STUDIES ON MOLECULAR BEHAVIOUR OF SOME DIELECTRIC LIQUIDS

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DEDICATED TO THE MEMORY OF MY
FATHER (Late Dinesh ch. Chatterjee)
AND MOTHER (Late Susama Chatterjee).

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CONTENTS

Page No.

Chapter - II

Chapter - III

Chapter - IV

Chapter - V

Chapter - VI

Chapter - VII

Chapter - VIII

Chapter - IX

Appendix -

INTRODUCTION

Molecular behaviour of dielectric liquids under the influence of electromagnetic radiation has been a subject of investigation for many years and the different aspects has been emphasized in different periods.

In 1912, Debye succeeded in deriving an extension of Clausius-Mosotti equation and showed that the dielectric constant depends not only on the molecular polarizability, but also on the permanent electric moment of the molecules. On the basis of this concept of molecular permanent dipole moment in the theory of dielectrics, he explained the anamolous dispersion of dielectric constant which was observed by Drude and others workers. He further pointed out that the process of orientation of the permanent electric moment connected with changes in the field requires a definite time interval, since it depends on the rotational movements accomplished by the molecules.

From Debye assumption concerning the molecular reorientation, it follows that after the removal of an externally applied field the average dipole orientation decay exponentially with time. The characteristic time of this exponential decay is called the dipole relaxation time.

Experimentally the relaxation time was found to depend exponentially with the reciprocal of temperature, this led to consideration of the dielectric relaxation process, which is nothing but a rate phenomenon.

Several modifications and extensions of Debye's theory for dielectric relaxation time have been proposed. This lead to the replacement of the single relaxation time by a set of different relaxation times in the description of the macroscopic relaxation process. For the description of the experimental results in the microwave region the continuous distribution of relaxation time was also proposed in many cases.

It appears from the above account that in this way in the near future further advancement may be achieved in the theory of dielectric polarization and dielectric dispersion in order to understand the molecular and intermolecular structure in the pure liquid and solution.

Thus, in order to have a clear idea of the subject of dielectric polarization and its relation with molecular structure a brief survey of various theories and their modification together with a brief review of earlier works are given in the following sections. The scope and object of the present investigations are given at the end of this section.

CHAPTER I

A BRIEF SURVEY OF THE THEORIES OF DIELECTRIC POLARIZATION, DIELECTRIC CONDUCTION TOGETHER WITH A BRIEF REVIEW OF PREVIOUS WORKS

1.1. Debye Theory of Dielectric Polarization and Complex Dielectric Constant:-

All matter is built up from electrically charged particles; negative electrons and positive nuclei, combining some times to neutral atoms and molecules, but in other case the particles with a net charges, such as ions in solution and in crystal. When a material is bring into an external electric field, then every particles in the material is subjected to an "internal field" which is proportional to applied electric field. Under the influence of external field in some materials the electrons in metals and ions in solution moved over a long distance, such materials are called conductors. But in the case of insulators or dielectries, a very small displacement of charges occurs. When an electric field is applied to the dielectric material the force acting upon the charges bring about a small displacement of the electrons relative to the nuclei, as the field tends to shift the positive and negative charges in opposite direction. This displacement is limited since the electrons are bound to the nuclei and therefore, reactive forces arise, which are proportional to the displacements for not too high field intensity. Thus when electrons of an atom are displaced by the electric field the dielectric is said to be polarized and this type of polarization is called electronic polarization. Another form of polarization is due to the fact that the applied fields tends to direct the permanent dipoles. During the formation of this polarization a certain amount of dielectric charges is transported through every plane elements in the dielectric. This transport is called the displacement current. After reaching the state of equilibrium in an applied electric field every volume element of the dielectric has aquired an induced moment.

The moment of a set of charges relative to a fixed point is defined by relation

$$\vec{m} = \sum_i e_i \vec{r}_i \qquad \ldots\ 1.1$$

where $\vec{r}_i$ is the radius vector, pointing from the chosen point to the ith. charge. The induced dipole moment in a volume element ΔV around a point is denoted by

$$\vec{m}_{ind} = \vec{p}\Delta V = \sum_i N_i e_i \vec{s}_i \Delta V \qquad \ldots\ 1.2$$

where $N_i \Delta V$ is the average number of charges e_i with displacement $\vec{S}_i$, in the volume element ΔV.

The vector $\vec{P}$ is generally called the "electric polarization" and it is the induced dipole moment per unit volume. The vector $\vec{P}$ is connected with the dielectric displacement vector $\vec{D}$ as

$$\vec{D} = \vec{E} + 4\pi\vec{P} \qquad \ldots 1.3a$$

or, $$\vec{P} = \frac{\vec{D} - \vec{E}}{4\pi} = \left(\frac{\epsilon - 1}{4\pi}\right)\vec{E} \qquad \ldots 1.3b$$

where $\vec{D} = \epsilon\vec{E}$, ϵ = dielectric permittivity and $\frac{\epsilon - 1}{4\pi} = \chi$ is the dielectric succeptibility $\vec{E}$ is the applied electric field.

Now, it consider that a dielectric sphere of radius 'a' in vacuum, then the formula for dipole moment becomes

$$\vec{m} = \frac{\epsilon - 1}{\epsilon + 2} a^3 \vec{E}_o \qquad \ldots 1.4$$

when a dielectric is placed in an electric field, $\vec{E}_o$ in vacuum, then due to induction, its polar molecules orientate themselves along the direction of the applied field. Each molecule is an electric dipole possessing an electric moment. This moment $\vec{m}$ is proportional to $\vec{E}_o$. So it can be written as

$$\vec{m} = \alpha\vec{E}_o \qquad \ldots 1.5$$

where α is a constant called polarizability of the dielectric, which is given by

$$\alpha = \frac{\epsilon - 1}{\epsilon + 2} a^3 \qquad \ldots 1.6$$

Thus polarizability has the dimension of volume. For conducting sphere polarizability $\alpha = a^3$.

The concept of the polarizability is very important for the molecular description of matter, since all atoms, ions and molecules are polarisable.

Polarisation $\vec{P}$ is divided into two parts $\vec{P}_\mu$ caused by the orientation of permanent dipoles and $\vec{P}_\alpha$ caused by the translational effect.

Thus

$$\vec{P} = \vec{P}_\alpha + \vec{P}_\mu \qquad \ldots 1.7$$

Then term

$$\vec{P}_\alpha = \sum_k N_K \alpha_K (\vec{E}_i)_K \qquad \ldots 1.8$$

and

$$\vec{P}_\mu = \sum_k N_k \bar{\mu}_k \qquad \ldots 1.9$$

where N is the number of perticles per unit volume, α the average polarizability of a particle and $\vec{E}_i$ the average field strength acting upon the particle. The index K refers to the k th. kind of particle. ($\vec{E}_i$ is the internal field which is equivalent to that of applied field $\vec{E}$). $\vec{\bar{\mu}}_k$ is the average value of permanent dipole moment for k th. molecule.

Now, in an uniform directing field $\vec{E}_r$ the average dipole moment vector $\bar{\vec{\mu}}$ of a dipole molecule in thermal equilibrium with a large number of other molecules is,

$$\bar{\vec{\mu}} = \frac{\mu^2}{3kT}\vec{E}_r \qquad \ldots\ 1.10$$

In the other theories $\vec{E}_r$ was taken equal to $\vec{E}_i$. However, Onsagar showed that this is only satisfactory for gases at low pressure, since in the general case only a part of the internal field $\vec{E}_i$ has a directing influence upon the permanent dipoles.

Combining eq. (1.9) and (1.10)

$$\vec{P}_\mu = \sum_k N_k \frac{\mu_k^2}{3kT}\left(\vec{E}_r\right)_k \qquad \ldots\ 1.11$$

From eq. (1.7), (1.8) and (1.11)

$$\vec{P} = \frac{\epsilon - 1}{4\pi}\vec{E} = \sum_k N_k\left[\alpha_k\left(\vec{E}_i\right)_k + \frac{\mu_k^2}{3kT}\left(\vec{E}_r\right)_k\right] \qquad \ldots\ 1.12$$

This is the fundamental equation.

To describe the dielectric behaviour of gases and polar molecules in a static and in a low frequency alternating field Debye equation is used. To obtain Debye equation by substituting $\vec{E}(\epsilon+2)/3$ both for $\left(\vec{E}_i\right)_k$ and $\left(\vec{E}_r\right)_k$ in eq. (1.12).

The result is

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} \sum_k N_k \left(\alpha_k + \frac{\mu_k^2}{3kT} \right) \qquad \ldots\ 1.13$$

The Debye equation is used for calculation of dipole moments from measurements on dilute solutions of a polar compound in a nonpolar solvent. But this is not very accurate method. Now introducing the molar polarization $[P]$ of the solution $[P] = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{\bar{M}}{d}$ where d = density and $\bar{M} = \sum_k x_k M_k$, average molecular weight, x_k are the molar fraction of the components and M_k their molecular weights. The Debye equation (1.13) becomes

$$[P] = \frac{4}{3} \pi N_A \sum_k x_k \left(\alpha_k + \frac{\mu_k^2}{3kT} \right) \qquad \ldots\ 1.14$$

where

$$N_A = \sum N_k \frac{M}{d}$$

is Avogardo's number.

In the solution of polar compound in nonpolar solvent

$$[P] = \frac{4}{3} \pi N_A \left[(1-x)\alpha_0 + x \left(\alpha + \frac{\mu^2}{3kT} \right) \right] \qquad \ldots\ 1.15$$

where α_0 is the polarizability of the solvent molecules, α, μ and x are the polarizability, permanent dipole moment and molar fractions of the solute respectively.

If $[P_s]$ is molar polarization of the pure solvent the Clausius-Mosotti equation becomes

$$[P_s] = \frac{4}{3}\pi N_A \alpha_0$$

or,

$$\frac{\epsilon - 1}{\epsilon + 2}\cdot\frac{M}{d} = \frac{4\pi N_A}{3}\alpha_0 \qquad \ldots\ 1.16$$

Further introducing the ideal molar polarization $[P]_d^0$ of the polar compound.

$$[P]_d^0 = \frac{4\pi}{3} N_A \left(\alpha + \frac{\mu^2}{3kT}\right)$$

or,

$$\frac{\epsilon_1 - 1}{\epsilon_1 + 2}\cdot\frac{M_1}{d_1} = \frac{4\pi N_A}{3}\left(\alpha + \frac{\mu^2}{3kT}\right) \qquad \ldots\ 1.17$$

Debye formula can be written in different form by eliminating α with the help of the Lorentz-Lorentz equation,

$$\frac{n_\infty^2 - 1}{n_\infty^2 + 2} = \frac{4\pi}{3} N\alpha \qquad \text{where} \qquad \epsilon = n_\infty^2$$

$$\therefore\ \mu^2 = \frac{9kT}{4\pi N}\cdot\frac{(\epsilon - n_\infty^2).3}{(\epsilon + 2)(n_\infty^2 + 2)} \qquad \ldots\ 1.18$$

Considering the correction for the reaction field and taking $\frac{4}{3}\pi a^3 N = 1$ Onsager reduced the eq.(1.18) to

$$\mu^2 = \frac{9kT}{4\pi N}\cdot\frac{(\epsilon - n_\infty^2)(2\epsilon + n_\infty^2)}{\epsilon(n_\infty^2 + 2)^2} \qquad \ldots\ 1.19$$

This is an important formula of Onsager's theory for calculating the dipole moments. But the difficulty is that, for determing the value of n_∞ the atomic polarisation should be known.

1.2. Physical Interpretation of Dielectric Loss (ϵ'') and Loss 'Tangent' ($\tan\delta$):

When a dielectric is subjected to an alternating electric field there are two possibilities are found, which depends on the frequency of the applied field, the temperature and the kind of material.

a) In some cases there are no measurable phase difference between $\vec{D}$ and $\vec{E}$ then the relation $\vec{D} = \epsilon \vec{E}$ is also valid for alternating field.

b) In other cases there is a suitable phase difference between $\vec{D}$ and $\vec{E}$. Then the simple relation $\vec{D} = \epsilon \vec{E}$ is not valid for and the phase difference between the potential and the true charges of the condenser makes it impossible to use the simple formula $C = \epsilon C_0$ for the capacity of the condenser.

The important difference between these two possibilities that in the first case no energy is absorbed by the dielectric from the electromagnetic field whereas in the second case there is a dissipation of energy in the dielectric. The dissipation of energy in the dielectric due to the absorption of electromagnetic wave is called the "dielectric loss".

A phase difference between $\vec{D}$ and $\vec{E}$ can be due to three different mechanisms:

I) Electrical conductivity (II) Relaxation effect due to permanent dipoles and (III) Resonance effect due to rotation or vibration of atoms, ions or electrons.

All alternating fields are associated with electromagnetic waves, thus the theory of dielectric loss is closer related to the theory of the absorption of electromagnetic waves by dielectric materials.

In the case of phase difference between $\vec{D}$ and $\vec{E}$ it is useful to describe the relationship between the scalars D and E with the aid of complex notation as

$$E^* = E_0 e^{j\omega t} \quad \text{and} \quad D^* = D_0 e^{j(\omega t - \delta)}$$

where δ is the phase difference and $\omega = 2\pi f$ is the frequency of the electromagnetic wave; But $D^* = \epsilon E^*$ or,

$$\epsilon = \frac{D^*}{E^*} = \frac{D_0}{E_0} e^{-j\delta} = \frac{D_0}{E_0}\left(\cos\delta - j\sin\delta\right) \qquad \ldots\ 1.20$$

Thus the dielectric constant becomes complex at high frequency. The complex dielectric constant ϵ^* can be split up into real and imaginary part ϵ' and ϵ'' respectively

$$\epsilon^* = \epsilon' - j\epsilon'' \qquad \ldots\ 1.21$$

where $$\epsilon' = \frac{D_o}{E_o}\cos\delta \text{ and } \epsilon'' = \frac{D_o}{E_o}\sin\delta$$

The dielectric loss at a certain frequency is often indicated by the value of tan δ

where $$\tan\delta = \frac{\epsilon''}{\epsilon'} \qquad \text{... 1.22}$$

Again, the dissipated energy per unit volume per second of the electric field is

$$W = \frac{\omega E_o^2}{8\pi}\epsilon\sin\delta = \frac{\omega E_o^2}{8\pi}\epsilon'' \qquad \text{... 1.23}$$

Thus the energy is directly proportional to ϵ'' and hence to sin δ. Therefore ϵ'' is generally called the loss factor and sin δ the power factor.

1.3. DIELECTRIC CONSTANT AND LOSS:

1.3a. Dielectric loss and relaxation time:-

Let in the static field the polarisation is

$$\vec{P}_s = \frac{\epsilon_s - 1}{4\pi}\vec{E}, \text{ then } \quad \vec{P}_s = \vec{P}_\infty + (\vec{P}_s)_{dip} \qquad \text{... 1.24}$$

where $(\vec{P}_s)_{dip}$ indicates the part of $\vec{P}_s$ due to permanent dipoles and $\vec{P}_\infty$ the part due to the polarizability of the particles

$$\vec{P}_\infty = \frac{\epsilon_\infty - 1}{4\pi}\vec{E} \qquad \text{...1.25}$$

The time in which the permanent dipoles needs to reach the equilibrium distribution subsequent to the application of a static electric field is of the order of magnitude between 10^{-6} and 10^{-13} seconds. This time depends on the temperature, the chemical composition and the structure of the dielectric molecules. During this time interval the part $(\vec{P}_s)_{dip}$ of $\vec{P}_s$ is build and polarisation increases from $\vec{P}_\infty$ to $(\vec{P}_s)$. Since the time required to established $\vec{P}_\infty$ relative to time required to build up $(\vec{P}_s)_{dip}$ is neglected. Then after a certain time t during this interval the relation becomes

$$\vec{P}_t = \vec{P}_\infty + \vec{P}_{dip} \qquad \ldots 1.26$$

where $\vec{P}_{dip}$ is the part of $(\vec{P}_s)_{dip}$ that has already been build up. Assuming the increase of $\frac{d\vec{P}_{dip}}{dt}$ is proportional to the difference between the final value $(\vec{P}_s)_{dip}$ and the actual value of $\vec{P}_{dip}$. Thus

$$\frac{d(\vec{P}_{dip})}{dt} = \frac{1}{\tau}\left\{(\vec{P}_s)_{dip} - \vec{P}_{dip}\right\} \qquad \ldots 1.27$$

τ is a constant which measures the time lag, so it is called the relaxation time.

The relaxation time τ may be defined as the time in which the polarisation is reduced to $\frac{1}{e}$ th. times of its original value, where e is the base of the natural logarithm.

Now integrating the eq. (1.27) and using the condition

$$(\vec{P}_{dip})_{t=0} = 0$$

$$\vec{P}_{dip} = (\vec{P}_s)_{dip}\left(1 - e^{-t/\tau}\right) \quad \ldots 1.28$$

At the alternating field at a time t,

$$(P_s^*)_{dip} = \frac{\epsilon_s - 1}{4\pi} E_t^* - \frac{\epsilon_\infty - 1}{4\pi} E_t^* \quad \ldots 1.29$$

from eq. (1.27) and eq. (1.29)

$$\frac{d(P_{dip}^*)}{dt} = \frac{1}{\tau}\left[\frac{\epsilon_s - \epsilon_\infty}{4\pi} E_0 e^{j\omega t} - P_{dip}^*\right] \quad \ldots 1.30$$

the general solution of the above equation is

$$P_{dip}^* = C e^{-t/\tau} + \frac{1}{4\pi}\frac{\epsilon_s - \epsilon_\infty}{1 + j\omega\tau} E_0 e^{j\omega t} \quad \ldots 1.31$$

The first term on the right hand side will decrease to an infinitely small value after some time and therefore it may be neglected.

Thus the total polarisation is given by

$$P^* = P_\infty^* + P_{dip}^*$$

or,

$$P^* = \left[\frac{\epsilon_\infty - 1}{4\pi} + \frac{1}{4\pi}\cdot\frac{\epsilon_s - \epsilon_\infty}{1 + j\omega\tau}\right] E_0 e^{j\omega t} \qquad \ldots\ 1.32$$

This formula indicates that P^* is a sinusoidal function of the time with the same frequency of the applied field. Now the dielectric displacement can be calculated from eqn (1.32) and $D^* = \epsilon^* E^*$,

$$D^* = E^* + 4.\pi.P^*$$

or, $$D^* = \left[\epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + j\omega\tau}\right] E_0 e^{j\omega t} \qquad \ldots\ 1.33$$

Thus the complex dielectric constant ϵ^* is

$$\epsilon^* = \left[\epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + j\omega\tau}\right] \qquad \ldots\ 1.34$$

or,

$$\epsilon^* = \left[\epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + \omega^2\tau^2}\left(1 - j\omega\tau\right)\right] \qquad \ldots\ 1.35$$

The real part of the eqn. (1.35) is

$$\epsilon' = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + \omega^2\tau^2} \qquad \ldots\ 1.36$$

and the imaginary part is

$$\epsilon'' = \frac{\epsilon_s - \epsilon_\infty}{1+\omega^2\tau^2}\cdot\omega\tau \qquad \ldots\ 1.37$$

1.3b. Distribution of relaxation time:-

According to the equations (1.36) and (1.37) it is possible to deduce

$$\frac{\epsilon' - \epsilon_\infty}{\epsilon_s - \epsilon_\infty} = \frac{1}{1+\omega^2\tau^2} \qquad \ldots\ 1.38$$

and

$$\frac{\epsilon''}{\epsilon_s - \epsilon_\infty} = \frac{\omega\tau}{1+\omega^2\tau^2} \qquad \ldots\ 1.39$$

By plotting the left hand side of these equations against log $\omega\tau$ symmetrical curves are obtained as shown in Fig. 1.1 and Fig. 1.2 respectively. The maximum value of absorption is reached for log $\omega\tau$ = 0. Thus the angular frequency corresponding to the maximum value of absorption is

$$\omega_m = \frac{1}{\tau} \qquad \ldots 1.40$$

This result can also be obtained from eq.(1.37) by taking $\frac{d\epsilon''}{d\omega} = 0$. The corresponding values ϵ'_{max} and ϵ''_{max} of ϵ' and ϵ'' are obtained by introducing $\omega\tau = 1$ in eq. (1.36) and eq. (1.37).

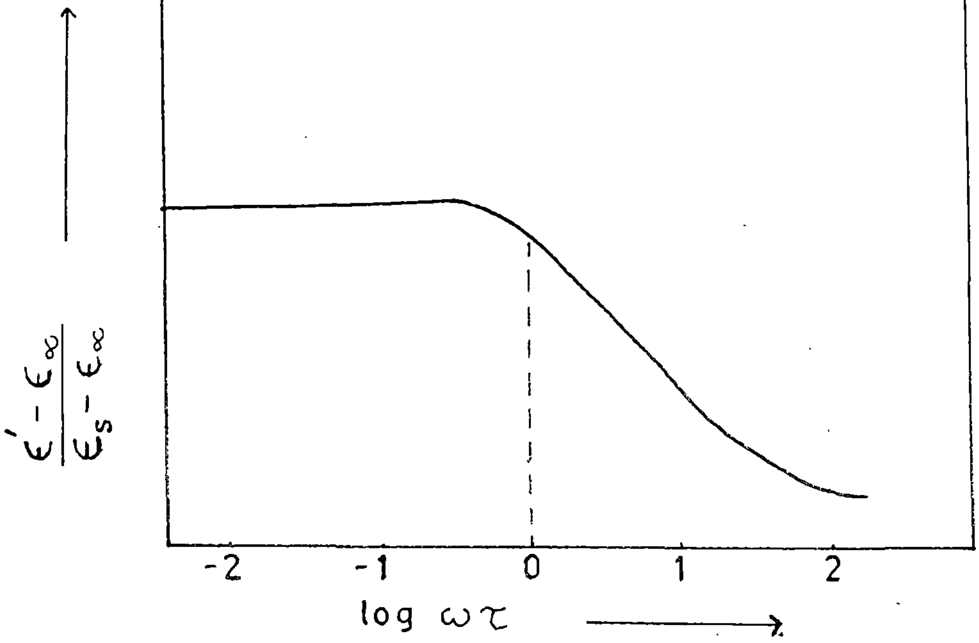

Fig -1.1 Plot of $\frac{\epsilon' - \epsilon_\infty}{\epsilon_s - \epsilon_\infty}$ versus $\log \omega\tau$.

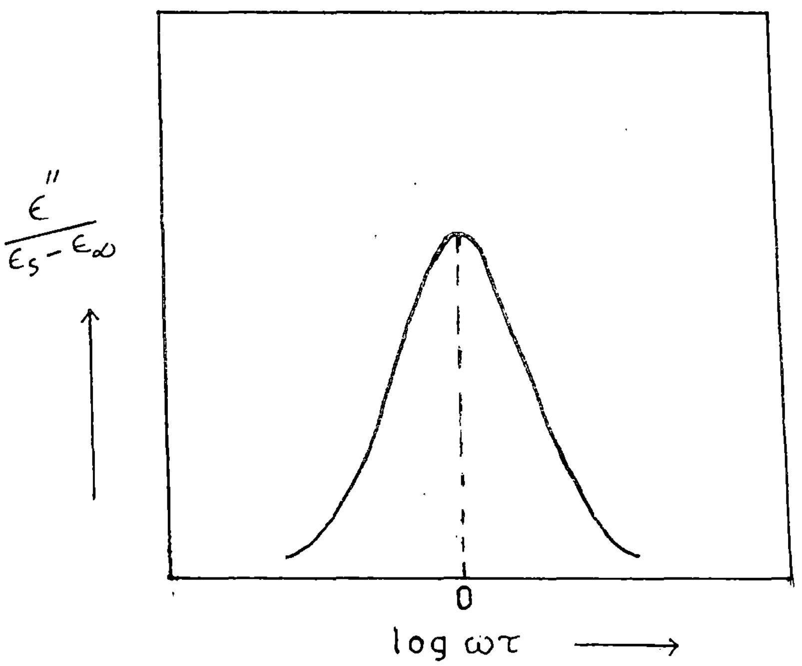

Fig-1.2 Plot of $\frac{\epsilon''}{\epsilon_s - \epsilon_\infty}$ versus log ωτ.

$$\epsilon'_{max} = \frac{\epsilon_s + \epsilon_\infty}{2} \qquad \ldots 1.41$$

and

$$\epsilon''_{max} = \frac{\epsilon_s - \epsilon_\infty}{2} \qquad \ldots 1.42$$

The cyclic frequency $f = \frac{\omega_m}{2\pi}$ corresponding to the angular frequency $\omega_{max} = \omega_m$ is generally called as critical frequency. The curves of Fig. 1.3 and Fig. 1.4 obtained from eq. (1.36) and eq. (1.37) are generally called Debye curve.

1.3c. Representation of permittivity in the complex plane:-

Debye Semi Circle

The equations for the complex permittivity

$$\frac{\epsilon' - \epsilon_\infty}{\epsilon_s - \epsilon_\infty} = \frac{1}{1+\omega^2\tau^2}, \quad \frac{\epsilon''}{\epsilon_s - \epsilon_\infty} = \frac{\omega\tau}{1+\omega^2\tau^2}$$

are the parametric equation of a circle in the ϵ' and ϵ'' plane, on eliminating the parameter $\omega\tau$ between two equations and rearranging

$$(\epsilon_s - \epsilon'')(\epsilon' - \epsilon_\infty) = \epsilon''^2 \qquad \ldots 1.43$$

$$\left(\epsilon' - \frac{\epsilon_s + \epsilon_\infty}{2}\right)^2 + \epsilon''^2 = \left(\frac{\epsilon_s - \epsilon_\infty}{2}\right)^2 \qquad \ldots 1.44$$

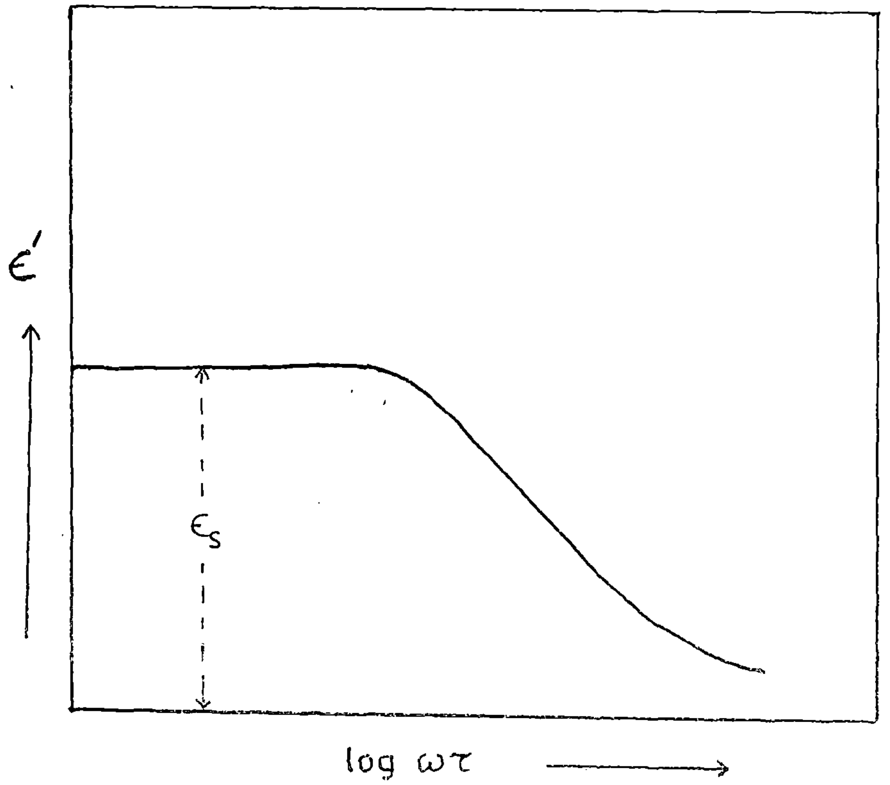

Fig-1.3 Plot of ϵ' versus log $\omega\tau$.

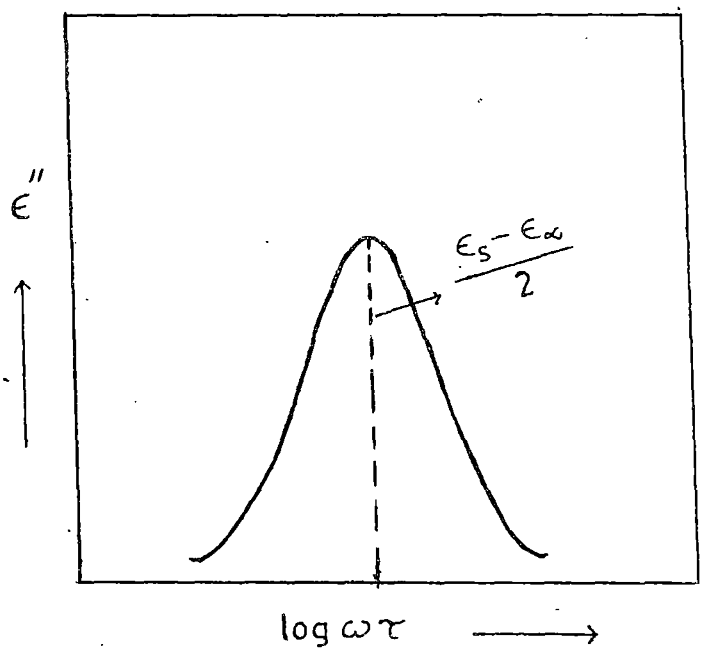

Fig-1.4 Plot of ϵ'' versus $\log\omega\tau$.

which is the equation of a circle whose centre is $\left\{\frac{\epsilon_s + \epsilon_\infty}{2}, 0\right\}$ and radius $\left(\frac{\epsilon_s - \epsilon_\infty}{2}\right)$.

The intersection points with the abscissa are characterised by $\epsilon' = \epsilon_\infty$ and $\epsilon' = \epsilon_s$ respectively. This semi circle is shown in Fig. 1.5. This semi circle is called Debye Semi Circle.

1.3d. Cole-Cole Distribution:-

The arc dispersion function of Cole and Cole has been applied to analysis the experimental dielectric data most frequent because of the attractively simple graphical form by which data of $\epsilon'(\omega)$ and $\epsilon''(\omega)$ can be analysis in its term. Cole and Cole have shown that the Fig. (1.6) Debye semi circle centre of which the arc is a part is depressed below the abscissa axis and the diameter drawn through the ϵ_∞ point makes an angle $\alpha < \frac{\pi}{2}$ with the abscissa axis. The angle α gives the measure of distribution of relaxation time which may vary with temperature but not with frequency. The value α lies between (0 and 1).

The Debye equation is modified by them as

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + (j\omega\tau_0)^{1-\alpha}} \qquad \ldots 1.45$$

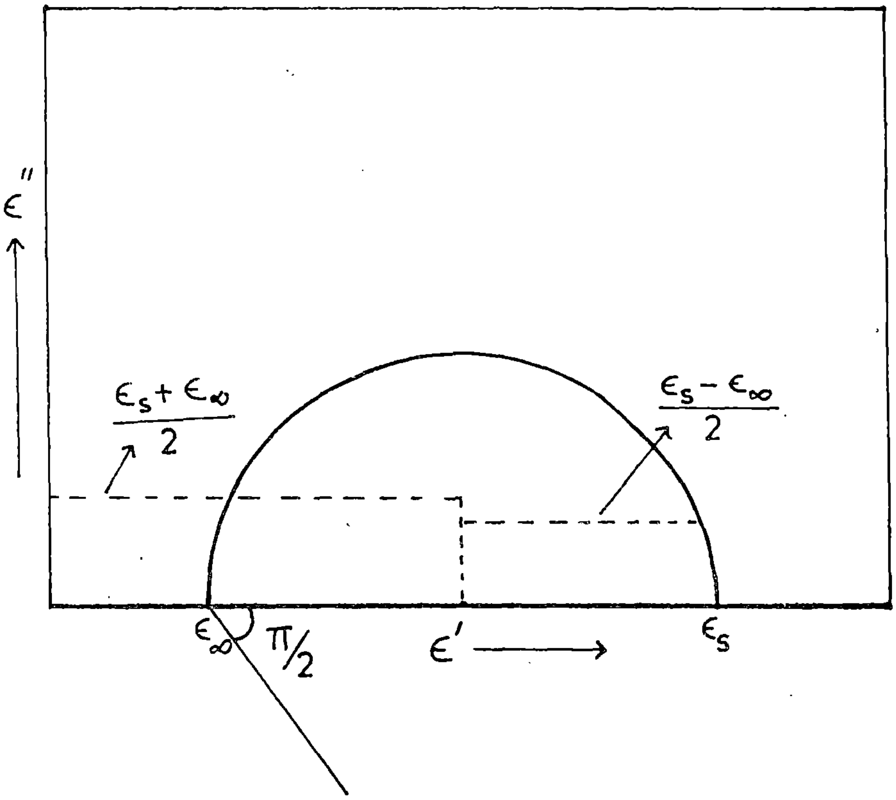

Fig - 1.5 Plot of ϵ'' versus ϵ'.

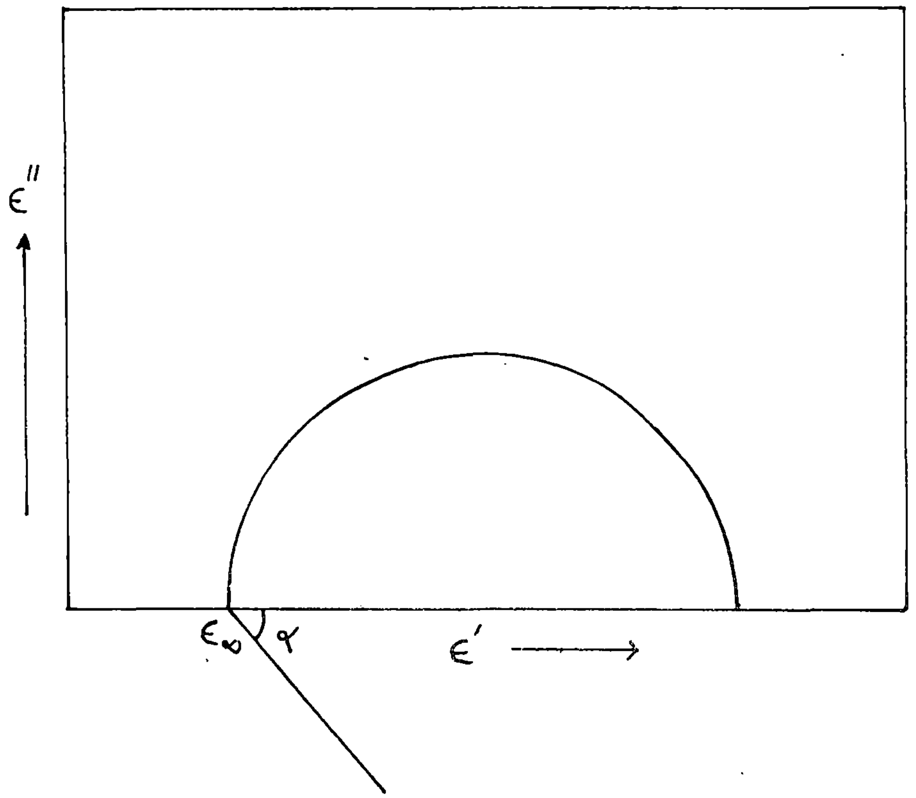

Fig-1.6 Cole-Cole Plot of ϵ'' versus ϵ'.

with the most probable relaxation time τ_0 which can be calculated from the relation

$$\frac{v}{u} = (\omega\tau_0)^{1-\alpha} \qquad \ldots 1.46$$

where v is the distance on the Cole-Cole plot from ϵ_s point to experimental point and u is the distance from the same experimental point to the ϵ_∞ point, if α is zero $\frac{v}{u}$ becomes equal to $\omega\tau_0$ which is the true Debye equation.

1.4. Expression for Dielectric Relaxation in Dilute Solution of Polar Molecules in Nonpolar Solvent:-

The expression for ϵ' and ϵ'' have already been derived and if ϵ' and ϵ'' are determined separately at certain frequency of the applied electric field the relaxation time τ may be determined.

If α_1 be the polarizability of a molecule of the first component (non-polar solvent) and α_2 that of a molecule of the second component (polar solute), and if n_1 and n_2 represent the number of molecules present in 1 c.c. of the solution then

$$\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} \cdot \frac{f_1 M_1 + f_2 M_2}{\rho} = \frac{4\pi}{3} N f_1 \alpha_1 + \frac{4\pi}{3} N f_2 \alpha_2 \qquad \ldots . 1.47$$

and

$$\frac{\epsilon_s-1}{\epsilon_s+2}\cdot\frac{f_1M_1+f_2M_2}{\rho}=\frac{4\pi}{3}Nf_1\alpha_1+\frac{4\pi}{3}Nf_2\alpha_2+\frac{4\pi}{3}Nf_2\frac{\mu^2}{3kT} \quad ...1.48$$

where ϵ_∞ and ϵ_s are the dielectric constant of the solution for infinite frequency and static field respectively. M_1 and M_2 are the molecular weights of the two components. The density of the solution is denoted by ρ, f_1 and f_2 the mole fractions of the two components are given by

$$f_1=\frac{n_1}{n_1+n_2}, \qquad f_2=\frac{n_2}{n_1+n_2}$$ respectively,

from eq. (1.47) and (1.48) we get

$$\epsilon_s-\epsilon_\infty=\frac{4\pi NC\mu^2}{27kT}(\epsilon_\infty+2)(\epsilon_s+2) \quad ...1.49$$

where C denotes the concentration of the solute molecules in mole/c.c.

Substituting the values of ($\epsilon_s-\epsilon_\infty$) in eq. (1.37) i.e.

$$\epsilon''=\frac{\epsilon_s-\epsilon_\infty}{1+\omega^2\tau^2}\cdot\omega\tau$$

or, $$\epsilon''=\frac{4\pi NC\mu^2(\epsilon_\infty+2)(\epsilon_s+2)}{27kT(1+\omega^2\tau^2)}\cdot\omega\tau$$

or,

$$\epsilon'' = \frac{(\epsilon_\infty+2)}{3}.\frac{(\epsilon_s+2)}{3}\left[\frac{4\pi NC\mu^2}{3}\right]\frac{\omega\tau}{1+\omega^2\tau^2} \qquad ...1.50$$

In case of dilute solution of polar solute in nonpolar solvent it is assume that $\epsilon_s \approx \epsilon_\infty$ and without causing much error ϵ_s and ϵ_∞ each can be taken equal to ϵ'.

Hence,

$$\epsilon'' = \left(\frac{\epsilon'+2}{3}\right)^2 \frac{4\pi NC\mu^2}{3kT}\frac{\omega\tau}{(1+\omega^2\tau^2)} \qquad ...\ 1.51$$

It is seen from the above equation (1.51) that for fairly low concentration the value of ϵ'' is linearly dependent on the concentration of polar solute molecules in nonpolar solvent and in the case of infinite dilution i.e. as $C \rightarrow 0$ the value of ϵ' may be replaced by ϵ_s the static dielectric constant of the solvent and eq. (1.51) becomes

$$\epsilon'' = \left(\frac{\epsilon_s+2}{3}\right)^2 . \frac{4\pi NC\mu^2}{3kT} . \frac{\omega\tau}{1+\omega^2\tau^2} \qquad ...\ 1.52$$

The eq. (1.52) has been used in the present investigations for determining the value of dipole moment and also relaxation time, whenever possible from experimentally determined value of dielectric loss ϵ'' at different frequencies, temperature and concentrations.

1.5a. Dielectric Loss and High Frequency Conductivity:

The experimental determination of dielectric absorption is a measure of energy dissipation in the medium and in practice most system show energy loss from this process other than dielectric relaxation. Generally these will be small and related to the d.c. conductivity of the medium. Assuming a homogenious medium of conductivity K (ohm^{-1} cm^{-1}) the Joule heating arising from the conductivity contributes a loss factor ϵ_c'' (conductance). So at a particular frequency,

$$\text{Total dielectric loss} = \epsilon''(\text{total}) = \epsilon''(\text{dielectric}) + \epsilon_c''(\text{conductance}) \quad \ldots 1.53$$

In an ideal dielectric there would be no free ions conduction but in actual insulating material Joules heat may be developed by the drift of free electrons and free ions in the applied field. Therefore, the total heat developed is the sum of the dielectric loss and Joule heat.

If a potential E is established between the parallel plate condenser whose dielectric material constant ϵ and distance between the plates and surface area are d and A respectively then a charge q per unit area will appear on each plate and a polarisation p will be created in the dielectric. The current flowing in the lead of the condenser is ($A\frac{dq}{dt}$). If it is assumed that conductivity due to free ions may be neglected then the conductivity is

$$K = \frac{1}{E}\cdot\frac{dq}{dt} \qquad \ldots 1.54$$

Since $E = \frac{V}{d} = \frac{D}{\epsilon}$ and $D = 4\pi q = E + 4\pi P$

The eq. (1.54) becomes

$$KE = \frac{dq}{dt} = \frac{1}{4\pi}\frac{dD}{dt} = \frac{\epsilon}{4\pi d}\cdot\frac{dV}{dt}.$$

where all the electrical quantities are expressed in e.s.u.

When the applied potential is alternating then V may be expressed as the real part of $V = V_0 e^{j\omega t}$ where $\omega = 2\pi f$ and the dielectric constant as complex $\epsilon^* = \epsilon' - j\epsilon''$.

Then the total current density in dielectric

$$I = \frac{dq}{dt} = \frac{\epsilon^*}{4\pi d}\frac{dV}{dt} = j\omega\frac{\epsilon^*}{4\pi d}\cdot V_0 e^{j\omega t}$$

$$= j\omega\frac{\epsilon' - j\epsilon''}{4\pi}\cdot\frac{V_0}{d}e^{j\omega t}$$

$$= \left(\frac{j\omega\epsilon' + \omega\epsilon''}{4\pi}\right)\cdot E_0 e^{j\omega t} \qquad \text{where } E_0 = \frac{V_0}{d}$$

$$\therefore \quad I = \left(\frac{\omega\epsilon''}{4\pi} + j\frac{\omega\epsilon'}{4\pi}\right)E_0 e^{j\omega t} \qquad \ldots 1.55$$

The total current density 'I' in the dielectric can be considered as the sum of displacement or capacitive current and conduction current

$$I = I_d + I_{cond} \qquad \ldots 1.56$$

Murphy and Morgan (1939) deduced an expression on total conductivity K which is a complex quantity and is the sum of conductivity due to displacement current (K") and conductivity due to conduction (K')

$$\therefore \quad K = K' + jK'' \qquad \ldots 1.57$$

Now comparing the eq. (1.55) and eq. (1.57), the real part of eq. (1.55) can be considered to

$$K' = \frac{\omega\epsilon''}{4\pi} \qquad \ldots 1.58$$

and the imaginary part $K'' = \frac{\omega\epsilon'}{4\pi}$ ... 1.59

Therefore, $I = \left(K' + jK''\right)E_0 e^{j\omega t}$ ... 1.60

For convenience in connection with subsequent account of methods of measurement, the admittance of the condenser may be expressed in terms of an equivalent parallel capacitance C_p and conductance G_p so that

$$\frac{dq}{dt} = \frac{0.9\times10^{12}}{A}\left(G_p + j\omega C_p\right)E_o e^{j\omega t} \qquad \ldots 1.61$$

where G_p in mhos, C_p in farads and 0.9×10^{12} is the ratio of the farad to the e.s.u. of capacitance and also of mhos to the e.s.u. of conductance. By using the expression for empty condenser capacitance C_o in farad

$$C_o = \frac{A}{4\pi d \times 0.9 \times 10^{12}} \qquad \text{... 1.62}$$

So we can write,

$$\frac{dq}{dt} = \frac{1}{4\pi C_o}\left(G_p + j\omega C_p\right) E_o e^{j\omega t} \qquad \text{... 1.63}$$

Comparing eq. (1.55) and (1.63) it is possible to get

$$\epsilon' = \frac{C_p}{C_o} \qquad \text{... 1.64}$$

$$\epsilon'' = \frac{G_p}{\omega C_o} \qquad \text{... 1.65}$$

and

$$K' = \frac{G_p}{4\pi C_o} = \frac{\omega \epsilon''}{4\pi} \qquad \text{... 1.66}$$

The K' in ohm^{-1} cm^{-1} can be written as

$$K' = \frac{\epsilon'' \omega}{4\pi \times 0.9 \times 10^{12}} = \frac{f \epsilon''}{1.8 \times 10^{12}} \qquad \text{... 1.67}$$

where f is the frequency of the applied field.

The instantaneous power or heat developed per second, which is the multiplication of current given in eq. (1.55) and voltage given by $E_0 \cos \omega t$ and integrating over half period, the mean power or heat developed

$$\overline{W} \text{ per second} = K' \frac{E_0^2}{2} = \frac{\omega \epsilon''}{4\pi} E_0^2 \text{ ergs/sec} \quad \ldots 1.68$$

Heat developed per cycle in the dielectric

$$\overline{W} \text{ per cycle} = \frac{\epsilon'' E_0^2}{4} \text{ ergs/sec} \quad \ldots 1.69$$

Eq. (1.68) and eq. (1.69) shows that K' is proportional to the heat developed per second and ϵ'' is proportional to the heat developed per cycle.

1.5b. High Frequency Conductivity of Dielectric Polar Molecules:-

In $K' = \frac{\omega \epsilon''}{4\pi}$, ϵ'' is substituted from the Debye equation (1.37) i.e.

$$\epsilon'' = \frac{\epsilon_s - \epsilon_\infty}{1 + \omega^2 \tau^2} \omega \tau$$

the high frequency conductivity K' becomes

$$K' = \frac{1}{4\pi} \cdot \frac{\epsilon_s - \epsilon_\infty}{1 + \omega^2 \tau^2} \omega^2 \tau \quad \ldots 1.70$$

This equation shows that K' does not pass through maximum as ϵ'', but increase with ω, approaching to limiting value K_∞, the infinite frequency conductivity, which is reached when 1 can be neglected in comparison with $\omega^2\tau^2$ that is as $\omega \to \infty$, $\omega^2\tau^2 \gg 1$, so that

$$K_\infty = \frac{\epsilon_s - \epsilon_\infty}{4\pi\tau} \qquad \ldots 1.71$$

1.5c. High Frequency Conductivity of Dilute Solution of Polar Molecules in Non-polar Solvent:-

It is seen in eq. (1.51) that for fairly low concentration the ϵ'' is linearly dependent on the concentration of polar solute molecules in nonpolar solvent

$$\epsilon'' = \left(\frac{\epsilon'+2}{3}\right)^2 \frac{4\pi N C \mu^2}{3kT} \cdot \frac{\omega\tau}{1+\omega^2\tau^2}$$

But at very low concentration that is at $C \longrightarrow 0$ the ϵ' may be replaced by ϵ_s dielectric constant of the solvent. Then the above equation becomes

$$\epsilon'' = \left(\frac{\epsilon_s+2}{3}\right)^2 \frac{4\pi N C \mu^2}{3kT} \cdot \frac{\omega\tau}{1+\omega^2\tau^2}$$

Substituting this value of ϵ'' in $K' = \frac{\omega\epsilon''}{4\pi}$

The high frequency conductivity of solution becomes

$$K' = \left(\frac{\epsilon_s+2}{3}\right)^2 \cdot \frac{NC\mu^2}{3kT} \cdot \frac{\omega^2\tau}{1+\omega^2\tau^2} \qquad \ldots\ 1.72$$

This eq. (1.72) has been used in the present investigation for determining the value of relaxation time τ and as well as the dipole moment (μ) of polar molecules.

1.6a. Relaxation Time (τ) and its Relation with Microscopic and Macroscopic Properties:-

In the previous sections the expression for ϵ' and ϵ'' have been given in terms of the relaxation time τ .

In Debye theory the turning couple on dipolar molecule caused by the applied field is opposed by a torque proportional to the angular velocity of the dipole and this constant denoted by ζ is dependent on the surrounding medium. Debye shown that if the dipoles are regarded as spheres of radius 'a' immersed in the medium with internal viscosity coefficient η_{int} the constant ζ is given by the stokes formula

$$\zeta = 8\pi\eta_{int}a^3 \qquad \ldots\ 1.73$$

and the relaxation time is obtained as

$$\tau = \frac{\zeta}{2kT} \qquad \ldots\ 1.74$$

combining eq. (1.73) and eq. (1.74) we get

$$\tau = \frac{4\pi a^3}{kT}\eta_{int}$$

Debye assumed that the internal viscosity η_{int} which is a microscopic property is equal to the macroscopic viscosity (η) of the polar liquid and thus the Debye relation can be written as

$$\tau = \frac{4\pi\eta a^3}{kT} \qquad \ldots 1.75$$

The above equation (1.75) shows that from the measured value of the relaxation time τ and the coefficient of viscosity η at a certain temperature T the size of the rotating polar molecule may be calculated from the equation

$$a^3 = \frac{\tau k T}{4\pi\eta} \qquad \ldots 1.76$$

where a = radius of the polar polecule. Alternatively if the size of the polar molecule is known from measurements, the determination of the value of the relaxation time τ afford a method of obtaining the value of η_{int} from which information on the structure of the polar medium may be obtained.

