

*CORRELATIONS OF PHYSICO-CHEMICAL
PROPERTIES OF SOME ORGANIC SOLVENT
MIXTURE*

*THESIS SUBMITTED FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY (SCIENCE) OF
THE UNIVERSITY OF NORTH BENGAL,
W.B. INDIA (2007)*



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STOCK TAKING - 2011

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*THIS RESEARCH WORKS PRESENTED IN THE
THESIS IS DEDICATED IN THE
MEMORY OF MY BELOVED MOTHER
LATE UMA RANI MITRA*

ACKNOWLEDGEMENT

I am highly grateful to Dr. pranab Ghosh, M.Sc. Ph.D , Reader in Chemistry of North Bengal University and Dr. Suprakash Acharyya , M.Sc, D.Phil(Cal), Reader in Physics of Raiganj University College, for their kind guidances, active co-peration and helpful supervisions for the research works presented in the thesis entitled " Correlations of Physico Chemical properties of some Organic solvent mixtures"

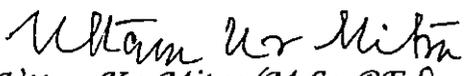
My heartily and never ending gratitude to Dr. Nilanjan Ghosh, M.Sc. Ph.D , Asstt. Teacher., S.D.P.U. Vidya Charka, Raiganj who not only inspired me but extended his tremendous help in every spheres of this thesis work,

The author is highly thankful to Dr. Achinta Chatterjee, Reader, Dept. of Physics, Malda College, for his guide line in calculation and Sri Kushal Aich , Computer Teacher, Raiganj Sri Sri R.K. Vidya Bhaban, Raiganj for his technical knowledge and laborious contribution in printing this thesis.

I convey my gratefulness to Dr. Swapan Kr. Sit and Dr. Koushik Dutta for their initial participations in the works presented in this thesis.

Heartily thanks also to Anirban, Arindam and Mrs. Anima Acharyya for their cooperation during the reaearch period.

Finally I like to express my appreciation to my wife Mrs. Manaswita Ghosh (Mitra) and my elder brother Mr. Gour Sankar Mitra for their continuous support and inspiration throughout the research period to complete the research works.


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PREFACE OF THE THESIS

PREFACE OF THE THESIS

The correlation of various properties of a large number of liquid solvents has gained much attention of a large number of workers[1-4]. Most of the workers have measured different parameters for some normal and simple liquids. The detail and extensive prediction of correlation from the available measurements of some associated and complicated organic dipolar liquids, fused salts, polymers etc. [5-7] is not made so far. Thus it is of considerable interest because of the important applications in the field of chemical process and to predict the theoretical models of polar – nonpolar liquid mixtures. The measured data on liquid mixtures are, however, very scanty and there exists still no sound theory in liquids. Further investigation in this area is of utmost importance to scientific community to correlate the various physical parameters of some polar liquids in nonpolar solvents of different concentrations and at different experimental temperatures. Attempts have been made to correlate them with the theoretical formulae so far prescribed and derived depending upon the available models of liquid dielectrics.

With this objective in view, the present thesis work is concerned with the measurements of relaxation times τ_j 's dipole moments μ_j 's of a large number of nonspherical polar dielectrics in non polar solvents like n-heptane, p-xylene, benzene etc. The selected dipolar liquids are N, N – dimethylsulphoxide (DMSO); N, N – dimethyl formamide (DMF), N, N – dimethylacetamide (DMA) and N, N – diethylformamide (DEF), 1-butanol, 1-hexanol, 1-heptanol, 1-decanol, 2-methyl-3heptanol, 3-methyl-3heptanol, 4-methyl-3-heptanol, 5-methyl-3-heptanol, 4-octanol, 2-octanol, 2,5-dichloronitrobenzene, 3,5-dichloronitrobenzene, 2,5-dibromonitrobenzene, 2,4-dinitrochlorobenzene, 3,4-dinitro chlorobenzene, p-hydroxypropiophenone, p-chloropropiophenone, p-acetamidobenzaldehyde, p-benzyloxybenzaldehyde, p-anisidine, p-phenitidine, o-chloro-p-nitroailine, p-bromonitrobenzene, m-diisopropylbenzene, p-methylbenzoylchloride, o-chloroaceto-phenone and mixture of two polar liquids DMF & DMSO chosen to investigate their correlation properties. The component of the liquid mixtures are very much interesting because the liquids are either polar aliphatic or aromatic compounds. The alcohols, on the other hand, are hydrogen bonded polymer type show some peculiar behaviour under environments. The purpose of their physico-chemical properties as well as to derive thermodynamic energy parameters in relevant solvents at different experimental temperatures through correlation of measured parameters is of considerable interest. The

variation of $\ln\tau_j T$ with $\ln\eta_i$, where η_i = viscosity of the solvents at different experimental temperatures TK to measure ΔH_η , enthalpy of activation, of the solvents due to viscous flow used to shed more light on their dielectric relaxation phenomena of the polar–nonpolar liquid mixtures.

Dielectric relaxation phenomena are the greatest unresolved problems of physics and chemistry of today. Nothing can relax from the perfections. The measured τ_j 's, double relaxations times τ_1 and τ_2 for the rotations of the flexible groups attached to the parent molecules and of the whole molecules respectively are, however, measured by the prescribed methods so far developed in this thesis. They are used to arrive at some conclusions of the physico – chemical properties of a large number of nonspherical polar molecules in suitable non polar solvents. The thermodynamic energy parameters i.e, ΔH_τ , ΔS_τ and ΔF_τ which are called the enthalpy of activation, entropy of activation and free energy of activation due to dielectric relaxations respectively, are, on the other hand measured from the Eyring's rate process theory equation like $\ln \tau_j T = \ln A + \frac{\Delta H_\tau}{RT}$. The above relation is a linear equation having a certain intercept $\ln A$ which contains the entropy of activation and the slope $\Delta H_\tau / R$ yield what is known as enthalpy of activation of a given dipolar liquid. The values of entropies thus measured from τ_j , τ_1 and τ_2 offer a valuable information of the fact that the activated states may or may not be in the stable positions rather than normal states of the polar liquids in solvents so far considered.

The dipole moments μ_j 's or μ_1 , μ_2 etc. in terms of the measured τ_j 's from τ_1 , τ_2 are, however, measured to throw much light on the conception of the shapes and sizes of the molecules. The measured μ_j 's in terms of measured τ_j 's give the information of the rotations of the part of the molecules. The μ_1 and μ_2 in terms of τ_1 and τ_2 of the double relaxation technique under the single frequency of the electric field of GHz range offer the fact of the rotations of the flexible groups attached to the parent ones and the rotations of the whole molecules under consideration. The excellent agreement of τ_1 's with τ_j 's is very interesting. The physical significance of Debye model is very simple from this observations.

The theoretical dipole moments μ_{theo} 's may be calculated from the available bond moments available from the infrared spectroscopic data, of the flexible groups attached to the parent molecules. In some cases μ_{theo} 's are larger or smaller depending upon the case that under the application hf electric fields the bond lengths may be increased or decreased depending upon the nature of the molecules under consideration.

This fact is, however, explained by the inductive, mesomeric and electromeric effects suffered by the flexible groups of the molecules. They may be counted by the required bond moments of the flexible groups when they are multiplied by the factor $\mu_{\text{exp}} / \mu_{\text{theo}}$ to yield the exact experimental μ 's of the molecules.

The static dipole moment or the low frequency dipole moment μ_s is also calculated from available data of permittivities ϵ_{0ij} , $\epsilon_{\infty ij}$, etc and presented in this thesis in chapter seven. The close agreement of μ_s with μ_1 from the double relaxation method in terms of τ_1 of the same method and μ_j 's from the measured τ_j 's of the ratio of $\{(d\chi_{ij}'' / d\omega) / (d\chi_{ij}' / d\omega)\}_{\omega \rightarrow 0}$ shows that the dipole moments are frequency independent of the applied electric field. The measured μ_j 's, μ_1 's, μ_2 's etc are the functions of the temperatures. Temperature effect on the polar-nonpolar liquid mixtures is very pronounced to yield the information of the symmetry or the asymmetry of the polar liquids in a given solvents.

All these observations are presented in several chapters of 3 to 9 in this thesis in a very lucid way so that the workers in this field of research can understand and realize the shapes and sizes of the nonspherical molecules in order to arrive at the conclusion of the correlations of the measured parameters in this thesis.

The chapter 1 contains the general introduction and a brief review of the previous workers in this line whereas in chapter 2 the theoretical models and formulations so far prescribed and developed based on the modern concepts of dielectric terminologies and parameters of the real χ_{ij}' and imaginary χ_{ij}'' parts of the high frequency (hf) susceptibilities are presented to get the desired relaxation parameters. They are found to give more light on the advancement of the recent knowledge to understand the relaxation phenomena of a large number of nonspherical polar liquids in suitable nonpolar solvents used, in different chapters of 3 to 9 of this thesis.

In chapter entitled 3 "*STRUCTURAL ASPECTS AND PHYSICO-CHEMICAL PROPERTIES OF SOME AROMATIC POLAR NITRO COMPOUNDS IN SOLVENT BENZENE AT DIFFERENT TEMPERATURES UNDER GIGA HERTZ ELECTRIC FIELD*" a few available nitro compounds such as 2,5-dichloronitrobenzene, 3,5-dichloronitrobenzene, 2,5-dibromonitrobenzene, 2,4-dinitrochlorobenzene, 3,4-dinitrochlorobenzene are studied in details to get their relaxation times τ_j 's and dipole moment μ_j 's in order to compare them with the reported ones

The compounds N,N-dimethylsulphoxide (DMSO); N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMA) and N,N-diethylformamide (DEF) are employed to

study their relaxation phenomena in chapter 4 under the heading "*DIELECTRIC RELAXATION PHENOMENA OF SOME APROTIC POLAR LIQUIDS UNDER GIGA HERTZ ELECTRIC FIELD*"

The chapter 5 entitled "*THE PHYSICO-CHEMICAL ASPECTS OF SOME LONG STRAIGHT CHAIN ALCOHOLS FROM SUSCEPTIBILITY MEASUREMENT UNDER A 24 GHz ELECTRIC FIELD AT 25°C*" deals with the compounds 1-butanol, 1-hexanol, 1-heptanol, 1-decanol, 2-methyl-3-heptanol, 3-methyl-3-heptanol, 4-methyl-3-heptanol, 5-methyl-3-heptanol, 4-octanol, 2-octanol to study the measured τ_j and μ_j with that reported values.

The phenomena of double relaxation of some normal alcohols like 1-butanol, 1-hexanol, 1-heptanol, 1-decanol are studied in chapter 6 entitled "*STUDIES ON PHYSICO CHEMICAL PROPERTIES WITH THE RELAXATION PHENOMENA OF SOME NORMAL ALIPHATIC ALCOHOLS IN NONPOLAR SOLVENT UNDER GIGA HERTZ ELECTRIC FIELD AT A SINGLE TEMPERATURE*"

The dipole moment μ'_j 's in terms of estimated τ_j 's of the polar compounds are, however, compared with the theoretical μ_{theo} 's from the available bond moments of the substituted flexible polar groups such as p-hydroxypropiophenone, p-chloropropiophenone, p-acetamidobenzaldehyde, p-benzyloxybenzaldehyde, p-anisidine, p-phenitidine, o-chloro-p-nitroaniline, p-bromonitrobenzene are given in chapter 7 having title "*DIELECTRIC RELAXATION OF AROMATIC PARA SUBSTITUTED DERIVATIVE POLAR LIQUIDS FROM DISPERSION AND ABSORPTION PHENOMENA UNDER GHz ELECTRIC FIELD*"

The chapter 8 entitled "*STRUCTURAL AND PHYSICO-CHEMICAL PROPERTIES OF POLYSUBSTITUTED BENZENES IN BENZENE FROM RELAXATION PHENOMENA*" gives a brief report on the physico-chemical properties and structural aspects of some polysubstituted benzenes of m-diisopropylbenzene, p-methylbenzoylchloride, o-chloroacetophenone.

Finally the chapter 9 "*THE STRUCTURAL ASPECTS AND PHYSICO CHEMICAL PROPERTIES OF BINARY POLAR LIQUIDS IN NONPOLAR SOLVENT UNDER A GIGAHERTZ ELECTRIC FIELD*" contains the mixtures of two polar liquids N,N-dimethylformamide DMF(j) and N,N-dimethylsulphoxide DMSO(k) to arrive at the structural and associational aspects of those polar liquids.

Thus the thesis work so far achieved during a few years investigations are so important that the results and the conclusions may encourage the future research workers to take up this line to study further in order to shed more information on the interactions of polar-nonpolar liquid solvents.

LIST OF SIX PUBLISHED AND ONE COMMUNICATED PAPERS

1. Structural aspects and physico chemical properties of some aromatic polar nitro compounds in solvent benzene at different temperatures under giga hertz electric field.(Published in J.Indian Chem.Soc. Vol.83 July 2006, pp.674-680)
2. Dielectric relaxation phenomena of some aprotic polar liquids under giga hertz electric field. (Published in Indian Journal of Pure & Applied Physics. Vol..44. November 2006.pp.856-866)
3. The Physico chemical aspects of some long straight chain alcohols from susceptibility measurement under a 24 GHz electric field at 25⁰C. (Published in Journal of Molecular Liquids.vol.126. 2006 pp.53-61)
4. Studies on physico chemical properties with the relaxation phenomena of some normal aliphatic alcohols in non polar solvent under giga hertz electric field at a single temperature (Published in J.Indian Chem.Soc. vol 84. March 2007. pp. 1-9)
5. Dielectric relaxation of aromatic para substituted derivative polar liquids from dispersion and absorption phenomena under GHz electric field (communicated to Indian Journal of Pure & Applied Physics)
6. Structural and physico chemical properties of polysubstituted benzenes in benzene from relaxation studies (Published in .Indian Chem.Soc. vol.83. December 2006. pp.1230-1235)
7. The structural aspects and physico chemical properties of binary polar liquids in non polar solvent under a giga hertz electric field (Published in Research Journal of Chemistry and Environment vol. 11 No.(1) March 2007)

CHAPTER – 1

GENERAL INTRODUCTION AND A BRIEF REVIEW OF PREVIOUS WORKS

1. GENERAL INTRODUCTION AND A BRIEF REVIEW OF PREVIOUS WORKS

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

$\sigma' = \omega \epsilon_0 \epsilon''$ and $\sigma'' = \omega \epsilon_0 \epsilon'$ 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 respectability, 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 $\varepsilon_{ij} = n_{Dij}^2$ where n_{Dij} is the refractive index of the solution, the eq. (1.33) for a neutral dielectrics is

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

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

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

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

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

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.

REFERENCES

- [1] W R Garbill *Chem Eng* **66(1)** (1959) 127
- [2] W R Garbill *Chem Eng* **66(3)** (1959) 123
- [3] L I Stiel and G Thodes *Ind. Eng. Chem Fundam.* **2** (1963) 23
- [4] A L Lee and R T Ellington *J Chem Eng Data* **10** (1965) 34
- [5] P Debye "*Polar Molecules*" The Chemical catalogue company Inc (1929)
- [6] H Fröhlich "*Theory of Dielectrics*" (Oxford University Press: Oxford (1949)
- [7] C P Smyth "*Dielectric Behaviour and Structure*" (New York: McGraw Hill 1055)
- [8] Nora E Hill, W E Vaughan, A H price and M Davis "*Dielectric Properties and Molecular Behaviour*" (Van Nostrand Reinhold Company: London 1969)
- [9] J W Smith "*Electro Dipole Moments*" Butterworths London (1955)
- [10] A K Jonscher "*Physics of Dielectric Solids*, Invited papers edited by CHL Goodman" (Canterbury 1980)
- [11] A K Chatterjee, P Acharyya ,I L Saha and S Acharyya , *Indian J Phys* **56B** (1982) 291
- [12] Mc Graw Hill *Encyclopedia of Science and Technology* **13** (1997) 269
- [13] A Budo *Phys Z* **39** (1938) 706
- [14] K Bergmann, D M Roberti and C P Smyth *J Phys Chem* **64** (1960) 665
- [15] J Bhattacharyya, A Hasan, S B Roy and G S Kastha *J Phys Soc Japan* **28** (1970) 204
- [16] K Higasi, Y Kaga and M Nakamura, *Bull Chem Soc Japan* **44** (1971) 988
- [17] U Saha, S K Sit, R C Basak and S Acharyya *J Phys D: Appl Phys* (U K) **27** (1994) 596

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- [18] S K Sit, R C Basak, U Saha and S Acharyya *J Phys D: Appl Phys* (U K) **27** (1994) 2194
- [19] U K Mitra, N Ghosh, P Ghosh and S Acharyya *J Mol Liquids* **126** (2006) 53
- [20] F J Murphy and S O Morghan *Bell Syst Tech J* **18** (1939) 502
- [21] M B R Murthy, R L Patil and D K Deshpande *Indian J Phys* **63B** (1989) 491
- [22] A Karmakar, U K Mitra, N Ghosh and S Acharyya *Indian J Pure & Appl Phys* communicated (2006)
- [23] K V Gopala Krishna *Trans Faraday Soc* **53** (1957) 767
- [24] P Debye "*Polar Molecules*" The chemical catalogue company (1929)
- [25] S I Mizushima *Phys Z* **28** (1926) 418
- [26] S I Mizushima *Sci papers Inst. Phys. Chem. Research* (Tokyo) **5** (1927) 201
- [27] J D Stranthein *Phys Rev.* **91** (1928) 653
- [28] L J Onsager *J chem. Phys* **2** (1934) 509
- [29] H J Phemely *Phys Rev.* **59** (1941) 200
- [30] C S Pao *Phys Rev.* **64** (1943) 60
- [31] E O Foster *Electro Chim Acta* **9** (1964) 1319
- [32] W Jackson & J W Powles *Trans Faraday Soc.* **24A** (1946) 101
- [33] G Kremling *Z Naturforsch* **5a** (1950) 101
- [34] W B Green *J Appl Phys.* **26** (1955) 1257
- [35] J Ph. Poley *J Appl. Sci. Res* **4** (1955) 337
- [36] S K Garg and C P Smyth *J Chem Phys* **42** (1956) 1397
- [37] K V Gopala Kkrishna *Trans Faradey Soc.* **53** (1957) 767
- [38] J A Schellman *J Chem Phys* **26** (1957) 1225
- [39] J Hart and A G Mungali *Trans. Am. Inst. Elec. Engrs* **76** (1957) 1295
- [40] K Higasi, K Bergmann and C P Smyth *J Phys Chem.* **64** (1960) 880
- [41] H Frölich *Theory of dielectric Oxford University Press; Oxford* 1949
- [42] K Bergmann, D M Roberti and C P Smyth *J Phys Chem* **64** (1960) 665
- [43] Krishanaji and A Mansingh *J Chem Phys* **42** (1964) 827
- [44] B Sinha, S B Roy and G S Kastha *Indian J Phys* **40** (1966) 101
- [45] B Sinha, S B Roy and G S Kastha *Indian J Phys.* **41** (1967)183
- [46] G H Berbenza *J Chem Phys* (France) **5** **65** (1968) 906
- [47] I Adamcrewski and B Jachym *Acta. Phys Polon* **34** (1968) 1015
- [48] J Bhattacharya, A Hasan, S B Roy and G S Kastha *J Phys Soc. Japan* **28** (1970) 204
- [49] K Higasi, Y Koga and M Nakamura *Bull. Chem Soc. Japan* **44** (1971) 988

- [50] H V Loheneysen and H Nageral *J phys D Appl Phys* **4** (1971) 1718
- [51] F Gaspared and J P Gosse *Electro Chim Acta (GB)* **15** (1970) 599
- [52] J Crossley, L Glasser and C P Smyth *J Chem Phys* **55** (1971) 2197
- [53] L Glasser, J Crossley and C P Smyth *J Chem Phys* **57** (1972) 3977
- [54] A D Vyas and V M Vashisth *J Mol Liquids* **38** (1988) 11
- [55] H D Purohit, H S Sharma, A D Vyas *Ind J Pure & Appl Phys* **12** (1974) 273
- [56] S Tripathy, G S Roy and B B Swain *Ind J Pure & Appl Phys* **31** (1993) 828
- [57] S N Sen and R Ghosh *J Phys Soc Japan* **36** (1974) 743
- [58] A K Ghosh and S N Sen *Ind J Pure & Appl Phys* **18** (1980) 586
- [59] A K Ghosh and S N Sen *J Phys Soc Japan* **48** (1980) 1219
- [60] R Ghosh and Ira Chowdhury *Pramana J Phys* **16** (1981) 319
- [61] R ghosh and Ira Chowdhury *Ind J Pure & Appl Phys* **20** (1982) 717
- [62] R Ghosh and A K Chatterjee *Ind J Pure & Appl Phys* **29** (1991) 650
- [63] J P shukla and M C Saxena *Ind J Pure & Appl Phys* **11** (1973) 896
- [64] R L Dhar, A Mathur, J P Shukla and M C Sexana *Ind J Pure & Appl Phys* **11** (1973) 568
- [65] Y Koga, H Takahashi and H Higasi *Bull. Chem Soc. Japan* **46** (1973) 3359
- [66] S K Srivastava and S L Srivastava *Ind J Pure & Appl Phys* **13** (1975) 179
- [67] S K S Somevanshi, S B I Misra and N K Mehotra *Ind J Pure & Appl Phys* **16** (1978) 57
- [68] C B Agarwal *Ind J Pure & Appl Phys* **24** (1986) 204
- [69] J M Gandhi and G L Sharma *J Mol Liquids (Netherlands)* **38** (1988) 23
- [70] C R Acharyya, A K Chatterjee, P K Sanyal and S Acharyya *Ind J Pure & Appl Phys* **24** (1986) 234
- [71] M B R Murthy, R L Patil and D K Deshpande *Ind J Phys* **63B** (1989) 491
- [72] A Sharma and D R Sharma *J Phys Soc. Japan* **61** (1992) 1049
- [73] A Sharma, D R Sharma and M S Chauhan *Ind J Pure & Appl Phys* **31** (1993) 841
- [74] P J Singh and K S Sharma *Ind J Pure & Appl Phys* **34** (1996) 1
- [75] U Saha and S Acharyya *Ind J Pure & Appl Phys* **32** (1994) 346
- [76] U Saha, S K Sit, R C Basak and S Acharyya *J Phys D, appl Phys* **27** (1994) 596
- [77] S N Elsayed, A Abdelghany, A H abou ElEla and N H Monsa *Ind J Pure & Appl Phys* **33** (1995) 13
- [78] R Varadarajan and A Rajagopal *Ind J Pure & Appl Phys* **36** (1998)13
- [79] R Varadarajan and A Rajagopal *Ind J Pure & Appl Phys* **36** (1990) 113

CHAPTER 2

SCOPE AND OBJECTIVE OF THE PRESENT WORK

2. SCOPE AND OBJECTIVE OF THE PRESENT WORK

2.1 INTRODUCTION

Almost all the liquids either organic or inorganic are usually called the solvents. Inorganic liquids are practically said to be ionic solvents. The main object of this thesis work is to find out the correlations among solutes and solvents. Some of the organic liquids are of highly nonspherical shapes and sizes and possess a considerable dipole moment μ . Under a high frequency (hf) electric field of Giga hertz (GHz) range, they give rise to what is known as dielectric relaxations. Dielectric relaxation phenomena of single polar solutes or binary polar solutes in non polar solvents under hf electric field are of considerable importance as the phenomena are considered to be an essential tool to investigate the physico-chemical properties as well as structural and associational aspects of the nonspherical polar molecules. The theories so far developed are based on the evaluation of relaxation times τ_j , double relaxation times τ_1 & τ_2 , hf dipole moments μ_1 , μ_2 and μ_j , static dipole moment μ_s , theoretical dipole moment μ_{theo} by bond angles and bond moments of substituted polar groups from the infra-red spectroscopic data. The thermodynamic energy parameters such as the enthalpy of activation ΔH_τ , the entropy of activation ΔS_τ , the free energy of activation ΔF_τ of dielectric relaxation and enthalpy of activation ΔH_η due to viscous flow of the solvents by the formulations advanced within the framework of Eyring's rate theory. Thus the main purpose of the work is to modify the existing theories to enhance new concept of the physico-chemical properties of the liquid molecules concerned in terms of dielectric relaxation phenomena.

2.2 THEORETICAL FORMULATIONS TO ESTIMATE hf τ_j and hf μ_j

The real ϵ'_{ij} and imaginary ϵ''_{ij} parts of hf complex dielectric permittivity ϵ^*_{ij} of a polar – non polar liquid mixture of weight fraction w_j are related by [1]:

$$\begin{aligned}\epsilon'_{ij} &= \epsilon_{\infty ij} + (1 / \omega \tau_j) \epsilon''_{ij} \\ \text{or } \epsilon'_{ij} - \epsilon_{\infty ij} &= (1 / \omega \tau_j) \epsilon''_{ij}\end{aligned}\tag{2.1}$$

With the internationally accepted real χ'_{ij} ($= \epsilon'_{ij} - \epsilon_{\infty ij}$) and imaginary χ''_{ij} ($= \epsilon''_{ij}$) parts of hf complex dimensionless dielectric orientational susceptibility χ^*_{ij} we get

$$\chi'_{ij} = (1 / \omega \tau_{ij}) \chi''_{ij} \quad \dots\dots (2.2)$$

which is clearly a straight line between the variables χ''_{ij} and χ'_{ij} as seen in Fig. 2.1, the slope of which can be used to get τ_{ij} 's of some solutes in terms of the angular frequency ω of the applied electric field.

But for most of the associative polar liquids like aromatic polar nitro compound [2], aprotic polar liquids [3] normal and octyl alcohols [4], the curves

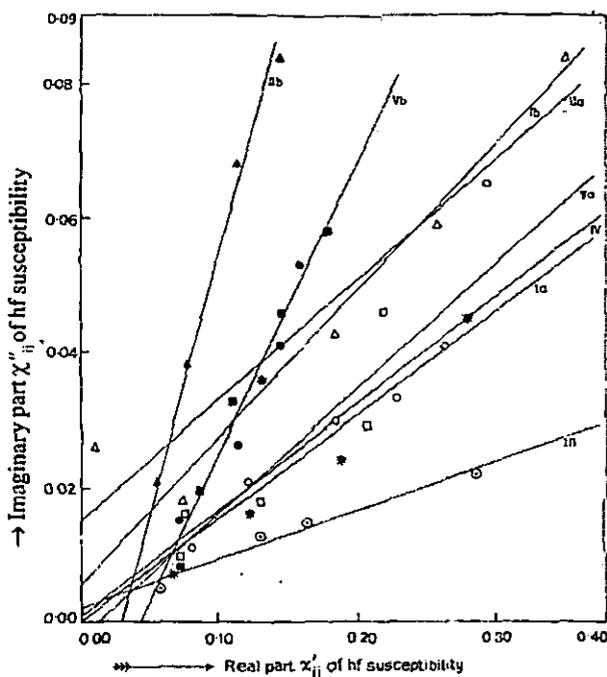


Fig. 2. 1 : Linear plot of imaginary part of hf susceptibility χ''_{ij} against real part χ'_{ij} of monosubstituted anilines in benzene at 35°C under GHz electric field.

(Ia) o-anisidine at 3.86 GHz (-O-), (Ib) o-anisidine at 22.06 GHz (-●-), (IIa) m-anisidine at 3.86 GHz (-Δ-), (IIb) m-anisidine at 22.06 GHz (-▲-), (III) o-toluidine at 2.02 GHz (-⊖-), (IV) m-toluidine at 3.86 GHz (-*-), (Va) p-toluidine at 3.86 GHz (-□-) and (Vb) p-toluidine at 22.06 GHz (-■-) respectively.

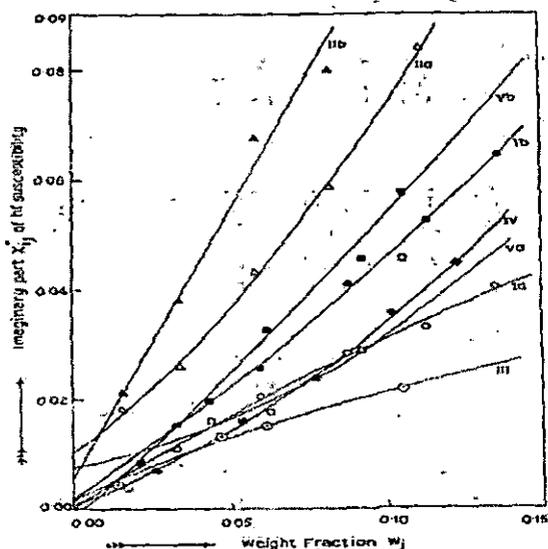


Fig. 2. 2 : Variation of imaginary part of hf susceptibility χ''_{ij} against weight fraction w_j of monosubstituted anilines in benzene at 35°C under GHz electric field.

(Ia) o-anisidine at 3.86 GHz (-O-), (Ib) o-anisidine at 22.06 GHz (-●-), (IIa) m-anisidine at 3.86 GHz (-Δ-), (IIb) m-anisidine at 22.06 GHz (-▲-), (III) o-toluidine at 2.02 GHz (-⊖-), (IV) m-toluidine at 3.86 GHz (-*-), (Va) p-toluidine at 3.86 GHz (-□-) and (Vb) p-toluidine at 22.06 GHz (-■-) respectively.

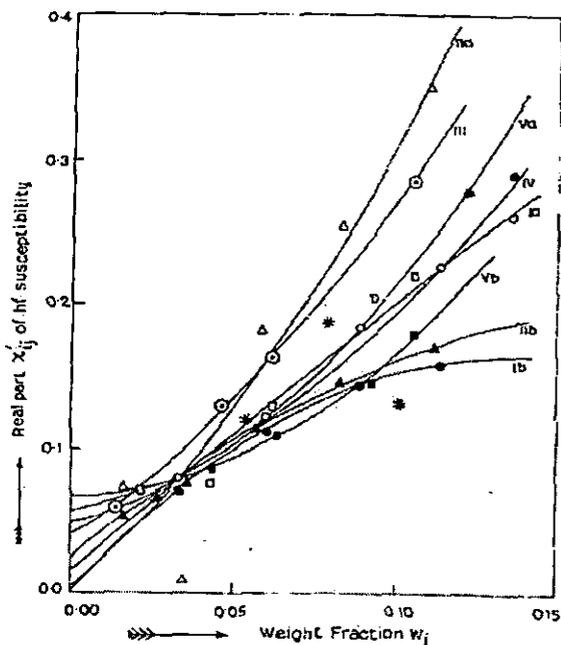


Fig 2. 3 Variation of real part of hf susceptibility χ'_{ij} against weight fraction w_j of monosubstituted anilines in benzene at 35°C under GHz electric field.

(Ia) o-anisidine at 3.86 GHz (-O-), (Ib) o-anisidine at 22.06 GHz (-●-), (IIa) m-anisidine at 3.86 GHz (-Δ-), (IIb) m-anisidine at 22.06 GHz (-▲-), (III) o-toluidine at 2.02 GHz (-⊖-), (IV) m-toluidine at 3.86 GHz (-*-), (Va) p-toluidine at 3.86 GHz (-□-) and (Vb) p-toluidine at 22.06 GHz (-■-) respectively.

showing the variations of χ''_{ij} against χ'_{ij} are not strictly linear. The ratio of linear coefficients of variations of χ''_{ij} and χ'_{ij} with w_j 's in Figs 2.2 and 2.3 is a better representation of slopes of eq. (2.2) in which polar-polar interactions are supposed to be almost eliminated [2-4].

$$\text{Thus } \frac{(d\chi''_{ij}/dw_j)_{w_j \rightarrow 0}}{(d\chi'_{ij}/dw_j)_{w_j \rightarrow 0}} = \omega\tau_j \quad (2.3)$$

The eq. (2.3) has widely been used to get τ_j of a polar solute for a large number of systems as seen in almost all the chapters of this thesis.

The imaginary part χ''_{ij} of hf complex susceptibility χ^*_{ij} is related to weight fraction w_j of a polar solute by [2,5]

$$\chi''_{ij} = \frac{N\rho_{ij}\mu_j^2}{27\varepsilon_0 M_j k_B T} \left(\frac{\omega\tau_j}{1+\omega^2\tau_j^2} \right) (\varepsilon_{ij} + 2)^2 w_j \quad (2.4)$$

which on differentiation with respect to w_j and at $w_j \rightarrow 0$ yields that

$$\left(\frac{d\chi''_{ij}}{dw_j} \right)_{w_j \rightarrow 0} = \frac{N\rho_{ij}\mu_j^2}{27\varepsilon_0 M_j k_B T} \left(\frac{\omega\tau_j}{1+\omega^2\tau_j^2} \right) (\varepsilon_i + 2)^2 \quad (2.5)$$

From eqs. (2.3) and (2.5) one obtains hf dipole moment in terms of measured τ_j 's by the

$$\mu_j = \left[\frac{27\varepsilon_0 M_j k_B T \beta}{N\rho_i (\varepsilon_i + 2)^2 \omega b} \right]^{1/2} \quad (2.6)$$

where

M_j = Molecular weight of solute in Kilogramme

ε_0 = Permittivity of free space = 8.854×10^{-12} Farad metre⁻¹

k_B = Boltzmann constant = 1.38×10^{-23} Joule mole⁻¹ K⁻¹

T = Temperature in absolute scale

β = Linear coefficients of $\chi'_{ij} - w_j$ curves of Fig 2.3 i.e, $(d\chi'_{ij}/dw_j)$

N = Avogadro's number = 6.023×10^{23}

ρ_i = Density of solvent in kgm⁻³

ε_i = Dielectric relative permittivity of solvent

$b = 1/(1+\omega^2\tau_j^2)$ a dimensionless parameter involved with the estimated τ_j of eq. (2.3)

The eq. (2.6) has been tested successfully for a large number of polar liquids to obtain hf μ_j of a polar solute as seen in almost all the chapters of this thesis.

Again the hf complex conductivity σ_{ij}^* of a polar non-polar liquid mixture is given by [6].

$$\sigma_{ij}^* = \sigma'_{ij} + j\sigma''_{ij} = \omega\epsilon_0 (\epsilon''_{ij} + \epsilon'^2_{ij})^{1/2} \quad (2.7)$$

The real σ'_{ij} and imaginary σ''_{ij} parts of σ_{ij}^* are related by [7]

$$\sigma''_{ij} = \sigma_{\infty ij} + \frac{1}{\omega\tau_j} \sigma'_{ij} \quad (2.8)$$

where $\sigma_{\infty ij}$ is the constant conductivity at infinite dilution i.e., at $w_j \rightarrow 0$. The eq. (2.8) on differentiation with respect to σ'_{ij} yields

$$\frac{d\sigma''_{ij}}{d\sigma'_{ij}} = \frac{1}{\omega\tau_j} \quad (2.9)$$

which provides also a convenient method to obtain τ_j of a polar solute.

It is again, better to use the ratio of the slopes of individual variations of σ''_{ij} and σ'_{ij} as functions of w_j 's and at $w_j \rightarrow 0$ to get τ_j from the relation

$$\frac{(d\sigma''_{ij}/dw_j)_{w_j \rightarrow 0}}{(d\sigma'_{ij}/dw_j)_{w_j \rightarrow 0}} = \frac{1}{\omega\tau_j} \quad (2.10)$$

The eq. (2.10) eliminates polar-polar interactions in a given solution and furnishes a method to estimate τ_j of a polar solute.

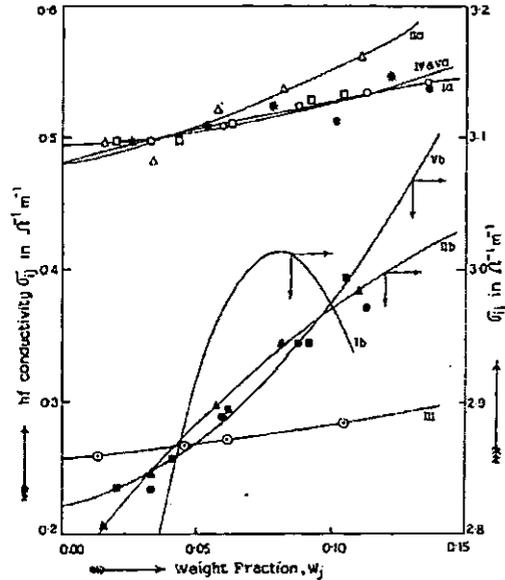


Fig 2.1 : Plot of σ_{ij} against weight fraction w_j of monosubstituted anilines in benzene at 35°C under GHz electric field.

(Ia) o-anisidine at 3.86 GHz (—○—), (Ib) o-anisidine at 22.06 GHz (—●—), (IIa) m-anisidine at 3.86 GHz (—△—), (IIb) m-anisidine at 22.06 GHz (—▲—), (III) o-toluidine at 2.02 GHz (—○—), (IV) m-toluidine at 3.86 GHz (—□—), (Va) p-toluidine at 3.86 GHz (—□—) and (Vb) p-toluidine at 22.06 GHz (—■—) respectively.

In the giga hertz range of applied electric field it is observed [8] that $\sigma''_{ij} \approx \sigma_{ij}$ = the total hf conductivity of the solution. So eq. (2.8) becomes

$$\sigma_{ij} = \sigma_{\infty ij} + \frac{1}{\omega \tau_j} \sigma'_{ij}$$

$$\text{Hence } (d\sigma'_{ij} / d\omega)_{\omega \rightarrow 0} = \omega \tau_j \beta \quad (2.11)$$

where $\beta = d\sigma'_{ij} / d\omega$ i.e, the linear coefficient of the curves of Fig 2.4

The real part σ'_{ij} of total hf conductivity of polar – nonpolar liquid mixture is given [5,8] by:

$$\sigma'_{ij} = \frac{N\rho_{ij}\mu_j^2}{27k_B T M_j} \left(\frac{\omega^2 \tau_j}{1 + \omega^2 \tau_j^2} \right) (\epsilon_j + 2)^2 \omega$$

which on differentiation with respect to ω and at $\omega \rightarrow 0$. yields

$$(d\sigma'_{ij} / d\omega)_{\omega \rightarrow 0} = \frac{N\rho_{ij}\mu_j^2}{27k_B T M_j} \left(\frac{\omega^2 \tau_j}{1 + \omega^2 \tau_j^2} \right) (\epsilon_j + 2)^2 \quad (2.12)$$

Now comparing (2.11) & (2.12) we get

$$\mu_j = \left(\frac{27 M_j k_B T \beta}{N\rho_{ij} (\epsilon_j + 2)^2 \omega} \right)^{\frac{1}{2}} \quad (2.13)$$

where $\omega (=2\pi f)$ is the angular frequency of the applied electric field and all the other symbols carry the usual meanings as discussed earlier. The eqs. (2.10) and (2.13) provide a convenient method to estimate τ_j and μ_j of a polar solute as seen in the chapter 4 of this thesis .

2.3 DOUBLE RELAXATION TIMES τ_1, τ_2 AND DIPOLE MOMENT μ_1, μ_2 DUE TO ROTATIONS OF THE FLEXIBLE POLAR GROUPS & ROTATIONS OF THE WHOLE MOLECULE

Saha et al [9] and Sit et al [10] , however, advanced an analytical method to estimate double relaxation times τ_1 & τ_2 from single frequency measurement in terms of measured

relative permittivities. Another object of the thesis is to detect τ_1 & τ_2 and hence μ_1 & μ_2 using χ_{ij} 's. The aspect of molecular orientational polarization, is, however, achieved by χ_{ij} 's because $\epsilon_{\infty ij}$ includes all the polarizations including the fast polarization. $\epsilon_{\infty ij}$ appears frequently as a subtracted term in Bergmann et al [11] equations. Thus to avoid the clumsiness of algebra and to use the modern concept of dielectric terminology and parameter one can write

$$\chi'_{ij} = \epsilon_{ij} - \epsilon_{\infty ij}, \quad \chi''_{ij} = \epsilon''_{ij}, \quad \chi_{0ij} = \epsilon_{0ij} - \epsilon_{\infty ij}$$

The Bergmann et al equations becomes

$$\frac{\chi''_{ij}}{\chi_{0ij}} = c_1 \frac{1}{1 + \omega^2 \tau_1^2} + c_2 \frac{1}{1 + \omega^2 \tau_2^2} \quad (2.14)$$

$$\frac{\chi'_{ij}}{\chi_{0ij}} = c_1 \frac{\omega \tau_1}{1 + \omega^2 \tau_1^2} + c_2 \frac{\omega \tau_2}{1 + \omega^2 \tau_2^2} \quad (2.15)$$

where χ_{0ij} is the low frequency susceptibility which is real. c_1 and c_2 are the relative weight factors such that $c_1 + c_2 = 1$. Putting $\omega \tau_1 = \alpha_1$ and $\omega \tau_2 = \alpha_2$ eqs. (2.14) and (2.15) are now solved to get

$$c_1 = \frac{(\chi'_{ij} \alpha_2 - \chi''_{ij} \alpha_1)(1 + \alpha_1^2)}{\chi_{0ij} (\alpha_2 - \alpha_1)} \quad (2.16)$$

and

$$c_2 = \frac{(\chi''_{ij} - \chi'_{ij} \alpha_1)(1 + \alpha_2^2)}{\chi_{0ij} (\alpha_2 - \alpha_1)} \quad (2.17)$$

provided $\alpha_2 - \alpha_1 > 0$

As $c_1 + c_2 = 1$, the eq. (2.16) and (2.17) yields

$$\frac{(\chi_{0ij} - \chi'_{ij})}{\chi'_{ij}} = \omega(\tau_1 + \tau_2) \frac{\chi''_{ij}}{\chi'_{ij}} - \omega^2 \tau_1 \tau_2 \quad (2.18)$$

which is clearly a straight line as illustrated in Fig 2.5 for some interesting liquids in suitable solvent previously studied between the variables $\left(\frac{\chi_{0ij} - \chi'_{ij}}{\chi'_{ij}} \right)$ and χ''_{ij} / χ'_{ij} with

slope $\omega (\tau_1 + \tau_2)$ and intercept $-\omega^2 \tau_1 \tau_2$ of eq. (2.18). They can be used to measure double relaxation times τ_1 & τ_2 due to rotations of the flexible polar groups attached to the parent ones and end over end rotations of the whole molecules in terms of known $\omega = 2\pi f$, where f is the frequency of the applied electric field in GHz range.

The estimated τ_1 and τ_2 can be used to obtain μ_1 and μ_2 from eqs. (2.6) and (2.13) of the flexible parts and the whole molecules.

This method of estimation of τ_1 and τ_2 & μ_1 and μ_2 has been applied on some alcohols at a single and different frequencies of the applied electric field, as seen in

chapters 5 and 6 of the thesis. The validity of eq. (2.18) is based on the fact that $c_1 + c_2 = 1$. The estimation of c_1 and c_2 can, however, be measured from Fröhlich's [12] theoretical equations and the graphical techniques [2,13] as discussed in those chapters. The later ones are shown graphically in Figs 2.6 and 2.7 for a large number of systems of polar – non polar mixtures.

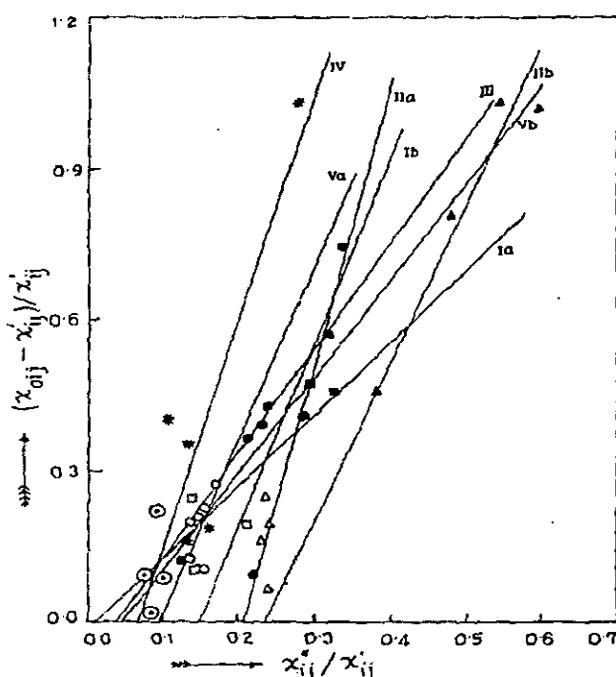


Fig 2.5: Linear variation of $(\chi_{0ij} - \chi'_{ij}) / \chi'_{ij}$ against χ''_{ij} / χ'_{ij} of monosubstituted anilines in benzene at 35°C under GHz electric field. (Ia) o-anisidine at 3.86 GHz (○), (Ib) o-anisidine at 22.06 GHz (●). (IIa) m-anisidine at 3.86 GHz (△), (IIb) m-anisidine at 22.06 GHz (▲). (III) o-toluidine at 2.02 GHz (⊙), (IV) m-toluidine at 3.86 GHz (*), (Va) p-toluidine at 3.86 GHz (□) and (Vb) p-toluidine at 22.06 (GHz (■) respectively.

2.4 FORMULATIONS TO ESTIMATE SYMMETRIC AND CHARACTERISTIC RELAXATION TIMES τ_s

& τ_{cs}

The solute like normal and octyl alcohols and amides (DMSO, DMF, DEF) under investigation appears to behave like non-rigid ones having symmetric and asymmetric distribution parameters γ and δ involved with the following equation

[14]:

$$\frac{\chi_{ij}^*}{\chi_{0ij}} = \frac{1}{1 + (j\omega\tau_s)^{1-\gamma}} \quad (2.19)$$

and

$$\frac{\chi_{ij}^*}{\chi_{0ij}} = \frac{1}{(1 + j\omega\tau_{cs})^\delta} \quad (2.20)$$

on separating the real and imaginary parts of eq. (2.19) & (2.20) and rearranging them in terms of χ'_{ij}/χ_{0ij} and χ''_{ij}/χ_{0ij} at $\omega_j \rightarrow 0$ as seen in Fig 2.6 and 2.7 one obtains

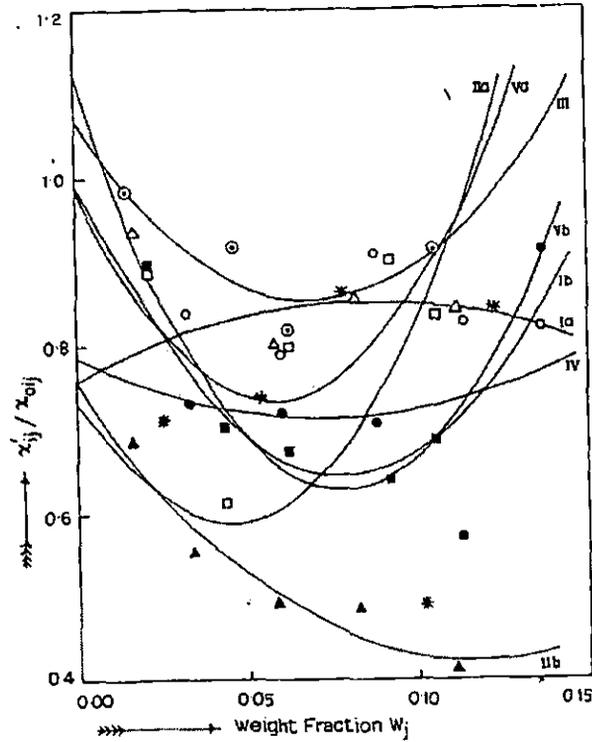


Fig. 2.6: Plot of χ'_{ij}/χ_{0ij} against weight fraction w_j of monosubstituted anilines in benzene at 35°C under GHz electric field.

(Ia) o-anisidine at 3.86 GHz (—○—), (Ib) o-anisidine at 22.06 GHz (—●—), (IIa) m-anisidine at 3.86 GHz (—△—), (IIb) m-anisidine at 22.06 GHz (—▲—), (III) O-toluidine at 2.02 GHz (—○—), (IV) m-toluidine at 3.86 GHz (—*—), (Va) p-toluidine at 3.86 GHz (—□—) and (Vb) p-toluidine at 22.06 GHz (—■—) respectively.

$$\gamma = \frac{2}{\pi} \tan^{-1} \left[\left(1 - \frac{\chi'_{ij}}{\chi_{0ij}} \right) \frac{\chi'_{ij}}{\chi''_{ij}} - \frac{\chi''_{ij}}{\chi_{0ij}} \right] \quad (2.21)$$

and

$$\tau_s = \frac{1}{\omega} \left[\frac{1}{\left(\frac{\chi'_{ij}}{\chi''_{ij}} \right) \cos \left(\frac{\gamma\pi}{2} \right) - \sin \left(\frac{\gamma\pi}{2} \right)} \right]^{1/(1-\gamma)} \quad (2.22)$$

similarly δ and τ_{cs} can be had from eq. (2.20) as

$$\tan(\phi\delta) = \frac{(\chi''_{ij} / \chi_{0ij})_{w_j \rightarrow 0}}{(\chi'_{ij} / \chi_{0ij})_{w_j \rightarrow 0}} \quad (2.23)$$

$$\text{and } \tan \phi = \omega \tau_{cs} \quad (2.24)$$

As ϕ can not be estimated directly, an ordinary theoretical curve between $(1/\phi) \log(\cos \phi)$ against ϕ in degree is drawn in Fig 2.8 from which

$$\left(\frac{1}{\phi} \right) \log(\cos \phi) = \frac{\log \{ (\chi'_{ij} / \chi_{0ij}) (\cos \phi \delta) \}}{\phi \delta}$$

can be known. The estimated $1/\phi \log(\cos \phi)$ is used to estimate ϕ from Fig 2.8. With known ϕ eqs. (2.23) and (2.24) δ and τ_{cs} estimated. This formulations has been applied with considerable success in chapters 4, 5, and 6 of the thesis.

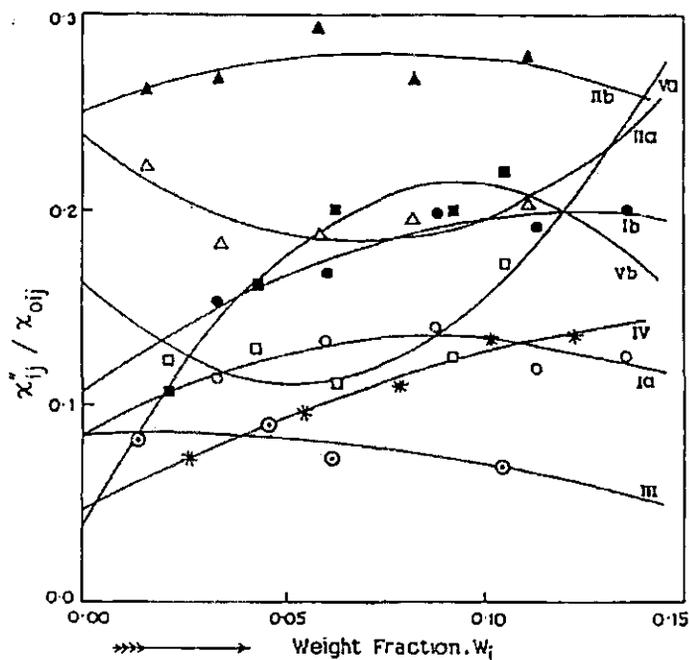


Fig 2.7: Plot of $\chi''_{ij} / \chi'_{0ij}$ against weight fraction w_j of monosubstituted anilines in benzene at 35°C under GHz electric field.

(Ia) o-anisidine at 3.86 GHz (—○—), (Ib) o-anisidine at 22.06 GHz (—●—), (IIa) m-anisidine at 3.86 GHz (—△—), (IIb) m-anisidine at 22.06 GHz (—▲—), (III) o-toluidine at 2.02 GHz (—○—), (IV) m-toluidine at 3.86 GHz (—*—), (Va) p-toluidine at 3.86 GHz (—□—) and (Vb) p-toluidine at 22.06 GHz (—■—) respectively.

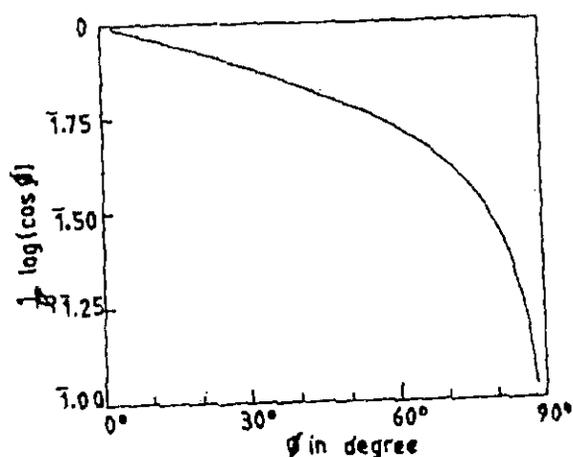


Fig 2.8 Plot of $(1/\phi) \log(\cos \phi)$ against ϕ in degree.

2.5 STATIC EXPERIMENTAL PARAMETER X_{ij} AND STATIC DIPOLE MOMENT μ_s

The static dipole moment μ_s of a polar solute (j) in a nonpolar solvent (i) is related with static relative permittivity ϵ_{0ij} and hf relative permittivity $\epsilon_{\infty ij}$ by [15]

$$\frac{\epsilon_{0ij} - 1}{\epsilon_{0ij} + 2} - \frac{\epsilon_{\infty ij} - 1}{\epsilon_{\infty ij} + 2} = \frac{\epsilon_{0i} - 1}{\epsilon_{0i} + 2} - \frac{\epsilon_{\infty i} - 1}{\epsilon_{\infty i} + 2} + \frac{N\mu_s^2}{9\epsilon_0 k_B T} c_j \quad (2.25)$$

The molar concentration c_j of solute is expressed in terms of w_j by

$$c_j = \frac{\rho_j w_j}{M_j}$$

The weight W_j and volume V_j of a polar solute when dissolved in a solvent of weight W_i and volume V_i to have the solution density ρ_{ij} of the mixture

$$\rho_{ij} = \frac{W_i + W_j}{V_i + V_j} = \frac{W_i + W_j}{\frac{W_i}{\rho_i} + \frac{W_j}{\rho_j}}$$

Or,

$$\rho_{ij} = \frac{\rho_i \rho_j}{\left(\frac{W_i}{W_i + W_j}\right) \rho_j + \left(\frac{W_j}{W_i + W_j}\right) \rho_i}$$

As

$$\frac{W_i}{W_i + W_j} = w_i \text{ and } \frac{W_j}{W_i + W_j} = w_j$$

The weight fractions of solvent and solute respectively . Again, the above equation can be written for ρ_{ij} as the density of the solution,

$$\rho_{ij} = \frac{\rho_i \rho_j}{w_i \rho_j + w_j \rho_i}$$

or,

$$\rho_{ij} = \frac{\rho_i}{w_i + \frac{\rho_i}{\rho_j} w_j}$$

$$\rho_{ij} = \frac{\rho_i}{1 - \left(1 - \frac{\rho_i}{\rho_j}\right) w_j} = \frac{\rho_i}{1 - \gamma w_j}$$

Or, $\rho_{ij} = \rho_i (1 - \gamma w_j)^{-1}$ [as $w_1 + w_2 = 1$ and $(1 - \rho_1 / \rho_2) = \gamma$]

$$\text{Or, } \rho_{ji} = \rho_i (1 + \gamma w_j + \dots) \tag{2.26}$$

where ρ_i and ρ_j are the densities of solvent and solute respectively. With eq. (2.26), and the eq.(2.25) becomes

$$\frac{\epsilon_{0ij} - \epsilon_{\infty ij}}{(\epsilon_{0ij} + 2)(\epsilon_{\infty ij} + 2)} = \frac{\epsilon_{0i} - \epsilon_{\infty i}}{(\epsilon_{0i} + 2)(\epsilon_{\infty i} + 2)} + \frac{N\mu_s^2 w_j \rho_i (1 + \gamma w_j + \dots)}{27\epsilon_0 M_j k_B T}$$

$$\text{or, } X_{ij} = X_i + \frac{N\rho_i \mu_s^2}{27\epsilon_0 M_j k_B T} w_j + \frac{N\rho_i \mu_s^2}{27\epsilon_0 M_j k_B T} \gamma w_j^2 + \dots \tag{2.27}$$

Since $0 < w_j < 1$, the above eq. (2.27) can be expressed as a polynomial equation of w_j like

$$X_{ij} = a_0 + a_1 w_j + a_2 w_j^2 + \dots \tag{2.28}$$

comparing the coefficient of first powers w_j 's of eqs. (2.27) and (2.28) one obtains

$$\mu_s = \left(\frac{27\epsilon_0 M_j k_B T}{N\rho_i} a_1 \right)^{1/2} \tag{2.29}$$

where a_1 is the linear coefficient of X_{ij} versus w_j

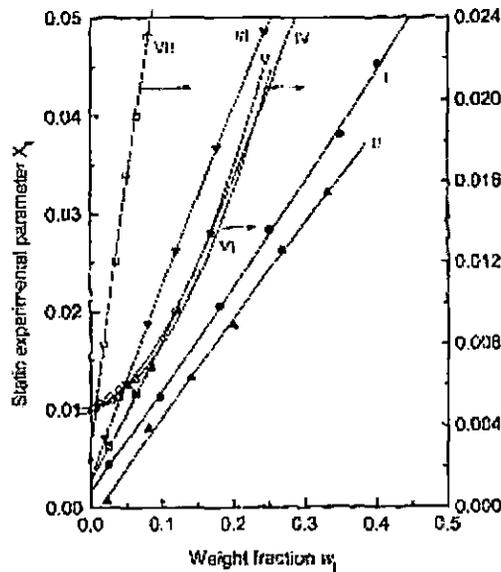


Fig 2.2 . Variation of the measured static experimental parameter X_{ij} with weight fraction w_j of the solutes for I - chloral in benzene (—●—); II - chloral in n-heptane (—▲—); III - ethyl trichloroacetate in benzene (—▼—); IV - ethyl trichloroacetate in n-hexane (—◼—); V - trifluoroethanol in benzene (—◊—); VI - trifluoroacetic acid in benzene (—△—) and VII - octanoyl chloride in benzene (—□—).

curves of Fig. 2.9 for a number of interesting compounds as seen elsewhere [8]. μ_s 's from higher powers of τ_j of eq. (2.27) are not reliable as the term γ is influenced by various effects like solute-solute interactions, relative density, macroscopic viscosity, internal field etc. This formulation of eq. (2.27) has been applied on some interesting polar liquids of para compounds in nonpolar solvents to have their static μ_s as seen in the 7 th chapter of this thesis

2.6 THEORETICAL FORMULATIONS TO ESTIMATE THERMODYNAMIC ENERGY PARAMETERS:

Dielectric relaxation is a process of rotation of a molecular dipole . The dipole requires an activation energy ΔF_τ , called free energy of activation to overcome the potential energy barrier between two equilibrium positions of normal and excited states.. Eyring's rate process [16] eq. (2.30) can be used with the temperature dependence of measured τ_j 's from eqs. (2.3) and (2.10).

According to Eyring's rate theory one gets that

$$\tau_j = \frac{A}{T} \exp(\Delta F_\tau / RT) \quad (2.30)$$

where $A = h / k$,is the ratio of Planck's and Boltzmann constants respectively and R is the gram molecular constant.

Again $\Delta F_\tau = \Delta H_\tau - T \Delta S_\tau$, the above eq. (2.30) becomes

$$\tau_j T = A \exp (\Delta H_\tau - T \Delta S_\tau) / RT$$

$$\text{or, } \tau_j T = A \exp (-\Delta S_\tau / R) \cdot \exp (\Delta H_\tau / RT)$$

$$\text{hence } \ln \tau_j T = \ln A' + \frac{\Delta H_\tau}{R} \cdot \frac{1}{T} \quad (2.31)$$

$$\text{where } A' = A \exp (-\Delta S_\tau / R)$$

The (2.31) represents a linear curve between $\ln (\tau_j T)$ against $1/T$, the intercept and slope of the curve have been employed to get ΔH_τ , ΔS_τ and ΔF_τ known as enthalpy, entropy and free energy of activation due to dielectric relaxation as illustrated in Fig. 2.10. for some p-compounds. These thermodynamic energy parameters so far measured help one to make strong comment on the physico-chemical properties of the systems as seen in chapters 3,7,8 & 9 of this thesis.

The Kalman factor $\tau_j T / \eta_i^\delta$ is equal to the volume of the rotating unit and is given by [17]:

$$A = \tau_j T / \eta_i^\delta$$

Hence $\ln \tau_j T = \ln a + \delta \ln \eta_i$ (2.32)

The slope $\delta (= \Delta H\tau / \Delta H\eta_i)$ of the linear eq. (2.32) is used to estimate the enthalpy of activation $\Delta H\eta_i$, due to viscous flow of the solvent as shown in the different chapters of this thesis to come to the conclusion of the solvent environment about the solute ones.

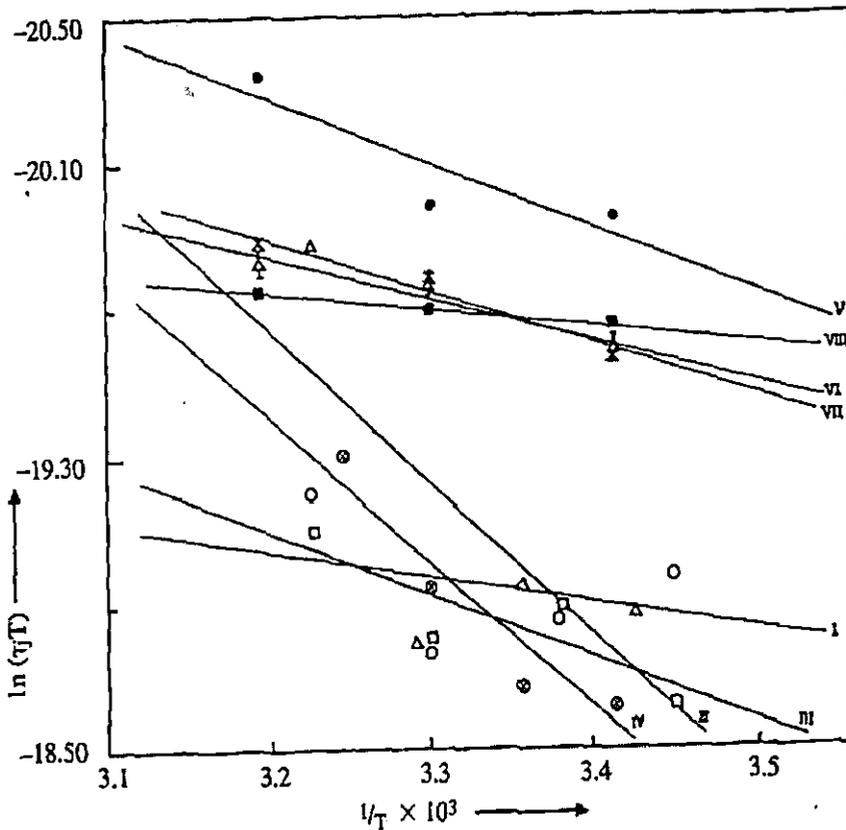


Fig 2.10 . Straight line plots of $\ln (\tau_j T)$ against $1/T$. (I) parahydroxypropiophenone ($-\circ-$), (II) parachloropropiophenone ($-\triangle-$), (III) paraacetamidobenzaldehyde ($-\square-$), (IV) parabenzoyloxybenzaldehyde ($-\otimes-$), (V) paraanisidine ($-\bullet-$) (VI) parafenitidine ($-\frac{\Delta}{\Delta}-$), (VII) orthochloroparanitroaniline ($-\times-$) and (VIII) parabromonitrobenzene ($-\blacksquare-$)

Chapter 2 , thus presents a brief account of the new theoretical formulations widely used in the several CHAPTERS 3,4,5,6,7 of this thesis to come to various conclusions in terms of measured parameters. They have significant contributions to study the physico-

chemical properties of a large number of polar liquids in non-polar solvents under hf and static electric fields.

REFERENCES

- [1] A K Jonscher, *Physics of Dielectric solids*, Invited papers edited by CHL Goodman Canterbury (1980)
- [2] U K Mitra, N Ghosh, P Ghosh and S Acharyya *J Indian Chem Soc* **83** (2006) 674
- [3] A Karmakar, U K Mitra, K Dutta and S Acharyya *Indian J Pure & Appl Phys* **44** (2006) 856
- [4] U K Mitra, N Ghosh, P Ghosh and S Acharyya *J Molecular Liquids* **126** (2006) 53
- [5] C P Smyth "*Dielectric Behaviour and structure*", (MC Graw Hill : New York) 1955
- [6] F J Morphy and S O Morgan *Bell Syst Tech J* **18** (1939) 502
- [7] M B R Murthy, R L Patil and D K Deshpande *Indian J Phys* **63B** (1989) 491
- [8] N Ghosh PhD Dissertation (North Bengal University, India), 2002
- [9] U Saha, S K Sit, R C Basak and S Acharyya *J Phys D: Appl Phys* (UK) **27** (1994) 596
- [10] S K Sit, R C Basak, U Saha and S Acharyya *J Phys D: Appl Phys* (UK) **27** (1994) 2194
- [11] K Bergmann, D Moberti and C P Smyth *J Phys Chem* **64** (1960) 665
- [12] H Fröhlich, "*Theory of Dielectrics*"(Oxford University Press: Oxford) 1949
- [13] U K Mitra, N Ghosh , P Ghosh and S Acharyya *J Indian Chem Soc* communicated (2006)
- [14] S C Srivastava and S Chandra '*Indian J Pure & Appl Phys* **13** (1975) 101
- [15] P Debye "*Polar molecules*" The Chemical Catalogue Company Inc (1929)
- [16] H Eyring, S Glasstone and K J Laidler "*The theory of Rate Process* " (MC Graw Hill: New York) 1941
- [17] B Sinha, S B Roy and G S Kastha '*Indian J Phys* **40** (1966) 101

CHAPTER 3

STRUCTURAL ASPECTS AND PHYSICO-CHEMICAL PROPERTIES OF
SOME AROMATIC POLAR NITRO COMPOUNDS IN SOLVENT BENZENE
AT DIFFERENT TEMPERATURES UNDER GIGA HERTZ ELECTRIC FIELD

3. STRUCTURAL ASPECTS AND PHYSICO-CHEMICAL PROPERTIES OF SOME AROMATIC POLAR NITRO COMPOUNDS IN SOLVENT BENZENE AT DIFFERENT TEMPERATURES UNDER GIGA HERTZ ELECTRIC FIELD

3.1. INTRODUCTION

The dielectric relaxation mechanism of polar liquid molecules in nonpolar solvents is of much importance as it provides an useful and essential tool to study their structural aspects and physico chemical properties. The method is involved with estimation of several dielectric relaxation parameters such as relaxation time τ_j , dipole moments μ_j , μ_{theo} and thermodynamic energy parameters. There exists several methods [1,2] for estimation of relaxation parameters, but all these methods are not so simple like our present one based on susceptibility measurement. Their method [1,2] consist of placing ϵ''_{ij} against ϵ'_{ij} measured at different frequencies of GHz range to get semicircular plot which cuts ϵ' -axis in the lower and higher points giving rise $\epsilon_{\infty ij}$ and ϵ_{0ij} respectively. Migahed et al [3] and Nandi et al [4] used the method of thermally stimulated depolarisation current density (TSDC) in terms of hf relative permittivities to study the relaxation mechanism of some polar liquids and the physico-chemical properties of some proteins, polymers, micelles etc. Although several workers [3,4] studied the relaxation mechanism of polar liquid molecules in nonpolar solvent in terms of measured relative permittivities of ϵ'_{ij} , the real part and ϵ''_{ij} , the imaginary part of high frequency (hf) complex permittivity ϵ^*_{ij} , but no such investigation on polar nitro compounds by susceptibility measurement has yet been made. The method includes the estimation of real χ'_{ij} ($= \epsilon'_{ij} - \epsilon_{\infty ij}$) and imaginary χ''_{ij} ($= \epsilon''_{ij}$) parts of high frequency (hf) complex dimensionless dielectric orientational susceptibility χ^*_{ij} at different experimental temperatures in °C under a gigahertz electric field from the measured permittivities of ϵ'_{ij} and ϵ''_{ij} of Pant et al [5]. χ'_{ij} 's are involved only with the molecular orientational polarisation and the evaluation of accurate relaxation parameters are made possible. It is evident from Fig. 3.1 that the variation of χ''_{ij} with χ'_{ij} is strictly linear, the slope of which presented in Table 3.1, is used to get τ_j 's of the polar solutes. Murthy et al [6], however, showed earlier that a similar linear relationship exists between hf imaginary part $K''_{ij}(\omega_j)$ and real part $K'_{ij}(\omega_j)$ of complex conductivity $K^*_{ij}(\omega_j)$ from which τ_j for polar molecules could be estimated. But for associative liquids in the higher concentration the variation of χ''_{ij} and χ'_{ij} is not always linear [7], the ratio of the linear coefficients of individual

polynomial variation of both χ'_{ij} and χ''_{ij} with weight fractions w_j 's like $\chi'_{ij} = \alpha + \beta w_j + \gamma w_j^2$ of solute [8] as displayed in Figs. 3.2 and 3.3 may be a better choice [9] to estimate τ_j 's of polar liquid compounds. τ_j 's so estimated, are presented in Table 3.1 for comparison with τ_j 's (11th column) calculated by Pant et al [5] by using Gopala Krishna's method [10]. The excellent agreement of τ_j 's by both of our prescribed methods in case of polar nitro compounds which includes the names of 2,5-dichloronitrobenzene, 3,5-dichloronitrobenzene, 2,5-dibromonitrobenzene, 2,4-dinitrochlorobenzene, 3,4-dinitrochlorobenzene indicates that the data of $\chi''_{ij}(w_j)$ and $\chi'_{ij}(w_j)$ are of low weight fractions w_j 's so that the polar-polar interactions are almost eliminated. The estimated τ_j 's involved with dimensionless parameter b 's are now used to obtain hf dipole moment μ_j in terms of linear coefficients β 's of curves of $\chi'_{ij} - w_j$ of Fig. 3.2 using Debye's relation [11]. The dimensionless parameter b 's, linear coefficients β 's and estimated μ_j 's are placed in Table 3.2 to compare with μ_j 's by Gopala Krishna's method [10] measured by Pant et al [5] and theoretical dipole moments μ_{theo} 's of Fig. 3.4, evaluated by vector addition of available bond moments of the substituent polar groups of the nitro compounds as seen in Table 3.2. The disagreement between estimated μ_j and μ_{theo} shows the probable existence of inductive, mesomeric and electromeric effects [12] suffered by the polar groups under the electric field of GHz frequency. μ_j 's thus measured when plotted against $t^{\circ}\text{C}$ shows convex and concave shapes as seen in Fig 3.5, which reflects the stability or instability of the polar-nonpolar liquid mixtures observed elsewhere [13]. The eq.(3.10) is a linear equation $\ln\tau_j T$ against $1/T$ of Fig.3.6. The slope and intercept are used to measure the required thermodynamic energy parameters. $\Delta H\tau$, $\Delta S\tau$ and $\Delta F\tau$ as placed in Table 3.3. The parameters so estimated provides a deep insight into the physico chemical properties [14] of the solute molecules in solvent benzene under GHz electric field. The Debye & Kalman factors as seen in Table 3.3 shows Debye relaxation mechanism obeyed by the molecules.

3.2. THEORETICAL FORMULATIONS

If $\epsilon_{\infty ij}$ be subtracted from ϵ'_{ij} the susceptibility contains only the orientational polarisation [15] and thus the fast polarisation is avoided unlike the ϵ^*_{ij} . In absence of reliable measured values of infinitely hf and low frequency (lf) permittivities $\epsilon_{\infty ij}$ and ϵ_{0ij} , the following Debye-

Pallate's equations[16] may safely be used from the measured values of the real ε'_{ij} and imaginary ε''_{ij} parts of the hf complex ε^*_{ij} of Pant et al [5].

$$\varepsilon'_{ij} = \varepsilon_{\infty ij} + \frac{\varepsilon_{0ij} - \varepsilon_{\infty ij}}{1 + \omega^2 \tau_j^2} \quad (3.1) \quad \text{and} \quad \varepsilon''_{ij} = \frac{\varepsilon_{0ij} - \varepsilon_{\infty ij}}{1 + \omega^2 \tau_j^2} \omega \tau_j \quad (3.2)$$

χ''_{ij} and χ'_{ij} 's of functions of ω_j 's are well displayed in Figs 3.3 and 3.2 respectively.

Both ε'_{ij} and ε''_{ij} parts of ε^*_{ij} are related by [11]

$$\varepsilon'_{ij} = \varepsilon_{\infty ij} + \frac{1}{\omega \tau_j} \varepsilon''_{ij} \quad (3.3)$$

In terms of real χ'_{ij} and imaginary χ''_{ij} parts of hf complex susceptibility χ^*_{ij} , one obtains

$$\chi''_{ij} = (\omega \tau_j) \chi'_{ij} \quad \text{or} \quad d\chi''_{ij} / d\chi'_{ij} = \omega \tau_j \quad (3.4)$$

Murthy et al [6] showed earlier that a similar linear relationship exists between hf conductivity $K''_{ij}(\omega_j)$ and $K'_{ij}(\omega_j)$ from which they estimated the relaxation time for polar molecules. The eq. (3.4) is a straight line between χ''_{ij} and χ'_{ij} observed graphically in Fig 3.1, the slope of which is used to get τ_j of a polar solute [6] as seen in Table 3.1. But for most of the associative liquids, the variation of χ''_{ij} against χ'_{ij} is not strictly linear [9]. For such associative polar-nonpolar liquid mixture χ'_{ij} is related with ω_j by $\chi'_{ij} = \alpha + \beta \omega_j + \gamma \omega_j^2$ the slope of eq. (3.4) can be represented by:

$$\frac{(d\chi''_{ij} / d\omega_j) \omega_j \rightarrow 0}{(d\chi'_{ij} / d\omega_j) \omega_j \rightarrow 0} = \omega \tau_j \quad (3.5)$$

The eq. (3.5) represents the ratio of linear coefficients of individual variation of both χ''_{ij} and χ'_{ij} with ω_j of a polar solute displayed graphically in Figs 3.2 and 3.3 respectively. τ_j 's estimated from eq. (3.5) are placed in Table 3.1 in order to compare them with τ_j 's obtained by direct slope $\chi''_{ij} - \chi'_{ij}$ of Fig. 3.1 and those of Gopala Krishna's method [10] measured by Pant et al [5].

The imaginary part χ''_{ij} of hf χ^*_{ij} is related to ω_j by of polar solute by [11].

$$\chi''_{ij} = \frac{N\rho_{ij}\mu_j^2}{27\varepsilon_0 M_j k_B T} \left(\frac{\omega \tau_j}{1 + \omega^2 \tau_j^2} \right) (\varepsilon_{ij} + 2)^2 \omega_j \quad (3.6)$$

which on differentiation with respect to w_j and in the limit of $w_j = 0$ yields that

$$\left(\frac{d\chi''_{ij}}{dw_j} \right)_{w_j=0} = \frac{N\rho_i\mu_j^2}{27\varepsilon_0M_jk_B T} \left(\frac{\omega\tau_j}{1+\omega^2\tau_j^2} \right) (\varepsilon_i + 2)^2 \quad (3.7)$$

from eqs. (3.5) and (3.7) one obtains hf μ_j by

$$\mu_j = \left[\frac{27\varepsilon_0M_jk_B T\beta}{N\rho_i(\varepsilon_i + 2)^2 b} \right]^{1/2} \quad (3.8)$$

M_j = Molecular weight of j th liquid in Kilogramme

ε_0 = Permittivity of free space = 8.854×10^{-12} Farad metre⁻¹

k_B = Boltzmann constant = 1.38×10^{-23} Joule mole⁻¹ K⁻¹

T = Temperature in absolute scale

$\beta = (d\chi'_{ij} / dw_j) =$ Linear coefficient of $\chi'_{ij} - w_j$ curves of

Fig.3.3 at $w_j \rightarrow 0$

N = Avogadro's number = 6.023×10^{23}

ρ_i = Density of solvent C₆H₆

ε_i = Dielectric relative permittivity of solvent C₆H₆

$b = 1/(1+\omega^2\tau_j^2)$, a dimensionless parameter involved with the estimated τ_j of eq. (3.5).

Dielectric relaxation is a process of rotation of the polar molecules under hf electric field and it requires an activation energy $\Delta F\tau$, known as free energy of activation to overcome the energy barrier between two equilibrium positions. $\Delta F\tau$, is ,however, related with estimated τ_j of eq. (3.5) by the relation [14]:

$$\tau_j = \frac{A}{T} \exp(\Delta F\tau / RT) \quad (3.9)$$

As $\Delta F\tau = \Delta H\tau - T\Delta S\tau$, so we have

$$\text{or, } \ln(\tau_j T) = \ln A' + \frac{\Delta H\tau}{R} \cdot \frac{1}{T} \quad (3.10)$$

$$\text{where } A' = Ae^{(-\Delta S_{\tau} / R)} \quad (3.11)$$

The eq (3.10) is a linear equation of $\ln\tau_j T$ against $1/T$ of Fig 3.6. The slope and intercept are used to measure the required thermodynamic energy parameters of the molecules as presented in Table 3.3 in agreement with those of Pant et al [5].

3.3. RESULTS AND DISCUSSION

The τ_j 's of aromatic polar nitro compounds in solvent C_6H_6 at different experimental temperatures in $^{\circ}C$ under 9.58 gigahertz electric field are worked out from the slope of the fitted linear eq. [4] between the variables χ''_{ij} and χ'_{ij} displayed graphically in Fig. 3.1 with the symbols showing the experimental points. τ_j 's so obtained are compared with τ_j 's estimated from the ratio of linear coefficients of individual variations of both χ''_{ij} and χ'_{ij} with ω_j 's shown graphically in Figs. 3.2 and 3.3. τ_j 's estimated by both the method are presented in Table 3.1. The excellent agreement of τ_j 's by both the methods at once indicates the data χ''_{ij} and χ'_{ij} are of low concentrations such that the polar-polar interactions are almost eliminated [9] at $\omega_j \rightarrow 0$. The τ_j 's by the latter method [21] are more reliable. Gopala Krishna's method [10] was employed by Pant et al [5] to get τ_j 's. They are presented in Table 3.1. The close agreement between τ_j 's of Pant et al [5] and estimated τ_j 's of eqs. (3.4) and (3.5) at once reflects the basic soundness [9] of our method to get τ_j in the limit $\omega_j = 0$. The correlation coefficient & % of error of both $\chi''_{ij} - \omega_j$ and $\chi'_{ij} - \omega_j$ curves of Figs. 3.2 and 3.3 are given in Table 3.1 only to show how far they are correlated with ω_j 's. It is evident from Table 3.1 that τ_j 's decrease with temperature. This can be explained on the basis of the fact that at constant temperature, the relaxation time depends upon the energy difference between the activated and normal states. At higher temperature thermal agitation causes an increase in energy loss due to large number of collisions and thereby decreasing the relaxation time [9,16]. Dipole moments μ_j 's of the polar solutes as estimated from eq. (3.8) are placed in Table 3.2 together with linear coefficients β 's of $\chi'_{ij} - \omega_j$ curves of Fig. 3.2 and dimensionless parameter b 's involved with τ_j of eq. (3.5) as seen in Table 3.2 respectively. They are, however, compared with μ_j 's of Pant et al [5] and theoretical μ_{theo} 's obtained from vector addition of bond moments [17] of the substituted polar groups of the compounds, as seen in the Table 3.2. The theoretical dipole moment and its orientation as

a consequence of known structure of the pertinent nitro-compound is displayed in Fig 3.4. The resonance effect thus obtained by solvent benzene compound into an inductive effect operated by the substituent polar groups in the ring is expected to play a prominent role [18] in the measured hf μ_j 's. The disagreement between hf μ_j 's and μ_{theo} 's is explained by the influence of hf electric field coupled with inductive and mesomeric moments on the flexible polar groups. μ_{theo} 's with reference to Fig. 3.4 gives a deep insight into the structures of the molecules concerned.

The symmetry and asymmetry of the molecules being a physico-chemical property can well be explained on the basis of $\mu_j - t$ curves of Fig. 3.5. It is seen that unlike system III all the systems show convex $\mu_j - t$ curves having minimum μ_j 's at lower and higher temperatures due to strong symmetry attained [8] at those temperatures. The system III shows maximum μ_j 's at lower and higher temperature due to asymmetric shape of the molecule. Physico-chemical properties of the systems can also be explained from the stand point of thermodynamics by estimating the energy parameters $\Delta H\tau$, $\Delta S\tau$ & $\Delta F\tau$ from the intercept and slope of a fitted linear equation of $\ln\tau_j T$ against $1/T$ shown graphically in Fig. 3.6 with the experimental points placed on them. They are placed in Table 3.3 together with those estimated by Pant et al [5] by using Gopala Krishna's method [10]. It is seen that except the first one the other systems are close to each other.. Unlike systems II & V all the systems possess negative $\Delta S\tau$'s which suggests that configuration involved in dipolar rotation has an activated state which is more ordered than the normal state [8,19] while the reverse is true for the rest two systems. $\Delta F\tau$'s for all the systems are nearly same in magnitude, as the activation is accomplished by the rupture of bond of dipolar groups in the same degrees of freedom [7,19]. Unlike 2,5 dichloro nitrobenzene and 2,5 dibromo nitrobenzene all the systems possess $\delta > 0.50$ as seen in Table 3.3 indicating solvent environment around the solute molecules [20]. Moreover, they show higher $\Delta H\eta_1$'s than that $\Delta H\tau$'s as seen in Table 3.3. It is due to the fact that $\Delta H\eta_1$ is involved with both translational and rotational motion of the molecules. Other systems possess lower values than that of $\Delta H\tau$ for high value of δ for those systems. Debye factor $\tau_j T / \eta$ and Kalman factor $\tau_j T / \eta^\delta$, being proportional to volume of the rotating unit are carefully estimated and are placed in Table 3.3. Debye factors are all of the order of 10^6 and Kalman factors although of different orders but found to have constant values for all systems at each temperature, indicating at once the validity of Debye model of dielectric relaxation mechanism for such aromatic polar nitro compounds in C_6H_6 under GHz electric field [9,13].

3.4. CONCLUSION

Our group [21] have developed a new method based on the complex susceptibility χ^*_{ij} in the limit $\omega_j = 0$ to study the structural aspects and physico-chemical properties of the polar nitro liquid compounds 2,5-dichloronitrobenzene, 3,5-dichloronitrobenzene, 2,5-dibromonitrobenzene, 2,4-dinitrochlorobenzene and 3,4-dinitrochlorobenzene in C_6H_6 under GHz electric field at different experimental temperatures. The excellent agreement of τ_j 's estimated by our methods of eqs. (3.4) and (3.5) at once establishes the applicability of the method suggested to get τ_j 's at $\omega_j \rightarrow 0$ as it eliminates polar-polar interaction [21] in a given solution. The correlation coefficients r 's and % of errors obtained by careful regression analysis between variables of curves of Figs. 3.2 and 3.3 show how far the variables χ''_{ij} and χ'_{ij} are correlated with ω_j 's to establish the statistical validity [15] of eq.(3.5). The thermodynamic energy parameters such as ΔH_τ , ΔS_τ and ΔF_τ worked out in terms of temperature variation of τ_j 's are useful and important tools to comment on the physico-chemical properties of dipolar liquid molecules. The theoretical dipole moment μ_{theo} 's and its comparison with measured hf μ_j 's of the eq.(3.8) explore new concept regarding structures of the molecules in addition to inductive, mesomeric and electromeric effects present in them. Almost the constant values of Debye & Kalman factors and the curves satisfied by experimental points in all the figures reflect the validity of the theoretical formulations advanced within the framework of Debye-Smyth model of dielectric relaxation. The significant contribution to study the structural aspects and physico-chemical properties of the polar liquid molecules as sketched in Fig. 3.4 in nonpolar solvent under nearly 10 GHz electric field are thus found out to be important to enhance scientific content of the the existing knowledge of dielectric relaxation processes.

Table-3.1:- Measured τ_j 's from ratio of slopes of individual variations of χ'_{ij} and χ''_{ij} with ω_j , relaxation time τ_j from Murthy et al, reported τ_j all are in pico second, correlation coefficient and % of error of $\chi'_{ij} - \omega_j$ & $\chi''_{ij} - \omega_j$ curves of Figs. 3.3 and 3.2, of aromatic polar nitro compounds in non polar solvent C_6H_6 at different experimental temperatures in $^{\circ}C$ under 9.58 GHz electric field frequency.

Systems with sl. No.	Tem p.in $^{\circ}C$	Individual slope of variation		slope χ''_{ij} vs χ'_{ij} (eq.3.4)	Ratio of slope of ind. variation	Correlation. Coeff. (r) of $\chi'_{ij} - \omega_j$ & $\chi''_{ij} - \omega_j$ curves	% of errors of $\chi'_{ij} - \omega_j$ & $\chi''_{ij} - \omega_j$ curves	τ_j in psec eq.3.4	τ_j in psec eq.3.5	Report ed τ_j in psec of pant et al [5]
		Slope of χ'_{ij} vs ω_j at $\omega_j \rightarrow 0$	Slope of χ''_{ij} vs ω_j at $\omega_j \rightarrow 0$							
1. 2,5-dichloro nitrobenzene	20	24.73	16.36	0.66	0.66	0.98	1.04	10.98	10.98	10.01
	30	77.03	45.93	0.60	0.60	0.92	4.81	9.90	9.90	9.43
	40	78.54	46.01	0.59	0.59	0.90	5.76	9.72	9.72	6.64
2. 3,5-dichloro nitrobenzene	20	27.35	21.10	0.77	0.77	0.96	2.55	12.81	12.81	11.95
	30	131.44	88.76	0.68	0.68	0.91	5.05	11.21	11.21	8.20
	40	39.69	20.04	0.50	0.50	0.99	0.71	8.38	8.38	7.48
3. 2,5-dibromo nitrobenzene	20	91.74	135.29	1.47	1.47	0.96	2.13	24.48	24.48	21.50
	30	3.40	4.63	1.36	1.36	0.99	0.87	22.62	22.62	19.63
	40	29.92	39.28	1.31	1.31	0.98	1.15	21.79	21.79	19.19
4. 2,4-dinitro chlorobenzene	20	5.23	5.36	1.02	1.02	0.98	1.48	17.00	17.00	15.24
	30	25.42	23.24	0.91	0.91	0.89	6.45	15.18	15.17	14.32
	40	20.00	14.47	0.72	0.72	0.94	3.56	12.01	12.01	11.21
5. 3,4-dinitro chlorobenzene	20	1.29	1.37	1.06	1.06	0.97	1.78	17.60	17.60	15.83
	30	9.59	8.24	0.86	0.86	0.96	2.44	14.25	14.25	13.01
	40	0.23	0.16	0.71	0.71	0.96	2.52	11.82	11.82	10.12

Table 3.2: The coefficients of α, β, γ of $\chi'_{ij} - \omega_j$ curves of Fig. 3.3, dimensionless parameters b's with τ_j of eq.(3.8), measured dipole moment μ_j , reported dipole moment μ_j (Gopala Krishna), theoretical dipole moments μ_j in coulomb metre (C.m) of some aromatic polar liquids in benzene at various experimental temperatures in $^{\circ}\text{C}$ under 9.58 GHz electric field frequency.

