

CHAPTER – 1

GENERAL INTRODUCTION AND A BRIEF REVIEW OF PREVIOUS WORKS

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1.1 INTRODUCTION

All the liquids both organic and inorganic are usually called the solvents. A few organic liquids are spherical in shape and have zero dipole moments, are, therefore, called nonpolar dielectrics. Most of the liquids, on the other hand, are highly asymmetric in shape and thus they possess dipole moments μ . These liquids are called polar dielectrics. An attempt to get the correlation of the physico-chemical properties of the organic liquids in non polar solvents is made in terms of measured parameters [1-4] of liquid dielectrics.

Liquid dielectric is an interesting branch of solid state physics and physical chemistry as it provides an important tool and technique to explore the shape, size and structure of a polar liquid solvent. Before 20 th century, the subject matter of dielectrics was published in different countries and in many languages. Debye carried out a noble job by concentrating this subject matter in his famous monograph "Polar Molecules"[5] in the year 1929. Series of monographs were, later on, published by a large number of workers: Fröhlich [6], Smyth [7], Hill [8], Smith [9], Jonscher [10] etc. to make this field interesting to scientific community all over the world. Physico-chemical properties of some organic polar mixtures can, however be achieved by the phenomena of dielectric relaxation involved with orientational polarization of the polar molecules.

1.2 DIELECTRIC DISPERSION

When a dielectric material is subjected to an alternating electric field electronic, atomic and orientational polarizations are called into play effectively. The springlike nature of the forces involved in electronic and atomic polarization tend to disappear with frequency of the applied electric field. When the frequency of the impressed electric field exceeds a critical value, the permanent dipoles can not follow the exact alternation of the electric field. The measurable lag in response to the electric field is called dielectric relaxation. When the electric field is switched off all the polarizations decay exponentially with time. The time in which the polarization drops to $1/e$ times its initial value is called relaxation time [11], usually denoted by τ . The electronic and atomic polarizations are effective within 10^{15} Hz

and 10^{12} Hz frequency respectively. But orientational polarization has a range of frequency lying between 10^4 to 10^9 Hz [12] depending upon nature of the material and temperature.

In Maxwell's electromagnetic theory it is assumed that

$$\vec{D} = \epsilon \vec{E} \quad (1.1)$$

Where \vec{D} and \vec{E} being the electric displacement and electric field vectors respectively. $\epsilon = \epsilon_0 \epsilon_r$, ϵ_0 is the permittivity of free space $= (1 / 4\pi c^2) \times 10^{-7} = 8.854 \times 10^{-12}$ Farad metre⁻¹, $c = 3 \times 10^{10}$ Cm/s = velocity of electromagnetic waves in vacuum and ϵ_r is the relative permittivity of medium of solute and solvent mixtures of a certain weight fraction w_j .

Each region of dispersion is associated with energy loss. The existence of energy loss means that electric displacement vector \vec{D} instead of being in phase with \vec{E} lags by an phase angle δ . So it is evident from Eq. (1.1) that ϵ_r is a complex quantity given

$$\text{by} \quad \epsilon_r^* = \epsilon_r' - j\epsilon_r'' \quad (1.2)$$

$$\epsilon_r'' / \epsilon_r' = \tan\delta \quad (1.3)$$

where ϵ_r' , ϵ_r'' and $\tan\delta$ are the real and imaginary parts of complex permittivity ϵ^* and loss tangent respectively.

1.3 DIELECTRIC SUSCEPTIBILITY

The introduction of a dielectric material between the two charged plates of a capacitor reduces the electric field by a factor ϵ_r . The reduction in electric field can be expressed as

$$\vec{E} = \frac{\vec{D} - \vec{P}}{\epsilon_0}$$

$$\text{or } \vec{D} - \vec{P} = \epsilon_0 \vec{E}$$

$$\text{or } \vec{P} / \epsilon_0 \vec{E} = \vec{D} / \epsilon_0 \vec{E} - 1$$

$$\text{or } \vec{P} / \epsilon_0 \vec{E} = \epsilon / \epsilon_0 - 1$$

The ratio of \vec{P} to $\epsilon_0 \vec{E}$ is called the dielectric susceptibility χ_e of the material