1.6b. Modification of Debye's relation:-

Perrin (1934) modified the Debye relation eq.(1.76) which is applicable for the spherically symmetric molecule. Perrin treated the rigid dipolar molecule as an ellipsoid with molecular dipole moment $\vec{\mu}$ having component μ_a μ_b and μ_c along the three principal axes (a, b, c) of the ellipsoid and obtained an expression for the average moment per molecule in which the term $\mu^2/1+j\omega\tau$ of equation

$$P^* = \frac{4\pi N_A}{3}\left[\alpha + \frac{\mu^2}{3kT}\cdot\frac{1}{1+j\omega\tau^*}\right] \qquad \ldots\ 1.77$$

is replaced by

$$\left[\frac{\mu_a^2}{1+j\omega\tau_a} + \frac{\mu_b^2}{1+j\omega\tau_b} + \frac{\mu_c^2}{1+j\omega\tau_c}\right] \qquad \ldots\ 1.78$$

So the eq. (1.77) becomes

$$P^* = \frac{\epsilon^* - 1}{\epsilon^* + 2}\cdot\frac{M}{\rho}$$

Or,

$$P^* = \frac{4\pi}{3}N_A\left[\alpha + \frac{1}{3kT}\left(\frac{\mu_a^2}{1+j\omega\tau_a} + \frac{\mu_b^2}{1+j\omega\tau_b} + \frac{\mu_c^2}{1+j\omega\tau_c}\right)\right] \ldots\ 1.79$$

where τ_a, τ_b and τ_c are the relaxation times of the dipole moment components along the three axes.

In many cases the rigid polar molecules is approximated by an ellipsoidal shape instead of being a perfect sphere. Moreover, the dipole may be along one of the axes of consideration. In such a case the time of relaxation is given by Fischer as

$$\tau = \frac{4\pi abcf}{kT}\eta_{int} \qquad \dots 1.80$$

where a, b, and c are the semi axes of the ellipsoid and f is a structure factor.

1.7 Radiofrequency Conductivity of Polar Dielectric Liquids and Relaxation Time:-

In an actual dielectric when a radiofrequency field ($E = E_0 e^{j\omega t}$) is applied, the total heat produced is due to the combined effect of dielectric loss and Joule's heating. Thus the radiofrequency conductivity measurement provides an information regarding the displacement current and conduction current in a dielectric liquid.

In reference to the previous theory of the dielectric conductivity eq. (1.58) it is observed that the product of angular frequency and loss factor is equivalent to a dielectric conductivity ($K' = \frac{\omega \epsilon''}{4\pi}$) The dielectric conductivity K' may represent as well an actual ohmic conductivity caused by migrating charge carrier as refer to an energy loss associated with a frequency dependence (dispersion) of ϵ'', for example, the friction accompanying the orientation of dipoles.

Sen and Ghosh (1974, 1978) put forward a theory on conductivity based on the assumption of existence of free ions in polar dielectric liquids, so that when a radio frequency field is applied in the polar liquid, there is not only the displacement component contributing to the conductivity as assumed by Murphy and Morgan, but the conduction current due to free ions plays a dominant role. Using Murphy and Morgan's eq. (1.58) of conductivity and Debye's dielectric loss equation (1.37) a general equation for conductivity has been obtained,

$$K' = \frac{1}{4\pi} \cdot \frac{(\epsilon_s - \epsilon_\infty)\omega^2 \tau}{1 + \omega^2 \tau^2} \qquad \ldots 1.81$$

Substituting the relaxation time $\tau = \frac{4\pi \eta a^3}{kT}$ in eq. (1.58) which is in most cases of common dielectric liquids is of the order of 10^{-11} secs. The eqn.(1.37) of the radio frequency conductivity becomes

$$K' = \frac{(\epsilon_s - \epsilon_\infty)}{kT} \omega^2 a^3 \eta \qquad \ldots 1.82$$

Here at radiofrequency stage $\omega^2 \tau^2$ considered to be very small i.e. $\omega^2 \tau^2 \ll 1$.

Thus it is evident that if measurement of radio-frequency conductivity are made at gradually higher and higher temperature then as ($\epsilon_s - \epsilon_\infty$) and η/T are both decreasing factor of temperature, therefore K' should decrease with the increase of temperature. But the experimental results showed that the radio frequency conductivity increases with the increase of temperature. It is well known that in case of electrolytes where conductivity is mainly due to ions, Walden's rule is valid, which states that the product of equivalent conductance at infinite dilution and the viscosity of the solvent is approximately constant and independent of the nature of dielectric.

A similar relation observed in case of polar dielectric liquids where $K'\eta$ = constant and it follows Walden's rule.

Taking the analogy from the motion of an electron in an ionized gas when the degree of ionization is small and assuming the resistive force as due to viscosity, the equation of motion of the ions is given by

$$M\frac{dv}{dt} = eE_0e^{j\omega t} - 6\pi\eta av \qquad \ldots 1.83$$

where "a" is the radius of the molecule and η the coefficient of viscosity then

$$v = \frac{eE_0e^{j\omega t}}{M(\nu + j\omega)} \qquad \ldots 1.84$$

where

$$\nu = \frac{6\pi\eta a}{M}$$

Now,

$$v = \frac{eE_0}{M}\left[\frac{\nu}{\nu^2+\omega^2} - j\frac{\omega}{\nu^2+\omega^2}\right]e^{j\omega t} \qquad \ldots\ 1.85$$

if n denotes the number of free ions/c.c. and the current $i_c = nev$

Then the conduction current

$$i_c = \frac{ne^2}{M}\left[\frac{\nu}{\nu^2+\omega^2} - j\frac{\omega}{\nu^2+\omega^2}\right]E_0 e^{j\omega t} \qquad \ldots 1.86$$

finding the real part of the conductivity

$$\sigma = \frac{ne^2\nu}{M(\nu^2+\omega^2)}$$

or,

$$\sigma = \frac{ne^2}{M}\cdot\frac{6\pi\eta a/M}{(6\pi\eta a/M)^2+\omega^2} \qquad \ldots\ 1.87$$

as $a = 10^{-8}$ cm, $\eta = 10^{-3}$ poise and $M = 10^{-28}$ gms.
then $\frac{6\pi\eta a}{M} \gg \omega$.

Thus conductivity due to free ions is

$$\sigma = \frac{ne^2}{6\pi\eta a} \qquad \ldots\ 1.88$$

Now, the total conductivity is given by K' = dielectric conductivity + ionic conductivity. Thus from eq. (1.70) and eq. (1.88)

$$K' = \left[\frac{(\epsilon_s - \epsilon_\infty)}{4\pi} \cdot \frac{\omega^2 \tau}{1 + \omega^2 \tau^2} + \sigma\right]$$

or,

$$K' = \frac{(\epsilon_s - \epsilon_\infty)}{4\pi} \omega^2 \tau + \left(\frac{n e^2}{6\pi a}\right) \frac{1}{\eta} \qquad \ldots\ 1.89$$

or, $K' = A + B/\eta$ ... 1.90

This is the fundamental equation for radiofrequency conductivity, where $A = \frac{1}{4\pi} \cdot (\epsilon_s - \epsilon_\infty)\, \omega^2 \tau$, $B = \frac{ne^2}{6\pi a}$ and $\omega = 2\pi f$ and considering $\omega^2 \tau^2 << 1$, B is the slope of the curve K' against $1/\eta$ and A is the intercept. From these values dielectric relaxations can be determined.

1.8. Ultra High Frequency Conductivity or Microwave Conductivity of Polar Molecules in Dilute Solution of Nonpolar Solvent:-

At the very dilute solution of the polar solute in nonpolar solvent the percentage of free ions present in solution is negligible. Again at U.H.F. and microwave field there will be no displacement of existing ions present in the dilute solution but only the oscillation can be expected. So the second part of the eq. (1.90) may be omitted. So at infinite dilute solution of polar solute in nonpolar solvent the equation (1.90) becomes,

K' = A' = The U.H.F. or microwave conductivity at infinite dilution,

or,

$$K' = \left(\frac{\epsilon_s + 2}{3}\right)^2 . \frac{NC\mu^2}{3kT} . \frac{\omega^2\tau}{1+\omega^2\tau^2} \qquad \ldots\ 1.91$$

since

$$A' = \left(\frac{\epsilon_s + 2}{3}\right)^2 . \frac{NC\mu^2}{3kT} . \frac{\omega^2\tau}{1+\omega^2\tau^2} \qquad \ldots\ 1.92$$

this eq. (1.91) is same as eq. (1.72).

In our present investigation this eq. (1.91) is used for determining the time of relaxation τ or dipole moment μ of the polar liquids.

1.9. A Brief Review of the Early Works:-

Dielectric Dispersion and Absorption and Some Related Phenomena of Some Organic Polar Dielectric Liquids:-

In the year 1850 Mossotti and in 1879 Clausius established a quantitative relation to reveal the nature of the liquid dielectrics in presence of an external electric field.

Lorentz (1892), Von-Helmholtz (1892) and Drude (1904) independently explained the anamolous dispersion of refractive index of dielectric liquids at optical frequencies. Similar anomalous dispersion of dielectric constant at very high frequency electric field was also modified by Drude in (1904).

Most of the earlier works were centered round the studies of applicability of Debye's equation in determining the molecular radii from the measurement of relaxation times and macroscopic viscosity and the experiments were done mainly on the polar rigid and non rigid molecules in nonpolar solvents.

In general the high frequency absorption in liquid system studies may be classified in two categories:

(a) Solution of polar rigid and non rigid molecules in non polar solvents.

(b) Pure polar liquids.

The first quantitative verification of Debye theory was attempted by Mizushima. He in 1926 carried out the investigation on dielectric dispersion of several alcohols and Ketones in metre wave length region and over a wide range of temperature and observed absorption peak at low temperature. He verified Debye theory in the case of alcohol by calculating molecular radii and found them to be almost of the right order with glycerine as an exception having too small a value for molecular radius.

J.D. Stranathan (1928) studied the dielectric behaviour of dilute solution of several alcohols in benzene solution. He found that the zero concentration (molecular volume Vs concentration curve at different temperatures) intercepts for methyl, ethyl, propyl and amyl alcohol lead to the values of electric moment of molecules which are essentially independent of temperatures thus is in agreement with Debye theory, it is contrast to the behaviour of the pure liquid alcohols.

Debye himself (1929) successfully explained the anamolous dispersion observed by Drude (1904) and postulated that the characteristic property of the liquid responsible for anamolous dispersion at radiofrequency range is the polarity of their molecules.

Fischer (1939) measured the relaxation times of a number of liquid compounds in dilute solutions and in pure liquid and found for the alephatic chain molecules (Ketones, monohalogenides, alcohols) the relative time increases in sequence alcohol, ketones, halogenides. The absolute values of relaxation times can be evaluated by introducing molecular viscosity which is smaller than macroscopic viscosity. The result show for acetone, nitrobenzene and monochlorobenzene in undiluted state in agreement with Debye theory of quasicrystalline structure of liquids, but the general theory does not explains the behaviour of alcohol with their strong interaction of (- OH) groups.

Spengler (1941) showed relaxation time as a function of concentration with two liquids C_6H_5NO and C_6H_5Cl. He pointed out that according to Debye's law, relaxation time (τ) varied with viscosity (η) holds for dilute solution where Brownian movement is a major factor in the arrangement of the dipole, with high concentration the mutual action between the dipoles is more important and the ratio (τ / η) the reduced relaxation time decreases.

Jackson and Powels (1946) determined the value of relaxation time in benzene and in paraffin solution and observed that the values only increased by 4 - 7 fold for an increase in viscosity of eight fold.

Curties (1952) and Smyth (1954) observed that although the viscosity of the liquid was same, value of relaxation time was different in solutions and in liquid state.

Müller (1956) observed that molecular radii calculated by using Debye equation for few molecules from experimental values of critical wavelength and critical frequency were too low compared with values obtained from other method. He further observed that the molecular radii becomes still lower with the increase of viscosity of the medium.

Sinha et al (1966) studied the influence of viscosity on relaxation time and concluded that the macroscopic viscosity did not correctly represent the internal viscosity of the liquid.

Mehrotra (1972) determined the relaxation time τ and mutual viscosity η_{12} of seven substituted benzene p-toludine, O-nitroaniline etc. in the microwave region at various temperatures and concluded that the mutual viscosity is a better representation of the resistance of the rotation of the individual solute molecules.

P.C.Gupta (1978) measured the dielectric loss (ϵ'') and dielectric permittivity in dilute solution of benzene in 3 cm. microwave region of benzoylacetone, p-fluoro, p-chloro, p-bromo and p-methyl benzoylacetones at 40°C and calculated the relaxation times, the dipole moments, the free energies of activation for dielectric relaxation and viscous flow.

Dielectric Dispersion and Absorption of Non-rigid Molecule in Nonpolar Solvents:-

Fischer and Frank (1939) using thermal method of measuring dielectric loss at 4.3 meter wavelength obtained relative values of relaxation times of some aromatic halides. The shorter relaxation times in larger molecules were explained by them as being associated with orientation of CH_2X group rotation around their bond ring.

F.R. Goss (1940) analysed the dielectric polarization of certain binary mixtures of polar with nonpolar liquids and showed that the solvent effect can be resolved into contributions depending on the anisotropy of the electric fields which varies with the shape of the non spherical molecules and on induction effect related to the dielectric constant of the liquids and arising both from the reaction field and from permanent dipoles.

Schallamarch (1946) experimentally showed that dielectric relaxation time and viscosity of a number of long chain liquids are not generally equal, in contradiction to the behaviour of liquids of low molecular weights.

Gopala Krishna (1957) gave a method for determining the dipole moment and relaxation time of polar substances in nonpolar solvents at microwave range of frequency. The special advantage of his method is that it need not required the density and concentration of solution for determining the relaxation time.

Since after the development of Budo's theory the molecular and intermolecular rotations have been observed in large number of molecules like - OCH_3, - NH_2, - CH_2Cl, - CH_2Br, - CH_2CN, - OH by Fong and Smyth (1963).

Jaiprakash (1969) developed a method based on Frolich's equation for calculating the relaxation time of spherical polar molecule in nonpolar solvent. The calculated relaxation time of five molecules were comparable with those calculated from Gopala Krishna's method.

Tay and Gossley (1972) analysed bromoalkanes and Ketones, interms of rotation of molecules as a whole but in amines the $-NH_2$ group rotation has been attributed to be responsible for dielectric relaxation.

Arrawatia et al (1977) determined the dielectric permitivity ϵ' and dielectric loss ϵ'' of O-Chlorobenzene, 4-chloro-3-nitrobenzotrifluoride and 4-chloro-3-nitrotoluene at 35°C in dilute solution of benzene and carbon tetrachloride in microwave region. The relaxation time (τ), the distribution parameter (α) and the dipole moment (μ) have been evaluated from the measured dielectric data.

Gupta et al (1978) studied the dielectric absorption of some simple liquids viz. fluorobenzene, O-dichlorobenzene and O-chlorotoluene and their binary mixtures in dilute benzene solutions at the 3 cm. microwave region over the temperature range 20°C - 60°C and determined the relaxation time and the thermodynamic parameters viz. free energy, enthalpy and entropy of activation.

The results obtained are explained on the basis of polarity, size of the molecules and the change in the molecular environment. Wassink and Bordeijk (1978) determined the dielectric relaxation times for mixtures of N-methylformide, N-ethyl acetamide in carbontetrachloride by time domain reflectometry.

Sharma et al (1985) used a standard microwave X-band technique and Gopala-Krishna's single frequency concentrational variational method determined the dielectric relaxation times (τ) of the dilute solutions of N,N-dimethyl formamide (DMF), methanol and several DMF + MeOH mixtures in benzene at different temperatures and also calculated the thermodynamical parameters.

Agarwal (1986) measured the dielectric constant (ϵ') and dielectric loss (ϵ'') of four different compounds of different shapes viz. n-butyl chloride (linear) chlorobenzene and bromobenzene (planer) and tert-butyl chloride (nearly spherical) in benzene solution at 32°C and 9.96 GHz and observed that for nearly the same molar volume of the solute molecule the relaxation time (τ) is affected by molecular shape in the following manner

$$\tau_{\text{linear}} > \tau_{\text{planner}} > \tau_{\text{spherical}}.$$

Madan (1987) studied the dielectric absorption of thiophone, acetone, benzophenon and their mixtures in dilute solutions in the microwave region over a wide range of temperatures and developed a relation for calculating the relaxation times and thermodynamic parameters. The values agrees with the given data.

Pure Liquids:-

The earlier studies of molecular shape and dielectric relaxation have been reviewed comprehensively by Smyth. According to simple dielectric theory the dielectric constant of the polar liquids should be directly derivable from their chemical structures. But Morgan and Yger (1940) observed these values greatly different. They explain the depertures may be due to association or interaction causing the molecules to act as anassociated pairs in which the electric moment is low because the dipoles are so directed (a) to oppose one another or (b) the effect of internal friction or viscosity is restricting the motion of the molecules. Whiffen and Thomson (1946) from dielectric measurement obtained (τ) value for toluene, O-xylene, p-cyanine etc. in pure liquid state, which are in according to the size of the molecules.

Hiafelin (1946) determined permittivity of iso-butyl alcohol in pure and in viscous solvents. Strong and weak solution in benzene behaved in accordance with

Debye theory but the medium solution behaved differently from the simple theory.

Petro and Smyth (1948) observed the same effect as observed by Whiffen and Thomson in (1946), Garner (1948) showed that simple Debye theory does not hold for many insoluting liquids such as glycerine, phenolic resines and suggested an equation

$$\frac{1}{\epsilon''} = B\left(x^n + \frac{1}{x^n}\right) \qquad ...1.93$$

when $0 < n < 1$ represents dielectric behaviour more correctly the loss factor ϵ'' and $x = \omega\tau$ where τ = relaxation time.

From dielectric loss measurement of some rigid molecules of monosubstituted benzene in liquid state, Poley (1955) obtained the relaxation times which increases with the molecular sizes.

Müller and Smyth (1956) examined the direction of dipole moment with respect to the molecular plane on the relaxation behaviour of the molecules of different shapes and size in liquid state and showed that though the molecules 2, 4, 6 trimethyl pyridine and 2, 4, 6-trimethyl 1,3,5-trioxane are of equal size, dipole moment and viscosity in the liquid state, the two molecules have quite different (τ) values, because of the direction of the dipole moment were parallel and perpendicular respectively to the spheroidal molecular plane.

Petro and Smyth (1957) from the investigation in substituted benzene and pyridine in the liquid state observed a regular increase in the (τ) values with the increase in the size of the substituents.

Higasi et al (1960) reanalysed the experimental data of n-alkyl bromide in liquid state in terms of distribution betwene two limits given by Frolich (1949). The (τ) values in lower limit was associated with the relaxation time of internal rotation of $-CH_2Br$ group, while the upper limit to the orientation of the whole molecule.

Relaxation time (τ) and viscosity (η) has been experimentally determined by Bhanumati (1963) at different temperatures for a few liquids, such as α - chloronapthalenes, butyl-phthalene and iso-anylphthalene etc. The values of potential barrier heights for dipole relaxation (ΔH_τ) and that for viscous flow (ΔH_η) were evaluated from the linear plots of log (τT) versus ($\frac{1}{T}$) and log (η) versus ($\frac{1}{T}$) respectively. The calculated values of (ΔH_η) were found to be greater than (ΔH_τ) as the phenomenon of viscous flow considered the process of translation as well as rotation but only rotational process was considered in dipole relaxation .

Krishnaji and Manshingh (1964) reported that the dielectric relaxation of alkyl cyanides and of alkylthiols in liquid state. The relaxation time was in the order of increasing size of the molecules in former case and more than two relaxation behaviour in the latter case was found.

Bhattacharyya et al (1966) reported in polar liquids with rigid dipoles having moment (μ = 1.5D or less), the effect of dipole interaction was negligible.

Sinha, Roy and Kastha (1967) showed in 7 mm microwave region the temperature dependence of relaxation time of a number of polar molecules of different shape, size and dipole moments in very dilute solution of non-polar solvents. The dependence of (τ) at any temperature (T) on viscosity (η) of the solution is represented by τT = (constant) η^{γ}, where γ is the ratio of the heats of activation for dielectric relaxation and viscous flow.

Garg and Smyth (1973) reanalysed the dielectric data of anisole and aniline in liquid state. They obtained values for methoxy group rotation as 3.2 p. sec. and its weight fraction as 0.2 while these values in dilute solution are about 8 to 0.8 respectively.

Molecular Association of Associated and Associato-Associated Polar Liquids:

Molecular association may be expected to influence dielectric relaxation by modifying the structure of the liquid. The investigation of dielectric relaxation in this connection continued actively in recent years.

Mecke and Reuter (1949) made precision measurements of permittivity on various solution of CH_3OH, C_2H_5OH, nC_4H_6OH, $nC_8H_{17}OH$, C_6H_5OH, $PC_6H_4(ON)CH_3$ in C_6H_6, CCl_4 and cyclohexane at 20°C and 40°C. They computed the molecular association and found for alcohols and phenols dipole moment is reduced by association and the binding moment of oil group is usually not much more than half the value of the free unassociated molecules.

Kremmling (1950) made absorption measurements on aliphatic chloride and alcohols. He found difficult to sort out the effects due to polar association, H-bond formation, change of molecular shape, internal rotation, multiple relaxation times etc.

Brot (1956) made a conclusions from his measurements on straight chain alcohols $CH_3(CH_2)_nOH$ with n = 5-9 and 11. In second dispersion region the principle of superposition of relaxation time did not hold good. A third dispersion region near λ = 1 cm was assigned to the reorientation of the dipoles in the interior of the polymeric species.

Schellman (1957) developed equations which take into account the association in liquids on dielectric saturation. Srivastava and Varshni (1957) also suggested an equation for variation of dielectric constant of mixture of polar liquids (associated-associated) with concentration C and temperature $T^{o}K$

$$\epsilon = \left(l + \frac{m}{T}\right) + \left(p + \frac{q}{T^{1/2}}\right) \times C + Z C^{2} \qquad \ldots 1.94$$

where p, q, l, m and z are constants, variation of ϵ with C is linear, the equation has been illustrated for water methyl alcohol and water butyl alcohol mixtures with satisfactory results.

Conway (1959) examined theory of absolute reaction rate for the case of relaxation in associated polar liquids and showed the mechanism of absolute reaction rate to be consistent with other theoretically derived quantities and with mechanism of proton mobility in water. Muralidhara, Rao (1959) studied the dielectric loss and dielectric constant of two liquid mixtures n-butyl alcohol + glycerol (both associated) and Isobutyl alcohol + n propyl bromide (asso-non-associated). Two picks were observed in both the cases in ϵ''-frequency and ϵ'' - temperature curves. Schallamarch's (1946) suggestion was that the process of dielectric relaxation cannot be directly connected with individual molecules but is an disturbance over an appreciable region in the liquid does not appear to be valid in the said mixture.

Mc.Duffie Jr. and Litovitz (1962) studied the dielectric properties of the associated liquids such as butanediol, 1, 3, 2-methyl pentanediol 2,4,glycerol and hexanetriol, 1,2,6 over the temperature range - 20°C to + 10°C and over a frequency range of 0.01 to 1200 MHz. Dielectric relaxation times and their distributions have been determined and observed that (a) all four liquids exibit an assymetric distribution of relaxation times of the Davidson and Cole form, (b) with the exception of hexanetriol 1,2,6, the distribution of relaxation times becomes narrower with increasing temperatures. They concluded that the dielectric orientation is closely related to the structural breakup of the group and the structural break up is a co-operative process. They explained the temperature dependence on the width of the distribution may be due to decrease of group size with increase of temperature and as the groups become smaller, the structural decay process becomes more exponential. McDuffie Jr, Quinn and Litovitz (1962) measured the dielectric relaxation time in MHz region and at low temperature for glycerol water mixture. The mixtures ranging from relatively pure glycerol to equal molar concentration of glycerol and water. From the data a single distribution of relaxation times was infered for these mixtures rather than two individual distributions. They explained their experimental findings in terms of the group concept of Schallamach in which it was assumed that in a mixtures of associated-associated liquids, such as glycerol and water dielectric orientation occurs through co-operative effect in groups of molecules and these groups containing molecules of both kinds.

Dielectric measurements of Garg and Smyth (1965) on the normal alcohol form propyl to dodecyl in pure liquid state have shown three distinct dispersion regions as was previously reported by other workers. The relaxation times for 1st, 2nd, and 3rd. were 1 to 2.2×10^{-10} secs. 1.7 to 5×10^{-11} and 1.7 to 4×10^{-12} secs. respectively. The long rela-xation times are associated with polymeric clusters resulting from the strong hydrogen bonding between (-OH) group shortest relaxation times was ascribed to the orientation of the (-OH) group and the intermediate relaxation time was attributed to the rotation of the free alcohol molecules.

Barbenza (1968) reported the dielectric property of methyl alcohol (pure) in temperature range 5° to 55°C and at wave length from 15 to 5 cm. Can be represented by a single relaxation time. The strong temperature dependence of extrapolated values of ϵ_{∞} leads to a second dispersion region. Moreover, the measurement show that the main dispersion can be described as a rate process with an activation energy of 3.4 K Cal/mol.

Rizk, I. Elanwar (1970) measured the frequency dependence of complex dielectric constant of glycerol-Iso propyl alcohol and glycerol-Isobutyl alcohol within the frequency band 10^5 to 10^7 c/s and the range of temperature -19 to + 50°C for entire concentration range. It is found for each mixture there is one main relaxation process. The average relaxation time in each system is found to vary exponentially with the molecular concentration of glycerol. The increase of glycerol content in each system is accompanied by a linear increase of the activation enthalpy and entropy change for dielectric relaxation. It is suggested that the dielectric relaxation in these mixtures occurs through a co-operative effect in groups containing molecules of both kinds and that the interaction between these molecules are stronger in glycerol-isobutyl alcohol system than in glycerol iso-propyl alcohol system.

Purohit and Sharma (1971) determined the dielectric constant (ϵ') and dielectric loss (ϵ'') of methanol, ethanol, 2-propanol, 3-methyl-1-butanol and 1-butanol in benzene solution for concentration varying from 0.004 to 0.08 weight fraction in the X-band. They found in all cases except 1-butanol, the tan δ - concentration curve shows a marked increase in the concentration range 0.03 - 0.04 mol. fraction and this behaviour has been explained as due to the formation of dimers by association and due to solute-solvent interaction.

Sen and Ghosh (1972) and Ghosh and Sen (1980) calculated the dielectric relaxation time of some normal primary alcohols in nonpolar solvents from radiofrequency conductivity measurements. They observed that the rate of breakup of the cluster of molecules is affected with dilution in different nonpolar solvents.

Van-Gemert and Deloor (1973) investigated dielectric relaxation and activation energies of some normal alcohols in nonpolar solvents. The relaxation time for alcohol benzene mixtures are found in all cases smaller than those observed for other solvents, the energy of activation in different solvents do not differ significantly, but are constantly higher than for the pure alcohols.

Rajyan, Ramasastry and Murthy (1977) studied dielectric dispersion of two pure liquids glycerol and diethylene glycol at radiofrequency, Uhf and microwave region at 80°C and confirmed the Cole Davidson type dispersion.

Mulecki and Balamicka (1980) studied the self association of t-butyl alcohol and developed a method for a simultaneous determination of three independent values of free energy of self association from experimental datas.

Prakash and Rai (1986) determined dielectric constant (ϵ'_{12}) and dielectric loss (ϵ''_{12}) at different concentration of five mixture of aniline and nitrobenzene mixture I (25% nitrobenzene and 75% aniline), mixture II (50% nitrobensene + 50% aniline) and mixture III (75% nitrobenzene + 25% aniline) and also of pure nitrobenzene using benzene as a nonpolar solvent at different temperatures and frequencies. ϵ'_{12} and ϵ''_{12} found to increase linearly with the addition of nitrobenzene in the aniline - nitrobenzene mixture except for mixture III. Similar deviation have also been recorded in relaxation times and thermodynamic parameters. These deviations may be attributed either to the existance of interassociation or to the complex formation in the last mixture (III).

Electrical Conductivity of Dielectric Liquids in D.C. And High Frequency Electric Fields:-

Quincke (1895) first showed that the current through the liquid depends upon voltage, gap width and nature of the liquid and concluded that the current is non-ohmic and probably electrolytic in origin.

Curie (1902) observed that the electrical conductivity of petroleum ether, carbon tetrachloride carbondisulphide and benzene was increased by exposure to gamma rays or X-rays.

Schweilder (1907) showed experimentally that the conductivity of saturated hydrocarbons decreased with increased purification.

Jaffe (1906) studied the current voltage characteristic of hexane when irradiated by gamma-ray and considered that the current as the sum of the two separate currents, one rising to a saturation value like the current in the gas, while the second is the ohmic current. In 1909 he succeded in measuring the small current developed when a voltage was impressed on highly purified hexane in a brass conductivity cell. His result shows that in pure state the conductivity of hexane was due to cosmic radiation and near about 146 ions were produced per c.c. per sec. similar result was obtained for heptane and petroleum ether, but Jaffe (1913) discarded this view of separate currents, in favour of a theory according to which the ions are produced in very densely packed column isolated from each other. The columns are the tracks of the photoelectrons reacted by γ -rays and he concluded that the field of less than 100 V/cm, a large part of the current is caused by external ionising radiation.

Nikuradse (1932) studied the current in liquid dielectrics over the wide range of field strength and gap width. He observed that current depends on the purification of the liquid, electrode geometry and electrode material, but independent of pressure but when all the ionizing agents such as X-rays and other radio active sources were removed there still exists a residual or natural conductivity in these liquids. The residual conductivity of a supposedly pure insoluting liquid has been reduced by a factor of a thousand or more by treating it in such a way as to remove traces of water. When a reasonable low limiting value of conductivity has been reached, the next problem is to find out, how it originates. However, there is no general agreement as to its characteristics.

Baker and Boltz (1937) and Dronte (1940) interpreted their investigation to mean that the conductivity is due to thermoionic emission from the cathode combined with Schottky effect. Lepage and Dubridge (1940) observed that log (I) is a linear function of (E) and later concluded that the current is due to field enhanced thermoionic emission and derived the following relation

$$J = AT^2 \exp\left[-\frac{\phi e}{kT} + \frac{1}{2.3RT}\left(\frac{e^3 E}{K'}\right)^{1/2}\right] \qquad \ldots 1.95$$

where K' is the dielectric constant of the liquid.

Plumley (1941) and Pao (1943) interpreted with experimental supports that the potential dissociation theory originally proposed by Onsager (1934) for very weak electrolytes. According to their view there are even in purest hydrocarbon such as hexane, a very small number of ions exist resulting from the sponteneous dissociation of molecules.

Ruhle (1943) developed the idea of induced conduction and Eck (1949) showed that the variation of current strength with time can be represented by the equation

$$\left(I - I_{\infty}\right) = \left(I_0 - I_{\infty}\right) e^{-kT} \qquad \ldots\ 1.96$$

where I_0 is the initial current, I_{∞} is the limiting current and K is the constant which contains the ionic mobilities. The effect is assumed to be due to initial existence of the ionic clusters in the body of the liquid which gradually disperse. He performed experiments on acetone, nitrobenzene and acetone substituted compounds.

Goodwin and Mac-Fadyen (1953) showed that the current is a function of electrode gap width and field strength. Extrapolation to zero gap width showed the existence of a zero width current that obey a field emission relation of the form

$$J = \left[A E^2 \exp\left(-b/E\right)\right] \qquad \ldots\ 1.97$$

Jaffe and LeMay (1953) studied time dependent current in hexane for wide gap and voltage of low value and concluded that the current are ionic. The breakdown in dielectric liquid gives additional information concerning the conduction current in dielectric liquid.

Green (1955) has studied the conduction and breakdown in hexane and assumed that positive ions are always present in the liquid, because of external radiation or dissociation of impurity molecules. When an external field is applied, these ions drift towards the cathode but the cathode surface layer impedes their immediate neutralization. The ions then set up a local field across the surface layer that tend to produce electron emission. The size of the local field depends upon the magnitude of the ionic current and the probability of neutralisation of the ions.

Standthammer and Sayer (1957) have obtained evidence for the formation of pure ions in cyclohexane and cyclohexane saturated with water.

Riehl (1955) and Keepler (1960) observed that the level of conduction of some polynuclear aromatic compounds, such as napthalene and anthracene increases by a factor 10^3 to 10^6 on melting. It has been suggested that the higher conduction in molten form is due to higher mobility of the charge carrier.

Hart and Mungali (1957) observed that the conduction current in chlorobenzene continued to decrease even after continuous distillation for as long as three months.

Le Blance (1959) suggest that electrons exist in n-hexane in quasi trapped state.

Forster (1962) studied the nature of conduction in pure hexane and benzene and also at different concentrations of n-hexane-benzene mixture and obtained a relation $\sigma_S = \sigma_H \cdot e^{CK}$ where σ_H is the conduction of n-hexane, K is the constant and C is the concentration. He further suggested that the transformation of electron from one benzene molecule to another is a function of the number of molecules located between the electrodes and assumed that only electron migration rather than electron diffusion is valid in the conduction process. The increase of conduction due to increase of temperature of the liquid would be the result of enhanced transfer probabilities resulting from an increase of molecular collision leading to electron transfer.

Forster (1964) again showed that conduction in alephatic hydrocarbons is most probably related to the presence of polar impurities or trapped electron present in the liquid or generated at the electrode surface. In unsaturated hydrocarbons experimental evidence suggested the existance of electronic conduction. He suggested an empirical relation for the activation energy of quasitrapped mechanism $\epsilon_a = 0.067$ P eV, where P is the number of peripherial π electrons and thus confirmed the electronic nature of the conduction current.

Silver (1965) has developed a theoretical model for conduction of current in insulating liquids which shows that it is possible to calculate from the measurement of potential distribution, the rate of formation and motion of charges. One consequence of his theory is that the conductivity is a function of electrode spacing and the form

$$V = \left(AJ^2 + BJL\right) \qquad \ldots 1.98$$

where A and B are constants, V is the applied voltage, J is the current density and L is the gap length. This theory explained successfully the variation of conductivity with electrode spacing at various constant voltage in benzene, but the result in nitrobenzene suggested that the cathode acts as an injector of electrons.

Felsenthan and Vonne Gut (1957) concluded that the enhancement of conductivity in insulating liquid may be due to the presence of depressed conducting particles in the insulating liquids.

Adamczewski and Jachym jointly (1968) investigated the electrical conductivity on number of saturated hydrocarbons which are characterised by the conductivities of two order of magnitude lower than those of other liquids and concluded that the natural conductivity values of organic liquids is a function of temperatures. They further observed that among all the investigated organic compound which occurs in liquid state the lowest conductivity values are found in nonpolar liquids.

Adamczewski (1969) measured the ionic mobilities in hexanes, heptanes and nonane, and other mixtures. He observed that mobility value in all cases lies between 7.2×10^{-5} to 5.8×10^{-4} $cm^2V^{-1}sec^{-1}$.

Gaspard and Gosse (1970) gave a clear evidence of ionic conduction in polar dielectric. They used membranes electrodes and gave evidence for three distinct regions of conduction and in each case the conduction is ionic in nature. It is due to the impurities at low and medium fields and injections of ions at high fields. They observed considerable erratic variation of current with time under electric field.

Lohneysen and Nagerl (1971) determined the mobility of polar liquids by temporal variation of current method and concluded that the existance of natural charge carriers in liquids are of two kinds having mobilities μ_1^+ and μ_2^- .

Nicolan, Secareanu and Moisescu (1971) studied the electrical conductance of n-butyl and amyl alcohol in the temperature range of 0-97°C. The variation of conductance with temperature for those alephatic alcohols was explained in the light of intermolecular hydrogen bonding and concluded that intermolecular hydrogen bonding plays an important role in the mechanism of electrical conduction.

Sen and Ghosh (1974) and Ghosh and Sen (1980) determined the r.f. conductivity of some polar associating and non-associating dielectric liquids in the solution of different non-polar solvents and temperatures and calculated the free ion density, ionic mobility and energy of activation for conductivity.

Ghosh, S.K., Ghosh A.K., and Acharyya S. (1980) established a relation for calculating the h.f. conductivity of polar liquids in infinitely dilute nonpolar solvents at microwave region and showed that the h.f. conductivity varies linearly with concentration.

Ghosh and Choudhury (1982) measured the r.f. conductivity of pure glycerol and glycerol water mixture at 1 MHz frequency and at various concentrations over the temperature range of 20° to 50°C and calculated the ionic mobility and the average ion number density. They observed a marked decrease in electrical resistance with the addition of water as impurity and thus confirmed that the impurity conduction prevails in pure polar liquid and the conduction of glycerol water mixture is an exponential function of concentration.

Critical Point Phenomena in Electric Resistivity of Binary Liquid Systems:

The phenomena of critical opalescence was first observed by Andrews (1869) in connection with his classical investigation of carbon-dioxide isothermal. After that many investigators came forward to unveil the different properties such as scattering, change of dielectric constant, viscosity, ultrasonic absorption and electrical resistance or conductivity of critical opalescent binary liquid mixture at and very near to critical temperature.

Friedlander (1901) probably the first worker to report on the study of transport phenomena for a binary liquid mixture near the critical point and showed qualitatively that the electrical conductivity is less sensative to critical behaviour than the viscosity in isobutyric acid-water mixture.

Gammel and Angell (1972) studied the temperature dependence of the resistivity for the system isobutyric acid + water but could not detect any influence due to critical fluctuations. Stein and Allen (1972) established the existance of a strong divergence in the temperature derivative of the resistivity for the same binary liquid mixture very close to critical temperature T_c.

Again Stein and Allen (1973) measured the electrical resistance of sealed solutions of isobutyric acid water at the critical composition in the reduced temperature range $3.3 \times 10^{-7} \leqslant \epsilon \leqslant 6.6 \times 10^{-2}$, using a Jones a.c. bridge and lock the amplifier. The temperature derivative of the resistance exhibits a strong divergense very close to T_c.

Further, Gammell and Angell (1974) measured the electrical conductivity of the same system for several concentration and also at critical concentration. Measurement were made using a hybrid conductance/viscosity cell a modified ubbelhode viscometer which permitted almost simultaneous measurements of viscosity and conductance. The results of their measurement indicated that, the electrical conductivity does not exhibit any critical anomaly down to $T_c + 0.03^\circ C$ even which it is well into the region (T_c to $T_c + 2^\circ c$), when the viscosity anomaly becomes apparent.

Jasnow, Goldburg and Samura (1974) analysed the data of Stein and Allen and showed that the data below a value of $\epsilon = \frac{T - T_c}{T_c} = 5 \times 10^{-5}$ may be influenced by gravitational effects which has been not accounted for the original analysis. They suggested a fit equation of the form $\frac{R_c - R}{R_c} \approx A t^{1-\alpha} + B t$ (where α is the specific heat exponent), when the temperature range is above the value $\epsilon = 5 \times 10^{-5}$.

Shaw and Goldburg (1976) measured the electrical conductivity of several binary liquid systems such as pure phenol-water, Kcl doped phenol water and isobutyric acid-water near their critical point. All the measurements were made within the reduced temperature range $10^{-5} \leqslant \epsilon \leqslant 10^{-2}$ and all the systems showed clearly the existance of a singular contribution to the conductivity. A least squares fit of the data for the equation $\left(\frac{\sigma - \sigma_c}{\sigma_c}\right) \propto \epsilon^{\theta} + \sigma_{bkg}$ showed that the singularity could be characterised by a critical exponent $\theta = 0.70^{+0.15}_{-0.10}$ Critical point phenomena in the electrical resistivity of binary liquid system $CS_2 + CH_3CN$ and $CS_2 + CH_3NO_2$ studied by Gopal et al (1976). They reported that the liquid mixture at the critical composition, the resistance of the system above T_c follow the relation $R = R_c - A(T - T_c)^b$ with the critical exponent b = 0.6 ± 1 and below the conductivity of the two phases obey a relation

$$(\sigma_2 - \sigma_1) = B(T_c - T)^{\beta}$$

with critical exponent $\beta = 0.34 \pm 0.02$.

Kumar and Gopal (1979) measured the electrical resistance of the binary liquid system, cyclohexane + acetic anhydride in the critical region ($\epsilon \approx 10^{-6}$) both in the pure mixture and when the mixture is doped with small amount ($\approx$ 100 ppm) of H_2O/D_2O impurities.

They showed that the critical exponent $b \approx 0.35$ in the fit of the resistance data to the equation appreciably by the impurities, but there is a sign reversal of $\frac{dR}{dT}$ in the non-critical region.

Sen and Ghosh (1980) measured the r.f. conductivity for methyl alcohol + nhexane, methyl alcohol + carbondisulphide and methyl alcohol + cyclohexane at critical temperature. Ghosh and Datta (1985) measured the electrical conductivity and mobility at critical solution temperature of five binary liquid systems and observed a sudden change in ionic mobility and viscosity of binary liquid solution at the critical point.

1.10. SCOPE AND OBJECT OF THE PRESENT INVESTIGATION-

It is evident from the brief review of the earlier works in both theoretical and experimental aspects on dielectric relaxation time and electrical conductivity of polar liquids that it is possible to obtain certain informations regarding the state of a system and the structure of the molecules. The interaction of electromagnetic field with polar molecules results into the orientation polarization of molecules which gives rise to dielectric relaxation. It has been admitted that dielectric relaxation offer an important method to study the dipole-moment and the shape and size of the molecule in the pure and dilute state.

Various methods have been reported for determining the relaxation time (τ) of pure liquids and even the relaxation time in dilute solution of nonpolar solvents, but it invites a slight personal error within a certain range. Recently in the process of determination of dipole moment (μ) of polar liquids in nonpolar solvent from the r.f. conductivity measurement shows that the relaxation time (τ), plays a very significant role in yielding the proper value of dipole moment (μ). This particular idea open the door to evaluate the relaxation time at dilute solution (τ_s) from the high frequency or microwave conductivity data. The method of determination of τ based on sound mathematical foundation. The accurate value of τ_s of the polar solute is of much importance as it throw much light on the structure of the molecule and also for calculating the exact value of dipole moment.

The ultra high frequency (UHF) and microwave conductivity data in the low concentration region are of much interest as they reveal a completely different situation in comparison to those of high concentration region.

The dipole-moment calculation from the value of relaxation time (τ_s) of polar solute in non polar solvent at lower and higher concentration gives an idea of the formation of monomer and dimer. It also predict the association of polar unit.

Thus it may be concluded that the variation in the value of dipole moment (μ_j) at different concentrations for the substituted molecules in benzene may be due to (i) the difference in the value of group moments and (ii) inductive effect.

Further the variation of r.f. conductivity, relaxation time and thermodynamical parameters of some alephatic monohydric alcohol in a nonpolar solvent at various concentrations and temperatures gives an idea of the rate of breaking of hydrogen bonding of the liquids with dilution and also the dipole orientation at infinite dilution.

Thus the scope and object of the present investigations were as follows : -

(I) To study the microwave conductivity and dipolemoment of polar dielectrics, it is expected that the experimental results will reveal some fresh ideas on the variation of dipolemoment with temperature of organic polar liquids.

(II) To study the microwave conductivity and dipolemoment of substituted benzenes, the experimental conductivity data of polar, nonpolar liquid mixtures at lower and higher concentration region may give some suggestion on the formation of dimer and monomer at higher and lower concentrations of the mixture.

(III) The ultra high frequency conductivity data of polar-nonpolar liquid mixtures at infinite dilution may be used to estimate the temperature and concentration dependence of dipole moment of the following liquids (a) N-methyl acetamide in benzene (b) N-methyl acetamide in dioxane and (c) p-Bromonitrobenzene in benzene.

(IV) The conductivity, relaxation time and energy of activation of some aliphatic alcohol in benzene at infinite dilution may suggest that the rotation of dipole molecule is not hindered by the interaction with the other neighbouring dipole molecules, the rotation is due to rotational orientation of the (-OH) group of a molecule.

(V) The experimental data of energy of activation and dipole moment of water may be used to calculate the correlation factor 'g' of water, which may be used to compute the bending of the bond angles with temperature.

(VI) The electrical conductivity of binary opalescent liquid mixture near critical temperature measured at radio frequency (400 KHz) in order to study the high frequency effect on critical exponent θ and to show that the results are consistent with the existance of a conductivity singularity of the form $\sigma_{\mathrm{sing}} = A\epsilon^{\theta}$

The experimental results and discussions of the works have been presented in chapter III to chapter VIII and a summary of the results is given in chapter IX.

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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)

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

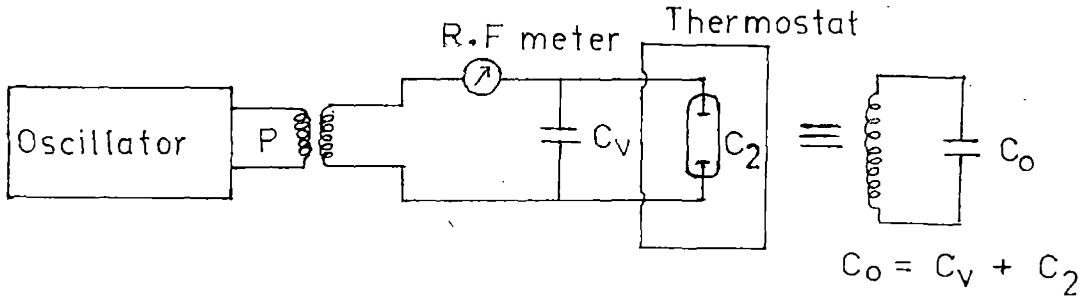
and

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

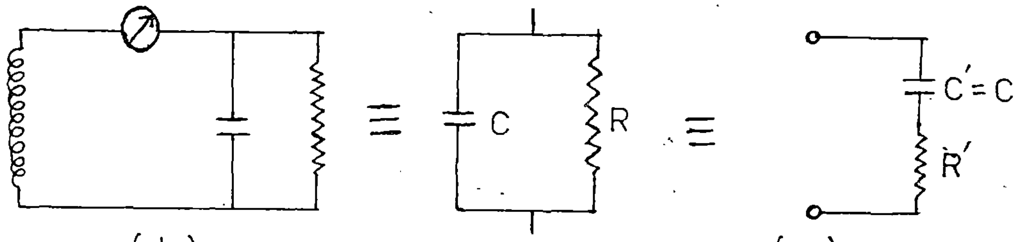
and as $\omega^2 C^2 R^2 >> 1$, then $C' = C$.

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

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



(a) COUPLED CIRCUIT



(b) (c)

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

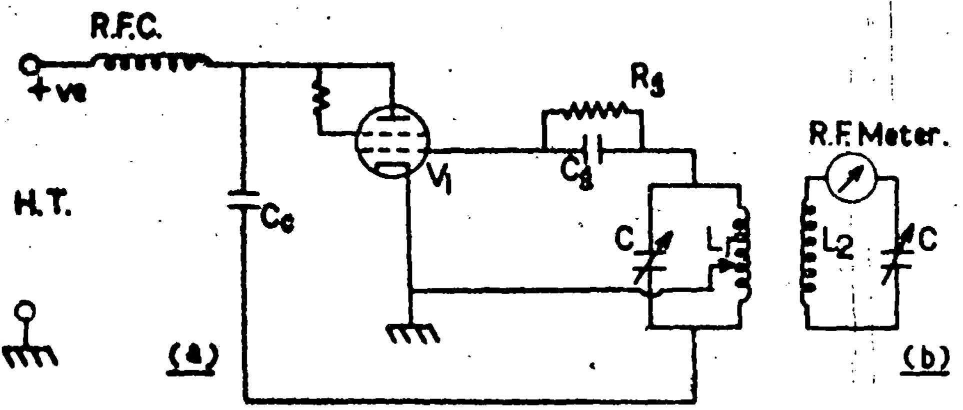


Fig. 2.2. (a) Radio frequency oscillator. (b) Secondary tuning circuit.

List of components.

V_1 = 6L.6.
R_g = 30 kΩ
C_g = 350 P.F.
C = 0-500 P.F.

C_c = ·01 μF.
R.F.C. = Radio frequency choke.
R.F. Meter = Radio frequency milli ammeter.

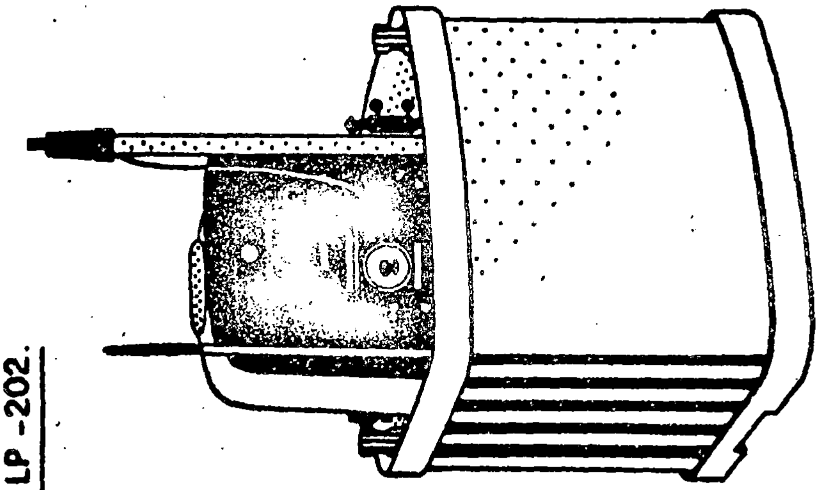


FIG. 2.6.

Neo-Thermostat
Type No. LP-202.

