

CHAPTER 2

THE SCOPE AND THE OBJECTIVE OF THE PRESENT WORKS

2.1 INTRODUCTION

It is a well known fact that Debye's theory is applicable to a rigid spherical polar molecule having one relaxation time τ . The nonrigid molecules, on the other hand, usually possess more than one relaxation time i.e., a distribution of relaxation times existing between two extreme values. In such cases an average macroscopic τ is always obtained with this theory. A large number of workers tried to estimate average τ_0 and other molecular relaxation parameters with the help of Cole-Cole and Cole-Davidson plots. In order to predict the double relaxation behaviour of nonspherical polar liquids it is, therefore, desirable to formulate a new theoretical technique derived on the basis of Debye and Smyth model. In this section a method is, however, suggested to estimate the molecular and intramolecular relaxation times τ_2 and τ_1 of a polar liquid dissolved in nonpolar solvents from the measured dielectric relaxation data under a single frequency electric field of GHz range.

Let $y(\tau) d\tau$ be the contribution to the static dielectric constant of a group of dipoles having individual relaxation times in the range τ to $\tau + d\tau$. Since in dilute solution polar-polar interaction is almost absent, the contribution to ϵ_0 by various groups superpose linearly. The total contribution to static dielectric constant is, therefore, given by

$$\epsilon_0 - \epsilon_\infty = \int_0^{\infty} y(\tau) d\tau \quad \text{.....(2.1)}$$

where $y(\tau)$ is the distribution function associated with the relaxation times.

To obtain the complex dielectric constant ϵ^* , we first consider the decay function $\alpha(t)$. The dipoles with relaxation times τ to $\tau + d\tau$ make a contribution to $\alpha(t)$ which is proportional to $\exp(-t/\tau)$ and $y(\tau) \frac{d\tau}{\tau}$. Therefore, the total contribution of all the dipoles is given by

$$\alpha(t) = \int_0^{\infty} e^{-t/\tau} y(\tau) \frac{d\tau}{\tau} \quad \text{.....(2.2)}$$

The complex dielectric constant ϵ^* is now obtained as

$$\begin{aligned}
\varepsilon^* - \varepsilon_\infty &= \int_0^\infty \alpha(x) e^{-i\omega x} dx \\
&= \int_0^\infty \left[e^{-i\omega x} \int_0^\infty \frac{d\tau}{\tau} e^{-x/\tau} y(\tau) \right] dx \\
&= \int_0^\infty \frac{y(\tau)}{\tau} d\tau \int_0^\infty e^{-i\omega x} e^{-x/\tau} dx \quad \dots\dots(2.3)
\end{aligned}$$

Let $I = \int_0^\infty e^{-i\omega x} e^{-x/\tau} dx$ which becomes as follows with integration by parts.

$$I = -\frac{1}{i\omega} \left[e^{-x/\tau} \cdot e^{-i\omega x} \right]_0^\infty - \frac{1}{i\omega\tau} \int_0^\infty e^{-x/\tau} e^{-i\omega x} dx$$

$$\text{or, } I = \frac{1}{i\omega} - \frac{1}{i\omega\tau} I$$

$$\text{or, } I = \frac{\tau}{1 + i\omega\tau}$$

so eq (2.3) can be written as

$$\varepsilon^* - \varepsilon_\infty = \int_0^\infty \frac{y(\tau) d\tau}{1 + i\omega\tau} \quad \dots\dots (2.4)$$

Substituting the value of ε^* from eq (1.17) and replacing the complex number 'i' one can write eq. (2.4) into the form:

$$\begin{aligned}
\varepsilon' - j\varepsilon'' - \varepsilon_\infty &= \int_0^\infty \frac{y(\tau) d\tau}{1 + j\omega\tau} \\
&= \int_0^\infty \frac{y(\tau) d\tau}{1 + \omega^2\tau^2} (1 - j\omega\tau) \\
&= \int_0^\infty \frac{y(\tau) d\tau}{1 + \omega^2\tau^2} - j \int_0^\infty \frac{y(\tau)\omega\tau}{1 + \omega^2\tau^2} d\tau
\end{aligned}$$

Equating the real and the imaginary parts from both sides of the above equation we have

$$\varepsilon' - \varepsilon_\infty = \int_0^\infty \frac{y(\tau)}{1 + \omega^2\tau^2} d\tau \quad \dots\dots(2.5)$$

$$\epsilon'' = \int_0^{\infty} \frac{y(\tau) \omega \tau}{1 + \omega^2 \tau^2} d\tau \quad \dots\dots(2.6)$$

For a detailed discussion of relations (2.5) and (2.6) the knowledge of distribution function $y(\tau)$ is to be known. Let us consider a model in which each molecule has two equilibrium positions with opposite dipolar directions and with equal energy in the ground level. The potential barrier between the two positions has different heights for each molecule. Let the heights H of the potential barriers are distributed equally over a range between H_0 and $H_0 + v_0$, i.e.

$$H = H_0 + v, \quad 0 \leq v \leq v_0 \quad \dots\dots(2.7)$$

Thus if N_0 is the total number of dipoles per unit volume.

$$N_0 \frac{dv}{v_0} \quad \dots\dots(2.8)$$

is the fraction with H -values in a range dv near $H_0 + v$.

For dilute solutions interaction between dipoles can be neglected. Therefore, the contribution of a dipolar molecule to ϵ_0 is the same for all molecules given by

$$\frac{\epsilon_0 - \epsilon_{\infty}}{N_0} \text{ per molecule} \quad \dots\dots(2.9)$$

The individual relaxation time τ , therefore, depends on H and covers the range $\tau_1 \leq \tau \leq \tau_2$

$$\text{where } \tau_2 = \tau_1 e^{\frac{v_0}{kT}} \quad \dots\dots(2.10)$$

To determine the distribution function $y(\tau)$, we note that $y(\tau) = 0$ outside the range of eq. (2.10). Now considering τ as a function of v , eq (2.1) can be written as

$$\begin{aligned} \epsilon_0 - \epsilon_{\infty} &= \int_{\tau_1}^{\tau_2} y(\tau) d\tau \\ &= \frac{1}{kT} \int_0^{v_0} y(\tau) \tau(v) dv \quad \dots\dots(2.11) \end{aligned}$$

