

**DIELECTRIC RELAXATION PARAMETERS OF POLAR LIQUIDS
FROM ULTRA-HIGH FREQUENCY CONDUCTIVITY OF
SOLUTES IN NON-POLAR SOLVENTS**

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**THESIS SUBMITTED FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY (SCIENCE)
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**BY
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DEDICATED TO THE SACRED MEMORY OF MY FATHER
LATE BIBHUTI BHUSAN SAHA WHO HAD UNBOUNDED
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INTRODUCTION

Dielectric behavior of pure polar liquids and polar liquids in non-polar solvents under the application of electric field of suitable frequency has been a subject of investigation for many years and their different aspects were emphasized in different periods.

In 1912 P Debye was successful to extend the Clausius-Mosotti relation and showed that the dielectric constant depends not only on the molecular polarizability, but also on the permanent electric moment of the molecules. He explained with the help of this concept of molecular permanent dipole moment, the anomalous dispersion of dielectric constant which was observed by Drude (1904) and other workers. Debye further pointed out that the process of orientation of the permanent electric moment connected with the change in the electric field, requires a definite time interval, since it depends on the rotational movements accomplished by the molecules. It follows from the assumption that after removal of an externally applied electric field the average dipole orientation decay exponentially with time. The characteristic time of such decay is called the relaxation time.

It was found experimentally that relaxation time depends on temperature. This led to consider the dielectric phenomenon as a rate process.

A large number of workers have proposed several modifications and extensions of Debye theory of dielectric absorption. The replacement of single relaxation time by a set of relaxation times was soon developed to describe the macroscopic relaxation process. In order to support the experimental results the introduction of distribution of relaxation times was also proposed in many cases. Cole and Cole, and Cole Davidson however, offered important graphical methods called Cole-Cole and Cole-Davidson plots to distinguish these cases from that of single relaxation time. It appears from the above discussion that further improvement in the theory of dielectric absorption and dispersion could, however, be made for a better understanding of the dielectric relaxation phenomena to throw much light on the molecular and intramolecular structures of the polar liquids in pure state and in solution also.

Thus in order to get a clear picture of the subject of dielectric polarization and its relation with shape, size and structure of polar molecules, a brief survey of the development of various theories of dielectric polarization and their extension and modifications together with a brief review of earlier works are given in the following section. The scope and the objects of the present works are given in the second chapter together with the radio frequency experimental technique and

theories of measurements. The rest of the subject matters of this thesis is distributed several chapters. The last chapter contains the results and conclusion of the present investigation.

CHAPTER I

GENERAL INTRODUCTION AND BRIEF REVIEW OF THE PREVIOUS WORKS

1.1 Debye Theory of Dielectric Polarization

When a substance is placed under an external electric field, an "internal field" being proportional to the applied electric field is called into play within the substance. Under the influence of the external electric field the electrons in some substance and the ions in some liquids move away over a long distance given rise to what is known as electric conduction. Such substances are called conductors. But in the case of insulators or dielectrics a very small displacement of positive and negative charges occurs in opposite directions. This sort of displacement of charges of atoms or molecules of a dielectric material under the application of the electric field causes what is known as dielectric polarization. This type of polarization is called distortion polarization. In some dielectrics, where permanent dipoles exist, the applied electric field tends to direct the permanent dipoles along the field direction. This is termed as orientational polarization. Orientation polarization results in the transport of charges through every plane elements in the dielectrics which is called displacement current. At equilibrium every volume element of the dielectric under the applied electric field acquires an induced dipole moment. The induced dipole moment in a volume element Δv around a point is given by

$$\vec{m}_{ind} = \vec{p}\Delta v = \sum N_i \cdot \vec{S}_i \Delta v \dots\dots\dots(1.1)$$

Where N_i is the average number of charges e_i per unit volume with displacement S_i . The vector \vec{P} is the induced dipole moment per unit volume and is known as "electronic polarization". It is connected with the dielectric displacement vector \vec{D} as

$$\vec{D} = \vec{E} + 4\pi \vec{P}$$

$$\text{or, } \vec{P} = \frac{\vec{D} - \vec{E}}{4\pi} = \frac{\epsilon - 1}{4\pi} \vec{E} \quad \dots\dots\dots(1.2)$$

Where $\vec{D} = \epsilon \vec{E}$, ϵ is the dielectric permittivity, $(\epsilon - 1)/4\pi = \chi$ is dielectric susceptibility and \vec{E} is the applied electric fields.

When a polar dielectric is placed under an electric field \vec{E}_0 the molecules themselves tend to orient along the field direction. The dipole moment of each molecule is proportional to \vec{E}_0 and it can be written as

$$\vec{m} = \alpha \vec{E}_0 \quad \dots\dots\dots(1.3)$$

Where α is a constant called polarizability of the dielectric.

In case of a dielectric sphere of radius 'a' the dipole moment is given by

$$\vec{m} = \frac{\epsilon - 1}{\epsilon + 2} a^3 \vec{E}_0 \quad \dots\dots\dots(1.4)$$

and hence from eq. (1.3) and (1.4) we get

$$\alpha = \frac{\epsilon - 1}{\epsilon + 2} a^3 \quad \dots\dots\dots(1.5)$$

The concept of polarizability is very important for the

molecular description of matter since all atoms, ions and molecules are polarizable. For polar dielectrics polarization \vec{P} consists of two parts \vec{P}_α and \vec{P}_μ due to translational effect and orientation of permanent dipoles respectively. Thus

$$\vec{P} = \vec{P}_\alpha + \vec{P}_\mu \quad \dots\dots\dots(1.6)$$

the terms $\vec{P}_\alpha = \sum_k N_k \alpha_k (\vec{E}_i)_k \quad \dots\dots\dots(1.7)$

and $\vec{P}_\mu = \sum_k N_k \mu_k \quad \dots\dots\dots(1.8)$

Where N_k is the number of particles per unit volume, α_k is the average polarizability of a particle and μ_k is the average value of permanent dipole moment for the kth. Kind of molecule. \vec{E}_i is the average field strength acting upon the particle called internal field, which is equivalent to the applied field \vec{E} .

Now in an uniform electric field \vec{E}_γ the average dipole moment $\vec{\mu}$ of a dipolar molecule in thermal equilibrium with a large number of other molecules is

$$\vec{\mu} = \frac{\mu^2}{3kT} \vec{E}_\gamma \quad \dots\dots\dots(1.9)$$

In general E'_y was taken equal to E'_i . However, Onsager (1934) showed that this is only possible for gases at low pressure, since in the general cases only a part of the internal field E'_i has a directing influence upon the permanent dipoles.

Substituting eq.(1.9) in eq.(1.8) and with eqs.(1.6) and (1.7) we have

$$P' = \frac{\epsilon - 1}{4\pi} E' = \sum_k N_k \left[\alpha_k (E'_i)_k + \frac{\mu_k^2}{3kT} (E'_y)_k \right] \dots\dots\dots(1.10)$$

This is the fundamental equation.

Assuming $E'(\epsilon+2)/3$ for both $(E'_i)_k$ and $(E'_y)_k$ the eq.(1.10) becomes

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} \sum_k N_k \left(\alpha_k + \frac{\mu_k^2}{3kT} \right) \dots\dots\dots(1.11)$$

The Debye equation is used to calculate the value of the dipole moment.

The molar polarization [P] for a solution can be given by

$$[P] = \frac{\epsilon - 1}{\epsilon + 2} \frac{\bar{M}}{d}$$

where $\bar{M} = \sum_k X_k M_k$ = average molecular weight of the solution, X_k being the mole fraction of the components having molecular weights M_k . The Debye equation (1.11) becomes

$$[P] = \frac{4\pi}{3} N_A \sum_k X_k \left[\alpha_k + \frac{\mu_k^2}{3kT} \right] \dots\dots\dots(1.12)$$

Where $N_A = \sum_k N_k \frac{M_k}{d}$ is the Avogadro number.

In case of a solution of polar compound in a non-polar solvent the above equation becomes

$$[P] = \frac{4\pi}{3} N_A \left[(1-x)\alpha_0 + x \left(\alpha + \frac{\mu^2}{3kT} \right) \right] \dots\dots\dots(1.13)$$

where α_0 is the polarizability of the solvent molecules, and α , μ and x are the polarizability, dipole moment and mole fraction of the polar solute respectively. If $[P_0]$ is the molar polarization of the pure solvent we get from eq.(1.13)

$$[P_0] = \frac{4\pi}{3} N_A \alpha_0$$

or $\frac{\epsilon - 1}{\epsilon + 2} \frac{M}{d} = \frac{4\pi}{3} N_A \alpha_0 \dots\dots\dots(1.14)$

This is the Clausius - Mosotti relation.

Again, for the pure polar compound, the Debye equation [eq.(1.13)] becomes

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

or
$$\frac{\epsilon - 1}{\epsilon + 2} \frac{M_1}{d_1} = \frac{4\pi}{3} N_A \left[\alpha + \frac{\mu^2}{3kT} \right] \dots\dots\dots(1.15)$$

With the help of Lorentz-Lorentz equation

$$(n_\alpha^2 - 1)/(n_\alpha^2 + 2) = \frac{4\pi}{3} N_A \alpha ,$$

Where $n_\alpha^2 = \epsilon$, the Debye formula can be written in different form

$$\mu^2 = \frac{27 kT}{4\pi N_A} - \frac{(\epsilon - n_\alpha^2)}{(\epsilon + 2)(n_\alpha^2 + 2)} \dots\dots\dots(1.16)$$

Considering the correction for the reaction field and taking

$$\frac{4\pi}{3} a^3 N_A = 1,$$

Onsager (1934) reduced the eq.(1.16) to

$$\mu^2 = \frac{9kT}{4\pi N_A} \frac{(\epsilon - n_\alpha^2)(2\epsilon + n_\alpha^2)}{\epsilon (n_\alpha^2 + 2)^2} \dots\dots\dots(1.17)$$

This is an important formula of Onsager's theory for calculating the dipole moment μ of a polar molecule. But the difficulty is to determine the value n_α the atomic polarization should be known.

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

When a dielectric material is subjected to an alternating

electric field, the following possibilities are found depending upon the frequency of the applied field, the temperature and the nature of the material :

a) In some cases there are no measurable phase difference between \vec{D} and \vec{E} . They are related by a simple relation $\vec{D} = \epsilon \vec{E}$. In these cases no energy is absorbed by the dielectric from the electromagnetic field.

b) In other cases there exist a suitable phase difference between \vec{D} and \vec{E} . The simple relationship $\vec{D} = \epsilon \vec{E}$ is not valid in these cases. Hence there is always a dissipation of energy in the dielectric due to the absorption of electromagnetic waves is called "dielectric loss". A phase difference between \vec{D} and \vec{E} is due to (i) electrical conduction, (ii) the relaxation effect due to permanent dipoles and (iii) the resonance effect due to rotation or vibration of atoms, ions or electrons of the dielectric materials.

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

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

where δ is the phase difference and $\omega = 2\pi f$, f being the frequency of the applied alternating electric field.

But $D^* = \epsilon^* E^*$

$$\text{or } \epsilon^* = \frac{D^*}{E^*} = \frac{D_0}{E_0} e^{-i\delta} = \frac{D_0}{E_0} (\cos\delta - j \sin\delta) \dots(1.18)$$

Thus the dielectric constant becomes complex at high frequency field

$$D^* = \epsilon' - j\epsilon'' \dots\dots\dots(1.19)$$

in which the real part $\epsilon' = \frac{D_0}{E_0} \cos \delta$, may be related to the usual dielectric constant, where as $\epsilon'' = \frac{D_0}{E_0} \sin \delta$, known as

dielectric loss which measures the ability of the medium to dissipate energy.

The dielectric loss at a certain frequency of the applied electric field gives the value of $\tan\delta$ where

$$\tan\delta = \frac{\epsilon''}{\epsilon'} \dots\dots\dots(1.20)$$

Again the dissipated energy per unit volume per unit time of the electric field is

$$W = \frac{\omega E_0^2}{8\pi} \epsilon \sin \delta = \frac{\omega E_0^2}{8\pi} \epsilon'' \dots\dots\dots(1.21)$$

Thus the energy is directly proportional to ϵ'' and hence $\tan \delta$. Therefore ϵ'' is generally called "dielectric Loss" and $\sin\delta$ is the phase factor.

1.3a Dielectric Loss and Relaxation Time

The polarization in the static field $P_e = (\epsilon - 1)E / 4\pi$ can be written by

$$P_e = P_\alpha + (P_e)_{dip} \dots \dots \dots (1.22)$$

Where $(P_e)_{dip}$ represents the part of P_e due to permanent dipoles and P_α , the part due to polarizability of the molecules,

$$P_\alpha = \frac{\epsilon_\alpha - 1}{4\pi} E \dots \dots \dots (1.23)$$

The time in which the permanent dipole attains the equilibrium position in a static electric field is of the order of between 10^{-6} and 10^{-13} second. This time depends upon the temperature, the chemical composition and the structure of the dielectric molecules. During this time interval the polarization increases from P_α to P_e . Let after time t within the time interval P_{dip} builds up. Assuming the rate of increase of P_{dip} with respect to time t is proportional to the difference of values of $(P_e)_{dip}$ and P_{dip} we have

$$\frac{dP_{dip}}{dt} = \frac{1}{\tau} \left[(P_e)_{dip} - P_{dip} \right] \dots \dots \dots (1.24)$$

where τ is a constant which measures the time lag and is called the relaxation time. The relaxation time τ may be defined as the time in which the polarization is reduced to $1/e$ of its original

value after the removal of the electric field, ϵ being equal to 2.718.

Integrating eq.(1.24) and using the condition $\bar{P}_{dip} = 0$ at $t = 0$ one can get

$$\bar{P}_{dip} = (\bar{P}_0)_{dip} (1 - e^{-t/\tau}) \dots\dots\dots(1.25)$$

Under an alternating electric field at a time t ,

$$(P_0^*)_{dip} = \frac{\epsilon_0 - 1}{4\pi} E_t^* - \frac{\epsilon_\alpha - 1}{4\pi} E_t^* \dots\dots\dots(1.26)$$

and from eq.(1.24) and eq.(1.26)

$$\frac{d}{dt} (P_{dip}^*) = \frac{1}{\tau} \left[\frac{\epsilon_0 - \epsilon_\alpha}{4\pi} E_0 e^{j\omega t} - P_{dip}^* \right] \dots\dots(1.27)$$

The general solution of the above equation is

$$P_{dip}^* = C e^{-t/\tau} + \frac{1}{4\pi} \frac{\epsilon_0 - \epsilon_\alpha}{1 + j\omega\tau} E_0 e^{j\omega t} \dots\dots\dots(1.28)$$

After a certain time the first term on the right hand side will diminish to an infinitely small value and hence it may be neglected. Therefore the total polarization in an alternating electric field is given by

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

$$\text{or } P^* = \left[\frac{\epsilon_{\alpha} - 1}{4\pi} + \frac{1}{4\pi} \frac{\epsilon_{\infty} - \epsilon_{\alpha}}{1 + j\omega\tau} \right] E_0 e^{j\omega t} \dots\dots(1.29)$$

The dielectric displacement can then be written as

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

$$D^* = \left[\epsilon_{\alpha} + \frac{\epsilon_{\infty} - \epsilon_{\alpha}}{1 + j\omega\tau} \right] E_0 e^{j\omega t} \dots\dots\dots(1.30)$$

Thus the complex dielectric constant, with equation $D^* = \epsilon^* E^*$, is

$$\epsilon^* = \left[\epsilon_{\alpha} + \frac{\epsilon_{\infty} - \epsilon_{\alpha}}{1 + j\omega\tau} \right] \dots\dots\dots(1.31)$$

$$\text{or } \epsilon' - j\epsilon'' = \left[\epsilon_{\alpha} + \frac{\epsilon_{\infty} - \epsilon_{\alpha}}{1 + \omega^2\tau^2} (1 - j\omega\tau) \right] \dots\dots\dots(1.32)$$

The real part of the eq.(1.32) i.e the dielectric permittivity is

$$\epsilon' = \epsilon_{\alpha} + \frac{\epsilon_{\infty} - \epsilon_{\alpha}}{1 + \omega^2\tau^2} \dots\dots\dots(1.33)$$

and the imaginary part i.e dielectric loss is

$$\epsilon'' = \frac{\epsilon_{\infty} - \epsilon_{\alpha}}{1 + \omega^2\tau^2} \omega\tau \dots\dots\dots(1.34)$$

Again from eq. (1.33) and (1.34) one can easily write

$$\frac{\epsilon' - \epsilon_\alpha}{\epsilon_\beta - \epsilon_\alpha} = \frac{1}{1 + \omega^2 \tau^2} \dots\dots\dots(1.35)$$

and

$$\frac{\epsilon''}{\epsilon_\beta - \epsilon_\alpha} = \frac{\omega\tau}{1 + \omega^2 \tau^2} \dots\dots\dots(1.36)$$

The plot of the left hand side of these equations against $\log(\omega\tau)$ give symmetrical curves as shown in Fig 1.1 and Fig 1.2 respectively. The maximum value of absorption is attained for $\log(\omega\tau) = 0$. Thus the angular frequency corresponding to maximum value of absorption is

$$\omega_m = \frac{1}{\tau} \dots\dots\dots(1.37)$$

This result can also be obtained from eq. (1.34) by using the condition $\frac{d\epsilon''}{d\nu} = 0$. The maximum values of dielectric permittivity and loss from eqs. (1.33) and (1.34), can be obtained by setting the condition $\omega\tau = 1$.

Thus we have

$$\epsilon'_{\max} = \frac{\epsilon_\beta + \epsilon_\alpha}{2} \dots\dots\dots(1.38)$$

$$\text{and } \epsilon''_{\max} = \frac{\epsilon_\beta - \epsilon_\alpha}{2} \dots\dots\dots(1.39)$$

The cyclic frequency $f_{\max} = \frac{\omega_m}{2\pi}$ is generally called critical frequency. The curves, as given in Figs. 1.3 and 1.4, obtained

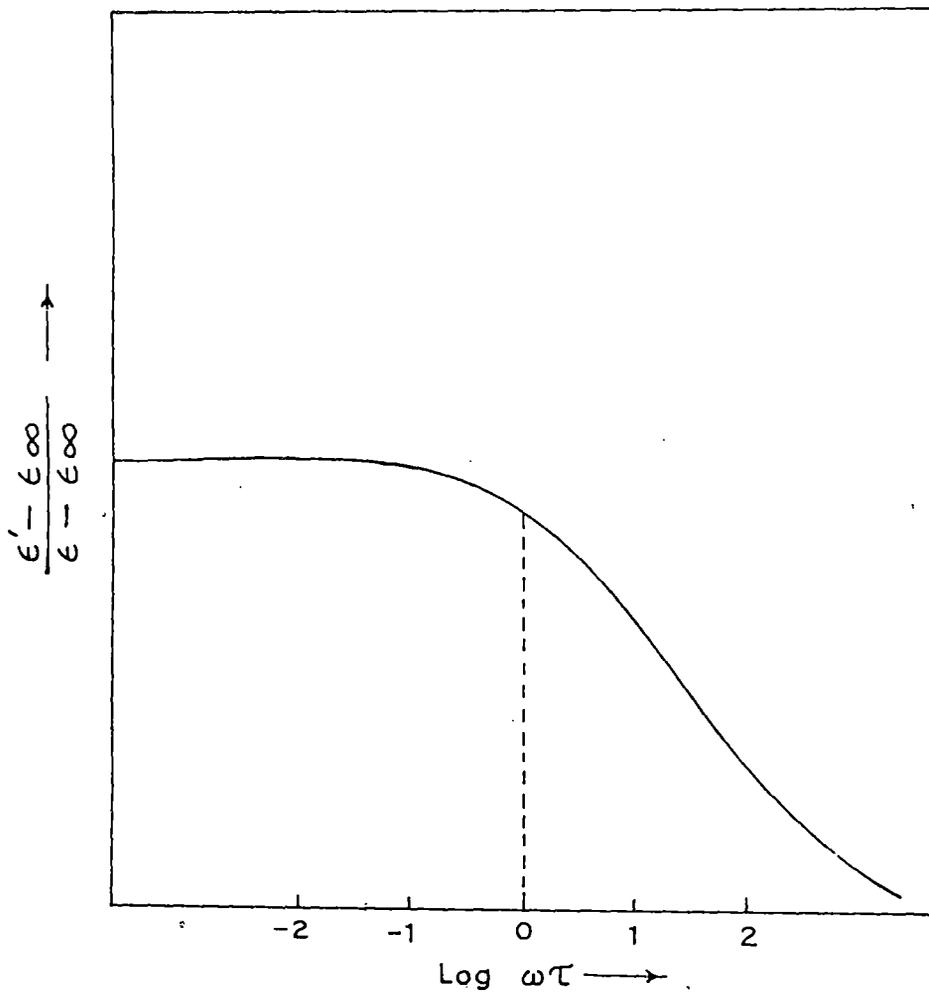


Fig. 1.1 - Plot of $\frac{\epsilon' - \epsilon_\infty}{\epsilon_s - \epsilon_\infty}$ vs $\omega\tau$

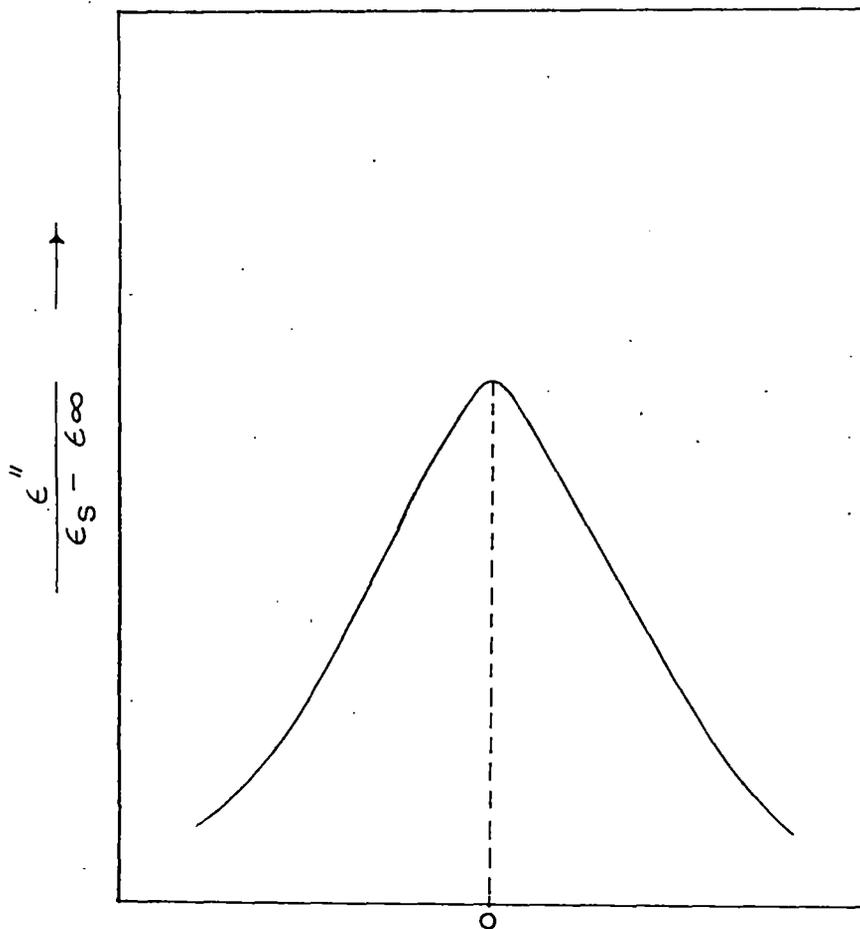


Fig. 1.2 - Plot of $\frac{\epsilon''}{\epsilon_s - \epsilon_\infty}$ vs $\text{Log } \omega\tau$

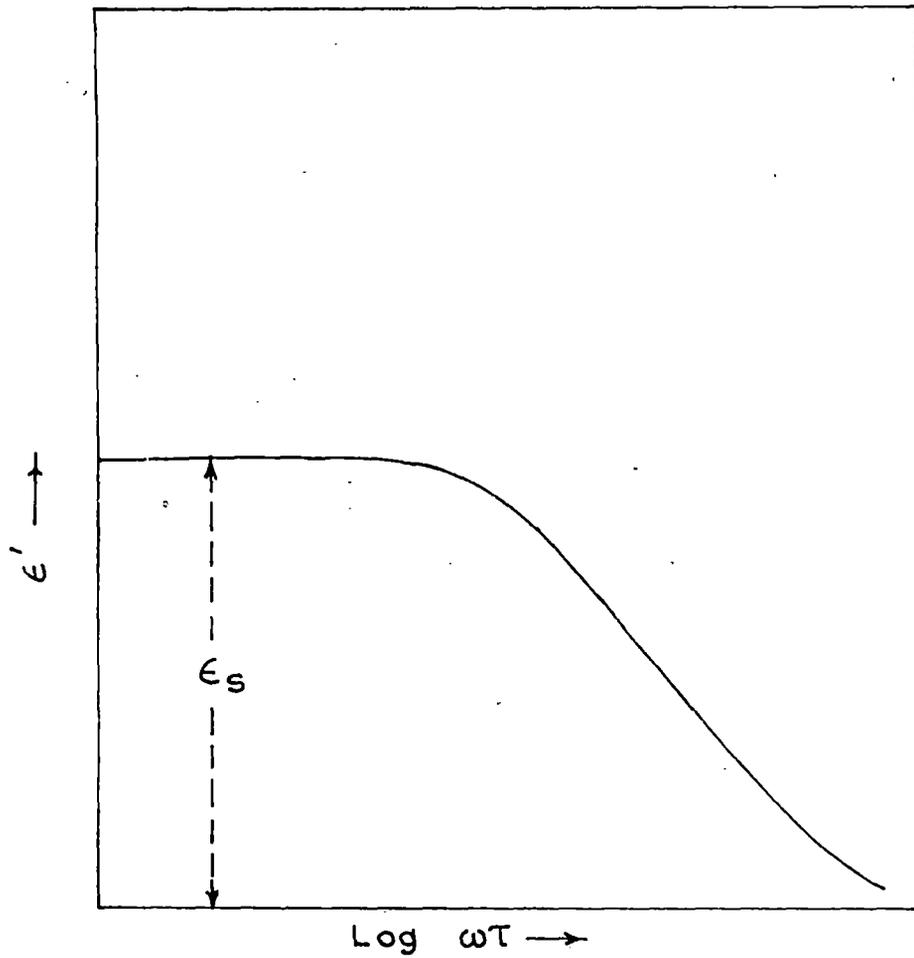


Fig. 1.3 - Plot of ϵ' vs $\log \omega\tau$

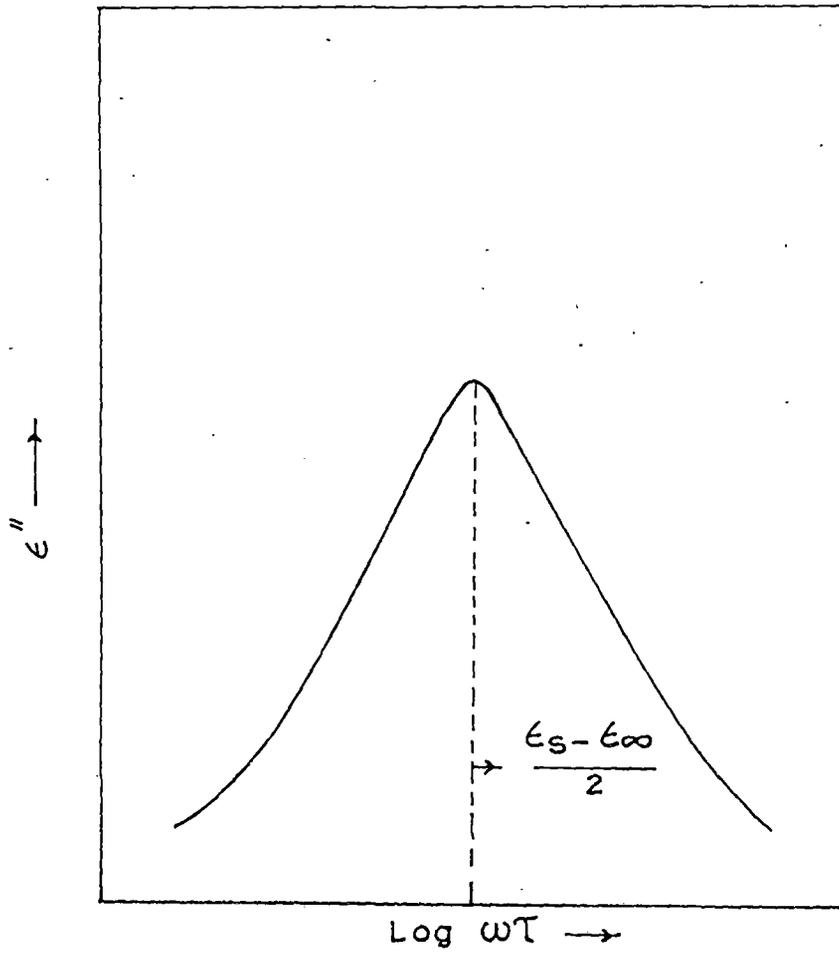


Fig. 1.4 - Plot of ϵ'' vs $\log \omega\tau$

from equations (1.33) and (1.34) are generally known as Debye curves.

1.3b Representation of Permittivity in the complex Plane : Debye Semi Circle

Eliminating $\omega\tau$ from eqs.(1.33) and (1.34) and rearranging the above two equations one gets the equation to a circle

$$\left[\epsilon' - \frac{\epsilon_s + \epsilon_\alpha}{2} \right]^2 + \epsilon''^2 = \left[\frac{\epsilon_s - \epsilon_\alpha}{2} \right]^2 \dots\dots\dots(1.40)$$

Hence a graph of ϵ'' against ϵ' in the complex plan gives a semicircle, as shown in Fig 1.5, whose centre is $\left[\frac{\epsilon_s + \epsilon_\alpha}{2}, 0 \right]$ and radius is $\left[\frac{\epsilon_s - \epsilon_\alpha}{2} \right]$. The intersection points with arc are characterized by $\epsilon' = \epsilon_\alpha$ and $\epsilon' = \epsilon_s$. This semicircle is known as Debye semicircle. Eqs.(1.33) and (1.34) together with this plot provide a basis for the interpretation of dielectric relaxation phenomena.

1.3C Cole-Cole Distribution

The arc dispersion function of Cole and Cole is frequently used to analyse the experimental dielectric data because of its simple and attractive graphical form of $\epsilon'(\omega)$ and $\epsilon''(\omega)$. Cole and

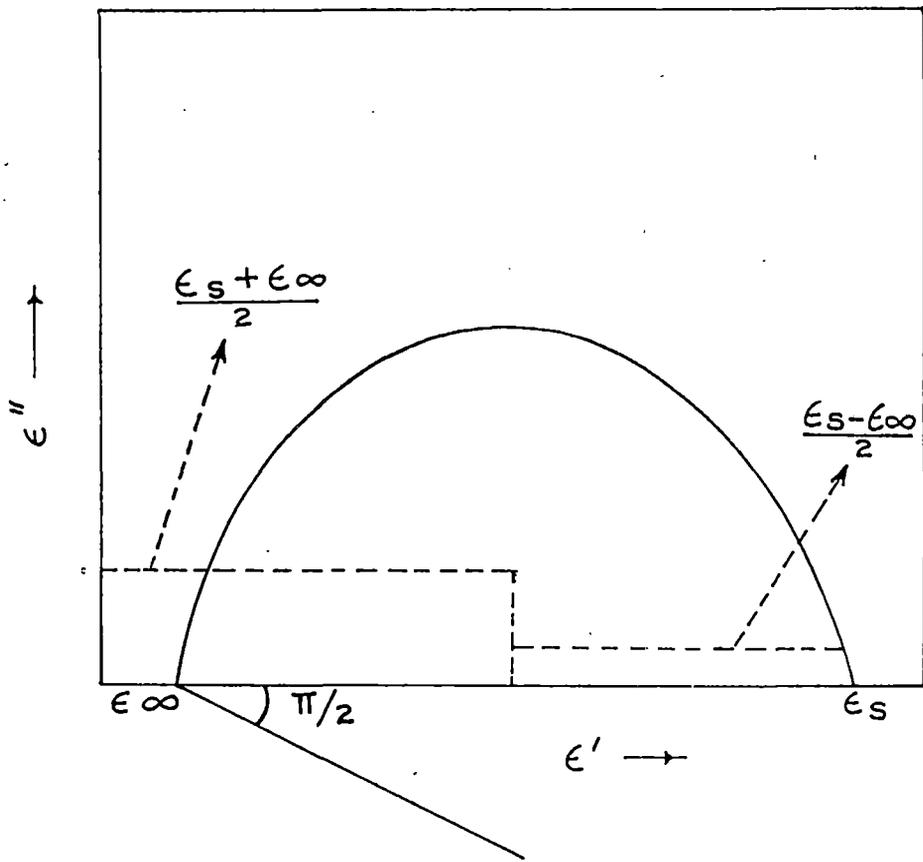


Fig. 1.5 - Plot of ϵ'' vs ϵ'

Cole (1941) have shown that the Debye semicircle centre (Fig.1.6) of which arc is a part is depressed below the abscissa axis. The diameter drawn through the point ϵ_α makes an angle $\alpha < \pi/2$ with the abscissa axis. The diameter drawn through the point ϵ gives a measure of distribution of relaxation time which may vary with temperature, but not with frequency. The value of α lies in the range 0 and 1.

The Debye equation is modified by Cole and Cole (1941) as

$$\epsilon^* = \epsilon_\alpha + \frac{\epsilon_\infty - \epsilon_\alpha}{1 + (j\omega\tau_0)^{1-\alpha}} \dots\dots\dots(1.41)$$

Where τ_0 is the most probable relaxation time which can be computed from the relation

$$\frac{v}{u} = (\omega\tau_0)^{1-\alpha} \dots\dots\dots(1.42)$$

The term v is distance on the Cole-Cole plot from ϵ_∞ point to experimental point and u is the distance of the same experimental point from the ϵ_α point. If α is equal to zero v/u becomes equal to $\omega\tau_0$ which is the true Debye equation.

1.4 Double Relaxation Time due to Molecular and Intramolecular Orientations

In case of some polar molecules the dielectric relaxation process involves an intramolecular rotation with a very short relaxation time in addition to the normal molecular orientation.

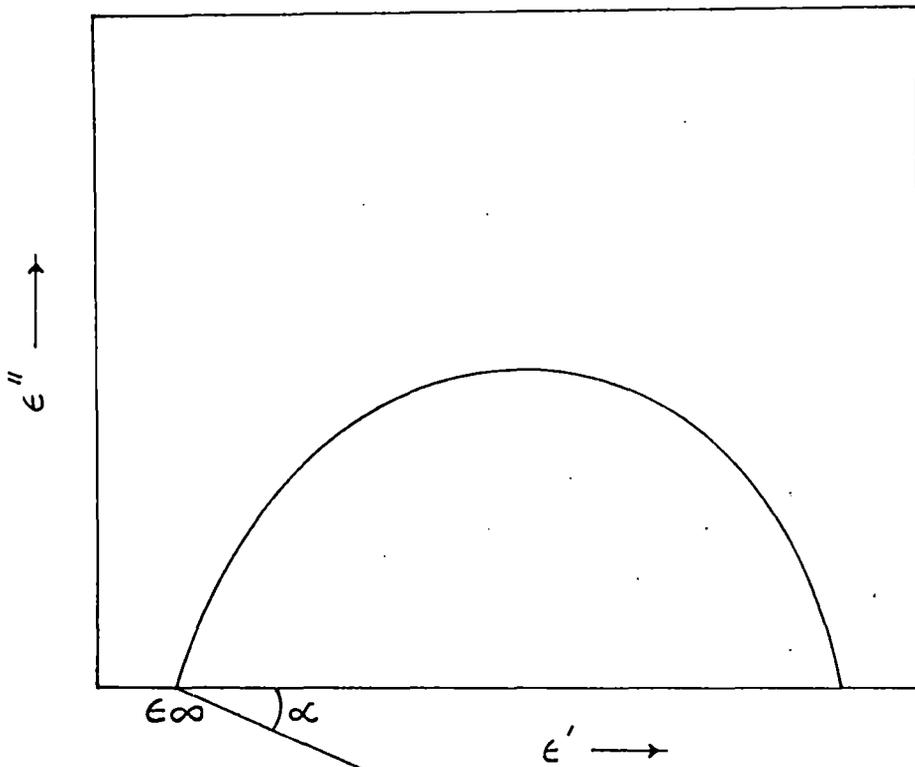


Fig. 1-6 - Cole-Cole plot of ϵ'' vs ϵ'

If τ_1 and τ_2 are the two relaxation times having their relative contributions C_1 and C_2 respectively, then one can write from eqs.(1.35) and (1.36)

$$\frac{\epsilon' - \epsilon_\alpha}{\epsilon_\beta - \epsilon_\alpha} = C_1 \frac{1}{1 + \omega^2 \tau_1^2} + C_2 \frac{1}{1 + \omega^2 \tau_2^2} \dots (1.43)$$

and
$$\frac{\epsilon''}{\epsilon_\beta - \epsilon_\alpha} = C_1 \frac{\omega \tau_1}{1 + \omega^2 \tau_1^2} + C_2 \frac{\omega \tau_2}{1 + \omega^2 \tau_2^2} \dots (1.44)$$

where $C_1 + C_2 = 1$.

Bergmann et al (1960) have suggested a graphical method to select the values of τ_1, τ_2 and C_1 by using eqs.(1.43) and (1.44) which may also be written in the following forms

$$Y = C_1 Y_1 + C_2 Y_2 \dots (1.45)$$

$$Z = C_1 Z_1 + C_2 Z_2 \dots (1.46)$$

where

$$Y = \frac{\epsilon''}{\epsilon_\beta - \epsilon_\alpha}, \quad Z = \frac{\epsilon' - \epsilon_\alpha}{\epsilon_\beta - \epsilon_\alpha}$$

$$Y_1 = \frac{\omega \tau_1}{1 + \omega^2 \tau_1^2}, \quad Z_1 = \frac{1}{1 + \omega^2 \tau_1^2}$$

$$Y_2 = \frac{\omega \tau_2}{1 + \omega^2 \tau_2^2}, \quad Z_2 = \frac{1}{1 + \omega^2 \tau_2^2}$$

By referring to Fig.1.7, it may be seen that the point (Y,Z) lies on the chord between the points (Y_1, Z_1) and (Y_2, Z_2) of the normalised Debye semicircle and divides the chord in the ratio $b/a = C_1/C_2$. The graphical analysis consists of plotting the normalised experimental points on a complex plane (Fig 1.7). Various chords of the semicircle are then drawn through the points until a set of parameters is found out in consistent of all the points.

Bhattacharyya et al (1970) have simplified the above method in order to calculate the double relaxation times τ_1 and τ_2 . Putting $x_1 = \omega\tau_1$ and $x_2 = \omega\tau_2$, and using the abbreviation $\xi = 1/(1+x^2)$ and $\eta = x/(1+x^2)$ eqs. (1.43) and (1.44) are written as

$$a = C_1 \xi_1 + C_2 \xi_2 \quad \dots\dots\dots(1.47)$$

$$b = C_1 \eta_1 + C_2 \eta_2 \quad \dots\dots\dots(1.48)$$

where $a = \frac{\epsilon' - \epsilon_\infty}{\epsilon_\infty - \epsilon_\alpha}$ and $b = \frac{\epsilon''}{\epsilon_\infty - \epsilon_\alpha}$

From eqs.(1.47) and (1.48) we obtain for $x_1 - x_2 \neq 0$ and $x_1 > x_2$

$$C_1 = \frac{(b - ax_2)(1 + x_1^2)}{x_1 - x_2} \quad \dots\dots\dots(1.49)$$

and $C_2 = \frac{(ax_1 - b)(1 + x_2^2)}{x_1 - x_2} \quad \dots\dots\dots(1.50)$

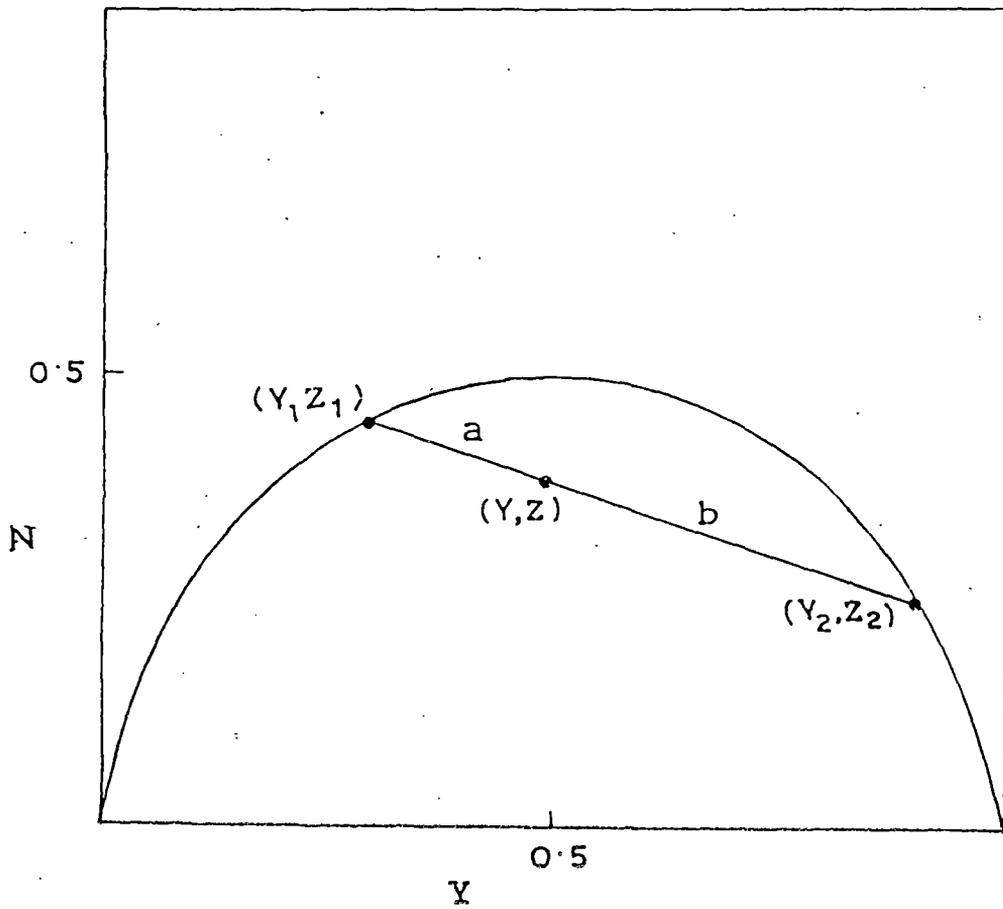


Fig. 1.7 - Plot of normalized semicircle .

Using the relation $C_1 + C_2 = 1$ we get with the help of eqs.(1.49) and (1.50)

$$\frac{1-a}{b} = (x_1 + x_2) - \frac{a}{b} x_1 x_2 \quad \dots\dots\dots(1.51)$$

Solving the above equation for two different known frequencies the values of $(\tau_1 + \tau_2)$ and $\tau_1 \tau_2$ are obtained to yield the values of τ_1 and τ_2 . The values of C_1 and C_2 are calculated from the corresponding expressions in eqs.(1.49) and (1.50)

1.5 Dielectric Relaxation in Dilute Solution of Polar Solute in Non-Polar Solvent

If α_i be the polarizability of a molecule of non-polar solvent having molecular weight M_i and α_j be that of a molecule of polar solute of molecular weight M_j , then in a solution of polar non-polar liquid mixture the Debye equation (1.15) is of the following forms

$$\frac{\epsilon_\alpha - 1}{\epsilon_\alpha + 2} \frac{f_i M_i + f_j M_j}{\rho_{ij}} = \frac{4\pi}{3} N f_i \alpha_i + \frac{4\pi}{3} N f_j \alpha_j \quad \dots\dots(1.53)$$

and
$$\frac{\epsilon_\bullet - 1}{\epsilon_\bullet + 2} \frac{f_i M_i + f_j M_j}{\rho_{ij}} = \frac{4\pi}{3} N f_i \alpha_i + \frac{4\pi}{3} N f_j \alpha_j$$

$$+ \frac{4\pi}{9} N f_j \frac{\mu_j^2}{3kT} \dots\dots\dots(1.54)$$

Where ϵ_α and ϵ_∞ are the dielectric constants of the solution at infinite frequency and static field respectively and ρ_{ij} is the density of the solution. The mole fractions f_i and f_j of the components are

$$f_i = \frac{n_i}{n_i + n_j} \text{ and } f_j = \frac{n_j}{n_i + n_j}$$

n_i and n_j being the number of molecules per c.c of the solution. From eqs.(1.53) and (1.54) we get

$$\epsilon_\infty - \epsilon_\alpha = \frac{4\pi N C_j \mu_j^2}{27kT} (\epsilon_\alpha + 2) (\epsilon_\infty + 2) \dots\dots\dots(1.55)$$

Where C_j denotes the concentration of the molecules in moles/c.c. Substituting the value of $(\epsilon_\infty - \epsilon_\alpha)$ in eq.(1.36) we get

$$\epsilon'' = \frac{(\epsilon_\alpha + 2) (\epsilon_\infty + 2)}{9} \left[\frac{4\pi N C_j \mu_j^2}{3kT} \right] \frac{\omega \tau}{1 + \omega^2 \tau^2} \dots\dots(1.56)$$

In case of dilute polar-non-polar mixture it is assumed

$$\epsilon_a \approx \epsilon_d \approx \epsilon'$$

and hence

$$\epsilon'' = \left(\frac{\epsilon' + 2}{3} \right)^2 \frac{4 \pi N C_j \mu_j^2}{3 K T} \frac{\omega \tau}{1 + \omega^2 \tau^2} \dots\dots\dots(1.57)$$

It is seen from the above equation that for extremely low concentration the value of ϵ'' is linearly dependent on the concentration of the polar solute in solution and at infinite dilution i.e. When $C_j \rightarrow 0$ the value of ϵ' may be replaced by ϵ_i the dielectric constant of solvent and eq.(1.57) becomes

$$\epsilon = \left(\frac{\epsilon_j + 2}{3} \right)^2 \frac{4 \pi N C_j \mu_j^2}{3 K T} \frac{\omega \tau}{1 + \omega^2 \tau^2} - \dots\dots\dots(1.58)$$

The eq.(1.58) has been used in the present investigation for determining the value of dielectric relaxation parameters.

1.6a 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 systems show energy loss from the process other than dielectric relaxation. Generally these are of smaller magnitude and related to the d.c. conductivity of the medium. Assuming a homogenous medium of conductivity K (mho cm^{-1}), the effect of Joule heating

arising from the conductivity contributes a loss factor ϵ'' (conductance). So at a particular frequency total dielectric loss is

$$\epsilon'' \text{ (total)} = \epsilon'' \text{ (dielectric)} + \epsilon'' \text{ (conductance)} \dots\dots\dots(1.59)$$

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

If a potential V is established between the parallel plates of a condenser having dielectric material of constant ϵ and d is the distance between the plates of surface area A , then a charge q per unit area will appear on each plate and a polarization P will also be created in the dielectric. If it is assumed that conductivity due to free ions is of negligible amount, then the conductivity is

$$K = \frac{1}{\epsilon} \frac{d q}{d t} \dots\dots\dots(1.60)$$

Where $K = \frac{v}{d} = \frac{D}{\epsilon}$

Again $D = 4\pi q = E + 4\pi P$ and eq(1.60) becomes

$$KE = \frac{d q}{d t} = \frac{1}{4 \pi} \frac{d D}{d t} = \frac{\epsilon}{4 \pi d} \frac{d v}{d t}$$

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

If the applied potential is alternating i.e. $V = V_0 e^{j\omega t}$, the dielectric constant is complex quantity $\epsilon^* = \epsilon' - j \epsilon''$. The total current density in dielectric is

$$I = \frac{d q}{d t} = \frac{\epsilon^*}{4 \pi d} \frac{d}{d t} \left[V_0 e^{j\omega t} \right]$$

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

Therefore $I = \left[\frac{\omega \epsilon''}{4 \pi} + j \frac{\omega \epsilon'}{4 \pi} \right] E_0 e^{j\omega t} \dots\dots\dots(1.61)$

Where $E_0 = V_0 / d$.

