Chapter 10

SUMMARY AND CONCLUSIONS

The subject matter of the thesis entitled "Dispersion and absorption phenomena of dipolar liquid in nonpolar solvent" has been divided into the following chapters. The Chapter1 entitled "General introduction and review of the previous works" contains the research works done by a large number of workers in dispersion and absorption phenomena of dipolar liquid in non-polar solvent developed chronologically from 1912 onwards. The present author in this chapter collects them. The Chapter2 under the caption of "Scope and objective of the present work" includes the different theoretical formulae developed by the present worker in order to apply them in a large number of polar-nonpolar liquid mixtures. Thus an important conclusion was, however, reached by the present research worker in order to publish them in reputed Indian and foreign journals.

The Chapter3 presents a derived linear 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 disubstituted benzenes and anilines (j) in aprotic and nonpolar solvents (i) C_6H_6 and CCl_4 under 9.945 GHz electric field are obtained from the available measured dielectric relative permittivities at 35^0C. The double relaxation times τ_1 and τ_2 of the flexible part and the whole molecule are estimated from the slope and intercept of the above equation. χ_{ij}' and χ_{ij}'' are the real and imaginary parts of the high frequency complex orientational dielectric susceptibility χ_{ij}^* and χ_{oij} is the low frequency dielectric susceptibility which is real. They are, however, related with the measured relative permittivities. τ_j's are calculated from the ratio of the individual slope of the variation of χ_{ij}'' and χ_{ij}' with w_j's at $w_j{\rightarrow}0$ assuming single Debye like dispersion and compared with Murthy et al (Ind. J. Phys. 1989 63B 491) and Gopalakrishna (Trans. Faraday Soc. 1957 53 767). The weighted contributions c_1 and c_2 towards dielectric relaxations for τ_1 and τ_2 can, however, be obtained from Fröhlich's theoretical formulations of χ_{ij}'/χ_{oij} and χ_{ij}''/χ_{oij} and compared with those from the experimentally measured values of $(\chi_{ij}'/\chi_{oij})_{wj{\rightarrow}0}$ and $(\chi_{ij}''/\chi_{oij})_{wj{\rightarrow}0}$. The latter measured values are employed to get symmetric distribution parameter γ to yield symmetric relaxation time τ_s. The curve of $(1/\phi)\log(\cos\phi)$ against ϕ in degrees together with the values of $(\chi_{ij}'/\chi_{oij})_{wj{\rightarrow}0}$ and $(\chi_{ij}''/\chi_{oij})_{wj{\rightarrow}0}$ experimentally obtained, give the asymmetric distribution parameter δ to get the characteristic relaxation time τ_{cs}. All these findings ultimately establish the different types of relaxation behaviours for such complex molecules. The dipole moments μ_1 and μ_2 for the flexible part and the whole molecule are ascertained from τ_1 and τ_2 and the linear coefficients β_1 of χ_{ij}'- w_j and

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β_2 of σ_{ij} - w_j curves respectively where σ_{ij} is the hf conductivity. The μ's are finally compared with the reported μ's and μ_{theo}'s derived from available bond angles and bond moments of the substituted polar groups of disubstituted anilines to conclude a part of the molecule is rotating while the whole molecular rotation occurs for disubstituted benzenes. The slight disagreement between measured μ's and μ_{theo}'s can, however, be interpreted by the inductive, mesomeric and electromeric effects of the polar groups of the parent molecules.

The ratio of the linear coefficients of the fitted individual equations of χ_{ij}''- w_j and χ_{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 ^{0}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_{τ}, entropy of activation ΔS_{τ}, and freee energy of activation ΔF_{τ}, 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}, 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 para compounds. Debye-Pellat's equations are, therefore, used to obtain static as well as infinitely hf permittivities ε_{oij} and $\varepsilon_{\infty ij}$ 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 χ_{ij}'- w_j equations to yield hf μ_j's interms 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 electromeric effects in them. All these factors are presented in Chapter4 of this thesis.

The Chapter5 reports 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) which 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 the solutes at various experimental temperatures [Saha etal 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 & μ_1 in Coulomb-metre (C.m) measured from the slope β's of χ_{ij}'–w_j curves are compared with those of conductivity σ_{ij} measurements using τ's from the ratio of individual slope of $(d\chi_{ij}''/dw_j)_{wj\rightarrow o}$ and $(d\chi_{ij}'/dw_j)_{wj\rightarrow o}$, linear slope of χ_{ij}''–χ_{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_τ, free energy of activation ΔF_τ and entropy of activation ΔS_τ'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.

The Chapter6 is concerned with a graphical method to measure the double relaxation times τ_2 and τ_1 for the rotations of the flexible part and the whole molecule of some long-chain alcohols in n-heptane under 24.33 GHz (K-Band), 9.25 GHz (X-Band) and 3.00 GHz (J-Band) electric fields on the basis of Debye and Fröhlich models. The fixed τ_1 and τ_2 at those frequencies are compared with the average τ_1 and τ_2 measured by the single frequency method of Saha et al (1994) and reported average τ's. This reveals the material property of the chemical systems in identical environments. τ's thus obtained agree well with the reported average τ's at three different experimental frequencies for most of the alcohols. This at once indicates the whole molecular rotation of the dipolar molecules at those

frequencies. The dipole moments μ_1 and μ_2 are, however, measured from the linear coefficients β's of hf susceptibilities χ_{ij}''s curves against weight fractions w_j's of the alcohols at all the frequencies in terms of the graphically obtained τ_1 and τ_2 and the reported τ's by the existing methods. Theoretical dipole moments μ_{theo}'s from the available bond angles and bond moments are also determined. The slight disagreement among the μ_{theo}'s, reported and estimated μ's indicates the existence of the inductive, electromeric and mesomeric effects of the substituent polar group –OH attached to the parent ones.