The contribution to ϵ_0 of the molecules in the range of dv is

$$\frac{y(\tau) \tau dv}{kT} \quad \dots\dots(2.12)$$

Eq. (2.12) can be written with the help of eqs (2.8) and (2.9) as

$$\frac{y(\tau)\tau dv}{kT} = \frac{\epsilon_0 - \epsilon_\infty}{N_0} \cdot \frac{N_0 dv}{v_0}$$

$$\text{or, } y(\tau) = (\epsilon_0 - \epsilon_\infty) \frac{kT}{v_0} \cdot \frac{1}{\tau} \text{ if } \tau_1 \leq \tau \leq \tau_2 = \tau_1 e^{\frac{v_0}{kT}}$$

$$= 0 \text{ if } \tau < \tau_1 \text{ and } \tau > \tau_2 \quad \dots\dots(2.13)$$

The dielectric constant ϵ' and ϵ'' can now be obtained from eq. (2.5) as

$$\frac{\epsilon' - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{kT}{v_0} \int_{\tau_1}^{\tau_2} \frac{d\tau}{\tau(1 + \omega^2\tau^2)} \quad \dots\dots(2.14)$$

$$\frac{\epsilon''}{\epsilon_0 - \epsilon_\infty} = \frac{kT}{v_0} \int_{\tau_1}^{\tau_2} \frac{\omega d\tau}{1 + \omega^2\tau^2} \quad \dots\dots(2.15)$$

Let $1 + \omega^2\tau^2 = Z$, eq. (2.14) can be written as :

$$\frac{\epsilon' - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{kT}{2v_0} \int_{1+\omega^2\tau_1^2}^{1+\omega^2\tau_2^2} \frac{dZ}{Z(Z-1)}$$

$$= - \frac{kT}{2v_0} \left\{ \ln \left(\frac{1 + \omega^2\tau_2^2}{1 + \omega^2\tau_1^2} \right) - \ln \frac{\omega^2\tau_2^2}{\omega^2\tau_1^2} \right\}$$

$$= \frac{kT}{2v_0} \left\{ \ln \frac{\frac{2v_0}{\tau_2^2 e^{kT}} (1 + \omega^2\tau_2^2)}{\frac{2v_0}{\tau_1^2} (1 + \omega^2\tau_2^2)} \right\} \quad \dots\dots(2.16)$$

Substituting $\tau_2 = \tau_1 e^{\frac{v_0}{kT}}$ in the R.H.S of the above eq. (2.16) one gets

$$\frac{\epsilon' - \epsilon_{\infty}}{\epsilon_0 - \epsilon_{\infty}} = 1 - \frac{1}{\frac{2v_0}{kT}} \ln \left(\frac{1 + \omega^2 \tau_1^2 e^{\frac{2v_0}{kT}}}{1 + \omega^2 \tau_1^2} \right)$$

$$= 1 - \frac{1}{2A} \ln \frac{1 + \omega^2 \tau_s^2 e^{2A}}{1 + \omega^2 \tau_s^2} \quad \dots\dots(2.17)$$

where τ_s is the small limiting relaxation time = τ_1 and A = Fröhlich parameter = $\frac{v_0}{kT} = \ln(\tau_2/\tau_1)$.

let us now put $\omega\tau = Z$ on the R.H.S of eq. (2.15) which after simplification yields :

$$\frac{\epsilon''}{\epsilon_0 - \epsilon_{\infty}} = \frac{kT}{v_0} \left\{ \frac{\omega\tau_2}{\omega\tau_1} \frac{dZ}{1 + Z^2} \right.$$

$$= \frac{1}{\frac{v_0}{kT}} \left[\tan^{-1}(\omega\tau_2) - \tan^{-1}(\omega\tau_1) \right]$$

$$= \frac{1}{A} \left[\tan^{-1}(e^A \omega\tau_s) - \tan^{-1}(\omega\tau_s) \right] \quad \dots\dots(2.18)$$

In case of a polar solute (j) dissolved in a nonpolar solvent (i) eqs. (2.17) and (2.18) are finally written as :

$$\frac{\epsilon'_{ij} - \epsilon_{\infty ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}} = x = 1 - \frac{1}{2A} \ln \frac{1 + \omega^2 \tau_s^2 e^{2A}}{1 + \omega^2 \tau_s^2} \quad \dots\dots(2.19)$$

$$\text{and } \frac{\epsilon''_{ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}} = y = \frac{1}{A} \left[\tan^{-1}(e^A \omega\tau_s) - \tan^{-1}(\omega\tau_s) \right] \quad \dots\dots (2.20)$$

These two formulae have already been used to find out relative contributions c_1 and c_2 towards dielectric relaxations in terms of τ_1 and τ_2 as estimated in our method discussed in detail in the latter parts of this thesis.

2.2 Multiple Relaxation Mechanism

The concept of existence of more than one relaxation time in a polar molecule was put forward by many workers. In 1938 Budo¹⁾, however, proposed a relation:

$$\frac{\epsilon^* - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \sum_j \frac{c_j}{1 + i\omega\tau_j} \quad \dots\dots(2.21)$$

to represent the complex dielectric constant ϵ^* as the sum of a number of noninteracting Debye type dispersions. The term c_j is the weight factor of the j th type relaxation mechanism; provided $\sum c_j = 1$

2.3 Double Relaxations

Bergmann et al²⁾ analysed the dielectric relaxation mechanism of some pure polar liquids from the measured relaxation data at different hf electric field of GHz range in terms of two Debye type dispersions. The larger and the smaller relaxation times τ_2 and τ_1 are, however, associated with molecular and intramolecular rotations of the molecule which follow the equations:

$$\frac{\epsilon' - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = c_1 \frac{1}{1 + \omega^2\tau_1^2} + c_2 \frac{1}{1 + \omega^2\tau_2^2} \quad \dots\dots(2.22)$$

$$\frac{\epsilon''}{\epsilon_0 - \epsilon_\infty} = c_1 \frac{\omega\tau_1}{1 + \omega^2\tau_1^2} + c_2 \frac{\omega\tau_2}{1 + \omega^2\tau_2^2} \quad \dots\dots(2.23)$$

The terms c_1 and c_2 are the relative contributions due to τ_1 and τ_2 . Both c_1 and c_2 are related by

$$c_1 + c_2 = 1 \quad \dots\dots(2.24)$$

Putting the eqs. (2.22) and (2.23) in the following form:

$$Y = c_1 Y_1 + c_2 Y_2 \quad \text{.....(2.25)}$$

$$Z = c_1 Z_1 + c_2 Z_2 \quad \text{.....(2.26)}$$

$$\text{where } Y = \frac{\epsilon''}{\epsilon_0 - \epsilon_\infty}; \quad Z = \frac{\epsilon' - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty}$$

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

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

A graphical analysis was, however, made by Bergmann et al²⁾ in order to estimate τ_1 , τ_2 and c_1 , c_2 which consists of plotting the normalised experimental points on a complex plane as shown in Fig 2.1. A number of chords were then drawn through the experimental points to obtain a set of parameters which is consistent for all the experimental points for a suitable value of ϵ_∞ . A point (Y,Z) was, however, selected between the points (Y₁,Z₁) and (Y₂, Z₂) of the normalised Debye semi-circle dividing the chord in the ratio b/a = c₁/c₂. From the known values of c₁ and c₂ one gets τ_1 and τ_2 from the appropriate values of ϵ' , ϵ'' , ϵ_0 and ϵ_∞ measured at different frequencies of GHz range.