The total current density in the dielectric is the sum of displacement or capacitive current and conduction current

$$I = I_d + I_{cond} \dots\dots\dots(1.62)$$

Murphy and Morgan (1939) deduced an expression of total conductivity K^* which is a complex quantity and sum of the conductivity due to displacement current K'' and conductivity due to conduction current K' i.e

$$K^* = K' + j K'' \dots\dots\dots(1.63)$$

Comparing eqs.(1.61) and (1.63) we have

$$K' = \frac{\omega \epsilon''}{4 \pi} \dots\dots\dots(1.64)$$

and $K'' = \frac{\omega \epsilon'}{4 \pi} \dots\dots\dots(1.65)$

as the real and imaginary parts of conductivities respectively.

1.6b High Frequency Conductivity of Dilute Solution of Polar Solute in Non-Polar Solvent

It is seen from eq.(1.58), for fairly dilute solution of polar-nonpolar liquid mixture, ϵ'' is linearly dependent on the concentration of polar component and is given by

$$\epsilon'' = \left[\frac{\epsilon_i + 2}{3} \right]^2 \frac{4 \pi N C_j \mu_j^2}{3 k T} \frac{\omega \tau}{1 + \omega^2 \tau^2}$$

Substituting the value ϵ'' in $K' = \frac{\omega \epsilon''}{4 \pi}$, the high frequency conductivity of solution becomes

$$K'_{ij} = \left[\frac{\epsilon_i + 2}{3} \right]^2 \frac{N C_j \mu_j^2}{3 k T} \frac{\omega \tau}{1 + \omega^2 \tau^2} \dots\dots\dots(1.66)$$

The eq.(1.66) has been used in the present investigation to determine the relaxation time τ as well as the dipole moment μ of polar molecules.

1.7a Relaxation Time and its Relation with Microscopic and Macroscopic Properties

Debye assumed that the torque applied to a dipolar molecule by electric field is counter balanced by frictional forces which are proportional to the angular velocity of the dipolar molecule at steady state. The torque can be given by

$$M = \zeta \frac{d \nu}{dt} \dots\dots\dots(1.67)$$

ζ is a constant called frictional coefficient which is dependent on the surrounding medium.

Debye showed that if the dipoles are regarded as sphere of radius 'a' immersed in a medium of internal viscosity η_{int} , the frictional coefficient ζ is then given by stokes formula

$$\zeta = 8 \pi \eta_{int} a^3 \dots\dots\dots(1.68)$$

The consideration of Brownian motion of dipole molecule in liquid state leads to the relationship between relaxation time τ and ζ as

$$\tau = \frac{\zeta}{2 k T} \dots\dots\dots(1.69)$$

From eqs. (1.68) and (1.69) we obtain

$$\tau = \frac{4 \pi a^3}{k T} \eta_{int} \dots\dots\dots(1.70)$$

Debye further considered that the the internal viscosity η_{int} , which is a microscopic property, is equal to the macroscopic viscosity η of the medium and the eq.(1.70) becomes

$$\tau = \frac{4 \pi a^3}{k T} \eta \dots\dots\dots(1.71)$$

The eq.(1.71) shows that from the measured values of the relaxation time τ and the coefficient of viscosity η at a certain temperature T the size of the rotating unit 'a' may be calculated. Alternately, if the size of the polar molecule is known, the determination of the value η_{int} from which information on the structure of the rotating unit may be obtained.

1.7b Modification of Debye Relation

Perrin (1934) modified the Debye equation (1.71) treating the rigid dipolar molecule as an ellipsoid instead of spherically symmetric molecule, with molecular dipole moment $\bar{\mu}$ having components μ_a , μ_b and μ_c along 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

$$P^* = \frac{4 \pi N}{3} \left[\alpha + \frac{\mu^2}{3 k T} \frac{1}{1 + j \omega \tau} \right] \dots\dots\dots(1.72)$$

is replaced by $\left[\frac{\mu_a^2}{1 + j \omega \tau_a} + \frac{\mu_b^2}{1 + j \omega \tau_b} + \frac{\mu_c^2}{1 + j \omega \tau_c} \right]$

and the eq.(1.72) can be written as

$$P^* = \frac{\epsilon^* - 1}{\epsilon^* + 2} \cdot \frac{M}{\rho} = \frac{4 \pi N}{3} \times \left[\alpha + \frac{1}{3 k T} \left(\frac{\mu_a^2}{1 + j \omega \tau_a} + \frac{\mu_b^2}{1 + j \omega \tau_b} + \frac{\mu_c^2}{1 + j \omega \tau_c} \right) \right] \dots(1.73)$$

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. Moreover, the dipole may be along one of the axes of consideration. In such a case the relaxation time is given by Fischer as

$$\tau = \frac{4 \pi a b c f}{k T} \eta_{int} \dots\dots\dots(1.74)$$

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

1.8a Radio Frequency Conductivity and Relaxation Time

In an actual dielectric when a radio frequency field ($E = E_0 e^{i\omega t}$) is applied, the total heat developed is due to the combined effect of dielectric loss and Joule heating. Thus the radio frequency conductivity measurement provides an information regarding the displacement current as well as conduction current

in the dielectric.

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 electric field is applied in the polar dielectric liquid, the conduction current due to free ions plays a dominant role to the conductivity than the displacement component suggested by Murphy and Morgan (1939). Using Debye's dielectric equation (1.34) and Murphy and Morgan's equation (1.64) a equation for conductivity has been obtained as

$$K' = \frac{1}{4\pi} \frac{\epsilon_s - \epsilon_\infty}{1 + \omega^2 \tau^2} \omega^2 \tau \dots\dots\dots(1.75)$$

Substituting the relaxation time $\tau = 4\pi a^3 \eta / kT$ in the above equation and as $\omega^2 \tau^2 \ll 1$ at the radio frequency conductivity can be written as

$$K' = \frac{\epsilon_s - \epsilon_\infty}{kT} \omega^2 a^3 \eta \dots\dots\dots(1.76)$$

The factors $(\epsilon_s - \epsilon_\infty)$ and η / T are both decreased with temperature and therefore it is expected that K' should decrease with the increase of temperature. But the experimental results show that the r.f. conductivity increases with 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. A similar relation is observed in case of polar dielectric liquids i.e $K' \eta = \text{constant}$.

To explain the above results it has to be assumed that besides the displacement current due to Murphy and Morgan, the existence of conduction current due to the presence of free ions has to be taken into consideration. On taking the analogy from the motion of an electron in an ionized gas when the degree of ionisation is small and assuming the resisting force is due to viscosity, the equation of motion of the ions is given by

$$M \frac{d v}{d t} = e E_0 e^{i \omega t} - 6 \pi a \eta v \dots\dots\dots(1.77)$$

Where 'a' is the radius of the molecule and η is the coefficient of viscosity, then

$$v = \frac{e E_0 e^{i \omega t}}{M (\gamma + j \omega)} \dots\dots\dots(1.78)$$

and $\gamma = \frac{6 \pi \eta a}{M}$

Now $v = \frac{e E_0}{M} \left[\frac{\gamma}{\gamma^2 + \omega^2} - j \frac{\omega}{\gamma^2 + \omega^2} \right] e^{i \omega t} \dots\dots\dots(1.79)$

If n denotes the number of free ions per c.c., then conduction current is $i_c = nev$

$$\text{or } i = \frac{ne^2}{M} \left[\frac{\gamma}{\gamma^2 + \omega^2} - j \frac{\omega}{\gamma^2 + \omega^2} \right] E_0 e^{i\omega t} \dots\dots(1.80)$$

Equating the real parts from both sides of eq. (1.80) the r.f. conductivity is given by

$$\sigma = \frac{ne^2 \gamma}{M(\gamma^2 + \omega^2)} = \frac{ne^2}{M} \frac{6\pi\eta a/M}{(6\pi\eta a/M)^2 + \omega^2} \dots\dots(1.81)$$

As $a \approx 10^{-8}$ cm, $\eta \approx 10^{-9}$ poise and $M \approx 10^{-28}$ gm, then

$6\pi\eta a/M \gg \omega$ and hence the r.f. conductivity due to free ions is

$$\sigma = \frac{ne^2}{6\pi\eta a} \dots\dots(1.82)$$

Therefore the total conductivity is

K' = dielectric conductivity + ionic conductivity and hence with eqs.(1,75) and (1.82) as $\omega^2 \tau^2 \ll 1$

$$K' = \frac{1}{4\pi} (\epsilon_s - \epsilon_\alpha) \omega^2 \tau + \frac{ne^2}{6\pi a \eta} \dots\dots(1.83)$$

$$\text{or } K' = A + \frac{B}{\eta} \dots\dots(1.84)$$

Where $A = \frac{1}{4\pi} (\epsilon_s - \epsilon_\alpha) \omega^2 \tau$ and $B = \frac{ne^2}{6\pi a}$

This is the fundamental equation of radio frequency conductivity.

1.8b Microwave Conductivity of Polar Liquids in Dilute Solution of Non-polar Solvent

For a very dilute solution of polar solute in non-polar solvent the percentage of free ions present in solution is negligible. Again in microwave electric field there will be no movement of free ions present in solution, but only oscillation can be expected. So the second part of eq.(1.84) may be omitted. Hence under microwave electric field where $\omega^2 \tau^2$ has appreciable value, the conductivity of the dilute polar nonpolar solution becomes

$$K = A = \frac{\epsilon_s - \epsilon_\infty}{4\pi} \frac{\omega^2 \tau}{1 + \omega^2 \tau^2} \dots\dots\dots(1.85)$$

Using eq. (1.55) we finally get

$$K = \left[\frac{\epsilon_s + 2}{3} \right]^2 \frac{N c_j \mu_j^2}{3 k T} \frac{\omega^2 \tau}{1 + \omega^2 \tau^2} \dots\dots\dots(1.86)$$

This eq.(1.86) is the same as the eq.(1.66)

In our present investigation this eq.(1.86) is used to compute the relaxation time τ or dipole moment μ of the polar molecules.

1.9a Energy of Activation for dipole Orientation

The Phenomenon of dielectric relaxation has been treated as a rate process in which polar molecules rotate from one equilibrium position to the other.

According to Eyring (1941) 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 is equal to $1/\tau$, where τ is the relaxation time. Therefore the rate Process equation of dielectric relaxation (Eyring et al 1941) can be written as

$$\tau = \frac{h}{k T} \exp \left(\frac{\Delta F_{\tau}}{R T} \right) \dots\dots\dots(1.87)$$

where h and k are the Plank's constant and Boltzmann constant respectively, T is the absolute temperature, R is the universal gas constant and ΔF_{τ} is the free energy of activation for dipole relaxation

Since $\Delta F_{\tau} = \Delta H_{\tau} - T\Delta S_{\tau}$ \dots\dots\dots(1.88)

the eq.(1.87) takes the form

$$\tau = \frac{h}{k T} \exp \left[- \frac{\Delta S_{\tau}}{R} \right] \exp \left[\frac{\Delta H_{\tau}}{R T} \right] \dots\dots\dots(1.89)$$

where ΔH_{τ} and ΔS_{τ} are the molar enthalpy and molar entropy of activation for dipole relaxation respectively. The ΔH_{τ} is computed from the slope of the linear plot of $\ln(\tau T)$ versus $1/T$ using the relation: slope = $\Delta H_{\tau}/2.303R$. Knowing ΔH_{τ} and τ , ΔS_{τ} can be calculated from the eq.(1.89) and hence ΔF_{τ} from eq.(1.88).

1.9b Energy of Activation for Viscous Flow

Like the dielectric relaxation process the viscous flow of liquids may also be considered as rate process. Viscous flow is preferred as the movement of one layer of molecules with respect to another layer involving translational as well as rotational motion of molecules with an activation energy to pass over a potential barrier. If η be the coefficient of viscosity of the medium, then we may write (Eyring et al 1984)

$$\eta = \frac{h V}{N} \exp \left(-\frac{\Delta F_{\eta}}{R T} \right) \dots\dots\dots(1.90)$$

where h is the Plank's constant, N is the Avogadro number, V is the molar volume and ΔF_{η} is the free energy of activation for viscous flow given by

$$\Delta F_{\eta} = \Delta H_{\eta} - T \Delta S_{\eta} \dots\dots\dots(1.91)$$

The eq.(1.90) with eq.(1.91) becomes

$$\eta = \frac{h \nu}{N} \exp \left[- \frac{\Delta S_{\eta}}{R} \right] \exp \left[\frac{\Delta H_{\eta}}{R T} \right] \dots\dots\dots(1.92)$$

where ΔS_{η} is the entropy of activation and ΔH_{η} is the enthalpy of activation for viscous flow. ΔH_{η} can be calculated from the slope of the linear plot $\ln \eta$ vs $1/T$. The values of ΔS_{η} and ΔH_{η} can be calculated from eq.(1.92) and (1.91) respectively.

1.10 A Brief Review of the Early Works

Dielectric dispersion and absorption of polar liquids

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

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

Most of the earlier works were centered around the studies of applicability of Debye's equation in determining the molecular radii from the measurement of relaxation time and macroscopic viscosity.

The first quantitative verification of Debye theory was attempted by Mizushima (1926). He measured the dispersion phenomena of several alcohols and ketones in meter wave length region for a wide range of temperature. The observed absorption peaks at low temperatures were verified by using Debye theory. In the case of alcohols the molecular radii as calculated were found to be almost of the right order with glycerin with an exception that the molecular radii have smaller values.

Stranathan (1928) studied the dielectric behavior of dilute solutions of several alcohols in benzene. He found that at the zero concentration the intercepts of molar volume vs concentration curves for methyl, ethyl, propyl and amyl alcohols led to the electric moment values which are essentially independent of temperature in agreement with Debye theory.

Debye (1929) himself successfully explained the anomalous dispersion as observed by Drude (1904). He postulated that the characteristic property of the liquid responsible for this anomalous dispersion at radio frequency region is the polarity of molecules.

Fischer (1939) measured the relaxation times of number of liquid compounds in dilute solutions as well as in pure liquids. He found that for aliphatic long chain molecules the relaxation time is increased in the sequence alcohol, ketone, halogenides.

The absolute value of relaxation time can be evaluated by introducing molecular viscosity which is smaller than the macroscopic viscosity. The results show that for acetone, nitrobenzene and monochlorobenzene in pure state are in agreement with Debye theory. But the general theory does not explain the behavior of alcohol with their strong interaction of (-OH) groups.

Whiffen and Thompson (1946) from the dielectric measurement obtained the relaxation time of toluene, O-xylene, P-cyanine etc in pure liquid state which are in accordance with the size of the molecule.

Jackson and Powles (1946) determined the values of relaxation time of some polar molecules in benzene as well as in paraffin and observed that the values is increased by 4 to 7 fold for an increase in viscosity of eight fold.

Schllamach (1946), from his study of temperature dependence of mixtures of complex polar molecules under a constant radio frequency electric field, concluded that dielectric relaxation in mixtures involves a rearrangement of relatively large region in the liquid and if the polar components is a mixture of both associative or both non-associative, the dielectric behaviour appears to a single relaxation process.

Curties (1952) and Smyth (1954) observed that the values of relaxation time were different in solution and in pure liquid

state although they have the same viscosity.

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

Muller (1956) found that molecular radii calculated by using Debye equation for few molecules from experimental values of critical wavelength and critical frequency, were too low in comparison with the values obtained from other methods. He further observed that molecular radii becomes still lower as the viscosity of the medium increases.

Higasi et al (1960) analysed the experimental data of n-alkyl bromide in liquid state in terms of distribution between two limits by Fröhlich (1949). The lower value of τ were associated with the relaxation time of internal rotation of $-\text{CH}_2\text{Br}$ group, while the higher ones to the end-over-end rotation of the whole molecule.

Bergmann et al (1960) using a graphical method analysed a few systems like diphenyl ether, anisol and O-dimethoxy benzene in terms of two relaxation times. The results are consistent with the interpretation of a large relaxation time due to molecular rotation and a smaller relaxation time due to intramolecular motion of a polar molecule.

Krishnaji and Mansingh (1964) reported the dielectric relaxation process of alkyl cyanides and alkylthiols in liquid state. The relaxation times were in the order of increasing size of the molecules.

Bhattacharyya et al (1970) analysed the dielectric data of pure phenetole, aniline and orthochloro aniline in terms of two relaxation times for molecular and intramolecular orientation using relation (Bergmann et al 1960) as modified by them.

Higasi et al (1970) showed that for non-rigid molecules having two relaxation times average relaxation time could, however, be obtained from Debye equations of dilute solution based on single frequency measurements. Under a certain condition of proper frequency used in the measurements and a suitable equation is employed for calculation, one may make a crude estimate regarding one of the two relaxation times.

Gupta (1978) measured the dielectric loss and permitivity in dilute solution of benzene in 3 cm microwave field of benzoylacetone, P-fluro, P-chloro P-bromo and P-methyl benzoylacetones at 40°C and calculated the relaxation time, the dipole moment, the free energies of activation for dielectric relaxation and viscous flow.

The most probable, the overall molecular and the group

relaxation time of four unsaturated triple bonded polar compounds were measured by Krishna and Sobhanadri (1983) from the values of dielectric permittivity and loss of solution at different concentrations, frequencies and temperatures. The dipole moments with the thermodynamic parameters of those compounds were also estimated.

A least square fit method was suggested by Suryavanshi and Mehrotra (1990) to determine the molecular properties viz. dipole moment and relaxation time etc in dilute solution of polar-nonpolar liquid mixtures.

Polar Liquid in non-polar solvent

The dielectric loss at 4.3 meter wavelength electric field were measured by Fischer and Frank (1939) in order to obtain the relative values of relaxation times of some aromatic halids. The shorter relaxation times in larger molecules were explained as being associated with $\text{CH}_2\text{-X}$ rotation around their bond ring.

Goss (1940) analysed the dielectric polarization of some binary polar-nonpolar liquid mixtures and showed that the solvent effect could be resolved into contribution depending upon the anisotropy of the electric field which varied with the shape of the non-spherical polar molecules and on the induction effect related to the dielectric constant of the liquids and arising both

from the reaction field and dipole moment.

A method in determining the dipole moment and relaxation time of a polar molecule in a non-polar solvent under microwave electric field was offered by Gopal Krishna (1957). The special advantage of this method is that it does not require the knowledge of density of solution.

Sinha, Roy and Kasta (1967) showed the temperature dependence of relaxation time of a number of polar molecules of different shape, size and dipole moments in extremely dilute solutions of non-polar solvents. The viscosity dependence of τ at any temperature T° K is, however, represented by $\tau T = \text{constant } \eta^\gamma$, where γ is the ratio of the enthalpies of activation for dielectric relaxation and viscous flow.

Joy Prakash (1969) developed a method based on Fröhlich equation for calculating τ of nearly spherical polar molecules in non-polar solvent. The calculated τ of five molecules were in agreement with those as obtained from Gopal Krishna method.

Tay and Crossley (1972) analysed bromoalkens and ketones in terms of rotation of molecule as a whole, but in aniline the $-\text{NH}_2$ group rotation has been attributed to be responsible for dielectric relaxation.

Arrawatia et al (1977) determined the dielectric permittivity and loss of several disubstituted benzene in benzene and carbon tetrachloride at 35°C under 9.945 GHz electric field. The relaxation time τ , distribution parameter α and dipole moment μ have been evaluated from the measured data.

The study of the dielectric absorption of fluorebenzene, O-dichlorobenzene and O-chlorotoluene and their binary mixtures in benzene under 3 cm electric field and in the temperature range 20 to 60°C were made by Gupta et al (1978) to determine τ and hence thermodynamic parameters. The results obtained are explained on the basis of polarity, size of the molecules and the change in the molecular environment.

Using a standard microwave X-band technique and Gopal Krishna's single frequency concentration variation method, Sharma et al (1985) determined τ and thermodynamic parameters of N, N-dimethyl formamide (DMF), methanol (MeOH) and several binary polar mixtures of DMF + MeOH in benzene at different temperatures.

In the year 1986, Agarwal measured dielectric constant and loss of n-butyl chloride, chlorobenzene, bromobenzene and tert butyl chloride in benzene at 32°C under 9.96 GHz electric field and observed that the relaxation time τ is affected by molecular

shape in the following manner

$$\tau_{\text{linear}} > \tau_{\text{planar}} > \tau_{\text{spherical}}$$

Madan in 1987 studied the dielectric absorption of thiophene, acetone, benzophenone and their mixtures in dilute solution in the microwave region over a wide range of temperature. The experimental and theoretical relaxation time, calculated using two relations, were found to agree with each other within the experimental error.

Gandhi and Sharma (1988) determined the most probable relaxation time τ_0 , $\tau(1)$ and $\tau(2)$. the distribution parameter of isobutyl-methacrylate and allyl-methacrylate and their mixtures in dilute benzene solutions using dielectric absorption data. The results indicate that the properties of single component systems such as the existence of intramolecular and molecular rotation are retained in two component systems.

A comparison of experimental τ_0 of the mixtures with those calculated on the basis of simple and reciprocal mixing rules and also by a equation suggested by Madan (1987) reveals that none of these procedures could successfully predict the experimental data.

Makosz in 1990 calculated dipole moment of five liquids in several non-polar solvents at 25°C by using the formula derived from Onsagar theory assuming an ellipsoidal shape of the molecules.

Murthy et al (1991) proposed a new method for the study of dielectric relaxation of polar molecules in non-polar solvent based on the effect of viscosity of medium on the dielectric absorption. The method was tested by a few number of binary and ternary mixtures in non-polar solvent.

Molecular association of polar liquids

Molecular association of polar liquids may be expected to influence dielectric relaxation by modifying the structure of the polar liquid. The investigation of dielectric relaxation in this connection is continued actively till date.

Mecke and Reuter (1949) made precision measurements of permittivity of various solutions of CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, $n\text{C}_4\text{H}_{10}\text{OH}$, $n\text{C}_8\text{H}_{17}\text{OH}$, $\text{C}_6\text{H}_5\text{OH}$, $p\text{C}_6\text{H}_4(\text{ON})\text{CH}_3$ in C_6H_6 , CCl_4 and cyclohexane at 20°C and 40°C. The molecular association are found for alcohols and phenols which reduced the dipole moment.

The dielectric absorption measurements of aliphatic chlorides and alcohols were performed by Kremmling (1950). It was found difficult to sort out the effects due to polar association and H-bond formation on change in molecular shape, internal rotation, multiple relaxation times etc.

Schellman (1957) developed equations which take into account of the association in liquids on dielectric saturation.

Srivastava and Vershni in 1957 also suggested an equation which explains the variation of dielectric constant of both associative binary polar mixtures with concentration C and temperature T^oK as

$$\epsilon' = \left(1 + \frac{m}{T}\right) + \left(p + \frac{q}{T^{1/2}}\right) \times C + zC^2$$

where p,q,l,m and z are constants. The equation was tested for water-methyl alcohol and water-butyl alcohol mixtures.

Dielectric measurements of Grag and Smyth (1956) on pure normal alcohols from propyl to dodecyl had shown three distinct dispersion regions as was reported earlier by other workers. The relaxation times for the three regions were 1 to 2.2 x 10⁻¹⁰ secs, 1.7 to 5 x 10⁻¹¹ and 1.7 to 4 x 10⁻¹² secs respectively. The long τ are associated with polymeric clusters formed by the strong

hydrogen bonding between (-OH) groups. The shortest τ values were ascribed to the orientation of the (-OH) group, while the intermediate τ values were attributed to the rotation of the free alcohol molecules.

Barbenza (1968) reported that the dielectric property of pure methyl alcohol in the temperature range 5°C to 55°C and at wavelength from 5 to 15 cm can be explained by a single relaxation time. The measurements showed that the main dispersion could be described as a rate process with an activation energy of 3.4 kcal/mol.

Purohit and Sharma (1971) determined the dielectric constant and loss of methanol, ethanol, 2-propanol, 3-methyl-1-butanol and 1-butanol in benzene for weight fraction W varying from 0.004 to 0.08 in the X-band electric field. They found in all cases except 1-butanol, the $\tan \delta$ vs W curves show a marked increase in the range of weight fraction 0.03-0.04. This behaviour has been explained as due to the formation of dimers by molecular associations.

The dielectric relaxation time of some normal primary alcohols in non-polar solvents from radio frequency conductivity measurements were done by Sen and Ghosh (1972) and, Ghosh and Sen (1980) and observed that the rate of break up of the cluster of molecules is affected with the dilution.

Rajyan, Ramasastry and Murthy (1977) studied dielectric dispersion of glycerol and diethylene glycol under the radio frequency, uhf and microwave electric fields at 80°C and confirmed the Cole-Davidson type dispersion.

Mulecki et al (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 data.

The dielectric constant ϵ'_{12} and loss ϵ''_{12} at different concentrations of aniline and nitrobenzene as well as mix I (25% nitrobenzene & 75% aniline), mix II (50% nitrobenzene & 50% aniline) and mix III (75% nitrobenzene & 25% aniline) at different temperatures and frequencies were experimentally determined by Prakash and Rai (1986). ϵ'_{12} and ϵ''_{12} were found to increase linearly with the addition of nitrobenzene in the mixture except for mix III. Similar deviations have also been reported in τ and the thermodynamic parameters. These deviations may be attributed to the existence of inter association or to the complex formation in the last mix III.

The study of the dielectric absorption of four aliphatic alcohols and their binary mixtures as well as mixtures of these alcohols with dimethyl formamide and 2-fluoroaniline in benzene under 3 cm electric field at 30°C was done by Vyas and Vashisth (1988). For alcohols and their mixtures $\tan \delta$ - weight fraction

curves show marked increase in the range 0.02 to 0.05. This behaviour has been explained by the complex formation via self and hetero-association of the polar molecules. The alcohols + DMF mixtures show complex formation at a very low concentration. The study of alcohol + 2-fluoro aniline mixture, however, indicates the evidence of dissociating effect.

Sharma and Sharma (1992) found the solute-solute type of molecular associations for dimethylsulphoxide (DMSO) and acetone (AC) mixture in carbon tetrachloride from the concentration variation of relaxation time at different temperatures. The thermodynamic relaxation parameters of 1:1 mixture have been compared with those for the Viscous flow.

Electrical conductivity of dielectric liquids in d.c. and high frequency electric field

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

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

Jaffe (1906) studies the current voltage characteristic of

hexane when irradiated by γ - rays and considered that the current consists of two separate parts, one rising to a saturation value like the current in the gas, while the second is the ohmic current. In 1909 he succeeded in measuring small current developed when a voltage was impressed on highly purified hexane in a brass conductivity cell. Jaffe (1913) discarded the 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 due to γ - rays.

Baker and Boltz (1937) and Drouete (1940) interpreted the conductivity is due to thermoionic emission from the cathod combined with Schottky effect. Lepage and Dubridge (1940) observed that $\text{Log}(I)$ is a linear function of E . The current is due to field enhanced thermoionic emission and the following relation was derived

$$J = AT^2 \exp \left[-\frac{Qe}{KT} + \frac{1}{2.3 RT} \left(\frac{e^2 E}{K} \right)^{1/2} \right]$$

where K is the dielectric constant of the liquid.

The potential dissociation theory originally proposed by Onsager (1934) for very weak electrolytes was also used by Plumley (1941) and Pao (1943) to interpret the origin of conductivities of liquids. According to their view there are a very small number of ions exist even in purest hydrocarbon such as hexane resulting in

the spontaneous dissociation of molecules.

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

$$(I - I_{\alpha}) = (I_0 - I_{\alpha}) e^{-kt}$$

where I_0 is the initial current, I_{α} 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.

The time dependent current in hexane for wide gap and voltage of low value was studied by Jaffe and LeMay (1953) and concluded that the current is ionic. The break down in dielectric liquid gives additional information concerning the 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 cathod, but the cathod 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 ions.

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

Froster (1964) showed that the conduction in aliphatic hydrocarbons is probably related with the presence of polar impurities or the trapped electrons present in the liquid or generated at the electrode surface. In unsaturated hydrocarbons experimental evidence suggested the existence of electronic conduction. He suggested an empirical relation for the activation energy of quasi trapped mechanism $\epsilon_a = 0.067 P$ eV, where P is the number of peripheral π - electrons and thus confirmed the electronic nature of conduction current.

Adamczewski and Jachym (1968) jointly found that 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 temperature. They further observed that among all/organic compounds, investigated the lowest conductivity values are found in non-polar liquids.

Gaspared and Gosse (1970) gave a clear evidence of ionic conduction in polar dielectric. They used membrane electrodes and

gave evidence for three distinct regions of conduction and in each case the conduction is ionic in nature. It is due to impurities at low and medium fields. They observed considerable erratic variation of current with time under electric field.

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

Sen and Ghosh (1974) and Ghosh and Sen (1980) used the r.f. conductivity of some polar associative and non-associative dielectric liquids in different non-polar solvents at different temperatures to calculate the free ion density, ionic mobility and activation energy.

Ghosh et al (1980) established a relation for calculating h.f. conductivity of polar liquids in dilute solutions of non-polar solvents under an electric field of microwave frequency 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 mixtures at 1 MHz frequency over the temperature range of 20 to 50°C and calculated the average ion density and ionic mobility. They observed a marked decrease in electrical resistance with the addition of water as the impurity.

They confirmed that the impurity conduction is prevailed in pure polar liquids and the conductivity of glycerol-water mixture is an exponential function of concentration.

Acharyya et al (1986) found that the concentration variation of uhf conductivity of polar liquids in non-polar solvents is perfectly linear in the low concentration region at a given temperature. But they differ radically at infinite dilution at different temperatures. In the high concentration region the uhf conductivity varies non linearly against concentration. These variations were finally used to estimate the temperature dependence of dipole moment.

Ghosh and Chatterjee (1991) determined the r.f. conductivity of water and glycerin mixtures at 5 MHz over 20 to 60°C. They found relaxation time of water τ_0 from the concentration variation of τ of mixtures at different temperatures and calculated the correlation parameter g of water.

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CHAPTER II

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

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

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

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

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

from the following equation

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

and

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

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

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

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

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

2B. Experimental technique and Theories of Measurements

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

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

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

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

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

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

respectively.

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

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

Further, the resonant current I_o without glass cell is

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

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

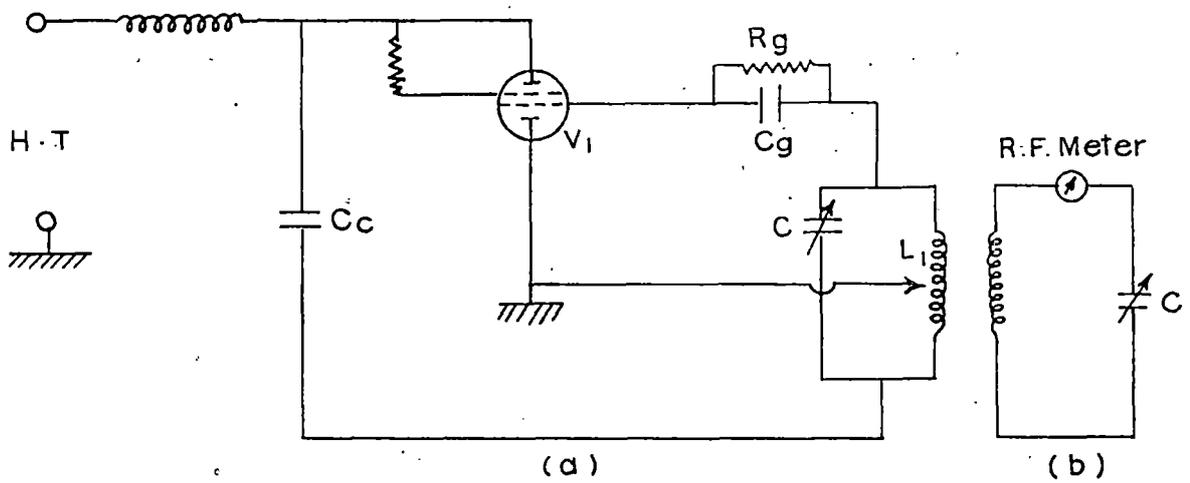


Fig. 2.2 (a) Radio frequency oscillator (b) Secondary tuning circuit.

List of components

$V_1 = 6L.6$

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

$C_g = 350\text{ PF}$

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

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

RFC = Radio frequency choke

R.F Meter = Radio frequency
milli ammeter.

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

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

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

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

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

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

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

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

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

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

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

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

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

The capacity of tuning condenser for the resonant current I_0 is

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

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

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

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

2B.2 Washing and Cleaning of Dielectric Cell

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

2B.3 Purification of Liquids

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

2B.4. Determination of Coefficient of Viscosity

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

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CHAPTER III

DIELECTRIC RELAXATION PARAMETERS FROM ULTRA-HIGH FREQUENCY
ELECTRIC CONDUCTIVITY OF POLAR -NONPOLAR MIXTURES

3.1 Introduction :

There are several methods (Gopal Krishna 1957, Sen and Ghosh 1972) to compute dipole moment μ_j as well as relaxation time τ_a of a polar liquid dissolved in non-polar solvent under the application of ultra high frequency such as microwave and radio frequency electric field. Both the methods mention above, unlike our method (Acharyya and Chatterjee 1985) suffer from extrapolation difficulties at infinite dilution. We in course of derivation of μ_j in terms of τ_a from uhf conductivity, observed that the imaginary and real parts K''_{ij} and K'_{ij} of the complex uhf conductivity K_{ij}^* vary linearly in the low concentration region and the slope of this linear variation can be used to evaluate the relaxation time τ_a of a polar solute. When an electric field is applied to dilute polar-nonpolar liquid mixture, the dipolar axis of polar molecule tends to orient in the field direction and the orientation period or the relaxation time depends upon size, shape and rigidity of polar molecules as well as the viscosity of the solvent.

Amides such as N-methyl acetamide (NMA), N,N-dimethyl acetamide (DMA) and N,N-dimethyl formamide (DMF) are very important non-aqueous i.e. protic liquids of assymmetric structure because of their high dielectric constant and wide biological applications. They thus attracted the attention of large number

of workers (Kumlar and porter 1934, Robinovitz and Pines 1969, Vyas and Vashith 1988) . Moreover the temperature variation of dielectric relaxation parameters, as obtained from uhf conductivity, are expected to detect the very existence of weak molecular associations. We are, therefore, tempted to report the uhf conductivity computed from the dielectric absorption data in the very low concentration region under 9.987 GHz electric field measured by Dhull et al (1982,1983), of DMF, DMF and NMA dissolved in benzene, dioxane and carbon tetrachloride at 25, 35, 45 and 55°C to calculate various dielectric relaxation parameters viz. relaxation time τ_a , dipole moment μ_j , free energy of activation ΔF_τ , enthalpy of activation ΔH_τ and entropy of activation ΔS_τ etc.

3.2 Theoretical formulation to estimate τ_a and μ_j of a polar solute

The uhf conductivity due to Morphy and Morgan (1939) of dilute polar non-polar liquid mixture is given by

$$K_{ij}^* = K'_{ij} + j K''_{ij} \dots\dots\dots(3.1)$$

Where $K'_{ij} = \omega \epsilon''_{ij} / 4\pi \dots\dots\dots(3.2)$

and $K''_{ij} = W \epsilon'_{ij} / 4\pi \dots\dots\dots(3.3)$

The magnitude of total uhf conductivity is usually computed from

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

The dielectric permittivity ϵ'_{ij} of solution in the uhf region although very small and is equal to optical dielectric constant, but still $\epsilon'_{ij} \gg \epsilon''_{ij}$, ϵ''_{ij} , the dielectric loss, is responsible for the absorption of electrical energy to offer resistance to the polarisation. Hence the total uhf conductivity becomes

$$K_{ij} = \frac{\omega}{4\pi} \epsilon'_{ij} \dots\dots\dots(3.5)$$

The real part of complex conductivity of solution having weight fraction W_j of polar solute at $T^\circ K$ is given

$$K'_{ij} = \frac{\mu_j^2 N \rho_{ij} F_{ij}}{9M_j k T} \frac{\omega^2 \tau_a}{1 + \omega^2 \tau_a^2} W_j \dots\dots\dots(3.6)$$

All other symbols have their usual significance (Acharyya and Chatterjee 1995). But for uhf region it can be shown that

$$\epsilon'_{ij} = \epsilon_{aij} + \epsilon''_{ij} / \omega \tau_a$$

and hence $K''_{ij} = K_{aij} + K'_{ij} / \omega \tau_a \dots\dots\dots(3.7)$

The slope m of the linear plot of K''_{ij} against K'_{ij} is given by

$$m = \frac{1}{\omega \tau_a} \text{ or } \tau_a = \frac{1}{2\pi f m} \dots\dots\dots(3.8)$$

Where f is the frequency of applied electric field.

Now from eqs (3.5) and (3.7) one can get

$$K_{ij} = K_{dij} + K'_{ij} / \omega \tau_a \dots\dots\dots(3.9)$$

Since K_{ij} is a function of W_j we obtain

$$\left(\frac{dK_{ij}}{dW_j} \right)_{W_j \rightarrow 0} = \omega \tau_a \beta \dots\dots\dots(3.10)$$

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

ρ_{ij} and F_{ij} become ρ_i and $F_i = \left[(\epsilon_i + 2) / 3 \right]^2$ of the solvent.

Differentiating eq.(3.6) with respect to W_j and as $W_j \rightarrow 0$ with eq.(3.10) we ultimately have

$$\mu_j = \left[\frac{9M_j k T}{N \rho_i F_i} - \frac{\beta}{\omega b} \right]^{1/2} \dots\dots\dots(3.11)$$

Where $b = 1 / (1 + \omega^2 \tau_a^2)$

Eqs. (3.8) and(3.11) are used to measure relaxation time τ_a and dipole moment μ_j of a polar solute in non-polar solvent respectively.

3.3 Results and discussion :

The magnitude of uhf conductivity K_{ij} and its real K'_{ij} and imaginary K''_{ij} parts of NMA in benzene and dioxane and of DMA and DMF both in benzene, dioxane and carbon tetrachloride at different W_j of polar solute were computed using eqs. (4), (2) and (3) respectively from the available data (Dhull et al 1982, 1983) of ϵ'_{ij} and ϵ''_{ij} at 25, 35, 45, and 55°C and given in Table 3.1.

The correlation coefficients (r) of the plots between K''_{ij} vs K'_{ij} of the systems at different temperature were calculated and listed in Table 3.2. They show that K''_{ij} vary linearly against K'_{ij} as required by eq.(3.7) in this low concentration region whose slopes and intercepts are presented in Table 3.2. The slopes are used to measure τ_a from eq.(3.8). The computed relaxation times along with the errors introduced and the reported (Dhull et al 1982, 1983) τ_a are tabulated in table 3.2. It is found that our τ_a are slightly higher than the reported ones and decrease with temperature. The temperature variation of relaxation time were then used to calculate the free energy of activation ΔF_τ , enthalpy of activation ΔH_τ and entropy of activation ΔS_τ by plotting $\ln(\tau_a \tau)$ against $1/\tau$ as required by the Eyring's rate process (1941) equations

$$\tau_a = \frac{h}{k T} \exp (\Delta F_\tau / RT) \quad \dots\dots\dots(3.12)$$

$$\Delta F_\tau = \Delta H_\tau - T\Delta S_\tau \quad \dots\dots\dots(3.13)$$

Table 3.1a

Values of uhf conductivity K_{ij} and its real K'_{ij} and imaginary K''_{ij} parts at different weight fractions W_j of DMF in various solvents at different temperatures

Solvent	Temp in oC	W_j	$K_{ij} \times 10^{-10}$ in esu	$K'_{ij} \times 10^{-9}$ in esu	$K''_{ij} \times 10^{-10}$ in esu
		0.0024	1.1580	0.0894	1.1580
		0.0047	1.1771	0.1908	1.1770
	25	0.0072	1.2017	0.2562	1.2014
		0.0093	1.2314	0.3595	1.2309
		0.0121	1.2446	0.4229	1.2439
b		0.0024	1.1465	0.0849	1.1465
		0.0047	1.1726	0.1693	1.1725
e	35	0.0072	1.1956	0.2217	1.1954
		0.0093	1.2218	0.2976	1.2214
n		0.0121	1.2384	0.3660	1.2379
z		0.0024	1.1405	0.0739	1.1405
		0.0047	1.1586	0.1178	1.1585
e	45	0.0072	1.1816	0.1888	1.1815
		0.0093	1.2027	0.2597	1.2024
n		0.0121	1.2273	0.3066	1.2269
e		0.0024	1.1315	0.0674	1.1315
		0.0047	1.1501	0.1523	1.1500
	55	0.0072	1.1711	0.1743	1.1710
		0.0093	1.1971	0.2047	1.1969
		0.0121	1.2152	0.2766	1.2149

Table 3.1a (continued)

Solvent	Temp in oC	W_j	$K_{ij} \times 10^{-10}$ in esu	$K'_{ij} \times 10^{-9}$ in esu	$K''_{ij} \times 10^{-10}$ in esu
d	25	0.0026	1.1272	0.1678	1.1270
		0.0048	1.1448	0.2696	1.1445
		0.0070	1.1696	0.3815	1.1690
		0.0088	1.1924	0.4649	1.1914
i		0.0124	1.2374	0.6207	1.2359
o		0.0026	1.1221	0.1498	1.1220
		0.0048	1.1428	0.2472	1.1425
x	35	0.0070	1.1625	0.3331	1.1620
		0.0088	1.1872	0.4264	1.1865
a		0.0124	1.2207	0.5573	1.2194
n		0.0026	1.1141	0.1348	1.1140
		0.0048	1.1382	0.2187	1.1380
e	45	0.0070	1.1609	0.2986	1.1605
		0.0088	1.1731	0.3720	1.1725
		0.0124	1.2130	0.5153	1.2119
		0.0026	1.1071	0.1218	1.1071
		0.0048	1.1362	0.1977	1.1360
	55	0.0070	1.1578	0.2751	1.1575
		0.0088	1.1680	0.3401	1.1675
		0.0124	1.2078	0.4544	1.2069

Table 3.1a (continued)

Solvent	Temp in oC	W_j	$K_{ij} \times 10^{-10}$ in esu	$K'_{ij} \times 10^{-9}$ in esu	$K''_{ij} \times 10^{-10}$ in esu
c		0.0011	1.1316	0.0974	1.1315
a	25	0.0030	1.1797	0.2452	1.1795
r		0.0049	1.1839	0.3211	1.1835
b		0.0071	1.2324	0.4939	1.2314
o					
n		0.0011	1.1201	0.0934	1.1200
	35	0.0030	1.1677	0.2237	1.1675
t		0.0049	1.1773	0.2951	1.1770
e		0.0071	1.2221	0.4010	1.2214
t					
r		0.0011	1.1116	0.0819	1.1116
a	45	0.0030	1.1482	0.2062	1.1480
c		0.0049	1.1703	0.2696	1.1700
h		0.0071	1.2135	0.3840	1.2129
l					
o		0.0011	1.1036	0.0704	1.1036
r	55	0.0030	1.1356	0.1703	1.1355
i		0.0049	1.1633	0.2557	1.1630
d		0.0071	1.2005	0.3525	1.1999
e					

Table 3.1b

Values of uhf conductivity K_{ij} and its real K'_{ij} and imaginary K''_{ij} parts at different weight fractions W_j of DMA in various solvents at different temperatures

Solvent	Temp in oC	W_j	$K_{ij} \times 10^{-10}$ in esu	$K'_{ij} \times 10^{-9}$ in esu	$K''_{ij} \times 10^{-10}$ in esu
c		0.0020	1.1331	0.1533	1.1330
a	25	0.0044	1.1679	0.3021	1.1675
r		0.0073	1.2064	0.4864	1.2054
b		0.0091	1.2321	0.5548	1.2309
o					
n		0.0020	1.1301	0.1473	1.1300
	35	0.0044	1.1613	0.2657	1.1610
t		0.0073	1.1952	0.4374	1.1944
e		0.0091	1.2210	0.5098	1.2199
t					
r		0.0020	1.1241	0.1253	1.1240
a	45	0.0044	1.1548	0.2527	1.1545
c		0.0073	1.1861	0.3795	1.1885
h		0.0091	1.2129	0.4789	1.2119
l					
o		0.0020	1.1141	0.1178	1.1140
r	55	0.0044	1.1432	0.2207	1.1430
i		0.0073	1.1760	0.3510	1.1755
d		0.0091	1.2016	0.4125	1.2009
e					

Table 3.1b (continued)

Solvent	Temp in oC	W_j	$K_{ij} \times 10^{-10}$ in esu	$K'_{ij} \times 10^{-9}$ in esu	$K''_{ij} \times 10^{-10}$ in esu
d	25	0.0028	1.1302	0.1688	1.1300
		0.0046	1.1418	0.2577	1.1415
		0.0070	1.1610	0.3431	1.1605
		0.0091	1.1768	0.4424	1.1760
i	35	0.0028	1.1231	0.1583	1.1230
		0.0046	1.1378	0.2292	1.1375
		0.0070	1.1544	0.3176	1.1540
		0.0091	1.1706	0.3930	1.1700
x	45	0.0028	1.1181	0.1468	1.1180
		0.0046	1.1332	0.2117	1.1330
		0.0070	1.1489	0.2821	1.1485
		0.0091	1.1656	0.3675	1.1650
e	55	0.0028	1.1101	0.1373	1.1101
		0.0046	1.1267	0.1883	1.1265
		0.0070	1.1418	0.2522	1.1415
		0.0091	1.1585	0.3361	1.1580

Table 3.1b (continued)

Solvent	Temp in oC	W_j	$K_{ij} \times 10^{-10}$ in esu	$K'_{ij} \times 10^{-9}$ in esu	$K''_{ij} \times 10^{-10}$ in esu
		0.0022	1.1585	0.0829	1.1585
	25	0.0064	1.1871	0.1903	1.1870
		0.0083	1.1992	0.2587	1.1989
b		0.0106	1.2133	0.3181	1.2129
e		0.0022	1.1465	0.0759	1.1465
	35	0.0064	1.1731	0.1803	1.1730
n		0.0083	1.1882	0.2252	1.1880
		0.0106	1.2058	0.2966	1.2054
z		0.0022	1.1355	0.0694	1.1355
e	45	0.0064	1.1606	0.1493	1.1605
		0.0083	1.1781	0.1932	1.1780
n		0.0106	1.1992	0.2467	1.1989
e		0.0022	1.1275	0.0629	1.1275
	55	0.0064	1.1541	0.1258	1.1540
		0.0083	1.1681	0.1768	1.1680
		0.0106	1.1947	0.2277	1.1944

Table 3.1c

Values of uhf conductivity K_{ij} and its real K'_{ij} and imaginary K''_{ij} parts at different weight fractions W_j of NMA in various solvents at different temperatures

Solvent	Temp in oC	W_j	$K_{ij} \times 10^{-10}$ in esu	$K'_{ij} \times 10^{-9}$ in esu	$K''_{ij} \times 10^{-10}$ in esu
b	25	0.0022	1.1570	0.1099	1.1570
		0.0053	1.1792	0.2277	1.1790
		0.0073	1.1940	0.3495	1.1934
		0.0094	1.2069	0.4749	1.2059
e n z	35	0.0022	1.1460	0.0974	1.1460
		0.0053	1.1707	0.2067	1.1705
		0.0073	1.1884	0.3416	1.1880
		0.0094	1.2037	0.4369	1.2029
e n	45	0.0022	1.1391	0.0909	1.1390
		0.0053	1.1591	0.1818	1.1590
		0.0073	1.1794	0.3096	1.1790
		0.0094	1.1986	0.4115	1.1979
e	55	0.0022	1.1291	0.0759	1.1290
		0.0053	1.1511	0.1678	1.1510
		0.0073	1.1718	0.2961	1.1715
		0.0094	1.1936	0.3955	1.1929

Table 3.1c (continued)

Solvent	Temp in °C	W_j	$K_{ij} \times 10^{-10}$ in esu	$K'_{ij} \times 10^{-9}$ in esu	$K''_{ij} \times 10^{-10}$ in esu
d	25	0.0030	1.1383	0.2442	1.1380
		0.0058	1.1542	0.4080	1.1535
		0.0091	1.1844	0.5932	1.1830
		0.0123	1.2117	0.7430	1.2094
o	35	0.0030	1.1223	0.2247	1.1220
		0.0058	1.1502	0.3880	1.1495
		0.0091	1.1829	0.5748	1.1815
		0.0123	1.2100	0.7141	1.2079
a	45	0.0030	1.1207	0.2002	1.1205
		0.0058	1.1446	0.3575	1.1440
		0.0091	1.1742	0.5353	1.1730
		0.0123	1.2078	0.6776	1.2059
e	55	0.0030	1.1192	0.1803	1.1190
		0.0058	1.1360	0.3241	1.1355
		0.0091	1.1725	0.4964	1.1715
		0.0123	1.2060	0.6202	1.2044

Table 3.2 - Values of correlation coefficients (r), intercepts (C & α) and slopes (m & β) of $K''_{ij} - K'_{ij}$ and $K'_{ij} - W_j$ curves and hence relaxation times τ_a and dipole moments μ_j with errors along with reported and theoretical ones

System	$t^\circ C$	$K''_{ij} - K'_{ij}$ curve's			Relaxation time, P Sec		$K'_{ij} - W_j$ curve's			Dipole moment, D		
		r	Intercept ($C \times 10^{-10}$)	Slope (m)	τ_a (comp) from eq(3.8)	τ (Rept) ^o	r	Intercept $\alpha \times 10^{-10}$	Slope $\beta \times 10^{-10}$	μ_j (comp.) from eq (3.11)	μ_j (Rept) ^o	μ_j (Theo)
DMF in Benzene	25	0.995	1.1312	2.6939	5.92±0.32	5.09	0.990	1.1353	9.4287	3.80±0.23	3.62	
	35	0.994	1.1185	3.3465	4.76±0.21	4.46	0.991	1.1260	9.6660	3.87±0.21	3.66	
	45	0.997	1.1148	3.5473	4.49±0.20	3.98	0.999	1.1174	9.0667	3.83±0.12	3.67	
	55	0.964	1.0981	4.2728	3.73±0.52	3.50	0.992	1.1094	8.9061	3.84±0.14	3.68	
DMF in Dioxane	25	0.995	1.0814	2.4188	6.59±0.44	5.58	0.996	1.0929	11.4241	3.98±0.21	3.69	
	35	0.998	1.0840	2.4061	6.57±0.17	5.26	0.995	1.0944	10.2062	3.86±0.16	3.70	3.82
	45	0.978	1.0817	2.5230	6.32±0.25	5.10	0.998	1.0894	9.8997	3.90±0.16	3.71	
	55	0.994	1.0750	2.8778	5.54±0.35	4.78	0.997	1.0848	9.9098	3.93±0.21	3.71	
DMF in CCl ₄	25	0.988	1.1107	2.4438	6.52±0.61	5.09	0.965	1.1197	15.4556	3.70±0.33	3.69	
	35	0.990	1.0907	3.1890	5.00±0.42	4.62	0.980	1.1079	15.8823	3.75±0.31	3.69	
	45	0.998	1.0816	3.3548	4.75±0.20	4.30	0.996	1.0945	16.5087	3.92±0.21	3.70	
	55	0.999	1.0784	3.3981	4.69±0.13	3.98	0.999	1.0863	15.9995	3.97±0.12	3.70	
DMA in Benzene	25	0.997	1.1408	2.2845	6.98±0.18	6.53	0.999	1.1446	6.5444	3.54±0.08	3.37	
	35	0.999	1.1258	2.6964	5.91±0.12	5.42	0.998	1.1300	7.0407	3.68±0.13	3.58	
	45	0.998	1.1093	3.5789	4.45±0.17	4.62	0.993	1.1166	7.5256	3.81±0.19	3.65	
	55	0.994	1.1026	3.9364	4.05±0.17	3.82	0.988	1.1077	7.3381	3.83±0.25	3.69	

Table 3.2 (continued)

System	t°C	K'_{ij} - K'_{ij} curve's			Relaxation time, P Sec		K_{ij} - H_j curve's			Dipole moment, D		
		r	Intercept (C x 10^{-10})	Slope (m)	τ _s (comp) from eq(3.8)	τ (Rept)*	r	Intercept α x 10^{-10}	Slope β x 10^{-10}	μ _j (comp.) from eq (3.11)	μ _j (Rept)*	μ _j (Theo)
DMA in	25	0.996	1.0996	1.7284	9.22±0.19	8.76	0.999	1.1085	7.4855	3.75±0.09	3.69	
	35	0.999	1.0917	1.9834	8.03±0.06	8.12	0.999	1.1027	7.4613	3.73±0.08	3.69	4.02
Dioxane	45	0.999	1.0875	2.1279	7.49±0.10	7.48	0.999	1.0980	7.3967	3.78±0.10	3.69	
	55	0.994	1.0797	2.3760	6.71±0.32	6.69	0.998	1.0903	7.4911	3.82±0.13	3.69	
DMA in	25	0.996	1.0962	2.3516	6.78±0.39	6.77	0.999	1.1059	13.8559	3.85±0.08	3.65	
	35	0.996	1.0956	2.3741	6.71±0.36	6.63	0.988	1.1049	12.6300	3.78±0.12	3.67	
CCl ₄	45	0.999	1.0924	2.4778	6.43±0.06	6.13	0.999	1.0997	12.2391	3.79±0.15	3.67	
	55	0.996	1.0796	2.8574	5.58±0.19	5.63	0.999	1.0894	12.1619	3.84±0.13	3.67	
NMA in	25	0.989	1.1445	1.3227	12.05±0.55	12.13	0.999	1.1421	6.9730	3.84±0.09	3.69	
	35	0.993	1.1328	1.6285	9.79±0.42	10.27	0.999	1.1283	8.0851	3.98±0.09	3.78	
Benzene	45	0.998	1.1240	1.7988	8.86±0.21	8.82	0.995	1.1186	8.3413	4.05±0.18	3.80	
	55	0.997	1.1157	1.9432	7.81±0.21	7.81	0.995	1.1070	8.9873	4.23±0.19	3.82	
NMA in	25	0.992	1.0990	1.4475	11.01±0.64	9.88	0.996	1.1114	8.0532	3.75±0.17	3.66	4.30
	35	0.999	1.0821	1.7481	9.12±0.13	8.41	0.999	1.0947	9.4813	3.96±0.13	3.69	
Dioxane	45	0.995	1.0827	1.7658	9.02±0.49	7.34	0.999	1.0913	9.3360	4.03±0.15	3.78	
	55	0.988	1.0785	1.9513	8.17±0.73	6.35	0.994	1.0865	9.5581	4.10±0.24	3.83	

* Ref. Dhull et al (1982, 1983)

The estimated ΔH_{τ} , ΔS_{τ} and ΔF_{τ} are placed in Table 3.3. The concept of viscous flow can also be considered as a rate process according to Eyring et al (1941) as

$$\eta = \frac{h N}{v} \exp (\Delta F_{\eta} / RT) \dots\dots\dots(3.14)$$

and $\Delta F_{\eta} = \Delta H_{\eta} - T \Delta S_{\eta} \dots\dots\dots(3.15)$

By using rate process equations for dielectric relaxation and viscous flow one can derive a simple relation $\tau_{\sigma} = A \eta^{\gamma} / T$, which satisfactorily represents the dependence of τ_{σ} upon viscosity and temperature (Kalman and Smyth 1960), A being the constant for each system and $\gamma = \Delta H_{\tau} / \Delta H_{\eta}$. The quantity γ is very important to indicate the solvent environment around solute molecule. The value of γ were, however, calculated from the slope of the plot $\ln (\tau_{\sigma} T)$ against $\ln (\eta)$ as required by: $\ln (\tau_{\sigma} T) = \ln (A) + \gamma \ln (\eta)$ and are shown in Table 3.3.

