

CHAPTER -11

SUMMARY AND CONCLUSION

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The subject matter of the thesis has been divided in several chapters. All the chapters are highly informative to analyse the structural and associational aspects of dielectropolar liquid molecules under low and high frequency (hf) electric fields.

A brief account of the dielectric terminologies and parameters in terms of relative permittivities under the static and hf electric fields has been made in **Chapter 1**. Different fundamental theories of polar dielectrics in nonpolar solvents have been well discussed to represent the chronological development of the subject. The theoretical equations had been used by previous experimental workers in terms of various plots, tables and figures to estimate the relaxation parameters. Short review on the experimental and theoretical technique has been included in this chapter to support different molecular associations. At the end, an extensive reference list of dielectric theories on liquids and solids has been added to acquire an overall knowledge.

In **Chapter 2** the derived theoretical formulations to estimate relaxation time τ_j , static dipole moment μ_s , double relaxation times τ_1 & τ_2 and dipole moments μ_1 & μ_2 under low and hf electric field of GHz range is presented. The block diagram of the experimental set up of radio frequency (rf) oscillator along with the theoretical formulations to estimate rf conductivity σ'_{ij} , τ_j and μ_j under rf electric field has been shown and well discussed. The overall outcome of **Chapter 2** is aimed at to conclude on the structural and associational aspects of polar liquid molecules in nonpolar solvents, under hf electric fields. The theories are based on Debye, Smyth and Hill model of dielectropolar liquids. The concept of structural and associational aspects of polar molecules in nonpolar solvents are, however, achieved through the study of thermodynamic energy parameters like enthalpy of activation ΔH_τ , entropy of activation ΔS_τ and free energy of activation ΔF_τ of dielectric relaxation of a polar molecule. The variation of τ

and μ with temperature and concentration helps one to estimate energy parameters from the rate theory of Eyring et. al. The theoretical formulations so far derived are tested by experimental measurements in the rf electric field signifying the applicability of the method.

The structural and associational aspects of binary (jk) polar-polar mixtures of N, N dimethyl formamide (DMF) and dimethyl sulphoxide (DMSO) together with a single (j or k) N, N diethyl formamide (DEF) and DMSO in nonpolar solvent (i) are studied in terms of relaxation times τ_j , τ_k or τ_{jk} and dipole moments μ_j , μ_k or μ_{jk} of the jth, kth or jk polar mixture of the solutes under GHz electric field at various experimental temperatures for different weight fractions w_{jk} 's of polar solutes in **Chapter 3**. The variation of τ_{jk} with mole fractions x_k 's of DMSO in DMF and C_6H_6 reveals the probable solute-solute molecular associations around $x_k = 0.5$ of DMSO. The solute-solvent molecular associations begin at and around 50 mole % of DMSO in DMF and continue upto 100 mole % of DMSO. The concentration and temperature variation of τ_{jk} of such aprotic liquids are in excellent agreement with the variation of τ_{jk} of jk polar mixture with x_k 's of DMSO. Thermodynamic energy parameters are, however, obtained from Eyrings' rate process equation with the estimated τ 's to support the molecular association. The slight disagreement between the theoretical dipole moments μ_{theo} 's from the bond angles and bond moments is noticed with the measured μ 's to indicate the temperature dependence of mesomeric and inductive effects of different substituent polar groups of the molecules.

The **Chapter 4**, however, reports the double relaxation behaviour of some isomeric octyl alcohols in n-heptane at 25°C under 24.33, 9.25 and 3.00 GHz electric fields. τ_1 and τ_2 for the flexible parts and the whole molecules are measured by a single frequency measurement of dielectric relaxation parameters. The alcohols are long straight chain hydrogen bonded polymer having methyl and hydroxyl groups attached to the — C — atoms which may bend, twist or

rotate internally each with a characteristic τ . The relative contributions c_1 and c_2 are estimated from Fröhlich's equations and graphical technique. τ_1 and τ_2 decreases with frequency (f) due to rupture of H-bonding in long chain alcohols causing self or solute-solvent association of molecules. μ_1 and μ_2 in terms of τ_1 and τ_2 are again found out for the rotation of their $-\text{OH}$ groups about $-\text{C}-\text{O}-$ bonds only. μ_1 and μ_2 are finally compared with μ_{theo} 's arising out of structural aspects of the bond angles and bond moments of the substituent polar groups of the molecules.