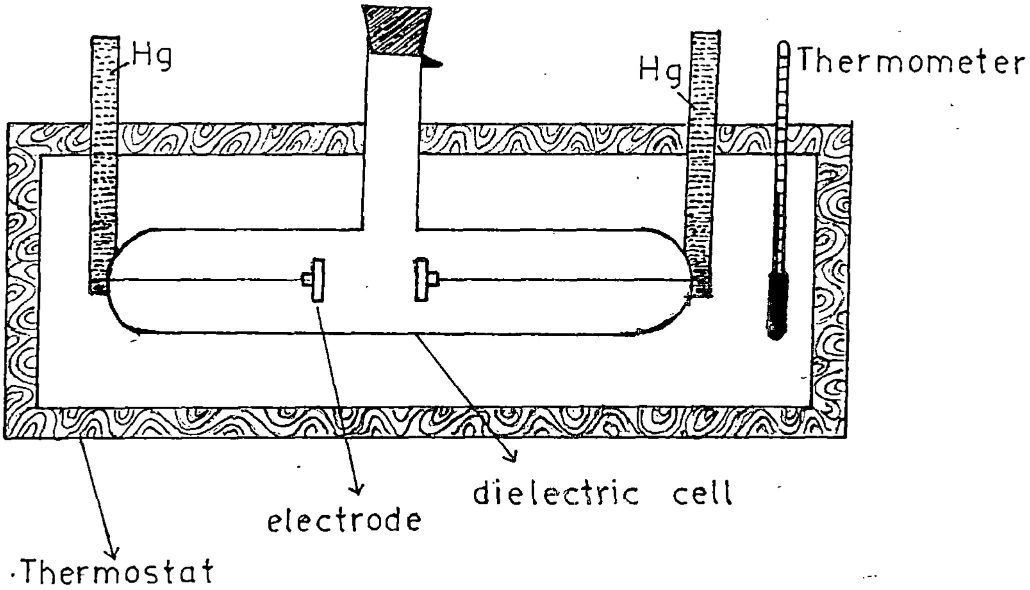


Fig - 2.3

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

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

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,

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

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

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

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

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

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

The complex dielectric constant of the solution can be written as

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

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 $\epsilon'_{ij} >> \epsilon''_{ij}$. Therefore microwave conductivity of the solution becomes,

$$K_{ij} = \frac{\omega}{4\pi} \epsilon'_{ij} \qquad \text{as} \quad \epsilon'_{ij} >> \epsilon''_{ij}$$

Considering Debye equation (1.36, 1.37) we can write

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

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

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

$$\epsilon'_{ij} = \epsilon_{ij\infty} + \frac{\epsilon''_{ij}}{\omega\tau} \qquad \ldots 2.17$$

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

$$K_{ij} = K_\infty + \frac{K'_{ij}}{\omega\tau_s} \qquad \ldots 2.18$$

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,

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

where μ_j is the dipole moment of polar solute, N is the Avogadro's number, k is the Boltzmann constant $C_j = \frac{\rho_i W_j}{M_j}$ 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 = $\left(\frac{\epsilon_i + 2}{3}\right)^2$, 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),

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

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

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

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

∴ Dipole moment

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

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

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

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

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

Therefore,

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

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

$$\eta = \frac{hV}{N} e^{\Delta F_\eta / RT} \qquad \ldots\ 2.25$$

where ΔF_η 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

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

Then eq. (2.25) may be written as

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

where $B = \frac{hN}{V}$, ΔH_η 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

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

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.

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

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

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

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.

CHAPTER III

MICROWAVE CONDUCTIVITY AND DIPOLE MOMENT OF POLAR DIELECTRICS

Introduction:

One of the main application of the dielectric theory in physics and chemistry is still the determination of permanent dipole moment of molecules. These values can be of great use, in both organic and inorganic chemistry for the elucidation of molecular structures and also in the study of the chemical bond. In view of the importance of the permanent dipole - moment of molecules we have tried to determine the dipole moment of the polar molecule in non polar solvent at different temperatures.

The temperature dependence of dipole moment of a polar liquid is not a new concept, (Ras and Bordewijk, 1971) yet it is found to occur when the polar - nonpolar liquid mixture is subjected to an alternating microwave electric field. There are several methods (Gopala Krishna,1957, Sen et al 1972) to compute the dipole relaxation time τ_S of polar liquid dissolved in nonpolar solvent under the application of radio - frequency and microwave alternating electric field.

Gopala Krishna's concentration variation method in the microwave region and Sen's graphical method in the r.f. region always invite a slight personal judgement to locate the exact and accurate value of τ_s within a certain considerable range. In order to avoid this difficulty we, in the process of derivation of the dipole moment μ_j of polar liquids in nonpolar solvent from the conductivity data in h.f. region devised a simple procedure (Ghosh et al, 1980, Datta et al 1981) to obtain the relaxation times τ_s of polar liquids from the microwave and radiofrequency conductivity data based on sound mathematical foundation. When the frequency of the impressed field exceeds a certain critical value, the permanent dipoles of solute molecules cannot follow the exact alternation of the applied field. This measurable lag is commonly known as dielectric relaxation, and the relaxation time of a solute is defined as the lag in response of polar solute with the forces to which it is subjected. Using the slope of concentration variation of total microwave conductivity K_{ij} at infinite dilution we attempted to obtain the relaxation time at different temperatures with the single μ_j value as obtain from literature. We found that the single value of μ_j could not yield the magnitude of τ_s though it gave the relative temperature dependence of computed τ_s only. This fact at once indicates that in the h.f. region μ_j is not a fixed quantity, but most probably it slightly varies with temperature to ascertain the actual magnitude of τ_s.

Theory: -

According to Murphy and Morgan (1939) the h.f. conductivity is a complex quantity K^*, where

$$K^* = K' + jK'' \qquad \ldots\ 3.1$$

In the case of polar nonpolar liquid mixture the high frequency conductivity can be represented as

$$K_{ij} = K'_{ij} + j K''_{ij} \qquad \ldots\ 3.2$$

where K'_{ij} is the real part of the conductivity $\left[K'_{ij} = \frac{\omega \epsilon''_{ij}}{4\pi} \right]$ and K''_{ij} is the imaginary part of the conductivity $\left[K''_{ij} = \frac{\omega \epsilon'_{ij}}{4\pi} \right]$ of the solution.

Now the magnitude of the total high frequency conductivity can be written as

$$K_{ij} = \left(K'^{2}_{ij} + K''^{2}_{ij} \right)^{1/2} \qquad \ldots\ 3.3$$

but the magnitude of K_{ij} is usually calculated from the relation

$$K_{ij} = \frac{\omega}{4\pi}\left(\epsilon''^{2}_{ij} + \epsilon'^{2}_{ij}\right)^{1/2} \quad \ldots 3.4$$

But in the microwave region ϵ'_{ij} of the solution is very small and equals to the optical dielectric constant, but still $\epsilon'_{ij} \gg \epsilon''_{ij}$ and ϵ''_{ij} is responsible for the absorption of electrical energy to yield to polarisation.

Now from the eq. (3.4) the total conductivity should be

$$K_{ij} = \frac{\omega\epsilon'_{ij}}{4\pi} = K''_{ij} \quad \ldots 3.5$$

Thus the total conductivity of the solution equals to the imaginary part of the conductivity in the microwave frequency.

But for high frequency it can be shown by using Debye equations

$$\epsilon' = \left(\epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1+\omega^2\tau^2}\right) \quad \text{and} \quad \epsilon'' = \frac{(\epsilon_s - \epsilon_\infty)\omega\tau}{1+\omega^2\tau^2}$$

the h.f. dielectric constant,

$$\epsilon'_{ij} = \epsilon_{ij\infty} + \epsilon''_{ij}/\omega\tau_s$$

or,

$$\frac{\omega \epsilon'_{ij}}{4\pi} = \frac{\omega \epsilon_{ij\infty}}{4\pi} + \frac{\omega \epsilon''_{ij}}{4\pi \omega \tau_s}$$

$$\therefore \quad K_{ij} = K_\infty + K'_{ij}/\omega\tau_s \qquad \ldots 3.6$$

where $\epsilon_{ij\infty}$ is the optical dielectric constant of the solution and K_∞ is a constant and τ_s is the relaxation time of the solute molecule in solution.

Now, the real part of h.f. conductivity K'_{ij} of polar nonpolar solution is obtained from eqn. (1.72) as

$$K'_{ij} = \left(\frac{\epsilon_{ij}+2}{3}\right)^2 \frac{N C_j \mu_j^2}{3kT} \frac{\omega^2 \tau_s}{1+\omega^2\tau_s^2} \qquad \ldots 3.7$$

Smyth (1955) introduced the idea of weight fraction W_j and replaced the molar concentration of solute C_j by $C_j = \rho_{ij} W_j / M_j$ where ρ_{ij} is the density of the solution, M_j is the molecular weight of the solute. Hence from eq. (3.7) we get

$$K'_{ij} = \frac{\mu_j^2 N \rho_{ij} F_{ij}}{3 M_j kT} \cdot \frac{\omega^2 \tau_s}{1+\omega^2\tau_s^2} W_j \qquad \ldots 3.8$$

where μ_j is the dipole moment of polar solute, N is the Avogadro number, k is the Boltzmann constant and

$$F_{ij} = \left(\frac{\epsilon_{ij} + 2}{3}\right)^2$$

is the local field.

Since K_{ij} is a function of W_j, so we have from eq. (3.6)

$$\left(\frac{dK_{ij}}{dW_j}\right)_{W_j \to 0} = \frac{1}{\omega\tau_s}\left(\frac{dK'_{ij}}{dW_j}\right)_{W_j \to 0}$$

or

$$\left(\frac{dK'_{ij}}{dW_j}\right)_{W_j \to 0} = \omega\tau_s\left(\frac{dK_{ij}}{dW_j}\right)_{W_j \to 0} = \omega\tau_s\beta \qquad \ldots 3.9$$

where β is the slope of K_{ij} vs W_j curve at $W_j \to 0$ the density ρ_{ij} of the solution becomes ρ_i the density of the solvent and the local field F_{ij} of the solution is F_i = the local field of the solvent = $\left[(\epsilon_i + 2)/3\right]^2$

Under the circumstances, eq.(3.8) on being differentiated with respect to W_j and as $W_j \to 0$ takes the form

$$\left(\frac{dK'_{ij}}{dW_j}\right)_{W_j \to 0} = \frac{\mu_j^2 N \rho_i F_i}{3 M_j kT}\left(\frac{\omega^2 \tau_s}{1 + \omega^2\tau_s^2}\right) \qquad \ldots 3.10$$

From eq. (3.9) and eq. (3.10) we get

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

or,

$$\frac{1}{1+\omega^2\tau_s^2} = \beta \Big/ \left(\frac{\mu_j^2 N \rho_i F_i}{3 M_j k T} \cdot \omega \right) = b \;(\text{say}) \qquad \ldots 3.11$$

or,

$$\tau_s = \frac{1}{\omega} \sqrt{\frac{1}{b} - 1}$$

or,

$$\tau_s = \frac{1}{2\pi f} \sqrt{\frac{1}{b} - 1}$$

when $\omega = 2\pi f$ is the frequency of the applied field. When $f = C/\lambda$ C is the velocity of electromagnetic radiation λ is the wave length.

$$\therefore \quad \tau_s = \frac{\lambda \times 10^{-10}}{18.84} \sqrt{\frac{1}{b} - 1} \qquad \ldots 3.12$$

Now from eq. (3.11) the dipole moment of the solute can be written in the form

$$\mu_j = \left(\frac{3 M_j k T}{N \rho_i F_i} \cdot \frac{\beta}{\omega b} \right)^{1/2} \qquad \ldots 3.13$$

The eq. (3.12) is used to compute b from reported τ_s data and hence the dipole moment of polar solute μ_j when it is dissolved in a nonpolar solvent.

Results and Discussions:

The radiofrequency and high frequency conductivity (Sen and Ghosh, 1972) of polar nonpolar liquid mixture is comparatively easy to measure down to very low concentration by the help of Hartley and Klystron valve oscillator in the laboratory. But as the experimental conductivity data under radio frequency and microwave electric fields are very scanty, it is therefore, used the available concentration, variation experimental data for ϵ''_{ij} and ϵ'_{ij} of seven systems in benzene such as: 2-5 dichloronitrobenzene and 2-5 dibromonitrobenzene under 3.13 cm. wavelength electric field (Pant et al, 1977) and 3-nitro-O-anisidine, 2-chloro-p-nitroaniline, p-phenetidine, O-nitroaniline and p-anisidine under 3.17 cms. wavelength electric field (Some Vanshi et al 1978) to obtain the corresponding experimental microwave conductivity K_{ij} values from the eq. (3.4) which is the extended relation of Murphy and Morgan

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

at various temperatures 20°C, 30°C and 40°C. The K_{ij} values of the above mention solutes in benzene solution are plotted against weight fraction (W_j) at different temperatures are shown in fig. (3.1) and Fig. (3.2).

The temperature dependence of K_{ij} for each system is vividly exposed in the plot. But at the lower concentration region the conductivity K_{ij} varies almost linearly with W_j . As the weight fraction W_j approaches to zero, it is assumed that the solvent benzene possesses a constant value of conductivity which is independent of experimental temperature. It is considered because of the fact that the quantity ($\rho_{ij} F_{ij} / T$) in eq.(3.8) approaches nearly a fixed value which is in the neighbourhood of 0.006. Consequently, at $W_j = 0$, the conductivity of a given system at all temperature remain the same. Nevertheless, at $W_j = 0$ the K_{ij} values of different systems are different. This is due to solvation effect (Datta et al 1981).

From Fig. (3.1, 3.2) it is clear that at $W_j = 0$ i.e. at infinite dilution where the solute molecules immersed in macroscopic amount of solvent and meeting of the curves at a point indicate that there are no effect of temperature on K_{ij} , therefore the change

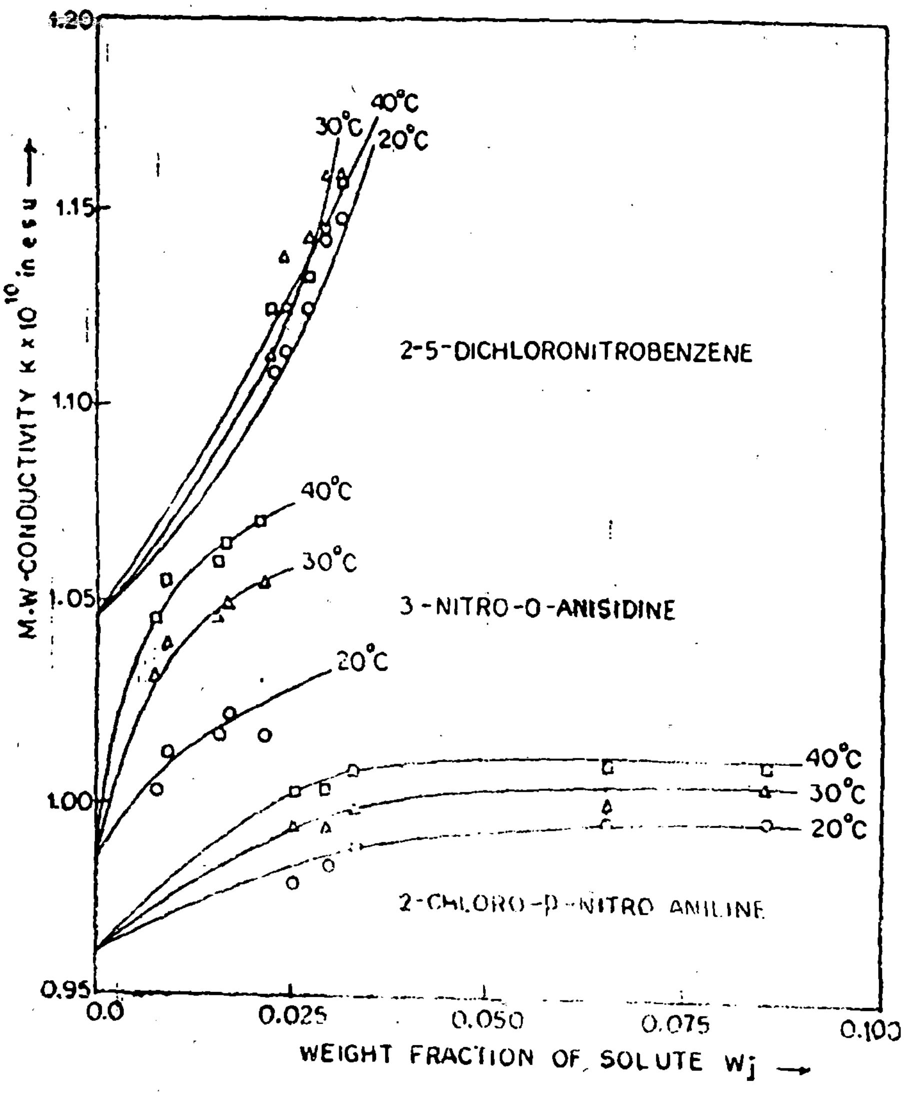


Figure 5.1-Microwave conductivity K is plotted against weight fraction ω_j at 20°C, 30°C and 40°C.

———○————○———at 20°C,

———△————△———at 30°C,

———□————□———at 40°C.

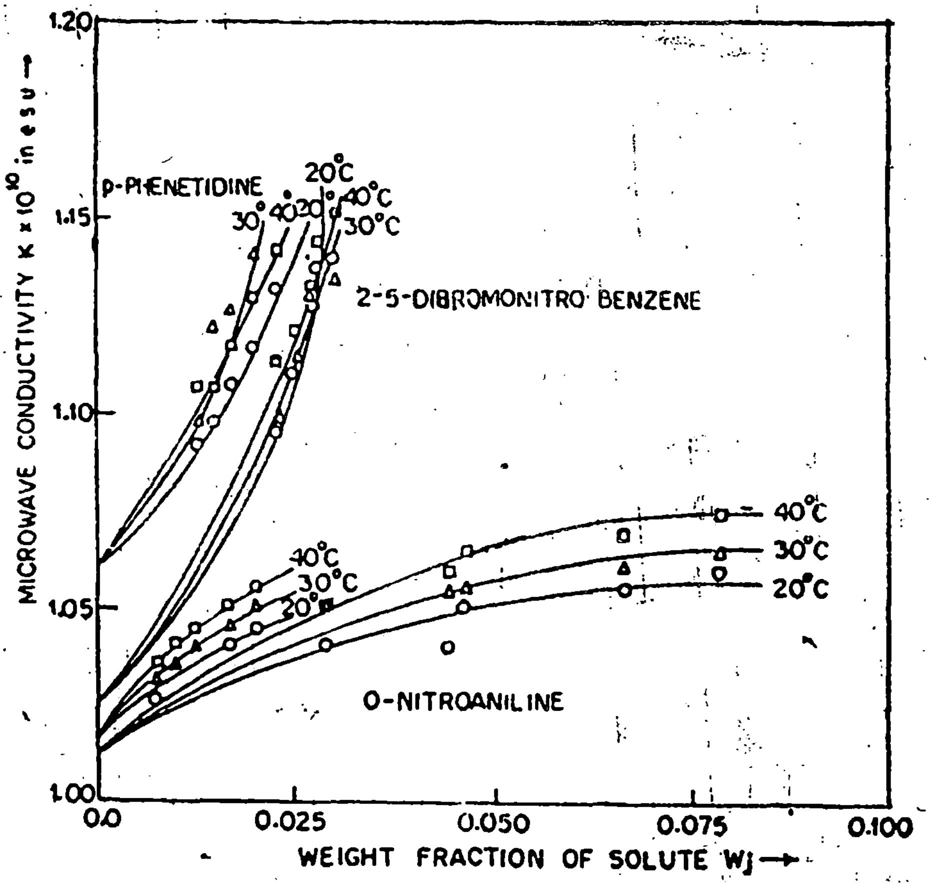


Figure 3.2 Microwave conductivity *K* is plotted against weight fraction ω_j at 20°C, 30°C and 40°C.

——— ○ ——— ○ ——— at 20°C,
——— △ ——— △ ——— at 30°C,
- - - - □ ——— □ ——— at 40°C.

in K_{ij} values at $W_j = 0$ may be considered due to solvation effect, which is independent of temperature over a large temperature range (Böttcher and Bordewijk, 1978).

For each systems in the lower concentration region there is a regularity in increase of slopes of the curves with temperature. At any experimental temperature the variation of K_{ij} with W_j is excellent to suggest that h.f. conductivity can be represented by a fitted formula

$$K_{ij} = \alpha + \beta W_j + \gamma W_j^2 \qquad \ldots 3.15$$

where α, β and γ are arbitrary constants depending upon the nature of the respective solution of polar nonpolar liquid mixture of which β plays a very important rôle in estimating dipole moment μ_j. Of course we have tried for determining the numerical values of α, β and γ by least square fitting technique. But unfortunately the process was abandoned because the available data are not smooth enough for the said technique. However, at linear portion the slope β of K_{ij} against W_j curve at $W_j \rightarrow 0$ was estimated by drawing a tangent to each curve at $W_j \rightarrow 0$ as demanded by the relation (3.9).

Though errors due (a) experimental uncertainty and (b) theoretical approximation done in obtaining eq.(3.9) may be expected to accumulate in determined μ_j by this method yet we have adopted this method because the (i) conductivity data are very scanty in the lower concentration region and (ii) the error due to theoretical approximation is negligibly small in the h.f. region.

Using eq. (3.12) the values of 'b' were determined with the reported relaxation time τ_s value for each systems at temperature 20°, 30° and 40°C and are placed in table (3.1). The corresponding μ_j values for all the chosen systems were also calculated from eq. (3.13) at those temperatures and are placed in table(3.1) along with the reported and theoretical ones for comparison. The dipole moment μ_j values thus obtained were found to satisfy the following empirical formulae:

(i) 2-5 dichloronitrobenzene:

$$\mu_j = 3.1729 - 3.143 \times 10^{-3}\ t + 4.51 \times 10^{-4}\ t^2$$

(ii) 2-5 dibromonitrobenzene:

$$\mu_j = 5.2209 + 2.7966 \times 10^{-2}\ t - 1.423 \times 10^{-4}\ t^2$$

(iii) 3-nitro-O-anisidine:

$$\mu_j = 2.154 + 1.8412 \times 10^{-2}\ t + 3.5226 \times 10^{-3}\ t^2$$

(iv) 2-chloro-p-nitroaniline:

$$\mu_j = 0.22158 + 0.11997\,t - 1.221 \times 10^{-3}\,t^2$$

(v) p-phenetidine:

$$\mu_j = 1.8453 + 6.3216 \times 10^{-2}\,t - 7.22 \times 10^{-4}\,t^2$$

(vi) O-nitroaniline:

$$\mu_j = 1.1532 + 4.873 \times 10^{-2}\,t - 2.616 \times 10^{-4}\,t^2$$

and

(vii) p-anisidine:

$$\mu_j = -1.4232 + 2.2068 \times 10^{-1}\,t - 2.958 \times 10^{-3}\,t^2$$

for different systems with temperature t in ^{o}C. The value of variation of the computed dipole moment μ_j of polar liquids against temperature in ^{o}C are shown graphically by the fitted lines in Fig. (3.3).

From table (3.1) it is obvious that μ_j in all the cases increases with experimental temperatures as observed by other workers (Ras et al, 1971) showed that dipole moments of some liquid compounds such as glycerol triacetate, glycerol tributriate etc. increase with temperature both in the pure form and in solution with benzene under the microwave alternating electric field though the values of pure compounds differ upto 7 percent from those determined in benzene. So far as the magnitude is concerned, the dipole moments of our

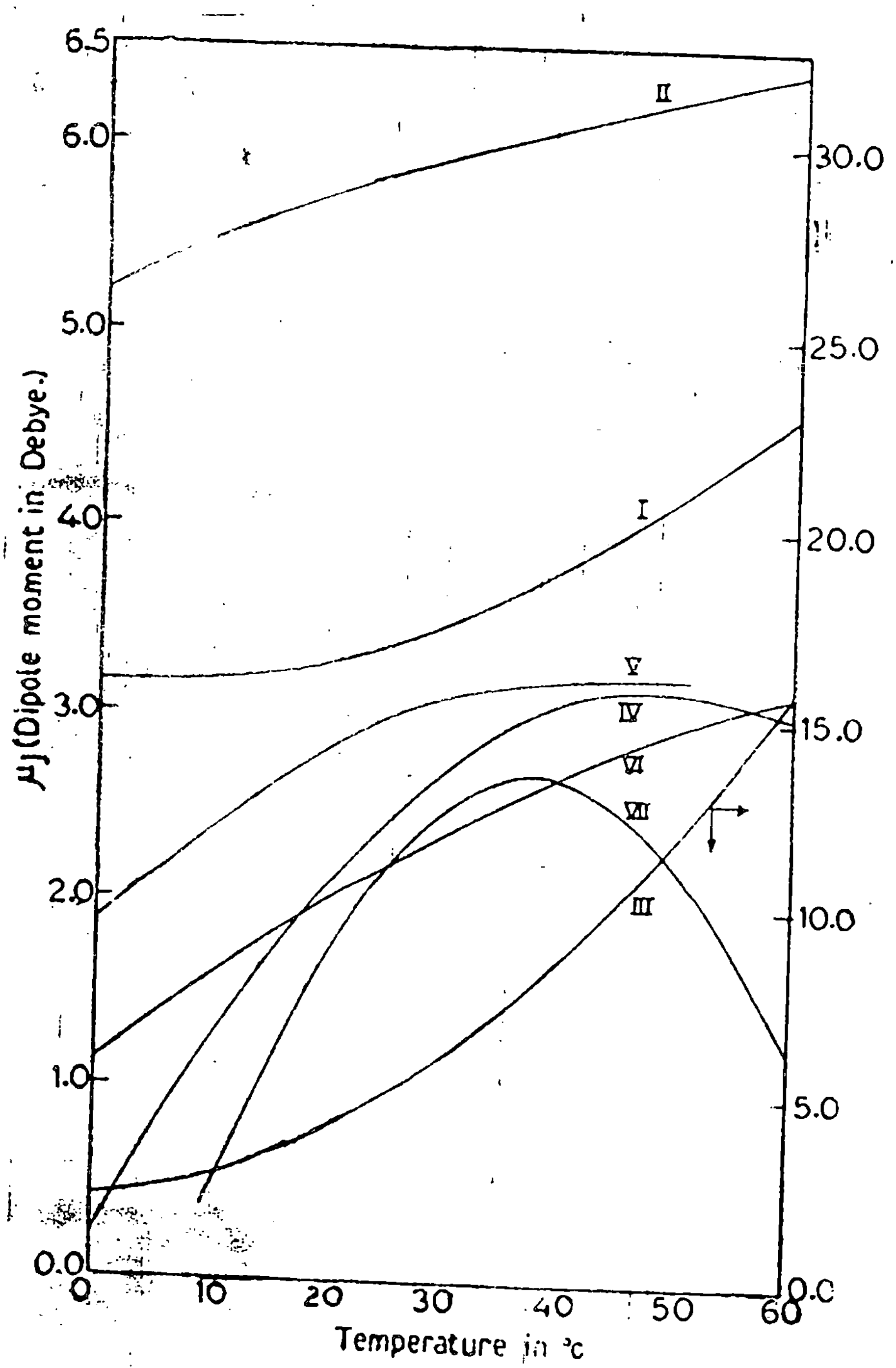


Figure 3.3–Computed dipole moments μ_j of seven polar liquids are plotted against temperature in °C.

For system III : μ_j $(0-15D)$ is shown on the right side of the graph while for other six systems : μ_j $(0-6{\cdot}5\ D)$ on the left side of the graph.

systems computed from eq. (3.13) are in excellent agreement with the reported ones based on Gopala Krishna's (1957) method and those theoretically calculated from vector atom model (Datta et al, 1981). However, for the system: 3-nitro-O-anisidine(III) the values at 20°C is very close to the reported data, but at 30°C and 40°C they are abnormally high. This could not be explained at present. Though the reported data of 2-5 dibromonitrobenzene (II) and 2-5 dichloronitrobenzene (I) are not available, the dipole moments as obtained from eq. (3.13) of the former is always greater than those of the latter. This indicates that the bulky molecule possesses a greater dipole moment to yield high τ_s values than those of lighter ones. Hence the size and shape of the molecules are important to locate the magnitudes of both relaxation time and dipole moment. The greater values of the dipole moments which are very close to the theoretical ones for 2-5 dibromonitrobenzene (II) undoubtedly confirms our methods to be a correct one. In fig. (3.3) the computed experimental μ_j of seven polar liquids are plotted against the temperature in °C in the range of 0 to 60°C. At present we are not interested to study to below and above this range of the said organic compounds.

It is observed that in all these cases that the dipole moment μ_j increases with temperatures in according to the mathematical relation given by

$$\mu_j = a' + b't + c't^2 \qquad \ldots \; 3.16$$

where a', b' and c' are the arbitrary constants depending upon the nature of the respective solute molecule in benzene under the h.f. alternating electric field and t is the temperature in degree centigrate.

The a' terms of all the systems are positive except the last one i.e. p-anisidine (VII) for which it is negative. For 2-5 dichloronitrobenzene (I) dipole moment increases monotonically with temperature producing a slight concave nature of the curve because the b' term of eq. (3.16) is negative while c' is positive. For 3-nitro-O-anisidine (III) a', b', and c' terms of eq. (3.16) are positive. As a result, the dipole moment of this compound becomes very high at comparatively higher temperatures, still, it agrees with the reported μ_j at 20°C. The most interesting system is p-anisidine (VII) for which a' and c' are negative, nevertheless, its dipole moment within the experimental range of temperature is finite which agrees fairly well with both the experimental and theoretical values. Beyond the experimental range of temperatures its dipole moment becomes zero at 7.1°C and at 67.5°C as observed from the curve (VII) of fig. (3.3) as well as from its empirical relation. This fact is also coroborated with the reported data which could also satisfy an empirical relation

$$\mu_j^{rept} = -7.46 + 6.49 \times 10^{-1}\, t + 9.90 \times 10^{-3}\, t^2 \quad \ldots\ 3.17$$

giving zero value of μ_j at 14.9°C and at 50.7°C. This trend is also visualised in curves (IV) and (V) of 2-chloro-p-nitroaniline and p-phenetidine respectively of fig. (3.3). We therefore, conclude that para molecules of organic polar liquids must show the zero value of dipole moment at lower and higher temperatures most probably due to association of polar units as well as due to the solvation effect, occured due to specific interactions between solute molecule and the solvent molecule and also to the bulk properties of the solvent especially the dielectric constant.

Table 3.1

Computed dipole moment μ_j (compt), rept. dipole moment μ_j (rept), relaxation times τ_s ; and b at temperature 20°, 30° and 40°C.

	System	Temp °C	b comp.	$\tau_s \times 10^{12}$ rep. in sec.	μ_j (compt.) in D	μ_j (rept.) in D	μ_j (theor.) in D
1)	2-5 dichloro-nitrobenzene	20	0.6620	11.87**	3.29		4.23***
		30	0.7060	10.72	3.48		
		40	0.7477	9.65	3.77		
2)	2-5 dibromonitrobenzene	20	0.3736	21.51**	5.72		4.23***
		30	0.4090	19.97	5.93		
		40	0.4369	18.86	6.11		
3)	3-nitro-O-anisidine	20	0.6165	13.27*	3.93	2.76	4.93***
		30	0.6793	11.56	5.88	3.11	
		40	0.7282	10.28	8.53	3.76	
4)	2-chloro-p-nitroaniline.	20	0.7170	10.57*	2.13	2.44	2.39***
		30	0.7432	9.89	2.72	3.28	
		40	0.7706	9.18	3.07	3.93	
5)	p-phenetidine	20	0.6975	11.08*	2.82	2.24	1.53***
		30	0.7147	10.63	3.09	2.78	
		40	0.7409	9.95	3.22	3.14	
6)	O-nitroaniline	20	0.7648	9.33*	2.02	3.95	4.25***
		30	0.7779	8.99	2.38	2.19	
		40	0.8050	8.28	2.68	2.24	
7)	p-anisidine	20	0.9493	3.89**	1.81	1.56	1.87***
		30	0.9546	3.67	2.51	3.10	
		40	0.9657	3.17	2.67	2.66	

* Somevanshi et al (1978), ** Pant et al (1977),

*** Calculated from the vector model assuming molecule to be planar.

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Microwave conductivity and dipole moment of polar dielectrics

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Abstract : The slope of the concentration variation of high frequency conductivity of polar-nonpolar liquid mixture at infinite dilution has been employed to estimate the dipole moment of polar solute at different temperatures. The calculations showed that in the microwave electric field the dipole moment of a polar unit is not fixed, but varies uniformly with temperature.

1. Introduction

The variation of dipole moment of a polar liquid with temperature is not a new concept (Ras and Bordewijk 1971) but it really occurs when the polar-nonpolar liquid mixture is subjected to the alternating microwave electric field. There are several methods (Gopala Krishna 1957, Sen *et al* 1972) to compute the relaxation times τ_s of polar liquid dissolved in nonpolar solvent under the application of radio frequency and microwave alternating electric field. Gopala Krishna's concentration variation method in the microwave region and Sen's graphical method in r.f. region always invite a slight personal judgement to locate the exact and accurate value of τ_s within a certain considerable range. In order to avoid this difficulty we, in the process of derivation of the dipole moment μ_j of polar liquids in solvent from the conductivity data (Ghosh and Acharyya 1977) in h.f. region, devised a simple procedure (Ghosh *et al* 1980, Datta *et al* 1981) to obtain the relaxation times τ_s of polar liquids from the m.w and r.f. conductivity data based on sound mathematical foundation. When the frequency of the impressed field exceeds a certain critical value, the permanent dipoles of solute molecules cannot follow the exact alternation of the applied field. This measurable lag is commonly known as dielectric relaxation, and the relaxation time of a solute is defined as the lag in response of polar solute with the forces to which it is subjected. Using the slope of concentration variation of total conductivity K at infinite dilution we attempted to obtain the ralaxation time at different temperatures with the single μ_j value as obtained from literature. We found that the single value of μ_j could not yield the magnitude of τ_s though it gave the relative temperature dependence of computed τ_s only. This fact at once indicates that in the h.f. region μ_j is not a fixed quantity, but most probably varies with temperature to ascertain the actual magnitude of τ_s.

All these points put us in a sound position to utilise the concentration variation of conductivity data to evaluate μ_j at different temperatures for the following seven systems of interest. μ_j values thus obtained were found to satisfy the following empirical formulae :

(i) 2-5 dichloronitrobenzene : $\mu_j = 3.1729 - 3.143 \times 10^{-3} t + 4.51 \times 10^{-4} t^2$.
(ii) 2-5 dibromonitrobenzene : $\mu_j = 5.2209 + 2.7966 \times 10^{-2} t - 1.423 \times 10^{-4} t^2$.
(iii) 3 nitro-*o*-anisidine : $\mu_j = 2.154 + 1.8412 \times 10^{-2} t + 3.5226 \times 10^{-3} t^2$.
(iv) 2-chloro-*p*-nitroaniline : $\mu_j = 0.22158 + 0.11997 t - 1.221 \times 10^{-3} t^2$.
(v) *p*-phenetidine : $\mu_j = 1.8453 + 6.3216 \times 10^{-2} t - 7.22 \times 10^{-4} t^2$.
(vi) *o*-nitroaniline : $\mu_j = 1.1532 + 4.873 \times 10^{-2} t - 2.616 \times 10^{-4} t^2$. and
(vii) *p*-anisidine : $\mu_j = -1.4232 + 2.2068 \times 10^{-1} t - 2.958 \times 10^{-3} t^2$.

for different systems with temperature in °C.

2. Theory

According to Murphy and Morgan (1939) the high frequency conductivity of a polar-nonpolar liquid mixture is given by $K = K' + jK''$, where K' = the real part of the conductivity $= \frac{\omega \epsilon''_{ij}}{4\pi}$, and K'' = the imaginary part of the conductivity $= \frac{\omega \epsilon'_{ij}}{4\pi}$. Now the magnitude of the total h.f. conductivity is usually calculated by the relation

$$K = \frac{\omega}{4\pi} [\epsilon''^2_{ij} + \epsilon'^2_{ij}]^{1/2} \tag{1}$$

But, in practice, as ϵ'_{ij} decreases with frequency and eventually equals the optical dielectric constant in the h.f. region, and ϵ''_{ij} increases with frequency to attain a maximum value at $\omega = \frac{1}{\tau}$ and then begins to decrease, the real part K' of h.f. conductivity of polar-nonpolar liquid mixture of weight fraction W_j of polar solute at any temperature T°K is given by

$$K' = \frac{\mu_j^2 N \rho_{ij} F_{ij}}{3 M_j k T} \left(\frac{\omega^2 \tau}{1 + \omega^2 \tau^2} \right) W_j \tag{2}$$

where μ_j is the dipole moment of polar solute of molecular weight M_j, N is the Avogadro number, k is the Boltzman constant and $F_{ij} = \left(\frac{\epsilon_{ij} + 2}{3} \right)^2$ is the local field. This ϵ_{ij} however, is the complex dielectric constant of the solution of density ρ_{ij} and is expressed as $\epsilon_{ij}=\epsilon'_{ij}-j\epsilon''_{ij}$ of which the emaginary part ϵ''_{ij} is responsible for the absorption of electrical energy to yield resistance to polarization. Now for microwave electric field $\epsilon'_{ij} \gg \epsilon''_{ij}$ and the conductivity of the solution becomes

$$K=\frac{\omega}{4\pi}\epsilon'_{ij} \tag{3}$$

But for h-f region it can be shown that

$$\epsilon'_{ij}=\epsilon_{ij,\infty}+\epsilon''_{ij}/\omega\tau \tag{4}$$

where $\epsilon_{ij,\infty}$ is the optical dielectric constant of the solution. From eqs. (3) and (4) the total h-f conductivity of the solution takes the form

$$K=K_\infty+K'/\omega\tau_s \tag{5}$$

where K_∞ is a constant and τ_s is the relaxation time of the solute molecule in solution. As K is a function of ω_j, we have from eq. (5)

$$\left(\frac{dK'}{d\omega_j}\right)_{\omega_j\to 0}=\omega\tau_s\left(\frac{dK}{d\omega_j}\right)_{\omega_j\to 0}=\omega\tau_s\beta \tag{6}$$

where β is the slope of $K-\omega_j$ curve at $\omega_j\to 0$. When ω_j approaches zero, the density ρ_{ij} of the solution becomes ρ_i the density of the solvent, and local field F_{ij} of the solution is F_i = the local field of the solvent $=\left(\frac{\epsilon_i+2}{3}\right)^2$. Under the circumstances, eq. (2) on being differentiated w.r. to ω_j as $\omega_j\to 0$ takes the form :

$$\left(\frac{dK'}{d\omega_j}\right)_{\omega_j\to 0}=\frac{\mu_j^2 N\rho_i F_i}{3M_jkT}\left(\frac{\omega^2\tau_s}{1+\omega^2\tau_s^2}\right) \tag{7}$$

Taking

$$b=\beta/\left(\frac{\mu_i^2 N\rho_i F_i}{3M_jkT}\cdot\omega\right) \tag{8}$$

we have from eqs. (6) and (7)

$$b=\frac{1}{1+\omega^2\tau_s^2} \text{ and whence}$$

$$\tau_s=\frac{\lambda}{2\pi C}\sqrt{\frac{1}{b}-1}=\frac{\lambda\times 10^{-10}}{18{\cdot}84}\sqrt{\frac{1}{b}-1} \tag{9}$$

Now from eq. (8) the dipole moment of the solute molecule can be written in the form

$$\mu_j=\left(\frac{3M_jkT}{N\rho_iF_i}\cdot\frac{\beta}{\omega b}\right)^{\frac{1}{2}} \tag{10}$$

With reported values of τ_s at experimental temperatures b may be calculated from eq. (9). With a knowledge of the slope β from $K-\omega_j$ curve at $\omega_j \rightarrow 0$ and corresponding b it is easy to calculate μ_j of the solute molecule from eq. (10) because all other quantities of the solvent benzene are known. Further, it is clear from eq. (9) that for a given frequency ω of the applied field the relaxation time τ_s depends upon the magnitude of b which in turn depends on μ_j. As τ_s changes with temperature, μ_j should change with temperature in order to locate the magnitude of τ_s in the microwave region because the change of the factor $\beta/\rho_i F_i$ with temperature of eq. (8) alone cannot cope with the pace of change of τ_s with temperature.

3. Results and discussions

The h.f. conductivity (Sen and Ghosh 1972) of polar-nonpolar liquid mixture is comparatively easy to measure down to very low concentration by Hartley oscillator and klystron valve in the laboratory. But the expt. conductivity data under radio-frequency and microwave electric fields are very scanty. We, therefore, used the available concentration variation expt. data for ϵ''_{ij} and ϵ'_{ij} of seven systems in benzene : 2-5 dichloronitrobenzene and 2-5 dibromonitrobenzene under 3.13 cm wavelength electric field (Pant *et al* 1977), and 3-nitro-*o*-anisidine, 2-chloro-*p*-nitroaniline, *p*-phenetidine, *o*-nitroaniline and *p*-anisidine under 3.17 cm wavelength electric field (Somevanshi *et al* 1978) to obtain corresponding experimental K values from Murphy-Morgan relation $K=\frac{\omega}{4\pi}\sqrt{\epsilon''^2_{ij}+\epsilon'^2_{ij}}$ at 20°, 30° and 40°C. The values of K thus obtained are shown graphically in Figures 1 and 2 for every stage of dilution for seven systems.

The temperature dependence of K for each system is vivid. K varies almost linearly with ω_j in the lower concentration region. As ω_j approaches zero, the solvent benzene assumes a constant value of conductivity independent of experimental temperature. This is because of the fact that the quantity $\rho_{ij}F_{ij}/T$ in eq. (2) assumes nearly a fixed value which is in the neighbourhood of 0.006. Consequently, at $\omega_j=0$ the conductivity of a given system at all temperatures remains the same. Nevertheless, at $\omega_j=0$ the K values of different systems are different. This is due to solvation effect (Datta *et al* 1981).

For each system in the lower concentration region there is a regularity in increase of slopes of the curves with temperature. At any experimental temperature the variation of K with ω_j is excellent to suggest that h.f. conductivity can be represented by a fitted formula $K=\alpha+\beta\omega_j+\gamma\omega_j^2$, where α, β and γ are arbitrary constants depending upon the nature of the respective solution of polar-nonpolar liquid mixture of which β plays a very important role in estimating μ_j. Of course we tried for numerical values of α, β and γ by fitting technique. But the process was abandoned because available data are not smooth enough for the said technique. However, the slope β of $K-\omega_j$ curve at $\omega_j \to 0$ was estimated by drawing a tangent to each curve at $\omega_j \to 0$ as demanded by the relation (6).

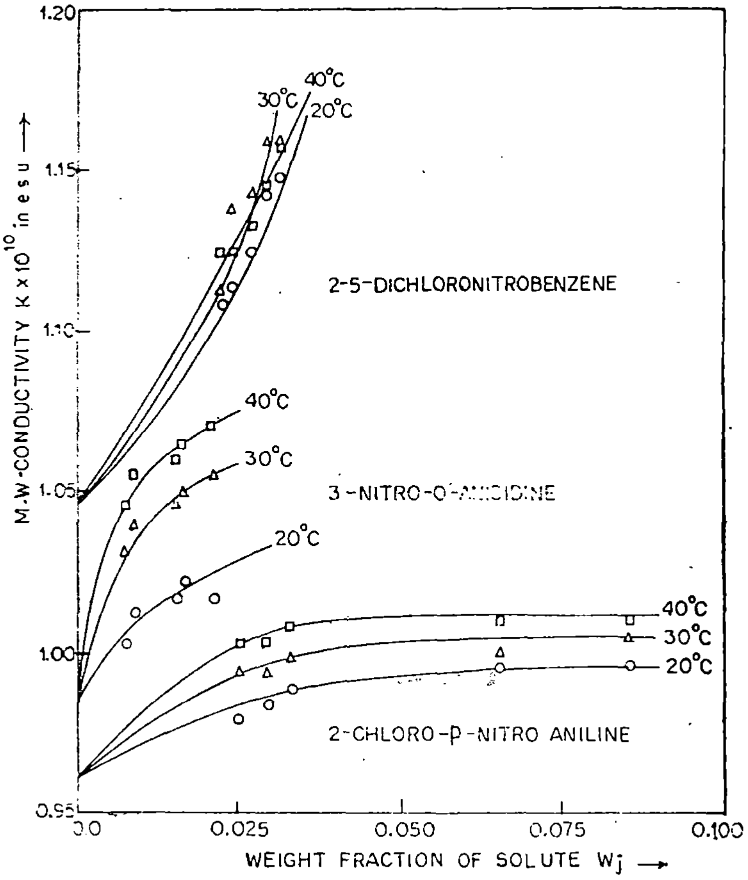

Figure 1. Microwave conductivity K is plotted against weight fraction ω_j at 20°C, 30°C and 40°C.

——○——○—— at 20°C,

——△——△—— at 30°C,

——□——□—— at 40°C.

Though errors due to (1) experimental uncertainty and (2) theoretical approximation done in obtaining eq. (6) may be accumulated in μ_j determined by this method. still we have adopted it because (i) conductivity data are very scanty in the lower concentration region and (ii) the error due to theoretical approximation is negligibly small in the h.f. region. Further, the uncertainty in drawing $K-\omega_j$ graph drawn with available ϵ'_{ij} data for different concentrations. is

5 very small.

Using eq. (9) values of b were determined with reported τ_s for each system at 20°, 30° and 40°C and are placed in Table 1. The corresponding μ_j values for all the chosen systems were also calculated from eq. (10) at these temperatures and are placed in Table 1, along with the reported and theoretical ones for comparison. The $\mu_j^{'s}$ thus obtained are also shown graphically by fitted lines in Figure 3.

Table 1. Computed dipole moment $\mu_{j\ \text{compt}}$, rept. dipole moment $\mu_{j\ \text{rept}}$, relaxation times τ_s and b at temperatures : 20°, 30° and 40°C.

System	Temp. °C	b compt.	$\tau_s \times 10^{12}$ rept in sec.	μ_j compt. in D	μ_j rept. in D	μ_j theor. in D
(i) 2-5 dichloronitrobenzene	20	0.6620	11.87**	3.29		4.23***
	30	0.7060	10.72	3.48		
	40	0.7477	9.65	3.77		
(ii) 2-5 dibromonitrobenzene	20	0.3736	21.51**	5.72		4.23***
	30	0.4090	19.97	5.93		
	40	0.4369	18.86	6.11		
(iii) 3-nitro-*o*-anisidine	20	0.6165	13.27*	3.93	2.76	4.93***
	30	0.6793	11.56	5.88	3.11	
	40	0.7282	10.28	8.53	3.76	
(iv) 2-chloro-*p*-nitroaniline	20	0.7170	10.57*	2.13	2.44	2.39***
	30	0.7432	9.89	2.72	3.28	
	40	0.7706	9.18	3.07	3.93	
(v) *p*-phenetidine	20	0.6975	11.08*	2.82	2.24	1.53***
	30	0.7147	10.63	3.09	2.78	
	40	0.7409	9.95	3.22	3.14	
(vi) *o*-nitroaniline	20	0.7648	9.33*	2.02	3.95	4.25***
	30	0.7779	8.99	2.38	2.19	
	40	0.8050	8.28	2.68	2.24	
(vii) *p*-anisidine	20	0.9493	3.89**	1.81	1.56	1.87***
	30	0.9546	3.67	2.54	3.10	
	40	0.9657	3.17	2.67	2.66	

* Somevanshi *et al* (1978)

** Pant *et al* (1977)

*** Calculated from the vector model assuming molecule to be planar.

From Table 1, it is obvious that μ_j in all the cases increases with experimental temperatures as observed by other workers (Ras *et al* 1971) who showed that dipole moments of some lipid compounds such as glycerol triacetate, glycerol tributriate etc. increase with temperature both in the pure form and in solution with benzene under the microwave alternating electric field though the values of pure compounds differ by up to 7% from those determined in benzene. So far as the magnitude is concerned, the dipole moments of our systems computed from eq. (10) are in excellent agreement with the reported

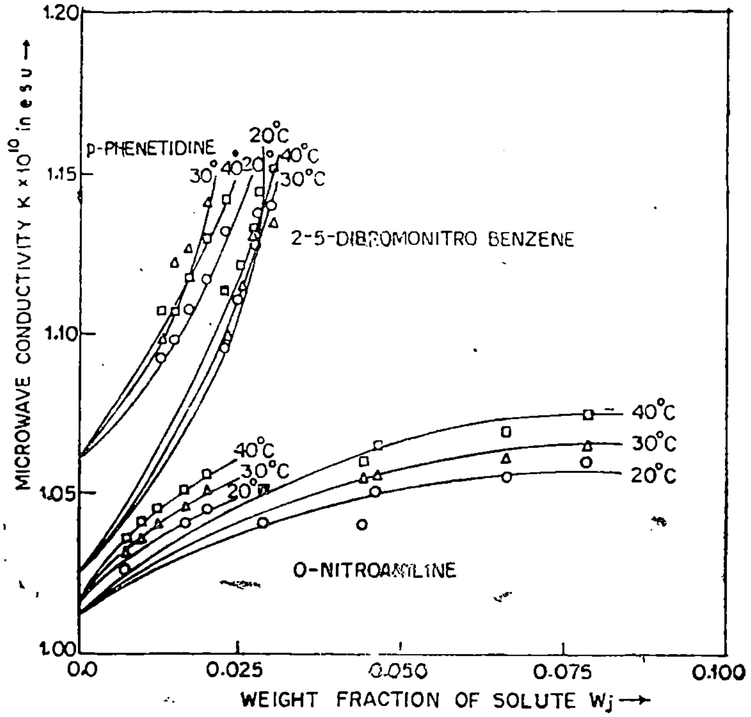

Figure 2. Microwave conductivity K is plotted against weight fraction ω_j at 20°C, 30°C and 40°C.