The calculated correlation coefficients (r), as shown in Table 3.2, between uhf conductivity K_{ij} of the solution and weight fraction W_j of solutes establish the truthness of their linear relationship whose slopes and intercepts are given in Table 3.2. The slope of $K_{ij} - W_j$ curve is very important parameter to yield the dipole moment μ_j of a polar molecule as evident from eq.(3.11). The measured dipole moments of DMF, DMA and NMA in the solvents at different temperatures are listed in Table 3.2, along with the reported (Dhull et al 1982, 1983) μ_j and theoretical

Table 3.3

Values of free energy of activation (ΔF_{τ} in KCal/mol), enthalpy of activation (ΔH_{τ} in KCal/mol), entropy of activation (ΔS_{τ} in Cal/mol/deg) and γ ($= \Delta H_{\tau} / \Delta H_{\eta}$)

t in oC	τ_a in P Sec	ΔF_{τ}	ΔH_{τ}	ΔS_{τ}	γ	τ_a in P Sec	ΔF_{τ}	ΔH_{τ}	ΔS_{τ}	γ
<u>DMF in benzene</u>						<u>DMF in dioxane</u>				
25	5.92	2.13		0.30		6.59	2.20		5.30	
35	4.76	2.10	2.22	0.41	0.91	6.57	2.29	0.62	5.43	0.21
45	4.49	2.15		0.24		6.32	2.36		5.47	
55	3.73	2.11		0.36		5.54	2.35		5.28	
<u>DMF in CCl₄</u>						<u>DMA in benzene</u>				
25	6.52	2.19		2.73		6.98	2.23		3.14	
35	5.00	2.12	1.38	2.42	0.55	5.91	2.22	3.17	3.07	1.29
45	4.75	2.18		2.55		4.45	2.15		3.22	
55	4.69	2.26		2.70		4.05	2.16		3.09	
<u>DMA in dioxane</u>						<u>DMA in CCl₄</u>				
25	9.22	2.40		3.49		6.78	2.22		5.48	
35	8.03	2.41	1.35	3.43	0.44	6.71	2.30	0.58	5.58	0.25
45	7.49	2.47		3.50		6.43	2.37		5.61	
55	6.71	2.49		3.47		5.58	2.38		5.46	
<u>NMA in benzene</u>						<u>NMA in dioxane</u>				
25	12.05	2.55		2.53		11.01	2.50		4.71	
35	9.79	2.54		2.39		9.12	2.49		4.52	
45	8.86	2.58	1.80	2.44	0.74	9.02	2.58	1.10	4.68	0.39
55	7.81	2.63		2.51		8.17	2.63		4.66	

ones for comparison. The errors introduced in computation of μ_j have also been calculated and placed in Table 3.2.

The values of relaxation time of a solute in different solvent show the lengthening of τ_2 with solvent viscosity, but do not exhibit direct proportionality to the solvent viscosity. It would, however, appear that the viscosity effect alone do not account for the relaxation behaviour of a polar molecule in the solvents. The reorientation of the polar molecules seems to be considerably influenced by solute-solvent molecular association. The factor $(\tau_2 T / \eta^\gamma)$, which is proportional to the volume of rotating unit, of DMF in benzene, carbon tetrachloride and dioxane are 1.85×10^{-7} , 2.61×10^{-8} and 5.01×10^{-9} respectively. The appreciable higher values of the factor in benzene and carbon tetrachloride than in dioxane indicate the presence of DMF-benzene and DMF-carbon tetrachloride molecular associations in the solutions. In case of DMA the values of $(\tau_2 T / \eta^\gamma)$ are 1.58×10^{-6} , 0.66×10^{-8} and 1.96×10^{-8} in benzene, carbon tetrachloride and dioxane respectively. These show that the solute-solvent associations occur in benzene only and the values 1.31×10^{-6} and 1.87×10^{-8} for NMA in benzene and dioxane respectively clearly exhibit the existence of strong interaction between NMA and benzene molecules only. A solute-solvent molecular association of the amides benzene may be due to the interaction of fractional positive charge on the nitrogen atom of amides with the π -electron cloud of benzene ring. The carbon

tetrachloride molecule has no molecular dipole moment, but contains four compensating $C \rightarrow Cl$ dipoles. The solute-solvent association of DMF in carbon tetrachloride may be attributed to the interaction of dipolar solute with a $C \rightarrow Cl$ dipole, whose local force field is not cancelled by the other three dipoles. A solute-solvent molecular associations of DMF in benzene and carbon tetrachloride are shown in Fig.3.1.

From Table 3.3 the free energy of activation difference ΔF_T between two equilibrium positions of the relaxing dipole in benzene and dioxane at all temperatures show an increase in order $NMA > DMA > DMF$. But in carbon tetrachloride solutions ΔF_T are in the reverse order i.e. $DMF > DMA$. These results confirm the formation of solute-solvent association in carbon tetrachloride only for DMF. The ΔH_T values of DMF in benzene is 2.22 KCal / mol whereas in carbon tetrachloride and dioxane they are 1.38 Kcal/ mol and 0.63 KCal / mol respectively. This suggests that the energy barriers encountered by the rotating units in benzene and carbon tetrachloride are higher than in dioxane inspite of the fact that dioxane is more viscous than benzene and carbon tetrachloride. This is consistent with already proposed solute-solvent association of DMF in benzene and carbon tetrachloride. The ΔH_T values of DMA and NMA. in the solvents (Table 3.3) support the presence of solute-solvent association only in benzene. The ΔS_T values show that for most of the systems the configuration involved in dipole orientation have an

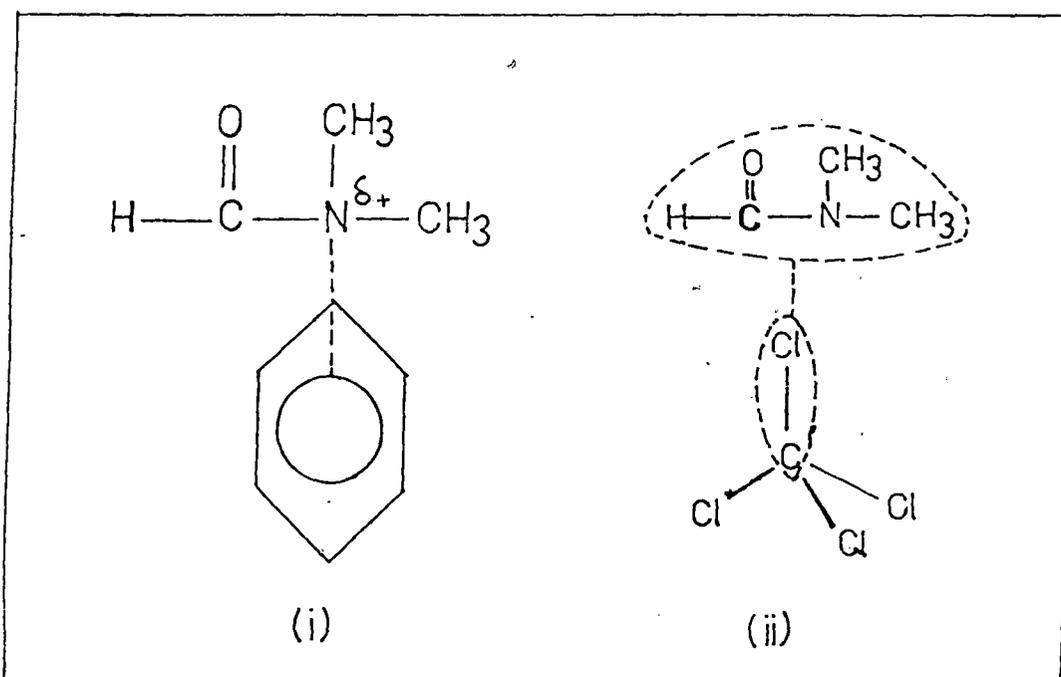


Fig. 3.1 - Solute - Solvent type of molecular association of DMF in (i) benzene and (ii) carbon tetrachloride

activated state which is more ordered than the normal state and the relaxation process involves the co-operation of neighbours. It has been observed from ΔS_{τ} values that the systems having unassociated molecules possess more ordered activated state than those containing associated relaxing units.

Again Krishnaji and Man Singh (1966) classified polar molecules in terms of γ and showed that the molecules for which $\gamma < 0.45$ behave as solid phase rotators and the molecules for which $\gamma > 0.5$ do not behave as solid phase rotators. An examination of γ values as presented in Table 3.3 suggests that DMF molecules in benzene and carbon tetrachloride, DMA and NMA molecules in benzene do not behave as solid phase rotators as expected due to solute-solvent association.

It is an established fact (Ras and Bordewijk 1971, Saha and Acharyya 1993) that the dipole moment μ_j of polar solute in non-polar solvent varies with temperature when subjected to uhf electric field. The measured μ_j of DMF, DMA and NMA, as given in Table 3.2, are found to vary appreciably with temperature. The temperature variation of μ_j have been shown by fitted curves in Fig.3.2 whose equations are:

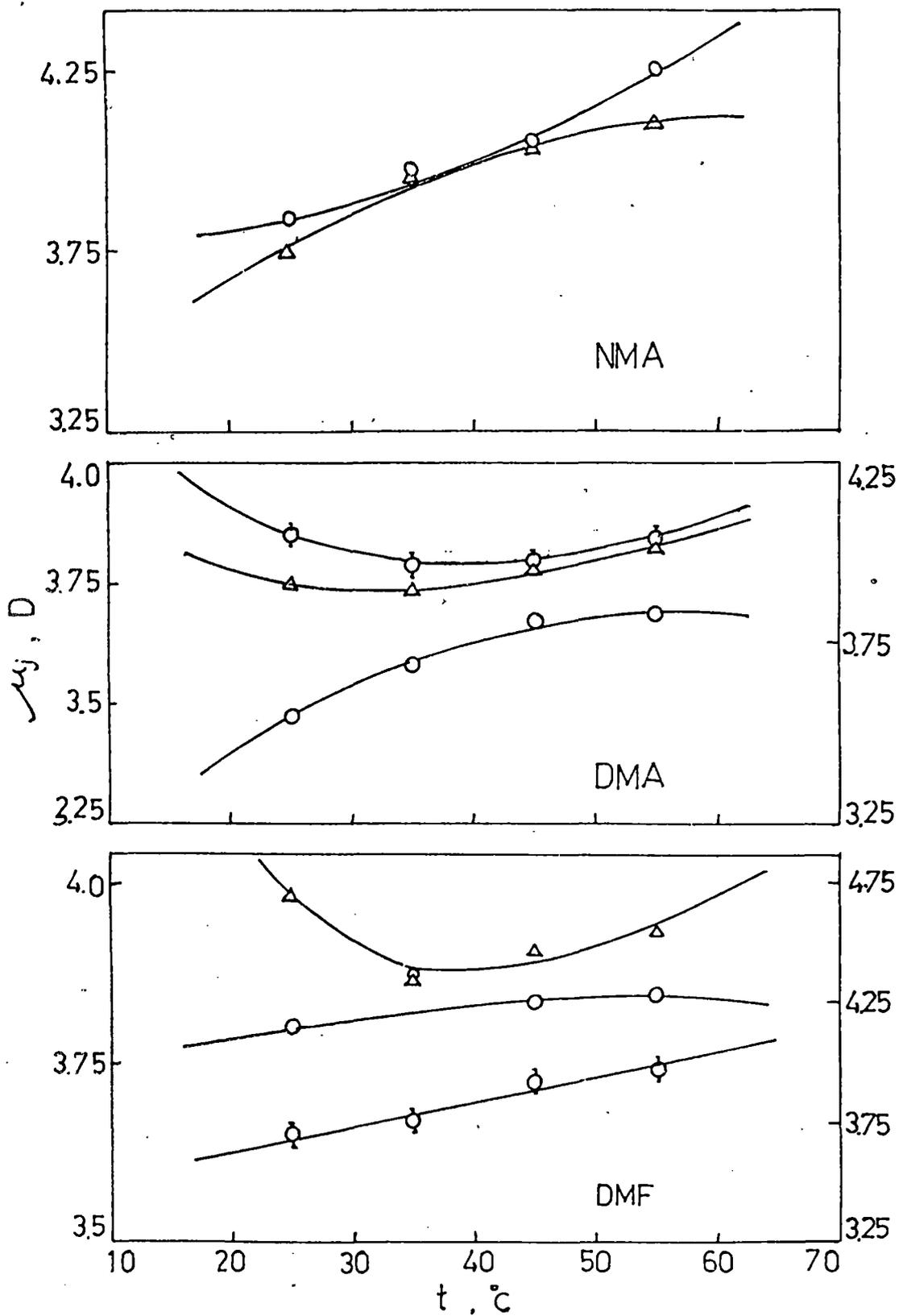


Fig. 3.2 - Temperature variation of dipole moment μ_j of DMF, DMA and NMA in benzene ($\circ-\circ-\circ$), dioxane ($\triangle-\triangle-\triangle$) and carbon tetrachloride ($\square-\square-\square$)

DMF

$$\text{In benzene: } \mu_j = 3.7438 + 2.6667 \times 10^{-8} t - 1.7 \times 10^{-5} t^2$$

$$\text{In dioxane: } \mu_j = 4.4953 - 0.0296 t + 3.5 \times 10^{-4} t^2$$

$$\text{In carbon tetrachloride: } \mu_j = 3.4430 + 9.8 \times 10^{-8} t$$

DMA

$$\text{In benzene: } \mu_j = 2.8725 + 0.0340 t - 3.0 \times 10^{-4} t^2$$

$$\text{In dioxane: } \mu_j = 3.9530 - 0.0132 t + 2.0 \times 10^{-4} t^2$$

$$\text{In carbon tetrachloride: } \mu_j = 4.2655 - 0.0242 t + 3.0 \times 10^{-4} t^2$$

NMA

$$\text{In benzene: } \mu_j = 3.6765 + 4.4000 \times 10^{-8} t + 1.0 \times 10^{-4} t^2$$

$$\text{In dioxane: } \mu_j = 2.9958 + 0.0392 t - 3.5 \times 10^{-4} t^2$$

The change in μ_j with temperature for unassociated molecules may be due to stretching of bond moments and change in bond angles, but for associated relaxing dipole perhaps the breaking of weak molecular associations is the additional factor. This may be the reason why the dipole moment of solute-solvent type of associated rotating unit always increases with temperature

(Fig.3.2).

The theoretical values of μ_j (Theo) of DMF, DMA and NMA have been calculated from the bond moments and bond angles by vector addition method assuming molecules to be planer ones as shown in Fig.3.3. The bond moments C = O and N-CH₃ act along a direction normal to C-N and other bond moments act along that of C-N. The theoretically calculated values are very close to the experimental values (Table 3.2) suggesting that the preferred conformation of the polar molecules investigated are correct ones as shown in Fig.3.3.

Thus our uhf method is a sensitive one to study the molecular structure and behaviour of polar solute in dilute solution.

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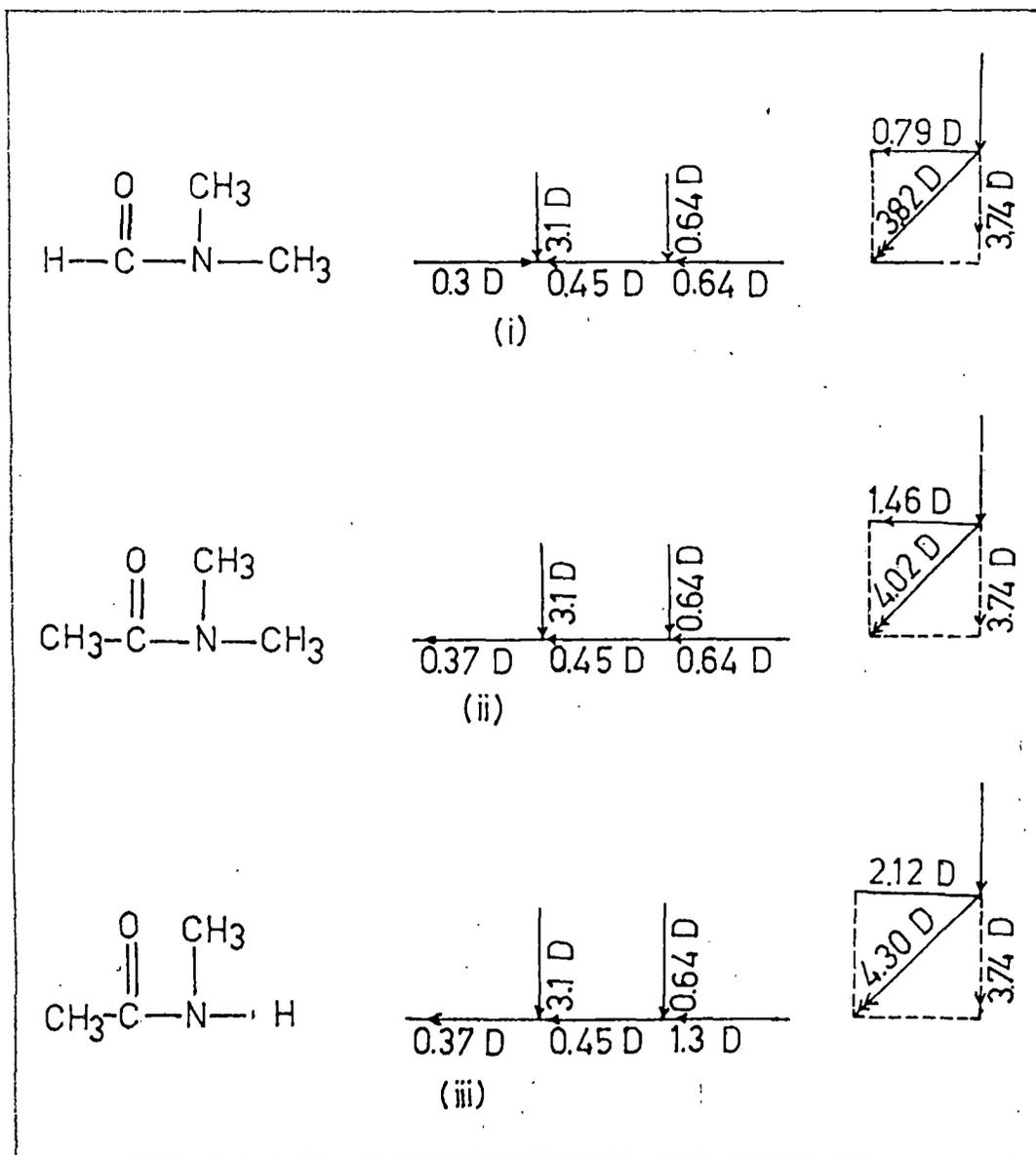


Fig. 3.3 - Structural form of (i) DMF, (ii) DMA and (iii) NMA

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CHAPTER IV

DIPOLE MOMENTS OF ASSOCIATED BINARY SOLUTES IN BENZENE FROM ULTRA
HIGH FREQUENCY CONDUCTIVITY OF SOLUTIONS.

4.1 Introduction

Now a days, the estimation of dipole moment μ_j as well as the relaxation time τ_a of a polar solute dissolved in non-polar solvent under ultra-high frequency electric field are really very encouraging (Acharyya and Chatterjee 1985, Acharyya et al 1986, Dhull et al 1982) as they throw much light on the monomer and dimer formations in a liquid mixture. But the measurement of μ_{jk} of binary polar mixtures in a given non-polar solvent are, however, very scanty. There are several methods (Gopala Krishna 1957, Sen and Ghosh 1972) to estimate τ_a and μ_j of polar solute dissolved in non-polar solvent under microwave or radio frequency electric field.

We (Acharyya and Chatterjee 1985), however, devised a method to find out relaxation time and dipole moment of a polar solute in non-polar solvent under uhf electric field. In this paper we thought to extend our method to compute the dipole moment of binary polar mixture in dilute solution of non-polar solvent. The uhf conductivity K_{ijk} of binary polar solute and non-polar solvent mixture is comparatively easy to measure down to very low concentration by using a Klystron or a r.f. Hartley oscillator in the laboratory. The data of uhf conductivity are, however, very limited (Sen and Ghosh 1972). Recently, Sharma and Sharma (1984, 1985) reported the measured values of ϵ'_{ijk} and ϵ''_{ijk} , the real and

imaginary parts of complex dielectric constant ϵ_{ijk}^* of binary polar mixtures consisting of N,N- dimethyl formamide (DMF) and N,N- tetramethyl urea (TMU) as well as DMF and N,N- dimethyl acetamide (DMA) in benzene under 9.885 GHz electric field. We, therefore, tempted to used these measured values of ϵ'_{ijk} and ϵ''_{ijk} of the polar mixtures for different mole fractions X_j of DMF at 15°C to 30°C to obtain uhf conductivities K_{ij} , K_{ik} and K_{ijk} using Murphy and Morgan relation (1939):

$$k = \frac{\omega(\epsilon'^2 + \epsilon''^2)^{1/2}}{4\pi}$$

The calculated conductivities are presented in Table 4.1. Amides are very important dielectric liquids for their wide biological applications and they form the basic building blocks in proteins. That is why amides attracted the attention of a large number of workers (Sato et al 1976). The K_{ijk} of DMF+TMU mixtures at 15°C in terms of weight fraction W_{jk} in benzene were found to be as :

$$K_{ik} \times 10^{-10} = 1.1670 - 1.2030 W_k + 795.72 W_k^2$$

$$K_{ijk} \times 10^{-10} = 1.1455 + 3.9273 W_{jk} - 21.4233 W_{jk}^2$$

$$K_{ijk} \times 10^{-10} = 1.1280 + 6.9023 W_{jk} - 51.4435 W_{jk}^2$$

$$K_{ijk} \times 10^{-10} = 1.1247 + 11.9614 W_{jk} - 249.0353 W_{jk}^2$$

$$K_{ijk} \times 10^{-10} = 1.1286 + 11.5870 W_{jk} - 120.3810 W_{jk}^2$$

Table 4.1a. Values of ultra high frequency conductivity K_{ijk} of polar solute in benzene at various concentration at 15°C

System	Mole fraction Of DMF X_j	Weight fraction of polar solute W_{jk}	Uhf. Conductivity $K_{ijk} \times 10^{-10}$, esu
DMF + TMU in benzene	1.0	0.0023	1.1715
		0.0048	1.1941
		0.0063	1.2089
		0.0079	1.2274
	0.9	0.0110	1.2629
		0.0026	1.1607
		0.0046	1.1733
		0.0073	1.2072
	0.7	0.0099	1.2399
		0.0122	1.2467
		0.0025	1.1542
		0.0053	1.1772
0.3	0.0072	1.2006	
	0.0097	1.2148	
	0.0112	1.2264	
	0.0019	1.1418	
	0.0040	1.1537	
	0.0068	1.1714	
	0.0084	1.1859	
	0.0105	1.1935	

Table 4.1a (continued)

System	Mole fraction Of DMF X_j	Weight fraction of polar solute w_{jk}	Uhf Conductivity $K_{ijk} \times 10^{-10} \text{ esu}$
		0.0020	1.1533
		0.0045	1.1607
	0.1	0.0073	1.1768
		0.0091	1.1780
		0.0120	1.1893
		0.0020	1.1680
		0.0037	1.1715
	0.0	0.0060	1.1866
		0.0078	1.2106
		0.0098	1.2286
		0.0023	1.1715
		0.0048	1.1941
	1.0	0.0063	1.2089
		0.0079	1.2274
		0.0110	1.2629
		0.0020	1.1551
		0.0041	1.1756
	0.9	0.0067	1.2165
		0.0085	1.2320
		0.0104	1.2476

Table 4.1a (continued)

System	Mole fraction of DMF x_j	Weight fraction of polar solute w_{jk}	Uhf Conductivity $K_{ijk} \times 10^{-10}$, esu
		0.0027	1.1606
		0.0044	1.1805
	0.7	0.0072	1.2168
		0.0090	1.2300
		0.0117	1.2653
		0.0028	1.1671
		0.0042	1.1806
	0.3	0.0070	1.1983
		0.0094	1.2272
DMF		0.0130	1.2578
+			
DMA		0.0021	1.1546
in		0.0041	1.1677
	0.1	0.0068	1.2050
benzene		0.0086	1.2210
		0.0109	1.2521
		0.0028	1.1645
		0.0039	1.1775
	0.0	0.0068	1.2020
		0.0089	1.2226
		0.0115	1.2470

Table 4.1b. Values of ultra high frequency conductivity K_{ijk} of (1:1) mixture of binary polar solute in benzene at different temperature

System	Temp. °C	Weight fraction of polar solute w_{jk}	UHF Conductivity $K_{ijk} \times 10^{-10}$ esu
	15	0.0019	1.1546
		0.0052	1.1672
		0.0073	1.1775
		0.0098	1.2031
		0.0127	1.2262
DMF + TMU in benzene	20	0.0019	1.1462
		0.0052	1.1563
		0.0073	1.1863
		0.0098	1.1914
		0.0127	1.2197
	30	0.0019	1.1324
		0.0052	1.1539
		0.0073	1.1664
		0.0098	1.1839
		0.0127	1.1970

Table 4.1b (continued)

System	Temp. in °C	Weight fraction of polar solute w_{jk}	Dhf Conductivity $K_{ijk} \times 10^{-10}$, esu ⁻¹
		0.0023	1.1690
		0.0039	1.1785
	15	0.0063	1.1991
		0.0105	1.2411
		0.0023	1.1541
		0.0039	1.1733
	20	0.0063	1.2005
DMF		0.0105	1.2357
+			
DMA		0.0023	1.1502
in		0.0039	1.1631
benzene	25	0.0063	1.1960
		0.0105	1.2242
		0.0023	1.1447
		0.0039	1.1611
	30	0.0063	1.1821
		0.0105	1.2187

$$\text{and } K_{ij} \times 10^{-10} = 1.1480 + 9.212 W_j + 109.655 W_j^2$$

respectively for the mole fractions $W_j = 0.0, 0.1, 0.3, 0.7, 0.9$ and 1.0 of DMF in DMF + TMU mixture. They are shown graphically in Fig. 4.1.

The usual behaviour of K_{ijk} of a ternary solution in the low concentration region is given by

$$K_{ijk} \times 10^{-10} = \alpha + \beta W_{jk} + \gamma W_{jk}^2$$

if the polar solute under consideration have different amount of polarities. When the individual polar solutes like DMF and DMA have almost of the same amount of polarity the K_{ijk} were found to be linear with W_j as $K_{ijk} \times 10^{-10} = \alpha + \beta W_{jk}$

The linear variation of uhf conductivity K_{ijk} of DMF + DMA mixtures in benzene as a function of W_{jk} of the solutes of was worked out to be :

$$K_{ij} \times 10^{-10} = 1.1447 + 10.5665 W_j$$

$$K_{ijk} \times 10^{-10} = 1.1326 + 11.4739 W_{jk}$$

$$K_{ijk} \times 10^{-10} = 1.1302 + 11.4907 W_{jk}$$

$$K_{ijk} \times 10^{-10} = 1.1413 + 8.9143 W_{jk}$$

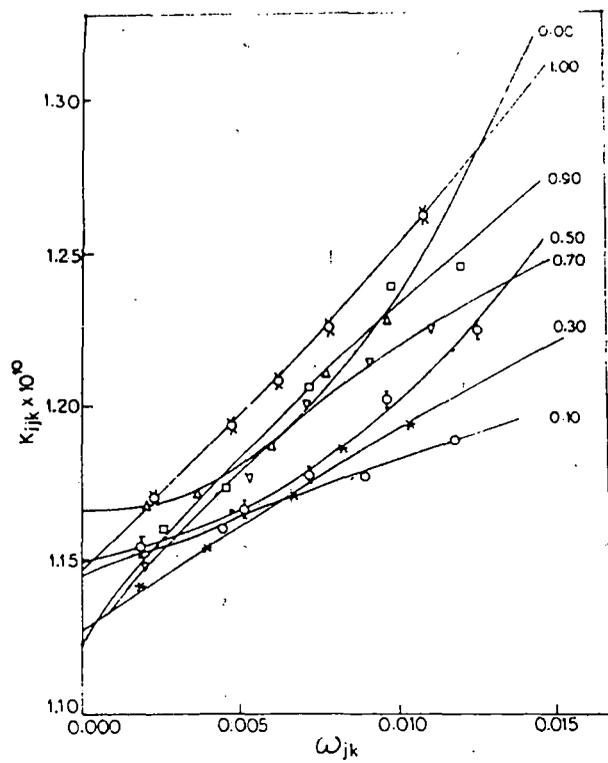


Fig 4.1. Concentration variation of K_{ijk} of DMF + TMU in benzene at different mole fractions of DMF at 15°C.

of

$$K_{ijk} \times 10^{-10} = 1.1268 + 11.2724 W_{jk}$$

$$\text{and } K_{ik} \times 10^{-10} = 1.1393 + 9.3479 W_k$$

for the mole fraction 1.0, 0.9, 0.7, 0.3, 0.1 and 0.0 of DMF in DMF + DMA at 15°C respectively.

Again K_{ijk} of 1:1 mixtures of DMF and TMU as well as DMF and DMA in benzene as a function W_{jk} were also arrived at.:

$$K_{ijk} \times 10^{-10} = 1.1497 + 1.554 W_{jk} + 359.0195 W_{jk}^2 \text{ at } 15^\circ\text{C}$$

$$K_{ijk} \times 10^{-10} = 1.1350 + 4.70 W_{jk} + 153.053 W_{jk}^2 \text{ at } 20^\circ\text{C}$$

$$K_{ijk} \times 10^{-10} = 1.1180 + 7.532 W_{jk} - 99.625 W_{jk}^2 \text{ at } 30^\circ\text{C}$$

$$\text{and } K_{ijk} \times 10^{-10} = 1.1455 + 8.9409 W_{jk} \text{ at } 15^\circ\text{C}$$

$$K_{ijk} \times 10^{-10} = 1.1342 + 9.8777 W_{jk} \text{ at } 20^\circ\text{C}$$

$$K_{ijk} \times 10^{-10} = 1.1303 + 9.2387 W_{jk} \text{ at } 25^\circ\text{C}$$

$$K_{ijk} \times 10^{-10} = 1.1252 + 8.9482 W_{jk} \text{ at } 30^\circ\text{C}$$

respectively.

The hf conductivity data of 1:1 mixtures of two polar solutes of DMF + TMU and DMF + DMA at different temperatures are shown in Figs. 4.2 and 4.3 respectively. It is found difficult to plot the

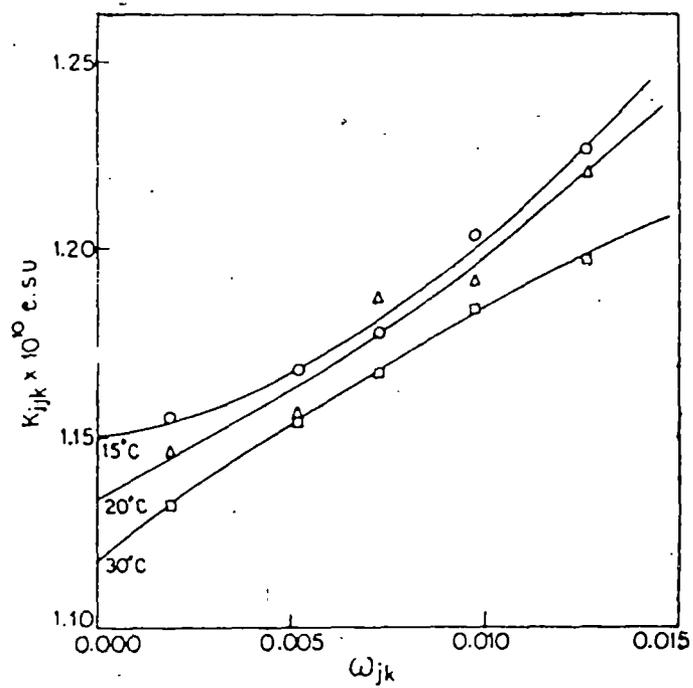


Fig. 4. 2. Concentration variation of K_{ijk} of DMF + TMU (50% each) in benzene at 15, 20 and 30°C.

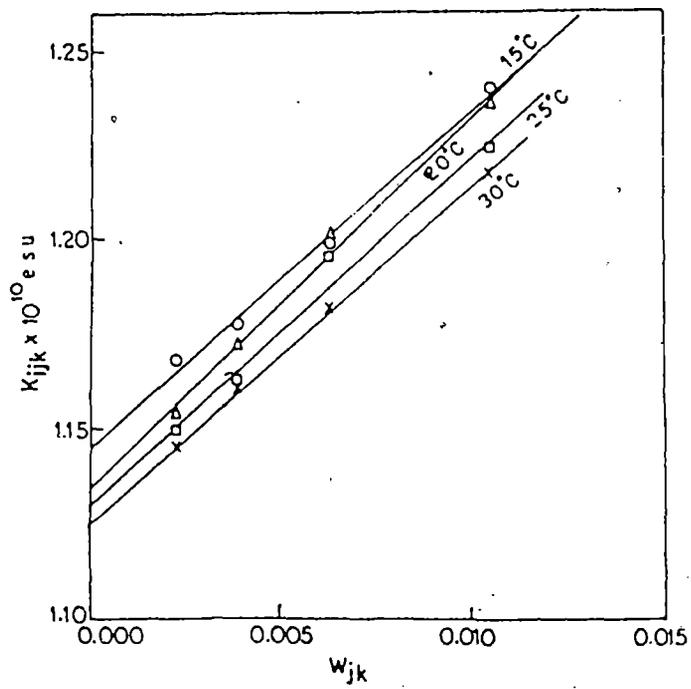


Fig 4.3. Concentration variation of K_{ijk} of DMF + DMA (50% each) in benzene at 15, 20, 25 and 30°C.

conductivities of DMF + DMA in benzene against w_{jk} for different mole fractions x_{jk} at 15°C as their slopes and intercepts are very close probably due to more or less same dipole moments of the two amides. The uhf conductivity data of polar-nonpolar liquid mixture are very sensitive to yield the dipole moment of single or binary polar solute. Hence the information regarding various types of molecular interactions could, however, be inferred from the estimated values of dipole moments. The variation of dipole moment with temperature is not a new concept, but it actually occurs when the polar-nonpolar liquid mixture is subjected to the high frequency electric field (Acharyya et al 1982, 1986, Ras and Bordewijk 1971), probably due to stretching of the bond lengths of molecules. The dipole moment μ_{jk} of (1:1) polar mixtures of DMF + TMU and DMF + DMA have been calculate from the concentration variation of uhf conductivity at different temperatures. The most probable variation of μ_{jk} of 50% DMF and 50% TMU mixture in benzene with respect to the temperature in °C is given by

$$\mu_{jk} = -4.393 + 0.6248 t - 1.157 \times 10^{-2} t^2$$

Showing the zero value of μ_{jk} at 8.31°C and 45.69°C due to orientation of the monomer dipole moments μ_j and μ_k of the individual solutes. The temperature variation of μ_{jk} of 1:1 mixture of DMF and DMA in benzene was also worked out to be :

$$\mu_{jk} = 2.97 + 0.133 t - 3 \times 10^{-3} t^2$$

showing a maximum value of μ_{jk} at 22.5°C. The temperature variation

of μ_{jk} for both the systems are displayed graphically in Fig 4.5

4.2 Theoretical Formulation

According to Murphy and Morgan (1939) the magnitude of total uhf conductivity K_{ijk} for weight fraction W_{jk} of a binary solute (j and K) dissolved in a non-polar solvent (i) is given by

$$K_{ijk} = \frac{\omega}{4\pi} \left(\epsilon'_{ijk}{}^2 + \epsilon''_{ijk}{}^2 \right)^{1/2} \dots\dots\dots(4.1)$$

Where $\omega = 2\pi f$, f being the frequency of the applied electric field. The values of ϵ'_{ijk} of the solution in the uhf electric field is very small and is often equal to optical dielectric constant, but still $\epsilon'_{ijk} \gg \epsilon''_{ijk}$, where ϵ''_{ijk} is the dielectric loss which is responsible for the absorption of electrical energy to offer resistance to the polarisation. Hence it is evident that in the electric field of microwave region, the magnitude of total conductivity become

$$K_{ijk} = \frac{\omega}{4\pi} \epsilon'_{ijk} \dots\dots\dots(4.2)$$

It can be shown that the real part $K'_{ijk} = \omega \epsilon''_{ijk} / 4\pi$

of uhf conductivity of solution of concentration W_{jk} of binary polar solute in non-polar solvent at temperature $T^{\circ}K$ is

$$K'_{ijk} = \frac{\mu_{jk}^2 N \rho_{ijk}}{3M_{jk} kT} \frac{\omega^2 \tau_a}{1 + \omega^2 \tau_a^2} W_{jk} \quad \dots (4.3)$$

where μ_{jk} is the dipole moment of polar solute of molecular weight

$$M_{jk} = x_j M_j + x_k M_k, \quad x_j \text{ and } x_k \text{ being the mole fractions of}$$

individual solutes of molecular weights M_j and M_k respectively in the binary polar mixture, N is the Avogadro number and k is the Boltzmann constant.

But for hf region

$$\epsilon'_{ijk} = \epsilon_\alpha + \frac{\epsilon''_{ijk}}{\omega \tau_a} \quad \dots (4.4)$$

and hence with eq.(4.2) we get

$$K_{ijk} = K_\alpha + K'_{ijk} / \omega \tau_a \quad \dots (4.5)$$

Where $K_\alpha = \omega \epsilon_\alpha / 4\pi$ is a constant conductivity and τ_a is the relaxation time of the associated solute.

Since K'_{ijk} is a function of W_{jk} , we have from eq (4.5)

$$\left[\frac{dK'_{ijk}}{dW_{jk}} \right]_{W_{jk} \rightarrow 0} = \omega \tau_a \left[\frac{dK_{ijk}}{dW_{jk}} \right]_{W_{jk} \rightarrow 0} = \omega \tau_a \beta \quad \dots (4.6)$$

Where β is the slope of $K_{ijk} - W_{jk}$ curve at $W_{jk} \rightarrow 0$.

When $W_{jk} \rightarrow 0$, ρ_{ijk} the density of the solution becomes ρ_i the

density of the solvent and local field F_{ijk} of the solution

becomes $F_i = \left[(\epsilon_i + 2) / 3 \right]^2$, the local field of the solvent.

Under this condition eq. (4.3) on differentiation with respect to W_{jk} takes the form

$$\left[\frac{dk'_{ijk}}{dW_{jk}} \right]_{W_{jk} \rightarrow 0} = \frac{\mu_{jk}^2 N \rho_j F_j}{3 M_{jk} k T} \left[\frac{\omega^2 \tau_a^2}{1 + \omega^2 \tau_a^2} \right] \dots\dots\dots(4.7)$$

From eqs. (4.6) and (4.7) the dipole moment of binary polar mixture becomes

$$\mu_{jk} = \left[\frac{3 M_{jk} k T}{N \rho_i F_i} \frac{\beta}{\omega b} \right]^{1/2} \dots\dots\dots(4.8)$$

Where $b = 1 / \left[1 + \omega^2 \tau_a^2 \right] \dots\dots\dots(4.9)$

Now b could, however, be estimated from eq.(4.9) in terms of the available relaxation time τ_a to obtain the dipole moment of associated solute from eq.(4.8) in a solvent.

4.3 Results and Discussion

The estimated uhf conductivity of DMF + TMU and DMF + DMA in benzene are given in Table 4.1. The equations of K_{ijk} against W_{jk} are already presented in the previous section. The variation of K_{ijk} with W_{jk} of DMF + TMU at different X_j at 15°C are shown in

Fig. 4.1 and that of (1:1) Mixtures of DMF + TMU and DMF + DMA at various temperatures are shown in Figs.4.2 and 4.3 respectively. The weight fraction W_{jk} of the binary solute changes in the solutions, the curves of K_{ijk} against W_{jk} have different intercepts and slopes (Figs. 4.2 and 4.3). This sort of behaviour of $K_{ijk} - W_{jk}$ curves does not occur for different X_j and for different temperatures, if we measure the conductivities in comparatively high concentration region (Acharyya et al 1982). The curves at all the experimental temperatures for a wide range of concentration when are drawn, are expected to meet at a common point on the K_{ijk} - axis because the term $\left[\rho_{ijk} F_{ijk} / T \right]$ in eq. (4.3) assumes a constant value 0.006 at $W_{jk} \rightarrow 0$ for benzene as solvent. At $W_{jk} \rightarrow 0$ the intercepts of $K_{ijk} - W_{jk}$ curves are incidentally different at different temperatures and decrease with the rise of temperature, as observed in Figs. 4.2 and 4.3, due to solvation effect (Datta et al 1981).