Systems with sl. No. & molecular Weight M_j	Temp in $^{\circ}\text{C}$	$\chi'_{ij} = \alpha + \beta\omega_j + \gamma\omega_j^2$			Dimensionless parameter $b = 1/(1 + \omega^2\tau_j^2)$	Measured $\mu_j \times 10^{30}$ in C.m.	$\mu_j \times 10^{30}$ in C.m. (by Pant et al)	$\mu_j(\text{theo}). \times$ 10^{30} in C.m. from bond moments
		α	β	γ				
1. 2,5-dichloro nitrobenzene $M_j = 0.1920$ kg	20	-284.43	24.727	-0.35	0.696	26.18	15.19	
	30	-1223.1	77.025	-1.06	0.738	45.99	15.44	14.17
	40	-1262.6	78.537	-1.07	0.745	47.33	14.82	
2. 3,5-dichloro nitrobenzene $M_j = 0.1920$ kg	20	-404.56	27.352	-0.36	0.627	29.01	8.87	
	30	-1978.7	131.44	-1.94	0.687	62.27	16.41	14.17
	40	-448.35	39.688	-0.69	0.797	32.52	17.06	
3. 2,5-dibromo nitrobenzene $M_j = 0.2810$ kg	20	-1456.2	91.74	-1.3	0.315	90.66	34.33	
	30	203.44	3.3988	-0.13	0.350	16.97	30.99	14.17
	40	-323.28	29.92	-0.46	0.367	50.33	30.81	
4. 2,4-dinitro chlorobenzene $M_j = 0.2025$ kg	20	37.556	5.2318	-0.15	0.488	14.77	17.74	
	30	-264.67	25.42	-0.47	0.545	31.58	12.37	12.36
	40	-186.98	20.003	-0.36	0.656	26.12	12.59	
5. 3,4-dinitro chlorobenzene $M_j = 0.2025$ kg	20	191.45	1.2885	0.019	0.471	7.46	17.76	
	30	-147.89	9.5948	-0.01	0.576	18.87	12.37	25.18
	40	199.23	0.2286	0.068	0.663	2.78	14.69	

Table 3.3: The thermodynamic energy parameters : enthalpy of activation ΔH_{τ} , entropy of activation ΔS_{τ} and free energy of activation ΔF_{τ} , value of δ from eq. $\ln\tau_j T = \ln a + \delta \ln \eta_j$, enthalpy of activation ΔH_{η_i} due to viscous flow of solvent, Debye factor and Kalman factor of some aromatic polar liquids in benzene at various experimental temperatures in $^{\circ}\text{C}$ under 9.58 GHz electric field frequency

Systems with Sl.no.	Temp. in $^{\circ}\text{C}$	ΔH_{τ} in KJ mole $^{-1}$	Δs_{τ} in J mole $^{-1}$	ΔF_{τ} in KJ mole $^{-1}$	Value of δ from $\ln\tau_j T = \ln a + \delta \ln \eta_j$	$\Delta H_{\eta_i} = (\Delta H_{\tau}/\gamma)$ in KJ mole $^{-1}$	Debye factor $(\tau_j T/\eta_j) \times 10^6$	Kalman factor $(\tau_j T/\eta_j^{\gamma})$
1. 2,5-dichloro nitrobenzene	20	2.16	-0.0277	10.28	0.36	5.99	5.22	4.61×10^{-8}
	30	2.16	-0.0274	10.45	0.36	5.99	5.35	4.45×10^{-8}
	40	2.16	-0.0277	10.83	0.36	5.99	5.82	4.63×10^{-8}
2. 3,5-dichloro nitrobenzene	20	13.58	0.0100	10.65	2.10	6.46	6.08	2.09×10^{-2}
	30	13.58	0.0093	10.77	2.10	6.46	6.05	2.30×10^{-2}
	40	13.58	0.0100	10.45	2.10	6.46	5.02	2.07×10^{-2}
3. 2,5-dibromo nitrobenzene	20	1.93	-0.0352	12.24	0.31	6.15	11.62	7.26×10^{-8}
	30	1.93	-0.0350	12.54	0.31	6.15	12.22	7.15×10^{-8}
	40	1.93	-0.0352	12.94	0.31	6.15	13.04	7.27×10^{-8}
4. 2,4-dinitro chlorobenzene	20	10.69	-0.0023	11.35	1.65	6.46	8.07	1.02×10^{-3}
	30	10.69	-0.0028	11.53	1.65	6.46	8.20	1.10×10^{-3}
	40	10.69	-0.0022	11.39	1.65	6.46	7.19	1.01×10^{-3}
5. 3,4-dinitro chlorobenzene	20	12.67	0.0042	11.43	2.00	6.33	8.36	1.37×10^{-2}
	30	12.67	0.0043	11.37	2.00	6.33	7.69	1.39×10^{-2}
	40	12.67	0.0042	11.34	2.00	6.33	7.07	1.37×10^{-2}

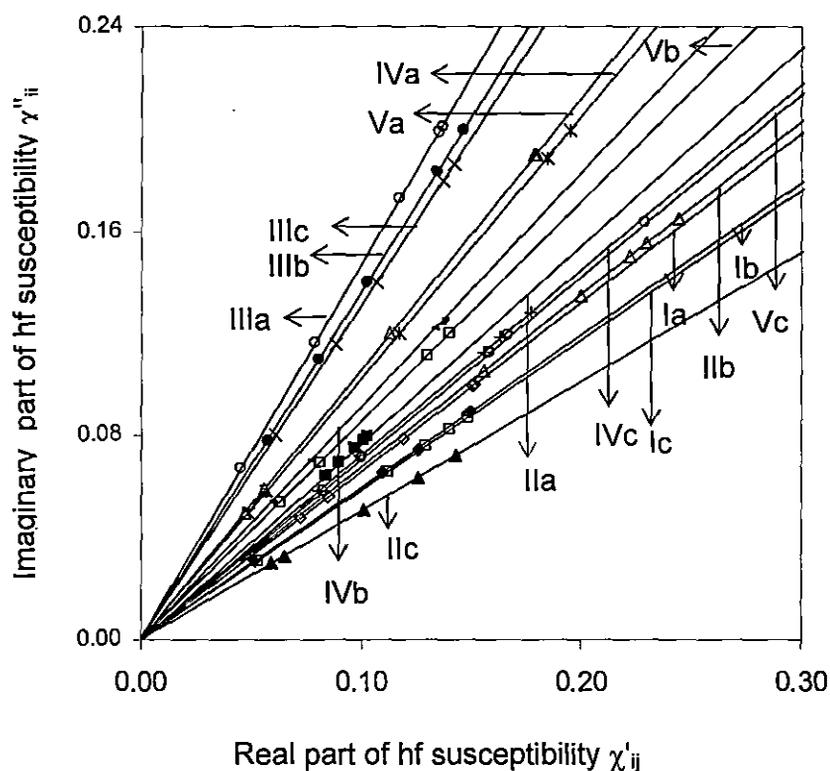


Fig. 3.1. Variation of imaginary part χ''_{ij} of hf orientational susceptibility against real part χ'_{ij} of hf orientation susceptibility of some polar nitro compounds in nonpolar solvent benzene at different temperatures in $^{\circ}\text{C}$ under 9.5846 GHz electric field frequency of 2,5-dichloro nitrobenzene- [Ia. at 20°C (\diamond), Ib. at 30°C (\blacklozenge), Ic. at 40°C (\square)] 3,5-dichloronitrobenzene- [IIa at 20°C (\blacksquare), IIb. at 30°C (\triangle), IIc. at 40°C (\blacktriangle)] 2,5-dibromonitobenzene- [IIIa. at 0°C (\circ), IIIb. at 30°C (\bullet), IIIc. at 40°C (\times)] 2,4-dinitrochlorobenzene- [IVa. at 20°C ($*$), IVb. at 30°C ($-$), IVc. at 40°C ($+$)] 3,4-ditrochlorobenzene- [Va. at 20°C (Δ), Vb. at 30°C (\square), Vc. at 40°C (\circ)]

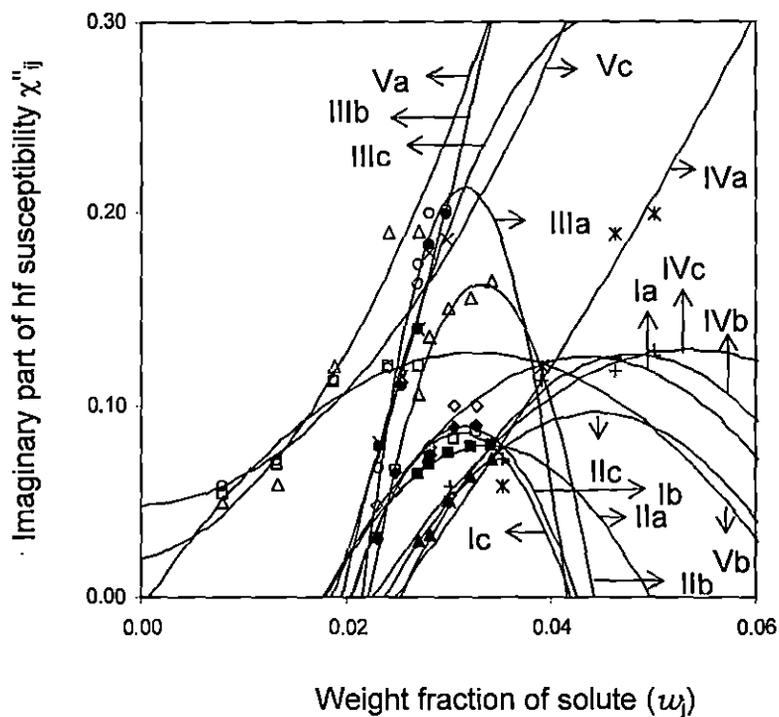


Fig. 3.2. Variation of imaginary part χ''_{ij} of hf orientational susceptibility against weight fraction w_j of some polar nitro compounds in nonpolar solvent benzene at different temperatures in $^{\circ}\text{C}$ under 9.5846 GHz electric field frequency of 2,5-dichloro nitrobenzene- [Ia. at 20°C (\diamond), Ib at 30°C (\blacklozenge), Ic.at 40°C (\square)] 3,5-dichloronitrobenzene-[IIa at 20°C (\blacksquare), IIb.at 30°C (Δ), IIc. at 40°C (\blacktriangle)] 2,5-dibromonitrobenzene- [IIIa. at 20°C (\circ), IIIb.at 30°C (\bullet), IIIc. at 40°C (\times)] 2,4-dinitrochlorobenzene- [IVa. at 20°C ($*$), IVb.at 30°C ($-$), IVc. at 40°C ($+$)] 3,4-ditrochlorobenzene- [Va. at 20°C (Δ), Vb.at 30°C (\square), Vc. at 40°C (\circ)]

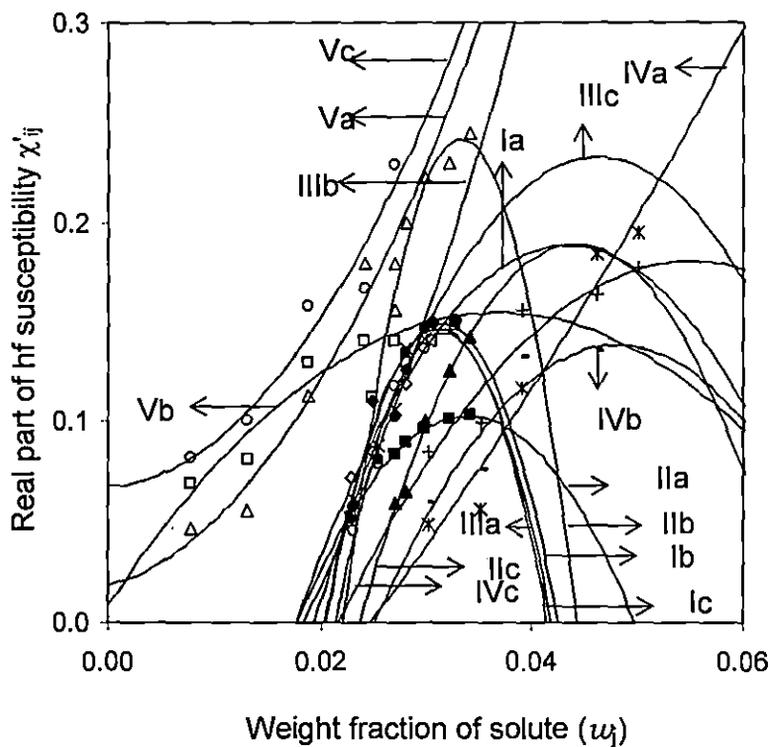


Fig. 3.3. Variation of real part χ'_{ij} of hf orientational susceptibility against weight fraction w_1 of some polar nitro compounds in nonpolar solvent benzene at different temperatures in $^{\circ}\text{C}$ under 9.5846 GHz electric field frequency of 2,5-dichloronitrobenzene- [Ia. at 20°C (\diamond), Ib. at 30°C (\blacklozenge), Ic. at 40°C (\square)] 3,5-dichloronitrobenzene-[Ila at 20°C (\blacksquare), Ilb. at 30°C (Δ), Ilc. at 40°C (\blacktriangle)] 2,5-dibromonitrobenzene- [IIIa. at 20°C (\circ), IIIb. at 30°C (\bullet), IIIc. at 40°C (\times)] 2,4-dinitrochlorobenzene- [IVa. at 20°C ($*$), IVb. at 30°C ($-$), IVc. at 40°C ($+$)] 3,4-ditrochlorobenzene- [Va. at 20°C (Δ), Vb. at 30°C (\square), Vc. at 40°C (\circ)]

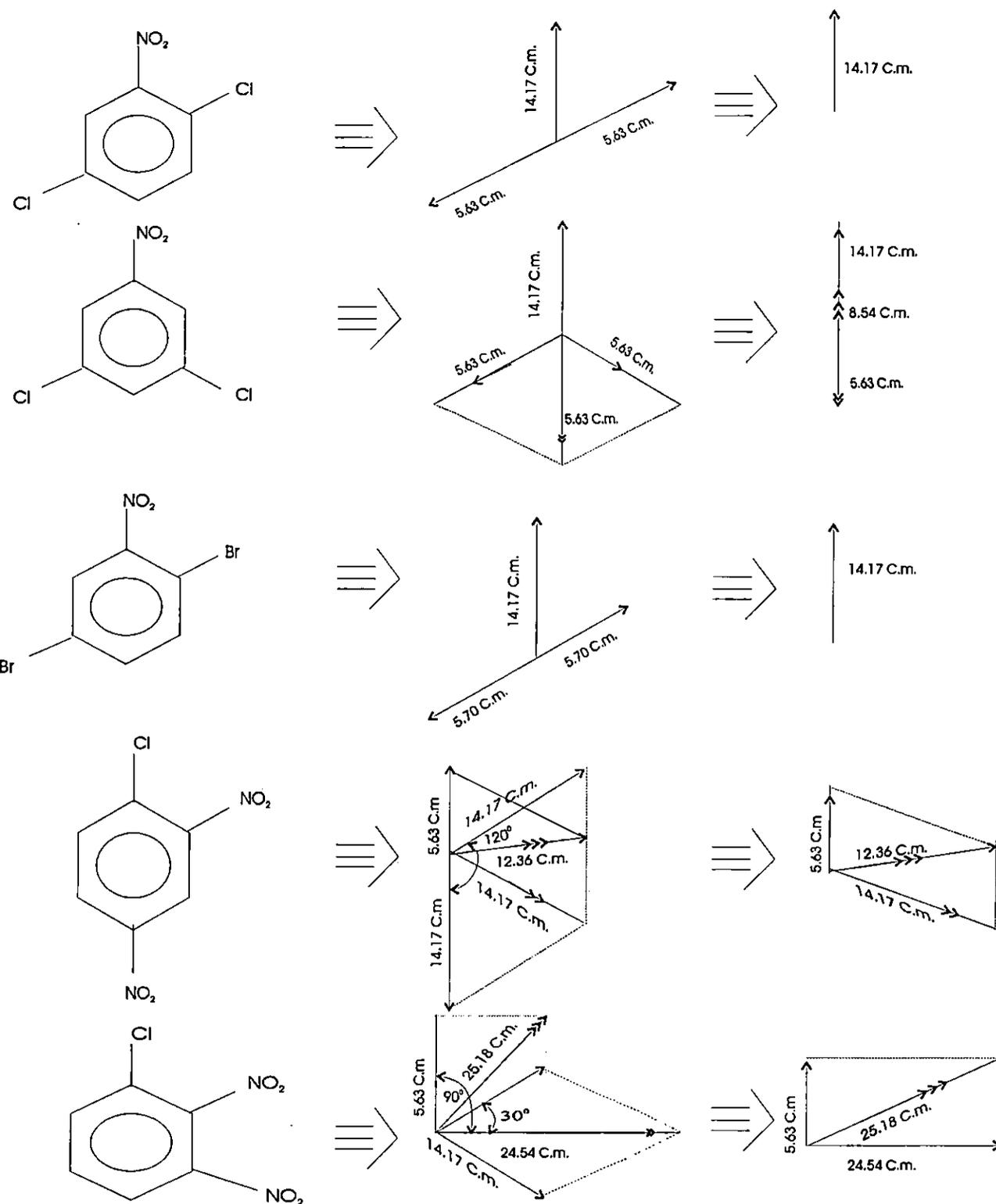


Fig. 3.4 Theoretical dipole moment μ_{theo} ($\times 10^{30}$) in coulomb. metre (C.m.) from available bond angle and bond moments of (I). 2,5- dichloro nitrobenzene (II).3,5- dichloro nitrobenzene (III). 2,5-dibromo nitrobenzene (IV). 2,4- dinitro chlorobenzene (V). 2,3- di nitro chlorobenzene.

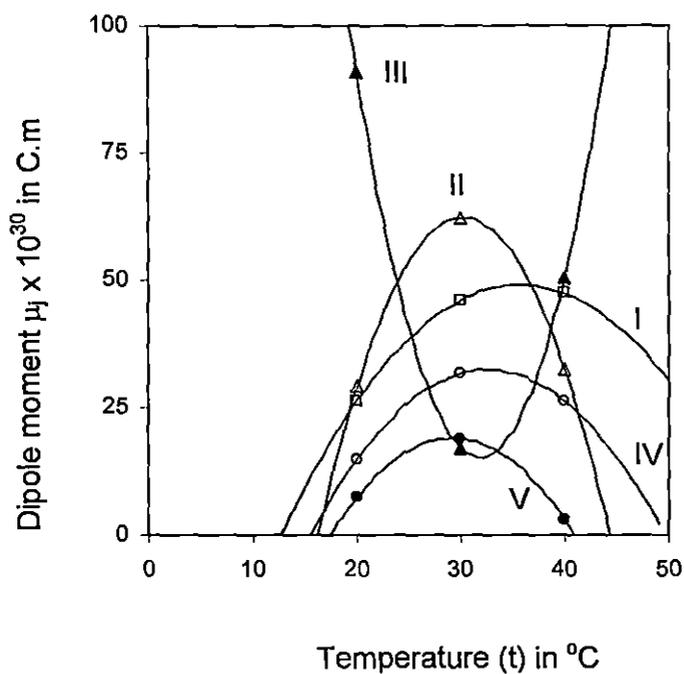


Fig. 3.5. Variation of dipole moment μ_j against temperature t in $^{\circ}\text{C}$ of some polar nitro compounds in nonpolar solvent benzene under 9.5846 GHz electric field frequency of I. 2,5-dichloro nitrobenzene (\square), II. 3,5-dichloro nitrobenzene (Δ), III. 2,5-dibromo nitrobenzene (\blacktriangle), IV. 2,4-dinitro chlorobenzene (\circ) V. 3,4-dinitro chlorobenzene (\bullet)

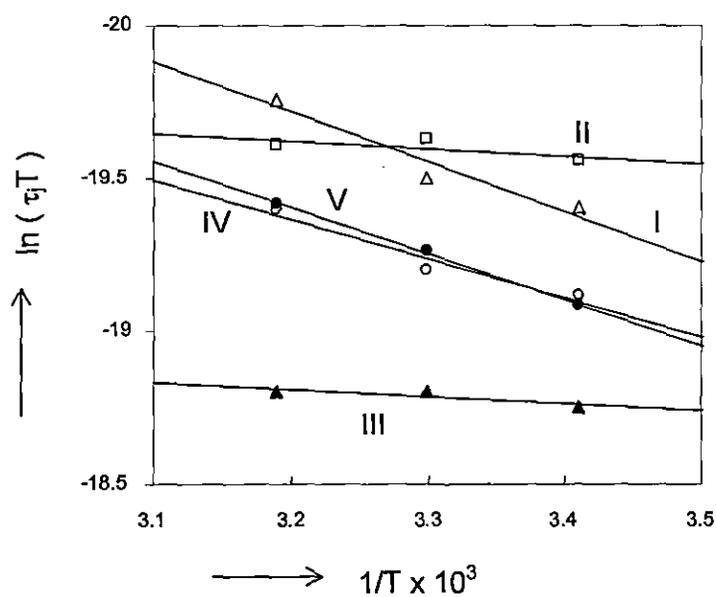


Fig. 3. 6. Variation of $\ln(\tau_j T)$ against $1/T$ of some polar nitro compounds in nonpolar solvent benzene under 9.5846 GHz electric field frequency of I. 2,5-dichloronitrobenzene (□), II. 3,5-dichloronitrobenzene (△), III. 2,5-dibromonitrobenzene (▲), IV. 2,4-dinitrochlorobenzene (○) V. 3,4-dinitrochlorobenzene (●)

REFERENCES

- [1] K S Cole and R H Cole, *J Chem Phys* **9** (1941) 341
- [2] E A Guggenheim, *Trans Faraday Soc.* **45** (1949) 714
- [3] M D Migahed , M T Ahmed & A E Kolp, *J Phys D: Appl Phys* (UK) **33** (2000) 2108
- [4] N Nandi, K Bhattacharyya and B Bagchi, *Chem.Rev.* **100** (2000) 2013
- [5] D C Pant, S K S Somevanshi, N K Mehrotra & N C Saxena, *Indian J Phys* **51** (1977) 305
- [6] M B R Murthy, R L Patil and D K Deshpande, *Indian J Phys* **63B** (1989) 491
- [7] U K Mitra, N Ghosh, P Ghosh and S Acharyya, *J Indian Chem. Soc* **83** (2006) 1230
- [8] N Ghosh, R C Basak, S K Sit and S Acharyya, *J Molecular Liquids* **85** (2000) 375
- [9] A Karmakar, U K Mitra, N Ghosh and S Acharyya, *J Phys D: Appl Phys* (UK) communicated 2005
- [10] K V Gopala Krishna, *Trans Faraday Soc* **53** (1957) 767
- [11] C P Smyth " Dielectric Behaviour and Structure" (New York: MC Graw Hill 1955)
- [12] S K Sit Ph D Dissertation (North Bengal University) INDIA 1997
- [13] N Paul, K P Sharma and S Chattopadhyay, *Indian J Phys* **71B** (1997) 711
- [14] H Eyring, S Glasstone and K J Laidler " *The Theory of Rate Process* (MC Graw Hill: New York) 1941
- [15] U K Mitra, N Ghosh, P Ghosh and S Acharyya, *J Molecular Liquids*, **126** (2006) 53
- [16] N E Hill, W E Vaughan, A H Price & M Davies , "Dielectric properties and molecular behaviour " Van Nostrand Reinhold Co. London (1969)
- [17] M V George, J Mohanty, P T Narasimhan & C N R Rao, "A Hand Book of Chemistry and Physics" Affiliated east-west press Pvt Ltd New Delhi (1967) 253
- [18] N Ghosh, A Karmakar, S K Sit and S Acharyya, *Indian J Pure & Appl Phys* **38** (2000) 574
- [19] R L Dhar, A Mathur, J P Shukla and M C Saxena ,*Indian J Pure & Appl Phys* **11**(1973) 568
- [20] A K Sharma and D R Sharma, *J Phys Soc Japan* **61**(1992) 1049
- [21] N Ghosh, S K Sit, A K Bothra & S Acharyya, *J Phys D: Appl Phys* (UK) **34** (2001) 379

CHAPTER 4

DIELECTRIC RELAXATION PHENOMENA OF SOME APROTIC POLAR LIQUIDS UNDER GIGA HERTZ ELECTRIC FIELD

4. DIELECTRIC RELAXATION PHENOMENA OF SOME APROTIC POLAR LIQUIDS UNDER GIGA HERTZ ELECTRIC FIELD

4.1. INTRODUCTION

The relaxation behaviour of polar-nonpolar liquid mixtures under high frequency (hf) electric field is of much importance to study the molecular shapes, sizes as well as associational behaviours [1-3] in them. Workers in this field usually analyse the experimental data obtained through relaxation mechanisms involved on the basis of various models [4-6] applicable to polar liquids. Dhull et al [7] and Sharma & Sharma [8] had, however, measured the real ϵ'_{ijk} , ϵ'_{ij} or ϵ'_{ik} and imaginary ϵ''_{ijk} , ϵ''_{ij} or ϵ''_{ik} parts of relative complex permittivities ϵ_{ijk}^* , ϵ_{ij}^* or ϵ_{ik}^* of some interesting binary or single polar liquids (jk, j or k) in a nonpolar solvent under X-band electric field at different or fixed temperatures. The purpose of the work was to detect monomer (solute-solvent) or dimer (solute-solute) molecular associations and molecular dynamics of the systems in terms of estimated relaxation time τ_j and dipole moment μ_j .

The measured [9] values of the relative permittivities ϵ_{ij} 's of some aprotic polar liquids like N,N-dimethylsulphoxide (DMSO); N,N-dimethylformamide (DMF); N,N-dimethyl acetamide (DMA) and N,N-diethylformamide (DEF) in benzene under the most effective dispersive region of nearly 10 GHz electric field at 25, 30, 35 and 40°C for DMSO; 25°C for DMA and DMF and 30°C for DEF respectively. DMSO is a ^{have} aprotic dipolar liquid of high penetrating power and ^{wide} application in medicine and industry. It acts as good constituent of binary mixtures because of its associative [10] nature. Amides, on the other hand, are the building blocks of proteins and enzymes and have wide biological applications. The liquids usually show two relaxation times τ_2 and τ_1 for the rotation of the whole molecules and the flexible parts attached to the parent molecules from the single frequency measurement technique. [11-12]

All these facts inspired us to study τ_2 and τ_1 and dipole moments μ_2 and μ_1 of these liquids in terms of real χ'_{ij} ($=\epsilon'_{ij}-\epsilon_{\infty ij}$) and imaginary χ''_{ij} ($=\epsilon''_{ij}$) parts of complex orientational susceptibility χ_{ij}^* ($=\epsilon_{ij}^*-\epsilon_{\infty ij}$) in benzene at different temperatures. The low frequency susceptibility χ_{0ij} ($=\epsilon_{0ij}-\epsilon_{\infty ij}$) is however real. χ'_{ij} can be obtained by subtracting either 1 or $\epsilon_{\infty ij}$ from the measured ϵ_{ij} 's. If 1 is subtracted from the relative permittivity ϵ'_{ij} and ϵ_{0ij} one

gets χ'_{ij} and χ_{oij} containing all types of polarisation processes including fast polarization. When high frequency relative permittivity or the optical permittivity $\epsilon_{\infty ij}$ be subtracted from ϵ_{ij}' and ϵ_{oij} of the solution at a certain weight fraction w_j 's of the solute the susceptibility χ'_{ij} , χ''_{ij} and χ_{oij} result due to orientational polarisation only. Our earlier study [9] was to calculate τ 's and μ 's in terms of either relative permittivities ϵ_{ij} 's or hf conductivities σ_{ij} 's. ϵ_{ij} 's are involved with all types of polarisations while σ_{ij} 's are related only to bound molecular charges of polar liquids. Nowadays relaxation mechanisms are studied in terms of χ_{ij} 's [13] because measurements of μ 's in terms of ϵ_{ij} 's or σ_{ij} 's include contributions due to all types of polarisations and bound molecular charges respectively. Moreover, relaxation processes are highly thermally activated to yield τ within the framework of Debye–Smith model of polar–nonpolar liquid mixture.

The purpose of the present work is to assess the contribution of fast polarisation and bound molecular charges in the measurement of μ 's when compared with μ 's from χ_{ij} and σ_{ij} measurements. The variation of μ 's with temperature provides knowledge of the state of the system through the measured energy parameters.

The detailed experimental technique involved in the measurement of dielectric relaxation parameters of solution has been described elsewhere [14]. A Hewlett Packard Impedance Analyser (HP–4192A) measured the capacitance and conductance of the cell containing polar–nonpolar liquid mixtures at different frequencies and temperatures for a fixed w_j of solute. The real and imaginary parts of relative permittivities ϵ_{ij}^* or susceptibility χ_{ij}^* are obtained from complex impedances of the cell measured within the range of frequencies from 5 Hz to 13 MHz. The measured ϵ_{ij} 's are then plotted in a Cole–Cole semicircular arc to get the values of ϵ'_{ij} , ϵ''_{ij} , ϵ_{oij} and $\epsilon_{\infty ij}$ at nearly 10 GHz electric field (Table.4.1). Again ϵ_{oij} is measured at 1 KHz whereas high frequency permittivity $\epsilon_{\infty ij}$ ($= n_{Dij}^2$) is measured by Abbe's Refractometer to compare the values obtained from Cole–Cole plot. The cell containing experimental liquid mixture is then kept in Mettler Hot Stage FP–52 chamber to regulate temperature. Multiply distilled C_6H_6 is used as a solvent in measurement after several times fractional distillation to get the purest quality of sample. The measured data ϵ'_{ij} or χ'_{ij} 's are accurate within $\pm 5\%$.

Bergmann et al [15], however, proposed a graphical technique to get τ_1 , τ_2 and c_1 , c_2 for a pure polar liquid at different frequencies of the microwave electric field. In order to

avoid clumsiness of algebra and fast polarisation processes, the molecular orientational polarisations in terms of established symbols of χ_{ij} 's can be written as [5]

$$\frac{\chi'_{ij}}{\chi_{oj}} = \frac{c_1}{1 + \omega^2 \tau_1^2} + \frac{c_2}{1 + \omega^2 \tau_2^2} \quad (4.1)$$

$$\frac{\chi''_{ij}}{\chi_{oj}} = c_1 \frac{\omega \tau_1}{1 + \omega^2 \tau_1^2} + c_2 \frac{\omega \tau_2}{1 + \omega^2 \tau_2^2} \quad (4.2)$$

assuming two separate broad Debye type dispersions of which $c_1 + c_2 = 1$.

Saha et al [11] and Sit et al [12] put forward an analytical technique to measure τ_1 , τ_2 and c_1 , c_2 of a polar–nonpolar liquid mixture in terms of measured χ'_{ij} , χ''_{ij} , χ_{oj} at different ω 's of solute under a single frequency electric field and temperature. eqs (4.1) and (4.2) are solved to get

$$\frac{\chi_{oj} - \chi'_{ij}}{\chi'_{ij}} = \omega(\tau_1 + \tau_2) \frac{\chi''_{ij}}{\chi'_{ij}} - \omega^2 \tau_1 \tau_2 \quad (4.3)$$

The eq. (4.3) gives a straight line when $(\chi_{oj} - \chi'_{ij})/\chi'_{ij}$ is plotted against χ''_{ij}/χ'_{ij} for different ω 's of solute for a given angular frequency $\omega (= 2\pi f)$, f being the frequency of the applied electric field. The slope $\omega(\tau_1 + \tau_2)$ and intercept $-\omega^2 \tau_1 \tau_2$ of straight line of eq. (4.3) are obtained through linear regression analysis as shown in Fig. 4.1. Relaxation times τ_2 and τ_1 are calculated from the slopes and intercepts of eq. (4.3) of Fig. 4.1 in terms of measured data of Table 4.1. They are then compared with measured τ_j 's from the linear slope of the χ''_{ij} against χ'_{ij} curve of Fig. 4.2 at different ω 's of the form:

$$\frac{d\chi''_{ij}}{d\chi'_{ij}} = \omega \tau \quad (4.4)$$

Both χ''_{ij} and χ'_{ij} are functions of ω 's of solute. It is better to use the individual slopes $\chi''_{ij} - \omega$ and $\chi'_{ij} - \omega$ curves in Figs. 4.3 and 4.4 at $\omega \rightarrow 0$ to measure τ using the following equation:

$$\frac{(d\chi''_{ij}/d\omega_j)_{\omega_j \rightarrow 0}}{(d\chi'_{ij}/d\omega_j)_{\omega_j \rightarrow 0}} = \omega \tau \quad (4.5)$$

τ 's from both the methods along with τ 's from conductivity measurement technique using eqs. (4.25) and (4.26) [see later] are placed in Table 4.2 in order to compare with τ measured by Gopala Krishna's method [16].

eqs. (4.1) and (4.2) are solved for c_1 and c_2 to get:

$$c_1 = \frac{(\chi'_{ij}\alpha_2 - \chi''_{ij})(1 + \alpha_1^2)}{\chi_{oij}(\alpha_2 - \alpha_1)} \quad (4.6)$$

$$c_2 = \frac{(\chi''_{ij} - \chi'_{ij}\alpha_1)(1 + \alpha_2^2)}{\chi_{oij}(\alpha_2 - \alpha_1)} \quad (4.7)$$

where $\alpha_1 = \omega \tau_1$ and $\alpha_2 = \omega \tau_2$, such that $\alpha_2 > \alpha_1$. The values of χ'_{ij}/χ_{oij} and χ''_{ij}/χ_{oij} are also obtained from following Fröhlich's equations. [17]:

$$\frac{\chi'_{ij}}{\chi_{oij}} = 1 - \frac{1}{2A} \ln \left(\frac{1 + \omega^2 \tau_2^2}{1 + \omega^2 \tau_1^2} \right) \quad (4.8)$$

$$\frac{\chi''_{ij}}{\chi_{oij}} = \frac{1}{A} \left[\tan^{-1}(\omega \tau_2) - \tan^{-1}(\omega \tau_1) \right] \quad (4.9)$$

where $A = \text{Fröhlich parameter} = \ln(\tau_2 / \tau_1)$. The theoretical values of relative contributions c_1 and c_2 towards dielectric relaxation processes for τ_1 and τ_2 are computed from eqs.(4.8) and (4.9). They are presented in Table 4.3. The graphical plots of χ'_{ij}/χ_{oij} and χ''_{ij}/χ_{oij} curves as a function of $\omega \tau_1$ are shown in Figs 4.5 and 4.6 respectively. The experimental values of c_1 and c_2 are also estimated from eqs(4.1) and (4.2) with the measured values of $(\chi'_{ij}/\chi_{oij})_{\omega \tau_1 \rightarrow 0}$ and $(\chi''_{ij}/\chi_{oij})_{\omega \tau_1 \rightarrow 0}$ of Figs 4.5 and 4.6. These c_1 and c_2 are finally compared with theoretical ones in Table 4.3.

The symmetric and asymmetric distribution parameters γ and δ of the molecules under study are calculated and placed in the last columns of the Table 4.3 along with all the c_1 and c_2 's in order to see that the relaxation mechanism for such liquids are symmetric.

The dipole moments μ_2 and μ_1 due to rotation of the whole molecule as well as the flexible parts of the molecules are determined from the slope β_1 of $\chi'_{ij} - \omega \tau_1$ curve of Fig. 4.4 at $\omega \tau_1 \rightarrow 0$ in terms of estimated τ_1 of eq. (4.3) as placed in Table 4.4. μ_1 's are again calculated from the τ 's of eqs. (4.4) and (4.25) of Murthy et al [18] and the ratio of the individual slopes of eqs. (4.5) and (4.26) from susceptibility and conductivity measurements using slope β_1 of $\chi'_{ij} - \omega \tau_1$ of Fig 4.4 and β_2 of $\sigma_{ij} - \omega \tau_1$ curve of Fig. 4.7. μ 's from both the measurements are entered in Table 4.4 along with estimated μ 's from Gopala Krishna's method [16] quoted as reported ones in the Table 4.4.

The variations of measured μ_2 and μ_1 for DMSO in benzene with temperature in $^{\circ}\text{C}$ are given by the equations:

$$\begin{aligned}\mu_2 &= -231.61 + 15.597 t - 0.2272 t^2 \\ \mu_1 &= 19.825 - 0.626 t + 0.0108 t^2\end{aligned}\quad (4.10)$$

μ_2 of the parent molecule attains a maximum value of 36 C.m at 34.32°C with zero dipole moments at 21.72°C and 46.92°C respectively due to monomer formation with C_6H_6 ring.

The theoretical dipole moment μ_{theo} 's of the molecules are calculated from the available infrared spectroscopic data of bond moments assuming the molecules are planar as sketched in Fig 4.8. They are found to vary with the measured μ_j 's. The difference, however, indicates that the effect of inductive, mesomeric and electromeric moments of the substituent polar groups within the molecules along with temperature in the hf electric field is to be considered to have the conformation of the molecules under interest.

The thermodynamic energy parameters like enthalpy of activation ΔH_{τ} , free energy of activation ΔF_{τ} and entropy of activation ΔS_{τ} were obtained from the slope and intercept of linear equation of $\ln(\tau_1 T)$ against $1/T$ for DMSO as given by the equation.

$$\begin{aligned}\ln(\tau_2 T) &= -4.8353 - 4.088 \times 10^3 (1/T) \\ \ln(\tau_1 T) &= -30.568 + 3.216 \times 10^3 (1/T)\end{aligned}\quad (4.11)$$

The variation of $\ln(\tau_1 T)$ or $\ln(\tau_2 T)$ against $1/T$ indicate that τ_1 obeys the Eyring rate process whereas τ_2 does not.

4.2 SYMMETRIC AND ASYMMETRIC DISTRIBUTION PARAMETER γ AND δ

The polar–nonpolar liquid mixtures under study are nonrigid in nature exhibiting two relaxation times τ_2 and τ_1 at a single frequency electric field. [19] The measured values of χ''_{ij}/χ_{oij} when plotted against χ'_{ij}/χ_{oij} at $\omega_j \rightarrow 0$ for different frequency ω at a fixed experimental temperature for DMSO may either show Cole–Cole semicircular arc or Cole–Davidson skewed arc having symmetric and asymmetric distribution of relaxation behaviour according to following equations:

$$\frac{\chi_{ij}^{\bullet}}{\chi_{oij}} = \frac{1}{1 + (j\omega\tau_s)^{1-\gamma}}\quad (4.12)$$

$$\frac{\chi_{ij}^*}{\chi_{oij}} = \frac{1}{(1 + j\omega\tau_{cs})^\delta} \quad (4.13)$$

where τ_s and τ_{cs} are symmetric and characteristics relaxation times related to symmetric and asymmetric distribution parameters γ and δ respectively. On separation the real and imaginary parts of eq. (4.12) one gets:

$$\gamma = \frac{2}{\pi} \tan^{-1} \left[\left(1 - \frac{\chi_{ij}'}{\chi_{oij}} \right) \frac{\chi_{ij}'/\chi_{oij}}{\chi_{ij}''/\chi_{oij}} - \frac{\chi_{ij}''}{\chi_{oij}} \right] \quad (4.14)$$

$$\tau_s = \frac{1}{\omega} \left[1 / \left(\frac{\chi_{ij}'/\chi_{oij}}{\chi_{ij}''/\chi_{oij}} \cos \frac{\gamma\pi}{2} - \sin \frac{\gamma\pi}{2} \right) \right]^{\frac{1}{1-\gamma}} \quad (4.15)$$

On simplification of eq. (4.13) further one gets :

$$\frac{1}{\phi} \log(\cos \phi) = \frac{\log[(\chi_{ij}'/\chi_{oij})/\cos(\phi\delta)]}{\phi\delta} \quad (4.16)$$

$$\tan(\phi\delta) = \frac{(\chi_{ij}''/\chi_{oij})_{\omega_j \rightarrow 0}}{(\chi_{ij}'/\chi_{oij})_{\omega_j \rightarrow 0}} \quad (4.17)$$

where $\tan \phi = \omega\tau_{cs}$

A theoretical curve of $(1/\phi)\log(\cos \phi)$ with ϕ in degrees was drawn [5] to get the known values of ϕ and δ in terms of measured parameter of $[\log\{(\chi_{ij}'/\chi_{oij})/\cos(\phi\delta)\}] / (\phi\delta)$ of eqs. (4.16) and (17). All the τ_s , τ_{cs} and δ ϕ are given in Tables 4.2 and 4.3 respectively.

4.3 DIPOLE MOMENT μ_j FROM SUSCEPTIBILITY MEASUREMENT

Debye equation [20] of relative permittivities of a polar solute (j) dissolved in a nonpolar solvent (i) in terms of complex dielectric orientational susceptibility χ_{ij}^* of solution can be written as:

$$\frac{\chi_{ij}^*}{\chi_{oij}} = \frac{1}{1 + j\omega\tau} \quad (4.18)$$

where χ'_{ij} ($=\epsilon'_{ij}-\epsilon_{\infty ij}$) and χ''_{ij} ($=\epsilon''_{ij}$) are the real and imaginary parts of $\chi^*_{ij} = \chi'_{ij}-j\chi''_{ij}$, $j = \sqrt{-1}$ is a complex number χ_{oij} ($=\epsilon_{oij}-\epsilon_{\infty ij}$) is the low frequency susceptibility which is real.

Again, the imaginary part of dielectric orientational susceptibility χ''_{ij} as a function of ω_j can be written according to Smith [21] as:

$$\chi''_{ij} = \frac{N\rho_{ij}\mu_j^2}{27\epsilon_o k_B T M_j} \frac{\omega\tau}{1+\omega^2\tau^2} (\epsilon_{ij} + 2)^2 \omega_j \quad (4.19)$$

On differentiation of eq. (4.19) w.r. t ω_j at $\omega_j \rightarrow 0$ one gets:

$$\left(\frac{d\chi''_{ij}}{d\omega_j} \right)_{\omega_j \rightarrow 0} = \frac{N\rho_{ij}\mu_j^2}{27\epsilon_o k_B T M_j} \frac{\omega\tau}{1+\omega^2\tau^2} (\epsilon_i + 2)^2 \quad (4.20)$$

where k_B = Boltzmann constant, N = Avogadro's Number ϵ_i = relative permittivity of the solute and ϵ_o = Absolute permittivity of free space = 8.854×10^{-12} F.m⁻¹, all expressed in S.I. units. Comparing eqs. (4.4) and (4.20) one gets :

$$\left(\frac{d\chi'_{ij}}{d\omega_j} \right)_{\omega_j \rightarrow 0} = \frac{N\rho_{ij}\mu_j^2}{27\epsilon_o k_B T M_j} \frac{1}{1+\omega^2\tau^2} (\epsilon_i + 2)^2 = \beta_1 \quad (4.21)$$

where β_1 is the slope of $\chi'_{ij}-\omega_j$ curves at $\omega_j \rightarrow 0$.

From eq. (4.21) one gets the dipole moment μ_j as:

$$\mu_j = \left(\frac{27\epsilon_o k_B T M_j \beta_1}{N\rho_{ij} (\epsilon_i + 2)^2 b} \right)^{\frac{1}{2}} \quad (4.22)$$

where $b = 1/(1+\omega^2\tau^2)$ is the dimensionless parameter involved with measured τ_j of Table 4.2. All the μ_j 's are placed in Table 4.4.

4.4 DIPOLE MOMENT μ_j FROM hf CONDUCTIVITY MEASUREMENT

The hf complex conductivity $\hat{\sigma}^*_{ij}$ of a polar-nonpolar liquid mixture is given by:

$$\hat{\sigma}^*_{ij} = \sigma'_{ij} + j\sigma''_{ij} = \omega\epsilon_o (\epsilon''_{ij} + j\epsilon'_{ij}) \quad (4.23)$$

the real σ'_{ij} and imaginary σ''_{ij} parts of $\hat{\sigma}^*_{ij}$ are related by

$$\sigma''_{ij} = \sigma_{\infty ij} + \frac{1}{\omega\tau_j} \sigma'_{ij} \quad (4.24)$$

where $\sigma_{\infty ij}$ is the constant conductivity at infinite dilution i.e. at $w_j \rightarrow 0$. The eq. (4.24) on differentiation w.r.t. σ'_{ij} yields:

$$\frac{d\sigma''_{ij}}{d\sigma'_{ij}} = \frac{1}{\omega\tau_j} \quad (4.25)$$

which provides a convenient method to obtain τ_j of a polar molecule. It is, however, better to use the ratio of the slopes of variation of σ''_{ij} and σ'_{ij} with w_j in order to avoid polar–polar interactions at $w_j \rightarrow 0$ in a given solvent to get τ_j from:

$$\frac{(d\sigma''_{ij}/dw_j)_{w_j \rightarrow 0}}{(d\sigma'_{ij}/dw_j)_{w_j \rightarrow 0}} = \frac{1}{\omega\tau_j} \quad (4.26)$$

In hf region of GHz range, it is generally observed that $\sigma''_{ij} \cong \sigma_{ij}$ the total hf conductivity [22] of the solution. Therefore, the eq. (4.24) can be written as:

$$\sigma_{ij} = \sigma_{\infty ij} + \frac{1}{\omega\tau_j} \sigma'_{ij} \quad (4.27)$$

$$\beta_2 = \frac{1}{\omega\tau_j} \left(\frac{d\sigma'_{ij}}{dw_j} \right)_{w_j \rightarrow 0}$$

where β_2 is the slope of $(d\sigma_{ij}/dw_j)_{w_j \rightarrow 0}$. The real part σ'_{ij} of a polar–nonpolar liquid mixture is given by [5]

$$\sigma'_{ij} = \frac{N\rho_{ij}\mu_j^2}{27k_B T M_j} \frac{\omega^2 \tau_j}{1 + \omega^2 \tau_j^2} (\epsilon_{ij} + 2)^2 w_j$$

$$\left(\frac{d\sigma'_{ij}}{dw_j} \right)_{w_j \rightarrow 0} = \frac{N\rho_i \mu_j^2}{27k_B T M_j} \frac{\omega^2 \tau_j}{1 + \omega^2 \tau_j^2} (\epsilon_i + 2)^2 \quad (4.28)$$

Now comparing eqs. (4.27) and (4.28) one gets hf μ_j from

$$\mu_j = \left(\frac{27k_B T M_j \beta_2}{N\rho_i (\epsilon_i + 2)^2 \omega b} \right)^{\frac{1}{2}} \quad (4.29)$$

where $b=1 / (1+\omega^2\tau^2)$ is involved with τ_j 's from eqs. (4.25) and (4.26). μ_j 's thus obtained from eq. (4.29) are placed in Table 4.4 along with Gopala Krishna's μ_j and μ_{theo} 's.

4.5 RESULT AND DISCUSSION

The relaxation parameters in terms of real χ'_{ij} ($=\epsilon'_{ij}-\epsilon_{\infty ij}$), imaginary χ''_{ij} ($=\epsilon''_{ij}$) and low frequency susceptibility χ_{oij} ($=\epsilon_{oij}-\epsilon_{\infty ij}$), which is real are extracted from the measured relative permittivities ϵ_{ij} 's for different ω_j 's of solute at 25, 30, 35 and 40°C for DMSO, 25°C for DMA and DMF and 30°C for DEF under nearly 10 GHz electric field as shown in Table 4.1. The curves of $(\chi_{oij}-\chi'_{ij})/\chi'_{ij}$ against χ''_{ij}/χ'_{ij} at different ω_j 's of solute are plotted from the measured data in Fig 4.1. All the curves show two relaxation times τ_2 and τ_1 due to rotation of the whole molecule and the flexible part attached to the parent ones as evident from Table 4.2. It indicates that the molecules are of non-rigid nature. Unlike τ_2 's, τ_1 's of DMSO at 25, 30, 35 and 40°C decrease gradually (Table 4.2). This indicates that τ_1 's obey the Debye relaxation mechanism. It is also evident from Table 4.2 and Fig. 4.1 that the graphs of $(\chi_{oij}-\chi'_{ij})/\chi'_{ij}$ against χ''_{ij}/χ'_{ij} for different ω_j 's of DMSO shift towards the origin with the increase of temperature. τ_2 's of all the liquids are much larger in magnitude than τ_1 . The parent molecule takes larger time to lag with the electric field frequency for its inertia in comparison to its flexible parts which are supported by the two relaxation model of polar unit under nearly 10 GHz electric field [23]. τ_j 's are estimated and placed in Table 4.2 from eqs. (4.4) and (4.5) using linear slope of χ''_{ij} against χ'_{ij} at different ω_j 's and the ratio of individual slopes of $\chi''_{ij}-\omega_j$ and $\chi'_{ij}-\omega_j$ curves at $\omega_j \rightarrow 0$ of Figs. 4.3 and 4.4 respectively. The values of τ_j from eq. (4.4) are larger than from eq. (4.5). Reported τ 's and τ_j 's calculated from both the Gopala Krishna's method [16] as well as conductivity measurement technique using eqs. (4.25) and (4.26) respectively. The agreement is better from the τ_j 's due to ratio of the individual slopes of $\chi''_{ij}-\omega_j$ and $\chi'_{ij}-\omega_j$ curves at $\omega_j \rightarrow 0$ of Figs. 4.3 and 4.4 because the polar-polar interactions are almost avoided. They are then compared with the reported τ_s and τ_{cs} of the molecules assuming symmetric and asymmetric distribution of relaxation processes only to show that the molecules obey symmetric distribution. The curves χ''_{ij} against χ'_{ij} of Fig. 4.2 of the molecules are found to meet at a point in the region of $0 < \omega_j < 0.02$ except DEF the data was measured at 30 °C. The experimental curves of $\chi''_{ij}-\omega_j$ and $\chi'_{ij}-\omega_j$ are not linear as

shown in Figs. 4.3 and 4.4 respectively. Like $\chi'_{ij}-w_j$ curves all the curves of $\chi''_{ij}-w_j$ of Fig. 4.3 are parabolic in nature and increase with the w_j 's of solute. The magnitude of χ''_{ij} is, however, maximum in lower temperature region and decrease with the rise of temperature. This indicates the absorption of electric energy in the polar–nonpolar mixture in the lower temperature region.

The relative contributions c_1 and c_2 due to τ_1 and τ_2 could, however, be estimated from the χ'_{ij}/χ_{oij} and χ''_{ij}/χ_{oij} of Fröhlich's eqs. (4.8) and (4.9) and placed in Table 4.3 assuming a continuous distribution of τ between limiting values of τ_1 and τ_2 . c_1 and c_2 are also calculated in terms of fixed values of $(\chi'_{ij}/\chi_{oij})_{w_j \rightarrow 0}$ and $(\chi''_{ij}/\chi_{oij})_{w_j \rightarrow 0}$ of the graphical plots of $(\chi'_{ij}/\chi_{oij})-w_j$ and $(\chi''_{ij}/\chi_{oij})-w_j$ curves of Figs. 4.5 and 4.6 respectively. All the curves are extrapolated to get the fixed values of (χ'_{ij}/χ_{oij}) and (χ''_{ij}/χ_{oij}) at $w_j \rightarrow 0$. They are substituted in the Bergmann's eqs. (4.6) and (4.7) to get c_1 and c_2 for the fixed values of τ_1 and τ_2 respectively. All the c 's are placed in Table 4.3 for comparison with Fröhlich's method. Both c_1 and c_2 from Fröhlich's [15] equations are all +ve for all the liquids. But c_2 for DMSO at 25 and 35°C are –ve from the graphical method. The –ve value of c_2 is physically meaningless as they are considered to be the relative contributions towards dielectric relaxation processes. This may indicate that the rotation of whole molecule under hf electric field is not in accord with the flexible part probably due to inertia as observed elsewhere [10,11]. The variation of χ'_{ij}/χ_{oij} and χ''_{ij}/χ_{oij} with w_j as shown in Figs. 4.5 and 4.6 are expected to be concave and convex [10,11] respectively. All the curves of Figs. 4.5 and 4.6 are, however, concave except systems VI ($-\oplus-$) of Fig. 4.6. This type of anomalous behaviour in the variation of χ'_{ij}/χ_{oij} and χ''_{ij}/χ_{oij} with w_j invariably demands careful measurement of data in low concentration region.

The dipole moments μ_1 and μ_2 are also calculated from the slope β_1 of $\chi'_{ij}-w_j$ curve of Fig. 4.4 and estimated τ_1 and τ_2 as shown in Table 4.4. They are compared with μ_j 's from τ_j 's of eqs. (4.4) and (4.5) respectively. μ_j 's from Gopala Krishna's method [16] and conductivity measurement technique [9] are also reported and placed in Table 4.4 for comparison among them. The total hf conductivity σ_{ij} is plotted against w_j 's of the polar–nonpolar liquid mixture as seen in Fig. 4.7 only to show that all the curves are parabolic in nature exhibiting maximum conductivity at lower temperature and higher concentration for DMSO. At $w_j \rightarrow 0$, the curves are found to yield different value of σ_{ij} probably due to the term $1/(M_j T)$ in the eq. (4.28) as seen in Fig. 4.7. The difference in estimated μ_2 and μ_1 from conductivity and susceptibility measurements suggests the involvement of bound molecular charges towards

μ 's of polar liquid. It is evident from Table 4.4 that μ_1 's of the polar liquids are found to be in excellent agreement with the reported μ 's. It thus reveals that a part of the molecule is rotating under 10 GHz electric field as observed earlier [24]. The variation of μ_1 and μ_2 with temperature for DMSO is given by eq. (4.10). The convex nature of μ_1 - t equation reveals the fact that the molecule DMSO attains higher asymmetry of larger μ_1 at a certain temperature. It also shows zero dipole moments at two different temperatures indicating the symmetric nature of the molecule. The variation of μ_1 with temperature may occur due to elongation of bond moments. This further invites the extensive study of the relaxation phenomena of highly nonspherical dipolar molecules at different experimental temperatures and in different solvents.

The theoretical dipole moment μ_{theo} 's of the polar molecules are calculated assuming the planar structure from the available bond moments of 7.83×10^{-30} C.m., 5.17×10^{-30} C.m. for polar groups $\text{S} \leftarrow \text{CH}_3$, $\text{O} \leftarrow \text{S}$ in DMSO 2.13×10^{-30} C.m., 2.60×10^{-30} C.m., 1.23×10^{-30} C.m. of $\text{N} \leftarrow \text{CH}_3$, $\text{N} \leftarrow \text{C}_2\text{H}_5$, $\text{CH}_3 \leftarrow \text{C}$ in DMF, DEF and DMA respectively. The other bond moments are 1×10^{-30} C.m., 1.50×10^{-30} C.m., 10.33×10^{-30} C.m. for $\text{C} \leftarrow \text{H}$, $\text{C} \leftarrow \text{N}$ and $\text{C} \leftarrow \text{O}$ in them. The bond moments are, however, reduced by a factor μ_1/μ_{theo} to yield exact μ 's as sketched in Fig. 4.8. The reduction or elongation in bond moments of the substituent polar groups may occur due to inductive, mesomeric and electromeric effects which in turn subsequently act as pusher or puller of electrons in them. The solvent C_6H_6 is a cyclic and planar compound and has three double bonds and six p -electrons on six C-atoms. The dipolar liquid molecules are aliphatic and planar ones. Hence π - π interaction or resonance effect combined with inductive effect commonly known as mesomeric effect in excited state called the electromeric effect may play the vital role in the estimation of μ_{theo} 's of Fig. 4.8.

The thermodynamic energy parameters like enthalpy of activation ΔH_τ entropy of activation ΔS_τ and free energy of activation ΔF_τ of DMSO were calculated from the slope and intercept of $\ln(\tau_1 T)$ against $(1/T)$ of eq. (4.11) on the basis of Eyrings theory considering the rotation of the polar molecule as a rate process. Unlike $\ln(\tau_2 T)$ against $(1/T)$; $\ln(\tau_1 T)$ against $(1/T)$ of DMSO is in accord with the Eyring's rate theory [20]. The value of ΔH_τ for DMSO is 6.85 in KJ mole^{-1} ΔS_τ are -8.21 , -8.15 , -11.65 , -11.48 in $\text{J mole}^{-1} \text{K}^{-1}$ and ΔF_τ are 9.30 , 9.32 , 10.43 and 10.45 . at 25 , 30 , 35 and 40°C respectively in KJ mole^{-1} . It is observed that ΔS_τ are $-ve$ indicating the activated states are more ordered than the normal states especially for DMSO.

4.6. CONCLUSION

The study of relaxation phenomena of aprotic polar liquids of amides in C_6H_6 in terms of the modern established symbols of dielectric terminologies and parameters of orientational susceptibilities χ_{ij} 's measured under a single frequency electric field is very encouraging and interesting. It seems to be more topical, significant and useful contribution to predict the conformational structures and various molecular associations of the molecules at any given temperatures. The intercept and slope of derived linear eq.(4.3) on the measured data of χ_{ij} of different ω_j 's are used to get τ_2 and τ_1 . The prescribed methodology in S I units is superior because of the unified, coherent and rationalised nature because χ_{ij} 's are directly linked only with orientational polarization of the molecules. The significant eqs (4.4) and (4.5) to obtain values of τ_j and hence values of μ_j from eq. (4.22) help the future workers to shed more light on the relaxation phenomena of complicated nonspherical polar liquids and liquid crystals. The present method to obtain values of τ_j from eq.(4.5) with the use of the ratio of the individual slopes of χ''_{ij} versus ω_j and χ'_{ij} versus ω_j curves at $\omega_j \rightarrow 0$ is a significant improvement over the existing ones, as it eliminates polar-polar interaction almost completely in τ_j 's and μ_j 's respectively.

The values of τ_j and μ_j are usually claimed to be accurate within 10% and 5% respectively. The tested correlation coefficients r 's and % of errors of eq.(4.3) demand that τ and μ are more than accurate. The DMSO, DMF, DMA and DEF molecules absorb electric energy much more strongly under nearly 10 GHz electric field, at which the variation of χ''_{ij} against frequency ω seem to be large. This at once indicates the attention to get the double relaxation phenomena from eq.(4.3). The sum of the experimental and theoretical values of weighted contributions c_1 and c_2 towards dielectric dispersions due to estimated τ_2 and τ_1 differ significantly to indicate more than two Debye type relaxations in such molecules because of their complexity. It can, further, be observed that only a part of the molecule is rotating under nearly 10 GHz electric field since $\ln(\tau_1 T)$ against $1/T$ obeys the Eyring's rate theory. The values of μ_2 and μ_1 due to τ_2 and τ_1 are expected to be smaller when they are measured from susceptibility measurement technique rather than the hf conductivity and permittivity methods, where approximation of $\sigma_{ij} \approx \sigma'_{ij}$ is usually made. The measurement of μ 's from hf conductivities σ_{ij} 's and hf permittivities ϵ_{ij} 's is involved with the contributions of the bound molecular charges and all types of polarisations including the fast one. The difference

of μ_1 and μ_j from μ_{theo} may arise, either by elongation or reduction of the bond moments of the substituted polar groups by factor μ_1/μ_{theo} in agreement with the measured μ 's to take into account of the inductive, mesomeric and electromeric effects of the substituted polar groups in the molecules under investigation. Thus the correlation between the conformational structures with the observed results enhances the scientific content to add a new horizon of understanding the existing knowledge of dielectric relaxation phenomena.

Table 4.1: The real χ'_{ij} and imaginary χ''_{ij} , parts of the complex dielectric orientational susceptibility χ_{ij}^* and static dielectric susceptibility χ_{oij} which is real for various weight fractions w_j 's of some aprotic polar liquids in benzenes at different temperatures under hf electric field.

System with sl. no	Temp. in °C	Weight fraction w_j	χ'_{ij}	χ''_{ij}	χ_{oij}
I. DMSO	25	0.0022	0.0611	0.0280	0.0731
		0.0043	0.0890	0.0420	0.1094
		0.0047	0.0950	0.0460	0.1181
		0.0069	0.1231	0.0616	0.1594
		0.0086	0.1520	0.0798	0.1982
II. DMSO	30	0.0022	0.0630	0.0274	0.074
		0.0043	0.0915	0.0400	0.1095
		0.0047	0.0980	0.0440	0.1220
		0.0069	0.1155	0.0526	0.1500
		0.0086	0.1340	0.0648	0.1802
III. DMSO	35	0.0022	0.0600	0.0234	0.0693
		0.0043	0.0800	0.0330	0.108
		0.0047	0.0825	0.0360	0.1135
		0.0069	0.1104	0.0496	0.1564
		0.0086	0.1260	0.0580	0.1830
IV. DMSO	40	0.0022	0.0499	0.0170	0.0648
		0.0043	0.0774	0.0282	0.1054
		0.0047	0.0784	0.0286	0.1094
		0.0069	0.1083	0.0420	0.1541
		0.0086	0.1155	0.0500	0.1775
V. DEF	30	0.0023	0.0850	0.0256	0.1137
		0.0042	0.0899	0.0288	0.1335
		0.0079	0.0997	0.0384	0.1822
		0.0095	0.1033	0.0448	0.2053
VI. DMF	25	0.0027	0.0742	0.0256	0.0948
		0.0036	0.0872	0.0302	0.1162
		0.0048	0.1045	0.0386	0.1423
		0.0063	0.1291	0.0484	0.1855
VII. DMA	25	0.0026	0.0818	0.0213	0.1201
		0.0045	0.1046	0.0278	0.1559
		0.0056	0.1198	0.0330	0.1851
		0.0066	0.1370	0.0381	0.2083

Table 4.2: The relaxation times τ_2 and τ_1 from the slope and intercept of straight line eq. (4.3), measured τ_j from different methods of susceptibility and conductivity measurement technique, reported τ , symmetric and characteristic relaxation times τ_s and τ_{cs} for different aprotic polar liquids under effective dispersive region of nearly 10 GHz electric field.

System	Temp in °C	Estimated		τ_j^a in ps	τ_j^b in ps	τ_j^c in ps	τ_j^d in ps	Rept* τ_j in ps	τ_s in ps	τ_{cs} in ps
		τ_1	τ_2							
I. DMSO	25	8.09	21.07	9.91	6.79	8.77	6.01	5.37	4.88	3.69
II. DMSO	30	7.51	52.02	9.07	6.34	8.04	5.86	4.96	4.82	3.05
III. DMSO	35	6.50	59.68	9.08	9.03	7.47	8.95	4.70	4.21	--
IV. DMSO	40	4.51	39.00	8.38	4.90	7.09	4.46	4.33	3.74	22.20
V. DEF	30	3.89	76.41	16.86	1.06	6.64	0.58	2.42	4.16	15.66
VI. DMF	25	4.60	56.24	6.73	6.69	5.87	5.58	5.09	3.02	8.47
VII. DMA	25	2.20	56.61	3.05	6.53	4.96	3.11	6.53	3.90	81.95

τ_j^a = relaxation time from direct slope of eq (4.4)

τ_j^b = relaxation time from ratio of individual slope of eq (4.5)

τ_j^c = relaxation time from direct slope of eq (4.25)

τ_j^d = relaxation time from ratio of individual slope of eq (4.26)

* reported τ_j by using Gopalakrishna's [16] method.

Table 4.3: Fröhlich's parameter $A [= \ln(\tau_2/\tau_1)]$, theoretical and experimental values of χ'_{ij}/χ_{oij} & χ''_{ij}/χ_{oij} of Fröhlich eqs (4.8) and (4.9) and from fitting eqs of Figs 4.5 and 4.6 at $\omega_j \rightarrow 0$ respectively, theoretical and experimental relative contributions c_1 and c_2 towards dielectric dispersion due to τ_1 and τ_2 , symmetric and asymmetric distribution parameters γ and δ for polar-nonpolar liquid mixtures of some aprotic polar liquids under effective dispersion region of nearly 10 GHz electric field.

System	Temp in °C	A	Theoretical values of χ'_{ij}/χ_{oij} & χ''_{ij}/χ_{oij} from eqs (4.8) & (4.9)		Theoretical values of c_1 and c_2		Experimental values of χ'_{ij}/χ_{oij} & χ''_{ij}/χ_{oij} at $\omega_j \rightarrow 0$ of Figs. 4.5 & 4.6		Experimental values of c_1 and c_2		Estimated values of γ and δ	
			c_1	c_2	c_1	c_2	c_1	c_2	γ	δ		
I. DMSO	25	0.957	0.629	0.466	0.485	0.571	0.874	0.380	1.095	-0.061	-0.07	2.00
II. DMSO	30	1.935	0.449	0.434	0.423	0.933	0.894	0.389	1.049	0.022	-0.08	2.37
III. DMSO	35	2.217	0.454	0.419	0.425	1.043	1.039	0.371	1.192	-0.076	-0.29	--
IV. DMSO	40	2.241	0.611	0.409	0.507	0.794	0.797	0.266	0.803	0.228	0.21	0.36
V. DEF	30	2.978	0.476	0.378	0.443	1.380	0.849	0.247	0.890	0.210	0.17	0.36
VI. DMF	25	2.505	0.497	0.405	0.451	1.086	0.855	0.262	0.921	0.065	0.13	0.61
VII. DMA	25	3.248	0.601	0.357	0.531	1.093	0.724	0.185	0.713	0.338	0.47	0.18

Table 4.4: Slope β_1 of χ'_{ij} vs ω_j and β_2 of σ_{ij} vs ω_j curves, measured dipole moments μ_2 and μ_1 from susceptibility measurement technique, μ_j 's from Eqs.(22) and (29) respectively, reported dipole moment, theoretical dipole moment μ_{theo} from available bond angles and bond moments expressed in Coulomb.metre (C.m) and the values of μ_1 / μ_{theo} for some aprotic polar liquids in benzene under effective dispersion region of nearly 10 GHz electric field.

System with sl.no. & mol.wt.	Slope of χ'_{ij} - ω_j & σ_{ij} - ω_j curves		Dipole moments μ_j (x 10 ⁻³⁰) in Coulomb.metre								$\frac{\mu_1}{\mu_{theo}}$	
			From Eq (22)		μ_j^a	μ_j^b	μ_j^c	μ_j^d	μ_j^r	μ_{theo}		
			μ_2	μ_1								
I.DMSO at 25 ^o C $M_j = 0.078$ Kg	β_1	β_2										
	10.943	6.280	14.69	10.30	10.75	10.03	11.10	10.48	12.65	15.18	0.67	
II.DMSO at 30 ^o C $M_j = 0.078$ Kg	16.440	9.096	36.69	12.64	13.09	12.35	13.31	12.75	12.79	15.18	0.83	
III.DMSO at 35 ^o C $M_j = 0.078$ Kg	8.950	4.621	31.09	9.27	9.79	9.78	9.50	9.82	13.49	15.18	0.61	
IV.DMSO at 40 ^o C $M_j = 0.078$ Kg	17.646	9.894	30.37	12.69	13.70	12.82	13.94	13.32	13.73	15.18	0.83	
V.DEF at 30 ^o C $M_j = 0.101$ Kg	2.870	2.922	26.62	5.67	7.91	5.53	8.18	7.58	12.96	13.30	0.42	
VI.DMF at 25 ^o C $M_j = 0.073$ Kg	10.938	7.282	33.21	9.37	9.81	9.80	10.54	10.48	12.09	12.73	0.74	
VII.DMA at 25 ^o C $M_j = 0.087$ Kg	5.147	2.792	24.97	6.83	7.07	6.89	7.00	6.81	11.26	13.37	0.51	

μ_j^a = dipole moment by using τ from the direct slope of Eq (4)

μ_j^b = dipole moment by using τ from the ratio of individual slopes of Eq (5)

μ_j^c = dipole moment by using τ from the direct slope of Eq (25)

μ_j^d = dipole moment by using τ from the ratio of individual slopes of Eq (26)

μ_j^r = reported dipole moment using Gopalakrishna's¹⁶ τ

μ_{theo} = theoretical dipole moment from the available bond moments.

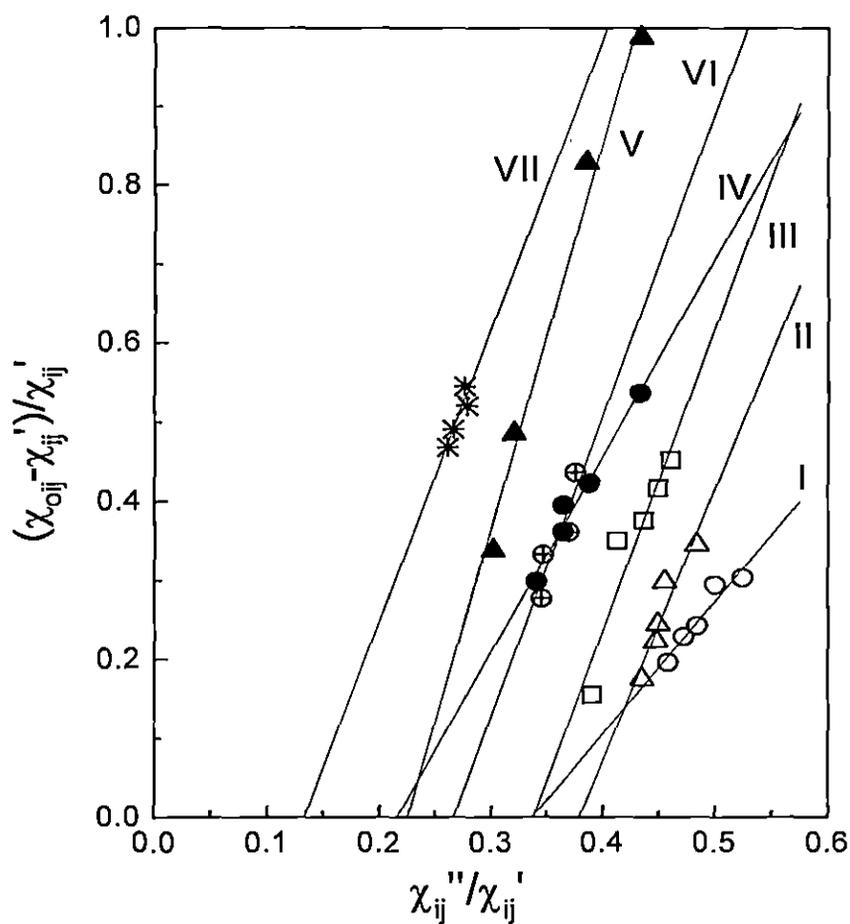


Fig. 4.1: Linear Plot of $(\chi_{oij} - \chi'_{ij}) / \chi'_{ij}$ against χ''_{ij} / χ'_{ij} for different w_j 's of DMSO, DEF, DMF and DMA in benzene.

(I) DMSO at 25 °C (-o-), (II) DMSO at 30 °C (-Δ-), (III) DMSO at 35 °C (-□-), (IV) DMSO at 40 °C (-●-), (V) DEF at 30 °C (-▲-), (VI) DMF at 25 °C (-⊕-) and (VII) DMA at 25 °C (-*-).

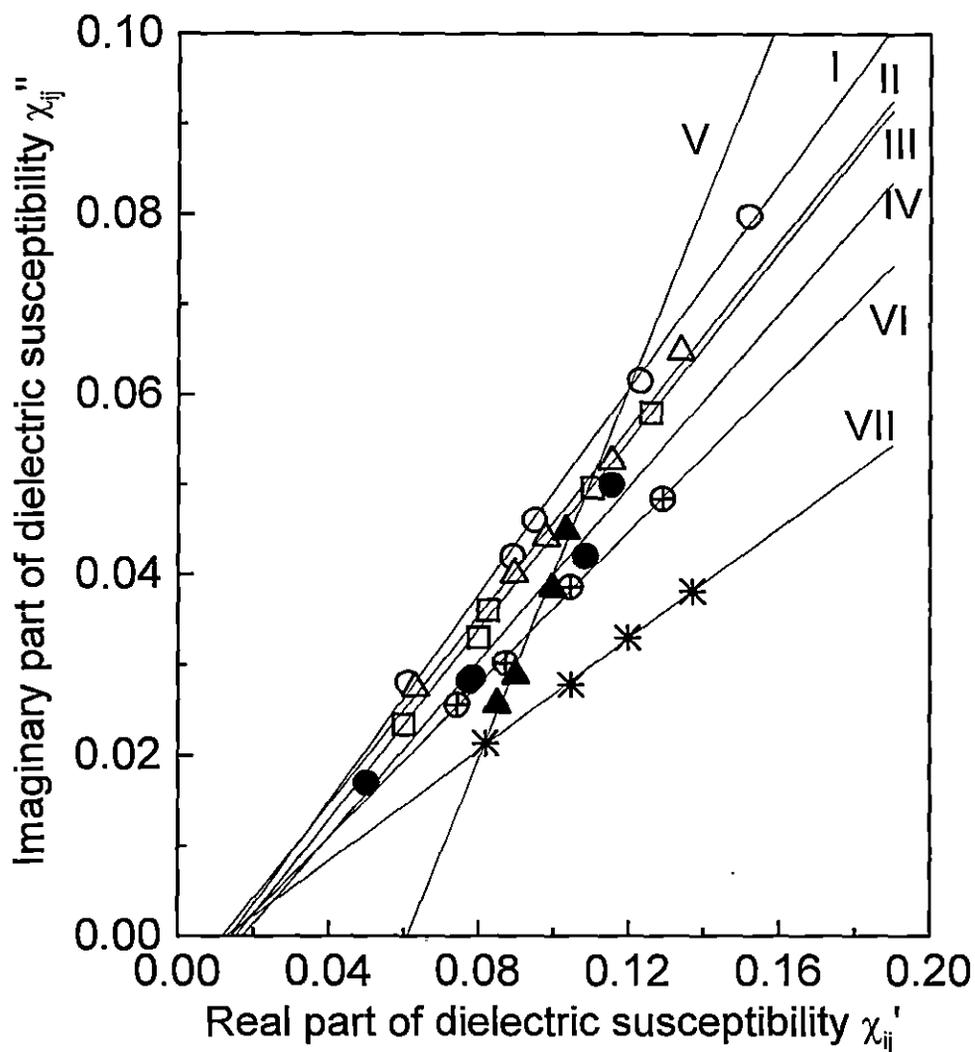


Fig. 4. 2: Linear variation of imaginary part of dielectric susceptibility χ''_{ij} against real part of dielectric susceptibility χ'_{ij} for different ω_j 's of DMSO, DEF, DMF and DMA in benzene.

(I) DMSO at 25 °C (-o-), (II) DMSO at 30 °C (-Δ-), (III) DMSO at 35 °C (-□-), (IV) DMSO at 40 °C (-●-), (V) DEF at 30 °C (-▲-), (VI) DMF at 25 °C (-⊕-) and (VII) DMA at 25 °C (-*-).

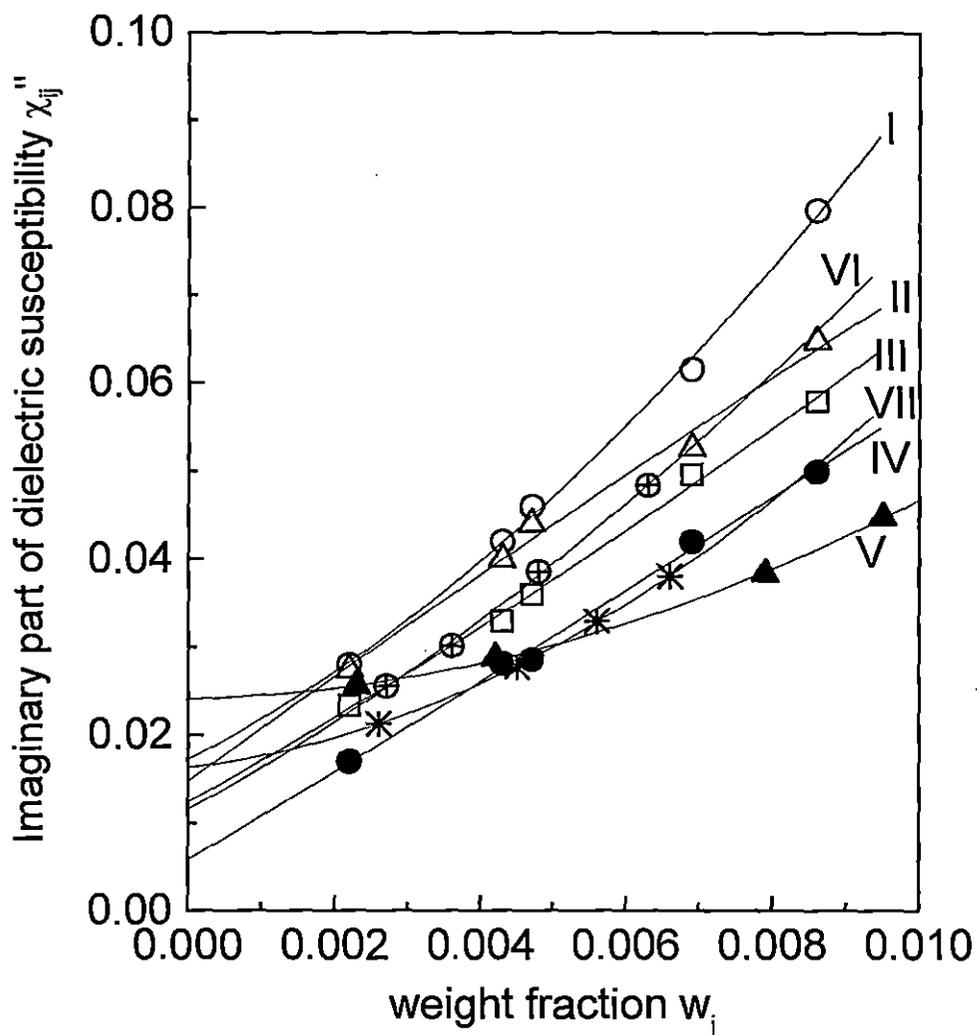


Fig. 4. 3: Plot of imaginary part of dielectric susceptibility χ''_{ij} with weight fraction w_j of DMSO, DEF, DMF and DMA in benzene.

(I) DMSO at 25 °C (-○-), (II) DMSO at 30 °C (-△-), (III) DMSO at 35 °C (-□-), (IV) DMSO at 40 °C (-●-), (V) DEF at 30 °C (-▲-), (VI) DMF at 25 °C (-⊕-) and (VII) DMA at 25 °C (-*-).

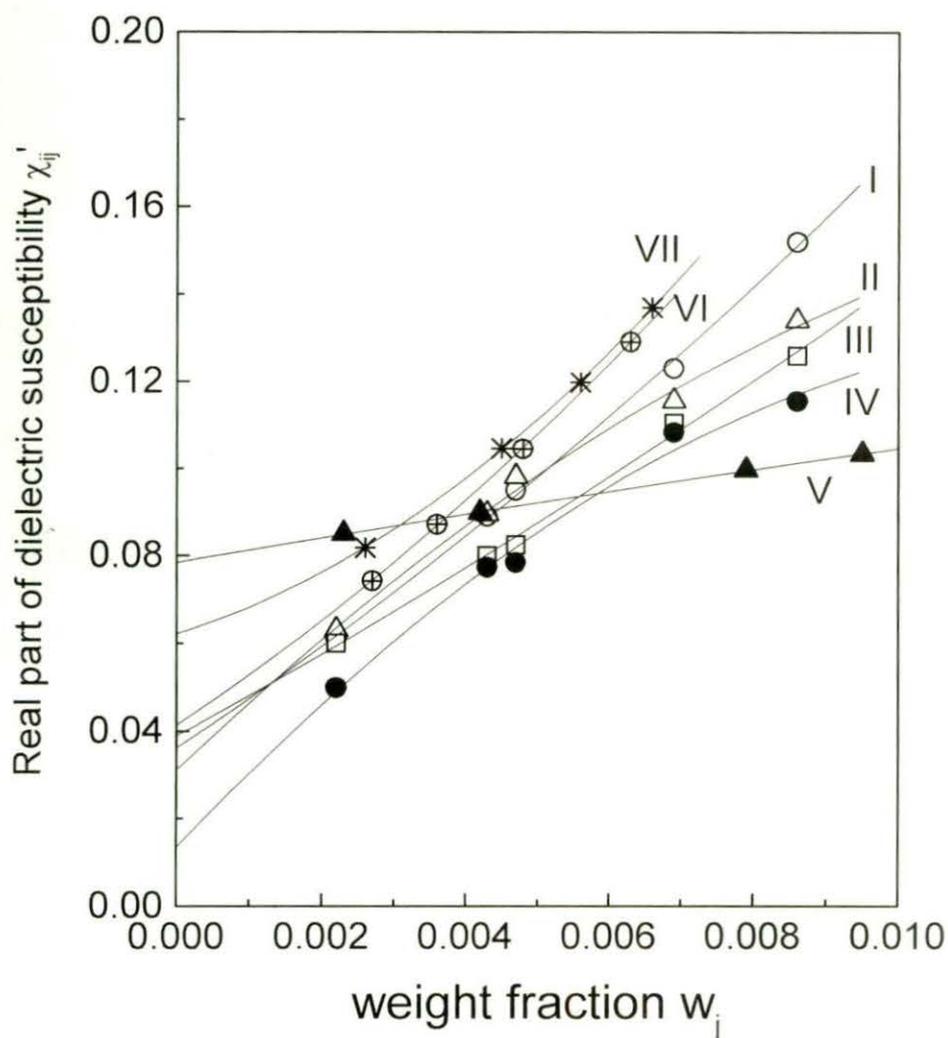


Figure 4.4. Plot of real part of dielectric susceptibility χ'_{ij} with weight fraction w_j of DMSO, DEF, DMF and DMA in benzene.

(I) DMSO at 25 °C (-○-), (II) DMSO at 30 °C (-△-), (III) DMSO at 35 °C (-□-), (IV) DMSO at 40 °C (-●-), (V) DEF at 30 °C (-▲-), (VI) DMF at 25 °C (-⊕-) and (VII) DMA at 25 °C (-*-).

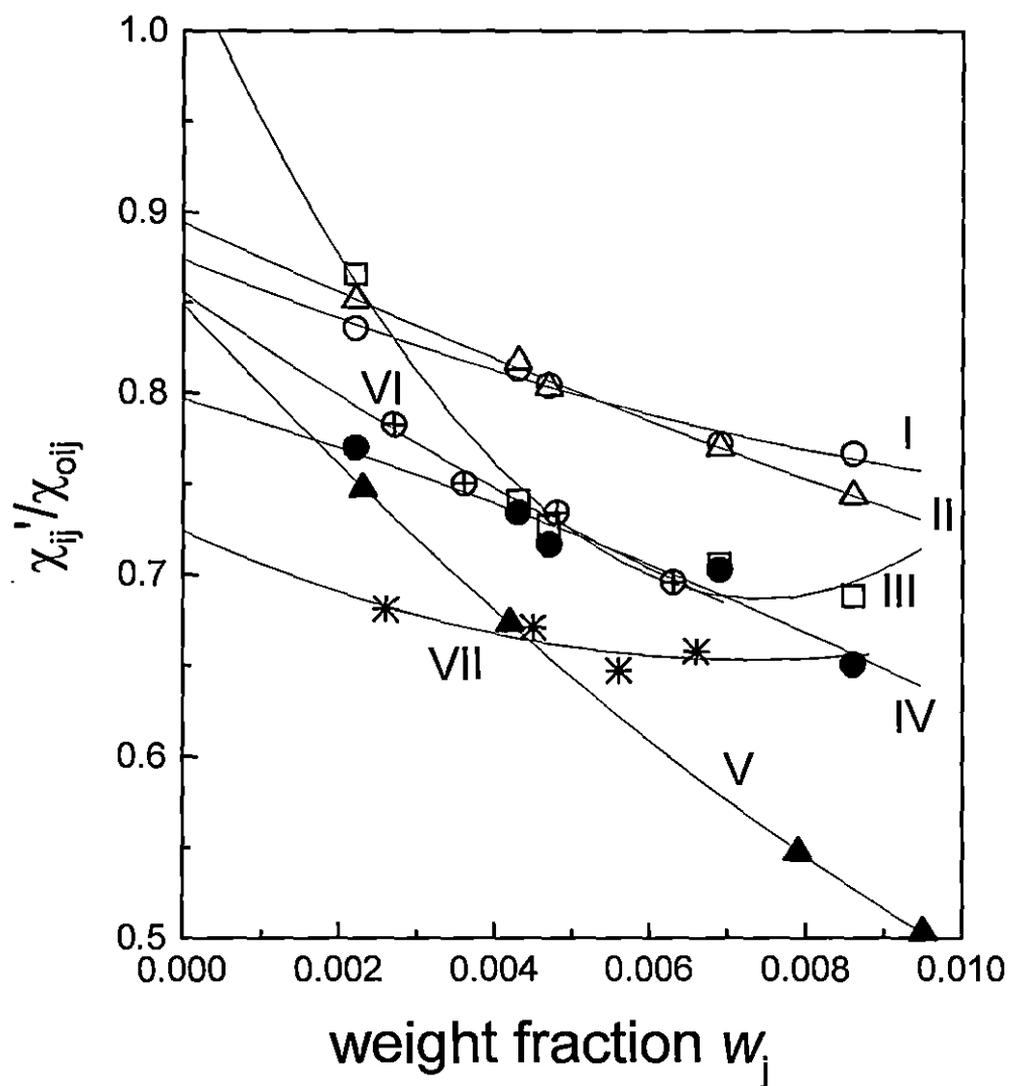


Fig. 4.5: Variation of χ'_{ij}/χ_{oij} with w_j 's of DMSO, DEF, DMF and DMA in benzene. (I) DMSO at 25 °C (-o-), (II) DMSO at 30 °C (-Δ-), (III) DMSO at 35 °C (-□-), (IV) DMSO at 40 °C (-●-), (V) DEF at 30 °C (-▲-), (VI) DMF at 25 °C (-⊕-) and (VII) DMA at 25 °C (-*-).

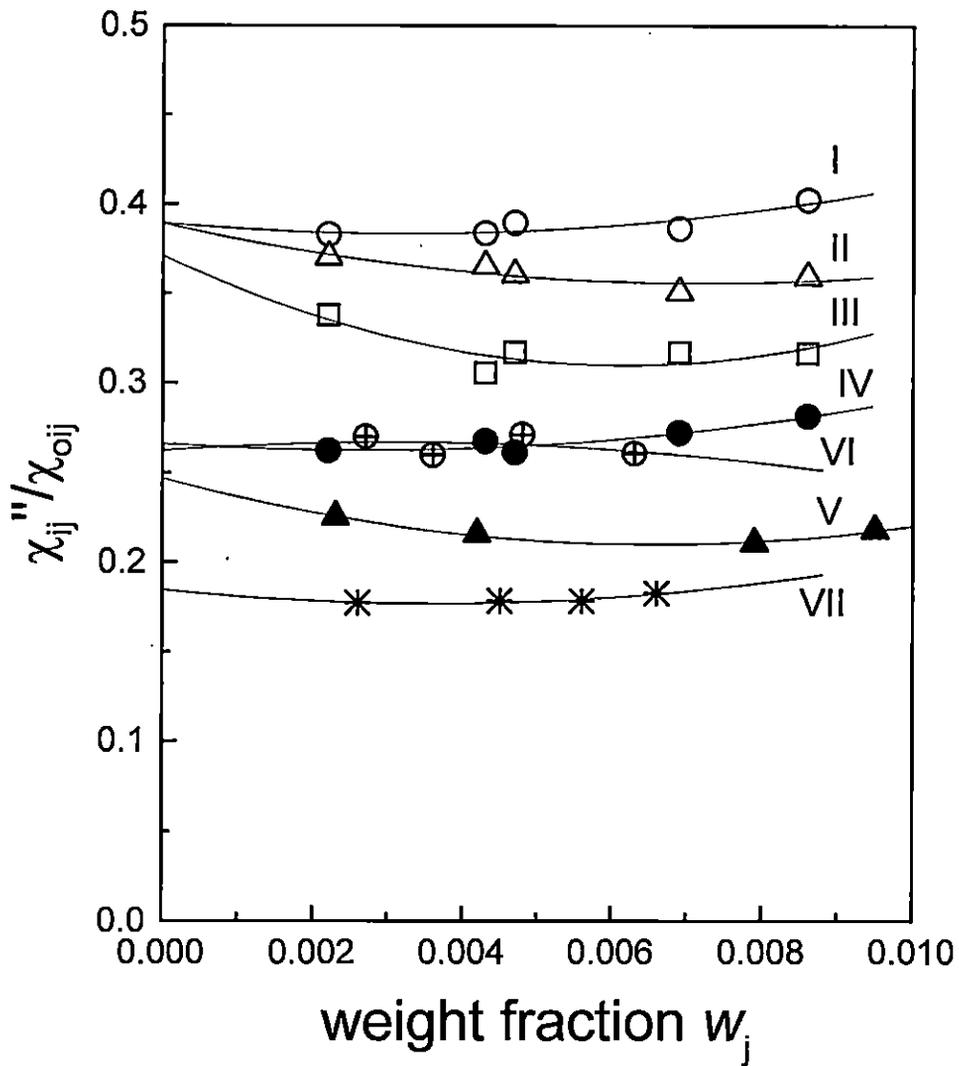


Fig. 4. 6: Variation of χ''_{ij}/χ'_{oij} with w_j 's of DMSO, DEF, DMF and DMA in benzene. (I) DMSO at 25 °C (-o-), (II) DMSO at 30 °C (-Δ-), (III) DMSO at 35 °C (-□-), (IV) DMSO at 40 °C (-●-), (V) DEF at 30 °C (-▲-), (VI) DMF at 25 °C (-⊕-) and (VII) DMA at 25 °C (-*-).

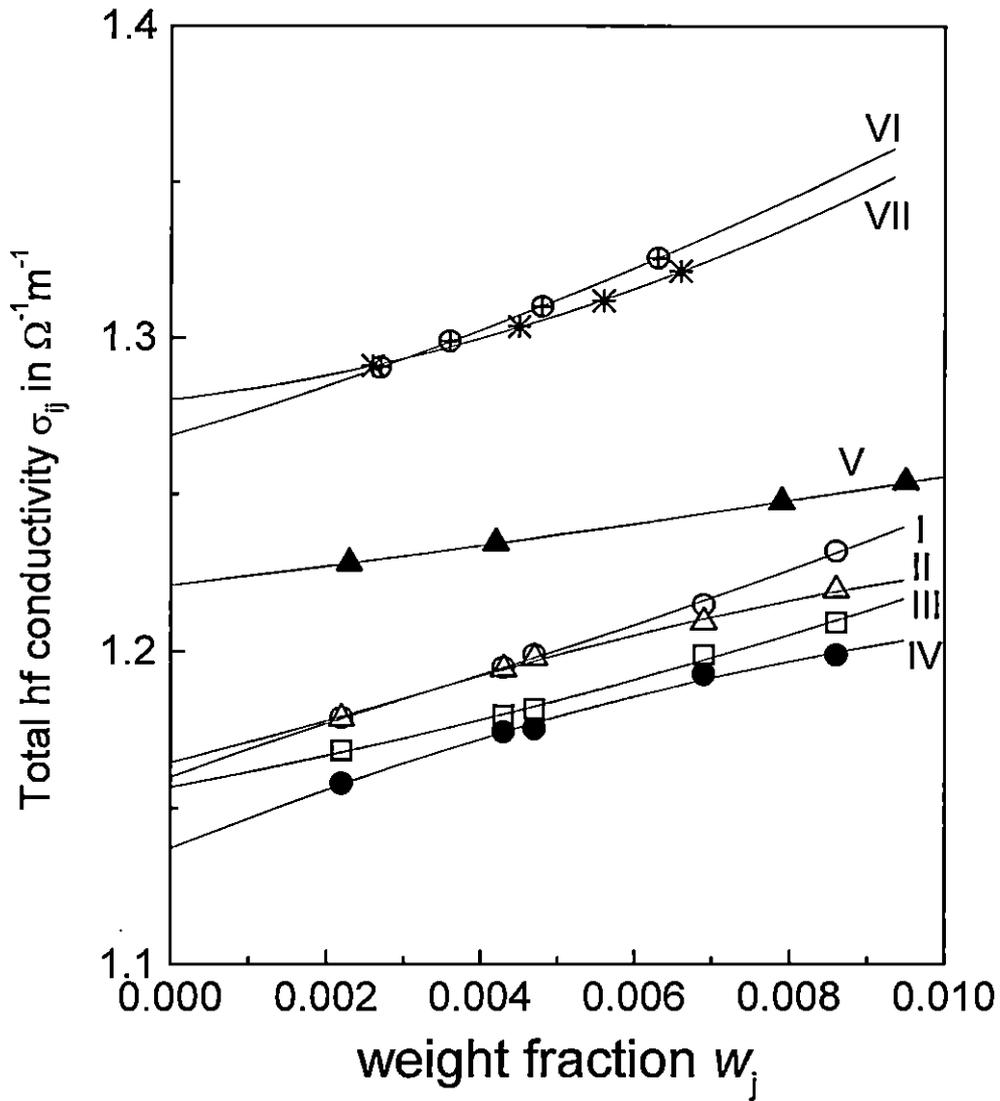


Fig. 4. 7: Variation of total hf conductivity σ_{ij} with w_j 's of DMSO, DEF, DMF and DMA in benzene.

(I) DMSO at 25 °C (-o-), (II) DMSO at 30 °C (-Δ-), (III) DMSO at 35 °C (-□-), (IV) DMSO at 40 °C (-●-), (V) DEF at 30 °C (-▲-), (VI) DMF at 25 °C (-⊕-) and (VII) DMA at 25 °C (-*-).

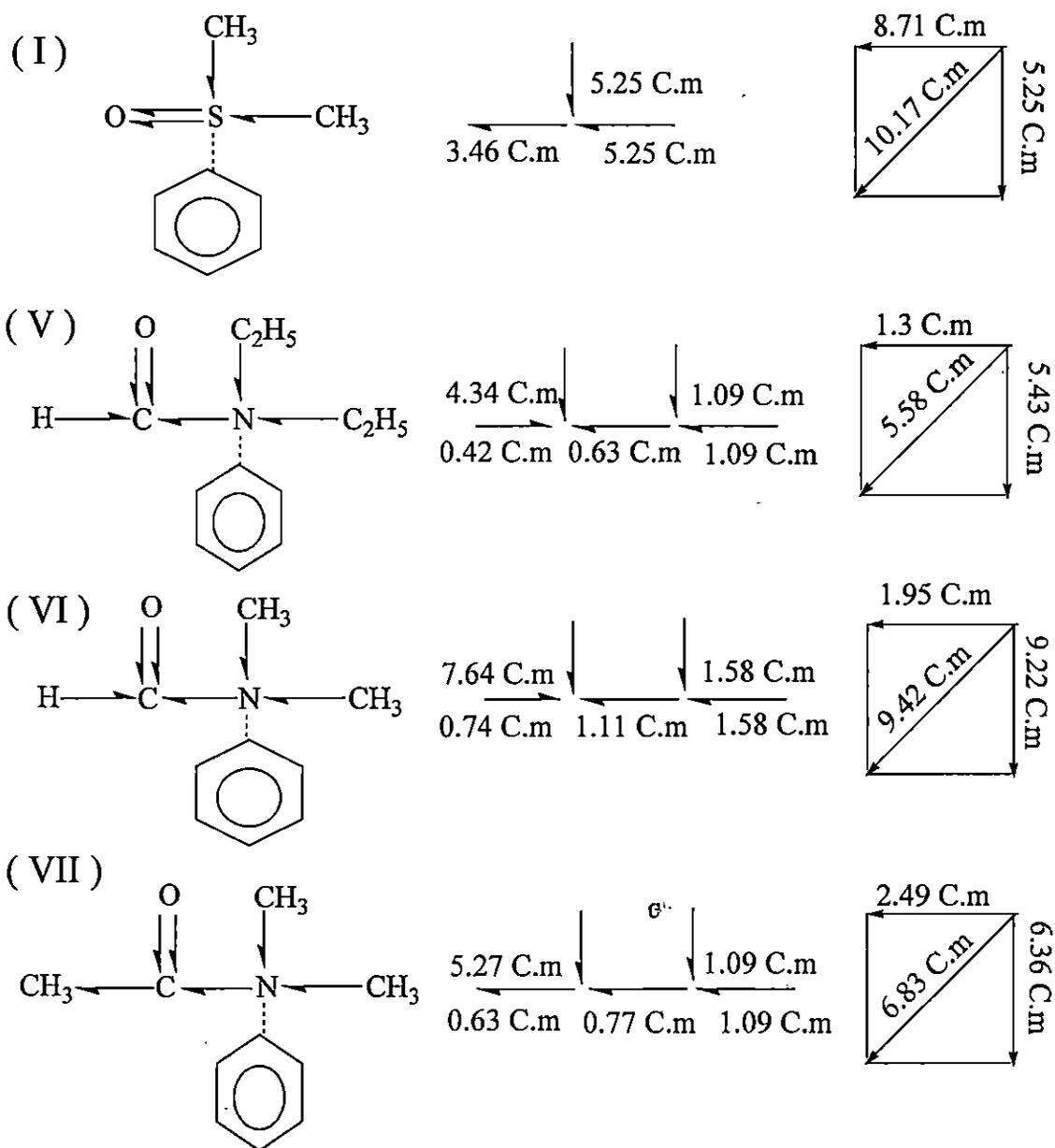


Fig. 4. 8: Conformational structures of aprotic polar liquids in terms of reduced bond length due to mesomeric and inductive moments in Coulomb metre (C.m.) $\times 10^{30}$ of the substituent polar groups:

(I) DMSO (II) DEF (III) DMF (IV) DMA

REFERENCES

- [1] S M Puranik, R Y Ghanabhadur, S N Helambe & S C Mehrotra, *Indian J Pure & Appl Phys* **29** (1991) 251
- [2] M B R Murthy, B S Dayasagar and R L Patil *Pramana J. Phys* **61** (2003) 725
- [3] K K Gupta, A K Bansal, P J Singh & K S Sharma, *Indian J Pure & Appl Phys* **42** (2004) 849
- [4] L J Onsager. *Am. Chem.Soc.* **58** (1936) 1485
- [5] K Dutta, S K Sit and S Acharyya, *Pramana J. Phys* **57** (2001) 775
- [6] N Ghosh, A Karmakar, S K Sit & S Acharyya, *Indian J Pure & Appl Phys* **38** (2000) 574
- [7] J S Dhull, D R Sharma and K N Laxminarayana, *Indian J.Phys* **B56** (1982) 334
- [8] A Sharma and D R Sharma, *J. Phys. Soc (Japan)* **61** (1992) 1049
- [9] S K Sit, K Dutta , S Acharyya, T Pal Majumder and S Roy, *J.Mole Liquids* **89** (2000) 111
- [10] S K Sit, N Ghosh, U Saha and S Acharyya, *Indian J. Phys* **71B** (1997) 533
- [11] U Saha, S K Sit, R C Basak and S Acharyya, *J. PhysD: Appl Phys* (London) **27** (1994) 596
- [12] S K Sit, R C Basak, U Saha and S Acharyya, *J. PhysD: Appl Phys* (London) **27**(1994) 2194
- [13] A K Jonscher, *Inst. Phys. Conference* Serial No. 58, Invited paper presented at physics of dielectrics Solids 8 – 11 (1980)
- [14] T Pal Majumder, *Ph.D thesis* (1996) Jadavpur University, Kolkata
- [15] K Bergmann, D M Roberti and C.P Smyth, *J. Phys. Chem* **64** (1960) 665
- [16] K V Gopalakrishna, *Trans Faraday Soc.* **53** (1957) 767
- [17] H Fröhlich, "*Theory of Dielectrics*" (Oxford university press) 1949
- [18] M B R Murthy, R L Patil and D K Deshpande, *Indian J. Phys* **B 63** (1989) 491
- [19] K Dutta, A Karmakar, L Dutta, S K Sit & S Acharyya, *Indian J Pure & Appl Phys* **40** (2002) 801
- [20] N E Hill, W E Vaughan, A H Price and M Davis " *Dielectric properties and Molecular Behaviour*" Van Nostrand Reinhold company Ltd (London), 1969
- [21] C P Smyth, "*Dielectric Behaviour and Structure*" (New York; Mc Graw Hill) 1955
- [22] K Dutta, A Karmakar, S K Sit & S Acharyya, *Indian J Pure & Appl Phys* **40** (2002) 588
- [23] S K Sit and S Acharyya, *Indian j. pure & appl. Phys* **34** (1996) 255
- [24] R C Basak, S K Sit and S Acharyya, *Indian J. Phys.* **B70** (1996) 37

CHAPTER 5

THE PHYSICO-CHEMICAL ASPECTS OF SOME LONG STRAIGHT CHAIN
ALCOHOLS FROM SUSCEPTIBILITY MEASUREMENT UNDER A 24 GHz
ELECTRIC FIELD AT 25⁰C

5. THE PHYSICO-CHEMICAL ASPECTS OF SOME LONG STRAIGHT CHAIN ALCOHOLS FROM SUSCEPTIBILITY MEASUREMENT UNDER A 24 GHz ELECTRIC FIELD AT 25°C

5.1 INTRODUCTION

The relaxation process of dipolar liquid or solid material (DRL or DRS) is very encouraging to study the physico-chemical molecular behaviour and structures through the different experimental techniques [1,2]. The methods consist of the measurements of high frequency (hf) conductivity [3], hf susceptibility [4], thermally stimulated depolarization current density (TSDC) [5], isothermal frequency domain of AC spectroscopy (IFDS) [6] etc. Although the latter two methods are very important as they provide one with the necessary information of dielectric relaxations, but these methods are very lengthy and often needs a tedious computer simulation work in comparison to the former methods. The hf conductivity or susceptibility measurement techniques are very simpler, straightforward and unique one within the framework of Debye model [7] to give the firm answer to the problem with which the present research group is usually dealing with.