2.4. Double Relaxations Measured under Two Different Frequencies

A polar molecule capable of rotation about its axis under a microwave electric field of angular frequency ω at a given temperature is presented by Bhattacharyya et al³⁾

$$\frac{\epsilon^* - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} \cdot \frac{\epsilon_0 + 2}{\epsilon^* + 2} = a - i b \quad \text{.....(2.27)}$$

$$\text{where } a = \frac{c_1}{1 + \omega^2 \tau_1^2} + \frac{c_2}{1 + \omega^2 \tau_2^2} \quad \text{.....(2.28)}$$

$$\text{and } b = c_1 \frac{\omega \tau_1}{1 + \omega^2 \tau_1^2} + c_2 \frac{\omega \tau_2}{1 + \omega^2 \tau_2^2}$$

The terms τ_1 , τ_2 and c_1 , c_2 carry usual meanings of eq (2.24).

Eq (2.27) after simplification for ϵ^* yields:

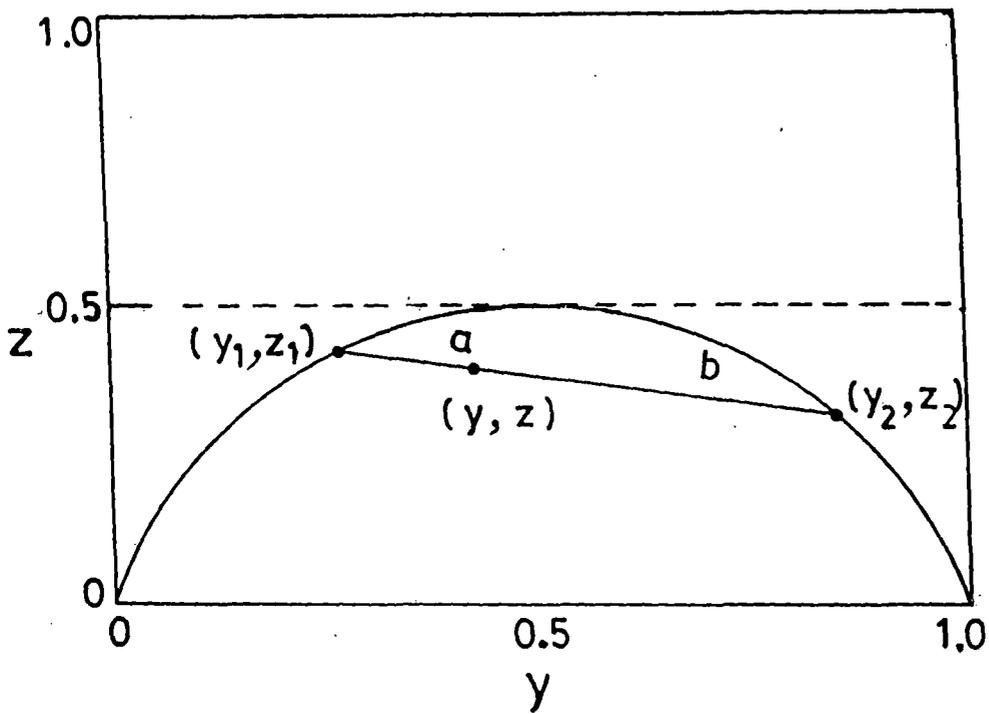


Figure 2.1 The graphical resolution of two independent Debye absorptions

$$\varepsilon^* = \frac{2\alpha(a - ib) + \varepsilon_\infty}{1 - \alpha(a - ib)}$$

$$\text{or, } \varepsilon^* - \varepsilon_\infty = \frac{\alpha(a - ib)(\varepsilon_\infty + 2)}{1 - \alpha(a - ib)}$$

$$\text{or, } \frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \frac{\alpha(a - ib)(\varepsilon_\infty + 2)}{(\varepsilon_0 - \varepsilon_\infty)\{1 - \alpha(a - ib)\}} \quad \dots\dots (2.29)$$

$$\text{where } \alpha = \frac{\varepsilon_0 - \varepsilon_\infty}{\varepsilon_0 + 2}$$

Separating the real and the imaginary parts from both sides of eq.(2.29) one gets:

$$\frac{\varepsilon' - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \frac{a\beta - (a^2 + b^2)(\beta - 1)}{\beta^2 - 2a\beta(\beta - 1) + (a^2 + b^2)(\beta - 1)^2} \quad \dots\dots(2.30)$$

$$\text{and } \frac{\varepsilon''}{\varepsilon_0 - \varepsilon_\infty} = \frac{b\beta}{\beta^2 - 2a\beta(\beta - 1) + (a^2 + b^2)(\beta - 1)^2}$$

$$\text{where } \beta = \frac{\varepsilon_0 + 2}{\varepsilon_\infty + 2} = \frac{1}{1 - \alpha}$$

The terms a and b are given by:

$$a = \frac{\epsilon_0 + 2}{\epsilon_0 - \epsilon_\infty} \left[\frac{(\epsilon' - \epsilon_\infty)(\epsilon' + 2) + \epsilon''^2}{(\epsilon' + 2)^2 + \epsilon''^2} \right]$$

$$\& \quad b = \frac{\epsilon_0 + 2}{\epsilon_0 - \epsilon_\infty} \left[\frac{\epsilon''(\epsilon_\infty + 2)}{(\epsilon' + 2)^2 + \epsilon''^2} \right] \quad \text{.....(2.31)}$$