When the mole fraction X_j of DMF in the mixtures are in the limit of $X_j = 0.0$ and $X_j = 1.0$ we get what are known as concentration variation of uhf conductivities K_{ik} and K_{lj} of TMU or DMA and DMF respectively at 15°C. The estimated slopes β of this concentration variation of uhf conductivity are very important to yield the dipole moments. The computed dipole moments are tabulated in Table 4.2 along with the slopes β . When $X_j = 0.0$ and 1.0 we get monomer dipole moments μ_k for TMU or DMA and μ_j for DMF respectively. The values of μ , computed from eq. (4.8) in terms of

Table 4.2- Dipole moments of N, N-dimethyl formamide (DMF) in DMF + N,N-tetramethyl urea (TMU) and in DMF + N, N-dimethyl acetamide (DMA) mixtures in benzene as a function of mole fraction x_j of DMF at 15°C as well as those of (1:1) DMF + TMU and (1:1) DMF + DMA mixtures in benzene at different experimental temperature in °C

System	temp t in °C	Mole Fraction DMF x_j	Slope of $K_{ijk} - \omega_{jk}$ curve $\beta \times 10^{-10}$	Assumed molecular wt. M_{jk} of solute	$b = 1/(1+\omega_{jk}^2 r_{jk}^2)$	Computed μ_j, μ_k and μ_{jk} in D (Expt.)	Calculated μ_j, μ_k and μ_{jk} in D from the values of bond moments and bond axes
DMF and TMU in benzene	15	1.00	9.2120	73.0920	0.8406	3.76	3.82
		0.90	11.5870	77.3986	0.6853	4.80	3.63
		0.70	11.9614	86.0118	0.6433	5.31	3.24
		0.30	6.9023	103.2362	0.5120	4.95	2.48
		0.10	3.9273	111.8514	0.6402	3.48	2.10
		0.00	1.2030	116.1580	0.6909	1.89	1.90
DMF and DMA in benzene	15	1.00	10.5665	73.0944	0.8406	4.02	3.82
		0.90	11.4739	74.4971	0.8193	4.29	3.84
		0.70	11.4907	77.3024	0.7543	4.56	3.88
		0.30	8.9143	82.9132	0.6929	4.23	3.96
		0.10	11.2724	85.7185	0.7575	4.74	4.00
		0.00	9.3479	87.1212	0.7660	4.33	4.02
DMF and TMU in benzene	15	0.50	1.5540	94.6250	0.4520	2.39	2.40
	20	0.50	4.7000	94.6250	0.6684	3.42	
	30	0.50	7.5320	94.6250	0.8770	3.94	
DMF and DMA in benzene	15	0.50	8.9409	80.1078	0.6929	4.27	4.27
	20	0.50	9.8777	80.1078	0.7120	4.49	
	25	0.50	9.2387	80.1078	0.7248	4.36	
	30	0.50	8.9482	80.1078	0.7470	4.28	

reported (Sharma and Sharma 1984, 1985) τ_{jk} , for TMU and DMF were thus found to be 1.89 D and 3.76 D respectively. The values of the dipole moment of the associated solutes (solute - solute molecular association) at 15°C, presented in Table 4.2, can, however, be fitted by a polynomial equation as a function of X_j of DMF:

$$\mu_{jk} = 2.5145 + 10.7785 X_j - 9.42 X_j^2$$

The graph of μ_{jk} against X_j satisfying the above equation is shown in Fig 4.4 with experimentally estimated μ_{jk} . The fitted curve, however, excludes two values of dipole moments : one $\mu_k = 1.89$ -D For TMU and the other $\mu_{jk} = 2.39$ D at $X_j = 0.0$ and 0.5 respectively. As X_j of DMF changes μ_{jk} gradually increase in a regular manner and then suddenly drops to a very low value at $X_j = 0.5$ (Fig. 4.4), after $X_j > 0.5$, μ_{jk} slowly decreases thus resembling the convex nature to terminate to $\mu_j = 3.76$ D of solute - solvent associated monomers of DMF at $X_j = 1.0$. This nature of variation of μ_{jk} against X_j may be due to formation of dimers in the liquid mixture of DMF and TMU. The sudden drop in the value of μ_{jk} from its regular behaviour is probable due to the maximum dimerisation in the liquid mixture having mole fraction nearly 0.5 of DMF. In case of DMF and DMA mixture in benzene the monomer for DMA and DMF were found to be $\mu_k = 4.33$ D and $\mu_j = 4.02$ D respectively. The curves in Fig.4.4 for DMF + DMA mixtures drawn with all experimental points shows two peaks : one at $X_j = 0.1$ and other at $X_j = 0.7$ and in the range $0.1 \leq X_j \leq 0.7$ it is simply a concave curve suggesting the formation of dimers in this region.

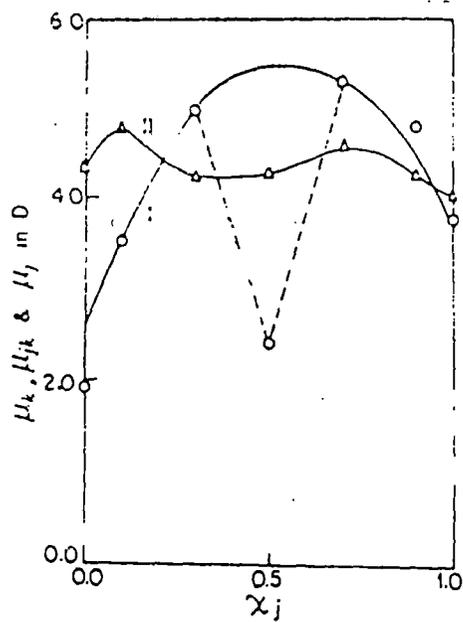


Fig. 4.4. Variation of experimentally observed dipole moments μ_k , μ_{jk} and μ_j with mole fraction of DMF in DMF + TMU and DMF + DMA mixtures at 15°C (-O-O- of DMF + TMU and - Δ - Δ - for DMF + DMA).

But the dipole moment μ_{jk} is to be minimum at $x_j = 0.3$ (Fig.4.4) and hence the dimerisation of this mixture may be maximum near $x_j = 0.3$ unlike the observation made by Sharma and Sharma (1984).

The nature of behaviour of μ_{jk} against temperature in $^{\circ}\text{C}$ are plotted in Fig. 4.5 with the experimentally measured values upon them. The curve of μ_{jk} for the 1st. mixture shows that the monomer solutes orient along their dipole axes such that the resultant dipole moments are zero at 8.31°C and 45.69°C . As shown in Fig.4.5 the μ_{jk} of the expected associate solute for (1.1) DMF + DMA mixture in benzene increases slowly from 2.97 D at 0°C to the maximum 4.49 D at 22.5°C and then slowly decrease to 3.49 D at 40°C . All these data show that the dipole moments of (1.1) binary polar mixtures in non-polar solvent do change with temperature in the hf region of alternating electric field.

Finally. to interpret the experimental monomer dipole moments of the solute, we calculated the theoretical μ_j and μ_k in terms of bond moments, bond axes and bond angles as sketched in Fig.4.5 for DMF, TMU and DMA respectively. In DMF the bond moments of C = O and CH_3 -N act along same direction making resultant moment of 3.74 D while those of CH_3 -N, H-C and N-C act along a common axis with a resultant dipole moment of 0.79 D and perpendicular to C-O [Fig.4.6(i)]. They thus gives rise to the monomer dipole moment 3.82 D of DMF in benzene. But the Table 4.2 shows 3.76 D and 4.02 D as the experimental dipole moments of DMF in the two mixtures respectively probably due to the effect of trace presence of TMU

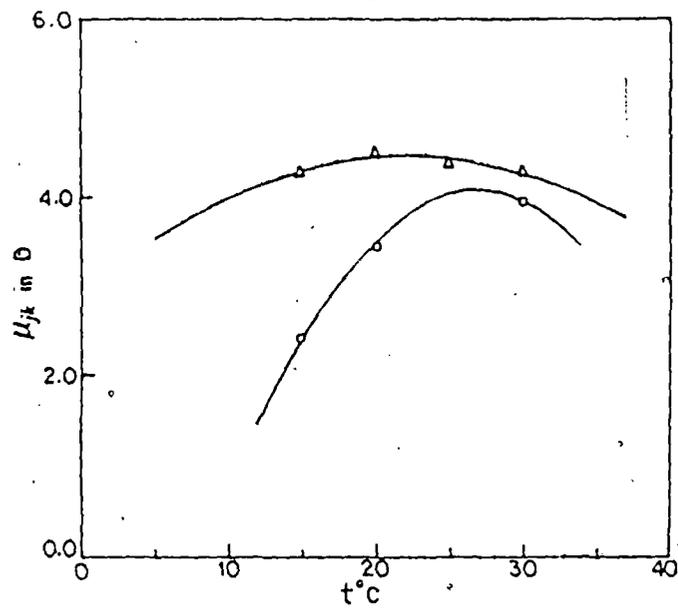


Fig 4.5. Variation of experimentally observed dipole moments with temperatures in °C for DMF + TMU and DMF + DMA in 1:1 mixtures (—O—O— for DMF and TMU and —Δ—Δ— for DMF + DMA).

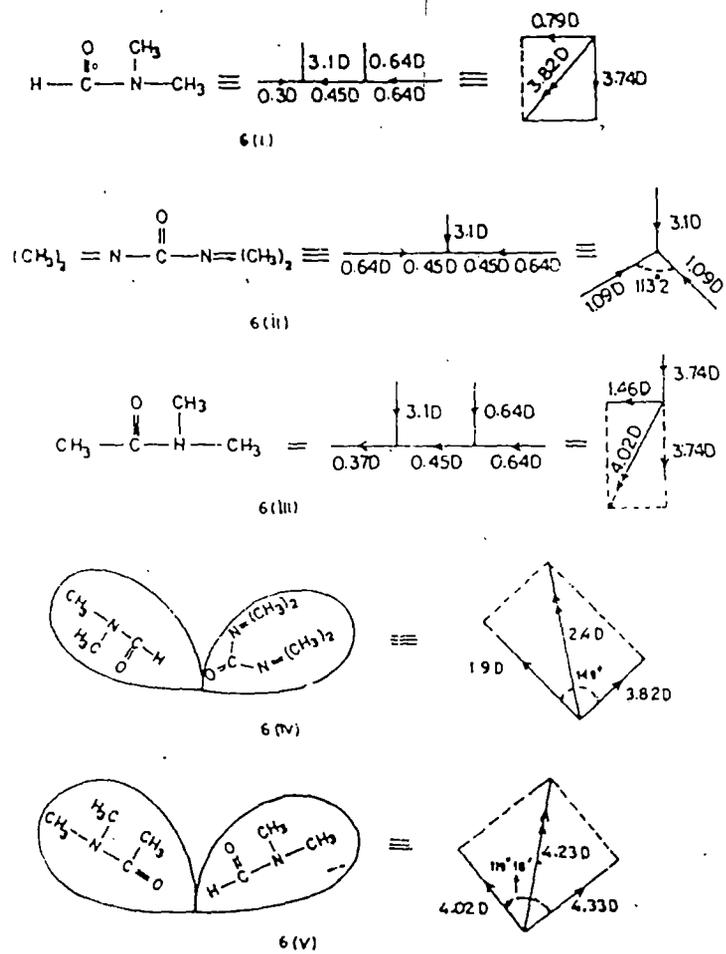


Fig 4.6. (i) Structural form of DMF, (ii) Structural form of TMU, (iii) Structural form of DMA, (iv) Structural form of dimer (DMF + TMU) and (v) Structural form of dimer (DMF + DMA)

and DMA in benzene at $W_{jk} \rightarrow 0$. Both the arms in TMU contain $(\text{CH}_3)_2 = \text{N}$ about a carbon atom in $\text{C} = \text{O}$ forming an angle 113.2° to give a resultant moment of nearly 1.2 D. This in its turn reduces the bond moment of 3.1D of $\text{C} = \text{O}$ to give rise to 1.9D as the monomer dipole moment of TMU [Fig. 4.6 (ii)]. Similarly in case of DMA the group moments of $\text{CH}_3\text{-N}$ and $\text{C} = \text{O}$ act along the same direction while the moments C-CH_3 , C-N , N-CH_3 are in the perpendicular direction [Fig. 4.6 (iii)] giving 4.02 D as the monomer dipole moment of DMA. With this preferred conformational directions for DMF, TMU and DMA the calculate values of dipole moments from vector model, assuming molecules to be planer ones, are in close agreement with the experimental values as evident in Table 4.2. The smaller values of μ_{jk} for 50:50 mixtures of DMF + TMU and DMF + DMA in benzene are due to dimer formation. For dimerisation between DMF and TMU [Fig. 4.6 (iv)] and between DMF and DMA [Fig. 4.6 (v)] in benzene the two monomers attach each other with there most electropositive (-H) and electronegative (-O) elements forming angles 149° and 119.18° in the two mixtures respectively as calculated from the experimental μ_j , μ_k and μ_{jk} values. The values of μ_{jk} of dimers change strongly with temperature probably due to the change of preferred conformational directional angle with temperature. The is more pronounced in the case of maximum dimerisation (Fig.4.5). This may be the reason that μ_{jk} of 50% of DMF in the mixture exhibit zero value at 8.31°C and 45.69°C where as in the 2nd mixture the μ_{jk} changes very

slowly as the maximum dimerisation occurs for 30% of DMF in this mixture.

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CHAPTER V

DIPOLE MOMENTS OF BINARY POLAR SOLUTES FROM ULTRA HIGH FREQUENCY CONDUCTIVITY OF SOLUTION IN NON-POLAR SOLVENT

5.1 Introduction

In recent years the study of dielectric relaxation mechanism of polar liquids dissolved in non-polar solvents from the concentration variation of the ultra high frequency (uhf) conductivity (Acharyya and Chatterjee 1985, Acharyya et al 1986, Ghosh and Chatterjee 1991) of solution is widely used in comparison to the pure liquids because of the absence of dipole-dipole interactions and low viscosity coefficients. The concentration variation on uhf conductivity in a microwave or radio frequency electric field for the polar-nonpolar liquid mixtures is very sensitive to yield the molecular parameters such as relaxation time τ_p , dipole moments μ_j , thermodynamic relaxation parameters ΔH_T , ΔS_T and ΔF_T etc. They also provide one with the information regarding the solute-solvent and solute-solute type of molecular association (Acharyya et al 1986). But the study of dielectric relaxation behaviour of binary polar liquid mixtures in non-polar solvent is of great interest although the data of such mixtures are very scanty. Schallamach (1946), however studied the temperature dependence of a few mixtures of relatively complex non-rigid molecules under a constant radio-frequency electric field and revealed that the mixtures of both associated or non-associated polar molecules correspond to a single relaxation process. The above conclusion was arrived at by Madan (1987) and Vyas and Vashisth (1988) on binary polar mixtures of alcohols, amids and ketones. In contrast, the results of other workers

(Forest and Smyth 1965, Klip et al 1966) suggests the possibility of two dispersion regions to describe the dielectric behaviour of polar mixtures. But still a few systems have been examined so far and even less information is available for polar mixtures in non-polar solvents. The binary polar mixtures of N, N-dimethyl formamide (DMF) with (I) methyl alcohol (MeOH) or (II) acetonitrile (AN) or (III) acetone (AC) respectively in benzene are studied here from our recently developed method (Chatterjee et al 1992). The present investigation is, however, concerned with the estimation of dipole moment of these polar mixtures from the slopes of concentration variation of uhf conductivity at infinite dilution. Sharma et al (1984, 1985) showed the probable solute-solute type of molecular association in the polar mixtures in terms of relaxation time τ_0 . We further studied these systems for understanding the molecular association from our theoretical formulation in terms of dipole moment of the systems and the molecular behaviour in the binary polar mixtures because of the possibility of optimum binary system corresponding to desired physical properties. Moreover in addition to other liquids under the present investigation formamide is a very important non-aqueous dielectric liquid for its wide biological applications. Hence it attracted the attention of a large number of workers (Vyas and Vashisth 1988, Kumler and Porter 1934, Rabinovitz and Pines 1969, Dhull and Sharma 1982). Thus the extensive study of the ternary mixtures of suitable dielectric liquids should be needed to throw much light on the solute-solute

molecular associations which is quite uncommon feature of liquids. The solute-solute type of molecular associations are, however, interpreted as a result of weak hydrogen bonding of the dipole-dipole interactions between the different solutes.

5.2 Theoretical Formulations

The uhf conductivity due to Murphy and Morgan (1939) of Binary solute in a non-polar solvent is given by

$$K_{ijk}^* = K_{ijk}' + j K_{ijk}'' \quad \dots\dots\dots(5.1)$$

where $K_{ijk}' = \omega \epsilon_{ijk}'^2 / 4\pi$ and $K_{ijk}'' = \omega \epsilon_{ijk}'' / 4\pi$

The magnitude of total uhf conductivity is usually computed from the relation

$$K_{ijk} = \frac{\omega}{4\pi} \left[\epsilon_{ijk}'^2 + \epsilon_{ijk}''^2 \right]^{1/2} \quad \dots\dots\dots(5.2)$$

The real part ϵ_{ijk}' of the complex dielectric constant ϵ_{ijk}^* although very small, but still $\epsilon_{ijk}' \gg \epsilon_{ijk}''$, where ϵ_{ijk}'' is the dielectric loss. Hence total uhf conductivity becomes

$$K_{ijk} = \frac{\omega}{4\pi} \epsilon_{ijk}'^2 \quad \dots\dots\dots(5.3)$$

The real part of uhf conductivity of solute having weight fraction W_{jk} of binary polar solute in a non-polar solvent at $T^{\circ}K$ is given by

$$K_{ijk} = \frac{\mu_{jk}^2 N \rho_{ijk} F_{ijk}}{3M_{jk} kT} \left(\frac{\omega^2 \tau_a}{1 + \omega^2 \tau_a^2} \right) W_{jk} \dots\dots\dots(5.4)$$

where τ_a and μ_{jk} are the relaxation time and the dipole moment of binary polar solute respectively having molecular weight $M_{jk} = X_j M_j + X_k M_k$, X_j being the mole fraction of polar liquid j in polar mixture of j and k , and $X_k = 1 - X_j$.

It can be shown in the hf region that $\epsilon'_{ijk} = \epsilon_{\alpha} + \epsilon''_{ijk}/\omega\tau_a$ and hence with the help of eq. (5.3) we get

$$K_{ijk} = K_{\alpha} + K'_{ijk} / \omega \tau_a \dots\dots\dots(5.5)$$

where K_{α} = the constant conductivity = $\omega \epsilon_{\alpha} / 4\pi$.

Since K'_{ijk} is a function of W_{jk} we have

$$\left(\frac{d K'_{ijk}}{d W_{jk}} \right) W_{jk} \rightarrow 0 = \omega \tau_a \beta \dots\dots\dots(5.6)$$

where β is the slope of K'_{ijk} versus W_{jk} curve at $W_{jk} \rightarrow 0$: At $W_{jk} \rightarrow 0$, ρ_{ijk} and F_{ijk} the density and local field of the solution become ρ_i and F_i of the solvent respectively, where

$$F_i = [(ε_i + 2)/3]^2.$$

Differentiating eq. (5.4) with respect to W_{jk} and using eq. (5.6) at $W_{jk} \rightarrow 0$ we ultimately get

$$\mu_{jk} = \left[\frac{3 M_{jk} kT}{N \rho_i F_i} \cdot \frac{\beta}{\omega b} \right]^{1/2} \dots\dots\dots(5.7)$$

Where $b = 1/(1 + \omega^2 \tau_a^2)$ is a dimensionless parameter. Eq.(5.7) can be used to measure the dipole moment of binary polar solute. When $K = 0$ or $j = 0$ the uhf conductivity becomes K_{ij} or K_{ik} to yield the dipole moment μ_j or μ_k of the j th. or the k th. polar solute respectively from eq.(5.7) with the reported τ_a .

5.3 Results and Discussion

The K_{ijk} of polar mixtures (I) DMF + MeOH, (II) DMF + AN and (III) DMF + AC in benzene at mole fractions $X_j = 1.0, 0.9, 0.7, 0.3, 0.1$ and 0.0 of DMF in the polar mixtures at 15°C and those of 1:1 polar mixture in benzene at $15, 20, 25$ and 30°C were estimated using Murphy and Morgan (1939) relation (eq.5.2) from the available measured data of ϵ'_{ijk} and ϵ''_{ijk} of Sharma et al (1984, 1985) under 3.035 cm wavelength electric field and presented in Table 5.1. The hf conductivity in the range $0 < X_j < 1$ are K_{ijk} of solution having binary polar mixture and for $X_j = 1.0$ and 0.0 we get K_{ij} and K_{ik} of solution containing single polar solute. The variation of K_{ij} , K_{ijk} and K_{ik} with the respective weight

Table 5.1a- Values of ultra high frequency conductivity K_{ijk} of binary polar mixtures in benzene at 15°C

System	Mole fraction of DMF X_j	Weight fraction of polar solute W_{jk}	Uhf conductivity $K_{ijk} \times 10^{-10}, \text{esu}$
DMF + MeOH in benzene	1.0	0.0023	1.1715
		0.0048	1.1941
		0.0063	1.2089
		0.0079	1.2274
		0.0110	1.2629
	0.9	0.0028	1.1626
		0.0051	1.1881
		0.0080	1.2231
		0.0098	1.2442
		0.0135	1.2834
	0.7	0.0025	1.1586
		0.0046	1.1830
		0.0070	1.2047
		0.0090	1.2207
		0.0117	1.2538
	0.3	0.0020	1.1506
		0.0040	1.1655
		0.0059	1.1715
0.0087		1.1995	
0.0106		1.2105	

Table 5.1a (continued)

System	Mole fraction of DMF X_j	Weight fraction of polar solute w_{jk}	Uhf conductivity $K_{ijk} \times 10^{-10}$, esu
		0.0025	1.1492
		0.0046	1.1645
	0.1	0.0060	1.1696
		0.0084	1.1944
		0.0116	1.1986
		0.0024	1.1497
		0.0050	1.1595
	0.0	0.0064	1.1645
		0.0086	1.1759
		0.0103	1.1825
		0.0023	1.1715
		0.0048	1.1941
	1.0	0.0063	1.2089
		0.0079	1.2274
		0.0110	1.2629
DMF		0.0020	1.1576
+		0.0057	1.1918
AN	0.9	0.0073	1.2118
in		0.0109	1.2521
benzene		0.0140	1.2931
		0.0025	1.1617
		0.0045	1.1915
	0.7	0.0063	1.2115
		0.0087	1.2365
		0.0108	1.2665

Table 5.1a (continued)

System	Mole fraction of DMF x_j	Weight fraction of polar solute w_{jk}	Uhf conductivity $K_{ijk} \times 10^{-10}, \text{esu}$
		0.0023	1.1665
		0.0041	1.2013
	0.3	0.0064	1.2215
		0.0086	1.2467
		0.0108	1.2915
		0.0024	1.1815
		0.0050	1.2163
	0.1	0.0064	1.2215
		0.0083	1.2514
		0.0103	1.2968
		0.0022	1.1616
		0.0045	1.2012
	0.0	0.0065	1.2263
		0.0081	1.2762
		0.0103	1.2962
		0.0023	1.1715
		0.0048	1.1941
	1.0	0.0063	1.2089
		0.0079	1.2274
		0.0110	1.2629
DMF		0.0025	1.1642
+		0.0040	1.1821
AC		0.0071	1.2201
in	0.95	0.0087	1.2322
benzene		0.0109	1.2675

Table 5.1a (continued)

System	Mole fraction of DMF x_j	Weight fraction of polar solute w_{jk}	Uhf conductivity $k_{ijk} \times 10^{-10}$, esu
		0.0029	1.1596
		0.0043	1.1923
	0.90	0.0063	1.2124
		0.0087	1.2293
		0.0104	1.2546
		0.0020	1.1625
		0.0040	1.1769
	0.70	0.0060	1.2028
		0.0080	1.2208
		0.0103	1.2432
		0.0020	1.1714
		0.0040	1.1813
	0.30	0.0057	1.1982
		0.0080	1.2122
		0.0103	1.2291
		0.0020	1.1620
		0.0038	1.1744
	0.10	0.0060	1.1878
		0.0078	1.2071
		0.0103	1.2215
		0.0017	1.1493
		0.0062	1.1784
	0.00	0.0080	1.1962
		0.0100	1.2185

Table 5.1b- Values of ultra high frequency conductivity K_{ijk} of (1:1) binary polar mixtures in benzene at different temperatures

System	Temperature °C	Weight fraction of polar solute w_{jk}	Uhf conductivity $K_{ijk} \times 10^{-10}$, esu
DMF + MeOH in benzene	15	0.0026	1.1536
		0.0046	1.1770
		0.0066	1.2000
		0.0091	1.2127
		0.0116	1.2384
	20	0.0026	1.1492
		0.0046	1.1742
		0.0066	1.1891
		0.0091	1.2031
		0.0116	1.2263
	25	0.0026	1.1433
		0.0046	1.1636
		0.0066	1.1835
		0.0091	1.2025
		0.0116	1.2173
30	0.0026	1.1383	
	0.0046	1.1621	
	0.0066	1.1846	
	0.0091	1.2000	
	0.0116	1.2152	

Table 5.1b (continued)

System	Temperature °C	Weight fraction of polar solute w_{jk}	Uhf conductivity $K_{ijk} \times 10^{-10}$, esu
		0.0025	1.1616
		0.0053	1.2015
	15	0.0068	1.2264
		0.0083	1.2514
		0.0119	1.2920
		0.0025	1.1517
		0.0053	1.1866
	20	0.0068	1.2214
		0.0083	1.2414
DMF +		0.0119	1.2816
AN in		0.0025	1.1518
		0.0053	1.1816
benzene	25	0.0068	1.2065
		0.0083	1.2364
		0.0119	1.2716
		0.0025	1.1467
		0.0053	1.1816
	30	0.0068	1.2015
		0.0083	1.2263
		0.0019	1.2628

Table 5.1b (continued)

System	Temperature °C	Weight fraction of polar solute w_{jk}	Uhf conductivity $K_{ijk} \times 10^{-10}$, esu
DMF + AC in benzene	15	0.0026	1.1626
		0.0039	1.1829
		0.0058	1.2037
		0.0083	1.2313
		0.0099	1.2420
	20	0.0026	1.1611
		0.0039	1.1794
		0.0058	1.1938
		0.0083	1.2209
		0.0099	1.2360
	25	0.0026	1.1542
		0.0039	1.1715
		0.0058	1.1810
		0.0083	1.2114
		0.0099	1.2229
30	0.0026	1.1408	
	0.0039	1.1680	
	0.0058	1.1750	
	0.0083	1.2050	
	0.0099	1.2169	

fractions was found to be linear. The intercepts α and slopes β of the linear variations of K_{ij} , K_{ijk} and K_{ik} are presented in Table 5.2. The K_{ijk} of 1:1 mixtures as a function of W_{jk} are shown graphically in Fig. 5.1 at 15, 20, 25 and 30°C which showed that the value of K_{ijk} decreases as the temperature increases. The constancy of the factor $(\rho_{ijk} F_{ijk})/T$ at $W_{jk} \rightarrow 0$ in eq. (5.4) suggests that at all the experimental temperatures K_{ijk} should meet at a common point on the K_{ijk} -axis at $W_{jk} = 0$. But in practice the intercepts are all different (Fig. 5.1) and decrease with temperature. This is perhaps due to the solvation effect (Datta et al 1981). The slopes of $K_{ij} - W_j$ and $K_{ik} - W_k$ curves are, however, used to compute dipole moments of single polar solutes from eq. (5.7). The measured values, $\mu = 4.02, 1.65, 3.78$ and 2.95 D for DMF, MeOH, AN and AC respectively (Table 5.2), are very close to the literature values (Dhull and Sharma 1982, Weast Editor 1976-77). The μ_j and μ_k may be considered as monomer dipole moments due to solute-solvent molecular associations. The solute-solvent association can arise due to the interaction of π -electron cloud of the benzene ring with the fractional positive charges on the nitrogen atom ($\frac{1}{2}\text{C}-\text{N}^{\delta+}$), the hydrogen atom ($-\text{O}-\text{H}^{\delta+}$), the nitrogen atom ($\text{C}=\text{N}^{\delta+}$) and the carbon atom ($>\text{C}^{\delta+}=\text{O}$) of DMF, MeOH, AN and AC respectively.

The slopes β of $K_{ijk} - W_{jk}$ curves at $W_{jk} \rightarrow 0$ in the mole fraction range $0 < X_j < 1$ gives us μ_{ij} , the dipole moment of binary polar solute (Table 5.2). For a mixture of two polar molecules j

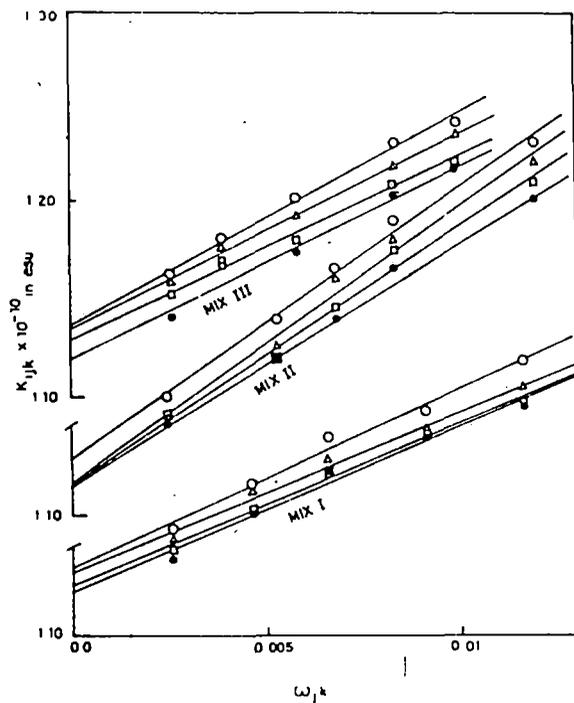


Fig.5.1—uhf Conductivity K_{ijk} of (I) DMF+MeOH, (II) DMF+AN and (III) DMF+AC in benzene against weight fraction ω_{jk} at different temperatures (—○— 15°C, —△— 20°C, —□— 25°C and —●— 30°C)

Table 5.2- Reports the values of experimental intercepts (α) and slopes (β) of conductivity versus concentration linear plots, reported τ_a , computed b, computed experimental dipole moments (μ_j , μ_k and μ_{jk}) with theoretical μ_j and μ_k

System	$t_{0.1}$ in °C	Mole fraction x_j of DMF	$\alpha \times 10^{-10}$ in esu	$\beta \times 10^{-10}$ in esu	Mol.Wt $M_{jk} =$ $(x_j M_j + x_k M_k)$	τ_a (Rept) * in ps	$b = \frac{1}{1 + \omega^2 \tau_a^2}$	μ_j, μ_k and μ_{jk} (Comt) in D	Average dipole moment μ_{jk} (av.) $(= x_j \mu_j + x_k \mu_k)$ in D	μ_j & μ_k (Theo) in D
DMF + MeOH in benzene	15	1.0	1.1447	10.5666	73.0944	7.01	0.8406	4.02	4.02	3.82
		0.9	1.1310	11.3857	68.9892	7.87	0.8072	4.14	3.78	
		0.7	1.1344	10.0244	60.7787	9.83	0.7285	3.84	3.31	
		0.3	1.1354	7.0783	44.3577	11.70	0.6544	2.91	2.36	
		0.1	1.1374	5.7261	36.1472	8.96	0.7643	2.18	1.89	
		0.0	1.1388	4.2240	32.0402	6.00	0.8781	1.65	1.65	1.64
DMF + AN in benzene	15	1.0	1.1447	10.5666	73.0944	7.01	0.8406	4.02	4.02	3.82
		0.9	1.1302	11.3961	69.8902	10.78	0.6905	4.51	4.00	
		0.7	1.1333	12.2275	63.4818	8.94	0.7643	4.23	3.95	
		0.3	1.1372	13.7086	50.6650	8.23	0.7928	3.93	3.85	
		0.1	1.1430	13.7588	44.2566	7.78	0.8107	3.66	3.80	
		0.0	1.1231	17.2720	41.0524	6.04	0.8766	3.78	3.78	3.67
benzene	15	0.5	1.1286	14.0757		8.74	0.7832	4.25	3.90	
	20	0.5	1.1179	14.1762		7.60	0.8178	4.23		
	25	0.5	1.1174	13.2377	57.0734	7.23	0.8322	4.11		
	30	0.5	1.1169	12.4521		6.94	0.8433	4.01		

Table 5.2 (continued)

System	t_0 in °C	Mole fraction x_j of DMF	$\alpha \times 10^{-10}$ in esu	$\beta \times 10^{-10}$ in esu	Mol. Wt $M_{jk} =$ $(x_j M_j + x_k M_k)$	τ_c (Rept) in ps	$b = \frac{1}{1 + \omega^2 \tau_c^2}$	μ_j, μ_k and μ_{jk} (Cont) in D	Average dipole moment μ_{jk} (av) $(= x_j \mu_j + x_k \mu_k)$ in D	μ_j & μ_k (Theo) in D
DMF + AC in benzene		1.0	1.1447	10.5666	73.0944	7.01	0.8406	4.02	4.02	3.82
		0.9	1.1419	10.6848	71.5929	7.94	0.8044	4.09	3.91	
		0.7	1.1409	9.9640	68.5900	10.73	0.6925	4.17	3.70	
	15	0.3	1.1559	7.0894	62.5842	8.76	0.7716	3.18	3.27	
		0.1	1.1473	7.3437	59.5813	5.17	0.9065	2.92	3.06	
		0.0	1.1372	8.1709	58.0798	3.35	0.9585	2.95	2.95	2.75
	15	0.5	1.1383	10.8577		13.34	0.5930	4.60	3.49	
20	0.5	1.1370	10.0415		11.85	0.6486	4.29			
25	0.5	1.1312	9.3474	65.5871	9.15	0.7571	3.88			
30	0.5	1.1209	9.8827		8.10	0.7860	3.97			

* Refs Sharmā et al (1984, 1985)

and k in dilute solute solution in a non-polar solvent there may appear two dispersion regions characterised by relaxation times τ_j and τ_k . Davidson (1961) has shown that, even in the case of two independent polarisation, the resolution of different dispersion regions is difficult unless the relaxation time of one component should be at least five times that the other. Therefore, the binary polar mixtures with τ_a which are not considerably different from one another, as in the present investigation, exhibit a broad dispersion-absorption behaviour in which separate loss peaks do not occur (Madan 1980, 1987). The relaxation of the mixture is thus the resultant of the relaxations of the individual molecules which is of course, strongly influenced by the variety of the molecular environments encountered in rotation as well as by the other factors such as size, shape, solute-solvent and solute-solute interactions etc. When a polar mixture is studied in a non-polar solvent, its ϵ_{ijk}^* is represented by the weighted sum of complex dielectric constants of individual components (Forest and Smyth 1965). Obviously if there is no solute-solute association in the mixture the τ_a as well as μ_{jk} , measured by our method, should vary linearly with the concentration of the components. The formation of dimer leads to τ_a considerably larger than the average value of the individual relaxation times (Crossley 1971, Prakash and Rai 1986). In such a case, the dielectric behaviour of polar mixture is mainly governed by the resulting molecular species.

The measured dipole moments (Table 5.2) of the mixture are plotted against x_j of DMF at 15°C and shown in Fig.5.2. The curves drawn through the experimental points are not the average values between two monomeric dipole moments. These sort of deviations at once indicate the existence of solute-solute molecular association in solutions. The deviations are found to be maximum at $x_j = 0.5$, 0.9 and 0.5 for DMF + MeOH, DMF + AN and DMF + AC respectively, suggesting the maximum dimerisation at those x_j for the mixtures, in agreement with the observations made by Sharma et al (1984, 1985). There may be also jj and kk dimers in the solutions. But the τ_a as well as μ_j and μ_k values, as shown in Table 5.2, exhibit no self-association for DMF, MeOH, AN and AC up to $W_j = 0.0110$ and $W_k = 0.0103$, 0.0100 and 0.0103 in benzene respectively. These W_j and W_k are considerably higher than the concentration of j and k in solution of jk in benzene. This rules out the possibility of jj and kk dimer formation in the solution of polar mixtures. The single relaxation times, measured by Sharma et al (1984, 1985) of these polar mixtures investigated, are found to follow the rate process equation. McDuffie and Litovitz (1962) have pointed out that if a single relaxation time is assumed, the degree of polarisation order in the polar mixtures should decay exponentially. Therefore, the relaxation behaviour of these mixtures in dilute solutions may be assumed to be mainly governed by the resulting relaxing units of jk dimers as an approximation to the true behaviour of the systems. Hence it is reasonable to consider the reported (Sharma et al 1984, 1985) τ_a and measured

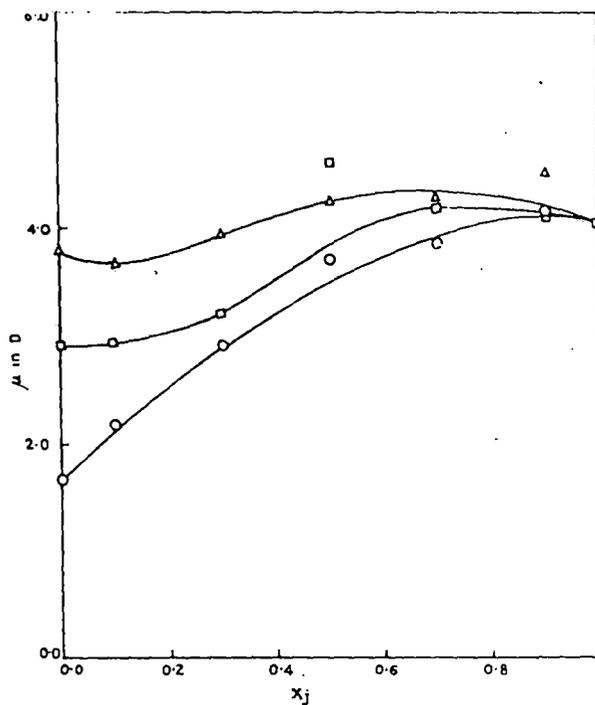


Fig.52—Variation of dipole moment μ against the mole fraction X_j of DMF in the binary polar mixtures of DMF with (I) MeOH (—O—), (II) AN (— Δ —) and (III) AC (— \square —) in benzene at 15°C

μ_{jk} of Table 5.2 as those for jk dimers.

The experimentally computed μ_j and μ_k are compared with theoretically calculated values in terms of bond moments and bond angles as sketched in Fig. 5.3. The moment of C-H, C-N and N-CH₃ groups of DMF act along a common axis, but the group moments C=O and N-CH₃ act \perp to that of C-N (Fig. 5.3a). In MeOH O-CH₃ and O-H make an angle 105° (Fig. 5.3b). In case of AN, C-CH₃ and C \equiv N act along the same axis (Fig. 5.3c) while in AC one of the two C-CH₃ act along C=O and the other is \perp to C=O (Fig. 5.3d). With this preferred conformations, the calculated values of μ_j and μ_k , from vector model, assuming molecules to be planar ones, are 3.82, 1.54, 3.67 and 2.75 D respectively for DMF, MeOH, AN and AC in close agreement with the experimental values of Table 5.2.

For dimer formation between DMF and MeOH the two monomers attach each other with their highly electropositive (-H) and highly electronegatively (-O-) elements forming certain angle viz. 112.7° at 15° C, as calculated from experimental μ_j , μ_k and μ_{jk} values (Fig. 5.3e). In case of DMF + AN, the molecules attach themselves by the interaction of fractional positive charge on N-atom of DMF with π - electron cloud of triple bond of AN molecule. But for DMF + AC fractional positive charge on (-H) of DMF interacts with fractional negative charge on (-O-) of AC to form dimer. The angle between two dipolar axes for mixtures II and III are found to be 114.05° and 98.98° respectively (Figs. 5.3f and 5.3g).

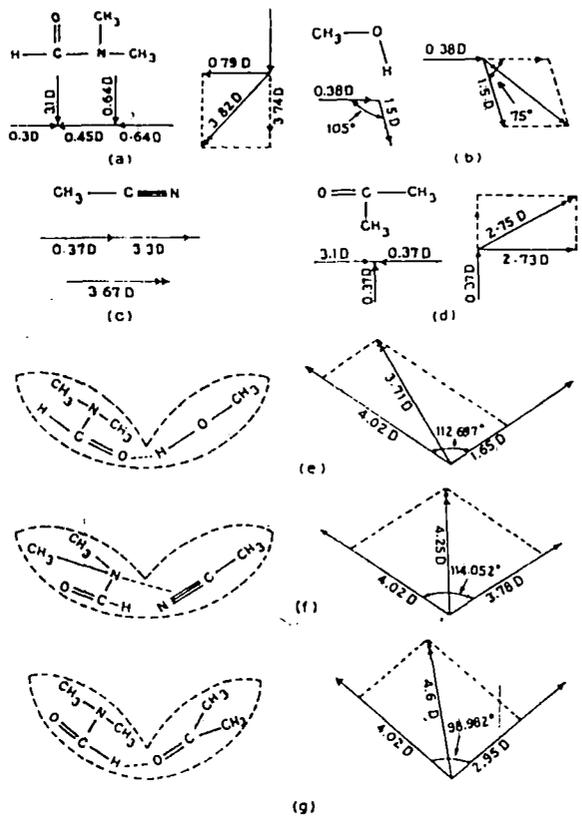


Fig.53—Conformations of different molecules showing orientations of the bond axes, bond moments and also dipole moments [Structural form of (a) DMF, (b) MeOH, (c) AN and (d) AC; structural form of dimers (e) DMF+MeOH, (f) DMF+AN and (g) DMF+AC in 15°C]

The measured μ_{jk} for 1:1 mixtures are plotted against temperature in Fig. 5.4. The variations are, however, represented by the following equations :

$$\begin{aligned} \text{DMF} + \text{MeOH} \quad \mu_{jk} &= 5.075 - 0.122 t + 2.0 \times 10^{-3} t^2 \\ \text{DMF} + \text{AN} \quad \mu_{jk} &= 4.148 + 0.019 t - 8.0 \times 10^{-4} t^2 \\ \text{and DMF} + \text{AC} \quad \mu_{jk} &= 7.120 - 0.226 t + 4.0 \times 10^{-3} t^2 \end{aligned}$$

As observed earlier (Acharyya et al 1986, Ras and Bordewijk 1971) the μ_j of a single polar solute in a non-polar solvent changes with temperature under uhf electric field. But in the present investigation the μ_{jk} of dimer decreases as the temperature rises (Fig. 5.4) and shows a tendency to yield the average value at a certain temperature. The result may be interpreted as an indication of the breaking of weak solute-solute molecular associations due thermal agitation. Therefore, we may conclude that for such binary mixtures there will be only j and k monomers in benzene at higher temperatures giving the average value of μ_j and μ_k .

In case of (1:1) DMF + AN mixture dimer dipole moment decreases very slowly so that the μ_{jk} remains almost constant in the studied temperature range (Fig. 5.4). In this mixture the maximum dimerisation does not occur at $x_j = 0.5$ and the interaction of fractional positive charge on N-atom of DMF with π -electron cloud of triple bond of AN results in greater bond energy compared to the interaction of other two dimers. This may

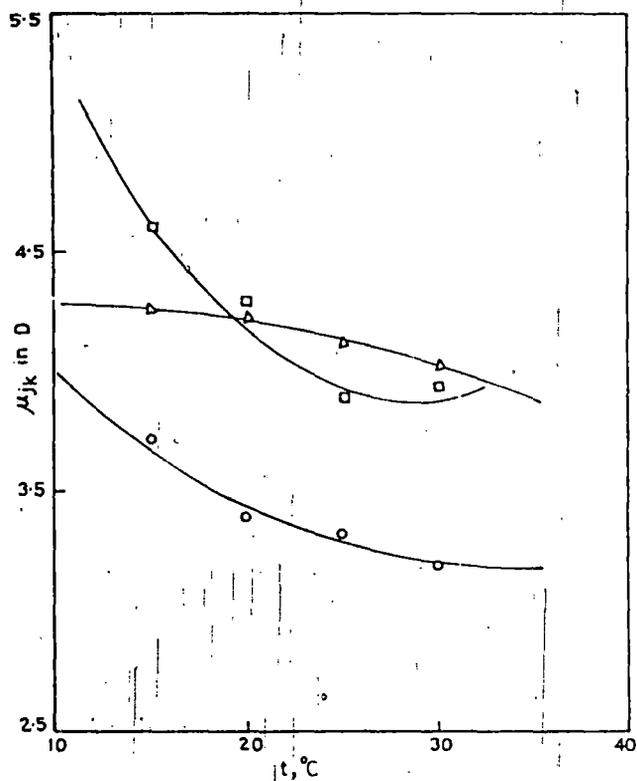


Fig. 4—Temperature variation of dipole moment μ_{jk} of (1:1) mixtures of DMF with (I) MeOH (—○—) (II) AN (—△—) and (III) AC (—□—) in benzene

be the reason that the breaking of molecular association for this (1:1) mixture is comparatively low causing small change in μ_{jk} with temperature unlike other two polar mixtures.

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CHAPTER VI

THEORETICAL RELAXATION TIME OF ASSOCIATED BINARY POLAR MIXTURE IN NON-POLAR SOLVENT

6.1 Introduction:

Study of dielectric relaxation phenomenon of a mixture of two polar liquids in dilute solution of a non-polar solvent under ultra-high frequency electric field is of considerable interest as it throws much light on the presence of various types of molecular associations. It also indicates the possibility of having optimum binary system corresponding to a desired physical property for a binary polar mixture of both associating components in a solvent. Schallamach (1946), from his study of temperature dependence of mixtures of polar molecules under radio frequency electric field, concluded that the dielectric relaxation in mixtures involves a rearrangement of relatively large region and if the components in a mixture are both associating or both non-associating, the dielectric behaviour appears to be correspond to a single relaxation process.

When a dipolar mixture is studied in a dilute solution its complex dielectric constant is represented by a weighted sum of the complex dielectric constants of individual components (Forest and Smyth 1965). Therefore the dependence of dielectric constants, dielectric loss and relaxation time on the concentration of the components should show linearity in the absence of solute-solute type of molecular association in the solution. The occurrence of polar molecular association results in relaxation time considerably higher than those for

unassociated molecules (Crossley 1971, Shama et al 1984, 1985, 1992). In these cases the dielectric behavior of the mixtures is mainly governed by the resulting molecular species.

Recently Yadav and Gandhi (1993) have proposed a theoretical relation for calculating relaxation time τ_{mix} of binary polar mixture in dilute solution of non-polar solvent from the knowledge of the relaxation of the constituent component. Madan (1980, 1987) has also formulated two theoretical relations for computing relaxation time of binary polar mixture. The methods give the theoretical τ_{mix} values which lie between the values of the individual components, but are unable to predict the τ_{mix} values of mixtures where solute-solute associations occur. In this chapter we proposed a theoretical formulation for calculating relaxation times of polar mixtures of two associating liquids in non-polar solvent where solute-solute type of molecular associations really happened.

6.2. Theoretical Formulations:

Debye (1929) has shown that for systems, which can be characterized by a single relaxation time, the complex dielectric constant ϵ^* is related to the relaxation time τ by

$$\frac{\epsilon^* - \epsilon_\alpha}{\epsilon_0 - \epsilon_\alpha} = \frac{1}{1 + j\omega\tau} \quad \dots\dots\dots(6.1)$$

where ϵ_α and ϵ_0 are the dielectric constants of the polar component at infinite frequency and static field respectively. Substituting $\epsilon^* = \epsilon' - j\epsilon''$, we have from real and imaginary parts

$$\omega\tau = \frac{\epsilon''}{\epsilon' - \epsilon_\alpha} \dots\dots\dots(6.2)$$

If τ_j and τ_k are the relaxation times of polar components and τ_{jk} that of their mixture in a non-polar solvent, from eq (6.2) we can write,

$$\omega\tau_j = \frac{\epsilon''_{ij}}{\epsilon'_{ij} - \epsilon_{\alpha ij}} \dots\dots\dots(6.3)$$

$$\omega\tau_k = \frac{\epsilon''_{ik}}{\epsilon'_{ik} - \epsilon_{\alpha ik}} \dots\dots\dots(6.4)$$

$$\omega\tau_{jk} = \frac{\epsilon''_{ijk}}{\epsilon'_{ijk} - \epsilon_{\alpha ijk}} \dots\dots\dots(6.5)$$

Now if the internal field of a polar mixture would not be much different from the internal field of its components, then it can be written as

$$\epsilon'_{ijk} = x_j \epsilon'_{ij} + x_k \epsilon'_{ik} \dots\dots\dots(6.6a)$$

$$\epsilon_{\alpha ijk} = x_j \epsilon_{\alpha ij} + x_k \epsilon_{\alpha ik} \dots\dots\dots(6.6b)$$

and $\epsilon''_{ijk} = x_j \epsilon''_{ij} + x_k \epsilon''_{ik} \dots\dots\dots(6.6c)$

where x_j and x_k are mole fractions of the respective solutes in the polar mixtures.

It has been found in dilute solutions of polar solute in non-polar solvent that the dielectric constants and loss are proportional to the solute concentration (Hassel et al 1964) i.e.

$$\epsilon'_{ij} = \epsilon_i + a'_j \omega_j \quad \dots\dots\dots(6.7a)$$

$$\epsilon''_{\alpha ij} = \epsilon_i + a_{\alpha j} \omega_j \quad \dots\dots\dots(6.7b)$$

and $\epsilon''_{ij} = a''_j \omega_j \quad \dots\dots\dots(6.7c)$

where ϵ_i is the dielectric constant of the solvent.