Straight chain alcohols behave almost like polymers in dispersion regions. The strong dipole of -OH group rotates about $>C=O$ bond without disturbing $-CH_3$ and $-CH_2$ groups. They thus have the possibility to exhibit intramolecular as well as intermolecular rotations. Glasser et al [8], and Crossley et al [9], however, measured the real ϵ'_{ij} and imaginary ϵ''_{ij} , parts of hf complex relative permittivity ϵ^*_{ij} along with the static ϵ_{oij} and optical ϵ_{oij} relative permittivities of alcohols at 25°C under different gigahertz electric field frequencies. As evident from Table 5.1 the available relative permittivities ϵ''_{ij} 's if plotted against frequency 'f' will show the sharp peak [10] at 24 GHz electric field frequency. At this resonance frequency the alcohol molecules in solvent n-heptane absorbs electric energy much more strongly to give exact and reliable values of relative permittivities. This at once suggests that 24 GHz electric field frequency is the most effective dispersive region of such normal and octyl alcohols and prompted the present workers to study the physico-chemical aspects of long straight chain alcohols in terms of hf susceptibilities χ'_{ij} , χ''_{ij} and χ_{oij} as the datas are available only at 25°C. The datas are, however, collected in Table 5.1 upto four decimal places. The hf dielectric

susceptibilities could, on the other hand, be obtained by the subtraction of either 1 or infinitely hf permittivity $\epsilon_{\alpha ij}$ from the real part ϵ'_{ij} and static ϵ_{oij} relative permittivities. If 1 is subtracted, the susceptibilities due to all operating polarization processes result, while if $\epsilon_{\alpha ij}$ is subtracted [11], the susceptibility due to only orientational polarization results. The imaginary part χ''_{ij} is numerically equal to ϵ''_{ij} as shown in Table 5.1.

Table-5.1. Measured relative permittivities ϵ'_{ij} , ϵ''_{ij} , ϵ_{oij} , $\epsilon_{\alpha ij}$, real χ'_{ij} , imaginary χ''_{ij} parts of hf complex susceptibility χ^*_{ij} and low frequency susceptibility χ_{oij} of some dipolar alcohols at 25°C for different weight fractions w_j of solutes under 24 GHz electric field in solvent n-heptane.

Systems with Mol.wt(Mj) in Kg.(in n-heptane)	Weight fraction w_j of solute	ϵ'_{ij}	ϵ''_{ij}	ϵ_{oij}	$\epsilon_{\alpha ij}$	χ'_{ij} (= $\epsilon'_{ij} - \epsilon_{\alpha ij}$)	χ''_{ij} (= ϵ''_{ij})	χ_{oij} (= $\epsilon_{oij} - \epsilon_{\alpha ij}$)
I. 1-butanol (Mj= 0.074)	0.0291	1.9570	0.0079	1.9710	1.9280	0.0290	0.0079	0.0430
	0.0451	1.9810	0.0147	2.0000	1.9450	0.0360	0.0147	0.0550
	0.0697	2.0110	0.0236	2.0500	1.9580	0.0530	0.0236	0.0920
	0.1163	2.0600	0.0425	2.1750	1.9780	0.0820	0.0425	0.1970
	0.1652	2.1050	0.0644	2.3810	2.0000	0.1050	0.0644	0.3810
	0.2072	2.1440	0.0818	2.6210	2.0200	0.1240	0.0818	0.6010
II. 1-hexanol (Mj= 0.102)	0.0458	1.9680	0.0131	1.9880	1.9440	0.0240	0.0131	0.0440
	0.0703	1.9840	0.0190	2.0150	1.9520	0.0320	0.0190	0.0630
	0.1028	2.0010	0.0296	2.0640	1.9700	0.0310	0.0296	0.0940
	0.1687	2.0370	0.0425	2.1960	1.9890	0.0480	0.0425	0.2070
	0.2335	2.0880	0.0569	2.3600	2.0020	0.0860	0.0569	0.3580
	0.2901	2.1340	0.0748	2.5800	2.0180	0.1160	0.0748	0.5620
III. 1-heptanol (Mj = 0.116)	0.0564	1.9680	0.0147	1.9850	1.9320	0.0360	0.0147	0.0530
	0.0735	1.9750	0.0182	2.0080	1.9450	0.0300	0.0182	0.0630
	0.1175	2.0070	0.0265	2.0660	1.9570	0.0500	0.0265	0.1090
	0.1909	2.0760	0.0482	2.1950	1.9890	0.0870	0.0482	0.2060
	0.2465	2.0970	0.0567	2.3150	2.0020	0.0950	0.0567	0.3130
	0.2970	2.1260	0.0693	2.4640	2.0080	0.1180	0.0693	0.4560
IV. 1-decanol (Mj = 0.158)	0.0572	1.9650	0.0120	1.9760	1.9400	0.0250	0.0120	0.0360
	0.0857	1.9790	0.0223	2.0030	1.9520	0.0270	0.0223	0.0510
	0.1351	2.0030	0.0273	2.0500	1.9640	0.0390	0.0273	0.0860
	0.2140	2.0360	0.0449	2.1470	1.9900	0.0460	0.0449	0.1570
	0.2640	2.0640	0.0513	2.2200	2.0080	0.0560	0.0513	0.2120
	0.3353	2.0970	0.0637	2.3460	2.0300	0.0670	0.0637	0.3160
V. 2-methyl 3-heptanol (Mj = 0.130)	0.0437	1.9600	0.0156	1.9710	1.9300	0.0300	0.0156	0.0410
	0.1299	2.0220	0.0361	2.0590	1.9660	0.0560	0.0361	0.0930
	0.2522	2.0950	0.0565	2.1720	2.0070	0.0880	0.0565	0.1650
	0.4081	2.1690	0.0809	2.3300	2.0540	0.1150	0.0809	0.2760

Systems with Mol.wt(M _j) in Kg.(in n- heptane)	Weight fraction <i>w_j</i> of solute	ϵ_{ij}'	ϵ_{ij}''	ϵ_{0ij}	$\epsilon_{\alpha ij}$	χ_{ij}' (= $\epsilon_{ij}' -$ $\epsilon_{\alpha ij}$)	χ_{ij}'' (= ϵ_{ij}'')	χ_{0ij} (= $\epsilon_{0ij} -$ $\epsilon_{\alpha ij}$)
VI. 3-methyl 3-heptanol (M _j = 0.130)	0.0450	1.9650	0.0137	1.9740	1.9340	0.0310	0.0137	0.0400
	0.1334	2.0280	0.0393	2.0690	1.9660	0.0620	0.0393	0.1030
	0.2538	2.1030	0.0674	2.1800	2.0040	0.0990	0.0674	0.1760
	0.4085	2.1680	0.0928	2.3340	2.0570	0.1110	0.0928	0.2770
VII. 4-methyl 3-heptanol (M _j = 0.130)	0.0466	1.9640	0.0146	1.9760	1.9360	0.0280	0.0146	0.0400
	0.1326	2.0250	0.0375	2.0650	1.9690	0.0560	0.0375	0.0960
	0.2590	2.1040	0.0616	2.1850	2.0110	0.0930	0.0616	0.1740
	0.4124	2.1800	0.0849	2.3520	2.0650	0.1150	0.0849	0.2870
VIII. 5-methyl 3-heptanol (M _j = 0.130)	0.1228	2.0080	0.0296	2.0480	1.9560	0.0520	0.0296	0.0920
	0.2489	2.0750	0.0511	2.1680	2.0040	0.0710	0.0511	0.1640
	0.3898	2.1480	0.0676	2.3150	2.0400	0.1080	0.0676	0.2750
IX. 4-octanol (M _j = 0.130)	0.1201	2.0000	0.0265	2.0400	1.9480	0.0520	0.0265	0.0920
	0.2445	2.0670	0.0449	2.1480	1.9970	0.0700	0.0449	0.1510
	0.3838	2.1400	0.0659	2.2820	2.0310	0.1090	0.0659	0.2510
X. 2-octanol (M _j = 0.130)	0.1236	2.0010	0.0245	2.0490	1.9540	0.0470	0.0245	0.0950
	0.2479	2.0680	0.0513	2.1950	1.9960	0.0720	0.0513	0.1990
	0.3844	2.1410	0.0680	2.4100	2.0360	0.1050	0.0680	0.3740

The commercially available alcohols were dried over anhydrous calcium sulphate and fractionally distilled . The portions were collected with their known boiling points before use. The solvent n-heptane was dried over sodium wire prior to its use to make solutions. The real ϵ'_{ij} and the imaginary ϵ''_{ij} parts of the hf complex relative permittivity ϵ^*_{ij} of the solutions were measured by an apparatus as described elsewhere [9,11] with a Boonton RX meter corrected by a hetrodyne beat method. The refractive index n_{Dij} (where $n^2_{Dij} = \epsilon_{\alpha ij}$) of the solutions was measured by Pulfrich refractometer using the sodium D line [11]. This may introduce some errors in the desired results. The weight fractions w_j 's is given by .

$$w_j = \frac{f_j M_j}{f_i M_i + f_j M_j} \quad (5.1)$$

in terms of mole fractions f_j 's of all the alcohols are defined [12] as the weight of the solute per unit weight of the solution upto four decimal places in Table 5.1.

All the alcohols may be supposed to possess three relaxation times. They may be attributed to the rotation of $-OH$ group, orientational motion of the molecular species while the 3rd one is associated with the hydrogen bonded structures. All these long straight chain hydrogen bonded polymer type dipolar alcohol molecules have wide applications in the fields of biological research, medicine and industry. Moreover, they can be used as good solvents to clean the desired parts of the instruments, in lubrication chemistry, viscosity modifiers, in the preparation of emulsifying agent, waxes etc.

Bergmann et al [13] proposed a graphical method to obtain τ_1 and τ_2 for a pure polar liquid. The respective weighted contributions c_1 and c_2 towards dielectric relaxations for τ_1 and τ_2 were also estimated. The single frequency measurement to get the double relaxation times is not a reliable one. Bhattacharyya et al [14] subsequently attempted to get τ_1 , τ_2 and c_1 , c_2 for a polar liquid from the relative permittivity measurements at least at two different frequencies in GHz range. The graphical analysis made by Higashi et al [15] on polar-nonpolar liquid mixtures suffers from a crude approximation.

Saha et al [16] and Sit et al [17], however, advanced an analytical treatment to study the single frequency measurements of the double relaxation times τ_1 and τ_2 from the measured relative permittivities. The object of the present paper is to detect τ_1 and τ_2 and hence to measure μ_1 and μ_2 using χ_{ij} 's. The aspect of molecular orientational polarization is, however, achieved by χ_{ij} 's because ϵ_{oij} includes the fast polarization and it frequently appears as a subtracted term in Bergmann's equations [15]. Thus to avoid the clumsiness of algebra and to exclude the fast polarization; Bergmann's equations [13] are simplified by the established symbols of χ'_{ij} , χ''_{ij} and χ_{oij} of Table 5.1 in S.I. units, into the following forms:

$$\frac{\chi'_{ij}}{\chi_{oij}} = \frac{c_1}{1 + \omega^2 \tau_1^2} + \frac{c_2}{1 + \omega^2 \tau_2^2} \quad (5.2)$$

$$\frac{\chi''_{ij}}{\chi_{oij}} = c_1 \frac{\omega \tau_1}{1 + \omega^2 \tau_1^2} + c_2 \frac{\omega \tau_2}{1 + \omega^2 \tau_2^2} \quad (5.3)$$

assuming two broad Debye-type dispersions for which $c_1 + c_2 = 1$.

The eqs (5.2) and (5.3) are then solved to get:

$$\frac{\chi_{oij} - \chi'_{ij}}{\chi'_{ij}} = \omega(\tau_1 + \tau_2) \frac{\chi''_{ij}}{\chi'_{ij}} - \omega^2 \tau_1 \tau_2 \quad (5.4)$$

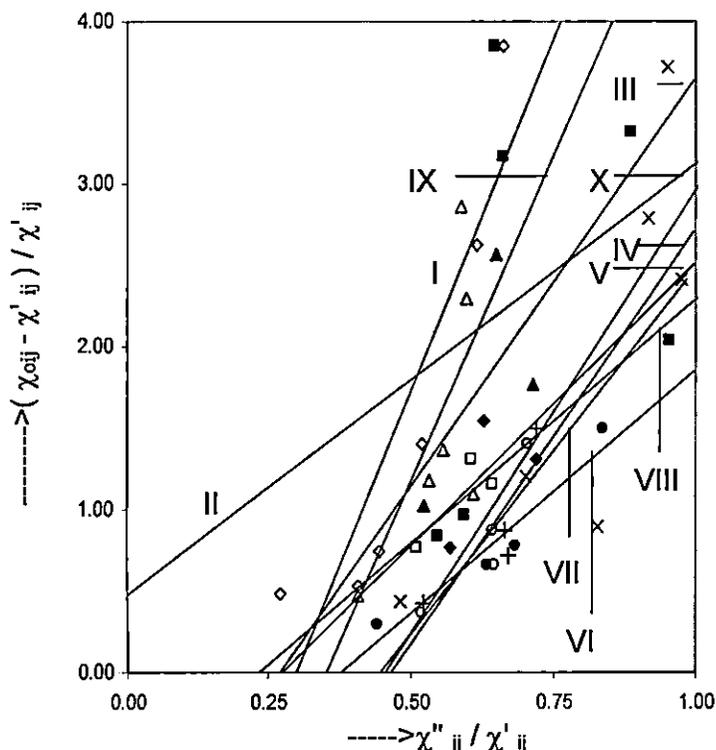


Fig.5.1 .Linear variation of $(\chi_{oij} - \chi'_{ij}) / \chi'_{ij}$ with χ''_{ij} / χ'_{ij} for different long straight chain dipolar alcohols in n-heptane at 25°C under 24 GHz electric field frequency I. 1-butanol (—◇—), II. 1-hexanol (—■—), III. 1-heptanol (—△—), IV. 1-decanol (—x—), V. 2-methyl-3-heptanol (—o—), VI. 3-methyl-3-heptanol(—●—), VII. 4-methyl-3-heptanol (—+—), VIII. 5-methyl-3-heptanol (—◆—), IX.4-octanol (—□—), X. 2-octanol (—▲—)

which is a linear equation between the variables $(\chi_{oij} - \chi'_{ij}) / \chi'_{ij}$ and χ''_{ij} / χ'_{ij} having intercept $-\omega^2 \tau_1 \tau_2$ and slope $\omega(\tau_1 + \tau_2)$ as illustrated in Fig. 5.1 for all the alcohols.

The intercepts and slopes of all the alcohols were then used to get τ_1 & τ_2 for the flexible part and the whole molecular species with known $\omega (=2\pi f)$, where f being the frequency of the applied electric field. as presented in Table 5.2.

The real ϵ'_{ij} and imaginary ϵ''_{ij} parts of hf complex relative permittivity are related by

$$\epsilon'_{ij} = \epsilon_{oij} + \frac{1}{\omega\tau_j} \epsilon''_{ij} \quad (5.5)$$

As $\epsilon'_{ij} - \epsilon_{oij}$ and ϵ''_{ij} are numerically equal to real and imaginary parts of hf complex dimensionless di-electric orientational susceptibility χ^*_{ij}

respectively. So we get $\chi''_{ij} = (\omega\tau_j) \chi'_{ij}$ (5.6)

which is clearly a straight line [18] between χ''_{ij} and χ'_{ij} , the slope, $\omega\tau_j$ can be used to get τ_j of a polar unit. But for associative liquids like normal and octyl alcohols under investigation the nature of variation of χ''_{ij} with χ'_{ij} is not strictly linear as seen in Fig. 5.2. Non linear variation of both χ'_{ij} and χ''_{ij} with weight fractions w_j 's of solute are presented graphically in Figs. 5.3 and 5.4 respectively. In such cases

$$\frac{(d\chi''_{ij}/dw_j)_{w_j \rightarrow 0}}{(d\chi'_{ij}/dw_j)_{w_j \rightarrow 0}} = \omega\tau_j \quad (5.7)$$

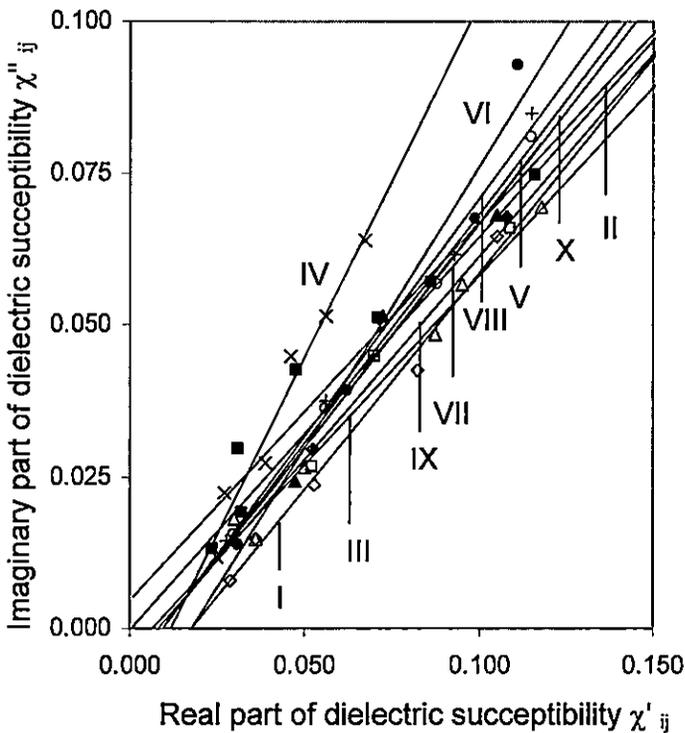


Fig 5.2. Linear variation of imaginary part χ''_{ij} of hf dielectric susceptibility against real part χ'_{ij} for different long straight chain dipolar alcohols in n - heptane at 25°C under 24GHz electric field frequency. I-butanol (--◇--), II. 1-hexanol (--■ - -), III. 1-heptanol (--△--), IV. 1-decanol (-- x --), V. 2 - methyl - 3 - heptanol (-- o --), VI. 3-methyl-3-heptanol (-- ● --), VII. 4-methyl-3-heptanol (-- + --), VIII. 5 - methyl - 3 - heptanol (-- ◆ --), IX. 4-octanol (-- □ --), X. 2-octanol (--▲ --)

is a better representation [19] of the slope of eq. (5.6) to get τ_j as it eliminates polar-polar interactions [20,21] in a given solution. τ_j 's from both eqs. (5.6) and (5.7) are placed in Table 5.2 to compare them with those obtained by the freshly calculated Gopala Krishna's [22] method.

The weighted contributions c_1 and c_2 towards dielectric relaxation in terms of estimated τ_1 and τ_2 are, however, worked out from Fröhlich's [23] theoretical equations are entered in Table 5.3 in order to compare them with the experimental ones obtained in terms of the intercepts of the variations of χ'_{ij}/χ_{oij} and χ''_{ij}/χ_{oij} with w_j 's of Figs 5.5 and 5.6.

Both χ'_{ij} / χ_{oij} and χ''_{ij} / χ_{oij} at $\omega_j=0$ together with curve of $(1/\phi) \log \cos\phi$ against ϕ^0 as seen in Fig. 5.7 are used to get symmetric and asymmetric distribution parameters γ and δ and hence symmetric and characteristic relaxation times τ_s and τ_{cs} . Both τ_s and τ_{cs} are given in Table 5.2 and γ, δ are presented in Table 5.3.

The dipole moments μ_1 and μ_2 by hf susceptibility measurement technique are, however, estimated from linear coefficient β 's of χ'_{ij} vs ω_j curves of Fig. 5.3 along with the dimensionless parameters b_1 & b_2 involved with estimated τ_1 and τ_2 of Table 5.2. The dipole moments μ_1 and μ_2 due to rotation of the flexible polar groups and end over end rotations of the whole molecule respectively are placed in Table 5.4 along with μ_{theo} 's and reported μ 's (Gopala Krishna) for comparison.

5.2 WEIGHTED CONTRIBUTIONS c_1 AND c_2 FOR ESTIMATED τ_1 AND τ_2 :

Taking $\omega\tau_1 = \alpha_1$ and $\omega\tau_2 = \alpha_2$ and solving eqs. (5.2) and (5.3) obtains

$$c_1 = \frac{(\chi'_{ij}\alpha_2 - \chi''_{ij})(1 + \alpha_1^2)}{\chi_{oij}(\alpha_2 - \alpha_1)} \quad (5.8)$$

and

$$c_2 = \frac{(\chi''_{ij} - \chi'_{ij}\alpha_1)(1 + \alpha_2^2)}{\chi_{oij}(\alpha_2 - \alpha_1)} \quad (5.9)$$

provided $\alpha_2 > \alpha_1$. c_1 and c_2 are estimated from known τ_1 and τ_2 by the double relaxation method. c_1 and c_2 can also be obtained with the known values of χ'_{ij} / χ_{oij} & χ''_{ij} / χ_{oij} from Fröhlich's [23] following theoretical equations with known τ_1 and τ_2 from eqs. (5.2) & (5.3).

$$\frac{\chi'_{ij}}{\chi_{oij}} = 1 - \frac{1}{2A} \ln \left[\frac{1 + \omega^2\tau_2^2}{1 + \omega^2\tau_1^2} \right] \quad (5.10)$$

$$\frac{\chi''_{ij}}{\chi_{oij}} = \frac{1}{A} [\tan^{-1}(\omega\tau_2) - \tan^{-1}(\omega\tau_1)] \quad (5.11)$$

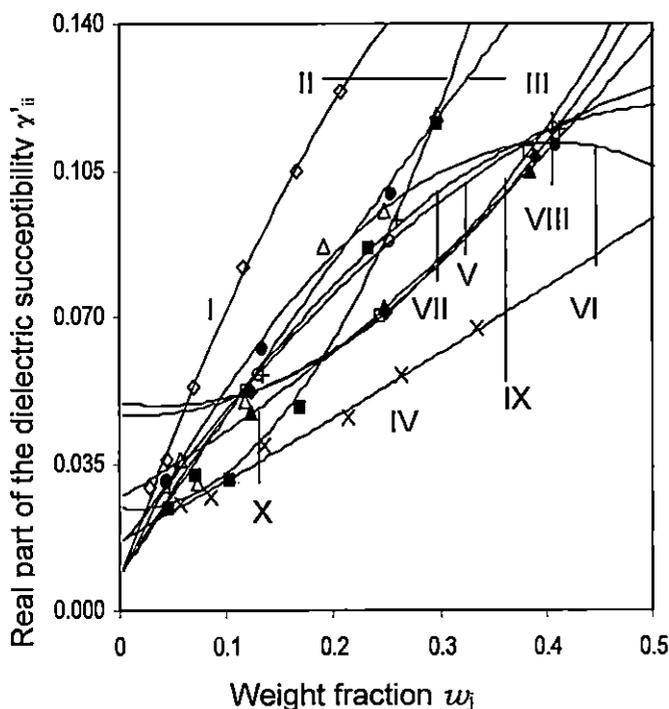


Fig 5. 3. Variation of real part χ'_{ij} of hf dielectric susceptibility with weight fraction w_j of some dipolar long straight chain alcohols in n-heptane at 25°C under 24GHz electric field frequency I.1-butanol (— \diamond —), II. 1-hexanol (— \blacksquare —), III. 1-heptanol (— \triangle —), IV. 1-decanol (— \times —), V. 2-methyl-3-heptanol (— \circ —), VI. 3-methyl-3-heptanol (— \bullet —), VII. 4-methyl-3-heptanol (— $+$ —), VIII. 5-methyl-3-heptanol (— \blacklozenge —), IX. 4-octanol (— \square —), X. 2-octanol (— \blacktriangle —)

c_1 and c_2 so estimated are placed in Table 5.3 for comparison with those worked out from intercept of the fitted polynomial plots of χ'_{ij} / χ_{oij} & χ''_{ij} / χ_{oij} against w_j curves of Figs. 5.5 and 5.6. Fröhlich's parameter A for each system are also placed in the same Table.

Table 5.2:-- The relaxation times τ_1 and τ_2 , from the slope and intercept of straightline equation.(4), correlation coefficient r 's and % of error in regression technique, measured τ_j from the slope of χ''_{ij} vs χ'_{ij} of eq (7) and the ratio of the individual slopes of χ''_{ij} vs ω_j and χ'_{ij} vs ω_j at $\omega_j \rightarrow 0$ of eq (7), reported τ , symmetric and characteristic relaxation times τ_s and τ_{cs} for different straight chain aliphatic alcohols in n-heptane under effective dispersive region of 24 GHz electric field at 25⁰C

System with St. No.	Slope and intercept of eq.(5.4)		Estimated τ_1 and τ_2 in psec		Corr. Coeff.	% of error	τ_j from (Murti et al) and (ratio of individual slope)		Reported τ_j in psec	τ_s in psec	τ_{cs} in pec
	Slope	Intercept	τ_1	τ_2							
I. 1-butanol (Mj= 0.074)	8.66	2.60	2.04	54.56	0.90	5.17	4.95	3.42	2.47	0.98	15.41
II. 1-hexanol (Mj= 0.102)	2.64	-0.47	-1.10	18.37	0.34	24.28	4.05	3.78	2.25	2.09	6.77
III. 1-heptanol (Mj = 0.116)	7.99	2.83	2.46	50.49	0.68	14.98	4.12	4.23	2.07	1.97	10.46
IV. 1-decanol (Mj = 0.158)	5.43	2.48	3.29	32.22	0.82	9.23	7.63	10.20	2.39	1.91	0.50
V. 2-methyl 3-heptanol (Mj = 0.130)	5.05	2.37	3.42	29.61	0.90	6.34	4.92	4.34	1.86	2.11	4.58
VI. 3-methyl 3-heptanol (Mj = 0.130)	3.00	1.14	2.91	16.68	0.96	2.33	6.06	4.30	2.26	1.65	5.29
VII. 4-methyl 3-heptanol (Mj = 0.130)	4.39	1.97	3.31	25.38	0.89	7.30	5.12	4.38	1.95	2.19	8.07
VIII. 5-methyl 3-heptanol (Mj = 0.130)	2.98	0.69	1.66	17.81	0.57	26.36	4.23	7.59	1.63	1.59	8.37
IX. 4-octanol (Mj = 0.130)	3.48	0.96	1.97	20.75	0.86	10.34	4.36	4.33	1.68	1.62	15.40
X. 2-octanol (Mj = 0.130)	5.02	1.37	1.89	30.94	0.63	23.30	4.82	15.91	1.93	2.33	37.08

Table-5.3: Fröhlich's parameter A, theoretical and experimental values of χ'_{ij} / χ_{oij} and χ''_{ij} / χ_{oij} of Fröhlich eqs. (5.10) and (5.11) and from fitted curves of Figs. 5.5 and 5.6 at $\omega_j \rightarrow 0$, respectively, theoretical and experimental relative contributions c_1 and c_2 towards dielectric dispersion due to τ_1 and τ_2 symmetric and asymmetric distribution parameters γ and δ for some straight chain aliphatic alcohols in solvent n-heptane under effective dispersive region of 24 GHz electric field at 25°C.

Systems with Sl.No.	A = In (τ_2/τ_1)	Theoretical values of $\chi'_{ij} /$ χ_{oij} & χ''_{ij} / χ_{oij} from Eqs (5.10) & (5.11)		Theoretical values of c_1 and c_2		Experimental values of $\chi'_{ij} /$ χ_{oij} & χ''_{ij} / χ_{oij} at $\omega_j \rightarrow 0$ of Figs 5.5 & 5.6		Experimental values of c_1 and c_2		Estimated values of γ and δ	
		χ_{oij}	χ''_{ij} / χ_{oij}	c_1	c_2	χ_{oij}	χ''_{ij} / χ_{oij}	c_1	c_2	γ	δ
I. 1-butanol	3.286	0.366	0.350	0.370	2.069	0.799	0.195	0.884	-0.474	0.357	0.21
II. 1-hexanol	—	—	—	—	—	0.740	0.348	0.598	1.412	0.128	0.55
III. 1-heptanol	3.023	0.347	0.359	0.358	1.878	0.721	0.298	0.816	0.247	0.230	0.39
IV. 1-decanol	2.281	0.341	0.396	0.364	1.283	0.870	0.404	1.100	-0.193	-0.079	2.49
V. 2-methyl 3-heptanol	2.157	0.345	0.404	0.369	1.198	0.776	0.386	0.995	-0.107	0.041	0.76
VI. 3-methyl 3-heptanol	1.746	0.474	0.446	0.435	0.837	0.814	0.319	1.000	-0.157	0.099	0.55
VII. 4-methyl 3-heptanol	2.036	0.374	0.417	0.386	1.084	0.729	0.358	0.920	-0.051	0.121	0.51
VIII. 5-methyl 3-heptanol	2.371	0.564	0.409	0.486	0.906	0.782	0.287	0.794	0.302	0.189	0.39
IX. 4-octanol	2.353	0.508	0.413	0.455	1.003	0.731	0.243	0.789	0.086	0.328	0.27
X. 2-octanol	2.797	0.451	0.387	0.426	1.351	0.683	0.193	0.741	-0.023	0.477	0.20

5.3 FORMULATIONS FOR SYMMETRIC AND CHARACTERISTIC RELAXATION TIMES AND ALSO SYMMETRIC AND ASYMMETRIC DISTRIBUTION PARAMETER:

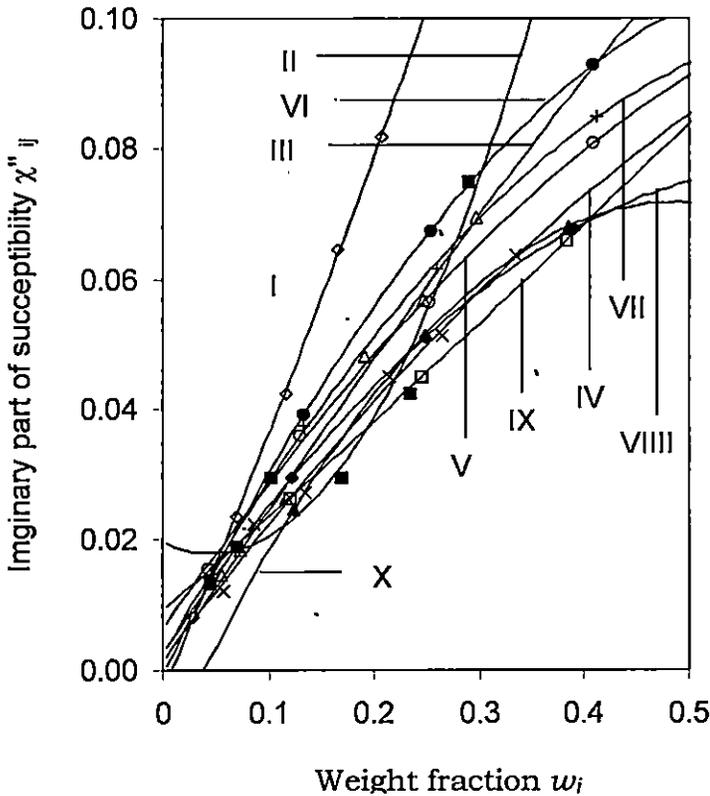


Fig 5.4. Variation of imaginary part χ''_{ij} of hf dielectric susceptibility with weight fraction w_i of some dipolar long straight chain alcohols in n-heptane at 25⁰ C under 24 GHz electric field frequency I. 1-butanol (-- \diamond --), II. 1-hexanol (-- \blacksquare --), III. 1-heptanol (-- \triangle --), IV. 1-decanol (-- x --), V. 2-methyl-3 - heptanol (-- o --), VI. 3-methyl-3 - heptanol (-- \bullet --), VII. 4-methyl-3-heptanol (-- + --), VIII. 5-methyl-3 - heptanol (-- \blacklozenge --), IX. 4-octanol (-- \square --), X. 2-octanol (-- \blacktriangle --)

$$\frac{\chi''_{ij}}{\chi_{oij}} = \frac{1}{1 + (j\omega\tau_s)^{1-\gamma}} \quad (5.12)$$

$$\frac{\chi''_{ij}}{\chi_{oij}} = \frac{1}{(1 + j\omega\tau_{cs})^\delta} \quad (5.13)$$

The molecules under investigation appear to behave like nonrigid ones under 24 GHz electric field frequency having either symmetric or asymmetric relaxation behaviour characterized by either symmetric τ_s and characteristic τ_{cs} relaxation times involved with the following equations:

separating the real and imaginary parts of the above equations and rearranging them in terms of intercepts viz $(d\chi'_{ij}/dw_j)_{w_j=0}$ and $(d\chi''_{ij}/dw_j)_{w_j=0}$ of the graphically fitted plots of Figs. 5.5 and 5.6 one gets γ and τ_s as :

$$\gamma = \frac{2}{\pi} \tan^{-1} \left[\left(1 - \frac{\chi'_{ij}}{\chi_{oij}} \right) \frac{\chi'_{ij}/\chi_{oij}}{\chi''_{ij}/\chi_{oij}} - \frac{\chi''_{ij}}{\chi_{oij}} \right] \quad (5.14)$$

and

$$\tau_s = \frac{1}{\omega} \left[\frac{1}{\{(\chi'_{ij}/\chi_{oij}) / (\chi''_{ij}/\chi_{oij})\} \cos(\gamma\pi/2) - \sin(\gamma\pi/2)} \right]^{1/1-\gamma} \quad (5.15)$$

similarly, δ and τ_{cs} can be evaluated from equation (13):

$$\tan(\phi\delta) = \frac{(\chi''_{ij}/\chi_{oij})_{w_j=0}}{(\chi'_{ij}/\chi_{oij})_{w_j=0}} \quad (5.16)$$

$$\text{and } \tan \phi = \omega\tau_{cs} \quad (5.17)$$

since ϕ can not be estimated directly, a theoretical curve between $(1/\phi) \log \cos \phi$ against ϕ in degrees has been drawn in Fig. 5.7. The value of $(1/\phi) \log \cos \phi$ can be estimated from the following relation

$$(1/\phi) \log \cos \phi = \log \left[\frac{\chi'_{ij}/\chi_{oij}}{\cos \phi \delta} \right] / \phi \delta \quad (5.18)$$

The known value of $(1/\phi) \log \cos \phi$ is used to get ϕ from the curve. With the known ϕ , eqs. (5.16) and (5.17) were used to obtain δ and τ_{cs} . Estimated τ_s and τ_{cs} are placed in Table 5.2 to compare with τ_j 's obtained by ratio of slopes of individual variations of χ'_{ij} & χ''_{ij} with w_j , τ_j 's by the method of Murthy et al [18], reported τ_j (Gopala Krishna) and τ_1 & τ_2 by the double relaxation method. Also γ and δ are shown in Table 5.3.

5.4. THEORETICAL FORMULATIONS TO OBTAIN hf DIPOLE MOMENT μ_j

The imaginary part χ''_{ij} of hf complex χ^*_{ij} is [4,20,24]

$$\chi''_{ij} = \frac{N\rho_{ij} \mu_j^2}{27 \epsilon_0 M_j k_B T} \frac{\omega \tau_j}{(1 + \omega^2 \tau_j^2)} (\epsilon_{ij} + 2)^2 \omega_j \quad (5.19)$$

which on differentiation with respect to ω_j and at $\omega_j = 0$ yields that

$$\left(\frac{d\chi''_{ij}}{d\omega_j} \right)_{\omega_j=0} = \frac{N\rho_{ij} \mu_j^2}{27 \epsilon_0 M_j k_B T} \frac{\omega \tau_j}{(1 + \omega^2 \tau_j^2)} (\epsilon_{ij} + 2)^2 \omega_j \quad (5.20)$$

From eqs. (5.7) and (5.19) one obtains

$$\omega \tau_j (d\chi'_{ij} / d\omega_j)_{\omega_j \rightarrow 0} = \frac{N\rho_{ij} \mu_j^2}{27 \epsilon_0 M_j k_B T} \frac{\omega \tau_j}{(1 + \omega^2 \tau_j^2)} (\epsilon_{ij} + 2)^2 \quad (5.21)$$

or

$$\omega \tau_j \beta = \frac{N\rho_{ij} \mu_j^2}{27 \epsilon_0 M_j k_B T} \frac{\omega \tau_j}{(1 + \omega^2 \tau_j^2)} (\epsilon_{ij} + 2)^2$$

or

$$\mu_j = \left[\frac{27 \epsilon_0 M_j k_B T \beta}{N\rho_{ij} (\epsilon_{ij} + 2)^2} \right]^{1/2} \quad (5.22)$$

where

ϵ_0 = Permittivity of free space = 8.854×10^{-12} Farad metre⁻¹

M_j = Molecular weight of solute in kilogramme

k_B = Boltzmann Constant = 1.38×10^{-23} J mole⁻¹ K⁻¹

T = Temperature in absolute scale

$\beta = (d\chi'_{ij} / dw_j) w_{j \rightarrow 0} =$ Linear coefficient of $\chi'_{ij} - w_j$ curve of Fig. 5.3 at $w_j \rightarrow 0$

N = Avogadro's number = 6.023×10^{23}

ρ_i = Density of solvent n-heptane = 680.15 Kg.m⁻³

ϵ_1 = Dielectric relative permittivity of the solvent = 1.917

$b = 1 / (1 + \omega^2 \tau_j^2)$ = a dimensionless parameter involved with estimated τ_j .

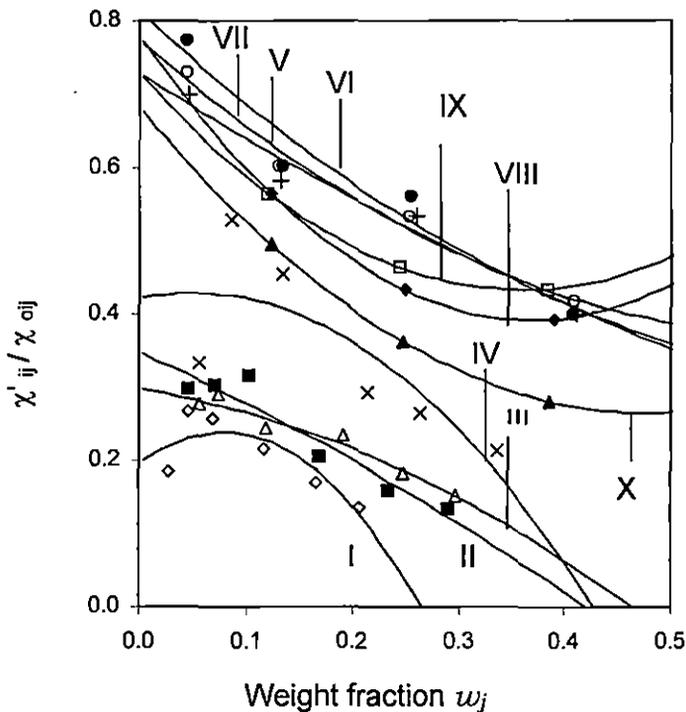


Fig 5.5. Plot of χ'_{ij} / χ_{oij} against weight fraction w_j of some dipolar long straight chain alcohols in n - heptane at 25°C under 24 GHz electric field frequency I. 1-butanol(-- \diamond --), II. 1-hexanol (-- \blacksquare --), III.1-heptanol (-- \triangle --), IV. 1-decanol (-- x --), V. 2-methyl-3 - heptanol (-- o --), VI. 3-methyl-3 - heptanol (-- \bullet --), VII. 4-methyl - 3 - heptanol (-- + --), VIII. 5-methy - 3 - heptanol (-- \blacklozenge --), IX. 4-octanol (-- \square --), X. 2-octanol (-- \blacktriangle --)

When $j = 1$ & 2 the dipole moments μ_1 & μ_2 associated with rotation of flexible polar groups and rotation of the whole molecule are evaluated in terms of b_1 & b_2 involved with τ_1 & τ_2 and are placed in Table 5.4 to compare them with μ_{theo} 's and reported μ 's (Gopala Krishna).

Table-5.4: linear coefficient β of χ'_{ij} Vs ω_j curves of Fig 5.3, dimensionless parameters b_1 , b_2 from τ_1 & τ_2 of eq.(5.4), correlation coefficient and % of error of $\chi'_{ij}-\omega_j$ estimated dipole moment μ_1 , μ_2 from eq. (5.22), computed dipole moment μ_j from τ_j of eq. (5.7), reported dipole moment (Gopala Krishna's method), all are expressed in Coulomb metre for different straight chain alcohols in solvent n-heptane at 25°C under 24 GHz electric field.

Systems with Sl.No. and Mol.Wt.M _j in Kg (in n- heptane)	Linear coeffi.of χ'_{ij} vs ω_j curves of Fig. 5.3 β	Dimensionl ess parameters		Correl. Coeffi. of $\chi'_{ij} - \omega_j$ curves	% of errors	Estimated Dipole moments $\mu \times 10^{30}$ in coulomb metre			Report ed $\mu \times$ 10^{30} in C.m	μ^*_{theo} X 10^{30} in C.m
		b_1	b_2			μ_1	μ_2	μ_j		
I. 1-butanol (M _j = 0.074)	0.719	0.911	0.014	0.997	0.00003	3.02	24.25	3.26	3.58	3.74
II. 1-hexanol (M _j = 0.102)	0.371	0.973	0.112	0.969	0.00037	2.47	7.25	2.81	3.35	3.49
III. 1-heptanol (M _j = 0.116)	0.392	0.879	0.017	0.987	0.00015	2.84	20.49	3.16	3.59	3.73
IV. 1-decanol (M _j = 0.158)	0.142	0.798	0.040	0.994	0.00007	2.10	9.43	3.47	3.55	3.68
V. 2-methyl 3-heptanol (M _j = 0.130)	0.359	0.785	0.047	0.998	0.00003	3.05	12.53	3.24	1.33	1.86
VI. 3-methyl 3-heptanol (M _j = 0.130)	0.508	0.835	0.133	0.985	0.00023	3.52	8.81	3.85	1.18	2.11
VII. 4-methyl 3-heptanol (M _j = 0.130)	0.429	0.796	0.062	0.996	0.00006	3.31	11.83	3.55	3.42	1.95
VIII. 5-methyl 3-heptanol (M _j = 0.130)	0.211	0.939	0.119	0.967	0.00056	2.14	6.01	3.17	3.54	1.39
IX. 4-octanol (M _j = 0.130)	0.217	0.917	0.090	0.985	0.00025	2.20	7.00	2.52	3.48	1.11
X. 2-octanol (M _j = 0.130)	0.143	0.923	0.043	0.977	0.00038	1.78	8.25	4.49	3.24	1.45

* Ghosh et al[10]

5.5. RESULTS AND DISCUSSION

The least squares fitted straight line equations : $(\chi_{oij} - \chi'_{ij}) / \chi'_{ij} = \omega (\tau_1 + \tau_2) \chi''_{ij} / \chi'_{ij} - \omega^2 \tau_1 \tau_2$ have been shown graphically in Fig. 5.1 for some normal and octyl alcohols with the symbols showing the experimental points in solvent n-heptane at 25°C under 24 GHz electric field frequency. The real χ'_{ij} and imaginary parts χ''_{ij} of hf complex dimensionless dielectric orientational susceptibility χ^*_{ij} and static or low frequency real dielectric susceptibility χ_{oij} have been derived from the measured relative permittivities [8,9] ϵ'_{ij} , ϵ''_{ij} , ϵ_{oij} and $\epsilon_{\infty ij}$. They are carefully collected in Table 5.1. The slopes and intercepts of eq. (5.4) used to get τ_1 & τ_2 are placed in the 2nd and 3rd columns of Table

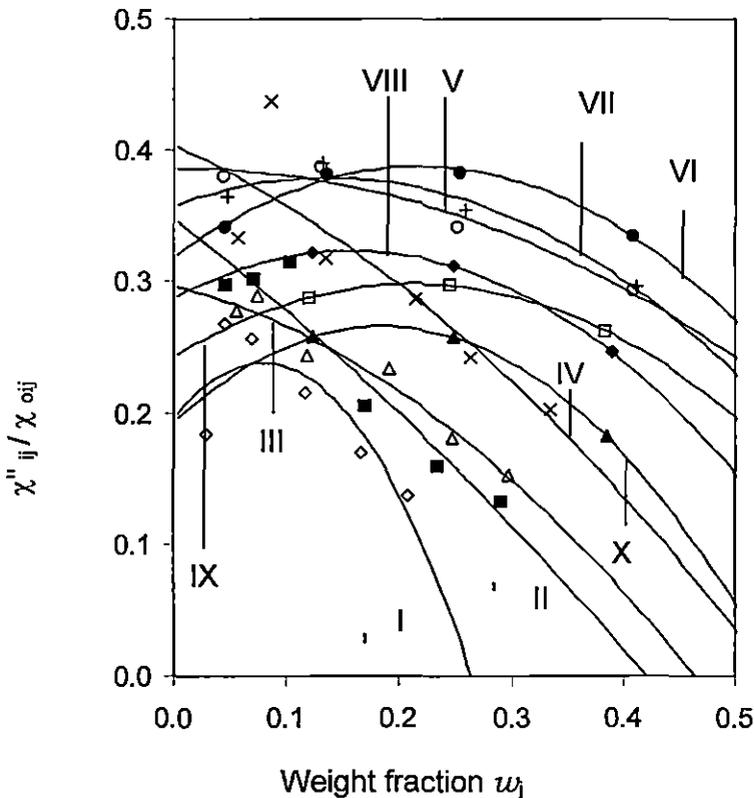


Fig 5. 6. Plot of χ''_{ij} / χ'_{ij} against weight fraction w_j of some dipolar long straight chain alcohols in n-heptane at 25°C under 24 GHz electric field frequency I. 1-butanol (--◇--), II. 1-hexanol (--■--), III. 1-heptanol (--△--), IV. 1-decanol (--x--), V. 2-methyl-3-heptanol (--o--), VI. 3-methyl-3-heptanol (--●--), VII. 4-methyl-3-heptanol (--+--), VIII. 5-methyl-3-heptanol (--◆--), IX. 4-octanol (--□--), X. 2-octanol (--▲--)

5.2 along with the estimated τ_1 & τ_2 in the 4th and 5th columns. Correlation coefficients (r) and % of errors of curves of Fig. 5.1 have been calculated and are placed in the 6th and 7th columns of Table 5.2 only to show how far the variables $(\chi_{oij} - \chi'_{ij}) / \chi'_{ij}$ and χ''_{ij} / χ'_{ij} are correlated with each other. It is seen that 'r' is very low and corresponding % of errors is very high for 5-methyl-3-heptanol and 2-octanol, which may be probably due to errors introduced in their permittivity ϵ_{ij} measurements. This fact

is further confirmed by remarkable deviations of experimental points from the fitted linear curves as seen in Fig. 5.1.

In absence of reliable τ_j values, the slopes of the linear curves [18] of Fig. 5.2 of the variables χ''_{ij} and χ'_{ij} are utilized to get τ_j . But for associative liquids like normal and octyl alcohols the variation of χ''_{ij} against χ'_{ij} is not strictly linear as seen in Fig. 5.2. Under such context, the ratio of slopes of individual variations of both χ'_{ij} and χ''_{ij} with ω_j 's is a better representation [20,21] of the method of Murthy et al [18] as it eliminates polar-polar interactions in a given solution [4]. τ_j 's estimated so far by this method are entered in the 9th column of Table 5.2 along with τ_j 's due to method of Murthy et al and reported ones as seen in the 8th and 10th columns. Non linear variation of both χ'_{ij} and χ''_{ij} against ω_j 's as seen in Figs 5.3 and 5.4 arises due to solute-solvent and solute-solute molecular associations which is supposed to be a physico-chemical property [21] of the solutes under consideration. Symmetric and characteristic relaxation times τ_s and τ_{cs} estimated from eqs (5.15) and (5.17) respectively in terms of γ and δ are seen in the 11th and 12th column of Table 5.2. It is observed that in comparison to τ_{cs} , τ_s is the same order of magnitude of τ_j 's from eq. (5.7) and reported (Gopala Krishna)

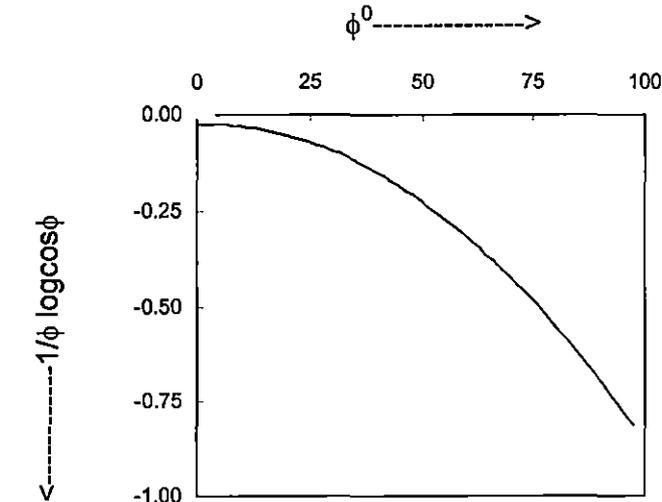
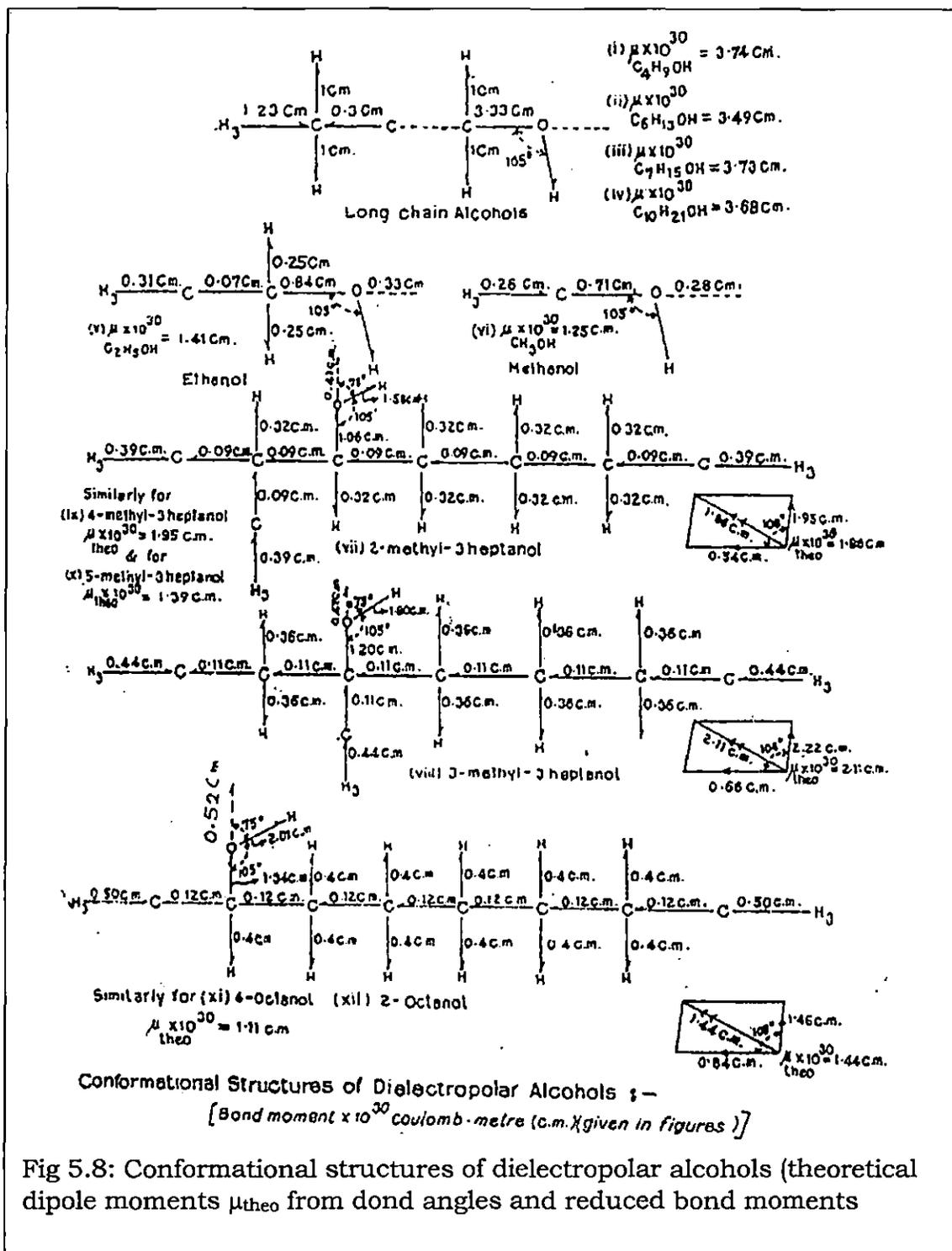


Figure 5.7. Variation of $(1/\phi) \log(\cos\phi)$ against

ones. This fact at once establishes the very basic soundness of our method [20,21] employed to get hf τ_j and also the symmetric relaxation behaviour [19] obeyed by the molecules. Larger τ_2 values arises for bigger size of rotating units $\tau_j T / \eta^j$ due to solute-solvent and solute solute molecular associations, supposed to be physico-chemical property of the solutes which is further supported by non linear variations of both χ'_{ij} and χ''_{ij} with ω_j 's as seen in Figs. 5.3 and 5.4.

The theoretical weighted contributions c_1 and c_2 towards dielectric relaxations from eqs.(5.8) and

(5.9) are, however, worked out with χ'_{ij} / χ_{oij} and χ''_{ij} / χ_{oij} values of eqs (5.10) & (5.11) and also with estimated τ_1 & τ_2 of Table 5.2. They are placed in the 5th and 6th columns of Table 5.3 in order to compare them with the experimental c_1 & c_2 estimated in terms of $(\chi'_{ij} / \chi_{oij}) \omega_{j \rightarrow 0}$ and $(\chi''_{ij} / \chi_{oij}) \omega_{j \rightarrow 0}$ of the graphically fitted plots of Figs. 5.5 and 5.6 and are placed in the 9th and 10th columns. Theoretical c 's for 1-hexanol could not be estimated as τ_1 is found to be negative probably due to errors [19] in the measurement of ϵ'_{ij} , ϵ''_{ij} , ϵ_{oij} and $\epsilon_{\infty ij}$. Both theoretical and experimental c_1 & c_2 shows that $c_1 + c_2 \approx 1$, which confirms the validity of eq. (5.4) to get τ_1 & τ_2 . It is seen that for some systems experimental c_2 is negative. This can, however, be explained on the basis of the fact that internal hydrogen bonding among -OH groups in dipolar alcohol molecules gives rise to inertia [25] of the flexible polar groups with respect to the whole molecule. Solute-solvent and solute-solute molecular interaction being a physico-chemical aspect is also supported by slight deviations of experimental points from the curves of Figs 5.5 and 5.6. The dipole moments μ_1 & μ_2 of the flexible polar groups and the whole molecules were estimated in terms of dimensionless parameters b_1 & b_2 involved with estimated τ_1 & τ_2 and linear coefficient β of $\chi'_{ij} - \omega_j$ curves of Fig. 5.3. They are entered in the 5th and 6th columns of Table 5.4 to compare them with μ_j 's estimated with τ_j 's of eq. (5.7), reported μ 's due to Gopala Krishna [22] and theoretical μ 's obtained with available bond angles and bond moments of the polar groups assuming the molecules to be planar ones, sketched here. Correlation coefficient's r 's and % of errors of $\chi'_{ij} - \omega_j$ curves of Fig. 5.3 were made by careful regression analysis of the measured data, are seen in the 5th and 6th columns of Table 5.4 only to suggest how far the variables $\chi'_{ij} - \omega_j$ are correlated with each other. Almost all the $\chi'_{ij} - \omega_j$ curves show a tendency to be closer within the range $0.00 \leq \omega_j \leq 0.10$, which is due to same polarity [4,25] of the molecules in addition to solute-solvent and solute-solute molecular interaction which is assumed to be physico-chemical behaviour [20,21] of the solutes in n-heptane. The close agreement of the estimated μ_1 & μ_2 with reported (Gopala Krishna) and theoretical μ 's establishes the very basic soundness of the present method to get hf μ_j 's in addition to the fact that a part of the molecule is rotating under GHz electric field [19]. It is seen that estimated μ_1 & μ_j 's are lower than that of μ_{theo} 's for normal alcohols while the reverse is true in octyl alcohols. It is probably due to the fact that strong hydrogen bonding among -OH groups in normal alcohols (1-butanol, 1-hexanol, 1-heptanol and 1-decanol) offers higher resistance due to



–OH groups to rotate under hf electric field to give lower μ_1 & μ_j values. In octyl alcohols hydrogen, on the otherhand, bonding between –OH groups is not so strong giving μ_1 's & μ_j 's higher than that of μ_{theo} 's as they are screened by a large number –CH₃ and –CH₂ groups. The conformations are presented in Fig. 5.8 in excellent agreement of the measured values in order to account of the mesomeric and electromeric effects of the substituted polar groups in alcohols by multiplying available bond moments by a factor $\mu_s / \mu_{\text{theo}}$ where μ_s is the low frequency or static dipole moment estimated elsewhere[10].

5.6. CONCLUSION

Theoretical formulations developed so far in SI unit within the frame work of Debye-Smyth model appears to be simpler straightforward and topical one to get the many interesting equations which are worked out in terms of χ_{ij} 's. They are useful to explain various physico-chemical aspects of several dipolar alcohol molecules in solvent n-heptane at 25^oC under 24 GHz (Q-band microwave) electric field frequency. The derived straight line eq. (5.4) have significant contribution in the field of dielectric relaxation as it gives microscopic τ_1 and macroscopic τ_2 due to both rotations of the flexible polar groups and the whole molecule while eq. (5.7) gives microscopic τ only [20,21]. Both theoretical and graphical experimental c_1 & c_2 confirm the validity of eq. (5.4). As seen in Table 5.3 that $c_1 + c_2 \cong 1$ is due to the fact that under 24 GHz electric field the rotations of the straight chained molecules are influenced by the moment of inertia of the flexible groups attached to the parent ones. $\epsilon_{\alpha ij} \cong 1$ to $1.5 n_{Dij}^2$. But $\epsilon_{\alpha ij} \cong n_{Dij}^2$ may introduce some errors in getting τ_1 & τ_2 and c_1 & c_2 also. Correlation coefficients r 's and % of errors between several variables involved in curves of Figs 5.1 and 5.3 are worked out only to establish the statistical validity [20,21] of eq. (5.4) and χ'_{ij} vs ω_j equations.. The close agreement of estimated relaxation parameters viz τ 's and μ 's with the reported ones confirms the very basic soundness of the theoretical formulations so far developed. The physico chemical properties of the systems are, however, inferred in terms of solute-solvent (monomer) and solute-solute (dimer) associations as supported by slight deviations of measured parameters from their reported and standard values and also observed by deviation of experimental points from the fitted polynomial plots of several Figs..

REFERENCES

- [1] N Paul, K P Sharma & S Chattoadhyay, *Indian J. Phys* **71B** (1997) 71
- [2] S N Sen & R Ghosh, *J. Phys. Soc. Japan* **33** (1972) 838
- [3] K Dutta, R C Basak, S K Sit & S Acharyya, *J. Molecular Liquids* **88** (2000) 229
- [4] N Ghosh, S K Sit, A K Bothra & S Acharyya, *J. Phys. D: Appl. Phys* (UK) **34** (2001) 379
- [5] M D Migahed, M T Ahmed & A E Kolp *J.Phys. D: Appl. Phys* **33** (2000) 2108
- [6] A Bello, E Laredo, M Girman, A Nogales & T A Ezqrearra, *J.Chem.Phys* **133** (2000) 863
- [7] P Debye, '*Polar Molecules*' (Chemical Catalogue) 1929
- [8] L Glasser, J Crossley & C P Smyth, *J.Chem.Phys* **57** (1972) 3977
- [9] J Crossley, L Glasser & C P Smyth *J.Chem.Phys* **55** (1971) 2197
- [10] N Ghosh, A Karmakar, S K Sit & S Acharyya, *Indian J. Pure & Appl. Phys* **38** (2000) 574
- [11] S K Garg and C P Smyth, *J. Phys. Chem.* **69** (1965) 1294
- [12] A K Ghosh & S Acharyya, *Indian J. Phys.* **52B** (1978) 129
- [13] K Bergmann, D M Roberti and C P Smyth, *J. Phys. Chem.* **64** (1960) 665
- [14] J Bhattacharyya, A Hasan, S B Roy and G S Kastha, *J. Phys. Soc.Japan* **28** (1970) 204
- [15] K Higasi, Y Koga and M Nakamura *Bull. Chem. Soc. Japan* **44** (1971) 988
- [16] U Saha, S K Sit, R C Basak & S Acharyya *J. Phys. D: Appl. Phys* (UK) **27** (1994) 596
- [17] S K Sit, R C Basak , U Saha & S Acharyya *J. Phys. D: Appl. Phys*(UK) **27** (1994) 2194
- [18] M B R Murthy, R L Patil and D K Deshpande, *Indian J. Phys* **63B** (1989) 491
- [19] N Ghosh, S K Sit and S Acharyya, *J. Molecular Liquids* **102** (2003) 29
- [20] U K Mitra, N Ghosh, P Ghosh and S Acharyya, *J.Indian Chem.Soc.* **83** (2006) 1230
- [21] A Karmakar, U K Mitra, N Ghosh and S Acharyya communicated *Indian J.Pure & Appl. Phys.* 2006
- [22] K V Gopala Krishna, *Trans Faraday Soc.* **53** (1957) 767
- [23] H Fröhlich '*Theory of Dielectrics*' (Oxford University Press) : Oxford 1949
- [24] C P Smyth, '*Dielectric Behaviour and Structure*' (McGraw Hill: New York) 1955
- [25] S K Sit, N Ghosh and S Acharyya, *Indian J.Pure & Appl. Phys.* **35** (1997) 329 .

CHAPTER 6

STUDIES ON PHYSICO-CHEMICAL PROPERTIES WITH THE
RELAXATION PHENOMENA OF SOME NORMAL ALIPHATIC ALCOHOLS
IN NONPOLAR SOLVENT UNDER GIGA HERTZ ELECTRIC FIELD AT A
SINGLE TEMPERATURE

6. STUDIES ON PHYSICO CHEMICAL PROPERTIES WITH THE RELAXATION PHENOMENA OF SOME NORMAL ALIPHATIC ALCOHOLS IN NONPOLAR SOLVENT UNDER GIGA HERTZ ELECTRIC FIELD AT A SINGLE TEMPERATURE

6.1. INTRODUCTION

Relaxation mechanism of polar molecules in non polar solvents under high frequency electric field is of special interest as it provides one with useful tool to study structural configuration and molecular associations in the formation of monomer [1] and dimer [2,3] through measured relaxation parameters like relaxation time τ and dipole moment μ obtained by any conventional method [4,5]. The technique also gives valuable information regarding stability or unstability [6] of the systems undergoing relaxation phenomena. Also τ_j obtained from the ratio of slopes of individual variations of $\chi''_{ij} - \omega_j$ and $\chi'_{ij} - \omega_j$ are conveniently used to shed more light on structural and associational aspects [7] in addition to physico-chemical properties of the polar molecules.

Glasser et al [8] measured the real ϵ'_{ij} and imaginary ϵ''_{ij} parts of complex hf dielectric relative permittivity ϵ^*_{ij} together with static and hf relative permittivity ϵ_{0ij} and $\epsilon_{\infty ij}$ of some normal alcohols like 1-butanol, 1-hexanol, 1-heptanol and 1-decanol at various mole fractions under different electric field frequencies in n-heptane at 25°C. The purpose of their study was to observe triple relaxation phenomena in them under different concentrations characterized by relaxation times τ_1, τ_2, τ_3 which arise respectively due to hydrogen bonded structure, orientational motion of the molecules and rotation of -OH groups about C-C bond. The alcohols under study are of special importance for their wide applications in the fields of biological research, medicine and industry.

But the modern trend is to study relaxation phenomena in polar-nonpolar liquid mixtures in terms of hf complex dimensionless dielectric orientational susceptibility χ^*_{ij} rather than permittivity ϵ^*_{ij} or conductivity σ^*_{ij} . As all types of polarizations are associated with ϵ^*_{ij} , while σ^*_{ij} includes within it transport of bound molecular charges, so it is more reasonable to work with χ_{ij} 's as it is directly linked with orientational polarization of the molecules. Moreover, the present study have

been carried out in modern concept of internationally accepted symbols of dielectric terminology and parameter in SI units because of its unified, coherent and rationalized nature. Under such context we have derived a straight line equation in terms of real χ'_{ij} and imaginary χ''_{ij} parts of hf complex susceptibility χ^*_{ij} together with low frequency real dielectric susceptibility χ_{oij} to have τ_1 and τ_2 of alcohol molecules in n-heptane at 25°C under GHz electric field. The frequency 24.33 GHz has been found out to be the most effective dispersive region of the alcohol molecules. When χ''_{ij} of the molecules are plotted against frequency (f) they showed peak in the neighbourhood of 24 GHz which is probably due to dielectric reorientation of polar molecules [9]. At this frequency the alcohol molecules absorb electrical energy much more strongly to show reliable τ_1 and τ_2 from intercept and slope of the least squares fitted straight line equation of $(\chi_{oij} - \chi'_{ij}) / \chi'_{ij}$ against χ''_{ij} / χ'_{ij} signifying the material property of the systems. The data of χ'_{ij} , χ''_{ij} and χ_{oij} so obtained are entered in Table 6.1

*Table—6.1 Concentration variation of measured real ϵ'_{ij} and imaginary ϵ''_{ij} parts of hf complex dielectric relative permittivity ϵ^*_{ij} , static and hf dielectric permittivity ϵ_{oij} and $\epsilon_{\infty ij}$ along with real χ'_{ij} and imaginary χ''_{ij} parts of hf complex dimensionless dielectric orientational susceptibility χ^*_{ij} , low frequency susceptibility χ_{oij} for alcohols in n-heptane at 25°C under different GHz electric field*

Systems with serial number & Mol.wt(Mj) in Kg.(in n-heptane)	Frequency f in GHz	Weight fraction w_j of solute	ϵ'_{ij}	ϵ''_{ij}	ϵ_{oij}	$\epsilon_{\infty ij}$	χ'_{ij} (= $\epsilon'_{ij} - \epsilon_{\infty ij}$)	χ''_{ij} (= ϵ''_{ij})	χ_{oij} (= $\epsilon_{oij} - \epsilon_{\infty ij}$)
I. 1-butanol Mj =0.074	a) 24.33	0.0291	1.9570	0.0079	1.9710	1.9280	0.0290	0.0079	0.0430
		0.0451	1.9810	0.0147	2.0000	1.9450	0.0360	0.0147	0.0550
		0.0697	2.0110	0.0236	2.0500	1.9580	0.0530	0.0236	0.0920
		0.1163	2.0600	0.0425	2.1750	1.9780	0.0820	0.0425	0.1970
		0.1652	2.1050	0.0644	2.3810	2.0000	0.1050	0.0644	0.3810
		0.2072	2.1440	0.0818	2.6210	2.0200	0.1240	0.0818	0.6010
		0.2072	2.1440	0.0818	2.6210	2.0200	0.1240	0.0818	0.6010
	b) 9.25	0.0291	1.9630	0.0059	1.9710	1.9280	0.0350	0.0059	0.0430
		0.0451	1.9850	0.0121	2.0000	1.9450	0.0400	0.0121	0.0550
		0.0697	2.0150	0.0220	2.0500	1.9580	0.0570	0.0220	0.0920
		0.1163	2.0660	0.0416	2.1750	1.9780	0.0880	0.0416	0.1970
		0.1652	2.1210	0.0637	2.3810	2.0000	0.1210	0.0637	0.3810
		0.2072	2.1720	0.0956	2.6210	2.0200	0.1520	0.0956	0.6010
		0.2072	2.1720	0.0956	2.6210	2.0200	0.1520	0.0956	0.6010

Systems with serial number & Mol.wt(Mj) in Kg.(in n-heptane)	Frequency f in GHz	Weight fraction w_j of solute	ϵ'_{ij}	ϵ''_{ij}	ϵ_{oij}	$\epsilon_{\infty ij}$	χ'_{ij} (= $\epsilon_{ij}' - \epsilon_{\infty ij}$)	χ''_{ij} (= ϵ_{ij}'')	χ_{oij} (= $\epsilon_{oij} - \epsilon_{\infty ij}$)	
II. 1-hexanol Mj = 0.102	c) 3.00	0.0291	1.9700	0.0044	1.9710	1.9280	0.0420	0.0044	0.0430	
		0.0451	1.9940	0.0114	2.0000	1.9450	0.0490	0.0114	0.0550	
		0.0697	2.0300	0.0188	2.0500	1.9580	0.0720	0.0188	0.0920	
		0.1163	2.1010	0.0460	2.1750	1.9780	0.1230	0.0460	0.1970	
		0.1652	2.1800	0.0782	2.3810	2.0000	0.1800	0.0782	0.3810	
		0.2072	2.2440	0.1119	2.6210	2.0200	0.2240	0.1119	0.6010	
	a) 24.33	0.0458	1.9680	0.0131	1.9880	1.9440	0.0240	0.0131	0.0440	
		0.0703	1.9840	0.0190	2.0150	1.9520	0.0320	0.0190	0.0630	
		0.1028	2.0010	0.0296	2.0640	1.9700	0.0310	0.0296	0.0940	
		0.1687	2.0370	0.0425	2.1960	1.9890	0.0480	0.0425	0.2070	
		b) 9.25	0.0458	1.9700	0.0083	1.9880	1.9440	0.0260	0.0083	0.0440
			0.0703	1.9900	0.0121	2.0150	1.9520	0.0380	0.0121	0.0630
			0.1028	2.0150	0.0226	2.0640	1.9700	0.0450	0.0226	0.0940
			0.1687	2.0740	0.0454	2.1960	1.9890	0.0850	0.0454	0.2070
			0.2335	2.1280	0.0688	2.3600	2.0020	0.1260	0.0688	0.3580
0.2901			2.1790	0.1000	2.5800	2.0180	0.1610	0.1000	0.5620	
c) 3.00		0.0458	1.9770	0.0065	1.9880	1.9440	0.0330	0.0065	0.0440	
		0.0703	2.0030	0.0117	2.0150	1.9520	0.0510	0.0117	0.0630	
	0.1028	2.0400	0.0214	2.0640	1.9700	0.0700	0.0214	0.0940		
	0.1687	2.1120	0.0446	2.1960	1.9890	0.1230	0.0446	0.2070		
	0.2335	2.1860	0.0755	2.3600	2.0020	0.1840	0.0755	0.3580		
	0.2901	2.2500	0.1097	2.5800	2.0180	0.2320	0.1097	0.5620		
III. 1-heptanol Mj = .116	a) 24.33	0.0735	1.9750	0.0182	2.0080	1.9450	0.0300	0.0182	0.0630	
		0.1175	2.0070	0.0265	2.0660	1.9570	0.0500	0.0265	0.1090	
		0.1909	2.0760	0.0482	2.1950	1.9890	0.0870	0.0482	0.2060	
		0.2465	2.0970	0.0567	2.3150	2.0020	0.0950	0.0567	0.3130	
		0.2970	2.1260	0.0693	2.4640	2.0080	0.1180	0.0693	0.4560	
		b) 9.25	0.0564	1.9750	0.0084	1.9850	1.9320	0.0430	0.0084	0.0530
	0.0735		1.9850	0.0129	2.0080	1.9450	0.0400	0.0129	0.0630	
	0.1175		2.0170	0.0232	2.0660	1.9570	0.0600	0.0232	0.1090	
	0.1909		2.0790	0.0438	2.1950	1.9890	0.0900	0.0438	0.2060	
	0.2465		2.1140	0.0609	2.3150	2.0020	0.1120	0.0609	0.3130	
	0.2970		2.1570	0.0774	2.4640	2.0080	0.1490	0.0774	0.4560	
	c) 3.00	0.0735	1.9980	0.0111	2.0080	1.9450	0.0530	0.0111	0.0630	
		0.1175	2.0430	0.0216	2.0660	1.9570	0.0860	0.0216	0.1090	
		0.1909	2.1170	0.0456	2.1950	1.9890	0.1280	0.0456	0.2060	
		0.2465	2.1750	0.0651	2.3150	2.0020	0.1730	0.0651	0.3130	
		0.2970	2.2250	0.0864	2.4640	2.0080	0.2170	0.0864	0.4560	

Systems with serial number & Mol.wt(Mj) in Kg.(in n-heptane)	Frequency f in GHz	Weight fraction w_j of solute	ϵ'_{ij}	ϵ''_{ij}	ϵ_{oij}	$\epsilon_{\infty ij}$	χ'_{ij} (= $\epsilon_{ij}' - \epsilon_{\infty ij}$)	χ''_{ij} (= ϵ_{ij}'')	χ_{oij} (= $\epsilon_{oij} - \epsilon_{\infty ij}$)
IV. 1-decanol Mj = .158	a) 24.33	0.0572	1.9650	0.0120	1.9760	1.9400	0.0250	0.0120	0.0360
		0.0857	1.9790	0.0223	2.0030	1.9520	0.0270	0.0223	0.0510
		0.1351	2.0030	0.0273	2.0500	1.9640	0.0390	0.0273	0.0860
		0.2140	2.0360	0.0449	2.1470	1.9900	0.0460	0.0449	0.1570
		0.2640	2.0640	0.0513	2.2200	2.0080	0.0560	0.0513	0.2120
		0.3353	2.0970	0.0637	2.3460	2.0300	0.0670	0.0637	0.3160
	b) 9.25	0.0572	1.9680	0.0090	1.9760	1.9400	0.0280	0.0090	0.0360
		0.0857	1.9770	0.0146	2.0030	1.9520	0.0250	0.0146	0.0510
		0.1351	2.0110	0.0228	2.0500	1.9640	0.0470	0.0228	0.0860
		0.2140	2.0550	0.0386	2.1470	1.9900	0.0650	0.0386	0.1570
		0.2640	2.0770	0.0484	2.2200	2.0080	0.0690	0.0484	0.2120
		0.3353	2.1230	0.0656	2.3460	2.0300	0.0930	0.0656	0.3160
	c) 3.00	0.0572	1.9720	0.0041	1.9760	1.9400	0.0320	0.0041	0.0360
		0.0857	1.9950	0.0086	2.0030	1.9520	0.0430	0.0086	0.0510
		0.1351	2.0310	0.0194	2.0500	1.9640	0.0670	0.0194	0.0860
		0.2140	2.0880	0.0371	2.1470	1.9900	0.0980	0.0371	0.1570
		0.2640	2.1290	0.0496	2.2200	2.0080	0.1210	0.0496	0.2120
		0.3353	2.1860	0.0690	2.3460	2.0300	0.1560	0.0690	0.3160

together with measured permittivities ϵ_{ij} 's. The validity of straight line equations of Fig.6.1 is tested by correlation coefficient(r) and % of errors which are entered in Table 6.2 along with estimated τ_1 and τ_2 . In absence of reliable τ_j 's of these normal alcohols the ratio of slopes of individual variations of χ''_{ij} and χ'_{ij} with w_j at $w_j \rightarrow 0$ as seen in Figs.6.2 and 6.3 were utilised to get hf τ_j to compare them with those of Murthy et al [10] of Fig.6.4 and Gopala Krishna's method [11].

The theoretical weighted contributions c_1 and c_2 towards dielectric dispersions in terms of measured τ_1 and τ_2 were worked out from Fröhlich's equations [12] to compare them with the experimental ones by graphical variation of χ'_{ij} / χ_{oij} and χ''_{ij} / χ_{oij} with w_j at $w_j = 0$ of Figs. 6.5 and 6.6. They are shown in Table 6.3. The symmetric γ and asymmetric δ distribution parameters were obtained from graphical extrapolation techniques of Figs. 6.5 and 6.6 in the limit $w_j = 0$ and from variation of $(1/\phi)\log(\cos\phi)$ against $\bar{\phi}$ of Fig. 6.7 respectively. Symmetric relaxation time τ_s from γ and

characteristic relaxation time τ_{cs} from δ and ϕ , were however, estimated to conclude about symmetric relaxation behaviour of polar molecules. τ_s and τ_{cs} so obtained are placed in Table 6.2 to compare them with τ_1 , τ_2 and τ_j .

The dipole moment's μ_1 and μ_2 in terms of b_1 and b_2 involved with estimated τ_1 and τ_2 and linear coefficient β 's of χ'_{ij} against ω_j curves of Fig. 6.3 were worked out to present them in Table 6.4 to compare with reported μ_j 's (Gopala Krishna) and μ_{theo} obtained from bond angles and reduced bond moments [13] of substituent polar groups attached to parent molecules. The comparison however suggests that the flexible part of the molecules rotate internally under GHz electric field [14,15]. The slight disagreement between experimental and theoretical μ 's establishes the very existence of strong internal hydrogen bonding among -OH groups of long straight chain alcohol molecules. Physico-chemical aspects of different solute molecules in nonpolar solvent can be explained by non linear variation of both τ_2 and μ_2 against frequency (f) of the applied electric field as shown in Fig. 6. 8.

6.2. EXPERIMENTAL

The dielectric constants ϵ'_{ij} and losses ϵ''_{ij} of the alcohols in n-heptane at different mole fractions of solutes were measured [8] with a Boonton RX meter corrected by a heterodyne beat method. Refractive indices ($n_{Dij} = \sqrt{\epsilon'_{ij}}$) of the solution were estimated by a Pulfrich refractometer for sodium D-line. The alcohols 1-butanol, 1-hexanol, 1-heptanol and 1-decanol were obtained from various commercial sources dried for a period over "Drierite" (anhydrous calcium sulphate) and fractionally distilled at atmospheric pressure. Commercial n-heptane was dried over sodium wire prior to its use and its relative permittivity ($\epsilon_i = 1.917$) was checked in agreement with literature value at 25°C.

6.3. THEORETICAL FORMULATION TO ESTIMATE DOUBLE RELAXATION

TIMES τ_1 , τ_2 AND C_1 , C_2

The hf complex dielectric relative permittivity ϵ^*_{ij} of polar-nonpolar liquid mixtures is associated with a number of non interacting Debye type dispersions in accordance with Budo's relation[16]

$$\frac{\varepsilon_{ij}^* - \varepsilon_{\infty ij}}{\varepsilon_{0ij} - \varepsilon_{\infty ij}} = \sum \frac{c_k}{1 + j\omega\tau_k} \quad (6.1)$$

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

But when ε_{ij}^* consists of two Debye type dispersions Budo's relation reduces to Bergmann's equations [17]. $\varepsilon_{\infty ij}$ includes within it fast polarization and frequently appears as a subtracted term in Bergmann's equations. Thus to avoid the clumsiness of algebra and to use the modern concept of dielectric terminology and parameter one gets

$$\chi'_{ij} = (\varepsilon'_{ij} - \varepsilon_{\infty ij}), \quad \chi''_{ij} = \varepsilon''_{ij}, \quad \chi_{0ij} = (\varepsilon_{0ij} - \varepsilon_{\infty ij})$$

The Bergmann's equations thus becomes

$$\frac{\chi'_{ij}}{\chi_{0ij}} = c_1 \frac{1}{1 + \omega^2\tau_1^2} + c_2 \frac{1}{1 + \omega^2\tau_2^2} \quad (6.2)$$

$$\frac{\chi''_{ij}}{\chi_{0ij}} = c_1 \frac{\omega\tau_1}{1 + \omega^2\tau_1^2} + c_2 \frac{\omega\tau_2}{1 + \omega^2\tau_2^2} \quad (6.3)$$

The relative weighted factors c_1 and c_2 are such that $c_1 + c_2 = 1$, χ'_{ij} and χ''_{ij} are the real and imaginary parts of hf complex dielectric orientational susceptibility χ_{ij}^* and χ_{0ij} is low frequency dielectric susceptibility which is real. The introduction of χ 's in Bergmann's equations are then concerned with the molecular orientational polarization alone.

Putting $\omega\tau_1 = \alpha_1$ and $\omega\tau_2 = \alpha_2$ eqs. (6.2) and (6.3) are solved to get

$$c_1 = \frac{(\chi'_{ij}\alpha_2 - \chi''_{ij})(1 + \alpha_1^2)}{\chi_{0ij}(\alpha_2 - \alpha_1)} \quad (6.4)$$

and

$$c_2 = \frac{(\chi''_{ij} - \chi'_{ij}\alpha_1)(1 + \alpha_2^2)}{\chi_{0ij}(\alpha_2 - \alpha_1)} \quad (6.5)$$

provided $\alpha_2 - \alpha_1 \neq 0$.

As $c_1 + c_2 = 1$, we have

$$\frac{(\chi'_{ij}\alpha_2 - \chi''_{ij})(1 + \alpha_1^2)}{\chi_{oij}(\alpha_2 - \alpha_1)} + \frac{(\chi''_{ij} - \chi'_{ij}\alpha_1)(1 + \alpha_2^2)}{\chi_{oij}(\alpha_2 - \alpha_1)} = 1$$

or, $\chi'_{ij}\alpha_2 + \chi'_{ij}\alpha_2\alpha_1^2 - \chi''_{ij} - \chi''_{ij}\alpha_1^2 + \chi''_{ij} + \chi''_{ij}\alpha_2^2 - \chi'_{ij}\alpha_1 - \chi'_{ij}\alpha_1\alpha_2^2 = \chi_{oij}(\alpha_2 - \alpha_1)$

or, $\chi'_{ij}(\alpha_2 - \alpha_1) - \chi'_{ij}\alpha_1\alpha_2(\alpha_2 - \alpha_1) + \chi''_{ij}(\alpha_2^2 - \alpha_1^2) = \chi_{oij}(\alpha_2 - \alpha_1)$

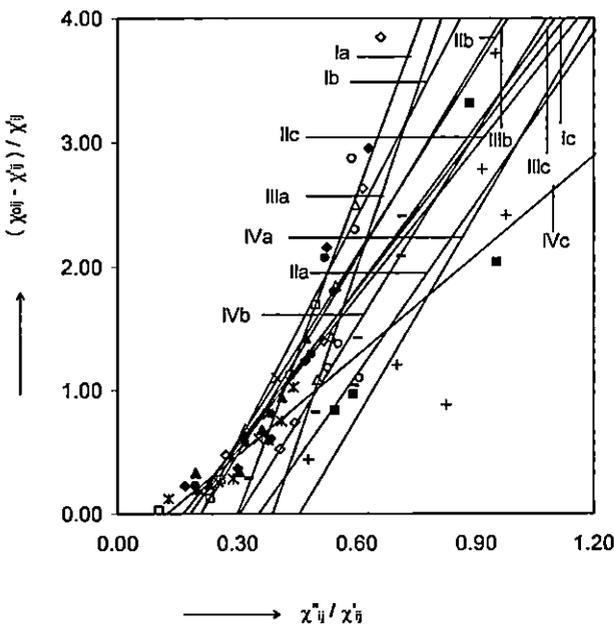
or, $\chi'_{ij} - \chi'_{ij}\alpha_1\alpha_2 + \chi''_{ij}(\alpha_2 + \alpha_1) = \chi_{oij}$

or, $\chi''_{ij}(\alpha_1 + \alpha_2) - \chi'_{ij}\alpha_1\alpha_2 = \chi_{oij} - \chi'_{ij}$

$$\text{or, } \frac{\chi_{oij} - \chi'_{ij}}{\chi'_{ij}} = (\alpha_1 + \alpha_2) \frac{\chi''_{ij}}{\chi'_{ij}} - \alpha_1\alpha_2$$

substituting $\alpha_1 = \omega\tau_1$ & $\alpha_2 = \omega\tau_2$ we have

$$\text{or } \frac{\chi_{oij} - \chi'_{ij}}{\chi'_{ij}} = \omega(\tau_1 + \tau_2) \frac{\chi''_{ij}}{\chi'_{ij}} - \omega^2\tau_1\tau_2 \tag{6.6}$$



which is a straight line equation between the variables $(\chi_{oij} - \chi'_{ij}) / \chi'_{ij}$ and χ''_{ij} / χ'_{ij} with slope $\omega(\tau_1 + \tau_2)$ and intercept $-\omega^2\tau_1\tau_2$. where $\omega = 2\pi f$, f being frequency of the applied electric field in GHz range. The above equation is, however, satisfied by experimental points as seen in Fig.6.1 for different weight fractions τ_i 's of solute at 25°C

Fig 6.1 .Linear variation of $(\chi_{oij} - \chi'_{ij}) / \chi'_{ij}$ with χ''_{ij} / χ'_{ij} for alcohols in n-heptane at 25°C of Ia. 1-butanol (\diamond) at 24.33 GHz, Ib. 1-butanol (\blacklozenge) at 9.25 GHz, Ic. 1-butanol (\square) at 3.00 GHz, IIa. 1-hexanol (\blacksquare) at 24.33 GHz, IIb. 1-hexanol (Δ) at 9.25 GHz IIc. 1-hexanol (\blacktriangle) at 3.00 GHz, IIIa. 1-heptanol (\circ) at 24.33 GHz, IIIb. 1-heptanol (\bullet) at 9.25 GHz, IIIc. 1-heptanol (\times) at 3.00 GHz, IVa. 1-decanol ($+$) at 24.33 GHz, IVb. 1-decanol ($-$) at 9.25 GHz, IVc. 1-decanol ($*$) at 3.00 GHz

under electric field frequencies of 24.33, 9.25 and 3.00 GHz. The eq.(6.6) has been used to estimate τ_1 and τ_2 in order to place them in Table 6.2.

*Table 6.2:-- The relaxation times τ_1 and τ_2 , from the slope and intercept of straight line eq.(6.6), correlation coefficient r 's and % of error in regression technique, measured τ_j from the slope of χ_{ij}'' vs χ_{ij}' of eq.(6.16) and the ratio of the individual slopes of χ_{ij}'' vs ω_j and χ_{ij}' vs ω_j at $\omega_j \rightarrow 0$ of eq. (6.17), reported τ_s symmetric and characteristic relaxation times τ_s and τ_{cs} for different straight chain aliphatic alcohols in *n*-heptane at 25°C under different GHz electric field.*

System with Sl. No.& Molecular weight M_j in Kg	Freque ncy (f) in GHz	Slope and inter-cept of eq.(6.6)		estimated τ_1 & and τ_2 in psec		Corrl. Coeff. (r)	% of error	Estimated τ_j in psec from method of Murti et al & ratio of individual slope)		Report -ed τ_j in psec	τ_s in psec	τ_{cs} in psec
		Slope	Inter cept	τ_1	τ_2							
I. 1-butanol $M_j = 0.074$	24.33	8.66	2.60	2.04	54.56	0.9973	0.000032	4.95	3.42	17.44	0.98	15.41
	9.25	6.13	1.28	3.72	101.78	0.9988	0.000014	12.52	6.79	43.86	1.40	4.61
	3.00	4.15	0.68	9.09	211.22	0.9980	0.000024	30.18	15.80	147.92	-	-
II. 1-hexanol $M_j = 0.102$	24.33	4.59	1.63	2.54	27.46	0.9573	0.000619	7.69	72.85	15.66	1.08	13.99
	9.25	5.17	1.08	3.75	85.16	0.9960	0.000048	11.42	7.79	42.45	10.50	163.63
	3.00	4.02	0.67	9.17	204.07	0.9983	0.000020	27.09	9.81	154.07	3.89	334.83
III. 1- heptanol $M_j = 0.116$	24.33	9.44	3.67	2.65	59.09	0.9891	0.000143	3.88	3.03	21.04	5.04	21.39
	9.25	5.01	0.92	3.29	82.96	0.9890	0.000132	11.02	26.84	48.86	1.31	3.03
	3.00	4.34	0.79	10.05	220.31	0.9970	0.000040	24.86	20.66	173.36	4.16	-
IV. 1- decanol $M_j = 0.158$	24.33	5.43	2.48	3.29	32.22	0.9940	0.000072	7.63	10.20	18.19	1.91	1.15
	9.25	5.16	1.57	5.60	83.06	0.9847	0.000184	14.00	11.10	51.02	3.19	13.43
	3.00	2.69	0.33	6.88	135.54	0.9993	0.000008	28.02	22.25	184.45	1.78	-

The theoretical weighted contributions c_1 and c_2 were, then obtained from eqs. (6.4) and (6.5) with the variables χ'_{ij} / χ_{oij} and χ''_{ij} / χ_{oij} of Fröhlich's eqs. (6.7) and (6.8) in terms of known τ_1 and τ_2 of Table 6.2.

$$\frac{\chi'_{ij}}{\chi_{oij}} = 1 - \frac{1}{2A} \ln \left(\frac{1 + \omega^2 \tau_2^2}{1 + \omega^2 \tau_1^2} \right) \quad (6.7)$$

$$\frac{\chi''_{ij}}{\chi_{oij}} = \frac{1}{A} [\tan^{-1}(\omega \tau_2) - \tan^{-1}(\omega \tau_1)] \quad (6.8)$$

c_1 and c_2 so obtained are entered in Table 6.3 in order to compare them with the experimental ones obtained from eqs. (6.4) and (6.5) with graphically extrapolated values of χ'_{ij} / χ_{oij} and χ''_{ij} / χ_{oij} in the limit $\omega \rightarrow 0$ of Figs. 6.5 and 6.6 respectively.

6.4. THEORETICAL FORMULATION TO ESTIMATE SYMMETRIC AND CHARACTERISTIC RELAXATION TIMES τ_s and τ_{cs}

The molecules under present investigation appear to behave like non-rigid ones having symmetric and asymmetric distribution parameters γ and δ involved with eqs. (6.9) and (6.10)

$$\frac{\chi^*_{ij}}{\chi_{oij}} = \frac{1}{1 + (j\omega\tau_s)^{1-\gamma}} \quad (6.9)$$

$$\frac{\chi^*_{ij}}{\chi_{oij}} = \frac{1}{(1 + j\omega\tau_{cs})^\delta} \quad (6.10)$$

The former one is associated with symmetric relaxation time τ_s while the later one with characteristic relaxation times τ_{cs} . On separating the real and imaginary parts of eqs. (6.9) and (6.10) and rearranging them in terms of χ'_{ij} / χ_{oij} and χ''_{ij} / χ_{oij} at $\omega \rightarrow 0$ as seen in Figs 6.5 and 6.6, the γ and τ_s were obtained as

$$\gamma = \frac{2}{\pi} \tan^{-1} \left[\left(1 - \frac{\chi'_{ij}}{\chi_{oij}} \right) \frac{\chi'_{ij}}{\chi''_{ij}} - \frac{\chi''_{ij}}{\chi_{oij}} \right] \quad (6.11)$$

And

$$\tau_s = \frac{1}{\omega} \left[\frac{1}{(\chi'_{ij} / \chi''_{ij}) \cos(\gamma\pi/2) - \sin(\gamma\pi/2)} \right]^{1/(1-\gamma)} \quad (6.12)$$

Similarly δ and τ_{cs} can be had from eq.(6.10) as

$$\tan(\phi\delta) = \frac{(\chi''_{ij} / \chi_{oij})_{\omega_j \rightarrow 0}}{(\chi'_{ij} / \chi_{oij})_{\omega_j \rightarrow 0}} \quad (6.13)$$

and $\tan\phi = \omega\tau_{cs}$ (6.14)

As ϕ can not be evaluated directly, an arbitrary theoretical curve between $(1/\phi) \log(\cos\phi)$ against ϕ in degree was drawn in Fig. 6.7 from which

$$(1/\phi) \log(\cos\phi) = \frac{\log \{(\chi'_{ij} / \chi_{oij}) / (\cos\phi\delta)\}}{\phi\delta} \quad (6.15)$$

can be known. The known value of $(1/\phi) \log(\cos\phi)$ is used to know ϕ from Fig. 6.7. With known ϕ eqs. (6.13) and (6.14) can be used to obtain δ and τ_{cs} respectively. τ_s and τ_{cs} in Table 6.2 can be compared with τ_j 's by Murthy et al[10], τ_j 's by the method of ratio of individual slope, Gopala Krishna [11] and τ_1, τ_2 by double relaxation method. Estimated values of γ and δ are seen in Table 6.3.

Table-6.3: Fröhlich's parameter A, theoretical and experimental relative contributions c_1 and c_2 towards dielectric dispersion with χ'_{ij} / χ_{oij} and χ''_{ij} / χ_{oij} estimated from Fröhlich's eqs. (6.7) and (6.8) and those by graphical technique of Figs.6.5 and 6.6, symmetric and asymmetric distribution parameters γ and δ of some normal alcohols in n-heptane at 25°C under different gigahertz electric field.