$$\text{i.e. } \chi_e = \epsilon_r - 1 \quad (1.4)$$

under hf electric field χ_e is also complex and is written as

$$\chi_e^* = \chi_e' - j\chi_e'' \quad (1.5)$$

The real χ_e' and imaginary χ_e'' parts of complex hf dimensionless orientational susceptibilities are related to complex ϵ_r^* by

$$\chi'_e = \varepsilon'_r - 1 \quad (1.6)$$

$$\chi''_e = \varepsilon''_r \quad (1.7)$$

1.4 REPRESENTATION OF PERMITTIVITY IN A COMPLEX PLANE

The variation of relative permittivity with angular frequency ω is given by [5]

$$\frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon_s - \varepsilon_\infty} = \frac{1}{1 + j\omega\tau} \quad (1.8)$$

where ε_s and ε_∞ are the relative permittivities at much lower and higher (optical) frequencies respectively. Equating the real and imaginary parts from both sides of the above equation one gets that

$$\frac{\varepsilon'_r - \varepsilon_\infty}{\varepsilon_s - \varepsilon_\infty} = \frac{1}{1 + \omega^2\tau^2} \quad (1.9)$$

$$\frac{\varepsilon''_r}{\varepsilon_s - \varepsilon_\infty} = \frac{\omega\tau}{1 + \omega^2\tau^2} \quad (1.10)$$

On eliminating the parameters of $\omega\tau$ from eqs.(1.9) and (1.10) the following equation is obtained

$$\left(\varepsilon'_r - \frac{\varepsilon_s + \varepsilon_\infty}{2} \right)^2 + \varepsilon_r''^2 = \left(\frac{\varepsilon_s - \varepsilon_\infty}{2} \right)^2 \quad (1.11)$$

Eq. (1.11) represents the equation of a circle . The value of ε_r'' when plotted against ε_r' gives a semicircle of radius $\left(\frac{\varepsilon_s - \varepsilon_\infty}{2} \right)$. Results of permittivity measurements were analysed in this way to many liquids and the experimental points are found to lie on the Debye semicircle.

1.5 DOUBLE RELAXATIONS DUE TO ROTATION OF THE FLEXIBLE POLAR GROUPS AND ROTATION OF THE WHOLE MOLECULES:

For k th type of relaxation process , Budo [13] assumed that Debye's eq. (1.8) can be written as

$$\frac{\epsilon'_r - \epsilon_\infty}{\epsilon_s - \epsilon_\infty} = \sum \frac{c_k}{1 + j\omega\tau_k} \quad (1.12)$$

where $\sum c_k = 1$ is the relative contribution of the k th type of relaxation process and $j = \sqrt{-1}$ is a complex number.

For almost all the dipolar liquids the relaxation process is involved with rotation of the flexible parts and the rotation of the whole molecule characterised by relaxation times τ_1 and τ_2 . With this assumption Budo's relation reduces to Bergmann's equations [14]:

$$\frac{\epsilon'_r - \epsilon_\infty}{\epsilon_s - \epsilon_\infty} = c_1 \frac{1}{1 + \omega^2\tau_1^2} + c_2 \frac{1}{1 + \omega^2\tau_2^2} \quad (1.13)$$

$$\frac{\epsilon''}{\epsilon_s - \epsilon_\infty} = c_1 \frac{\omega\tau_1}{1 + \omega^2\tau_1^2} + c_2 \frac{\omega\tau_2}{1 + \omega^2\tau_2^2} \quad (1.14)$$

Such that $c_1 + c_2 = 1$

Bergmann et al [14] used a graphical method to obtain τ_1 & τ_2 from eqs.(1.13) and (1.14). Bhattacharyya et al [15] simplified the Bergmann's procedure to calculate τ_1 and τ_2 when the different frequencies of the electric field. Higasi et al [16] made a crude graphical analysis to estimate τ_1 and τ_2 of polar liquid molecules in nonpolar solvent under single frequency electric field. Saha et al [17] and Sit et al [18] extended the single frequency measurement analytical technique to calculate τ_1 and τ_2 in terms of relative permittivities ϵ'_{ij} , ϵ''_{ij} , ϵ_{0ij} and $\epsilon_{\infty ij}$ of a large number of polar nonpolar liquid mixture of different weight fractions w_j 's of solutes. Recently, Mitra et al [19] has derived a technique in terms of dielectric orientational susceptibilities to obtain τ_1 and τ_2 as discussed in chapter 2 of this thesis.