In case of pure polar liquids if $\epsilon_0 \approx \epsilon' \approx \epsilon_\infty$ and ϵ'' is very small, eq (2.30) is reduced to

$$\frac{\epsilon' - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = a \text{ and } b = \frac{\epsilon''}{\epsilon_0 - \epsilon_\infty}$$

which are similar like eqs (2.22) and (2.23) respectively. Putting $x_1 = \omega\tau_1$ and $x_2 = \omega\tau_2$ and using the abbreviations $\xi = 1/(1+x^2)$ and $\eta = x/(1+x^2)$, eqs (2.28) are finally written as

$$a = c_1 \xi_1 + c_2 \xi_2$$

$$\text{and } b = c_1 \eta_1 + c_2 \eta_2 \quad \text{.....(2.32)}$$

From eqs (2.32) one gets (for $x_2 - x_1 \neq 0$ and $x_2 > x_1$)

$$c_1 = \frac{(a x_2 - b)(1 + x_1^2)}{x_2 - x_1}$$

$$c_2 = \frac{(b - a x_1)(1 + x_2^2)}{x_2 - x_1} \quad \text{.....(2.33)}$$

Using the relation $c_1 + c_2 = 1$, eq (2.33) yields:

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

$$\text{or, } \frac{1 - a}{b\omega} = (\tau_1 + \tau_2) - \frac{a\omega}{b} \tau_1 \tau_2 \quad \text{.....(2.34)}$$

when ϵ' , ϵ'' , ϵ_0 and ϵ_∞ at two different frequencies ω_1 and ω_2 of the electric fields are measured at any given temperature, eq (2.34) becomes

$$\frac{1 - a_1}{b_1 \omega_1} = (\tau_1 + \tau_2) - \frac{a_1}{b_1} \omega_1 \tau_1 \tau_2$$

and
$$\frac{1 - a_2}{b_2 \omega_2} = (\tau_1 + \tau_2) - \frac{a_2}{b_2} \omega_2 \tau_1 \tau_2$$

From the above two equations τ_1 , τ_2 and hence c_1 , c_2 from eqs. (2.33) are usually estimated. In order to test the theoretical formulations described above, Bhattacharyya et al³⁾ used the polar liquid like phenetole, aniline and orthochloro aniline to get τ_1 , τ_2 and c_1 , c_2 respectively from the measured relaxation data under 3.58 cm and 1.64 cm wavelength electric field at 45°, 60° and 75°C respectively. The data thus reported were of reasonable values.

2.5. Double Relaxation Phenomena of Polar- Nonpolar liquid Mixture under Single Frequency Electric Field.

The existing method of Bhattacharyya et al³⁾ although provides one with the significant improvement over the other²⁾ still both of them within the framework of Debye and Smyth model²³⁾ suffer from the following inherent approximations:

- i) polar-polar interactions in a pure polar liquid can not be avoided.
- ii) the approximations of the equalities of $\epsilon_0 \approx \epsilon_\infty \approx \epsilon'$ and $\epsilon_0 = 0$ are not true because the dielectric relaxation parameters are usually found to be different experimentally
- iii) the eq (2.27) of Bhattacharyya et al³⁾ seems to be complicated and is reduced to Bergmann's equations under the above approximations only and
- iv) the estimated values of τ_2 and τ_1 were supposed to be constant at two different frequencies, but really they are little affected by the frequencies of the electric field of GHz range.

We, under such context proposed a very simple technique to get molecular and intra-molecular relaxation times τ_2 and τ_1 in terms of slopes and intercepts of a derived straight line equation. The equation is based on the solution data like real ϵ'_{ij} , imaginary ϵ''_{ij} parts of complex dielectric constant ϵ^*_{ij} as well as static ϵ_{0ij} and hf dielectric constant $\epsilon_{\infty ij}$ of a solute (j) dissolved in a nonpolar solvent (i) measured under a single frequency electric field of GHz range at a given temperature. If a polar solute possesses two distinct Debye type dispersions each with a characteristic relaxation time, the eqs (2.22) and (2.23) can now be written as:

$$\frac{\epsilon'_{ij} - \epsilon_{\infty ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}} = \frac{c_1}{1 + \omega^2 \tau_1^2} + \frac{c_2}{1 + \omega^2 \tau_2^2} \quad \text{.....(2.35)}$$

$$\frac{\epsilon''_{ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}} = c_1 \frac{\omega \tau_1}{1 + \omega^2 \tau_1^2} + c_2 \frac{\omega \tau_2}{1 + \omega^2 \tau_2^2} \quad \text{.....(2.36)}$$

Here, τ_1 , τ_2 and c_1 , c_2 carry usual significance³⁾ provided $c_1 + c_2 = 1$.

Substituting $\frac{\epsilon'_{ij} - \epsilon_{\infty ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}} = x$ and $\frac{\epsilon''_{ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}} = y$

with $\omega\tau = \alpha$ in the eqs (2.35) and (2.36) one gets:

$$x = c_1 a_1 + c_2 a_2 \quad \text{.....(2.37)}$$

$$y = c_1 b_1 + c_2 b_2 \quad \text{.....(2.38)}$$

where $a = 1/1 + \alpha^2$ and $b = \alpha/1 + \alpha^2$

The suffices 1 and 2 with a and b are, however, related. to τ_1 and τ_2 respectively. From eqs (2.37) and (2.38) since $\alpha_2 \neq \alpha_1$, we have

$$c_1 = \frac{(x \alpha_2 - y)(1 + \alpha_1^2)}{\alpha_2 - \alpha_1} \quad \text{.....(2.39)}$$

$$c_2 = \frac{(y - x \alpha_1)(1 + \alpha_2^2)}{\alpha_2 - \alpha_1} \quad \text{.....(2.40)}$$

Now, using the relation $c_1 + c_2 = 1$, one can easily get the following equation with the help of eqs (2.39) and (2.40):

$$\frac{1-x}{y} = (\alpha_1 + \alpha_2) - \frac{x}{y} \alpha_1 \alpha_2 \quad \text{.....(2.41)}$$

Substituting the values of x, y and α in the above expression we have

$$\frac{\epsilon_{0ij} - \epsilon'_{ij}}{\epsilon'_{ij} - \epsilon_{\infty ij}} = \omega (\tau_1 + \tau_2) \frac{\epsilon''_{ij}}{\epsilon'_{ij} - \epsilon_{\infty ij}} - \omega^2 \tau_1 \tau_2 \quad \text{.....(2.42)}$$

This is simply a straight line between $(\epsilon_{0ij} - \epsilon'_{ij}) / (\epsilon'_{ij} - \epsilon_{\infty ij})$ and $\epsilon''_{ij} / (\epsilon'_{ij} - \epsilon_{\infty ij})$ having intercept $-\omega^2 \tau_1 \tau_2$ and slope $\omega (\tau_1 + \tau_2)$ respectively. Here $\omega = 2\pi f$, f being the frequency of the alternating electric field. In order to get the slope and intercept, the eq (2.42) could, however, be fitted with the data of ϵ'_{ij} , ϵ''_{ij} , ϵ_{0ij} and $\epsilon_{\infty ij}$ at different ω_j 's measured under a single frequency electric field at a given temperature. The estimated slope and intercept are finally used to get τ_2 and τ_1 to represent molecular and intramolecular relaxation times of a polar liquid in nonpolar solvent.