Systems with Sl. No.	Frequency (f) in GHz	A = ln (τ_2/τ_1)	Theoretical values of χ'_{ij} / χ_{oij} & χ''_{ij} / χ_{oij} from eqs (6.7) & (8)		Theoretical values of c_1 and c_2		Experimental values of χ'_{ij} / χ_{oij} & χ''_{ij} / χ_{oij} at $\omega_j \rightarrow 0$ of Figs 6.5 & 6.6		Experimental values of c_1 and c_2		Estimated values of γ and δ	
			c_1	c_2	c_1	c_2	γ	δ				
I. 1-butanol	24.33	3.286	0.366	0.350	0.370	2.069	0.799	0.195	0.884	-0.474	0.357	0.21
	9.25	3.308	0.465	0.360	0.439	1.637	0.973	0.132	1.033	-0.499	0.043	0.51
	3.00	3.146	0.556	0.367	0.498	1.203	1.112	0.069	1.178	-0.537	-0.688	-
II.1-hexanol	24.33	2.381	0.415	0.406	0.404	1.197	0.796	0.211	0.946	-0.479	0.323	0.23
	9.25	3.122	0.489	0.370	0.454	1.423	0.697	0.158	0.729	0.031	0.552	0.15
	3.00	3.103	0.560	0.369	0.500	1.171	0.840	0.109	0.875	-0.157	0.538	0.09
III.1-heptanol	24.33	3.103	0.313	0.346	0.335	2.101	0.475	0.312	0.537	1.140	0.289	0.46
	9.25	3.227	0.511	0.365	0.470	1.398	0.980	0.122	1.031	-0.346	0.025	0.70
	3.00	3.088	0.535	0.372	0.484	1.244	1.003	0.108	1.061	-0.376	-0.088	-
IV. 1-decanol	24.33	2.281	0.341	0.396	0.364	1.283	0.870	0.404	1.100	-0.193	-0.079	2.49
	9.25	2.696	0.427	0.390	0.411	1.355	0.862	0.259	0.959	-0.118	0.125	0.44
	3.00	2.981	0.664	0.359	0.561	0.846	1.007	0.037	1.063	-0.290	-0.145	-

6.5. THEORETICAL FORMULATION O OBTAIN RELAXATION TIME τ_j AND hf

DIPOLE MOMENT μ_j

The real ϵ'_{ij} and imaginary ϵ''_{ij} parts of hf complex dielectric relative permittivity ϵ^*_{ij} are related by

$$\begin{aligned}
 \epsilon'_{ij} &= \epsilon_{oij} + (1/\omega\tau) \epsilon''_{ij} \\
 \text{or, } (\epsilon'_{ij} - \epsilon_{oij}) &= (1/\omega\tau) \epsilon''_{ij} \\
 \text{or, } \chi'_{ij} &= (1/\omega\tau) \chi''_{ij} \\
 \text{or, } (d\chi''_{ij} / d\chi'_{ij}) &= \omega\tau_j
 \end{aligned}
 \tag{6.16}$$

χ''_{ij} 's are found to vary almost linearly[10] with χ'_{ij} as seen in Fig.6.4, the slope $\omega\tau_j$ is

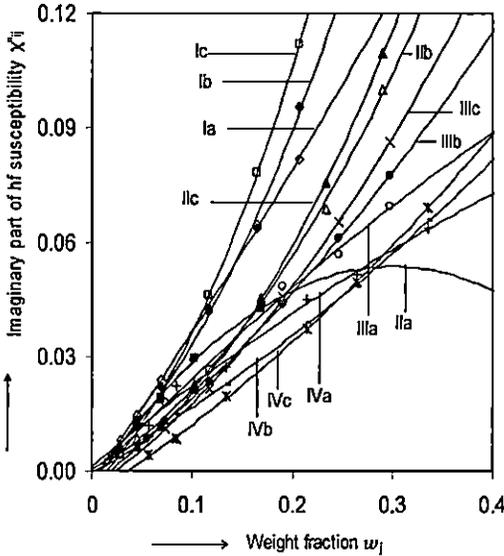


Fig 6.2 .Variation of imaginary part of hf susceptibility χ''_{ij} with weight fraction w_j for alcohols in n-heptane at 25°C of Ia.1-butanol(\diamond) at 24.33 GHz,Ib.1-butanol(\blacklozenge) at 9.25 GHz, Ic. 1-butanol (\square) at 3.00 GHz, Ila.1-hexnol (\blacksquare) at 24.33 GHz,Ilb.1-hexnol (\triangle) at 9.25 GHz Ilc.1-hexnol (\blacktriangle) at 3.00 GHz,IIla.1-heptanol (\circ) at 24.33 GHz,IIlb 1-heptanol (\bullet) at 9.25 GHz, IIlc. 1-heptanol (\times) at 3.00 GHz,IVa. 1-decanol ($+$) at 24.33 GHz, IVb. 1-decanol ($-$) at 9.25 GHz, IVc. 1-decanol ($*$) at 3.00 GHz

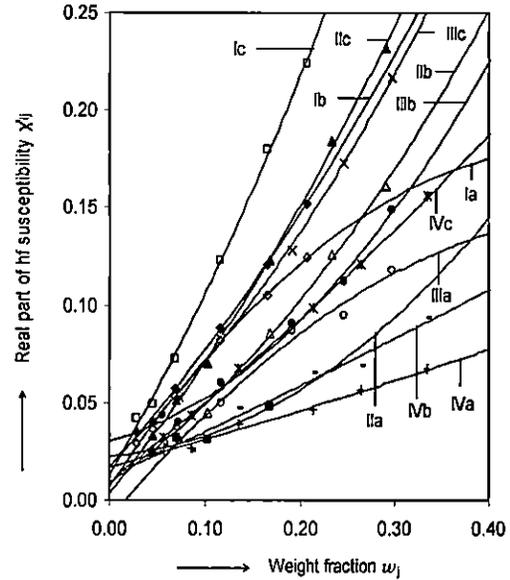


Fig 6.3 .Variation of real part of hf susceptibility χ'_{ij} with weight fraction w_j for alcohols in n-heptane at 25°C of Ia.1-butanol(\diamond) at 24.33 GHz,Ib.1-butanol(\blacklozenge) at 9.25 GHz, Ic. 1-butanol (\square) at 3.00 GHz, Ila.1-hexnol (\blacksquare) at 24.33 GHz,Ilb.1-hexnol (\triangle) at 9.25 GHz Ilc.1-hexnol (\blacktriangle) at 3.00 GHz,IIla.1-heptanol (\circ) at 24.33 GHz,IIlb 1-heptanol (\bullet) at 9.25 GHz, IIlc. 1-heptanol (\times) at 3.00 GHz,IVa. 1-decanol ($+$) at 24.33 GHz, IVb. 1-decanol ($-$) at 9.25 GHz, IVc. 1-decanol ($*$) at 3.00 GHz

used to obtain τ_j as seen in the 9th column of Table 6.2.

But earlier investigation on some isomers of anisidines and toluidines [15] and the present investigation on normal alcohols shows that variation of χ''_{ij} against χ'_{ij} as seen in Fig. 6.4 are strictly not linear. The ratio of slopes of individual variations of χ''_{ij} and χ'_{ij} with w_j 's in Figs 6.2 and 6.3 is a better representation of eq. (6.16) to get τ_j where polar-polar interactions are almost avoided [15]. Thus

$$\frac{(d\chi''_{ij} / dw_j)_{w_j \rightarrow 0}}{(d\chi'_{ij} / dw_j)_{w_j \rightarrow 0}} = \omega\tau_j \quad (6.17)$$

The Imaginary part χ''_{ij} of χ^*_{ij} can be represented [18,19] as

$$\chi''_{ij} = \frac{N\rho_{ij} \mu_j^2}{27 \epsilon_0 M_j k_B T} \frac{\omega\tau_j}{(1 + \omega^2\tau_j^2)} (\epsilon_{ij} + 2)^2 w_j \quad (6.18)$$

which on differentiation with respect to ω_j and at $\omega_j \rightarrow 0$ yields that

$$(d\chi''_{ij} / d\omega_j)_{\omega_j \rightarrow 0} = \frac{N\rho_i \mu_j^2}{27 \varepsilon_0 M_j k_B T} \frac{\omega \tau_j}{(1 + \omega^2 \tau_j^2)} (\varepsilon_i + 2)^2 \quad (6.19)$$

Now in comparison to earlier works presented elsewhere[6,13] the approximation that $\chi_{ij} \cong \chi''_{ij}$ like $\sigma_{ij} \cong \sigma''_{ij}$ is not necessary to obtain μ_j from τ_j where σ''_{ij} is the imaginary part of complex hf conductivity and σ_{ij} is the total hf conductivity of polar – nonpolar liquid mixture. From eqs. (6.17) and (6.19) one gets

$$\omega \tau_j (d\chi'_{ij} / d\omega_j) = \frac{N\rho_i \mu_j^2}{27 \varepsilon_0 M_j k_B T} \frac{\omega \tau_j}{(1 + \omega^2 \tau_j^2)} (\varepsilon_i + 2)^2$$

$$\text{or, } \omega \tau_j \beta = \frac{N\rho_i \mu_j^2}{27 \varepsilon_0 M_j k_B T} \omega \tau_j b (\varepsilon_i + 2)^2$$

$$\text{or, } \beta = \frac{N\rho_i \mu_j^2}{27 \varepsilon_0 M_j k_B T} b (\varepsilon_i + 2)^2$$

$$\text{or, } \mu_j = \left[\frac{27 \varepsilon_0 M_j k_B T \beta}{N\rho_i (\varepsilon_i + 2)^2 b} \right]^{1/2} \quad (6.20)$$

which is directly interrelated with the measured τ 's through b, where

ε_0 = Permittivity of free space = 8.854×10^{-12} Farad metre⁻¹

M_j = Molecular weight of solute in kilogramme

k_B = Boltzmann Constant = 1.38×10^{-23} J mole⁻¹ K⁻¹

T = Temperature in absolute scale

$\beta = d\chi'_{ij} / d\omega_j$ = Linear coefficient of $\chi'_{ij} - \omega_j$ curves of Fig.6.3 at $\omega_j \rightarrow 0$

N = Avogadro's number = 6.023×10^{23}

ρ_i = Density of solvent n-heptane at 25°C = 680.15 Kg.m⁻³

ϵ_i = Relative permittivity of the solvent n-heptane = 1.917

$b = 1 / (1 + \omega^2 \tau^2)$ = a dimensionless parameter involved with estimated τ_1 & τ_2 of eq. (6.6) and τ_j of eq. (6.17).

Dipole moments μ_1 and μ_2 obtained with the knowledge of b_1 and b_2 involved with estimated τ_1 and τ_2 by double relaxation method are entered in the 8th and 9th column of Table 6.4. They are, however, compared to μ_j with τ_j of eq. (6.17) and reported μ 's (Gopala Krishna) and μ_{theo} as seen in 10th, 12th and 13th columns.

Table-6.4: Linear coefficient β of χ'_{ij} Vs w_j curves of Fig. 6.3, dimensionless parameters b_1 , b_2 from τ_1 & τ_2 of eq. (6.6), correlation coefficient (r) and % of errors, estimated dipole moment μ_1 , μ_2 from eq. (6.20), computed dipole moment μ_j from τ_j of eq. (6.17), reported dipole moment (Gopala Krishna's method), all are expressed in Coulomb-metre for different straight chain alcohols in n-heptane at 25°C under different GHz electric field.

System with Sl. No. & mol. weight M _j in kg	Frequ- ency (f) in GHz	Linear coeffi- cient of χ'_{ij} vs w_j curves of fig 6.3 β	Dimensionless parameters		Correlation coefficient of $\chi'_{ij} - w_j$ & χ''_{ij} - w_j curves	% of errors of both $\chi'_{ij} - w_j$ & $\chi''_{ij} - w_j$ curves	Estimated Dipole moments $\mu \times 10^{30}$ in coulomb metre			$\mu_1 =$ $\mu_2 (C_1/C_2)^{1/2}$ in c.m	Reported $\mu \times 10^{30}$ in C.m by	μ_{theo} $\times 10^{30}$ in C.m
			b_1	b_2			μ_1	μ_2	μ_j			
I.1-butanol (M _j = 0.074)	24.33	0.719	0.911	0.0142	0.997347	0.000032	3.02	24.25	3.26	10.25	3.58	
	9.25	0.539	0.955	0.0278	0.998805	0.000014	2.56	14.99	2.69	7.77	3.80	3.74
	3.00	0.830	0.971	0.0593	0.998034	0.000024	3.14	12.72	3.23	8.19	4.30	
II.1-hexanol (M _j =0.102)	24.33	0.034	0.869	0.0537	0.957348	0.000619	0.79	3.18	8.25	1.85	3.35	
	9.25	0.330	0.955	0.0392	0.996042	0.000048	2.35	11.59	2.52	6.55	3.87	3.49
	3.00	0.609	0.971	0.0633	0.998317	0.000020	3.16	12.39	3.17	8.10	4.27	
III.1- heptanol (M _j = 0.116)	24.33	0.588	0.859	0.0121	0.989149	0.000143	3.52	29.69	3.60	11.86	3.59	
	9.25	0.131	0.965	0.0412	0.989026	0.000132	1.57	7.59	2.86	4.40	3.60	3.73
	3.00	0.447	0.965	0.0548	0.996990	0.000040	2.90	12.17	3.06	7.59	4.27	
IV.1- decanol (M _j =0.158)	24.33	0.142	0.798	0.0395	0.994031	0.000072	2.10	9.43	3.47	5.03	3.55	
	9.25	0.227	0.904	0.0411	0.984662	0.000184	2.49	11.67	2.82	6.42	3.83	3.68
	3.00	0.388	0.983	0.1328	0.999324	0.000008	3.12	8.50	3.36	6.92	4.33	

6.6. RESULTS AND DISCUSSIONS

The least square fitted straight line eq. of $(\chi_{oij} - \chi'_{ij}) / \chi'_{ij}$ against χ''_{ij} / χ'_{ij} for

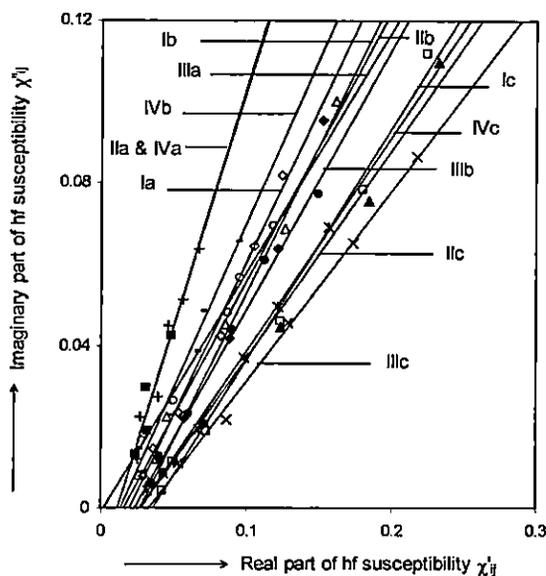


Fig 6.4 Variation of imaginary part of hf susceptibility χ''_{ij} with real part of hf susceptibility χ'_{ij} of alcohols in n-heptane at 25°C of Ia. 1-butanol (\diamond) at 24.33 GHz, Ib. 1-butanol (\blacklozenge) at 9.25 GHz, Ic. 1-butanol (\square) at 3.00 GHz, IIa. 1-hexanol (\blacksquare) at 24.33 GHz, IIb. 1-hexanol (\triangle) at 9.25 GHz, IIc. 1-hexanol (\blacktriangle) at 3.00 GHz, IIIa. 1-heptanol (\circ) at 24.33 GHz, IIIb. 1-heptanol (\bullet) at 9.25 GHz, IIIc. 1-heptanol (\times) at 3.00 GHz, IVa. 1-decanol ($+$) at 24.33 GHz, IVb. 1-decanol ($-$) at 9.25 GHz, IVc. 1-decanol ($*$) at 3.00 GHz

different weight fractions w_j 's of solute at 25°C in n-heptane under different GHz electric field frequency are shown graphically in Fig. 6.1 together with experimental points placed on them. The real χ'_{ij} and imaginary χ''_{ij} parts of hf complex dimensionless dielectric orientational susceptibility χ^*_{ij} and low frequency real dielectric susceptibility χ_{oij} are, however, derived from measured [8] permittivities $\epsilon\epsilon'_{ij}$, ϵ''_{ij} , ϵ_{oij} and ϵ_{ooij} of

Table 6.1. The linearity of all curves of Fig. 6.1 are confirmed by correlation coefficients r 's and percentage of errors placed in the 7th and 8th columns of Table 6.2. The relaxation times τ_1 and τ_2 estimated from eq. (6.6) are placed in the 5th and 6th columns of Table 6.2. It is seen that both τ_1 and τ_2 are of low values at 24.33 GHz and tends to increase with the lower frequencies of 9.25 and 3.00 GHz electric fields. It may be explained on the basis of the fact that at higher frequencies the rate of hydrogen bond rupture is maximum in such long chain alcohols to reduce τ for each rotating unit [20].

In absence of reliable τ_j of such molecules it was tried to calculate τ_j from the least square fitted straight line eq. of χ''_{ij} against χ'_{ij} in Fig. 6.4 as claimed by Murthy et al [10] to place them in the 9th column of Table 6.2. But the experimental points are found to deviate from linearity as seen in Fig. 6.4 which is probably due to various associational aspects of polar molecules in non polar solvent [13]. The

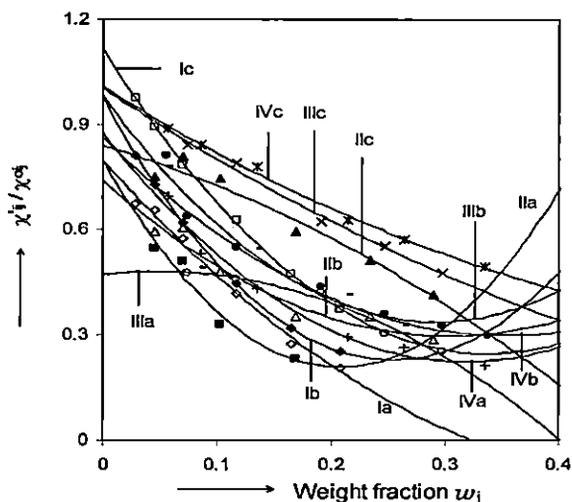


Fig 6.5 i. Variation χ''_{ij} / χ'_{oj} with weight fraction ω_j for alcohols in n-heptane at 25°C of Ia. 1-butanol (\diamond) at 24.33 GHz, Ib. 1-butanol (\blacklozenge) at 9.25 GHz, Ic. 1-butanol (\square) at 3.00 GHz, IIa. 1-hexanol (\blacksquare) at 24.33 GHz, IIb. 1-hexanol (\triangle) at 9.25 GHz, IIc. 1-hexanol (\blacktriangle) at 3.00 GHz, IIIa. 1-heptanol (\circ) at 24.33 GHz, IIIb. 1-heptanol (\bullet) at 9.25 GHz, IIIc. 1-heptanol (\times) at 3.00 GHz, IVa. 1-decanol ($+$) at 24.33 GHz, IVb. 1-decanol ($-$) at 9.25 GHz, IVc. 1-decanol ($*$) at 3.00 GHz

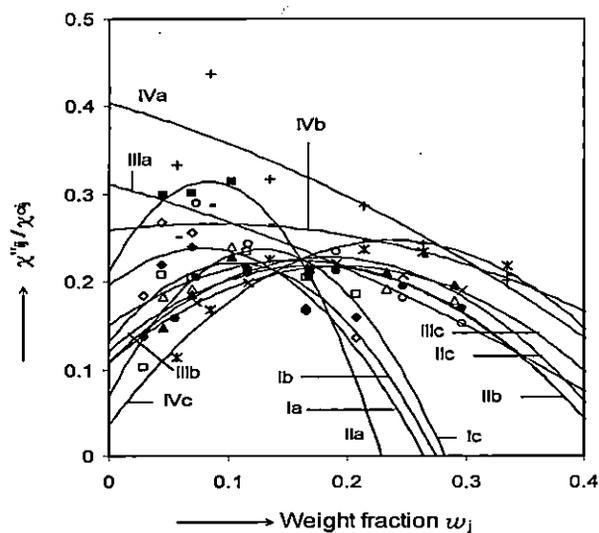


Fig 6.6 . Variation χ''_{ij} / χ'_{oj} with weight fraction ω_j for alcohols in n-heptane at 25°C of Ia. 1-butanol (\diamond) at 24.33 GHz, Ib. 1-butanol (\blacklozenge) at 9.25 GHz, Ic. 1-butanol (\square) at 3.00 GHz, IIa. 1-hexanol (\blacksquare) at 24.33 GHz, IIb. 1-hexanol (\triangle) at 9.25 GHz, IIc. 1-hexanol (\blacktriangle) at 3.00 GHz, IIIa. 1-heptanol (\circ) at 24.33 GHz, IIIb. 1-heptanol (\bullet) at 9.25 GHz, IIIc. 1-heptanol (\times) at 3.00 GHz, IVa. 1-decanol ($+$) at 24.33 GHz, IVb. 1-decanol ($-$) at 9.25 GHz, IVc. 1-decanol ($*$) at 3.00 GHz

individual plots of χ''_{ij} and χ'_{ij} against ω_j of normal alcohols are not linear as seen in Figs 6.2 and 6.3 which confirms the probable solute-solute (dimer) and solute-solvent (monomer) molecular associations. The reliability of both $\chi''_{ij} - \omega_j$ and $\chi'_{ij} - \omega_j$ variations are confirmed by correlation coefficients r 's and

% of errors as placed in Table 6.4. This fact at once inspired us to evaluate τ_j from the ratio of slopes of individual variations of χ''_{ij} and χ'_{ij} with ω_j at $\omega_j \rightarrow 0$. τ_j so obtained shows close agreement with τ_1 from double relaxation and Gopala krishna's method

[11]. This approach further confirms that polar – polar interactions are fully avoided

[6, 15] in the later method. Thus hf dielectric susceptibility measurement yields the

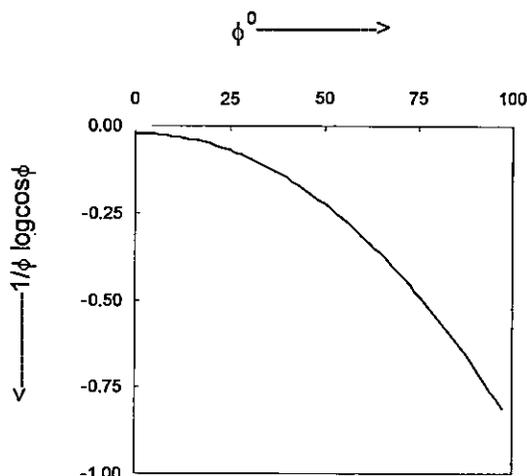


Figure 7. Variation of $(1/\phi) \log(\cos\phi)$ against ϕ^0

Fig 6.7

and asymmetric distribution parameters γ and δ of such molecules from eqs. (6.11) and (6.13) with graphical extrapolation values of χ'_{ij}/χ_{oij} and χ''_{ij}/χ_{oij} at $\omega_j = 0$ of Figs.

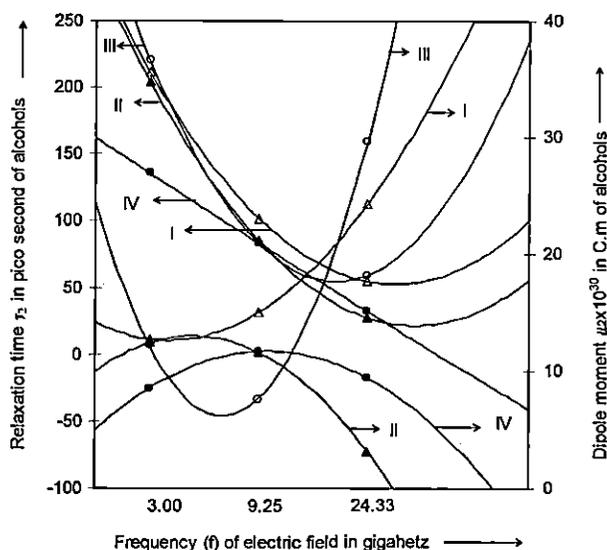


Fig 6.8 Variation of Relaxation time and Dipole moment against frequency(f) of the applied electric field for some alcohols in n-heptane at 25°C I.1-butanol(Δ) II.1-hexanol (\blacktriangle) III.1-heptanol (\circ) IV. 1-decanol (\bullet)

accurate microscopic τ due to orientational polarization whereas double relaxation method gives both microscopic and macroscopic τ 's [15,20].

Higher values of τ_2 's results in bigger size of rotating unit ($\tau_j T / \eta^\gamma$) which is due to solute-solvent (monomer) associations under GHz electric field. Distribution of τ 's between two limiting values τ_1 & τ_2 prompts one to estimate the symmetric

and asymmetric distribution parameters γ and δ of such molecules from eqs. (6.11) and (6.13) with graphical extrapolation values of χ'_{ij}/χ_{oij} and χ''_{ij}/χ_{oij} at $\omega_j = 0$ of Figs. 6.5 and 6.6. Values of γ so obtained is used to evaluate τ_s from eq. (6.12). The arbitrary curve of $(1/\phi) \log(\cos\phi)$ against ϕ in degree is essential to know ϕ for known value of $(1/\phi) \log(\cos\phi)$ from eq. (6.15). Known ϕ from Fig. 6.7 was however used to evaluate δ and τ_{cs} from eqs. (6.13) and (6.14). τ_s and τ_{cs} thus so estimated are entered in the 12th and 13th columns of Table 6.2 to compare them

with τ_1 , τ_2 and τ_j . Both γ and δ are placed in 12th and 13th columns of Table 6.3. The value of γ establishes the non-rigid behaviour of the molecules signifying the applicability of Debye–Smyth model of dielectric relaxation to some extent in such normal alcohols in n-heptane under GHz electric field.

Symmetric relaxation time τ_s obtained from eq. (6.12) with known γ agrees well with τ_1 's by double relaxation and τ_j 's by Gopala Krishna's method except at 3.00 GHz electric field frequency. This discrepancy may be explained on the basis of the fact that at lower frequency the rate of hydrogen bond rupture is small resulting in higher value of τ for each rotating unit. High value of τ_{cs} eventually rules out the possibility of occurring asymmetric relaxation behaviour for the alcohols. Fig. 6.8 represents the plot of both τ_2 and μ_2 against frequency (f) of the applied electric field. It is evident from the plot that τ_2 of the alcohols decreases with frequency. It is due to the fact that at higher frequency the rate of hydrogen bond rupture is maximum, reducing thereby τ_2 for each rotating unit [20]. For system II and IV the variation of μ_2 against frequency is convex in nature having zero μ_2 values at two frequencies due to strong symmetry attained by the molecules. 1-butanol (system I) and 1-heptanol (system III) shows minimum μ_2 for their symmetry attained between 3.00 and 9.25 GHz electric field frequency. Beyond 9.25 GHz μ_2 increases with f showing asymmetric nature of the molecules. All types of symmetries and asymmetries arises probably due to various types of molecular associations between solute and solvent molecules which are supposed to be physico-chemical behaviour of the systems [19].

The relative contributions c_1 and c_2 towards dielectric dispersions as seen in the 6th and 7th columns of Table 6.3 have been evaluated from eqs. (6.4) and (6.5) for fixed τ_1 and τ_2 as predicted from eq. (6.6) and with estimated χ'_{ij}/χ_{oij} and χ''_{ij}/χ_{oij} from Fröhlich's eq. (6.7) and (6.8). The same are, however, obtained experimentally from the graphical variation of χ'_{ij} / χ_{oij} and χ''_{ij} / χ_{oij} with ω_j of Figs. 6.5 and 6.6 at $\omega_j = 0$. They are also shown in 10th and 11th column of Table 6.3 to compare with the former ones. The Fröhlich's parameter A is the temperature variation of the width of distribution of τ and is equal to $\ln(\tau_2/\tau_1)$.

Variation of χ'_{ij}/χ_{oij} and χ''_{ij}/χ_{oij} with ω_j as seen in Figs. 6.5 and 6.6 are concave and convex in nature which are in accordance with Bergmann's eqs. (6.2) and (6.3) as observed elsewhere [14,21]. The estimated c_2 is greater than c_1 for almost all the alcohols in Fröhlich's method, while the reverse is true for graphical technique. Formation of internal hydrogen bonding among -OH groups in polar alcohol molecules gives rise to inertia [15,20] of the flexible part with respect to whole molecule which results in negative c_2 satisfying the condition $c_1 + c_2 \cong 1$ in graphical technique. For Fröhlich method $c_1 + c_2 > 1$, indicating the possibility of occurrence of more than two relaxation processes [8] in them.

Dipole moments μ_1 and μ_2 estimated from dimensionless parameters b_1 and b_2 for measured τ_1 & τ_2 and linear coefficient β 's of $\chi'_{ij} - \omega_j$ curves of Fig. 6.3 are shown in the 8th and 9th columns of Table 6.4. Correlation coefficient 'r' and % of errors involved in $\chi'_{ij} - \omega_j$ variations are placed in 6th and 7th columns of Table 6.4 only to show how far χ'_{ij} 's are correlated with ω_j 's. Values of r's and % of errors in terms of r's gives reliable β to yield accurate μ_1 and μ_2 . Almost all the curves of Fig. 6.3 shows a tendency to become closer within the limit $0.00 \leq \omega_j \leq 0.05$ probably due to the same polarity of the molecules arising out of monomer and dimer formations [13,15].

The theoretical dipole moments μ_{theo} were, however, obtained from bond angles and bond moments of a number of dipolar groups like $\text{H}_3 \rightarrow \text{C}$, $\text{C} \rightarrow \text{O}$ and $\text{O} \leftarrow \text{H}$ of 1.23×10^{-30} , 3.33×10^{-30} and 1.30×10^{-30} Coulomb metre [13] and are entered in 13th column of Table 6.4. The -OH group in all the alcohols making an angle 105° with the C-C bond plays an important role to yield theoretical dipole moment μ_{theo} . In absence of reliable μ_j values Gopala Krishna's method were employed to get μ_j (Reported data) to compare with μ_1 's estimated from the relation $\mu_1 = \mu_2 (c_1/c_2)^{1/2}$ assuming two relaxation processes are equally probable in them. But the agreement is poor as seen in the 11th and 12th columns of Table 6.4, probably due to the fact that sum of c_1 and c_2 as estimated from Fröhlich's method is not strictly equal to one. The close agreement between μ_1 from double relaxation method, μ_{theo} and reported μ 's establishes the basic soundness of the method [19] for getting hf μ_j in addition to the fact that a part of the molecule is rotating [15]

under GHz electric field. Slight disagreement between μ_{theo} and μ_1 arises due to the formation of H bonds among the –OH groups in dipolar liquid molecules which results in solute – solute molecular association increasing thereby the value of μ_{theo} 's.

6.7. CONCLUSIONS

The methodology so far developed in SI units with internationally accepted symbols of dielectric terminologies and parameters appears to be simple, straightforward and topical one to predict relaxation parameters as χ 's are directly linked with molecular orientational polarization. The significant and interesting equations to evaluate relaxation parameters gives deep insight into the solute–solute and solute–solvent molecular interactions in a solution. The simple straight line eq. (6.6) provides one with microscopic and macroscopic relaxation times. Evaluation of τ_j from eq. (6.17) by ratio of slopes of individual variations of χ''_{ij} and χ'_{ij} against ω_j in the limit $\omega_j = 0$ is a better representation of eq. (6.16) of Murthy et al as it eliminates polar–polar interactions in a solution. The results obviously show that the former method in long straight chain hydrogen bonded associative alcohol molecules may be applicable to get the accurate τ 's of the molecules only due to orientational polarization. Validity of the method so far advanced to evaluate hf τ_j and μ_j is also supported by τ_j and μ_j values estimated from freshly calculated Gopala Krishna's method. The close agreement between measured τ_j and τ_{cs} confirms the non-rigid behaviour of the molecules which at once invites the applicability of Debye-Smyth model of dielectric relaxation in such alcohol molecules. Molecular association is however confirmed by conformational structure in which internal H bonding plays the prominent role. Graphical variation of χ'_{ij}/χ_{oij} and χ''_{ij}/χ_{oij} with ω_j as seen in Figs. 6.5 and 6.6 to estimate c_1 and c_2 are concave and convex in nature which are inaccordance with Bergmann's equations. Reliable τ_1 and τ_2 obtained for alcohols at three electric field frequencies indicate the fact that double relaxation is a material property of the system. Although Figs. 6.1 to 6.6 appear to be crowded, they provides a clear comparison between the results obtained for different systems. Some experimental points are found not to

fall on the smooth curves of different Figs. probably due to various molecular associations between solute and solvent molecules which supports the physico-chemical behaviour of the systems. Concave and convex nature of curves of Fig. 6.8 shows that stability and instability of the alcohol molecules depends on frequency of the applied electric field ever shown. Thus the correlation between the conformational structures [19] with the observed results enhances the scientific content to add a new horizon of understanding to the existing knowledge of dielectric relaxation phenomena in addition to physico-chemical properties of the polar liquid molecules.

REFERENCES

- [1]. A Sharma and D R Sharma , *J Phys Soc Japan* **61** (1992) 1049
- [2]. A Sharma, D R Sharma and M S Chowhan, *Indian. J pure & Appl. Phys* **31** (1993) 841
- [3]. S K Sit, N Ghosh, U saha and S Acharyya, *Indian . J Phys* **71B** (1997) 533
- [4]. K S Cole and R H Cole, *J Chem Phys* **9** (1941) 341
- [5]. E A Guggenheim, *Trans Faraday Soc* **45** (1949) 714
- [6]. N Ghosh, R C Basak, S K Sit and S Acharyya , *J Molecular Liquids* **85** (2000) 375
- [7]. A K Jonscher, *Physics of dielectric Solids*, invited papers edited by C H L Goodman 1980
- [8]. L Glasser, J Crossley and C P Smyth, *J Chem.Phys* **57** (1972) 3977
- [9]. A K Jonscher, invited papers presented at *Inst.Phys.conference*, Canterbury, edited by CHL Goodman 1980
- [10]. M B R Murthy, R L Palit and D K Deshpande, *Indian .J Phys* **63B** (1989) 491
- [11]. K V Gopalakrishna, *Trans Faraday Soc.* **53** (1957) 767
- [12]. H Ffóhlich, *Theory of Dielectrics (Oxford University press: Oxford)* 1949
- [13]. N Ghosh, A Karmakar, S K Sit and S Acharyya, *Indian . J pure & Appl. Phys* **38V**(2000) 574
- [14]. U Saha, S K Sit, R C Basak and S Acharyya, *J phys D: Appl phys (U K)*

27 (1994) 596

- [15]. N Ghosh, S K Sit, A K Bothra and S Acharyya, *J Phys D: Appl Phys*, (UK) **34** (2001) 379
- [16]. A Budo, *Phys Z* **39** (1938) 706
- [17]. K Bergmann, D M Roberti and C P Smyth, *J Phys Chem* **64** (1960) 665
- [18]. C P Smyth, *Dielectric Behaviour and Structure* (M C graw Hill: New York) 1955
- [19]. U K Mitra, N Ghosh, P Ghosh and S Acharyya *J Molecular Liquids*, **126** (2006) 53
- [20]. S K Sit, N Ghosh, and S Acharyya, *Indian J Pure & Appl. Phys* **35** (1997) 329
- [21]. S K Sit and S Acharyya *Indian. J. Phys* **70B** (1996) 19.

CHAPTER 7

DIELECTRIC RELAXATION OF AROMATIC PARA SUBSTITUTED
DERIVATIVE POLAR LIQUIDS FROM DISPERSION AND ABSORPTION
PHENOMENA UNDER GIGA HERTZ ELECTRIC FIELD

7. DIELECTRIC RELAXATION OF AROMATIC PARA SUBSTITUTED DERIVATIVE POLAR LIQUIDS FROM DISPERSION AND ABSORPTION PHENOMENA UNDER GIGA HERTZ ELECTRIC FIELD

7.1. INTRODUCTION

Both aliphatic and aromatic polar liquid molecules having substituted polar groups attached to the parent ones are often characterized by more than one relaxation time τ_j 's corresponding to rotations of over all molecule and flexible parts attached to it. In long chain compounds, the molecules having polar flexible parts at their ends may have multiple relaxation processes [1,2]. It is, of course, possible to measure these τ 's while in some cases, the average τ 's are, however, determined since the resolution of more than two distinct dispersive regions cannot often be detected. Para polar aromatic liquid molecules usually, attracted the attention of a large number of workers [3-5] to study their physico-chemical aspects from the dispersion and absorption phenomena.

Dhar et al [6] and Somevanshi et al [7] measured real ϵ'_{ij} and imaginary ϵ''_{ij} parts of hf complex relative permittivity ϵ^*_{ij} under 10 GHz electric field, of some interesting para substituted derivative polar liquid molecules in solvent dioxane and benzene respectively in the temperature range of 17 to 40°C as collected in Table 7.1. p-hydroxypropiophenone, p-chloropropiophenone, p-benzyloxybenzaldehyde were available in the purest form from Aldrich Chemicals and p-acetamidobenzaldehyde from Central Drug Research Institute, Lucknow, India. The liquids dioxane, benzene, p-anisidine, p-phenitidine etc. were, however, obtained from M/S BDH. London. The liquids were purified through repeated fractional distillations. The physical constants of the solvents like density ρ , viscosity η , and the relative permittivity ϵ_r at different temperatures in °C were collected from the literature [8].

Nowadays, the usual and conventional trend to study the dielectric relaxation phenomena of a polar liquid (DRL) is being advanced with the established symbols of dielectric terminology and parameter of hf, complex orientational susceptibility χ^*_{ij} of which $\chi'_{ij} (= \epsilon'_{ij} - \epsilon_{\infty ij})$ and $\chi''_{ij} (= \epsilon''_{ij})$ are the

real and the imaginary parts in S.I. units. If 1 is subtracted from ε'_{ij} to get the real part χ'_{ij} in which all operating processes result, while if infinitely *hf* permittivity $\varepsilon_{\omega ij}$ is subtracted from *hf* ε'_{ij} and static ε_{0ij} one gets χ'_{ij} and χ_{0ij} due to only orientational polarisation process. χ_{0ij} is a real quantity.

Ghosh et al [9] recently studied all these p-compounds in terms of the complex *hf* conductivity σ^*_{ij} [10] where

$$\sigma^*_{ij} = \sigma'_{ij} + j\sigma''_{ij} = \omega\varepsilon_0\varepsilon''_{ij} + j\omega\varepsilon_0\varepsilon'_{ij} \quad (7.1)$$

ε'_{ij} and ε''_{ij} are the real and imaginary parts of the *hf* complex relative permittivity ε^*_{ij} related by

$$\varepsilon^*_{ij} = \varepsilon'_{ij} - j\varepsilon''_{ij} \quad (7.2)$$

$j = \sqrt{-1}$ is a complex number and $\varepsilon_0 =$ permittivity of free space $= 8.854 \times 10^{-12}$ Farad metre⁻¹, to show that all these p-compounds obey Debye-relaxation mechanism. Both σ''_{ij} and σ'_{ij} are related by [11]

$$\sigma''_{ij} = \sigma_{\omega ij} + \frac{1}{\omega\tau_j} \sigma'_{ij} \quad (7.3)$$

$$\text{or, } \frac{d\sigma''_{ij}}{d\sigma'_{ij}} = \frac{1}{\omega\tau_j} \quad (7.4)$$

τ_j 's may, therefore, be determined by the slopes of σ''_{ij} against σ'_{ij} linear curves [11]. A better representation of eq (7.4) can, however, be given by

$$\left(\frac{d\sigma''_{ij}}{d\omega_j} \right)_{\omega_j \rightarrow 0} \bigg/ \left(\frac{d\sigma'_{ij}}{d\omega_j} \right)_{\omega_j \rightarrow 0} = \frac{1}{\omega\tau_j} \quad (7.5)$$

to eliminate polar-polar interactions in the solution when $\omega_j \rightarrow 0$ to measure τ_j 's by Ghosh et al [12] by the conductivity method and known $\omega = 2\pi f$ where $f =$ frequency of the applied electric field = 10 GHz.. Hence Debye Pellat's equation. [13]

$$\varepsilon'_{ij} = \varepsilon_{\infty ij} + \frac{\varepsilon_{0ij} - \varepsilon_{\infty ij}}{1 + \omega^2 \tau_j^2} \quad (7.6)$$

$$\text{and } \varepsilon''_{ij} = \frac{\varepsilon_{0ij} - \varepsilon_{\infty ij}}{1 + \omega^2 \tau_j^2} \omega \tau_j \quad (7.7)$$

can be used to obtain the concentration variation of ε_{0ij} and $\varepsilon_{\infty ij}$ of any polar liquid in close agreement with the experimentally measured data within $\pm 1\%$ error as tested. The data are placed in Table 7.1 together with χ'_{ij} ($= \varepsilon'_{ij} - \varepsilon_{\infty ij}$), χ''_{ij} ($= \varepsilon''_{ij}$) to measure τ_j 's and hf μ_j 's and the static parameters X_{ij} as a function of ω_j 's to get the static μ_s 's. The estimated value of μ_s confirms the data are much more accurate. This indicates the very soundness of the method so far suggested. Thus a faithful measurement of χ'_{ij} and χ''_{ij} is possible to study the relaxation phenomena where the orientational polarisation alone plays the important role. In σ_{ij} 's measurements, the transfer of bound molecular charges are responsible to yield hf μ_j 's with an approximation that $\sigma_{ij} \approx \sigma''_{ij}$ where σ_{ij} is the total hf conductivity $\sigma_{ij} = \omega \varepsilon_0 (\varepsilon''_{ij}{}^2 + \varepsilon'_{ij}{}^2)^{1/2}$ as a function of ω_j at each temperature.

Some sample curves of both χ'_{ij} and χ''_{ij} against ω_j 's are shown in Figs. 7.1 and 7.2 respectively. The linear equations of $\ln \tau_j T$ against $1/T$ with τ_j 's from the susceptibility measurements are shown graphically in Fig. 7.3 with the experimental points placed upon them. The values of intercepts and slopes are entered in the Table 7.3, to compute thermodynamic energy parameters like enthalpy ΔH_τ , entropy ΔS_τ and free energy ΔF_τ of activation due to dielectric relaxation from Eyring's rate process equations [14]. The enthalpy of activation ΔH_η due to viscous flow was estimated from ΔH_τ and the slope δ of the linear equations of $\ln \tau_j T$ against $\ln \eta_i$ where η_i is the coefficient of viscosity of the solvents used. The data as seen in Table 7.2 throw much light on the stability as well as on the physico-chemical properties of the systems. Kalman and Debye factors placed in the Table 7.3 reflect the applicability of Debye model of relaxation for such p-compounds [9].

The *hf* μ_j 's of all the para liquid molecules due to orientational prolarization alone were carefully worked out from the linear coefficients β 's of $\chi'_{ij} - \omega_j$ equations and the dimensionless parameters 'b' involved with estimated μ_j 's at different temperatures and are placed in Table 7.2. They are compared with the reported *hf* μ_j 's, static μ_s 's obtained from linear coefficient a_1 of static $X_{ij} - \omega_j$ equations, and μ_{theo} 's from the available infrared spectroscopic data of bond moments of the substituted polar groups attached to the parent molecules. The disagreement of measured *hf* μ_j with μ_{theo} establishes the existence of inductive and mesomeric moments which in excitd state offers the electromeric effects suffered by the polar groups of the molecules under GHz electric field. The close agreement between μ_j and μ_{theo} is, however, achieved when the bond moments are corrected by multiplying with $\frac{\mu_j}{\mu_{theo}}$ and $\frac{\mu_s}{\mu_{theo}}$ respectively as required.

7.2. THEORETICAL FORMULATONS TO MEASURE τ_j AND μ_j OF A POLAR

UNIT

The real and imaginary parts of *hf* complex relative permittivity ϵ^*_{ij} are related by

$$\epsilon'_{ij} = \epsilon_{\infty ij} + \frac{1}{\omega\tau_j} \epsilon''_{ij} \quad (7.8)$$

replacing $\epsilon'_{ij} - \epsilon_{\infty ij}$ by χ'_{ij} and ϵ''_{ij} by χ''_{ij} we have

$$\chi''_{ij} = (\omega\tau_j) \chi'_{ij}$$

$$\text{or } d\chi''_{ij} / d\chi'_{ij} = (\omega\tau_j) \quad (7.9)$$

χ''_{ij} varies linearly with χ'_{ij} . The slope of eq. (7.9) which is used to measure τ_j of a polar unit.

But for associative liquids like p-anisidine, p-phenitidine etc the variation of χ''_{ij} with χ'_{ij} is not strictly linear as claimed elsewhere [15]. The ratio of slopes of individual variations of χ''_{ij} and χ'_{ij} against w_j 's are found to be a better representation of the slope of eq. (7.9) in which polar - polar interactions are supposed to be almost eliminated [16].

$$\text{Thus } \frac{(d\chi''_{ij}/dw_j)_{w_j \rightarrow 0}}{(d\chi'_{ij}/dw_j)_{w_j \rightarrow 0}} = \omega\tau_j \quad (7.10)$$

The imaginary part χ''_{ij} of hf χ^*_{ij} is [17, 18].

$$\chi''_{ij} = \left(\frac{N\rho_{ij}\mu_j^2}{27\varepsilon_0 M_j k_B T} \right) (\varepsilon_i + 2)^2 \cdot \frac{\omega\tau_j}{1 + \omega^2\tau_j^2} w_j \quad (7.11)$$

which on differentiation w.r.t. w_j and in the limit $w_j \rightarrow 0$ becomes :

$$\left(\frac{d\chi''_{ij}}{dw_j} \right)_{w_j \rightarrow 0} = \left(\frac{N\rho_{ij}\mu_j^2}{27\varepsilon_0 M_j k_B T} \right) (\varepsilon_i + 2)^2 \cdot \frac{\omega\tau_j}{1 + \omega^2\tau_j^2} \quad (7.12)$$

From eqs (7.10) and (7.12) one obtains

$$\omega\tau_j \left(\frac{d\chi'_{ij}}{dw_j} \right)_{w_j \rightarrow 0} = \left(\frac{N\rho_{ij}\mu_j^2}{27\varepsilon_0 M_j k_B T} \right) \frac{\omega\tau_j}{1 + \omega^2\tau_j^2} (\varepsilon_i + 2)^2$$

which at once provides μ_j as :

$$\mu_j = \left[\frac{27\varepsilon_0 M_j k_B T \beta}{N\rho_{ij} (\varepsilon_i + 2)^2 b} \right]^{\frac{1}{2}} \quad (7.13)$$

to measure hf dipole moments μ_j 's in terms of τ_j 's obtained from eq.(7.10) where ε_0 = Permittivity of free space = 8.854×10^{-12} Farad. metre⁻¹.

M_j = Molecular weight of solute in Kg

k_B = Boltzmann constant = 1.38×10^{-23} J mole⁻¹K⁻¹

β = Linear coefficient of $\chi'_{ij} - w_j$ curves of Fig.7.1 at $w_j \rightarrow 0$

T = Temperature in Kelvin

$N = \text{Avogadro's number} = 6.023 \times 10^{23}$

$\epsilon_j = \text{Dielectric relative permittivity of the solvent and}$

$b = \frac{1}{1 + \omega^2 \tau_j^2}$, a dimensionless parameter involved with estimated τ_j 's.

Thus the eq. (7.13) can be employed to measure $hf \mu_j$'s of all para-polar liquid molecules under investigation, in benzene and dioxane at different experimental temperatures. They are presented in Table 7.2. The temperature variations of $hf \mu_j$'s are shown graphically in Fig. 7.4. It is evident from Fig 7.4 that the temperature variation μ_j 's offers a valuable information about the structural aspects in addition to the physico chemical properties of the liquid molecules.

7.3. THEORETICAL FORMULATION OF STATIC PARAMETER X_{ij} TO

ESTIMATE STATIC DIPOLE MOMENT μ_s

The static dipole moment μ_s of a polar solute (j) in a non-polar solvent (i) at TK is given in terms of ϵ_{0ij} and $\epsilon_{\infty ij}$ of Table 7.1, by [12, 13]

$$\frac{\epsilon_{0ij} - 1}{\epsilon_{0ij} + 2} - \frac{\epsilon_{\infty ij} - 1}{\epsilon_{\infty ij} + 2} = \frac{\epsilon_{0i} - 1}{\epsilon_{0i} + 2} - \frac{\epsilon_{\infty i} - 1}{\epsilon_{\infty i} + 2} + \frac{N \mu_s^2}{9 \epsilon_0 k_B T} c_j \quad (7.14)$$

The molar concentration c_j is expressed by w_j of the polar solute

$$c_j = \frac{\rho_{ij}}{M_j} w_j$$

The weight W_j and volume V_j of a polar solute is dissolved in a non-polar solvent of weight W_i and volume V_i to have the solution density ρ_{ij} where

$$\rho_{ij} = \frac{W_j + W_i}{V_j + V_i} = \frac{W_j + W_i}{(W_j / \rho_j) + (W_i / \rho_i)}$$

$$\begin{aligned}
 &= \frac{\rho_i \rho_j}{\rho_j w_i + \rho_i w_j} = \rho_i (1 - \gamma w_j)^{-1} \\
 &= \rho_i (1 + \gamma w_j + \gamma w_j^2 + \dots) \quad (7.15)
 \end{aligned}$$

The weight fractions w_i and w_j of the solvent and solute are

$$w_i = \frac{W_i}{W_i + W_j} \quad \text{and} \quad w_j = \frac{W_j}{W_i + W_j} \quad \text{respectively}$$

such that $w_i + w_j = 1$ and $\gamma = \left(1 - \frac{\rho_i}{\rho_j}\right)$ where ρ_i and ρ_j are the densities of pure solvent and pure solute respectively in S.I. units.

Hence eq. (7.14) becomes:

$$\begin{aligned}
 \frac{\epsilon_{0ij} - \epsilon_{\infty ij}}{(\epsilon_{0ij} + 2)(\epsilon_{\infty ij} + 2)} &= \frac{\epsilon_{oi} - \epsilon_{\alpha i}}{(\epsilon_{oi} + 2)(\epsilon_{\alpha i} + 2)} + \frac{N\rho_i \mu_s^2}{27\epsilon_0 M_j k_B T} \times w_j (1 + \gamma w_j + \dots) \\
 \text{or, } X_{ij} &= X_i + \frac{N\rho_i \mu_s^2}{27\epsilon_0 M_j k_B T} w_j + \frac{N\rho_i \mu_s^2}{27\epsilon_0 M_j k_B T} \gamma w_j^2 + \dots \quad (7.16)
 \end{aligned}$$

Since $0 < w_j < 1$, the above eq. (7.16) can be expressed by the polynomial equation of w_j upto the third term only like

$$X_{ij} = a_0 + a_1 w_j + a_2 w_j^2 + \dots \quad (7.17)$$

Comparing the coefficients of first power of w_j of eqs. (7.16) and (7.17) one gets the static μ_s as:

$$\mu_s = \left[\frac{27\epsilon_0 M_j k_B T}{N\rho_i} a_1 \right]^{\frac{1}{2}} \quad (7.18)$$

where a_1 is the linear coefficient of $X_{ij} - w_j$ curves, a few of which are shown in Fig. 7.5 as for example. μ_s 's from coefficient of higher powers of w_j of eq. (7.16) are not reliable as the term γ is involved with various effects like solute-solute interaction, relative density, macroscopic viscosity, internal field etc. The μ_s 's thus obtained establish the very soundness of the methods so far advanced where

ϵ_{0ij} and $\epsilon_{\infty ij}$ are not experimentally measured. The μ_s 's thus estimated for the p-compounds are seen in Table 7.2 to compare with *hf* μ_j 's from the orientational susceptibility measurements and theoretical μ_{theo} 's from the available bond angles and bond moments of the substituted polar groups attached to the parent molecules.

7.4. RESULTS AND DISCUSSION

The concentration variation of χ'_{ij} and χ''_{ij} of all the p-compounds in solvents dioxane and benzene respectively at different experimental temperatures in $^{\circ}\text{C}$ are collected in Table 7.1 to show some variations of χ'_{ij} and χ''_{ij} with w_j 's in Figs.7.1 and 7.2 respectively as for example. The relaxation times τ_j 's have been measured under 3 cm wave length electric field from eqs. (7.9) and (7.10) by using χ'_{ij} and χ''_{ij} of Table 7.1. τ_j 's from eq. (7.10) are presented in the Table 7.2 to compare with those placed in the same Table 7.2 recalculated from eq.(7.5) by conductivity σ_{ij} method [9] and reported ones [6, 7]. The close agreement between all the τ_j 's at once reflects the validity of eq.(7.10) derived from the susceptibility χ_{ij} 's measurements. Thus the method of ratio of slopes of individual variations of χ'_{ij} and χ''_{ij} with w_j 's in the limit $w_j = 0$ to get τ_j from eq.(7.10) is superior one where the effects of fast polarization in addition to polar-polar interactions are reduced to a large extent [16]. Although not shown in Table 7.2, they were interesting to see that the direct slope of χ''_{ij} against χ'_{ij} gives rise to almost the same τ_j 's with those obtained from the ratio of the individual slopes of χ''_{ij} and χ'_{ij} against w_j 's of eq. (7.10). The τ_j 's at all the temperatures for p-hydroxypropiophenone, p-chloropropiophenone, p-acetamidobenzaldehyde, p-benzyloxy benzaldehyde are of high values probably due to their larger molecular sizes [9] while the reverse is true for p-anisidine, p-phenitidine, o-chloroparanitroaniline and p-bromonitrobenzene. The observation indicates that τ_j 's of all the liquids decrease with the rise of temperature in $^{\circ}\text{C}$ for the lower values of the coefficients of viscosity [6] of solution. The variation of some τ_j 's with $t^{\circ}\text{C}$ of all the p-liquids were found to be (see Table 7.2) irregular and in disagreement with the Debye relaxation [19]. This is, however, explained on the

basis of the fact that as the temperature rises the stretching of bond angles and distributions of bond moments of all the flexible polar groups attached to the parent ones lead to either symmetric or asymmetric shapes of the molecules [9].

The process of rotation of the rotating molecular dipole requires an activation energy sufficient to overcome the energy barrier between two equilibrium positions. Eyrings rate process equation [14] can be used with the known τ_j 's, where

$$\tau_j = \frac{A}{T} \exp(\Delta F_\tau / RT)$$

$$\text{or, } \ln \tau_j T = \ln A' + \frac{\Delta H_\tau}{RT} \quad (7.19)$$

$$\text{since } \Delta F_\tau = \Delta H_\tau - T\Delta S_\tau \quad \text{and } A' = Ae^{-\Delta S_\tau / R}$$

to measure thermodynamic energy parameters like ΔF_τ , ΔH_τ and ΔS_τ usually known as free energy, enthalpy and entropy of activations due to dielectric relaxation processes.

The linear eq.(7.19) of $\ln \tau_j T$ against $1/T$ having intercept and slope are presented in Table 7.3 together with the values of ΔF_τ , ΔH_τ and ΔS_τ as obtained from eq. (7.19). The least square fitted linear plots of $\ln \tau_j T$ against $1/T$ with the experimental points placed on them have been shown in Fig. 7.3. Some of the experimental points are found not to fall on the smooth curves of Fig. 7.3 due to irregular variations of τ_j 's with temperature [9] probably due to the fact that the non spherical dipolar molecules are known to be non Debye in their relaxation behaviours. As seen in Table 7.3 ΔF_τ 's for most of the systems are higher in comparison to ΔH_τ 's. This implies that a large number of flexible polar groups surrounding the parent molecules are rotating under GHz electric field [6]. The -ve ΔS_τ for all the systems except p-benzyloxybenzaldehyde and p-anisidine is due to co-operative orientations of the steric forces [20] indicating thereby that the activated states are more ordered [4,21] while the +ve ΔS_τ 's for other systems refers to the instability of the activated states. Enthalpy of activation due

to viscous flow ΔH_η , has been estimated from slope δ of $\ln \tau_j T$ with $\ln \eta_i$ fitted linear equation and known ΔH_τ in order to place them in Table 7.3. $\delta (= \Delta H_\tau / \Delta H_\eta)$ for all the molecules > 0.50 except p-hydroxypropiophenone and p-acetamidobenzaldehyde indicates the solvent environment around the solute molecules to behave as solid phase rotators [9]. Low value of δ for systems as seen in Table 7.3 arises for the weak interaction of the solvent and solute [9]. Almost constant values of Debye factor $\tau_j T / \eta_i$ rather than Kalman factor $\tau_j T / \eta_i^\delta$ at all the temperatures for each molecule implies the applicability of Debye relaxation for such p-liquids [9,22].

This at once prompted us to recalculate *hf* τ_j 's from conductivity, measurements in the GHz range. From eq.(7.3) one gets

$$\beta = \frac{1}{\omega \tau_j} \left(\frac{d\sigma'_{ij}}{dw_j} \right)_{w_j \rightarrow 0} \quad (7.20)$$

where β is the slope of $\sigma_{ij} - w_j$ curve of a polar-nonpolar liquid mixture at $w_j \rightarrow 0$

The real part of *hf* complex σ_{ij}^* is [12, 17]

$$\begin{aligned} \text{Now } \sigma'_{ij} &= \frac{N\rho_i \mu_j^2}{27M_j k_B T} (\epsilon_{ij} + 2)^2 \frac{\omega^2 \tau_j}{1 + \omega^2 \tau_j^2} w_j \\ \text{or, } \left(\frac{d\sigma'_{ij}}{dw_j} \right)_{w_j \rightarrow 0} &= \frac{N\rho_i \mu_j^2}{27M_j k_B T} (\epsilon_i + 2)^2 \frac{\omega^2 \tau_j}{1 + \omega^2 \tau_j^2} \end{aligned} \quad (7.21)$$

Comparing eqs (7.20) and (7.21) the following formula is obtained to get *hf* μ_j from σ_{ij} in $\Omega^{-1}m^{-1}$ which takes into account of the contribution of bound molecular charge transfer among the solute molecules

$$\mu_j = \left[\frac{27M_j k_B T}{N\rho_i (\epsilon_i + 2)^2} \cdot \frac{\beta}{\omega b} \right]^{\frac{1}{2}} \quad (7.22)$$

where b is a dimensionless parameter involved with τ_j 's measured from eq. (7.5). The recalculated τ_j 's are presented in Table 7.2 for comparison with those measured from eq. (7.10) and reported ones [6,7]. Estimation of τ_j by eq. (7.5) is significant one, as it is useful to obtain ϵ_{0ij} and $\epsilon_{\infty ij}$ by Debye – Pellat's equation, to have static μ_s as entered in Table 7.2. μ_j 's by susceptibility measurements are shown in Table 7.2 to see how far they agree with μ_{theo} 's of the bond moments of the flexible parts as calculated in Fig. 7.6 and the static μ_s from eq. (7.18). μ_s 's thus computed from ϵ_{0ij} and $\epsilon_{\infty ij}$ data of Table 7.1 show the fact that they are very close to hf μ_j . Thus the frequency effect is almost nil in hf μ_j 's obtained by susceptibility method. A comparison between hf μ_j from eqs. (7.13) and (7.22) may, however, be interesting which is to be studied later on. The values of n_{Dij}^2 ($\approx \epsilon_{\infty ij}$) had been tested from the literature [8] where they were available.

$\mu_j - t$ of least square fitted curves of I, III, IV and V of p-hydroxypropiophenone, p-acetamidobenzaldehyde, p-benzyloxybenzaldehyde and p-anisidine initially increases with temperature and then attain the highest value to show maximum asymmetries at different temperatures as seen in Fig. 7.4. μ_j 's of those compounds go on decreasing with temperature to attain symmetries. These curves are convex in nature showing $\mu_j = 0$ at lower and higher temperatures due to strong symmetry attained at those temperatures [9]. The curve of VII for o-chloro-p-nitroaniline shows gradual decrease of μ_j values with temperature. On the other hand the least square fitted curves of μ_j against t in $^{\circ}\text{C}$ of II, VI and VIII are concave in nature. The curve VI of p-phenitidine reaches the highest symmetry and then goes on increasing with the rise in temperature. The curve shows 0 (zero) values at lower and higher temperature, as shown by the dotted line to maintain the continuity of the curves. The above nature of $\mu_j - t$ curves are explained by the rupture of solute-solvent (monomer) and solute-solute (dimer) associations due to stretching of bond angles and bond moments of substituted polar groups at different temperatures. [4,9].

Ghosh et al [9] obtained the μ 's of p-compounds i.e. systems I – VIII as 8.27, 9.73, 13.12, 6.23, 6.82, 15.04, 15.93 & 8.40 each multiplied by 10^{-30} in C.m. respectively. A special attention is to be paid to the contributions of the available bond moments and bond angles due to different substituent groups of parent molecules in calculating theoretical dipole moments μ_{theo} 's. But μ_{theo} 's as sketched elsewhere [9] are found to be slightly deviated from the measured hf μ_j 's and μ_s 's because of the existence of the inductive and the mesomeric moments for different flexible groups. The reduced or elongated bond moments of the substituted polar groups are calculated by multiplying the μ_{theo} 's by the factor μ_j / μ_{theo} around 20^0 C. The results for systems I to VIII are 14.27, 7.27, 12.62, 10.22, 8.56, 29.36, 2.41 and 4.23 each multiplied by 10^{-30} in C.m. respectively. They are placed in the last column of Table 7.2 and displayed in Fig. 7.6. The reduction or elongation in bond moments exhibits the presence of mesomeric, inductive and electromeric effects under static and hf electric fields.

7.5. CONCLUSION

Theoretical consideration in S.I units for the effective utilization of the established symbols of dielectric terminologies and parameters in terms of dielectric susceptibilities obtained from dielectric relative permittivities appears to be more topical, significant and useful one to have valuable information in the study of dispersion and absorption phenomena as they are directly linked with the molecular orientational polarisation. A convenient method is, therefore, suggested to calculate τ_j and μ_j under GHz electric field along with the static μ_s in S.I units of some p-compounds. The ratio of slopes of individual variations of χ''_{ij} and χ'_{ij} with w_j 's is a better representation over the previous one of Murthy et al as it eliminates polar-polar interactions almost completely in a given solution. Thermodynamic energy parameters ; enthalpy ΔH_r , entropy ΔS_r , and free energy ΔF_r of activation due to dielectric relaxation and enthalpy of 'activation due to viscous flow of solvent provides information about the stability or unstabilities of the states of polar-nonpolar liquid mixture in a given temperature range. The physico chemical properties could, also be studied in terms of conformations of such p-compounds. The temperature variation of measured μ_j 's reveals that the

molecules may attain either symmetric or asymmetric shapes with the rise in temperature. The slight difference between experimental μ_j 's and theoretical μ_{theo} 's suggests the existence of inductive, mesomeric and electromeric effects of the polar flexible groups of the molecules due to their aromaticity. Theoretical formulations, so far developed, are in S.I. units because of its unified, coherent and rationalised nature. The experimental points in some cases are slightly deviated from the least squares fitted plots indicating that the highly nonspherical polar molecules are slightly non Debye in relaxation behaviour. However, the $X_{ij} - \omega_j$ curves used to get μ_s , can be used to test the accuracies of the measurements of static ϵ_{0ij} and hf $\epsilon_{\infty ij}$.

The X_{ij} 's are involved with the low and infinitely hf permittivities ϵ_{0ij} and $\epsilon_{\infty ij}$ derived from Debye- pellet's equations in terms of measured concentration variation of ϵ'_{ij} and ϵ''_{ij} of polar-non polar liquid mixtures. The μ_j 's and μ_s 's are almost equal in some cases only to show that μ_j 's are little affected by the applied electric field frequency. The computation of τ_j , μ_j and μ_s from σ_{ij} , χ_{ij} and X_{ij} measurements of a polar unit in a given solvent appears to be more simple, straight forward and topical one to locate the accuracies of τ_j , μ_j and μ_s which are claimed to be accurate within 10% and 5% respectively. The calculated results appear to be of more archival values to reveal some interest in the process of dielectric relaxation. The factors of μ_i / μ_{theo} and μ_j / μ_{theo} are almost constant for all the molecules revealing the material property of the systems [23]. The correlation between the conformational structures presented in Fig. 7.6 of the p-compounds with the observed results enhances the scientific content and adds a new horizon to understand the existing knowledge of dielectric relaxation from dispersion and absorption phenomena.

Table 7.1: Concentration variation of the real and imaginary parts of dielectric permittivity ϵ^*_{ij} , static permittivity ϵ_{0ij} , infinitely high frequency permittivity $\epsilon_{\infty ij}$, real and imaginary parts of dielectric susceptibilities χ'_{ij} and χ''_{ij} of hf complex susceptibility χ^*_{ij} and static experimental parameters X_{ij} , of some parapolar liquids in non polar solvents at different experimental temperatures under 10 GHz electric field

System with Sl. No.	Temp in $^{\circ}\text{C}$	Weight fraction	Dielectric permittivities				Dielectric susceptibilities		static experimental parameter
			ϵ'_{ij}	ϵ''_{ij}	ϵ_{0ij}	$\epsilon_{\infty ij}$	χ'_{ij}	χ''_{ij}	X_{ij}
1. p-hydroxy- propiophenone (in dioxane)	17	0.0040	2.0930	0.0320	2.1316	2.0665	0.0265	0.0320	0.00388
		0.0066	2.0970	0.0420	2.1477	2.0622	0.0348	0.0420	0.00507
		0.0089	2.0980	0.0440	2.1511	2.0615	0.0365	0.0440	0.00531
		0.0107	2.0990	0.0470	2.1557	2.0601	0.0389	0.0470	0.00567
		0.0116	2.1210	0.0620	2.1958	2.0696	0.0514	0.0620	0.00739
	23	0.0040	2.1250	0.0310	2.1663	2.1018	0.0232	0.0310	0.00378
		0.0066	2.1330	0.0470	2.1957	2.0978	0.0352	0.0470	0.00570
		0.0090	2.1410	0.0590	2.2197	2.0968	0.0442	0.0590	0.00711
		0.0117	2.1560	0.0720	2.2520	2.1020	0.0540	0.0720	0.00860
	30	0.0041	2.1490	0.0360	2.2035	2.1252	0.0238	0.0360	0.00451
		0.0067	2.1550	0.0440	2.2216	2.1259	0.0291	0.0440	0.00549
		0.0091	2.1560	0.0470	2.2271	2.1249	0.0311	0.0470	0.00586
		0.0109	2.1570	0.0490	2.2312	2.1246	0.0324	0.0490	0.00610
		0.0118	2.1730	0.0710	2.2805	2.1261	0.0469	0.0710	0.00874
	37	0.0041	2.1580	0.0350	2.1896	2.1192	0.0388	0.0350	0.00408
		0.0068	2.1750	0.0440	2.2147	2.1263	0.0487	0.0440	0.00509
		0.0092	2.1780	0.0510	2.2241	2.1215	0.0565	0.0510	0.00589
		0.0110	2.1840	0.0560	2.2346	2.1220	0.0620	0.0560	0.00645
		0.0119	2.1860	0.0590	2.2393	2.1207	0.0653	0.0590	0.00679
	2. p-chloro- propiophenone (in dioxane)	19	0.0050	2.1100	0.0280	2.1301	2.0709	0.0391	0.0280
0.0068			2.1200	0.0320	2.1429	2.0754	0.0446	0.0320	0.00400
0.0080			2.1220	0.0340	2.1464	2.0746	0.0474	0.0340	0.00425
0.0093			2.1270	0.0400	2.1557	2.0712	0.0558	0.0400	0.00499
0.0112			2.1330	0.0450	2.1653	2.0702	0.0628	0.0450	0.00561
0.0123			2.1430	0.0490	2.1781	2.0746	0.0684	0.0490	0.00608
25		0.0051	2.1230	0.0290	2.1581	2.0990	0.0240	0.0290	0.00347
		0.0069	2.1250	0.0320	2.1637	2.0986	0.0264	0.0320	0.00382
		0.0081	2.1280	0.0340	2.1692	2.0999	0.0281	0.0340	0.00405
		0.0094	2.1290	0.0390	2.1762	2.0968	0.0322	0.0390	0.00464
		0.0113	2.1340	0.0430	2.1861	2.0985	0.0355	0.0430	0.00510
		0.0124	2.1410	0.0500	2.2015	2.0997	0.0413	0.0500	0.00591
31		0.0051	2.1350	0.0290	2.1817	2.1170	0.0180	0.0290	0.00376
		0.0069	2.1380	0.0330	2.1911	2.1175	0.0205	0.0330	0.00427
		0.0082	2.1390	0.0340	2.1937	2.1179	0.0211	0.0340	0.00439
		0.0095	2.1480	0.0390	2.2108	2.1238	0.0242	0.0390	0.00501
		0.0114	2.1490	0.0410	2.2150	2.1235	0.0255	0.0410	0.00526
		0.0125	2.1510	0.0630	2.2524	2.1119	0.0391	0.0630	0.00804
37		0.0052	2.1450	0.0270	2.1574	2.0861	0.0589	0.0270	0.00419
		0.0070	2.1680	0.0290	2.1813	2.1048	0.0632	0.0290	0.00446
	0.0083	2.1730	0.0330	2.1881	2.1011	0.0719	0.0330	0.00507	
	0.0115	2.1740	0.0360	2.1905	2.0955	0.0785	0.0360	0.00553	
	0.0126	2.1790	0.0400	2.1974	2.0918	0.0872	0.0400	0.00615	

System with Sl. No.	Temp in °C	Weight fraction	Dielectric permittivities				Dielectric susceptibilities		static experimental parameter
			w_j	ϵ'_{ij}	ϵ''_{ij}	ϵ_{oij}	$\epsilon_{\infty ij}$	χ'_{ij}	χ''_{ij}
3. p-acetamido benzaldehyde (in dioxane)	17	0.0023	2.1530	0.0290	2.2024	2.1360	0.0170	0.0290	0.00382
		0.0042	2.1540	0.0380	2.2187	2.1317	0.0223	0.0380	0.00499
		0.0073	2.1600	0.0530	2.2503	2.1289	0.0311	0.0530	0.00692
		0.0078	2.1690	0.0610	2.2729	2.1332	0.0358	0.0610	0.00791
		0.0112	2.1750	0.0670	2.2891	2.1357	0.0393	0.0670	0.00865
	23	0.0023	2.1580	0.0340	2.2031	2.1324	0.0256	0.0340	0.00407
		0.0043	2.1650	0.0440	2.2233	2.1318	0.0332	0.0440	0.00524
		0.0073	2.1710	0.0480	2.2346	2.1348	0.0362	0.0480	0.00570
		0.0078	2.1740	0.0560	2.2482	2.1318	0.0422	0.0560	0.00664
		0.0113	2.1820	0.0670	2.2708	2.1315	0.0505	0.0670	0.00790
	30	0.0154	2.1840	0.0680	2.2741	2.1327	0.0513	0.0680	0.00801
		0.0074	2.1750	0.0350	2.2275	2.1517	0.0233	0.0350	0.00432
		0.0079	2.1860	0.0430	2.2505	2.1573	0.0287	0.0430	0.00527
		0.0098	2.1870	0.0530	2.2665	2.1517	0.0353	0.0530	0.00648
		0.0114	2.1950	0.0590	2.2835	2.1557	0.0393	0.0590	0.00718
37	0.0155	2.2010	0.0710	2.3075	2.1537	0.0473	0.0710	0.00860	
	0.0075	2.2110	0.0370	2.2600	2.1831	0.0279	0.0370	0.00432	
	0.0080	2.2210	0.0470	2.2832	2.1855	0.0355	0.0470	0.00545	
	0.0099	2.2320	0.0550	2.3048	2.1905	0.0415	0.0550	0.00634	
	0.0115	2.2410	0.0730	2.3377	2.1859	0.0551	0.0730	0.00836	
4. p- benzyloxy- benzaldehyde (in dioxane)	20	0.0157	2.2420	0.0760	2.3426	2.1846	0.0574	0.0760	0.00870
		0.004	2.1450	0.027	2.1910	2.1292	0.0158	0.0270	0.00358
		0.0066	2.1500	0.029	2.1994	2.1330	0.0170	0.0290	0.00383
		0.0089	2.1520	0.031	2.2049	2.1338	0.0182	0.0310	0.00409
		0.0104	2.1530	0.035	2.2127	2.1325	0.0205	0.0350	0.00461
	25	0.0116	2.1540	0.036	2.2154	2.1329	0.0211	0.0360	0.00473
		0.0153	2.1560	0.045	2.2327	2.1296	0.0264	0.0450	0.00590
		0.0041	2.167	0.028	2.1947	2.1387	0.0283	0.0280	0.00323
		0.0067	2.172	0.034	2.2057	2.1377	0.0343	0.0340	0.00391
		0.009	2.174	0.038	2.2117	2.1357	0.0383	0.0380	0.00436
	30	0.0105	2.175	0.039	2.2136	2.1356	0.0394	0.0390	0.00448
		0.0117	2.18	0.044	2.2236	2.1356	0.0444	0.0440	0.00504
		0.0154	2.187	0.047	2.2336	2.1396	0.0474	0.0470	0.00536
		0.0041	2.1780	0.0310	2.2151	2.1521	0.0259	0.0310	0.00360
		0.0067	2.1920	0.0350	2.2339	2.1627	0.0293	0.0350	0.00404
35	0.009	2.1930	0.0390	2.2397	2.1604	0.0326	0.0390	0.00449	
	0.0106	2.1940	0.0400	2.2419	2.1606	0.0334	0.0400	0.00461	
	0.0118	2.1960	0.0440	2.2486	2.1592	0.0368	0.0440	0.00506	
	0.0155	2.2060	0.0620	2.2802	2.1542	0.0518	0.0620	0.00709	
	0.0041	2.2030	0.0320	2.2290	2.1636	0.0394	0.0320	0.00371	
35	0.0091	2.2090	0.036	2.2382	2.1647	0.0443	0.0360	0.00417	
	0.0119	2.2160	0.042	2.2501	2.1643	0.0517	0.0420	0.00485	
	0.0156	2.2190	0.0450	2.2556	2.1636	0.0554	0.0450	0.00519	

System with Sl. No.	Temp in °C	Weight fraction	Dielectric permittivities				Dielectric susceptibilities		static experimental parameter
			ϵ'_{ij}	ϵ''_{ij}	ϵ_{oij}	$\epsilon_{\infty ij}$	χ'_{ij}	χ''_{ij}	X_{ij}
5. p-anisidine (in benzene)	20	0.0071	2.1700	0.0300	2.1854	2.1117	0.0583	0.0300	0.00428
		0.0098	2.1900	0.0350	2.2080	2.1220	0.0680	0.0350	0.00496
		0.0121	2.2000	0.0400	2.2206	2.1223	0.0777	0.0400	0.00565
		0.0165	2.2000	0.0440	2.2227	2.1146	0.0854	0.0440	0.00622
		0.0198	2.2100	0.0480	2.2347	2.1168	0.0932	0.0480	0.00676
	30	0.0071	2.1800	0.0300	2.1919	2.1041	0.0759	0.0300	0.00510
		0.0098	2.1900	0.0350	2.2038	2.1014	0.0886	0.0350	0.00594
		0.0121	2.2000	0.0400	2.2158	2.0987	0.1013	0.0400	0.00677
		0.0165	2.2100	0.0450	2.2278	2.0961	0.1139	0.0450	0.00760
		0.0198	2.2200	0.0450	2.2378	2.1061	0.1139	0.0450	0.00757
	40	0.0071	2.1900	0.0400	2.1997	2.0247	0.1653	0.0400	0.01035
		0.0098	2.2000	0.0420	2.2102	2.0265	0.1735	0.0420	0.01084
		0.0121	2.2100	0.0440	2.2206	2.0282	0.1818	0.0440	0.01132
		0.0165	2.2200	0.0460	2.2311	2.0299	0.1901	0.0460	0.01180
		0.0198	2.2300	0.0500	2.2421	2.0234	0.2066	0.0500	0.01281
6. p-phenitidine (in benzene)	20	0.0132	2.3100	0.0300	2.3296	2.2642	0.0458	0.0300	0.00355
		0.0149	2.3200	0.0500	2.3527	2.2436	0.0764	0.0500	0.00591
		0.0168	2.3400	0.0700	2.3858	2.2330	0.1070	0.0700	0.00823
		0.0199	2.3800	0.0800	2.4324	2.2577	0.1223	0.0800	0.00925
		0.0231	2.3900	0.0900	2.4489	2.2525	0.1375	0.0900	0.01038
	30	0.0132	2.3200	0.0300	2.3373	2.2681	0.0519	0.0300	0.00374
		0.0149	2.3700	0.0400	2.3931	2.3008	0.0692	0.0400	0.00489
		0.0168	2.3800	0.0500	2.4089	2.2935	0.0865	0.0500	0.00610
		0.0199	2.4100	0.0600	2.4447	2.3061	0.1039	0.0600	0.00724
		0.0231	2.4100	0.0800	2.4562	2.2715	0.1385	0.0800	0.00970
	40	0.0132	2.3400	0.0400	2.3604	2.2615	0.0785	0.0400	0.00532
		0.0149	2.3400	0.0500	2.3655	2.2419	0.0981	0.0500	0.00668
		0.0168	2.3600	0.0600	2.3906	2.2422	0.1178	0.0600	0.00796
		0.0199	2.3900	0.0700	2.4257	2.2526	0.1374	0.0700	0.00920
		0.0231	2.4100	0.0800	2.4508	2.2530	0.1570	0.0800	0.01045
7. o-chloro-p- nitro aniline (in benzene)	20	0.0251	2.0700	0.0200	2.0832	2.0398	0.0302	0.0200	0.00264
		0.0293	2.0800	0.0200	2.0932	2.0498	0.0302	0.0200	0.00262
		0.0331	2.0900	0.0300	2.1098	2.0446	0.0454	0.0300	0.00392
		0.0652	2.1000	0.0300	2.1198	2.0546	0.0454	0.0300	0.00390
		0.0851	2.1000	0.0400	2.1265	2.0395	0.0605	0.0400	0.00522
	30	0.0251	2.1000	0.0200	2.1100	2.0600	0.0400	0.0200	0.00300
		0.0293	2.1000	0.0200	2.1100	2.0600	0.0400	0.0200	0.00300
		0.0331	2.1100	0.0250	2.1225	2.0600	0.0500	0.0250	0.00373
		0.0652	2.1100	0.0250	2.1225	2.0600	0.0500	0.0250	0.00373
		0.0851	2.1200	0.0300	2.1350	2.0600	0.0600	0.0300	0.00447
	40	0.0251	2.1200	0.0300	2.1344	2.0575	0.0625	0.0300	0.00459
		0.0293	2.1200	0.0300	2.1344	2.0575	0.0625	0.0300	0.00459
		0.0331	2.1300	0.0325	2.1456	2.0623	0.0677	0.0325	0.00495
		0.0652	2.1300	0.0325	2.1456	2.0623	0.0677	0.0325	0.00495
		0.0851	2.1300	0.0350	2.1468	2.0571	0.0729	0.0350	0.00533

System with Sl. No.	Temp in °C	Weight fraction	Dielectric permittivities				Dielectric susceptibilities		static experimental parameter
			ϵ'_{ij}	ϵ''_{ij}	ϵ_{oij}	$\epsilon_{\infty ij}$	χ'_{ij}	χ''_{ij}	X_{ij}
8. p-bromo- nitro benzene (in benzenè)	20	0.0162	2.2100	0.0263	2.2267	2.1686	0.0415	0.0263	0.00330
		0.0202	2.2313	0.0302	2.2504	2.1837	0.0476	0.0302	0.00375
		0.0342	2.2352	0.0350	2.2574	2.1801	0.0551	0.0350	0.00434
		0.0375	2.2423	0.0375	2.2661	2.1832	0.0591	0.0375	0.00464
		0.0416	2.2540	0.0400	2.2794	2.1910	0.0630	0.0400	0.00493
	30	0.0162	2.2483	0.0270	2.2634	2.2003	0.0480	0.0270	0.00353
		0.0202	2.2621	0.0320	2.2801	2.2051	0.0570	0.0320	0.00416
		0.0342	2.2670	0.0351	2.2867	2.2044	0.0625	0.0351	0.00456
		0.0375	2.2739	0.0441	2.2987	2.1953	0.0786	0.0441	0.00573
		0.0416	2.2880	0.0460	2.3138	2.2061	0.0819	0.0460	0.00594
	40	0.0162	2.2756	0.0276	2.2898	2.2218	0.0538	0.0276	0.00375
		0.0202	2.2931	0.0332	2.3101	2.2283	0.0648	0.0332	0.00449
		0.0342	2.2982	0.0353	2.3162	2.2294	0.0688	0.0353	0.00476
		0.0375	2.3056	0.0463	2.3293	2.2153	0.0903	0.0463	0.00625
		0.0416	2.3220	0.0478	2.3465	2.2287	0.0933	0.0478	0.00641

Table-7.2:- Measured τ_j 's from ratio of slopes of individual variations of χ'_{ij} and χ''_{ij} with w_j , estimated relaxation time τ_i , reported τ_i all are in pico second, estimated dipole moments (μ_j) using τ_j of eq. (7.10), estimated μ_s , reported μ_j and theoretical dipole moment μ_{theo} using bond moments in Coulomb - metre of some para compounds in non-polar solvents at different experimental temperatures under 10 GHz electric field.

System with Sl.no. & molecular weight (Mj) in Kg	Temp. in $^{\circ}\text{C}$	Measured τ_j in p-sec using eq.(7.10)	τ_j in p-sec by eq.(5)	Reported τ_j in p-sec	Estimated hf $\mu_j \times 10^{30}$ in C.m.	Estimated $\mu_s \times 10^{30}$ in C.m.	Reported $\mu \times 10^{30}$ in C.m.	Corrected $\mu_{theo} \times 10^{30}$ in C.m.
1. p-hydroxy propiophenone Mj = 0.150 Kg	17	19.20	19.20	-	-	-		
	23	21.21	21.21	25.40	14.28	14.65	10.20	14.27
	30	24.08	24.08	24.20		-		
	37	14.37	14.37	23.10	10.25	10.16		
2. P-chloro propiophenone Mj = 0.1685 Kg	19	11.40	11.40	20.80	5.33	5.61	9.84	7.27
	25	19.26	19.26	19.20	-	-		
	31	25.60	25.60	18.20	-	-		
	37	7.30	7.30	17.10	7.28	6.46		
3. P-acetamido benzaldehyde Mj = 0.163 Kg	17	27.10	27.10	21.80	15.96	16.07		
	23	21.09	21.09	20.80	12.62	12.60	10.37	12.62
	30	23.86	23.86	19.00	20.57	20.40		
	37	21.07	21.06	18.60	26.85	26.12		
4. P-benzyloxy benzaldehyde Mj = 0.212 Kg	20	27.13	27.12	20.00	-	-		
	25	15.77	15.77	19.40	10.22	10.34	10.63	10.22
	30	19.03	19.03	18.00	-	-		
	35	12.92	12.92	16.90	6.12	6.05		
5. P-anisidine Mj = 0.123 Kg	20	8.19	9.21	3.89	9.29	9.38	5.20	8.56
	30	6.28	10.86	3.67	12.43	12.78	10.33	
	40	3.85	11.34	3.17	4.84	4.47	8.87	
6. P-phenitidine Mj = 0.0.137 Kg	20	10.41	9.82	11.08	29.35	29.22	7.47	29.36
	30	9.19	10.17	10.63	11.06	9.55	9.27	
	40	8.10	9.91	9.95	20.32	20.26	10.47	
7. O-chloro p-nitro aniline Mj = 0.1725 Kg	20	10.52	10.52	10.57	2.41	2.33	8.13	2.41
	30	7.95	20.47	9.89	1.87	1.97	10.93	
	40	7.64	30.59	9.18	1.38	1.17	13.10	
8. P-bromo nitrobenzene Mj = 0.202 kg	20	10.10	8.40	-	4.23	4.36	-	4.23
	30	8.93	8.93	-	-	-	-	
	40	8.15	8.16	-	-	-	-	

Table-7.3 :The intercepts and slopes of $\ln\tau_j T$ against $1/T$ curves of Fig. 7.3, thermodynamic energy parameters like enthalpy of activation ΔH_τ in Kilo Joule mole⁻¹, the entropy of activation ΔS_τ in Joule mole⁻¹ K⁻¹, free energy of activation ΔF_τ in Kilo Joule mole⁻¹ for dielectric relaxation process, enthalpy of activation ΔH_η in kilo Joule mole⁻¹ due to viscous flow, δ as the ratio of ΔH_τ and ΔH_η , kalman factor $(\tau_j T/\eta^\delta)$, Debye factor $(\tau_j T/\eta)$ at different experimental temperatures in °C and the coefficients of $\mu_j - t$ equations $\mu_j = a + bt + ct^2$ of different para compounds in dioxane and benzene under 10 GHz electric field frequency.

System with Sl.no. & mole ular weight (Mj) in Kg	Tem p in °C	Intercept & slope of $\ln\tau_j T$ Vs $1/T$ equation		ΔH_τ i n KJ mole ⁻¹	ΔS_τ in J mole ⁻¹ K ⁻¹	ΔF_τ in KJ mole ⁻¹	$\gamma =$ ($\Delta H_\tau /$ ΔH_η)	ΔH_η in KJ mole ⁻¹	Kalman factor ($\tau_j T / \eta^\delta$)	Debye factor ($\tau_j T / \eta$) $\times 10^6$	Coefficients in the eqs μ_j $\times 10^{30} = a + bt + ct^2$ equation		
		Intercept	slope								a	b	c
p-hydroxy propiofenone Mj = 0.150 Kg	17				-19.29	11.50			1.40×10^{-7}	3.88			
	23	-21.33	708.00	5.91	-20.71	12.03	0.49	11.99	1.66×10^{-7}	4.83	-0.02	1.15	-11.49
	30				-22.42	12.70			2.06×10^{-7}	6.40			
	37				-18.74	11.72			1.30×10^{-7}	4.52			
P-chloro propiofenone Mj = 0.1685 g	19				-1.59	10.33			1.48×10^{-6}	2.40			
	25	-23.20	1182.4	9.86	-6.81	11.89	0.92	10.68	2.81×10^{-6}	4.57	0.0875	-4.8	65.11
	31				-10.01	12.90			4.22×10^{-6}	6.95			
	37				-0.33	9.96			1.38×10^{-6}	2.30			
P- acetamido benzaldehyde Mj = 0.163 Kg	17				-27.27	12.33			5.48×10^{-8}	5.48			
	23	-20.56	530.45	4.42	-25.66	12.02	0.30	14.92	4.48×10^{-8}	4.80	0.0595	-2.06	35.89
	30				-27.23	12.68			5.40×10^{-8}	6.34			
	37				-26.71	12.71			5.09×10^{-8}	6.63			
P-benzyloxy benzaldehyde Mj = 0.212 Kg	20				53.72	12.49			1.50×10^{-3}	5.81			
	25	-30.30	3384.2	28.23	56.49	11.39	1.84	15.32	1.04×10^{-3}	3.74	-0.041	2.42	30.10
	30				53.21	12.10			1.53×10^{-3}	5.06			
	35				54.79	11.35			1.31×10^{-3}	3.94			
P-anisidine Mj = 0.123 Kg	20				56.96	9.56			2.78×10^{-4}	3.89			
	30	-30.55	3147.2	26.25	55.93	9.30	4.07	6.45	3.24×10^{-4}	3.39	-0.054	3.00	29.22
	40				56.98	8.42			2.73×10^{-4}	2.30			
P- phenitidine Mj 0.0.137 Kg	20				-10.58	10.15			2.44×10^{-5}	4.94			
	30	-22.49	844.99	7.05	-10.62	10.26	1.11	6.37	2.08×10^{-5}	4.96	0.1377	-8.71	148.55
	40				-10.58	10.36			2.48×10^{-5}	4.85			
O-chloro p- nitro aniline Mj = 0.1725 g	20				-1.22	10.17			4.22×10^{-4}	5.00			
	30	-23.65	1177.0	9.82	-0.26	9.90	1.60	6.14	3.85×10^{-4}	4.29	0.0002	-0.06	3.575
	40				-1.24	10.21			4.27×10^{-4}	4.57			
P-bromo nitrobenzene Mj = 0.202 kg	20				-15.07	10.07			1.95×10^{-6}	4.79			
	30	-21.96	678.44	5.66	-14.96	10.19	0.90	6.32	1.94×10^{-6}	4.82	0.0211	-1.48	25.35
	40				-15.07	10.38			1.95×10^{-6}	4.88			

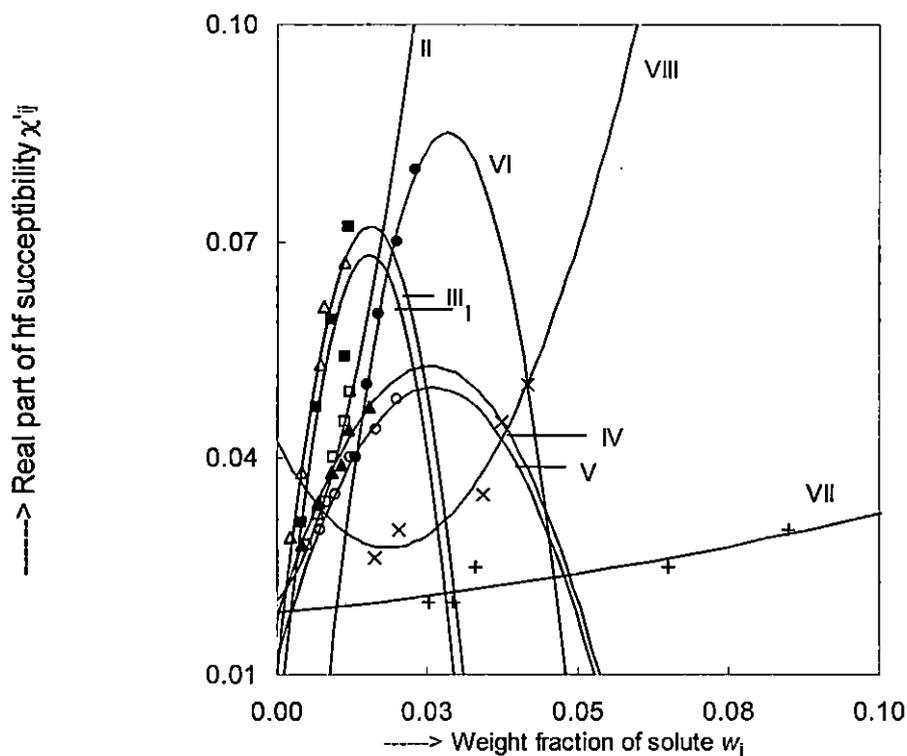


Fig-7.1:Variation of real part χ'_{ij} of hf complex orientational susceptibility against weight fraction w_j of solute of some para compounds at selected temperatures in nonpolar solvents (dioxane and benzene) under 10 GHz electric field frequency I. p-hydroxypropiofenone (-- ■ --) at 23^o C, II.p-chloropropiofenone (-- □ --) at 19^o C, III.P-acetamidobenzaldehyde (-- △ --) at 17^o C, IV .p-benzyloxybenzaldehyde (-- ▲ - -) at 25^o C, V. p-anisidine (-- o--) at 20^o C, VI. p-phenitidine (-- • --) at 40^o C, VII. o-chloro-p-nitroaniline (-- + --) at 30^o C, VIII. p-bromonitrobenzene (-- x --) at 20^o C .

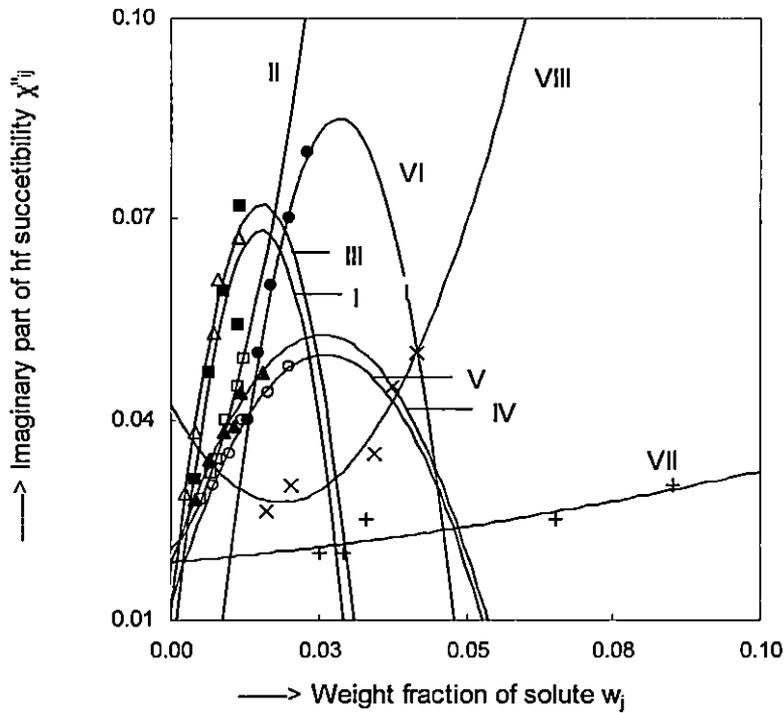


Fig.7.2: Variation of imaginary part χ''_{ij} of hf complex orientational susceptibility against weight fraction w_j of solute of some para compounds at selected temperatures in nonpolar solvents (dioxane and benzene) under 10 GHz electric field frequency. I. p-hydroxypopiophenone (-- ■ --) at 23^o C, II.p-chloropropiophenone (-- □ --) at 19^oC, III.P-acetamidobenzaldehyde (-- △ --) at 17^oC, IV .p-benzyloxybenzaldehyde (-- ▲ --) at 25^oC, V. p-anisidine (-- o--) at 20^oC, VI. p-phenitidine (-- • --) at 40^oC, VII. o-chloro-p-nitroaniline (-- + --) at 30^oC, VIII. p-bromonitrobenzene (-- x --) at 20^oC .