The structural and associational aspects of nonspherical para polar liquids (j) in nonpolar solvents (i) are studied through hf conductivities σ_{ij} 's of solutions in **Chapter 5**. These liquids are widely used in pharmaceuticals, dyes, fragrances, agrochemicals, explosives and plastics. τ 's of the associative liquids under 3 cm wavelength electric field at different experimental temperatures in $^{\circ}\text{C}$, are estimated from the ratio of slopes of the individual variations of real σ'_{ij} and imaginary σ''_{ij} parts of hf complex conductivity σ^*_{ij} with w_j 's of polar liquids. The variation of τ with temperature for comparatively larger nonspherical para molecules in dioxane is not strictly obeyed by Debye model unlike other simpler para di or tri-substituted benzenes in C_6H_6 . The thermodynamic energy parameters ΔH_{τ} , ΔS_{τ} and ΔF_{τ} are obtained from Eyrings' rate process equation with the estimated τ 's in order to get solvent environment around the solute. The value of $\gamma (= \Delta H_{\tau} / \Delta H_{\eta}) > 0.50$ for all p-liquids except for p-bromonitrobenzene indicating solvent environment around solute molecules. The higher values of γ are due to solid phase rotators for the liquids. The estimated Kalman and Debye factors $\tau_j T / \eta^{\gamma}$ and $\tau_j T / \eta$ establish the Debye relaxation mechanism for almost all the para molecules. The obtained μ_j 's with the estimated τ_j 's are then compared with the reported μ 's and μ_{theo} 's. The temperature variation of μ_j explains the rupture of solute-solute association to form solute-solvent association due to stretching of bond angles and bond moments of polar molecules. The non associative nature of p-bromonitrobenzene in C_6H_6 is also confirmed by typical

nature of μ_j -t curve. Association or non-association of polar solutes in C_6H_6 and dioxane is, however, established from negative and positive ΔS_τ 's of Table 5.2. μ_j 's of some para molecules are often zero indicating the symmetric shape of the molecules. At other temperatures some p-molecules show the net moments. The slight disagreement between the measured and theoretical μ 's reveals the presence of inductive and mesomeric effects of the substituent polar groups in molecules at different experimental temperatures.

In **Chapter 6** the structural and associational aspects of some straight chain aliphatic alcohols are inferred from their static μ_s 's and hf μ_j 's in terms of τ_j 's under effective dispersive region of nearly 24 GHz electric field. Since dielectric dispersion is governed by frequency domain of AC spectroscopy, the dipolar liquids of normal and octyl alcohols absorb electric energy much more strongly at 24 GHz to yield accurate relative permittivities. Taking this fact into account the study of dielectric relaxation was carried out on such dielectropolar liquids. τ_j 's are estimated from the slope of linear variation of the imaginary part σ''_{ij} with the real part σ'_{ij} of hf complex conductivity σ_{ij}^* for different w_j 's in order to compare with those obtained from the ratio of individual slopes of σ''_{ij} and σ'_{ij} with w_j 's of solute. Non linear variation of both σ''_{ij} and σ'_{ij} with w_j indicates various types of molecular association in long chain dielectropolar alcohols. The linear coefficient a_1 of static experimental parameter X_{ij} with w_j is used to obtain μ_s . The $X_{ij}-w_j$ curves are closer within the region $0.1 \leq w_j \leq 0.2$ indicating same polarity of the molecules arising out of solute-solvent molecular associations. The slopes β of $\sigma_{ij}-w_j$ curves are employed to get hf μ_j 's in terms of τ_j 's obtained by two methods only to see how far they agree with μ_1 and μ_2 from double relaxation method. Unlike methanol and ethanol μ_s 's are lower than μ_j 's and μ_1 's for all the alcohols. This at once reveals the possible formation of monomers and dimers in the static and hf electric field. The dimer formation is favourable in octyl alcohols than the normal alcohols due to existence of strong inductive effect for their - OH groups at the end of molecular chains. It is,

however, observed that — OH groups of alcohols rotates about — C — O — bond under GHz electric field. The slight disagreement of μ_{theo} 's with μ_j 's and μ_s 's suggest the strong hydrogen bonding in them, in addition to mesomeric and inductive effects of the substituent polar groups attached to the parent molecules. Comparatively higher values of both μ_{theo} 's and μ_j 's in octyl alcohols indicates the solute-solvent association due to strong hydrogen bonding supported by the fact that — OH groups being screened by —CH₃ and a large number of >CH₂ groups.