——○——○—— at 20°C,
——△——△—— at 30°C,
——□——□—— at 40°C.

ones based on Gopala Krishna's (1957) method and those theoretically calculated from vactor atom model (Datta *et al* 1981). However, for the system : 3 nitro-*o*-anisidine (III) the values at 20°C is very close to the reported data, but at 30°C and 40°C they are abnormally high. This could not be explained at present. Though the reported data of 2-5 dibromonitrobenzene (II) and 2-5 dichloronitrobenzene (I) are not available, the dipole moments as obtained from eq. (10) of the former is always greater than those of the latter. This indicates that the bulky molecule possesses a greater dipole moment to yield high τ_s values than those of lighter ones. Hence the size and shape of the molecule are important to locate the magnitudes of both relaxation time and dipole moment. The greater values of the dipole moments which are very close to the theoretical ones for 2-5 dibromonitrobenzene (II) undoubtedly confirms our method to be a correct one. In Figure 3, the computed experimental μ_j of seven polar liquids are plotted against the temperature in °C in the range of 0 to 60°C. Below and above

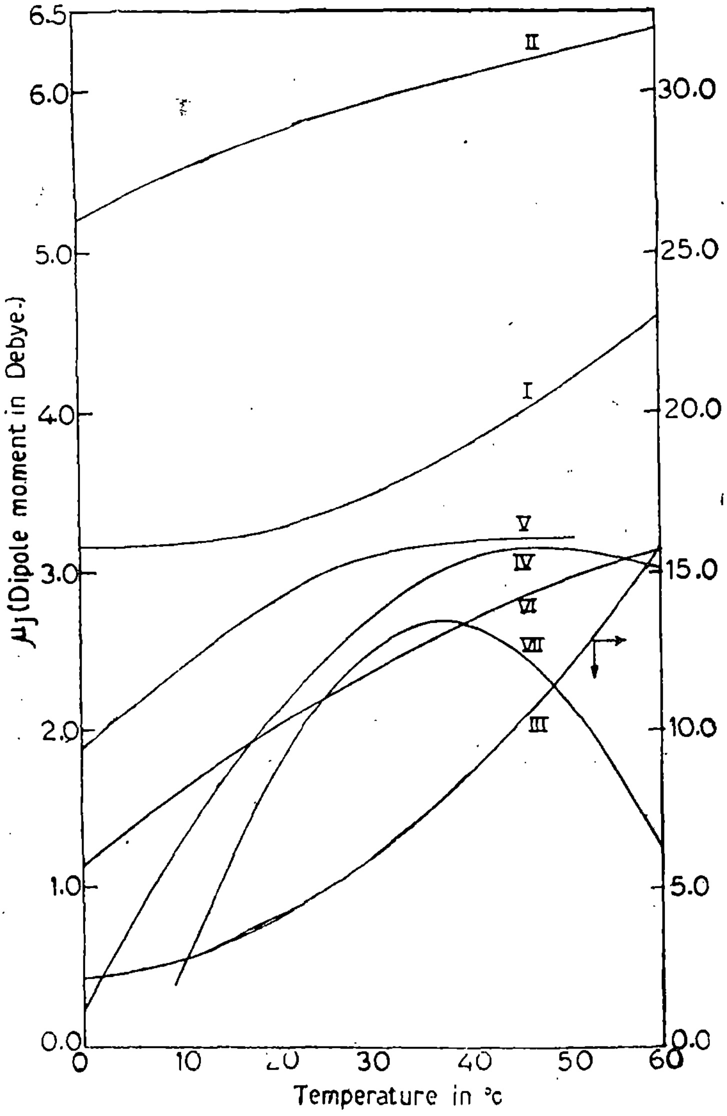

Figure 3. Computed dipole moments μ_j of seven polar liquids are plotted against temperature in °C.
For system III : μ_j (0–15*D*) is shown on the right side of the graph while for other six systems : μ_j (0–6·5 *D*) on the left side of the graph.

this range we are not interested because the liquids are organic compounds. However, in all these cases, dipole moment increases in the fashion

$$\mu_j = a' + b't + C't^2 \tag{11}$$

with temperature in °C, where a', b' and c' are the arbitrary constants depending upon the nature of the respective solute molecule in benzene under the h.f. alternating electric field.

The a' terms of all the systems are positive except the last one i.e. *p*-anisidine (VII) for which it is negative. For 2-5 dichloronitrobenzene (I) dipole moment increases monotonically with temperature producing a slight concave nature of the curve because the b' term of eq. (11) is negative while c' is positive. For 3-nitro-*o*-anisidine (III) a', b' and c' terms of eq. (11) are positive. As a result, the dipole moment of this compound becomes very high at comparatively higher temperatures, still, it agrees with the reported μ_j at 20°C. The most interesting system is *p*-anisidine (VII) for which both a' and c' are negative ; nevertheless, its dipole moment within the experimental range of temperature is finite which agrees fairly well with both the experimental and theoretical values. Beyond the experimental range of temperatures its dipole moment becomes zero at 7.1°C and at 67.5°C as observed from the curve (VII) of Figure 3 as well as from its empirical relation. This fact is also coroborated with the reported data which could also satisfy an empirical relation :

$$\mu_j^{expt} = -7.46 + 6.49 \times 10^{-1} t - 9.90 \times 10^{-3} t^2 \tag{12}$$

giving zero value of μ_j at 14.9°C and at 50.7°C. This trend is also visualised in curves (IV) and (V) of 2-chloro-*p*-nitroaniline and *p*-phenetidine respectively of Figure 3. We, therefore, conclude that para molecules of organic polar liquids must show the zero value of dipole moment at lower and higher temperatures most probably due to association of polar units as well as solvation effect.

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CHAPTER IV

MICROWAVE CONDUCTIVITY AND DIPOLE MOMENT OF SOME SUBSTITUTED BENZENE

Introduction:

In recent years, much attention has been drawn to study the concentration variation of high frequency conductivity (Ghosh S K et al, 1980 and Datta S K et al 1981) to yield the dielectric relaxation parameters such as: relaxation time (τ), dipole moment (μ_j) of polar dielectrics, heat enthalpy (ΔH_τ), entropy of dielectric relaxation (ΔS_τ) and the activation energy (E_τ) etc. In the previous chapter (III) it has been shown that under the microwave electric field the dipole moment is not a fixed quantity, but varies with temperature though it is supposed to be constant under the low frequency and the d.c. electric fields.

The present chapter will report the permanent dipole moment and bond moment of the following seven dielectric liquids. The dipole moment were calculated from the concentration variation of microwave conductivity method. The theory and method of determination of dipole moment (μ_j) from variation of h.f. conductivity with weight fraction W_j are given in chapter (III).

The seven dielectric liquids (i) m-aminobenzotrifluoride (ii) O-nitrobenzotrifluoride (iii) m-nitrobenzotrifluoride (iv) O-chlorobenzotrifluoride at 3.0166 cm wave length, (v) O-chloronitrobenzene (vi) 4-chloro-3-nitrobenzotrifluoride and (vii) 4-chloro-3-nitrotoluene at 3.0 cm wavelength electric field, the systems are very interesting regarding the sizes and shapes of the molecule whose dipole moments and bond moment have been reported.

Result and Discussion:

The microwave conductivity K_{ij} of polar - nonpolar liquid mixtures were calculated with the help of the fundamental eq. (3.4), i.e.

$$K_{ij} = \frac{\omega}{4\pi}\left(\epsilon_{ij}''^{2} + \epsilon_{ij}'^{2}\right)^{1/2} \qquad \ldots 4.1$$

Further the total conductivity K_{ij} for the h.f. region is represented by eq. (3.6) i.e.

$$K_{ij} = K_{\infty} + K_{ij}'/\omega\tau_s \qquad \ldots 4.2$$

where K_{∞} and τ_s are constants (d.c. conductivity and relaxation time of the solute molecules in the dilute solution respectively). Therefore the total conductivity can be written with the help of eq. (3.8) and eq. (4.2) as

$$K_{ij} = K_{\infty} + \frac{\mu_j^2 N \rho_{ij} F_{ij}}{3 M_j k T}\left(\frac{\omega}{1+\omega^2\tau_s^2}\right) W_j \qquad \ldots 4.3$$

The eq. (4.3) clearly shows that the K_{ij} is a function of weight fraction. Hence the variation of K_{ij} with W_j could be expressed according to mathematical relation

$$K_{ij} = \alpha + \beta W_j \qquad \ldots 4.4$$

where α and β are constants. The constant β is the most important factor for determining the τ_s and μ_j. The slope β could be obtained from the graphical plot of K_{ij} against W_j at $W_j \longrightarrow 0$ or from the eqn. (4.4). The K_{ij} of the seven respective solutions computed by using the following least square fit relations are

i) $K_{ij} \times 10^{-10} = 1.1106 + 2.3536\,W_j$

ii) $K_{ij} \times 10^{-10} = 1.1169 + 4.1557\,W_j$

iii) $K_{ij} \times 10^{-10} = 1.1262 + 1.7747\,W_j$

iv) $K_{ij} \times 10^{-10} = 1.1199 + 2.0159\,W_j$

v) $K_{ij} \times 10^{-10} = 1.1265 + 4.0539\,W_j$

vi) $K_{ij} \times 10^{-10} = 1.1286 + 1.1894\,W_j$ and

vii) $K_{ij} \times 10^{-10} = 1.1250 + 2.8594\,W_j$

To calculate the variation of K_{ij} at various weight fraction W_j, the experimental data of ϵ'_{ij} and ϵ''_{ij} given the paper of (Arrawatia et al.1977), and Gupta P C et al, (1978) have been considered.

The K_{ij} values thus obtained are tabulated in table (4.1a, 1b). The nature of variation of K_{ij} with weight fraction W_j and also the nature of their fitted curves are shown in fig. (4.1a -4.1 g).

The dipole moments of seven systems of interest have been computed with the help of eq. (3.13) i.e.

$$\mu_j = \left(\frac{3M_jkT}{N\rho_iF_i}\cdot\frac{\beta}{\omega b}\right)^{1/2}$$

and it is observed that the dipole moment values of many molecules measured in solution were consistently different from one solvent to another and this effect has been considered as due to solvent effect. So the correct values of induce dipole moment calculated from the most convenient Müllers empirical equation

$$\mu_j^{\langle s\rangle} = \mu_j\left[1 - c\left(\epsilon_i - 1\right)^2\right]$$

are also tabulated in table (4.2) along with the available literature data for comparison. The μ_j data have also been computed from the bond dipole moment and bond angles, assuming that the benzene molecule is a planer one. The molecular parameters needed for this computation of theoretical values of μ_j are shown in fig. 4.2 and placed in table (4.3).

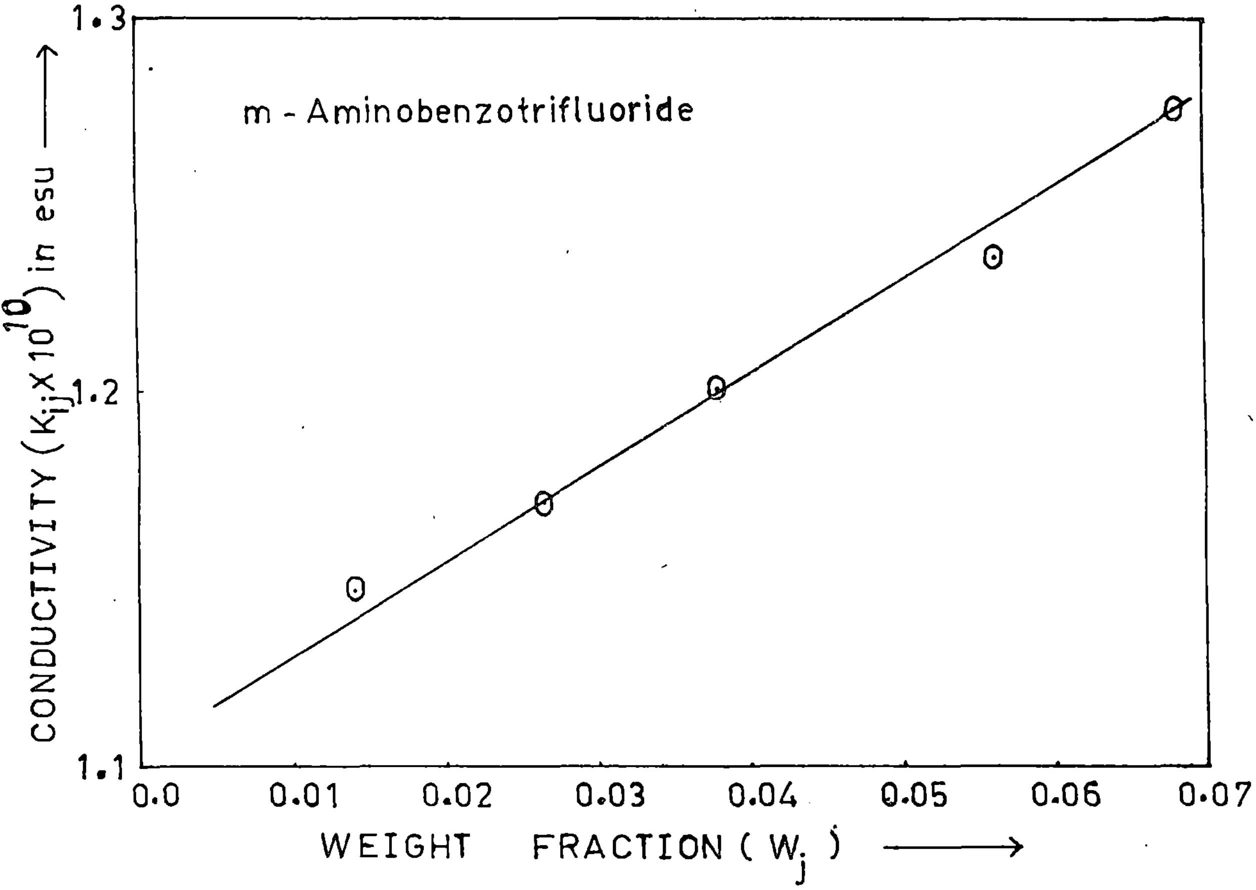

Fig - 4.1a Conductivity K_{ij} is plotted against Weight fraction W_j of solute.

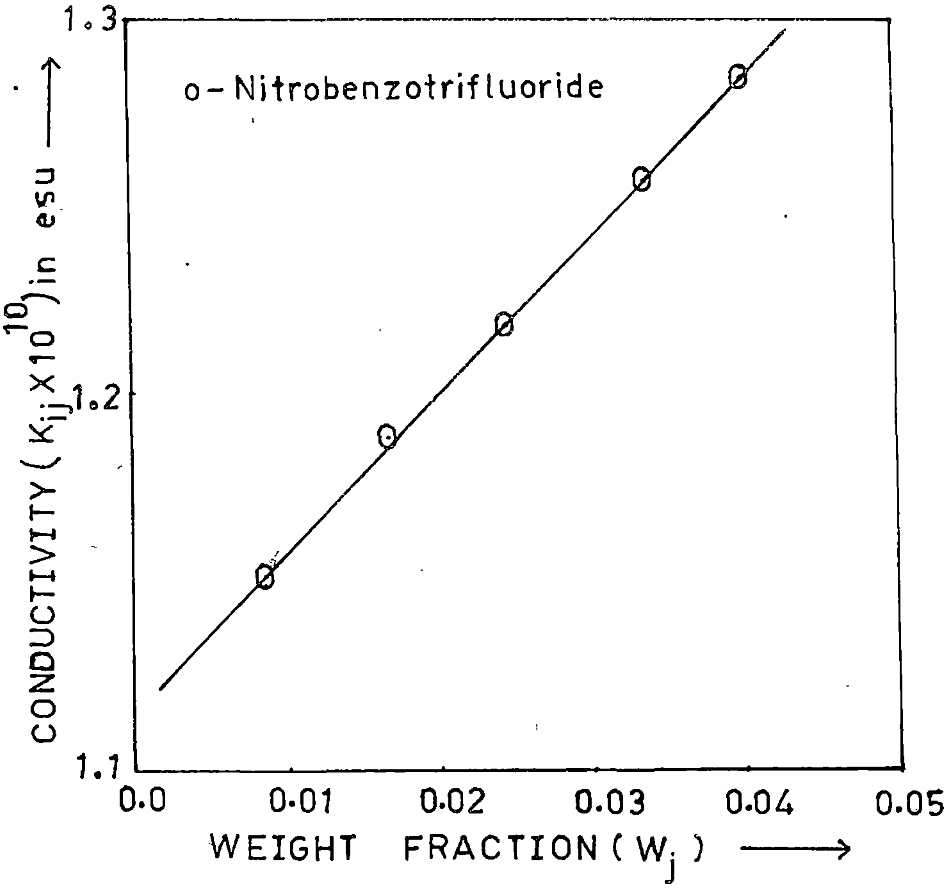

Fig-4.1b Conductivity K_{ij} is plotted against Weight fraction W_j of solute.

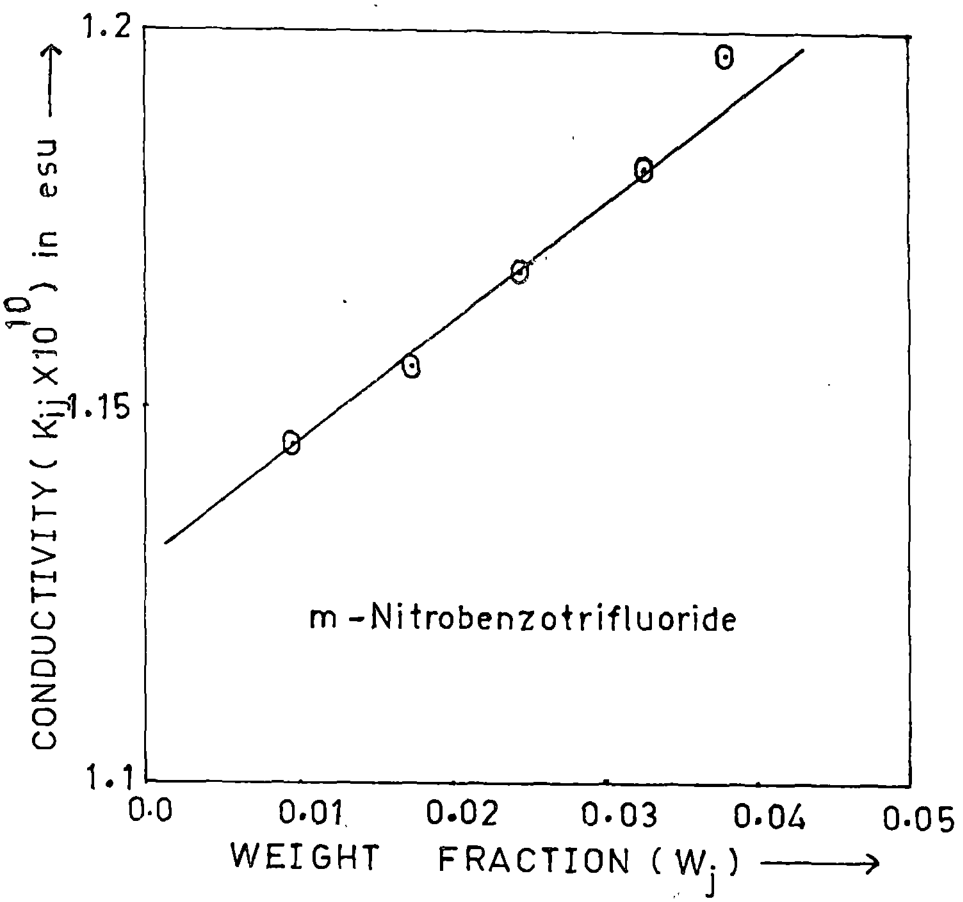

Fig-4.1c Conductivity K_{ij} is plotted against Weight fraction W_j of solute.

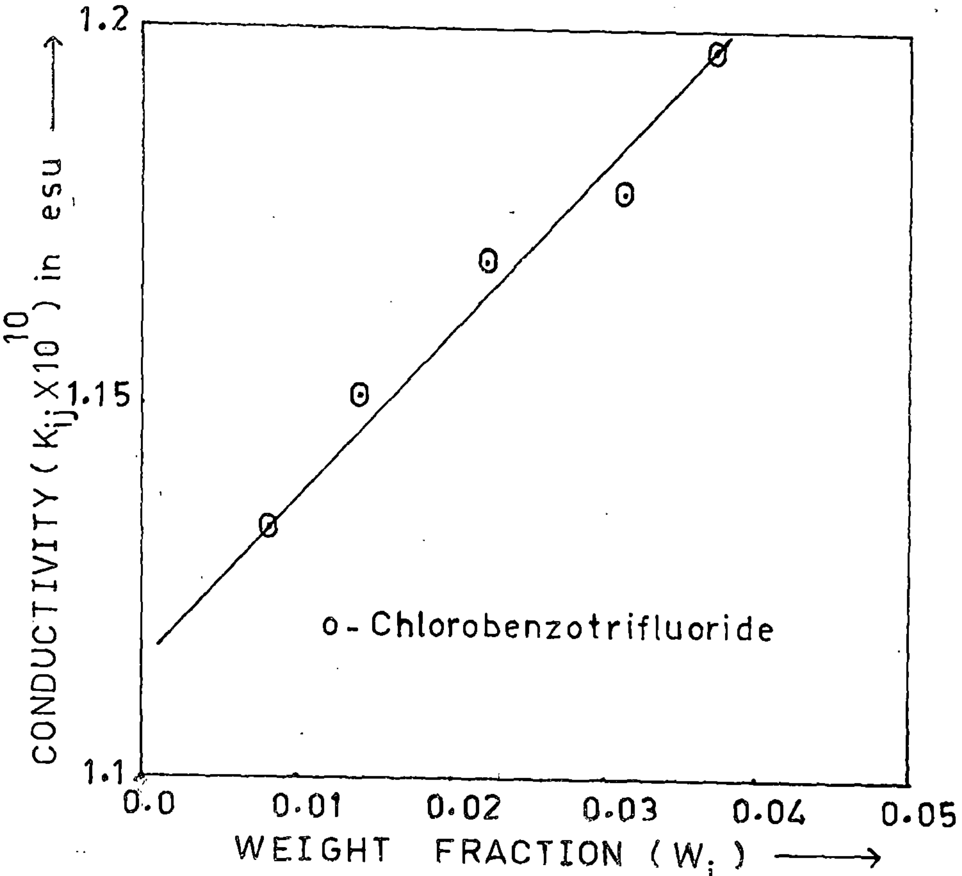

Fig-4.1d Conductivity K_{ij} is plotted against Weight fraction W_j of solute.

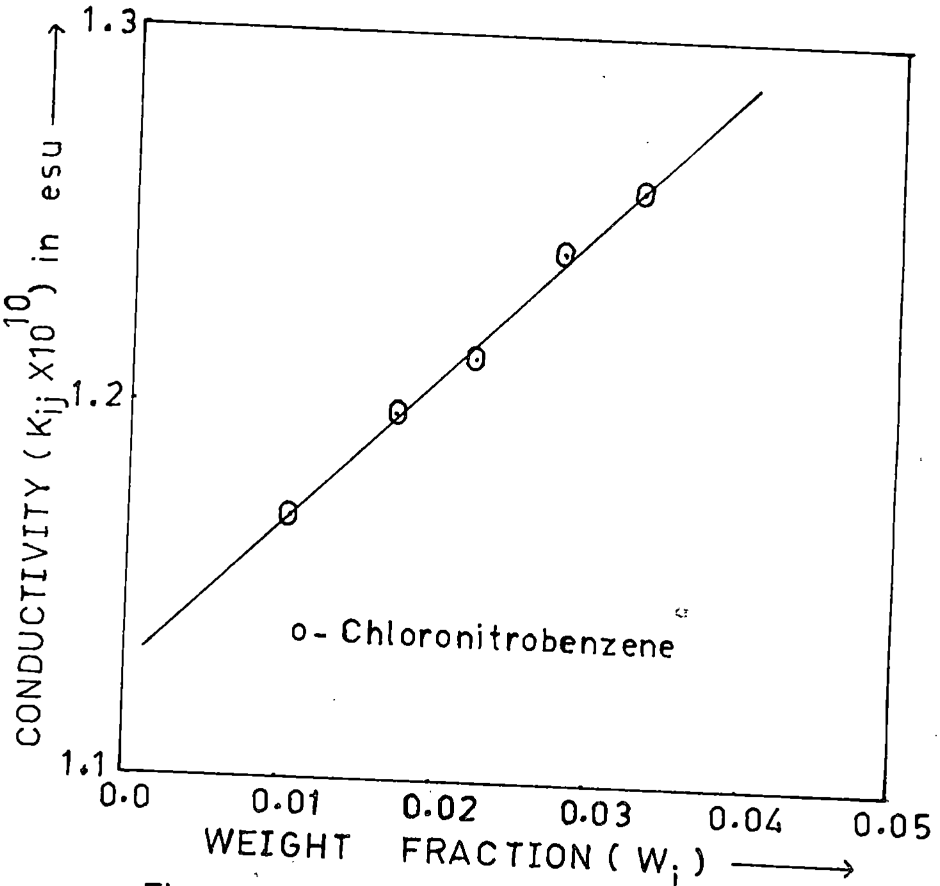

Fig-4.1e Conductivity K_{ij} is plotted against Weight fraction W_j of solute.

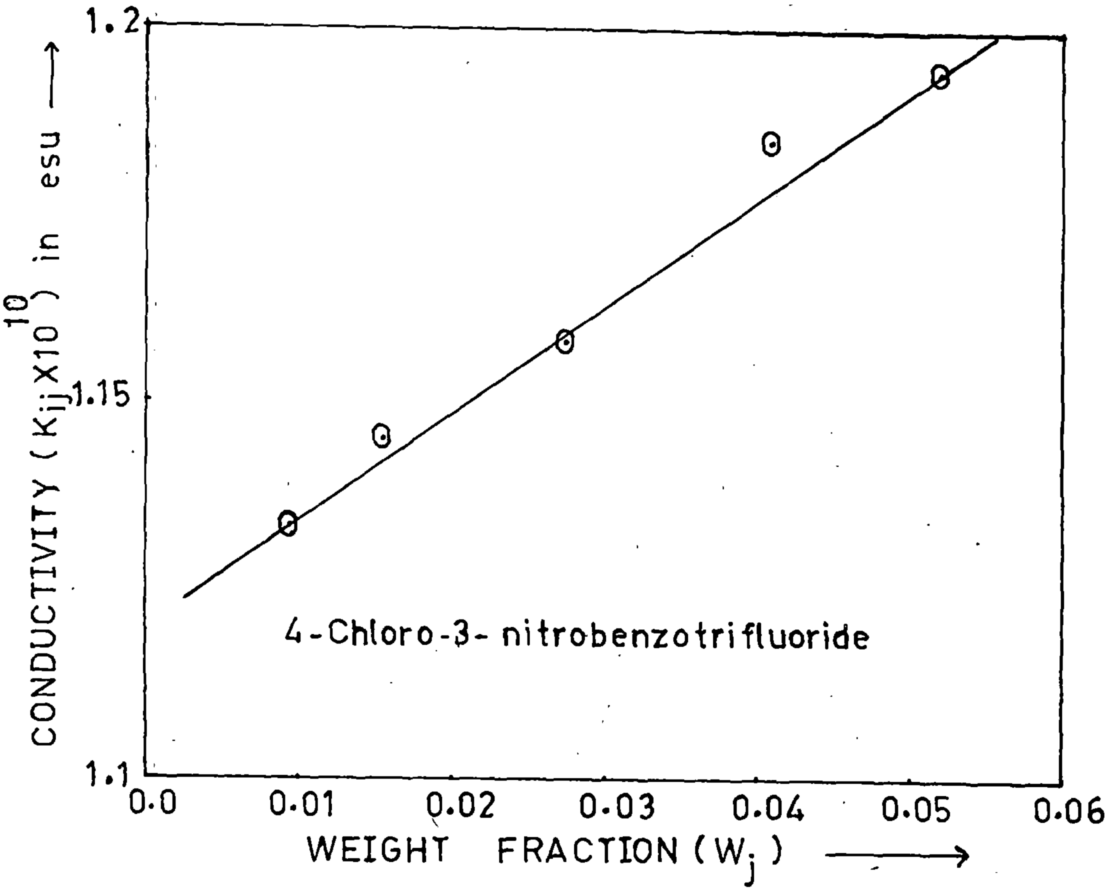

Fig-4.1f Conductivity K_{ij} is plotted against Weight fraction W_j of solute .

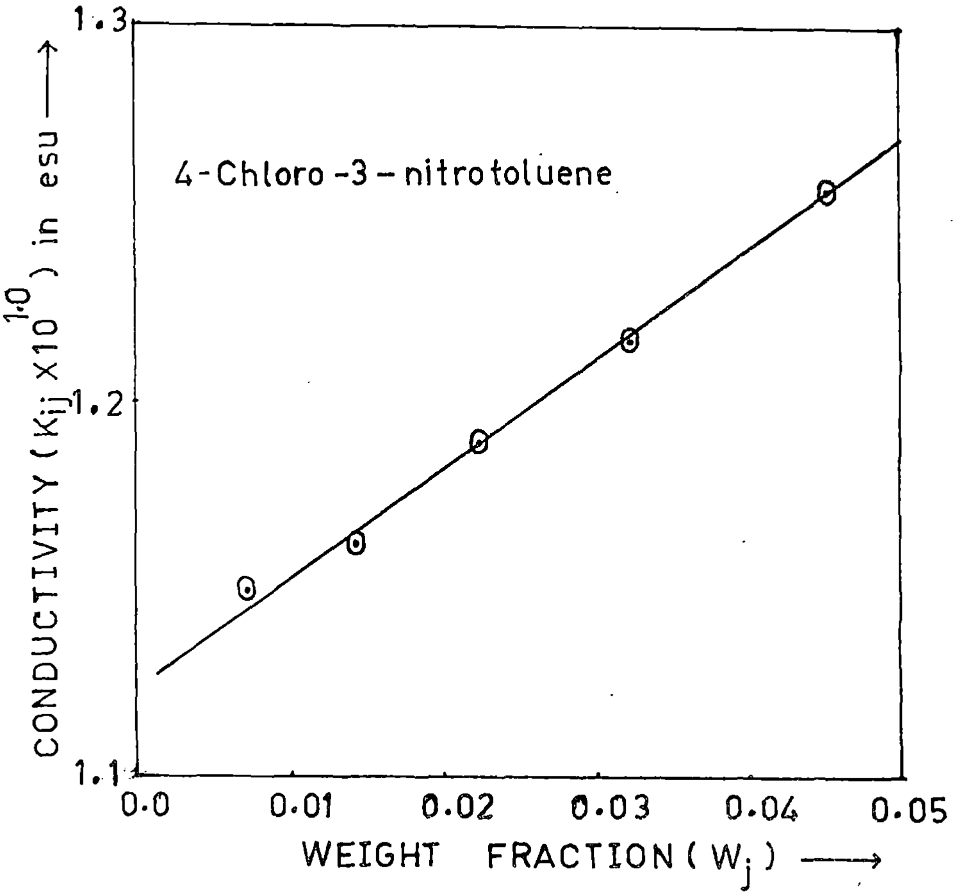

Fig.- 4.1g Conductivity K_{ij} is plotted against Weight fraction W_j of solute.

The microwave conductivity data in the low concentration region are of much interest as they reveal a completely different situation in comparison to those of high concentration which is shown in the previous chapter (III). This is the reason which led us to study the systems reported here and to calculate their dipole moments. High concentration conductivity data of a polar nonpolar liquid mixture is liable to yield the dipole moment due to dimer formation while those in low concentration region behave linearly with the weight fraction and give the dipole moment due to monomer formation i.e. solute-solvent association. The computed dipole moments agree with those reported experimentally as well as computed theoretical ones, as illustrated in table (4.2). This fact suggests the basic soundness of the method adopted here.

The variation in the μ_j values for these substituted molecules in benzene might be due to
(i) the difference in values of group moments and
(ii) inductive effect. The dipole moment of O-nitrobenzotrifluoride is always greater than that of m-nitrobenzotrifluoride (Table 4.2) both shown by the computed and theoretical μ_j's due to the two different positions of the NO_2 (shown in fig. 4.2) group in the compound.

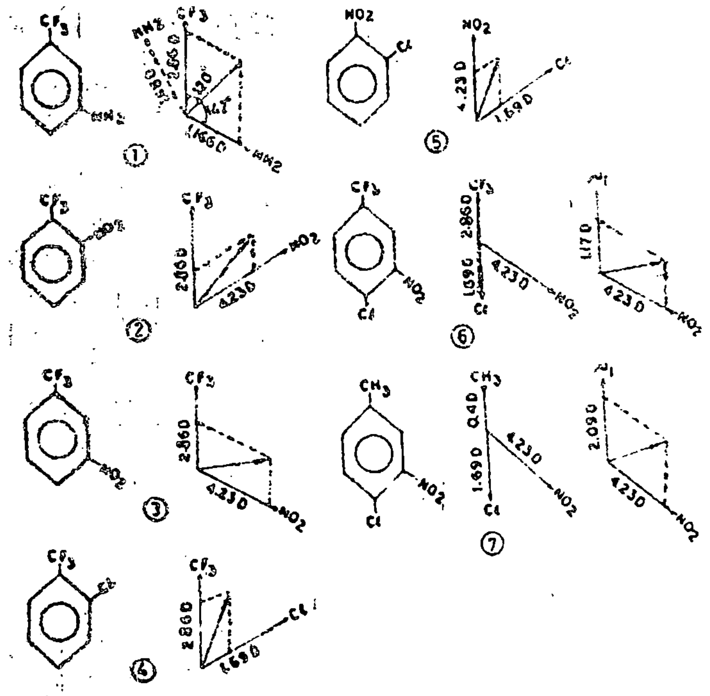

Fig.4.2-Conformation of the different molecules studied showing the orientation of the bond axes and the dipole moments and also bond moments: [1, *m*-Aminobenzotrifluoride; 2, *o*-nitrobenzotrifluoride; 3, *m*-nitrobenzotrifluoride; 4, *o*-chlorobenzotrifluoride; 5, *o*-chloronitrobenzene; 6, 4-chloro-3-nitrobenzotrifluoride & 7, 4-chloro-3-nitrotoluene]

The other two compounds, viz. m-aminobenzotrifluoride and O-chlorobenzotrifluoride have smaller values of dipole moments due to the same reasons as mentioned earlier.

The group moment of $-CF_3$ groups acts in the reverse direction to that of $-Cl$ group and hence its net effect is to reduce the total moment along the common axis. 4-chloro-3-nitrobenzotrifluoride thus shows the lower value of μ_j in benzene than in O-chloronitrobenzene. The group moment of $-CH_3$ group acts in the direction of $-Cl$ group and hence the resultant dipole moment increases along the common axis. That is why the last compound in table (4.2) and in fig. (4.2), i.e. 4-chloro-3-nitrotoluence has higher dipole moment in benzene than in O-chloronitrobenzene. The close agreement between the computed μ_j values with the theoretical ones shows that the dipole moments of these compounds have a preferred conformation, as depicted in fig. (4.2). Regarding the group moments assumed by us, they compensate each other to a certain extent.

Table 4.1a

Values of dielectric constant (ϵ'_{ij}), loss factor (ϵ''_{ij}) conductivity (K_{ij}) and weight fraction (W_j) at wave length λ = 3.0166 cms.

	Systems	W_j	ϵ'_{ij}	ϵ''_{ij}	$K_{ij} \times 10^{-10}$ in esu
1.	m-Aminobenzotrifluoride	0.0142	2.306	0.053	1.147
		0.0265	2.351	0.088	1.170
		0.0379	2.412	0.131	1.201
		0.0561	2.480	0.178	1.236
		0.0682	2.556	0.233	1.276
2.	O-Nitrobenzotrifluoride	0.0085	2.315	0.058	1.151
		0.0167	2.386	0.108	1.188
		0.0244	2.445	0.159	1.218
		0.0335	2.515	0.205	1.255
		0.0402	2.571	0.255	1.285
3.	m-Nitrobenzotrifluoride	0.0096	2.302	0.032	1.145
		0.0173	2.322	0.060	1.155
		0.0245	2.347	0.082	1.168
		0.0326	2.375	0.106	1.182
		0.0380	2.404	0.128	1.197
4.	O-chlorobenzotrifluoride	0.0081	2.278	0.027	1.133
		0.0142	2.315	0.048	1.151
		0.0225	2.350	0.061	1.169
		0.0312	2.368	0.087	1.178
		0.0374	2.404	0.106	1.197

Table 4.1b

Values of dielectric constant (ϵ'_{ij}), loss factors (ϵ''_{ij}) conductivity (K_{ij}) weight fractions (W_j) at wavelength λ = 3.0cms.

System	W_j	ϵ'_{ij}	ϵ''_{ij}	K_{ij} x 10^{-10} in esu
5. O-chloronitrobenzene	0.0109	2.340	0.066	1.170
	0.0173	2.393	0.100	1.198
	0.0217	2.422	0.126	1.213
	0.0280	2.479	0.165	1.242
	0.0330	2.511	0.192	1.259
6. 4-chloro-3-nitrobenzotrifluoride	0.0096	2.266	0.021	1.133
	0.0154	2.289	0.035	1.145
	0.0275	2.316	0.058	1.158
	0.0410	2.369	0.093	1.185
	0.0519	2.386	0.112	1.194
7. 4-chloro-3-nitrotoluene	0.0072	2.298	0.046	1.149
	0.0144	2.322	0.088	1.162
	0.0224	2.375	0.133	1.189
	0.0323	2.426	0.179	1.216
	0.0453	2.499	0.252	1.256

Table 4.2

The Computed Values of b, $\mu_j^{\langle s\rangle}$, μ_j (Compt.), μ_j (Rept) at 35°C

System	b	$\tau_s \times 10^{12}$ (Rept)	$\mu_j^{\langle s\rangle}$ in D (Compt)	μ_j in D (Compt)	μ_j in D (Rept)	μ_j in D (Theor)
λ = 3.0166 cm.						
m-Aminobenzotrifluoride	0.7234	9.9	3.1971	3.40	3.16	2.48
O-Nitrobenzotrifluoride	0.6913	10.7	4.7332	5.03	4.54	6.18
m-Nitrobenzotrifluoride	0.6403	12.0	3.2138	3.42	3.33	3.74
O-Chlorobenzotrifluoride	0.7356	9.6	3.1062	3.30	3.15	3.98
λ = 3.0 cm.						
O-Chloronitrobenzene	0.5816	13.5	4.6137	4.91	4.71	5.28
4-Chloro-3-nitrobenzotrifluoride	0.7088	10.2	2.7084	2.88	3.17	3.78
4-Chloro-3-nitro-toluene	0.3670	20.9	5.0899	5.41	4.88	5.58

Table 4.3

Electric moment of groups and bonds.

Group or bond	Electric moments in Debye units.
- CF_3	2.86
- NH_2	1.166
- NO_2	4.23
- Cl	1.69
- CH_3	-0.4

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Microwave Conductivity & Dipole Moment of Substituted Benzenes

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The slope of the curve of the variation of the microwave conductivity with concentration at infinite dilution, is used to obtain the dipole moments of some substituted benzotrifluorides and substituted benzenes at 35°C, subjected to the 3.0166 and 3.0 cm wavelength electric fields respectively. The data thus estimated are in agreement with the reported μ_j values, suggesting the uniqueness of the method adopted.

In recent years, much attention has been drawn to study the concentration variation of high frequency conductivity[1,2] to yield the dielectric relaxation parameters: relaxation time (τ), dipole moment (μ_j) of polar dielectrics, heat of enthalpy (ΔH_τ), entropy of dielectric relaxation (ΔS_τ) and the activation energy (E_τ), etc. Recently, it has been shown by Acharyya *et al.*[3] that under the microwave electric field the dipole moment is not a fixed quantity, but varies with temperature though it is supposed to be constant under the low-frequency and the dc electric fields.

The microwave conductivities (K_{ij}) of (i) *m*-aminobenzotrifluoride, (ii) *o*-nitrobenzotrifluoride, (iii) *m*-nitrobenzotrifluoride, (iv) *o*-chlorobenzotrifluoride at 3.0166 cm wavelength electric field are found to vary linearly with the concentration expressed in weight fractions (W_j). Similarly do those of (v) *o*-chloronitrobenzene, (vi) 4-chloro-3-nitrobenzotrifluoride and (vii) 4-chloro-3-nitrotoluene at 3.0 cm wavelength electric field, thereby yielding a constant slope β at any stage of dilution and thus makes the procedure more reliable than those done earlier[3]. Moreover, the systems mentioned above are very interesting regarding the sizes and shapes of these molecules. Of the seven systems, five are benzotrifluorides and two are comparatively less simple. The variation of K_{ij} with W_j could be expressed by $K_{ij}=\alpha+\beta W_j$ of which β is the most important to yield both τ_s as well as μ_j of the polar liquids. The K_{ij} of the respective solutions are computed by using the following relations:

$$K_{ij}\times 10^{-10}=1.1106+2.3536\,W_j$$
$$K_{ij}\times 10^{-10}=1.1169+4.1557\,W_j$$
$$K_{ij}\times 10^{-10}=1.1262+1.7747\,W_j$$
$$K_{ij}\times 10^{-10}=1.1199+2.0159\,W_j$$
$$K_{ij}\times 10^{-10}=1.1265+4.0539\,W_j$$
$$K_{ij}\times 10^{-10}=1.1286+1.1894\,W_j$$
$$K_{ij}\times 10^{-10}=1.1250+2.8594\,W_j$$

with the help of the available data[4,5].

Theoretical Formulations—The high frequency conductivity[6] of a polar-nonpolar liquid mixture is given by $K_{ij}=K'_{ij}+jK''_{ij}$ where K'_{ij} is the real part of the conductivity $=\omega\varepsilon''_{ij}/4\pi$, and K''_{ij} is the imaginary part of the conductivity $=\omega\varepsilon'_{ij}/4\pi$. Now the magnitude of the total high frequency conductivity is usually computed from the relation

$$K_{ij}=\frac{\omega}{4\pi}[\varepsilon''^2_{ij}+\varepsilon'^2_{ij}]^{1/2} \qquad \ldots(1)$$

The ε'_{ij} of the solution in the microwave region is very small and equals the optical dielectric constant, but still $\varepsilon'_{ij}\gg\varepsilon''_{ij}$ and ε''_{ij} is responsible for the absorption of electrical energy to yield resistance to polarization; hence the real part K'_{ij} of hf conductivity of solution of weight fraction W_j of polar solute at temperature T K is given by

$$K'_{ij}=\frac{\mu_j^2 N\rho_{ij}F_{ij}}{3M_jkT}\left(\frac{\omega^2\tau}{1+\omega^2\tau^2}\right)W_j \qquad \ldots(2)$$

where μ_j is the dipole moment of polar solute of molecular weight M_j, N is the Avogadro number, k is the Boltzmann constant and $F_{ij}=\left(\frac{\varepsilon_{ij}+2}{3}\right)^2$ is the local field. Hence, it requires that the total conductivity should be

$$K_{ij}=\frac{\omega}{4\pi}\varepsilon'_{ij} \qquad \ldots(3)$$

But for hf region it can be shown that

$$\varepsilon'_{ij}=\varepsilon_{ij,\infty}+\varepsilon''_{ij}/\omega\tau \qquad \ldots(4)$$

where $\varepsilon_{ij,\infty}$ is the optical dielectric constant of the solution. From Eqs (3) and (4) the total hf conductivity of the solution takes the form

$$K_{ij}=K_\infty+K'_{ij}/\omega\tau_s \qquad \ldots(5)$$

where K_∞ is a constant and τ_s is the relaxation time of the solute molecule in solution. As K_{ij} is a function of W_j, we have from Eq. (5)

$$\left(\frac{dK'_{ij}}{dW_j}\right)_{W_j\to 0}=\omega\tau_s\left(\frac{dK_{ij}}{dW_j}\right)_{W_j\to 0}=\omega\tau_s\beta \qquad \ldots(6)$$

where β is the slope of $K_{ij}-W_j$ curve at $W_j\to 0$ the density ρ_{ij} of the solution becomes ρ_i, the density of the solvent, and the local field F_{ij} of the solution is $F_i =$ the local field of the solvent $= \left(\frac{\varepsilon_i + 2}{3}\right)^2$. Under the circumstances, Eq. (2) on being differentiated with respect to W_j and as $W_j \rightarrow 0$ takes the form

$$\left(\frac{dK'_{ij}}{dW_j}\right)_{W_j \rightarrow 0} = \frac{\mu_j^2 N \rho_i F_i}{3M_j kT}\left(\frac{\omega^2 \tau_s}{1 + \omega^2 \tau_s^2}\right) \qquad \ldots(7)$$

Taking

$$b = \beta \bigg/ \left(\frac{\mu_j^2 N \rho_i F_i}{3M_j kT} \cdot \omega\right) \qquad \ldots(8)$$

We have from Eqs (6) and (7)

$$b = \frac{1}{1 + \omega^2 \tau_s^2}$$

and whence

$$\tau_s = \frac{\lambda}{2\pi C}\sqrt{\frac{1}{b} - 1} = \frac{\lambda \times 10^{-10}}{18.84}\sqrt{\frac{1}{b} - 1} \qquad \ldots(9)$$

Now from Eq. (8) the dipole moment of the solute molecule can be written in the form

$$\mu_j = \left(\frac{3M_j kT}{N \rho_i F_i} \cdot \frac{\beta}{\omega b}\right)^{1/2} \qquad \ldots(10)$$

The Eq. (9) is used to compute b from the reported τ_s data and thence the dipole moment of polar solute $\mu_j^{\langle S \rangle}$ when it is dissolved in a solvent. From Eq. (10), Müller[7] gave a relation between $\mu_j^{\langle S \rangle}$ and μ_j

$$\mu_j^{\langle S \rangle} = \mu_j [1 - C(\varepsilon_i - 1)^2] \qquad \ldots(11)$$

where $\mu_j^{\langle S \rangle}$ is the dipole moment of the solute in a solvent and μ_j the dipole moment of the polar solute, $C = 0.038$ which is claimed to be a constant for a large number of liquids, and ε_i the dielectric constant of the solvent.

Results and discussion—The dipole moments of seven systems of interest have been computed and listed in Table 1 with the reported μ_j data available from the literature for comparison. The μ_j data have also been computed from the bond dipole moment and bond angles, assuming that the benzene molecule is a planar one. The molecular parameters needed for this computation of theoretical values of μ_j are shown in Fig. 1.

The microwave conductivity data in the low-concentration region are of much interest as they reveal a completely different situation in comparison to those of high-concentration region, as recently shown by Acharyya *et al.*[8] This is the reason which led us to study the systems reported here and to calculate their dipole moments. High-concentration conductivity data of a polar-nonpolar liquid mixture is liable to yield the dipole moment due to dimer formation while those in low-concentration region behave linearly with the weight fraction and give the dipole moment due to monomer formation, i.e. solute-solvent association. The computed dipole moments agree with those reported experimentally as well as computed theoretical ones, as illustrated in Table 1. This fact suggests the basic soundness of the method adopted here.

The variation in the μ_j values for these substituted molecules in benzene might be due to (i) the difference in the values of group moments and (ii) inductive effect. The dipole moment of *o*-nitrobenzofluoride is always greater than that of *m*-nitrobenzotrifluoride (Table 1), both shown by the computed and theoretical μ_j's due to the two different positions of the $-NO_2$ group in the

Table 1—The Computed Values of b, $\mu_j^{\langle s \rangle}$, μ_j (Compt), μ_j(Rept) at 35°C

System	b	$\tau_s \times 10^{12}$ (Rept)	$\mu_j^{\langle s \rangle}$ (Compt)	μ_j (Compt)	μ_j (Rept)	$_j$ (Theo)
		$\lambda = 3.0166$ cm				
m-Aminobenzotrifluoride	0.7234	9.9	3.1971	3.40	3.16	2.48
o-Nitrobenzotrifluoride	0.6913	10.7	4.7332	5.03	4.54	6.18
m-Nitrobenzotrifluoride	0.6403	12.0	3.2138	3.42	3.33	3.74
o-Chlorobenzotrifluoride	0.7356	9.6	3.1062	3.30	3.15	3.98
		$\lambda = 3.0$ cm				
o-Chloronitrobenzene	0.5816	13.5	4.6137	4.91	4.71	5.28
4-Chloro-3-nitrobenzotrifluoride	0.7088	10.2	2.7084	2.88	3.17	3.78
4-Chloro-3-nitrotoluene	0.3670	20.9	5.0899	5.41	4.88	5.58

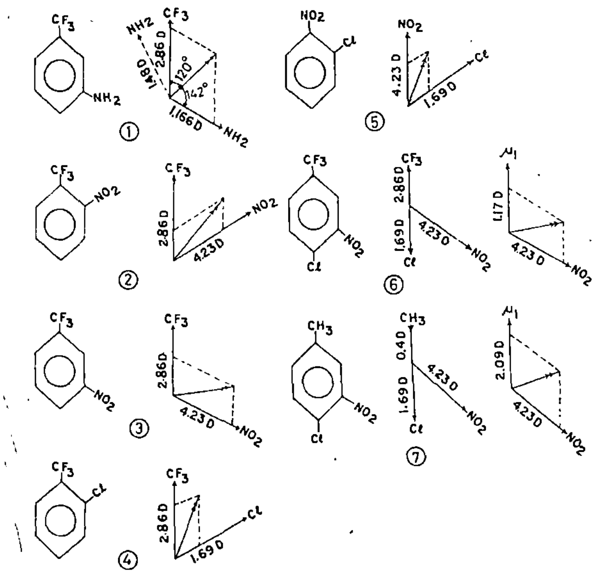

Fig. 1—Conformation of the different molecules studied showing the orientation of the bond axes and the dipole moments and also bond moments: [1, *m*-Aminobenzotrifluoride; 2, *o*-nitrobenzotrifluoride; 3, *m*-nitrobenzotrifluoride; 4, *o*-chlorobenzotrifluoride; 5, *o*-chloronitrobenzene; 6, 4-chloro-3-nitrobenzotrifluoride & 7, 4-chloro-3-nitrotoluene]

compound. The other two compounds, viz. *m*-aminobenzotrifluoride and *o*-chlorobenzotrifluoride have smaller values of dipole moments due to the same reasons as mentioned earlier.