1.6 HIGH FREQUENCY CONDUCTIVITY

An ideal dielectric when subjected to an alternating electric field, there is no conduction of

free ions but Joule heat is produced due to drift electrons and free ions. If a potential difference v is established between the two plates of a capacitor separated by a distance d , creates an electric displacement Vector \vec{D} in the dielectric. The current density is given by

$$i = \frac{dq}{dt} \quad (1.15)$$

In SI units, $q = D = \epsilon_r^* \epsilon_0 E$, where $E = v / d =$ intensity of electric field

Hence
$$i = \epsilon_r^* \epsilon_0 \frac{d}{dt} \left(\frac{v}{d} \right) \quad (1.16)$$

As the field is alternating we have $v = v_0 e^{j\omega t}$

So
$$i = \frac{\epsilon_r^* \epsilon_0}{d} \frac{d}{dt} (v_0 e^{j\omega t})$$

$$i = j\omega \frac{\epsilon_r^* \epsilon_0}{d} (v_0 e^{j\omega t})$$

$$i = j\omega \epsilon_r^* \epsilon_0 E \quad (1.17)$$

The current density i in terms of hf complex conductivity σ^* is

$$i = \sigma^* E \quad (1.18)$$

From (1.17) and (1.18) one obtains

$$\sigma^* = j\omega \epsilon_r^* \epsilon_0 \quad (1.19)$$

Murphy and Morgan [20] deduced σ^* as

$$\sigma^* = \sigma' + j\sigma''$$

$$\text{hence } \sigma' + j\sigma'' = j\omega \epsilon_0 (\epsilon' - j\epsilon'')$$

$$\text{or, } \sigma' + j\sigma'' = j\omega \epsilon_0 \epsilon' + \omega \epsilon_0 \epsilon'' \quad (1.20)$$

comparing real and imaginary parts from both sides we get

$$\sigma' = \omega \epsilon_0 \epsilon'' \text{ and } \sigma'' = \omega \epsilon_0 \epsilon' \text{ as the real and imaginary parts of hf}$$

complex conductivity.

1.7 ESTIMATION OF RELAXATION TIME τ_j BY HIGH FREQUENCY CONDUCTIVITY :

Deby's equation in S I unit is written as
$$\frac{\epsilon_r - 1}{\epsilon_r + 2} \frac{M}{\rho} = \frac{N}{3\epsilon_0} \left(\alpha_d + \frac{\mu^2 \rho}{3KT} \right) \quad (1.21)$$

Where M = molecular weight , ρ mass density of dielectric material, α_d = polarizability due to fast polarization, μ_p = dipole moment of a polar molecule.

If α_i and α_j be the polarizabilities of a nonpolar and polar molecule of molecular weights M_i and M_j respectively, then eq. (1.21) becomes

$$\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} \frac{f_i M_i + f_j M_j}{\rho_{ij}} = \frac{N}{3\varepsilon_0} (f_i \alpha_i + f_j \alpha_j) \quad (1.22)$$

or

$$\frac{\varepsilon_s - 1}{\varepsilon_s + 2} \frac{f_i M_i + f_j M_j}{\rho_{ij}} = \frac{N}{3\varepsilon_0} (f_i \alpha_i + f_j \alpha_j) + \frac{N \mu^2 f_j}{9\varepsilon_0 K T} \quad (1.23)$$

where ε_∞ and ε_s are the dielectric constants of the solution of infinite i.e, optical frequency and in static electric fields respectively. The mole fractions f_i and f_j of the components are

$$f_i = \frac{n_i}{n_i + n_j} \quad \text{and} \quad f_j = \frac{n_j}{n_i + n_j} \quad , \quad \text{where } n_i \text{ and } n_j \text{ be the number of}$$

solvent and solute molecules per unit volume of the solutions.