The Fröhlich parameter $A (= \ln \tau_2/\tau_1)$ as seen in eq.(2.17) for polar solutes exhibiting the double relaxation phenomena are used to evaluate both x and y of eqs. (2.17) and (2.18) in terms of ω and the small limiting relaxation time $\tau_s = \tau_1$. The computed values of x and y are used to obtain c_1 and c_2 from eqs (2.39) and (2.40). In the framework of Debye and Smyth model, the values of c_1 and c_2 are estimated for the fixed values of x and y at infinite dilutions. The plots of x and y against ω_j 's could, however, be made. They vary usually concave and convex manner respectively in accordance with the eqs. (2.35) and (2.36). The graphs are then extrapolated to get x and y at $\omega_j \rightarrow 0$. This is really in conformity with the fixed values of τ_1 & τ_2 and c_1 & c_2 when substituted in the R.H.S of eqs. (2.35) and (2.36) for fixed x and y in the L.H.S of those eqs. (2.35) and (2.36).

2.6. Theoretical Formulation to Estimate μ_1, μ_2 in Terms of τ_1, τ_2

The hf conductivity K_{ij} for a polar nonpolar liquid mixture (ij) has already been given by Murphy and Morgan eq (1.58) which is a function of ω_j of a polar solute. In the hf electric field, although $\epsilon''_{ij} \ll \epsilon'_{ij}$, the term ϵ''_{ij} still offers resistance to polarisation. Thus the real part K'_{ij} of the hf conductivity of a polar nonpolar liquid mixture at T K is ⁴⁾

$$K'_{ij} = \frac{\mu_j^2 N \rho_{ij} F_{ij}}{3 M_j k T} \left(\frac{\omega^2 \tau}{1 + \omega^2 \tau^2} \right) \omega_j \quad \dots\dots(2.43)$$

Differentiating the eq (2.43) with respect to ω_j and for $\omega_j \rightarrow 0$ yields that

$$\left(\frac{d K'_{ij}}{d \omega_j} \right)_{\omega_j \rightarrow 0} = \frac{\mu_j^2 N \rho_i F_i}{3 M_j k T} \left(\frac{\omega^2 \tau}{1 + \omega^2 \tau^2} \right) \quad \dots\dots(2.44)$$

where M_j is the molecular weight of a polar solute, N is the Avogadro's number, k is the Boltzmann constant, the local field $F_{ij} = 1/9 (\epsilon_{ij} + 2)^2$, becomes $F_i = 1/9 (\epsilon_i + 2)^2$ and the density $\rho_{ij} \rightarrow \rho_i$ the density of the solvent at $\omega_j \rightarrow 0$

Again, total hf conductivity $K_{ij} = \frac{\omega}{4 \pi} \epsilon'_{ij}$ can be written as

$$K_{ij} = K_{\infty ij} + \frac{1}{\omega \tau} K'_{ij}$$

$$\text{or, } \left(\frac{d K'_{ij}}{d \omega_j} \right)_{\omega_j \rightarrow 0} = \omega \tau \left(\frac{d K_{ij}}{d \omega_j} \right)_{\omega_j \rightarrow 0} = \omega \tau \beta \quad \dots\dots(2.45)$$

where β is the slope of the $K_{ij} - \omega_j$ curve at $\omega_j \rightarrow 0$. From eqs. (2.44) and (2.45) we thus get.

$$\mu_j = \sqrt{\frac{27 M_j k T \beta}{N \rho_i (\epsilon_i + 2)^2 \omega b}} \quad \dots\dots(2.46)$$

as the dipole moments μ_1 and μ_2 in terms of b , where b is a dimensionless parameter given by

$$b = \frac{1}{1 + \omega^2 \tau^2} \quad \dots\dots(2.47)$$

for τ_0 , τ_1 and τ_2 respectively.

2.7. A Brief Review Works

The process of derivation of dipole moments μ from hf conductivity measurements shows that the relaxation time plays a significant role in yielding the dipole moment μ of polar liquids.

Acharyya and Chatterjee⁵⁾ used the slope of the curve of the variation of the microwave conductivity with concentration at infinite dilutions to obtain μ of some substituted benzotrifluorides and benzenes at 35°C under nearly 3cm wavelength electric field. The estimated μ showed the excellent agreement with the reported ones, suggesting the uniqueness of the method adopted.

Acharyya et al⁶⁾ used the uhf conductivity K_{ijk} of N, methyl acetamide in several nonpolar solvents in the lower as well as higher concentrations to throw much light regarding constant conductivity at $\omega_j \rightarrow 0$ due to solvation effect at different temperatures. Chatterjee et al⁷⁾ measured the concentration variation of uhf conductivity K_{ijk} of ternary solutions at 9.885 GHz electric field for different mole fractions of N, N-dimethyl formamide (DMF) with N,N tetramethyl urea (TMU) and N,N-dimethyl acetamide (DMA) at different temperatures. The mole fraction and temperature variation of μ as seen in Figs (2.2) and (2.3) indicate the very existence of solute-solvent and solute-solute molecular associations in liquids. All these facts mentioned above inspired us to study high frequency absorptions by different nonspherical polar liquids in nonpolar solvents to arrive at the definite conclusions regarding monomer and dimer formations in liquid mixture.

We ⁸⁾ in the mean time developed the theoretical procedure to estimate the double relaxation times τ_1 and τ_2 of some nonspherical polar liquids in solvent benzene and carbon tetrachloride at 9.945 GHz electric field using the single frequency measured relaxation data. The hf conductivity technique had also been used to get μ_1 and μ_2 in terms of slope β of $K_{ij} - \omega_j$ curve. The close agreement of computed μ_2 with the μ 's in literature indicates the correctness of the method suggested. This is beautifully presented and displayed in Chapter III of this thesis.