Substituting eq. (6.6) in eq (6.5) and using eqs (6.3), (6.4) and (6.7) we obtain the relaxation time of polar mixture in dilute solution as

$$\tau_{jk} = \frac{\tau_j + x \tau_k a}{1 + x a} \quad \dots\dots\dots(6.8)$$

or $\tau_{jk} = \frac{a'_j + x a'_k}{\frac{a'_j}{\tau_j} + x \frac{a'_k}{\tau_k}} \quad \dots\dots\dots(6.9)$

where $x = \frac{x_k}{x_j}$ and $a = \frac{a'_k - a_{\alpha k}}{a'_j - a_{\alpha j}}$

The relation (6.8) or (6.9) gives the τ_{jk} values of polar mixtures which are average of the individual components. The relation is not fitted to the solutions of two associating polar mixtures where τ_{jk} become higher than the average value due to solute-solute associations.

The assumption of linear variations of dielectric constants and loss with concentration, as given by eq (6.6), are not true for associating-associating polar mixtures. An examination of the dielectric constants and loss values of both associating binary polar mixtures in a non-polar solvent shows that the ϵ' and ϵ'' values first decrease with the concentration and then increase whereas ϵ'' first increase and then decrease. We can represent these variations by the equations:

$$\epsilon'_{ijk} = x_j \epsilon'_{ij} + (1 - x_j) \epsilon'_{ik} \quad \dots\dots\dots(6.10a)$$

$$\epsilon''_{ijk} = x_j \epsilon''_{ij} + (1 - x_j) \epsilon''_{ik} \quad \dots\dots\dots(6.10b)$$

and $\epsilon''_{ijk} = x_j \epsilon''_{ij} + (1 - x_j^2) \epsilon''_{ik} \quad \dots\dots\dots(6.10c)$

Substituting eqs (6.10) in eq (6.5) with eqs (6.3), (6.4) and (6.7) we get

$$\tau_{jk} = \frac{x_j \tau_j + (1 - x_j^2) \tau_k a}{x_j^2 + x_k^2} \dots\dots\dots(6.11)$$

$$\text{or } \tau_{jk} = \frac{x_j a_j'' + (1 - x_j^2) a_k''}{x_j^2 \frac{a_j''}{\tau_j} + x_k^2 \frac{a_k''}{\tau_k}} \dots\dots\dots(6.12)$$

where $a = (a_k' - a_{\alpha k}) / (a_j' - a_{\alpha j})$

The eq (6.11) or (6.12) may be used to calculate the theoretical values of relaxation time of mixture of two associating polar liquids in a non-polar solvent in terms of individual relaxation time. For $x_j = 1$ eq.(6.11) or (6.12) reduces to $\tau_{jk} = \tau_j$ and for $x_j = 0$ the equation gives $\tau_{jk} = \tau_k$. The slopes of the linear plots of dielectric constants or loss against concentration, as given by eq.(6.7), be used to calculate τ_{jk} from eq. (6.11) or (6.12) with the advantage that individual errors in particular values of dielectric constants and loss are minimized.

6.3 Results and Discussion:

The simple theoretical relations for calculating τ_{jk} , which are developed here, have been tested by six selected polar mixtures of two associating liquids containing forty one compositions in dilute solution of non-polar solvent using available dielectric relaxation data in the literature (Sharma et

al 1984, 1985, 1992). The theoretical values of τ_{jk} , calculated by the eqs (6.9) and (6.12) using τ_j and τ_k of the individual components and the slopes a_j'' and a_k'' of the linear variations of dielectric loss against weight fraction, are placed in Table 6.1 along with a_j'' and a_k'' .

The development of suitable theoretical relation is of considerable importance for obtaining information about the relaxation phenomena of binary polar mixtures as well as for the formulation of adequate models of dielectric liquid relaxation. The eq.(6.8) or (6.9) has been developed with the assumption that the internal field of the pure component would not be different from the internal field of the mixture and ϵ'_{ijk} , ϵ''_{ijk} and ϵ'_{ijk} , can be expressed by a simple mixing relation as in eq.(6.6). This relation is not different from the relation recently developed by Yadav and Gandhi (1993). The τ_{jk} values of the systems, calculated by eq.(6.9), are always within τ_j and τ_k values and are very close to the average values obtained by the equation $\tau_{jk} = x_j \tau_j + x_k \tau_k$, as shown in Table 6.1. These values show relatively large deviations from the experimental values (Table 6.1) for the systems studied. The relations to compute τ_{jk} given by Madan (1980, 1987) also yield the values which lie between the τ values of the individual components. These relations are not applicable to the polar mixtures of both associating solutes in dilute solution where τ_{jk} values are expected to be higher than the average values due to increase in size in rotating unit as a

Table 6.1 Theoretical relaxation time (τ_{jk}) of binary polar mixtures in benzene* with experimental ones at 15°C

Mixtures	x_j	a''_j	a''_k	Relaxation Time In P Sec			
				Computed from eq(6.9)	$\tau_{jk} = x_j \tau_j + x_k \tau_k$	Computed from eq(6.12)	Experimental τ_{jk}
Dimethyl formide (DMF)	1.0			7.01	7.01	7.01	7.01
+ Methyl alcohol (MeOH)	0.9			6.96	6.91	7.98	7.87
	0.7			6.85	6.71	10.05	9.83
	0.5	10.9381	4.1223	6.70	6.51	11.67	12.87
	0.3			6.50	6.30	11.32	11.70
	0.1			6.20	6.10	8.16	8.94
	0.0			6.00	6.00	6.00	6.00
DMF	1.00			7.01	7.01	7.01	7.01
	0.95			6.84	6.83	7.34	7.43
	0.90			6.67	6.64	7.64	7.94
+ Acetone (AC)	0.70			5.98	5.91	8.47	10.73
	0.50	10.9381	4.7975	5.26	5.18	8.21	13.34
	0.30			4.52	4.45	6.70	8.76
	0.10			3.75	3.72	4.48	5.17
	0.00			3.35	3.35	3.35	3.35

Table 6.1 (continued)

Mixtures	x_j	a''_j	a''_k	Relaxation Time In P Sec			
				Computed from eq(6.9)	$\tau_{jk} = x_j \tau_j + x_k \tau_k$	Computed from eq(6.12)	Experimental τ_{jk}
	1.0			7.01	7.01	7.01	7.01
DMF	0.9			6.89	6.91	8.28	10.78
+	0.7			6.67	6.72	10.12	8.94
Acetonitrile	0.5	10.9381	11.6772	6.47	6.53	10.49	8.47
(AN)	0.3			6.29	6.33	9.31	8.23
	0.1			6.12	6.14	7.21	7.78
	0.0			6.04	6.04	6.04	6.04
AC	1.0			5.08	5.08	5.08	5.08
+	0.7			5.07	5.07	7.42	7.98
Dimethylsul-	0.5	16.7589	9.8830	5.06	5.06	8.18	11.27
phoxide	0.3			5.05	5.05	7.33	4.46
(DMSO)	0.0			5.03	5.03	5.03	5.03

Table 6.1 (continued)

Mixtures	x_j	a''_j	a''_k	Relaxation Time in P Sec			
				Computed from eq(6.9)	$\tau_{jk} = x_j \tau_j + x_k \tau_k$	Computed from eq(6.12)	Experimental τ_{jk}
	1.0			7.01	7.01	7.01	7.01
DMF	0.9			7.25	7.39	8.68	10.91
+	0.7	10.9381	10.3073	7.79	8.14	12.28	11.99
Tetramethylu- rea (TMU)	0.5			8.44	8.89	15.20	17.73
	0.3			9.22	9.64	15.62	15.47
	0.1			10.19	10.39	12.88	12.07
	0.0			10.77	10.77	10.77	10.77
	1.0			7.01	7.01	7.01	7.01
	0.9			7.14	7.20	8.49	7.56
DMF	0.7			7.44	7.58	11.52	9.19
+	0.5	10.9381	9.4159	7.77	7.96	13.63	10.72
Dimethylacet- amide (DMA)	0.3			8.17	8.33	13.45	9.83
	0.1			8.63	8.71	10.76	9.11
	0.0			8.90	8.90	8.90	8.90

* For AC + DMSO mixture temperature is 25°C and solvent is carbon tetrachloride

result of solute-solute molecular association.

The internal field of polar mixture depends upon the dipole moments of its components and dipole-dipole interactions. Hence the internal field of associated polar mixtures in non-polar solvent may be expected to be different from the internal field of individual components. This change in internal field perhaps the reason of non-linear variation of dielectric constants and loss against concentration in the polar mixtures as given by eq.(6.10). The eq.(6.12) formulated with the above assumption, has been used to calculate τ_{jk} of the systems. These values are close to the experimental values for most of the systems. The deviations of the theoretical τ_{jk} values from the experimental ones, that have been appeared in case of some systems, are appreciably less than the deviations of τ_{jk} values calculated by other methods. These theoretical τ_{jk} values are plotted against mole fractions of one of the components in six binary mixtures containing both associated solute in dilute solution as shown in Fig 6.1. The figure shows that the relaxation time increases from τ_j at $x_k = 0.0$ as x_k is increased and reaching peak values decreases and finally drop to τ_k at $x_k = 1.0$ for all the mixtures. These curves (Fig 6.1) indicate the presence of associated solutes due to solute-solute molecular association and the molecular association is maximum through a small region of x_k which is consistent with the experimental results (Sharma et al 1984, 1985, 1992). In most of the systems the region of maximum

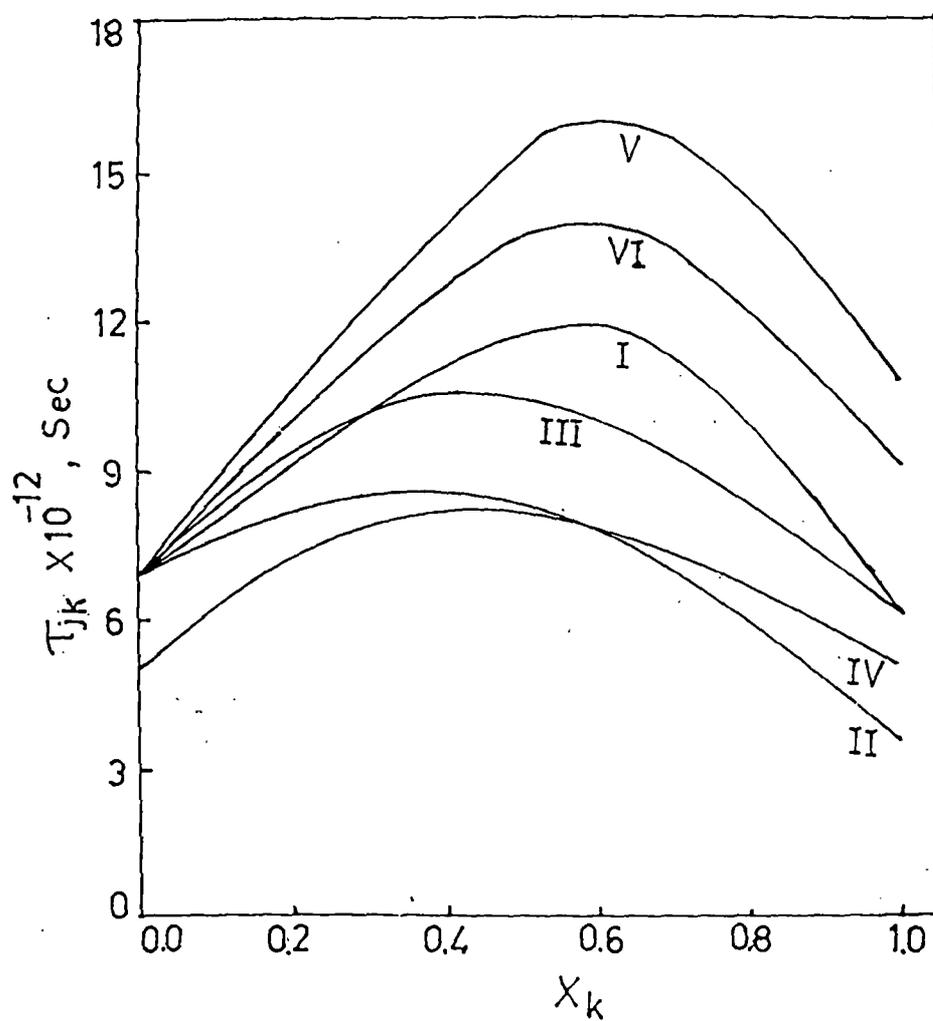


Fig. 6.1 - Variation of theoretical τ_{jk} against mole fraction X_k (I DMF + MeOH, II DMF + AC, III DMF + AN, IV AC + DMSO, V DMF + TMU and VI DMF + DMA)

molecular associations as given by the theoretical curves agree well with results given by Sharma et al (1984, 1985, 1992) on the basis of experimental τ_{jk} . It is thus obvious from the results that the predictions of τ_{jk} values calculated by eq (6.12), which is based on Debye (1929) equation, for a polar mixture containing two associating liquids in a non-polar solvent is better than those by the other methods.

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CHAPTER VII

DOUBLE RELAXATION TIME OF NON-SPHERICAL POLAR LIQUIDS IN
NON-POLAR SOLVENT - A NEW APPROACH BASED ON SINGLE FREQUENCY
MEASUREMENT

7.1 Introduction

The dielectric relaxation of polar liquid in non-polar solvent is much more simpler in comparison to pure polar liquid because in dilute solution of polar liquid the effects of the macroscopic viscosity, the dipole interaction, the internal field etc. are made to be minimised. The dielectric relaxation parameters viz the relaxation times τ_1 and τ_2 , the dipole moments μ_1 and μ_2 etc. are effective tools to investigate the molecular and intra molecular rotation, sizes, shapes and structures of polar molecules. Careful investigation of the phenomenon of dielectric relaxation in binary (Acharyya and Chatterjee 1985) and ternary (Chatterjee et al 1992, Saha and Acharyya, 1993) mixtures of solute solvent is therefore necessary to throw much light on the structures of the polar liquids.

Khamesharq and Sisodia (1980), Gupta et al (1978) and Arrawatia et al (1977) measured the static dielectric constant ϵ_{oij} , the square of the refractive indices η_{Dij}^2 , the real ϵ'_{ij} and the imaginary ϵ''_{ij} parts of the complex dielectric constant ϵ_{ij}^* of five and seven disubstituted anilines and benzene respectively in solvents benzene and carbon tetrachloride at 35°C under a single high frequency 9.945 GHz electric field. Aniline as well as benzene derivatives are expected to absorb much strong in microwave electric field due to presence of the flexible

parts such as methyl or other groups. They are, therefore, expected to have more than one relaxation times because of the existence of internal rotation of these groups. Although one could not make strong conclusion based on single frequency measurement provided the experimental values of ϵ_{oij} and $\epsilon_{\alpha ij}$ are not accurately known. The nonspherical molecular liquids on the other hand, are known to be non-Debye in their relaxation behaviour.

The existing methods due to Bergmann et al (1960) was involved with the measurements of ϵ'_{ij} , ϵ''_{ij} , $\epsilon_{\alpha ij}$ and ϵ_{oij} of a nonspherical polar liquid (j) in solvent (i) for various frequencies at a given experimental temperature in $^{\circ}\text{C}$ to yield τ_1 and τ_2 . They (1960) actually used the Cole - Cole plot to achieve τ_1 and τ_2 to represent the relaxation times of the smallest flexible unit attached to the parent ring and the molecular itself. Kasta et al (1969) subsequently simplified the procedure due to Bergmann et al (1960) by measuring the experimental parameters at two given frequencies of the electric field in the microwave region.

We, under this context, therefore, thought to suggest an alternative method in which the single frequency measurements of dielectric relaxation parameters like ϵ'_{ij} , ϵ''_{ij} , $\epsilon_{\alpha ij}$ and ϵ_{oij} (Khameshard and Sisodia 1980, Gupta et al 1978 and Arrawatia et al 1977) for some highly nonspherical polar liquids like aniline and benzene derivatives in solvents benzene and carbon

tetrachloride respectively are enough to estimate τ_1 and τ_2 within the framework of Debye model (Bergmann et al 1960). The systems of polar-nonpolar liquid mixtures under investigation are placed in the first column of each table. Moreover, such rigorous studies on various types of di- or even mono - substituted polar compounds in nonpolar solvents could, however, be made in order to detect the existence of double relaxation phenomena from available data measured under a single frequency electric field of GHz region. Finally, τ_1 and τ_2 thus estimated from our method based on single frequency measurement which appears to be much more simpler, can be used to obtain μ_1 and μ_2 of the polar molecules from the slope β of the concentration variation of ultra high frequency conductivity K_{1j} of the solution in order to explore their conformations.

7.2 Theoretical formulation to estimate τ_1 , τ_2 and c_1 , c_2

The relative contribution of c_1 and c_2 towards the dielectric relaxation by the two extreme values τ_1 and τ_2 (Higasi et al 1960) can be given by (Bergmann et al 1960):

$$\frac{\epsilon'_{ij} - \epsilon_{\infty ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}} = c_1 \frac{1}{1 + \omega^2 \tau_1^2} + c_2 \frac{1}{1 + \omega^2 \tau_2^2} \dots\dots\dots(7.1)$$

$$\frac{\epsilon''_{ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}} = c_1 \frac{\omega \tau_1}{1 + \omega^2 \tau_1^2} + c_2 \frac{\omega \tau_2}{1 + \omega^2 \tau_2^2} \dots\dots\dots(7.2)$$

provided $c_1 + c_2 = 1$. The symbols used in equations (7.1) and (7.2) convey their usual meanings.

$$\text{Let } x = \frac{\epsilon'_{ij} - \epsilon_{\alpha ij}}{\epsilon_{\alpha ij} - \epsilon_{\alpha ij}}, \quad y = \frac{\epsilon''_{ij}}{\epsilon_{\alpha ij} - \epsilon_{\alpha ij}} \quad \text{and } w \tau = \alpha$$

The above equations (7.1) and (7.2) can be written as:

$$x = c_1 a_1 + c_2 a_2 \quad \dots\dots\dots(7.3)$$

$$y = c_1 b_1 + c_2 b_2 \quad \dots\dots\dots(7.4)$$

where $a = \frac{1}{1 + \alpha^2}$ and $b = \frac{\alpha}{1 + \alpha^2}$. The suffices 1 and 2

are related with τ_1 and τ_2 respectively. Solving equations (7.3) and (7.4) for c_1 and c_2 one gets

$$c_1 = \frac{(\alpha \alpha_2 - y)(1 + \alpha_1^2)}{\alpha_2 - \alpha_1} \quad \dots\dots\dots(7.5)$$

$$c_2 = \frac{(y - \alpha \alpha_1)(1 + \alpha_2^2)}{\alpha_2 - \alpha_1} \quad \dots\dots\dots(7.6)$$

provided $\alpha_2 > \alpha_1$. Now adding equation (7.5) and (7.6) we get since $c_1 + c_2 = 1$,

$$\frac{1 - x}{y} = (\alpha_1 + \alpha_2) - \frac{x}{y} \alpha_1 \alpha_2$$

$$\text{or, } \frac{\epsilon'_{oi j} - \epsilon'_{ij}}{\epsilon'_{ij} - \epsilon_{\alpha ij}} = \omega (\tau_1 + \tau_2) \frac{\epsilon''_{ij}}{\epsilon'_{ij} - \epsilon_{\alpha ij}} - \omega^2 \tau_1 \tau_2 \dots\dots\dots(7.7)$$

which is simply a straight line between $\frac{\epsilon'_{oi j} - \epsilon'_{ij}}{\epsilon'_{ij} - \epsilon_{\alpha ij}}$ and

$$\frac{\epsilon''_{ij}}{\epsilon'_{ij} - \epsilon_{\alpha ij}} \text{ having intercept } - \omega^2 \tau_1 \tau_2 \text{ and slope } \omega (\tau_1 + \tau_2)$$

where $\omega = 2 \pi f$, f being the frequency of the applied electric field in GHz region. When equation (7.7) is fitted with the experimental data ϵ'_{ij} , ϵ''_{ij} , $\epsilon_{oi j}$ and $\epsilon_{\alpha ij}$ for different concentrations w_j of each of the polar molecules at 35°C, we get the intercept and slope and the corresponding values of τ_1 and τ_2 found as shown in table (7.1) along with the reported τ . The error as well as Correlation Coefficient were also found out for each curve of equation (7.7) and placed in table 7.1, only to see how far they are linear as shown in figure (7.1).

The Fröhlich parameters A , were $A = \ln (\tau_2 / \tau_1)$ shown in table 7.2 for all the polar compounds are used to evaluate both x and y of equation (7.3) and (7.4) in terms of ω and small limiting relaxation time τ_a , where $\tau_a = \tau_1$ by the following

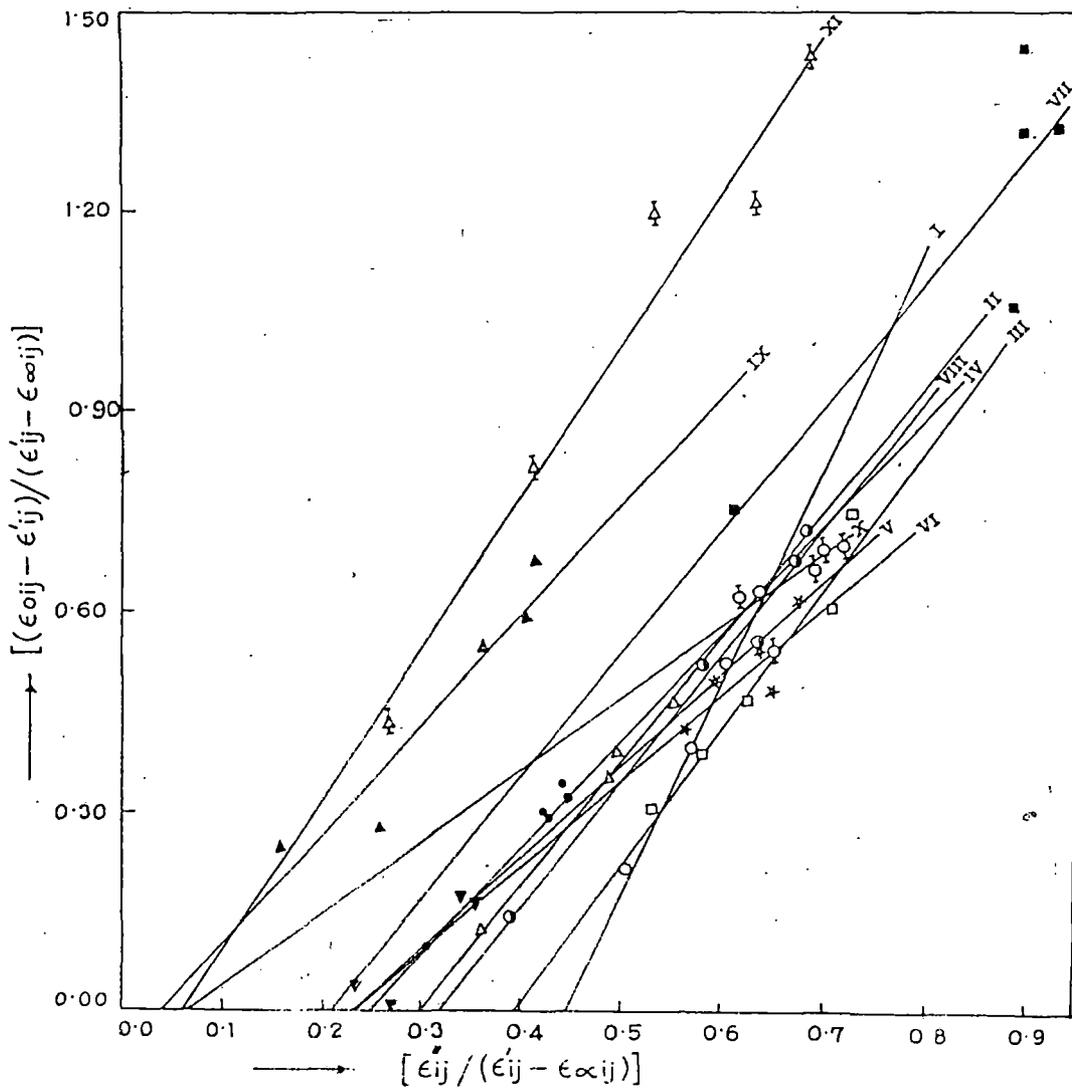


Fig. 7.1 - Straight line plot of $[(\epsilon'_{0ij} - \epsilon'_{ij}) / (\epsilon'_{ij} - \epsilon_{\infty ij})]$ against $[\epsilon''_{ij} / (\epsilon'_{ij} - \epsilon_{\infty ij})]$ for the polar-nonpolar liquid mixtures at 35°C (Table 7.1)

Table 7.1: The double relaxation times τ_1 (smaller) and τ_2 (larger) estimated from intercepts and slopes of equation (7) with errors and correlation coefficients along with rept. τ of polar liquids.

System with sl.no. and molecular wt (M_j) in gm.	Intercept & slope of equation (7)	Correlation coefficient (r)	% error in regression technique	Estimated value of τ_1 & τ_2 in psec.	Reported τ in psec.
i) 4 chloro 2 methyl aniline in benzene $M_j = 141.52$	-1.4276 3.2169	0.9964	1.33	8.51 42.97	18.5
ii) 3 chloro 4 methyl aniline in benzene $M_j = 141.52$	-0.5605 1.8913	0.9982	0.76	5.89 24.38	13.6
iii) 5 chloro 2 methyl aniline in benzene $M_j = 141.52$	-0.8107 2.0749	0.9727	3.67	8.36 24.85	16.6
iv) 3 chloro 2 methyl aniline in benzene $M_j = 141.52$	-0.3862 1.5960	0.9918	1.09	4.76 20.78	9.9
v) 2 chloro 6 methyl aniline in benzene $M_j = 141.52$	-0.3132 1.3711	0.9250	2.77	4.63 17.31	7.8
vi) 0 chloro nitro-benzene in benzene $M_j = 157.5$	-0.3033 1.3129	0.8170	3.77	4.79 16.22	13.5

Table 7.1 (continued)

System with sl.no. and molecular wt (M_j) in gm.	Intercept & slope of equation (7)	Correlation coefficient (γ)	% error in regression technique	Estimated value of τ_1 & τ_2 in $\mu\text{sec.}^2$	Reported τ in psec.
vii) 4 chloro 3 nitro- toluent in benzene $M_j = 171.5$	-0.3863 1.8623	0.8776	11.90	3.81 25.99	20.9
viii) m-nitrobenzotrifluo- ride in benzene $M_j = 191.0$	-0.6003 1.9038	0.9929	2.44	6.38 24.09	19.7
ix) 4 chloro 3 nitrobenz- otrifluoride in carbon tetrachloride $M_j = 225.5$	-0.0587 1.6634	0.9524	5.33	0.58 26.04	21.1
x) O-nitro benzotriflu- oride in benzene $M_j = 191.039$	-0.0620 1.0560	0.6992	4.17	0.99 15.90	13.7
xi) 4 chloro 3 nitro- toluent in carbon tetrachloride $M_j = 171.5$	-0.1335 2.2819	0.9771	7.51	0.96 35.56	35.0
xii) 4 chloro 3 nitrobenz- otrifluoride in benzene $M_j = 225.5$	2.5194 -3.0302	-0.8599	13.07 10.87	10.2

Table 7.1 (continued)

	System with sl.no. and molecular wt (M_j) in gm.	Intercept & slope of equation (7)		Correlation coefficient (γ)	% error in regression technique	Estimated value of τ_1 & τ_2 in μ psec.		Reported τ in psec.
xiii)	m-amino benzotrifluoride in benzene $M_j = 161.05$	0.8445	0.0452	0.0088	11.38	15.07	14.5
xiv)	O-chloro 3 nitrobenzene in carbon tetrachloride $M_j = 157.5$	0.0194	1.2973	0.9277	5.57	21.00	15.8
xv)	O-chloro benzotrifluoride in benzene $M_j = 180.5$	0.2856	0.5696	0.1405	19.10	14.25	12.3

equations (Fröhlich 1949):

$$\frac{\epsilon'_{ij} - \epsilon_{\infty ij}}{\epsilon_{\infty ij} - \epsilon_{\infty ij}} = 1 - \frac{1}{2A} \ln \frac{1 + e^{2A} \omega^2 \tau_a^2}{1 + \omega^2 \tau_a^2} \dots\dots\dots(7.8)$$

$$\frac{\epsilon''_{ij}}{\epsilon'_{ij} - \epsilon_{\infty ij}} = \frac{1}{A} \left[\tan^{-1} (e^A \omega \tau_a) - \tan^{-1} (\omega \tau_a) \right] \dots\dots\dots(7.9)$$

The computed values of x and y from the above equations and the corresponding c_1 and c_2 from equations (7.1) and (7.2) are presented in table 7.2. Again the left hand sides of equation (7.1) and (7.2) are obviously the functions of W_j of the solute in a given solvent as evident from the plots of x and y against W_j in figures 7.2 and 7.3 respectively. This at once prompted us to get the fixed values of x and y when $W_j \rightarrow 0$ from figures 7.2 and 7.3 to estimate c_1 and c_2 which are shown in table 7.2 for comparison with those of Fröhlich (1949). This is really in conformity with the fixed estimated values of τ_1 and τ_2 from the slope and intercept of equation (7.7) for each compound when substituted on the right hand sides of equations (7.1) and (7.2).

7.3 Mathematical formulations to estimate μ_1 and μ_2 .

According to Murphy and Morgan (1939) the uhf conductivity K_{ij} as given by

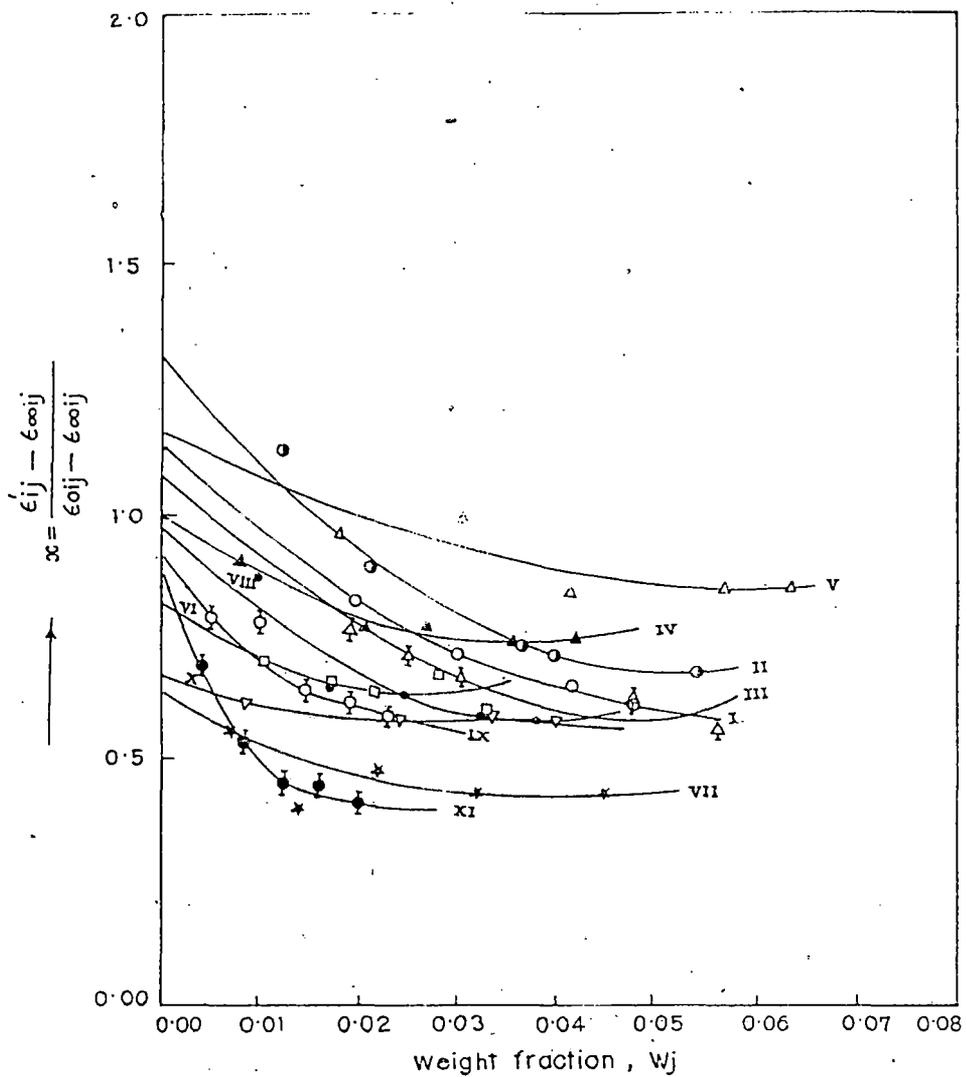


Fig. 7.2 - Variation of $\left[\frac{\epsilon'_{ij} - \epsilon_{\infty ij}}{\epsilon_{oij} - \epsilon_{\infty ij}} \right]$ against weight fraction W_j of polar solutes in dilute solution of non-polar solvent at 35°C (Table 7.2)

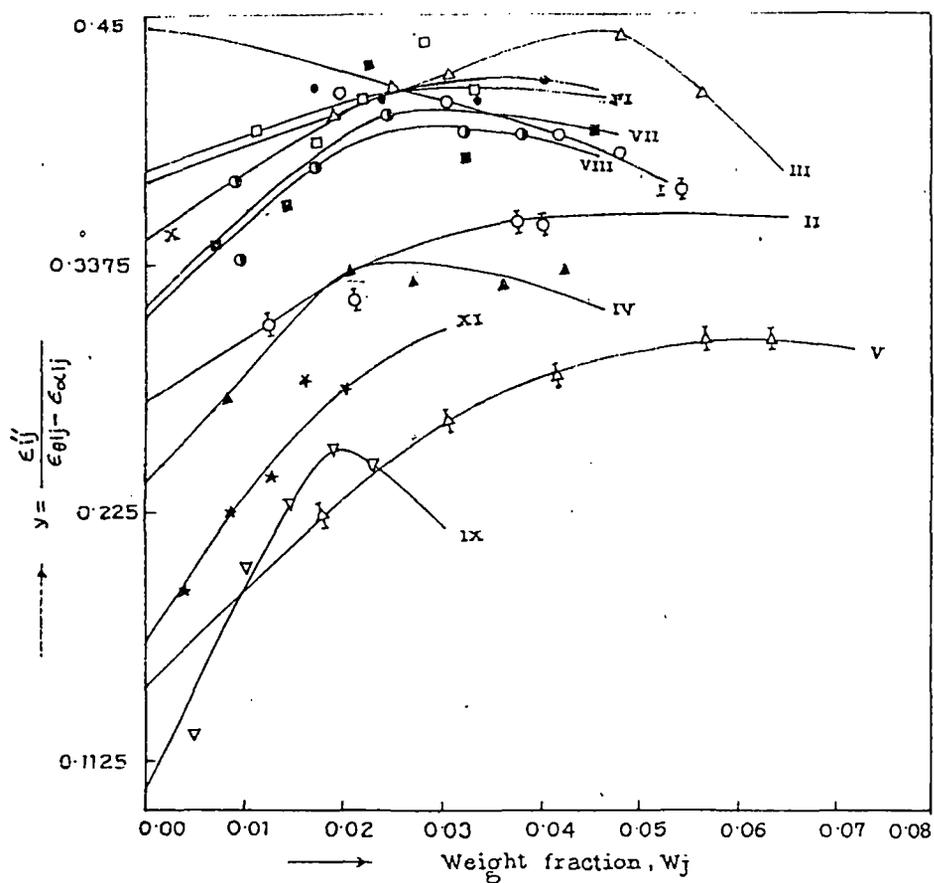


Fig. 7.3 - Variation of $\left[\frac{\epsilon''_{ij}}{(\epsilon_{0ij} - \epsilon_{\infty ij})} \right]$ against weight fraction W_j of polar solutes in dilute solution of non-polar solvent at 35°C (Table 7.3)

Table 7.2: Report of Fröhlich parameter A, relative contributions C_1 and C_2 towards dielectric relaxations with estimated values X and Y due to Fröhlich equation (8) and (9) and those by our method

System with sl.no & molecular wt. M_j in gm	Fröhlich parameter $A = \ln(\tau_2/\tau_1)$	Theoretical values of X & Y using Eqs.(8) & (9)		Theoretical values of C_1 & C_2		Estimated values of		Estimated values of	
		X	Y	C_1	C_2	$x = \left(\frac{\epsilon' - \epsilon_a}{\epsilon_0 - \epsilon_a} \right) w_j \rightarrow 0$	$y = \left(\frac{\epsilon''}{\epsilon_0 - \epsilon_a} \right) w_j \rightarrow 0$	C_1	C_2
i) 4 chloro 2 methyl aniline in benzene $M_j = 141.52$	1.6193	0.4269	0.4478	0.4159	0.8418	1.14	0.4455	1.5577	-0.6112
ii) 3 chloro 4 methyl aniline in benzene $M_j = 141.52$	1.4205	0.8448	0.4483	0.8239	0.3953	1.32	0.2745	1.7061	-0.6065
iii) 5 chloro 2 methyl aniline in benzene $M_j = 141.52$	1.0894	0.5478	0.4745	0.4642	0.6239	1.08	0.3758	1.6069	-0.6227
iv) 3 chloro 2 methyl aniline in benzene $M_j = 141.52$	1.4737	0.6937	0.4241	0.5180	0.5845	0.99	0.2385	1.1382	-0.1497
v) 2 chloro 5 methyl aniline in benzene $M_j = 141.52$	1.3187	0.7369	0.4114	0.5272	0.5430	1.17	0.1440	1.5339	-0.5334

Table 7.2 (continued)

System with sl.no & molecular wt. M_j in gm	Frönlich parameter $A = \ln(\tau_2/\tau_1)$	Theoretical values of X & Y using Eqs.(8) & (9)		Theoretical values of C_1 & C_2		Estimated values of		Estimated values of C_1 & C_2	
		X	Y	C_1	C_2	$X = \left[\frac{\epsilon' - \epsilon_a}{\epsilon_o - \epsilon_a} \right] W_j \rightarrow 0$	$Y = \left[\frac{\epsilon''}{\epsilon_o - \epsilon_a} \right] W_j \rightarrow 0$	C_1	C_2
vi) 0 chloro nitro-benzene in benzene $M_j = 157.5$	1.2197	0.7456	0.4107	0.5259	0.5326	0.82	0.3803	0.6874	0.3832
vii) 4 chloro 3 nitro-toluene in benzene $M_j = 171.5$	1.9201	0.6783	0.4086	0.5282	0.6486	0.64	0.3173	0.5504	0.4328
viii) m-nitrobenzotrifluoride in benzene $M_j = 191.0$	1.3286	0.6103	0.4551	0.4852	0.6252	0.97	0.3128	0.2013	-0.2176
ix) 4 chloro 3 nitrobenzotrifluoride in carbon tetrachloride $M_j = 225.5$	3.8044	0.8302	0.2583	0.6876	0.5231	0.91	0.1012	0.8682	0.1565
x) 0-nitro benzotrifluoride in benzene $M_j = 191.039$	2.7764	0.8771	0.2592	0.6595	0.4371	0.67	0.3487	0.3413	0.655
xi) 4 chloro 3 nitro toluene in carbon tetra chloride $M_j = 171.5$	3.6120	0.7540	0.3010	0.6379	0.7022	0.88	0.1642	0.8314	0.306

$$K_{ij} = \frac{\omega}{4\pi} \left[\epsilon'_{ij}{}^2 + \epsilon''_{ij}{}^2 \right]^{1/2} \dots\dots\dots(7.10)$$

which is a function of W_j of a polar solute. In the hf electric field $\epsilon''_{ij} \ll \epsilon'_{ij}$. Hence the real part K'_{ij} of hf conductivity of a polar nonpolar liquid mixture at a given temperature T K is given by (Smyth 1955):

$$K'_{ij} = \frac{\mu_j^2 N \rho_{ij} F_{ij}}{3 M_j kT} \left[\frac{\omega^2 \tau}{1 + \omega^2 \tau^2} \right] W_j \dots\dots\dots(7.11)$$

where M_j is the molecular weight of a polar solute, N is the Avogadro's number, k is the Boltzmann constant and

$F_{ij} = \left[\left[(\epsilon_{ij} + 2) / 3 \right]^2 \right]$ is the local field. The total hf

conductivity $K_{ij} = \omega \epsilon''_{ij} / 4\pi$ can be represented by:

$$K_{ij} = K_{ij\alpha} + K'_{ij} / \omega \tau$$

or, $\left[\frac{dK'_{ij}}{dW_j} \right]_{W_j \rightarrow 0} = \omega \tau \left[\frac{dK_{ij}}{dW_j} \right]_{W_j \rightarrow 0} = \omega \tau \beta \dots\dots(7.12)$

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

Equation (7.11) on being differentiated w.r.to W_j for $W_j \rightarrow 0$, becomes

$$\left(\frac{dK'_{ij}}{dW_j} \right)_{W_j \rightarrow 0} = \frac{\mu_j^2 N \rho_i F_i}{3 M_j kT} \left(\frac{\omega^2 \tau}{1 + \omega^2 \tau^2} \right) \dots\dots(7.13)$$

because $\rho_{ij} \rightarrow \rho_i$, the density of the solvent and $F_{ij} \rightarrow F_i$ the local field of the solvent in the limit $W_j = 0$. Using equations (7.12) and (7.13) we finally get

$$\mu_j = \left[\frac{3 M_j k T \beta}{N \rho_i F_i \omega b} \right]^{1/2} \dots\dots\dots(7.14)$$

to evaluate μ_1 and μ_2 in terms of b , where b is a dimensionless parameter given by:

$$b = \frac{1}{1 + \omega^2 \tau^2} \dots\dots\dots(7.15)$$

for τ_1 and τ_2 respectively. The values of b as well as μ_1 and μ_2 thus computed from equations (7.14) and (7.15) are placed in table 7.3.

Table 7.3 Reports the estimated intercepts and slopes of the concentration variation of uhf conductivity, the dimensionless parameter 'b', the dipole moments μ_1 and μ_2 in Debye (D) for the flexible part and the end over end rotation of a polar molecule, reported μ_1 and μ_2 in D due to existing methods, the theoretical μ_s ' from the bond length and bond moments respectively

Sl. No. & Systems	Intercepts and slopes of K_{ij} against ω_j		Dimensionless parameters "b"		Estimated dipole moment		Reported μ s' in Debye		μ s' (theo) in Debye	Expt μ_1 in Debye
	$\alpha \times 10^{-10}$ in esu	$\beta \times 10^{-10}$	$b_1 = \frac{1}{1+\omega^2 \tau_1^2}$	$b_2 = \frac{1}{1+\omega^2 \tau_2^2}$	μ_1 in D	μ_2 in D	Guggenheim	Higasi et al	μ_2 from bond length & bond moments	using $\mu_1 = \mu_2 (c_1/c_2)^{1/2}$
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
1) 4 Chloro 2 methyl aniline in C_6H_6	1.1323	1.7863	0.7797	0.1219	2.51	6.36	3.28	3.12	3.06	4.47
2) 3 Chloro 4 methyl aniline in C_6H_6	1.1220	1.2865	0.8808	0.3014	2.01	3.43	2.61	2.43	2.20	4.95
3) 5 Chloro 2 methyl aniline in C_6H_6	1.1189	1.6848	0.7858	0.2934	2.43	3.98	3.10	2.92	2.83	3.43
4) 4 Chloro 2 methyl aniline in C_6H_6	1.1144	2.1490	0.9188	0.3725	2.54	3.99	3.02	2.86	2.48	3.75
5) 2 Chloro 6 methyl aniline in C_6H_6	1.1135	1.3766	0.9228	0.4611	2.03	2.87	2.32	2.20	1.85	2.83
6) 0-Chloro nitrobenzene in C_6H_6	1.1265	4.0539	0.9178	0.4935	3.68	5.02	4.35	4.43	5.28	4.99
7) 4 Chloro 3 nitro-tollune in C_6H_6	1.1250	2.8594	0.9464	0.2751	3.18	5.89	4.49	4.59	5.58	5.31

Table 7.3 (continued)

Sl. No. & Systems	Intercepts and slopes of K_{ij} against ω_j		Dimensionless parameters "b"		Estimated dipole moment		Reported μ 's in Debye		μ 's (theo) in Debye	Expt μ_1 in Debye
	$\alpha \times 10^{-10}$ in esu	$\beta \times 10^{-10}$	$b_1 = \frac{1}{1+\omega^2 \tau_1^2}$	$b_2 = \frac{1}{1+\omega^2 \tau_2^2}$	μ_1 in D	μ_2 in D	Guggenheim	Higasi et al	μ_2 from bond length & bond moments	using $\mu_1 = \mu_2 (c_1/c_2)^{1/2}$
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
8) m-nitrobenzotrifluoride in C_6H_6	1.1262	1.7747	0.8630	0.3064	2.77	4.64	3.67	3.80	3.74	4.08
9) 4-Chloro 3 nitrobenzotrifluoride in CCl_4	1.0999	1.5781	0.9987	0.2744	1.99	3.79	3.17	3.15	3.78	4.34
10) O-nitrobenzene trifluoride in C_6H_6	1.1169	4.1557	0.9962	0.5035	3.94	5.54	4.96	5.07	6.18	6.80
11) 4-Chloro 3 nitrotoluene in CCl_4	1.1044	3.2769	0.9964	0.1686	2.50	6.07	4.68	4.63	5.58	5.78
12) 4-Chloro 3 nitrobenzotrifluoride in C_6H_6	1.1286	1.1894	----	0.6845	----	2.76	2.97	2.98	3.78	----
13) m-aminobenzotrifluoride in C_6H_6	1.1106	2.3536	----	0.5303	----	3.73	3.51	3.60	2.48	----
14) O-chloro nitrobenzene in CCl_4	1.0973	5.4508	----	0.3676	----	5.08	4.19	4.13	5.28	----
15) O-chlorobenzotrifluoride in C_6H_6	1.1199	2.0159	----	0.5580	----	3.57	3.38	3.49	3.98	----

7.4. Results and Discussions

Figure 1 represents the linear relationship of

$$\left[\frac{\epsilon_{\alpha ij} - \epsilon'_{ij}}{\epsilon'_{ij} - \epsilon_{\alpha ij}} \right] \text{ with}$$

$$\left[\frac{\epsilon''_{ij}}{\epsilon'_{ij} - \epsilon_{\alpha ij}} \right] \text{ satisfying the equation 7.7) having}$$

intercepts and slopes presented in table 7.1 with the experiment points placed on each curve for eleven systems possessing the double relaxation phenomena. The error involved in such regressions as well as the correlation coefficients for all the curves were also calculated and placed in table 7.1 in order to test their linearity and to assess the errors introduced in τ values which may normally be claimed to be accurate up to $\pm 10\%$. The double relaxation times of the molecules as mentioned in tables 7.1 - 7.3 were attempted to measure in order to calculate μ_1 and μ_2 of the flexible parts as well as the whole molecules. They are shown in tables 7.1 and 7.3 respectively. The eleven systems out of fifteen, nevertheless, exhibit double relaxation phenomena by showing the lower as well as higher values of τ_1 and τ_2 respectively. As shown in table 7.1 eight molecules i.e all disubstituted anilines and three benzene derivatives namely O-chloronitrobenzene, 4 chloro 3 nitrotoluene and m-nitrobenzotrifluoride all in C_6H_6 show considerable larger

values of τ_1 in their relaxation behaviours. This is perhaps due to the fact that the flexible $-\text{CH}_3$ group in aniline and those attached to the benzene rings mentioned above, absorb energy much more strongly in the microwave electric field and thereby yield large values of τ_1 . 4 chloro 3 nitrobenzotrifluoride in CCl_4 have their τ_1 much smaller, presumably due to the fact that their flexible parts are comparatively rigidly fixed with the parent ones (table 7.1). It is, however, interesting to note that the last four systems of table 7.1 show single relaxation process probably for their rigid attachment with the flexible parts. The slopes and intercepts of equation (7.7) yield τ_1 with negative sign for the aforesaid molecules.

Again, O-chloronitrobenzene shows double relaxation phenomenon in C_6H_6 while single relaxation process in CCl_4 . The reverse case, however, occurs in 4 chloro 3 nitrobenzotrifluoride which shows low value of τ_1 in CCl_4 and single relaxation process in C_6H_6 . This sort of affairs may perhaps be attributed to the solvent effect upon the polar molecules. So a strong conclusion on solvent effect seems to be of utmost importance if measurements would be performed on single polar molecule in different nonpolar solvents.