From eqs. (1.22) and (1.23) one obtains

$$\varepsilon_s - \varepsilon_\infty = \frac{N c_j \mu^2}{27 \varepsilon_0 K T} (\varepsilon_s + 2)(\varepsilon_\infty + 2) \quad (1.24)$$

Where c_j is the concentrations of the solute molecules in moles / c.c. Now eq. (1.24) with eq. (1.10) becomes

$$\varepsilon_r'' = \frac{N c_j \mu^2}{27 \varepsilon_0 K T} (\varepsilon_s + 2)(\varepsilon_\infty + 2) \frac{\omega \tau}{1 + \omega^2 \tau^2} \quad (1.25)$$

In dilute polar-nonpolar liquid mixture it is assumed that $\varepsilon_s \approx \varepsilon_\infty \approx \varepsilon_r'$

Hence

$$\varepsilon_r'' = \frac{N c_j \mu^2}{27 \varepsilon_0 K T} (\varepsilon_r' + 2)^2 \frac{\omega \tau}{1 + \omega^2 \tau^2} \quad (1.26)$$

At infinite dilution ϵ'_r may be replaced by ϵ_i , the relative permittivity of the solvent

$$\epsilon''_r = \frac{Nc_j \mu^2_j}{27\epsilon_o KT} (\epsilon_i + 2)^2 \frac{\omega\tau}{1 + \omega^2\tau^2} \quad (1.27)$$

As $\sigma' = \omega\epsilon_o\epsilon''_r$ we have

$$\sigma' = \frac{Nc_j \mu^2_j}{27KT} (\epsilon_i + 2)^2 \frac{\omega^2\tau}{1 + \omega^2\tau^2} \quad (1.28)$$

The eq. (1.28) may be used to estimate μ_j of a dipolar molecule to comment about its physico-chemical aspects of polar liquid in non polar solvents. From eq. (1.9) it can be written as

$$\epsilon'_r = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + \omega^2\tau^2} \quad (1.29)$$

Multiplying both sides by $\omega\epsilon_o$ and introducing the term $\sigma'' = \omega\epsilon_o\epsilon'_r$ and $\sigma' = \omega\epsilon_o\epsilon''_r$, the eq. (1.29) with the help of eq.(1.10) becomes

$$\sigma'' = \sigma_\infty + \left(\frac{1}{\omega\tau_j} \right) \sigma' \quad (1.30)$$

which shows a linear relationship between σ'' and σ' , the slope $(1 / \omega\tau_j)$ may conveniently be used [21] to estimate τ_j of a polar solute.

1.8 ESTIMATION OF DIPOLE MOMENT μ_s OF A POLAR SOLUTE FROM DEBYE EQUATION UNDER LOW FREQUENCY OR STATIC ELECTRIC FIELD:

For a polar (j) and a nonpolar (i) liquid mixture the eq. (1.21) can be used to estimate static μ_s under static or low frequency electric field. The eq. (1.21) can be written as

$$\frac{\epsilon_{ij} - 1}{\epsilon_{ij} + 2} \frac{M_i f_i + M_j f_j}{\rho_{ij}} = \frac{N}{3\epsilon_o} \left(\alpha_i f_i + \alpha_j f_j + \frac{\mu_s^2}{3KT} f_j \right) \quad (1.31)$$

ϵ_{ij} is the relative permittivity of (i,j) solution. As $\alpha_i = \alpha_j$ the eq. (1.31) reduces to

$$\frac{\epsilon_{ij} - 1}{\epsilon_{ij} + 2} v_{ij} = \frac{N\alpha_i}{3\epsilon_o} + \frac{N}{3\epsilon_o} \frac{\mu_s^2}{3KT} f_i \quad (1.32)$$

$$\frac{\varepsilon_{ij} - 1}{\varepsilon_{ij} + 2} v_{ij} = \frac{\varepsilon_i - 1}{\varepsilon_i + 2} v_i + \frac{N\mu^2_s}{9\varepsilon_o KT} f_i. \quad (1.33)$$