The Chapter IV is concerned with the use of the single frequency measurement technique on the dielectric relaxation parameters to measure τ_2 and τ_1 of some monosubstituted anilines for three different electric field frequencies of GHz range at 35°C. The o-and m-anisidine like p-toluidines exhibit double relaxation phenomena at 3.86 and 22.06 GHz. o-and m-toluidines show the same effect at 2.02 and 3.86 GHz respectively. p-anisidine alone shows the monorelaxation behaviour at all frequencies. The relative contributions c_1 and c_2 towards dielectric relaxations are calculated in terms of x, y and τ_1, τ_2 . The dipole moments μ_1, μ_2 were also calculated in terms of slopes β 's of concentration variation of their conductivity curves in order to compare with those from bond angles and bond moments of the molecules concerned.

An attempt has been made in Chapter V to show the fact that monosubstituted anilines exhibit double relaxation times at 9.945 GHz electric field which seems to be the most effective dispersive region for such molecules. All the anilines also possess symmetric distribution of relaxation behaviour at nearly 10 GHz electric field.

2.8. Symmetric Distribution of Relaxation Times

Cole and Cole ⁹⁾ presented a relation:

$$\frac{\epsilon_{ij}^* - \epsilon_{\infty ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}} = \frac{1}{1 + (j \omega \tau_s)^{1-\gamma}} \quad \dots\dots(2.48)$$

in order to represent the symmetric distribution behaviour of nonrigid molecules. Here, γ = symmetric distribution parameter associated with symmetric relaxation times τ_s .

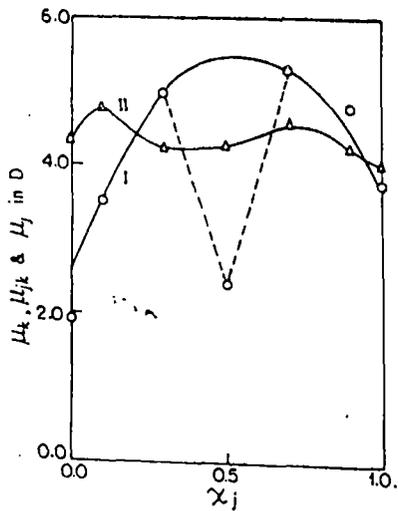


Figure 2.2 Variation of experimentally observed dipole moments μ_k , μ_{jk} and μ_j with mole fraction of DMF in (DMF+TMU) and (DMF+DMA) mixtures at 15°C (-o- for DMF+TMU and -Δ- for DMF+DMA)

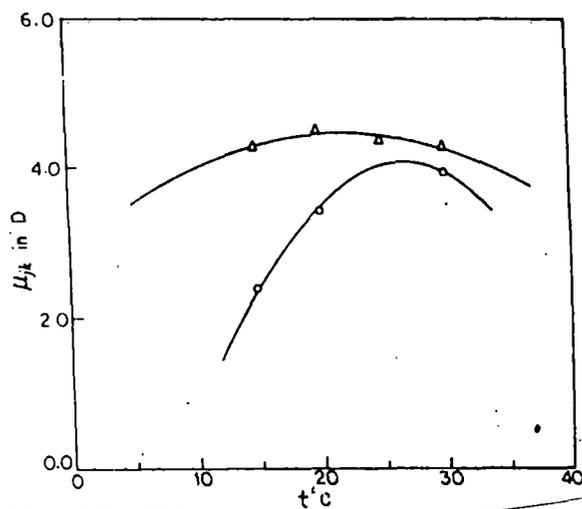


Figure 2.3 Variation of experimentally observed dipole moments with temperature in °C for DMF+TMU and DMF+DMA in 1:1 mixtures at 15°C (-o- for DMF+TMU and -Δ- for DMF+DMA)

$$\text{or, } \frac{\varepsilon_{ij}^* - \varepsilon_{\infty ij}}{\varepsilon_{0ij} - \varepsilon_{\infty ij}} = \frac{1}{1 + j \left[\cos\left(\frac{\gamma\pi}{2}\right) - j \sin\left(\frac{\gamma\pi}{2}\right) \right] (\omega \tau_s)^{1-\gamma}}$$

$$= \frac{1 + (\omega \tau_s)^{1-\gamma} \sin\left(\frac{\gamma\pi}{2}\right) - j (\omega \tau_s)^{1-\gamma} \cos\left(\frac{\gamma\pi}{2}\right)}{1 + 2 (\omega \tau_s)^{1-\gamma} \sin\left(\frac{\gamma\pi}{2}\right) + (\omega \tau_s)^{2(1-\gamma)}}$$

Separating real and imaginary parts from both sides one gets

$$\frac{\varepsilon'_{ij} - \varepsilon_{\infty ij}}{\varepsilon_{0ij} - \varepsilon_{\infty ij}} = x = \frac{1 + (\omega \tau_s)^{1-\gamma} \sin\left(\frac{\gamma\pi}{2}\right)}{1 + 2 (\omega \tau_s)^{1-\gamma} \sin\left(\frac{\gamma\pi}{2}\right) + (\omega \tau_s)^{2(1-\gamma)}}$$

$$\frac{\varepsilon''_{ij}}{\varepsilon_{0ij} - \varepsilon_{\infty ij}} = y = \frac{(\omega \tau_s)^{1-\gamma} \cos\left(\frac{\gamma\pi}{2}\right)}{1 + 2 (\omega \tau_s)^{1-\gamma} \sin\left(\frac{\gamma\pi}{2}\right) + (\omega \tau_s)^{2(1-\gamma)}} \quad \dots\dots\dots(2.49)$$

The symmetric distribution parameter γ and relaxation time τ_s can be given by the relations:

$$\gamma = \frac{2}{\pi} \tan^{-1} \left[(1 - x) \frac{x}{y} - y \right] \quad \dots\dots\dots(2.50)$$

$$\tau_s = \frac{1}{\omega} \left\{ \frac{1}{\left[\frac{x}{y} \cos\left(\frac{\gamma\pi}{2}\right) - \sin\left(\frac{\gamma\pi}{2}\right) \right]} \right\}^{\frac{1}{1-\gamma}} \quad \dots\dots\dots(2.51)$$

where x and y are the fixed estimated values at $\omega_j \rightarrow 0$ as obtained from graphical plot of eqs (2.35) and (2.36).