The group moment of $-CF_3$ group acts in the reverse direction to that of $-Cl$ group and hence its net effect is to reduce the total moment along the common axis. 4-Chloro-3-nitrobenzotrifluoride thus shows the lower value of μ_j in benzene than in *o*-chloronitrobenzene. The group moment of $-CH_3$ group acts in the direction of $-Cl$ group and hence the resultant dipole moment increases along the common axis. That is why the last compound in Table 1 and in Fig. 1, i.e. 4-chloro-3-nitrotoluene has higher dipole moment in benzene than in *o*-chloronitrobenzene. The close agreement between the computed μ_j values with the theoretical ones shows that the dipole moments of these compounds have a preferred conformation, as depicted in Fig. 1. Regarding the group moments assumed by us, they compensate each other to a certain extent.

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CHAPTER V

ULTRA HIGH FREQUENCY CONDUCTIVITY OF POLAR - NONPOLAR LIQUID MIXTURES.

Introduction

The dipole moment of polar liquids varies with temperature when the dielectric liquid mixture is subjected to microwave field or rather to an alternating high frequency electric field. There are several methods (Gopala Krishna, 1957, Sen and Ghosh, 1972 and Ghosh et al, 1980) to compute the relaxation times as well as dipole moment of polar liquids dissolved in nonpolar solvents under the application of microwave and radiofrequency electric fields. But most of these methods suffer from extrapolation difficulties at infinite dilution i.e. $W_j \longrightarrow 0$. The microwave conductivity data for nitromethyl acetamide (NMA), have been computed from the recent studies on dielectric absorption in the very low concentration region by Dhull et al(1982) at temperature 25°C, 35°C, 45°C and 55°C in two different nonpolar solvents benzene and dioxane and also in the high concentration region in benzene at 25°C. Nitromethyl acetamide is supposed to be an important dielectric solute due to its very high values of dielectric constant and moreover its wide applications in biological research. Hence it attracted the attention of a large number of workers Sato et al (1976) to study its different dielectric parameters.

We too get interested to this system and an attempt has been taken to study the variation of microwave conductivity of NMA in very dilute solution of benzene and dioxane at various temperatures, viz. 25°C, 35°C, 45°C and 55°C and also at relatively high concentration region at 25°C. So it is thought that the calculated data of UHF conductivity of the mixture K_{ij} can be used to show that the low concentration region of this solution the association is solute-solvent type, i.e. monomer which changes into the solute-solute association or dimer at relatively high concentrations. Moreover, the extremely low concentration conductivity data may reveal new information regarding the solvation effect. As the information regarding the various types of interactions of solutes in solution could, however, be inferred from the estimated values of the dipole moments. Hence the dipole moments μ_j's of NMA as well as p-bromonitrobenzene (p-BNB) have been calculated from the concentration variation of UHF conductivity of the solution.

<u>Theory:-</u>

The HF conductivity due to Murphy and Morgan (1939) of polar-nonpolar liquid mixture is given by $K_{ij} = K'_{ij} + jK''_{ij}$ where K'_{ij} is the real part of the conductivity = $\left(\frac{\omega \epsilon''_{ij}}{4\pi}\right)$ and K''_{ij} is the imaginary part = $\left(\omega \epsilon'_{ij}/4\pi\right)$. The magnitude of total hf conductivity is usually given by

$$K_{ij} = \frac{\omega}{4\pi}\left(\epsilon''^2_{ij} + \epsilon'^2_{ij}\right)^{1/2} \qquad \ldots 5.1$$

ϵ'_{ij} of solution in the microwave region ($\lambda = 3.004$cm) though very small and is equal to optical dielectric constant, but still $\epsilon'_{ij} \gg \epsilon''_{ij}$ where ϵ''_{ij} is responsible for the absorption of electrical energy to offer resistance to polarization. Hence the real part of K_{ij} of HF conductivity of solution of weight fraction W_j of polar solute at temperature T K is

$$K'_{ij} = \frac{\mu_j^2 N \rho_{ij} F_{ij}}{3M_j kT}\left(\frac{\omega^2\tau}{1+\omega^2\tau^2}\right)W_j \qquad \ldots 5.2$$

where μ_j is the dipole moment of polar solute of molecular weight M_j , N the Avogadro's number, k is the Boltzmann constant and $F_{ij} = \left[(\epsilon_{ij}+2)/3\right]^2$ is the local field. Hence it is evident that, for the microwave electric field, the total conductivity becomes:

$$K_{ij} = \frac{\omega}{4\pi}\epsilon'_{ij} \qquad \ldots 5.3$$

But, for HF region, it can be shown that

$$\epsilon'_{ij} = \epsilon_{ij\infty} + \epsilon''_{ij}/\omega\tau \qquad \ldots 5.4$$

Using eqn. (5.3) and (5.4) it is shown that

$$K_{ij} = K_{\infty} + K'_{ij}/\omega\tau_s \qquad \ldots 5.5$$

where K_{∞} is a constant conductivity and τ_s is the relaxation time of the solute molecule in the solvent. Since K_{ij} is a function of W_j from eq. (5.5) we have :

$$\left(\frac{d K'_{ij}}{d W_j}\right)_{W_j \rightarrow 0} = \omega\tau_s\left(\frac{d K_{ij}}{d W_j}\right)_{W_j \rightarrow 0} = \omega\tau_s\beta \qquad \ldots 5.6$$

where β is the slope of $K_{ij} - W_j$ curve at $W_j \longrightarrow 0$. When $W_j \longrightarrow 0$ the density of the solution ρ_{ij} becomes ρ_i the density of the solvent and the local field F_{ij} of the solution becomes

$$F_i = \left[(\epsilon_i + 2)/3\right]^2 ,$$

the local field of the solvent.

Under this condition eq. (5.2) on differentiation with respect to W_j and as $W_j \longrightarrow 0$ takes the form:

$$\left(\frac{dK'_{ij}}{dW_j}\right)_{W_j \to 0} = \frac{\mu_j^2 N \rho_i F_i}{3 M_j k T}\left(\frac{\omega^2 \tau_s}{1+\omega^2\tau_s^2}\right) \quad \ldots 5.7$$

Taking

$$b = \beta \Big/ \left(\frac{\mu_j^2 N \rho_i F_i \omega}{3 M_j k T}\right) \quad \ldots 5.8$$

and using eqs. (5.6) and (5.7), we can have

$$b = \frac{1}{1+\omega^2\tau_s^2}$$

Hence

$$\tau_s = \frac{\lambda}{2\pi C}\left(\frac{1}{b}-1\right)^{1/2} = \frac{\lambda \times 10^{-10}}{18.84}\left(\frac{1}{b}-1\right)^{1/2} \quad \ldots 5.9$$

From eq. (5.8) the dipole moment, μ_j of polar solute can be evaluated by

$$\mu_j^{\langle s \rangle} = \left(\frac{3 M_j k T}{N \rho_i F_i} \cdot \frac{\beta}{b\,\omega}\right)^{1/2} \quad \ldots 5.10$$

Eq. (5.9) is used to compute 'b' from the reported τ_s data thence the dipole moment $\mu_j^{\langle s \rangle}$ of polar solute when it is dissolved in solvent, from eq. (5.10).

Müller (1934) gave a relation between $\mu_j^{\langle s \rangle}$ and the corrected μ_j of solute by

$$\mu_j^{\langle s \rangle} = \mu_j\left[1 - c(\epsilon_i - 1)^2\right] \qquad \ldots \; 5.11$$

where c is a constant which is claimed to be 0.038 for a large number of liquids and ϵ_i is the dielectric constant of the solvent.

Results and Discussions:

The eq. (5.2) shows that the real part of K_{ij} of h.f. conductivity of solution of weight fraction W_j of polar solute at temperature T K is function of concentration. So it is observed that the microwave conductivities (K_{ij}) of NMA in e.s.u. in benzene solvent at different temperatures, is a function of concentration and which can be written as :

$$K_{ij} \times 10^{-10} = 1.1415 + 7.0699 W_j \quad , \text{ at } 25^{\circ}\text{C}$$

$$K_{ij} \times 10^{-10} = 1.1278 + 8.1738 W_j \quad \text{at } 35^{\circ}\text{C}$$

$$K_{ij} \times 10^{-10} = 1.1178 + 8.4588 W_j \quad \text{at } 45^{\circ}\text{C}$$

and

$$K_{ij} \times 10^{-10} = 1.1062 + 9.1398 W_j \quad \text{at } 55^{\circ}\text{C}$$

Similarly it follows in dioxane solvent also and h.f. conductivity can be represented as:

$$K_{ij} \times 10^{-10} = 1.1107 + 8.1173 W_j \quad \text{at } 25^{\circ}\mathrm{C}$$

$$K_{ij} \times 10^{-10} = 1.0943 + 9.5319 W_j \quad \text{at } 35^{\circ}\mathrm{C}$$

$$K_{ij} \times 10^{-10} = 1.0922 + 9.2835 W_j \quad \text{at } 45^{\circ}\mathrm{C}$$

and

$$K_{ij} \times 10^{-10} = 1.0859 + 9.6132 W_j \quad \text{at } 55^{\circ}\mathrm{c}.$$

The results can be shown graphically by the help of fitted curves along with the experimental points on them. The microwave conductivities in e.s.u. are plotted against the weight fractions W_j of the solute shown in fig. (5.1) and (5.2). It is observed from the linear plot that from the region $W_j = 0.0022$ to $W_j = 0.0094$ of the solute in benzene and also from $W_j = 0.0030$ to $W_j = 0.0123$ of the solute in dioxane as the temperature of the systems increases, the UHF conductivity decreases, but maintaining a regular increase in slopes. The h.f. conductivity in the lower concentration region would vary linearly with W_j because ($\rho_{ij} F_{ij} / T$) in eqn. (5.2) assumed to be a constant value in the neighbourhood of 0.006 in

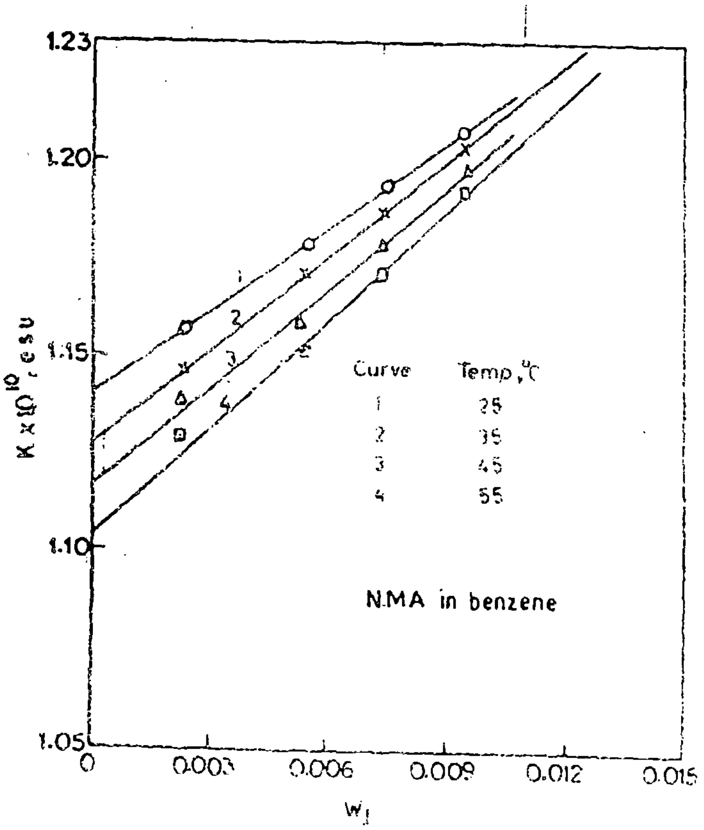

Fig.5.1—Concentration variation of K of NMA in benzene at different temperatures .

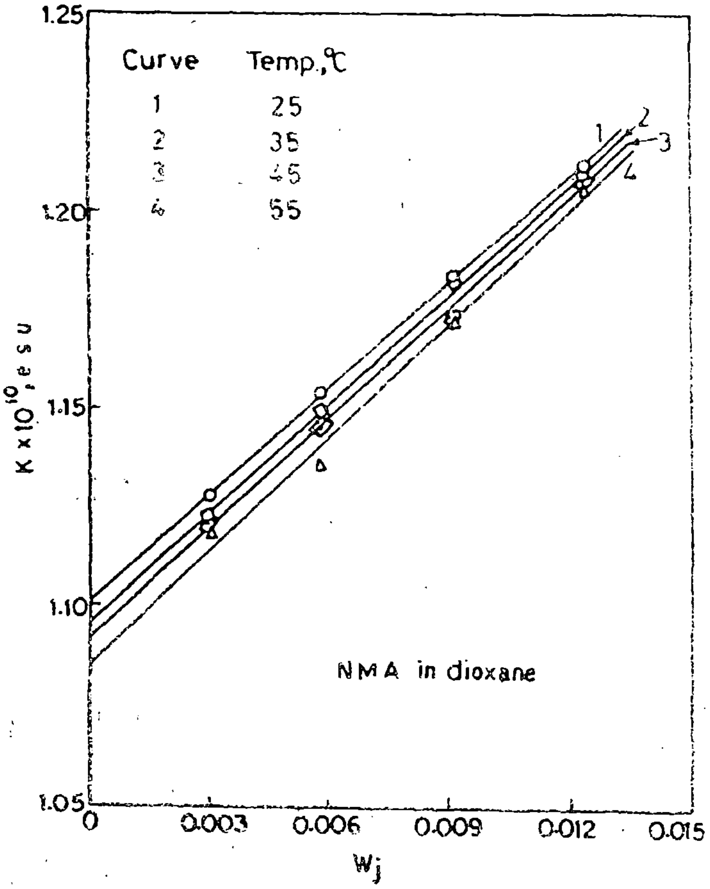

Fig. 5.2–Concentration variation of *K* of NMA in dioxane at different temperatures

the limit $W_j = 0$, at all the experimental temperatures. But at higher concentration the plot of K_{ij} with W_j will be mostly nonlinear. This is shown in Fig.(5.3) in which the h.f. conductivity of NMA in benzene at 25°C. It has been only plotted with W_j having its range from $W_j = 0.0212$ to $W_j = 0.0520$. This fact is also corroborated by the data of p-bromonitrobenzene in benzene, its nature of concentration variation also is shown in Fig. (5.4).

The nature of variation of conductivity K_{ij} with weight fraction W_j both in benzene and dioxane shown in Figs. (5.1) and (5.2) indicate that the conductivities at different temperature have tending to meet within a certain zone in the higher concentration region, which clearly indicate that higher values of K_{ij} with respect to increasing temperature are expected at higher concentration region. The curves of the high concentration K_{ij} data thus available are found to be temperature dependent quantities, i.e. the elevated temperature of the mixture gives rise to higher value of K_{ij} after a certain concentration zone. Thus for high concentration the conductivity data of mixture of polar-nonpolar liquids forced us to draw the curves of K_{ij} against W_j at all experimental temperatures to meet at a common point on the K_{ij}

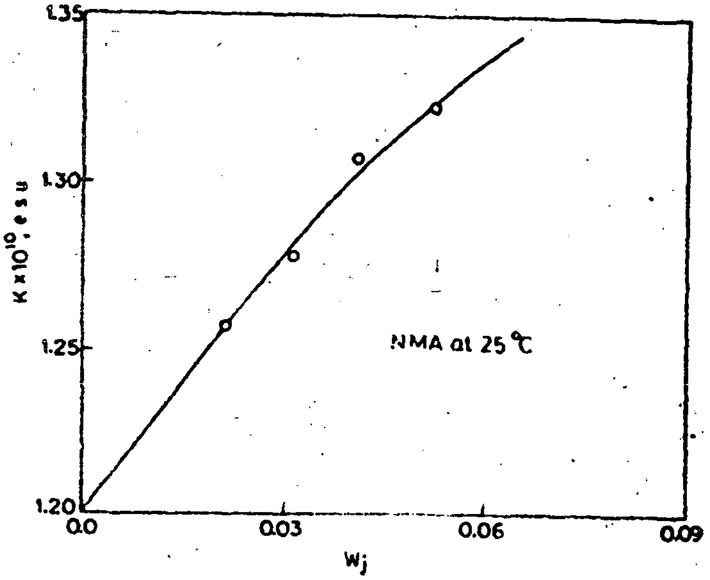

Fig.5.3-Concentration variation of K of NMA in benzene at 25°C

axis in the limit $W_j = 0$ which is apriori determined value from

$$\left(K_{ij}\right)_{W_j \to 0} = \left(\omega \epsilon'_{ij} / 4\pi\right)_{W_j \to 0}$$

for most of the solute-solvent systems. This is usually attributed to the solvation effect. When the conductivity data of p - BNB in benzene are considered then the curves in Fig. (5.4) presenting the conductivity data at different temperatures, measured at relatively higher concentrations from $W_j = 0.0162$ to $W_j = 0.0416$, are found to meet at a common point on the K_{ij} axis at $W_j = 0$.

In fact, the information regarding the low concentration conductivities of polar compounds in nonpolar solvents can no longer be borrowed from high concentration conductivity data.

The data of K_{ij} (table 5.1a,b, c) for NMA in benzene and dioxane available from the dielectric absorption studies by Dhull et al (1982) revealed a new picture regarding the concentration variation of K_{ij} data at all stages of dilution, so far as the lower concentration region is concerned, Both in benzene and dioxane as solvents, the UHF conductivities of the present system at $W_j \to 0$ gradually decrease as the temperature increases from 25°C to 55°C shown by the normal

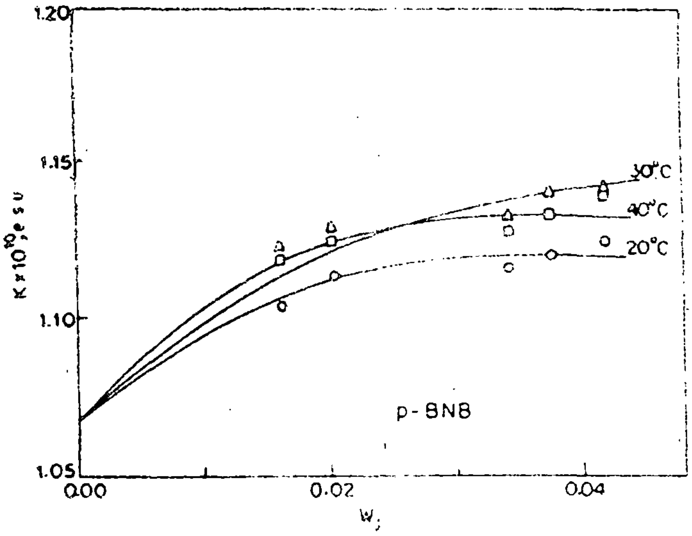

Fig.5.4–Concentration variation of *K* of *p*-BNB in benzene at different temperatures

equations relating K_{ij} and W_j as derived from the available experimental data and also as illustrated graphically in Figs. 5.1 and 5.2 respectively. But there may exist a certain link between the low and high concentration data of K_{ij} against W_j. In the limit $W_j = 0$, the graphs using lower concentration conductivity data for some suitable system in any solvent like benzene or dioxane, do not meet at a common point, but at different points on the K_{ij} axis as shown is Figs. 5.1 and 5.2. The value of the intercepts for K_{ij} at $W_j = 0$ decreases with increase in temperature. But both these features are not exhibited in case of aromatic compounds like p-BNB in benzene. In the higher concentration region, the experimental curves (Fig. 5.1 and 5.2) have a tendency to meet each other within a certain higher concentration zone, below and above which the system investigated has most probably a different physical nature.

Dipole Moment And Structural Form:

The dipole moments μ_j of NMA and p-BNB at different temperatures were then computed from eq.(5.10) and the equation of fitted curves of the variation of μ_j as function of temperature in ^{o}C for the given solute of interest are given below:

$$\mu_j = 3.6071 + 0.0112\,t - 8.3 \times 10^{-6}t^2$$ for NMA in benzene

$$\mu_j = 3.4294 + 0.0126t - 6.7 \times 10^{-5}t^2$$ for NMA in dioxane

and

$$\mu_j = 2.114 + 0.0747t - 3.8 \times 10^{-4}t^2$$ for p-BNB in benzene

The μ_j's of these systems were found to increase in a regular fashion with temperature in °C. The corrected μ_j values were obtained from eq. (5.11). However, both the values of dipole moments computed from eq.(5.10) and (5.11) using the reported values of τ_s are higher than those of actual values because of the estimated error (Bhull et al 1982) of the order of 10 percent in the calculated values of τ_s and hence the computed values of the dipole moments from these data would naturally be higher. Both these values of μ_j's are given in table (5.2), with those of reported μ_j, τ_s etc.

The computed μ_j values from eq. (5.10) are finally shown graphically in fig. 5.5 against temperature. From table (5.2) it is evident that μ_j's are always higher when measured from low concentration conductivity data of NMA in benzene and dioxane, but at 25°C the high concentration data (Fig. 5.3) always gives us the low value of

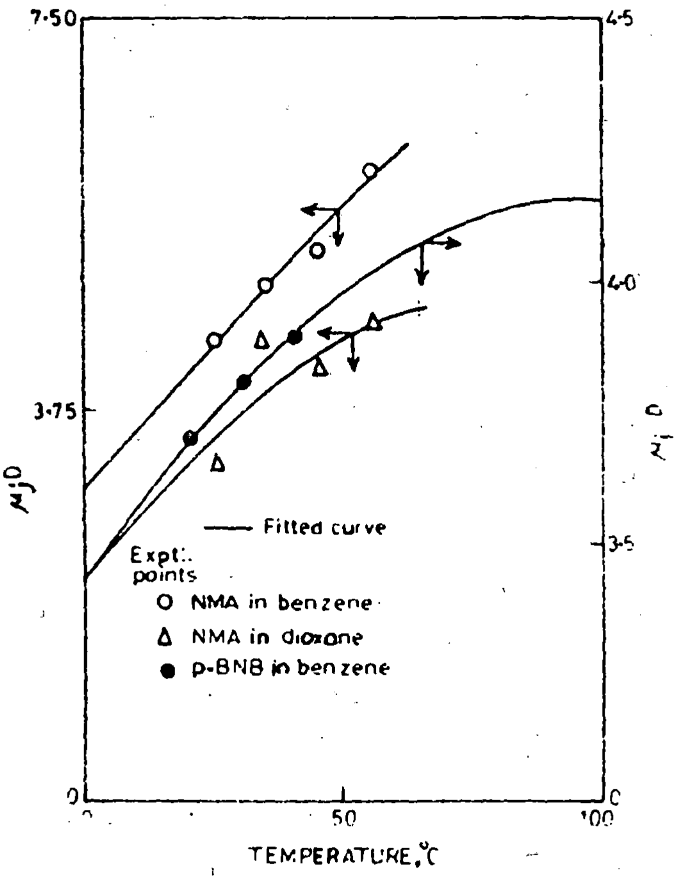

Fig.5.5-Variation of experimentally observed dipole moment with temperature in °C along with the fitted curves

dipole moment. However, p-BNB in benzene does not fall in this category. As observed by Dhull et al (1982), the high values of dipole moments of NMA in benzene and dioxane are due to monomers, i.e. solute-solvent association which may actually occur in the lower concentration region. This state of affairs changes above a certain concentration zone to dimer, i.e. solute-solute association. The variation in the theoretically computed μ_j values for these molecules, one aliphatic ketonic group and the other substituted benzene might be due to (i) the difference in the values of group moments and (ii) inductive effect. The dipole moments of NMA in solvents at lower concentrations (Table 5.2), shown both by the experimentally computed and theoretically obtained μ_j's due to the solute-solute association, i.e. dimer formation. For p-BNB group moments of $C-NO_2$ and C-Br act at a certain angle, assuming the benzene ring as a planar one (Fig. 5.6). With this conformation in view, the theoretical value of μ_j in terms of bond moments and bond angles gives us only the monomer μ_j value in case of p-BNB as it excellently agrees with the computed μ_j's (Table 5.2). Thus p-BNB gives the dipole moments at higher concentration due to monomer formation. The group moments of $C-CH_3$, C-N and N-H groups act along a common axis as sketched in Fig. 5.6. But the group

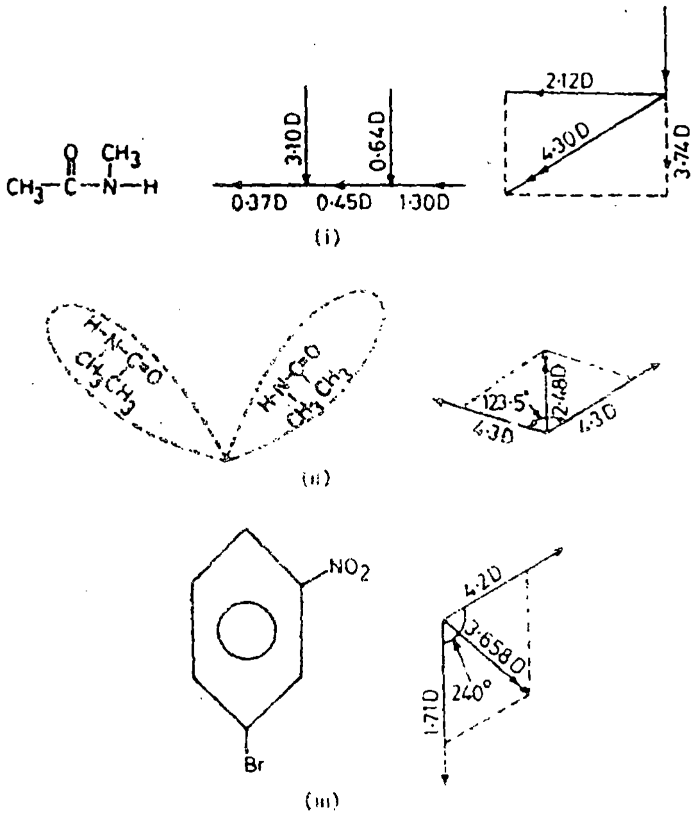

Fig. 5·6– Conformation of the different molecules showing the orientation of the bond axes, bond moments and also the dipole moments [(i) structural form of NMA; (ii), structural form of dimers; and (iii) structural form of *p*-BNB] moments of C = O and N-CH_3 act along the direction normal to that of C-CH_3. With this preferred conformational directions for NMA as depicted in Fig. 5.6, the resultant μ_j value was obtained for monomer formation. These data for μ_j's thus obtained also excellently agree with the computed μ_j's (Table 5.2). But for the dimer formation of NMA in benzene the two monomers attach each other with their most electropositive and electronegative elements, i.e. [-H] and [-O-] form a certain angle viz. 123.5° as calculated both from experimental and theoretical μ_j values as shown in Fig. 5.6, while the electropositive and electronegative elements project themselves along the dipole axes. Thus the monomer due to this preferred angle, the immediate obvious feature in fig. 5.6 (ii). Further the dipole moment (Fig. 5.5) is a temperature dependent quantity when the system is subjected to UHF alternating fields. Hence it is concluded that the high values of dipole moments are due to formation of monomer and less value due to formation of dimer in dielectrics, particularly in the case of NMA in benzene and dioxane.

Table 5.1a

Values of dielectric constant (ϵ'_{ij}), loss factor (ϵ''_{ij}) uhf conductivity (K_{ij}) weight fractions (W_j) at different temperatures (t).

Systems	Temp. t ^oC	W_j	ϵ'_{ij}	ϵ''_{ij}	K_{ij} x 10^{-10} in esu
N-methylacetamide in benzene	25	0.0022	2.317	0.0220	1.157
		0.0053	2.361	0.0456	1.179
		0.0073	2.390	0.0700	1.194
		0.0094	2.415	0.0951	1.207
	35	0.0022	2.295	0.0195	1.146
		0.0053	2.344	0.0414	1.171
		0.0073	2.379	0.0684	1.188
		0.0094	2.409	0.0875	1.204
	45	0.0022	2.281	0.0182	1.139
		0.0053	2.321	0.0364	1.159
		0.0073	2.361	0.0620	1.179
		0.0094	2.399	0.0824	1.199
	55	0.0022	2.261	0.0152	1.129
		0.0053	2.305	0.0336	1.151
		0.0073	2.346	0.0593	1.172
		0.0094	2.389	0.0792	1.194
N-methylacetamide in benzene in high concentration.	25	0.0212	2.512	0.1532	1.257
		0.0310	2.553	0.1866	1.278
		0.0406	2.594	0.2020	1.307
		0.0520	2.638	0.2369	1.323.

Table 5.1b

Values of dielectric constants (ϵ'_{ij}), loss factor (ϵ''_{ij}) uhf conductivity (K_{ij}) and weight fraction (W_j) at different temperatures (t)

Systems	Temp t °C	W_j	ϵ'_{ij}	ϵ''_{ij}	K_{ij} x 10^{-10} in esu
N-methyl acetamide in dioxane	25	0.0030	2.279	0.0489	1.138
		0.0058	2.310	0.0817	1.154
		0.0091	2.369	0.1188	1.184
		0.0123	2.422	0.1488	1.212
	35	0.0030	2.247	0.0450	1.122
		0.0058	2.303	0.0777	1.150
		0.0091	2.366	0.1151	1.183
		0.0123	2.419	0.1430	1.210
	45	0.0030	2.244	0.0401	1.121
		0.0058	2.291	0.0716	1.144
		0.0091	2.349	0.1072	1.174
		0.0123	2.415	0.1357	1.208
	55	0.0030	2.241	0.0361	1.119
		0.0058	2.274	0.0649	1.136
		0.0091	2.346	0.0994	1.173
		0.0123	2.412	0.1242	1.206

Table 5.1c

Values of dielectric constant (ϵ'_{ij}), loss factor (ϵ''_{ij}) uhf conductivity (K_{ij}) and weight fraction (W_j) at different temperature (t).

System	Temp. t ^oC	W_J	ϵ'_{ij}	ϵ''_{ij}	K_{ij} x 10^{-10} in esu
p-Bromonitrobenzene in benzene	20	0.0162	2.21	0.0263	1.104
		0.0202	2.2313	0.0302	1.114
		0.0342	2.2352	0.0346	1.116
		0.0375	2.2423	0.0436	1.120
		0.0416	2.2539	0.0447	1.126
	30	0.0162	2.2483	0.0265	1.123
		0.0202	2.2621	0.0316	1.130
		0.0342	2.2670	0.0346	1.132
		0.0375	2.2739	0.0374	1.140
		0.0416	2.2880	0.0458	1.143
	40	0.0162	2.2394	0.0346	1.118
		0.0202	2.2531	0.0447	1.125
		0.0342	2.2582	0.0583	1.128
		0.0375	2.2691	0.0632	1.134
		0.0416	2.2789	0.0793	1.139

Table 5.2

Values of $(\mu_j)_{compts}$ $(\mu_j)_{rept}$ $(\mu_j)_{theor}$ $(\tau_s)_{rept}$ and b(comput) at different temperatures.

System	Temp. in ^oC	b(compt)	τ_s (rept.)x 10^{+12} Sec.	μ_j (comp.) [Eq.10] D	μ_j (corr) [Eq.11] D	(μ_j) theor. D	(μ_j) rept. D
N-methyl acetamide in benzene	25	0.6334	12.13	3.882	4.135	4.30	3.69
	35	0.7068	10.27	4.008	4.262		3.78
	45	0.7637	8.87	4.064	4.313		3.80
	55	0.8065	7.81	4.216	4.467		3.82
N-methyl acetamide in dioxane	25	0.7185	9.88	3.647	3.862		3.66
	35	0.7824	8.41	3.886	4.109		3.69
	45	0.8252	7.34	3.830	4.043		3.78
	55	0.8631	6.35	3.907	4.117		3.83
N-methyl acetamide in benzene in high concentration.	25	0.6987	10.47	2.236	2.383	2.48	1.87
p-Bromonitrobenzene in benzene	20	0.7905	8.21	3.456	3.687	3.658	
	30	0.8259	7.32	4.013	4.272		
	40	0.8657	6.28	4.494	4.774		

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The variation of UHF conductivity K_{ij} of nitromethylacetamide in benzene and dioxane solvents in the lower as well as higher concentration regions of a polar solute, has been extensively studied to throw light regarding a constant conductivity at infinite dilution due to solvation effect at different temperatures. It is found that the measured data of K_{ij} for the lower concentration region is perfectly linear with W_j, the weight fraction of the solute, but differs radically at $W_j \to 0$ due to solute-solvent association or monomer formation in dielectrics. This observation, however, escapes detection when the K_{ij} data for higher concentration region are used as found in the case of *p*-bromonitrobenzene in benzene. The slope of curves showing UHF conductivity data versus concentration of the solution at infinite dilution, is finally used to estimate the temperature dependence of dipole moments for these liquids.

1 Introduction

The dipole moment of polar liquids varies[1,2] with temperature when the dielectric mixture is subjected to an alternating microwave or rather high frequency electric field. There are several methods[3-5] to compute the relaxation times as well as dipole moments of polar liquids dissolved in nonpolar solvents under the application of microwave and radio frequency electric fields. But these methods[3,4], unlike our method[5], suffer from extra-polation difficulties at $W_j \to 0$. The microwave conductivity data for nitro-methyl acetamide (NMA), have been computed from the recent studies on dielectric absorption in the very low concentration region by Dhull *et al.*[6] at temperatures 25°C, 35°C, 45°C, and 55°C in two different solvents (benzene and dioxane) and also in the high concentration regions at 25°C in benzene. NMA is an important dielectric solute because of its very high dielectric constant, and its wide biological applications. Hence it attracted the attention of a large number of workers[7].

We, therefore have chosen this system is order to report the microwave conductivity data of NMA in benzene and dioxane at different temperatures, viz. 25°C, 35°C, 45°C and 55°C in the extremely low concentration region as well as those at relatively high concentration region only at 25°C. The data for K_{ij} are then used to show that in the low concentration range of this solution the association is solute-solvent type, i.e. monomer which changes into the solute-solute association or dimer at relatively high concentrations. Moreover, the extremely low concentration conductivity data may reveal new information regarding the solvation effect[8].

Finally, the information regarding the various types of interactions of solutes in solution could, however, be inferred from the estimated values of the dipole moments. Hence the dipole moments μ_j's of NMA as well as *p*-bromonitrobenzene (*p*BNB) have been calculated from the concentration variation of UHF conductivity of the solution by the method described elsewhere[1]. The μ_j values thus obtained are found to increase with temperature as already shown by Acharyya *et al.*[1] for other systems. The fitted curves of the variation of μ_j as a function of temperature in °C for the given solutes of interest are

$$\mu_j = 3.6071 + 0.0112t - 8.3 \times 10^{-6}t^2 \quad \text{for NMA in benzene}$$

$$\mu_j = 3.4294 + 0.0126t - 6.7 \times 10^{-5}t^2 \quad \text{for NMA in dioxane}$$

and

$$\mu_j = 2.114 + 0.0747t - 3.8 \times 10^{-4}t^2 \quad \text{for } p\text{-BNB in benzene}$$

The μ_j's of these systems were found to increase in a regular fashion with temperature (in °C).

2 Theory

The HF conductivity due to Murphy and Morgan[9] of polar-nonpolar liquid mixture is given by $K_{ij} = K'_{ij} + jK''_{ij}$ where K'_{ij} is the real part of the conductivity $= \omega\varepsilon''_{ij}/4\pi$ and K''_{ij} is the imaginary part $= \omega\varepsilon'_{ij}/4\pi$. The magnitude of total hf conductivity is usually given by

$$K_{ij} = \frac{\omega}{4\pi}(\varepsilon''^2_{ij} + \varepsilon'^2_{ij})^{1/2} \quad \ldots(1)$$

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ε'_{ij} of solution in the microwave region ($\lambda = 3.004\,\mathrm{cm}$), though very small and is equal to optical dielectric constant, but still $\varepsilon'_{ij} \gg \varepsilon''_{ij}$ where ε''_{ij} is responsible for the absorption of electrical energy to offer resistance to polarization. Hence the real part of K_{ij} of HF conductivity of solution of weight fraction W_j of polar solute at temperature TK is

$$K'_{ij}=\frac{\mu_j^2 N\rho_{ij}F_{ij}}{3M_jkT}\left(\frac{\omega^2\tau}{1+\omega^2\tau^2}\right)W_j \qquad \ldots(2)$$

where μ_j is the dipole moment of polar solute of molecular weight M_j, N the Avogadro number, k is the Boltzmann constant and $F_{ij}=[(\varepsilon_{ij}+2)/3]^2$ is the local field. Hence it is evident that, for the microwave electric field, the total conductivity becomes:

$$K_{ij}=\frac{\omega}{4\pi}\varepsilon'_{ij} \qquad \ldots(3)$$

But, for HF region, it can be shown that

$$\varepsilon'_{ij}=\varepsilon_{ij\infty}+\varepsilon''_{ij}/\omega\tau \qquad \ldots(4)$$

Using Eqs (2), (3) and (4) it is shown that

$$K_{ij}=K_\infty+\frac{K'_{ij}}{\omega\tau_s} \qquad \ldots(5)$$

where K_∞ is a constant conductivity and τ_s is the relaxation time of the solute molecule in the solvent. Since K_{ij} is a function of W_j from Eq. (5) we have:

$$\left(\frac{\mathrm{d}K'_{ij}}{\mathrm{d}W_j}\right)_{W_j\to 0}=\omega\tau_s\left(\frac{\mathrm{d}K_{ij}}{\mathrm{d}W_j}\right)_{W_j\to 0}=\omega\tau_s\beta \qquad \ldots(6)$$

where β is the slope of $K_{ij}-W_j$ curve at $W_j\to 0$. When $W_j\to 0$ the density of the solution ρ_{ij} becomes ρ_i the density of the solvent and the local field F_{ij} of the solution becomes $F_i=[(\varepsilon_i+2)/3]^2=$ the local field of the solvent.

Under this condition, Eq. (2) on differentiation with respect to W_j and as $W_j\to 0$ takes the form:

$$\left(\frac{\mathrm{d}K'_{ij}}{\mathrm{d}W_j}\right)_{W_j\to 0}=\frac{\mu_j^2 N\rho_iF_i}{3M_jkT}\left(\frac{\omega^2\tau_s}{1+\omega^2\tau_s^2}\right) \qquad \ldots(7)$$

Taking

$$b=\beta\bigg/\left(\frac{\mu_j^2 N\rho_iF_i\omega}{3M_jkT}\right) \qquad \ldots(8)$$

and using Eqs (6) and (7), we can have

$$b=\frac{1}{1+\omega^2\tau_s^2}$$

Hence

$$\tau_s=\frac{\lambda}{2\pi c}\left(\frac{1}{b}-1\right)^{1/2}=\frac{\lambda\times 10^{-10}}{18.84}\left(\frac{1}{b}-1\right)^{1/2} \qquad \ldots(9)$$

From Eq. (8) the dipole moment μ_j of polar solute can be evaluated by

$$\mu_j^{<s>}=\left(\frac{3M_jkT}{N\rho_iF_i}\cdot\frac{\beta}{b\omega}\right)^{1/2} \qquad \ldots(10)$$

Eq. (9) is used to compute b from the reported τ_s data and thence the dipole moment $\mu_j^{<s>}$ of polar solute when it is dissolved in solvent, from Eq. (10).

Müller[10] gave a relation between $\mu_j^{<s>}$ and the corrected μ_j of solute by

$$\mu_j^{<s>}=\mu_j[1-C(\varepsilon_i-1)^2] \qquad \ldots(11)$$

where C is a constant which is claimed to be 0.038 for a large number of liquids and ε_i is the dielectric constant of the solvent.

3 Results and Discussion

The microwave conductivities of NMA in benzene at different temperatures, as a function of concentration, are given by:

$K\times 10^{-10}=1.1415+7.0699\,W_j$ at 25°C

$K\times 10^{-10}=1.1278+8.1738\,W_j$ at 35°C

$K\times 10^{-10}=1.1178+8.4588\,W_j$ at 45°C

and

$K\times 10^{-10}=1.1062+9.1398\,W_j$ at 55°C

while those in dioxane are:

$K\times 10^{-10}=1.1107+8.1173\,W_j$ at 25°C

$K\times 10^{-10}=1.0943+9.5319\,W_j$ at 35°C

$K\times 10^{-10}=1.0922+9.2835\,W_j$ at 45°

and

$K\times 10^{-10}=1.0859+9.6132\,W_j$ at 55°C

and have been shown graphically by the fitted curves along with the experimental points on them in Figs 1 and 2, in which the microwave conductivities in e.s.u. are plotted against the weight fractions W_j of the solute. It is found that from the region $W_j=0.0022$ to $W_j=0.0094$ of the solute in benzene and also from $W_j=0.0030$ to $W_j=0.0123$ of the solute in dioxane as the temperature of the systems increases, the UHF conductivity decreases, but maintaining a regular increase in slopes. The HF conductivity in the lower concentration region would vary linearly with W_j, because $\rho_{ij}F_{ij}/T$ in Eq. (2) assumes a constant value in the neighbourhood of 0.006 in the limit $W_j=0$, at all the experimental temperatures, but at higher concentration the plot of K_{ij} with W_j will be mostly nonlinear. This is shown in Fig. 3 in which the HF conductivity of NMA in benzene at 25°C only has been plotted with W_j having its range from $W_j=0.0212$ to $W_j=0.0520$. This fact is also corroborated by the data *p*-bromonitrobenzene[11] in benzene (Fig. 4).

In the variation of K_{ij} with W_j both in benzene and dioxane the K_{ij}'s as shown in Figs 1 and 2 have tendency to meet within a certain zone in the higher concentration region and then they are expected to

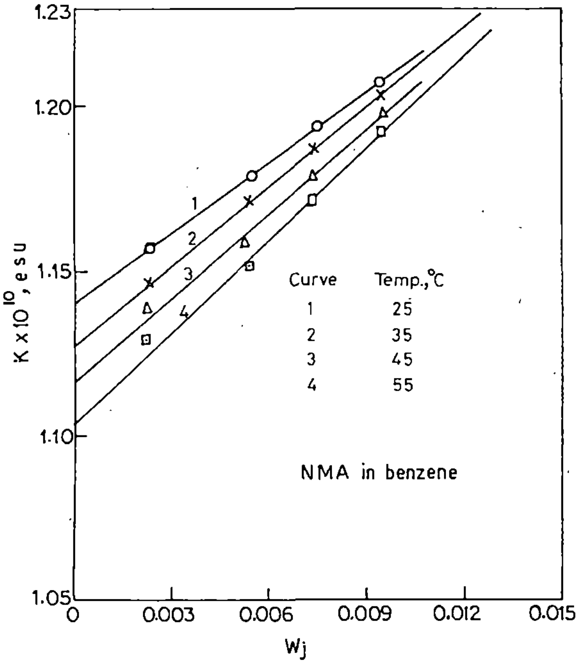

Fig. 1—Concentration variation of K of NMA in benzene at different temperatures

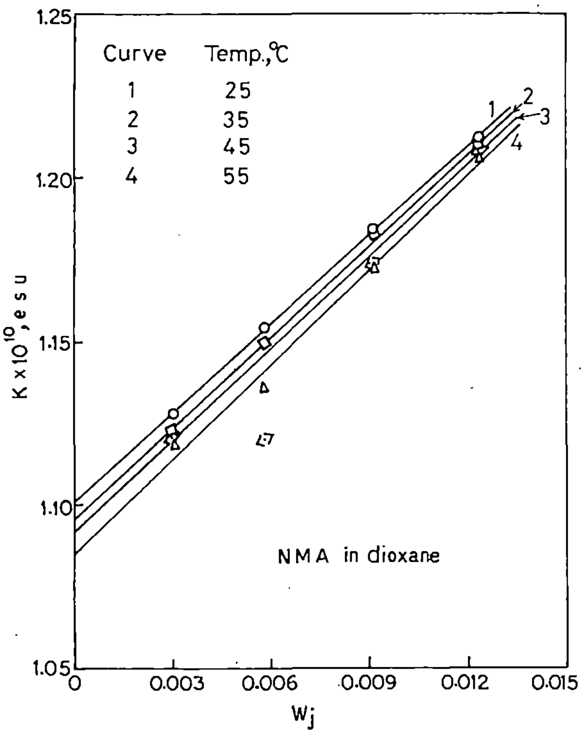

Fig. 2—Concentration variation of K of NMA in dioxane at different temperatures

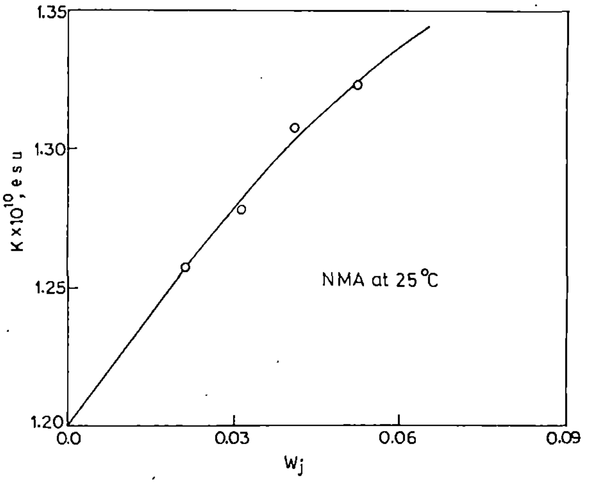

Fig. 3—Concentration variation of K of NMA in benzene at 25°C

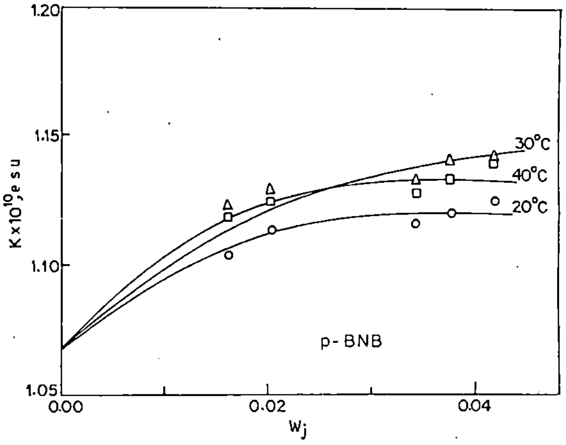

Fig. 4—Concentration variation of K of p-BNB in benzene at different temperatures

give the higher values of K_{ij} data with respect to increasing temperatures in the higher concentration region. The curves of the high concentration K_{ij} data thus available are found to be temperature-dependent quantities, i.e. the elevated temperature of the mixture gives rise to higher value of K_{ij} after a certain concentration zone. This had already been demonstrated by Acharyya *et al.*[1] for a large number of polar compounds in benzene at relatively higher concentrations. Thus, for high concentrations, conductivity data of polar-nonpolar liquid mixture forced the experimentalists to draw curves of K_{ij} against W_j at all experimental temperatures to meet at a common point on the K_{ij} axis in the limit $W_j = 0$ which is apriori determined value from $(K_{ij})_{W_j \to 0} = (\omega \varepsilon'_{ij}/4\pi)_{W_j \to 0}$ for most of the solute-solvent systems. This is usually attributed to the solvation effect[8]. In the case of p-BNB in benzene (Fig. 4), the curves presenting the conductivity data[9] at different temperatures, measured at relatively higher concentrations from $W_j = 0.0162$ to $W_j = 0.0416$, are found to meet at a common point on the K_{ij} axis at $W_j = 0$.

In fact, the information regarding the low-concentration conductivities of polar compounds in nonpolar solvents can no longer be borrowed from high concentration conductivity data. The high as well as low-concentration data of K_{ij} are very scanty. This is why the data of K_{ij} for NMA in benzene and dioxane available from the dielectric absorption studies by Dhull *et al.*[6] revealed a new picture regarding the concentration variation of K_{ij} data at all stages of dilution so far as the lower-concentration region is concerned. Both in benzene and dioxane as solvents, the UHF conductivities of the present system at $W_j \rightarrow 0$ gradually decrease as the temperature increases from 25°C to 55°C as shown by the normal equations relating K_{ij} and W_j, as derived from the available experimental data and also as illustrated graphically in Figs 1 and 2 respectively. But there may exist a certain link between the low and high concentration data of K_{ij} against W_j. In the limit $W_j = 0$, the graphs using lower-concentration conductivity data for some suitable system in any solvent like benzene or dioxane, do not meet at a common point, but at different points on the K axis as shown in Figs 1 and 2. The value of the intercepts for K_{ij} at $W_j = 0$ decreases with increase in temperature. But both these features are not exhibited in case of aromatic compounds like *p*-BNB in benzene. In the higher-concentration region, the experimental curves (Figs 1 and 2) have a tendency to meet each other within a certain higher-concentration zone, below and above which the system investigated has most probably a different physical nature.