Table 7.2 reports the relative contributions C_1 and C_2 due to τ_1 and τ_2 (table 7.1) towards relaxation as computed from

Fröhlich's equations (7.8) and (7.9) for x and y as well as by our graphical technique (figures 7.2 and 7.3). Eventually, C_2 calculated for six polar molecules are negative although they fulfill the condition : $C_1 + C_2 = 1$. The disagreements in C_1 and C_2 with those of Fröhlich (1949) indicate their flexible parts loosely bound to them. In hf electric field the contribution by the rest molecule towards relaxation could not be in accord with the flexible one due to inertia.

The intercept α and the slope β of the variation of hf conductivities $K_{ij} S'$ of five disubstituted anilines with respect to polar solutes are placed in table 7.3 to compute μ_1 and μ_2 using the relaxation times τ_1 and τ_2 of table 7.1 from equations (7.14) and (7.15). The values of b_1 and b_2 are also placed in the 4th and the 5th columns of table 7.3. The corresponding μ_1 and μ_2 from equation (7.14) are shown in table 7.3. They are compared with μ s' due to Guggenheim (1949) and Higasi et al (1952). The disubstituted benzenes were already studied by Acharyya and Chatterjee (1985) from the conductivity method. The μ_j (theo) from the bond lengths and bond angles were also previously studied. The same data with those of disubstituted anilines are again shown in table 7.3 only for comparison.

In figure (7.4) the bond moments of $\text{CH}_3 \rightarrow \text{C}$ and $\text{C} \rightarrow \text{Cl}$ are 0.37D and 1.69D respectively. The bond moment 1.48D of $\text{C} \rightarrow$

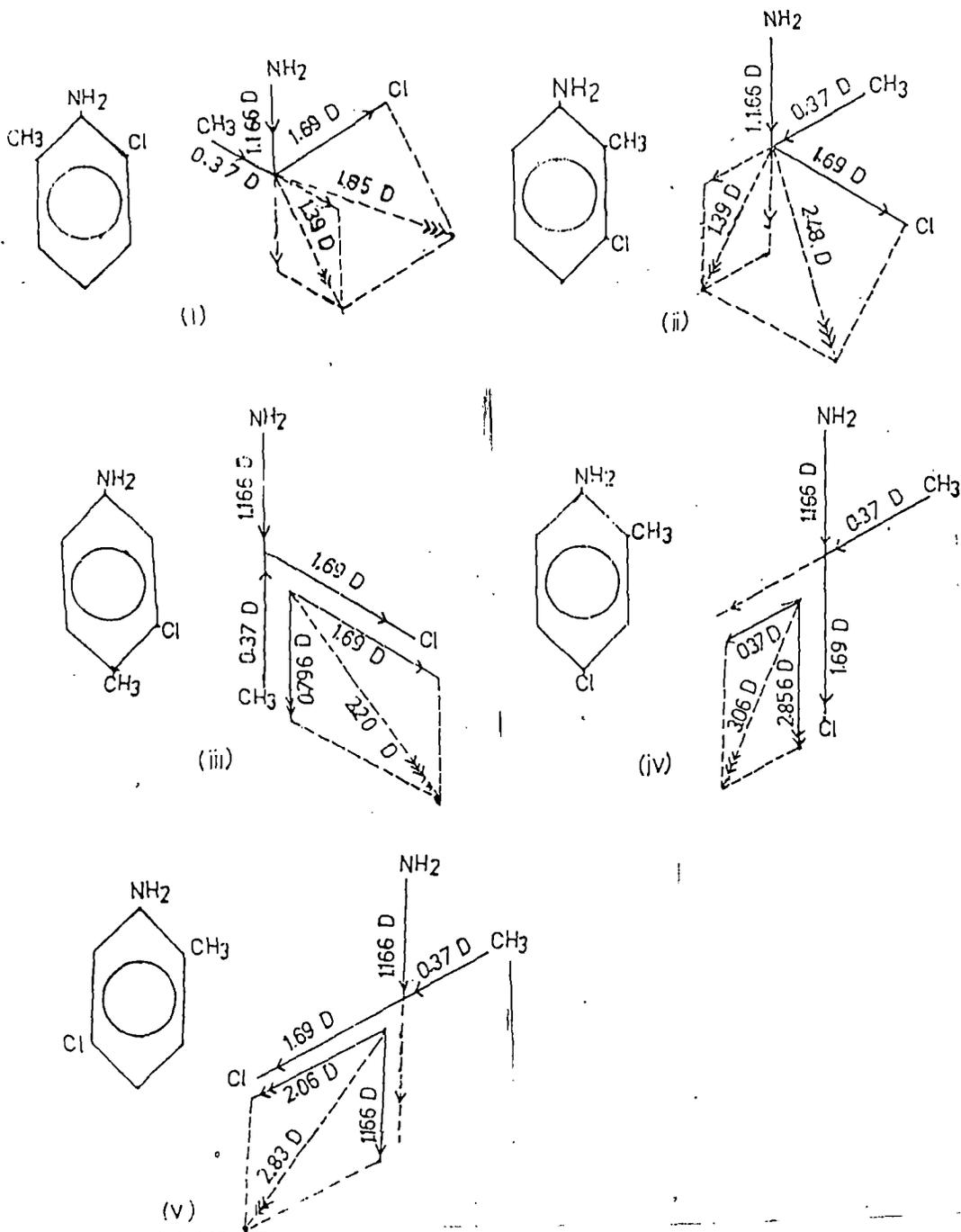


Fig. 7.4 - Conformations of five disubstituted anilines showing the orientation of bond axes, bond moments and dipole moments

NH₂ makes angle 142° with the bond axis. The component along the bond axis in these molecules becomes 1.166D. With these preferred conformational structures of the disubstituted anilines the theoretical $\mu_j(\text{theo})$ were computed by the vector addition method and are placed in table 7.3. The close agreement of $\mu_j(\text{theo})$ with our experimental μ_2 's suggests their correct conformational structures as shown in figure(7.4).

The values of μ_1 from $\mu_1 = \mu_2 (c_1 / c_2)^{1/2}$ is possible when the two relaxation phenomena are equally probable (Fröhlich 1949) But the present investigation finds μ_1 's as calculated from the above relation are larger for c_1 and c_2 due to Frohlich's equations. The γ values gradually decrease due to various conformations of the disubstituted anilines (figure 7.4 and table 7.1) probably due to decrease in the effective radii of the rotating units under hf electric field. Although the molecules are in the same environment and their molecular weights are the same, the most probable relaxation time due to Higasi (1966) and Guggenheim (1957) also show the similar trend like ours as shown in table 7.1

7.5 Conclusions

The close agreement of μ_2 's with those of literature values at once suggests that our new approach is justifyingly claimed to be a simple, straightforward and useful one. The method of single

frequency measurements of dielectric relaxation data at a given temperature is comparatively easy to perform. It requires an easy and time saving calculations unlike the other existing methods to detect the very existence of double relaxation phenomena in polar-nonpolar liquid mixtures. Thus the present procedure offers a significant improvement to the derivation of τ_1 & τ_2 and μ_1 & μ_2 because it not only allows to find an estimate of the errors, but also the correlation coefficients between the desired values generated from the dielectric relaxation.

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CHAPTER VIII

RELAXATION TIME AND ENERGY OF ACTIVATION OF NITROBENZENE IN
BENZENE FROM RADIO FREQUENCY CONDUCTIVITY MEASUREMENT

8.1 Introduction

It is well known fact that solutions of dielectric polar molecules in simple non - polar solvent may be expected to exhibit significant dielectric loss ϵ'' at radio and microwave frequency electric field. The studies on the pure polar liquid as well as polar liquid in non - polar solvent have provided informations on the effects of molecular size and shape upon dielectric relaxation. These also help to understand the effect of viscosity on the process of dielectric relaxation of polar molecules.

The Debye equation (1929), $\tau = 4\pi a^3 \eta / kT$, shows the proportionality between relaxation time τ and viscosity η of the medium. The validity of Debye equation in the dilute solutions of polar - nonpolar mixtures has been established in the low viscosity range. But the theory has not been satisfactorily applied to explain the relaxation characteristics when the viscosity of the solution is high.

Therefore it raises a question as to what extent the macroscopic viscosity can be regarded as a measure of the internal viscosity. Jackson and Powles (1946) determined directly the relaxation time of some polar solute namely benzophenone, nitrobenzene and bromobenzene in non-polar solvent benzene. He attributed that dilute solution of polar solute in various non-polar solvents satisfy the Debye equation. Whiffen and

Thompson (1946) and Whiffen (1950) showed that the ratio (τ / η) varies with temperature and concluded that the Debye simple expression is inadequate to explain the proportionately between τ and η . Therefore it is incorrect to regard the macroscopic viscosity as an internal viscosity of the medium.

The purpose of the present work is to carry out a careful study of the applicability of Debye equation in pure and dilute solution of nitrobenzene in non-polar benzene at various concentrations and temperatures from the radio frequency conductivity measurements.

8.2 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.

The dielectric cell was made up of a pyrex glass tube of diameter 2 cm with a pair of stainless steel circular electrodes of diameter 1.5 cm, 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 nitrobenzene and benzene were all Analar grade obtained from M/S British Drug House, London.

The viscosity of the liquids and their mixtures were measured

with Ostwald viscometer at different temperatures. The temperature variation was regulated by a good thermostat whose accuracy is better than $\pm 1^{\circ}\text{C}$. All the measurements were accurate upto $\pm 2\%$.

8.3 Results and Discussion

8.3.1 RF Conductivity and Relaxation Time

Most of the polar dielectric liquids display electrical conduction which arises not from the effect of the displacement current, but from the actual charge transport like ionic conduction in electrolyte. The evidence of existence of free ions in organic polar dielectric liquids has been shown by many workers (Lohneysen and Nagerl 1971, Rao and Raju 1970, Sen and Ghose 1974). Such conduction would normally be described by volume conductivity. In the microwave region the dependence of absorption upon charge transport is unimportant, but below 20 MHz that is at radio frequency region the conduction loss becomes important in some organic polar liquids. These liquids may be considered to be semiconducting liquids or liquid semiconductors.

The dielectric phenomena with which we are principally concerned are most conveniently discussed in electrostatic units, in which complex dielectric constant, $\epsilon^* = \epsilon' - j\epsilon''$, is a dimension less quantity. The dielectric loss is a parameter which describes the motion of electric charge in a conduction phenomenon.

In semiconducting organic polar liquids the effect of volume conductivity K' ($\Omega^{-1} \text{ cm}^{-1}$) would be an additional term to the dielectric loss ϵ'' given by

$$\epsilon'' = \epsilon''_{\text{displacement}} + \frac{K'}{\omega} \left(\frac{1}{4\pi} \times \frac{1}{9 \times 10^{11}} \right) \dots\dots(8.1)$$

The above expression (Hasted 1973) shows that the frequency variation of dielectric loss might be described as a frequency variation of apparent conductivity arises from the relaxation process.

The radio frequency conductivity K' of nitrobenzene and its solution in benzene at various concentration over the temperature range 15°C to 50°C have been measured. The charge density n of pure solute and solutions in benzene has been calculated from the slope of the linear plot (Fig 8.1) of K' against the inverse of viscosity $1/\eta$ (Sen and Ghosh 1974). The values of viscosity η , r.f. conductivity K' , number of ions/CC n and the mobility ν , calculated from the expression $\nu = K'/ne$, are listed in Tables 8.1 and 8.2. So it is evident that if we consider the additional term of dielectric loss ϵ'' due to the volume conductivity, then the presence of free ions or electrons has to be taken into consideration for calculating the effective dielectric loss ϵ'' at radio frequency electric field. The variation of ion density n against mole fraction of nitrobenzene in benzene x_1 is shown in Fig.8.2.

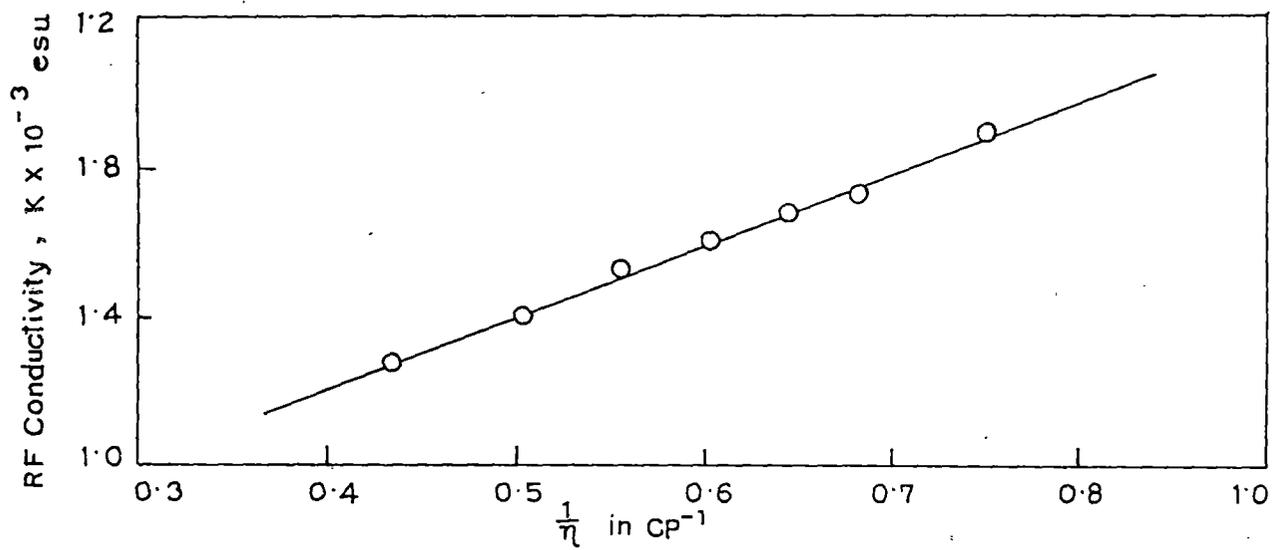


Fig. 8-1. Plot of K' vs $1/\eta$ of Nitrobenzene ,

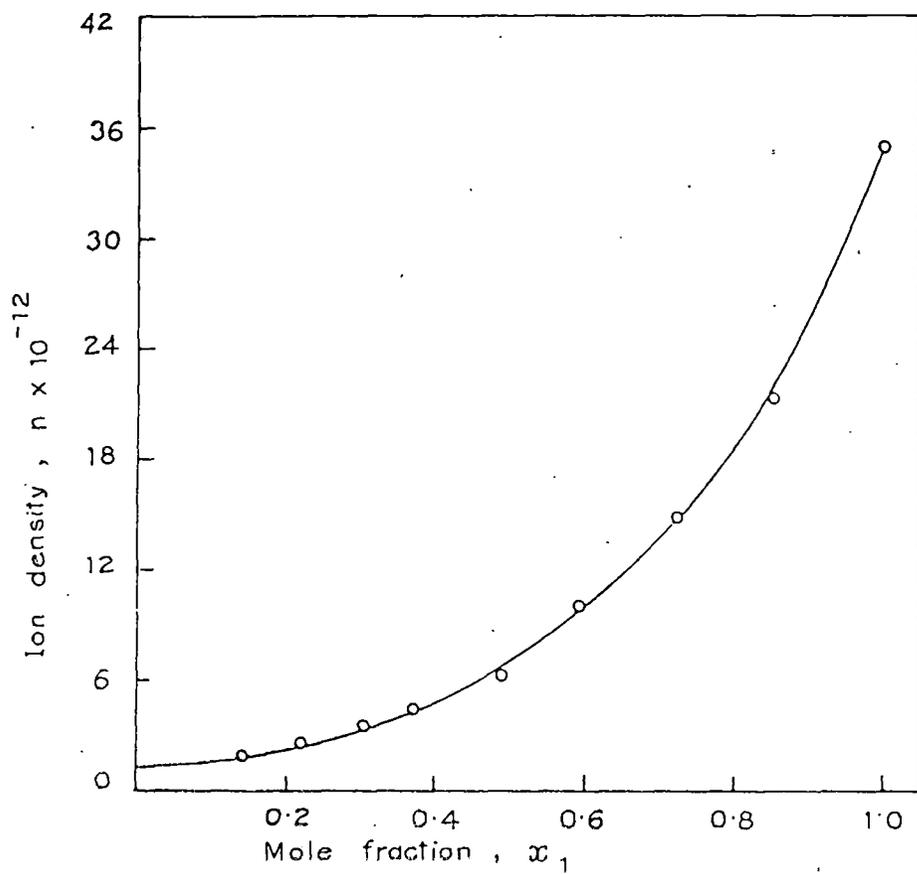


Fig. 8.2. Plot of ion density n against mole fraction of nitrobenzene in benzene mixture.

TABLE - B.1 Values of RF Conductivity k' , ion density n , mobility v , macroscopic and molecular relaxation times τ and τ' , thermodynamic parameters, γ , $\tau'T/\eta$ and γ , $\tau'T/\eta^\gamma$ of nitrobenzene (NB) at different temperatures

t °C	η in CP	$k' \times 10^{-9}$ in esu	$n \times 10^{-13}$ in ions/cc	$v \times 10^4$ in cm ² /V/Sec	$\tau \times 10^{-11}$ in Sec	$\tau' \times 10^{-11}$ in Sec	$\Delta H_{\tau'}$ in KCal/mol	$\Delta S_{\tau'}$ in Cal/mol/ deg	$\Delta F_{\tau'}$ in KCal/mol	ΔH_{η} in KCal/mol	ΔS_{η} in Cal/mol/deg	ΔF_{η} in KCal/mol	$\gamma = \frac{\Delta H_{\tau'}}{\Delta H_{\eta}}$	$\frac{\tau'T}{\eta}$ $\times 10^7$	$\frac{\tau'T}{\eta^\gamma}$ $\times 10^7$
15	2.30	1.2712		2.5244	6.11	4.07		-4.01	3.15		-4.55	3.57		5.10	3.27
20	1.98	1.3978		2.7758	5.46	3.64		-3.94	3.15		-4.40	3.55		5.39	3.40
25	1.79	1.5280		3.0343	4.91	3.27		-3.88	3.15		-4.34	3.55		5.44	3.40
30	1.65	1.5986	3.5	3.1745	4.62	3.08	1.99	-4.02	3.21	2.26	-4.31	3.56	0.88	5.66	3.49
35	1.55	1.6693		3.3149	4.35	2.90		-4.04	3.24		-4.32	3.59		5.76	3.53
40	1.46	1.7275		3.4305	4.14	2.76		-3.96	3.23		-4.33	3.61		5.92	3.60
50	1.23	1.8837		3.7407	3.67	2.45		-3.98	3.28		-4.24	3.63		6.43	3.84

TABLE - 8.2 Values of viscosity η , RF Conductivity k' , ion density n , mobility v , relaxation times τ , thermodynamic parameters, γ , $\tau T/\eta$ and $\tau T/\eta^\gamma$ of nitrobenzene - benzene mixture at different mole fraction of nitrobenzene x_1 and temperatures

x_1	t °C	η CP	$k' \times 10^{-9}$ esu	$n \times 10^{-12}$	$v \times 10^8$ in cm ² /v/Sec	$\tau \times 10^{+11}$ in Sec	ΔH_τ KCal/mol	ΔS_τ Cal/mol/ deg	ΔF_τ KCal/ mol	ΔH_η KCal/mol	ΔS_η Cal/mol/ /deg	ΔF_η KCal/mol	$\gamma = \frac{\Delta H_\tau}{\Delta H_\eta}$	$\frac{\tau T}{\eta}$ $\times 10^7$	$\frac{\tau T}{\eta^\gamma}$ $\times 10^7$
0.14	25	0.70	0.3005		1.1529	1.30		-5.21	2.60		-2.28	2.99		5.53	0.37
	30	0.66	0.3128		1.2001	1.23		-5.19	2.62		-2.29	3.01		5.68	0.36
	40	0.58	0.3320	1.81	1.2738	1.12	1.05	-5.18	2.67	2.32	-2.31	3.04	0.45	6.00	0.36
	50	0.52	0.3480		1.3352	1.04		-5.19	2.73		-2.34	3.07		6.51	0.37
0.22	25	0.77	0.3812		1.0589	1.41		-5.28	2.65		-2.46	3.05		5.49	0.40
	30	0.72	0.3983		1.1064	1.33		-5.26	2.67		-2.48	3.06		5.63	0.40
	40	0.64	0.4239	2.50	1.1775	1.21	1.07	-5.25	2.72	2.31	-2.50	3.09	0.47	5.94	0.40
	50	0.56	0.4407		1.2242	1.13		-5.28	2.78		-2.53	3.19		6.46	0.41
0.30	25	0.83	0.49		0.9823	1.52		-5.33	2.69		-2.65	3.10		5.43	0.45
	30	0.78	0.51		1.0282	1.43		-5.30	2.71		-2.66	3.11		5.57	0.44
	40	0.69	0.54	3.46	1.0860	1.31	1.10	-5.31	2.77	2.31	-2.68	3.15	0.48	5.92	0.44
	50	0.62	0.57		1.1358	1.21		-5.32	2.82		-2.71	3.18		6.35	0.45
0.37	25	0.90	0.5729		0.9083	1.64		-5.44	2.74		-2.81	3.14		5.37	0.48
	30	0.84	0.5985		0.9489	1.55		-5.43	2.76		-2.82	3.16		5.54	0.47
	40	0.75	0.6305	4.38	0.9947	1.42	1.12	-5.43	2.82	2.30	-2.85	3.19	0.48	5.89	0.47
	50	0.67	0.6623		1.0501	1.31		-5.45	2.87		-2.87	3.23		6.30	0.48
0.49	25	1.03	0.65		0.7354	2.03		-5.77	2.86		-3.09	3.22		5.88	0.59
	30	0.96	0.68		0.7632	1.92		-5.76	2.89		-3.10	3.24		6.09	0.59
	40	0.85	0.72	6.17	0.8133	1.75	1.14	-5.76	2.95	2.30	-3.12	3.28	0.50	6.45	0.59
	50	0.76	0.75		0.8485	1.62		-5.78	3.01		-3.15	3.32		6.89	0.59

Table 8.2 (Continued)

x_1	t °C	η CP	$k' \times 10^{-3}$ esu	$n \times 10^{-12}$	$\nu \times 10^8$ in cm ² /v/Sec	$\tau \times 10^{+11}$ in Sec	ΔH_τ KCal/mol	ΔS_τ Cal/mol/ deg	ΔF_τ KCal/ mol	ΔH_η KCal/mol	ΔS_η Cal/mol/ deg	ΔF_η KCal/mol	$\gamma = \frac{\Delta H_\tau}{\Delta H_\eta}$	$\frac{\tau T}{\eta}$ $\times 10^7$	$\frac{\tau T}{\eta^2}$ $\times 10^7$
0.59	25	1.15	0.8412		0.5901	2.53		-5.75	2.99		-3.33	3.28		6.60	0.92
	30	1.06	0.8792		0.6167	2.38		-5.74	3.02		-3.36	3.31		6.80	0.92
	40	0.91	0.9398	1.90	0.6592	2.16	1.28	-5.74	3.08	2.29	-3.37	3.34	0.60	7.18	0.92
	50	0.85	0.9968		0.6992	1.97		-5.75	3.14		-3.39	3.38		7.53	0.92
0.72	25	1.32	1.0013		0.4695	3.18		-5.81	3.13		-3.62	3.36		7.18	1.34
	30	1.22	1.0508		0.4927	2.98		-5.79	3.15		-3.63	3.39		7.39	1.33
	40	1.09	1.1311	14.81	0.5340	2.68	1.40	-5.79	3.21	2.29	-3.65	3.43	0.61	7.74	1.33
	50	0.98	1.2017		0.5635	2.44		-5.81	3.27		-3.68	3.47		8.07	1.34
0.85	25	1.52	1.2311		0.4014	3.72		-5.86	3.22		-3.92	3.45		7.28	1.66
	30	1.40	1.2920		0.4212	3.49		-5.85	3.25		-3.93	3.47		7.53	1.67
	40	1.24	1.3938	21.30	0.4544	3.13	1.48	-5.86	3.31	2.28	-3.95	3.52	0.65	7.87	1.67
	50	1.13	1.4805		0.4827	2.85		-5.88	3.37		-3.98	3.57		8.17	1.67

The two fundamental equations (Smyth 1955) of Debye for calculating relaxation time τ of polar molecule in pure state and in dilute solution of non-polar solvent from dielectric loss ϵ'' measurement are given by

$$\epsilon'' = \frac{\epsilon_0 - \epsilon_\infty}{1 + \omega^2 \tau^2} \omega \tau \dots\dots\dots(8.2)$$

an
$$\epsilon'' = \frac{4\pi CN \mu^2 (\epsilon_0 + 2) (\epsilon_\infty + 2) \omega \tau}{27 kT (1 + \omega^2 \tau^2)} \dots\dots\dots(8.3)$$

respectively. But these equations have not taken into consideration of existence of free ions or electrons.

Therefore in the absence of any other suitable expression which takes this aspect into consideration, an equation (Ghosh and Chaudhury 1980) for calculating dipole relaxation time has been used, which is given by

$$\tau = \frac{2}{3} \frac{a^2 e}{\nu kT} \dots\dots\dots(8.4)$$

where k is the Boltzmann constant, T is the temperature in Kelvin, a is the radius and e is the electric charge.

The values of relaxation time τ , calculated from eq. (8.4), for pure nitrobenzene at various temperatures and for nitrobenzene in benzene at different concentrations and temperatures are tabulated in Table 8.1 and 8.2. The τ values of pure nitrobenzene agree fairly well with the literature values. The observed high values of τ of pure nitrobenzene at r.f. field indicates that the

interionic forces may hinder the rotation of dipolar molecules. Moreover in the concentrated and pure polar liquids the internal field of the dipoles influences the orientation of the molecules. Therefore relaxation of dipoles must occur by a co-operative effect which involves a group of molecules rather than a single one. Thus the calculated values of relaxation time of pure nitrobenzene are the macroscopic relaxation times τ and these have been corrected to get the values of molecular relaxation time τ' by using the relaxation of Powels (1953):

$$\tau' = \left(\frac{2\epsilon_0 + \epsilon_\alpha}{2\epsilon_0} \right) \tau \dots\dots\dots(8.5)$$

All the values of relaxation times τ and τ' are given in Tables 8.1 and 8.2 and found that relaxation time decreases with temperature. The relaxation time of nitrobenzene molecule at infinite dilution τ_α has been obtained at different temperatures from the extrapolation of the curves of τ against x_1 as shown in Fig. 8.3. The curves indicate that at a particular temperature the increase of benzene concentration accompanied by exponential decrease of τ . The values of τ_α are given in Table 8.3 which are in fair agreement with the values of the other workers (Cripwell and Sutherland 1946, Madan 1973).

It is apparent from Table 8.1 that the values of $(\tau T/\eta)$ for nitrobenzene molecule do not, remain constant with the variation of temperature. The factor increases with the increase of temperature or it can be interpreted as it decreases with the

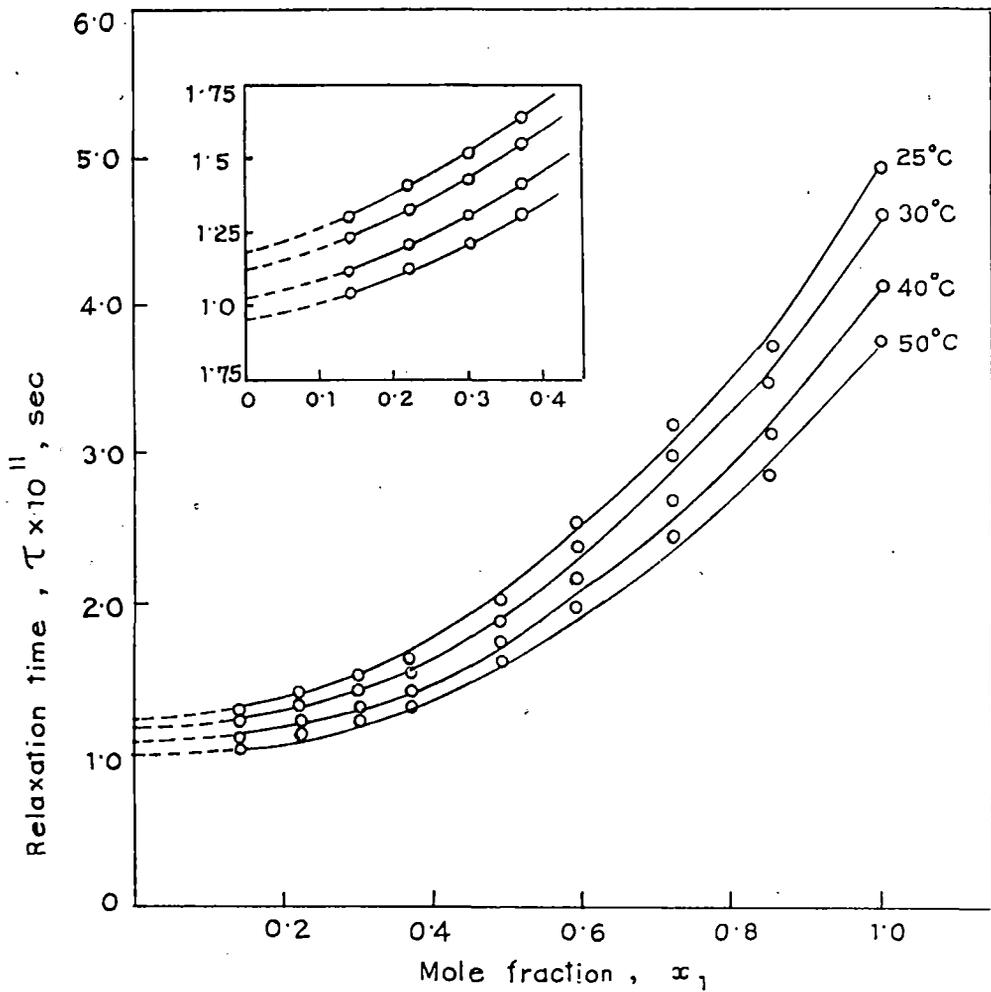


Fig. 8.3. Plot of τ against mole fraction of nitrobenzene in benzene mixture.

TABLE - 8.3 Values of relaxation times τ_α , thermodynamic parameters, γ , τ/η and τ/η^γ of nitrobenzene in benzene at infinite dilution at different temperatures

t °C	η CP	$\tau_\alpha \times 10^{11}$ sec	$\Delta H\tau_\alpha$ kCal/mol deg	$\Delta S\tau_\alpha$ Cal/mol/ deg	$\Delta F\tau_\alpha$ kCal/mol	$\Delta H\eta$ kCal/mol	$\Delta S\eta$ Cal/mol/deg	$\Delta F\eta$ kCal/mol	$\gamma = \frac{\Delta H\tau_\alpha}{\Delta H\eta}$	$\frac{\tau}{\eta} \times 10^7$	$\frac{\tau}{\eta^\gamma} \times 10^7$
25	0.60	1.17		-5.10	2.54		-1.95	2.90		5.81	0.33
30	0.56	1.12	1.02	-5.10	2.56	2.32	-1.96	2.92	0.44	6.02	0.33
40	0.50	1.03		-5.11	2.62		-1.99	2.94		6.41	0.33
50	0.44	0.95		-5.11	2.67		-2.01	2.97		6.94	0.33

increase of macroscopic viscosity. But the variation of the factor $(\tau T/\eta)$ at different temperatures could be minimized if the numerical value of macroscopic viscosity is replaced by η^γ where $\gamma = \Delta H_\tau / \Delta H_\eta$ and η^γ is considered to be internal viscosity coefficient η_{int} . The data of Tables 8.1, 8.2 and 8.3 reveals that the Kalman (Kalman and Smyth 1960) factor $(\tau T/\eta^\gamma)$ for the given nitrobenzene molecules practically remains constant. This observation further support the previous conclusion drawn by the other workers (Higari 1961) that η^γ is a better representation of internal viscosity. The internal viscosity η_{int} is function of macroscopic viscosity η which may be represented by the equation

$$\eta_{int} = \text{Cont.} \cdot \eta^\gamma$$

If the constant is unity the relation becomes $\eta_{int} = \eta^\gamma$

8.3.2 Determination of Thermodynamic Parameters and the value of γ

The temperature variation of relaxation time has been used to calculate the molar heat activation energy using Eyring theory of rate process (1941)

$$\tau = \frac{A}{T} \exp \left[\frac{\Delta F_\tau}{RT} \right] \dots\dots\dots(8.6)$$

Where $A = h/R$, is a constant, h and R being the Plank's constant and gas constant respectively.

The heat of activation energy ΔH_τ and the entropy of

activation energy ΔS_{τ} for dipole relaxation may be determined by putting

$$\Delta F_{\tau} = \Delta H_{\tau} - T\Delta S_{\tau} \dots\dots\dots(8.7)$$

and hence the eqs. (8.6) becomes

$$\tau = \frac{h}{RT} \left[\exp - \frac{\Delta S_{\tau}}{R} \right] \left[\exp \frac{\Delta H_{\tau}}{RT} \right] \dots\dots\dots(8.8)$$

Taking the concept of viscous flow of a liquid as a rate process an analogous equation for viscosity can be written as (Eyring et al 1941)

$$\eta = B \exp (\Delta F_{\eta} / RT)$$

$$= B \left[\exp \left(- \frac{\Delta S_{\eta}}{R} \right) \right] \left[\exp \left(\frac{\Delta H_{\eta}}{RT} \right) \right] \dots\dots\dots(8.9)$$

Where ΔF_{η} , ΔH_{η} and ΔS_{η} are the molar free energy, heat and entropy of activation for viscons flow of the liquid and $B = hN/v$, N is the Avogadro number and v is the molar volume respectively.

Figs.8.4 and 8.5 show the linear plots of $\ln(\tau T)$ vs $1/T$ and $\ln\eta$ Vs $1/T$. From the slopes of the curves the values of ΔH_{τ} , ΔS_{τ} and ΔF_{τ} and also ΔH_{η} , ΔS_{η} and ΔF_{η} have been determined and are given in Table 8.1, 8.2 and 8.3.

It is observed from the Tables that the values of free energy of activation ΔF_{τ} are high compared to enthatpy of activation ΔH_{τ} It may be due to the size of the molecules whose potential barrier

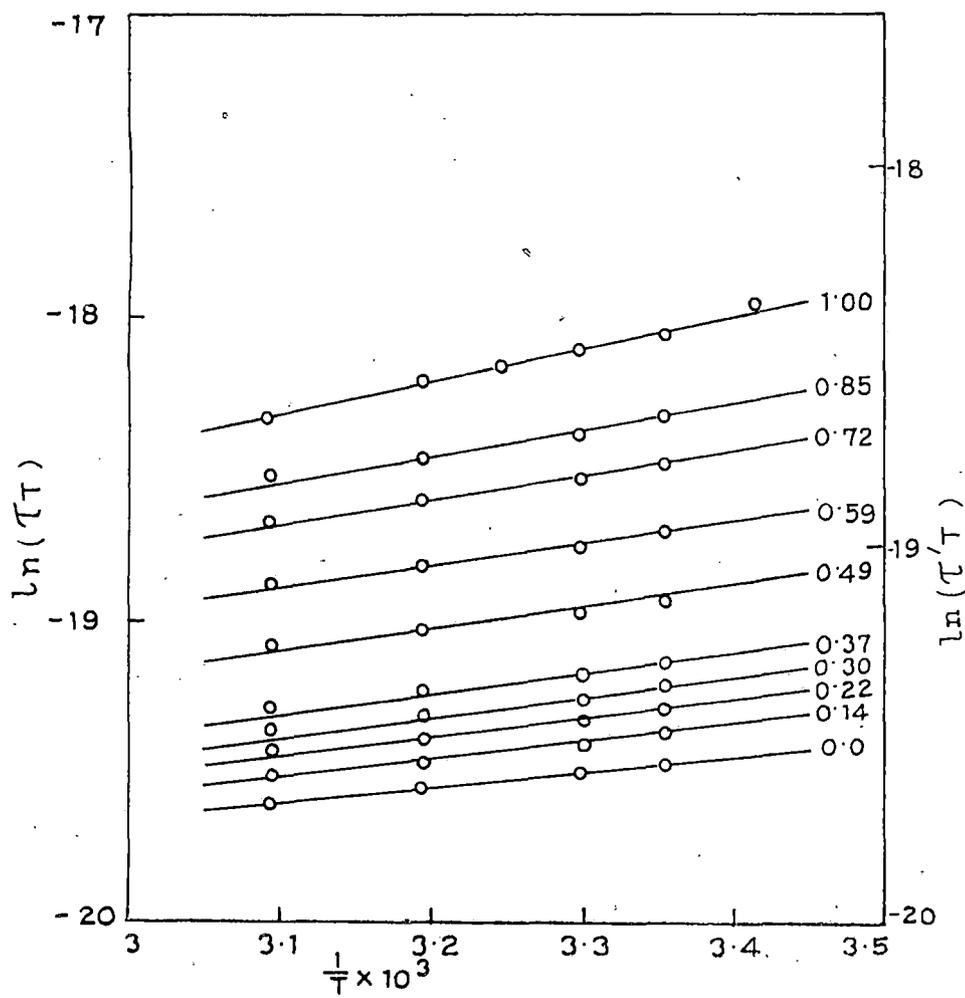


Fig. 8.4. Plot of $\ln(\tau T)$ against $1/T$ at different mole fractions of nitrobenzene in nitrobenzene and benzene mixture.

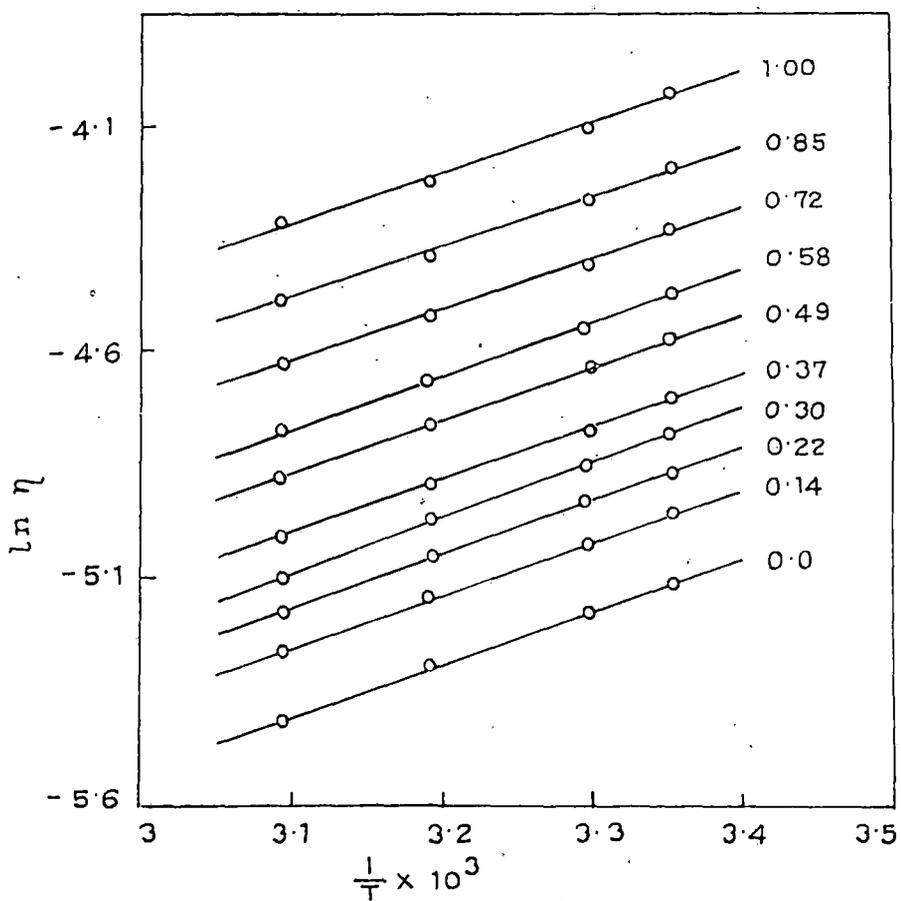


Fig. 8.5. Plot of $\ln \eta$ against $1/T$ at different mole fractions of nitrobenzene in nitrobenzene and benzene mixture.

hinder the rotation of the dipolar molecules. Again it is seen that free energy of activation increases with the rise of temperature. This suggest that with the increase in temperature the thermal agitation increases resulting in the increase of potential barrier height which hinder rotation of the molecules.

It is apparent from the Table 8.1 - 8.3 that the enthalpies of activation are less than the corresponding free energy of activation. That is why the entropy of activation values are negative. The negative and high values of entropy suggest that there are larger number of molecules surrounding to one which rotates in the process of orientation and due to this group rotation a primary single long time of relaxation is expected. It is further appeared from the Tables 8.1 and 8.3 that the enthalpy of activation of pure nitrobenzene (ΔH_T) is high compared to the enthalpy of activation of nitrobenzene at infinite dilution (ΔH_{T_α}). Therefore it may be assumed that large molecular region is involved in the relaxation process of pure nitrobenzene whereas the nitrobenzene molecule at infinite dilution does not form any molecular complex with the surrounding molecules that is the molecule is freely rotating in benzene.

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CHAPTER IX

RADIO FREQUENCY CONDUCTIVITY AND RELAXATION TIME OF NITROBENZENE
IN BENZENE AND PARAFFIN SOLUTIONS

9.1 INTRODUCTION

The relation between dielectric relaxation time of dipolar molecule of polar liquid with its viscosity and size of the molecule has been studied by number of workers (Bottcher C.J.F. 1952). The measurement of relaxation time provides a means of investigating molecular motion and inter molecular action in liquid. In the Debye (1929) treatment the relaxation time τ of dipolar molecule was assumed to be due to the rotation of a sphere of radius a in a continuous viscous fluid whose internal viscosity is η and obtained an expression as $\tau = 4 \pi a^3 \eta / kT$. This expression has been applied with varying degree of success and failure using the value of directly measured macroscopic viscosity as internal viscosity.

Whiffen and Thompson (1946), Hall et al (1946), Cripwell and Sutherland (1946), Chaw, Le Fevre and Tardif (1957) showed that the Debye expression for dielectric loss ϵ'' due to microwave absorption by the solution of nitrobenzene in non-polar solvent C_6H_6 and CCl_4 , and in the mixed solvents of high viscous paraffin and CCl_4 , C_6H_6 , C_6H_{14} and CS_2 is fairly obeyed, but the Debye relation connecting relaxation time of polar molecule with macroscopic viscosity of the solution and radius of polar molecule does not hold good in these solutions. Jackson and Powles (1946) made a comparative study of the behavior of bromobenzene - benzene solution and bromobenzene - paraffin

solution and confirmed the inadequacy of the Debye relation of relaxation time τ with macroscopic viscosity η .

In continuation of the work described in the preceding chapter a further study has been made to know whether the Debye relation between τ and η is valid in the radio frequency electric field. In order to have a better idea of the above mentioned problem a comparative study has been done on the variation of r.f. conductivity K' and relaxation time τ at radio frequency electric field with the variation of viscosity η produced by changing temperature as well as by gradually adding high viscous paraffin solvent at room temperature.

9.2 RESULTS AND DISCUSSION

Experimental arrangement for the measurement of r.f. conductivity of polar liquid and its solutions in non-polar solvent at various concentration and temperatures has been given in Chapter VIII. Chemically pure nitrobenzene and benzene were used as solute and solvent respectively. Medicinal paraffin whose viscosity is 20 Cp and density is 0.81 gm/cc at 20°C was used as another non-polar solvent for making variable high viscous solution at a fixed temperature. The values of the viscosity η of nitrobenzene, paraffin and the mixed solutions were determined experimentally with the help of Oswald's viscometer. The values η of pure nitrobenzene have been compared with those given in International Critical Table.

In the previous chapter (Chapter VIII) the r.f. conductivity were measured for pure nitrobenzene at different temperatures and nitrobenzene in benzene at various concentrations and temperatures. In the present Chapter the values of r.f. conductivity of (i) nitrobenzene in liquid paraffin at different concentrations (ii) a fixed solution of 0.78 mole fraction of nitrobenzene in benzene at different temperatures and (iii) the fixed solution of nitrobenzene in benzene mixed with various percentage of solvent paraffin at room temperatures, have been measured. The values of r.f. conductivity K' , viscosity η ion density n calculated from the slopes of $K'-1/n$ curves, mobility ν and the relaxation time τ calculated from Ghosh and Chaudhury (1980) relation $\tau = \frac{2}{9} \frac{a e}{\nu k T}$ which is applicable for semi conducting organic polar liquid at r.f. field, are listed in Tables 9.1, 9.2 and 9.3.