τ_1 and τ_2 for isomers of anisidine and toluidine in C₆H₆ under 9.945 GHz electric field are predicted from the slope and intercept of a derived linear equation of $(\chi_{\text{ojj}} - \chi'_{\text{ij}}) / \chi'_{\text{ij}}$ against $\chi''_{\text{ij}} / \chi'_{\text{ij}}$ for different w_j 's solute at 35°C. χ'_{ij} and χ''_{ij} are the real and imaginary parts of hf complex orientational susceptibility χ^*_{ij} and χ_{ojj} is the low frequency real dielectric susceptibility. Larger values of τ_2 occur due to larger size of rotating units governed by solute-solvent i.e. monomer formation under hf electric field. Highly dispersive region is again established by the isomers of anisidine and toluidine which absorbed electric energy much more strongly at 9.945 GHz electric field to show reasonable τ_1 and τ_2 . The τ 's, dimensionless parameter b 's and the linear coefficients β 's of $\chi'_{\text{ij}} - w_j$ curves are used to obtain μ_1 and μ_2 of the molecules. Almost all $\chi'_{\text{ij}} - w_j$ curves have a tendency to be closer within the region $0.00 \leq w_j \leq 0.03$ showing the possible formation of monomers and dimers. c_1 and c_2 due to τ_1 and τ_2 from Fröhlich's equations are compared with the experimental ones by concentration variation of $\chi'_{\text{ij}} / \chi_{\text{ojj}}$ and $\chi''_{\text{ij}} / \chi_{\text{ojj}}$ curves at $w_j \rightarrow 0$. Theoretical and experimental values of c_1 and c_2 showed $|c_2 + c_2| \simeq 1$ establishing the validity of the linear equation in such liquids also. The estimated τ 's from the ratio of the individual slopes of variations of χ''_{ij} and χ'_{ij} with w_j at $w_j \rightarrow 0$ are compared with the existing methods. The symmetric and characteristic τ_s and τ_{cs} by symmetric and asymmetric distribution parameters γ and δ suggest the symmetric relaxation behaviour of the molecules. The measured μ_1 and μ_2 by double relaxation method

and reported μ suggest that a part of the molecule is rotating under GHz electric field. The slight disagreement between μ_{theo} and measured μ_1 demands the inductive and mesomeric effects of the substituted polar groups in addition to structural and associational aspects of such molecules. All these findings are beautifully presented in **Chapter 7**.

The linear equation $(\chi_{\text{oij}} - \chi'_{\text{ij}}) / \chi'_{\text{ij}} = \omega(\tau_1 + \tau_2) (\chi''_{\text{ij}} / \chi'_{\text{ij}}) - \omega^2 \tau_1 \tau_2$ for different ω_j 's of monosubstituted anilines (j) in C_6H_6 at 35°C under electric field frequencies of 2.02, 3.86 and 22.06 GHz are plotted graphically in **Chapter 8** to yield τ_1 and τ_2 . Larger τ_2 signify the monomer associations. τ 's from the ratio of the individual slopes of χ''_{ij} and χ'_{ij} with ω_j at $\omega_j \rightarrow 0$ are compared with the existing methods. Theoretical c_1 and c_2 for τ_1 and τ_2 from Fröhlich's equations and the experimental ones from graphically extrapolated values of the fitted curves of $\chi'_{\text{ij}} / \chi_{\text{oij}}$ and $\chi''_{\text{ij}} / \chi_{\text{oij}}$ with ω_j at $\omega_j \rightarrow 0$ are also compared. The findings reveals that $|c_1 + c_2| \simeq 1$. The applicability of derived linear equation is thereby established. The latters are employed to get γ and δ to yield τ_s and τ_{cs} in order to establish that monosubstituted anilines obey symmetric relaxation behaviour. μ_1 and μ_2 from τ_1 and τ_2 and linear coefficient β of variations of χ'_{ij} and σ_{ij} with ω_j are estimated. Higher μ 's from $\sigma_{\text{ij}} - \omega_j$ curves arise due to all types of polarisations involved with σ_{ij} 's while χ_{ij} 's is concerned with orientational polarisation. The difference $\Delta\mu_j$ between μ_j 's from $\sigma_{\text{ij}} - \omega_j$ and $\chi'_{\text{ij}} - \omega_j$ curves provides one to infer the bound charges of the molecules due to σ_{ij} measurements. μ_1 and μ_2 are compared with reported μ 's and μ_{theo} 's. The slight disagreement of measured μ_j 's from μ_{theo} 's is explained by inductive, mesomeric and electromeric effects.