Where V_{ij} and V_i are the specific volumes of solution and solvent respectively. As $\varepsilon_{ij} = n^2_{Dij}$ where n_{Dij} is the refractive index of the solution, the eq. (1.33) for a neutral dielectrics is

$$\frac{n^2_{Dij} - 1}{n^2_{Dij} + 2} v_{ij} = \frac{n^2_{Di} - 1}{n^2_{Di} + 2} v_i \quad (1.34)$$

From eqs. (1.33) and (1.34) one obtains

$$\left(\frac{\varepsilon_{ij} - 1}{\varepsilon_{ij} + 2} - \frac{n^2_{Dij} - 1}{n^2_{Dij} + 2} \right) = \left(\frac{\varepsilon_i - 1}{\varepsilon_i + 2} - \frac{n^2_{Di} - 1}{n^2_{Di} + 2} \right) \frac{V_i}{V_{ij}} + \frac{N}{3\varepsilon_o} \frac{\mu^2_s}{3KT} \frac{f_i}{V_{ij}}. \quad (1.35)$$

$f_i / V_{ij} = c_j$, the molar concentration per unit volume and at infinite dilution $V_i / V_{ij} \rightarrow 1$. So we have

$$\left(\frac{\varepsilon_{ij} - 1}{\varepsilon_{ij} + 2} - \frac{n^2_{Di} - 1}{n^2_{Di} + 2} \right) = \left(\frac{\varepsilon_{ij} - 1}{\varepsilon_{ij} + 2} - \frac{n^2_{Dij} - 1}{n^2_{Dij} + 2} \right) \frac{N\mu^2_s}{9\varepsilon_o KT} c_j. \quad (1.36)$$

which is the Debye's equation for a polar – nonpolar liquid mixture . The eq.(1.36) can be used to obtain static dipole moment μ_s of a polar solute under low frequency electric field. The disadvantage of this method is that it can not be applied for a concentrated solution. This equation has been developed by Mitra et al [22] for estimation of μ_s as discussed in Chapter -7 of this thesis.

1.9 GOPALAKRISHNA'S METHOD TO ESTIMATE τ AND μ :

Debye's (1.8) for complex dielectric constant ε^*_{ij} of a solution

$$\frac{\varepsilon^*_{ij} - 1}{\varepsilon^*_{ij} + 2} = \frac{\varepsilon_{\infty ij} - 1}{\varepsilon_{\infty ij} + 2} + \frac{n\mu^2}{9\varepsilon_o KT} \cdot \frac{1}{1 + j\omega\tau} \quad (1.37)$$

Equating the real and imaginary parts from both sides of the above equation i.e, eq. (1.37) one gets,

$$\frac{\varepsilon'^2_{ij} + \varepsilon'_{ij} + \varepsilon''^2_{ij} - 1}{(\varepsilon'_{ij} + 2)^2 + \varepsilon''^2_{ij}} = \frac{\varepsilon_{\infty ij} - 1}{\varepsilon_{\infty ij} + 2} + \frac{n\mu^2}{9\varepsilon_o KT} \cdot \frac{1}{1 + \omega^2\tau^2} \quad (1.38)$$

And

$$\frac{3\varepsilon''_{ij}}{(\varepsilon'_{ij} + 2)^2 + \varepsilon''^2_{ij}} = \frac{n\mu^2}{9\varepsilon_o KT} \cdot \frac{\omega\tau}{1 + \omega^2\tau^2} \quad (1.39)$$

Writing $(\varepsilon'^2_{ij} + \varepsilon'_{ij} + \varepsilon''^2_{ij} - 1) / \{(\varepsilon'_{ij} + 2)^2 + \varepsilon''^2_{ij}\} = x$,

$3\varepsilon''_{ij} / \{(\varepsilon'_{ij} + 2)^2 + \varepsilon''^2_{ij}\} = y$ and $(\varepsilon_{\infty ij} - 1) / (\varepsilon_{\infty ij} + 2) = p$

equating (1.38) and (1.39) takes the form:

$$x = p + (1 / \omega\tau) \cdot y \quad (1.40)$$

which is a straight line between x and y and the slope $(1 / \omega\tau)$ can be used [23] to estimate τ of a polar molecule to explore their physico – chemical aspects.