The dipole moments μ_j of NMA and *p*-BNB at different temperatures were then computed from Eq. (10). The corrected μ_j values were obtained from Eq. (11). However both the values of dipole moments computed from Eqs (10) and (11) using the reported values of τ_s are higher than those of the actual values because of the estimated error[6] of the order of 10% in the calculated values of τ_s and hence the computed values of the dipole moments from these data would naturally be higher. Both these values of μ_j's are given in Table 1, with those of reported μ_j, τ_s, etc. The computed μ_j values from Eq. (10) are finally shown graphically in Fig. 5 against temperature. From Table 1 it is evident that μ_j's are always higher when measured from low-concentration conductivity data of NMA in benzene and dioxane, but at 25°C the high concentration data (Fig. 3) always gives us the low value of dipole moment. However, *p*-BNB in benzene does not fall in this category. As observed by Dhull *et al.*[6], the high values of dipole moments of NMA in benzene and dioxane are due to monomers, i.e. solute-solvent association which may actually occur in the lower-concentration region. This state of affairs changes above a certain concentration zone to dimer, i.e. solute-solute association. The variation in the theoretically computed μ_j values for these molecules, one aliphatic ketonic group and the other substituted benzene might be due to (i) the difference in the values of group moments and (ii) the inductive effect[12]. The dipole moments of NMA in solvents at lower concentrations will be greater than those at higher concentrations (Table 1), shown both by the experimentally computed and theoretically obtained μ_j's due to the solute-solute association, i.e. dimer formation. For *p*-BNB the group moments of $C-NO_2$ and $C-Br$ act at a certain angle, assuming the benzene ring as a planar one (Fig. 6). With this conformation in view, the theoretical value of μ_j in terms of bond moments and bond angles gives us only the monomer μ_j value in case of *p*-BNB as it excellently agrees with the computed μ_j's (Table 1). Thus *p*-BNB gives the dipole moments at higher concentration due to

Table 1—Values of $(\mu_j)_{\text{comput}}$, $(\mu_j)_{\text{rept}}$, $(\mu_j)_{\text{theor}}$, $(\tau_s)_{\text{rept}}$ and *b*(comput) at Different Temperatures

System	Temp. in °C	*b*(Comput.)	τ_s rept. 10^{-12}s	(μ_j) comput. [Eq. 10]	(μ_j) corr. [Eq. 11]	$(\mu_j)_\lambda$ D	$(\mu_j)_\lambda$ rept D
N-methyl acetamide in benzene	25	0.6334	12.13	3.882	4.135		3.69
	35	0.7068	10.27	4.008	4.262		3.78
	45	0.7637	8.87	4.064	4.313	4.30	3.80
	55	0.8065	7.81	4.216	4.467		3.82
N-methyl acetamide in dioxane	25	0.7185	9.88	3.647	3.862		3.66
	35	0.7824	8.41	3.886	4.109		3.69
	45	0.8252	7.34	3.830	4.043		3.78
	55	0.8631	6.35	3.907	4.117		3.83
N-methyl acetamide in benzene in high concentration	25	0.6987	10.47	2.236	2.383	2.48	1.87
p-Bromonitrobenzene in benzene	20	0.7905	8.21	3.456	3.687		
	30	0.8259	7.32	4.013	4.272	3.658	
	40	0.8657	6.28	4.494	4.774		

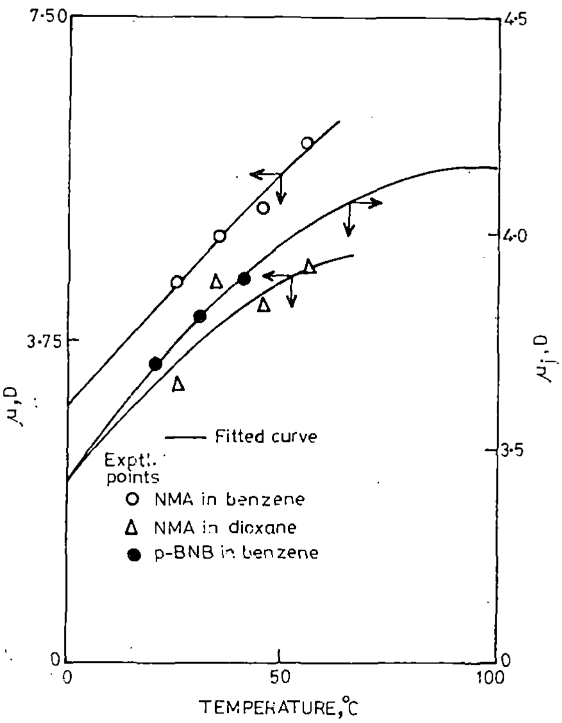

Fig. 5—Variation of experimentally observed dipole moment with temperature in °C along with the fitted curves

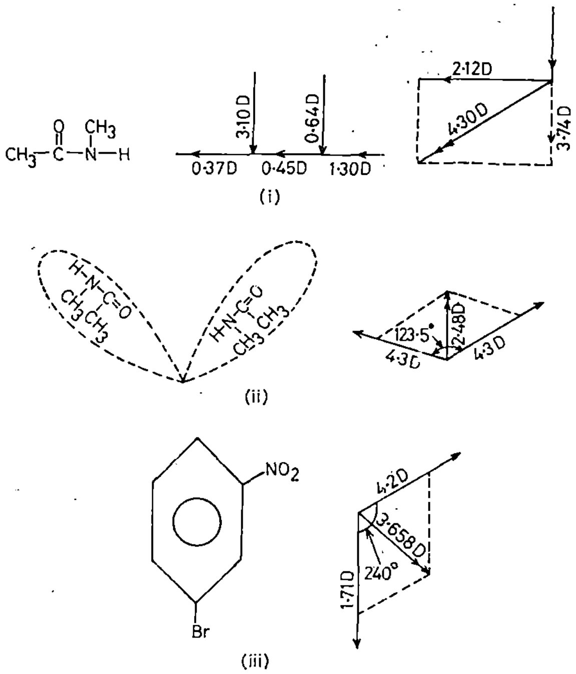

Fig. 6—Conformation of the different molecules showing the orientation of the bond axes, bond moments and also the dipole moments [(i) structural form of NMA; (ii), structural form of dimers; and (iii) structural form of *p*-BNB]

monomer formation. The group moments of $C-CH_3$, $C-N$ and $N-H$ groups act along a common axis as sketched in Fig. 6. But the group moments of $C=O$ and $N-CH_3$ act along the direction normal to that of $C-CH_3$. With this preferred conformational directions for NMA as depicted in Fig. 6, the resultant μ_j value was obtained for monomer formation. These data for μ_j's thus obtained also excellently agree with the computed μ_j's (Table 1). But for the dimer formation of NMA in benzene the two monomers attach each other with their most electropositive and electronegative elements, i.e. $-H$ and $-O-$ form a certain angle viz. 123.5° as calculated both from experimental and theoretical. μ_j values as shown in Fig. 6, while the electropositive and electronegative elements project themselves along the dipole axes. Thus the dipole moment of dimer formation is less than those of monomer due to this preferred angle—the immediate obvious feature in Fig. 6 (ii). Further, the dipole moment (Fig. 5) is a temperature-dependent quantity when the system is subjected to UHF alternating fields. Hence it is concluded that the high values of dipole moments are due to formation of monomer and less value due to the formation of dimer in dielectrics, particularly in the case of NMA in benzene and dioxane.

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CHAPTER VI

CONDUCTIVITY, RELAXATION TIME AND ENERGY OF ACTIVATION OF SOME ALCOHOL + BENZENE MIXTURE AT RADIO FREQUENCY FIELD.

INTRODUCTION:

Alcohols presents a complex and interesting problem in liquid structure because of the possibility of strong hydrogen bonding between adjacent molecules. The dielectric properties of alcohol was initially carried out by Mizushima (1927) and then by Debye (1929). Lateron many workers extensively investigated the dielectric properties of pure aliphatic alcohols and also of dilute solution in different nonpolar solvents. Measurement over a very large frequency range later on showed that in aliphatic alcohols, the anomalous dispersion and absorption cannot be described by a single relaxation time. The different behaviour of the alcohols in pure state and in dilute solution in nonpolar solvent indicates that the dipole orientation is essentially determined by the association of -OH groups via hydrogen bridge and not by the properties of the individual group. Garg and Smyth (1965) measured the dielectric constant and losses of the normal alcohols at various temperatures and frequencies and obtained three different relaxation times for each alcohol viz. (a) in the low frequency region it is around 1 to 22 x 10^{-10} sec. (b) in the intermediate frequency region it is about the order of 1.7 to 5 x 10^{-11} sec. and (c) in the high frequency region it is around 1.7 to 4 x 10^{-12} sec. which can be taken as dipole rotation of single molecule. Sen and Ghosh (1972) estimated the time of relaxation of some pure normal alcohol in radio frequency region which fall in the low frequency region. As there is no suitable expression for finding out the relaxation time for normal alcohols in dilute solution of nonpolar solvents from radio frequency conductivity data, we used the Debye dispersion equation (Smyth, 1955)

$$K' = \frac{\mu^2 N \rho_{ij} F_{ij}}{3 M_j k T}\left(\frac{\omega^2 \tau}{1+\omega^2\tau^2}\right) W_j \qquad \ldots 6.1$$

where r.f. conductivity $K' = \frac{\omega \epsilon''}{4\pi}$ and ϵ'' is the dielectric loss. It has already been established that the dielectric properties of the liquid varies with temperature, concentration in nonpolar solvent as well as with frequency in the dispersion region. Therefore a relatively large change in dielectric relaxation is expected by decreasing or by increasing the viscosity of liquids, either by temperature variation or by varying the concentration of the polar molecules in nonpolar solvents.

So in the present paper an attempt has been taken to study the nature of variation of dipolar relaxation time of three normal alcohols such as methyl, ethyl and propyl alcohols at various concentrations in benzene and at different temperatures from radio frequency conductivity measurements. The activation energy which characterised the dipole relaxation process in reaction kinetic energy consideration can be determined by using Eyring (1941) rate equations

$$\tau = \frac{A}{T}\exp\left(\frac{\Delta F_\tau}{RT}\right) \qquad \ldots 6.2$$

This equation has been utilised to calculate the variation of thermodynamical quantities of orientation, such as free energy of activation ΔF_τ, enthalpy of activation ΔH_τ and entropy of activation ΔS_τ of the three normal alcohols.

Experimental Arrangement:

The schematic diagram of the experimental arrangement and the method of determination of radio frequency conductivity at 1 MHz. has been described in detail in chapter II section 1.

The dielectric cell was made up of a pyrex glass tube of diameter 2 cms. with a pair of stainless steel circular electrodes of diameter 1.5 cms., separated by a distance of 1 cm. Before filling the dielectric liquids, the glass cell was cleaned with chromic acid, then with distilled water and finally with benzene. The liquids under investigation such as methyl alcohol ethyl alcohol, propyl alcohol and benzene were all Analar grade obtained from Messrs, British Drug House, London. The viscosity of the liquids were measured with an Ostwald viscometer taking water as a standard liquid for comparison. The temperatures in all the experiments were controlled within ± 1°C by a thermostat. The method of measurement of viscosity and purification of chemicals are given in chapter II section 2.5 and 2.6 respectively.

Results and Discussion:

The high frequency conductivity of polar dielectric liquid in nonpolar solvent is expressed (Smyth, 1955) as

$$K^*_{ij} = K'_{ij} + jK''_{ij} \qquad \ldots 6.3$$

where K'_{ij} is the real part and K''_{ij} is the imaginary part of the r.f. conductivity of the dielectric solution. Assuming there is no free ion present in the dielectric liquid, the real part of the conductivity has been expressed by the relation

$K'_{ij} = \frac{\omega \epsilon''_{ij}}{4\pi}$ where ϵ''_{ij} and ω

are the dielectric loss and angular frequency of the applied field respectively. Now the number of experimental facts has established that, polar liquids especially alcohols contain atleast some percentage of free ions which are responsible for their higher conductivity. But in our present experiment we have tactfully eliminated the effect of free ions by estimating the r.f. conductivity at infinite dilution of alcohols in nonpolar solvent.

The r.f. conductivity (K'_{ij}) in esu of polar and nonpolar liquid mixture of different weight fractions (Wj) and temperatures can be expressed by the three terms polynomial equation in weight fraction Wj as

$$K'_{ij} = \alpha + \beta W_j + \gamma W_j^2 \qquad \ldots 6.4$$

where α , β and γ are the constants. The computed values of the K'_{ij} in esu of various weight fractions at different temperatures of the three systems (1) methanol + benzene, (2) ethanol + benzene and (3) propanol + benzene are given in the table (6.1.a,b,c) Table (6.2.a,b,c,d) and Table (6.3.a,b,c) respectively.

System 1

Methanol in Benzene.

$K'_{ij} \times 10^{-3} = 0.552 - 1.499\,W_j + 2.792\,W_j^2$ at temp. t = 30°C

$K'_{ij} \times 10^{-3} = 1.269 - 3.91\,W_j + 4.93\,W_j^2$ at temp. t = 40°C

$K'_{ij} \times 10^{-3} = 1.192 - 3.986\,W_j + 5.471\,W_j^2$ at temp. t = 50°C.

System 2

Ethanol in Benzene.

$K'_{ij} \times 10^{-2} = 2.178 - 8.321\,W_j + 10.515\,W_j^2$ at temp. t = 30°C

$K'_{ij} \times 10^{-2} = 3.922 - 14.37\,W_j + 16.87\,W_j^2$ at temp. t = 40°C

$K'_{ij} \times 10^{-2} = 4.356 - 15.404\,W_j + 18.527\,W_j^2$ at temp t = 50°C

$K'_{ij} \times 10^{-2} = 3.624 - 12.195\,W_j + 17.059\,W_j^2$ at temp. t = 60°C.

and System 3

1-Propanol in Benzene

$$K'_{ij} \times 10^{-2} = 4.851 - 8.624\,W_j + 6.119\,W_j^2 \quad \text{at temp. } t = 30^{\circ}C$$

$$K'_{ij} \times 10^{-2} = 4.39 - 7.065\,W_j + 5.771\,W_j^2 \quad \text{at temp. } t = 40^{\circ}C$$

$$K'_{ij} \times 10^{-2} = 3.684 - 5.539\,W_j + 6.266\,W_j^2 \quad \text{at temp. } t = 50^{\circ}C$$

The coefficients of W_j of the above equations are important to evaluate the relaxation time τ_s of polar solute in dilute solution of nonpolar solvent.

Eq. (6.1) on being differentiated with respect to W_j as $W_j \longrightarrow 0$ takes the following form:

$$\left(\frac{dK'_{ij}}{dW_j}\right)_{W_j \to 0} = \frac{\mu^2 N \rho_i F_i}{3 M_j k T}\left(\frac{\omega^2 \tau_s}{1 + \omega^2 \tau_s^2}\right) = \beta \quad \ldots 6.5$$

since $\omega^2 \tau_s^2 \ll 1$ in the radio frequency region so eq. (6.5) finally becomes

$$\tau_s = \frac{3 M_j k T \beta}{\mu^2 N \rho_j F_j \omega^2} \quad \ldots 6.6$$

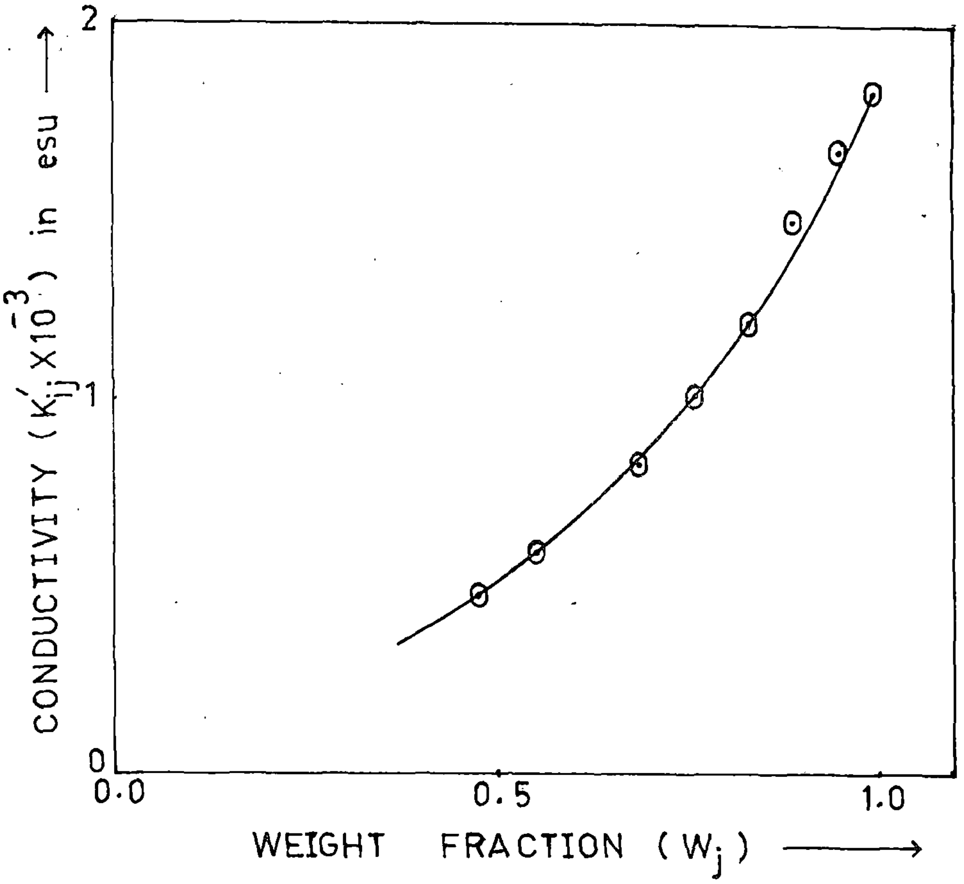

Fig-6.1 Conductivity K'_{ij} is plotted against Weight fraction W_j for methanol in benzene at 30°C.

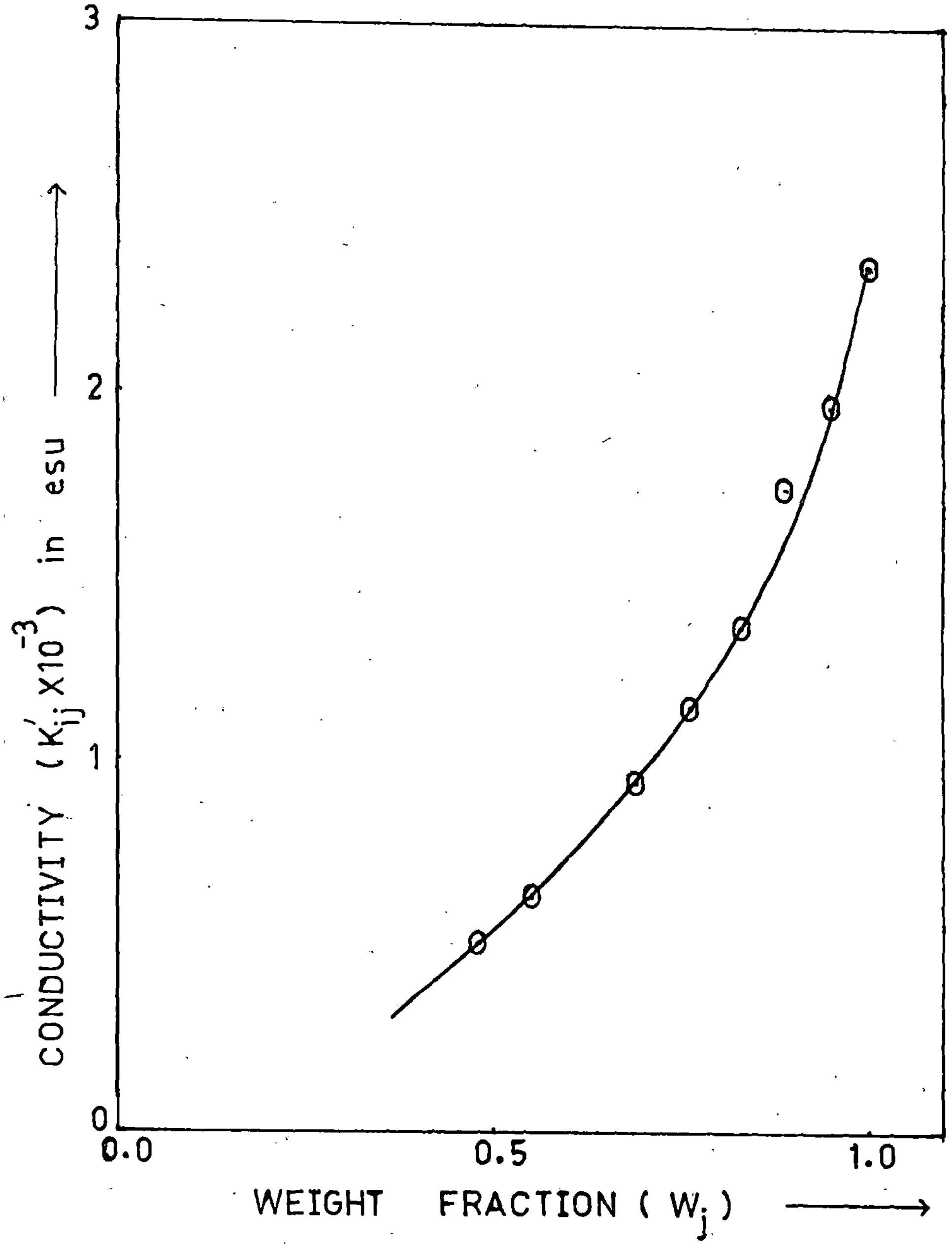

Fig-6.2 Conductivity K'_{ij} is plotted against Weight fraction W_j for methanol in benzene at 40°C.

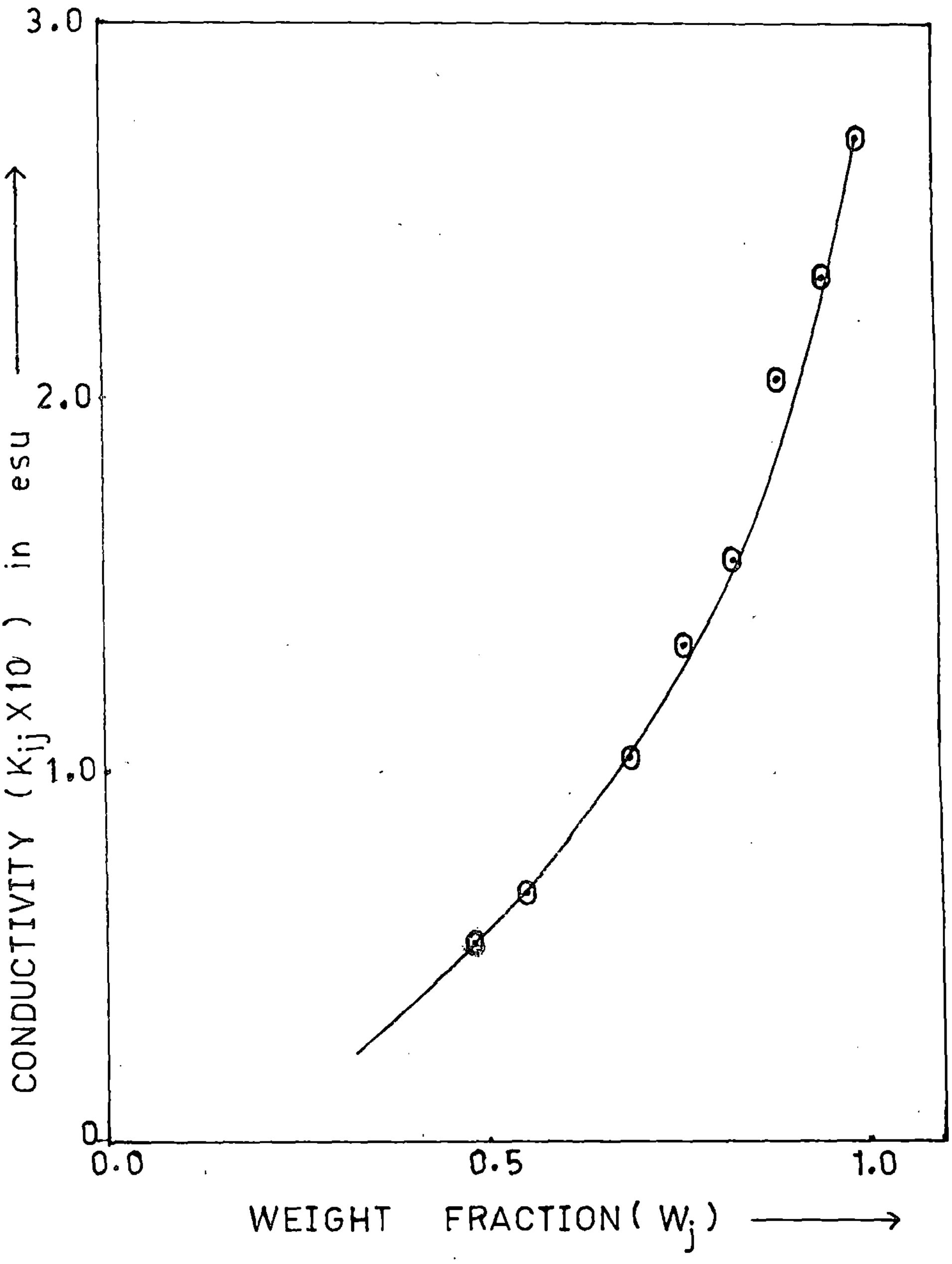

Fig-6.3 Conductivity K'_{ij} is plotted against Weight fraction W_j for methanol in benzene at 50°C.

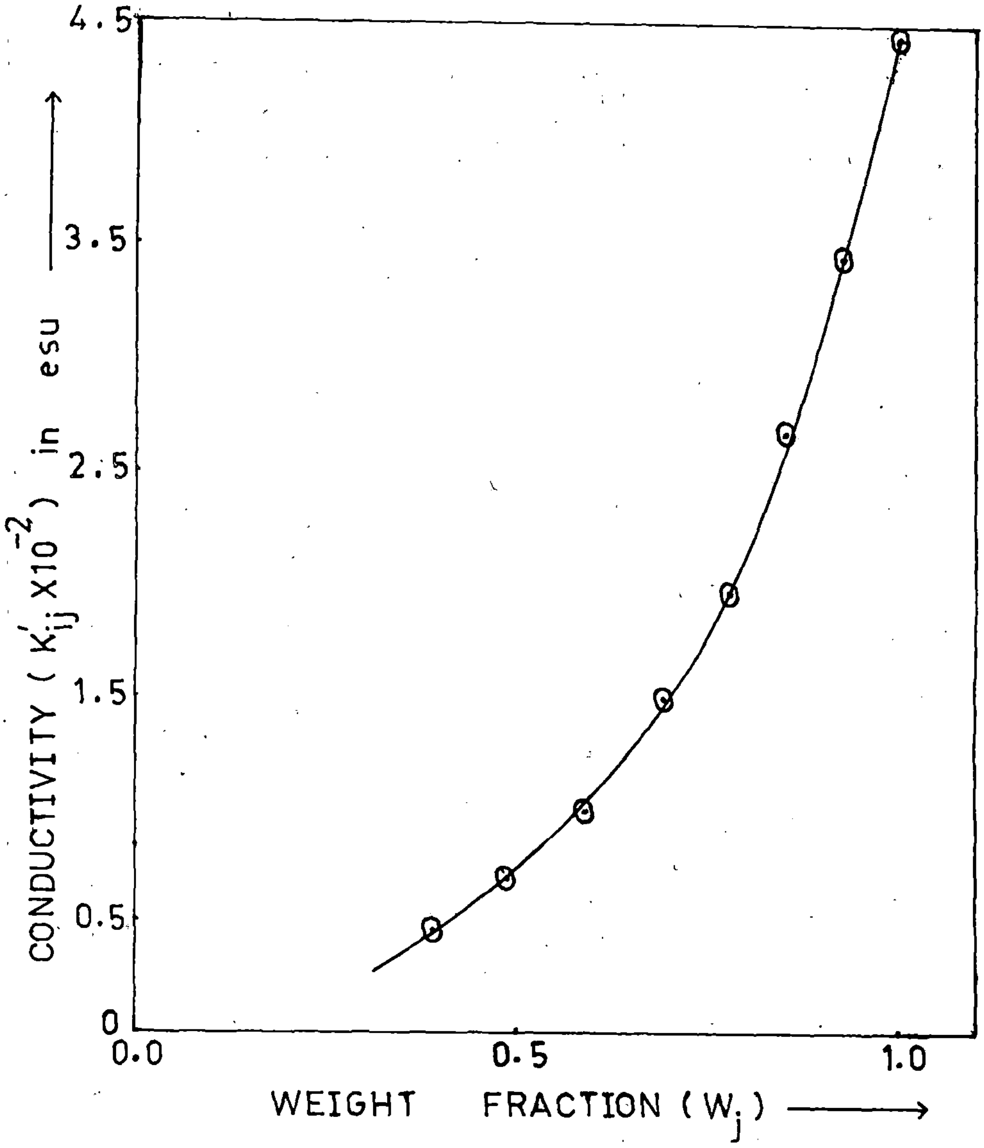

Fig-6.4 Conductivity K'_{ij} is plotted against Weight fraction W_j for ethanol in benzene at 30°C.

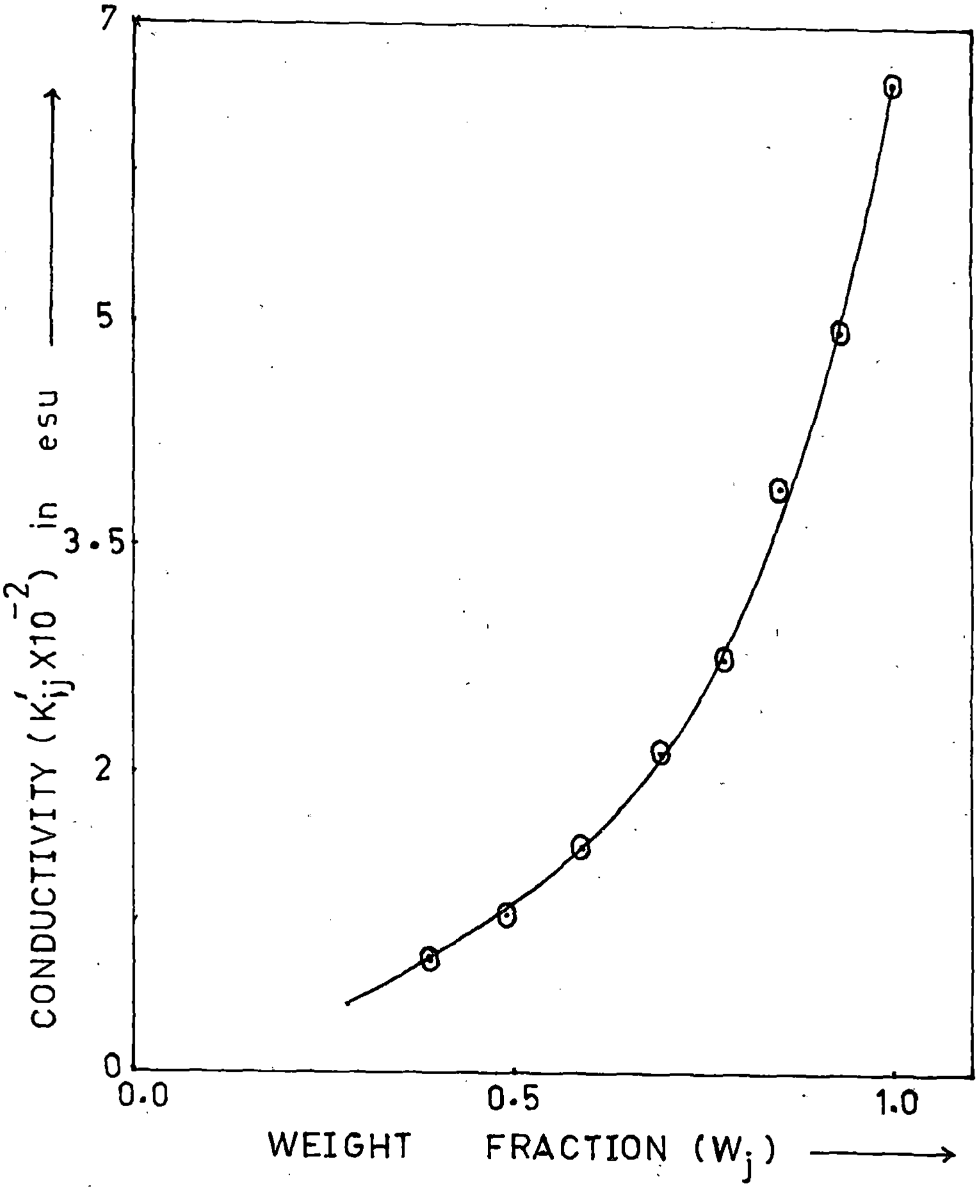

Fig-6.5 Conductivity K'_{ij} is plotted against Weight fraction W_j for ethanol in benzene at 40°C .

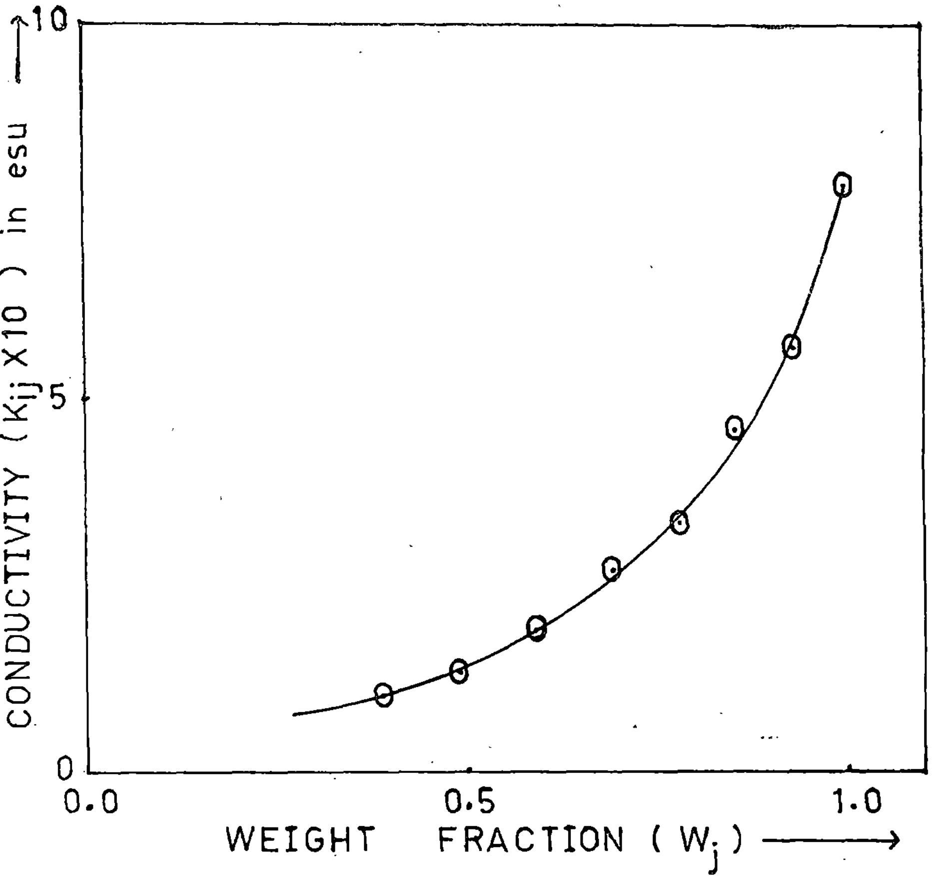

Fig-6.6 Conductivity K'_{ij} is plotted against Weight fraction W_j for ethanol in benzene at 50°C.

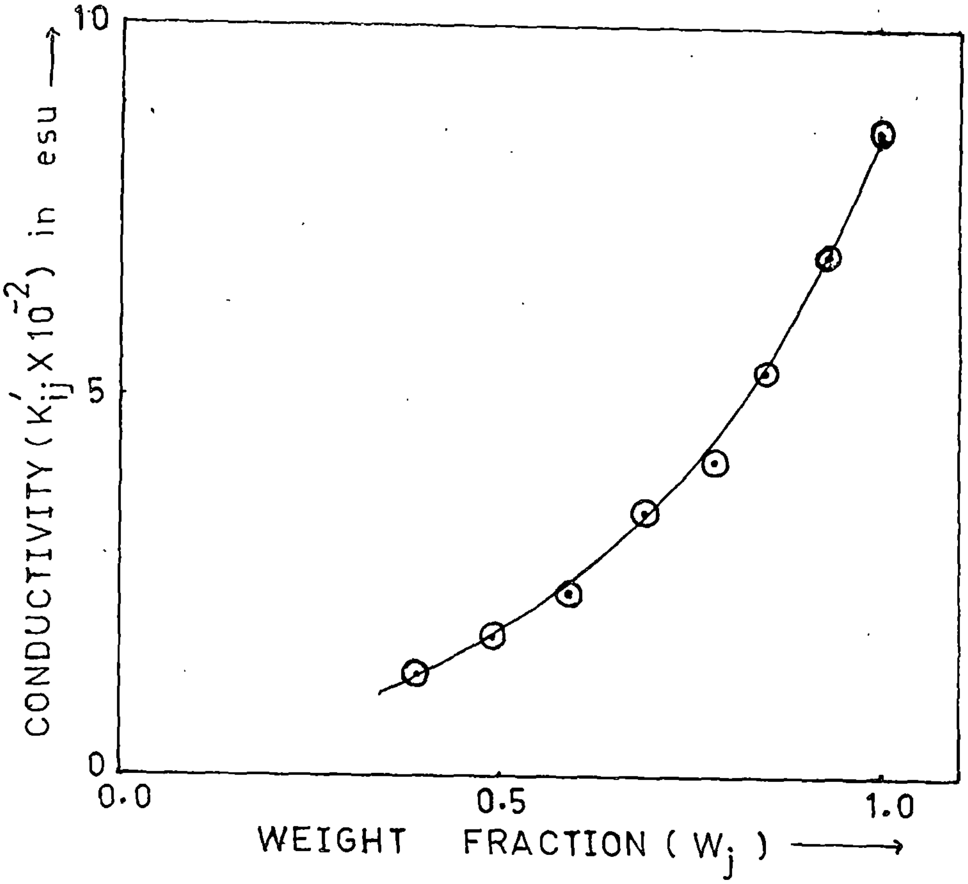

Fig-6.7 Conductivity K'_{ij} is plotted against Weight fraction W_j for ethanol in benzene at 60°C .

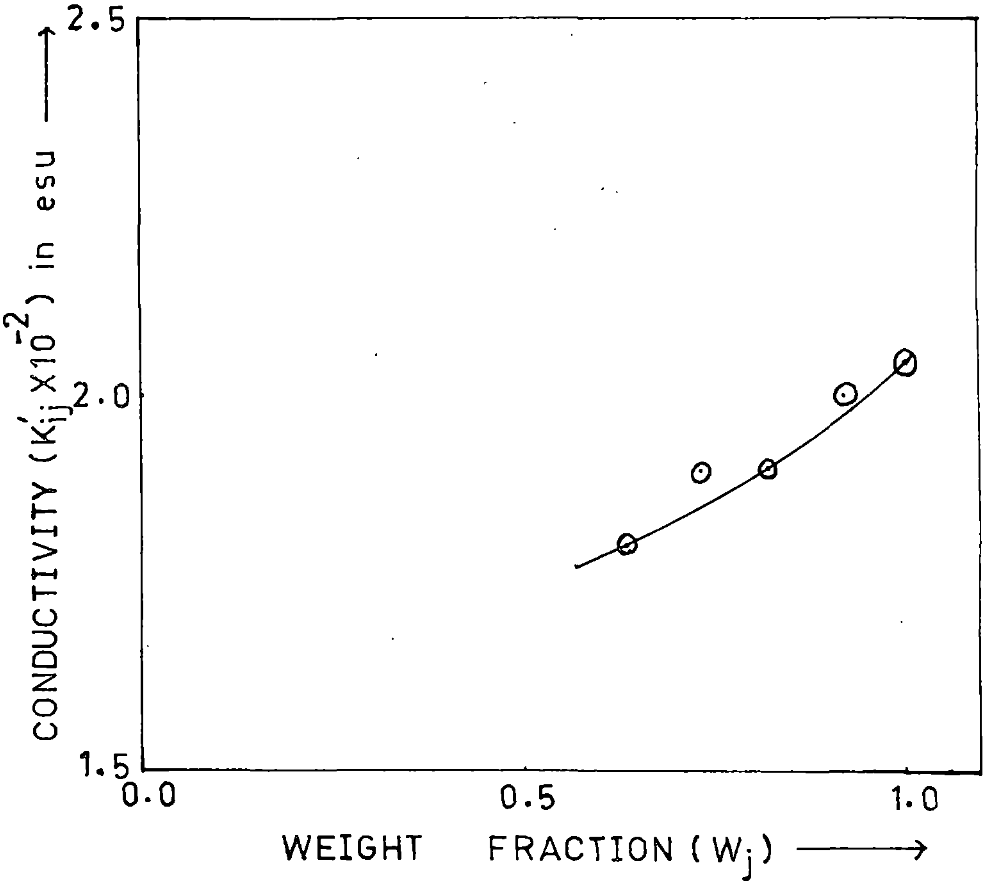

Fig-6.8 Conductivity K'_{ij} is plotted against Weight fraction W_j for 1-propanol in benzene at 30°C.

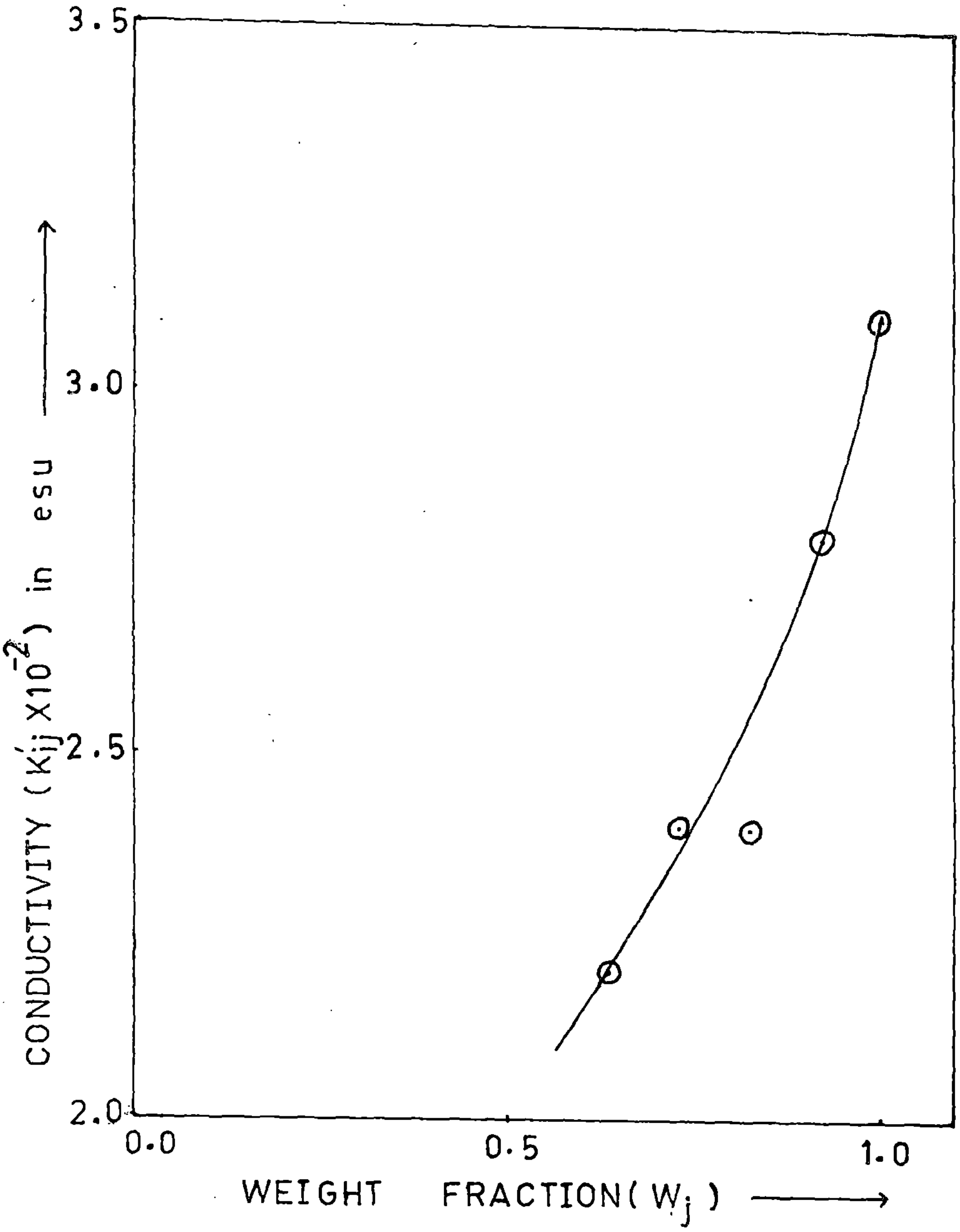

Fig-6.9 Conductivity K'_{ij} is plotted against Weight fraction W_j for 1-propanol in benzene at 40°C.

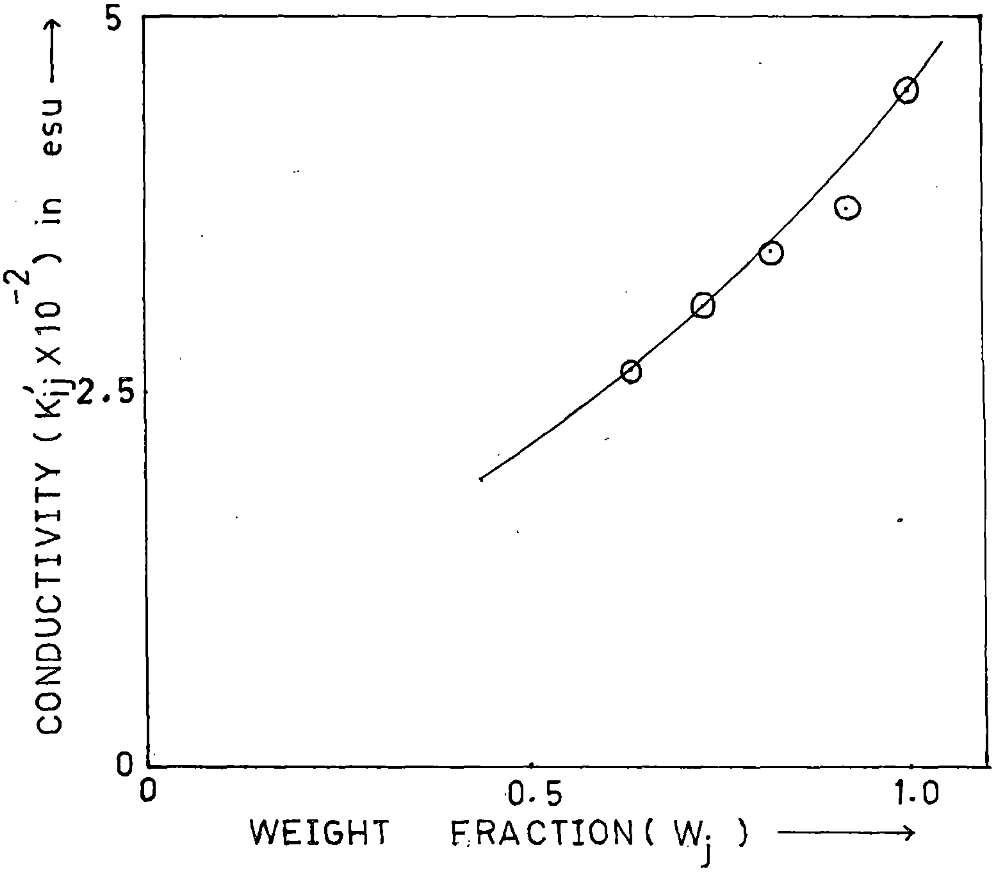

Fig - 6.10 Conductivity K'_{ij} is plotted against Weight fraction W_j for 1-propanol in benzene at 50°C .

where β is the slope of $K'_{ij} - W_j$ plot at $W_j \longrightarrow 0$ and ρ_i the density of the solvent, F_i the local field, μ the dipole moment of the solute, M_j, N and k are the molecular weight, Avogadro's number and Boltzmann's constant respectively.

It is evident that the dielectric properties of polar liquid varies with temperature, concentration and also with the frequency in the dispersion region. Therefore relatively a large change in dielectric relaxation time is expected by decreasing or by increasing the microscopic viscosity of the liquid either by temperature variation or by variation of concentration of polar molecules in nonpolar solvents. So in this paper an attempt has been made to study, the nature of variation of dipole relaxation time of some monohydric alcohol at various temperatures and concentration in nonpolar liquid benzene. The values of relaxation time τ_s for various concentrations of alcohol in benzene solution and at different temperatures (T) have been computed from the equation (6.6). The time of relaxation at infinite dilute (τ_∞) has been calculated from the relation,

$$\tau_\infty = \left(\frac{\eta_0}{\eta_s}\right)\tau_s \qquad \ldots 6.7$$

where η_o and η_s are viscosities of nonpolar solvent and of the extremely low concentration of solute respectively. Again the Onsager (N.E.Hill et al, 1969) model $\tau'_\infty = \left(\frac{2}{3}\right)\tau_s$ has been applied to calculate the molecular relaxation τ'_∞ of the polar molecule. All these calculated values of relaxation time are placed in the Table 6.4. It is observed from the table that the calculated values of relaxation times agrees fairly well with literature (Böttcher, 1952) values and also indicate the tendency of decreasing with the increase of temperature. Further it is observed that τ_∞ slightly varies with number of carbon atoms. The effect of solvent on the measurement of dipole moment of polar solute is well known and with this view in mind the solvent effect of benzene on the relaxation time of polar molecules at infinite dilution τ^*_∞ has been calculated from the relation

$$\tau^*_\infty = \frac{\tau_\infty}{\left[1 - C(\epsilon - 1)^2\right]^2} \qquad \ldots 6.8$$

where C is the constant for which Müller (Smyth, 1955) gave a value of 0.038 and ϵ is the dielectric constant of the solvent. The values of τ^*_∞ thus calculated for each alcohol molecules from eq. (6.8) are entered in table 6.4. The higher values of τ^*_∞ for a particular temperature indicate that the variation of local environment has a definite influence upon relaxation time. It is further observed that the computed values of relaxation times of polar molecules at infinite dilution are much lower than those of the pure compound, which indicates that at an infite dilute solution in nonpolar solvent the rotation of a dipole molecules is not hindered by the interaction with other neighbouring dipole molecules.

The dielectric mechanism may be explained in terms of absolute rate theory (Glasstone et al,1941) by treating the dipole orientation as a rate process in which polar molecules rotate from one equilibrium position to another. The process of rotation requires an activation energy sufficient to overcome the energy barrier separating the two mean equilibrium position and is given by

$$\tau = \frac{A}{T} \exp\left(\frac{\Delta F_\tau}{RT}\right) \qquad \ldots 6.9$$

where A is known as frequency factor and is given by $A = \frac{h}{k}$ where h and k are Plank's constant and Boltzmann's constant respectively and R is the universal gas constant.