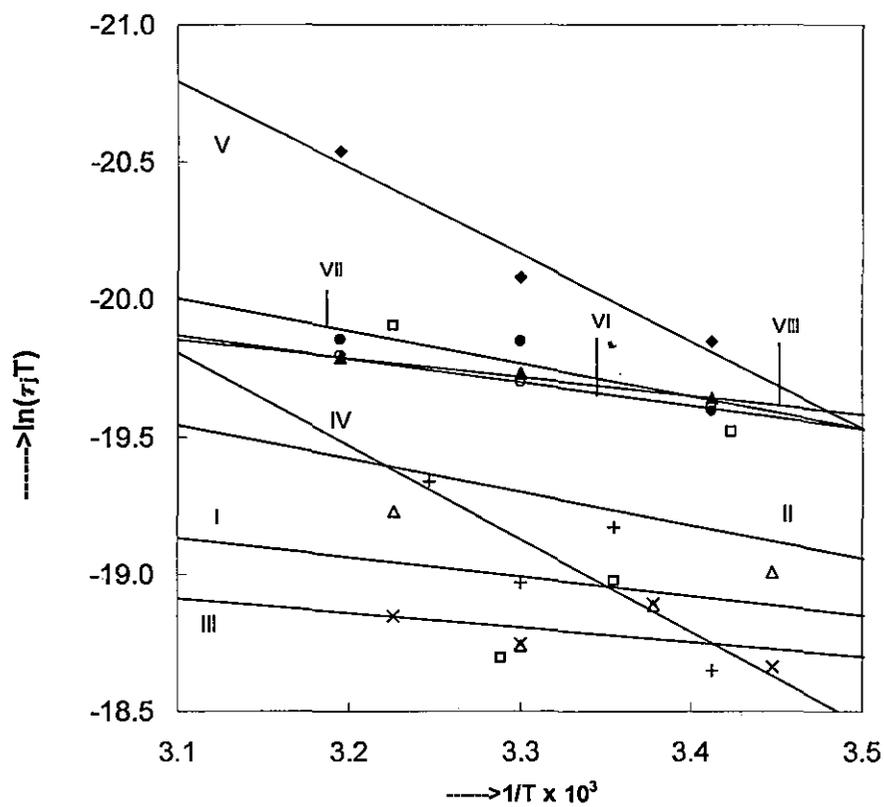


Fig. 7.3 .Straight line plots of $\ln(\tau_i T)$ against $1/T$ I. p-hydroxypropiophenone ($-\Delta-$). II. P-chloroprolohenone ($-\square-$). III. P-acetamidobenzaldehyde ($-\times-$). IV. P-benzyloxybenzaldehyde ($-\+-$). V. P-anisidine ($-\blacklozenge-$). VI. P-phenitidine ($-\circ-$). VII. o-chloro-p-nitroaniline ($-\bullet-$). VIII. P-bromonitrobenzene ($-\blacktriangle-$).

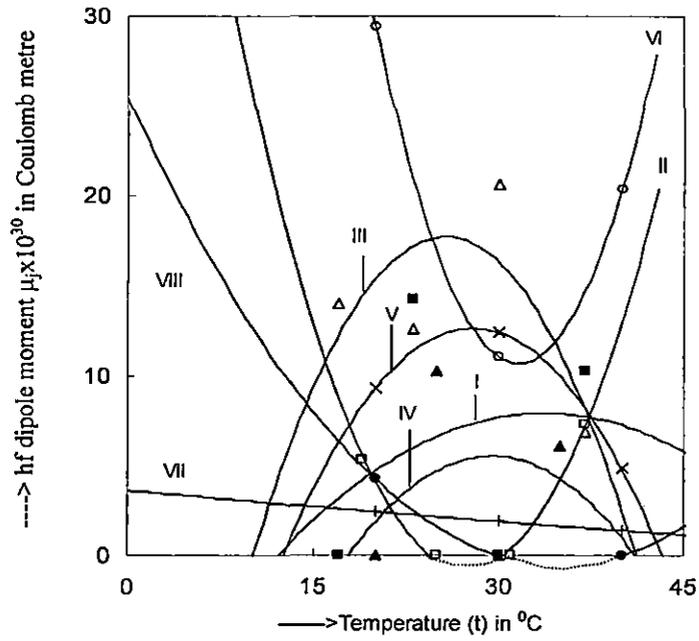


Fig. 7.4 Variation of estimated hf dipole moments $\mu_j \times 10^{30}$ in Coulomb metre against t in $^{\circ}\text{C}$. I. p-hydroxy propiophenone (— ■ —) II. p-chloropropiophenone (— □ —) III. p-acetamidobenzaldehyde (— △ —) IV. p-benzyloxybenzaldehyde (— ▲ —) V. p-anisidine (— x —) VI. p-phenitidine (— o —) VII. o-chloro-p-nitroaniline (— + —) VIII. p-bromonitrobenzene (— ● —)

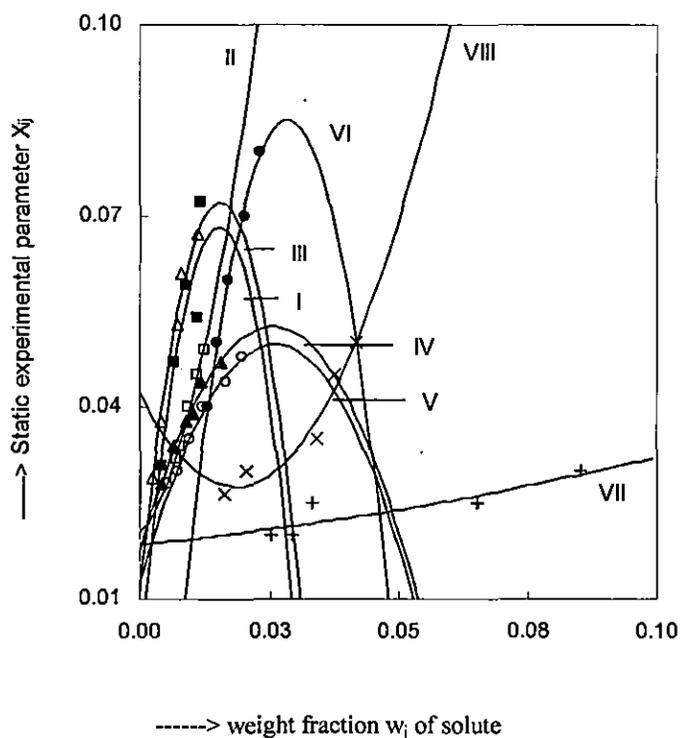


Fig. 7.5 Variation of static experimental parameter X_j against weight fraction w_1 of solute of some para compounds at temperatures in nonpolar solvents (dioxane 7 benzene) under 10 GHz electric field frequency. I. p-hydroxypropiphenone (— ■ —) at 23°C, II. p-chloropropiphenone (— □ —) at 19°C III. P-acetamidobenzaldehyde (— △ —) at 17°C, IV. P-benzyloxybenzaldehyde (— ▲ —) at 5°C, V p-anisidine (— o —) at 20°C, VI.p-phenitidine (— ● —) at 40°C, VII.o-chloro p-nitroaniline (— + —) at 30°C,VIII.p-bromonitrobenzene (— x —) at 20°C

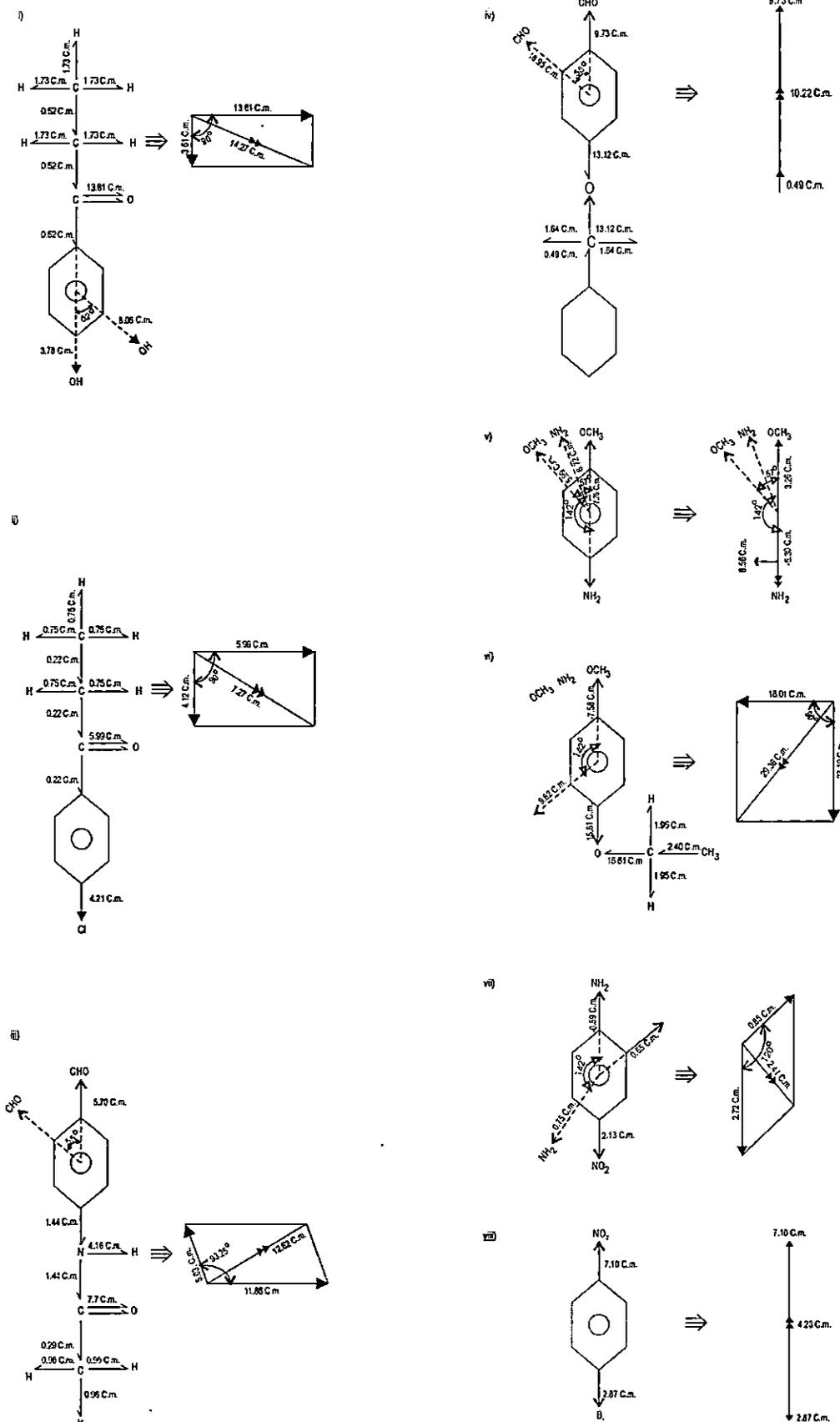


Fig. 7.6 Confrontational structures from available bond moments and bond angles of para compounds: (i) para-hydroxypropiophenone (ii) para-chloropropiophenone (iii) para-acetamidobenzaldehyde (iv) para-benzyloxybenzaldehyde (v) para-anisidine (vi) para-phenitidine (vii) ortho-chloroparanitroaniline and (viii) para-bromonitrobenzene

REFERENCES

- [1] H D Purohit, and H S Sharma, *Bull. Chem. Soc. Japan.* **50** (1977) 2606
- [2] F L Mopisk and R H Cole, *J Chem.Phys* **44** (1966) 1015
- [3] S Acharyya, A K Chatterjee , P Acharyya and I L Saha , *Ind J Phys* **56** (1982) 291
- [4] S K Sit , N Ghosh, U Saha and S Acharyya , *Indian J Phys* **71B** (1997) 533
- [5] N Paul , K P Sharma and S Chattopadhyay, *Indian J Phys* **71B** (1997) 711
- [6] R L Dhar , A Mathur , J P Shukla and M C Saxena ,*Indian J Pure & ApplPhys* **11** (1973) 568
- [7] S K S Somevanshi, S B I Misra and N K Mehrotra , *Indian J Pure & Appl Phys* **16** (1978) 57
- [8] *Hand Book of Chemistry and Physics*. CRC Press 58th Edition 1977-78
- [9] N Ghosh, R C Basak, S K Sit and S Acharyya, *J Mol Liquids (Germany)* **85** (2000) 375
- [10] F J Murphy and S O Morgan , *Bell Syst Tech J* **18** (1939) 502
- [11] M B R Murthy, R L Patil and D K Deshpande, *Indian J Phys* **63B** (1980) 491
- [12] N Ghosh, A Karmakar, S K Sit and S Acharyya, *Indian J Pure & Appl Phys* **38** (2000) 574
- [13] P Debye '*Polar Molecules*' (*Chemical Catalogue*) 1929
- [14] H Eyring, S Glasstone and K J Laidler '*The Theory of Rate Process*' (*Mc Graw Hill: New York*) 1941
- [15] K Dutta, A Karmakar, L Dutta, S K Sit and S Acharyya, *Indian J Pure & Appl Phys* **40** (2002) 801
- [16] N Ghosh, S K Sit, A K Bothra and S Acharyya, *J Phys D : Appl Phys* **34** (2001) 379
- [17] C P Smyth, '*Dielectric Behaviour and Structure*' (*Mc Graw Hill: New York*) 1955
- [18] N Ghosh, S K Sit, and S Acharyya , *J Mol Liquids (Germany)* **102** (2003) 29
- [19] S C Srivastava and S Chandra, *Indian J Pure & Appl Phys* **13** (1975) 101
- [20] F H Branin (Jr) and C P Smyth J.,*Chem Phys* **02** (1952) 1120
- [21] S K Garg and C P Smyth, *J Phys Chem* **69** (1965) 1294
- [22] K Dutta, S K Sit and S Acharyya, *J Mol liquids* **92** (2001) 263
- [23] K Dutta, A Karmakar, S K Sit, and Acharyya, *Pramana J phys* (communicated) 2004

CHAPTER-8

STRUCTURAL ASPECTS AND PHYSICO-CHEMICAL PROPERTIES OF POLYSUBSTITUTED BENZENES IN BENZENE FROM RELAXATION PHENOMENA

8. STRUCTURAL ASPECTS AND PHYSICO-CHEMICAL PROPERTIES OF POLYSUBSTITUTED BENZENES IN BENZENE FROM RELAXATION PHENOMENA

8. 1 INTRODUCTION

Relaxation phenomena of polar liquid molecules in nonpolar solvents under oscillating electric field in the GHz range at different experimental temperatures are of special importance as they are useful tools to investigate their physico-chemical properties as well as structural and associational aspects.[1,2]. The method is based on evaluation of relaxation time τ_j , dipole moment μ_j and thermodynamic energy parameters. There exists several methods [3,4] to get τ_j 's and μ_j 's, but all these methods are not as simple as the present one in which a simultaneous determination of μ_j and τ_j is possible. Although several workers [5-7] studied the relaxation mechanism of polar liquid molecules, but no such investigation on polysubstituted benzenes in terms of high frequency (hf) dielectric susceptibilities χ_{ij} 's has yet been made. The formulations derived so far may be used to study proteins, micelles, polymers and many other complex fluids [8] including liquid crystals as well. Even binary mixtures of polar liquids can give rise to slow relaxation [9]. The formulations are concerned with the real χ'_{ij} ($= \epsilon'_{ij} - \epsilon_{\infty ij}$) and imaginary χ''_{ij} ($= \epsilon''_{ij}$) parts of hf complex dimensionless dielectric orientational susceptibility χ^*_{ij} .

The real ϵ'_{ij} and imaginary ϵ''_{ij} parts of high frequency permittivity ϵ^*_{ij} of polysubstituted benzenes like 1,3 di-isopropylbenzene, p-methylbenzoylchloride and o-chloroacetophenone in benzene at different weight fractions w_j 's of solutes in the temperature range of 30 to 45°C under 10 GHz electric field were measured by Paul et al [10]. The useful optical relative permittivities $\epsilon_{\infty ij}$'s to get concentration variation of χ'_{ij} were generated from Debye-Pallet's equations [11].

$$\epsilon'_{ij} = \epsilon_{\infty ij} + \frac{\epsilon_{0ij} - \epsilon_{\infty ij}}{1 + \omega^2 \tau_j^2} \quad (8.1)$$

and

$$\epsilon''_{ij} = \frac{\epsilon_{0ij} - \epsilon_{\infty ij}}{1 + \omega^2 \tau_j^2} \omega \tau_j \quad (8.2)$$

with the available τ_j 's previously determined by conductivity measurements [12]. Paul et al [10] used the Gopala Krishna's method [13] to measure τ_j 's from ϵ_{ij} 's in which all the polarizations including the fast polarisation exist. If 1 is subtracted from low frequency ϵ_{oij} and real ϵ'_{ij} , the corresponding static susceptibilities χ_{oij} and real χ'_{ij} contain all the polarisations. When hf $\epsilon_{\infty ij}$ is subtracted from ϵ'_{ij} or static ϵ_{oij} one obtains susceptibilities χ'_{ij} or χ_{oij} respectively, involved with the orientational polarization alone to get accurate τ_j 's and μ_j 's.

Both the real ϵ'_{ij} and imaginary ϵ''_{ij} parts of ϵ^*_{ij} are related by [14]

$$\epsilon'_{ij} = \epsilon_{\infty ij} + (1/\omega\tau_j) \epsilon''_{ij} \quad (8.3)$$

which in terms of established symbols of χ'_{ij} and χ''_{ij} becomes

$$\chi''_{ij} = \omega\tau_j \chi'_{ij} \quad (8.4)$$

eq. (8.4) exhibit linear relationship between χ''_{ij} and χ'_{ij} as seen in Fig. 8.1. The slope $\omega\tau_j$ is used to get τ_j of a polar solute [15]. For most of the associative liquids studied elsewhere [16], however, the variation of χ''_{ij} against χ'_{ij} is not strictly linear as seen in Figs 8.2 and 8.3. Hence the slope of eq.(8.4) can be written as:

$$\frac{(d\chi''_{ij} / d\omega_j)_{\omega_j \rightarrow 0}}{(d\chi'_{ij} / d\omega_j)_{\omega_j \rightarrow 0}} = \omega\tau_j \quad (8.5)$$

containing τ_j 's of the present polar solutes. The τ_j 's estimated using eq.(8.5) and (8.4) from both the methods are presented in Table 8.1. The excellent agreement between τ_j 's indicates that the polar-polar interactions are almost eliminated in the limit of $\omega_j = 0$ to give reliable τ_j by the latter method [17]. The correlation coefficients r 's and relative errors of both the plots in Figs 8.2 and 8.3 were obtained by regression analysis. They are within the range of 0.93 to 0.99 and 0.0008 to 0.0001 respectively, hereby indicating how far both χ''_{ij} 's and χ'_{ij} 's are correlated with ω_j 's. It is evident from Table 8.1 that τ_j 's decrease with temperature. At constant temperature τ_j depends on the energy difference between the activated and normal states. At higher temperatures thermal agitation causes an increase in energy loss due to larger number of collisions and thereby decreases the values of τ_j 's. For m-diisopropylbenzenes the τ_j 's are greater in comparison to p-methylbenzoylchloride and o-chloroacetophenone probably due to bigger size of the molecules containing higher number of carbon atoms. For systems II and III τ_j 's do not vary much with temperature because of the presence of the same number of C-atoms in both the molecules. p-methylbenzoyl

chloride shows reverse variation of τ_j with temperature. Inductive effect of CH_3 group put the $\text{C}=\text{O}$ group of COCl to exist as dipolar structure ($>\text{C}^+-\text{O}^-$), therefore increase in temperature has no significant effect on τ_j of this system.

Dielectric relaxation is a process of rotation of polar molecule under hf electric field and it requires an activation energy ΔF_τ to overcome the potential energy barrier between two equilibrium positions. ΔF_τ is related to estimated τ_j by [18].

$$\tau_j = (A/T) e^{\Delta F_\tau / RT} \quad (8.6)$$

$$\text{where } \Delta F_\tau = \Delta H_\tau - T \Delta S_\tau \quad (8.7)$$

From eqs. (8.6) and (8.7) it follows that

$$\ln \tau_j T = \ln A' + (\Delta H_\tau / R) 1/T \quad (8.8)$$

$$\text{where } A' = A e^{-\Delta S_\tau / R}$$

eq. (8.8) is a straight line when $\ln(\tau_j T)$ is plotted against $1/T$ as seen in Fig.8.4, the slope and intercept are used to get enthalpy of activation ΔH_τ , entropy of activation ΔS_τ and free energy of activation ΔF_τ due to dielectric relaxation as presented in Table 8.1. The enthalpy of activation ΔH_η due to viscous flow of the solvent is ascertained from the slope δ ($= \Delta H_\tau / \Delta H_\eta$) of the linear equation of $\ln \tau_j T$ against $\ln \eta_i$, where η_i is the coefficient of viscosity of the solvent used.

It is evident from Table 8.1 and Fig.8.4 that for system II the linear eq. (8.8) has negative slope to give negative ΔH_τ because for that system τ_j 's increases with temperature. The systems I and III shows positive ΔS_τ 's which suggest that the configuration involved in dipolar rotation has an activated state which is less ordered than the normal state [19]. Unlike p-methylbenzoylchloride both systems I and III show $\delta > 0.50$ (as seen in Table 8.1) indicating solvent environment around solute molecules to behave as solid phase rotators[19,20]. ΔH_{η_i} in Table 8.1 involved with translational and rotational motions of the molecule is of lower value than those of ΔH_τ 's in which only the rotational motion occurs. The Debye factors $\tau_j T / \eta_i$ unlike Kalman factors $\tau_j T / \eta_i^\gamma$ at all temperatures are of constant orders for each system. This at once reflects the validity of Debye model [20] of dielectric relaxation for such compounds in benzenes under 10 GHz electric field.

8. 2 THEORETICAL FORMULATION

In order to obtain hf dipole moment μ_j , the Debye-Smyths relation [21,22] in terms of hf χ''_{ij} is used, where

$$\chi''_{ij} = \frac{N\rho_{ij}\mu_j^2}{27\varepsilon_0 M_j k_B T} \left(\frac{\omega\tau_j}{1+\omega^2\tau_j^2} \right) (\varepsilon_{ij} + 2)^2 w_j \quad (8.9)$$

where M_j = molecular weight of the solute in kg.

ε_{ij} = relative permittivity of solution (ij)

ρ_{ij} = density of solution (ij)

k_B = Boltzmann constant

eq. (8.9) on differentiation with respect to w_j and at $w_j \rightarrow 0$

$$\left(\frac{d\chi''_{ij}}{dw_j} \right)_{w_j \rightarrow 0} = \frac{N\rho_i\mu_j^2}{27\varepsilon_0 M_j k_B T} \left(\frac{\omega\tau_j}{1+\omega^2\tau_j^2} \right) (\varepsilon_i + 2)^2 \quad (8.10)$$

in the limit $w_j = 0$, because $\rho_{ij} \rightarrow \rho_i$, $\varepsilon_{ij} \rightarrow \varepsilon_i$ are the density, relative permittivity of solvent benzene

From eqs.(8.5) and (8.10) one obtains

$$\mu_j = \left[\frac{27\varepsilon_0 M_j k_B T \beta}{N\rho_i (\varepsilon_i + 2)^2 b} \right]^{1/2} \quad (8.11)$$

where $b = 1 / (1 + \omega^2\tau_j^2)$ is a dimensionless parameter associated with estimated τ_j of eq.(8.5), β is the linear coefficient of $\chi'_{ij} - w_j$ curves of Fig. 8.3

8. 3 EXPERIMENTAL

The microwave radiations of frequency 10 GHz, generated by a Gunn oscillator fed by 10 volt dc power supply were passed through the isolator, tuner, frequencymeter, attenuator and a slotted line fitted with a probe connected with a crystal detector and a VSWR meter. The other end of the slotted line was connected to a 6.4 cm. long silvered waveguide cell which was connected to a thermostat by a 90° bend to carry out the experimental values of ε'_{ij} and ε''_{ij} at different temperatures [10].

The viscosity η_i and density ρ_i of benzene at various experimental temperatures were measured using an Ubbelohde viscometer and a pycnometer respectively. The analytical grade polysubstituted benzenes like 1,3-diisopropylbenzene, p-methylbenzoyl chloride and o-chloroacetophenone as well as the solvent benzene were supplied by Central Drug Research Institute, Lucknow. They were further purified by repeated fractional distillations and the physical constants like density, viscosity and relative permittivity ϵ_i of solvent C_6H_6 were checked in agreement with the literature values [10]. The polar liquids were kept over molecular sieve of mesh 4Å for 48 hours with occasional shaking. They were then distilled through a long vertical fractionating column and the middle fractions were used for the present study. Benzene (BDH Analar) was purified by refluxing over sodium metal for 6 hours and then distilled through a long vertical fractionating column. The middle fraction of the solvent was used to make solutions of different w_j 's of the respective solutes at different experimental temperatures [23]

8. 4 RESULTS AND DISCUSSION

The μ_j 's thus measured at all temperatures are entered in Table 8.1. Almost all the $\chi'_{ij} - w_j$ curves have a tendency to come closer within the range $0.00 < w_j < 0.03$ probably due to almost same polarity of the molecules [22] arising out of solute – solvent or solute – solute molecular association which may be supposed to be physico-chemical properties [14] of the systems. This can be inferred from the nonlinear variation of $\mu_j - t$ curves of Fig. 8.5. Unlike the system I & II, o-chloroacetophenone (system III) shows minimum μ_j 's at lower and higher temperatures. In the vicinity of $-COCH_3$ and Cl, the electronic factor may operate between the carbonyl oxygen and Cl atom at ortho position may be the reason for its anomalous behaviour towards μ_j value as seen in Fig 8.6. The minimum μ_j 's indicate the attainment of slight symmetry in the molecules at those temperatures [20]. The monotonic increase of μ_j with temperature for p-methylbenzoylchloride occurs for its increasing molecular asymmetry at higher temperatures. The above nature of $\mu_j - t$ curves arises due to alignment of different types of bondings among the solute and solvent molecules which are either formed or broken to some extent [24,25]. Thus the measured μ_j 's reflects the stability or unstability of the molecules. This is confirmed by different thermodynamic energy parameters in order to make a strong comment on their physico-chemical properties.

Theoretical dipole moment's μ_{theo} 's, as seen in Fig. 8.6. are, however, considered by vector addition of bond moments of substituted polar groups of molecules from the available infrared spectroscopic data of bond moments assuming the molecules to be planar ones. They are placed in Table 8.1 to compare them with the measured hf μ_j 's. The molecules under study have polar groups and there is large probability of intramolecular group rotations and, therefore, these molecules may not be represented by simple Debye type dielectric dispersions. On the otherhand, Higasi's equation. [7] for single frequency in dilute solutions or Higasi's frequency variation method could, however, be used to evaluate those group rotations for such molecules. But the molecules are very simple and the purpose of the paper is to see the applicability of Debye type dispersions in them in evaluating τ_j and μ_j which are claimed to be accurate with 10% and 5% respectively. The molecules of polysubstituted benzenes referred to Tables and figures are planar and have the property of cyclic delocalization of π electrons on each C-atom. The solvent benzene is a cyclic and planar compound with three double bonds and six p-electrons on six carbon atoms of the benzene ring. Hence π - π interaction or resonance effect combined with an inductive effect commonly known as mesomeric effect in excited state called the electromeric effect is expected to play the prominent role in hf μ_j 's. The slight disagreement between hf μ_j 's and μ_{theo} 's of Fig 8.6 is explained on the basis of the fact that the flexible polar groups of the molecules are greatly influenced by hf electric field to yield the inductive, mesomeric and electromeric effects in them to give higher μ_j values, especially for m-diisopropylbenzene. All these effects, are, however, incorporated in their structures by multiplying the bond moments by a factor $\mu_j / \mu_{\text{theo}}$ to make μ_{theo} 's closer to μ_j 's as sketched in Fig.8.6. The electromeric effect caused by $>C=O$ in the 2nd and 3rd molecules may be the reason to make μ_j 's more closer to μ_{theo} 's [26].

8. 5 CONCLUSION

The theoretical formulations in terms of internationally accepted and established symbols of dielectric terminologies and parameters in S.I. units are more topical, significant and simpler one to have deep insight into the physico-chemical, structural and associational aspects of polysubstituted benzenes in C_6H_6 at different temperatures under 10 GHz electric field. The conformational structures so far sketched in Fig. 8.6 are also significant because they enhance the scientific content of the existing knowledge of dielectric

relaxation processes. The curves satisfied by experimental points in all the figures reflect the validity of the theoretical formulations based on Debye model to estimate several physical parameters such as τ_j 's, μ_j 's and ΔH_τ , ΔF_τ , ΔS_τ etc which are more of archival values to study the temperature variation of physico-chemical properties of dipolar molecules. The uncertainty in the evaluated τ_j ' and μ_j values are of 10% and 5% errors which are claimed to be accurate.

ACKNOWLEDGEMENT

The authors express their heartfelt thanks to the Central Drug Research Institute, Lucknow, India for supplying the materials.

Table-8.1. Estimated relaxation times τ_j 's , enthalpy ΔH_τ , entropy ΔS_τ and free energy ΔF_τ due to relaxation, dimensionless parameter γ ($= \Delta H_\tau / \Delta H_{\eta_i}$) from slope of $\ln \tau_j T$ vs. $\ln \eta_i$ equation. enthalpy of activation ΔH_{η_i} due to viscous flow of the solvent, estimated hf dipole moment μ_j and theoretical dipole moment μ_{theo} in coulomb metre(C.m.) of some polysubstituted benzenes in solvent C_6H_6 at different experimental temperatures in $^{\circ}C$ under 10 GHz electric field frequency.

System with sl. no.& mol. wt.in Kg.	Temp in $^{\circ}C$	τ_j in psec (eq. 8.4)	τ_j in psec from eq. (8.5)	ΔH_τ in KJ mole $^{-1}$	ΔS_τ in J mole $^{-1}$ K $^{-1}$	ΔF_τ in KJ mole $^{-1}$	Value of δ	$\Delta H_{\eta_i} = (\Delta H_\tau / \gamma)$ in KJ mole $^{-1}$	Estimated dipole moment $\mu_j \times 10^{30}$ C.m. with τ_j from eq. (8.5)	$\mu_{theo} \times 10^{30}$ C.m. from bond angles & reduced bond moments
I. m-di-isopropyl-benzene (Mj = 0.162)	30	8.80	8.80		109.01	10.12			12.70	
	35	7.33	7.33		108.09	9.86			13.87	
	40	5.46	5.46	43.15	108.16	9.30	6.96	6.20	13.99	3.77
	45	3.74	3.76		109.01	8.49			14.76	
II.p-methyl-benzoyl chloride (Mj = 0.156)	30	2.72	2.72		-59.09	7.16			9.63	
	35	3.30	3.30		-60.26	7.82			9.82	
	40	3.23	3.23	-10.74	-59.66	7.93	-1.61	6.67	9.95	8.80
	45	3.24	3.24		-59.28	8.11			10.10	
III.o-chloro-acetophenone (Mj = 0.156)	30	4.20	4.20		255.12	8.26			6.83	
	35	3.04	3.04		253.09	7.61			7.72	
	40	1.26	1.26	85.56	255.84	5.48	13.56	6.31	7.05	7.40
	45	0.90	0.90		254.21	4.72			6.48	

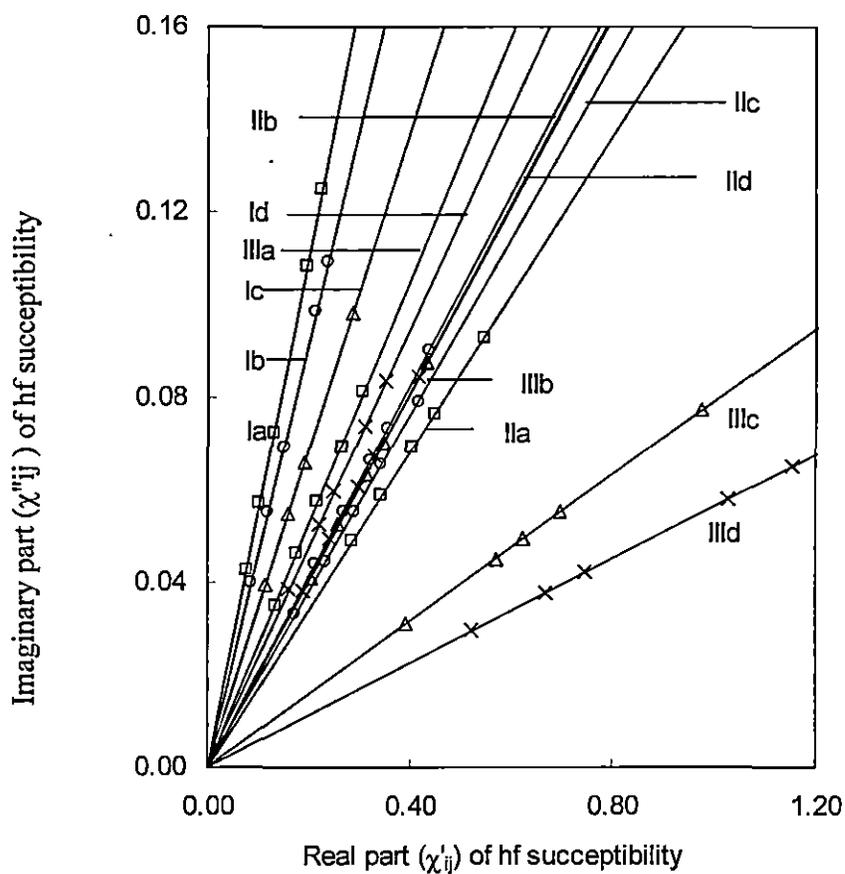


Fig. 8.1 : Variation of imaginary part χ''_{ij} against real part χ'_{ij} of the complex hf dielectric orientational susceptibility χ^*_{ij} of some polysubstituted benzenes in C_6H_6 under 10 GHz electric field at various experimental temperatures.

m-di-isopropylbenzene- Ia (-□-) at 30^oc, Ib (-o-) at 35^oc, Ic (-Δ-) at 40^oc, Id (-X-) at 45^oc
 p-methylbenzylchloride-IIa (-□-) at 30^oc, IIb (-o-) at 35^oc, IIc (-Δ-) at 40^oc, IIId (-X-) at 45^oc
 o-chloroacetophenone -IIIa (-□-) at 30^oc, IIIb (-o-) at 35^oc, IIIc (-Δ-) at 40^oc, IIIId (-X-) at 45^oc

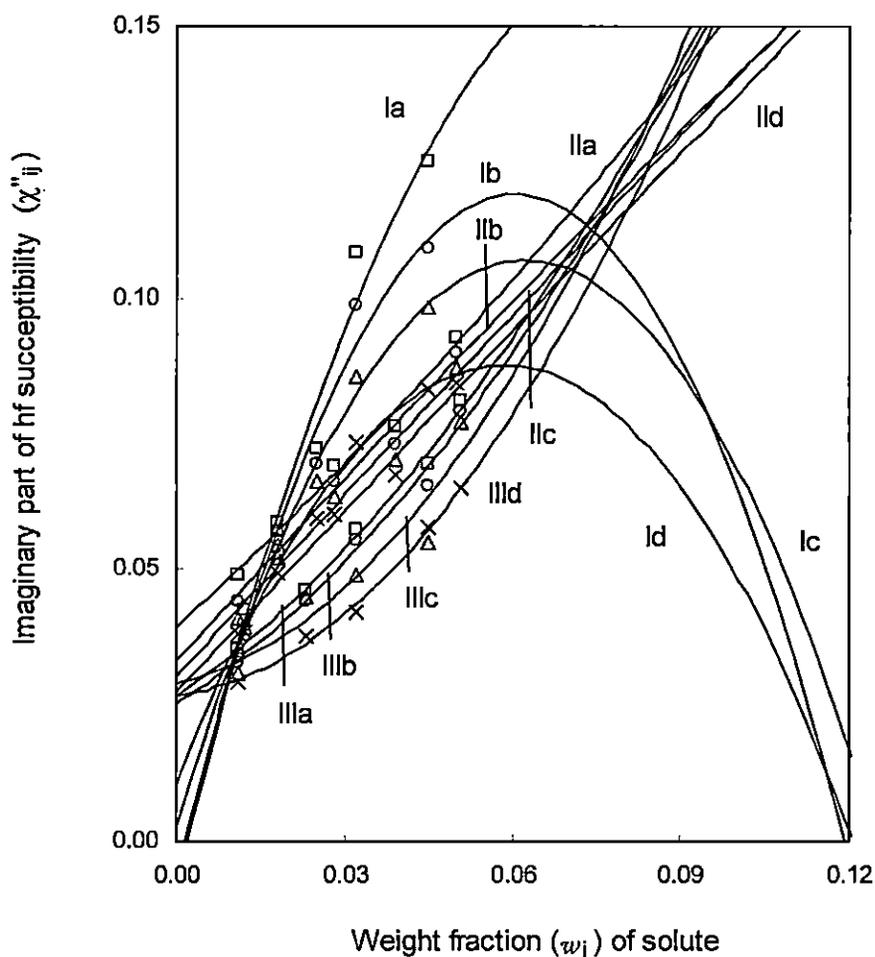


Fig. 8.2 Variation of imaginary part χ''_{ij} of hf susceptibility with weight fraction w_j 's of some polysubstituted benzenes in C_6H_6 under 10 GHz electric field at various experimental temperatures

m-di-isopropylbenzene- Ia (-□-) at 30⁰C, Ib (-o-) at 35⁰ C, Ic (-Δ-) at 40⁰ C, Id (-X-) at 45⁰ C
 p-methylbenzylchloride -IIa (-□-)at 30⁰ C, IIb (-o-) at 35⁰ C, IIc (-Δ-) at 40⁰C, IIId (-X-) at 45⁰ C
 o-chloroacetophenone-IIIa (-□-)at 30⁰ C, IIIb(-o-) at 35⁰ C, IIIc (-Δ-) at 40⁰ C, IIId (-X-)at 45⁰ C

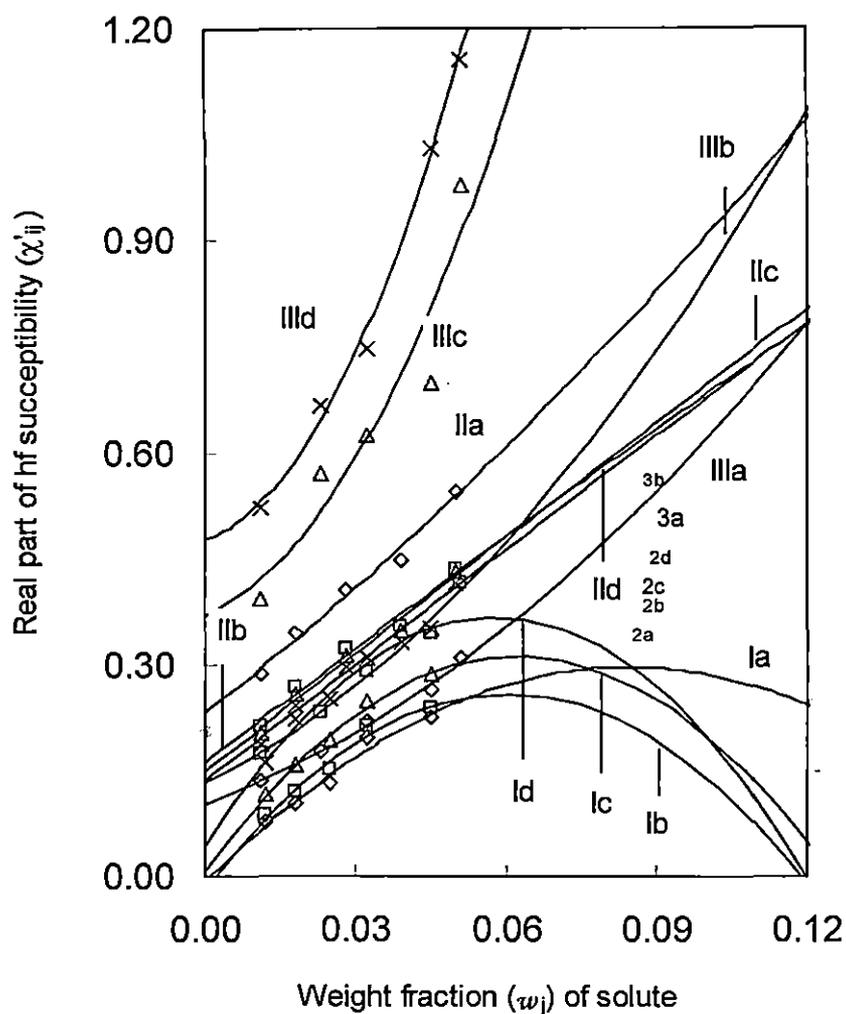


Fig. 8.3 Variation of real part χ'_{ij} of hf susceptibility with weight fraction w_j 's of some polysubstituted benzenes in C_6H_6 under 10 GHz electric field at various experimental temperatures

m-di-isopropylbenzene- Ia (\diamond) at $30^\circ C$, Ib (\square) at $35^\circ C$, Ic (Δ) at $40^\circ C$, Id (\times) at $45^\circ C$
 p-methylbenzylchloride-IIa (\diamond) at $30^\circ C$, IIb (\square) at $35^\circ C$, IIc (Δ) at $40^\circ C$, IIId (\times) at $45^\circ C$
 o-chloroacetophenone -IIIa (\diamond) at $30^\circ C$, IIIb (\square) at $35^\circ C$, IIIc (Δ) at $40^\circ C$, IIIId (\times) at $45^\circ C$

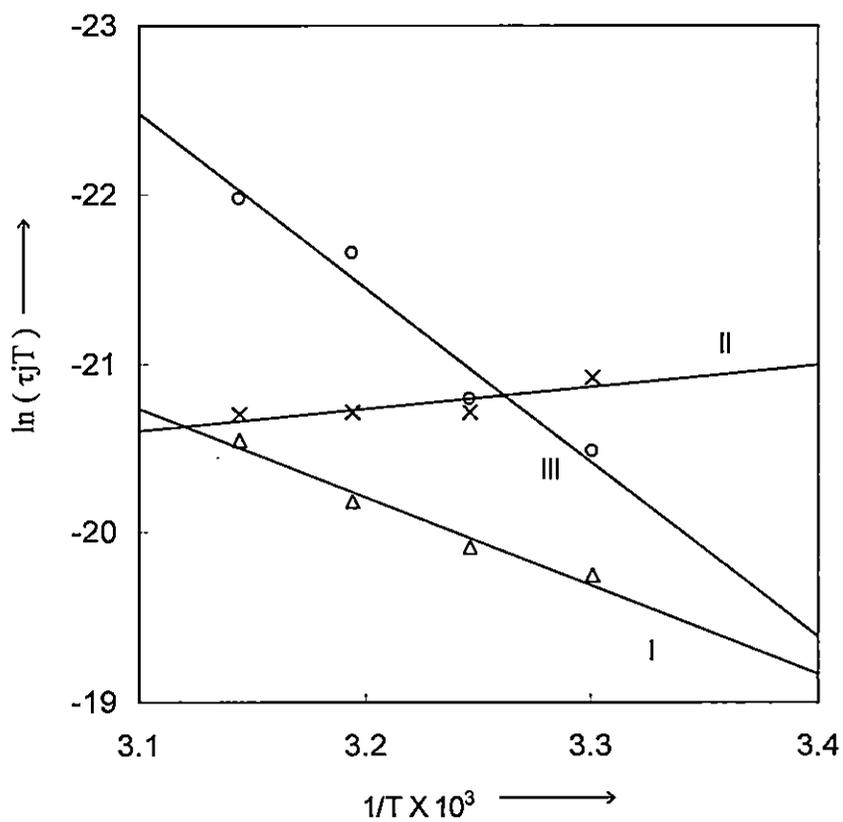


Fig. 8.4 The linear plot of $\ln(\tau_j T)$ against $1/T$ of some polysubstituted benzenes in C_6H_6 under 10 GHz electric field .

I. m-di-isopropylbenzene (- △ -) using τ_j of eq.(2). II. p-methylbenzoylchloride (- × -) using τ_j of eq.(2). III. o-chloroacetophenone : (- ○ -) using τ_j of eq.(2)

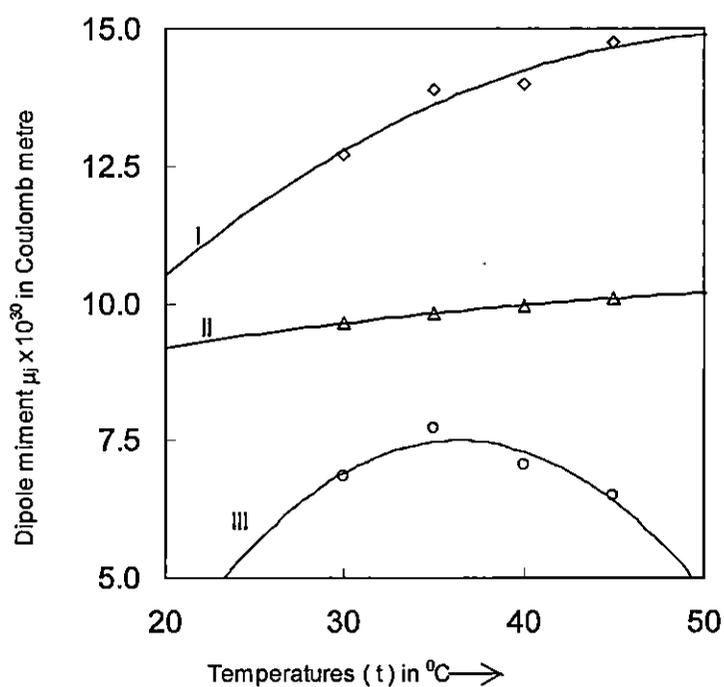


Fig. 8.5 Plot of measured dipole moment μ_j in Coulomb metre [using τ_j by our method i.e, eq.(5)] with temperatures t in $^{\circ}\text{C}$ of some polysubstituted benzenes in C_6H_6 under 10 GHz electric field .

- I. .m-di-isopropylbenene : (- □ -) using τ_j on eq.(2), II.p-ethylbenzoylchloride:
 (- Δ -) using τ_j on eq.(2), III. o-chloroacetophenone:(- o -) using τ_j on eq.(2),

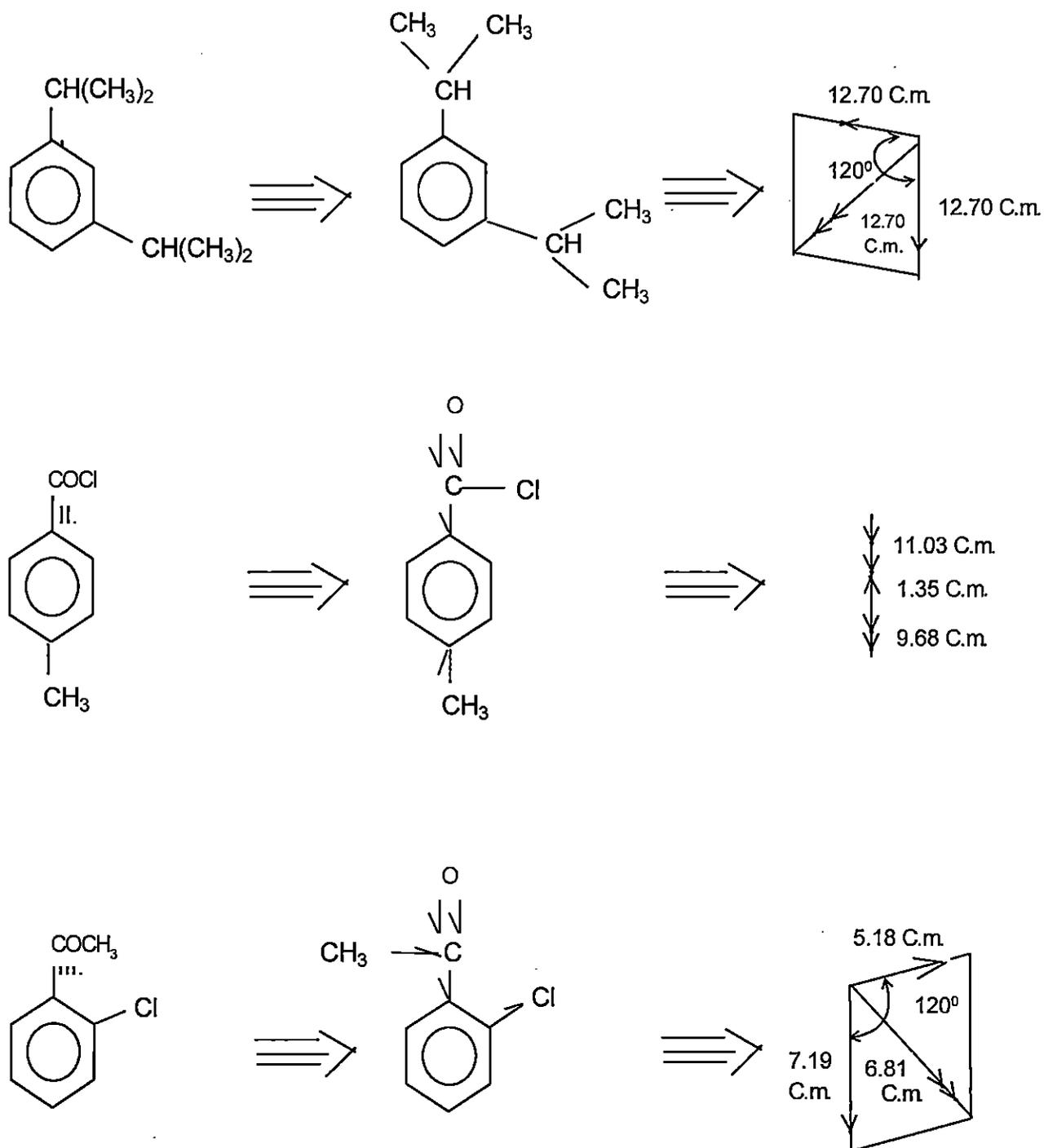


Figure 6. Conformational structures of different polysubstituted benzenes

Fig. 8.6 th dipole moment $\mu_{\text{theo}} \times 10^{30}$ in Coulomb metre (C.m.)]

I m-diisopropylbenzene

II p-methylbenzoylchloride

III o-chloroacetophenone

REFERENCES

- [1]. L Glasser, J Crossley & C P Smyth, *J Chem Phys* **57** (1972) 3977
- [2]. C B Agarwal, *Indian J pure & Appl Phys* **24** (1986) 204
- [3]. S K Cole & R H Cole, *J Chem Phys* **9** (1941) 341
- [4]. E A Guggenheim, *Trans Faraday Soc* **45** (1949) 714
- [5]. A Sharma & D R Sharma, *J Phys Soc Japan* **61** (1992) 1049
- [6]. U Saha & R Ghosh, *J Phys D : Appl Phys* (U K) **32** (1999) 820
- [7]. K Higasi, Y Koga & M Nakamura, *Bull Chem Soc Japan* **44** (1971) 988
- [8]. N Nandi, K Bhattacharyya & B Bagchi, *Chem.Rev.* **100** (2000) 2013
- [9]. N Nandi & B Bagchi, *J. Phys. Chem*, **B101** (1997) , 10954
- [10]. N Paul, K P Sharma & S Chattopadhyay, *Indian J Phys* **71B** (1997) 711
- [11]. N E Hill, W E Vaughan, A H Price & M Davies, "Dielectric properties and molecular behaviour" Van Nostrand Reinhold Company. London 1969
- [12]. N Ghosh, A Karmakar, S K Sit & S Acharyya, *Indian J Pure & Appl Phys* **38** (2000) 574
- [13]. K V Gopalakrishna, *Trans Faraday Soc* **53** (1957) 767
- [14]. U K Mitra, N Ghosh, P Ghosh & S Acharyya, *J Molecular Liquids* **126** (2006) 53
- [15]. M B R Murthy, R L Patil & D K Deshpande, *Indian J Phy* **63B** (1989) 491
- [16]. N Ghosh, S K Sit & S Acharyya, *J Molecular Liquids* **102** (2003) 29
- [17]. R C Basak, S K Sit, N Nandi & S Acharyya, *Indian J Phys* **70B** (1996) 37
- [18]. S K Sit, N Ghosh, U Saha & S Acharyya, *Indian J phys* **71B** (1997) 533
- [19]. N Ghosh, R C Basak, S K Sit & S Acharyya, *J Molecular Liquids* **85** (2000) 375
- [20]. H Eyring, S Glasstone & K J Laidler, *The Theory of Rate Process* (McGraw Hill : NewYork) 1941
- [21]. C P Smyth, 'Dielectric Behaviour and Structure' (McGraw Hill ; New York) 1955
- [22]. N Ghosh, S K Sit, A K Bothra & S Acharyya, *J Phys D: Appl Phys* (UK) **34** (2001) 379
- [23]. P Ghosh, R P Singh, C P Sinha & J Das, *J Chem Eng Data* **35** (1990) 93
- [24]. R L Dhar, A Mathur, J P Shukla & M C Saxena, *Indian J Pure & Appl Phys* **11** (1973) 568
- [25]. S K S Somevanshi, S B I Misra & N K Mehrotra, *Indian J Pure & Appl Phys* **16** (1978) 57

CHAPTER 9

STRUCTURAL ASPECTS AND PHYSICO CHEMICAL PROPERTIES OF BINARY POLAR LIQUIDS IN NONPOLAR SOLVENT UNDER A GIGAHERTZ ELECTRIC FIELD

9. STRUCTURAL ASPECTS AND PHYSICO CHEMICAL PROPERTIES OF BINARY POLAR LIQUIDS IN NONPOLAR SOLVENT UNDER A GIGAHERTZ ELECTRIC FIELD

9. 1 INTRODUCTION

The dielectric relaxation phenomena of two polar liquid mixtures in a nonpolar solvent is gaining much attention from a large number of workers [1,2] for its inherent ability to predict the associational and structural aspects of the dipolar molecules in a suitable solvent. The method is directed to the estimation of dielectric relaxation parameters in terms of real χ'_{ijk} and imaginary χ''_{ijk} parts of high frequency complex dimensionless dielectric orientational susceptibility χ^*_{ijk} along with the static dielectric susceptibility χ_{oijk} which is real. All these parameters are involved only with the orientational polarisations. According to Murphy and Morgan [3], the hf complex conductivity σ^*_{ijk} of binary jk polar mixture in a nonpolar solvent

(i) can be written as
$$\sigma^*_{ijk} = \sigma'_{ijk} + j\sigma''_{ijk} \quad (9.1)$$

where σ'_{ijk} ($= \omega \epsilon_0 \epsilon''_{ijk}$) and σ''_{ijk} ($= \omega \epsilon_0 \epsilon'_{ijk}$) are the real and imaginary parts of hf complex conductivity of a binary solution σ^*_{ijk} . ϵ'_{ijk} and ϵ''_{ijk} are the real and imaginary parts of hf complex relative permittivity ϵ^*_{ijk} which contain all the polarisations including the fast polarisation, ϵ_0 is the permittivity of free space $= 8.854 \times 10^{-12}$ Farad metre⁻¹ and $j = \sqrt{-1}$ is a complex number.

Both σ'_{ijk} and σ''_{ijk} are linearly related by [4]

$$\sigma''_{ijk} = \sigma_{\inftyijk} + (1/\omega\tau_{jk}) \sigma'_{ijk} \quad (9.2)$$

which is a straight line between the variables σ''_{ijk} and σ'_{ijk} . The slope $(1/\omega\tau_{jk})$ has already been used to get τ_{jk} by conductivity measurement as measured elsewhere [5]. Both the static and infinitely hf permittivities ϵ_{oijk} and ϵ_{\inftyijk} are obtained from the following Debye-Pellat equations [6] and known $\omega = (2\pi f)$, where f being the frequency of the applied electric field,

$$\epsilon'_{ijk} = \epsilon_{\inftyijk} + \frac{\epsilon_{oijk} - \epsilon_{\inftyijk}}{1 + \omega^2 \tau_{jk}^2} \quad (9.3)$$

$$\epsilon''_{ijk} = \frac{\epsilon_{oijk} - \epsilon_{\inftyijk}}{1 + \omega^2 \tau_{jk}^2} \omega \tau_{jk} \quad (9.4)$$

In order to get the data χ'_{ijk} ($= \epsilon'_{ijk} - \epsilon_{\inftyijk}$) and χ''_{ijk} ($= \epsilon''_{ijk}$) which are, however, presented in Table 9.1 and displayed graphically in Figs. 9.1 and 9.2 respectively.

The real and imaginary parts hf complex relative permittivity ϵ^*_{ijk} are related by

$$\epsilon'_{ijk} = \epsilon_{\alpha ij k} + \frac{1}{\omega \tau_{jk}} \epsilon''_{ijk} \quad (9.5)$$

Replacing $\epsilon'_{ijk} - \epsilon_{\alpha ij k}$ by χ'_{ijk} and ϵ''_{ijk} by χ''_{ijk} the eq. (9.5) becomes

$$\chi''_{ijk} = (\omega \tau_{jk}) \chi'_{ijk} \quad (9.6)$$

which is a straight line between χ''_{ijk} and χ'_{ijk} . The slope $\omega \tau_{jk}$ is now used to measure τ_{jk} of a polar – polar dimer in which the only orientational polarisation exists.

But for associative liquids like dimethyl formamide (DMF), dimethyl sulphoxide (DMSO) under investigation the variation of χ''_{ijk} with χ'_{ijk} is not strictly linear as claimed elsewhere [7]. The ratio of slopes of individual variations of χ''_{ijk} and χ'_{ijk} against w_{jk} , of Figs. 9.2 and 9.1 the weight fraction of jk polar mixture are found to be a better representation [8] of the slope of eq. (9.6). Thus we have

$$\frac{(d\chi''_{ijk} / dw_{jk})_{w_{jk} \rightarrow 0}}{(d\chi'_{ijk} / dw_{jk})_{w_{jk} \rightarrow 0}} = \omega \tau_{jk} \quad (9.7)$$

τ_{jk} 's so estimated are presented in Table 9.2 to compare them with those of Gopala Krishna's method [9]. Fig. 9.3 shows the variation of relaxation time τ_{jk} of jk polar unit with mole% of DMSO (k). It is evident from the plot that τ_{jk} attains a maximum value showing maximum dimerisation of j and k polar mixtures around 40 mole % of DMSO in benzene (i). The formation of dimer between DMF (j) and DMSO (k) polar unit is supposed to be a physico-chemical aspect of the polar solutes in benzene. The gradual fall of τ_{jk} between 40 to 100 mole % of DMSO in C_6H_6 is probably due to rupture of dimerisation i.e, change over to self association. When $w_{jk} \rightarrow 0$ we get what is known as τ_j of DMF. Similarly, when $w_{jk} \rightarrow 100$ mole%, the plot in Fig. 9.3 reports τ_k of DMSO

The phenomenon of dielectric relaxation is a rotation of the dipolar molecules in response to the hf electric field and it requires an activation energy $(\Delta F\tau)_{jk}$ to overcome the potential energy barrier between the polarised and the free states. The free energy of activation $(\Delta F\tau)_{jk}$ is related to τ_{jk} by the rate process equation of Eyring et al [10] as

$$\tau_{jk} = \frac{A}{T} \exp [(\Delta F\tau)_{jk} / RT] \quad (9.8)$$

$$\text{or, } \ln (\tau_{jk} T) = \ln A' + \frac{(\Delta H\tau)_{jk}}{R} \cdot \frac{1}{T} \quad (9.9)$$

since $[(\Delta F\tau)_{jk}] = (\Delta H\tau)_{jk} - T(\Delta S\tau)_{jk}$ and $A' = Ae^{[-(\Delta S\tau)_{jk} / R]}$

The eq. (9.9) is a straight line of $\ln(\tau_{jk}T)$ against $1/T$ as shown graphically in Fig. 9.4 with the symbols showing the experimental points on them.. The intercepts and slopes of eq. (9.9) are estimated by fit method and are presented in Table 9.3. They are used to get the enthalpy $(\Delta H\tau)_{jk}$, the entropy $(\Delta S\tau)_{jk}$ and free energy $(\Delta F\tau)_{jk}$ of activation due to dielectric relaxation. The enthalpy of activation $\Delta H\eta_i$ due to viscous flow of the solvent was estimated from slope (γ) of the linear equation of $\ln(\tau_{jk}T)$ against $\ln\eta_i$, where η_i is the coefficient of viscosity of the solvent used. The dimensionless parameter δ and $\Delta H\eta_i$ thus obtained are seen in Table 9.3. The Kalman and Debye factors estimated with known τ_{jk} are entered in Table 9.3 to show the applicability of Debye model of dielectric relaxation for such binary polar mixtures.

The μ_{jk} 's of binary polar units are estimated in terms of linear coefficient β 's of χ'_{ijk} vs w_{jk} curves of Fig. 9.1 and dimensionless parameters 'b' where $b=1/(1+\omega^2\tau_{jk}^2)$, from Table 9.2. They are presented in Table 9.2 to compare them with the μ_{theo} estimated in terms of vector addition of bond moments of the substituted polar groups to support their molecular conformations. The disagreement between μ_{jk} 's and μ_{theo} 's suggests the very existence of inductive, mesomeric and electromeric effects suffered by the substituted polar groups attached to the parent molecules under hf electric field in addition to strong hydrogen bonding between DMF and DMSO molecule. The compounds DMF, DMSO are basically amides. They act as building blocks of proteins and enzymes. The barrier to internal rotation around C-N bonds in such compounds falls in the region of magnetic resonance frequency. DMSO, on the other hand, has high penetrating power with its wide application in the field of medicine and industry. Moreover, DMSO is a good constituent of a binary mixture of required characteristic.

9.2 EXPERIMENTAL

Sharma et al [11] estimated the real ϵ'_{ijk} and imaginary ϵ''_{ijk} parts of hf complex dielectric relative permittivity ϵ^*_{ijk} of two polar mixtures in a nonpolar solvent at different mole percentage of the k th polar solute (DMSO) in solvent C_6H_6 in the temperature range of $25^0C - 40^0C$ under 9.174 GHz electric field frequency. An X-band microwave bench was used to measure the wavelength in the dielectric and the voltage standing-wave ratio (VSWR) using a short circuiting plunger. The experimental techniques of Arrawatia et al [12] for microwave measurements were used. A range of DMF concentrations was

prepared in C_6H_6 and all the measurements were made at 25,30,35 and 40°C by circulating thermostatted water around the dielectric cell. The temperature control of the thermostat (MLW Baureihe U7⁰) was $\pm 0.05^\circ C$. The precision and equipment was tested by measuring the dipole moments of purified acetone, methanol and pyridine. The dipole moments measured were found to be within $\pm 2\%$, in agreement with the literature values (Pimental and Meclellan 1960, Smyth 1955). The viscosity and density of benzene at various experimental temperatures were measured using an Ubbelohde viscometer and a pycnometer respectively. The analytical grade DMF, DMSO and C_6H_6 were supplied by Central drug Research Institute, Lucknow. They were further purified by repeated fractional distillations and the physical constants like density ρ_i , viscosity η_i and relative permittivity ϵ_i of solvent C_6H_6 were checked in agreement with the literature values [13]. The DMF and DMSO were kept over molecular sieve of mesh 4Å for 48 hours with occasional shaking. They were then distilled through a long vertical fractionating column and the middle fractions were used for the present study. Benzene (BDH Analar) was purified by refluxing over sodium metal for 6 – 8 hours and then distilled through a long vertical fractionating column. The middle fraction of the solvent was used.

9.3 THEORETICAL FORMULATIONS TO ESTIMATE hf DIPOLE MOMENT (μ_{jk}):

The imaginary part χ''_{ijk} of hf complex dielectric orientational susceptibility χ^*_{ijk} is [14,15]

$$\chi''_{ijk} = \frac{N\rho_{ijk}\mu_{jk}^2}{27\epsilon_0 M_{jk} k_B T} \left(\frac{\omega\tau_{jk}}{1+\omega^2\tau_{jk}^2} \right) (\epsilon_{ijk} + 2)^2 w_{jk} \quad (9.10)$$

which on differentiation with respect to w_{jk} and at $w_{jk} \rightarrow 0$ yields that

$$\left(\frac{d\chi''_{ijk}}{dw_{jk}} \right)_{w_{jk} \rightarrow 0} = \frac{N\rho_i \mu_{jk}^2}{27\epsilon_0 M_{jk} k_B T} \left(\frac{\omega\tau_{jk}}{1+\omega^2\tau_{jk}^2} \right) (\epsilon_i + 2)^2 \quad (9.11)$$

From eqs (9.7) and (9.11) one obtains

$$\mu_{jk} = \left[\frac{27\epsilon_0 M_{jk} k_B T \beta}{N\rho_i (\epsilon_i + 2)^2 \omega b} \right]^{1/2} \quad (9.12)$$

where

M_{jk} = Molecular weight of j & k polar mixture in Kilogramme

ϵ_0 = Permittivity of free space = 8.854×10^{-12} Farad metre⁻¹

k_B = Boltzmann constant = 1.38×10^{-23} Joule mole⁻¹ K⁻¹

T = Temperature in absolute scale

β = Linear coefficients of $\chi'_{ijk} - w_{jk}$ curves of Fig. 9.1 at $w_{jk} \rightarrow 0$

N = Avogadro's number = 6.023×10^{23}

ρ_i = Density of solvent C_6H_6 in kg/m^3

ϵ_i = Dielectric relative permittivity of solvent C_6H_6

$b = 1/(1 + \omega^2 \tau_{jk}^2)$, a dimensionless parameter involved with the estimated τ_{jk} .

9.4 RESULTS AND DISCUSSION

The relaxation time τ_{jk} of j and k polar dimer in C_6H_6 at different experimental temperatures in $^{\circ}C$ under 9.174 GHz electric field frequency are worked out from ratio of slopes of individual variation of both χ'_{ijk} and χ''_{ijk} with w_{jk} of polar-polar mixture and are placed in Table 9.2 to compare them with those of Gopala Krishna [9] measured by permittivity measurement of sharma et al [11] The excellent agreement between both the τ_{jk} 's at once reflects the basic soundness of the present method [16] suggested to get τ_{jk} . The real χ'_{ijk} and imaginary χ''_{ijk} parts of hf complex dielectric orientational susceptibility χ^*_{ijk} are derived from estimated relative permittivities ϵ'_{ijk} , ϵ''_{ijk} , $\epsilon_{\infty ij k}$. They are collected in Table 9.1. Correlation coefficients r 's and % of errors of both $\chi'_{ijk} - w_{jk}$ and $\chi''_{ijk} - w_{jk}$ curves are given in Table 9.2 only to show how far both χ'_{ijk} and χ''_{ijk} are correlated with w_{jk} 's. It is seen in Table 9.2 that τ_{jk} 's decrease with temperature. It can be explained on the basis of the fact that at constant temperature, the relaxation time depends upon the energy difference between the activated and normal states. At higher temperature thermal agitation causes an increase in energy loss [15] only due to collision effect to decrease the τ_{jk} . The Fig. 9.3 shows the variation of τ_{jk} with mole% of the k th polar solute, DMSO. τ_{jk} increases upto 40 mole% DMSO yielding both τ_j and τ_k of the respective solutes at $w_{jk \rightarrow 0}$ and $w_{jk \rightarrow 100}$ mole% respectively probably due to polar-polar dimer association and then due to rupture of dimerisation [17] gradually decreases and attains a minimum value at 100 mole% DMSO. Formation of j & k polar-polar dimer and rupture of dimerisation i.e. self association is supposed to be a physico-chemical behaviour [16] of the solutes in a solvent.

Temperature variation of τ_{jk} of jk polar dimer enables one to estimate the thermodynamic energy parameters $(\Delta H\tau)_{jk}$, $(\Delta S\tau)_{jk}$ and $(\Delta F\tau)_{jk}$ from the intercept and slope of fitted linear plots of $\ln(\tau_{jk}T)$ against $1/T$ of Fig. 9.4, due to rate process equation of Eyring et al [10]. The intercepts and slopes, calculated by regression analysis on the measured τ_{jk} at different experimental temperatures in Kelvin are presented in Table 9.3. It is seen that system VI shows negative $\Delta H\tau$ probably for unreliable τ_{jk} at $35^{\circ}C$ which

may be due to experimental error involved in the permittivity measurement. Unlike system I & II all the systems show negative $\Delta S\tau$'s, which suggests that configuration involved in the dipolar rotation has an activated state which is more ordered than the normal state [18]. This fact is further supported by gradual decrease of τ_{jk} with concentration of DMSO beyond 40 mole% as seen in Fig. 9.3. $\Delta F\tau$'s for each system are constant in magnitude at all temperatures, as the activation is accomplished by the rupture of bond of dipolar groups in the same degree of freedom [19]. All the systems except VI show $\gamma > 0.50$, seen in Table 9.3 which indicate solvent environment around jk polar dimer to behave as solid phase rotator [8,15] $\Delta H\eta$, the enthalpy of activation due to viscous flow of the solvent is involved with translational and rotational motions of molecule possess lower values than that of $\Delta H\tau$ due to high value of δ except for system VI. Kalman factor $\tau_{jk}T / \eta^\delta$, and Debye factor $\tau_{jk}T / \eta$ which are proportional to volume of rotating unit are carefully estimated and are entered in the 10th and 11th column of Table 9.3 respectively only to show the applicability of Debye model of dielectric relaxation for such binary polar mixtures in C_6H_6 under GHz electric field.

Dipole moments μ_{jk} estimated from eq.(9.12) are placed in Table 9.2 to compare them with μ_{theo} 's as seen in same Table 9.2. The slope β of $\chi'_{ijk} - w_{jk}$ curves in Fig. 9.1 is used to get the measured dipole moments μ_{jk} . μ_{jk} 's for system VI can not be estimated as it gives negative β owing to the abnormal behaviour of available permittivity data. It is seen in Fig. 9.3 that in analogy with τ_{jk} , μ_{jk} increases gradually with concentration of the k th solute DMSO and attains a maximum value around 40 mole% of DMSO in C_6H_6 showing maximum dimerisation at that concentration and then gradually decreases to attain a minimum value at 80 mole% of DMSO. This gradual fall of τ_{jk} is probably due to rupture of the polar-polar dimerisation and to assume the state of monomer.

The dimerisation or the self association being a physico-chemical property [15] of the solute can also be inferred from μ_{jk} with $t^\circ C$ fitted polynomial plots of Fig. 9.5. It is evident from the plot that unlike systems II & IV all the curves are convex in nature showing minimum μ_{jk} at lower and higher temperatures, probably due to weak symmetry [19] attained at those temperatures, while system II & IV shows maximum μ_{jk} 's at lower and higher temperatures probably due to solute-solute dimer association to have a bigger molecular shape. The nature of variation of μ_{jk} with temperature $t^\circ C$ curves are explained on the basis of symmetric shape and dimerisation of solute molecules. This reflects the internal stability and instability of the systems which are also confirmed by positive and negative $\Delta S\tau$'s [19,20]. Dimerisation between two polar units of DMF & DMSO can also be explained by the hydrogen bonding between the fractional negative charge δ^- of

oxygen atom which is highly electronegative of DMSO molecule and the fractional positive charge δ^+ of hydrogen atom of DMF molecule. This is also supported by their conformations as sketched in Fig. 9.6.

Theoretical dipole moment μ_{theo} estimated from vector addition of bond moments of the substituted polar groups attached to the parent ones, assuming the molecules to be planar ones provides a deep insight into the geometry of the molecules concerned. The solute-solvent molecular interaction is a physico-chemical behaviour which arises due to interactions of fractional positive charges of 'N' and 'S' atoms of the molecules as δ^+ with the π delocalised electron cloud of C_6H_6 ring. The interactions are sketched in Fig. 9.6 (i) & 9.6 (ii). Fig. 9.6 (iii), however, shows a certain angle ϕ ($=106^\circ$) between monomeric μ_j of DMF and μ_k of DMSO to have $\mu_{\text{theo}} = 15.90 \times 10^{-30}$ Coulomb-metre in close agreement with measured value of μ_{jk} in Table 9.2. The slight deviations of μ_{jk} 's from μ_{theo} 's occur due to inductive, electromeric and mesomeric moments of substituted polar groups attached to such molecules. This can be rectified by the multiplying by $\mu_{\text{theo}} / \mu_{\text{exp}}$ a factor which may account of all these effects mentioned above.

9. 5 CONCLUSION

The structural and associational aspects of DMF and DMSO dimer have been studied in terms of measured parameters with derived theoretical formulations. The interesting equations in terms of χ_{ijk} 's helps one to explore new physical insight about the systems as χ_{ijk} 's are directly linked only with the molecular orientational polarization. Relaxation times τ_{jk} obtained from eq.(9.7) and its excellent agreement with those of Gopala Krishna's method used by Sharma et al [11] at once reflects the validity of our theoretical formulations so far achieved. Now linear variations of τ_{jk} and dipole moment μ_{jk} with mole% of k-th solute (DMSO) reflects strong dimer association between two polar units which is supposed to be a physico-chemical property of the systems. Strong association between the polar units arises due to strong H-bonding (Fig. 9.6 iii) which are also supported by positive and negative $\Delta S\tau$'s giving additional information about unstability and stability of the systems. Higher μ_{jk} 's in comparison to μ_{theo} arises due to solute-solute (dimer) association between DMF & DMSO molecules in addition to inductive, mesomeric and electromeric effects suffered by polar groups attached to the parent polar molecules. All these effects give another information about physico-chemical property of the molecules. Correlation coefficients (r's) and % of errors estimated between different parameters of several curves

establishe the statistical validity of our theoretical formulations based on Debye model to estimate several physical parameters which are more of archival values to study the temperature variation of physico-chemical properties and structural and associational aspects of the aprotic polar liquid of dipolar molecules.

Table 9.1: Temperature variation of the real and imaginary parts of dielectric relative permittivity ϵ^*_{ijk} , infinitely high frequency relative permittivity $\epsilon_{\infty ij k}$, real and imaginary parts of dielectric susceptibilities χ'_{ijk} and χ''_{ijk} of hf complex susceptibility χ^*_{ijk} of binary polar liquids in non polar solvent C_6H_6 at different experimental temperatures under 9.174 GHz electric field.

Systems with Sl. No.	Temp in $^{\circ}C$	Weight fraction	Dielectric permittivities			Dielectric susceptibilities	
			w_{jk}	ϵ'_{ijk}	ϵ''_{ijk}	$\epsilon_{\infty ij k}$	χ'_{ijk}
1. DMF + 0 mole% DMSO	25	0.0036	2.3700	0.0510	2.2532	0.1168	0.0510
		0.0057	2.4000	0.0640	2.2534	0.1466	0.0640
		0.0080	2.4500	0.0820	2.2621	0.1879	0.0820
		0.0101	2.4700	0.0960	2.2501	0.2199	0.0960
	30	0.0036	2.3600	0.0430	2.2599	0.1001	0.0430
		0.0057	2.3700	0.0610	2.2280	0.1420	0.0610
		0.0080	2.4400	0.0760	2.2631	0.1769	0.0760
		0.0101	2.4500	0.0870	2.2475	0.2025	0.0870
	35	0.0036	2.3400	0.0400	2.2280	0.1120	0.0400
		0.0057	2.3700	0.0550	2.2160	0.1540	0.0550
		0.0080	2.4300	0.0700	2.2340	0.1960	0.0700
		0.0101	2.4400	0.0780	2.2217	0.2183	0.0780
	40	0.0036	2.3300	0.0370	2.2246	0.1054	0.0370
		0.0057	2.3700	0.0500	2.2275	0.1425	0.0500
		0.0080	2.4200	0.0650	2.2348	0.1852	0.0650
		0.0101	2.4300	0.0730	2.2220	0.2080	0.0730
2. DMF + 17 mole% DMSO	25	0.0033	2.3600	0.0620	2.2899	0.0701	0.0620
		0.0048	2.4000	0.1040	2.2824	0.1176	0.1040
		0.0067	2.4300	0.1330	2.2795	0.1505	0.1330
		0.0105	2.4600	0.1520	2.2948	0.1652	0.1520
	30	0.0033	2.3500	0.0590	2.2714	0.0786	0.0590
		0.0048	2.3800	0.0940	2.2547	0.1253	0.0940
		0.0067	2.4200	0.1180	2.2627	0.1573	0.1180
		0.0105	2.4500	0.1380	2.2660	0.1840	0.1380
	35	0.0033	2.3400	0.0490	2.2702	0.0698	0.0490
		0.0048	2.3700	0.0810	2.2545	0.1155	0.0810
		0.0067	2.4200	0.1070	2.2675	0.1525	0.1070
		0.0105	2.4500	0.1300	2.2647	0.1853	0.1300
	40	0.0033	2.3100	0.0470	2.2334	0.0766	0.0470
		0.0048	2.3500	0.0710	2.2343	0.1157	0.0710
		0.0067	2.4100	0.1040	2.2406	0.1694	0.1040
		0.0105	2.4400	0.1270	2.2331	0.2069	0.1270

Systems with Sl. No.	Temp in °C	Weight fraction	Dielectric permittivities			Dielectric susceptibilities	
			w_{jk}	ϵ'_{ijk}	ϵ''_{ijk}	$\epsilon_{\infty ij}$	χ'_{ijk}
3. DMF + 50 mole% DMSO	25	0.0036	2.3700	0.0500	2.3146	0.0554	0.0500
		0.0042	2.3800	0.0630	2.3102	0.0698	0.0630
		0.0072	2.4500	0.1320	2.3038	0.1462	0.1320
		0.0100	2.4800	0.1490	2.3150	0.1650	0.1490
	30	0.0036	2.3500	0.0450	2.2957	0.0543	0.0450
		0.0042	2.3600	0.0570	2.2912	0.0688	0.0570
		0.0072	2.4400	0.1240	2.2903	0.1497	0.1240
		0.0100	2.4600	0.1370	2.2946	0.1654	0.1370
	35	0.0036	2.3300	0.0420	2.2734	0.0566	0.0420
		0.0042	2.3500	0.0560	2.2745	0.0755	0.0560
		0.0072	2.4200	0.1110	2.2704	0.1496	0.1110
		0.0100	2.4500	0.1300	2.2748	0.1752	0.1300
	40	0.0036	2.3100	0.0390	2.2550	0.0550	0.0390
		0.0042	2.3400	0.0510	2.2680	0.0720	0.0510
		0.0072	2.4000	0.1030	2.2546	0.1454	0.1030
		0.0100	2.4400	0.1260	2.2622	0.1778	0.1260
4. DMF + 60 mole% DMSO	25	0.0038	2.3600	0.0700	2.2454	0.1146	0.0700
		0.0051	2.3800	0.0810	2.2474	0.1326	0.0810
		0.0072	2.4200	0.1170	2.2285	0.1915	0.1170
		0.0110	2.5000	0.1540	2.2479	0.2521	0.1540
	30	0.0038	2.3500	0.0600	2.2529	0.0971	0.0600
		0.0051	2.3700	0.0720	2.2535	0.1165	0.0720
		0.0072	2.4000	0.1030	2.2334	0.1666	0.1030
		0.0110	2.4800	0.1390	2.2551	0.2249	0.1390
	35	0.0038	2.3100	0.0460	2.2304	0.0796	0.0460
		0.0051	2.3600	0.0670	2.2441	0.1159	0.0670
		0.0072	2.3900	0.0980	2.2205	0.1695	0.0980
		0.0110	2.4600	0.1290	2.2368	0.2232	0.1290
	40	0.0038	2.3000	0.0350	2.2344	0.0656	0.0350
		0.0051	2.3500	0.0660	2.2264	0.1236	0.0660
		0.0072	2.3800	0.0920	2.2076	0.1724	0.0920
		0.0110	2.4400	0.1100	2.2339	0.2061	0.1100

Systems with Sl. No.	Temp in °C	Weight fraction	Dielectric permittivities			Dielectric susceptibilities	
			w_{jk}	ϵ'_{ijk}	ϵ''_{ijk}	$\epsilon_{\infty ij}$	χ'_{ijk}
5. DMF + 80 mole% DMSO	25	0.0042	2.3800	0.0460	2.2769	0.1031	0.0460
		0.0069	2.4400	0.0820	2.2562	0.1838	0.0820
		0.0082	2.4600	0.0960	2.2448	0.2152	0.0960
		0.0120	2.5800	0.1360	2.2752	0.3048	0.1360
	30	0.0042	2.3500	0.0430	2.2442	0.1058	0.0430
		0.0069	2.4200	0.0780	2.2281	0.1919	0.0780
		0.0082	2.4500	0.0920	2.2237	0.2263	0.0920
		0.0120	2.5500	0.1250	2.2425	0.3075	0.1250
	35	0.0042	2.3400	0.0370	2.2442	0.0958	0.0370
		0.0069	2.4100	0.0690	2.2314	0.1786	0.0690
		0.0082	2.4300	0.0870	2.2048	0.2252	0.0870
		0.0120	2.5400	0.1140	2.2449	0.2951	0.1140
	40	0.0042	2.3200	0.0340	2.2310	0.0890	0.0340
		0.0069	2.4000	0.0640	2.2324	0.1676	0.0640
		0.0082	2.4200	0.0750	2.2236	0.1964	0.0750
		0.0120	2.5200	0.1100	2.2319	0.2881	0.1100
6. DMF + 100 mole% DMSO	25	0.0021	2.3100	0.0270	2.2338	0.0762	0.0270
		0.0047	2.3500	0.0440	2.2258	0.1242	0.0440
		0.0084	2.4400	0.0580	2.2763	0.1637	0.0580
		0.0100	2.4800	0.0970	2.2062	0.2738	0.0970
	30	0.0021	2.3000	0.0260	2.2262	0.0738	0.0260
		0.0047	2.3400	0.0400	2.2265	0.1135	0.0400
		0.0084	2.4200	0.0540	2.2668	0.1532	0.0540
		0.0100	2.4700	0.0940	2.2033	0.2667	0.0940
	35	0.0021	2.2800	0.0200	2.2269	0.0531	0.0200
		0.0047	2.3200	0.0320	2.2350	0.0850	0.0320
		0.0084	2.3900	0.0520	2.2518	0.1382	0.0520
		0.0100	2.4500	0.0880	2.2162	0.2338	0.0880
	40	0.0021	2.2700	0.0180	2.2166	0.0534	0.0180
		0.0047	2.3000	0.0250	2.2258	0.0742	0.0250
		0.0084	2.3700	0.0480	2.2275	0.1425	0.0480
		0.0100	2.4400	0.0760	2.2143	0.2257	0.0760

Table-9.2:- Measured τ_{jk} 's from ratio of slopes of individual variations of χ'_{ijk} and χ''_{ijk} with ω_{jk} , reported τ_{jk} in pico second, correlation coefficient and % of error of χ'_{ijk} - ω_{jk} & χ''_{ijk} - ω_{jk} curves of Figs. 9.1 and 9.2, dipole moments (μ_{jk}) using τ_{jk} of eq.(9.7) and theoretical dipole moment μ_{theo} using bond moments in Coulomb - metre of binary polar mixtures in solvent C_6H_6 at different experimental temperatures under 9.174 GHz electric field.

Systems with Sl.no. & molecular weight (M_{jk}) in Kg	Temp. in $^{\circ}C$	Estimated τ_{jk} in psec using eq.(9.7)	Reported τ_{jk} in psec	Correl. coeff. $\chi'_{ijk}-\omega_{jk}$ & $\chi''_{ijk}-\omega_{jk}$ curves	% of error. $\chi'_{ijk}-\omega_{jk}$ & $\chi''_{ijk}-\omega_{jk}$ curves	Estimated hf $\mu_{jk} \times 10^{30}$ in C.m.	$\mu_{theo} \times 10^3$ in C.m.
1.DMF + 0 mole% DMSO $M_{jk} = 0.07300$	25	7.57	7.50	0.9991	0.06	11.30	12.74
	30	7.45	6.90	0.9943	0.38	15.88	
	35	6.20	6.10	0.9921	0.53	16.61	
	40	6.09	5.50	0.9944	0.37	15.55	
2.DMF +17 mole% DMSO $M_{jk} = 0.07385$	25	15.33	16.40	0.9013	6.33	26.48	15.90
	30	13.01	14.10	0.9412	3.85	23.86	
	35	12.17	12.60	0.9570	2.84	23.60	
	40	10.65	11.10	0.9665	2.22	23.53	
3.DMF +50mole% DMSO $M_{jk} = 0.07550$	25	15.66	15.70	0.9673	2.17	28.15	15.90
	30	14.36	13.50	0.9602	2.63	28.76	
	35	12.86	11.20	0.9763	1.58	26.11	
	40	12.29	9.90	0.9853	0.98	24.51	
4.DMF +60 mole% DMSO $M_{jk} = 0.07600$	25	10.59	11.20	0.9925	0.51	17.85	15.90
	30	10.72	10.90	0.9955	0.30	17.05	
	35	10.02	10.00	0.9859	0.95	22.11	
	40	9.26	9.30	0.9393	3.97	27.04	
5.DMF +80 mole% DMSO $M_{jk} = 0.07700$	25	7.74	7.80	0.9977	0.16	18.55	15.90
	30	7.05	7.70	0.9934	0.44	20.46	
	35	6.70	7.40	0.9878	0.82	21.73	
	40	6.62	6.20	0.9984	0.11	18.06	
6.DMF +100 mole% DMSO $M_{jk} = 0.07800$	25	6.14	5.40	0.9286	4.64	—	15.17
	30	6.11	5.00	0.9164	5.41	—	
	35	6.53	4.70	0.9394	3.97	—	
	40	5.84	4.30	0.9492	3.34	—	

Table-9.3 :Intercepts and slopes of $\ln\tau_{jk}T$ against $1/T$ curves of Fig. 9.4, thermodynamic energy parameters like enthalpy of activation ΔH_τ in Kilo Joule mole⁻¹, the entropy of activation ΔS_τ in Joule mole⁻¹ K⁻¹, free energy of activation ΔF_τ in Kilo Joule mole⁻¹, enthalpy of activation ΔH_η in Kilo Joule mole⁻¹ due to viscous flow of solvent, δ (slope of $\ln\tau_{jk}T$ vs. $\ln\eta_i$ equation), Kalman factor ($\tau_{jk}T / \eta^\delta$) and Debye factor ($\tau_{jk}T / \eta$) at different experimental temperatures and the coefficients of $\mu_{jk} - t$ of equations $\mu_{jk} = a + bt + ct^2$ of mixture of liquids in benzene under 9.174 GHz electric field frequency.