The variations of r.f. conductivity K' of nitrobenzene as well as the fixed solution of 0.78 mole fraction of nitrobenzene in benzene with macroscopic viscosity η of the medium either by changing temperature or varying the proportion of liquid paraffin added to the system at 25°C are shown in Fig.9.1 and 9.2 respectively. Fig. 9.1 shows that the conductivity K' decreases exponentially with the increase of viscosity of the medium. This nature of variation of K' against η does not depend upon whether the change of η is due to the variation of temperature of the solution or by increasing the percentage of liquid paraffin in

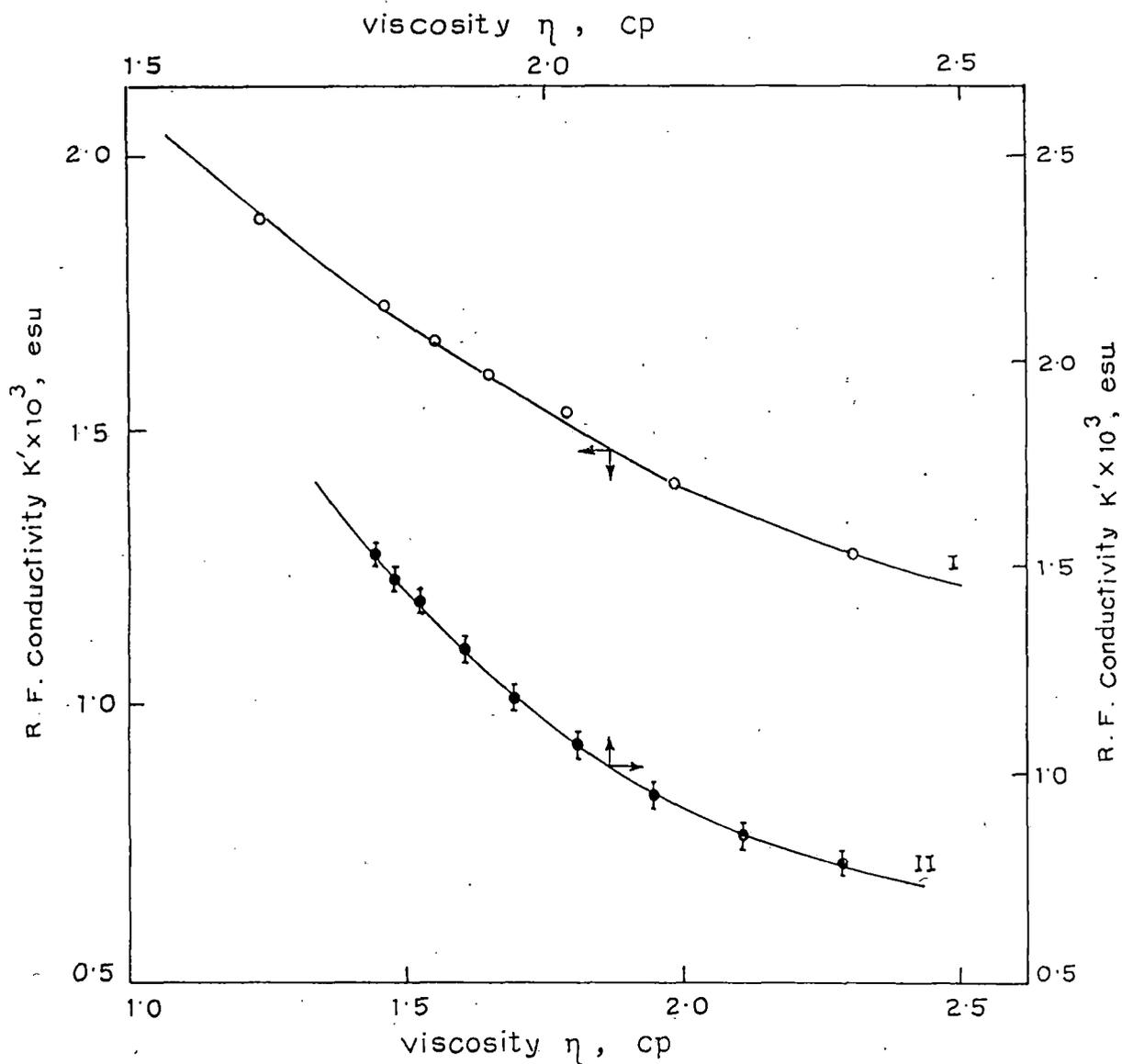


Fig. 9.1. Plot of $K' \times 10^{-3}$ vs viscosity (η) of
 I (—○—) Nitrobenzene at different temperatures
 II (—●—) Nitrobenzene + Paraffin mix at 25°C

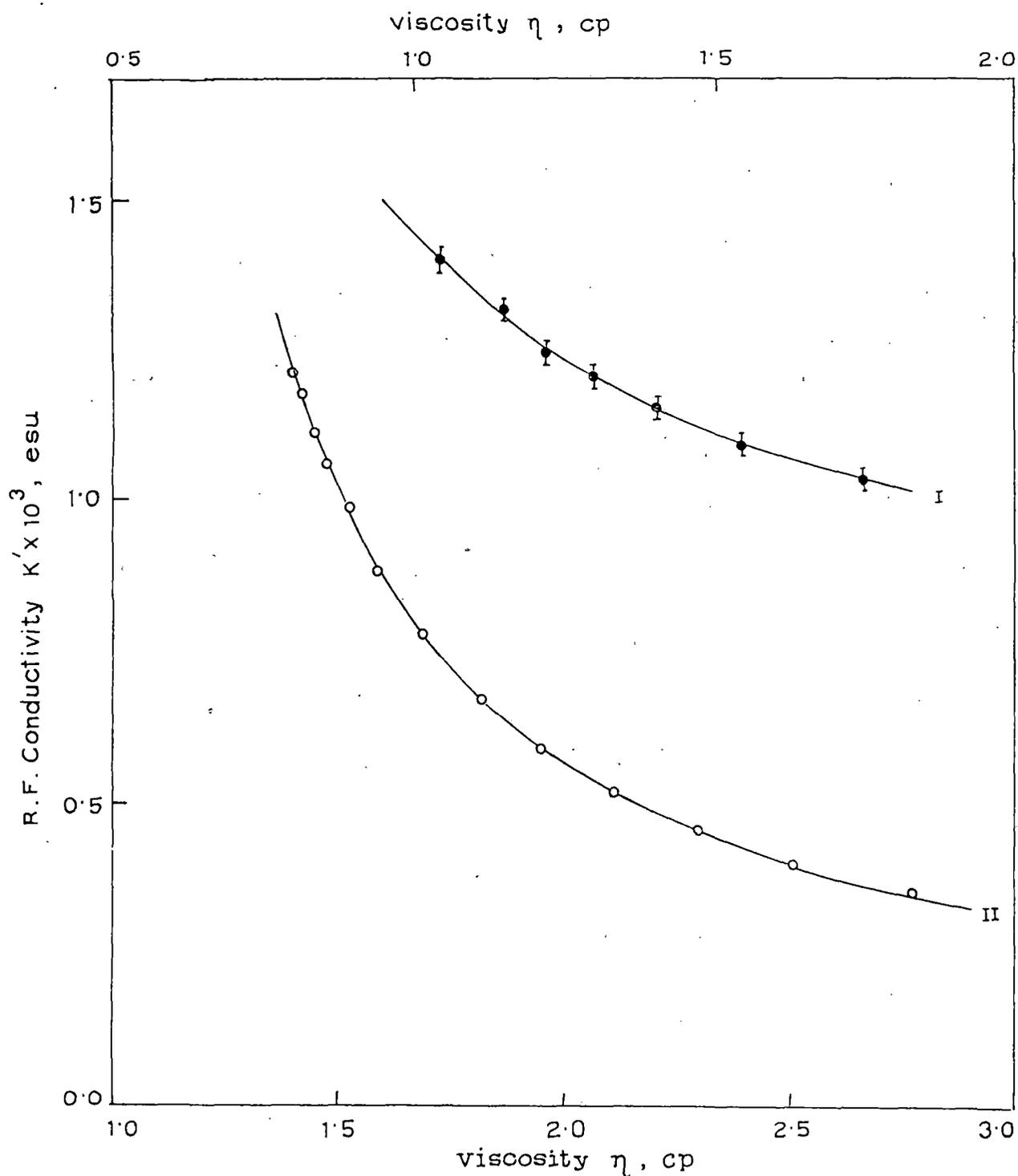


Fig. 9.2. Plot of $K' \times 10^3$ vs viscosity η
 I (—●—) a fixed solution of 0.78 mole fraction of nitrobenzene
 in benzene at various temperatures.
 II (—○—) the fixed solution + Paraffin at 25°C

Table 9.1 - Values of viscosity η , ion density n , r.f. conductivity mobility ν , relaxation time τ ,

$\gamma = \Delta H\tau/\Delta H\eta$, and radius a of nitrobenzene in nitrobenzene plus paraffin mixture at 25°C

% of Paraffin	η CP	$n \times 10^{-12}$	$K \times 10^{-9}$ esu	$\nu \times 10^4$ cm ² /volt/sec	$\tau \times 10^{11}$ sec	γ From Graph	$\frac{\tau}{\eta} \times 10^9$	$\frac{\tau}{\eta^\gamma} \times 10^9$	$a^{\circ A}$ with $\eta_{int} = \eta$	$a^{\circ A}$ with $\eta_{int} = \eta^\gamma$
0.0	1.79	34.9	1.5280	3.0343	4.91		2.74	9.51	2.08	3.15
0.9	1.82	34.3	1.4700	2.9762	5.02		2.76	9.57	2.08	3.15
2.0	1.85	33.4	1.4205	2.9535	5.05		2.73	9.41	2.08	3.13
3.7	1.90	31.9	1.2953	2.8198	5.29		2.78	9.49	2.09	3.14
5.5	1.97	30.5	1.1761	2.6761	5.56	1.31	2.83	9.56	2.10	3.15
7.5	2.04	28.9	1.0640	2.5549	5.84		2.87	9.58	2.11	3.15
9.8	2.13	27.1	0.9484	2.4285	6.15		2.89	9.52	2.11	3.15
12.3	2.24	25.2	0.8502	2.3429	6.37		2.85	9.25	2.10	3.12
14.0	2.35	23.9	0.7844	2.2792	6.55		2.78	8.87	2.09	3.07

Table 9.2 - Values of viscosity η , ion density n , r.f. conductivity K' , mobility v , relaxation time τ ,

$\gamma = \Delta H\tau/\Delta H\eta$, and radius a of nitrobenzene in a fixed solution (0.78 mole fraction of nitrobenzene in benzene) plus paraffin mixture at 25°C

% of Paraffin	η CP	$n \times 10^{-12}$	$K' \times 10^{-9}$ esu	$v \times 10^4$ cm ² /volt/sec	$\tau \times 10^{11}$ sec	γ From Graph	$\frac{\tau}{\eta} \times 10^9$	$\frac{\tau}{\eta\gamma} \times 10^9$	a °A with $\eta_{int} = \eta$	a °A with $\eta_{int} = \eta\gamma$
0.00	1.40	18.9	1.2100	4.4412	3.36		2.40	9.37	1.99	1.45
0.72	1.43	18.6	1.1709	4.3669	3.42		2.40	9.42	1.99	1.46
1.71	1.45	18.2	1.1069	4.2328	3.53		2.44	9.61	2.00	1.47
3.20	1.48	17.6	1.0576	4.1635	3.59		2.43	9.61	2.00	1.47
5.20	1.52	16.8	0.9824	4.0608	3.68		2.42	9.62	1.99	1.47
8.00	1.59	15.7	0.8790	3.8979	3.83		2.41	9.70	1.99	1.47
11.50	1.69	14.4	0.7759	3.7418	3.99	0.78	2.37	9.64	1.98	1.47
15.85	1.81	13.0	0.6714	3.5976	4.15		2.29	9.48	1.96	1.46
19.77	1.95	11.8	0.5927	3.4881	4.28		2.20	9.24	1.93	1.45
23.76	2.11	10.6	0.5187	3.3854	4.41		2.09	8.96	1.90	1.43
27.75	2.30	9.5	0.4528	3.3030	4.52		1.96	8.57	1.86	1.41
31.68	2.51	8.6	0.4010	3.2456	4.60		1.83	8.14	1.82	1.39
35.20	2.77	7.6	0.3525	3.2041	4.66		1.68	7.63	1.77	1.36

Table 9.3 - Values of viscosity η , r.f. conductivity, K' , mobility ν , relaxation timer ,

$\gamma = \Delta H\tau/\Delta H\eta$, and radius of nitrobenzene in a fixed solution of 0.78 mole fraction

of nitrobenzene in benzene at different temperatures.

t °C	η CP	$K \times 10^{-9}$ esu	$\nu \times 10^4$ cm ² /volt/sec	$\tau \times 10^{11}$ sec	γ From Activa- tion energy	γ From Graph	$\frac{\tau T}{\eta} \times 10^7$	$\frac{\tau T}{\eta \gamma} \times 10^7$ with $\gamma = 0.78$	a ^o A with $\eta_{int} = \eta$	a ^o A with $\eta_{int} = \eta^\gamma$
15	1.75	1.0354	3.8004	3.93			6.4588	2.6531	1.92	1.43
20	1.54	1.0901	4.0011	3.79			7.2010	2.8759	1.99	1.47
25	1.40	1.1527	4.2309	3.53			7.4989	2.9332	2.02	1.48
30	1.30	1.2094	4.4390	3.31	0.53	0.78	7.7393	2.9748	2.04	1.48
35	1.22	1.2472	4.5778	3.16			7.9941	3.0309	2.06	1.49
40	1.15	1.3146	4.8251	2.95			8.0648	3.0087	2.07	1.49
50	1.04	1.0380	5.1169	2.69			8.3706	3.0642	2.09	1.50

the solution at a fixed temperature. Similar results have been obtained in case of the fixed solution of nitrobenzene in benzene (Fig 9.2).

It has been suggested (Smyth 1955) that when the polar molecules are surrounded by non-polar ones, the relaxation time τ is influenced by the nature of non-polar molecules as well as by the viscosity of the solution as a whole. If the shape of the molecule, undergoing dipole orientation, depart little from that of a sphere, it can rotate without any considerable displacement of the surrounding molecules. In this case the relaxation time is relatively insensitive to the macroscopic viscosity of the solution, which is obtained with the help of usual Laboratory method. But if the molecule is not spherical in shape, its rotation must involve the displacement of the neighboring molecules and corresponding τ should depend markedly upon the viscosity of the solution as well as upon the molecular size. Nitrobenzene is a non-spherical molecule. So it is of great interest to ascertain whether the relaxation time τ of nitrobenzene molecule in low viscous benzene solvent and in high viscous paraffin solvent are related in an analogous manner to the macroscopic viscosity η of the solution. A desired comparative statements of the results are given in Table 9.4. It indicates that the relation taken from Debye expression:

Table 9.4 - Comparison of relaxation time and macroscopic viscosity of nitrobenzene at 25°C

Solvent	Viscosity η CP	Relaxation time $\tau \times 10^{11}$ Sec.	Viscosity Ratio $\frac{\eta_{\text{para}}}{\eta_{\text{Ben}}}$	Relaxation time ratio $\frac{\tau_{\text{para}}}{\tau_{\text{Ben}}}$
Benzene	0.70	1.30		
Paraffin	2.36	6.55	3.4	5.0

$$\frac{\tau_{\text{NB} + \text{Prffn}}}{\tau_{\text{NB} + \text{Bnzn}}} = \frac{\eta_{\text{NB} + \text{Prffn}}}{\eta_{\text{NB} + \text{Bnzn}}} \dots\dots\dots(9.1)$$

is not valid. Thus τ is far from being proportional to η originally suggested by Debye equation: $\tau = 4 \pi a^3 \eta / kT$, a being the molecular radius.

Fig. 9.3 shows the variation of τ with the % of benzene in nitrobenzene as well as with the % of paraffin in nitrobenzene and the fixed solution. As the % of paraffin increases the τ value increases given convex nature in both the solutions. But in benzene solution τ of nitrobenzene increases in a concave manner with the decrease of % of benzene. The variations of relaxation time τ of nitrobenzene of the fixed solution against macroscopic viscosity η by changing temperature as well as by gradually adding paraffin liquid are shown in Fig.9.4. The figure shows that the τ increases linearly as the viscosity η increases upto a particular value of macroscopic viscosity η_{c1} and then increases but markedly deviates from from the linearity. The value of the critical macroscopic viscosity after which $\tau \propto \eta$ does not hold good has been found from the graphs (Fig 7.4), to be $\eta_{c1} = 1.52$ cp. It suggests that the Debye equation is inapplicable to the cases where the viscosity of the solution is greater than of about 1.52 cp.

Jackson and Powles (1946) determined the relaxation time τ of benzophenone in benzene and paraffin at 19°C and observed that

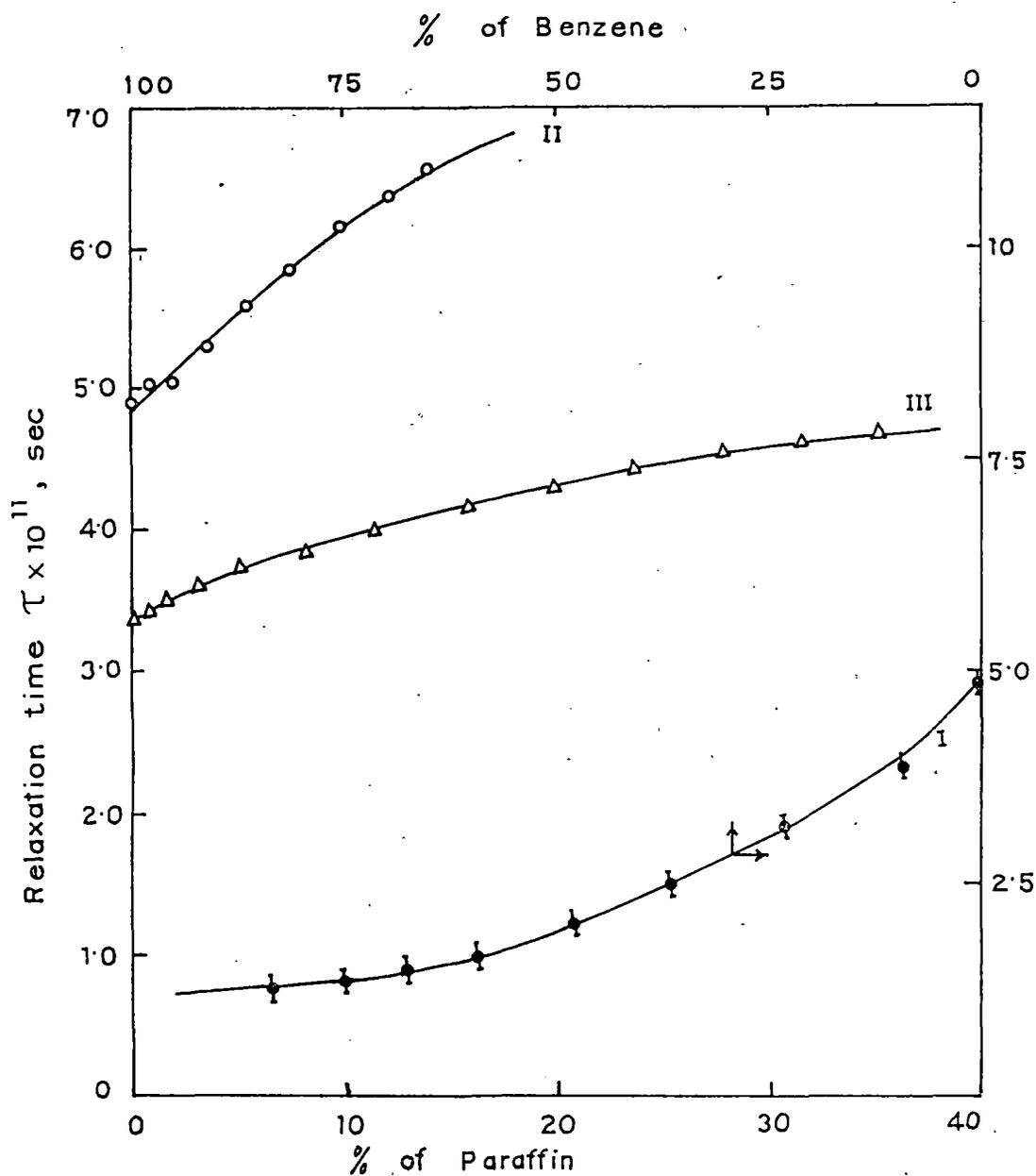


Fig. 9.3. Variation of relaxation time τ against % of benzene or paraffin.
 I (—●—) nitrobenzene + benzene at 25°C
 II (—○—) nitrobenzene + paraffin at 25°C
 III (—△—) [0.78 mole fraction of nitrobenzene in benzene] + paraffin at 25°C.

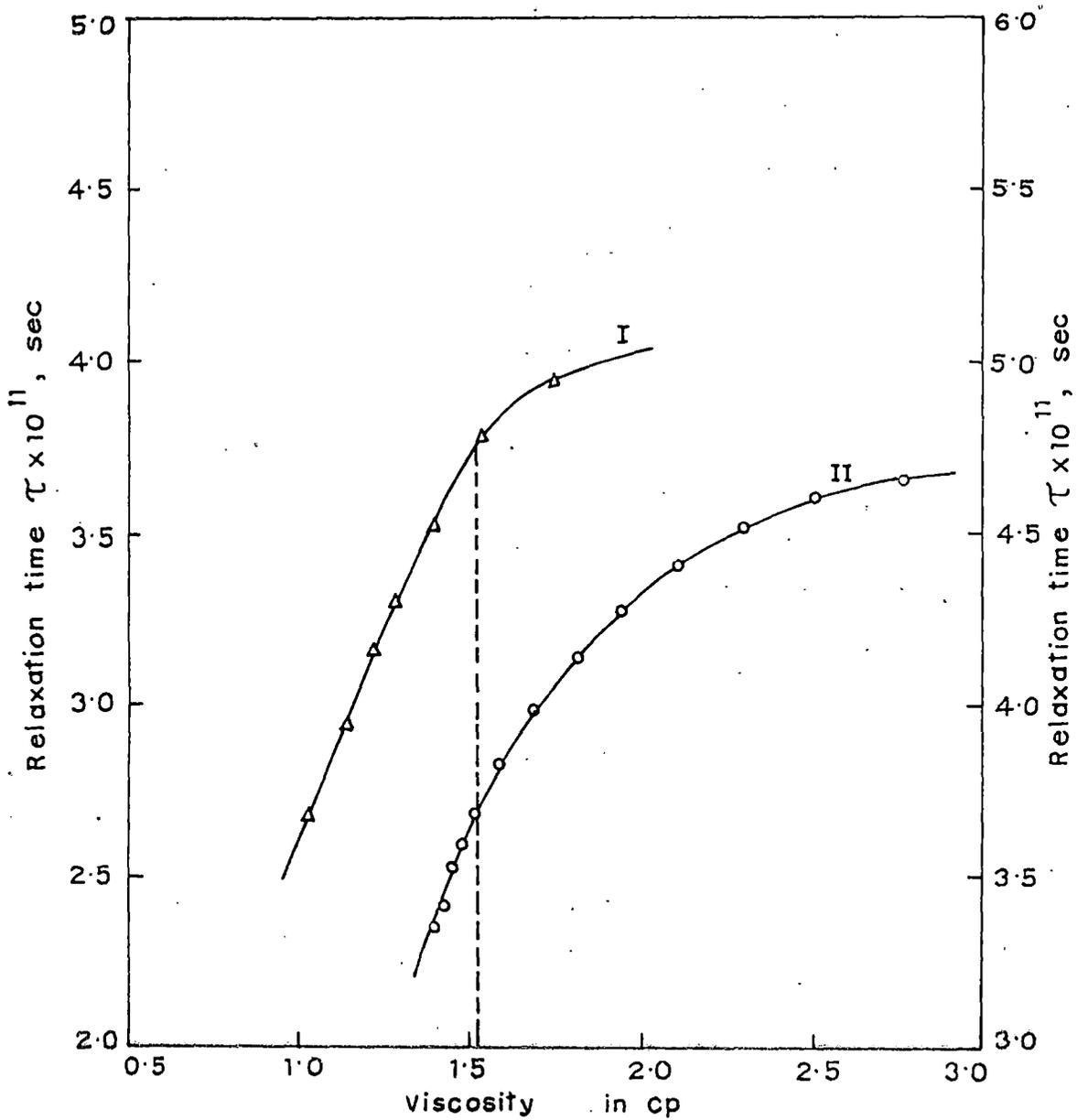


Fig. 9.4. Plot of relaxation time τ against viscosity η
 I (\triangle) a fixed solution of 0.78 mole fraction
 of nitrobenzene in benzene at various temperatures
 II (\circ) the fixed solution + paraffin at 25°C

the τ in paraffin appears to be 18 times that in benzene solution when the ratio of viscosities of paraffin and benzene is 2.98 at this temperature. A systematic examination of the influence of different solvents on the relaxation time τ of nitrobenzene was made by Whiffen (1950) and the results are given in Table 9.5. It is observed from Table 9.5 that the τ for nitrobenzene are not closely parallel to the viscosity of the solvents as given by Debye formula. Higasi (1961) emphasized that not only the solute molecules will slip in rotation past the solvent molecules, but also showed that the intermolecular interactions exceeding KT in energy may cause appreciable sticking of molecules. He observed that the ratio of the relaxation time of a polar molecule in two non-polar solvents CCl_4 and C_6H_{12} whose viscosity differs not more than 1% becomes $\tau_{CCl_4} / \tau_{C_6H_{12}} = 1.8 \pm 0.3$ and suggested an expression $\tau = \text{const. } \eta^\gamma$ where $\gamma = \Delta H_\tau / \Delta H_\eta$.

The variation of τ and η with temperature can be expressed in terms of following equations (Whiffen and Thompson 1946)

$$\tau = A \exp (\Delta H_\tau / RT) \quad \dots\dots\dots(9.2)$$

$$\eta = B \exp (\Delta H_\eta / RT) \quad \dots\dots\dots(9.3)$$

Where A and B are approximately constant over the temperature range of the present experiment and ΔH_τ and ΔH_η are the enthalpies of activation for dielectric relaxation and viscous flow respectively.

Table 9.5 - Relaxation time of nitrobenzene in different solvents

according to the measurements of Whiffen (1950) at 20°C

Solvent	Viscosity η CP	Relaxation time $\tau \times 10^{11}$ Sec	$\frac{\tau}{\eta} \times 10^9$
Carbon disulphide	0.37	0.86	2.32
n - Heptane	0.42	0.68	1.62
Benzene	0.65	1.28	1.97
Cyclohexane	0.97	0.95	0.98
Carbon-tetra- chloride	0.97	1.52	1.57

From eqn (9.2) and (9.3) we get

$$\tau/\eta = (A/B) \exp (\Delta H\tau - \Delta H\eta) /RT \dots\dots\dots(9.4)$$

Taking $\Delta H\tau = \eta \Delta H\eta$ we have from eq (9.4)

$$\begin{aligned} \tau &= (AB^{-\gamma}) \eta^\gamma \\ \tau &= \text{const. } \eta^\gamma \end{aligned} \dots\dots\dots(9.5)$$

This equation (9.5) indicates the relaxation time is a simple function of η^γ . Therefore the plot of $\log \tau$ against $\log \eta$ should be a straight line. Fig. 9.5 and 9.6 represents the plot of $\log \tau$ versus $\log \eta$ for nitrobenzene + paraffin mixtures and the fixed solution (0.78 mole fraction of nitrobenzene in benzene) + paraffin mixtures at 25°C. These figures show that the curves are straight line, but at the higher viscosity region the linearity does not hold. The critical viscosity η_{c2} upto which the linearity $\tau \propto \eta^\gamma$ holds good has been found to be 1.93 cp and 2.1 cp from the Figs 9.5 and 9.6 respectively. Again the values of τ/η and τ/η^γ indicates the same results (Table 9.1 to 9.3).

Even allowing the free space between packed molecules the value of the molecular radius 'a' calculated from the density of nitrobenzene is 3.4°A, which is much higher than the values obtained from Debye relation $\tau = 4\pi a^3 \eta_{int}/kT$ using η_{int} is equal to macroscopic viscosity η and η^γ as shown in Table 9.1 to 9.3. The calculated values of radius 'a' using $\eta_{int} = \eta$ are found to be

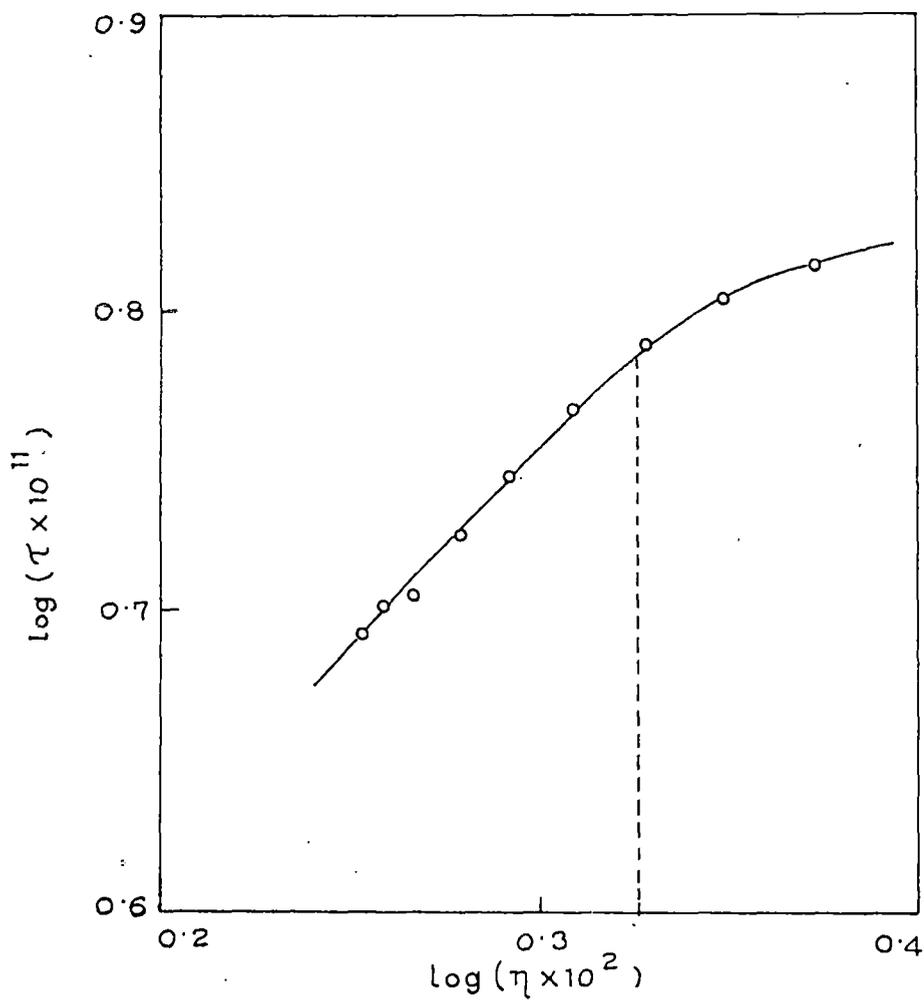


Fig. 9.5. Plot of $\log(\tau \times 10^{11})$ vs $\log(\eta \times 10^2)$ of nitrobenzene + paraffin at 25°C.

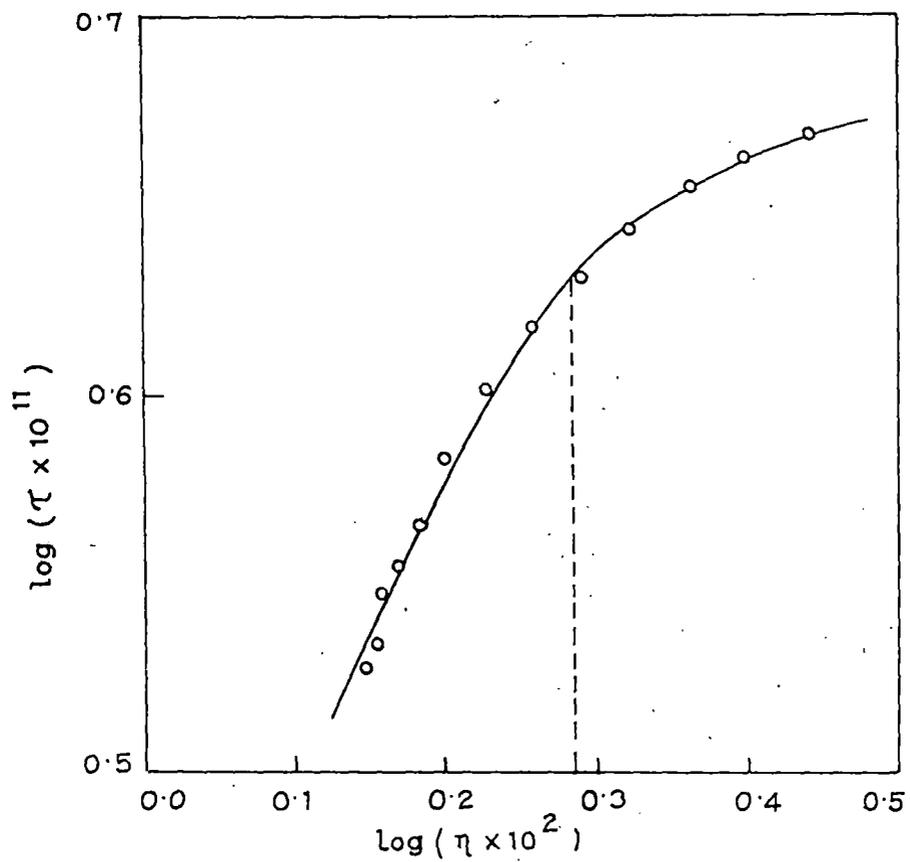


Fig. 9.6. Plot of $\log(\tau \times 10^{11})$ vs $\log(\eta \times 10^2)$ of (0.78 mole fraction of nitrobenzene in benzene) + paraffin at 25°C.

nearly constant upto $\eta \approx 1.5$ cp, but the 'a' values calculated using $\eta_{int} = \eta^x$ are fairly constant upto η is about 2cp.

Therefore it may be suggested that the relaxation time τ is far from being proportional to the macroscopic viscosity η . So it may be assumed that the Debye equation is inadequate in describing the relation between τ and η . This discrepancy probably arises from the experimental facts that the macroscopic viscosity η is used in place of internal viscosity η_{int} . Thus the assumption $\eta_{int} = \eta$ is inapplicable in representing the variation of relaxation time of a polar molecule with the viscosity of the medium also in the radio frequency electric field.

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CHAPTER X

SUMMARY OF THE RESULTS OF PRESENT WORKS AND CONCLUSION

The results and discussion of the present works have been described in detail in chapter III to IX. Here a chapterwise summary of the results are given below.

Chapter III: "Dielectric Relaxation Parameters From Ultra-High Frequency Electric Conductivity of Polar-Nonpolar liquid Mixtures".

The dipole moments μ_j of N,N - dimethyl formamide (DMF) and N,N - dimethyl acetamide (DMA) both in benzene, dioxane and carbon tetrachloride as well as of N-methyl acetamide (NMA) in benzene and dioxane at 25, 35, 45 and 55°C have been measured from the slope of concentration variation of ultra high frequency conductivity at infinite dilution with the help of relaxation time τ_a using the following equation

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

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

The relaxation times τ_a have simultaneously determined from the slopes of the linear plots of the imaginary part against the real part of uhf conductivity as given by the equation

$$K''_{ij} = K'_\alpha + K'_{ij} / \omega \tau_a$$

The temperature variation of τ_a has been used to evaluate

energy parameters ΔF_T , ΔH_T , and ΔS_T of the dielectric relaxation. The dielectric relaxation parameters, thus obtained, in different solvents at various temperatures suggested the presence of appreciable solute - solvent type of molecular associations for DMF in benzene and carbontetrachloride and for DMA and NMA in benzene only.

Chapter IV: The chapter IV under the title "Dipole Moments of Associated Binary Solutes in Benzene from Ultra-High Frequency Conductivities of Solutions" presents a method of determining the dipole moments μ_{jk} of binary polar mixture in non-polar solvent. The dipole moments of polar mixtures of N, N - dimethyl formamide (DMF) with N, N - tetramethyl urea (TMU) and N, N - dimethyl acetamide (DMA) for different mole fractions of DMF at 15°C as well as those of (1:1) polar mixture in benzene in the temperature range 15°C to 30°C have been measured from the concentration variation of uhf 9.885 GHz electric conductivity K_{ijk} of the solutions. The mole fraction and temperature variations of dipole moments μ_{jk} thus obtained when compared with the theoretical values from bond moments and bond axes indicate the very existence of solute - solvent i.e. monomer and solute-solute i.e. dimer formation in the solutions.

Chapter V: "Dipole Moments of Binary Polar Solutes from Ultra-High Frequency Conductivities of Solutions in Non-Polar Solvent".

The dipole moments μ_j and μ_k of the respective monomers and μ_{jk} of dimer of binary polar solutes like N, N - dimethyl formamide (DMF) with (I) methyl alcohols (MeOH), (II) acetonitrile (AN) and (III) acetone (AC) at different mole fractions X_j of DMF have been computed from the concentration variation of u_{hf} conductivities of solution in benzene at 15°C under 3.035 cm wavelength electric field only to locate the maximum solute - solute molecular association at $X_j = 0.5, 0.9$ and 0.5 in DMF + MeOH, DMF + AN and DMF + AC respectively. The μ_{jk} of 1:1 binary polar mixtures at 15, 20, 25 and 30°C have also been estimated only to support the above facts by showing that the dimer moments μ_{jk} decrease with temperature for all the mixtures except for DMF + AN where μ_{jk} remains almost constant.

Chapter VI: In this Chapter entitled "Theoretical Relaxation Time of Associated Binary Polar Mixture in Non-Polar Solvent", a theoretical relation based on Debye equation for calculating dielectric relaxation time τ_{jk} of a polar mixture of two associating liquids in a non-polar solvent interms of a slopes of linear variation of dielectric constants or loss against solute concentration and relaxation times τ_j and τ_k of individual components has been proposed. The relation is

$$\tau_{jk} = \frac{x_j \tau_j + (1-x_j^2) \tau_k a}{x_j^2 + a(1-x_j)}$$

or,

$$\tau_{jk} = \frac{x_j a'' + (1-x_j^2) a''}{x_j^2 \frac{a''}{\tau_j} + (1-x_j) \frac{a''}{\tau_k}}$$

where $a = \frac{(a'_k - \alpha_k a)}{(a'_j - \alpha_j a)}$

It has been tested by forty one system of six binary polar mixtures, and is found to predict better results for associated polar mixtures than the relations proposed by other workers.

Chapter VII: Double Relaxation Times of Nonspherical polar Liquids in Non-Polar Solvents - A New Approach Based on Single Frequency Measurement"

A new approach based on single frequency measurement has been suggested to estimate the double relaxation times τ_1 and τ_2 of some highly nonspherical polar molecules in non-polar solvent. The smaller relaxation time τ_1 refers to the rotation of the smallest flexible part attached to the parent molecule while the larger one τ_2 due to the end-over-end rotation of the polar molecule. The weighted contributions C_1 and C_2 towards relaxations have been calculated from Frohlich's equations as well as by a new technique adopted here. The method has been tested by fifteen

nonspherical polar liquids of which eleven molecules show double relaxation phenomenon. The dipole moments μ_1 and μ_2 have also been computed from the slope β of the ultra high frequency conductivity K_{ij} against weight fractions ω_j for the compounds in terms of τ_1 and τ_2 . The close agreement of μ_2 , thus computed with those of the existing methods, at once indicate that the approach suggested is a correct one.

Chapter VIII: "Relaxation Time and Energy of Activation of Nitrobenzene in Benzene From Radio Frequency conductivity Measurement"

The relaxation time and energy of activation of pure nitrobenzene at different temperatures and of nitrobenzene in benzene at different concentrations and temperatures -have been computed from the radio frequency conductivity measurement. The results show that in the Debye equation $\tau = 4\pi a^3 \eta / kT$, η the experimentally measured macroscopic viscosity can not be regarded as a measure of the internal viscosity in the high viscosity range. The Debye relation will be a true representation of relaxation time and viscosity if the internal viscosity η_{int} is represented by the equation $\eta_{int} = \eta^\gamma$, where γ is the ratio of enthalpies of activation for dielectric relaxation and viscous flow.

Chapter IX: "Radio Frequency conductivity and Relaxation

Time of Nitrobenzene in Benzene in Benzene and Paraffin Solutions".

In continuation of the work described in chapter VIII, the r.f conductivity of (i) nitrobenzene in liquid paraffin at different concentration (ii) a fixed solution of 0.78 mole fraction of nitrobenzene in benzene at different temperatures and (iii) the fixed solution of nitrobenzene in benzene mixed with various percentage of solvent paraffin at room temperature, have been measured. The relaxation times have been computed using Ghosh and Chaudhury (1980) relation $\tau = 2a^2e/3gkT$. The variations of τ against viscosity η and $\log \tau$ vs. $\log \eta$ show that the Debye relation connecting τ and η is inapplicable to the cases where the viscosity of the solution is greater than of about 1.52 cp. Again it is found that the representation of internal viscosity by $\eta_{int} = \eta^\gamma$ is adequate up to macroscopic viscosity $\eta \approx 2$ cp.

The discussions of the results of this thesis, thus summarised in this chapter, reveal the fact that it has opened a new and vast scope to work further in the investigation of dielectric relation phenomena of polar - nonpolar liquid mixtures under uhf electric field.

APPENDIX

LIST OF PUBLISHED AND COMMUNICATED PAPERS

1. Dielectric Relaxation Parameters From Ultra-High Frequency Electric Conductivity of Polar-Nonpolar Liquid Mixtures - U.Saha and S.Acharyya, Ind. J.Pure & Appl. Physics
(Accepted)
2. Dipole Moments of Associated Binary Solutes in Benzene From Ultra - High Frequency conductivities of Solutions - A.K.Chatterjee, U.Saha, N.Nandi, R.C.Basak and S.Acharyya, Indian J.Physics 66B (1992) 291-302.
3. Dipole Moments of Binary Polar Solutes From Ultra - High Frequency conductivities of Solutions - in Non-Polar Solvents - U.Saha, and S.Acharyya, Ind J.Pure & Appl. Phys 31 (1993) 181-186.
4. Theoretical Relaxation Time of Associated Binary Polar Mixture in Non-Polar Solvent - U. Saha and S. Acharyya, J. Phys D: Appl Phys (G.B)(communicated)
5. Double Relaxation Times of Nonspherical Polar Liquids in Non-Polar Solvents - A New Approach Based on Single Frequency Measurement - U.Saha, S.K.Sit, R.C. Basak, and S.Acharyya, J.Phys D: Appl Phys (G.B.) (in Press).

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**Dipole moments of associated binary solutes
in benzene from ultra high frequency
conductivities of solutions**

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Dipole moments of associated binary solutes in benzene from ultra high frequency conductivities of solutions

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Abstract : The dipole moments of the binary polar mixtures in benzene of NN-dimethyl-formamide (DMF) with NN-tetramethyl-urea (TMU) and NN-dimethyl-acetamide (DMA) respectively for different mole fractions of DMF as well as those of their (1 : 1) mixtures in benzene in the temperature range of 15°C to 30°C are measured from the concentration variation of ultra high frequency 9.885 GHz electric conductivity K_{ijk} of the solutions. The method used here is an extension of our previous work for a polar-nonpolar liquid mixture. The mole fraction and temperature variations of dipole moments thus obtained when compared with the theoretical values from the bond moments and bond axes indicate the very existence of solute-solvent i.e. monomer and solute-solute i.e. dimer formations which occur in the liquid mixtures when subjected to the ultra high frequency alternating electric fields.

Keywords : Uhf conductivity, dipole moment, monomer and dimer.

PACS Nos. : 35.20. My, 31.70. Dk

1. Introduction

Now a days, the estimation of dipole moment μ_j as well as the relaxation time τ_r of a single polar solute dissolved in a nonpolar solvent like benzene or dioxane or carbontetrachloride etc. under the application of ultra-high-frequency electric field are really very encouraging (Acharyya and Chatterjee 1985, Acharyya *et al* 1986, Dhull *et al* 1982) as they throw much light on the structures of monomer and dimer formations in a liquid mixture. But the measurements of μ_{jk} of a binary polar mixtures in a given nonpolar solvent are, however, very scanty. There are several methods (Gopala Krishna 1957, Sen and Ghosh 1972) to estimate μ_j of a polar solute dissolved in a nonpolar solvent under an alternating microwave or radio frequency electric field.

We (Acharyya and Chatterjee 1985), however, devised a method to find out the relaxation time and the dipole moment of a polar solute in a nonpolar solvent under the *uhf* electric field. In this paper we thought to extend our previous method to obtain the dipole moment of binary polar solutes in a nonpolar solvent. The *uhf* conductivity K_{ijk} of binary polar solutes dissolved in a nonpolar solvent is comparatively easy to measure down to very

low concentration by using a klystron or a radiofrequency Hartley oscillator in the laboratory. The data of *uhf* conductivity under the radiofrequency or the microwave electric field is very limited (Sen and Ghosh 1972). Recently, Shärma and Sharma (1984, 1985) reported the measured values of ϵ'_{ijk} and ϵ''_{ijk} the real and the imaginary parts of the complex dielectric constant ϵ^*_{ijk} of binary polar mixtures consisting of N,N-dimethyl formamide (DMF) and N,N-tetramethyl urea (TMU) as well as N,N-dimethyl formamide (DMF) and N,N-dimethyl acetamide (DMA) in benzene solution using microwave absorption technique at a frequency of 9.885 GHz electric field, in order to collect information regarding the solute-solvent and solute-solute molecular association in the liquid mixtures. We, therefore tempted to use these measured values of ϵ'_{ijk} and ϵ''_{ijk} of the two binary polar mixtures for different mole fractions x_j of DMF at 15°C to 30°C to obtain *hf* conductivities K_{ij} , K_{ik} and K_{ijk} 's for different weight fractions of single and binary polar solutes using Murphy-Morgan (1939) relation :

$$K_{ijk} = K'_{ijk} + jK''_{ijk}, \text{ where } K'_{ijk} = \frac{\omega\epsilon''_{ijk}}{4\pi} \text{ is the real part and } K''_{ijk} = \frac{\omega\epsilon'_{ijk}}{4\pi} \text{ is the}$$

imaginary part of the *hf* conductivity. Amides are very important dielectric solutes for their wide biological applications and they form the basic building blocks in proteins. That is why amides attracted much attention of a large number of workers (Sato *et al* 1976). The K_{ijk} 's of DMF + TMU mixtures at 15°C in terms of the weight fractions ω_{jk} in benzene were found to be of the following equations :

$$K_{ik} \times 10^{-10} = 1.167 - 1.203\omega_k + 795.72\omega_k^2$$

$$K_{ijk} \times 10^{-10} = 1.1455 + 3.9273\omega_{jk} - 21.4223\omega_{jk}^2$$

$$K_{ij} \times 10^{-10} = 1.128 + 6.9023\omega_{jk} - 51.4435\omega_{jk}^2$$

$$K_{ijk} \times 10^{-10} = 1.1247 + 11.9614\omega_{jk} - 249.0353\omega_{jk}^2$$

$$K_{ik} \times 10^{-10} = 1.1286 + 11.587\omega_{jk} - 120.381\omega_{jk}^2$$

$K_{ij} \times 10^{-10} = 1.148 + 9.212\omega_j + 109.655\omega_j^2$ respectively for the mole fractions 0.0, 0.1, 0.3, 0.7, 0.9 and 1.0 of DMF in TMU and benzene solutions. They are shown graphically in Figure 1 with the measured values of K_{ijk} upon the fitted lines.

The usual behaviour of K_{ijk} of a ternary solution in the low concentration region is thus given by $K_{ijk} \times 10^{-10} = \alpha + \beta\omega_{jk} + \gamma\omega_{jk}^2$ if the polar solutes under consideration have different amount of polarities. When the individual polar solutes like DMF and DMA have almost of the same amount of polarity the *h-f* conductivity K_{ijk} were found to be linear like $K_{ijk} \times 10^{-10} = \alpha + \beta\omega_{jk}$. The linear variation of *uhf* conductivities K_{ijk} of DMF + DMA mixtures in benzene as a function of weight fraction ω_{jk} of the solutes was worked out to be :

$$K_{ij} \times 10^{-10} = 1.1447 + 10.5665\omega_j$$

$$K_{ijk} \times 10^{-10} = 1.1326 + 11.4739\omega_{jk}$$

$$K_{ik} \times 10^{-10} = 1.1302 + 11.4907\omega_{jk}$$

$$K_{ijk} \times 10^{-10} = 1.1413 + 8.9143\omega_{jk}$$

$$K_{ijk} \times 10^{-10} = 1.1268 + 11.2724\omega_{jk} \text{ and}$$

$K_{ik} \times 10^{-10} = 1.1393 + 9.3479\omega_k$ for the given mole fractions 1.0, 0.9, 0.7, 0.3, 0.1 and 0.0 of DMF in DMA and benzene solution at 15°C.

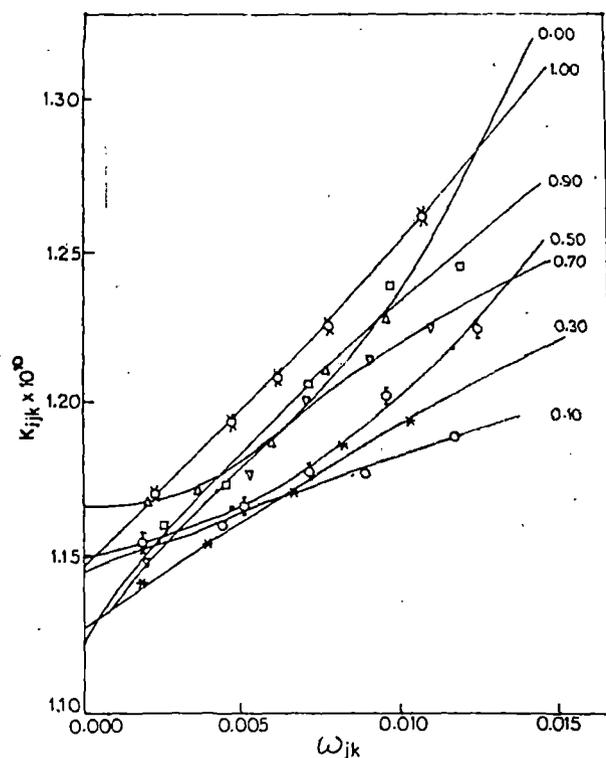


Figure 1. Concentration variation of K_{ijk} of DMF + TMU in benzene at different mole fractions of DMF at 15°C.

Again K_{ijk} of 1 : 1 mixtures of DMF and TMU as well as DMF and DMA in benzene as a function of ω_{jk} were also arrived at :

$$K_{ijk} \times 10^{-10} = 1.1497 + 1.554\omega_{jk} + 359.0195\omega_{jk}^2 \text{ at } 15^\circ\text{C},$$

$$K_{ijk} \times 10^{-10} = 1.135 + 4.70\omega_{jk} + 153.053\omega_{jk}^2 \text{ at } 20^\circ\text{C},$$

$$K_{ijk} \times 10^{-10} = 1.118 + 7.532\omega_{jk} - 99.625\omega_{jk}^2 \text{ at } 30^\circ\text{C},$$

and $K_{ijk} \times 10^{-10} = 1.1455 + 8.9409\omega_{jk} \text{ at } 15^\circ\text{C},$

$$K_{ijk} \times 10^{-10} = 1.1342 + 9.8777\omega_{jk} \text{ at } 20^\circ\text{C},$$

$$K_{ijk} \times 10^{-10} = 1.1303 + 9.2387\omega_{jk} \text{ at } 25^\circ\text{C}, \text{ and}$$

$$K_{ijk} \times 10^{-10} = 1.1252 + 8.9482\omega_{jk} \text{ at } 30^\circ\text{C}, \text{ respectively.}$$

The h - f conductivity data of 1 : 1 mixtures of two polar solutes consisting of DMF + TMU and DMF + DMA respectively at different experimental temperatures are graphically shown in Figures 2 and 3 along with the experimentally measured K_{ijk} 's upon them. It is found

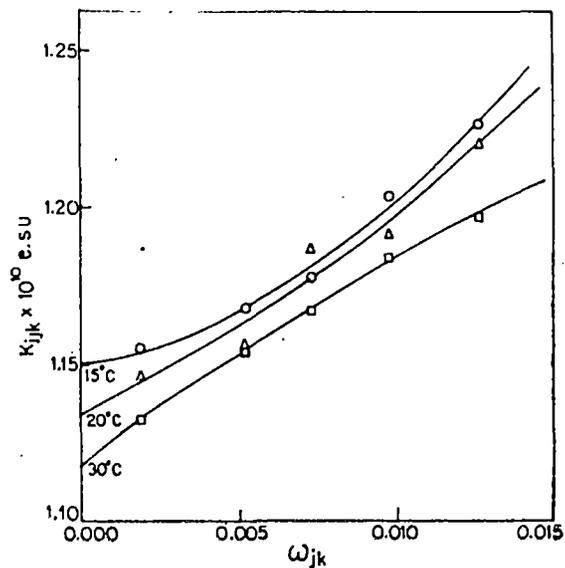


Figure 2. Concentration variation of K_{ijk} of DMF + TMU (50% each) in benzene at 15, 20 and 30°C.