The enthalpy of activation ΔH_τ and the entropy of activation ΔS_τ for dipole relaxation are related with free energy of activation ΔF_τ by the equation

$$\Delta F_{\tau} = \left[\Delta H_{\tau} - T\Delta S_{\tau}\right] \qquad \ldots\ 6.10$$

Hence from the equation (6.9), we can get

$$\tau = \frac{A}{T}\exp\left(-\frac{\Delta S_{\tau}}{R}\right)\exp\left(\frac{\Delta H_{\tau}}{RT}\right) \qquad \ldots\ 6.10a.$$

or

$$\tau = \frac{A'}{T}\exp\left(\frac{\Delta H_{\tau}}{RT}\right) \qquad \ldots\ 6.10b.$$

where $A' = A\exp\left(-\frac{\Delta S_{\tau}}{R}\right)$

Further the molar free energy of activation for viscous flow ΔF_{η} , the heat activation energy ΔH_{η} and the entropy of activation ΔS_{η} for viscous flow of the infinitly dilute solution of alcohol in benzene also have been calculated for the purpose of comparison by using the relation

$$\eta = B\exp\left(\frac{\Delta F_{\eta}}{RT}\right) \qquad \ldots 6.11a$$

or

$$\eta = B\exp\left(-\frac{\Delta S_{\eta}}{R}\right)\exp\left(\frac{\Delta H_{\eta}}{RT}\right) \qquad \ldots\ 6.11b$$

Here $B = \frac{hN}{V}$ known as the frequency factor, where N is the Avogadro's number, V is the molar volume, h is the Plank's constant and η is the coefficient of viscosity of the liquid.

In this chapter the temperature dependence of relaxation time have been utilized for determining the molar free energy of activation ΔF_{τ}, ethalpy of activation energy ΔH_{τ} and the entropy of activation energy ΔS_{τ} for the dipole orientation of polar molecules in nonpolar solvent. The computed values of ΔH_{τ_∞} for the three alcohols, methanol, ethanol and propanol, have been determined from the slope of the usual plot $\log_e (\tau_\infty T)$, against $(\frac{1}{T})$, shown in the figure, (6.11, 12,13) The intercept of the plot of the curves gives the values of the factor A', which have been used for computing the values of entropy ΔS_{τ_∞} and the magnitudes of ΔF_{τ_∞} for different systems have been determined from equation (6.10). The computed values of ΔF_{τ_∞}, ΔH_{τ_∞} and ΔS_{τ_∞} for the three different systems at various temperatures are tabulated in table (6.4). The values of ΔH_{τ_∞} are very nearly same to the values as refer by Bordewijk and Böttcher (1978). Similarly the heat of activation energy for viscous flow ΔH_{η_∞} has been calculated from the linear plot of $\log_e \eta$ against $1/T$

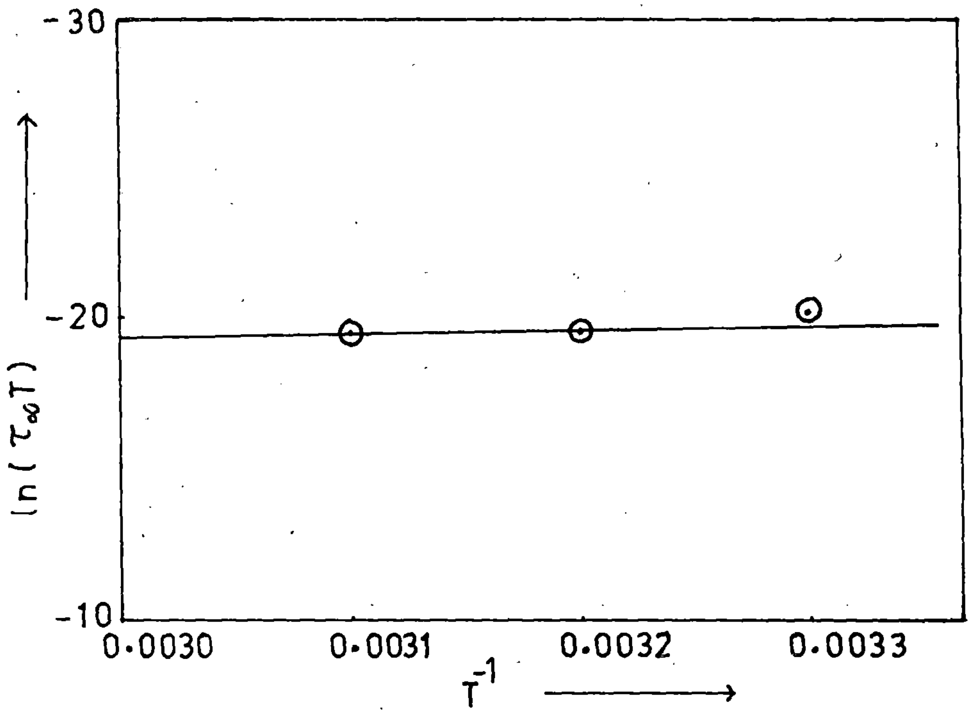

Fig-6.11 Value of $\ln(\tau_\infty T)$ versus reciprocal of absolute temperature (T^{-1}) for methanol in benzene.

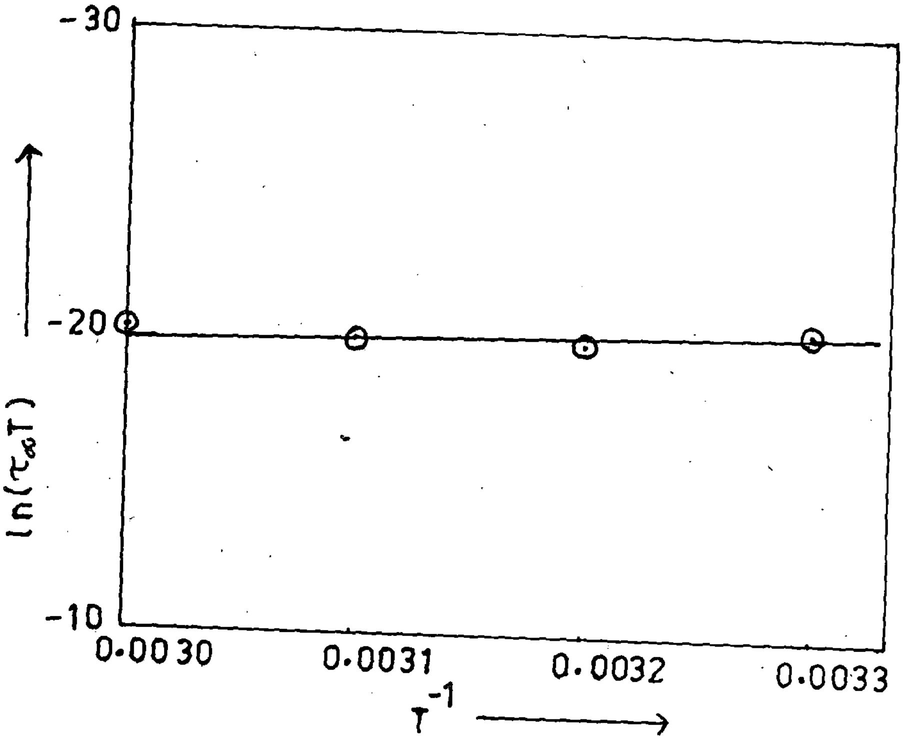

Fig. 6.12 Value of $\ln(\tau_\infty T)$ versus reciprocal of absolute temperature (T^{-1}) for ethanol in benzene.

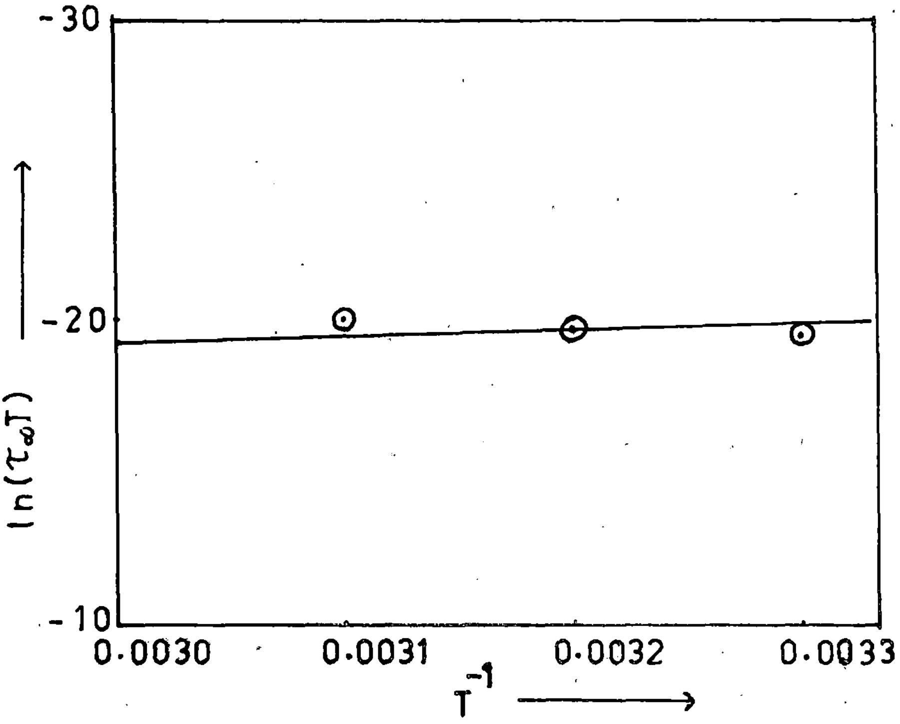

Fig-6.13 Value of ln(τ_∞T) versus reciprocal of absolute temperature (T^{-1}) for 1-propanol in benzene.

shown in figure (6.14). Here the activation energy for viscosity ΔH_{η} has been considered due to the effect of viscosity of unit mole fraction of benzene in alcohol benzene solution, which is eventually the viscosity of benzene at pure state. The activation energy for relaxation of dipole orientation is often compared with that for the activation energy for viscosity and it is found that these are approximately equal ($\Delta F_{\eta} \approx \Delta F_{\tau_\infty}$) for rigid molecules. From the table (6.4), we observed that ΔH_{τ_∞} and ΔH_{η} are approximately equal for the first two systems whereas it differ widely in the case of 1-propanol, the third system.It is further observed from the table (6.4) that the heat activation energy ΔH_{τ_∞} for methanol, ethanol and 1-propanol gradually increases with the increase of chain length or with carbon atoms and the values are closely agree with the values given by other workers (Bordewijk, et al,1978). The slightly higher value of ΔH_{η} compare to ΔH_{τ_∞} for methanol and ethanol may be interpreted as that for viscous flow the molecules involves both translational as well as rotational motion whereas for dipole relaxation it is only related to orientational motion of the dipole molecules. But the very high value of ΔH_{τ_∞} for 1-propanol compare to ΔH_{η} indicate that the energy concentration due to its higher chain length.

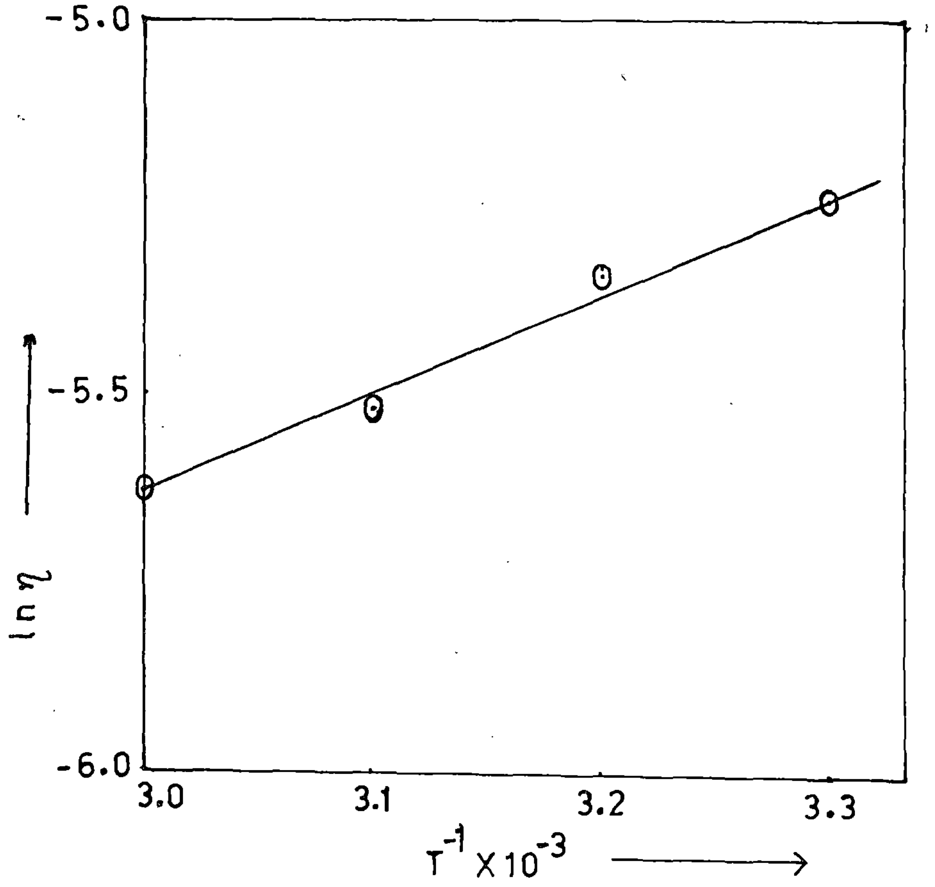

Fig-6.14 Value of ln η versus reciprocal of absolute temperature (T^{-1}) .

The positive value of ΔS_{τ_∞} implies that, certain number of molecules surrounding the one, rotates during the process of orientation, but, momentarily, complete discharge occurs between one another under the applied field. But again they resume their configuration with net displacement orientation in the new-direction, which exhibited as, increase in the freedom of activation. Further it is observed that due to the positive value of ΔS_{τ_∞} the calculated values of ΔF_{τ_∞} becomes relatively small compared to ΔH_η .

Debye (1929) equation $\tau = 4\pi\eta a^3/kT$ has been used here to calculate the radius of the molecule. All the radii values thus calculated are placed in the Table (6.4). It is found that the values are nearly equal to the actual values. This suggest that the Debye equation is not adequately represented the relation between relaxation time (τ), molecular radius (a) and the macroscopic viscosity (η) of the medium.

All most uniform values of radius of the molecules given in table (6.4), further suggest that the relaxation time τ_∞ at infinite dilution of alcohol molecule in nonpolar solvent, is relatively low in comparison to the time of relaxation of pure solute (Böttcher,1952) and also depend very little upon the size of the molecules and temperatures. Therefore, we may conclude that, the dipole relaxation at infinite dilution in nonpolar solvent is due to the rotational orientation of the (-OH) group of a molecule.

Table 6.1a, b, c

Values of r.f. conductivity K'_{ij} in e.s.u., wiehgt fraction (W_j), constants of the fitting equations and dielectric parameters i.e. static dielectric constant (ϵ_0) dielectric constant at infinite frequency (ϵ_∞) and dipole moment (μ) of the different systems at different temperatures.

Table 6.1a

System - Methanol + Benzene at temperature 30°C.

Weight fraction W_j	R.F. conductivity $K'_{ij} \times 10^{-3}$ in esu	Weight fraction W_j^2	Weight fraction W_j^3	Weight fraction W_j^4	$K'_{ij} \times W_j \times 10^{-3}$	$K'_{ij} \times W_j^2 \times 10^{-3}$	Fitting equation constants	Dielectric parameters		
								ϵ_0 in esu	ϵ_∞ in esu	μ in D
1.00	1.81	1.00	1.00	1.00	1.81	1.81				
0.95	1.67	0.9025	0.8574	0.8145	1.5865	1.5072	α=0.552			
0.89	1.48	0.7921	0.7049	0.6274	1.3172	1.1723				
0.83	1.21	0.6889	0.5718	0.4746	1.0043	0.8336	β=-1.499	31.55	3.30	1.69
0.76	1.02	0.5776	0.4390	0.3336	0.7752	0.5892				
0.69	0.82	0.4761	0.3285	0.2266	0.5658	0.3904	γ= 2.792			
0.55	0.59	0.3025	0.1664	0.0915	0.3239	0.1782				
0.48	0.47	0.2304	0.1106	0.0531	0.2270	0.1089				

Table 6.1b

System - Methanol + Benzene at temperature 40°C

Weight fraction W_j	R.F. conductivity $K'_{ij} \times 10^{-3}$ in esu	Fitting eq. constants.	Dielectric parameters		
			ϵ_o in esu	ϵ_∞ in esu	μ in D
1.00	2.32				
0.95	1.96	$\alpha = 1.269$			
0.89	1.74				
0.83	1.37	$\beta = -3.91$	31.53	3.45	1.69
0.76	1.15				
0.69	0.94	$\gamma = 4.93$			
0.55	0.63				
0.48	0.51				

Table 6.1c

System - Methanol + Benzene at temperature 50°C

Weight fraction W_j	R.F. conductivity $K'_{ij} \times 10^{-3}$ in esu	Fitting equation constants	Dielectric parameters		
			ϵ_o in esu	ϵ_∞ in esu	μ in D
1.00	2.69				
0.95	2.32	$\alpha = 1.192$			
0.89	2.05				
0.83	1.57	$\beta = -3.986$	31.50	3.62	1.69
0.76	1.34				
0.69	1.04	$\gamma = 5.471$			
0.55	0.67				
0.48	0.54				

<u>Table 6.2a</u>

System - Ethanol + Benzene at Temp. 30°C

Weight fraction W_j	R.F. conductivity $K'_{ij}\times10^{-2}$ in esu	Weight fraction W_j^2	Weight fraction W_j^3	Weight fraction W_j^4	$K'_{ij}\times W_j\times10^{-2}$	$K'_{ij}\times W_j^2\times10^{-2}$	Fitting Equation constant	Dielectric parameters		
								ϵ_0 in esu	ϵ_∞ in esu	μ in D
1.00	4.46	1.00	1.00	1.00	4.46	4.46				
0.93	3.47	0.8649	0.8044	0.7480	3.2271	3.0012				
0.85	2.68	0.7225	0.6141	0.5220	2.278	1.9363	α= 2.178			
0.78	1.96	0.6084	0.4746	0.3702	1.5288	1.1925				
0.69	1.51	0.4761	0.3285	0.2267	1.0419	0.7189	β= -8.321	23.52	2.23	1.67
0.59	0.99	0.3481	0.2054	0.1212	0.5841	0.3446				
0.49	0.69	0.2401	0.1176	0.0576	0.3381	0.1656	γ=10.515			
0.39	0.46	0.1521	0.0593	0.0231	0.1794	0.0699				

Table 6.2b

System - Ethanol + Benzene at temperature 40°C

Weight fraction W_j	R.F. conductivity $K'_{ij} \times 10^{-2}$ in esu	Fitting Equation constants	Dielectric parameters		
			ϵ_0 in esu	ϵ_∞ in esu	μ in D
1.00	6.64				
0.93	4.93	$\alpha = 3.922$			
0.85	3.89				
0.78	2.75	$\beta = -14.37$	23.50	2.30	1.67
0.69	2.13				
0.59	1.48				
0.49	1.04	$\gamma = 16.87$			
0.39	0.74				

Table 6.2c

System - Ethanol + Benzene at temperature 50°C

Weight fraction W_j	R.F. conductivity $K'_{ij} \times 10^{-2}$ in esu	Fitting Equation constants	Dielectric parameters		
			ϵ_0 in esu	ϵ_∞ in esu	μ in D
1.00	7.80				
0.93	5.72	$\alpha = 4.356$			
0.85	4.62				
0.78	3.36	$\beta = -15.404$	23.48	2.40	1.67
0.69	2.71				
0.59	1.91	$\gamma = 18.527$			
0.49	1.34				
0.39	1.02				

Table 6.2d

System - Ethanol + Benzene at Temperature 60°C.

Weight fraction W_j	RF. conductivity $K'_{ij} \times 10^{-2}$ in esu	Fitting Equation constants.	Dielectric parameters		
			ϵ_0 in esu	ϵ_∞ in esu	μ in D
1.00	8.64				
0.93	6.99	$\alpha = 3.624$			
0.85	5.44				
0.78	4.24	$\beta = -12.195$	23.46	2.55	1.67
0.69	3.56				
0.59	2.45				
0.49	1.84	$\gamma = 17.059$			
0.39	1.34				

Table 6.3a

System - 1 Propanol + Benzene at temperature 30°C.

Weight fraction W_j	R.F. conductivity $K'_{ij}\times 10^{-2}$ in esu	Weight fraction W_j^2	Weight fraction W_j^3	Weight fraction W_j^4	$K'_{ij}\times W_j\times 10^{-2}$	$K'_{ij}\times W_j^2\times 10^{-2}$	Fitting Equation constants	Dielectric parameters		
								ϵ_0 in esu	ϵ_∞ in esu	μ in D
1.00	2.4	1.00	1.00	1.00	2.4	2.4				
0.921	2.0	0.8482	0.7812	0.7195	1.842	1.6965	α = 4.851			
0.823	1.9	0.6773	0.5574	0.4588	1.5637	1.2869		17.30	2.10	1.66
0.730	1.9	0.5329	0.3890	0.2839	1.387	1.0125	β = -8.624			
0.635	1.8	0.4032	0.2560	0.1626	1.143	0.7258	γ = 6.119			

Table 6.3b

System - 1 Propanol + Benzene at temperature 40°C

Weight fraction W_j	R.F. conductivity $K'_{ij} \times 10^{-2}$ in esu	Fitting Equation constants	Dielectric parameters		
			ϵ_0 in esu	ϵ_∞ in esu	μ in D
1.00	3.1				
0.921	2.8	$\alpha = 4.39$			
0.823	2.4	$\beta = -7.065$	17.28	2.12	1.66
0.730	2.4				
0.635	2.2	$\gamma = 5.771$			

Table 6.3c

System - 1 Propanol + Benzene at Temp. 50°C

Weight fraction W_j	R.F. conductivity $K'_{ij} \times 10^{-2}$ in esu	Fitting Equation constants	Dielectric parameters		
			ϵ_0 in esu	ϵ_∞ in esu	μ in D
1.00	4.50				
0.921	3.72	$\alpha = 3.684$			
0.823	3.42	$\beta = -5.539$	17.26	2.15	1.66
0.730	3.07				
0.635	2.64	$\gamma = 6.266$			

Table 6.4

Values of relaxation times for solution (τ_s), for infinite dilution (τ_∞), molecular relaxation times (τ'_∞) and due to solvent effect (τ^*_∞), thermodynamical parameters [Heat activation energy (ΔH_{τ_∞}), entropy of activation (ΔS_{τ_∞}), free energy of activation (ΔF_{τ_∞}) for dipole relaxation and heat activation energy (ΔH_η), entropy of activation (ΔS_η), free energy of activation (ΔF_η) for viscous flow)] viscosity coefficient (η) and radius of the molecule (a).

System	Temp. in K	Relaxation times in secs.				ΔH_{τ_∞} KCal/mole	ΔS_{τ_∞} Cal/mole	ΔF_{τ_∞} KCal/mole	η in CP	ΔH_η Kcal/mole	ΔS_η cal/mole	ΔF_η KCal/mole	Radius (a) in Å
		$\tau_s \times 10^{11}$	$\tau_\infty \times 10^{11}$	$\tau'_\infty \times 10^{11}$	$\tau^*_\infty \times 10^{11}$								
1. Methanol	303	0.515	0.45	0.343	0.51	2.381	1.173	2.026	0.53	2.60	-0.984	2.898	1.48
	313	1.365	1.09	0.91	1.23		-0.9126	2.095	0.48		-1.087	2.940	2.14
	323	1.407	0.94	0.938	1.06		-0.9149	2.085	0.40		-1.002	2.924	2.32
2. Ethanol	303	0.696	0.61	0.464	0.69	2.419	0.6898	2.210	0.53	2.60	-0.984	2.898	1.63
	313	1.234	0.99	0.823	1.12		-0.5987	2.606	0.48		-1.087	2.940	2.07
	323	1.348	0.899	0.899	1.01		-0.7081	2.648	0.40		-1.002	2.924	2.29
	333	1.076	0.65	0.717	0.73		-0.3453	2.534	0.36		-1.056	2.952	2.22
3. 1-Propanol	303	1.299	1.11	0.866	1.26	4.167	5.2614	2.573	0.53	2.60	-0.984	2.898	2.01
	313	1.104	0.85	0.736	0.96		5.2909	2.511	0.48		-1.087	2.940	1.992
	323	0.897	0.58	0.589	0.65		5.5802	2.365	0.40		-1.002	2.924	1.996

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CHAPTER VII

ENERGY OF ACTIVATION, DIPOLE MOMENT AND CORRELATION PARAMETER OF WATER.

Introduction:

Considerable amount of work has been carried out by different workers in an endeavour to clarify the dielectric behaviour of liquid-water under the alternating electric stress. Despite its apparent complex molecular structure, liquid-water closely follows a simple Debye type relaxation ($\tau = 4\pi\eta a^3/kT$) Sexton and Lane (1946) described measurements of the dielectric properties of water at microwave frequency range and at different temperatures. After that Collie et al (1948) established that, the dispersion observed in water seems to be explicable in terms of single relaxation time, They calculated the value of $\tau = 0.85 \times 10^{-11}$ secs. from Debye equation at a given temperature.

Lane and Sexton (1952) gave a very accurate method for measuring the refractive index and absorption coefficient of water and showed that the dielectric properties of water can be expressed in terms of only one relaxation time at any given temperature.

It has been further observed that the associated mixture which contain group of molecules of both kinds also shows a single relaxation time. Dalbert et al (1949), compared the various available measured values for τ of water and aliphatic alcohols and concluded that it is difficult to get reliable values for relaxation time from dielectric measurements.

Considering the above mentioned facts, we have paid special attention in our present experiment to study the temperature dependence of relaxation time (τ), the thermodynamical parameters (ΔH_τ , ΔS_τ , ΔF_τ), the dipole moment (μ) and correlation factor (g) of water in the radio frequency field.

Experimental Arrangement:

The schematic diagram of the experimental arrangement and the method of determining the r.f. conductivity of the mixture has been described in detail in the chapter II section 2.1. The oscillator frequency was fixed at 5 MHz. The dielectric cell was made up of a pyrex glass tube of diameter 2.5 cm., fitted with one pair of stainless steel circular electrodes of diameter 1.5 cms. and separated by a distance of 1 cm. Analar grade glycerine supplied by M/s. British Drug House (London) was used without further purification and highly pure distilled water (H_2O) was used for this experiment.

The viscosity of the experimental water was measured with Ostwald viscometer at different temperatures. The temperature variation was regulated by a good thermostat whose accuracy is better than ± 1°C. All the measurements were accurate upto ± 2 percent.

Results and Discussion:

The dielectric phenomena with which we are principally concerned and most conveniently discussed in electrostatic units, in which the complex dielectric constant ϵ^* represent by

$$\epsilon^* = \epsilon' - j\epsilon'' \qquad \ldots 7.1$$

The dielectric loss ϵ'' is a parameter, which describes the motion of electric charge, i.e. the electrical conduction phenomenon. Certain dielectrics are found to display conduction which arises not from the effect of polarization on the displacement current, but from the actual charge transport just like ionic conduction in electrolytes. Such conduction would normally be described by volume conductivity K' $\text{ohm}^{-1}\text{cm}^{-1}$. The effect of conductivity is an additional term of the dielectric loss. Therefore, the conductivity term K' can be expressed as $K' = \frac{\omega \epsilon''}{4\pi}$ where ω is the angular frequency.

A mathematical expression connecting radio frequency conductivity K' and the macroscopic viscosity η of the dielectric liquid given by Sen and Ghosh (1974) as

$$K' = A + \frac{B}{\eta} \qquad \ldots\ 7.2$$

where A and B are constants. The detail deduction of the equation (7.2) is given in chapter I, section 1.9. The constant B gives the ion density 'n' of the liquid mixture. Using the eq. (7.2) the average number of ion density has been obtained from the slope B is of the order of 1.7×10^{18} ions/c.c.

The radio frequency conductivity of the glycerine + water mixture at 50 percent concentration to down to unit mole fraction of water has been measured at 5 MHz over the temperature range 20°C to 60°C. The measured conductivities at different temperatures and concentrations are accurate upto ± 2 percent.

In the present paper an attempt has been taken to calculate the time of relaxation τ of the mixture at various concentrations and temperatures using the given relation deduced by Ghosh et al (1980).

$$\tau_s = \frac{2}{3}\,\frac{a^2 e}{v k T} \qquad \ldots\ 7.3.$$

where 'a' is the radius of the molecule, 'e' is the electronic charge, v is the mobility of the free ions obtained from the equation $K' = nev$, k is the Boltzmann's constant and T is the absolute temperature. The time of relaxation values (τ_s) thus calculated are placed in the table (7.1). The fig. (7.1) shows the plot of exponential variation of relaxation time (τ_s) with mole fraction 'f' of mixture. It is observed that at a particular temperature the increase of water concentration is accompanied by exponential decrease of relaxation time which eventually become the time of relaxation of water (τ_0) at unit mole fraction of water at pure state. The time of relaxation τ_0 determined from extrapolation curve at unit mole fraction of water at different temperatures are placed in table (7.2). The observed τ_0 values obtain from r.f. conductivity measurements are little greater than the values obtained by Mason et al (Von Hipple, 1954) from microwave data of pure water at different temperatures. Von Hipple (1954) had calculated the value of $\tau_0 = 0.25 \times 10^{-10}$ sec. at room temperature, considering the radius of the molecule 'a' = 2Å and viscosity $\eta = 10$ m poise. He showed graphically that τ_0 for water is located near the wavelength $\lambda = 1$ cm. It may be ascribed that slight high value of τ_0 for water at the present experiment may be due to the presence of certain minute quantity of glycerine

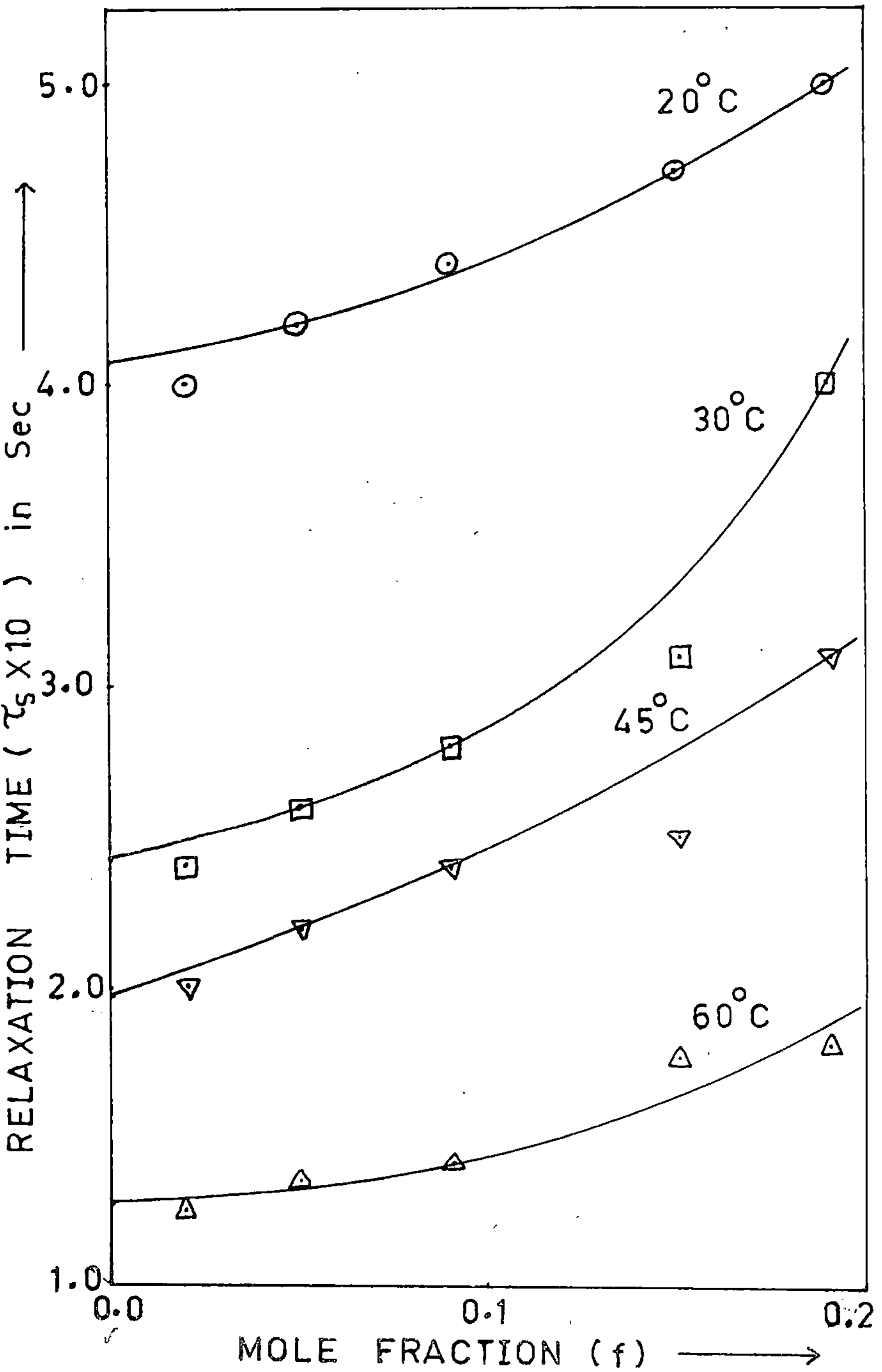

Fig-7.1 Relaxation time (τ_s) is plotted against Mole fraction(f) at different temperatures.

as an impurity, which increases the hydrogen bonding between water molecules with the impurity molecules. Thus the existance of the organic molecule increase the relaxation time for water. Generally it is observed that the τ_0 decreases with temperature. A number of studies revealed that the neutral molecules especially alcohol group increase the value of relaxation time for water. The decrease of τ_0 value for water with temperature has been suggested by Oster (1946), may be due to breaking of hydrogen bond with rise of temperature. Powles (1953) equation

$$\tau_0' = \frac{2\epsilon_s + \epsilon_\infty}{3\epsilon_s}\tau_0 \qquad \ldots 7.3a$$

has been applied for calculating the molecular relaxation time τ_0'. The different values of τ_0' at various temperatures are tabulated in Table 7.2.

Determination of molar enthalpy of activation ΔH_{τ_0}.

It is possible to treat the dipole relaxation process as analogous to a chemical rate process (Glasstone et al, 1941). The theory of rate process applied to the temperature variation of single relaxation time yields the equation

$$\tau_0 = \frac{h}{kT}\exp\left(\frac{\Delta F_{\tau_0}}{RT}\right) \qquad \ldots 7.4a$$

or,

$$\tau_0 = \frac{h}{kT} \exp\left(\frac{-\Delta S_{\tau_0}}{R}\right) \exp\left(\frac{\Delta H_{\tau_0}}{RT}\right) \qquad \ldots\ 7.4b$$

where ΔS_{τ_0} is the molar entropy of activation, ΔH_{τ_0} is the molar enthalpy of activation and ΔF_{τ_0} is the free energy of activation. From the equation (7.4a) it follows that a graph of $\log_e (\tau_0 T)$ against $1/T$ should be rectilinear and from the slope of the graph shown in Fig. (7.2), the molar enthalpy of activation ΔH_{τ_0} has been calculated. The order of magnitude of the enthalpy ΔH_{τ_0} clearly shows some involvement of molecular energy in the dipole relaxation process of water. An individual water molecules may require one, two, three or four (OH-O) bonds in all, in order to build a tetrahedral structure. Again the reorientation of dipole due to the effect of external applied field involves in breaking of typical (OH-O) hydrogen bond which give the principal relaxation time for water. The amount of enthalpy of activation energy ΔH_{τ_0} needed to rapture such bond in water is generally of the order of 4.5 Kcal/mole (Hasted,1973). in our present experiment we obtained $\Delta H_{\tau_0} = 4.8$ Kcal/mole which agrees very well with the literature value.

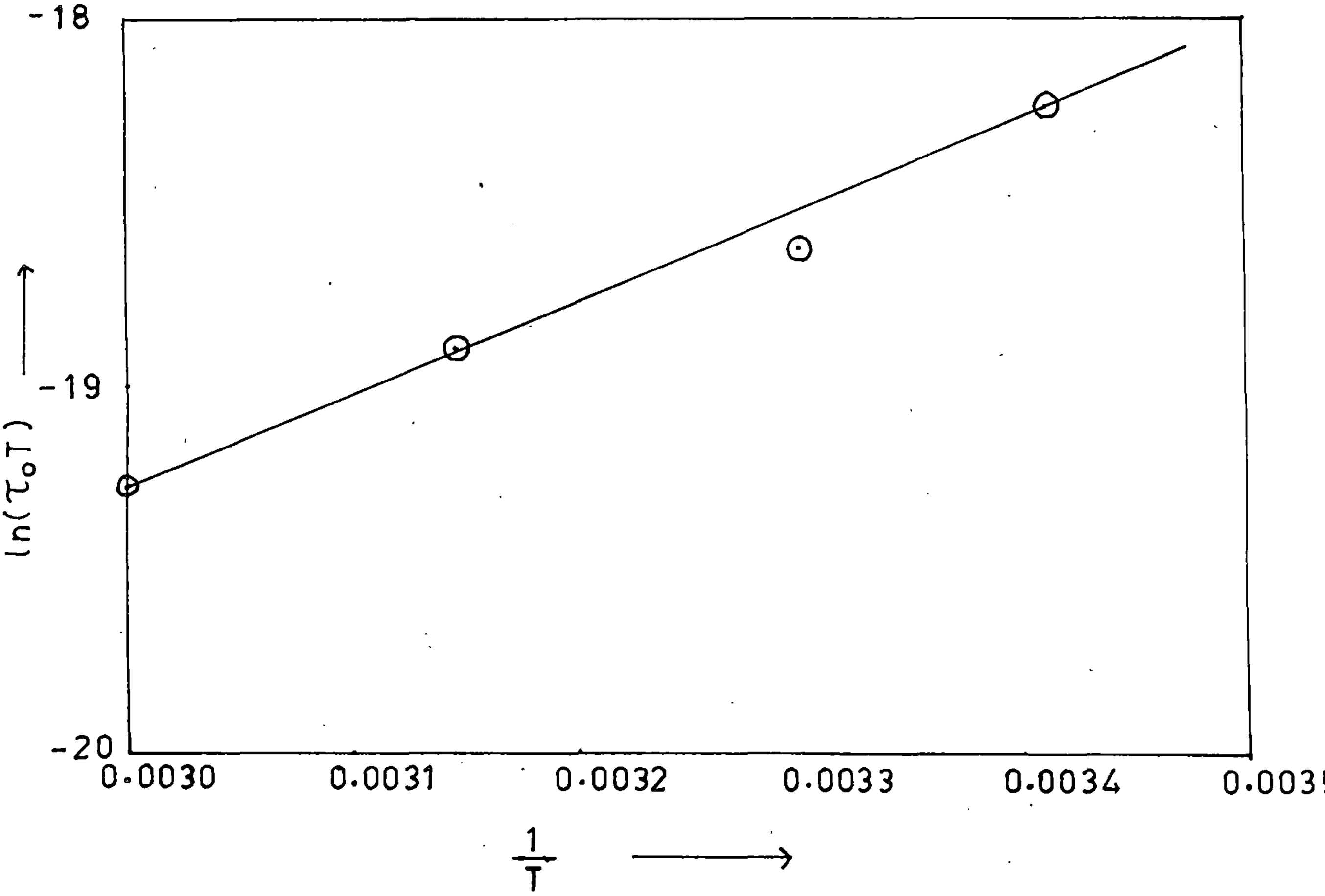

Fig → 7.2 Value of $\ln(\tau_o T)$ is plotted against reciprocal value of absolute temperature (T^{-1}).

The values of free energy of activation ΔF_{τ_0} enthalpy of activation ΔH_{τ_0} and entropy of activation ΔS_{τ_0} at different temperatures are placed in Table (7.2).

If we consider ΔH_{τ_0} to be of the same order of magnitude of dipole-dipole interaction energy then it gives us an opportunity to calculate the apparent dipole moment of water by applying Debye-Keesom (Ketelaar, 1953) expression.

Determination of Correlation Parameter 'g' and Apparent Dipole Moment μ_{app}.

Polar liquid such as water posses its own static dielectric constant, dipole moment, relaxation time and correlation factor 'g'. The correlation parameter 'g' is a measure of the local ordering in the material. The structure of water has been the subject of such study till today. Kirwood assumed a single structure similar to that suggested by Bernal and Fowler (1933) in order to calculate the correlation parameters g. The Kirkwood (Smyth, 1955) correlation parameter 'g' can be determined by using the equation

$$\mu_{app}^2 = g\mu_{Vapour}^2 \qquad \ldots 7.5$$

where μ_{app} is the apparent dipole moment of the water and μ_{Vapour} is the dipole moment of water at gaseous state. Assuming the enthalpy of activation $\Delta H_{\tau_o} = 4.8$ Kcal/mole is of the same order of magnitude as the dipole-dipole interaction energy, the apparent dipole moment value μ_{app} at different temperature has been calculated from the Debye-Keesom (Ketelaar, 1953) expression

$$\Delta H_{\tau_o} = \frac{2}{3} \cdot \frac{\mu_{app}^4}{a^6 k T} \qquad \ldots \; 7.6$$

where a = 1.48 Å is the average intermolecular distance. The μ_{app} thus calculated from equation (7.6) are placed in Table (7.2) and found that the values of $\mu_{app} > \mu_{Vapour}$ has tendency to increase slowly with rise of temperature. It may be interpreted as, with the rise of temperature, the rotational vibration of the molecules increases, which causes the slight increase of dipole moment. It is observed that the correlation parameter is large in associated or associated - associated liquid (Bordewijk et al, 1978) because the material possesses high degree of correlation between dipoles. In liquid water the local forces between dipole molecules are very large. So, it could be expected that 'g' value should differ appreciably from unity. Here also we found that the 'g' values thus calculated from the relation $g = \left(\mu_{app} / \mu_{Vapour}\right)^2$

are greater than unit. But the variation of g values is small, that can be taken as constant within our experimental range of temperatures, and the values are given in Table (7.2).

After the work of Bernal and Fowler (1933), almost all the theories adopted a tetrahedrally arranged hydrogen bonded model of water. Haggis et al (1952) modified the model further and proposed that each water molecule may be hydrogen - bonded to four other water molecules. In the case of water Kirkwood (Smyth,1955) gave a relation

$$g = 1 + Z \cos^2 \frac{\theta}{2} \quad \ldots 7.7$$

where θ is the angle of (H-O-H) bond taken as 104° and Z = 4, is the number of nearest neighbour molecules, which surround each water molecules. The bond angles have been calculated at various temperatures using equation (7.7) and the values are listed in Table (7.2). Thus we may conclude that the correlation parameter of water $g > 1$, suggest that the structure of water has appreciable effect on dipolar polarization which causes $\mu_{app} > \mu_{Vapour}$ and the rise of temperature results in bending of hydrogen bond.

Table 7.1

Values of conductivities (K'), mobilities (ν) and relaxation times (τ_s) of the solution at different temperatures (t) and mole fractions (f):

Temp. in °C	20°C			30°C			45°C			60°C		
Mole fraction f	$K' \times 10^5$ mho/cm	$\nu \times 10^4$ cm^2V^{-1} Sec^{-1}	$\tau_s \times 10^{11}$ secs.	$K' \times 10^5$ mho/cm	$\nu \times 10^4$ cm^2V^{-1} sec^{-1}	$\tau_s \times 10^{11}$ sec.	$K' \times 10^5$ mho/cm	$\nu \times 10^4$ cm^2V^{-1} sec^{-1}	$\tau_s \times 10^{11}$ secs.	$K' \times 10^5$ mho/cm	$\nu \times 10^4$ cm^2V^{-1} sec^{-1}	$\tau_s \times 10^{11}$ secs.
0.19	3.699	1.156	5.0	4.458	1.393	4.01	5.494	1.717	3.10	9.04	2.825	1.80
0.15	3.933	1.229	4.7	5.770	1.803	3.10	6.815	2.1297	2.50	9.245	2.889	1.76
0.09	4.202	1.313	4.4	6.387	1.996	2.80	7.098	2.218	2.40	11.622	3.632	1.40
0.05	4.403	1.376	4.2	6.877	2.149	2.60	7.744	2.420	2.20	12.051	3.766	1.35
0.02	4.624	1.445	4.0	7.45	2.328	2.40	8.518	2.662	2.00	13.018	4.068	1.25

Table 7.2

Values of relaxation time (τ_0), molar relaxation time (τ_0'), viscosity (η), enthalpy of activation (ΔH_{τ_0}), entropy of activation (ΔS_{τ_0}), free energy of activation (ΔF_{τ_0}), apparent dipole moments (μ_{app}), dipole moment in vapour state (μ_{Vapour}), correlation factors (g), bond angle (θ) of water and radius of the molecule 'a' at different temperatures.

Temp. in ^{o}C	$\tau_0 \times 10^{11}$ secs.	τ_0' $\times 10^{11}$ secs	η mpoise	ΔH_{τ_0} Kcal/mole	ΔS_{τ_0} Cal/mole	ΔF_{τ_0} Kcal/mole	μ_{app} in D	μ_{Vapour} in D	'g'	θ^{o}	a in Å
20	4.075	2.72	10.01		5.358	3.230	2.83		2.47	105.36	2.3
30	2.425	1.62	8.0	4.80	5.788	3.046	2.86	1.8	2.52	103.9	2.16
45	1.963	1.32	6.05		5.366	3.094	2.89		2.58	102.1	2.25
60	1.275	0.85	4.77		5.457	2.983	2.92		2.63	100.7	2.14

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CHAPTER VIII

ELECTRICAL CONDUCTIVITY ANOMALY IN BINARY LIQUID MIXTURES NEAR THE CRITICAL POINT.

Introduction:

A number of publications have appeared concerning the temperature dependence of the electrical resistance R(T) of some selected binary liquid mixture near the critical points has attracted considerable attention recently. The behaviour of the transport properties for a binary liquid mixture was first reported by Friedlander (1901). Later on, it was observed by number of authors (Stein et al, 1972) that the viscosity of binary liquid at critical system shows a anomaly as T_c is approached from single phase region. Stein and Allen (1973) established the existance of strong divergence in the temperature dependence of resistivity for isobutyric acid + water very close to critical tempe rature T_c. Gammell and Angell (1974) studied the temperature dependence of the electrical resistance for the above mention system, but could not detect any anomaly at all due to critical fluctuation. Stein and Allen (1973) further analysed their data by the help of four methods at very close to T_c($\epsilon \approx 10^{-7}$) and found the critical exponent 'd' in the range $0.50 < d < 0.77$ and concluded that the derivative $\left(\frac{dR}{dT}\right)$ is strongly divergent near T_c. Jasnow, Goldburg and Semura (1974) reanalysed the data of Stein and Allen and showed that over a limited range of reduced temperature $2 \times 10^{-5} < \epsilon < 10^{-2}$, their data could be fitted to the functional form

$$\frac{R_c - R}{R_c} = a\epsilon^{1-\alpha} - b\epsilon \qquad \ldots 8.1$$

where $a = 4.1$, $b = 1.6$ and $\alpha = 0.12$. Jasnow et al. (1974) discarded those data which were very close to the critical point ($3.3 \times 10^{-7} \leqslant \epsilon \leqslant 10^{-5}$) on the ground that they might be subjected to gravitational effects. Shaw and Goldburg (1976) have repeated the Isobutyric acid + water experiment of Stein and Allen and also have carried out similar studies in a critical mixture of pure phenol + water and KCl - doped phenol - water mixture. They observed that their experimental data as well as the data given by Stein and Allen were nicely fitted to the equation

$$\sigma_R = \left(\frac{\sigma - \sigma_c}{\sigma_c}\right) = A\epsilon^{\theta} + B_1\epsilon + B_2\epsilon^2 \qquad \ldots 8.2$$

in the reduced temperature range $10^{-5} \leqslant \epsilon \leqslant 10^{-2}$ and noticed that their results were consistent with the existence of a conductivity singularity of the form

$$\sigma_{sing} = A\,\epsilon^{\theta} \qquad \text{where} \quad \theta = 0.70^{+.15}_{-.10}$$

Gopal et al (1976, 1977) and Ramkrishna (1978) have studied the temperature dependence of electrical resistivity of several polar, nonpolar critical mixture system near critical point and found the critical coefficient $\beta = b = 0.35$, which is becoming the accepted value for giving singularity in derivative $\left(\frac{dR}{dT}\right)$.

The purpose of the present experiment is to measure the electrical conductivity of the three binary liquid systems such as (Methyl alcohol + carbondisulphide), (Nitrobenzene + n Hexane) and (Aniline + Cyclohexane), in the critical temperature region at a frequency of 400 KHz in order to study whether our conductivity data also exhibit a singularity of the form $\sigma_{sing} = A\,\epsilon^{\theta = 2\beta}$ or not.

Experimental Arrangement:

The schematic diagram of the experimental arrangement and the method of determining the r.f. conductivity of the mixture has been described in detail in the chapter II section 2.1.

The oscillator frequency for measurement of r.f. conductivity was fixed at 400 KHz. A dielectric cell was made up of pyrex glass tube of diameter of 2.5 cms., fitted with a pair of stainless steel circular electrodes of diameter 1.5 cms. and 5 mm apart.