Since $n = (N\rho_{ij} / M_j) \cdot \omega_j$, the number of dipoles per unit volume, the eq. (1.38) takes the form

$$x = p + k\rho_{ij} \cdot \omega_j \quad (1.41)$$

where

$$k = \frac{N\mu^2}{9\varepsilon_o KTM_j} \cdot \frac{\omega\tau}{1 + \omega^2\tau^2}$$

The slope of the linear relation between x and ω_j be used to estimate μ of a polar unit [23] under hf electric field.

1.10 A BRIEF REVIEW OF PREVIOUS WORKS

After debye [24] a large number of workers engaged themselves to estimate several relaxation parameters of different dipolar liquid molecules. Their works provide an useful and essential tool to study the physico-chemical properties of liquid solute and solvents.

The radii of alcohols, ketones and glycerines were determined by Mizushima [25,26] which are found to be smaller than the gas kinetic values, but maintaining the same order [27]. The estimated dipole moments μ 's of methyl, ethyl and amyl alcohols are found to be independent of temperature. Onsager [28], Plumely [29], Pao [30] and Foster [31] interpreted the origin of conduction in case of pure hydrocarbons such as hexane. Jackson and Powles [32] estimated τ_j of polar molecules in C_6H_6 and in paraffin and showed that τ_j 's depend on the viscosity of the solvents used. The dielectric absorption measurement of

aliphatic chlorides and alcohols was performed by Kremmling [33] and as a result the internal rotations and hence multiple relaxation times of the molecules were observed.

The presence of some bound ions in dielectric liquids are noticed by Green [34]. τ_j 's were estimated by Poley [35] from the imaginary part of complex permittivity ϵ^* measurement for monosubstituted benzenes. The increase of τ_j occurs with molecular sizes. Garg and Smyth [36] showed three different τ_j 's for three different dispersion regions of alcohol molecules. They arise respectively due to hydrogen bonded structure, orientational motions of the molecules and rotations of $-OH$ groups about C-C bond. A convenient and useful method to estimate τ_j and μ_j of polar molecules was developed by Gopala Krishna [37] in terms of density of the solvent. Schellman [38] studied the associations in saturated dielectric liquids.

Hart and Mungali [39] observed the electric conduction in chlorobenzene. Higasi et al [40] analysed the experimental data of n-alkyl bromide in liquid state in terms of distribution of τ_j 's between two Fröhlich's [41] limiting τ 's. Bergmann et al [42] however devised a graphical method to estimate double relaxation times τ_1 and τ_2 due to rotations of functional groups attached to the parent molecules and end over end rotation of the whole molecule respectively for diphenyl ether, anisol and o-dimethoxy benzene. Krishnaji and Mansingh [43] studied the dielectric relaxation mechanism in alkyl cyanides and alkythiols and observed that τ_j 's increases with sizes of the molecules. Sinha et al [44,45] observed the temperature dependence of τ_j and μ_j of some polar molecules in nonpolar solvent. The viscosity dependence of τ_j i.e, $\tau_j T / \eta^\gamma = \text{const.}$ is however, predicted; where $\gamma (= \Delta H_\tau / \Delta H_{\eta_i})$ is the ratio of enthalpies of activation due to dielectric relaxation and viscous flow of the solvent used.

Berbenza [46] studied the dielectric relaxation behaviour of methyl alcohol in the temperature range of 5°C to 55°C under electric field of wave length 5 c.m. to 15 c.m. and the results were interpreted by single relaxation process. Adamczewski and Jackym [47] observed that conductivity σ is a function of temperature for some organic liquids. Bhattacharyya et al [48] observed intramolecular and intermolecular τ_1 and τ_2 due to rotation of flexible polar groups and where molecule itself from the equations of Bergmann et al [42]. Non rigid molecules having two τ 's could, however, be obtained by Higasi et al [49] based on single frequency measurement method.