Systems with SI.no.	Temp in °C	Intercept & slope of $\ln\tau_{jk}T$ Vs $1/T$ equation		ΔH_τ in KJ mole ⁻¹	ΔS_τ in J mole ⁻¹ K ⁻¹	ΔF_τ in KJ mole ⁻¹	δ =slope of $\ln(\tau_{jk}T)$ vs $\ln\eta_i$ equation	ΔH_η in KJ mole ⁻¹	Kalman factor ($\tau_{jk}T/\eta^\delta$)	Debye factor ($\tau_{jk}T/\eta$) $\times 10^6$	Coefficients of the eqs $\mu_{jk} \times 10^{30} = a + bt + ct^2$ equation		
		Intercept	slope								a	b	c
1.DMF + 0 mole% DMSO	25			10.50	3.10	9.57			6.49x10 ⁻⁴	3.83			
	30	-24.11	1258.40	10.50	2.52	9.73	1.69	6.22	7.04x10 ⁻⁴	4.02	-0.056	3.937	-51.746
	35			10.50	3.36	9.46			6.46x10 ⁻⁴	3.57			
	40			10.50	2.83	9.61			6.69x10 ⁻⁴	3.64			
2.DMF + 17 mole% DMSO	25			15.53	14.10	11.33			2.78x10 ⁻¹	7.76			
	30	-25.47	1861.70	15.53	14.48	11.14	2.41	6.44	2.70x10 ⁻¹	7.03	0.025	-1.840	56.429
	35			15.53	14.07	11.20			2.88x10 ⁻¹	7.01			
	40			15.53	14.24	11.07			2.70x10 ⁻¹	6.37			
3.DMF + 50 mole% DMSO	25			10.49	-2.98	11.38			1.25x10 ⁻³	7.93			
	30	-23.49	1257.60	10.49	-2.98	11.39	1.68	6.26	1.26x10 ⁻³	7.76	-0.022	1.170	12.967
	35			10.49	-2.76	11.34			1.24x10 ⁻³	7.41			
	40			10.49	-3.06	11.45			1.25x10 ⁻³	7.35			
4.DMF + 60 mole% DMSO	25			4.75	-18.99	10.41			4.96x10 ⁻⁷	5.36			
	30	-21.46	569.05	4.75	-19.49	10.65	0.68	6.94	5.28x10 ⁻⁷	5.79	0.057	-3.067	58.458
	35			4.75	-19.33	10.70			5.18x10 ⁻⁷	5.78			
	40			4.75	-19.04	10.71			4.94x10 ⁻⁷	5.54			
5.DMF + 80 mole% DMSO	25			5.55	-13.67	9.63			2.16x10 ⁻⁶	3.92			
	30	-22.23	665.73	5.55	-13.34	9.59	0.92	6.03	2.09x10 ⁻⁶	3.81	-0.056	3.626	-37.420
	35			5.55	-13.35	9.66			2.11x10 ⁻⁶	3.86			
	40			5.55	-13.67	9.83			2.17x10 ⁻⁶	3.96			
6.DMF + 100 mole% DMSO	25			-1.25	-34.58	9.05			2.89x10 ⁻¹⁰	3.51			
	30	-19.69	-150.21	-1.25	-34.61	9.23	-0.31	4.01	1.80x10 ⁻¹⁰	3.26	-	-	-
	35			-1.25	-35.23	9.60			1.79x10 ⁻¹⁰	3.47			
	40			-1.25	-34.37	9.50			1.93x10 ⁻¹⁰	3.84			

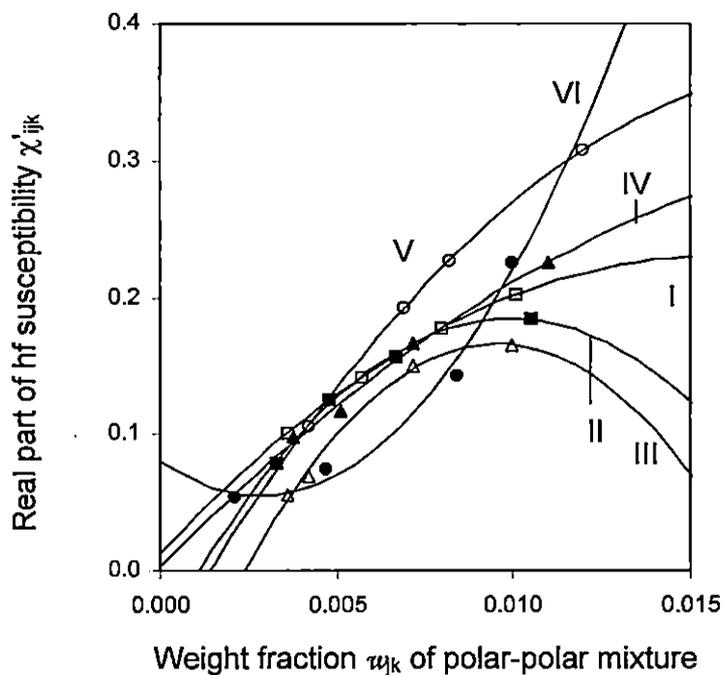


Fig 9.1. Some sample curves showing the variation of imaginary part χ'_{ijk} of hf dielectric susceptibility against weight fraction w_{jk} of polar-polar mixture in solvent C_6H_6 under 9.174 GHz electric field frequency of I. DMF + 0 mole% DMSO (-- □ --) II. DMF + 17 mole% DMSO (-- ■ --) III. DMF + 50 mole% DMSO (-- Δ --) IV. DMF + 60 mole% DMSO (-- ▲ --) V. DMF+ 80 mole% DMSO (-- o --) VI. DMF+ 100 mole% DMSO (-- ● --)

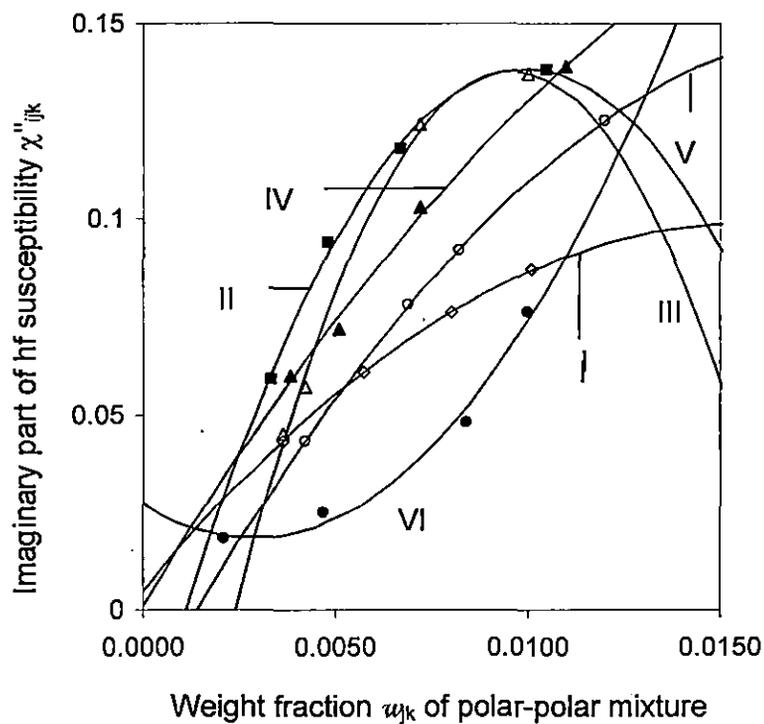


Fig 9.2. Some sample curves showing the variation of imaginary part χ''_{ijk} of hf dielectric susceptibility against weight fraction w_{jk} of polar-polar mixture in solvent C_6H_6 under 9.174 GHz electric field frequency of I. DMF + 0 mole% DMSO (— \square —) II. DMF + 17 mole% DMSO (— \blacksquare —) III. DMF + 50 mole% DMSO (— \triangle —) IV. DMF + 60 mole% DMSO (— \blacktriangle —) V. DMF + 80 mole% DMSO (— \circ —) VI. DMF + 100 mole% DMSO (— \bullet —)

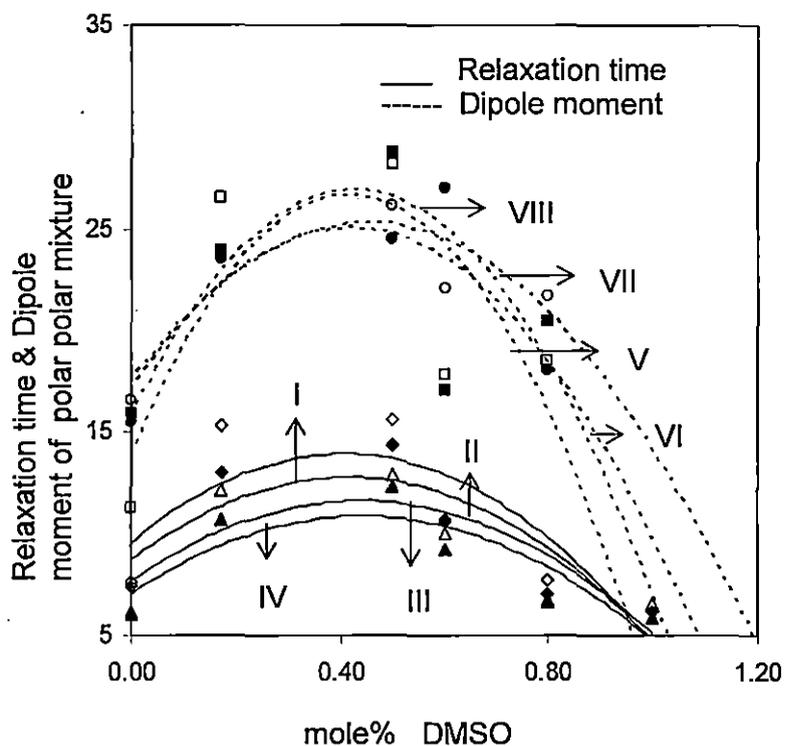


Fig-9.3. Variation of relaxation time τ_{jk} and Dipole moment $\mu_{jk} \times 10^{30}$ in C.m of polar-polar binary mixture against mole% of DMSO in C_6H_6 at different temperature in $^{\circ}C$ under 9.174 GHz electric field frequency I. τ_{jk} (\diamond) at $25^{\circ}C$ II. τ_{jk} (\blacklozenge) at $30^{\circ}C$, III. τ_{jk} (\triangle) at $35^{\circ}C$, IV. τ_{jk} (\blacktriangle) at $40^{\circ}C$, V. μ_{jk} (\square) at $25^{\circ}C$, VI. μ_{jk} (\blacksquare) at $30^{\circ}C$, VII. μ_{jk} (\circ) at $35^{\circ}C$, VIII. μ_{jk} (\bullet) at $40^{\circ}C$

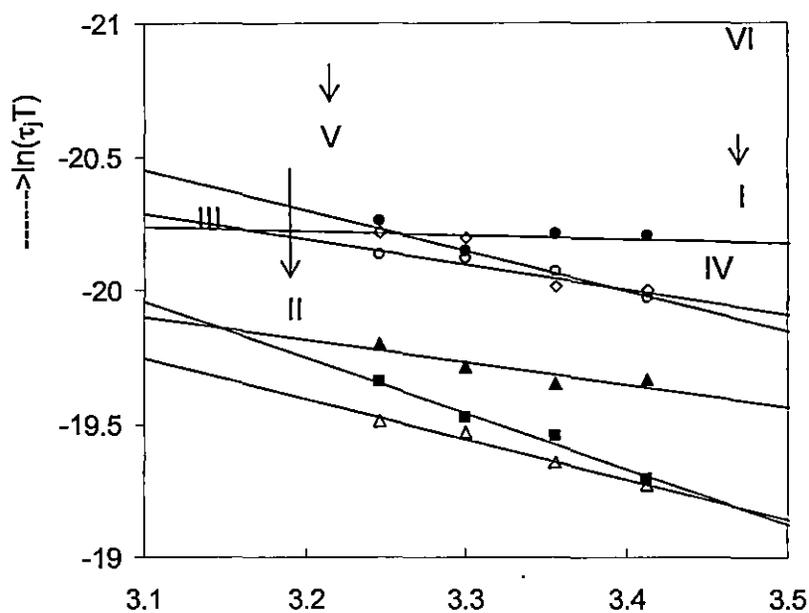


Figure 9.4. Variation of $\ln(\tau_j T)$ against $1/T$ of binary polar mixtures in solvent C_6H_6 under 9.174 GHz electric field frequency I. DMF + 0 mole% DMSO (-- \square --) II. DMF + 17 mole% DMSO (-- \blacksquare --) III. DMF + 50 mole% DMSO (-- \triangle --) IV. DMF + 60 mole% DMSO (-- \blacktriangle --) V. DMF + 80 mole% DMSO (-- \circ --) VI. DMF + 100 mole% DMSO (-- \bullet --)

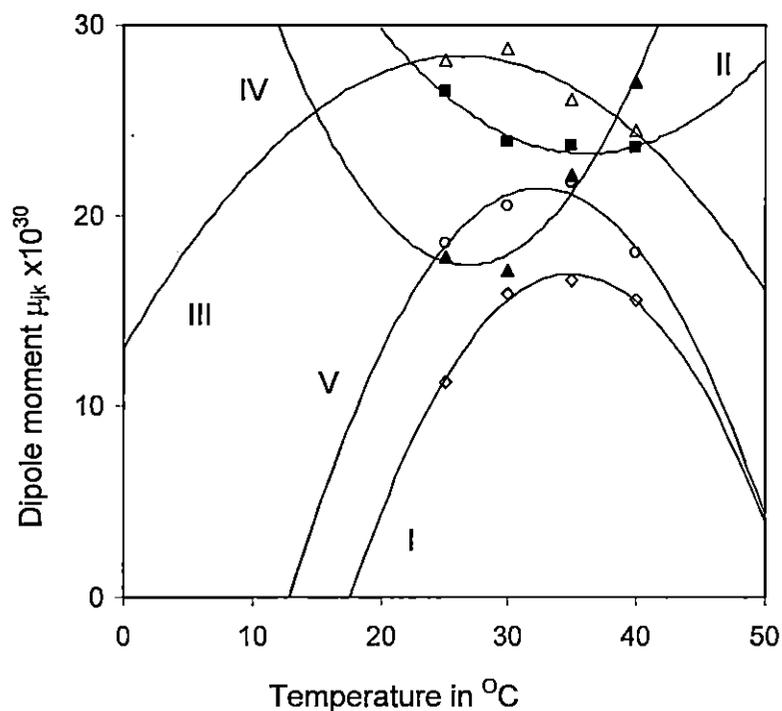
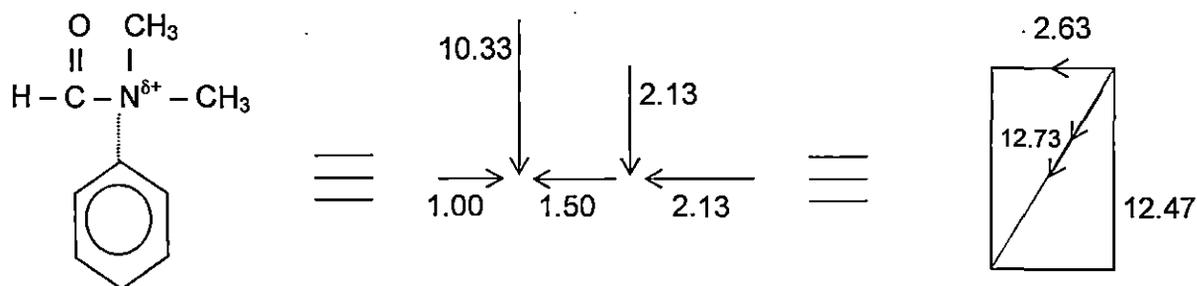
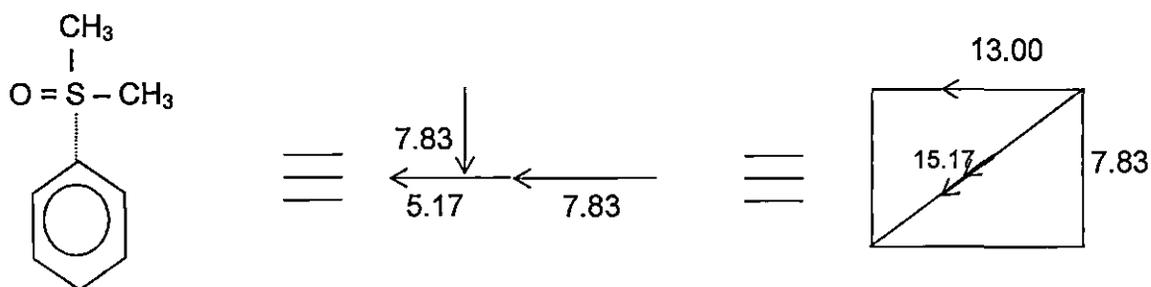


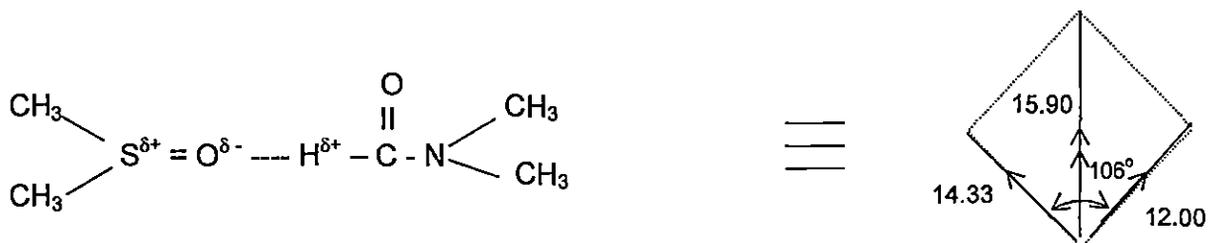
Figure 9.5. Variation of dipole moment $\mu_{jk} \times 10^{30}$ in Coulomb-metre of binary polar - polar mixture against temperature in $^{\circ}\text{C}$ under 9.174 GHz electric field frequency of I. DMF + 0 mole% DMSO (-- \square --) II. DMF + 17 mole% DMSO (-- \blacksquare --) III. DMF + 50 mole% DMSO (-- \triangle --) IV. DMF + 60 mole% DMSO(-- \blacktriangle --) V. DMF + 80 mole% DMSO (-- \circ --) VI. DMF + 100 mole% DMSO (-- \bullet --)



(i)



(ii)



(iii)

Figure 9.6: CONFORMATIONAL STRUCTURES
(Bond moment $\times 10^{30}$ Coulomb metre given in figures)

- (i) DMF in benzene
- (ii) DMSO in benzene
- (iii) DMF – DMSO dimer

REFERENCES

- [1] M P Madan, *J Mol Liquids* **33** (1987) 203
- [2] A D Vyas & Vashisth, *J Mol Liquids* **38** (1988) 11
- [3] F J Murphy and S O Morgan, *Bell Syst Tech J* **18** (1930) 502
- [4] M B R Murthy, R L Patil and D K Deshpande, *Indian J Phys* **63B** (1989) 491
- [5] N Ghosh, A Karmakar, S K Sit & S Acharyya, *Indian J Pure & Appl Phys.* **38** (2000) 574
- [6] P Debye, *Polar Molecules (Chemical Catalogue)* 1929
- [7] P Ghosh, S K Sit, A K Bothra and S Acharyya, *J Phys D: Appl Phys (U K)* **34** (2001) 379
- [8] A Karmakar, U K Mitra, N Ghosh and S Acharyya, *Indian J Pure & Appl Phys* communicated 2006
- [9] K V Gopala Krishna, *Trans Faraday Soc.* **53** (1957) 767
- [10] H Eyring, S Glasstone and K J Laidler, *The Theory of Rate Process* (New York: Mc Graw Hill) 1941
- [11] A Sharma, D R Sharma and M S Chauhan, *Indian J Pure & Appl Phys* **31** (1993) 841
- [12] M L Arrawatia, P C Gupta and M L Sisodia, *Indian J Pure & Appl Phys* **15** (1977) 770
- [13] *Hand Book of Chemistry and Physics*, CRC press 58th edition 1977-78
- [14] Smyth C P, *Dielectric Behaviour and Structure* (New York: Mc Graw Hill) 1955
- [15] U K Mitra, N Ghosh, P Ghosh and S Acharyya, *J.Indian Chem.Soc.* **83** (2006) 1230
- [16] U K Mitra, N Ghosh, P Ghosh and S Acharyya, *J Mol. Liquids* **126** (2006) 53
- [17] N Ghosh, Ph.D dissertation (North Bengal University (W.B.) INDIA) 2002
- [18] A K Sharma and D R Sharma *J, Phys Soc Japan* **61** (1992) 1049
- [19] N Ghosh, R C Basak, S K Sit and S Acharyya, *J Mol Liquids* **85** (2000) 375
- [20] R L Dhar, A Mathur, J P Shukla and M C Saxena, *Indian J Pure & Appl Phys* **11** (1973) 568

CHAPTER 10

SUMMARY AND CONCLUSION OF THE THESIS WORKS

10. SUMMARY AND CONCLUSION OF THE THESIS WORKS

The subject matter of the thesis works has been divided into several CHAPTERS from 1 to 10. All the chapters are highly informative to shed more light on physico-chemical properties of the polar solvents under static and high frequency electric fields. The physico – chemical aspects of the solvents and solute liquids have been studied in detail and presented in terms of the variation of the measured relaxation parameters with weight fractions w_j 's of the polar solutes at a single or different temperatures to enhance the present knowledge of relaxation phenomena. Dielectric relaxation is one of the difficult unresolved problems of physics and chemistry today. The point which needs to be kept in mind is that all relaxation phenomena are of necessity connected with the presence in the systems under study of some form of disorder. There can be no relaxation in a perfectly ordered system, because nothing can relax from perfection. It is very interesting to note that many workers in this field of research do not know how to use the data of dielectric relaxation for the maximum effective utilisation. The First CHAPTER entitled "GENERAL INTRODUCTION AND REVIEW OF THE PREVIOUS WORKS" helps the reader to get a first hand information on the topic of correlation in the liquid solvents like polar and non polar liquids mixtures. The handy and new theories have been derived and presented in the SECOND CHAPTER having the heading "SCOPE AND OBJECTIVE OF THE PRESENT WORKS". The theories so far prescribed are widely used in different CHAPTERS of 3 to 9 in order to arrive at the conclusion of the works studied so far of the thesis of CHAPTER 10 called the "SUMMARY AND CONCLUSION OF THE THESIS WORKS". In which all the important findings are incorporated chapterwise from chapters 3 to 9 respectively.

The CHAPTER 3 entitled "STRUCTURAL ASPECTS AND PHYSICO-CHEMICAL PROPERTIES OF SOME AROMATIC POLAR NITRO COMPOUNDS IN SOLVENT BENZENE AT DIFFERENT TEMPERATURES UNDER GIGA HERTZ ELECTRIC FIELD" in which an interesting method based on complex orientational susceptibilities χ_{ij}^* s to study the dielectric relaxation

mechanism of some standard polar nitro compounds in non polar solvent benzene has been prescribed and applied successfully to arrive at their structural and physico-chemical properties. The dielectric orientational susceptibilities χ'_{ij} , the real and χ''_{ij} , the imaginary parts of χ^*_{ij} are involved with the measured relative permittivities ϵ'_{ij} and ϵ''_{ij} of ϵ^*_{ij} of Pant et al to measure the relaxation time τ_j of all the polar solutes from the ratio of the linear coefficients of individual variations of χ''_{ij} and χ'_{ij} with weight fractions w_j 's of the respective solute. They are further compared with τ_j 's obtained from the direct slope of the linear variations of χ''_{ij} and χ'_{ij} and Gopala Krishna's method measured by Pant et al. The temperature variation of τ_j 's from the former method helps one to get the thermodynamic energy parameters i.e. enthalpy of activation ΔH_τ , entropy of activation ΔS_τ and free energy of activation ΔF_τ of dielectric relaxation by using the rate process equation of Eyring et al to throw much light on their structural and physico chemical properties. The dimensionless parameter δ ($= \Delta H_\tau / \Delta H\eta_1$) which is the slope of the linear equation of $\ln\tau_j T = \ln a + \delta \ln \eta_1$, where η_1 the coefficient of viscosity of the solvent, is used to get Debye and Kalman factors. They reflect the associative nature along with the applicability of Debye-Smyth model of dielectric relaxation for such polar nitro molecules. The estimated dipole moments μ_j 's in terms of linear coefficient β 's of χ'_{ij} vs w_j like $\chi'_{ij} = \alpha + \beta w_j + \gamma w_j^2$ curves and dimensionless parameters b 's involved with measured τ_j 's are finally compared with theoretical dipole moments μ_{theo} 's, obtained from available bond angles and bond moment of the substituent polar groups of the molecules as well as with μ_j 's of Gopala Krishna's method used by Pant et al to shed more light on the conformations of the molecules, in addition to inductive, mesomeric and electromeric effects.

The "DIELECTRIC RELAXATION PHENOMENA OF SOME APROTIC LIQUIDS UNDER GIGA HERTZ ELECTRIC FIELD" in CHAPTER 4 presents the double relaxation times τ_1 and τ_2 due to rotations of the flexible parts and the whole molecules of some aprotic polar liquids (j) like N,N-dimethylsulphoxide (DMSO); N,N-dimethylformamide (DMF), N,N-

dimethylacetamide (DMA) and N, N-diethylformamide (DEF) in benzene (i) estimated from the measured real χ'_{ij} and imaginary χ''_{ij} part of hf complex dielectric orientational susceptibility χ^*_{ij} and low frequency susceptibility χ_{oij} at different weight fractions w_j 's of solute at various experimental temperatures. The relative contributions c_1 and c_2 due to τ_1 and τ_2 are calculated from Fröhlich's equations. and graphical technique. All the c 's are positive from Fröhlich's equations. while some c_2 's are negative from graphical method. The dipole moments μ_2 & μ_1 in Coulomb-metre (C.m) measured from the slope β 's of $\chi'_{ij} - w_j$ curves are compared with those τ 's from ratio of individual slope of $(d\chi''_{ij}/dw_j)w_j \rightarrow 0$ and $(d\chi'_{ij}/dw_j)w_j \rightarrow 0$, linear slope of $\chi''_{ij} - \chi'_{ij}$, conductivity measurement technique along with those of Gopala krishna's method. The estimated μ_1 's agree with the measured and reported μ 's to indicate that a part of the molecule is rotating under GHz electric field. The theoretical dipole moment μ_{theo} 's are obtained in terms of available bond angles and bond moments of the substituent polar groups attached to the parent molecules acting as pusher or puller of electrons due to inductive, mesomeric and electromeric effects in them under hf electric field. The variation of μ_1 with temperature suggests the elongation of bond moments. The energy parameters such as enthalpy of activation ΔH_τ , free energy of activation ΔF_τ and entropy of activation ΔS_τ 's were obtained for DMSO only assuming dielectric relaxation as a rate process to know the molecular dynamics of the system. The plot of $\ln(\tau_1 T)$ against $1/T$ of DMSO reveals that it obeys Eyring rate theory unlike $\ln(\tau_2 T) - 1/T$ curve.

The straight line equation $(\chi_{oij} - \chi'_{ij}) / \chi'_{ij} = \omega (\tau_1 + \tau_2) (\chi''_{ij} / \chi'_{ij}) - \omega^2 \tau_1 \tau_2$ for different weight fractions w_j 's of some dipolar long straight chain alcohols (j) in n-heptane (i) derived from the available relative permittivities ϵ'_{ij} , ϵ''_{ij} , ϵ_{oij} and $\epsilon_{\alpha ij}$ at 25°C under nearly 24 GHz electric field. The intercepts and slopes of the above equation. are used to get relaxation times τ_1 and τ_2 of the rotation of flexible part and the whole molecules. $\chi'_{ij} (= \epsilon'_{ij} - \epsilon_{\alpha ij})$ and $\chi''_{ij} (= \epsilon''_{ij})$ are the real and imaginary parts of hf dimensionless complex dielectric

orientational susceptibility χ_{ij}^* and χ_{oij} ($=\epsilon_{oij} - \epsilon_{\infty ij}$) is the low frequency dielectric susceptibility which is real. τ_j 's of such alcohols are also measured from the ratio of the slopes of the individual variations of χ'_{ij} and χ''_{ij} with ω_j 's at $\omega_j \rightarrow 0$ and the direct slope of χ''_{ij} versus χ'_{ij} equations of Muthy et al . These τ_j 's are finally compared with the reported τ_j 's of Gopala Krishna and τ_1, τ_2 by double relaxation method to see that the flexible part of the molecule is only rotating under the most effective dispersive region of 24 GHz electric field. The weighted contributions c_1 and c_2 towards dielectric relaxations for estimated τ_1, τ_2 are, however, obtained from Fröhlich's theoretical formulations of χ'_{ij} / χ_{oij} and χ''_{ij} / χ_{oij} to compare them with those of graphical ones of $(\chi'_{ij} / \chi_{oij})\omega_j \rightarrow 0$ and $(\chi''_{ij} / \chi_{oij})\omega_j \rightarrow 0$. The latter ones are employed to get symmetric distribution parameter γ to have the symmetric relaxation times τ_s . The arbitrary curve of $(1/\phi) \log \cos\phi$ against ϕ in degree together with $(\chi'_{ij} / \chi_{oij}) \omega_j \rightarrow 0$ and $(\chi''_{ij} / \chi_{oij}) \omega_j \rightarrow 0$ experimentally obtained, gives the asymmetric distribution parameter δ to get the characteristic relaxation time τ_{cs} . All these findings finally establish the symmetric relaxation behaviour for such compounds. The dipole moments μ_1 and μ_2 for the flexible part and the whole molecule are determined from τ_1 and τ_2 and the linear coefficient β of χ'_{ij} versus ω_j 's curves . All the measured μ_j 's are compared with the reported μ_j 's and μ_{theo} 's derived from the bond angles and bond moments of the substituted polar groups of the compounds to arrive at the physico chemical properties by the conformations sketched in this chapter The slight disagreement of estimated μ_j 's and μ_{theo} 's is , however, explained with the consideration of inductive and mesomeric moments in addition to strong hydrogen bonding of the flexible polar groups attached to the parent molecule. All these findings are presented in CHAPTER 5 having title "THE PHYSICO-CHEMICAL ASPECTS OF SOME LONG STRAIGHT CHAIN ALCOHOLS FROM SUSCEPTIBILITY MEASUREMENT UNDER A 24 GHz ELECTRIC FIELD AT 25⁰C"

The CHAPTER 6 "STUDIES ON PHYSICO-CHEMICAL PROPERTIES WITH THE RELAXATION PHENOMENA OF SOME NORMAL

ALIPHATIC ALCOHOLS IN NONPOLAR SOLVENT UNDER GIGA HERTZ ELECTRIC FIELD AT A SINGLE TEMPERATURE” in which double relaxations of some normal aliphatic alcohols have been studied to get relaxation times τ_1 and τ_2 due to rotation of flexible part and end over end rotation of the whole molecule from the intercept and slope of a linear equation of $(\chi_{oij} - \chi'_{ij}) / \chi'_{ij}$ against χ''_{ij}/χ'_{ij} for different weight fractions w_j 's of solute in n-heptane at 25°C under electric field frequencies of 24.33, 9.25 and 3.00 GHz. Alcohols like 1-butanol, 1-hexanol, 1-heptanol and 1-decanol are long straight chain hydrogen bonded polymer type molecules having -OH groups which may bend twist or rotate internally about C-C bond under GHz electric field exhibiting characteristic τ . Estimated τ_j obtained from ratio of slopes of individual variation of χ''_{ij} and χ'_{ij} against w_j at $w_j \rightarrow 0$ are compared with those of Murthy et al, Gopala krishna (reported data) and τ_1 , τ_2 by double relaxation method. Relative contributions c_1 and c_2 due to τ_1 and τ_2 towards dielectric relaxations estimated from Fröhlich's equations are compared with the experimental ones obtained by graphical technique. Graphical variations of χ'_{ij} / χ_{oij} and χ''_{ij} / χ_{oij} with w_j at $w_j=0$ together with arbitrary curve of $(1/\phi) \log(\cos\phi)$ against ϕ in degree have been utilised to get symmetric γ and asymmetric δ distribution parameters. The symmetric relaxation time τ_s by γ and characteristic relaxation time τ_{cs} by δ and ϕ are computed to suggest symmetric relaxation behaviour of the molecules. Linear coefficient β 's of $\chi'_{ij} - w_j$ curves and dimensionless parameters b_1 and b_2 involved with estimated τ_1 and τ_2 are used to get dipole moments μ_1 and μ_2 due to rotation of flexible part and the whole molecule which are compared with reported μ 's (Gopalakrishna) and μ_{theo} 's. The slight disagreement between μ_1 and μ_{theo} obtained from available bond angles and reduced bond moments of substituent polar groups attached to parent molecules arises due to strong internal hydrogen bonds present among the -OH groups of dipolar liquid molecules.

The ratio of the linear coefficients of the fitted individual equations of $\chi''_{ij} - w_j$ and $\chi'_{ij} - w_j$ of some para substituted derivative polar liquid molecules in solvents

dioxane and benzene, are used to get their relaxation times τ_j 's under 10 GHz electric field at various experimental temperatures in $^{\circ}\text{C}$. χ'_{ij} and χ''_{ij} are the real and imaginary parts of the high frequency (hf) complex dielectric susceptibility χ_{ij}^* as a function of weight fractions w_j 's of polar solutes at each experimental temperature. The measured τ_j 's of solutes at different temperatures, by Eyring's rate process equations, yield thermodynamic energy parameters: enthalpy of activation ΔH_r , entropy of activation ΔS_r and free energy of activation ΔF_r due to dielectric relaxation to study stability and physico-chemical properties of the systems. The parameter δ from the slope of linear variation of $\ln \tau_j T$ with $\ln \eta_i$ provides the information of the solvent environment around the solute molecules and also gives ΔH_{η_i} , the enthalpy of activation due to viscous flow of the solvent. η_i is the coefficient of viscosity of the solvent used. The estimated Debye and Kalman factors $\tau_j T / \eta$ and $\tau_j T / \eta^\delta$ confirm Debye relaxation mechanism in such p-compounds. Debye–Pellat's equations are, therefore, used to obtain static as well as infinitely hf permittivities ϵ_{0ij} and $\epsilon_{\infty ij}$ respectively to get static parameter X_{ij} where X_{ij} vs w_j equations are used to get static dipole moments μ_s 's while the slopes β 's of $\chi'_{ij} - w_j$ equations to yield hf μ_j 's in terms of estimated τ_j 's. They are, however, compared with the theoretical μ_{theo} 's from the available bond moments of the substituted flexible polar groups attached to the parent molecules to show the existence of the inductive, mesomeric and often electrometric effects in them. All these facts are given in CHAPTER 7 called "DIELECTRIC RELAXATION OF AROMATIC PARA SUBSTITUTED DERIVATIVE POLAR LIQUIDS FROM DISPERSION AND ABSORPTION PHENOMENA UNDER GHz ELECTRIC FIELD"

The CHAPTER 8 titled "STRUCTURAL AND PHYSICO-CHEMICAL PROPERTIES OF POLYSUBSTITUTED BENZENES IN BENZENE FROM RELAXATION PHENOMENA" in which a brief report on the physico-chemical properties and structural aspects of some polysubstituted benzenes in benzene

at different experimental temperatures under 10 GHz electric field is made to estimate relaxation times τ_j 's, dipole moments μ_j and thermodynamic energy parameters like enthalpy ΔH_τ , entropy ΔS_τ and free energy of activation ΔF_τ due to dielectric relaxation with formulations derived from orientational susceptibilities χ_{ij} 's. τ_j 's of the polar solutes obtained from the slope of the linear equation of χ''_{ij} and χ'_{ij} are, however, compared with those obtained from the ratio of the linear coefficients of individual variations of χ''_{ij} and χ'_{ij} with weight fractions w_j 's of the solute. τ_j 's from the later method are used to get thermodynamic energy parameters from the Eyring's rate process equation to shed more light on the physico-chemical properties of the polar liquid molecules concerned. The estimated μ_j 's in terms of linear coefficients β 's of $\chi'_{ij} - w_j$ curves and dimensionless parameters b 's involved with measured τ_j 's are finally compared with theoretical dipole moments μ_{theo} 's obtained from vector addition of available bond angles and bond moments of substituted polar groups. The estimated μ_{theo} gives valuable information regarding structures of the molecules. The slight disagreement between high frequency μ_j 's and μ_{theo} 's provides an interesting insight on the inductive, mesomeric and electromeric effects of the substituted polar groups attached to the parent molecules.

Finally, the CHAPTER 9 of "THE STRUCTURAL ASPECTS AND PHYSICO CHEMICAL PROPERTIES OF BINARY POLAR LIQUIDS IN NONPOLAR SOLVENT UNDER A GIGAHERTZ ELECTRIC FIELD" contains the mixtures of two polar liquids N,N-dimethylformamide DMF(j) and N,N-dimethylsulphoxide DMSO(k) in a nonpolar solvent benzene C_6H_6 (i) are studied in terms of the ternary(ijk) high frequency (hf) orientational susceptibilities χ_{ijk} 's at different experimental temperatures in $^{\circ}C$ to arrive at the structural and associational aspects of those polar liquids. The estimation of binary relaxation time τ_{jk} and dipole moment μ_{jk} and several thermodynamic energy parameters like the enthalpy of activation $(\Delta H_\tau)_{jk}$, the entropy of activation $(\Delta S_\tau)_{jk}$, the free energy of activation $(\Delta F_\tau)_{jk}$ of the binary solutes are, however, obtained in order to reach

the conclusion. The dimensionless parameter $\delta = (\Delta H_{\tau})_{jk} / \Delta H_{\eta_i}$ estimated from the slope of the linear equation of $\ln \tau_{jk} T$ against $\ln \eta_i$ where η_i is the coefficient of viscosity of the solvent used, provides one with the information of the solute-solute and solute-solvent molecular associations among the molecules concerned. Almost constant values of Debye factor $\tau_{jk} T / \eta_i$ unlike Kalman factors $\tau_{jk} T / \eta_i^{\delta}$ indicate the Debye relaxation mechanism obeyed by the solutions of binary associated molecules in C_6H_6 . The measured hf binary dipole moment μ_{jk} in terms of estimated binary relaxation time τ_{jk} are compared with the theoretical dipole moments μ_{theo} 's obtained from the bond moments of the substituent polar groups attached to the parent molecules only to support their conformations of associations. The disagreement between μ_{jk} 's and μ_{theo} 's indicates the inductive, mesomeric and electromeric effects of the substituent polar groups in addition to their H-bonding in a gigahertz electric field.

The theoretical formulations so far derived in S.I. units with internationally accepted symbols of dielectric terminologies and parameters are found out to be simple, straight forward and unique one to measure the dielectric relaxation parameters of several polar liquid molecules in non polar solvents under hf electric fields. All the curves satisfied by experimental points in many Figures of different CHAPTERS show the correctness of the theoretical formulations so far presented within the frame work of Debye-Smyth and Hill model of dielectric theories. Although, there exists different models like Kirkwood, Fröhlich and Onsagar. But they are not so simple like the new direct method so far suggested. The methods like thermally stimulated depolarization current density (TSDC) and isothermal frequency domain of AC spectroscopy (IFDS) may give a firm answer to the problem of dielectric relaxation with which the present author is involved. But the weak point of these methods are that they are comparatively very lengthy and often need tedious computer simulation technique. A sound theoretical formulations with the help of Newton – Raphson method may be developed for molecules of high molecular weights by considering their moments of inertia about the central axes. Future workers are, therefore, advised in this field of research of dielectrics and liquid crystals to deal

with this problem. Finally it can be concluded that the CHAPTERS 3,4,5,6,8 and 9 published in the reputed Indian and foreign journals establish the correctness of the present theoretical formulations to predict the physico – chemical problems of some simple polar liquid molecules in non polar solvents under high frequency electric field.

REPRINTS OF PUBLISHED PAPERS

Structural aspects and physico-chemical properties of some aromatic polar nitro compounds in solvent benzene at different temperatures under Giga Hertz electric field

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Manuscript received 14 September 2005, revised 22 March 2006, accepted 4 April 2006

Abstract : An interesting method based on complex orientational susceptibilities χ_{ij}^* to study the dielectric relaxation mechanism of some standard polar nitro compounds in nonpolar solvent benzene has been prescribed and applied successfully to arrive at their structural and physico-chemical properties. The dielectric orientational susceptibilities χ_{ij}' , the real and χ_{ij}'' , the imaginary part of χ_{ij}^* are involved with the measured relative permittivities ϵ_{ij}' and ϵ_{ij}'' of ϵ_{ij}^* of Pant *et al.* to measure the relaxation time τ_j of all the polar solutes from the ratio of the linear coefficients of individual variations of χ_{ij}'' and χ_{ij}' with weight fraction w_j 's of the respective solute. They are further compared with τ_j 's obtained from the direct slope of the linear variations of χ_{ij}'' and χ_{ij}' and Gopala Krishna's method measured by Pant *et al.* The temperature variation of τ_j 's from the former method helps one get the thermodynamic energy parameters i.e. enthalpy of activation ΔH_τ , entropy of activation ΔS_τ , and free energy of activation ΔF_τ of dielectric relaxation by using the rate process equation of Eyring *et al.*, to throw much light on their structural and physico-chemical properties. The dimensionless parameter δ ($= \Delta H_\tau / \Delta H \eta_\tau$) which is the slope of the linear equation of $\ln \tau_j T = \ln a + \delta \ln \eta_i$, where η_i is the coefficient of viscosity of the solvent, is used to get Debye and Kalman factors. They reflect the associative nature along with the applicability of Debye-Smyth model of dielectric relaxation for such polar nitro molecules. The estimated dipole moments μ_j 's in terms of linear coefficient β 's of χ_{ij}' vs w_j like $\chi_{ij}' = \alpha + \beta w_j + \gamma w_j^2$ curves and dimensionless parameters b 's involved with measured τ_j 's are finally compared with theoretical dipole moments μ_{theo} 's, obtained from available bond angles and bond moments of the substituent polar groups of the molecules as well as with μ_j 's of Gopala Krishna's method used by Pant *et al.* to shed more light on the conformations of the molecules, in addition to inductive, mesomeric and electromeric effects.

Keywords : Structural aspects, nitro compounds, Giga Hertz electric field.

The dielectric relaxation mechanism of polar liquid molecules in nonpolar solvents is of much importance as it provides an useful and essential tool to study their structural aspects and physico-chemical properties. The method is involved with estimation of several dielectric relaxation parameters such as relaxation time τ_j , dipole moments μ_j , μ_{theo} and thermodynamic energy parameters. There exists several methods^{1,2} for estimation of relaxation parameters, but all these methods are not so simple like our present one based on susceptibility measurement. Their method^{1,2} consist of placing ϵ_{ij}'' against ϵ_{ij}' measured at different frequencies of GHz range to get semicircular plot which cuts ϵ' -axis in the lower and higher points giving rise ϵ_{oi} and ϵ_{oi} respectively. Migahed *et al.*³ and Nandi *et al.*⁴ used the method of thermally stimulated depolarisation current density (TSDC) in terms of *hf* relative permittivities to study

the relaxation mechanism of some polar liquids and the physico-chemical properties of some proteins, polymers, micelles etc. Although several workers^{3,4} studied the relaxation mechanism of polar liquid molecules in nonpolar solvent in terms of measured relative permittivities of ϵ_{ij}' , the real part and ϵ_{ij}'' , the imaginary part of high frequency (*hf*) complex permittivity ϵ_{ij}^* , but no such investigation on polar nitro compounds by susceptibility measurement has yet been made. The method includes the estimation of real χ_{ij}' ($= \epsilon_{ij}' - \epsilon_{\text{oi}}$) and imaginary χ_{ij}'' ($= \epsilon_{ij}''$) parts of high frequency (*hf*) complex dimensionless dielectric orientational susceptibility χ_{ij}^* at different experimental temperatures in °C under a Giga Hertz electric field from the measured permittivities of ϵ_{ij}' and ϵ_{ij}'' of Pant *et al.*⁵. χ_{ij}^* 's are involved only with the molecular orientational polarisation and the evaluation of accurate relaxation parameters are made pos-

Table 1. Measured τ_j 's from ratio of slopes of individual variations of χ_{ij} and χ_{ij}'' with w_j , relaxation time τ_j from Murthy *et al.*, reported τ_j all are in pico second, correlation coefficient and % of error of $\chi_{ij} - w_j$ and $\chi_{ij}'' - w_j$ curves of Figs. 2 and 3, of aromatic polar nitro compounds in nonpolar solvent C_6H_6 at different experimental temperatures in $^{\circ}C$ under 9.58 GHz electric field frequency

Sl. no.	Systems	Temp. ($^{\circ}C$)	Individual slope of variation		Slope of χ_{ij}'' vs χ_{ij}' (eq. (4))	Ratio of slope of ind. variation	Correlation coeff. (<i>r</i>) of $\chi_{ij} - w_j$ and $\chi_{ij}'' - w_j$ curves	% of errors of $\chi_{ij} - w_j$ and $\chi_{ij}'' - w_j$ curves	τ_j in psec (eq. (4))	τ_j in psec (eq. (5))	Reported τ_j in psec of Pant <i>et al.</i> ⁵
			Slope of χ_{ij}' vs w_j at $w_j \rightarrow 0$	Slope of χ_{ij}'' vs w_j at $w_j \rightarrow 0$							
1.	2,5-Dichloro-nitrobenzene	20	24.73	16.36	0.66	0.68	0.98	1.04	10.98	10.98	10.01
		30	77.03	45.93	0.60	0.60	0.92	4.81	9.90	9.90	9.43
		40	78.54	46.01	0.59	0.59	0.90	5.76	9.72	9.72	6.64
2.	3,5-Dichloro-nitrobenzene	20	27.35	21.10	0.77	0.77	0.96	2.55	12.81	12.81	11.95
		30	131.44	88.76	0.68	0.68	0.91	5.05	11.21	11.21	8.20
		40	39.69	20.04	0.50	0.50	0.99	0.71	8.38	8.38	7.48
3.	2,5-Dibromo-nitrobenzene	20	91.74	135.29	1.47	1.47	0.96	2.13	24.48	24.48	21.50
		30	3.40	4.63	1.36	1.36	0.99	0.87	22.62	22.62	19.63
		40	29.92	39.28	1.31	1.31	0.98	1.15	21.79	21.79	19.19
4.	2,4-Dinitro-chlorobenzene	20	5.23	5.36	1.02	1.02	0.98	1.48	17.00	17.00	15.24
		30	25.42	23.24	0.91	0.91	0.89	6.45	15.18	15.17	14.32
		40	20.00	14.47	0.72	0.72	0.94	3.56	12.01	12.01	11.21
5.	3,4-Dinitro-chlorobenzene	20	1.29	1.37	1.06	1.06	0.97	1.78	17.60	17.60	15.83
		30	9.59	8.24	0.86	0.86	0.96	2.44	14.25	14.25	13.01
		40	0.23	0.16	0.71	0.71	0.96	2.52	11.82	11.82	10.12

Table 2. The coefficients of α , β , γ of $\chi_{ij} - w_j$ curves of Fig. 3, dimensionless parameters b 's with τ_j of eq. (8), measured dipole moment μ_j , reported dipole moment μ_j (Gopala Krishna), theoretical dipole moments μ_j in coulomb metre (C.m.) of some aromatic polar liquids in benzene at various experimental temperatures in $^{\circ}C$ under 9.58 GHz electric field frequency

Sl. no.	Systems (Molecular weight, M_j)	Temp. ($^{\circ}C$)	$\chi_{ij} = \alpha + \beta w_j + \gamma w_j^2$			Dimensionless parameter $b = 1/(1 + \omega^2 \tau_j^2)$	Measured $\mu_j \times 10^{30}$ (C.m.)	$\mu_j \times 10^{30}$ in C.m. (Pant <i>et al.</i>)	μ_j (theo.) $\times 10^{30}$ in C.m. from bond moments
			α	β	γ				
1.	2,5-Dichloro-nitrobenzene ($M_j = 0.1920$ kg)	20	-284.43	24.727	-0.35	0.696	26.18	15.19	
		30	-1223.1	77.025	-1.06	0.738	45.99	15.44	14.17
		40	-1262.6	78.537	-1.07	0.745	47.33	14.82	
2.	3,5-Dichloro-nitrobenzene ($M_j = 0.1920$ kg)	20	-404.56	27.352	-0.36	0.627	29.01	8.87	
		30	-1978.7	131.44	-1.94	0.687	62.27	16.41	14.17
		40	-448.35	39.688	-0.69	0.797	32.52	17.06	
3.	2,5-Dibromo-nitrobenzene ($M_j = 0.2810$ kg)	20	-1456.2	91.74	-1.3	0.315	90.66	34.33	
		30	203.44	3.3988	-0.13	0.350	16.97	30.99	14.17
		40	-323.28	29.92	-0.46	0.367	50.33	30.81	
4.	2,4-Dinitro-chlorobenzene ($M_j = 0.2025$ kg)	20	37.556	5.2318	-0.15	0.488	14.77	17.74	
		30	-264.67	25.42	-0.47	0.545	31.58	12.37	12.36
		40	-186.98	20.003	-0.36	0.656	26.12	12.59	
5.	3,4-Dinitro-chlorobenzene ($M_j = 0.2025$ kg)	20	191.45	1.2885	0.019	0.471	7.46	17.76	
		30	-147.89	9.5948	-0.01	0.576	18.87	12.37	25.18
		40	199.23	0.2286	0.068	0.663	2.78	14.69	

sible. It is evident from Fig. 1 that the variation of χ_{ij}'' with χ_{ij}' is strictly linear, the slope of which presented in Table 1, is used to get τ_j 's of the polar solutes. Murthy *et al.*⁶, however, showed earlier that a similar linear relationship exists between hf imaginary part $K_{ij}''(w_j)$ and real part $K_{ij}'(w_j)$ of complex conductivity $K_{ij}^*(w_j)$ from which τ_j for polar molecules could be estimated. But for associative liq-

uids in the higher concentration the variation of χ_{ij}'' and χ_{ij}' is not always linear⁷, the ratio of the linear coefficients of individual polynomial variation of both χ_{ij}' and χ_{ij}'' with weight fractions w_j 's like $\chi_{ij}' = \alpha + \beta w_j + \gamma w_j^2$ of solutions⁸ as displayed in Figs. 2 and 3, may be a better choice⁹ to estimate τ_j 's of polar liquid compounds τ_j 's so estimated, are presented in Table 1 for comparison with τ_j 's (11th col-

Table 3. The thermodynamic energy parameters : enthalpy of activation ΔH_{τ} , entropy of activation ΔS_{τ} and free energy of activation ΔF_{τ} , measured by our method (a) and measured by Pant *et al.* (b), value of δ from equation $\ln \tau_j T = \ln a + \delta \ln \eta_j$, enthalpy of activation ΔH_{η_j} due to viscous flow of solvent, Debye factor and Kalman factor of some aromatic polar liquids in benzene at various experimental temperatures in °C under 9.58 GHz electric field frequency

Sl. no.	System	Temp. (°C)	ΔH_{τ} (kJ mol ⁻¹)		ΔS_{τ} (J mol ⁻¹)		ΔF_{τ} (kJ mol ⁻¹)		Value of δ	$\Delta H_{\eta_j} = (\Delta H_{\tau}/\delta)$ (kJ mol ⁻¹)	Debye factor $(\tau_j T/\eta_j) \times 10^6$	Kalman factor $(\tau_j T/\eta_j^{\delta})$
			a	b	a	b	a	b				
			1.	2,5-Dichloro-nitrobenzene	20	2.16	13.00	-0.0277				
		30	2.16	13.00	-0.0274	0.0088	10.45	10.33	0.04	5.99	5.35	4.45×10^{-8}
		40	2.16	13.00	-0.0277	0.0101	10.83	9.84	0.36	5.99	5.82	4.63×10^{-8}
2.	3,5-Dichloro-nitrobenzene	20	13.58	15.44	0.0100	0.0169	10.65	10.49	2.10	6.46	6.08	2.09×10^{-2}
		30	13.58	15.44	0.0093	0.0181	10.77	9.97	2.10	6.46	6.05	2.30×10^{-2}
		40	13.58	15.44	0.0100	0.0169	10.45	10.15	2.10	6.46	5.02	2.07×10^{-2}
3.	2,5-Dibromo-nitrobenzene	20	1.93	1.86	-0.0352	-0.0343	12.24	11.92	0.31	6.15	11.62	7.26×10^{-8}
		30	1.93	1.86	-0.0350	-0.0341	12.54	12.18	0.31	6.15	12.22	7.15×10^{-8}
		40	1.93	1.86	-0.0352	-0.0344	12.94	12.61	0.31	6.15	13.04	7.27×10^{-8}
4.	2,4-Dinitro-chorobenzene	20	10.69	9.12	-0.0023	-0.0067	11.35	11.08	1.65	6.46	8.07	1.02×10^{-3}
		30	10.69	9.12	-0.0028	-0.0075	11.53	11.38	1.65	6.46	8.20	1.10×10^{-3}
		40	10.69	9.12	-0.0022	-0.0067	11.39	11.21	1.65	6.46	7.19	1.01×10^{-3}
5.	3,4-Dinitro-chorobenzene	20	12.67	14.50	0.0042	0.0114	11.43	11.17	2.00	6.33	8.36	1.37×10^{-2}
		30	12.67	14.50	0.0043	0.0111	11.37	11.14	2.00	6.33	7.69	1.39×10^{-2}
		40	12.67	14.50	0.0042	0.0114	11.34	10.94	2.00	6.33	7.07	1.37×10^{-2}

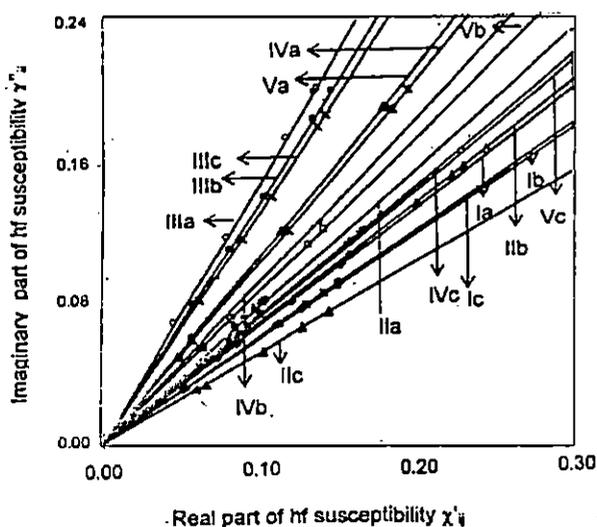


Fig. 1. Variation of imaginary part χ''_{ij} of hf orientational susceptibility against real part χ'_{ij} of hf orientation susceptibility of some polar nitro compounds in nonpolar solvent benzene at different temperatures in °C under 9.5846 GHz electric field frequency of 2,5-dichloronitrobenzene [Ia at 20 °C (◇), Ib at 30 °C (◆), Ic at 40 °C (□)], 3,5-dichloronitrobenzene [IIa at 20 °C (■), IIb at 30 °C (Δ), IIc at 40 °C (▲)], 2,5-dibromonitrobenzene [IIIa at 20 °C (○), IIIb at 30 °C (●), IIIc at 40 °C (×)], 2,4-dinitrochlorobenzene [IVa at 20 °C (*), IVb at 30 °C (-), IVc at 40 °C (+)], 3,4-dinitrochlorobenzene [Va at 20 °C (Δ), Vb at 30 °C (□), Vc at 40 °C (○)].

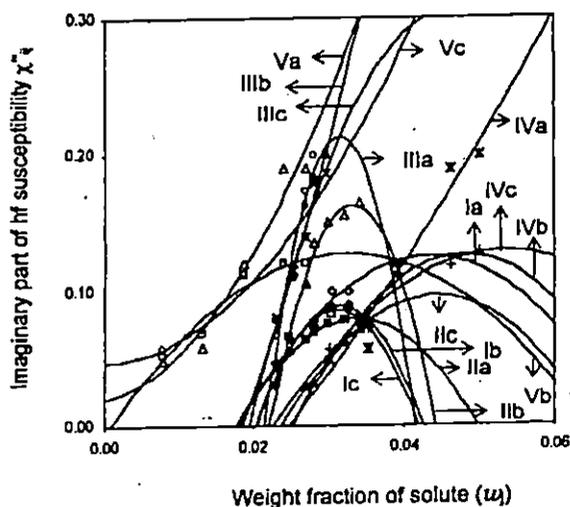


Fig. 2. Variation of imaginary part χ''_{ij} of hf orientational susceptibility against weight fraction w_j of some polar nitro compounds in nonpolar solvent benzene at different temperatures in °C under 9.5846 GHz electric field frequency of 2,5-dichloronitrobenzene [Ia at 20 °C (◇), Ib at 30 °C (◆), Ic at 40 °C (□)], 3,5-dichloronitrobenzene [IIa at 20 °C (■), IIb at 30 °C (Δ), IIc at 40 °C (▲)], 2,5-dibromonitrobenzene [IIIa at 20 °C (○), IIIb at 30 °C (●), IIIc at 40 °C (×)], 2,4-dinitrochlorobenzene [IVa at 20 °C (*), IVb at 30 °C (-), IVc at 40 °C (+)], 3,4-dinitrochlorobenzene [Va at 20 °C (Δ), Vb at 30 °C (□), Vc at 40 °C (○)].

umn) calculated by Pant *et al.*⁵ by using Gopala Krishna's method¹⁰. The excellent agreement of τ_j 's by both of our

prescribed methods in case of polar nitro compounds which includes the names of 2,5-dichloronitrobenzene, 3,5-dichloronitrobenzene, 2,5-dibromonitrobenzene, 2,4-dinitro-

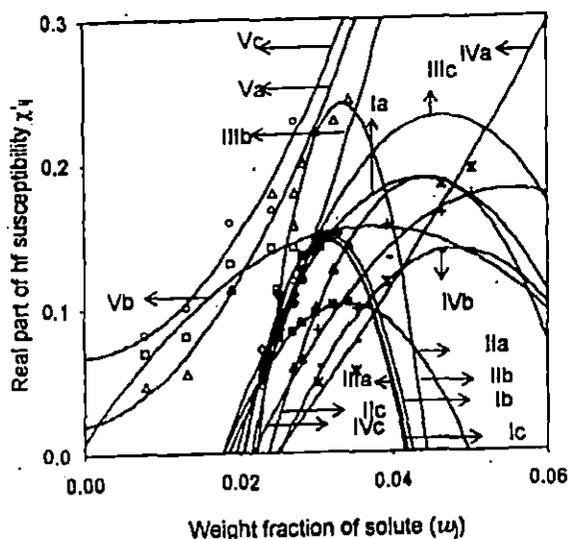


Fig. 3. Variation of real part χ'_{ij} of *hf* orientational susceptibility against weight fraction w_j of some polar nitro compounds in nonpolar solvent benzene at different temperatures in $^{\circ}\text{C}$ under 9.5846 GHz electric field frequency of 2,5-dichloronitrobenzene [Ia at 20 $^{\circ}\text{C}$ (○), Ib at 30 $^{\circ}\text{C}$ (◊), Ic at 40 $^{\circ}\text{C}$ (◻)], 3,5-dichloronitrobenzene [IIa at 20 $^{\circ}\text{C}$ (■), IIb at 30 $^{\circ}\text{C}$ (Δ), IIc at 40 $^{\circ}\text{C}$ (▲)], 2,5-dibromonitrobenzene [IIIa at 20 $^{\circ}\text{C}$ (○), IIIb at 30 $^{\circ}\text{C}$ (◊), IIIc at 40 $^{\circ}\text{C}$ (×)], 2,4-dinitrochlorobenzene [IVa at 20 $^{\circ}\text{C}$ (*), IVb at 30 $^{\circ}\text{C}$ (-), IVc at 40 $^{\circ}\text{C}$ (+)], 3,4-dinitrochlorobenzene [Va at 20 $^{\circ}\text{C}$ (Δ), Vb at 30 $^{\circ}\text{C}$ (◻), Vc at 40 $^{\circ}\text{C}$ (○)].

chlorobenzene. 3,4-dinitrochlorobenzene indicates that the data of $\chi''_{ij}(w_j)$ and $\chi'_{ij}(w_j)$ are of low weight fractions w_j 's so that the polar-polar interactions are almost eliminated. The estimated τ_j 's involved with dimensionless parameter b 's are now used to obtain *hf* dipole moment μ_j in terms of linear coefficients β 's of curves of $\chi'_{ij} - w_j$ of Fig. 2 using Debye's relation¹¹. The dimensionless parameter b 's, linear coefficients β 's and estimated μ_j 's are placed in Table 2 to compare with μ_j 's by Gopala Krishna's method¹⁰ measured by Pant *et al.*⁵ and theoretical dipole moments μ_{theo} 's of Fig. 4, evaluated by vector addition of available bond moments of the substituent polar groups of the nitro compounds as seen in Table 2. The disagreement between estimated μ_j and μ_{theo} shows the probable existence of inductive, mesomeric and electromeric effects¹² suffered by the polar groups under the electric field of GHz frequency. μ_j 's thus measured when plotted against t $^{\circ}\text{C}$ shows convex and concave shapes as seen in Fig. 5, which reflects the stability or instability of the polar-nonpolar liquid mixtures observed elsewhere¹³. The eq. (10) is a linear equation in $\tau_j T$ against $1/T$ of Fig. 6. The slope and intercept are used to measure the required thermodynamic energy parameters. ΔH_{τ} , ΔS_{τ} and ΔF_{τ} as placed in Table 3. The parameters so estimated provides a deep insight into the physico-chemical properties¹⁴ of the solute molecules in solvent benzene under GHz electric field. The Debye and Kalman factors as seen in Table 3 shows Debye relaxation mechanism obeyed by the molecules.

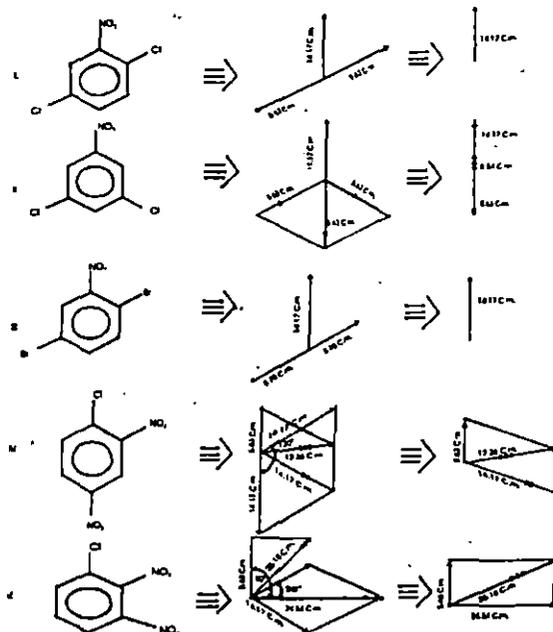


Fig. 4. Theoretical dipole moment μ_{theo} ($\times 10^{30}$) in coulomb metre (C.m.) from available bond angle and bond moments of (I) 2,5-dichloronitrobenzene, (II) 3,5-dichloronitrobenzene, (III) 2,5-dibromonitrobenzene, (IV) 2,4-dinitrochlorobenzene, (V) 3,4-dinitrochlorobenzene.

Theoretical formulations :

If $\epsilon_{\alpha ij}$ be subtracted from ϵ'_{ij} , the susceptibility contains only the orientational polarisation¹⁵ and thus the fast polarisation is avoided unlike the ϵ_{ij}^* . In absence of reliable measured values of infinitely *hf* and low frequency (*lf*) permittivities $\epsilon_{\alpha ij}$ and ϵ_{Oij} , the following Debye-Pallate's equations¹⁶ may safely be used from the measured values of the real ϵ'_{ij} and imaginary ϵ''_{ij} parts of the *hf* complex ϵ_{ij}^* of Pant *et al.*⁵

$$\epsilon'_{ij} = \epsilon_{\alpha ij} + \frac{\epsilon_{\text{Oij}} - \epsilon_{\alpha ij}}{1 + \omega^2 \tau_j^2} \quad (1)$$

and

$$\epsilon''_{ij} = \frac{\epsilon_{\text{Oij}} - \epsilon_{\alpha ij}}{1 + \omega^2 \tau_j^2} \omega \tau_j \quad (2)$$

χ''_{ij} and χ'_{ij} 's of functions of w_j 's are well displayed in Figs. 3 and 2 respectively. Both ϵ'_{ij} and ϵ''_{ij} parts of ϵ_{ij}^* are related by¹¹

$$\epsilon'_{ij} = \epsilon_{\alpha ij} + \frac{1}{\omega \tau_j} \epsilon''_{ij} \quad (3)$$

In terms of real χ'_{ij} and imaginary χ''_{ij} parts of *hf* complex susceptibility χ_{ij}^* , one obtains

$$\chi''_{ij} = (\omega \tau_j) \chi'_{ij} \text{ or } d\chi''_{ij} / d\chi'_{ij} = \omega \tau_j \quad (4)$$

Murthy *et al.*⁶ showed earlier that a similar linear relationship exists between *hf* conductivity $K''_{ij}(w_j)$ and $K'_{ij}(w_j)$ from

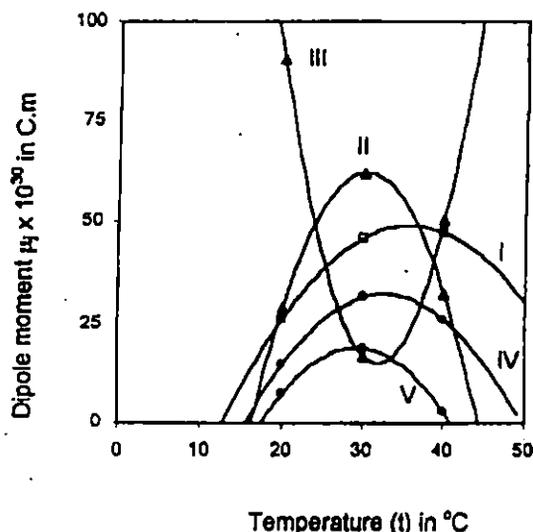


Fig. 5. Variation of dipole moment μ_j against temperature t in $^{\circ}\text{C}$ of some polar nitro compounds in nonpolar solvent benzene under 9.5846 GHz electric field frequency of (I) 2,5-dichloronitrobenzene (\square), (II) 3,5-dichloronitrobenzene (Δ), (III) 2,5-dibromonitrobenzene (\blacktriangle), (IV) 2,4-dinitrochlorobenzene (\circ), (V) 3,4-dinitrochlorobenzene (\bullet).

which they estimated the relaxation time for polar molecules. The eqs. (4) is a straight line between χ''_{ij} and χ'_{ij} observed graphically in Fig. 1, the slope of which is used to get τ_j of a polar solute⁶ as seen in Table 1. But for most of the associative liquids, the variation of χ''_{ij} against χ'_{ij} is not strictly linear⁹. For such associative polar-nonpolar liquid mixture χ'_{ij} is related with w_j by $\chi'_{ij} = \alpha + \beta w_j + \gamma w_j^2$ the slope of eq. (4) can be represented by :

$$\frac{(d\chi''_{ij}/dw_j)_{w_j \rightarrow 0}}{(d\chi'_{ij}/dw_j)_{w_j \rightarrow 0}} = \omega\tau_j \quad (5)$$

The eq. (5) represents the ratio of linear coefficients of individual variation of both χ''_{ij} and χ'_{ij} with w_j of a polar solute displayed graphically in Figs. 2 and 3 respectively, τ_j 's estimated from eq. (5) are placed in Table 1 in order to compare them with τ_j 's obtained by direct slope $\chi''_{ij} - \chi'_{ij}$ of Fig. 1 and those of Gopala Krishna's method¹⁰ measured by Pant *et al.*⁵.

The imaginary part χ''_{ij} of $hf \chi_{ij}^*$ is related to w_j of polar solute by¹¹

$$\chi''_{ij} = \frac{N\rho_{ij}\mu_j^2}{27\epsilon_0 M_j k_B T} \left(\frac{\omega\tau_j}{1 + \omega^2\tau_j^2} \right) (\epsilon_{ij} + 2)^2 w_j \quad (6)$$

which on differentiation with respect to w_j and in the limit of $w_j = 0$ yields that

$$\left(\frac{d\chi''_{ij}}{dw_j} \right)_{w_j=0} = \frac{N\rho_{ij}\mu_j^2}{27\epsilon_0 M_j k_B T} \left(\frac{\omega\tau_j}{1 + \omega^2\tau_j^2} \right) (\epsilon_{ij} + 2)^2 \quad (7)$$

From eqs. (5) and (7) one obtains $hf \mu_j$ by

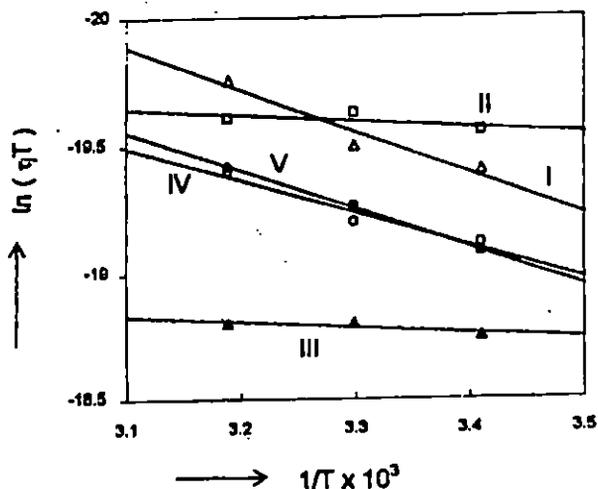


Fig. 6. Variation of $\ln(\tau_j T)$ against $1/T$ of some polar nitro compounds in nonpolar solvent benzene under 9.5846 GHz electric field frequency of (I) 2,5-dichloronitrobenzene (\square), (II) 3,5-dichloronitrobenzene (Δ), (III) 2,5-dibromonitrobenzene (\blacktriangle), (IV) 2,4-dinitrochlorobenzene (\circ), (V) 3,4-dinitrochlorobenzene (\bullet).

$$\mu_j = \left[\frac{27\epsilon_0 M_j k_B T \beta}{N\rho_{ij} (\epsilon_{ij} + 2)^2 b} \right]^{1/2} \quad (8)$$

M_j = Molecular weight of j -th liquid in Kilogram, ϵ_0 = permittivity of free space = 8.854×10^{-12} Farad metre⁻¹, k_B = Boltzmann constant = 1.38×10^{-23} J mol⁻¹ K⁻¹, T = temperature in absolute scale, $\beta = (d\chi''_{ij}/dw_j)_{w_j \rightarrow 0}$ = linear coefficient of $\chi''_{ij} - w_j$ curves of Fig. 3 at $w_j \rightarrow 0$, N = Avogadro's number = 6.023×10^{23} , ρ_{ij} = density of solvent C_6H_6 , ϵ_{ij} = dielectric relative permittivity of solvent C_6H_6 , $b = 1/(1 + \omega^2\tau_j^2)$, a dimensionless parameter involved with the estimated τ_j of eq. (5).

Dielectric relaxation is a process of rotation of the polar molecules under hf electric field and it requires an activation energy ΔF_{τ} , known as free energy of activation to overcome the energy barrier between two equilibrium positions. ΔF_{τ} is, however, related with estimated τ_j of eq. (5) by the relation¹⁴.

$$\tau_j = \frac{A}{T} \exp(\Delta F_{\tau}/RT) \quad (9)$$

As $\Delta F_{\tau} = \Delta H_{\tau} - T\Delta S_{\tau}$, so we have

$$\text{or, } \ln(\tau_j T) = \ln A' + \frac{\Delta H_{\tau}}{R} \frac{1}{T} \quad (10)$$

$$\text{where } A' = A e^{(-\Delta S_{\tau}/R)} \quad (11)$$

The eq. (10) is a linear equation of $\ln \tau_j T$ against $1/T$ of Fig. 6. The slope and intercept are used to measure the required thermodynamic energy parameters of the molecules as presented in Table 3 in agreement with those of Pant *et al.*⁵.

Results and discussion

The τ_j 's of aromatic polar nitro compounds in solvent C_6H_6 at different experimental temperatures in $^\circ C$ under 9.58 Giga Hertz electric field are worked out from the slope of the fitted linear eq. (4) between the variables χ_{ij}'' and χ_{ij}' displayed graphically in Fig. 1 with the symbols showing the experimental points. τ_j 's so obtained are compared with τ_j 's estimated from the ratio of linear coefficients of individual variations of both χ_{ij}'' and χ_{ij}' with w_j 's shown graphically in Figs. 2 and 3. τ_j 's estimated by both the method are presented in Table 1. The excellent agreement of τ_j 's by both the methods at once indicates the data χ_{ij}'' and χ_{ij}' are of low concentrations such that the polar-polar interactions are almost eliminated⁹ at $w_j \rightarrow 0$. The τ_j 's by the latter method²¹ are more reliable. Gopala Krishna's method¹⁰ was employed by Pant *et al.*⁵ to get τ_j 's. They are presented in Table 1. The close agreement between τ_j 's of Pant *et al.*⁵ and estimated τ_j 's of eqs. (4) and (5) at once reflects the basic soundness of our method to get τ_j in the limit $w_j = 0$. The correlation coefficient and % of error of both $\chi_{ij}'' - w_j$ and $\chi_{ij}' - w_j$ curves of Figs. 2 and 3 are given in Table 1 only to show how far they are correlated with w_j 's. It is evident from Table 1 that τ_j 's decrease with temperature. This can be explained on the basis of the fact that at constant temperature, the relaxation time depends upon the energy difference between the activated and normal states. At higher temperature thermal agitation causes an increase in energy loss due to large number of collisions and thereby decreasing the relaxation time^{9,16}. Dipole moments μ_j 's of the polar solutes as estimated from eq. (8) are placed in Table 2 together with linear coefficients β 's of $\chi_{ij}' - w_j$ curves of Fig. 2 and dimensionless parameter b 's involved with τ_j of eq. (5) as seen in Table 2 respectively. They are, however, compared with μ_j 's of Pant *et al.*⁵ and theoretical μ_{theo} 's obtained from vector addition of bond moments¹⁷ of the substituted polar groups of the compounds, as seen in the Table 2. The theoretical dipole moment and its orientation as a consequence of known structure of the pertinent nitro-compound is displayed in Fig. 4. The resonance effect thus obtained by solvent benzene compound into an inductive effect-operated by the substituent polar groups in the ring is expected to play a prominent role¹⁸ in the measured $hf\mu_j$'s. The disagreement between $hf\mu_j$'s and μ_{theo} 's is explained by the influence of hf electric field coupled with inductive and mesomeric moments on the flexible polar groups. μ_{theo} 's with reference to Fig. 4 gives a deep insight into the structures of the molecules concerned.

The symmetry and asymmetry of the molecules being a physico-chemical property can well be explained on the basis of $\mu_j - t$ curves of Fig. 5. It is seen that unlike system III all the systems show convex $\mu_j - t$ curves having minimum μ_j 's at lower and higher temperatures due to strong symmetry attained⁸ at those temperatures. The system III shows maximum μ_j 's at lower and higher temperature due to asymmetric shape of the molecule. Physico-chemical properties of the systems can also be explained from the stand point of thermodynamics by estimating the energy parameters ΔH_τ , ΔS_τ and ΔF_τ from the intercept and slope of a fitted linear equation of $\ln \tau_j T$ against $1/T$ shown graphically in Fig. 6 with the experimental points placed on them. They are placed in Table 3 together with those estimated by Pant *et al.*⁵ by using Gopala Krishna's method¹⁰. It is seen that except the first one the other systems are close to each other. Unlike systems II and V all the systems possess negative ΔS_τ 's which suggests that configuration involved in dipolar rotation has an activated state which is more ordered than the normal state^{8,19} while the reverse is true for the rest two systems. ΔF_τ 's for all the systems are nearly same in magnitude, as the activation is accomplished by the rupture of bond of dipolar groups in the same degrees of freedom^{7,19}. Unlike 2,5-dichloronitrobenzene and 2,5-dibromonitrobenzene all the systems possess $\delta > 0.50$ as seen in Table 3 indicating solvent environment around the solute molecules¹⁵. Moreover, they show higher ΔH_{η_i} 's than that ΔH_τ 's as seen in Table 3. It is due to the fact that ΔH_{η_i} is involved with both transitional and rotational motion of the molecules. Other systems possess lower values than that of ΔH_τ for high value of δ for those systems. Debye factor $\tau_j T / \eta$ and Kalman factor $\tau_j T / \eta^6$, being proportional to volume of the rotating unit are carefully estimated and are placed in Table 3. Debye factors are all of the order of 10^6 and Kalman factors although of different orders but found to have constant values for all systems at each temperature, indicating at once the validity of Debye model of dielectric relaxation mechanism for such aromatic polar nitro compounds in C_6H_6 under GHz electric field^{9,13}.

Conclusion :

Our group²¹ have developed a new method based on the complex susceptibility χ_{ij}^* in the limit $w_j=0$ to study the structural aspects and physico-chemical properties of the polar nitro liquid compounds 2,5-dichloronitrobenzene, 3,5-dichloronitrobenzene, 2,5-dibromonitrobenzene, 2,4-dinitrochlorobenzene and 3,4-dinitrochlorobenzene in C_6H_6 under GHz electric field at different experimental temperatures. The excellent agreement of τ_j 's estimated by our methods of eqs. (4) and (5) at once establishes the ap-

plicability of the method suggested to get τ_j 's at $w_j \rightarrow 0$ as it eliminates polar-polar interaction²¹ in a given solution. The correlation coefficients r 's and % of errors obtained by careful regression analysis between variables of curves of Figs. 2 and 3 show how far the variables χ''_{ij} and χ'_{ij} are correlated with w_j 's to establish the statistical validity¹⁵ of eq. (5). The thermodynamic energy parameters such as ΔH_τ , ΔS_τ and ΔF_τ worked out in terms of temperature variation of τ_j 's are useful and important tools to comment on the physico-chemical properties of dipolar liquid molecules. The theoretical dipole moment μ_{theo} 's and its comparison with measured $hf \mu_j$'s of the eq. (8) explore new concept regarding structures of the molecules in addition to inductive, mesomeric and electromeric effects present in them. Almost the constant values of Debye and Kalman factors and the curves satisfied by experimental points in all the figures reflect the validity of the theoretical formulations within the framework of Debye-Smyth model of dielectric relaxation. The significant contribution to study the structural aspects and physico-chemical properties of the polar liquid molecules as sketched in Fig. 4 in nonpolar solvent under nearly 10 GHz electric field are thus found to be important to enhance scientific content of the existing knowledge of dielectric relaxation processes.

References

1. K. S. Cole and R. H. Cole, *J. Chem. Phys.*, 1941, 9, 341.
2. E. A. Guggenheim, *Trans. Faraday Soc.*, 1949, 45, 714.
3. M. D. Migahed, M. T. Ahmed and A. E. Kolp, *J. Phys. D: Appl. Phys. (UK)*, 2000, 33, 2108.
4. N. Nandi, K. Bhattacharyya and B. Bagechi, *Chem. Rev.*, 2000, 100, 2013.
5. D. C. Pant, S. K. S. Somevanshi, N. K. Mehrotra and N. C. Saxena, *Indian J. Phys.*, 1977, 51, 305.
6. M. B. R. Murthy, R. L. Patil and D. K. Deshpande, *Indian J. Phys.*, 1989, 63B, 491.
7. U. K. Mitra, N. Ghosh, P. Ghosh and S. Acharyya, *Indian J. Chem., Sect. A*, 2005.
8. N. Ghosh, R. C. Basak, S. K. Sit and S. Acharyya, *J. Molecular Liquids*, 2000, 85, 375.
9. A. Karnakar, U. K. Mitra, N. Ghosh and S. Acharyya, *J. Phys. D: Appl. Phys. (UK)*, 2005.
10. K. V. Gopala Krishna, *Trans. Faraday Soc.*, 1957, 53, 767.
11. C. P. Smyth, "Dielectric Behaviour and Structure", Mc-Graw Hill, New York, 1955.
12. S. K. Sit, PhD Dissertation, North Bengal University, India, 1997.
13. N. Paul, K. P. Sharma and S. Chattopadhyay, *Indian J. Phys.*, 1997, 71B, 711.
14. H. Eyring, S. Glasstone and K. J. Laidler, "The Theory of Rate Process", Mc-Graw Hill, New York, 1941.
15. U. K. Mitra, N. Ghosh, P. Ghosh and S. Acharyya, *J. Molecular Liquids*, 2005.
16. N. E. Hill, W. E. Vaughan, A. H. Price and M. Davies, "Dielectric Properties and Molecular Behaviour", Van Nostrand Reinhold Co., London, 1969.
17. M. V. George, J. Mohanty, P. T. Narasimhan and C. N. R. Rao, "A Hand Book of Chemistry and Physics," Affiliated East-West Press Pvt. Ltd., New Delhi, 1967, p. 253.
18. N. Ghosh, A. Karnakar, S. K. Sit and S. Acharyya, *Indian J. Pure Appl. Phys.*, 2000, 38, 574.
19. R. L. Dhar, A. Mathur, J. P. Shukla and M. C. Saxena, *Indian J. Pure Appl. Phys.*, 1973, 11, 568.
20. A. K. Sharma and D. R. Sharma, *J. Phys. Soc. Jpn.*, 1992, 61, 1049.
21. N. Ghosh, S. K. Sit, A. K. Bothra and S. Acharyya, *J. Phys. D: Appl. Phys. (UK)*, 2001, 34, 379.

Dielectric relaxation phenomena of some aprotic polar liquids under giga hertz electric field

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Received 17 October 2005; revised 27 June 2006; accepted 5 July 2006

The two relaxation times τ_1 and τ_2 due to rotations of the flexible parts and the whole molecules of some aprotic polar liquids (j) like N, N-dimethyl sulphoxide (DMSO); N, N-dimethyl formamide (DMF), N, N-dimethyl acetamide (DMA) and N, N-diethyl formamide (DEF) in benzene (i) are estimated from the measured real χ_{ij}' and imaginary χ_{ij}'' part of *hf* complex dielectric orientational susceptibility χ_{ij}^* and low frequency susceptibility χ_{oij} at different weight fractions w_j 's of solute at various experimental temperatures [Saha *et al.*, *J Phys. D: Appl Phys*, 27 (1994) 596]. The relative contributions c_1 and c_2 due to τ_1 and τ_2 are calculated from Fröhlich's equations and graphical technique. All the c 's are positive from Fröhlich's equations while some c_2 's are negative from graphical method. The dipole moments μ_2 and μ_1 in Coulomb-metre (C.m) measured from the slope β 's of $\chi_{ij}'-w_j$ curves are compared with those of conductivity σ_{ij} measurements using τ 's from the ratio of individual slope of $(d\chi_{ij}''/dw_j)_{w_j \rightarrow 0}$ and $(d\chi_{ij}'/dw_j)_{w_j \rightarrow 0}$, linear slope of $\chi_{ij}^*-\chi_{ij}'$ along with Gopalakrishna's method [Trans Faraday Soc, 53 (1957) 767]. The estimated μ_1 's agree with the measured and reported μ 's to indicate that the flexible part of the molecule is rotating under GHz electric field. The theoretical dipole moment μ_{theo} 's are obtained in terms of available bond moments of the substituent polar groups attached to the parent molecules acting as pusher or puller of electrons due to inductive, mesomeric and electromeric effects in them under *hf* electric field. The variation of μ_1 with temperature suggests the elongation of bond moments. The energy parameters such as enthalpy of activation ΔH_a , free energy of activation ΔF_a and entropy of activation ΔS_a 's are obtained for DMSO only assuming dielectric relaxation as a rate process to know the molecular dynamics. The variation of $\ln(\tau_1 T)$ against $1/T$ of DMSO reveals that it obeys Eyring rate theory unlike $\ln(\tau_2 T)$ against $1/T$ curve.

Keywords: Dielectric relaxation, Aprotic polar liquids, Dipole moment

IPC Code: G01R27/26

1 Introduction

The relaxation behaviour of polar-nonpolar liquid mixtures under high frequency (*hf*) electric field is of much importance to study the molecular shapes, sizes as well as associational behaviour¹⁻³ in them. Researchers in this field usually analyse the experimental data obtained through relaxation mechanisms involved on the basis of various models⁴⁻⁶ applicable to polar liquids. Dhull *et al.*⁷ and Sharma and Sharma⁸ had, however, measured the real ϵ_{ijk}' , ϵ_{ij}' or ϵ_{ik}' and imaginary ϵ_{ijk}'' , ϵ_{ij}'' or ϵ_{ik}'' parts of relative complex permittivities ϵ_{ijk}^* , ϵ_{ij}^* or ϵ_{ik}^* of some interesting binary or single polar liquids (jk, j or k) in a non-polar solvent under X-band electric field at different or fixed temperatures. The purpose of the work was to detect monomer (solute-solvent) or dimer (solute-solute) molecular associations and molecular dynamics of the systems in terms of estimated relaxation time τ_j and dipole moment μ_j .

The measured⁹ values of the relative permittivities ϵ_{ij} 's of some aprotic polar liquids like N, N-dimethyl sulphoxide (DMSO); N, N-dimethyl formamide (DMF); N, N-dimethyl acetamide (DMA) and N, N-diethyl formamide (DEF) in benzene under the most effective dispersive region of nearly 10 GHz electric field at 25, 30, 35 and 40°C for DMSO; 25°C for DMA and DMF and 30°C for DEF respectively. DMSO is a aprotic dipolar liquid of high penetrating power and wide applications in medicine and industry. It acts as good constituent of binary mixtures because of its associative¹⁰ nature. Amides, on the other hand, are the building blocks of proteins and enzymes and have wide biological applications. The liquids usually show two relaxation times τ_2 and τ_1 , for the rotation of the whole molecules and the flexible parts attached to the parent molecules from the single frequency measurement technique^{11,12}.

All these facts inspired us to study τ_2 and τ_1 and dipole moments μ_2 and μ_1 of these liquids in terms of real χ_{ij}' ($=\epsilon_{ij}' - \epsilon_{\infty ij}$) and imaginary χ_{ij}'' ($=\epsilon_{ij}''$) parts of complex orientational susceptibility χ_{ij}^* ($=\epsilon_{ij}^* - \epsilon_{\infty ij}$) in benzene at different temperatures. The low frequency susceptibility χ_{oij} ($=\epsilon_{oij} - \epsilon_{\infty ij}$) is, however, real. χ_{ij}' can be obtained by subtracting either 1 or $\epsilon_{\infty ij}$ from the measured ϵ_{ij} 's. If 1 is subtracted from the relative permittivity ϵ_{ij}' and ϵ_{oij} one gets χ_{ij}' and χ_{oij} containing all types of polarisation processes including fast polarisations. When high frequency relative permittivity or the optical permittivity $\epsilon_{\infty ij}$ be subtracted from ϵ_{ij}' and ϵ_{oij} of the solution at a certain weight fraction w_j 's of the solute the susceptibility χ_{ij}' , χ_{ij}'' and χ_{oij} result due to orientational polarisation only. Our earlier study⁹ was to calculate τ 's and μ 's in terms of either relative permittivities ϵ_{ij} 's or hf conductivities σ_{ij} 's. ϵ_{ij} 's are involved with all types of polarisations while σ_{ij} 's are related only to bound molecular charges of polar liquids. Now-a-days relaxation mechanisms are studied in terms¹³ of χ_{ij} 's because measurements of μ 's in terms of ϵ_{ij} 's or σ_{ij} 's include contributions due to all types of polarisations and bound molecular charges, respectively. Moreover, relaxation processes are highly thermally activated to yield τ within the framework of Debye-Smith model of polar-nonpolar liquid mixture.

The purpose of the present work is to assess the contribution of fast polarisation and bound molecular charges in the measurement of μ 's when compared with μ 's from χ_{ij} and σ_{ij} measurements. The variation of μ 's with temperature provides knowledge of the state of the system through the measured energy parameters.

The detailed experimental technique involved in the measurement of dielectric relaxation parameters of solution has been described elsewhere¹⁴. A Hewlett Packard Impedance Analyser (HP-4192A) measured the capacitance and conductance of the cell containing polar-nonpolar liquid mixtures at different frequencies and temperatures for a fixed w_j of solute. The real and imaginary parts of relative permittivities ϵ_{ij}^* or susceptibility χ_{ij}^* are obtained from complex impedances of the cell measured within the range of frequencies from 5 Hz to 13 MHz. The measured ϵ_{ij} 's are then plotted in a Cole-Cole semicircular arc to get the values of ϵ_{ij}' , ϵ_{ij}'' , ϵ_{oij} and $\epsilon_{\infty ij}$ at nearly 10 GHz electric field (Table 1). Again ϵ_{oij} is measured at 1 kHz whereas high frequency permittivity $\epsilon_{\infty ij}$ ($=n_{Dij}^2$) is

measured by Abbe's refractometer to compare the values obtained from Cole-Cole plot. The cell containing experimental liquid mixture is then kept in Mettler Hot Stage FP-52 chamber to regulate temperature. Multiply distilled C_6H_6 is used as a solvent in measurement after several times fractional distillation to get the purest quality of sample. The measured data ϵ_{ij}' or χ_{ij}' 's are accurate within $\pm 5\%$.

Bergmann *et al.*¹⁵, however, proposed a graphical technique to get τ_1 , τ_2 and c_1 , c_2 for a pure polar liquid at different frequencies of the microwave electric field. In order to avoid clumsiness of algebra and fast polarisation processes, the molecular orientational polarisations in terms of established symbols of χ_{ij}' 's can be written as⁵

$$\frac{\chi_{ij}'}{\chi_{oij}} = \frac{c_1}{1 + \omega^2 \tau_1^2} + \frac{c_2}{1 + \omega^2 \tau_2^2} \quad \dots (1)$$

$$\frac{\chi_{ij}''}{\chi_{oij}} = c_1 \frac{\omega \tau_1}{1 + \omega^2 \tau_1^2} + c_2 \frac{\omega \tau_2}{1 + \omega^2 \tau_2^2} \quad \dots (2)$$

assuming two separate broad Debye type dispersions of which $c_1 + c_2 = 1$.

Saha *et al.*¹¹ and Sit *et al.*¹² put forward an analytical technique to measure τ_1 , τ_2 and c_1 , c_2 of a polar-nonpolar liquid mixture in terms of measured χ_{ij}' , χ_{ij}'' , χ_{oij} at different w_j 's of solute under a single frequency electric field and temperature. Eqs (1) and (2) are solved to get:

$$\frac{\chi_{oij} - \chi_{ij}'}{\chi_{ij}'} = \omega(\tau_1 + \tau_2) \frac{\chi_{ij}''}{\chi_{ij}'} - \omega^2 \tau_1 \tau_2 \quad \dots (3)$$

Eq. (3) gives a straight line when $(\chi_{oij} - \chi_{ij}')/\chi_{ij}'$ is plotted against χ_{ij}''/χ_{ij}' for different w_j 's of solute for a given angular frequency ω ($=2\pi f$), f being the frequency of the applied electric field. The slope $\omega(\tau_1 + \tau_2)$ and intercept $-\omega^2 \tau_1 \tau_2$ of straight line of Eq. (3) are obtained through linear regression analysis as shown in Fig. 1. Relaxation times τ_2 and τ_1 are calculated from the slopes and intercepts of Eq. (3) of Fig. 1 in terms of measured data of Table 1. They are then compared with measured τ_j 's from the linear slope of the χ_{ij}'' against χ_{ij}' curve of Fig. 2 at different w_j 's of the form:

$$\frac{d\chi_{ij}''}{d\chi_{ij}'} = \omega \tau \quad \dots (4)$$

Both χ_{ij}'' and χ_{ij}' are functions of w_j 's of solute. It is better to use the individual slopes $\chi_{ij}''-w_j$ and $\chi_{ij}'-w_j$

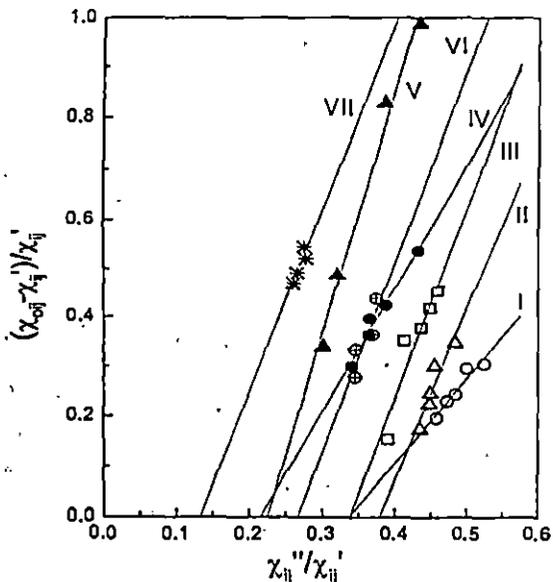


Fig. 1—Linear plot of $(\chi'_{oij} - \chi'_{ij})/\chi'_{oij}$ against χ''_{ij}/χ'_{ij} for different w_j 's of DMSO, DEF, DMF and DMA in benzene (I) DMSO at 25°C (-o-), (II) DMSO at 30°C (-Δ-), (III) DMSO at 35°C (-□-), (IV) DMSO at 40°C (-●-), (V) DEF at 30°C (-▲-), (VI) DMF at 25°C (-⊕-) and (VII) DMA at 25°C (-*-)

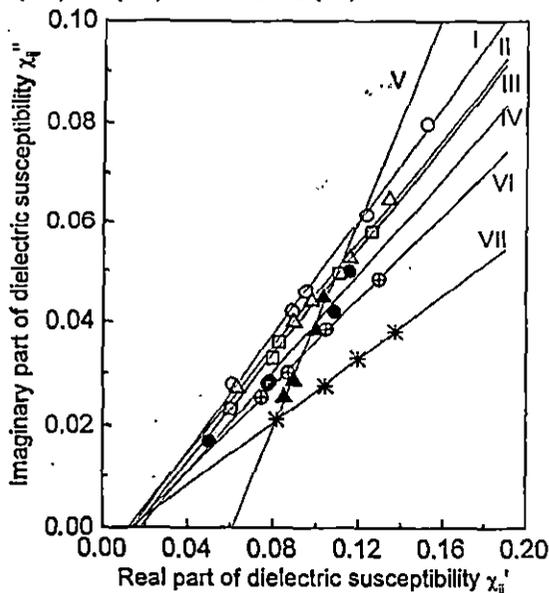


Fig. 2—Linear variation of imaginary part of dielectric susceptibility χ''_{ij} against real part of dielectric susceptibility χ'_{ij} for different w_j 's of DMSO, DEF, DMF and DMA in benzene (I) DMSO at 25°C (-o-), (II) DMSO at 30°C (-Δ-), (III) DMSO at 35°C (-□-), (IV) DMSO at 40°C (-●-), (V) DEF at 30°C (-▲-), (VI) DMF at 25°C (-⊕-) and (VII) DMA at 25°C (-*-)

curves in Figs 3 and 4 at $w_j \rightarrow 0$ to measure τ using the following equation:

$$\frac{(d\chi''_{ij}/dw_j)_{w_j \rightarrow 0}}{(d\chi'_{ij}/dw_j)_{w_j \rightarrow 0}} = \omega\tau \quad \dots (5)$$

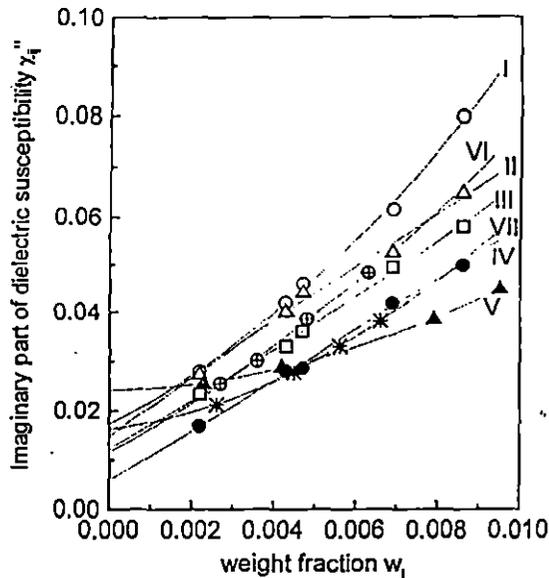


Fig. 3—Plot of imaginary part of dielectric susceptibility χ''_{ij} with weight fraction w_j of DMSO, DEF, DMF and DMA in benzene (I) DMSO at 25°C (-o-), (II) DMSO at 30°C (-Δ-), (III) DMSO at 35°C (-□-), (IV) DMSO at 40°C (-●-), (V) DEF at 30°C (-▲-), (VI) DMF at 25°C (-⊕-) and (VII) DMA at 25°C (-*-)

τ 's from both the methods along with τ 's from conductivity measurement technique using Eqs (25) and (26) are placed in Table 2 in order to compare with τ measured by Gopalakrishna's method¹⁶.

Eqs (1) and (2) are solved for c_1 and c_2 to get:

$$c_1 = \frac{(\chi'_{ij}\alpha_2 - \chi''_{ij})(1 + \alpha_1^2)}{\chi'_{oij}(\alpha_2 - \alpha_1)} \quad \dots (6)$$

$$c_2 = \frac{(\chi''_{ij} - \chi'_{ij}\alpha_1)(1 + \alpha_2^2)}{\chi'_{oij}(\alpha_2 - \alpha_1)} \quad \dots (7)$$

where $\alpha_1 = \omega\tau_1$ and $\alpha_2 = \omega\tau_2$, such that $\alpha_2 > \alpha_1$. The values of χ'_{ij}/χ'_{oij} and χ''_{ij}/χ'_{oij} are also obtained from following Fröhlich's equations¹⁷:

$$\frac{\chi'_{ij}}{\chi'_{oij}} = 1 - \frac{1}{2A} \ln \left(\frac{1 + \omega^2\tau_2^2}{1 + \omega^2\tau_1^2} \right) \quad \dots (8)$$

$$\frac{\chi''_{ij}}{\chi'_{oij}} = \frac{1}{A} \left[\tan^{-1}(\omega\tau_2) - \tan^{-1}(\omega\tau_1) \right] \quad \dots (9)$$

where $A = \text{Fröhlich parameter} = \ln(\tau_2/\tau_1)$. The theoretical values of relative contributions c_1 and c_2 towards dielectric relaxation processes for τ_1 and τ_2 are computed from Eqs (8) and (9). They are presented in Table 3. The graphical plots of χ'_{ij}/χ'_{oij} and χ''_{ij}/χ'_{oij} curves as a function of w_j are shown in Figs 5 and 6, respectively. The experimental values of c_1 and c_2 are

Table 1—Real χ_{ij}' and imaginary χ_{ij}'' , parts of the complex dielectric orientation susceptibility χ_{ij}^* and static dielectric susceptibility χ_{oij} which are real for various weight fractions w_j 's of some aprotic polar liquids in benzenes at different temperatures under hf electric field

System	Temp. °C	Weight fraction w_j	χ_{ij}'	χ_{ij}''	χ_{oij}
I. DMSO	25	0.0022	0.0611	0.0280	0.0731
		0.0043	0.0890	0.0420	0.1094
		0.0047	0.0950	0.0460	0.1181
		0.0069	0.1231	0.0616	0.1594
		0.0086	0.1520	0.0798	0.1982
II. DMSO	30	0.0022	0.0630	0.0274	0.074
		0.0043	0.0915	0.0400	0.1095
		0.0047	0.0980	0.0440	0.1220
		0.0069	0.1155	0.0526	0.1500
		0.0086	0.1340	0.0648	0.1802
III. DMSO	35	0.0022	0.0600	0.0234	0.0693
		0.0043	0.0800	0.0330	0.108
		0.0047	0.0825	0.0360	0.1135
		0.0069	0.1104	0.0496	0.1564
		0.0086	0.1260	0.0580	0.1830
IV. DMSO	40	0.0022	0.0499	0.0170	0.0648
		0.0043	0.0774	0.0282	0.1054
		0.0047	0.0784	0.0286	0.1094
		0.0069	0.1083	0.0420	0.1541
		0.0086	0.1155	0.0500	0.1775
V. DEF	30	0.0023	0.0850	0.0256	0.1137
		0.0042	0.0899	0.0288	0.1335
		0.0079	0.0997	0.0384	0.1822
		0.0095	0.1033	0.0448	0.2053
VI. DMF	25	0.0027	0.0742	0.0256	0.0948
		0.0036	0.0872	0.0302	0.1162
		0.0048	0.1045	0.0386	0.1423
		0.0063	0.1291	0.0484	0.1855
VII. DMA	25	0.0026	0.0818	0.0213	0.1201
		0.0045	0.1046	0.0278	0.1559
		0.0056	0.1198	0.0330	0.1851
		0.0066	0.1370	0.0381	0.2083

also estimated from Eqs (1) and (2) with the measured values of $(\chi_{ij}'/\chi_{oij})_{w_j \rightarrow 0}$ and $(\chi_{ij}''/\chi_{oij})_{w_j \rightarrow 0}$ of Figs 5 and 6. These c_1 and c_2 are finally compared with theoretical ones in Table 3.