Analar grade sample supplied by BDH (London) were used without further purification. The cell was filled with the liquids in proper proportion to the critical mixture was then flamed sealed at the top. To avoid the self-heating of a sample only a low voltage given to the electrodes of the cell by making the very loose coupling. All the measurements were made while looking the liquid from the one phase to two phase region. A thermostat having millidegree temperature stability was used for this study. The detection of T_c was supplemented by a visual observation.

Results and Discussion:

The self diffusion coefficient of organic polar liquid, which is usually closely associated with ionic mobility do not show any unusual behaviour near the critical temperature T_c. But it has been possible to detect (Dutta, Thesis, 1983) a suitable change in ionic mobility by the help of resistance measurement of mixture at critical solution temperature. On this basis it has been thought that the electrical resistance of binary liquid mixture should show some anomaly due to the critical fluctuation near T_c.

In order to show the existence of a singular contribution to the electrical resistance of the several binary liquid system near the critical solution temperature and to determine the critical exponent 'b', number of authors (Jasnow et al, 1974), choose various functional forms to fit the data of temperature dependence resistance R(T) of the systems. The singularity in ($\frac{dR}{dT}$) of binary liquid arises from the critical concentration fluctuation which grow in range and magnitude in the critical region. In the one phase region the functional form of the resistance is given (Gopal, et al, 1976) by

$$R = R_c - A\left(T - T_c\right)^b \qquad \ldots 8.3$$

where $b = 0.3$ is the critical exponent and Rc is the electrical resistance at critical temperature Tc. Also in the one phase region Show and Goldburg (1976) showed that the conductivity of the binary critical mixture must contain a term of the form $\sigma_{sing} = A\epsilon^{\theta = 2\beta}$ where the reduced temperature $\epsilon = \left(\frac{T - T_c}{T_c}\right)$ and the critical exponent $\theta = 2\beta$ where β is an exponent which characterise the shape of the coexistence curve. They further outline a percolation model of the electrical conduction process in the effective medium approximation and showed the critical exponent $\theta = 2\beta$.

A Simple Expression for Conductivity $\sigma(T)$ From Percolation Theory:

The percolation theory is more directly applicable to σ (T) rather than R (T). At a particular instant of time there exists a spatial variation of composition in the mixture of polar, nonpolar liquid i.e. $C_{12} = (C_c + \delta C_o)$ and this variation gives rise to a spatial variation of the local conductivity $\sigma(r,t)$ of correlation length ξ . But if the life time of the concentration fluctuation is sufficiently long and the composition of the mixture of spatially inhomogeneous medium considered as static then only the percolation theory is applicable. Approximating the distribution function of composition, the conductivity as a bimodel one reduced temperature $\epsilon << 1$ and latter on averaging the fluctuation over a correlation volume (ξ^3) we get a relation

$$\sigma_{sing} \propto \epsilon^{2\beta} \qquad \text{... (8.4 a)}$$

or

$$\sigma_{sing} = M \epsilon^{2\beta} \qquad \text{... 8.4 b}$$

where M is the parameter $\epsilon = \left(\frac{T - T_c}{T_c}\right)$ is the reduced temperature and β is the critical coefficient which characterises the shape of the coexistence curve.

Further considering effective medium approximation and taking equation (12) of Reference (Landaner, 1952) the conductivity σ can be written as

$$\sigma = \sigma_0 + \sigma_0 B \langle (\delta c)^2 \rangle_{\xi^3} \qquad \text{... 8.5 a}$$

or

$$\sigma = \sigma_0 \left[1 + B \langle (\delta c)^2 \rangle_{\xi^3} \right] \qquad \text{... 8.5 b}$$

where

$$B = \frac{1}{3} \left\{ 2 \left(\frac{\left(\frac{\delta \eta}{\delta c}\right)_0}{\eta_0} \right)^2 - \left(\frac{\left(\frac{\delta n}{\delta c}\right)_0}{n_0} \right)^2 - \frac{\left(\frac{\delta \eta}{\delta c}\right)_0 \left(\frac{\delta n}{\delta c}\right)_0}{n_0 \eta_0} \right\} \qquad \text{... 8.6}$$

where η is the viscosity, and n is the ion density of system and n_0 , η_0 and σ_0 denotes the value of mean ion density, viscosity and conductivity at C = Cc (critical concentration). Using scaling theory and standard statistical arguments, one find (Jasnow, 1975)

$$C_c^{-2} \langle (\delta c)^2 \rangle_{\xi^3} = d \epsilon^{2\beta} \qquad \text{...8.7}$$

where d is of order unity.

On combining equations (8.6) and (8.7), we get the desired relation

$$\sigma = \sigma_0 + \sigma_0 Bd\,\epsilon^{2\beta} \qquad \ldots\ 8.8\ \text{a}$$

or,

$$\sigma = \sigma_0 + M\,\epsilon^{2\beta} \qquad \ldots\ 8.8\ \text{b}$$

or,

$$\sigma = \sigma_0 + \sigma_{sing} \qquad \ldots\ 8.8\ \text{c}$$

where M = (σ_0 Bd) and actually σ_0 has been regarded here as analytic in ϵ .

All the experimental binary liquid systems were brought into one phase region about 5°C above T_c. The liquids were allowed for few minutes to attain thermal equilibrium. Then the system were slowly cooled with millidegree steps till the mixture comes down to the critical or opalescence region. The r.f. conductivity (K') of the binary liquid mixtures, such as (a) methyl alcohol + carbon disulphide ($CH_3OH + CS_2$) (b) Nitrobenzene + n - hexane ($C_6H_5NO_2 + C_6H_{14}$) and (c) Aniline + cyclohexane ($C_6H_5NH_2 + C_6H_{12}$) have been measured at 400 KHz and at various temperature starting from one phase region to down to T_c. Much care has been taken on measurement of K'_c , the critical temperature r.f.

conductivity. The values of the r.f. conductivity of the three systems at various temperatures above T_c and at T_c are placed in Table (8.1a- 3a). As it is the temperature derivative of electrical resistance is strongly divergent near T_c. So an attempt has been taken to study the r.f. conductivity anomaly near critical temperature of the three polar - nonpolar liquid mixtures at critical concentrations. The r.f. conductivity data are plotted against the reduced temperatures for the three systems shown in Fig. (8.1, 8.2, 8.3). It is observed that the temperature variation conductivity closer to T_c is quite large but when it is away from T_c the variation is small. This clearly indicate the asymtotic behaviour of derivative of conductivity and strongly suggest the existance of r.f. conductivity anomaly near T_c.

Stein and Allen chose to fit the resistance versus temperature data to various functional forms

(a) $$\frac{dR}{dT} = A\epsilon^{-d} + B\epsilon^{2} + C\epsilon + D \qquad \text{... 8.9a}$$

(b) $$\frac{R_c - R}{\epsilon . R_c} = \left(\frac{A'}{1-d}\right)\epsilon^{-d} + B'\epsilon^{2} + C'\epsilon + D' \qquad \text{... 8.9b}$$

(c) $$R - R_{ideal} = A''\epsilon^{1-d} + B''\epsilon + C'' \qquad \text{... 8.9c}$$

(d) $$\left(\Delta R_j - \Delta R_i\right) = A'''\left(\epsilon_i^{1-d} - \epsilon_j^{1-d}\right) + B'''\left(\epsilon_i - \epsilon_j\right) \qquad \text{... 8.9 d}$$

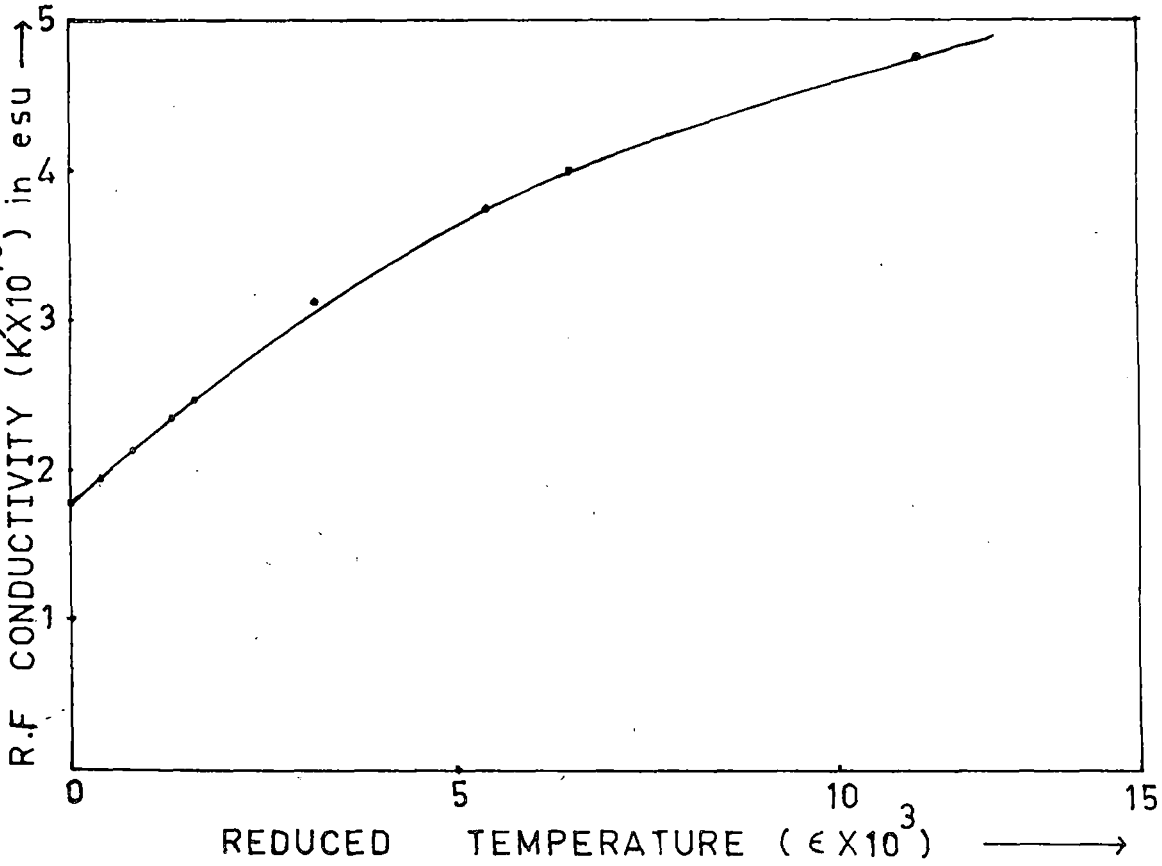

Fig - 8.1 Plot of R.F Conductivity K' against Reduced temperature ϵ for $CH_3OH + CS_2$.

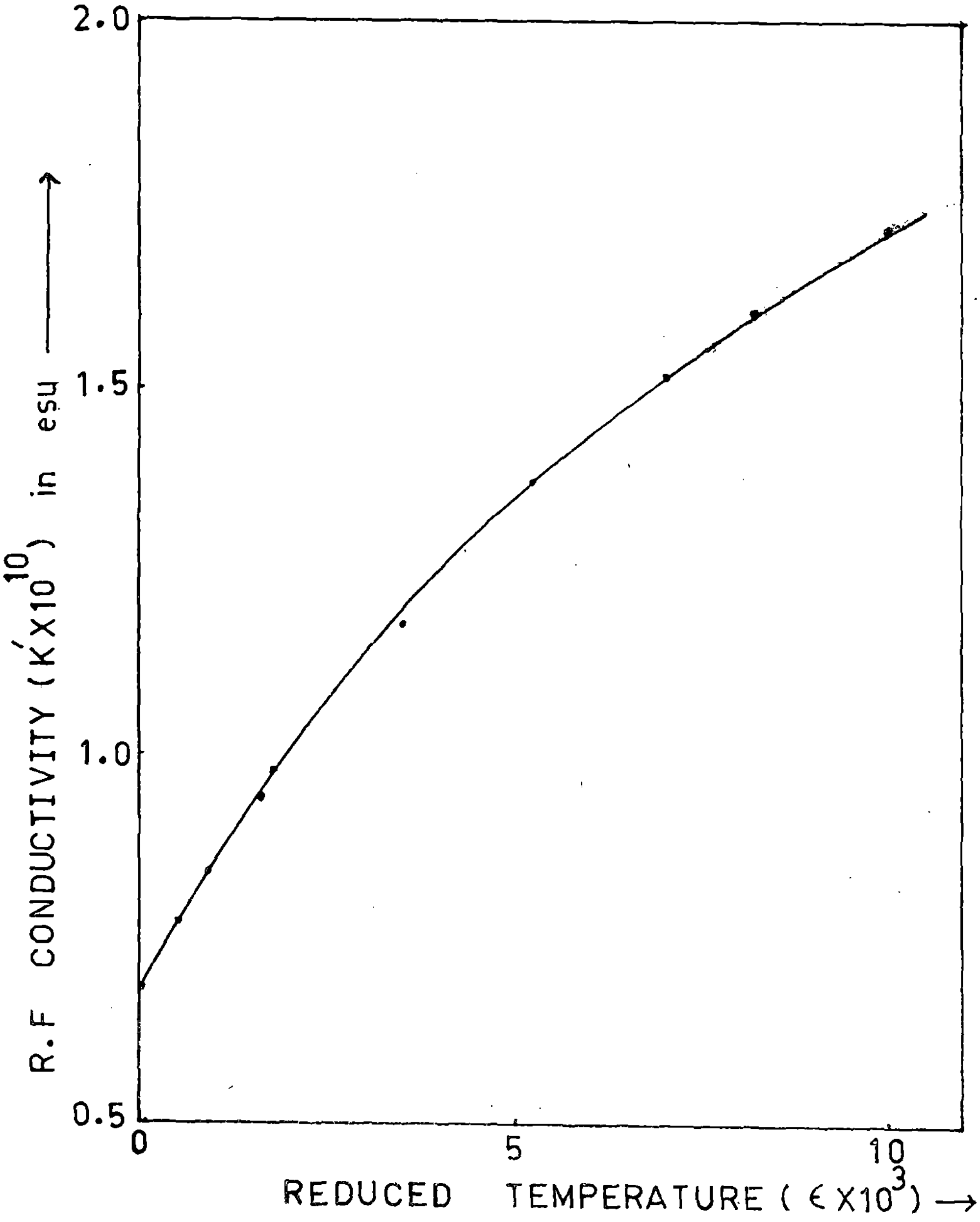

Fig - 8.2 Plot of R.F Conductivity K′ against Reduced temperature ε for $C_6H_5NO_2 + C_6H_{14}$.

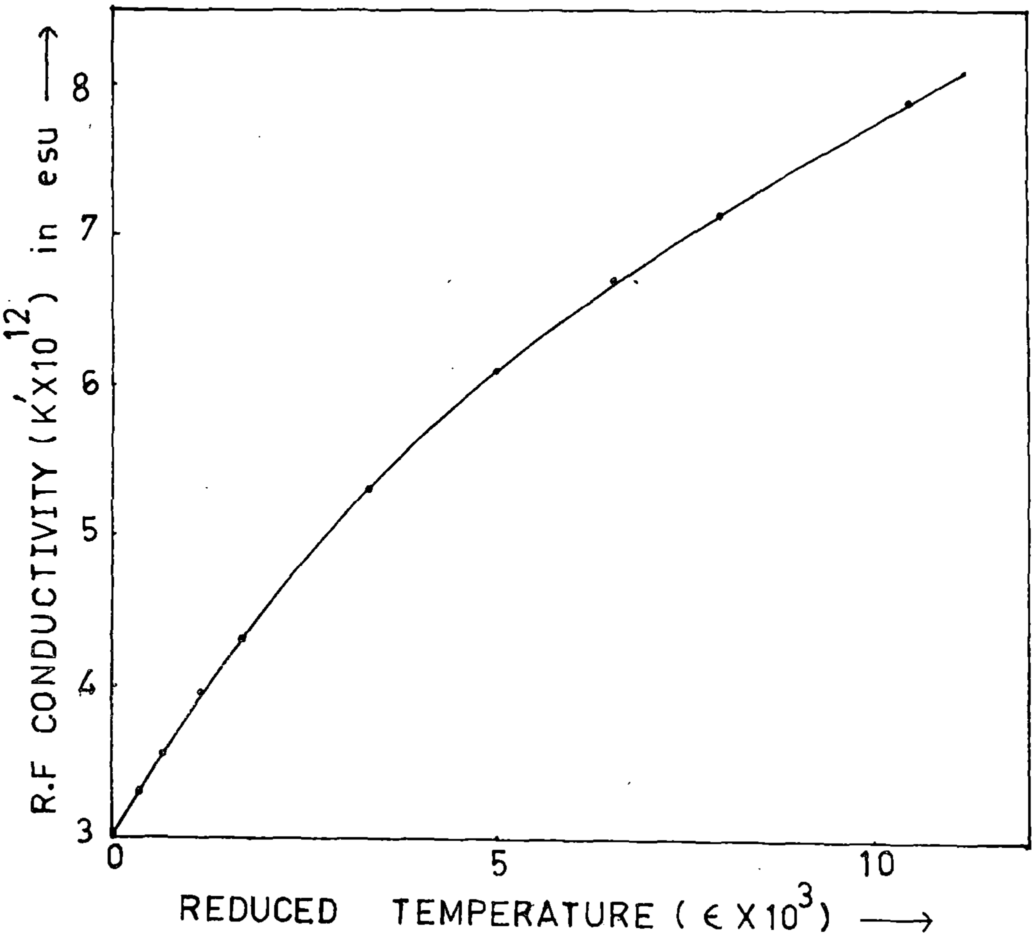

Fig- 8.3 Plot of R.F Conductivity K' against Reduced temperature ϵ for $C_6H_5NH_2 + C_6H_{12}$.

where R_{ideal} is the back ground resistance and

$\Delta R = (R - R_{ideal})$ and parameter $A''' = \left(\frac{A}{1-d}\right)$,
$B''' = -B''$

As the percolation theory is applicable only to temperature variation of conductivity rather than R (T). So we tried to analyse and least squares fits our r.f. conductivity data K' (T) to the Shaw and Goldburg empirical equation of conductivity,

$$\sigma = A' \epsilon^{\theta} + \sigma_c + B_1' \epsilon + B_2' \epsilon^2 \qquad \text{... 8.10}$$

Therefore we can write the equation (8.10) of form

$$K' = A' \epsilon^{\theta} + K_c' + B_1' \epsilon + B_2' \epsilon^2 \qquad \text{... 8.11 a}$$

or

$$K' - K_c' = K'_{singular} + K'_{bkg} \qquad \text{... 8.11 b}$$

where A', B'_1, and B'_2 and θ are the least squares fit values or parameter, singular conductivity $K'_{singular} = A' \epsilon^{\theta}$ and background conductivity $K'_{bkg} = B_1' \epsilon + B_2' \epsilon^2$

Writting the above equation (8.11 a) for conductivity in dimension less unit, we have reduced conductivity

$$K'_R = \frac{K' - K'_c}{K'_c} = \frac{A'}{K'_c} \epsilon^{\theta} + \frac{B'_1 \epsilon}{K'_c} + \frac{B'_2 \epsilon^2}{K'_c} \qquad \ldots\ 8.12$$

or

$$K'_R = A\epsilon^{\theta} + B_1\epsilon + B_2\epsilon^2 \qquad \ldots\ 8.13$$

where the least squares parameters $A = \frac{A'}{K'_c}$, $B_1 = \frac{B'_1}{K'_c}$ and $B_2 = \frac{B'_2}{K'_c}$.

In our present analysis we did not use the higher power of ϵ, so we have eliminated the term $B_2\epsilon^2$. Therefore, the equation (8.13) becomes,

$$K'_R = A\epsilon^{\theta} + B_1\epsilon \qquad \ldots\ 8.14$$

In order to get the best least squares fits parameters, we have varied the range of reduced temperature of the order $10^{-4} \leqslant \epsilon \leqslant 10^{-2}$ and determined least squares fit parameters for three sets of ϵ, using the equation (8.14) for each systems. The values of the fits parameters are placed in the Table (8.1 a, 2a, 3a).

It is further observed that all our measured data for three different systems are fits well in equation (8.14) if we consider the critical exponent value $\theta = 0.71$, which is the slope of plot $\log_{10} K_R'$ against $\log_{10} \epsilon$. Figures (8.4, 5 and 6) shows the results of second set ($10^{-4} \leqslant \epsilon \leqslant 10^{-2}$) of all the systems ($CH_3OH + CS_2$) , ($C_6H_5NO_2 + C_6H_{14}$) and ($C_6H_5NH_2 + C_6H_{12}$) respectively. In the graph of $\log_{10} K_R'$ plotted against $\log_{10} \epsilon$ the upper dashed line running through the experimental data points which are the least square fits data obtained from equation (8.14). The lower dashed line is the same as upper one but with background conductivity K_{bkg}' subtracted. In the data analysis, only linear background terms ($B_1 \epsilon$) was considered. The values of $\log K'(\epsilon)$, $\log(K_R' - K_{bkg}')$ and $\log \epsilon$ of the three systems are tabulated in table (8.2 a, 2b, and 2c) respectively.

So we find that our data are best fitted to the equation (8.14) in the reduced temperature range $10^{-4} \leqslant \epsilon \leqslant 10^{-2}$ and the amplitude ratio of singular to background $A/B_1 < 1$, provides strong evidence that the conductivity singularities which we have observed, is an experimental fact.

The striking observation made in this studies is that apart from the shape of the conductivity curves Fig. (8.1, 8.2, 8.3) the critical exponent θ for the

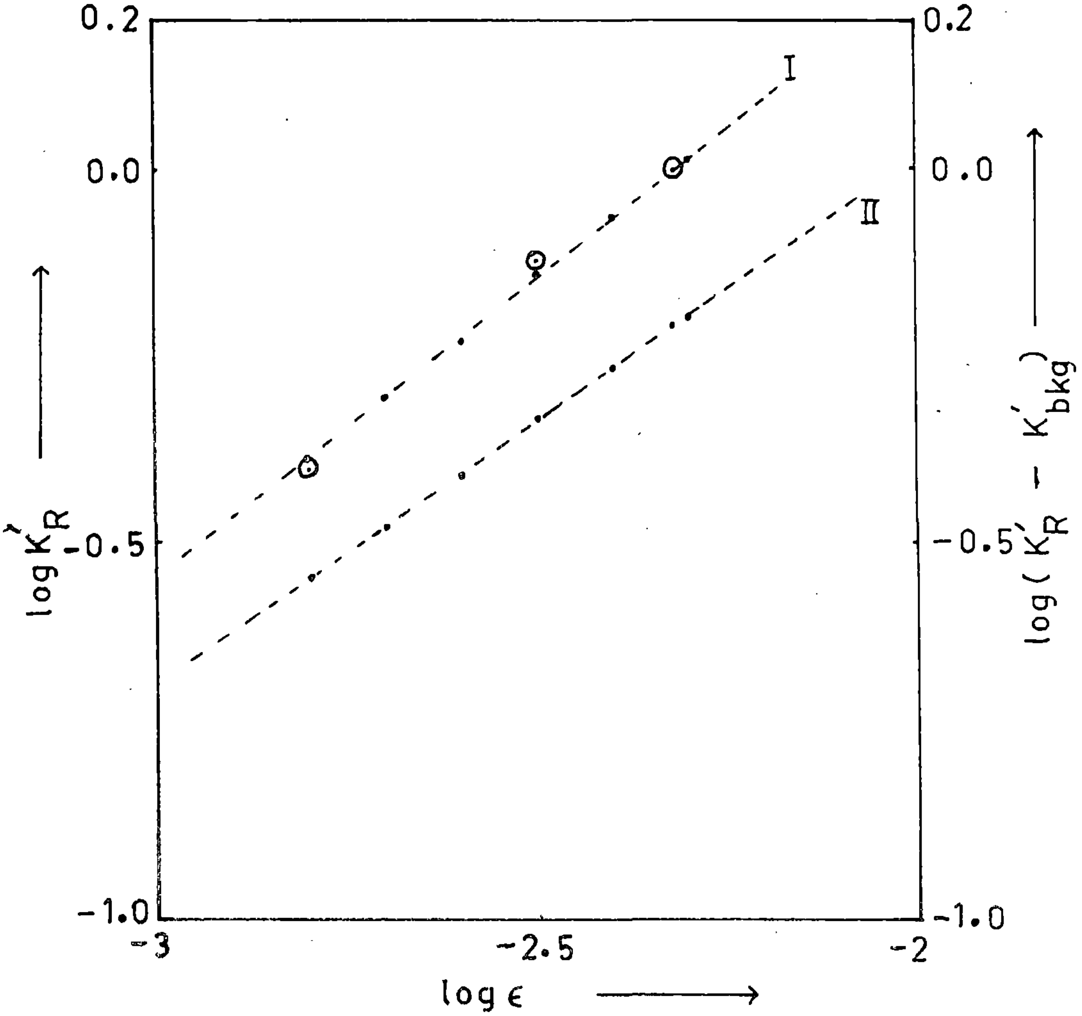

Fig - 8.4 Log-Log plot of reduced conductivity K'_R versus reduced temperature ϵ (I) and also background term K'_{bkg} subtracted (II) for $CH_3OH + CS_2$.

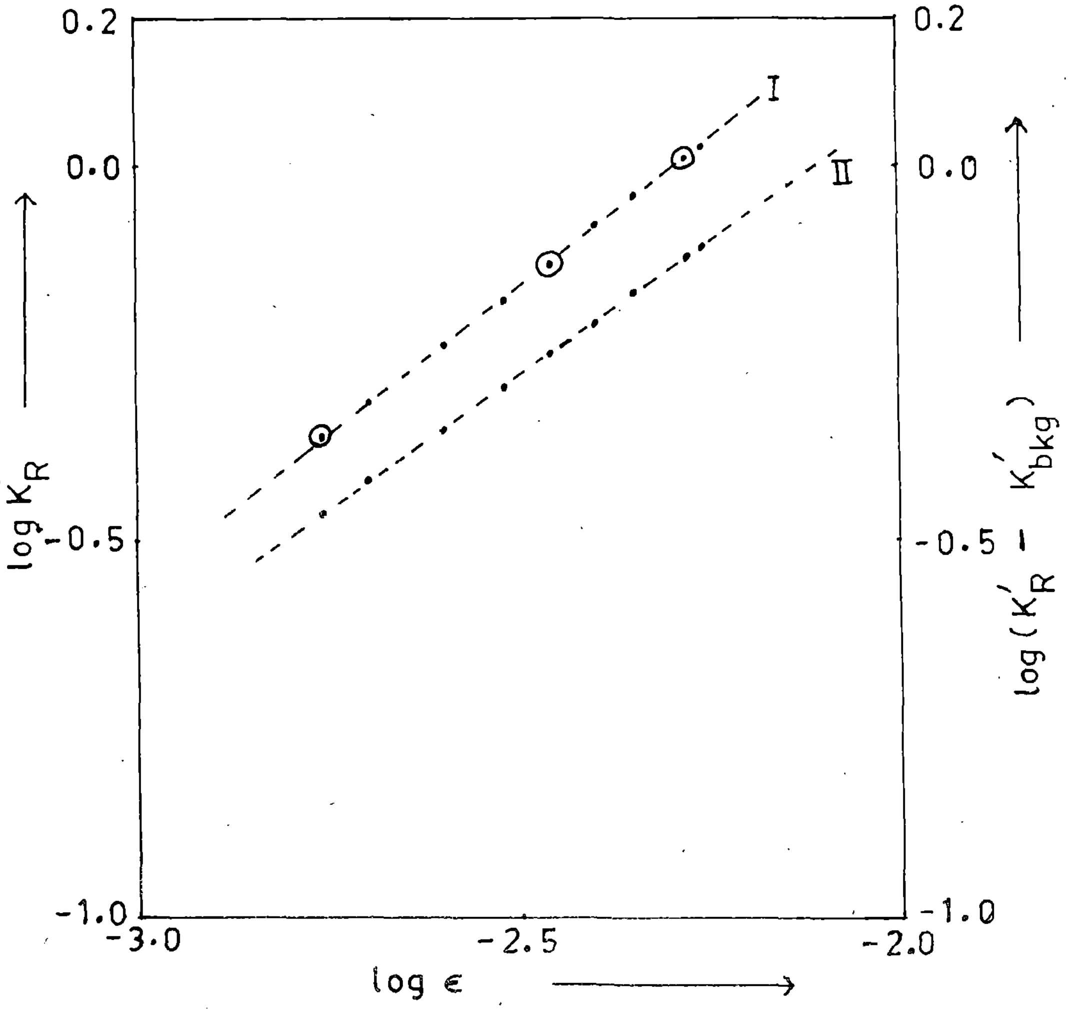

Fig-8.5 Log-Log plot of reduced conductivity K_R' versus reduced temperature ε (I) and also background term K_{bkg}' subtracted (II) for $C_6H_5NO_2 + C_6H_{14}$.

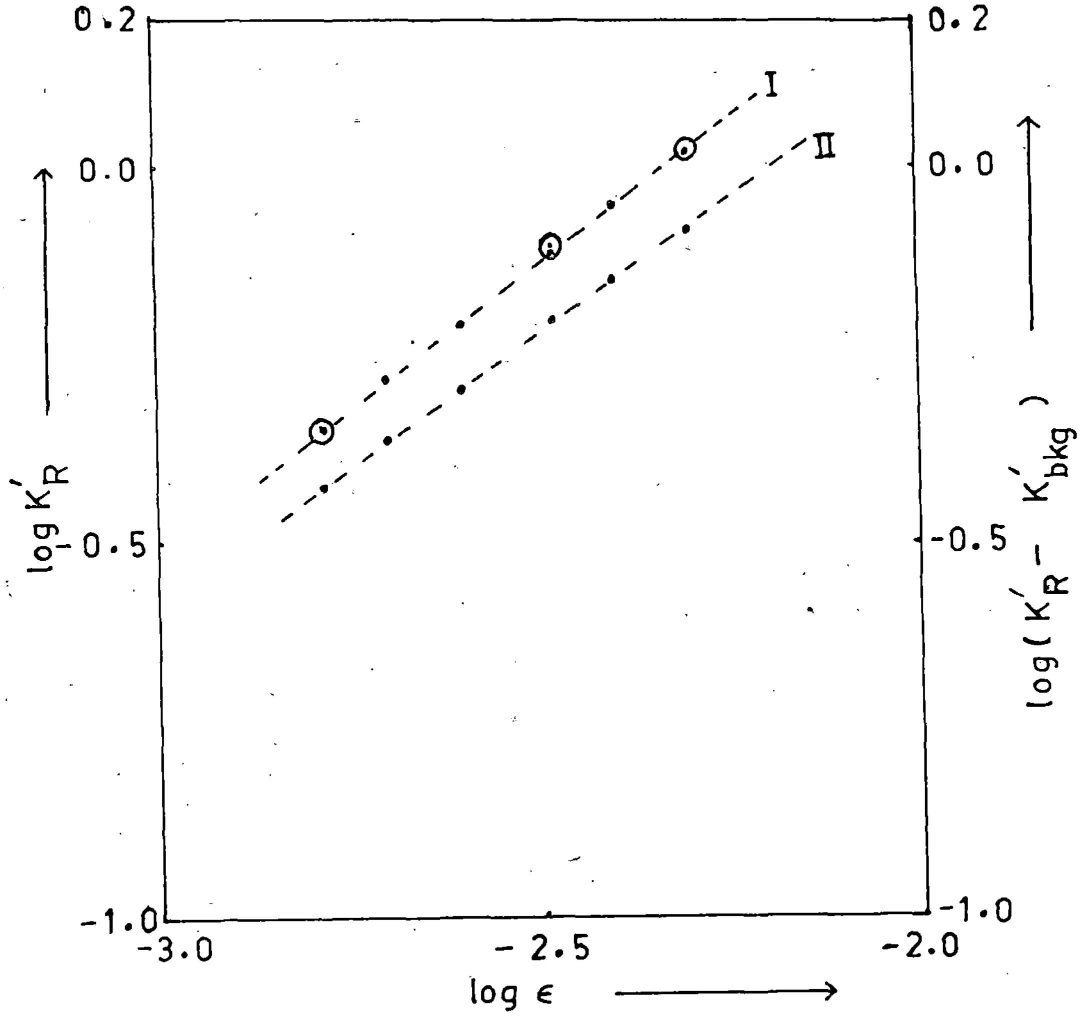

Fig-8.6 Log-Log plot of reduced conductivity K'_R versus reduced temperature ϵ (I) and also background term K'_{bkg} subtracted (II) for $C_6H_5NH_2 + C_6H_{12}$.

three different systems almost have the same value $\theta \simeq 0.71$ which agree excellently with the value reported by previous workers (Gopal, 1976).

It has been reported that very near to T_c there is every possibility to expect frequency dependent conductivity anomaly (i.e. of the inverse of the applied frequency) being of the same order of magnitude as the fluctuation life time. But the frequency dependent relaxation effect occurs in the 10^{10} to 10^{12} Hz region in the pure and dilute solution of polar liquid in nonpolar solvent and little high value may be expected at critical opalescence temperature T_c.

But in our present experiment we have taken the frequency 400 KHz, which is quite low compare to the time constant for decay of composition fluctuation at critical temperature. So we can consider that there is no noticeable effect of frequency on critical exponent θ has taken place at that frequency.

Thus we can conclude that in the one phase region, the conductivity of the binary liquid mixture near critical temperature T_c must contain the term of the form, $K'_{sing} = A\,\epsilon^{\theta=2\beta}$ with $\theta = 0.71$ and $\beta \simeq 0.35$, which is an universal value for the temperature variation of the order parameter in critical phenomena.

Table 8.1a

Values of r.f. conductivity (K'), reduced r.f. conductivity (K'_R) at different reduced temperatures (ϵ), fitting equation parameters (θ , A, B_1) and the amplitude ratio A/B_1, R.F. conductivity at critical temperature ($T_c = 40.5^oC$) $K'_c = 1.792 \times 10^{-10}$ esu.

System	No. of sets	$\epsilon \times 10^3$	$K' \times 10^{10}$ esu	K'_R	θ	A	B_1	A/B_1
Methyl alcohol (15 per-cent by weight) + Carbon disulphide (85 percent by weight) Solution	1	1.3	2.35	0.3114	0.12	-0.017	248.23	-6.8×10^{-5}
		0.8	2.15	0.1998				
		0.4	1.95	0.088				
		0	1.792					
	2	4.78	3.568	0.99	0.71	27.42	80.59	0.34
		3.19	3.138	0.75				
		1.59	2.496	0.393				
		0	1.792					
	3	11.10	4.75	1.651	0.50	13.26	23.22	0.57
		6.5	4.0	1.232				
		5.4	3.75	1.093				
		0	1.792					

Table 8.1b

Fitted values of reduced temperature (ϵ), reduced conductivity (K'_R) and reduced conductivity with background term subtracted ($K'_R - K'_{bkg}$) . Fitted equation is $K'_R = 27.42\,\epsilon^{.71} + 80.59\,\epsilon$.

System	$\epsilon \times 10^3$	K'_R	$K'_R - K'_{bkg}$	$\log \epsilon$	$\log K'_R$	$\log(K'_R - K'_{bkg})$
Methyl alcohol + carbon disulphide	1.00	0.2839	0.2033	-3.00	-0.5468	-0.692
	1.59	0.4107	0.2825	-2.799	-0.3865	-0.549
	2.00	0.4937	0.3325	-2.699	-0.3065	-0.478
	2.5	0.5911	0.3896	-2.602	-0.2283	-0.409
	3.19	0.7203	0.4632	-2.496	-0.1425	-0.339
	4.00	0.8663	0.5439	-2.398	-0.0623	-0.264
	4.78	1.002	0.6173	-2.321	+0.00087	-0.2095
	5.00	1.040	0.6373	-2.301	+0.017	-0.196

Table 8.2a

Values of r.f. conductivity (K'), reduced r.f. conductivity (K'_R) at different reduced temperature (ϵ), fitting equation parameters (θ, A, B_1) and the amplitude ratio A/B_1. Taking r.f. conductivity at critical temperature ($T_c = 14^\circ C$) $K'_c = 0.678 \times 10^{-10}$ esu.

System	No. of sets	$\epsilon \times 10^3$	$K' \times 10^{10}$ esu	K'_R	θ	A	B_1	A/B_1
Nitrobenzene(50 percent by weight) + n-hexane (50 percent by weight) Solution	1	1.6	0.94	0.386	0.85	59.0	89.58	0.66
		0.9	0.84	0.239				
		0.5	0.77	0.136				
		0.0	0.678					
	2	5.226	1.378	1.032	0.71	31.36	52.69	0.60
		3.484	1.178	0.737				
		1.742	0.978	0.442				
		0.0	0.678					
	3	10.0	1.72	1.537	0.70	52.34	-56.32	-0.94
		8.2	1.62	1.375				
		7.0	1.52	1.242				
		0.0	0.678					

Table 8.2b

Fitted values of reduced temperature (ϵ), reduced conductivity (K'_R) and reduced conductivity with back ground term subtracted ($K'_R-K'_{bkg}$).

Fitted equation is $K'_R = 31.36\ \epsilon^{0.71} + 52.69\epsilon$.

System	ϵ x10^3	K'_R	$K'_R-K'_{bkg}$	Log ϵ	Log K'_R	log $(K'_R-K'_{bkg})$
Nitro-benzene + n-hexane	1.00	0.2852	0.2325	-3.00	-0.545	-0.634
	1.742	0.4365	0.3448	-2.759	-0.360	-0.462
	2.0	0.4857	0.3803	-2.699	-0.314	-0.420
	2.5	0.5773	0.4456	-2.602	-0.239	-0.351
	3.0	0.6652	0.5071	-2.523	-0.177	-0.295
	3.484	0.7475	0.5639	-2.458	-0.126	-0,249
	4.0	0.8328	0.6221	-2.398	-0.079	-0.206
	4.5	0.9134	0.6763	-2.347	-0.039	-0.170
	5.226	1.0274	0.7521	-2.282	+0.012	-0.124
	5.5	1.0697	0.780	-2.260	+0.029	-0.108

Table 8.3a

Values of r.f. conductivity (K'), reduced r.f. conductivity (K'_R) at different reduced temperature (ϵ), fitting equation parameters (θ , A, B_1) and the amplitude ratio A/B_1. Taking r.f. conductivity at critical temperature (T_c = 31°C) K'_c = 3.0 x 10^{-12} esu.

System	No. of sets.	$\epsilon \times 10^3$	$K' \times 10^{12}$ esu	K'_R	θ	A	B_1	A/B_1
Aniline (46 percent by weight) + Cyclohexane (54 percent by weight) Solution	1	1.1	3.95	0.317	0.87	490.28	-950.1	-0.52
		0.6	3.55	0.183				
		0.3	3.30	0.10				
		0.0	3.0					
	2	4.93	6.11	1.037	0.71	35.60	45.53	0.78
		3.29	5.33	0.777				
		1.64	4.333	0.444				
		0.0	3.0					
	3	10.4	7.895	1.632	0.67	50.07	-71.23	-0.70
		7.9	7.15	1.383				
		6.5	6.70	1.233				
		0.0	3.0					

Table 8.3b

Fitted values of reduced temperature (ϵ), reduced conductivity (K'_R) and reduced conductivity with background term subtracted ($K'_R - K'_{bkg}$). Fitted equation is $K'_R = 35.6\,\epsilon^{.71} + 45.53\,\epsilon$.

System	$\epsilon \times 10^3$	K'_R	$K'_R - K'_{bkg}$	$\log \epsilon$	$\log K'_R$	$\log(K'_R - K'_{bkg})$
Aniline + cyclohexane	1.0	0.3094	0.2639	-3.0	-0.509	-0.579
	1.64	0.4496	0.3749	-2.785	-0.347	-0.426
	2.0	0.5228	0.4317	-2.699	-0.282	-0.365
	2.5	0.6196	0.5058	-2.602	-0.208	-0.296
	3.29	0.7645	0.6147	-2.483	-0.117	-0.211
	4.0	0.8883	0.7062	-2.398	-0.051	-0.151
	4.93	1.0436	0.8192	-2.307	+0.0185	-0.087

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CHAPTER IX

SUMMARY OF THE RESULTS OF PRESENT WORK AND CONCLUSION

The result and discussions of the present investigation have been described in detail in Chapter III to VIII. Here a chapterwise summary of the results are given below.

Chapter III

MICROWAVE CONDUCTIVITY AND DIPOLE MOMENT OF POLAR DIELECTRICS.

The high frequency conductivity of the seven systems in benzene, such as (i) 2-5dichloronitrobenzene, (ii) 2-5 dibromonitrobenzene, (iii) 3-nitro-O-anisidine (iv) 2-chloro-p-nitroaniline (v) p-phenitidine, (vi) O-nitroaniline, (vii) p-anisidine have been calculated from the relation

$$K_{ij} = \frac{\omega}{4\pi}\sqrt{\epsilon_{ij}'^2 + \epsilon_{ij}''^2} \quad \text{where } \epsilon_{ij}''$$

is the dielectric loss and ϵ_{ij}' is the dielectric constant at various temperatures. The computed conductivity K_{ij} for each systems varies almost linearly with weight fraction W_j ; specially in the lower concentration region. The slope of the concentration variation of h.f. conductivity of polar - nonpolar liquid mixture at infinite dilution has been employed to estimate the dipole moment μ_j of polar solute at different temperatures by using the relation $\mu_j = \left[\frac{3M_j kT\beta}{N\rho_j F_j \omega b}\right]^{1/2}$ where β is the slope of the curve, ρ_j is the density, F_j is the local field and $b = \frac{1}{1+\omega^2\tau^2}$. It is further observed that in all the systems, the increase of dipole moment can be expressed by the relation $\mu_j = a' + b't + c't^2$ where a', b' and c' are the least square fits constants which depends upon the nature of the respective molecules in benzene under the high frequency alternating electric field. It is observed from the computed values of dipole moment at different temperatures that, in microwave electric field the dipole moment of a polar unit is not fixed, but varies uniformly with temperature.

Chapter IV

MICROWAVE CONDUCTIVITY AND DIPOLE MOMENT OF SOME SUBSTITUTED BENZENE

This chapter reported the measurement of permanent dipole moment and bond moment of the following dielectric liquids -

(a) m-Aminobenzotrifluoride, (b) O-Nitrobenzotrifluoride (c) m-Nitrobenzotrifluoride (d) O-Chlorobenzotrifluoride (e) O-chloronitrobenzene (f) 4-chloro-3-nitrobenzo trifluoride (g) 4-chloro-3-nitrotoluene.

The theory and method of determination of dipole moment (μ_j) from the microwave conductivity method in the 3 cms. wavelength range is same as previous chapter. The data of dipole moment at higher and lower concentration explain the formation of dimer and monomer. The μ_j values have also been computed from the bond moment and bond angles, assuming that the benzene molecules is a planer one. It has been considered that the variation of μ_j for the substituted molecules in benzene may be due to the difference in values of group moment and the inductive effect.

Chapter V

ULTRA HIGH FREQUENCY CONDUCTIVITY OF POLAR - NONPOLAR LIQUID MIXTURES

The UHF conductivity of nitromethyl acetamide (NMA) in benzene and in dioxane solvent in the lower as well as higher concentration region of polar solute have been determined from dielectric absorption data in the temperature range of 25°C to 55°C. It is observed that at lower concentration region the UHF conductivity data varies linearly with the weight fraction of the solute, but differ radically at weight fraction $W_j \rightarrow 0$, which has been considered due to the solute solvent association effect. At the higher concentration the above mentioned effect was not detected in the case of NMA but found in p-bromonitrobenzene (p-BNB). From the slope of the curve of UHF conductivity against concentration of solute molecules at infinite dilution, the dipole moment have been estimated for above mentioned liquids at various temperatures using the equation given in chapter III. It has been suggested that in the case of NMA in benzene and dioxane, the higher (computed) values of dipole moment are due to the formation of monomer and slightly lower estimated values may be due to the formation of dimer.

Chapter VI

CONDUCTIVITY, RELAXATION TIME AND ENERGY OF ACTIVATION OF SOME ALCOHOL + BENZENE MIXTURE AT RADIO FREQUENCY FIELD

A study has been made on the nature of variation of dipolar relaxation time (τ) for three normal alcohols such as, methyl alcohol, ethyl alcohol and 1-propyl alcohol at very dilute solution in nonpolar solvent benzene and at various temperatures. The time of relaxation has been determined from radiofrequency conductivity measurements at 1 MHz. The radio frequehcy conductivities of the three systems at various dilute solution and at different temperatures have been computed from least square fit equation

$$K' = \alpha + \beta W_j + \gamma W_j^2$$

and the time of relaxation τ_s determined from the relation given in chapter III. The relaxation time of dipole at infinite dilution (τ_∞) at various temperatures ($30^\circ C$ to $60^\circ C$) were computed from the relation $\tau_\infty = (2/3)\tau_s$ and also the changes due to solvent effect were estimated. It has been concluded that the lower values of τ_∞ compared to τ_s indicates that at infinite dilution the rotation of a molecule is not hindered by the interaction with other molecules, which suggests that rotational orientation occured due to (-OH) group of a molecule.

The temperature dependence of relaxation time has been utilised for determining the molecular free energy of activation ΔF_{τ_∞}, enthalpy of activation energy ΔH_{τ_∞} and entropy of activation energy ΔS_{τ_∞} for the dipole orientation of polar alcohols in nonpolar solvent. It is observed that ΔH_{τ_∞} and activation energy for viscosity ΔH_η are almost same for two systems where as it differ widely in the case of propanol. It has been considered that slightly higher value of ΔH_{τ_∞} for propanol compared to ΔH_η may be due to the energy concentration for its higher chain length.

Chapter VII

ENERGY OF ACTIVATION, DIPOLE MOMENT AND CORRELATION PARAMETER OF WATER.

In this chapter the radio frequency conductivity K' of water and glycerine mixture at 50% concentration down to unit mole fraction of water has been determined at 5 MHz over the temperature range $20^{\circ}C$ to $60^{\circ}C$. The relaxation time τ_s for the mixture at various temperatures and concentration have been calculated from the relation $\tau_s = \frac{2}{3} \cdot \frac{a^2 e}{v k T}$, where a is the radius of the molecule, e is the electronic charge and v is the mobility of the free ions calculated from the relation K' = Nev . The time of relaxation of water τ_0 at various temperatures have been determined from the extrapolation curve at unit molefraction of water. It has been thought that the little high value of τ_0 may be due to the presence of minute quantity of glycerine as impurity, which increases the hydrogen bonding between water molecules with the impurity molecules. The decrease of τ_0 value with the rise of temperature suggested due to the breaking of the hydrogen bond.

The theory of rate process has been used to the temperature variation of single relaxation time in order to calculate the thermodynamical parameters

ΔF_{τ_0} , ΔH_{τ_0} and ΔS_{τ_0}).

for water. Assuming the $\Delta H_{\tau_0} = 4.8$ Kcal/mole is of the same order of magnitude as the dipole-dipole interaction energy, the apparent dipole moment for water has been calculated from the Debye-Keesom relation

$$\Delta H_{\tau_0} = \frac{2}{3}\,\frac{\mu^4_{app}}{a^6 kT_0},$$

where $a = 1.48$ Å is the average intermolecular distance. The correlation parameter for water $g = (\mu_{app}/\mu_{gas})^2$ was calculated and found greater than unity ($g > 1$) The bond angle θ of (H-OH) has been calculated at various temperatures from Kirkwood relation $g = 1 + Z\cos^2\frac{\theta}{2}$.

Analysing the results a conclusion has been drawn that, the structure of water has an appreciable effect on dipolar polarisation which causes $\mu_{app} > \mu_{gas}$ and the bending of hydrogen bond with the rise of temperature.

Chapter VIII

ELECTRICAL CONDUCTIVITY ANOMALY IN BINARY LIQUID MIXTURES NEAR THE CRITICAL POINT

In this chapter a study has been made on the electrical conductivity anomaly of three critical binary liquid mixtures at the critical temperature region. The electrical conductivities of the three binary liquid mixtures such as, (a) Methyl alcohol + carbondisulphide, (b) Nitrobenzene + n-Hexane, (c) Aniline + cyclohexane have been determined at various temperature starting from one phase region to down to T_c at 400 KHz. The conductivity (K') data fitted against reduced temperature (ϵ) for three systems indicated the asymptotic behaviour of derivative of conductivity and existence of conductivity anomaly near critical temperature T_c.

As the percolation theory is applicable only to temperature variation of conductivity rather than resistivity R(T) near T_c, so it has been tried to fit the reduced conductivity data $K'_R = \frac{K' - K'_c}{K'_c}$ at the reduced temperature range $10^{-4} \leqslant \epsilon \leqslant 10^{-2}$ in the least square fit equation $K'_R = A\epsilon^{\theta} + B_1\epsilon + B_2\epsilon^2$ where A, B_1 and B_2 are the least square fit parameters and θ is the critical exponent, which is the slope of the linear plot $\log_{10} K'_R$ against $\log_{10} \epsilon$. The linear plot further proved that the validity of the above mentioned fit equation, when the calculated fitted data points run smoothly through the experimental data points. The striking observation made in this studies that apart from the shape of the conductivity curves of the three systems, the critical exponent θ for the three different systems are almost have the same value $\theta = 0.71$. Therefore it has been suggested that in the one phase region, the conductivity of the binary liquid mixture near critical temperature must contain the term of the form $K'_{singular} = A\epsilon^{\theta=2\beta}$, with $\theta = 0.71$ and $\beta = 0.35$ which is an universal value for the temperature variation of the order parameter in critical phenomena.

APPENDIX

10.0 List of publications

1. Microwave conductivity and dipole moment of polar dielectrics - Indian J phys 56 (1982) 291 .

2. Microwave conductivity and dipole moment of some substituted benzene - Indian J pure and Appl phys 23 (1985) 484 .

3. Ultra high frequency conductivity of polar non-polar liquid mixtures - Indian J pure and Appl phys 24 (1986) 234 .