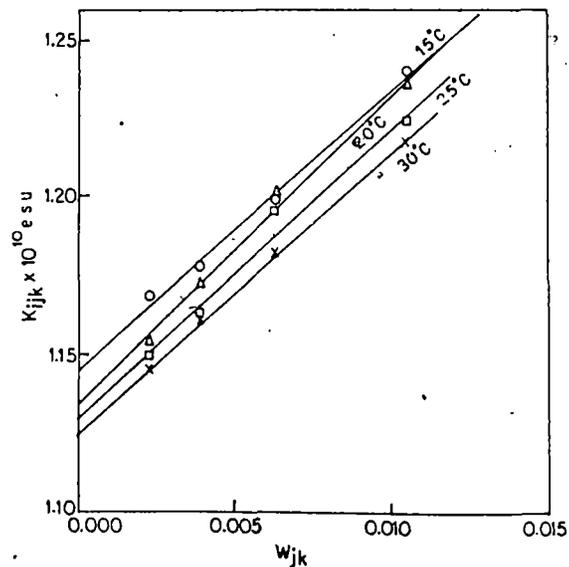


Figure 3. Concentration variation of K_{ijk} of DMF + DMA (50% each) in benzene at 15, 20, 25 and 30°C.

difficult to plot the estimated h - f conductivities of DMF and DMA as a function of weight fraction ω_{jk} for different mole fractions of DMF at 15°C as their slopes and intercepts are very close probably due to the more or less same dipole moments of the two amides under investigation. The ultra high frequency conductivity data of polar-nonpolar liquid mixture are very much sensitive to yield the dipole moment of single or binary polar solutes. Hence the information regarding the various types of molecular interactions of solute-solute and solute-solvent could, however, be inferred from the estimated values of the dipole moments. The variation of dipole moment with temperature is not a new concept, but it actually occurs when the polar-nonpolar liquid mixture is subjected to the high frequency electric field of GHz region (Acharyya *et al* 1982, 1986, Ras and Bordewijk 1971), probably due to stretching of the bond lengths of the molecules at an elevated temperature. The dipole moments μ_{jk} 's of the associated polar solutes of 50% DMF and 50% TMU as well as 50% DMF and 50% DMA dissolved in benzene have been calculated from the concentration variation of uhf conductivity K_{ijk} at different experimental temperatures $t^\circ\text{C}$. The most probable variation of μ_{jk} with respect to the temperature change in $^\circ\text{C}$ is given by :

$$\mu_{jk} = -4.393 + 0.6248t - 1.157 \times 10^{-2}t^2$$

for DMF and TMU mixtures in benzene showing the zero value of μ_{jk} at 8.31°C and 45.69°C respectively due to orientation of the monomer dipole moments μ_j and μ_k of the individual solutes. The temperature variation of μ_{jk} of 1 : 1 mixture of DMF and DMA in Benzene was also worked out to be :

$$\mu_{jk} = 2.97 + 0.133t - 3 \times 10^{-3}t^2.$$

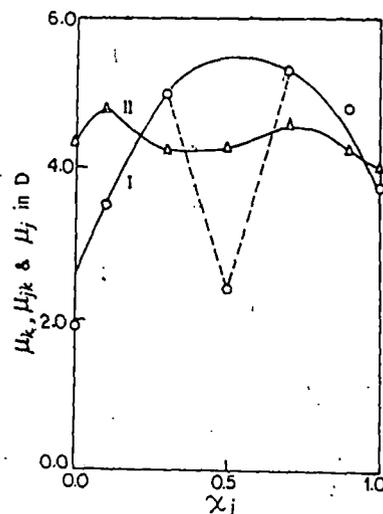


Figure 4. Variation of experimentally observed dipole moments μ_k , μ_{jk} and μ_j with mole fraction of DMF in DMF + TMU and DMF + DMA mixtures at 15°C (—O—O— of DMF + TMU and —Δ—Δ— for DMF + DMA).

showing a maximum value of μ_{jk} at 22.5°C. Both the μ_{jk} 's thus obtained are displayed graphically in Figure 5.

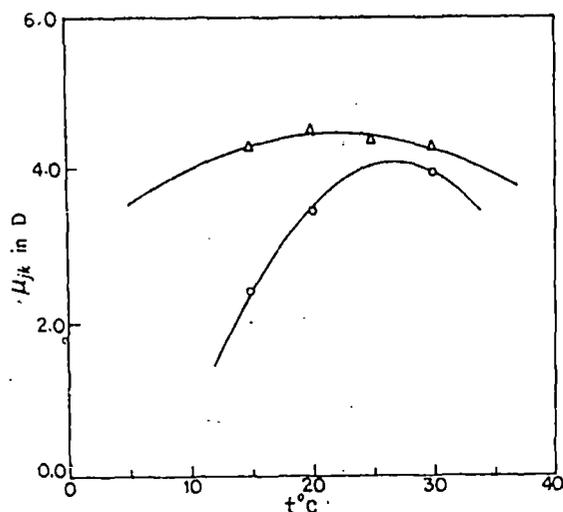


Figure 5. Variation of experimentally observed dipole moments with temperatures in °C for DMF + TMU and DMF + DMA in 1 : 1 mixtures (—O—O— for DMF + TMU and —Δ—Δ— for DMF + DMA).

As evident from Table 1, when the mole fractions of DMF are 0% and 100% respectively at 15°C indicate $\mu_j = 3.82\text{D}$ for DMF, $\mu_k = 1.90\text{D}$ for TMU and $\mu_k = 4.02\text{D}$ for DMA (Figure 4) as their individual theoretical dipole moments whereas the experimentally measured values are $\mu_j = 3.76\text{D}$ and 4.02D for DMF in two mixtures, $\mu_k = 1.89\text{D}$ for TMU and $\mu_k = 4.33\text{D}$ for DMA respectively.

2. Theoretical formulations

According to Murphy and Morgan (1939) relation the magnitude of the total h - f conductivity K_{ijk} for a given weight fraction ω_{jk} of a binary solute (j and k) dissolved in a nonpolar solvent (i) is usually given by

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

where $\omega = 2\pi f$; $f = 9.885\text{ GHz}$ being the frequency of the applied h - f electric field in the present work. The value of real part of the dielectric constant ε'_{ijk} of the solution in the microwave electric field is very small and is often equal to optical dielectric constant, but still $\varepsilon'_{ijk} \gg \varepsilon''_{ijk}$ where ε''_{ijk} is the dielectric loss which is responsible for the absorption of electrical energy to offer resistance to the polarisation. Hence it is evident that in the electric field of microwave region, the magnitude of the total conductivity becomes

$$K_{ijk} = \frac{\omega}{4\pi} \varepsilon'_{ijk} \quad (2)$$

Table 1. Dipole moments of N,N-dimethyl formamide (DMF) in DMF+N,N-tetramethyl urea (TMU) and in DMF+N,N-dimethyl acetamide (DMA) mixtures in benzene as a function of mole fraction x_j of DMF at 15°C as well as those of (1 : 1) DMF+TMU and (1 : 1) DMF+DMA mixtures in benzene at different experimental temperatures in °C.

System	temp. t in °C	Mole fractions of DMF x_j	Slope of $K_{ijk} - \omega_{jk}$ curve $\beta \times 10^{-10}$	Assumed molecular wt. M_{jk} of solutes	$b = 1/(1 + \omega^2 \tau^2)$	Computed μ_j, μ_k and μ_{jk} in D (expt.)	Calculated μ_j, μ_k and μ_{jk} in D from the values of bond moments and bond axes
DMF and TMU in benzene	15	1.00	9.2120	73.0920	0.8406	3.76	3.82
		0.90	11.5870	77.3986	0.6853	4.80	3.63
		0.70	11.9614	86.0118	0.6433	5.31	3.24
		0.30	6.9023	103.2382	0.5120	4.95	2.48
		0.10	3.9273	111.8514	0.6402	3.48	2.10
		0.00	1.2030	116.1580	0.6909	1.89	1.90
DMF and DMA in benzene	15	1.00	10.5665	73.0944	0.8406	4.02	3.82
		0.90	11.4739	74.4971	0.8193	4.29	3.84
		0.70	11.4907	77.3024	0.7543	4.56	3.88
		0.30	8.9143	82.9132	0.6929	4.23	3.96
		0.10	11.2724	85.7185	0.7575	4.74	4.00
		0.00	9.3479	87.1212	0.7660	4.33	4.02
DMF and TMU in benzene	15	0.50	1.5540	94.6250	0.4520	2.39	2.40
	20	0.50	4.7000	94.6250	0.6684	3.42	
	30	0.50	7.5320	94.6250	0.8770	3.94	
DMF and DMA in benzene	15	0.50	8.9409	80.1078	0.6929	4.27	4.27
	20	0.50	9.8777	80.1078	0.7120	4.49	
	25	0.50	9.2387	80.1078	0.7248	4.36	
	30	0.50	8.9482	80.1078	0.7470	4.28	

It can be shown that the real part $K'_{ijk} = \omega \epsilon''_{ijk} / 4\pi$ of h - f conductivity of solution of weight fraction ω_{jk} of binary polar solute in non-polar solvent at temperature T °K is

$$K'_{ijk} = \frac{\mu_{jk}^2 N \rho_{ijk} F_{ijk}}{3M_{jk} kT} \frac{\omega^2 \tau_s}{1 + \omega^2 \tau_s^2} \omega_{jk} \quad (3)$$

where μ_{jk} is the dipole moment of polar solutes of molecular weight $M_{jk} = x_j M_j + x_k M_k$, x_j and x_k being the mole fraction of individual solutes in binary mixtures of polar solute having molecular weights M_j and M_k respectively, N is the Avogadro number, k is the Boltzmann constant and $F_{ijk} = [(\epsilon_{ijk} + 2)/3]^2$ is the local field.

$$\text{But for } hf \text{ region } \epsilon'_{ijk} = \epsilon''_{ijk} + \epsilon''_{ijk} / \omega \tau_s \quad (4)$$

and from eqs. (2) and (4) we get

$$K_{ijk} = K''_{ijk} + K'_{ijk} / \omega \tau_s \quad (5)$$

where $K''_{ijk} = \omega \epsilon''_{ijk} / 4\pi$ is a constant conductivity and τ_s is the relaxation time of the associated solutes. Since K_{ijk} is a function of ω_{jk} from eq. (5) we have

$$\left(\frac{dK'_{ijk}}{d\omega_{jk}} \right)_{\omega_{jk} \rightarrow 0} = \omega \tau_s \left(\frac{dK_{ijk}}{d\omega_{jk}} \right)_{\omega_{jk} \rightarrow 0} = \omega \tau_s \beta \quad (6)$$

where β is the slope of $K_{ijk} - \omega_{jk}$ curve at $\omega_{jk} \rightarrow 0$. When $\omega_{jk} \rightarrow 0$ ρ_{ijk} the density of the solution becomes ρ_i , the density of the solvent and local field F_{ijk} of the solution becomes $F_i = [(\epsilon_i + 2)/3]^2$, local field of the solvent. Under this condition, eq. (3) on the differentiation with respect to ω_{jk} takes the form:

$$\left(\frac{dK'_{ijk}}{d\omega_{jk}} \right)_{\omega_{jk} \rightarrow 0} = \frac{\mu_{jk}^2 N \rho_i F_i}{3M_{jk} kT} \left(\frac{\omega^2 \tau_s}{1 + \omega^2 \tau_s^2} \right) \quad (7)$$

From eqs. (6) and (7) the dipole moment of associated polar solutes μ_{jk} is

$$\mu_{jk} = \left(\frac{3M_{jk} kT}{N \rho_i F_i} \cdot \frac{\beta}{\omega b} \right)^{1/2} \quad (8)$$

$$\text{where } b = \frac{1}{(1 + \omega^2 \tau_s^2)} \quad (9)$$

Now b could, however, be estimated from eq. (9) in terms of the available relaxation time τ to obtain the dipole moment of associated solutes from eq. (8) in a suitable solvent.

3. Results and discussion

The estimated uhf conductivity of DMF + TMU and DMF + DMA in benzene respectively at 15°C are already presented by the fitted polynomial equations in terms of the weight fractions ω_{jk} of the respective binary solutes for different mole fractions of DMF in Section 1. The K_{ijk} 's of DMF + TMU mixtures for different mole fractions of DMF are shown graphically in Figure 1, with respect to ω_{jk} of the solutes. Similarly those of 1:

mixtures of DMF in TMU and DMF in DMA with benzene as solvent in terms of ω_{jk} at different experimental temperatures in the range of 15°C to 30°C respectively are also shown graphically in Figures 2 and 3. The weight fractions ω_{jk} of the binary solutes as changes in the mixtures, the curves of K_{ijk} against ω_{jk} have different intercepts and slopes. This sort of behaviour of $K_{ijk} - \omega_{jk}$ curves do not occur for different x_j and for different experimental temperatures if we measure the conductivities in comparatively higher concentration region (Acharyya *et al* 1982). The K_{ijk} curves at all the experimental temperatures for a wide range of concentration when are drawn, are expected to meet at a common point on the K_{ijk} axis because the term $(\rho_{ijk} F_{ijk} / T)$ in eq. (3) assumes a constant value 0.006 at $\omega_{jk} \rightarrow 0$ for benzene as solvent. At $\omega_{jk} \rightarrow 0$, the intercepts of $K_{ijk} - \omega_{jk}$ curves at different temperatures are incidentally different and decrease with increase of temperature as observed in Figures 2 and 3, due to solvation effect (Datta *et al* 1981).

When the mole fractions x_j of DMF in the two mixtures are in the limit of $x_j = 0.0$ and $x_j = 1.0$ we get what are known as the concentration variation of *hf* conductivities K_{ik} and K_{ij} of TMU or DMA and DMF respectively in benzene against weight fractions ω_k and ω_j of the solutes (Figure 1) at 15°C. The estimated slopes β as obtained from fitted equations of the K_{ijk} against ω_{jk} are very important to yield the dipole moments. When $x_j = 0.0$ and 1.0 we get monomer dipole moments μ_k for TMU or DMA and μ_j for DMF respectively. The slope β of $K_{ijk} - \omega_{jk}$ curves are placed in Table 1. The dipole moments thus obtained are considered as monomer because the concentration of solutes in the solution is very low and lies within the range of about 0.0023 to 0.0110 weight fraction. The values of μ_k for TMU and μ_j for DMF were thus found out to be 1.89D and 3.76D respectively. The values of μ_{jk} , the dipole moments of the associated solutes (solute-solute molecular association) at 15°C, presented in Table 1, can, however, be fitted by a polynomial equation of μ_{jk} as a function of x_j of DMF :

$$\mu_{jk} = 2.5145 + 10.7785 x_j - 9.42 x_j^2$$

The graph of μ_{jk} against x_j satisfying the above equation is shown in Figure 4, with the experimentally estimated values of μ_k , μ_{jk} and μ_j respectively from eq. (8) with the knowledge of the reported τ_s (Sharma and Sharma 1985). The fitted curve, however, excludes two values of the dipole moments : one $\mu_k = 1.89D$ for TMU alone and the other $\mu_{jk} = 2.39D$ for dimer at $x_j = 0$ and $x_j = 0.5$ respectively. As x_j of DMF changes μ_{jk} gradually increases in a regular manner and then suddenly drops to a very low value at $x_j = 0.5$ (Figure 4). after $x_j > 0.5$, μ_{jk} slowly decreases thus resembling the convex nature to terminate to $\mu_j = 3.76D$ of the solute-solvent associated monomer of DMF at $x_j = 1.0$. The sudden drop in the value of μ_{jk} from its regular behaviour with x_j is probably due to the formation of dimer in the liquid mixture having mole fraction nearly 0.5 of DMF. In the case of DMF and DMA mixture in benzene the monomer dipole moments for DMA and DMF are $\mu_k = 4.33D$ and $\mu_j = 4.02D$ respectively from eq. (8) in terms of reported τ_s (Sharma and Sharma 1984). From Figure 4, as x_j of DMF is $0.0 < x_j < 1.0$, we get μ_{jk} 's at

15°C using the slopes of $K_{ijk} - \omega_{jk}$ linear equations presented in Section 1. The curve in Figure 4 drawn with all μ_k, μ_{jk} 's and μ_j at 15°C as a function of x_j shows two peaks : one at $x_j = 0.1$ and the other at $x_j = 0.7$ and in the range of $0.1 \leq x_j \leq 0.7$ it is simply a concave curve suggesting the formation of dimer in this region. But the dipole moment μ_{jk} is to be minimum at $x_j = 0.3$ (Figure 4) and hence the dimerisation of this mixture may be yet to be maximum near $x_j = 0.3$ unlike the observation made by Sharma and Sharma (1984). The data of μ_j, μ_k and μ_{jk} 's of DMF, TMU or DMA and their respective binary solutes at 15°C as well as μ_{jk} 's of 1 : 1 mixtures of DMF + TMU and DMF + DMA in benzene at different experimental temperatures which are listed in the seventh column of Table 1, are plotted in Figures 4 and 5 as the functions of x_j of DMF and temperature t in °C respectively.

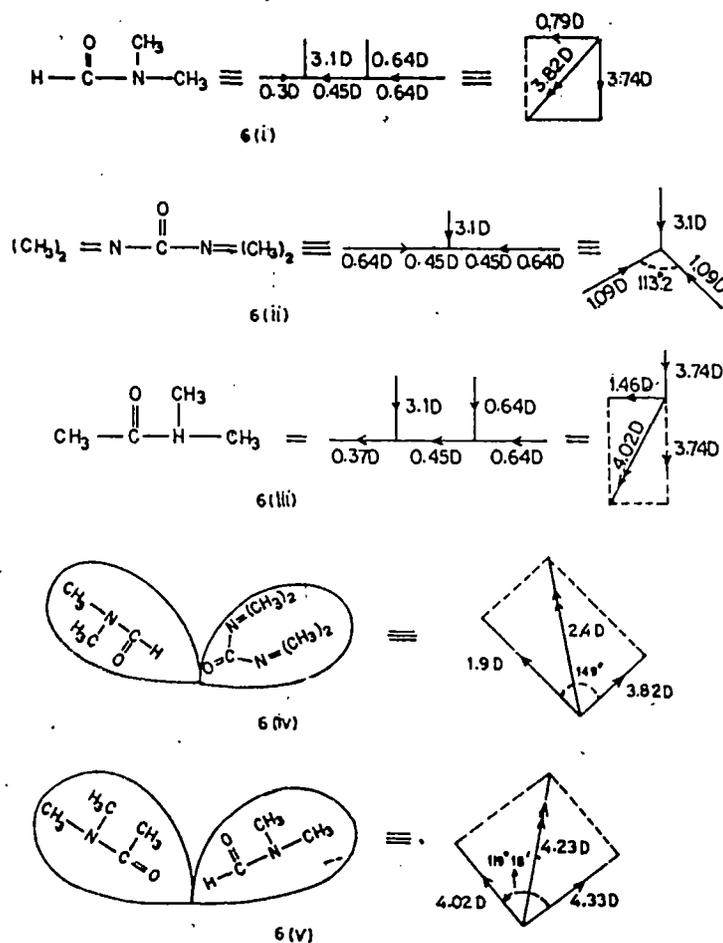


Figure 6. (i) Structural form of DMF, (ii) Structural form of TMU, (iii) Structural form of DMA, (iv) Structural form of dimer (DMF + TMU) and (v) Structural form of dimer (DMF + DMA)

The nature of behaviour of μ_{jk} against the temperature t in °C are plotted in Figure with the experimentally measured values upon them. The curve of μ_{jk} for the 1st mixture

shows that the monomer solutes orient along their dipole axes such that the resultant dipole moments are zero at 8.31°C and 45.69°C respectively. As shown in Figure 5, the μ_{jk} 's of the expected associated solutes for 1 : 1 mixture of DMF and DMA in benzene increases slowly from 2.97D at 0°C to the maximum 4.49D at 22.5°C and then slowly decreases to 3.49D at 40°C. All these data show that the dipole moments of the 1 : 1 binary polar solute mixture in benzene do change with temperature in the *hf* region of alternating electric field.

Finally, to interpret the experimental monomer dipole moments of the solutes we calculated the theoretical μ_j and μ_k as sketched in Figure 6, for DMF, TMU and DMA in terms of bond moments, bond axes and bond angles respectively. In DMF, the bond moments of C = O and CH₃ — N act along a common axis, being sketched in Figure 6(i), with a resultant dipole moment of 3.74D while those of CH₃ — N, H — C and N — C make the resultant moment 0.79D acting in other direction. They, thus give rise to the monomer dipole moment 3.82D of pure DMF in benzene. But the Table 1 shows 3.76D and 4.02D respectively as the experimental dipole moments of DMF in the two mixtures under consideration probably due to the effect of trace presence of TMU and DMA in benzene at $\omega_{jk} \rightarrow 0$. Both the arms in TMU contain (CH₃) = N about a carbon atom in C = O form an angle 113°.2 to give the resultant moment of nearly 1.2D. This in its turn reduces the bond moment of 3.1D of C = O to give rise to 1.9D as the monomer dipole moment of TMU (Figure 6 (ii)) in close agreement with the experimental $\mu = 1.89$ D (Table 1). Similarly in case of DMA, the group moments of CH₃—N and C = O act along the same direction having the resultant moment 3.74D which with the resultant moment of 1.46D for C—CH₃, C—N and N—CH₃ (Figure 6 (iii)) yields 4.02D (Table 1) as the monomer dipole moment of DMA. With these preferred conformational directions for DMF and TMU and DMA as sketched in Figure 6, the calculated values of dipole moments from the vector model, assuming molecules to be planer are in close agreement with the experimental values as evident in Table 1 in which all the data are placed for comparison. The smaller values of μ_{jk} for 50 : 50 and 30 : 70 mixtures of DMF + TMU and DMF + DMA in benzene are due to dimer formation. For dimer formation between DMF and TMU (Figure (6 iv)) and DMF and DMA (Figure (6 v)) in benzene, the two monomers attach each other with their most electropositive (—H) and electronegative (—O—) elements forming angles 149° and 119°.18 at mole fractions $x_j = 0.5$ and $x_j = 0.3$ for DMF in the two mixtures respectively as calculated from the experimental μ_j , μ_k and μ_{jk} values. The values of μ_{jk} 's of dimers change strongly with temperature probably due to this preferred conformational directional angle which changes with temperature. The change is more pronounced in the case of maximum dimerisation (Figure 5). This is the reason that μ_{jk} of 50% of DMF in the mixture exhibit zero value at 8.31°C and 45.69°C whereas in the 2nd mixture the μ_{jk} changes very slowly as the maximum dimerisation occurs for 30% of DMF in this mixture.

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Dipole moments of binary polar solutes from ultra high frequency conductivities of solutions in non-polar solvent

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The dipole moments μ_j and μ_k of the respective monomers and μ_{jk} of dimer of binary polar solutes like N,N-dimethyl formamide (DMF) with (I) methyl alcohol (MeOH), (II) acetonitrile (AN) and (III) acetone (AC) at different mole fractions X_j of DMF are computed from the concentration variation of ultra high frequency conductivities of solutions in benzene at 15°C under 3.035 cm wavelength electric field only to locate the maximum solute-solute molecular associations at $X_j = 0.5, 0.9$ and 0.5 in DMF+MeOH, DMF+AN and DMF+AC respectively. The μ_{jk} of 1:1 binary polar mixtures at 15, 20, 25 and 30°C are also estimated only to support the above facts by showing that the dimer moments μ_{jk}^2 decrease with temperature for all the mixtures except for DMF+AN where μ_{jk} remains almost constant.

1 Introduction

Now a days the study of dielectric relaxation mechanism of polar liquids dissolved in non-polar solvents from the concentration variation of the ultra high frequency (uhf) conductivity¹⁻⁴ of solutions is widely used in comparison to the pure liquids because of the absence of dipole-dipole interactions and low viscosity coefficients. The concentration variation of uhf conductivity in a microwave or radio-frequency electric field for the polar-non-polar liquid mixtures is very much sensitive to yield the molecular parameters such as relaxation times τ_s , dipole moment μ_j , thermodynamic relaxation parameters ΔH_τ , ΔS_τ and ΔF_τ etc. They also provide one with the information regarding the solute-solvent and solute-solute type of molecular associations^{2,4}. But the study of dielectric relaxation behaviour of binary polar liquid mixtures in a non-polar solvent is of great interest although the data of such mixtures are very scanty. Schallamach⁵, however, studied the temperature dependence of a few mixtures of relatively complex non-rigid molecules under a constant radio-frequency electric field and revealed that the mixtures of both associated or non-associated polar molecules correspond to a single relaxation process. The above conclusion was also arrived at by Madan⁶ and, Vyas and Vashisth⁷ on binary polar mixtures of alcohols, amides and ketones. In contrast, the results of other workers^{8,9} suggest the possibility of two dispersion regions to describe the dielectric behaviour of binary polar mix-

tures. But still a few systems have been examined so far and even less information is available for polar mixtures in non-polar solvents. The binary polar mixtures of N,N-dimethyl formamide (DMF) with (I) methyl alcohol (MeOH) or (II) acetonitrile (AN) or (III) acetone (AC) respectively in benzene from our recently developed method¹⁰ are studied. The present investigation is, however, concerned with the estimation of dipole moment of these polar mixtures from the slopes of uhf conductivity at infinite dilution. Sharma *et al.*¹¹⁻¹³ showed the probable solute-solute type of molecular association in the polar mixtures in terms of relaxation times τ_s . We further studied these systems for understanding the molecular association from our theoretical formulation in terms of dipole moment of the systems and the molecular behaviour in the binary polar mixtures because of the possibility of having optimum binary system corresponding to desired physical properties. Moreover in addition to other liquids under the present investigation formamide is a very important non-aqueous dielectric liquid for its wide biological applications. Hence it attracted the attention of a large number of workers^{7,14-16}. Thus, the extensive study of the ternary mixtures of suitable dielectric liquids should be needed to throw much light on the solute-solute type of molecular associations which is quite uncommon feature of liquids. The solute-solute molecular formations, are, however, interpreted as a result of weak hydrogen bonding of the dipole-dipole interactions between the different solutes.

2 Theoretical Formulations

The uhf conductivity due to Murphy and Morgan¹⁷ of binary solutes in a non-polar solvent is given by

$$K_{ijk}^* = K_{ijk}' + jK_{ijk}'' \quad \dots (1)$$

where $K_{ijk}' = \omega \varepsilon_{ijk}'' / 4\pi$ and $K_{ijk}'' = \omega \varepsilon_{ijk}' / 4\pi$. The magnitude of total uhf conductivity is usually computed from the relation

$$K_{ijk} = \frac{\omega}{4\pi} (\varepsilon_{ijk}'^2 + \varepsilon_{ijk}''^2)^{1/2} \quad \dots (2)$$

The real part ε_{ijk}' of the complex dielectric constant ε_{ijk}^* of the solution in the microwave region although very small and equals the optical dielectric constant, but still $\varepsilon_{ijk}' \gg \varepsilon_{ijk}''$, where ε_{ijk}'' is the dielectric loss which is responsible for the absorption of electrical energy to offer resistance to the polarisation. Hence total uhf conductivity becomes

$$K_{ijk} = \frac{\omega}{4\pi} \varepsilon_{ijk}' \quad \dots (3)$$

The real part of uhf conductivity of solution having weight fraction ω_{jk} of binary polar solute in a non-polar solvent at T K is given by

$$K_{ijk}' = \frac{\mu_{jk}^2 N \rho_{ijk} F_{ijk}}{3 M_{jk} k T} \left(\frac{\omega^2 \tau_s}{1 + \omega^2 \tau_s^2} \right) \omega_{jk} \quad \dots (4)$$

where τ_s and μ_{jk} are the relaxation time and the dipole moment of binary polar solute respectively having molecular weight $M_{jk} = (X_j M_j + X_k M_k)$, X_j being the mole fraction of polar liquid j in polar mixture of j and k and $X_k = 1 - X_j$.

It can be shown in the hf region that $\varepsilon_{ijk}' = \varepsilon_\infty + \varepsilon_{ijk}'' / \omega \tau_s$, and hence with the help of Eq. (3) we get

$$K_{ijk} = K_\infty + K_{ijk}' / \omega \tau_s \quad \dots (5)$$

where $K_\infty =$ the constant conductivity $= \omega \varepsilon_\infty / 4\pi$.

Since K_{ijk} is a function of ω_{jk} we have

$$\left(\frac{dK_{ijk}'}{d\omega_{jk}} \right)_{\omega_{jk} \rightarrow 0} = \omega \tau_s \beta \quad \dots (6)$$

where β is the slope of K_{ijk} versus ω_{jk} curve at $\omega_{jk} \rightarrow 0$. At $\omega_{jk} \rightarrow 0$, ρ_{ijk} and F_{ijk} the density and local field of the solution become ρ_i and F_i of the solvent respectively, where $F_i = [(\varepsilon_i + 2)/3]^2$. Differentiating Eq. (4) w.r. to ω_{jk} and using Eq. (6) at $\omega_{jk} \rightarrow 0$, we ultimately get

$$\mu_{jk} = \left(\frac{3 M_{jk} k T \beta}{N \rho_i F_i \omega b} \right)^{1/2} \quad \dots (7)$$

where $b = 1/(1 + \omega^2 \tau_s^2)$ is a dimensionless parameter. Eq. (7) can be used to measure the dipole moment of binary polar solute. When $k=0$ or $j=0$ the uhf conductivity becomes K_{ij} or K_{ik} to yield the dipole moment μ_j or μ_k of the j th or the k th polar solute respectively from Eq. (7) with the reported τ_s .

3 Result and Discussion

The K_{ijk} of polar mixtures (I) DMF+MeOH, (II) DMF+AN and (III) DMF+AC in benzene at mole fractions $X_j = 1.0, 0.9, 0.7, 0.3, 0.1$ and 0.0 of DMF in the polar mixtures at 15°C and those of 1:1 polar mixtures in benzene at $15, 20, 25$ and 30°C were estimated using Murphy and Morgan¹⁷ relation (Eq. 2) from the available measured data of ε_{ijk}' and ε_{ijk}'' of Sharma *et al.*¹¹⁻¹³ under 3.035 cm wavelength electric field. The hf conductivity in the range $0 < X_j < 1$ are K_{ijk} of solution having binary polar mixture, and for $X_j = 1.0$ and 0.0 we get K_{ij} and K_{ik} of solutions containing single polar solute. The variation of K_{ijk} , K_{ij} and K_{ik} with the respective weight fractions was found to be linear. The intercepts α and slopes β of the linear variations of K_{ij} , K_{ik} and K_{ijk} are presented in Table 1. The K_{ijk} of 1:1 mixtures as a function of ω_{jk} are shown graphically in Fig. 1 at $15, 20, 25$ and 30°C which showed that the value of K_{ijk} decreases as the temperature increases. The constancy of the factor $(\rho_{ijk} F_{ijk})/T$ at $\omega_{jk} \rightarrow 0$ in Eq. (4) suggests that at all the experimental temperatures K_{ijk} should meet at a common point on the K_{ijk} -axis at $\omega_{jk} = 0$. But in practice the intercepts are all different (Fig. 1) and decrease with temperature. This is perhaps due to the solvation effect¹⁸. The slopes of $K_{ij} - \omega_j$ and $K_{ik} - \omega_k$ curves, are however, used to compute dipole moments of single polar solutes from Eq. (7). The measured values, $\mu = 4.02, 1.65, 3.78$ and 2.95 D for DMF, MeOH, AN and AC respectively (Table 1) are very close to the literature values^{16,19}. The μ_j and μ_k 's may be considered as monomer dipole moments due to solute-solvent molecular associations. The solute-solvent molecular associations can arise due to the interactions of π -electron cloud of the benzene ring with the fractional positive charges on the nitrogen atom ($-\overset{\delta+}{\text{C}}-\overset{\delta+}{\text{N}}-\overset{\delta-}{\text{O}}$), the hydrogen atom ($-\overset{\delta-}{\text{O}}-\overset{\delta+}{\text{H}}$) the nitrogen atom ($-\overset{\delta+}{\text{C}}\equiv\overset{\delta+}{\text{N}}$) and the carbon atom ($>\overset{\delta+}{\text{C}}=\overset{\delta-}{\text{O}}$) of DMF, MeOH, AN and AC respectively.

The slopes β of $K_{ijk} - \omega_{jk}$ curves at $\omega_{jk} \rightarrow 0$ in the mole fraction range $0 < X_j < 1$ give us μ_{jk} , the dipole moment of binary polar solute (Table 1). For a mixture of two polar molecules j and k in

Table 1—Reports the values of experimental intercepts (α) and slopes (β) of conductivity versus concentration linear plots; reported τ_s , computed b , computed experimental dipole moments (μ_p , μ_k and μ_{jk} 's) with theoretical μ_j and μ_k

System	t in °C	Mol. fraction X_j of DMF	$\alpha \times 10^{-10}$ in esu	$\beta \times 10^{-10}$ in esu	Mol. Wt M_{jk} = $(X_j M_j$ + $X_k M_k)$	τ_s (Rept) in ps	b = $\frac{1}{1 + \omega^2 \tau_s^2}$	μ_p , μ_k & μ_{jk} (Comt) in D	Average dipole moment μ_{jk} (av) (= $X_j \mu_j + X_k \mu_k$) in D	μ_j & μ_k (Theo) in D
DMF +	15	1.0	1.1447	10.5666	73.0944	7.01	0.8406	4.02	4.02	3.82
		0.9	1.1310	11.3857	68.9892	7.87	0.8072	4.14	3.78	
		0.7	1.1344	10.0244	60.7787	9.83	0.7285	3.84	3.31	
		0.3	1.1354	7.0783	44.3577	11.70	0.6544	2.91	2.36	
		0.1	1.1374	5.7261	36.1472	8.96	0.7643	2.18	1.89	
MeOH in benzene	0.0	1.1388	4.2240	32.0420	6.00	0.8781	1.65	1.65	1.64	
DMF +	15	0.5	1.1337	9.0717		12.87	0.6101	3.71	2.84	3.82
		0.9	1.1302	11.3961	69.8902	10.78	0.6905	4.51	4.00	
		0.7	1.1333	12.2275	63.4818	8.94	0.7643	4.23	3.95	
		0.3	1.1372	13.7086	50.6650	8.23	0.7928	3.93	3.85	
AN in benzene	0.0	1.1231	17.2720	41.0524	6.04	0.8766	3.78	3.78	3.67	
DMF +	15	0.5	1.1286	14.0757		8.74	0.7832	4.25	3.90	3.82
		0.9	1.1419	10.6848	71.5929	7.94	0.8044	4.09	3.91	
		0.7	1.1409	9.9640	68.5900	10.73	0.6925	4.17	3.70	
		0.3	1.1559	7.0894	62.5842	8.76	0.7716	3.18	3.27	
AC in benzene	0.0	1.1372	8.1709	58.0798	3.35	0.9585	2.95	2.95	2.75	
DMF +	15	0.5	1.1473	7.3437	59.5813	5.17	0.9065	2.92	3.06	3.49
		0.9	1.1473	7.3437	59.5813	5.17	0.9065	2.92	3.06	
		0.7	1.1473	7.3437	59.5813	5.17	0.9065	2.92	3.06	
		0.3	1.1473	7.3437	59.5813	5.17	0.9065	2.92	3.06	
DMF +	15	0.5	1.1383	10.8577		13.34	0.5930	4.60	3.49	3.88
		0.9	1.1370	10.0415		11.85	0.6486	4.29	3.88	
		0.7	1.1312	9.3474	65.5871	9.12	0.7571	3.88	3.88	
		0.3	1.1209	9.8827		8.10	0.7860	3.97	3.97	

Refs 11-13

dilute solution in a non-polar solvent there may appear two dispersion regions characterised by relaxation times τ_j and τ_k . Davidson²⁰ has shown that, even in the case of two independent polarisation, the resolution of different dispersion regions is difficult unless the relaxation time of one component should be at least 5 times that of the

other. Therefore, the binary polar mixtures with τ_s ' which are not considerably different from one another, as in the present investigation, exhibit a broad dispersion-absorption behaviour in which separate loss peaks do not occur^{6,21}. The relaxation of the mixture is thus the resultant of the relaxations of the individual molecule which is of

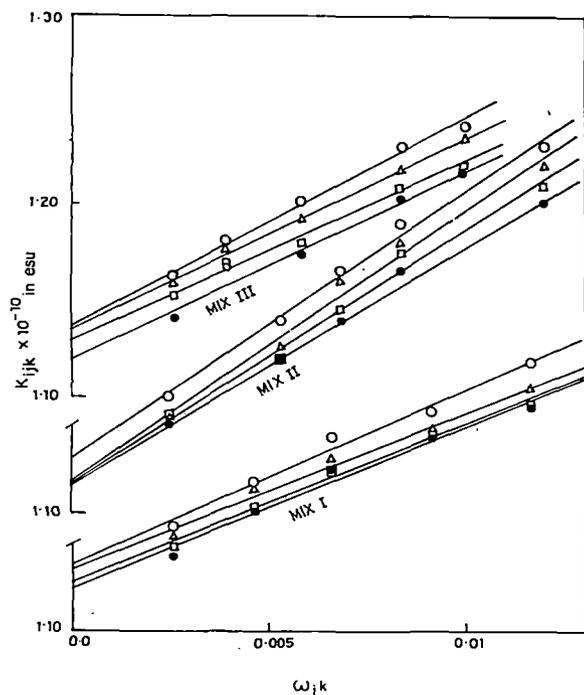


Fig. 1—uhf Conductivity K_{jk} of (I) DMF+MeOH, (II) DMF+AN and (III) DMF+AC in benzene against weight fraction ω_{jk} at different temperatures (—○— 15°C, —△— 20°C, —□— 25°C and —●— 30°C)

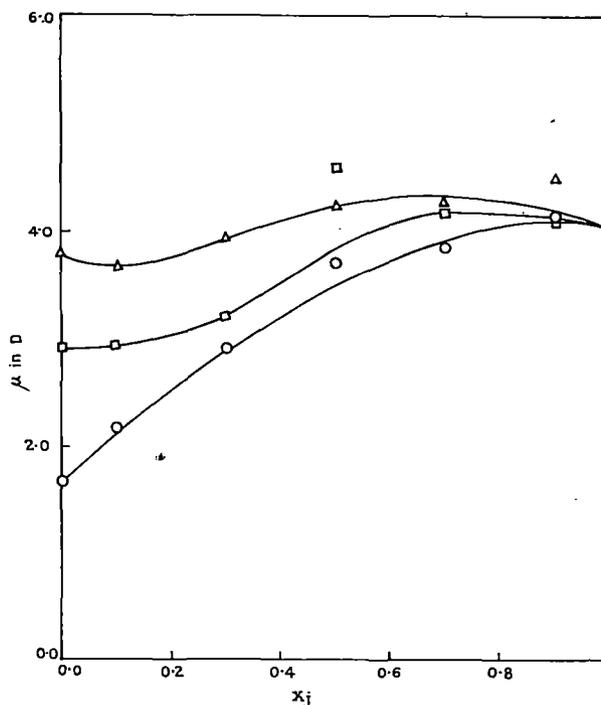


Fig. 2—Variation of dipole moment μ against the mole fraction X_j of DMF in the binary polar mixtures of DMF with (I) MeOH (—○—), (II) AN (—△—) and (III) AC (—□—) in benzene at 15°C

course, strongly influenced by the variety of the molecular environments encountered in rotation as well as by the other factors such as size, shape, solute-solvent, solute-solute interactions etc. When a polar mixture is studied in a non-polar solvent, its ϵ_{ijk}^* is represented by the weighted sum of complex dielectric constants of individual components²². Obviously if there is no solute-solute association in the mixture, the τ_s as well as μ_{jk} , measured by our method, should vary linearly with the concentration of the components. The formation of dimer leads to τ_s considerably larger than the average value of the individual relaxation times^{23,24}. In such a case, the dielectric behaviour of polar mixture is mainly governed by the resulting molecular species.

The measured dipole moments (Table 1) of the mixtures are plotted against X_j of DMF at 15°C and shown in Fig. 2. The curves drawn through the experimental points are not the average values between two monomeric dipole moments. These sort of deviation at once indicate the existence of solute-solute molecular association in solutions. The deviations are found to be maximum at $X_j = 0.5$, 0.9 and 0.5 for DMF+MeOH, DMF+AN and DMF+AC respectively, suggesting the maximum dimerisation at those X_j for the mixtures, in agreement with the observation made

by Sharma *et al.*¹¹⁻¹³. There may be also jj and kk dimers in the solutions. But the τ_s as well as μ_j and μ_k values as shown in Table 1 exhibit no self-association for DMF, MeOH, AN and AC up to $\omega_j = 0.0110$ and $\omega_k = 0.0103$, 0.0100 and 0.0103 in benzene respectively. These ω_j and ω_k are considerably higher than the concentration of j and k in solution of jk in benzene. This rules out the possibility of jj or kk dimer formation in the solutions of polar mixtures. The single relaxation times, measured by Sharma *et al.*¹¹⁻¹³ of these polar mixtures investigated, are found to follow the rate process equation. McDuffie and Litovitz²⁵ have pointed out that if a single relaxation time is assumed, the degree of polarisation order in the polar mixtures should decay exponentially. Therefore, the relaxation behaviour of these mixtures in dilute solutions may be assumed to be mainly governed by the resulting relaxing units of jk dimers, as an approximation to the true behaviour of the systems. Hence it is reasonable to consider the reported τ_s and measured μ_{jk} of Table 1 as those for jk dimers.

The experimentally computed μ_j and μ_k are compared with theoretically calculated values in terms of bond moments and bond angles as sketched in Fig. 3. The moments of C—H, C—N and N—CH₃ groups of DMF act along a com-

mon axis, but the group moments C=O and N-CH₃ act \perp to that of C-N (Fig. 3a). In MeOH, O-CH₃ and O-H make an angle 105° (Fig. 3b). In case of AN, C-CH₃ and C \equiv N not along the same axis (Fig. 3c) while in AC one of the two C-CH₃ acts along C=O and the other is \perp to C=O (Fig. 3d). With these preferred conformations, the calculated values of μ_j and μ_k 's, from vector model, assuming molecules to be planar ones, are 3.82, 1.54, 3.67 and 2.75 D respectively for DMF, MeOH, AN and AC in close agreement with the experimental values of Table 1.

For dimer formation between DMF and MeOH the two monomers attach each other with their highly electropositive (-H) and highly electronegative (-O-) elements forming certain angle viz. 112.7° at 15°C, as calculated from experimental μ_j , μ_k and μ_{jk} values (Fig. 3e). In case of DMF+AN, the molecules attach themselves by the interaction of fractional positive charge on N-atom of DMF with π -electron cloud of triple bond of AN molecule. But for DMF+AC frac-

tional positive charge on (-H) of DMF interacts with fractional negative charge on (-O-) of AC to form dimer. The angle between two dipolar axes for mixtures II and III are found to be 114.05° and 98.98° respectively (Figs 3f and 3g).

The measured μ_{jk} for 1:1 mixtures are plotted against temperature in Fig. 4. The variations are, however, represented by the following equations:

$$\text{DMF+MeOH } \mu_{jk} \\ = 5.075 - 0.122 t + 2.0 \times 10^{-3} t^2,$$

$$\text{DMF+AN } \mu_{jk} = 4.148 + 0.019 t - 8.0 \times 10^{-4} t^2 \\ \text{and}$$

$$\text{DMF+AC } \mu_{jk} = 7.120 - 0.226 t + 4.0 \times 10^{-3} t^2.$$

As observed earlier^{2,26} the μ_j of a single polar solute in a non-polar solvent increases with temperature under uhf electric field. But in the present investigation the μ_{jk} of dimer decreases as the temperatures rises (Fig. 4) and shows a tendency to yield the average value at a certain temperature. The result may be interpreted as an indication of the breaking of weak solute-solute molecular associations due to thermal agitation. Therefore, we may conclude that for such binary mix-

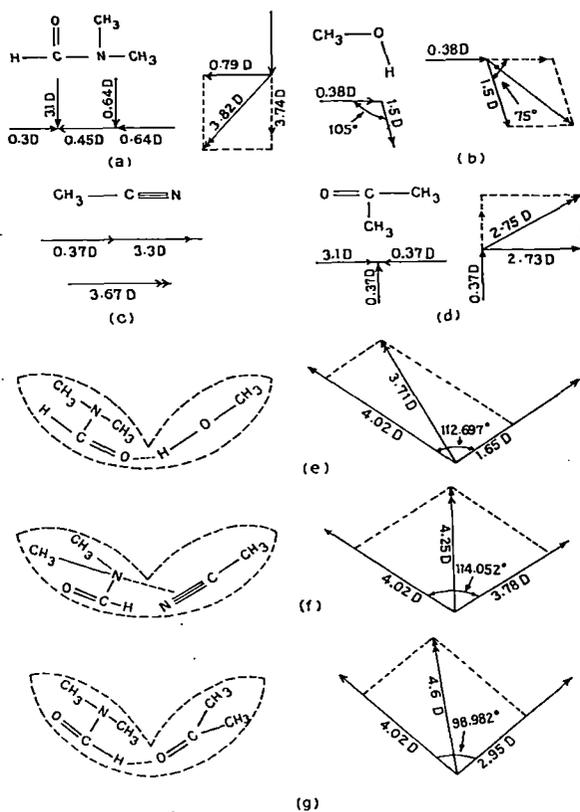


Fig. 3—Conformations of different molecules showing orientations of the bond axes, bond moments and also dipole moments [Structural form of (a) DMF, (b) MeOH, (c) AN and (d) AC; structural form of dimers (e) DMF+MeOH, (f) DMF+AN and (g) DMF+AC in 15°C]

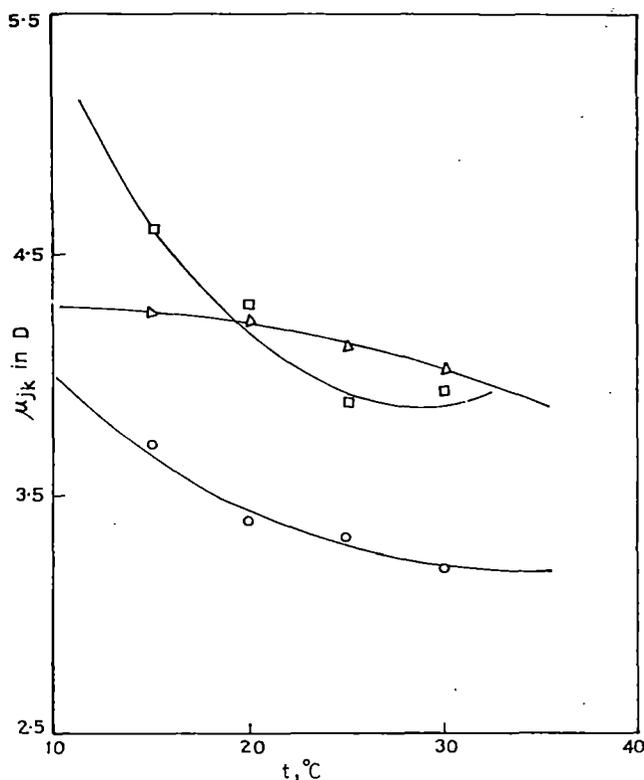


Fig. 4—Temperature variation of dipole moment μ_{jk} of (1:1) mixtures of DMF with (I) MeOH (—○—) (II) AN (—△—) and (III) AC (—□—) in benzene

tures there will be only j and k monomers in benzene at higher temperatures giving the average value of μ_{jk} .

In case of (1:1) DMF+AN mixture dimer dipole moment decreases very slowly so that the μ_{jk} remains almost constant in the studied temperature range (Fig. 4). In this mixture the maximum dimerisation does not occur at $X_j=0.5$ and the interaction of fractional positive charge on N-Atom of DMF with π -electron cloud of triple bond of AN results in greater bond energy compared to the interactions of other two dimers. This may be the reason that the breaking of molecular association for this (1:1) mixture is comparatively low causing small change in μ_{jk} with temperature unlike other two polar mixtures.

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