2.9. Asymmetric Distribution of Relaxation Times

Davidson and Cole¹⁰⁾ showed the following relation for the molecules possessing asymmetric distribution of relaxation times as:

$$\frac{\epsilon_{ij}^* - \epsilon_{\infty ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}} = \frac{1}{(1 + j \omega \tau_{cs})^\delta} \quad \dots\dots(2.52)$$

where δ = asymmetric distribution parameter associated with characteristic relaxation time τ_{cs} . Let $\omega \tau_{cs} = \tan \phi$. On substitution in eq (2.52) and after simplification one can write.

$$\begin{aligned} \frac{\epsilon_{ij}^* - \epsilon_{\infty ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}} &= \frac{(\cos \phi)^\delta}{\cos \delta \phi + j \sin \delta \phi} \\ &= (\cos \phi)^\delta \cos(\delta \phi) - j (\cos \phi)^\delta \sin \delta \phi \end{aligned}$$

Separating real and imaginary parts yields

$$\frac{\epsilon'_{ij} - \epsilon_{\infty ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}} = x = (\cos \phi)^\delta \cos(\delta \phi) \quad \dots\dots(2.53)$$

$$\frac{\epsilon''_{ij}}{\epsilon_{0ij} - \epsilon_{\infty ij}} = y = (\cos \phi)^\delta \sin(\delta \phi) \quad \dots\dots(2.54)$$

Similarly, δ and τ_{cs} can be had in terms of x and y at $\omega_j \rightarrow 0$ as.

$$\tan(\delta \phi) = \frac{y}{x} \quad \dots\dots(2.55)$$

and $\tan \phi = \omega \tau_{cs} \quad \dots\dots(2.56)$

As the values of ϕ can not be estimated directly we draw a theoretical curve for $\log(\cos \phi)^{\frac{1}{\phi}}$ against ϕ from which

$$\log(\cos \phi)^{\frac{1}{\phi}} = \frac{\log \frac{x}{\cos(\delta\phi)}}{\delta\phi} \quad \dots\dots(2.57)$$

can be known. With the known ϕ one can estimate τ_{cs} and δ from eqs (2.56) and (2.55) respectively. On comparison the symmetric and asymmetric distribution behaviours it is found that all the mono-substituted anilines show the symmetric distribution of relaxation times. This has been discussed in Chapter V of the thesis.

The double relaxation behaviours of several normal and isomeric octyl alcohols dissolved in n-heptane under 24.33, 9.25 and 3.00 GHz electric fields at 25°C have been studied using single frequency measurement technique of dielectric relaxation parameters.

The results are, however, presented in Chapter VI for normal alcohols and Chapter VII for isomeric octyl alcohols respectively.

It is interesting to note that all the alcohols show double relaxation times at each frequency with the exception of methanol in C_6H_6 at 9.84 GHz electric field. Although, Onsager's equation may be a better choice for such polymeric long chain molecules, but our method seems to be very much simple and straightforward within the framework of Debye and Smyth model. The corresponding μ_1, μ_2 were also calculated from slopes of $K_{ij}-\omega_j$ curves and compared with those due to bond angles and bond moments. The conformational structures also accord with the measured data.

The structural and associational aspects of some binary and single polar solutes in nonpolar solvents are given in Chapter VIII with the use of hf conductivity measurement of solutions. The valuable information on monomer and dimer formations of polar liquids at 9.945 GHz electric field as well as the temperature dependence of mesomeric and inductive moments of the various substituent groups of such polar molecules were observed.

2.10. Experimental Techniques

It is clear from the above chapters that the relaxation data of polar-nonpolar liquid mixtures under the microwave electric fields of nearly 10 GHz are expected to yield very interesting results. We, therefore, are very much tempted to perform experiments on some aprotic polar liquids like dimethyl sulphoxide (DMSO), N,N-dimethyl formamide (DMF); N,N-dimethyl acetamide (DMA) and N,N-tetra methyl urea (TMU) in C_6H_6 under 9.945 GHz electric field at different temperatures. The liquids are widely used in medicine and industry. They are already investigated in Chapter VIII to reveal their associational aspects. Thus, the purpose of the present experiment is only to observe whether they show either the double or monorelaxation behaviour at 9.945 GHz electric fields.

2.10 (a) Experimental Set up

The Block diagram of the experimental set up for the measurements of dielectric relaxation solution (ij) data is given in Fig(2.4). It consists of sample holder, temperature chamber, temperature controller and Hewlett Packard Bridge 4192A. The real ϵ'_{ij} and imaginary ϵ''_{ij} parts of complex dielectric constant ϵ_{ij}^* as well as static dielectric constant ϵ_{0ij} of the polar-nonpolar mixture were measured at different temperatures at the desired electric field frequencies. The permittivity at infinite frequency $\epsilon_{\infty ij}$ ($= n^2_{Dij}$) were, however, measured by Abbe's Refractometer.

2.10 (b) The Cell Construction and Sample Holder

A cell with a sample holder consists of two glass plates. The inner surfaces are coated with conducting layer of ITO (Indium Tin Oxide) as shown in Fig (2.5). A capacitor is thus formed with the active area of 1 cm^2 . The glass plates are separated by $40 \mu\text{m}$ apart. The connecting leads of 1 m length are used for measurements. The sample for measurements is placed on the lower glass plate in contact with front edge of the upper glass plate and kept on Mettler Hot Stage FP 52. The sample is filled up by capillary action and during fill up it is essential to avoid air bubble.

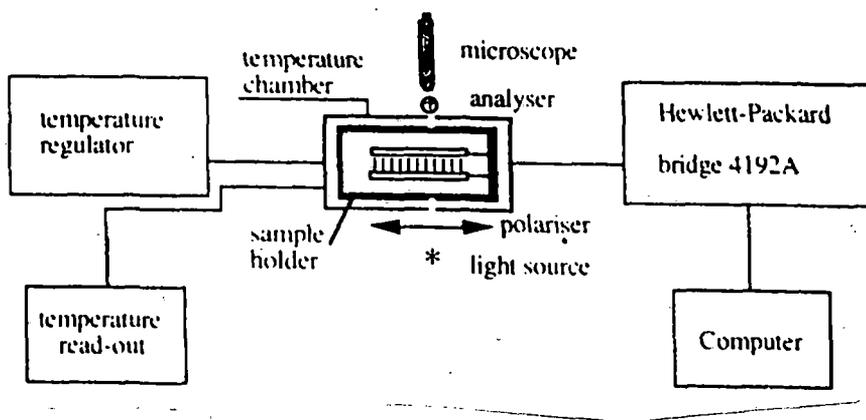


Figure 2.4 Block Diagram of the experimental set up used for dielectric measurements