The symmetric and asymmetric distribution parameters γ and δ of the molecules under study are calculated and placed in the last columns of the Table 3 along with all the c_1 and c_2 's in order to see that the relaxation mechanism for such liquids are symmetric. The dipole moments μ_2 and μ_1 due to rotation of the whole molecule as well as the flexible parts of the molecules are determined from the slope β_1 of $\chi_{ij}'-w_j$ curve of Fig. 4 at $w_j \rightarrow 0$ in terms of estimated τ_1 and τ_2 of Eq. (3) as placed in Table 4. μ_2 's are again calculated from the τ 's of Eqs (4) and (25) of Murthy *et*

*al.*¹⁸ and the ratio of the individual slopes of Eqs (5) and (26) from susceptibility and conductivity measurements using slope β_1 of $\chi_{ij}'-w_j$ of Fig. 4 and β_2 of $\sigma_{ij}-w_j$ curve of Fig. 7. μ 's from both the measurements are entered in Table 4 along with estimated μ 's from Gopalakrishna's method¹⁶ quoted as reported ones in the Table 4.

The variations of measured μ_2 and μ_1 for DMSO in benzene with temperature in °C are given by the equations:

$$\begin{aligned} \mu_2 &= -231.61 + 15.597 t - 0.2272 t^2 \\ \mu_1 &= 19.825 - 0.626 t + 0.0108 t^2 \end{aligned} \quad \dots (10)$$

μ_2 of the parent molecule attains a maximum value of 36 C.m at 34.32°C with zero dipole moments at 21.72

Table 2—Relaxation times τ_2 and τ_1 from the slope and intercept of straight line Eq. (3), measured τ_j from different methods of susceptibility and conductivity measurement technique, reported τ , symmetric and characteristic relaxation times τ_s and τ_{cs} for different aprotic polar liquids under effective dispersive region of nearly 10 GHz electric field

System	Temp °C	Estimated τ_1 and τ_2 , ps		τ_j^a ps	τ_j^b ps	τ_j^c ps	τ_j^d ps	Rept [*] τ_j ps	τ_s ps	τ_{cs} ps
		τ_1	τ_2							
I. DMSO	25	8.09	21.07	9.91	6.79	8.77	6.01	5.37	4.88	3.69
II. DMSO	30	7.51	52.02	9.07	6.34	8.04	5.86	4.96	4.82	3.05
III. DMSO	35	6.50	59.68	9.08	9.03	7.47	8.95	4.70	4.21	—
IV. DMSO	40	4.51	39.00	8.38	4.90	7.09	4.46	4.33	3.74	22.20
V. DEF	30	3.89	76.41	16.86	1.06	6.64	0.58	2.42	4.16	15.66
VI. DMF	25	4.60	56.24	6.73	6.69	5.87	5.58	5.09	3.02	8.47
VII. DMA	25	2.20	56.61	3.05	6.53	4.96	3.11	6.53	3.90	81.95

τ_j^a = relaxation time from direct slope of Eq. (4); τ_j^b = relaxation time from ratio of individual slope of Eq. (5); τ_j^c = relaxation time from direct slope of Eq. (25); τ_j^d = relaxation time from ratio of individual slope of Eq. (26) and reported τ_j by using Gopalakrishna's¹⁶ method

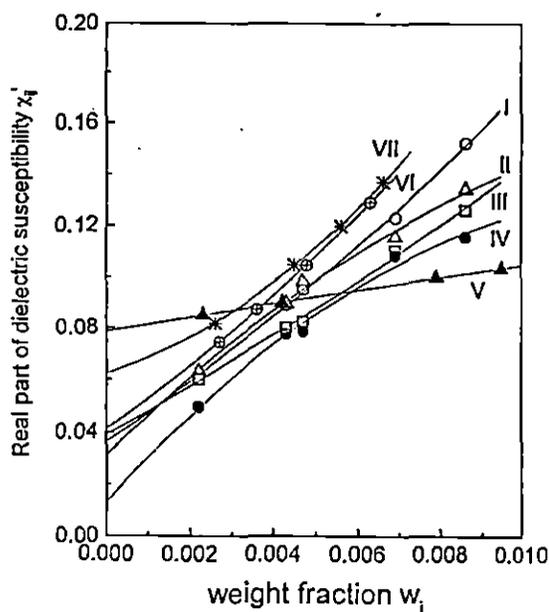


Fig. 4—Plot of real part of dielectric susceptibility χ'_{ij} with weight fraction w_j of DMSO, DEF, DMF and DMA in benzene (I) DMSO at 25°C (-o-), (II) DMSO at 30°C (-Δ-), (III) DMSO at 35°C (-□-), (IV) DMSO at 40°C (-●-), (V) DEF at 30°C (-▲-), (VI) DMF at 25°C (-⊕-) and (VII) DMA at 25°C (-*-)

and 46.92°C, respectively due to monomer formation with C_6H_6 ring.

The theoretical dipole moment μ_{theo} 's of the molecules are calculated from the available infrared spectroscopic data of bond moments assuming the molecules are planar as sketched in Fig. 8. They are found to vary with the measured μ_j 's. The difference, how-

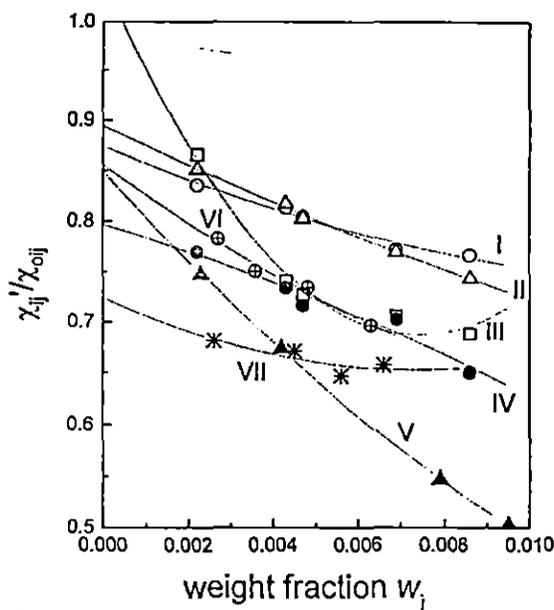


Fig. 5—Variation of χ'_{ij}/χ_{oij} with w_j 's of DMSO, DEF, DMF and DMA in benzene (I) DMSO at 25°C (-o-), (II) DMSO at 30°C (-Δ-), (III) DMSO at 35°C (-□-), (IV) DMSO at 40°C (-●-), (V) DEF at 30°C (-▲-), (VI) DMF at 25°C (-⊕-) and (VII) DMA at 25°C (-*-)

ever, indicates that the effect of inductive, mesomeric and electromeric moments of the substituent polar groups within the molecules along with temperature in the hf electric field is to be considered to have the conformation of the molecules under interest.

The thermodynamic energy parameters like enthalpy of activation ΔH_τ , free energy of activation ΔF_τ

Table 3—Fröhlich's parameter A [$=\ln(\tau_2/\tau_1)$], theoretical and experimental values of χ_{ij}'/χ_{oij} and χ_{ij}''/χ_{oij} of Fröhlich Eqs (8) and (9) and from fitting equations of Figs 5 and 6 at $\omega_j \rightarrow 0$, respectively, theoretical and experimental relative contributions c_1 and c_2 towards dielectric dispersion due to τ_1 and τ_2 , symmetric and asymmetric distribution parameters γ and δ for polar-nonpolar liquid mixtures of some aprotic polar liquids under effective dispersion region of nearly 10 GHz electric field

System	Temp °C	A	Theoretical values of χ_{ij}'/χ_{oij} and χ_{ij}''/χ_{oij} from Eqs (8) and (9)		Theoretical values of c_1 and c_2		Experimental values of χ_{ij}'/χ_{oij} and χ_{ij}''/χ_{oij} at $\omega_j \rightarrow 0$ of Figs 5 and 6		Experimental values of c_1 and c_2		Estimated values of γ and δ	
			χ_{ij}'/χ_{oij}	χ_{ij}''/χ_{oij}	c_1	c_2	χ_{ij}'/χ_{oij}	χ_{ij}''/χ_{oij}	c_1	c_2	γ	δ
I. DMSO	25	0.957	0.629	0.466	0.485	0.571	0.874	0.380	1.095	-0.061	-0.07	2.00
II. DMSO	30	1.935	0.449	0.434	0.423	0.933	0.894	0.389	1.049	0.022	-0.08	2.37
III. DMSO	35	2.217	0.454	0.419	0.425	1.043	1.039	0.371	1.192	-0.076	-0.29	--
IV. DMSO	40	2.241	0.611	0.409	0.507	0.794	0.797	0.266	0.803	0.228	0.21	0.36
V. DEF	30	2.978	0.476	0.378	0.443	1.380	0.849	0.247	0.890	0.210	0.17	0.36
VI. DMF	25	2.505	0.497	0.405	0.451	1.086	0.855	0.262	0.921	0.065	0.13	0.61
VII. DMA	25	3.248	0.601	0.357	0.531	1.093	0.724	0.185	0.713	0.338	0.47	0.18

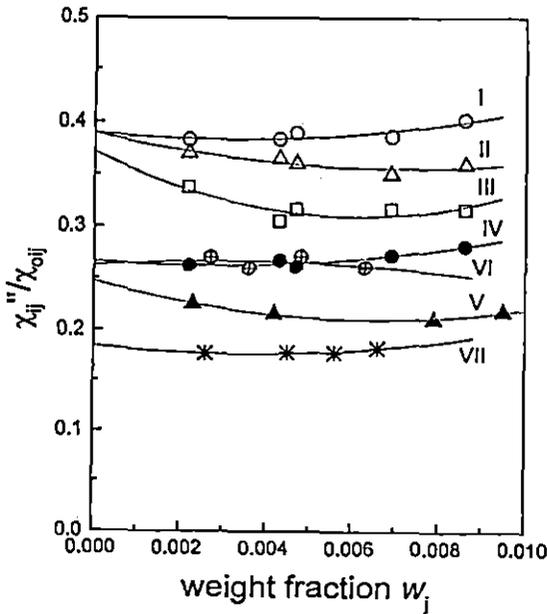


Fig. 6—Variation of χ_{ij}''/χ_{oij} with w_j 's of DMSO, DEF, DMF and DMA in benzene (I) DMSO at 25°C (-o-), (II) DMSO at 30°C (-Δ-), (III) DMSO at 35°C (-□-), (IV) DMSO at 40°C (-●-), (V) DEF at 30°C (-▲-), (VI) DMF at 25°C (-⊕-) and (VII) DMA at 25°C (-*-))

and entropy of activation ΔS_τ were obtained from the slope and intercept of linear equation of $\ln(\tau_1 T)$ against $1/T$ for DMSO as given by the equation:
 $\ln(\tau_2 T) = -4.8353 - 4.088 \times 10^3(1/T)$
 $\ln(\tau_1 T) = -30.568 + 3.216 \times 10^3(1/T)$... (11)

The variation of $\ln(\tau_1 T)$ or $\ln(\tau_2 T)$ against $1/T$ indicates that τ_1 obeys the Eyring rate process whereas τ_2 does not.

2 Symmetric and Asymmetric Distribution Parameters γ and δ

The polar-nonpolar liquid mixtures under study are non-rigid in nature exhibiting two relaxation times τ_2 and τ_1 at a single frequency electric field¹⁹. The measured values of χ_{ij}''/χ_{oij} when plotted against χ_{ij}'/χ_{oij} at $\omega_j \rightarrow 0$ for different frequency ω at a fixed experimental temperature for DMSO may either show Cole-Cole semicircular arc or Cole-Davidson skewed arc having symmetric and asymmetric distribution of relaxation behaviour according to following equations:

$$\frac{\chi_{ij}'}{\chi_{oij}} = \frac{1}{1 + (j\omega\tau_s)^{1-\gamma}} \quad \dots (12)$$

$$\frac{\chi_{ij}''}{\chi_{oij}} = \frac{1}{(1 + j\omega\tau_{cs})^\delta} \quad \dots (13)$$

where τ_s and τ_{cs} are symmetric and characteristics relaxation times related to symmetric and asymmetric distribution parameters γ and δ , respectively. On separation, the real and imaginary parts of Eq. (12), one gets:

$$\gamma = \frac{2}{\pi} \tan^{-1} \left[\left(1 - \frac{\chi_{ij}'}{\chi_{oij}} \right) \frac{\chi_{ij}'/\chi_{oij}}{\chi_{ij}''/\chi_{oij}} - \frac{\chi_{ij}''}{\chi_{oij}} \right] \quad \dots (14)$$

$$\tau_s = \frac{1}{\omega} \left[\frac{1}{\left(\frac{\chi_{ij}'/\chi_{oij}}{\chi_{ij}''/\chi_{oij}} \cos \frac{\gamma\pi}{2} - \sin \frac{\gamma\pi}{2} \right)^{1-\gamma}} \right] \quad \dots (15)$$

Table 4—Slope β_1 of χ'_{ij} versus w_j and β_2 of σ_{ij} versus w_j curves, measured dipole moments μ_2 and μ_1 from susceptibility measurement technique, μ_j^a 's from Eqs (22) and (29), respectively, reported dipole moment, theoretical dipole moment μ_{theo} from available bond angles and bond moments expressed in Coulomb metre (C.m) and the values of μ_1/μ_{theo} for some aprotic polar liquids in benzene under effective dispersion region of nearly 10 GHz electric field

System mol wt	Slope of χ'_{ij} - w_j and σ_{ij} - w_j curves		Dipole moments μ_j ($\times 10^{-30}$) in Coulomb metre							μ_1/μ_{theo}	
	β_1	β_2	From Eq (22)		μ_j^a	μ_j^b	μ_j^c	μ_j^d	μ_j^e		μ_{theo}
			μ_2	μ_1							
I.DMSO at 25°C $M_j=0.078$ kg	10.943	6.280	14.69	10.30	10.75	10.03	11.10	10.48	12.65	15.18	0.67
II.DMSO at 30°C $M_j=0.078$ kg	16.440	9.096	36.69	12.64	13.09	12.35	13.31	12.75	12.79	15.18	0.83
III.DMSO at 35°C $M_j=0.078$ kg	8.950	4.621	31.09	9.27	9.79	9.78	9.50	9.82	13.49	15.18	0.61
IV.DMSO at 40°C $M_j=0.078$ kg	17.646	9.894	30.37	12.69	13.70	12.82	13.94	13.32	13.73	15.18	0.83
V.DEF at 30°C $M_j=0.101$ kg	2.870	2.922	26.62	5.67	7.91	5.53	8.18	7.58	12.96	13.30	0.42
VI.DMF at 25°C $M_j=0.073$ kg	10.938	7.282	33.21	9.37	9.81	9.80	10.54	10.48	12.09	12.73	0.74
VII.DMA at 25°C $M_j=0.087$ kg	5.147	2.792	24.97	6.83	7.07	6.89	7.00	6.81	11.26	13.37	0.51

μ_j^a = dipole moment by using τ from the direct slope of Eq. (4); μ_j^b = dipole moment by using τ from the ratio of individual slopes of Eq. (5); μ_j^c = dipole moment by using τ from the direct slope of Eq. (25); μ_j^d = dipole moment by using τ from the ratio of individual slopes of Eq. (26); μ_j^e = reported dipole moment using Gopalakrishna's¹⁶ τ and μ_{theo} = theoretical dipole moment from the available bond moments.

On simplification of Eq. (13) further, one gets :

$$\frac{1}{\phi} \log(\cos \phi) = \frac{\log \left[\left(\chi'_{ij} / \chi_{oij} \right) / \cos(\phi\delta) \right]}{\phi\delta} \quad \dots (16)$$

$$\tan(\phi\delta) = \frac{\left(\chi''_{ij} / \chi_{oij} \right)_{w_j \rightarrow 0}}{\left(\chi'_{ij} / \chi_{oij} \right)_{w_j \rightarrow 0}} \quad \dots (17)$$

where $\tan \phi = \omega\tau_{cs}$

A theoretical curve of $(1/\phi) \log(\cos \phi)$ with ϕ in degrees was drawn⁵ to get the known values of ϕ and δ in terms of measured parameter of $[\log \{ (\chi'_{ij} / \chi_{oij}) / \cos(\phi\delta) \}] / (\phi\delta)$ of Eqs (16) and (17). All the τ_s , τ_{cs} and δ ϕ are given in Tables 2 and 3, respectively.

3 Dipole Moment μ_j from Susceptibility Measurement

Debye equation²⁰ of relative permittivities of a polar solute (j) dissolved in a non-polar solvent (i) in terms of complex dielectric orientational susceptibility χ^*_{ij} of solution can be written as:

$$\frac{\chi^*_{ij}}{\chi_{oij}} = \frac{1}{1 + j\omega\tau} \quad \dots (18)$$

where $\chi_{ij}' (= \epsilon_{ij}' - \epsilon_{\infty ij})$ and $\chi_{ij}'' (= \epsilon_{ij}'')$ are the real and imaginary parts of $\chi^*_{ij} = \chi_{ij}' - j\chi_{ij}''$. $j = \sqrt{-1}$ is a complex number $\chi_{oij} (= \epsilon_{oij} - \epsilon_{\infty ij})$ is the low frequency susceptibility which is real.

Again, the imaginary part of dielectric orientational susceptibility χ_{ij}'' as a function of w_j can be written according to Smith²¹ as:

$$\chi''_{ij} = \frac{N\rho_{ij}\mu_j^2}{27\epsilon_o k_B T M_j} \frac{\omega\tau}{1 + \omega^2\tau^2} (\epsilon_{ij} + 2)^2 w_j \quad \dots (19)$$

On differentiation of Eq. (19) w.r. to w_j at $w_j \rightarrow 0$, one gets:

$$\left(\frac{d\chi''_{ij}}{dw_j} \right)_{w_j \rightarrow 0} = \frac{N\rho_{ij}\mu_j^2}{27\epsilon_o k_B T M_j} \frac{\omega\tau}{1 + \omega^2\tau^2} (\epsilon_i + 2)^2 \quad \dots (20)$$

where k_B is the Boltzmann constant, N the Avogadro's Number ϵ_i the relative permittivity of the solute and ϵ_o

is the absolute permittivity of free space = $8.854 \times 10^{-12} \text{ F.m}^{-1}$, all expressed in SI units. Comparing Eqs (4) and (20), one gets:

$$\left(\frac{d\chi_{ij}'}{dw_j} \right)_{w_j \rightarrow 0} = \frac{N\rho_i \mu_j^2}{27\epsilon_0 k_B T M_j} \frac{1}{1 + \omega^2 \tau^2} (\epsilon_i + 2)^2 = \beta_1 \quad \dots (21)$$

where β_1 is the slope of $\chi_{ij}' - w_j$ curves at $w_j \rightarrow 0$.

From Eq. (21), one gets the dipole moment μ_j as:

$$\mu_j = \left(\frac{27\epsilon_0 k_B T M_j \beta_1}{N\rho_i (\epsilon_i + 2)^2 b} \right)^{\frac{1}{2}} \quad \dots (22)$$

where $b = 1/(1 + \omega^2 \tau^2)$ is the dimensionless parameter involved with measured τ_j of Table 2. All the μ_j 's are placed in Table 4.

4 Dipole Moment μ_j from hf Conductivity Measurement

The hf complex conductivity σ_{ij}^* of a polar-non-polar liquid mixture is given by:

$$\sigma_{ij}^* = \sigma_{ij}' + j\sigma_{ij}'' = \omega\epsilon_0 (\epsilon_{ij}' + j\epsilon_{ij}'') \quad \dots (23)$$

the real σ_{ij}' and imaginary σ_{ij}'' parts of σ_{ij}^* are related by:

$$\sigma_{ij}'' = \sigma_{\infty ij} + \frac{1}{\omega\tau_j} \sigma_{ij}' \quad \dots (24)$$

where $\sigma_{\infty ij}$ is the constant conductivity at infinite dilution i.e. at $w_j \rightarrow 0$. The Eq. (24) on differentiation w.r.t. σ_{ij}' yields:

$$\frac{d\sigma_{ij}''}{d\sigma_{ij}'} = \frac{1}{\omega\tau_j} \quad \dots (25)$$

which provides a convenient method to obtain τ_j of a polar molecule. It is, however, better to use the ratio of the slopes of variation of σ_{ij}'' and σ_{ij}' with w_j in order to avoid polar-polar interactions at $w_j \rightarrow 0$ in a given solvent to get τ_j from:

$$\frac{(d\sigma_{ij}''/dw_j)_{w_j \rightarrow 0}}{(d\sigma_{ij}'/dw_j)_{w_j \rightarrow 0}} = \frac{1}{\omega\tau_j} \quad \dots (26)$$

In hf region of GHz range, it is generally observed that $\sigma_{ij}'' \cong \sigma_{ij}$ the total hf conductivity²² of the solution. Therefore, the Eq. (24) can be written as:

$$\sigma_{ij} = \sigma_{\infty ij} + \frac{1}{\omega\tau_j} \sigma_{ij}' \quad \dots (27)$$

$$\beta_2 = \frac{1}{\omega\tau_j} \left(\frac{d\sigma_{ij}'}{dw_j} \right)_{w_j \rightarrow 0}$$

where β_2 is the slope of $(d\sigma_{ij}'/dw_j)_{w_j \rightarrow 0}$. The real part σ_{ij}' of a polar-nonpolar liquid mixture is given by⁵:

$$\sigma_{ij}' = \frac{N\rho_{ij} \mu_j^2}{27k_B T M_j} \frac{\omega^2 \tau_j}{1 + \omega^2 \tau_j^2} (\epsilon_{ij} + 2)^2 w_j$$

$$\left(\frac{d\sigma_{ij}'}{dw_j} \right)_{w_j \rightarrow 0} = \frac{N\rho_{ij} \mu_j^2}{27k_B T M_j} \frac{\omega^2 \tau_j}{1 + \omega^2 \tau_j^2} (\epsilon_i + 2)^2 \quad \dots (28)$$

Now comparing Eqs (27) and (28), one gets hf μ_j from:

$$\mu_j = \left(\frac{27k_B T M_j \beta_2}{N\rho_{ij} (\epsilon_i + 2)^2 \omega b} \right)^{\frac{1}{2}} \quad \dots (29)$$

where $b = 1/(1 + \omega^2 \tau^2)$ is involved with τ_j 's from Eqs (25) and (26). μ_j 's thus obtained from Eq. (29) are placed in Table 4 along with Gopalakrishna's μ_j and μ_{theo} 's.

5 Results and Discussion

The relaxation parameters in terms of real χ_{ij}' ($=\epsilon_{ij}' - \epsilon_{\infty ij}$), imaginary χ_{ij}'' ($=\epsilon_{ij}''$) and low frequency susceptibility χ_{oij} ($=\epsilon_{oij} - \epsilon_{\infty ij}$), which are real and extracted from the measured relative permittivities ϵ_{ij} 's for different w_j 's of solute at 25, 30, 35 and 40°C for DMSO, 25°C for DMA and DMF and 30°C for DEF under nearly 10 GHz electric field as shown in Table 1. The curves of $(\chi_{oij} - \chi_{ij}')/\chi_{ij}'$ against χ_{ij}''/χ_{ij}' at different w_j 's of solute are plotted from the measured data in Fig. 1. All the curves show two relaxation times τ_2 and τ_1 due to rotation of the whole molecule and the flexible part attached to the parent ones as evident from Table 2. It indicates that the molecules are of non-rigid nature. Unlike τ_2 's, τ_1 's of DMSO at 25, 30, 35 and 40°C decrease gradually (Table 2). This indicates that τ_1 's obey the Debye relaxation mechanism. It is also evident from Table 2 and Fig. 1 that the graphs of $(\chi_{oij} - \chi_{ij}')/\chi_{ij}'$ against χ_{ij}''/χ_{ij}' for different w_j 's of DMSO shift towards the origin with the increase of temperature. τ_2 's of all the liquids are much larger in magnitude than τ_1 . The parent mole-

cule takes larger time to lag with the electric field frequency for its inertia in comparison to its flexible parts which are supported by the two relaxation model of polar unit under nearly 10 GHz electric field²³. τ_j 's are estimated and placed in Table 2 from Eqs (4) and (5) using linear slope of χ_{ij}'' against χ_{ij}' at different w_j 's and the ratio of individual slopes of $\chi_{ij}''-w_j$ and $\chi_{ij}'-w_j$ curves at $w_j \rightarrow 0$ of Figs 3 and 4, respectively. The values of τ_j from Eq. (4) are larger than from Eq. (5). Reported τ 's and τ_j 's calculated from both the Gopalakrishna's method¹⁶ as well as conductivity measurement technique using Eqs (25) and (26), respectively. The agreement is better from the τ_j 's due to ratio of the individual slopes of $\chi_{ij}''-w_j$ and $\chi_{ij}'-w_j$ curves at $w_j \rightarrow 0$ of Figs 3 and 4 because the polar-polar interactions are almost avoided. They are then compared with the reported τ_s and τ_{cs} of the molecules assuming symmetric and asymmetric distribution of relaxation processes only to show that the molecules obey symmetric distribution. The curves χ_{ij}'' against χ_{ij}' of Fig. 2 of the molecules are found to meet at a point in the region of $0 < w_j < 0.02$ except DEF the data was measured at 30°C. The experimental curves of $\chi_{ij}''-w_j$ and $\chi_{ij}'-w_j$ are not linear as shown in Figs 3 and 4, respectively. Like $\chi_{ij}'-w_j$ curves all the curves of $\chi_{ij}''-w_j$ of Fig. 3 are parabolic in nature and increase with the w_j 's of solute. The magnitude of χ_{ij}'' is, however, maximum in lower temperature region and decrease with the rise of temperature. This indicates the absorption of electric energy in the polar-non-polar mixture in the lower temperature region.

The relative contributions c_1 and c_2 due to τ_1 and τ_2 could, however, be estimated from the χ_{ij}''/χ_{oij} and χ_{ij}'/χ_{oij} of Fröhlich's Eqs (8) and (9) and placed in Table 3 assuming a continuous distribution of τ between limiting values of τ_1 and τ_2 . c_1 and c_2 are also calculated in terms of fixed values of $(\chi_{ij}''/\chi_{oij})_{w_j \rightarrow 0}$ and $(\chi_{ij}'/\chi_{oij})_{w_j \rightarrow 0}$ of the graphical plots of $(\chi_{ij}''/\chi_{oij})-w_j$ and $(\chi_{ij}'/\chi_{oij})-w_j$ curves of Figs 5 and 6 respectively. All the curves are extrapolated to get the fixed values of (χ_{ij}''/χ_{oij}) and (χ_{ij}'/χ_{oij}) at $w_j \rightarrow 0$. They are substituted in the Bergmann's Eqs (6) and (7) to get c_1 and c_2 for the fixed values of τ_1 and τ_2 , respectively. All the c 's are placed in Table 3 for comparison with Fröhlich's method. Both c_1 and c_2 from Fröhlich's¹⁵ equations are all +ve for all the liquids. But c_2 for DMSO at 25 and 35°C are -ve from the graphical method. The -ve value of c_2 is physically

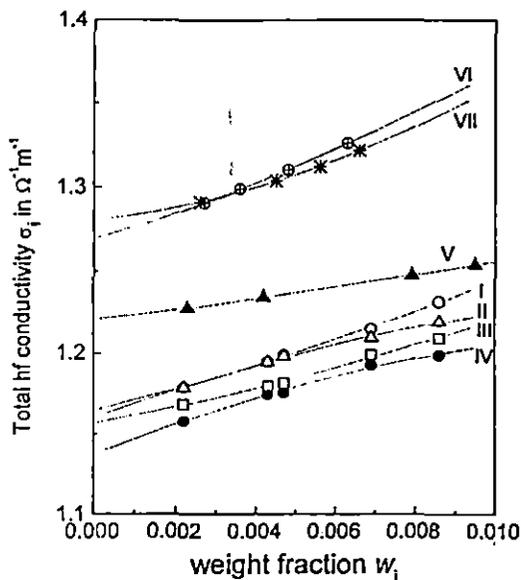


Fig. 7—Variation of total hf conductivity σ_{ij} with w_j 's of DMSO, DEF, DMF and DMA in benzene (I) DMSO at 25°C (-o-), (II) DMSO at 30°C (-Δ-), (III) DMSO at 35°C (-□-), (IV) DMSO at 40°C (-●-), (V) DEF at 30°C (-▲-), (VI) DMF at 25°C (-⊕-) and (VII) DMA at 25°C (-*-)

meaningless as they are considered to be the relative contributions towards dielectric relaxation processes. This may indicate that the rotation of whole molecule under hf electric field is not in accord with the flexible part probably due to inertia as observed elsewhere^{10,11}. The variation of χ_{ij}''/χ_{oij} and χ_{ij}'/χ_{oij} with w_j as shown in Figs 5 and 6 are expected to be concave and convex^{10,11} respectively. All the curves of Figs 5 and 6 are, however, concave except systems VI (-⊕-) of Fig. 6. This type of anomalous behaviour in the variation of χ_{ij}''/χ_{oij} and χ_{ij}'/χ_{oij} with w_j invariably demands careful measurement of data in low concentration region.

The dipole moments μ_1 and μ_2 are also calculated from the slope β_1 of $\chi_{ij}'-w_j$ curve of Fig. 4 and estimated τ_1 and τ_2 as shown in Table 4. They are compared with μ_j 's from τ_j 's of Eqs (4) and (5), respectively. μ_j 's from Gopalakrishna's method¹⁶ and conductivity measurement technique⁹ are also reported and placed in Table 4 for comparison among them. The total hf conductivity σ_{ij} is plotted against w_j 's of the polar-nonpolar liquid mixture as seen in Fig. 7 only to show that all the curves are parabolic in nature exhibiting maximum conductivity at lower temperature and higher concentration for DMSO. At $w_j \rightarrow 0$, the curves are found to yield different value of σ_{ij} probably due to the term $1/(M_j T)$ in the Eq. (28) as seen in Fig. 7. The difference in estimated μ_2 and μ_1 from conductivity and susceptibility measurements

suggests the involvement of bound molecular charges towards μ 's of polar liquid. It is evident from Table 4 that μ_1 's of the polar liquids are found to be in excellent agreement with the reported μ 's. It, thus, reveals that a part of the molecule is rotating under 10 GHz electric field as observed earlier²⁴. The variation of μ_1 and μ_2 with temperature for DMSO is given by Eq. (10). The convex nature of μ_1 - t equation reveals the fact that the molecule DMSO attains higher asymmetry of larger μ_1 at a certain temperature. It also shows zero dipole moments at two different temperatures indicating the symmetric nature of the molecule. The variation of μ_1 with temperature may occur due to elongation of bond moments. This further invites the extensive study of the relaxation phenomena of highly non-spherical dipolar molecules at different experimental temperatures and in different solvents.

The theoretical dipole moment μ_{theo} 's of the polar molecules are calculated assuming the planar structure from the available bond moments of 7.83×10^{-30} C.m., 5.17×10^{-30} C.m. for polar groups $S \leftarrow \text{CH}_3$, $\text{O} \leftarrow \text{S}$ in DMSO 2.13×10^{-30} C.m., 2.60×10^{-30} C.m., 1.23×10^{-30} C.m. of $\text{N} \leftarrow \text{CH}_3$, $\text{N} \leftarrow \text{C}_2\text{H}_5$, $\text{CH}_3 \leftarrow \text{C}$ in DMF, DEF and DMA respectively. The other bond moments are 1×10^{-30} C.m., 1.5×10^{-30} C.m., 10.33×10^{-30} C.m. for $\text{C} \leftarrow \text{H}$, $\text{C} \leftarrow \text{N}$ and $\text{C} \leftarrow \text{O}$ in them. The bond moments are, however, reduced by a factor μ_1/μ_{theo} to yield exact μ 's as sketched in Fig. 8. The reduction or elongation in bond moments of the substituent polar groups may occur due to inductive, mesomeric and electromeric effects which in turn subsequently act as pusher or puller of electrons in them. The solvent C_6H_6 is a cyclic and planar compound and has three double bonds and six p-electrons on six C-atoms. The dipolar liquid molecules are aliphatic and planar ones. Hence, π - π interaction or resonance effect combined with inductive effect commonly known as mesomeric effect in excited state called the electromeric effect may play the vital role in the estimation of μ_{theo} 's of Fig. 8.

The thermodynamic energy parameters like enthalpy of activation ΔH_τ entropy of activation ΔS_τ and free energy of activation ΔF_τ of DMSO were calculated from the slope and intercept of $\ln(\tau_1 T)$ against $(1/T)$ of Eq. (11) on the basis of Eyrings theory considering the rotation of the polar molecule as a rate process. Unlike $\ln(\tau_2 T)$ against $(1/T)$; $\ln(\tau_1 T)$ against $(1/T)$ of DMSO is in accord with the Eyring's rate

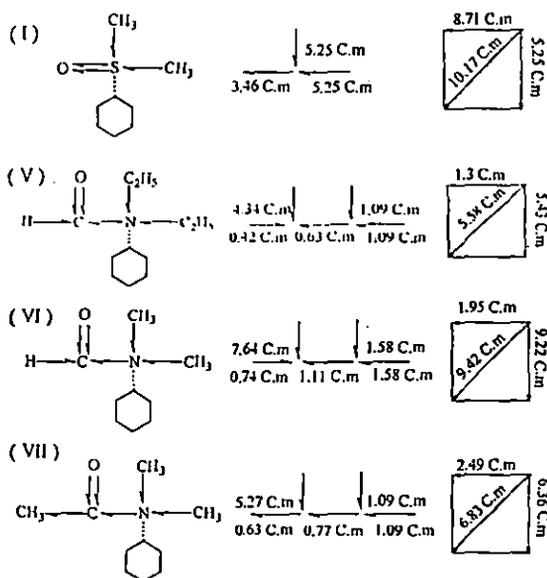


Fig. 8—Conformational structures of aprotic polar liquids in terms of reduced bond length due to mesomeric and inductive moments in Coulomb metre (Cm) $\times 10^{30}$ of the substituent polar groups: (I) DMSO (II) DEF (III) DMF (IV) DMA

theory²⁰. The value of ΔH_τ for DMSO is 6.85 in KJ mole⁻¹ ΔS_τ are -8.21, -8.15, -11.65, -11.48 in J mole⁻¹ K⁻¹ and ΔF_τ are 9.30, 9.32, 10.43 and 10.45. at 25, 30, 35 and 40°C, respectively in KJ. mole⁻¹. It is observed that ΔS_τ are -ve indicating the activated states are more ordered than the normal states especially for DMSO.

6 Conclusions

The study of relaxation phenomena of aprotic polar liquids of amides in C_6H_6 in terms of the modern established symbols of dielectric terminologies and parameters of orientational susceptibilities χ_{ij} 's measured under a single frequency electric field is very encouraging and interesting. It seems to be more topical, significant and useful contribution to predict the conformational structures and various molecular associations of the molecules at any given temperatures. The intercept and slope of derived linear Eq. (3) on the measured data of χ_{ij} of different w_j 's are used to get τ_2 and τ_1 . The prescribed methodology in SI units is superior because of the unified, coherent and rationalised nature because χ_{ij} 's are directly linked only with orientational polarisation of the molecules. The significant Eqs (4) and (5) to obtain values of τ_j and hence, values of μ_j from Eq. (22) help the future researchers to shed more light on the relaxation phenomena of complicated non-spherical polar liquids and liquid crystals. The present method to obtain val-

ues of τ_j from Eq. (5) with the use of the ratio of the individual slopes of χ_{ij}'' versus w_j and χ_{ij}' versus w_j curves at $w_j \rightarrow 0$ is a significant improvement over the existing ones, as it eliminates polar-polar interaction almost completely in τ_j 's and μ_j 's, respectively.

The values of τ_j and μ_j are usually claimed to be accurate within 10 and 5%, respectively. The tested correlation coefficients r 's and % of errors of Eq. (3) demand that τ and μ are more than accurate. The DMSO, DMF, DMA and DEF molecules absorb electric energy much more strongly under nearly 10 GHz electric field, at which the variation of χ_{ij}'' against frequency ω seem to be large. This at once indicates the attention to get the double relaxation phenomena from Eq. (3). The sum of the experimental and theoretical values of weighted contributions c_1 and c_2 towards dielectric dispersions due to estimated τ_2 and τ_1 differ significantly to indicate more than two Debye type relaxations in such molecules because of their complexity. It can, further, be observed that only a part of the molecule is rotating under nearly 10 GHz electric field since $\ln(\tau_1 T)$ against $1/T$ obeys the Eyring's rate theory. The values of μ_2 and μ_1 due to τ_2 and τ_1 are expected to be smaller when they are measured from susceptibility measurement technique rather than the hf conductivity and permittivity methods, where approximation of $\sigma_{ij} \approx \sigma'_{ij}$ is usually made. The measurement of μ 's from hf conductivities σ_{ij} 's and hf permittivities ϵ_{ij} 's is involved with the contributions of the bound molecular charges and all types of polarisations including the fast one. The difference of μ_1 and μ_j from μ_{theo} may arise, either by elongation or reduction of the bond moments of the substituted polar groups by factor μ_1/μ_{theo} in agreement with the measured μ 's to take into account of the inductive, mesomeric and electromeric effects of the substituted polar groups in the molecules under investigation. Thus, the correlation between the conformational structures with the observed results enhances the scientific content to add a new horizon of understanding the existing knowledge of dielectric relaxation phenomena.

References

- 1 Puranik S M, Ghanabhadur R Y, Helambe S N & Mehrotra S C, *Indian J Pure & Appl Phys* 29 (1991) 251.
- 2 Murthy M B R, Dayasagar B S & Patil R L, *Pramana: J Phys*, 61 (2003) 725.
- 3 Gupta K K, Bansal A K, Singh P J & Sharma K S, *Indian J Pure & Appl Phys*, 42 (2004) 849.
- 4 Onsager L, *J American Chem Soc*, 58 (1936) 1485.
- 5 Dutta K, Sit S K & Acharyya S, *Pramana: J Phys*, 57 (2001) 775.
- 6 Ghosh N, Karmakar A, Sit S K & Acharyya S, *Indian J Pure & Appl Phys*, 38 (2000) 574.
- 7 Dhull J S, Sharma D R & Laxminarayana K N, *Indian J Phys B*, 56 (1982) 334.
- 8 Sharma A & Sharma D R, *J Phys Soc (Japan)*, 61 (1992) 1049.
- 9 Sit S K, Dutta K, Acharyya S, Pal Majumder T & Roy S, *J Molecular Liquids*, 89 (2000) 111.
- 10 Sit S K, Ghosh N, Saha U & Acharyya S, *Indian J Phys*, 71B (1997) 533.
- 11 Saha U, Sit S K, Basak R C & Acharyya S, *J Phys D: Appl Phys (London)*, 27 (1994) 596.
- 12 Sit S K, Basak R C, Saha U & Acharyya S, *J Phys D: Appl Phys (London)*, 27 (1994) 2194.
- 13 Jonscher A K, *Inst Phys Conference Serial No 58*. Invited paper presented at physics of dielectrics Solids 8-11 (1980).
- 14 Pal Majumder T, *Ph D thesis* Jadavpur University, Kolkata (1996)
- 15 Bergmann K, Roberti D M & Smyth C P, *J Phys Chem*, 64 (1960) 665.
- 16 Gopalakrishna K V, *Trans Faraday Soc*, 53 (1957) 767.
- 17 Fröhlich H, *Theory of Dielectrics* (Oxford University press) 1949.
- 18 Murthy M B R, Patil R L & Deshpande D K, *Indian J Phys B*, 63 (1987) 491.
- 19 Dutta K, Karmakar A, Dutta L, Sit S K & Acharyya, *Indian J Pure & Appl Phys*, 40 (2002) 801.
- 20 Hill N E, Vaughan W E, Price A H & Davis M *Dielectric properties and Molecular Behaviour* Van Nostrand Reinhold, London, 1969.
- 21 Smyth C P, *Dielectric Behaviour and Structure* (McGraw Hill, New York) 1955.
- 22 Dutta K, Karmakar A, Sit S K & Acharyya, *Indian J Pure & Appl Phys*, 40 (2002) 588.
- 23 Sit S K & Acharyya S, *Indian J Pure & Appl Phys*, 34 (1996) 255.
- 24 Basak R C, Sit S K & Acharyya S, *Indian J Phys B*, 70 (1996) 37.

The physico-chemical aspects of some long straight chain alcohols from susceptibility measurement under a 24 GHz electric field at 25 °C

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Received 20 December 2004; accepted 10 May 2005

Available online 10 February 2006

Abstract

The straight line equation $(\chi_{oij} - \chi_{ij}')/\chi_{ij}' = \omega(\tau_1 + \tau_2)(\chi_{ij}''/\chi_{ij}') - \omega^2\tau_1\tau_2$ for different weight fractions w_j 's of some dipolar long straight chain alcohols (j) in *n*-heptane (i) is derived from the available relative permittivities ϵ_{ij}' , ϵ_{ij}'' , ϵ_{oij} and ϵ_{oij}' at 25 °C under 24 GHz electric field. The intercepts and slopes of the above equation are used to get relaxation times τ_1 and τ_2 of the rotation of the flexible part and the whole molecule itself. $\chi_{ij}' (= \epsilon_{ij}' - \epsilon_{oij})$ and $\chi_{ij}'' (= \epsilon_{ij}'' - \epsilon_{oij}'')$ are the real and imaginary parts of hf dimensionless complex dielectric orientational susceptibility χ_{ij}^* and χ_{oij} ($= \epsilon_{oij} - \epsilon_{oij}'$) is the low frequency dielectric susceptibility which is real. τ_j 's of such alcohols are also measured from the ratio of the slopes of the individual variations of χ_{ij}' and χ_{ij}'' with w_j at $w_j \rightarrow 0$ and the direct slope of χ_{ij}'' versus χ_{ij}' equations of Murthy et al. [M.B.R. Murthy, R.L. Patil and D.K. Deshpande, Indian J. Phys 63B (1989) 491]. These τ_j 's are finally compared with the reported τ_j 's of Gopalakrishna [K.V. Gopalakrishna, Trans Faraday Soc. 53 (1957) 767] and τ_1 , τ_2 by double relaxation method to see that the flexible part of the molecule is only rotating under the most effective dispersive region of the 24 GHz electric field. The weighted contributions c_1 and c_2 towards dielectric relaxations for estimated τ_1 , τ_2 are, however, obtained from Fföhlich's theoretical formulations of χ_{ij}'/χ_{oij} and χ_{ij}''/χ_{oij} to compare them with those of graphical ones of $(\chi_{ij}'/\chi_{oij})_{w_j \rightarrow 0}$ and $(\chi_{ij}''/\chi_{oij})_{w_j \rightarrow 0}$. The latter ones are used to get the symmetric distribution parameter γ to have the symmetric relaxation times τ_s . The arbitrary curve of $(1/\phi) \log \cos \phi$ against ϕ in degree together with $(\chi_{ij}'/\chi_{oij})_{w_j \rightarrow 0}$ and $(\chi_{ij}''/\chi_{oij})_{w_j \rightarrow 0}$ experimentally obtained gives the asymmetric distribution parameter δ to get the characteristic relaxation time τ_{cs} . All these findings finally establish the symmetric relaxation behaviour for such compounds. The dipole moments μ_1 and μ_2 for the flexible part and the whole molecule are determined from τ_1 and τ_2 and the linear coefficient β of χ_{ij}' versus w_j 's curves. All the measured μ_j 's are compared with the reported μ_j 's and μ_{theo} 's derived from the bond angles and bond moments of the substituted polar groups of the compounds to arrive at the physico-chemical properties by the conformations sketched in the paper. The slight disagreement of estimated μ_j 's and μ_{theo} 's is, however, explained with the consideration of inductive and mesomeric moments in addition to strong hydrogen bonding of the flexible polar groups attached to the parent molecule.

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1. Introduction

The relaxation process of dipolar liquid or solid material (DRL or DRS) is very encouraging in the study of the physico-chemical molecular behaviour and structures through the different experimental techniques [1,2]. The methods consist of the measurements of high frequency (hf) conductivity [3], hf susceptibility [4], thermally stimulated depolarization current density (TSDC) [5], isothermal frequency domain of AC spectroscopy (IFDS) [6], etc. Although the latter two methods are very important as they provide one with the necessary information of dielectric relaxations, these methods are very lengthy and often needs a tedious computer simulation work in

comparison to the former methods. The hf conductivity or susceptibility measurement techniques are much simpler, straightforward and unique one within the framework of the Debye model [7] to give the firm answer to the problem with which the present research group is usually dealing with.

Straight chain alcohols behave almost like polymers in dispersion regions. The strong dipole of the -OH group rotates about the C=O bond without disturbing -CH₃ and -CH₂ groups. They thus have the possibility to exhibit intramolecular as well as intermolecular rotations. Glasser et al. [8] and Crossley et al. [9], however, measured the real ϵ_{ij}' , imaginary ϵ_{ij}'' , parts of hf complex relative permittivity ϵ_{ij}^* along with the static ϵ_{oij} and optical ϵ_{oij}' of relative permittivities of alcohols at 25 °C under different gigahertz electric field frequencies. As evident from Table 1, the

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Table 1
Measured relative permittivities ϵ'_{ij} , ϵ''_{ij} , ϵ_{oij} , $\epsilon_{a ij}$, real χ'_{ij} , imaginary χ''_{ij} parts of hf complex susceptibility χ^*_{ij} and low frequency susceptibility χ_{oij} of some dipolar alcohols at 25 °C for different weight fractions w_j of solutes under 24 GHz electric field in solvent *n*-heptane

Systems with mol. wt. (M_j) in kg (in <i>n</i> -heptane)	Weight fraction w_j of solute	ϵ'_{ij}	ϵ''_{ij}	ϵ_{oij}	$\epsilon_{a ij}$	χ'_{ij} (= $\epsilon'_{ij} - \epsilon_{a ij}$)	χ''_{ij} (= ϵ''_{ij})	χ_{oij} (= $\epsilon_{oij} - \epsilon_{a ij}$)
I. 1-butanol ($M_j=0.074$)	0.0291	1.9570	0.0079	1.9710	1.9280	0.0290	0.0079	0.0430
	0.0451	1.9810	0.0147	2.0000	1.9450	0.0360	0.0147	0.0550
	0.0697	2.0110	0.0236	2.0500	1.9580	0.0530	0.0236	0.0920
	0.1163	2.0600	0.0425	2.1750	1.9780	0.0820	0.0425	0.1970
	0.1652	2.1050	0.0644	2.3810	2.0000	0.1050	0.0644	0.3810
	0.2072	2.1440	0.0818	2.6210	2.0200	0.1240	0.0818	0.6010
II. 1-hexanol ($M_j=0.102$)	0.0458	1.9680	0.0131	1.9880	1.9440	0.0240	0.0131	0.0440
	0.0703	1.9840	0.0190	2.0150	1.9520	0.0320	0.0190	0.0630
	0.1028	2.0010	0.0296	2.0640	1.9700	0.0310	0.0296	0.0940
	0.1687	2.0370	0.0425	2.1960	1.9890	0.0480	0.0425	0.2070
	0.2335	2.0880	0.0569	2.3600	2.0020	0.0860	0.0569	0.3580
	0.2901	2.1340	0.0748	2.5800	2.0180	0.1160	0.0748	0.5620
III. 1-heptanol ($M_j=0.116$)	0.0564	1.9680	0.0147	1.9850	1.9320	0.0360	0.0147	0.0530
	0.0735	1.9750	0.0182	2.0080	1.9450	0.0300	0.0182	0.0630
	0.1175	2.0070	0.0265	2.0660	1.9570	0.0500	0.0265	0.1090
	0.1909	2.0760	0.0482	2.1950	1.9890	0.0870	0.0482	0.2060
	0.2465	2.0970	0.0567	2.3150	2.0020	0.0950	0.0567	0.3130
	0.2970	2.1260	0.0693	2.4640	2.0080	0.1180	0.0693	0.4560
IV. 1-decanol ($M_j=0.158$)	0.0572	1.9650	0.0120	1.9760	1.9400	0.0250	0.0120	0.0360
	0.0857	1.9790	0.0223	2.0030	1.9520	0.0270	0.0223	0.0510
	0.1351	2.0030	0.0273	2.0500	1.9640	0.0390	0.0273	0.0860
	0.2140	2.0360	0.0449	2.1470	1.9900	0.0460	0.0449	0.1570
	0.2640	2.0640	0.0513	2.2200	2.0080	0.0560	0.0513	0.2120
	0.3353	2.0970	0.0637	2.3460	2.0300	0.0670	0.0637	0.3160
V. 2-methyl 3-heptanol ($M_j=0.130$)	0.0437	1.9600	0.0156	1.9710	1.9300	0.0300	0.0156	0.0410
	0.1299	2.0220	0.0361	2.0590	1.9660	0.0560	0.0361	0.0930
	0.2522	2.0950	0.0565	2.1720	2.0070	0.0880	0.0565	0.1650
	0.4081	2.1690	0.0809	2.3300	2.0540	0.1150	0.0809	0.2760
VI. 3-methyl-3-heptanol ($M_j=0.130$)	0.0450	1.9650	0.0137	1.9740	1.9340	0.0310	0.0137	0.0400
	0.1334	2.0280	0.0393	2.0690	1.9660	0.0620	0.0393	0.1030
	0.2538	2.1030	0.0674	2.1800	2.0040	0.0990	0.0674	0.1760
	0.4085	2.1680	0.0928	2.3340	2.0570	0.1110	0.0928	0.2770
VII. 4-methyl-3-heptanol ($M_j=0.130$)	0.0466	1.9640	0.0146	1.9760	1.9360	0.0280	0.0146	0.0400
	0.1326	2.0250	0.0375	2.0650	1.9690	0.0560	0.0375	0.0960
	0.2590	2.1040	0.0616	2.1850	2.0110	0.0930	0.0616	0.1740
	0.4124	2.1800	0.0849	2.3520	2.0650	0.1150	0.0849	0.2870
VIII. 5-methyl-3-heptanol ($M_j=0.130$)	0.1228	2.0080	0.0296	2.0480	1.9560	0.0520	0.0296	0.0920
	0.2489	2.0750	0.0511	2.1680	2.0040	0.0710	0.0511	0.1640
	0.3898	2.1480	0.0676	2.3150	2.0400	0.1080	0.0676	0.2750
IX. 4-octanol ($M_j=0.130$)	0.1201	2.0000	0.0265	2.0400	1.9480	0.0520	0.0265	0.0920
	0.2445	2.0670	0.0449	2.1480	1.9970	0.0700	0.0449	0.1510
	0.3838	2.1400	0.0659	2.2820	2.0310	0.1090	0.0659	0.2510
	0.1236	2.0010	0.0245	2.0490	1.9540	0.0470	0.0245	0.0950
X. 2-octanol ($M_j=0.130$)	0.2479	2.0680	0.0513	2.1950	1.9960	0.0720	0.0513	0.1990
	0.3844	2.1410	0.0680	2.4100	2.0360	0.1050	0.0680	0.3740

available relative permittivities ϵ''_{ij} 's, if plotted against frequency ' f ', will show the sharp peak [10] at 24 GHz electric field frequency. At this resonance frequency, the alcohol molecules in the solvent *n*-heptane absorb electric energy much more to give exact and reliable values of relative permittivities. This at once suggests that the 24 GHz electric field frequency is the most effective dispersive region of such normal and octyl alcohols and prompted the present workers to study the physico-chemical aspects of long straight chain alcohols in terms of the hf susceptibilities χ'_{ij} , χ''_{ij} and χ_{oij} as the data are available only at 25 °C. The data are, however, collected in Table 1 upto four decimal places. The hf dielectric susceptibilities could, on the other hand, be

obtained by the subtraction of either 1 or the hf permittivity $\epsilon_{a ij}$ from the real part ϵ'_{ij} and static ϵ_{oij} relative permittivities. If 1 is subtracted, the susceptibilities due to all operating polarization processes result, while if $\epsilon_{a ij}$ is subtracted [11], the susceptibility due to only orientational polarization results. The imaginary part χ''_{ij} is numerically equal to ϵ''_{ij} as shown in Table 1.

The commercially available alcohols were dried over anhydrous calcium sulphate and fractionally distilled. The portions were collected with their known boiling points before use. The solvent *n*-heptane was dried over sodium wire prior to its use to make solution. The real ϵ'_{ij} and the imaginary ϵ''_{ij} parts of the hf complex relative permittivity ϵ^*_{ij} of the solutions were

measured by an apparatus as described elsewhere [9,11] with a Boonton RX meter corrected by a heterodyne beat method. The refractive index n_{Dij} (where $n_{Dij}^2 = \epsilon_{oij}$) of the solutions was measured by a Pulfrich refractometer using the sodium D line [11]. This may introduce some errors in the desired results. The weight fractions w_j 's are given by

$$\omega_j = \frac{f_j M_j}{f_i M_i + f_j M_j} \quad (1)$$

in terms of mole fractions f_j 's of all the alcohols are defined [12] as the weight of the solute per unit weight of the solution up to four decimal places in Table 1.

All the alcohols may be supposed to possess three relaxation times. They may be attributed to the rotation of -OH group, the orientational motion of the molecular species while the 3rd one is associated with the hydrogen bonded structures. All these long straight chain hydrogen bonded polymer type dipolar alcohol molecules have wide applications in the fields of biological research, medicine and industry. Moreover, they can be used as good solvents to clean the desired parts of the instruments, in lubrication chemistry, viscosity modifiers, in the preparation of emulsifying agents, waxes etc.

Bergmann et al. [13] proposed a graphical method to obtain τ_1 and τ_2 for a pure polar liquid. The respective weighted contributions c_1 and c_2 towards dielectric relaxations for τ_1 and τ_2 were also estimated. The single frequency measurement to get the double relaxation times is not a reliable one. Bhattacharyya et al. [14] subsequently attempted to get τ_1 , τ_2 and c_1 , c_2 for a polar liquid from the relative permittivity measurements at least at two different frequencies in the GHz range. The graphical analysis made by Higassi et al. [15] on polar–nonpolar liquid mixtures suffers from a crude approximation.

Saha et al. [16] and Sit et al. [17], however, advanced an analytical treatment to study the single frequency measurements of the double relaxation times τ_1 and τ_2 from the measured relative permittivities. The object of the present paper is to detect τ_1 and τ_2 and hence to measure μ_1 and μ_2 using χ_{ij} 's. The aspect of molecular orientational polarization is, however, achieved by χ_{ij} 's because ϵ_{oij} includes the fast polarization and it frequently appears as a subtracted term in Bergmann's equations [15]. Thus to avoid the clumsiness of algebra and to exclude the fast polarization, Bergmann's equations [13] are simplified by the established symbols of χ'_{ij} , χ''_{ij} and χ_{oij} of Table 1 in S.I. units, into the following forms:

$$\frac{\chi'_{ij}}{\chi_{oij}} = \frac{c_1}{1 + \omega^2 \tau_1^2} + \frac{c_2}{1 + \omega^2 \tau_2^2} \quad (2)$$

$$\frac{\chi''_{ij}}{\chi_{oij}} = c_1 \frac{\omega \tau_1}{1 + \omega^2 \tau_1^2} + c_2 \frac{\omega \tau_2}{1 + \omega^2 \tau_2^2} \quad (3)$$

assuming two broad Debye-type dispersions for which $c_1 + c_2 = 1$.

The Eqs. (2) and (3) are then solved to get:

$$\frac{\chi_{oij} - \chi'_{ij}}{\chi'_{ij}} = \omega(\tau_1 + \tau_2) \frac{\chi''_{ij}}{\chi'_{ij}} - \omega^2 \tau_1 \tau_2 \quad (4)$$

which is a linear equation between the variables $(\chi_{oij} - \chi'_{ij})/\chi'_{ij}$ and χ''_{ij}/χ'_{ij} having the intercept $-\omega^2 \tau_1 \tau_2$ and the slope $\omega(\tau_1 + \tau_2)$ as illustrated in Fig. 1 for all the alcohols.

The intercepts and slopes of all the alcohols were then used to get τ_1 and τ_2 for the flexible part and the whole molecular species with known $\omega (=2\pi f)$, where f being the frequency of the applied electric field, as presented in Table 2.

The real ϵ'_{ij} and imaginary ϵ''_{ij} parts of hf complex relative permittivity are related by

$$\epsilon'_{ij} = \epsilon_{oij} + \frac{1}{\omega \tau_j} \epsilon''_{ij} \quad (5)$$

as $\epsilon'_{ij} - \epsilon_{oij}$ and ϵ''_{ij} are numerically equal to real and imaginary parts of hf complex dimensionless di-electric orientational susceptibility χ_{ij}^* , respectively. So we get

$$\chi''_{ij} = (\omega \tau_j) \chi'_{ij} \quad (6)$$

which is clearly a straight line [18] between χ''_{ij} and χ'_{ij} ; the slope $\omega \tau_j$ can be used to get τ_j of a polar unit. But for associative liquids like normal and octyl alcohols under investigation the nature of variation of χ''_{ij} with χ'_{ij} is not strictly linear as seen in Fig. 2. Non-linear variation of both χ'_{ij} and χ''_{ij} with weight fractions, w_j 's, of the solute are

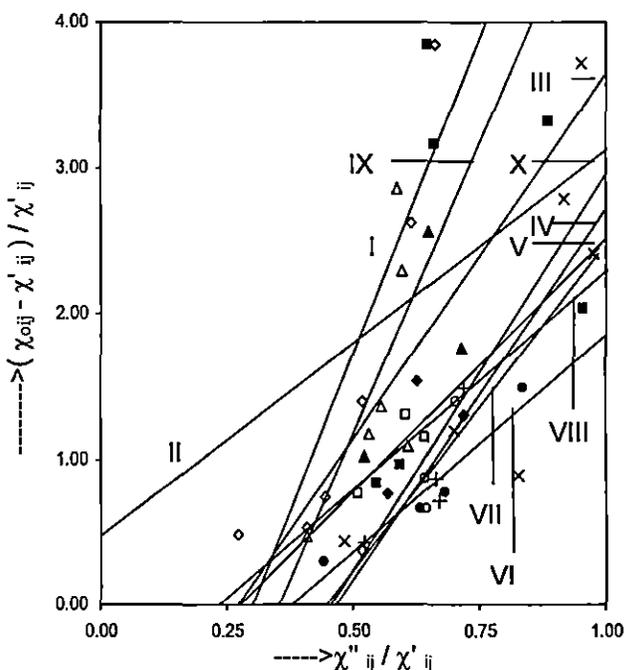


Fig. 1. Linear variation of $(\chi_{oij} - \chi'_{ij})/\chi'_{ij}$ with χ''_{ij}/χ'_{ij} for different long straight chain dipolar alcohols in *n*-heptane at 25 °C under 24 GHz electric field frequency: I. 1-butanol (-○-), II. 1-hexanol (-■-), III. 1-heptanol (-△-), IV. 1-decanol (-×-), V. 2-methyl-3-heptanol (-○-), VI. 3-methyl-3-heptanol (-●-), VII. 4-methyl-3-heptanol (-+-), VIII. 5-methyl-3-heptanol (-◆-), IX. 4-octanol (-□-), X. 2-octanol (-▲-).

Table 2
The relaxation times τ_1 and τ_2 , from the slope and intercept of the straightline Eq. (4), correlation coefficient r 's and % of error in regression technique, measured τ_j from the slope of χ''_{ij} vs χ'_{ij} of Eq. (7) and the ratio of the individual slopes of χ''_{ij} vs. w_j and χ'_{ij} vs. w_j at $w_j \rightarrow 0$ of Eq. (7), reported τ_s , symmetric and characteristic relaxation times τ_{cs} and τ_{cs} for different straight chain aliphatic alcohols in *n*-heptane under effective dispersive region of 24 GHz electric field at 25 °C

System with Sl. No.	Slope and intercept of Eq. (4)		Estimated τ_1 and τ_2 in ps		Correlation coefficient	% of error	τ_j from (Murthy et al.) and (ratio of individual slope)		Reported τ_s in ps	τ_{cs} in ps	τ_{cs} in ps
	Slope	Intercept	τ_1	τ_2							
I. 1-butanol ($M_j=0.074$)	8.66	2.60	2.04	54.56	0.90	5.17	4.95	3.42	2.47	0.98	15.41
II. 1-hexanol ($M_j=0.102$)	2.64	-0.47	-1.10	18.37	0.34	24.28	4.05	3.78	2.25	2.09	6.77
III. 1-heptanol ($M_j=0.116$)	7.99	2.83	2.46	50.49	0.68	14.98	4.12	4.23	2.07	1.97	10.46
IV. 1-decanol ($M_j=0.158$)	5.43	2.48	3.29	32.22	0.82	9.23	7.63	10.20	2.39	1.91	0.50
V. 2-methyl 3-heptanol ($M_j=0.130$)	5.05	2.37	3.42	29.61	0.90	6.34	4.92	4.34	1.86	2.11	4.58
VI. 3-methyl 3-heptanol ($M_j=0.130$)	3.00	1.14	2.91	16.68	0.96	2.33	6.06	4.30	2.26	1.65	5.29
VII. 4-methyl 3-heptanol ($M_j=0.130$)	4.39	1.97	3.31	25.38	0.89	7.30	5.12	4.38	1.95	2.19	8.07
VIII. 5-methyl 3-heptanol ($M_j=0.130$)	2.98	0.69	1.66	17.81	0.57	26.36	4.23	7.59	1.63	1.59	8.37
IX. 4-octanol ($M_j=0.130$)	3.48	0.96	1.97	20.75	0.86	10.34	4.36	4.33	1.68	1.62	15.40
X. 2-octanol ($M_j=0.130$)	5.02	1.37	1.89	30.94	0.63	23.30	4.82	15.91	1.93	2.33	37.08

presented graphically in Figs. 3 and 4, respectively. In such cases

$$\frac{(d\chi''_{ij}/dw_j)_{w_j \rightarrow 0}}{(d\chi'_{ij}/dw_j)_{w_j \rightarrow 0}} = \omega\tau_j \quad (7)$$

is a better representation [19] of the slope of Eq. (6) to get τ_j as it eliminates polar-polar interactions [20,21] in a given solution. τ_j 's from both Eqs. (6) and (7) are placed in Table 2 to compare them with those obtained by the freshly calculated Gopalakrishna's [22] method.

The weighted contributions c_1 and c_2 towards dielectric relaxation in terms of estimated τ_1 and τ_2 are, however, worked

out from Ffóhlich's [23] theoretical equations and given in Table 3 in order to compare them with the experimental ones obtained in terms of the intercepts of the variations of χ''_{ij}/χ_{oij} and χ'_{ij}/χ_{oij} with w_j 's of Figs. 5 and 6. Both χ''_{ij}/χ_{oij} and χ'_{ij}/χ_{oij} at $w_j=0$ together with the curve of $(1/\phi) \log \cos \phi$ against ϕ^0 as seen in Fig. 7 are used to get symmetric and asymmetric distribution parameters γ and δ and hence symmetric and characteristic relaxation times τ_s and τ_{cs} . Both τ_s and τ_{cs} are given in Table 2 and γ , δ are presented in Table 3.

The dipole moments μ_1 and μ_2 by hf susceptibility measurement technique are, however, estimated from linear coefficient β 's of χ''_{ij} vs. w_j curves of Fig. 3 along with the dimensionless parameters b_1 and b_2 involved with estimated τ_1

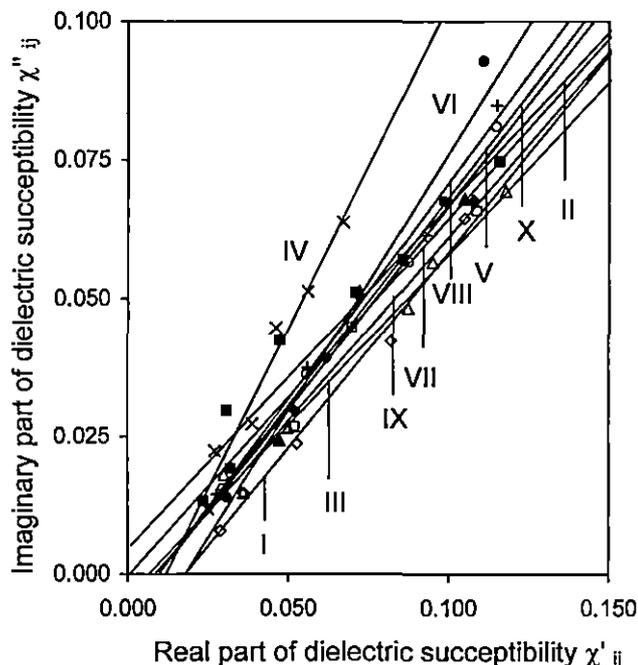


Fig. 2. Linear variation of imaginary part χ''_{ij} of hf dielectric susceptibility against real part χ'_{ij} for different long straight chain dipolar alcohols in *n*-heptane at 25 °C under 24 GHz electric field frequency: I. 1-butanol (○), II. 1-hexanol (■), III. 1-heptanol (△), IV. 1-decanol (×), V. 2-methyl-3-heptanol (○), VI. 3-methyl-3-heptanol (●), VII. 4-methyl-3-heptanol (+), VIII. 5-methyl-3-heptanol (●), IX. 4-octanol (□), X. 2-octanol (▲).

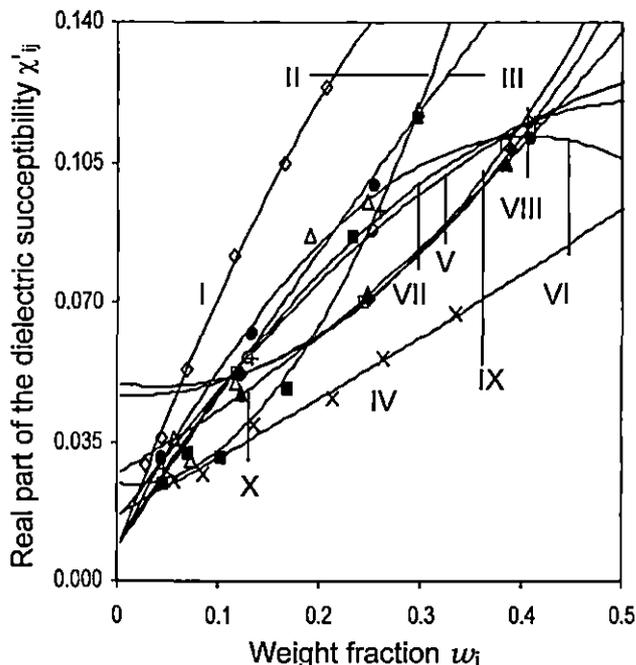


Fig. 3. Variation of real part χ'_{ij} of hf dielectric susceptibility with weight fraction w_j of some dipolar long straight chain alcohols in *n*-heptane at 25 °C under 24 GHz electric field frequency: I. 1-butanol (○), II. 1-hexanol (■), III. 1-heptanol (△), IV. 1-decanol (×), V. 2-methyl-3-heptanol (○), VI. 3-methyl-3-heptanol (●), VII. 4-methyl-3-heptanol (+), VIII. 5-methyl-3-heptanol (●), IX. 4-octanol (□), X. 2-octanol (▲).

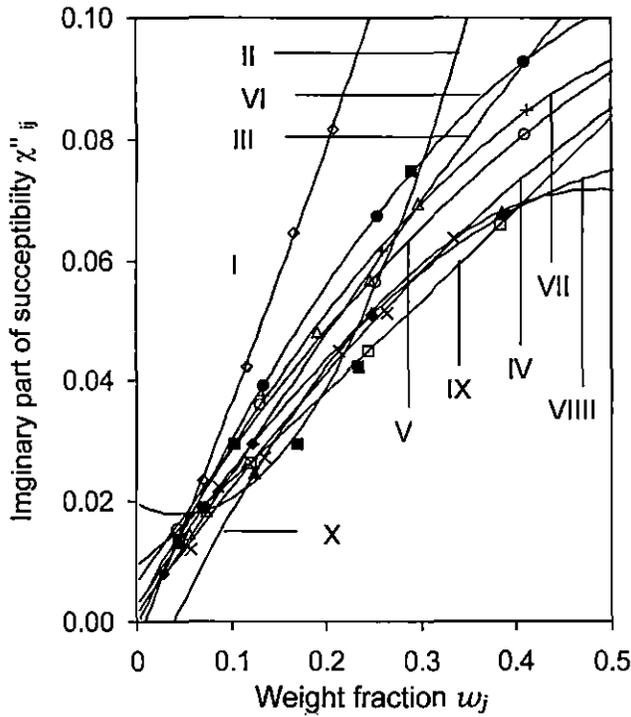


Fig. 4. Variation of imaginary part χ''_{ij} of hf dielectric susceptibility with weight fraction w_j of some dipolar long straight chain alcohols in *n*-heptane at 25 °C under 24 GHz electric field frequency: I. 1-butanol (-○-), II. 1-hexanol (-■-), III. 1-heptanol (-△-), IV. 1-decanol (-×-), V. 2-methyl-3-heptanol (-○-), VI. 3-methyl-3-heptanol (-●-), VII. 4-methyl-3-heptanol (-+-), VIII. 5-methyl-3-heptanol (-◆-), IX. 4-octanol (-□-), X. 2-octanol (-▲-).

and τ_2 of Table 2. The dipole moments μ_1 and μ_2 due to rotation of the flexible polar groups and end over end rotations of the whole molecule respectively are placed in Table 4 along with μ_{theo} 's and reported μ 's (Gopalakrishna) for comparison.

2. Weighted contributions c_1 and c_2 for estimated τ_1 and τ_2

Taking $\omega\tau_1 = \alpha_1$ and $\omega\tau_2 = \alpha_2$ and solving Eqs. (2) and (3) yields

$$c_1 = \frac{(\chi''_{ij}\alpha_2 - \chi''_{ij}) (1 + \alpha_1^2)}{\chi_{oij}(\alpha_2 - \alpha_1)} \quad (8)$$

Table 3
Fröhlich's parameter A , theoretical and experimental values of χ'_i/χ_{oij} and χ''_i/χ_{oij} of Fröhlich Eqs. ((10) and (11)) and from fitting curves of Figs. 5 and 6 at $w_j \rightarrow 0$, respectively, theoretical and experimental relative contributions c_1 and c_2 towards dielectric dispersion due to τ_1 and τ_2 symmetric and asymmetric distribution parameters γ and δ for some straight chain aliphatic alcohols in solvent *n*-heptane under effective dispersive region of 24 GHz electric field at 25 °C

Systems with Sl. No.	$A = \ln(\tau_2/\tau_1)$	Theoretical values of χ'_i/χ_{oij} and χ''_i/χ_{oij} from Eqs. (10) and (11)		Theoretical values of c_1 and c_2		Experimental values of χ'_i/χ_{oij} and χ''_i/χ_{oij} at $w_j \rightarrow 0$ of Figs. 5 and 6		Experimental values of c_1 and c_2		Estimated values of γ and δ	
		χ'_i/χ_{oij}	χ''_i/χ_{oij}	c_1	c_2	χ'_i/χ_{oij}	χ''_i/χ_{oij}	c_1	c_2	γ	δ
I. 1-butanol	3.286	0.366	0.350	0.370	2.069	0.799	0.195	0.884	-0.474	0.357	0.21
II. 1-hexanol	-	-	-	-	-	0.740	0.348	0.598	1.412	0.128	0.55
III. 1-heptanol	3.023	0.347	0.359	0.358	1.878	0.721	0.298	0.816	0.247	0.230	0.39
IV. 1-decanol	2.281	0.341	0.396	0.364	1.283	0.870	0.404	1.100	-0.193	-0.079	2.49
V. 2-methyl 3-heptanol	2.157	0.345	0.404	0.369	1.198	0.776	0.386	0.995	-0.107	0.041	0.76
VI. 3-methyl 3-heptanol	1.746	0.474	0.446	0.435	0.837	0.814	0.319	1.000	-0.157	0.099	0.55
VII. 4-methyl 3-heptanol	2.036	0.374	0.417	0.386	1.084	0.729	0.358	0.920	-0.051	0.121	0.51
VIII. 5-methyl 3-heptanol	2.371	0.564	0.409	0.486	0.906	0.782	0.287	0.794	0.302	0.189	0.39
IX. 4-octanol	2.353	0.508	0.413	0.455	1.003	0.731	0.243	0.789	0.086	0.328	0.27
X. 2-octanol	2.797	0.451	0.387	0.426	1.351	0.683	0.193	0.741	-0.023	0.477	0.20

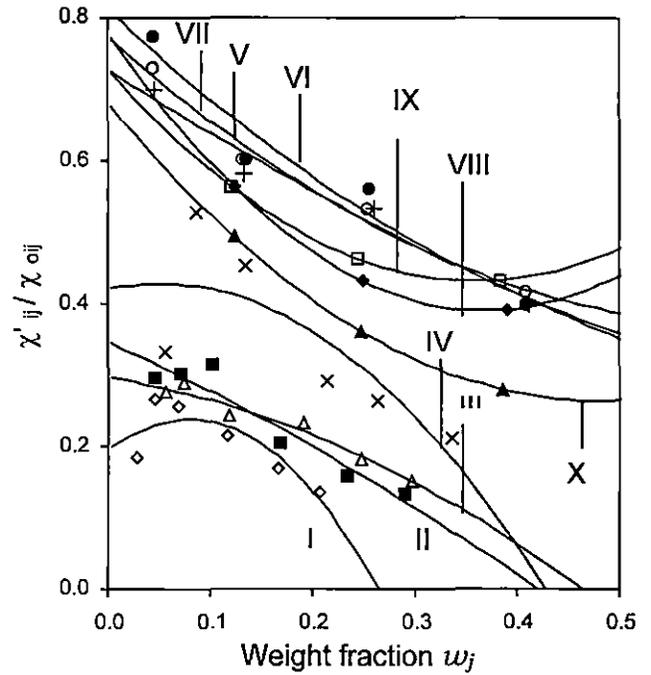


Fig. 5. Plot of χ'_i/χ_{oij} against weight fraction w_j of some dipolar long straight chain alcohols in *n*-heptane at 25 °C under 24 GHz electric field frequency: I. 1-butanol (-○-), II. 1-hexanol (-■-), III. 1-heptanol (-△-), IV. 1-decanol (-×-), V. 2-methyl-3-heptanol (-○-), VI. 3-methyl-3-heptanol (-●-), VII. 4-methyl-3-heptanol (-+-), VIII. 5-methyl-3-heptanol (-◆-), IX. 4-octanol (-□-), X. 2-octanol (-▲-).

and

$$c_2 = \frac{(\chi''_{ij} - \chi''_{ij}\alpha_1) (1 + \alpha_2^2)}{\chi_{oij}(\alpha_2 - \alpha_1)} \quad (9)$$

provided that $\alpha_2 > \alpha_1$. c_1 and c_2 are estimated from known τ_1 and τ_2 by the double relaxation method. c_1 and c_2 can also be obtained with the known values of χ'_i/χ_{oij} and χ''_i/χ_{oij} from Fröhlich's following theoretical equations [23] with known τ_1 and τ_2 from Eqs. (2) and (3).

$$\frac{\chi'_i}{\chi_{oij}} = 1 - \frac{1}{2A} \ln \left[\frac{1 + \omega^2\tau_2^2}{1 + \omega^2\tau_1^2} \right] \quad (10)$$

$$\frac{\chi''_i}{\chi_{oij}} = \frac{1}{A} [\tan^{-1}(\omega\tau_2) - \tan^{-1}(\omega\tau_1)] \quad (11)$$

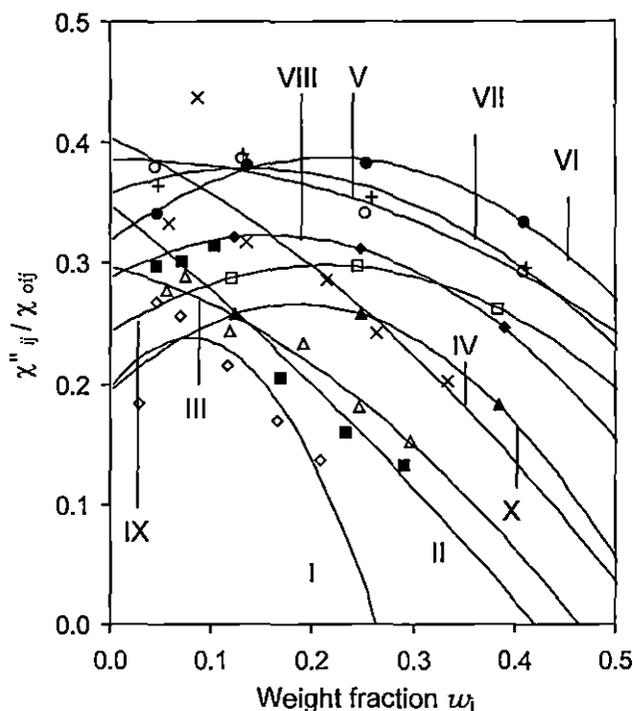


Fig. 6. Plot of χ''_{ij}/χ_{oij} against weight fraction w_j of some dipolar long straight chain alcohols in *n*-heptane at 25 °C under 24 GHz electric field frequency: I. 1-butanol (-○-), II. 1-hexanol (-■-), III. 1-heptanol (-△-), IV. 1-decanol (-×-), V. 2-methyl-3-heptanol (-○-), VI. 3-methyl-3-heptanol (-●-), VII. 4-methyl-3-heptanol (-+-), VIII. 5-methyl-3-heptanol (-◆-), IX. 4-octanol (-□-), X. 2-octanol (-▲-).

c_1 and c_2 thus estimated are placed in Table 3 for comparison with those worked out from the intercept of the fitted polynomial plots of χ'_{ij}/χ_{oij} and χ''_{ij}/χ_{oij} against w_j curves of Figs. 5 and 6. Fäöhlich's parameter A for each system is also placed in the same table.

3. Formulations for symmetric and characteristic relaxation times and also symmetric and asymmetric distribution parameter

The molecules under investigation appear to behave like nonrigid ones under 24 GHz electric field frequency having either symmetric or asymmetric relaxation behaviour characterized by either symmetric τ_s and characteristic τ_{cs} relaxation times involved with the following equations:

$$\frac{\chi_{ij}^*}{\chi_{oij}} = \frac{1}{1 + (j\omega\tau_s)^{1-\gamma}} \quad (12)$$

$$\frac{\chi_{ij}^*}{\chi_{oij}} = \frac{1}{(1 + j\omega\tau_{cs})^\delta} \quad (13)$$

separating the real and imaginary parts of the above equations and rearranging them in terms of intercepts viz. $(d\chi'_{ij}/dw_j)_{w_j=0}$ and $(d\chi''_{ij}/dw_j)_{w_j=0}$ of the graphically fitted plots of Figs. 5 and 6 one gets γ and τ_s as:

$$\gamma = \frac{2}{\pi} \tan^{-1} \left[\left(1 - \frac{\chi'_{ij}}{\chi_{oij}} \right) \frac{\chi'_{ij}/\chi_{oij}}{\chi''_{ij}/\chi_{oij}} - \frac{\chi''_{ij}}{\chi_{oij}} \right] \quad (14)$$

$$\tau_s = \frac{1}{\omega} \left[\frac{1}{\left\{ \left(\chi'_{ij}/\chi_{oij} \right) / \left(\chi''_{ij}/\chi_{oij} \right) \cos(\gamma\pi/2) - \sin(\gamma\pi/2) \right\}^{1/\gamma}} \right] \quad (15)$$

Similarly, δ and τ_{cs} can be evaluated from Eq. (13):

$$\tan(\phi\delta) = \frac{\left(\chi''_{ij}/\chi_{oij} \right)_{w_j=0}}{\left(\chi'_{ij}/\chi_{oij} \right)_{w_j=0}} \quad (16)$$

and

$$\tan\phi = \omega\tau_{cs} \quad (17)$$

since ϕ can not be estimated directly, a theoretical curve between $(1/\phi) \log \cos\phi$ against ϕ in degrees has been drawn in Fig. 7. The value of $(1/\phi) \log \cos\phi$ can be estimated from the following relation

$$(1/\phi) \log \cos\phi = \log \left[\frac{\chi'_{ij}/\chi_{oij}}{\cos\phi\delta} \right] / \phi\delta. \quad (18)$$

The known value of $(1/\phi) \log \cos\phi$ is used to get ϕ from the curve. With the known ϕ , Eqs. (16) and (17) were used to obtain δ and τ_{cs} . Estimated τ_s and τ_{cs} are placed in Table 2 to compare with τ_j 's obtained by ratio of slopes of individual variations of χ'_{ij} and χ''_{ij} with w_j , τ_j 's by the method of Murthy et al. [18], reported τ_j (Gopalakrishna) and τ_1 and τ_2 by the double relaxation method. Also γ and δ are shown in Table 3.

4. Theoretical formulations to obtain hf dipole moment μ_j

The imaginary part χ''_{ij} of hf complex χ_{ij}^* is [4,20,24]

$$\chi''_{ij} = \frac{N\rho_{ij}\mu_j^2}{27\varepsilon_0 M_j k_B T} \frac{\omega\tau_j}{(1 + \omega^2\tau_j^2)} (\varepsilon_{ij} + 2)^2 w_j \quad (19)$$

which on differentiation with respect to w_j and at $w_j=0$ yields that

$$\left(\frac{d\chi''_{ij}}{dw_j} \right)_{w_j=0} = \frac{N\rho_{ij}\mu_j^2}{27\varepsilon_0 M_j k_B T} \frac{\omega\tau_j}{(1 + \omega^2\tau_j^2)} (\varepsilon_{ij} + 2)^2 w_j \quad (20)$$

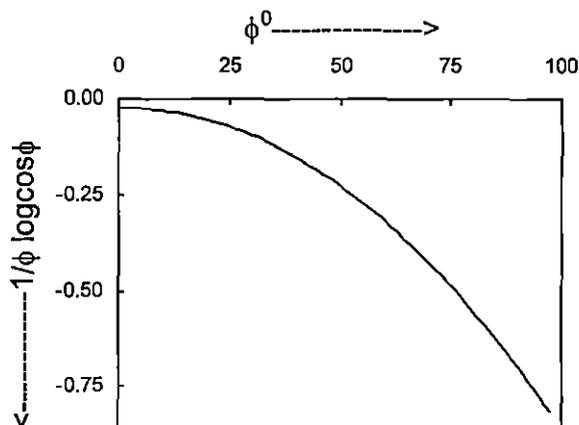


Fig. 7. Variation of $(1/\phi) \log(\cos\phi)$ against ϕ^0 .

Table 4

Linear coefficient β of χ'_{ij} vs. w_j curves of Fig. 3, dimensionless parameters b_1, b_2 from τ_1 and τ_2 of Eq. (4), correlation coefficient and % of error of $\chi'_{ij}-w_j$ estimated dipole moment μ_1, μ_2 from Eq. (22), computed dipole moment μ_j from τ_j of Eq. (7), reported dipole moment (Gopalakrishna's method), all are expressed in C m for different straight chain alcohols in solvent *n*-heptane at 25 °C under 24 GHz electric field

Systems with SI. No. and mol. wt. M_j in kg mol ⁻¹ (in <i>n</i> -heptane)	Linear coefficients of χ'_{ij} vs. w_j curves of Fig. 3 β	Dimensionless parameters		Correlation coefficients of $\chi'_{ij}-w_j$	% of errors	Estimated dipole moments $\mu \times 10^{30}$ in C m			Reported $\mu \times 10^{30}$ in C m Gopalakrishna's method	$\mu_{theo}^a \times 10^{30}$ in C m
		b_1	b_2			μ_1	μ_2	μ_j		
I. 1-butanol ($M_j=0.074$)	0.719	0.911	0.014	0.997	0.00003	3.02	24.25	3.26	3.58	3.74
II. 1-hexanol ($M_j=0.102$)	0.371	0.973	0.112	0.969	0.00037	2.47	7.25	2.81	3.35	3.49
III. 1-heptanol ($M_j=0.116$)	0.392	0.879	0.017	0.987	0.00015	2.84	20.49	3.16	3.59	3.73
IV. 1-decanol ($M_j=0.158$)	0.142	0.798	0.040	0.994	0.00007	2.10	9.43	3.47	3.55	3.68
V. 2-methyl 3-heptanol ($M_j=0.130$)	0.359	0.785	0.047	0.998	0.00003	3.05	12.53	3.24	1.33	1.86
VI. 3-methyl 3-heptanol ($M_j=0.130$)	0.508	0.835	0.133	0.985	0.00023	3.52	8.81	3.85	1.18	2.11
VII. 4-methyl 3-heptanol ($M_j=0.130$)	0.429	0.796	0.062	0.996	0.00006	3.31	11.83	3.55	3.42	1.95
VIII. 5-methyl 3-heptanol ($M_j=0.130$)	0.211	0.939	0.119	0.967	0.00056	2.14	6.01	3.17	3.54	1.39
IX. 4-octanol ($M_j=0.130$)	0.217	0.917	0.090	0.985	0.00025	2.20	7.00	2.52	3.48	1.11
X. 2-octanol ($M_j=0.130$)	0.143	0.923	0.043	0.977	0.00038	1.78	8.25	4.49	3.24	1.45

^a Ghosh et al. [10].

From Eqs. (7) and (19) one obtains

$$\omega\tau_j(d\chi'_{ij}/dw_j)_{w_j \rightarrow 0} = \frac{N\rho_i\mu_j^2}{27\varepsilon_0M_jk_B T} \frac{\omega\tau_j}{(1+\omega^2\tau_j^2)}(\varepsilon_i+2)^2 \quad (21)$$

or

$$\omega\tau_j\beta = \frac{N\rho_i\mu_j^2}{27\varepsilon_0M_jk_B T} \frac{\omega\tau_j}{(1+\omega^2\tau_j^2)}(\varepsilon_i+2)^2$$

or

$$\mu_j = \left[\frac{27\varepsilon_0M_jk_B T\beta}{N\rho_i(\varepsilon_i+2)^2b} \right]^{1/2} \quad (22)$$

where

- ε_0 =Permittivity of free space= 8.854×10^{-12} F m⁻¹
- M_j =Molecular weight of solute in kg mol⁻¹
- k_B =Boltzmann constant= 1.38×10^{-23} J k⁻¹
- T =Temperature in K
- $\beta=(d\chi'_{ij}/dw_j)_{w_j \rightarrow 0}$ =Linear coefficient of $\chi'_{ij}-w_j$ curve of Fig. 5 at $w_j \rightarrow 0$
- N =Avogadro's number= 6.023×10^{23} mol⁻¹
- ρ_i =Density of solvent *n*-heptane= 680.15 kg m⁻³
- ε_i =Dielectric relative permittivity of the solvent= 1.917
- $b=1/(1+\omega^2\tau_j^2)$ =a dimensionless parameter involved with estimated τ_j .

When $j=1$ and 2 the dipole moments μ_1 and μ_2 associated with rotation of flexible polar groups and rotation of the whole molecules are evaluated in terms of b_1 and b_2 involved with τ_1 and τ_2 and are placed in Table 4 to compare them with μ_{theo} 's and reported μ 's (Gopalakrishna).

5. Results and discussion

The least squares fitted straight line equations: $(\chi_{oij}-\chi'_{ij})/\chi'_{ij}=\omega(\tau_1+\tau_2)\chi''_{ij}/\chi'_{ij}-\omega^2\tau_1\tau_2$ have been shown graphically in Fig. 1 for some normal and octyl alcohols with the symbols showing the experimental points in the solvent *n*-heptane at 25 °C under 24 GHz electric field frequency. The real χ'_{ij} and imaginary parts χ''_{ij} of hf complex dimensionless dielectric orientational susceptibility χ_{ij}^* and static or low frequency real dielectric susceptibility χ_{oij} have been derived from the measured relative permittivities [8,9] $\varepsilon'_{ij}, \varepsilon''_{ij}, \varepsilon_{oij}$ and ε_{oij} . They are carefully collected in Table 1. The slopes and intercepts of Eq. (4) used to get τ_1 and τ_2 are placed in the 2nd and 3rd columns of Table 2 along with the estimated τ_1 and τ_2 in the 4th and 5th columns. Correlation coefficients (r) and % of errors of curves of Fig. 1 have been calculated and are placed in the 6th and 7th columns of Table 2 only to show how far the variables $(\chi_{oij}-\chi'_{ij})/\chi'_{ij}$ and χ''_{ij}/χ'_{ij} are correlated with each other. It is seen that ' r ' is very low and corresponding % of errors is very high for 5-methyl 3-heptanol and 2-octanol, which may be probably due to errors introduced in their permittivity ε_{ij} measurements. This fact is further confirmed by remarkable deviations of experimental points from the fitted linear curves as seen in Fig. 1.

In absence of reliable τ_j values, the slopes of the linear curves [18] of Fig. 2 of the variables χ''_{ij} and χ'_{ij} are utilized to get τ_j . But for associative liquids like normal and octyl alcohols, the variation of χ''_{ij} against χ'_{ij} is not strictly linear as seen in Fig. 2. Under such context, the ratio of the slopes of individual variations of both χ'_{ij} and χ''_{ij} with w_j 's is a better representation [20,21] of the method of Murthy et al. [18] as it eliminates polar-polar interactions in a given solution [4]. τ_j 's estimated so far by this method are entered in the 9th column of

Table 2 along with τ_j 's due to the method of Murthy et al. and reported ones as seen in the 8th and 10th columns. Nonlinear variation of both χ_{ij}^I and χ_{ij}^{II} against w_j 's as seen in Figs. 3 and 4 arises due to solute–solvent and solute–solute molecular associations which is supposed to be a physico-chemical property [21] of the solutes under consideration. Symmetric and characteristic relaxation times τ_s and τ_{cs} estimated from Eqs. (15) and (17), respectively, in terms of γ and δ are seen in the 11th and 12th column of Table 2. It is observed that in comparison to τ_{cs} , τ_s is the same order of magnitude of τ_j 's from Eq. (7) and reported (Gopalakrishna) ones. This fact at once establishes the very basic soundness of our method [20,21] employed to get hf τ_j and also the symmetric relaxation behaviour [19] obeyed by the molecules. Larger τ_2 values arise for bigger size of rotating units $\tau_j T / \eta \gamma$ due to solute–solvent and solute–solute molecular associations, supposed to be

physico-chemical property of the solutes which is further supported by non linear variations of both χ_{ij}^I and χ_{ij}^{II} with w_j 's as seen in Figs. 3 and 4.

The theoretical weighted contributions c_1 and c_2 towards dielectric relaxations from Eqs. (8) and (9) are, however, worked out with χ_{ij}^I/χ_{oij} and $\chi_{ij}^{II}/\chi_{oij}$ values of Eqs. (10) and (11) and also with estimated τ_1 and τ_2 of Table 2. They are placed in the 5th and 6th columns of Table 3 in order to compare them with the experimental c_1 and c_2 estimated in terms of $(\chi_{ij}^I/\chi_{oij})_{w_j=0}$ and $(\chi_{ij}^{II}/\chi_{oij})_{w_j=0}$ of the graphically fitted plots of Figs. 5 and 6 and are placed in the 9th and 10th columns. Theoretical c 's for 1 hexanol could not be estimated as τ_1 is found to be negative probably due to errors [19] in the measurement of ϵ_{ij}^I , ϵ_{ij}^{II} , ϵ_{oij} and ϵ_{oij} . Both theoretical and experimental c_1 and c_2 shows that $c_1 + c_2 \approx 1$, which confirms the validity of Eq. (4) to get τ_1 and τ_2 . It is seen that for some systems experimental c_2 is

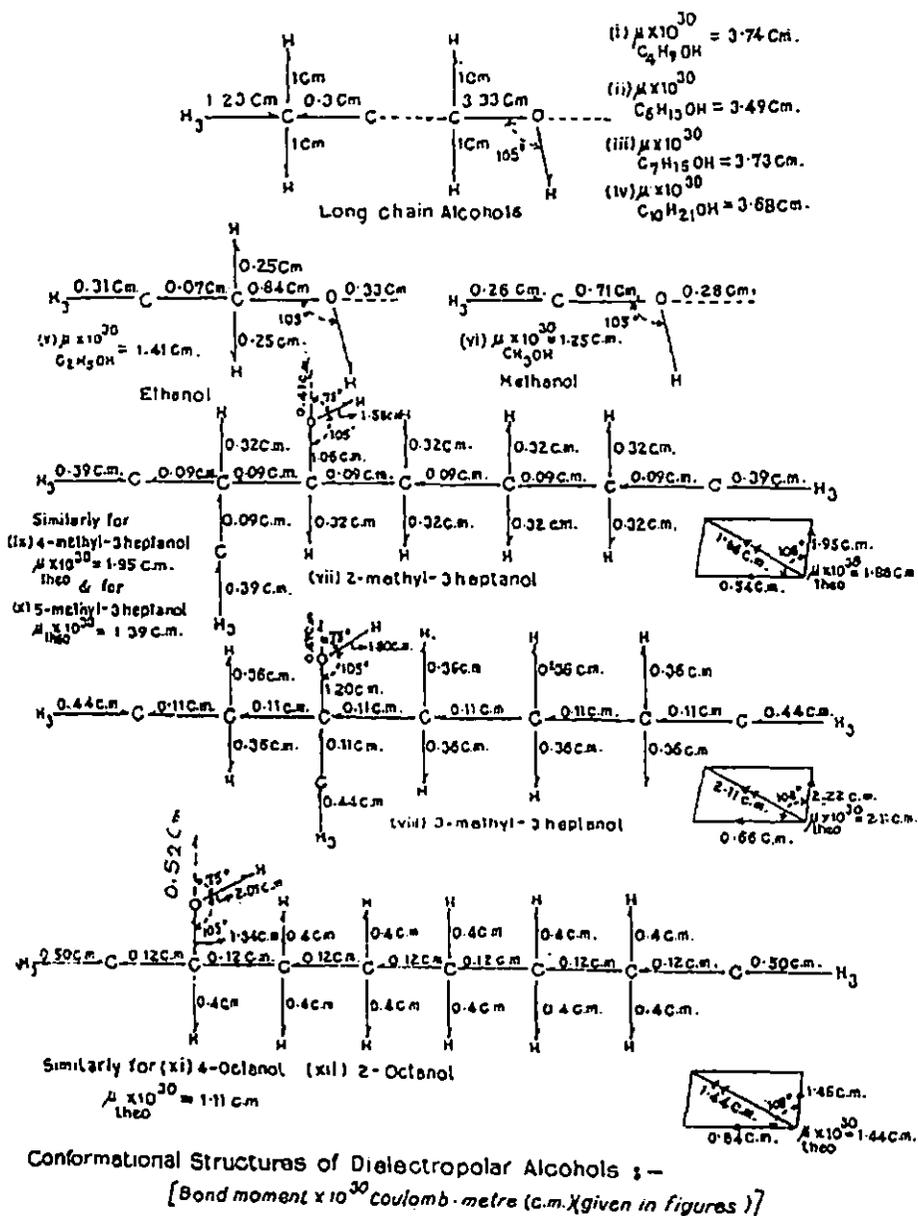


Fig. 8. Conformational structures of dielectropolar alcohols (theoretical dipole moments μ_{theo} from bond angles and reduced bond moments).

negative. This can, however, be explained on the basis of the fact that internal hydrogen bonding among –OH groups in dipolar alcohol molecules gives rise to inertia [25] of the flexible polar groups with respect to the whole molecule. Solute–solvent and solute–solute molecular interaction being a physicochemical aspect is also supported by slight deviations of experimental points from the curves of Figs. 5 and 6.