The relaxation time τ and dipole moment μ of some methyl benzenes and ketones (j) in a nonpolar solvent benzene (i) at 25^0C under 9.585 GHz electric field are obtained from the measured real and imaginary parts ε_{ij}' and ε_{ij}'' of hf complex relative permittivity ε_{ij}^* at various weight fractions w_j's of a polar liquid. The methodology to get τ from the ratio of the individual slopes of real $\sigma_{ij}'(=\omega\varepsilon_0\varepsilon_{ij}'')$ and imaginary $\sigma_{ij}''(=\omega\varepsilon_0\varepsilon_{ij}')$ of complex hf conductivity σ_{ij}^* curve against w_j's, seems to be a significant improvement over the existing one like the linear slope of σ_{ij}''– σ_{ij}' curve. The variation of σ_{ij} – w_j curve like σ_{ij}''– w_j curve is often convex indicating the probable occurrence of phase change in the polar-nonpolar liquid mixture after a certain concentration. The convex nature of σ_{ij}'– w_j curves for some systems indicate the maximum absorption of hf electric energy unlike other systems. The estimated μ's from slope β of hf conductivity σ_{ij} – w_j curve and τ from both the methods are compared with the work of Gopalakrishna to establish the applicability of the methods. Theoretical dipole moment μ_{theo}'s from available bond angles and bond moments are calculated by considering inductive, mesomeric and electromeric effects of the substituent polar groups of the molecules. All this information is presented in Chapter7.

In Chapter8 the use of slopes of individual variation of the imaginary σ_{ij}'' and real σ_{ij}' parts of high frequency (hf) conductivity σ_{ij}^* with the weight fractions w_j's of a solute is employed to determine the relaxation times τ_j's of some monosubstituted anilines in C_6H_6. The dipole moments μ_j's of such polar molecules in terms of estimated τ_j's are calculated and compared with those by using the existing methods for τ_j' (Murthy et al 1989). Excellent agreement of μ_j's in all cases except m-toluidine indicates the applicability of both the methods. The hf μ_j as well as static μ_s differ from μ_{theo}'s as obtained from the available bond angles and bond moments. The reduced bond moments are, however,

calculated from the estimated μ_j, μ_s and μ_{theo} to yield the exact μ's in close agreement with μ_s and μ_j only to establiash the presence of inductive and mesomeric moments of the substituent groups, in addition to solute-solute or solute-solvent molecular associations among the molecules in the solution. The μ_j's being little affected by the frequency of the electric field, are finally compared with μ_2 and μ_1 (Sit and Acharyya, 1996) due to rotations of the whole and a part of the molecules. They are very close to μ_1 indicating the fact that a part of the molecule is rotating under the electric field of 10 GHz.

Similarly the Chapter9 gives the structural and associational aspects of some straight chain alcohols from their static dipole moments μ_s's and high frequency (hf) dipole moments μ_j's in terms of relaxation times τ_j's under effective dispersive region of nearly 24 GHz electric field. τ_j's are estimated from the slope of the linear variation of imaginary part σ_{ij}'' with real part σ_{ij}' of hf complex conductivity σ_{ij}^* for different weight fractions w_j in order to compare with those obtained from the ratio of the individual slopes of σ_{ij}'' and σ_{ij}' with w_j's of solutes. The linear coefficients of the static experimental parameter X_{ij} with w_j are used to obtain μ_s. The slopes β's of σ_{ij} with w_j's are employed to get hf μ_j in terms of τ_j's obtained by two methods only to see how far they agree with μ_2 and μ_1 from double relaxation method (Sit & Acharyya, 1996 and Sit et al 1997). It is observed that –OH bond of alcohols about $\equiv$C–O– bond rotates under GHz electric field. The slight disagreement of theoretical dipole moments μ_{theo}'s from available bond angles and bond moments with μ_j's and μ_s's suggest the strong hydrogen bonding in them, in addition to mesomeric and inductive moments of the substituent polar groups attached to the parent molecule.

Theories of dispersions and absorptions have been formulated in terms of relative permittivities ε_{ij}'s. Measurement of τ_j's and μ_j's were carried out in terms of hf conductivity σ_{ij} which is concerned with bound molecular charges of polar molecules. Nowadays, it is preferred to study in terms of dielectric orientation susceptibility χ_{ij}'s in SI units. χ_{ij}'s are supposed to be involved only with orientation polarisation of molecules. It is to be noted that the dielectric susceptibilities χ's are given by the subtraction of either 1 or ε_∞ from relative permittivity ε_r. If 1 is subtracted, the susceptibility due to all operating polarisation processes results, while if ε_∞ is subtracted from the low frequency value of ε_r, the susceptibility due only to orientation polarisation processes is given. The methods appear to

be much simpler, straightforward and easy to arrive at the expected conclusion. Moreover, the polar-nonpolar liquid mixtures can be studied by taking into account of the concept of other models like Onsager, Kirkwood, Fröhlich etc. But those models are not so simpler like Debye-Smyth. Recently Thermally Stimulated Depolarisation Current Density (TSDCD) and Isothermal Frequency Domain AC Spectroscopy (IFDS) are used to study the dispersion and absorption phenomena of dielectropolar liquids.

The correlation between the conformational structures obtained from the available bond angles and bond lengths with the observed results enhances the scientific contents and adds a new horizon of understanding to the existing knowledge of dispersion and absorption. The thesis thus provides the future workers in this field to open a new and vast scope to work further in polar-nonpolar liquid mixtures under hf electric field.