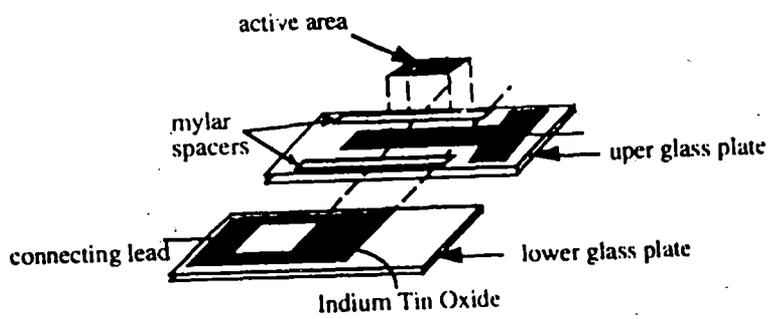


Figure 2.5 Inner surfaces of the lower and upper conducting glass plates

2.10 (c) Capacitance and Conductance Measurement by HP LF Impedance Analyser

The Block diagram of Hewlett Packard Impedance Analyser (HP 4192A) for measuring the capacitance and conductance of the cell in the frequency range of 5Hz to 13 MHz is shown in Fig (2.6). It can perform impedance measurement in the above frequency range in an almost continuous sweep. The frequency may be scanned either linearly or logarithmically. The generator generates AC signal with an amplitude variable from 5mv to 1.1 Volt. One of the disadvantage of the bridge is that its capability of impedance measurements is limited to 3 MΩ. This restricts the accuracy of the measurements at lower frequencies. However, if the capacitance of the sample is large enough, the accuracy is improved because the impedance become measurable by the bridge. When the bridge is balanced as shown in Fig (2.6), the current I_d is zero, i.e.

$$I_x = I_r \quad \dots\dots\dots(2.58)$$

The voltage drop across the sample is equal to that across the range resistor R_r . The complex impedance of the sample Z_x^* is given by

$$Z_x^* = R_r \frac{e_s^*}{e_r^*} \quad \dots\dots\dots(2.59)$$

where e_s^* and e_r^* are the complex voltages respectively. From the measurements of the complex impedance; the bridge evaluates the capacitance and conductance values.

2.10 (d) Cell Calibration

Our measurement cell consists of a parallel plate capacitor connected with relatively short leads. The cell thickness is determined by the myler spacer or glass spacer between glass plates. The measured air capacitance C_0 has a contribution from the capacitance of the active area of the plates. The stray capacitance arises from the leads and the nonhomogeneities of the field lines at the edges of the active area. The spacers do not

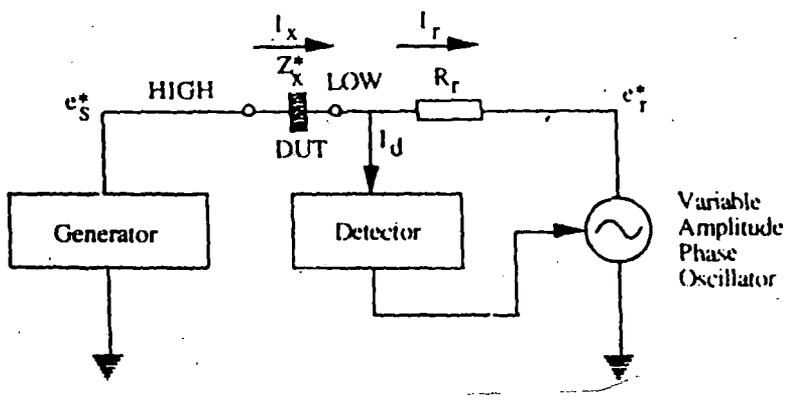


Figure 2.6 Block diagram of the HP 4192A bridge (5Hz to 13 MHz)

contribute to the capacitance because they are placed outside the active area. In this case C_0 is written as

$$C_0 = C_L + C_s \quad \text{.....(2.60)}$$

where C_L is the capacitance of the empty cell excluding the stray capacitance. To determine the stray capacitance, two standard liquids (Spec-pure benzene and para-xylene) with known dielectric permittivity were used. When the cell is filled with a liquid of known dielectric permittivity ϵ , the measured capacitance will be given by

$$C = \epsilon C_L + C_s \quad \text{.....(2.61)}$$

From the above two, eqs (2.60) and (2.61), the value of C_s is calculated. The error in measurement of C_s for standard liquids is $\pm 1\%$. The real part of the dielectric permittivity of the sample is then given by

$$\epsilon'_{ij} = (C - C_s) / (C_0 - C_s) \quad \text{.....(2.62)}$$

where C is the capacitance of the cell filled with the sample. The dielectric absorption for the sample is calculated from conductance measurement by

$$\epsilon''_{ij} = G_{ij} / 2\pi f C_0 \quad \text{.....(2.63)}$$

where G_{ij} is the conductance and f is the frequency of the electric field. In order to get the real and imaginary permittivity of the dielectric sample at 9.945 GHz, graphs were plotted with ϵ'_{ij} and ϵ''_{ij} against f for a fixed temperature and concentration of the sample. Lastly, an extrapolation procedure was adopted to get values at 9.945 GHz electric field. The findings of the experimental data are displayed column-wise in Chapter IX.

2.11. Dipole Moments of Isotopomer Molecules

The dipole moments of isotopomer molecular ions play a significant role in the photon induced dissociation process of such molecules. Photo-dissociation is used in the study of modelling the ionised atmosphere, photo chemical reactions and is, therefore, an important mechanism for destruction of inter stellar molecules. Moreover, the observed asymmetry

in the forward and backward scattering process of the fragments produced from the collision induced dissociation of heteronuclear molecular ions depends on their dipole moments.

We, in the Chapter X have calculated the dipole moments of HD^+ , HT^+ molecular ions using Morse function since the diatomic molecular ions are supposed to obey the Morse potential excellently. The calculated values of μ by using Morse potential when compared with those of Saha ¹¹⁾ reveal the applicability of the method suggested.

Although, Morse-Kratzer ¹²⁾ potential was supposed to be the most real potential for such heteronuclear molecular ions, but the calculated values did not yield better result.

In the last chapter XI, we have given the summary and concluding remarks of the whole thesis.

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