The dipole moments μ_1 and μ_2 of the flexible polar groups and the whole molecules were estimated in terms of dimensionless parameters b_1 and b_2 involved with estimated τ_1 and τ_2 and linear coefficient β of $\chi'_{ij}-w_j$ curves of Fig. 3. They are entered in the 5th and 6th columns of Table 4 to compare them with μ_j 's estimated with τ_j 's of Eq. (7), reported μ 's due to Gopalakrishna [22] and theoretical μ 's obtained with available bond angles and bond moments of the polar groups assuming the molecules to be planar ones, sketched here. Correlation coefficients r 's and % of errors of $\chi'_{ij}-w_j$ curves of Fig. 3 were made from by careful regression analysis of the measured data, are seen in the 5th and 6th columns of Table 4 only to suggest how far the variables $\chi'_{ij}-w_j$ are correlated with each other. Almost all the $\chi'_{ij}-w_j$ curves show a tendency to be closer within the range $0.00 \leq w_j \leq 0.10$, which is due to equal polarity [4,25] of the molecules in addition to solute–solvent and solute–solute molecular interaction which is assumed to be physico-chemical behaviour [20,21] of the solutes in *n*-heptane. The close agreement of the estimated μ_1 and μ_2 with reported (Gopalakrishna) and theoretical μ 's establishes the very basic soundness of the present method to get hf μ_j 's in addition to the fact that a part of the molecule is rotating under GHz electric field [19]. It is seen that estimated μ_1 and μ_j 's are lower than those of μ_{theo} 's for normal alcohols while the reverse is true in octyl alcohols. It is probably due to the fact that strong hydrogen bonding among –OH groups in normal alcohols (1-butanol, 1-hexanol, 1-heptanol and 1-decanol) offers higher resistance due to –OH groups to rotate under hf electric field to give lower μ_1 and μ_j values. In octyl alcohols hydrogen, on the otherhand, bonding between –OH groups is not so strong giving μ_1 's and μ_j 's higher than that of μ_{theo} 's as they are screened by a large number of –CH₃ and –CH₂ groups. The conformations are presented in Fig. 8 in excellent agreement of the measured values in order to account of the mesomeric and electromeric effects of the substituted polar groups in alcohols by multiplying available bond moments by a factor μ_s/μ_{theo} where μ_s is the low frequency or static dipole moment estimated elsewhere [10].

6. Conclusion

Theoretical formulations developed so far in SI units within the frame work of the Debye-Smyth model appear to be the simpler straightforward and topical ones to get the many interesting equations which are worked out in terms of χ'_{ij} 's. They are useful to explain various physico-chemical aspects of several dipolar alcohol molecules in solvent *n*-heptane at 25 °C under 24 GHz (Q-band microwave) electric field frequency. The derived straight line Eq. (4) has significant contribution in the field of dielectric relaxation

as it gives microscopic τ_1 and macroscopic τ_2 due to both rotations of the flexible polar groups and the whole molecule while Eq. (7) gives microscopic τ only [20,21]. Both theoretical and graphical experimental c_1 and c_2 confirm the validity of Eq. (4). As seen in Table 3 $c_1+c_2 \approx 1$ is due to the fact that under 24 GHz electric field the rotations of the straight chained molecules are influenced by the moment of inertia of the flexible groups attached to the parent ones. $\epsilon_{\alpha ij} \approx 1 - 1.5n_{Dij}^2$. But $\epsilon_{\alpha ij} \approx n_{Dij}^2$ may introduce some errors in getting τ_1 and τ_2 and c_1 and c_2 also. Correlation coefficients r 's and % of errors between several variables involved in the curves of Figs. 1 and 3 are worked out only to establish the statistical validity [20,21] of Eq. (4) and χ'_{ij} vs. w_j equations. The close agreement of estimated relaxation parameters viz. τ 's and μ 's with the reported ones confirms the very basic soundness of the theoretical formulations so far developed. The physico-chemical properties of the systems are, however, inferred in terms of solute–solvent (monomer) and solute–solute (dimer) associations as supported by slight deviations of measured parameters from their reported and standard values and also observed by deviation of experimental points from the fitted polynomial plots of several figures.

References

- [1] N. Paul, K.P. Sharma, S. Chattoadhyay, Indian J. Phys. 71B (1997) 71.
- [2] S.N. Sen, R. Ghosh, J. Phys. Soc. Jpn. 33 (1972) 838.
- [3] K. Dutta, R.C. Basak, S.K. Sit, S. Acharyya, J. Mol. Liq. 88 (2000) 229.
- [4] N. Ghosh, S.K. Sit, A.K. Bothra, S. Acharyya, J. Phys., D, Appl. Phys. (UK) 34 (2001) 379.
- [5] M.D. Migahed, M.T. Ahmed, A.E. Kolp, J. Phys., D, Appl. Phys. 33 (2000) 2108.
- [6] A. Bello, E. Laredo, M. Girman, A. Nogales, T.A. Ezqrearra, J. Chem. Phys. 133 (2000) 863.
- [7] P. Debye, 'Polar Molecules' (Chemical Catalogue) 1929
- [8] L. Glasser, J. Crossley, C.P. Smyth, J. Chem. Phys. 57 (1972) 3977.
- [9] J. Crossley, L. Glasser, C.P. Smyth, J. Chem. Phys. 55 (1971) 2197.
- [10] N. Ghosh, A. Karmakar, S.K. Sit, S. Acharyya, Indian J. Pure Appl. Phys. 38 (2000) 574.
- [11] S.K. Garg, C.P. Smyth, J. Phys. Chem. 69 (1965) 1294.
- [12] A.K. Ghosh, S. Acharyya, Indian J. Phys. 52B (1978) 129.
- [13] K. Bergmann, D.M. Roberti, C.P. Smyth, J. Phys. Chem. 64 (1960) 665.
- [14] J. Bhattacharyya, A. Hasan, S.B. Roy, G.S. Kastha, J. Phys. Soc. Jpn. 28 (1970) 204.
- [15] K. Higasi, Y. Koga, M. Nakamura, Bull. Chem. Soc. Jpn. 44 (1971) 988.
- [16] U. Saha, S.K. Sit, R.C. Basak, S. Acharyya, J. Phys., D, Appl. Phys. (UK) 27 (1994) 596.
- [17] S.K. Sit, R.C. Basak, U. Saha, S. Acharyya, J. Phys., D, Appl. Phys. (UK) 27 (1994) 2194.
- [18] M.B.R. Murthy, R.L. Patil, D.K. Deshpande, Indian J. Phys. 63B (1989) 491.
- [19] N. Ghosh, S.K. Sit, S. Acharyya, J. Mol. Liq. 102 (2003) 29.
- [20] U.K. Mitra, N. Ghosh, P. Ghosh and S. Acharyya, Pramana J. Phys. (communicated) 2004.
- [21] A. Karmakar, U.K. Mitra, N. Ghosh and S. Acharyya, J. Phys., D, Appl. Phys. (UK) (communicated) 2004.
- [22] K.V. Gopalakrishna, Trans. Faraday Soc. 53 (1957) 767.
- [23] H. Fröhlich, Theory of Dielectrics, Oxford University Press, Oxford, 1949.
- [24] C.P. Smyth, Dielectric Behaviour and Structure, McGraw Hill, New York, 1955.
- [25] S.K. Sit, N. Ghosh, S. Acharyya, Indian J. Pure Appl. Phys. 35 (1997) 329.

Studies on physico-chemical properties with the relaxation phenomena of some normal aliphatic alcohols in non polar solvent under Giga Hertz electric field at a single temperature

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Manuscript received 23 March 2006, revised 7 November 2006, accepted 16 November 2006

Abstract : Double relaxations of some normal aliphatic alcohols have been studied to get relaxation times τ_1 and τ_2 due to rotation of flexible part and end over end rotation of the whole molecule from the intercept and slope of a linear equation of $(\chi_{oij} - \chi'_{ij})/\chi'_{ij}$ against χ''_{ij}/χ'_{ij} for different weight fractions w_j 's of solute in *n*-heptane at 25 °C under electric field frequencies of 24.33, 9.25 and 3.00 GHz. Alcohols like 1-butanol, 1-hexanol, 1-heptanol and 1-decanol are long straight chain hydrogen bonded polymer type molecules having -OH groups which may bend twist or rotate internally about C-C bond under GHz electric field exhibiting characteristic τ . Estimated τ_j obtained from ratio of slopes of individual variation of χ''_{ij} and χ'_{ij} against w_j at $w_j \rightarrow 0$ are compared with those of Murthy *et al.*, Gopalakrishna (reported data) and τ_1, τ_2 by double relaxation method. Relative contributions c_1 and c_2 due to τ_1 and τ_2 towards dielectric relaxations estimated from Fröhlich's equations are compared with the experimental ones obtained by graphical technique. Graphical variations of χ'_{ij}/χ_{oij} and χ''_{ij}/χ_{oij} with w_j at $w_j=0$ together with arbitrary curve of $(1/\phi) \log(\cos \phi)$ against ϕ in degree have been utilised to get symmetric γ and asymmetric δ distribution parameters. The symmetric relaxation time τ_s by γ and characteristic relaxation time τ_{cs} by δ and ϕ are computed to suggest symmetric relaxation behaviour of the molecules. Linear coefficient β 's of $\chi'_{ij} - w_j$ curves and dimensionless parameters b_1 and b_2 involved with estimated τ_1 and τ_2 are used to get dipole moments μ_1 and μ_2 due to rotation of flexible part and the whole molecule which are compared with reported μ 's (Gopalakrishna) and μ_{theo} 's. The slight disagreement between μ_j and μ_{theo} obtained from available bond angles and reduced bond moments of substituent polar groups attached to parent molecules arises due to strong internal hydrogen bonds present among the -OH groups of dipolar liquid molecules.

Keywords : Relaxation, aliphatic alcohol, non-polar solvent.

Relaxation mechanism of polar molecules in non polar solvents under high frequency electric field is of special interest as it provides one with useful tool to study structural configuration and molecular associations in the formation of monomer¹ and dimer^{2,3} through measured relaxation parameters like relaxation time τ and dipole moment μ obtained by any conventional method^{4,5}. The technique also gives valuable information regarding stability or unstability⁶ of the systems undergoing relaxation phenomena. Also τ_j obtained from the ratio of slopes of individual variations of $\chi''_{ij} - w_j$ and $\chi'_{ij} - w_j$ are conveniently used to shed more light on structural and associational aspects⁷ in addition to physico-chemical properties of the polar molecules.

Glasser *et al.*⁸ measured the real ϵ'_{ij} and imaginary ϵ''_{ij} parts of complex hf dielectric relative permittivity ϵ^*_{ij} together with static and hf relative permittivity ϵ_{oij}

and ϵ_{oij} of some normal alcohols like 1-butanol, 1-hexanol, 1-heptanol and 1-decanol at various mole fractions under different electric field frequencies in *n*-heptane at 25 °C. The purpose of their study was to observe triple relaxation phenomena in them under different concentrations characterized by relaxation times τ_1, τ_2, τ_3 which arise respectively due to hydrogen bonded structure, orientational motion of the molecules and rotation of -OH groups about C-C bond. The alcohols under study are of special importance for their wide applications in the fields of biological research, medicine and industry.

But the modern trend is to study relaxation phenomena in polar-non polar liquid mixtures in terms of hf complex dimensionless dielectric orientational susceptibility χ^*_{ij} rather than permittivity ϵ^*_{ij} or conductivity σ^*_{ij} . As all types of polarisations are associated with ϵ^*_{ij} , while σ^*_{ij} includes within it transport of bound molecular charges,

so it is more reasonable to work with χ_{ij} 's as it is directly linked with orientational polarisation of the molecules. Moreover, the present study have been carried out in modern concept of intemationally accepted symbols of dielectric terrninology and parameter in SI units because of its unified, coherent and rationalized nature. Under such context we have derived a straight line equation interms of real χ'_{ij} and imaginary χ''_{ij} parts of hf complex susceptibility χ^*_{ij} together with low frequency real dielectric susceptibility χ_{oij} to have τ_1 and τ_2 of alcohol molecules in *n*-heptane at 25 °C under GHz electric field. The frequency 24.33 GHz has been found out to be the most effective dispersive region of the alcohol molecules. When χ''_{ij} of the molecules are plotted against frequency (*f*) they showed peak in the neighbourhood of 24 GHz which is probably due to dielectric reorientation of polar molecules⁹. At this frequency the alcohol molecules absorb electrical energy much more strongly to show reliable τ_1 and τ_2 from intercept and slope of the least squares fitted straight line equation of $(\chi_{oij} - \chi'_{ij})/\chi'_{ij}$ against χ''_{ij}/χ'_{ij} signifying the material property of the systems.

The validity of straight line equations of Fig. 1 is tested by correlation coefficient (*r*) and % of errors. In absence of reliable τ_j 's of these normal alcohols the ratio of slopes of individual variations of χ''_{ij} and χ'_{ij} with w_j at $w_j \rightarrow 0$ as seen in Figs. 2 and 3 were utilised to get hf τ_j to compare them with those of Murthy *et al.*¹⁰ of Fig. 4 and Gopalakrishna's method¹¹.

The theoretical weighted contributions c_1 and c_2 towards dielectric dispersions interms of measured τ_1 and τ_2 were worked out from Fröhlich's equations¹² to compare them with the experimental ones by graphical variation of χ'_{ij}/χ_{oij} and χ''_{ij}/χ_{oij} with w_j at $w_j \rightarrow 0$ of Figs. 5 and 6. The symmetric γ and asymmetric δ distribution parameters were obtained from graphical extrapolation techniques of Figs. 5 and 6 in the limit $w_j=0$ and from variation of $(1/\phi) \log(\cos \phi)$ against ϕ^0 of Fig. 7 respectively. Symmetric relaxation time τ_s from γ and characteristic relaxation time τ_{cs} from δ and ϕ , were however, estimated to conclude about symmetric relaxation behaviour of polar molecules.

The dipole moment's μ_1 and μ_2 interms of b_1 and b_2 involved with estimated τ_1 and τ_2 were worked out to present them in Table 1 to compare with reported μ_j 's (Gopalakrishna) and μ_{theq} obtained from bond angles and reduced bond moments¹³ of substituent polar groups attached to parent molecules. The comparison however suggests that the flexible part of the molecules rotate internally under GHz electric field^{14,15}. The slight

disagreement between experimental and theoretical μ 's estestablishes the very existence of strong internal hydrogen bonding among -OH groups of long straight chain alcohol molecules. Physico-chemical aspects of different solute molecules in non polar solvent can be explained by non linear variation of both τ_2 and μ_2 against frequency (*f*) of the applied electric field as shown in Fig. 8.

Experimental

The dielectric constants ϵ'_{ij} and losses ϵ''_{ij} of the alcohols in *n*-heptane at different mole fractions of solutes were measured⁸ with a Boonton RX meter corrected by a heterodyne beat method. Refractive indices ($n_{Dij} = \sqrt{\epsilon_{ij}}$) of the solution were estimated by a Pulfrich refractometer for sodium D-line. The alcohols 1-butanol, 1-hexanol, 1-heptanol and 1-decanol were obtained from various commercial sources dried for a period over "Drierite" (anhydrous calcium sulphate) and fractionally distilled at atmospheric pressure. Commercial *n*-heptane was dried over sodium wire prior to its use and its relative permittivity ($\epsilon_1 = 1.917$) was checked in agreement with literature value at 25 °C.

Theoretical formulations to estimate double relaxation times τ_1 , τ_2 and c_1 , c_2 :

The hf complex dielectric relative permittivity ϵ^*_{ij} of polar-non polar liquid mixtures is associated with a number of non-interacting Debye type dispersions in accordance with Budo's relation¹⁶

$$\frac{\epsilon^*_{ij} - \epsilon_{\infty ij}}{\epsilon_{oij} - \epsilon_{\infty ij}} = \sum \frac{c_k}{1 + j\omega\tau_k} \quad (1)$$

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

But when ϵ^*_{ij} consists of two Debye type dispersions Budo's relation reduces to Bergmann's equations¹⁷. $\epsilon_{\infty ij}$ includes within it fast polarization and frequently appears as a subtracted term in Bergmann's equations. Thus to avoid the clumsiness of algebra and to use the modern concept of dielectric terminology and parameter one gets

$$\chi'_{ij} = (\epsilon'_{ij} - \epsilon_{\infty ij}), \chi''_{ij} = \epsilon''_{ij}, \chi_{oij} = (\epsilon_{oij} - \epsilon_{\infty ij})$$

The Bergmann's equations thus becomes

$$\frac{\chi'_{ij}}{\chi_{oij}} = c_1 \frac{1}{1 + \omega^2\tau_1^2} + c_2 \frac{1}{1 + \omega^2\tau_2^2} \quad (2)$$

$$\frac{\chi''_{ij}}{\chi_{oij}} = c_1 \frac{\omega\tau_1}{1 + \omega^2\tau_1^2} + c_2 \frac{\omega\tau_2}{1 + \omega^2\tau_2^2} \quad (3)$$

The relative weighted factors C_1 and C_2 are such that $C_1 + C_2 = 1$. χ'_{ij} and χ''_{ij} are the real and imaginary parts of hf complex dielectric orientational susceptibility χ_{ij}^* and χ_{oij} is low frequency dielectric susceptibility which is real. The introduction of χ 's in Bergmann's equations are then concerned with the molecular orientational polarization alone.

Putting $\omega\tau_1 = \alpha_1$ and $\omega\tau_2 = \alpha_2$ eqs. (2) and (3) are solved to get

$$c_1 = \frac{(\chi'_{ij}\alpha_2 - \chi''_{ij})(1 + \alpha_1^2)}{\chi_{oij}(\alpha_2 - \alpha_1)} \quad (4)$$

and

$$c_2 = \frac{(\chi''_{ij} - \chi'_{ij}\alpha_1)(1 + \alpha_2^2)}{\chi_{oij}(\alpha_2 - \alpha_1)} \quad (5)$$

provided $\alpha_2 - \alpha_1 \neq 0$.

As $c_1 + c_2 = 1$, we have

$$\frac{(\chi'_{ij}\alpha_2 - \chi''_{ij})(1 + \alpha_1^2)}{\chi_{oij}(\alpha_2 - \alpha_1)} + \frac{(\chi''_{ij} - \chi'_{ij}\alpha_1)(1 + \alpha_2^2)}{\chi_{oij}(\alpha_2 - \alpha_1)} = 1$$

$$\text{or, } \chi'_{ij}\alpha_2 + \chi'_{ij}\alpha_2\alpha_1^2 - \chi''_{ij} - \chi''_{ij}\alpha_1^2 + \chi''_{ij} + \chi''_{ij}\alpha_2^2 - \chi'_{ij}\alpha_1 - \chi'_{ij}\alpha_1\alpha_2^2 = \chi_{oij}(\alpha_2 - \alpha_1)$$

$$\text{or, } \chi'_{ij}(\alpha_2 - \alpha_1) - \chi'_{ij}\alpha_1\alpha_2(\alpha_2 - \alpha_1) + \chi''_{ij}(\alpha_2^2 - \alpha_1^2) = \chi_{oij}(\alpha_2 - \alpha_1)$$

$$\text{or, } \chi'_{ij} - \chi'_{ij}\alpha_1\alpha_2 + \chi''_{ij}(\alpha_2 + \alpha_1) = \chi_{oij}$$

$$\text{or, } \chi''_{ij}(\alpha_1 + \alpha_2) - \chi'_{ij}\alpha_1\alpha_2 = \chi_{oij} - \chi'_{ij}$$

$$\text{or, } \frac{\chi_{oij} - \chi'_{ij}}{\chi'_{ij}} = (\alpha_1 + \alpha_2) \frac{\chi''_{ij}}{\chi'_{ij}} - \alpha_1\alpha_2$$

substituting $\alpha_1 = \omega\tau_1$ and $\alpha_2 = \omega\tau_2$ we have

$$\text{or, } \frac{\chi_{oij} - \chi'_{ij}}{\chi'_{ij}} = \omega(\tau_1 + \tau_2) \frac{\chi''_{ij}}{\chi'_{ij}} - \omega^2\tau_1\tau_2 \quad (6)$$

which is a straight line equation between the variables $(\chi_{oij} - \chi'_{ij})/\chi'_{ij}$ and χ''_{ij}/χ'_{ij} with slope $\omega(\tau_1 + \tau_2)$ and intercept $\omega^2\tau_1\tau_2$, where $\omega = 2\pi f$, f being frequency of the applied electric field in GHz range. The above equation is, however, satisfied by experimental points as seen in Fig. 1 for different weight fractions w_j 's of solute at 25 °C under electric field frequencies of 24.33, 9.25 and 3.00 GHz. The eq. (6) has been used to estimate τ_1 and τ_2 in order to place them in Table 1.

The theoretical weighed contributions c_1 and c_2 were, then obtained from eqs. (4) and (5) with the variables χ''_{ij}/χ_{oij} and χ''_{ij}/χ_{oij} of Fröhlich's eqs. (7) and (8) in

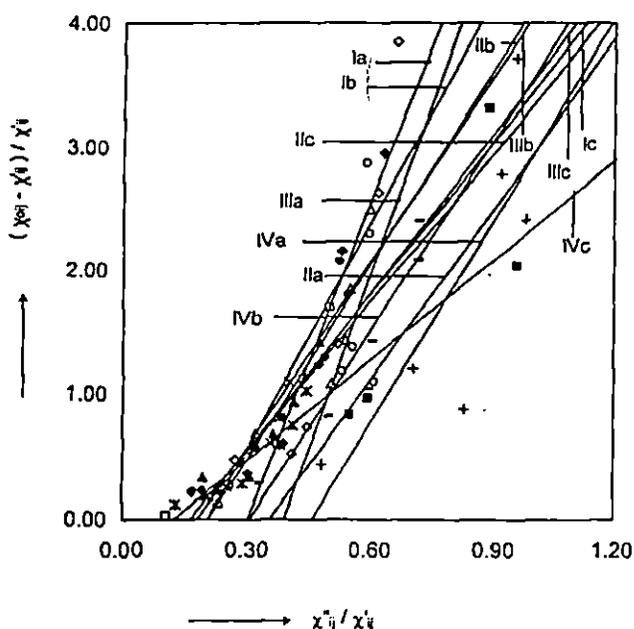


Fig. 1. Linear variation of $(\chi_{oij} - \chi'_{ij})/\chi'_{ij}$ with χ''_{ij}/χ'_{ij} for alcohols in *n*-heptane at 25 °C of (Ia) 1-butanol (○) at 24.33 GHz, (Ib) 1-butanol (◊) at 9.25 GHz, (Ic) 1-butanol (◻) at 3.00 GHz, (IIa) 1-hexanol (■) at 24.33 GHz, (IIb) 1-hexanol (Δ) at 9.25 GHz, (IIc) 1-hexanol (▲) at 3.00 GHz, (IIIa) 1-heptanol (○) at 24.33 GHz, (IIIb) 1-heptanol (●) at 9.25 GHz, (IIIc) 1-heptanol (×) at 3.00 GHz, (IVa) 1-decanol (+) at 24.33 GHz, (IVb) 1-decanol (-) at 9.25 GHz, (IVc) 1-decanol (*) at 3.00 GHz.

terms of known τ_1 and τ_2 .

$$\frac{\chi'_{ij}}{\chi_{oij}} = 1 - \frac{1}{2A} \ln \left(\frac{1 + \omega^2\tau_2^2}{1 + \omega^2\tau_1^2} \right) \quad (7)$$

$$\frac{\chi''_{ij}}{\chi_{oij}} = \frac{1}{A} \left[\tan^{-1}(\omega\tau_2) - \tan^{-1}(\omega\tau_1) \right] \quad (8)$$

Theoretical formulations to estimate symmetric and characteristic relaxation times τ_s and τ_{cs} :

The molecules under present investigation appear to behave like non-rigid ones having symmetric and asymmetric distribution parameters γ and δ involved with eqs. (9) and (10)

$$\frac{\chi_{ij}^*}{\chi_{oij}} = \frac{1}{1 + (j\omega\tau_s)^{1-\gamma}} \quad (9)$$

$$\frac{\chi_{ij}^*}{\chi_{oij}} = \frac{1}{(1 + j\omega\tau_{cs})^\delta} \quad (10)$$

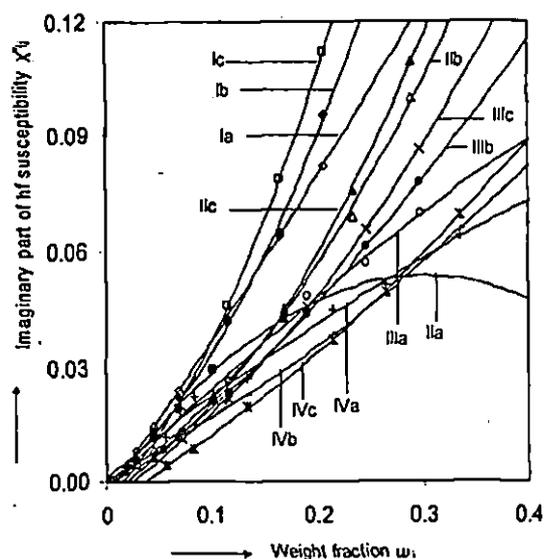


Fig. 2. Variation of imaginary part of hf susceptibility χ''_{ij} with weight fraction w_j for alcohols in *n*-heptane at 25 °C of (Ia) 1-butanol (\diamond) at 24.33 GHz, (Ib) 1-butanol (\blacklozenge) at 9.25 GHz, (Ic) 1-butanol (\square) at 3.00 GHz, (IIa) 1-hexanol (\blacksquare) at 24.33 GHz, (IIb) 1-hexanol (\triangle) at 9.25 GHz, (IIc) 1-hexanol (\blacktriangle) at 3.00 GHz, (IIIa) 1-heptanol (\circ) at 24.33 GHz, (IIIb) 1-heptanol (\bullet) at 9.25 GHz, (IIIc) 1-heptanol (\times) at 3.00 GHz, (IVa) 1-decanol ($+$) at 24.33 GHz, (IVb) 1-decanol ($-$) at 9.25 GHz, (IVc) 1-decanol ($*$) at 3.00 GHz.

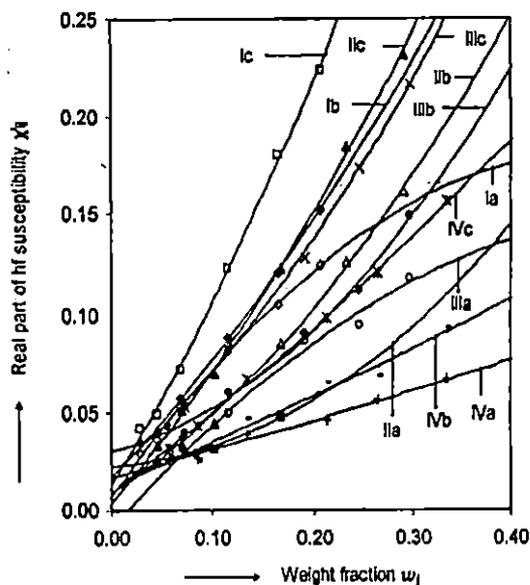


Fig. 3. Variation of real part of hf susceptibility χ'_{ij} with weight fraction w_j for alcohols in *n*-heptane at 25 °C of (Ia) 1-butanol (\diamond) at 24.33 GHz, (Ib) 1-butanol (\blacklozenge) at 9.25 GHz, (Ic) 1-butanol (\square) at 3.00 GHz, (IIa) 1-hexanol (\blacksquare) at 24.33 GHz, (IIb) 1-hexanol (\triangle) at 9.25 GHz, (IIc) 1-hexanol (\blacktriangle) at 3.00 GHz, (IIIa) 1-heptanol (\circ) at 24.33 GHz, (IIIb) 1-heptanol (\bullet) at 9.25 GHz, (IIIc) 1-heptanol (\times) at 3.00 GHz, (IVa) 1-decanol ($+$) at 24.33 GHz, (IVb) 1-decanol ($-$) at 9.25 GHz, (IVc) 1-decanol ($*$) at 3.00 GHz.

The former one is associated with symmetric relaxation time τ_s while the later one with characteristic relaxation times τ_{cs} . On separating the real and imaginary parts of eqs. (9) and (10) and rearranging them in terms of χ'_{ij}/χ_{oij} and χ''_{ij}/χ_{oij} at $w_j \rightarrow 0$ as seen in Figs. 5 and 6, the γ and τ_s were obtained as

$$\gamma = \frac{2}{\pi} \tan^{-1} \left[\left(1 - \frac{\chi'_{ij}}{\chi_{oij}} \right) \frac{\chi'_{ij}}{\chi''_{ij}} - \frac{\chi''_{ij}}{\chi_{oij}} \right] \quad (11)$$

and

$$\tau_s = \frac{1}{\omega} \left[\frac{1}{\left(\frac{\chi'_{ij}}{\chi''_{ij}} \right) \cos(\gamma\pi/2) - \sin(\gamma\pi/2)} \right]^{1/(1-\gamma)} \quad (12)$$

Similarly δ and τ_{cs} can be had from eq. (10) as

$$\tan(\phi\delta) = \frac{(\chi''_{ij}/\chi_{oij})_{w_j \rightarrow 0}}{(\chi'_{ij}/\chi_{oij})_{w_j \rightarrow 0}} \quad (13)$$

$$\text{and } \tan \phi = \omega\tau_{cs} \quad (14)$$

As ϕ can not be evaluated directly, an arbitrary theoretical curve between $(1/\phi) \log(\cos \phi)$ against ϕ in degree was drawn in Fig. 7 from which

$$(1/\phi) \log(\cos \phi) = \frac{\log \{ (\chi'_{ij}/\chi_{oij}) / (\cos \phi\delta) \}}{\phi\delta} \quad (15)$$

can be known. The known value of $(1/\phi) \log(\cos \phi)$, is used to know ϕ from Fig. 7. With known ϕ eqs. (13) and (14) can be used to obtain δ and τ_{cs} respectively.

Theoretical formulations to obtain relaxation time τ_j and hf dipole moment μ_j :

The real ϵ'_{ij} and imaginary ϵ''_{ij} parts of hf complex dielectric relative permittivity ϵ^*_{ij} are related by

$$\begin{aligned} \epsilon'_{ij} &= \epsilon_{\infty ij} + (1/\omega\tau)\epsilon''_{ij} \\ \text{or, } (\epsilon'_{ij} - \epsilon_{\infty ij}) &+ (1/\omega\tau)\epsilon''_{ij} \\ \text{or, } \chi''_{ij} &= (1/\omega\tau)\chi''_{ij} \\ \text{or, } (d\chi''_{ij}/d\chi'_{ij}) &= \omega\tau_j \end{aligned} \quad (16)$$

χ''_{ij} 's are found to vary almost linearly¹⁰ with χ'_{ij} as seen in Fig. 4, the slope $\omega\tau_j$ is used to obtain τ_j .

But earlier investigation on some isomers of anisidines and toluidines¹⁵ and the present investigation on normal alcohols shows that variation of χ''_{ij} against χ'_{ij} as seen in Fig. 4 are strictly not linear. The ratio of slopes of

individual variations of χ''_{ij} and χ'_{ij} with w_j 's in Figs. 2 and 3 is a better representation of eq. (16) to get τ_j where polar-polar interactions are almost avoided¹⁵. Thus

$$\frac{(d\chi''_{ij}/dw_j)_{w_j \rightarrow 0}}{(d\chi'_{ij}/dw_j)_{w_j \rightarrow 0}} = \omega\tau_j \quad (17)$$

Imaginary part χ''_{ij} of χ^*_{ij} can be represented^{18,19} as

$$\chi''_{ij} = \frac{N\rho_{ij}\mu_j^2}{27 \epsilon_0 M_j k_B T} \frac{\omega\tau_j}{(1 + \omega^2\tau_j^2)} (\epsilon_{ij} + 2)^2 w_j \quad (18)$$

which on differentiation with respect to w_j and at $w_j \rightarrow 0$ yields that

$$(d\chi''_{ij}/dw_j)_{w_j \rightarrow 0} = \frac{N\rho_{ij}\mu_j^2}{27 \epsilon_0 M_j k_B T} \frac{\omega\tau_j}{(1 + \omega^2\tau_j^2)} (\epsilon_i + 2)^2 \quad (19)$$

Now in comparison to earlier works presented elsewhere^{6,13} the approximation that $\chi_{ij} \approx \chi''_{ij}$ like $\sigma_{ij} \approx \sigma''_{ij}$ is not necessary to obtain μ_j from τ_j where σ''_{ij} is the imaginary part of complex hf conductivity and σ_{ij} is the total hf conductivity of polar-nonpolar liquid mixture. From eqs. (17) and (19) one gets

$$(d\chi''_{ij}/dw_j) = \frac{N\rho_{ij}\mu_j^2}{27 \epsilon_0 M_j k_B T} \frac{\omega\tau_j}{(1 + \omega^2\tau_j^2)} (\epsilon_i + 2)^2$$

$$\text{or, } \omega\tau_j\beta = \frac{N\rho_{ij}\mu_j^2}{27 \epsilon_0 M_j k_B T} \omega\tau_j b (\epsilon_i + 2)^2$$

$$\text{or, } \beta = \frac{N\rho_{ij}\mu_j^2}{27 \epsilon_0 M_j k_B T} b (\epsilon_i + 2)^2$$

$$\text{or, } \mu_j = \left[\frac{27 \epsilon_0 M_j k_B T \beta}{N\rho_{ij}(\epsilon_i + 2)^2 b} \right]^{1/2} \quad (20)$$

which is directly interrelated with the measured τ 's through b , where

ϵ_0 = Permittivity of free space = 8.854×10^{-12} Farad metre⁻¹,

M_j = Molecular weight of solute in kilogramme,

k_B = Boltzmann constant = 1.38×10^{-23} J mol⁻¹ K⁻¹,

T = Temperature in absolute scale,

$\beta = d\chi'_{ij}/dw_j =$ Linear coefficient of $\chi'_{ij} - w_j$ curves of Fig. 3 at $w_j \rightarrow 0$,

Table 1. The relaxation times τ_1 and τ_2 from the slope and intercept of straight line eq. (6), estimated dipole moment μ_1, μ_2 from eq. (20). Computed dipole moment μ_j from τ_j of eq. (17), reported dipole moment (Gopalakrishna's method), all are expressed in Coulomb-metre for different straight chain alcohols in *n*-heptane at 20 °C under different GHz electric field

System with sl. no. and mol. weight in kg	Frequency (f) in GHz	Estimated τ_1 and τ_2 in psec		Estimated dipole moment $\mu \times 10^{30}$ in Coulomb metre (C.m.)			Reported $\mu \times 10^{30}$ in C.m. by Gopalakrishna's method	$\mu_{\text{theo}}^a \times 10^{30}$ in C.m. from reduced bond moments
		τ_1	τ_2	μ_1	μ_2	μ_j		
I. 1-Butanol ($M_j = 0.074$)	24.33	2.04	54.56	3.02	24.25	3.26	3.58	
	9.25	3.72	101.78	2.56	14.99	2.69	3.80	3.74
	3.00	9.09	211.22	3.14	12.72	3.23	4.30	
II. 1-Hexanol ($M_j = 0.102$)	24.33	2.54	27.46	0.79	3.18	8.25	3.35	
	9.25	3.75	85.16	2.35	11.59	2.52	3.87	3.49
	3.00	9.17	204.07	3.16	12.39	3.17	4.27	
III. 1-Heptanol ($M_j = 0.116$)	24.33	2.65	59.09	3.52	29.69	3.60	3.59	
	9.25	3.29	82.96	1.57	7.59	2.86	3.60	3.73
	3.00	10.05	220.31	2.90	12.17	3.06	4.27	
IV. 1-Decanol ($M_j = 0.158$)	24.33	3.29	32.22	2.10	9.43	3.47	3.55	
	9.25	5.60	83.06	2.49	11.67	2.82	3.83	3.68
	3.00	6.88	135.54	3.12	8.50	3.36	4.33	

^aRef. 19.

$N = \text{Avogadro's number} = 6.023 \times 10^{23}$,

$\rho_i = \text{Density of solvent } n\text{-heptane at } 25^\circ\text{C} = 680.15 \text{ kg m}^{-3}$,

$\epsilon_i = \text{Relative permittivity of the solvent } n\text{-heptane} = 1.917$,

$b = 1/(1 + \omega^2\tau^2)$ = a dimensionless parameter involved with estimated τ_1 and τ_2 of eq. (6) and τ_j of eq. (17).

Dipole moments μ_1 and μ_2 obtained with the knowledge of b_1 and b_2 involved with estimated τ_1 and τ_2 by double relaxation method are entered in the 5th and 6th column of Table 1. They are, however, compared to μ_j with τ_j of eq. (17) and reported μ 's (Gopalakrishna) and μ_{theo} as seen in 7th, 8th and 9th columns.

Results and discussion

The least square fitted straight line equation of $(\chi_{oij} - \chi'_{ij})/\chi'_{ij}$ against χ''_{ij}/χ'_{ij} for different weight fractions w_j 's of solute at 25°C in n -heptane under different GHz electric field frequency are shown graphically in Fig. 1 together with experimental points placed on them. The real χ'_{ij} and imaginary χ''_{ij} parts of hf complex dimensionless dielectric orientational susceptibility χ^*_{ij} and low frequency real dielectric susceptibility χ_{oij} are, however, derived

from measured⁸ permittivities ϵ'_{ij} , ϵ''_{ij} , ϵ_{oij} and $\epsilon_{\infty ij}$. The linearity of all curves of Fig. 1 are confirmed by correlation coefficients r 's and percentage of errors. The relaxation times τ_1 and τ_2 estimated from eq. (6) are placed in the 3rd and 4th columns of Table 1. It is seen that both τ_1 and τ_2 are of low values at 24.33 GHz and tends to increase with the lower frequencies of 9.25 and 3.00 GHz electric fields. It may be explained on the basis of the fact that at higher frequencies the rate of hydrogen bond rupture is maximum in such long chain alcohols to reduce τ for each rotating unit²⁰.

In absence of reliable τ_j of such molecules it was tried to calculate τ_j from the least square fitted straight line equation of χ''_{ij} against χ'_{ij} in Fig. 4 as claimed by Murthy *et al.*¹⁰. But the experimental points are found to deviate from linearity as seen in Fig. 4 which is probably due to various associational aspects of polar molecules in non polar solvent¹³. The individual plots of χ''_{ij} and χ'_{ij} against w_j of normal alcohols are not linear as seen in Figs. 2 and 3 which confirms the probable solute-solute (dimer) and solute-solvent (monomer) molecular associations. The reliability of both $\chi''_{ij} - w_j$ and $\chi'_{ij} - w_j$ variations are confirmed by correlation coefficients r 's and % of errors. This fact at once inspired us to evaluate τ_j from the ratio of slopes of individual variations of χ''_{ij} and χ'_{ij} with w_j at $w_j \rightarrow 0$. τ_j so obtained shows close agreement with τ_1

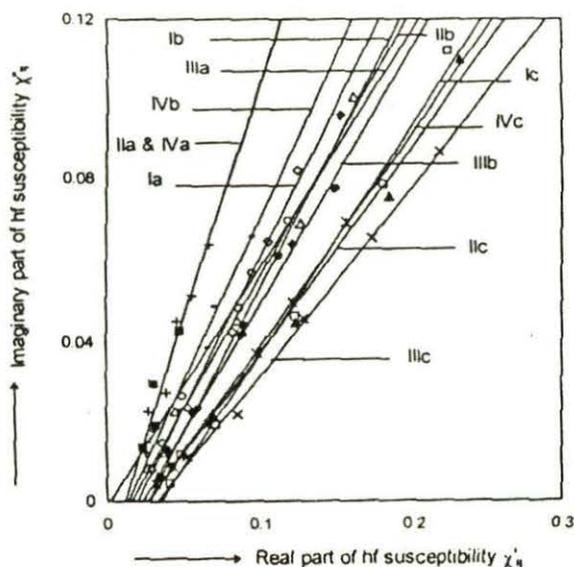


Fig. 4. Variation of imaginary part of hf susceptibility χ''_{ij} with real part of hf susceptibility χ'_{ij} of alcohols in n -heptane at 25°C of (Ia) 1-butanol (\circ) at 24.33 GHz, (Ib) 1-butanol (\blacklozenge) at 9.25 GHz, (Ic) 1-butanol (\square) at 3.00 GHz, (IIa) 1-hexanol (\blacksquare) at 24.33 GHz, (IIb) 1-hexanol (Δ) at 9.25 GHz, (IIc) 1-hexanol (\blacktriangle) at 3.00 GHz, (IIIa) 1-heptanol (\circ) at 24.33 GHz, (IIIb) 1-heptanol (\bullet) at 9.25 GHz, (IIIc) 1-heptanol (\times) at 3.00 GHz, (IVa) 1-decanol ($+$) at 24.33 GHz, (IVb) 1-decanol ($-$) at 9.25 GHz, (IVc) 1-decanol ($*$) at 3.00 GHz.

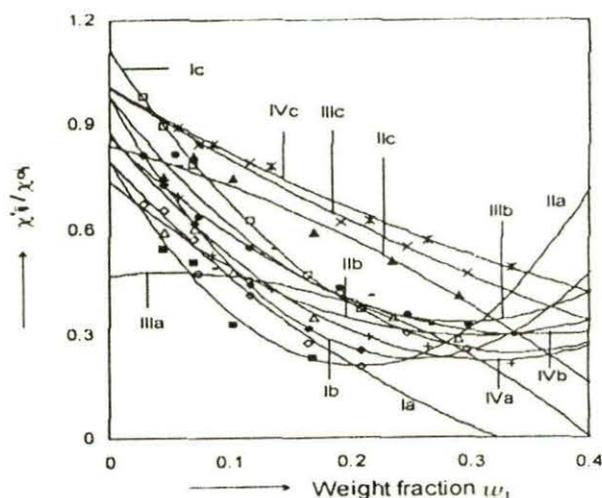


Fig. 5. Variation χ''_{ij}/χ'_{oij} with weight fraction w_j for alcohols in n -heptane at 25°C of (Ia) 1-butanol (\circ) at 24.33 GHz, (Ib) 1-butanol (\blacklozenge) at 9.25 GHz, (Ic) 1-butanol (\square) at 3.00 GHz, (IIa) 1-hexanol (\blacksquare) at 24.33 GHz, (IIb) 1-hexanol (Δ) at 9.25 GHz, (IIc) 1-hexanol (\blacktriangle) at 3.00 GHz, (IIIa) 1-heptanol (\circ) at 24.33 GHz, (IIIb) 1-heptanol (\bullet) at 9.25 GHz, (IIIc) 1-heptanol (\times) at 3.00 GHz, (IVa) 1-decanol ($+$) at 24.33 GHz, (IVb) 1-decanol ($-$) at 9.25 GHz, (IVc) 1-decanol ($*$) at 3.00 GHz.

from double relaxation and Gopalakrishna's method¹¹. This approach further confirms that polar-polar interactions are fully avoided^{6,15} in the later method. Thus hf dielectric susceptibility measurement yields the accurate microscopic τ due to orientational polarisation whereas double relaxation method gives both microscopic τ 's^{15,20}.

Higher values of τ_2 's results in bigger size of rotating unit ($\tau_2 T / \eta'$) which is due to solute-solvent (monomer) associations under GHz electric field. Distribution of τ 's between two limiting values τ_1 and τ_2 prompts one to estimate the symmetric and asymmetric distribution parameters γ and δ of such molecules from eqs. (11) and (13) with graphical extrapolation values of χ'_{ij}/χ_{oij} and χ''_{ij}/χ_{oij} at $w_j = 0$ of Figs. 5 and 6. Values of γ so obtained is used to evaluate τ_s from eq. (12). The arbitrary curve of $(1/\phi) \log(\cos \phi)$ against ϕ in degree is essential to know ϕ for known value of $(1/\phi) \log(\cos \phi)$ from eq. (15). Known ϕ from Fig. 7 was however used to evaluate δ and τ_{cs} from eqs. (13) and (14). The value of γ establishes the non-rigid behaviour of the molecules signifying the applicability of Debye-Smyth model of dielectric relaxation to some extent in such normal alcohols in *n*-heptane under GHz electric field.

Symmetric relaxation time τ_s obtained from eq. (12) with known γ agrees well with τ_1 's by double relaxation

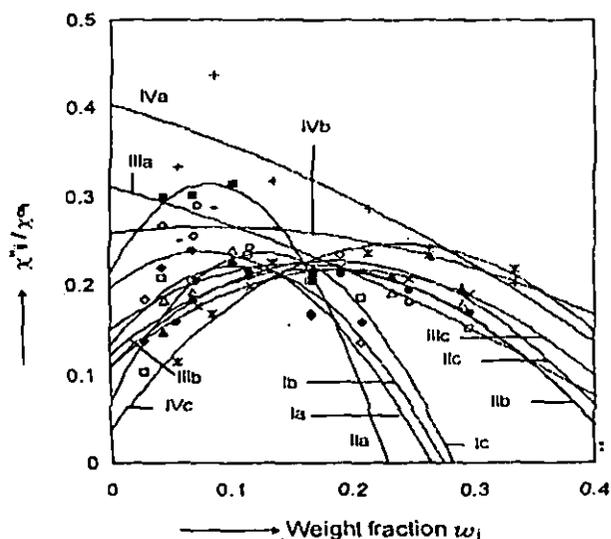


Fig. 6. Variation χ''_{ij}/χ_{oij} with weight fraction w_j for alcohols in *n*-heptane at 25 °C of (Ia) 1-butanol (○) at 24.33 GHz, (Ib) 1-butanol (◆) at 9.25 GHz, (Ic) 1-butanol (□) at 3.00 GHz, (IIa) 1-hexanol (■) at 24.33 GHz, (IIb) 1-hexanol (Δ) at 9.25 GHz, (IIc) 1-hexanol (▲) at 3.00 GHz, (IIIa) 1-heptanol (○) at 24.33 GHz, (IIIb) 1-heptanol (●) at 9.25 GHz, (IIIc) 1-heptanol (×) at 3.00 GHz, (IVa) 1-decanol (+) at 24.33 GHz, (IVb) 1-decanol (-) at 9.25 GHz, (IVc) 1-decanol (*) at 3.00 GHz.

and τ_1 's by Gopalakrishna's method except at 3.00 GHz electric field frequency. This discrepancy may be explained on the basis of the fact that at lower frequency the rate of hydrogen bond rupture is small resulting in higher value of τ for each rotating unit. High value of τ_{cs} eventually rules out the possibility of occurring asymmetric relaxation behaviour for the alcohols. Fig. 8 represents the plot of both τ_2 and μ_2 against frequency (f) of the applied electric field. It is evident from the plot that τ_2 of the alcohols decreases with frequency. It is due to the fact that at higher frequency the rate of hydrogen bond rupture is maximum, reducing thereby τ_2 for each rotating unit²⁰. For system II and IV the variation of μ_2 against frequency is convex in nature having zero μ_2 values at two frequencies due to strong symmetry attained by the molecules. 1-Butanol (system I) and 1-heptanol (system III) shows minimum μ_2 for their symmetry attained between 3.00 and 9.25 GHz electric field frequency. Beyond 9.25 GHz μ_2 increases with f showing asymmetric nature of the molecules. All types of symmetries and asymmetries arises probably due to various types of molecular associations between solute and solvent molecules which are supposed to be physico-chemical behaviour of the systems¹⁹.

The relative contributions c_1 and c_2 towards dielectric dispersions have been evaluated from eqs. (4) and (5) for fixed τ_1 and τ_2 as predicted from eq. (6) and with estimated χ'_{ij}/χ_{oij} and χ''_{ij}/χ_{oij} from Fröhlich's eqs. (7) and (8). The same are, however, obtained experimentally from the graphical variation of χ'_{ij}/χ_{oij} and χ''_{ij}/χ_{oij} with w_j of Figs. 5 and 6 at $w_j = 0$. The Fröhlich's parameter A is the temperature variation of the width of distribution of τ and is equal to $\ln(\tau_2/\tau_1)$. Variation of χ'_{ij}/χ_{oij} and χ''_{ij}/χ_{oij}

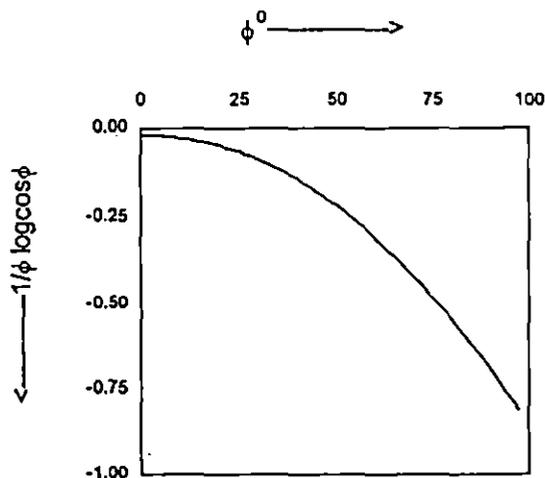


Fig. 7. Variation of $(1/\phi) \log(\cos \phi)$ against ϕ^0 .

χ_{oij} with w_j as seen in Figs. 5 and 6 are concave and convex in nature which are in accordance with Bergmann's eqs. (2) and (3) as observed elsewhere^{14,21}. The estimated c_2 is greater than c_1 for almost all the alcohols in Fröhlich's method, while the reverse is true for graphical technique. Formation of internal hydrogen bonding among -OH groups in polar alcohol molecules gives rise to inertia^{15,20} of the flexible part with respect to whole molecule which results in negative c_2 satisfying the condition $c_1 + c_2 \approx 1$ in graphical technique. For Fröhlich method $c_1 + c_2 > 1$, indicating the possibility of occurrence of more than two relaxation processes⁸ in them.

Dipole moments μ_1 and μ_2 estimated from dimensionless parameters b_1 and b_2 for measured τ_1 and τ_2 and linear coefficient β 's of $\chi'_{ij} - w_j$ curves of Fig. 3 are shown in the 5th and 5th columns of Table 1. Values of r 's and % of errors in terms of r 's gives reliable β to yield accurate μ_1 and μ_2 . Almost all the curves of Fig. 3 shows a tendency to become closer within the limit $0.00 \leq w_j \leq 0.05$ probably due to the same polarity of the molecules arising out of monomer and dimer formations^{13,15}.

The theoretical dipole moments μ_{theo} were, however, obtained from bond angles and bond moments of a number of dipolar groups like $H_3 \rightarrow C$, $C \rightarrow O$ and $O \leftarrow H$ of 1.23×10^{-30} , 3.33×10^{-30} and 1.30×10^{-30} Coulomb metre¹³ and are entered in 9th column of Table 1. The -OH group

in all the alcohols making an angle 105° with the C-C bond plays an important role to yield theoretical dipole moment μ_{theo} . In absence of reliable μ_j values Gopalakrishna's method were employed to get μ_j (reported data) to compare with μ_j 's estimated from the relation $\mu_1 = \mu_2 (c_1/c_2)^{1/2}$ assuming two relaxation processes are equally probable in them. But the agreement is poor probably due to the fact that sum of c_1 and c_2 as estimated from Fröhlich's method is not strictly equal to one. The close agreement between μ_1 from double relaxation method, μ_{theo} and reported μ 's establishes the basic soundness of the method¹⁹ for getting hf μ_j in addition to the fact that a part of the molecule is rotating¹⁵ under GHz electric field. Slight disagreement between μ_{theo} and μ_1 arises due to the formation of H bonds among the -OH groups in dipolar liquid molecules which results in solute-solute molecular association increasing thereby the value of μ_{theo} 's.

Conclusion :

The methodology so far developed in SI units with internationally accepted symbols of dielectric terminologies and parameters appears to be simple, straightforward and topical one to predict relaxation parameters as χ 's are directly linked with molecular orientational polarisation. The significant and interesting equations to evaluate relaxation parameters gives deep insight into the solute-solute and solute-solvent molecular interactions in a solution. The simple straight line eq. (6) provides one with microscopic and macroscopic relaxation times. Evaluation of τ_j from eq. (17) by ratio of slopes of individual variations of χ'_{ij} and χ''_{ij} against w_j in the limit $w_j = 0$ is a better representation of eq. (16) of Murthy *et al.* as it eliminates polar-polar interactions in a solution. The results obviously show that the former method in long straight chain hydrogen bonded associative alcohol molecules may be applicable to get the accurate τ 's of the molecules only due to orientational polarization. Validity of the method so far advanced to evaluate hf τ_j and μ_j is also supported by τ_j and μ_j values estimated from freshly calculated Gopalakrishna's method. The close agreement between measured τ_j and τ_{cs} confirms the non-rigid behaviour of the molecules which at once invites the applicability of Debye-Smyth model of dielectric relaxation in such alcohol molecules. Molecular association is however confirmed by conformational structure in which internal H bonding plays the prominent role. Graphical variation of χ'_{ij}/χ_{oij} and χ''_{ij}/χ_{oij} with w_j as seen in Figs. 5 and 6 to estimate c_1 and c_2 are concave and convex in nature which are in accordance with Bergmann's equations. Reliable τ_1 and τ_2 obtained for alcohols at three electric

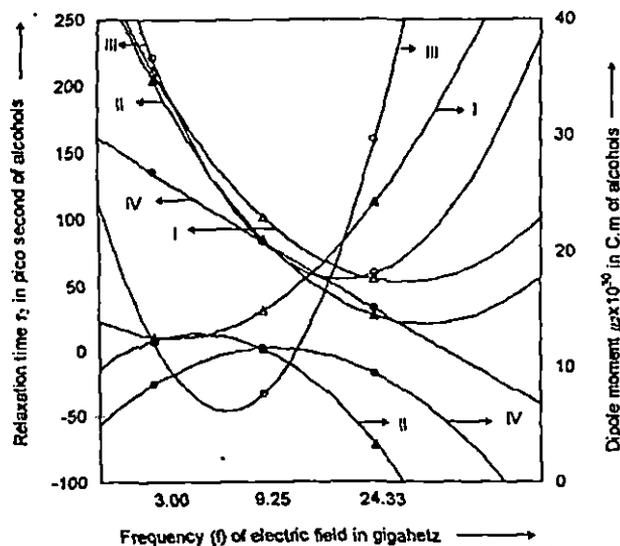


Fig. 8. Variation of relaxation time and dipole moment against frequency (f) of the applied electric field for some alcohols in *n*-heptane at 25 °C (I) 1-butanol (Δ), (II) 1-hexanol (\blacktriangle), (III) 1-heptanol (\circ), (IV) 1-decanol (\bullet).

field frequencies indicate the fact that double relaxation is a material property of the system. Although Figs. 1 to 6 appear to be crowdy, they provides a clear comparison between the results obtained for different systems. Some experimental points are found not to fall on the smooth curves of different figures probably due to various molecular associations between solute and solvent molecules which supports the physico-chemical behaviour of the systems. Concave and convex nature of curves of Fig. 8 shows that stability and instability of the alcohol molecules depends on frequency of the applied electric field ever shown. Thus the correlation between the conformational structures¹⁹ with the observed results enhances the scientific content to add a new horizon of understanding to the existing knowledge of dielectric relaxation phenomena in addition to physico-chemical properties of the polar liquid molecules.

References

1. A. Sharma and D. R. Sharma, *J. Phys. Soc. Jpn.*, 1992, 61, 1049.
2. A. Sharma, D. R. Sharma and M. S. Chowhan, *Indian J. Pure Appl. Phys.*, 1993, 31, 841.
3. S. K. Sit, N. Ghosh, U. Saha and S. Acharyya, *Indian J. Phys.*, 1997, 71B, 533.
4. K. S. Cole and R. H. Cole, *J. Chem. Phys.*, 1941, 9, 341.
5. E. A. Guggenheim, *Trans. Faraday Soc.*, 1949, 45, 714.
6. N. Ghosh, R. C. Basak, S. K. Sit and S. Acharyya, *J. Molecular Liquids*, 2000, 85, 375.
7. A. K. Jonscher, "Physics of Dielectric Solids", invited papers edited by C. H. L. Goodman, 1980.
8. L. Glasser, J. Crossley and C. P. Smyth, *J. Chem. Phys.*, 1972, 57, 3977.
9. A. K. Jonscher, invited papers presented at Inst. Phys. Conference, Canterbury, edited by C. H. L. Goodman, 1980.
10. M. B. R. Murthy, R. L. Palit and D. K. Deshpandé, *Indian J. Phys.*, 1989, 63B, 491.
11. K. V. Gopalakrishna, *Trans. Faraday Soc.*, 1957, 53, 767.
12. H. Fröhlich, "Theory of Dielectrics", Oxford University Press, Oxford, 1949.
13. N. Ghosh, A. Karmakar, S. K. Sit and S. Acharyya, *Indian J. Pure Appl. Phys.*, 2000, 38, 574.
14. U. Saha, S. K. Sit, R. C. Basak and S. Acharyya, *J. Phys. D : Appl. Phys. (UK)*, 1994, 27, 596.
15. N. Ghosh, S. K. Sit, A. K. Bothra and S. Acharyya, *J. Phys. D : Appl. Phys. (UK)*, 2001, 34, 379.
16. A. Budo, *Phys. Z.*, 1938, 39, 706.
17. K. Bergmann, D. M. Roberti and C. P. Smyth, *J. Phys. Chem.*, 1960, 64, 665.
18. C. P. Smyth, "Dielectric Behaviour and Structure", McGraw Hill, New York, 1955.
19. U. K. Mitra, N. Ghosh, P. Ghosh and S. Acharyya, *J. Molecular Liquids*, 2006, 126, 53.
20. S. K. Sit, N. Ghosh and S. Acharyya, *Indian J. Pure Appl. Phys.*, 1997, 35, 329.
21. S. K. Sit and S. Acharyya, *Indian J. Phys.*, 1996, 70B, 19.

Structural aspects and physico-chemical properties of polysubstituted benzenes in benzene from relaxation phenomena

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Manuscript received 22 March 2006, accepted 16 October 2006

Abstract : A brief report on the physico-chemical properties and structural aspects of some polysubstituted benzenes in benzene at different experimental temperatures under 10 GHz electric field is made to estimate relaxation times τ_j 's, dipole moments μ_j and thermodynamic energy parameters like enthalpy ΔH_τ , entropy ΔS_τ and free energy of activation ΔF_τ due to dielectric relaxation with formulations derived from orientational susceptibilities χ_{ij} 's, τ_j 's of the polar solutes obtained from the slope of the linear equation of χ''_{ij} and χ'_{ij} are, however, compared with those obtained from the ratio of the linear coefficients of individual variations of χ''_{ij} and χ'_{ij} with weight fractions w_j 's of the solute. τ_j 's from the later method are used to get thermodynamic energy parameters from the Eyring's rate process equation to shed more light on the physico-chemical properties of the polar liquid molecules concerned. The estimated μ_j 's in terms of linear coefficients β 's of χ'_{ij-w_j} equations and dimensionless parameters b 's involved with measured τ_j 's are finally compared with theoretical dipole moments μ_{theo} 's obtained from vector addition of available bond angles and bond moments of substituted polar groups. The estimated μ_{theo} gives valuable information regarding structures of the molecules. The slight disagreement between high frequency μ_j 's and μ_{theo} 's provides an interesting insight on the inductive, mesomeric and electromeric effects of the substituted polar groups attached to the parent molecules.

Keywords : Dipole moment, relaxation time, susceptibility.

Relaxation phenomena of polar liquid molecules in non-polar solvents under oscillating electric field in the GHz range at different experimental temperatures are of special importance as they are useful tools to investigate their physico-chemical properties as well as structural and associational aspects^{1,2}. The method is based on evaluation of relaxation time τ_j , dipole moment μ_j and thermodynamic energy parameters. There exists several methods^{3,4} to get τ_j 's and μ_j 's, but all these methods are not as simple as the present one in which a simultaneous determination of μ_j and τ_j is possible. Although several workers⁵⁻⁷ studied the relaxation mechanism of polar liquid molecules, but no such investigation on polysubstituted benzenes in terms of high frequency (hf) dielectric susceptibilities χ_{ij} 's has yet been made. The formulations derived so far may be used to study proteins, micelles, polymers and many other complex fluids⁸ including liquid crystals as well. Even binary mixtures of polar liquids can give rise to slow relaxation⁹. The formulations are concerned with the real χ'_{ij} ($= \epsilon'_{ij} - \epsilon_{\infty ij}$) and imaginary χ''_{ij} ($= \epsilon''_{ij}$) parts of hf complex dimensionless dielectric orientational susceptibility χ^*_{ij} .

The real ϵ'_{ij} and imaginary ϵ''_{ij} parts of high frequency permittivity ϵ^*_{ij} of polysubstituted benzenes like 1,3-diisopropyl benzene, *p*-methyl benzoyl chloride and *o*-chloroacetophenone in benzene at different weight fractions w_j 's of solutes in the temperature range of 30 to 45 °C under 10 GHz electric field were measured by Paul *et al.*¹⁰. The useful optical relative permittivities $\epsilon_{\infty ij}$'s to get concentration variation of χ'_{ij} were generated from Debye-Pallet's equations¹¹.

$$\epsilon'_{ij} = \epsilon_{\infty ij} + \frac{\epsilon_{0ij} - \epsilon_{\infty ij}}{1 + \omega^2 \tau_j^2} \quad (1)$$

and

$$\epsilon''_{ij} = \frac{\epsilon_{0ij} - \epsilon_{\infty ij}}{1 + \omega^2 \tau_j^2} \omega \tau_j \quad (2)$$

with the available τ_j 's previously determined by conductivity measurements¹². Paul *et al.*¹⁰ used the Gopalakrishna's method¹³ to measure τ_j 's from ϵ_{ij} 's in which all the polarisations including the fast polarisation

exist. If 1 is subtracted from low frequency ϵ_{0ij} and real ϵ'_{ij} , the corresponding static susceptibilities χ_{0ij} and real χ'_{ij} contain all the polarizations. When hf $\epsilon_{\infty ij}$ is subtracted from ϵ'_{ij} or static ϵ_{0ij} one obtains susceptibilities χ'_{ij} or χ_{0ij} respectively, involved with the orientational polarization alone to get accurate τ_j 's and μ_j 's.

Both the real ϵ'_{ij} and imaginary ϵ''_{ij} parts of ϵ^*_{ij} are related by¹⁴

$$\epsilon'_{ij} = \epsilon'_{\infty ij} + (1/\omega\tau_j) \epsilon''_{ij} \quad (3)$$

which in terms of established symbols of χ'_{ij} and χ''_{ij} becomes

$$\chi''_{ij} = \omega\tau_j \chi'_{ij} \quad (4)$$

Eq. (4) exhibit linear relationship between χ''_{ij} and χ'_{ij} as seen in Fig. 1. The slope $\omega\tau_j$ is used to get τ_j of a polar solute¹⁵. For most of the associative liquids studied elsewhere¹⁶, however, the variation of χ''_{ij} against χ'_{ij} is not strictly linear as seen in Figs. 2 and 3. Hence the slope of eq. (4) can be written as :

$$\frac{(d\chi''_{ij} / d\omega_j)_{\omega_j \rightarrow 0}}{(d\chi'_{ij} / d\omega_j)_{\omega_j \rightarrow 0}} = \omega\tau_j \quad (5)$$

containing τ_j 's of the present polar solutes. The τ_j 's estimated using eqs. (5) and (4) from both the methods are presented in Table 1. The excellent agreement between

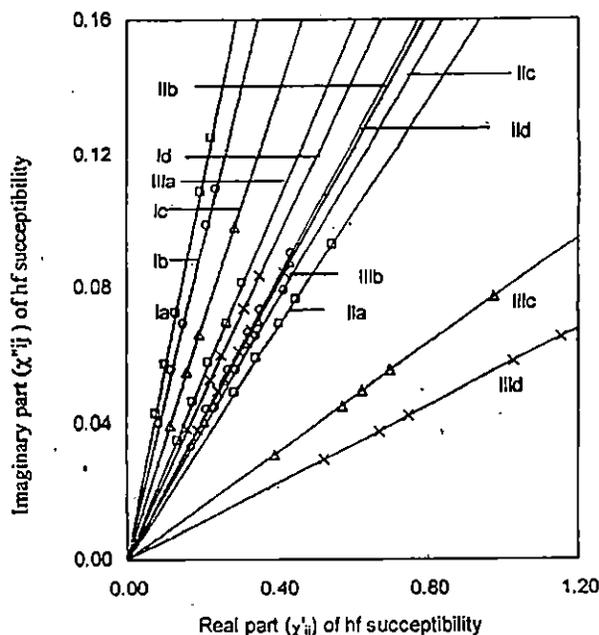


Fig. 1. Variation of imaginary part χ''_{ij} against real part χ'_{ij} of the complex hf dielectric orientational susceptibility χ^*_{ij} of some polysubstituted benzenes in C_6H_6 under 10 GHz electric field at various experimental temperatures. *m*-Di-isopropylbenzene : Ia (\square) at 30°, Ib (O) at 35°, Ic (Δ) at 40°, Id (\times) at 45°; *p*-methylbenzylchloride : IIa (\square) at 30°, IIb (O) at 35°, IIc (Δ) at 40°, IIId (\times) at 45°; *o*-chloroacetophenone : IIIa (\square) at 30°, IIIb (O) at 35°, IIIc (Δ) at 40°, IIIId (\times) at 45°C.

Table 1. Estimated relaxation times τ_j 's, enthalpy ΔH_τ , entropy ΔS_τ and free energy ΔF_τ of activation due to dielectric relaxation, dimensionless parameter $\gamma (= \Delta H_\tau / \Delta H_{\eta_i})$ from slope of $\ln \tau_j T$ vs $\ln \eta_i$ equation, enthalpy of activation ΔH_{η_i} due to viscous flow of the solvent, estimated hf dipole moment μ_j and theoretical dipole moment μ_{theo} in coulomb metre (c.m.) of some polysubstituted benzenes in solvent C_6H_6 at different experimental temperatures in °C under 10 GHz electric field frequency

System with sl. no. and mol. wt. (kg)	Temp. (°C)	τ_j in psec (eq. 4)	τ_j in psec from eq. (5)	ΔH_τ (kJ mol ⁻¹)	ΔS_τ (J mol ⁻¹ K ⁻¹)	ΔF_τ (kJ mol ⁻¹)	Value of δ	$\Delta H_{\eta_i} = (\Delta H_{\tau_j})$ (kJ mol ⁻¹)	Estimated dipole moment $\mu \times 10^{30}$ c.m. with τ_j from eq. (5)	$\mu_{theo} \times 10^{30}$ c.m. from bond angles and reduced bond moments
(I) <i>m</i> -Di-isopropyl-benzene ($M_j = 0.162$)	30	8.80	8.80		109.01	10.12			12.70	
	35	7.33	7.33		108.09	9.86			13.87	
	40	5.46	5.46	43.15	108.16	9.30	6.96	6.20	13.99	3.77
	45	3.74	3.76		109.01	8.49			14.76	
(II) <i>p</i> -Methylbenzoyl chloride ($M_j = 0.156$)	30	2.72	2.72		-59.09	7.16			9.63	
	35	3.30	3.30		-60.26	7.82			9.82	
	40	3.23	3.23	-10.74	-59.66	7.93	-1.61	6.67	9.95	8.80
	45	3.24	3.24		-59.28	8.11			10.10	
(III) <i>o</i> -Chloroacetophenone ($M_j = 0.156$)	30	4.20	4.20		255.12	8.26			6.83	
	35	3.04	3.04		253.09	7.61			7.72	
	40	1.26	1.26	85.56	255.84	5.48	13.56	6.31	7.05	7.40
	45	0.90	0.90		254.21	4.72			6.48	

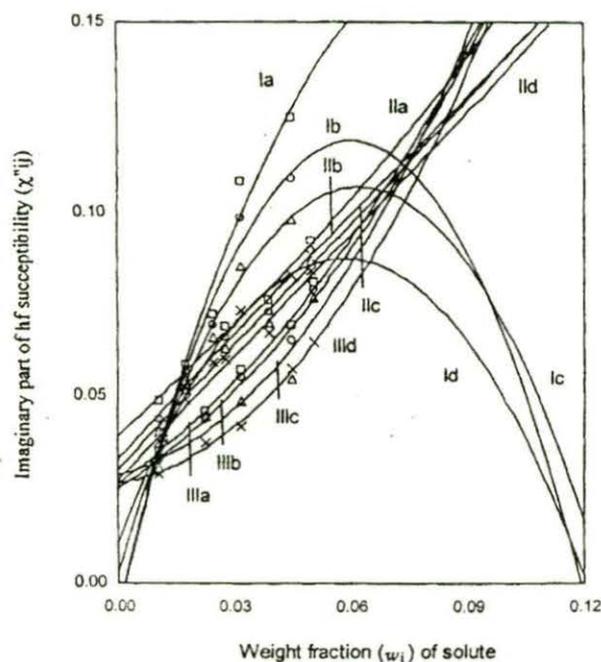


Fig. 2. Variation of imaginary part χ''_{ij} of hf susceptibility with weight fraction w_j 's of some polysubstituted benzenes in C_6H_6 under 10 GHz electric field at various experimental temperatures. *m*-Di-isopropylbenzene : Ia (\square) at 30°, Ib (O) at 35°, Ic (Δ) at 40°, Id (\times) at 45°; *p*-methylbenzylchloride : IIa (\square) at 30°, IIb (O) at 35°, IIc (Δ) at 40°, IID (\times) at 45°; *o*-chloroacetophenone : IIIa (\square) at 30°, IIIb (O) at 35°, IIIc (Δ) at 40°, IIId (\times) at 45°C.

τ_j 's indicates that the polar-polar interactions are almost eliminated in the limit of $w_j = 0$ to give reliable τ_j by the latter method¹⁷. The correlation coefficients r 's and relative errors of both the plots in Figs. 2 and 3 were obtained by regression analysis. They are within the range of 0.93 to 0.99 and 0.0008 to 0.0001 respectively, hereby indicating how far both χ''_{ij} 's and χ'_{ij} 's are correlated with w_j 's. It is evident from Table 1 that τ_j 's decrease with temperature. At constant temperature τ_j depends on the energy difference between the activated and normal states. At higher temperatures thermal agitation causes an increase in energy loss due to larger number of collisions and thereby decreases the values of τ_j 's. For *m*-diisopropyl benzenes the τ_j 's are greater in comparison to *p*-methyl benzoyl chloride and *o*-chloro acetophenone probably due to bigger size of the molecules containing higher number of carbon atoms. For systems II and III τ_j 's do not vary much with temperature because of the presence of the same number of C-atoms in both the molecules. *p*-Methyl benzoyl chloride shows reverse variation of τ_j with temperature. Inductive effect of CH_3 group put the $C=O$ group of $COCl$ to exist as dipolar structure

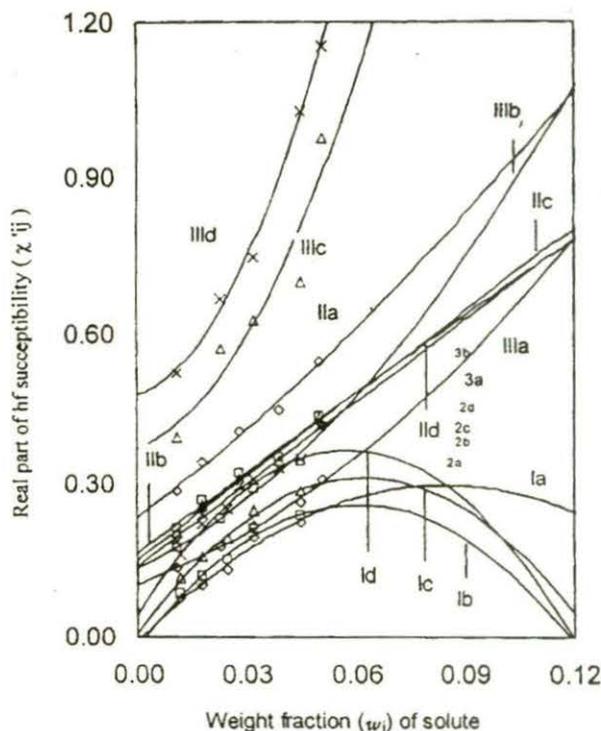


Fig. 3. Variation of imaginary part χ''_{ij} of hf susceptibility with weight fraction w_j 's of some polysubstituted benzenes in C_6H_6 under 10 GHz electric field at various experimental temperatures. *m*-Di-isopropylbenzene : Ia (\diamond) at 30°, Ib (\square) at 35°, Ic (Δ) at 40°, Id (\times) at 45°; *p*-methylbenzylchloride : IIa (\diamond) at 30°, IIb (\square) at 35°, IIc (Δ) at 40°, IID (\times) at 45°; *o*-chloroacetophenone : IIIa (\diamond) at 30°, IIIb (\square) at 35°, IIIc (Δ) at 40°, IIId (\times) at 45°C.

($>C^+-O^-$), therefore increase in temperature has no significant effect on τ_j of this system.

Dielectric relaxation is a process of rotation of polar molecule under hf electric field and it requires an activation energy ΔF_τ to overcome the potential energy barrier between two equilibrium positions. ΔF_τ is related to estimated τ_j by¹⁹

$$\tau_j = (A/T) e^{\Delta F_\tau/RT} \quad (6)$$

$$\text{where } \Delta F_\tau = \Delta H_\tau - T\Delta S_\tau \quad (7)$$

From eqs. (6) and (7) it follows that

$$\ln \tau_j T = \ln A' + (\Delta H_\tau/R) 1/T \quad (8)$$

$$\text{where } A' = Ae^{-\Delta S_\tau/R}$$

Eq. (8) is a straight line when $\ln(\tau_j T)$ is plotted against $1/T$ as seen in Fig. 4, the slope and intercept are used to get enthalpy of activation ΔH_τ , entropy of activation ΔS_τ and free energy of activation ΔF_τ due to dielectric relaxation as presented in Table 1. The enthalpy of activation ΔH_τ

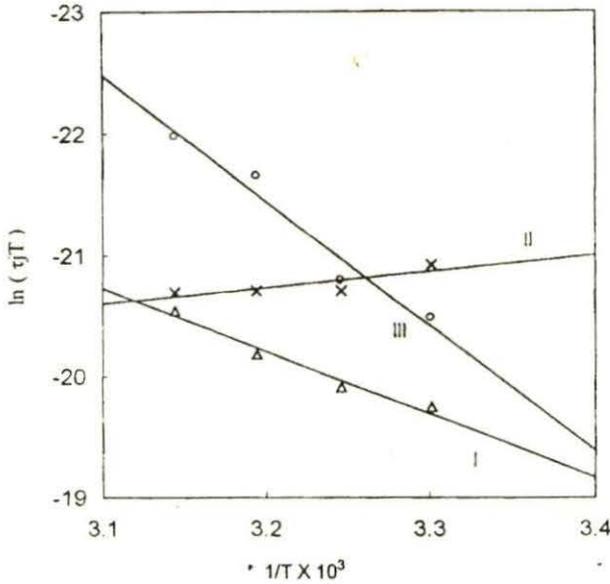


Fig. 4. The linear plot of $\ln(\tau_j T)$ against $1/T$ of some polysubstituted benzenes in C_6H_6 under 10 GHz electric field. (I) *m*-Diisopropylbenzene (Δ) using τ_j of eq. (2), (II) *p*-methylbenzylchloride (\times) using τ_j of eq. (2), (III) *o*-chloroacetophenone (O) using τ_j of eq. (2).

due to viscous flow of the solvent is ascertained from the slope δ ($= \Delta H_\tau / \Delta H_{\eta_i}$) of the linear equation of $\ln \tau_j T$ against $\ln \eta_i$, where η_i is the coefficient of viscosity of the solvent used.

It is evident from Table 1 and Fig. 4 that for system II the linear eq. (8) has negative slope to give negative ΔH_τ because for that system τ_j 's increases with temperature. The systems I and III shows positive ΔS_τ 's which suggest that the configuration involved in dipolar rotation has an activated state which is less ordered than the normal state²⁰. Unlike *p*-methyl benzoyl chloride both systems I and III show $\delta > 0.50$ (as seen in Table 1) indicating solvent environment around solute molecules to behave as solid phase rotators^{18,20}. ΔH_{η_i} in Table 1 involved with translational and rotational motions of the molecule is of lower value than those of ΔH_τ 's in which only the rotational motion occurs. The Debye factors $\tau_j T / \eta_i$ unlike Kalman factors $\tau_j T / \eta_i^\gamma$ at all temperatures are of constant orders for each system. This at once reflects the validity of Debye model¹⁸ of dielectric relaxation for such compounds in benzenes under 10 GHz electric field.

Theoretical formulations :

In order to obtain hf dipole moment μ_j , the Debye-Smyth's relation^{21,22} in terms of hf χ_{ij} 's is used

$$\chi''_{ij} = \frac{N\rho_{ij}\mu_j^2}{27\epsilon_0 M_j k_B T} \left(\frac{\omega\tau_j}{1 + \omega^2\tau_j^2} \right) (\epsilon_{ij} + 2)^2 w_j \quad (9)$$

where M_j = molecular weight of the solute in kg.

ϵ_{ij} = relative permittivity of solution (ij)

ρ_{ij} = density of solution (ij)

k_B = Boltzmann constant

Eq. (9) on differentiation with respect to w_j and at $w_j \rightarrow 0$

$$\left(\frac{d\chi''_{ij}}{dw_j} \right)_{w_j \rightarrow 0} = \frac{N\rho_i\mu_j^2}{27\epsilon_0 M_j k_B T} \left(\frac{\omega\tau_j}{1 + \omega^2\tau_j^2} \right) (\epsilon_j + 2)^2 \quad (10)$$

in the limit $w_j = 0$, because $\rho_{ij} \rightarrow \rho_i$, $\epsilon_{ij} \rightarrow \epsilon_i$ are the density, relative permittivity of solvent benzene. From eqs. (5) and (10) one obtains

$$\mu_j = \left[\frac{27\epsilon_0 M_j k_B T \beta}{N\rho_i (\epsilon_i + 2)^2 b} \right]^{1/2} \quad (11)$$

where $b = 1/(1 + \omega^2\tau_j^2)$ is a dimensionless parameter associated with estimated τ_j of eq. (5), β is the linear coefficient of $\chi'_{ij} - w_j$ curves of Fig. 3.

Experimental

The microwave radiations of frequency 10 GHz, generated by a Gunn oscillator fed by 10 volt dc power supply were passed through the isolator, tuner, frequency meter, attenuator and a slotted line fitted with a probe connected with a crystal detector and a VSWR meter. The other end of the slotted line was connected to a 6.4 cm long silvered waveguide cell which was connected to a thermostat by a 90° bend to carry out the experimental values of ϵ'_{ij} and ϵ''_{ij} at different temperatures¹⁰.

The viscosity η_i and density ρ_i of benzene at various experimental temperatures were measured using an Ubbelohde viscometer and a pycnometer respectively. The analytical grade polysubstituted benzenes like 1,3-diisopropyl benzene, *p*-methyl benzoyl chloride and *o*-chloroacetophenone as well as the solvent benzene were supplied by Central Drug Research Institute, Lucknow. They were further purified by repeated fractional distillations and the physical constants like density, viscosity and relative permittivity ϵ_i of solvent C_6H_6 were checked in agreement with the literature values¹⁰. The polar liquids were kept over molecular sieve of mesh 4 Å for 48

h with occasional shaking. They were then distilled through a long vertical fractionating column and the middle fractions were used for the present study. Benzene (B.D.H., Analar) was purified by refluxing over sodium metal for 6 h and then distilled through a long vertical fractionating column. The middle fraction of the solvent was used to make solutions of different w_j 's of the respective solutes at different experimental temperatures²⁶.

Results and discussion

The μ_j 's thus measured at all temperatures are entered in Table 1. Almost all the $\chi'_{ij}-w_j$ curves have a tendency to come closer within the range $0.00 < w_j < 0.03$ probably due to almost same polarity of the molecules²² arising out of solute-solvent or solute-solute molecular association which may be supposed to be physico-chemical properties¹⁴ of the systems. This can be inferred from the nonlinear variation of μ_j-t curves of Fig. 5. Unlike the system I and II, *o*-chloroacetophenone (system III) shows minimum μ_j 's at lower and higher temperatures. In the vicinity of $-\text{COCH}_3$ and Cl, the electronic factor may operate between the carbonyl oxygen and Cl atom at *ortho* position may be the reason for its anomalous behaviour towards μ_j value as seen in Fig. 6. The minimum μ_j 's indicate the attainment of slight symmetry in the molecules at those temperatures¹⁸. The monotonic increase of μ_j with temperature for *p*-methyl benzoyl chloride oc-

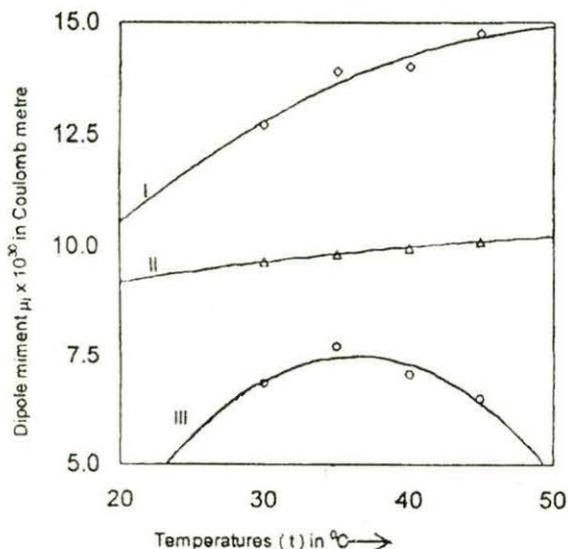


Fig. 5. Plot of measured dipole moment μ_j in Coulomb metre [using τ_j by our method i.e. eq. (5)] with temperatures t in °C of some polysubstituted benzenes in C_6H_6 under 10 GHz electric field. (I) *m*-Di-isopropylbenzene (□) using τ_j of eq. (2), (II) *p*-methylbenzylchloride (Δ) using τ_j of eq. (2), (III) *o*-chloroacetophenone (O) using τ_j of eq. (2).

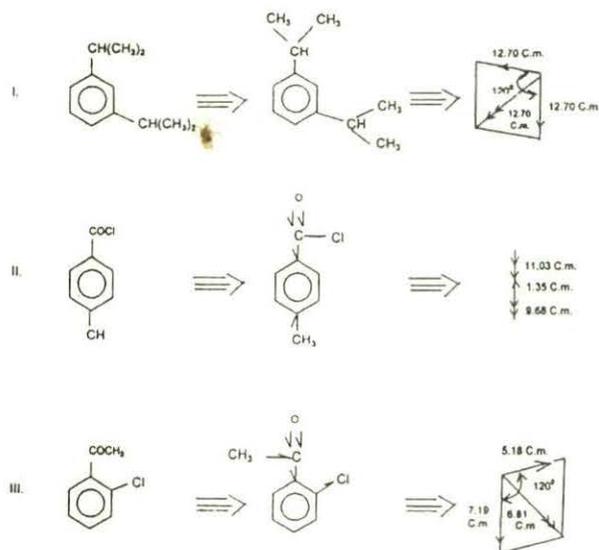


Fig. 6. Conformational structures of different polysubstituted benzenes with dipole moment $\mu_{\text{theo}} \times 10^{30}$ in Coulomb metre (c.m.). (I) *m*-Di-isopropylbenzene, (II) *p*-methylbenzylchloride, (III) *o*-chloroacetophenone.

curs for its increasing molecular asymmetry at higher temperatures. The above nature of μ_j-t curves arises due to alignment of different types of bondings among the solute and solvent molecules which are either formed or broken to some extent^{23,24}. Thus the measured μ_j 's reflects the stability or instability of the molecules. This is confirmed by different thermodynamic energy parameters in order to make a strong comment on their physico-chemical properties.

Theoretical dipole moment's μ_{theo} 's, as seen in Fig. 6. are, however, considered by vector addition of bond moments of substituted polar groups of molecules from the available infrared spectroscopic data of bond moments assuming the molecules to be planar ones. They are placed in Table 1 to compare them with the measured hf μ_j 's. The molecules under study have polar groups and there is large probability of intramolecular group rotations and, therefore, these molecules may not be represented by simple Debye type dielectric dispersions. On the otherhand, Higasi's equation⁷ for single frequency in dilute solutions or Higasi's frequency variation method could, however, be used to evaluate those group rotations for such molecules. But the molecules are very simple and the purpose of the paper is to see the applicability of Debye type dispersions in them in evaluating τ_j and μ_j which are claimed to be accurate with 10% and 5% respectively. The molecules of polysubstituted benzenes

referred to tables and figures are planar and have the property of cyclic delocalization of π electrons on each C-atom. The solvent benzene is a cyclic and planar compound with three double bonds and six p -electrons on six carbon atoms of the benzene ring. Hence π - π interaction or resonance effect combined with an inductive effect commonly known as mesomeric effect in excited state called the electromeric effect is expected to play the prominent role in μ_j 's. The slight disagreement between hf μ_j 's and μ_{theo} 's of Fig. 6 is explained on the basis of the fact that the flexible polar groups of the molecules are greatly influenced by hf electric field to yield the inductive, mesomeric and electromeric effects in them to give higher μ_j values, especially for *m*-diisopropyl benzene. All these effects, are, however, incorporated in their structures by multiplying the bond moments by a factor μ_j/μ_{theo} to make μ_{theo} 's closer to μ_j 's as sketched in Fig. 6. The electromeric effect caused by $>C=O$ in the 2nd and 3rd molecules may be the reason to make μ_j 's more closer to μ_{theo} 's²⁵.

Conclusion :

The theoretical formulations in terms of internationally accepted and established symbols of established dielectric terminologies and parameters in SI units are more topical, significant and simpler one to have deep insight into the physico-chemical, structural and associational aspects of polysubstituted benzenes in C_6H_6 at different temperatures under 10 GHz electric field. The conformational structures so far sketched in Fig. 6 are also significant because they enhance the scientific content of the existing knowledge of dielectric relaxation processes. The curves satisfied by experimental points in all the figures reflect the validity of the theoretical formulations based on Debye model to estimate several physical parameters such as τ_j 's, μ_j 's and ΔH_τ , ΔF_τ , ΔS_τ etc. which are more of archival values to study the temperature variation of physico-chemical properties of dipolar molecules. The uncertainty in the evaluated τ_j and μ_j values are of 10% and 5% errors which are claimed to be accurate.

Acknowledgement

The authors express their heartfelt thanks to the Central Drug Research Institute, Lucknow, India for supplying the materials.

References

1. L. Glasser, J. Crossley and C. P. Smyth, *J. Chem. Phys.*, 1972, **57**, 3977.

2. C. B. Agarwal, *Indian J. Pure Appl. Phys.*, 1986, **24**, 204.
3. S. K. Cole and R. H. Cole, *J. Chem. Phys.*, 1941, **9**, 341.
4. E. A. Guggenheim, *Trans. Faraday Soc.*, 1949, **45**, 714.
5. A. Sharma and D. R. Sharma, *J. Phys. Soc. Jpn.*, 1992, **61**, 1049.
6. U. Saha and R. Ghosh, *J. Phys. D : Appl. Phys. (UK)*, 1999, **32**, 820.
7. K. Higasi, Y. Koga and M. Nakamura, *Bull. Chem. Soc. Jpn.*, 1971, **44**, 988.
8. N. Nandi, K. Bhattacharyya and B. Bagchi, *Chem. Rev.*, 2000, **100**, 2013.
9. N. Nandi and B. Bagchi, *J. Phys. Chem.*, 1997, **B101**, 10954.
10. N. Paul, K. P. Sharma and S. Chattopadhyay, *Indian J. Phys.*, 1997, **71B**, 711.
11. N. E. Hill, W. E. Vaughan, A. H. Price and M. Davies, "Dielectric Properties and Molecular Behaviour", Van Nostrand Reinhold Company, London, 1969.
12. N. Ghosh, A. Karmakar, S. K. Sit and S. Acharyya, *Indian J. Pure Appl. Phys.*, 2000, **38**, 574.
13. K. V. Gopalakrishna, *Trans. Faraday Soc.*, 1957, **53**, 767.
14. U. K. Mitra, N. Ghosh, P. Ghosh and S. Acharyya, *J. Mole. Liq.*, 2006, **126**, 53.
15. M. B. R. Murthy, R. L. Patil and D. K. Deshpande, *Indian J. Phys.*, 1989, **63B**, 491.
16. N. Ghosh, S. K. Sit and S. Acharyya, *J. Mole. Liq.*, 2003, **102**, 29.
17. R. C. Basak, S. K. Sit, N. Nandi and S. Acharyya, *Indian J. Phys.*, 1996, **70B**, 37.
18. N. Ghosh, R. C. Basak, S. K. Sit and S. Acharyya, *J. Mole. Liq.*, 2000, **85**, 375.
19. H. Eyring, S. Glasstone and K. J. Laidler, "The Theory of Rate Process", McGraw Hill, New York, 1941.
20. S. K. Sit, N. Ghosh, U. Saha and S. Acharyya, *Indian J. Phys.*, 1997, **71B**, 533.
21. C. P. Smyth, "Dielectric Behaviour and Structure", McGraw Hill, New York, 1955.
22. N. Ghosh, S. K. Sit, A. K. Bothra and S. Acharyya, *J. Phys. D : Appl. Phys. (UK)*, 2001, **34**, 379.
23. R. L. Dhar, A. Mathur, J. P. Shukla and M. C. Saxena, *Indian J. Pure Appl. Phys.*, 1973, **11**, 568.
24. S. K. S. Somevanshi, S. B. I. Misra and N. K. Mehrotra, *Indian J. Pure Appl. Phys.*, 1978, **16**, 57.
25. "Internal Rotation in Molecules", ed. W. J. Thomas, Orville, John Wiley, 1974.
26. P. Ghosh, R. P. Singh, C. P. Sinha and J. Das, *J. Chem. Eng. Data*, 1990, **35**, 93.

The Structural Aspects and Physico Chemical Properties of Binary Polar Liquids in Nonpolar Solvent under a Gigahertz Electric Field

U. K. Mitra*, N. Ghosh, S. Acharyya and P. Ghosh

The mixtures of two polar liquids N,N-dimethyl formamide DMF(j) and N,N-dimethyl sulphoxide DMSO(k) in a nonpolar solvent benzene C_6H_6 (i) are studied in terms of the ternary(ijk) high frequency (hf) orientational susceptibilities χ_{ijk} 's at different experimental temperatures in $^{\circ}C$ to arrive at the structural and associational aspects of those polar liquids. The estimation of binary relaxation time τ_{jk} and dipole moment μ_{jk} and several thermodynamic energy parameters like the enthalpy of activation $(\Delta H\tau)_{jk}$, the entropy of activation $(\Delta S\tau)_{jk}$, the free energy of activation $(\Delta F\tau)_{jk}$ of the binary solutes are, however, obtained in order to reach the conclusion. The dimensionless parameter $\delta = (\Delta H\tau)_{jk} / \Delta H\eta_i$ estimated from the slope of the linear equation of $\ln\tau_{jk}T$ against $\ln\eta_i$ where η_i is the coefficient of viscosity of the solvent used, provides one with the information of the solute-solute and solute-solvent molecular associations among the molecules concerned. Almost constant values of Debye factor $\tau_{jk}T / \eta_i$ unlike Kalman factors $\tau_{jk}T / \eta_i^{\delta}$ indicate the Debye relaxation mechanism obeyed by the solutions of binary associated molecules in C_6H_6 . The measured hf binary dipole moment μ_{jk} in terms of estimated binary relaxation time τ_{jk} are compared with the theoretical dipole moments μ_{theo} 's obtained from the bond moments of the substituent polar groups attached to the parent molecules only to support their conformations of associations. The disagreement between μ_{jk} 's and μ_{theo} 's indicates the inductive, mesomeric and electromeric effects of the substituent polar groups in addition to their H-bonding in a gigahertz electric field.

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