The existence of natural charge carries in dielectric liquid was, however, observed by Loheneysen and Nageral [50], Gaspared and Gosse [51], Crossley et al [52] and

Glasser et al [53]. They measured concentration variation of ϵ' and ϵ'' of some aliphatic alcohols in n-heptane at 25⁰C under electric field frequencies of gigahertz range. They observed three distinct τ 's, the lowest τ_j 's are due to rotation of -OH groups, the intermediate τ_j 's for monomer and small multimers formed by polar chain and while largest τ_j 's are due to hydrogen bonded structure. Vyas and Vashisth [54] conducted an observation on four aliphatic alcohols and the mixtures of alcohols with DMF and 2 fluoroaniline in C₆H₆ under 3 c.m. wavelength electric field at 30⁰C and showed complex formations at very low concentration.

Purohit et al [55] and Tripathy et al [56] studied the relaxation parameters of trifluoro ethanol, trifluoro acetic acid, n-propanol, n-butanol, n-butylamine, n-propylamine and observed strong -H bonding among the molecules. Some workers [57-62] estimated τ_j from 'n', the number density of free ions, 'a', the radius of rotating units and thermodynamic energy parameters for some interesting polar liquid molecules in nonpolar solvent under hf electric field. They observed that τ_j increases with the number of C-atoms of molecules and ΔE_j increases with size of the molecules. Other workers [63-67] measured relative permittivities ϵ' and ϵ'' of some substituted toluidines, para compounds etc. and estimated τ_j , μ_j and thermodynamic energy parameters. Molecular associations are found to play a vital role in explaining the observed results. Agarwal [68] estimated τ_j of n-butyl chloride, chlorobenzene, tertiary butyl alcohol in benzene at 25⁰C under 9.96 GHz electric field frequency and also detected that τ_j is influenced by configuration in the given order $\tau_{linear} > \tau_{planer} > \tau_{spherical}$.

Gandhi and Sharma [69] determined τ_1 , τ_2 and τ_0 ($= \sqrt{\tau_1\tau_2}$) of isobutyl-methacrylate and allyl-methacrylate and their mixtures in C₆H₆ and the observed results show the intramolecular and molecular rotations.

Taking into consideration of the work of Acharyya et al [70], Murthy et al [71] added a new dimension in the theoretical formulaton by which the interrelation of τ_j and μ_j is achieved. Sharma & Sharma [72] and Sharma et al [73] estimated ϵ' and ϵ'' of DMA, DMSO in C₆H₆ in the temperature range of 25⁰C to 40⁰C under 9.174 GHz electric field frequency to estimate τ_j , μ_j and thermodynamic energy parameters. The existence of monomer and dimer associations has been observed. A similar study on acetophenone and DMSO in C₆H₆ is also made by Singh and Sharma [74]. Non linear variation of τ with concentration w_j (weight fraction) of solute reveals the existence of solute solvent molecular associations.

Almost identical observation was carried out by Saha & Acharyya [75] and Saha et al [76] on DMF, DMA, DEF, CH₃OH and mixtures of DMF + CH₃OH, DMF + Acetonitrile, DMF + Acetone and on some disubstituted anilines and benzenes in solvent C₆H₆ and CCl₄ at single temperature under nearly 3 c.m. wave length electric field. The estimated τ_j , μ_j , τ_1 , τ_2 , μ_1 , μ_2 etc. were explained on the basis of polarity, size of the molecules and solvent environment around the solute molecules. Elsayed et al [77] estimated the ΔH_τ , ΔF_τ , ΔS_τ from the temperature variation of τ_j for Ag, Sb, Te in solid and liquid phase under 1 MHz electric field frequency. They gave an explanation that τ_j decreases with temperature due to increase of thermal agitation to weaken the intermolecular forces. Varadarajan and Rajagopal [78,79] showed the rotation of -OH group about the whole molecule and also observed the dipole-dipole interactions of a no. of alcohols in C₆H₆.

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