The **Chapter 9 and 10** present the results of the rf conductivity σ' (real part) measurements to arrive at the structural and associational aspects of some normal alcohols in C_6H_6 only, aprotic polar liquids in C_6H_6 and CCl_4 and pure polar-polar liquid mixtures at single and different temperatures. The slope of σ' and $1/\eta$ is used to get number density 'n' of free ions of the liquid. τ_j 's and τ_{jk} 's

are, however, obtained in terms of measured 'n' from Einstein - Stokes relation with the values of gas kinetic molecular radius 'a'. Non linear variation of τ_j with w_j arises probably due to solute-solvent interactions. Higher τ_{jk} is due to formation of polymeric clusters by molecular association between j and k polar solutes. τ_j thus measured together with slopes β of $\sigma'_{ij}-w_j$ curves, yields rf μ_j from Smyth's relation to compare them with μ_{theo} 's. σ_{ij} 's for normal alcohols increases gradually with w_j to attain the maximum value at $w_j=0.5$, except for n-propanol, indicating a change of phase, arising out of solute-solvent molecular association. The μ_{theo} 's, on the other hand, gives an insight into the distribution of bond moments of different $-\text{CH}_3$ and $-\text{OH}$ groups to yield important information on structure of alcohols. The convex and concave nature of μ_j-t curves for aprotic polar liquids are interpreted by rupture of monomer and dimer associations due to stretching of bond moments of the substituent polar groups by thermal agitation. The disagreement between rf μ_j and μ_{theo} arises due to short range ionic forces influencing the whole dipolar rotations. Temperature variation of τ_j again helps one to obtain ΔH_τ , ΔS_τ , ΔF_τ and $\gamma(=\Delta H_\tau/\Delta H_\eta)$ from Eyrings' rate process equation to conclude the stability or instability of the chemical systems and solvent environment around solute molecules. Debye and Kalman factors $\tau_j T/\eta$ and $\tau_j T/\eta^\gamma$ showed the molecules obeyed Debye relaxation. The semiconduction activation energies ΔE_j or ΔE_{jk} are obtained from temperature variation of rf σ' . They are finally compared with the literature values only to arrive at the structural and associational aspects of such molecules under 1 MHz and 500KHz rf electric field respectively.

In **Chapters 3 to 7 and 9** μ_{theo} 's of a large number of dipolar molecules under investigation have been obtained in terms of available bond angles and bond moments of substituent polar groups of parent molecules by vector addition method. This study invariably gives an important information of structures of the molecules concerned. The disagreement between μ_{theo} 's and estimated μ_j 's at once indicates the existence of inductive, mesomeric and electromeric effects

of substituent polar groups of the molecules, in addition to short range ionic forces.

In some chapters the dielectric theories are presented in SI units because of its unified, coherent and rationalised nature. The curves with the available experimental points in several figures of different chapters show the validity of the derived theoretical formulations. These are supported by the correlation coefficients r 's, % of errors and minimum chisquare testing on the data of polar-nonpolar liquid mixture of different w_j 's of solute in various nonpolar solvents at given experimental temperature. Many theories of dielectric relaxations 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, the study of dielectric relaxation phenomena is preferred in terms of dielectric orientational susceptibilities χ_{ij} 's in SI units as seen in **Chapter 7 and 8** of the thesis. χ_{ij} 's are supposed to be involved only with orientational polarisation of molecules. But the dielectric relaxation phenomena can recently be studied by Thermally Stimulated Depolarisation Current (TSDC) density and Isothermal Frequency Domain of AC Spectroscopy. These may give a firm answer to the problem of polar-nonpolar liquid mixtures including polymer and liquid crystal about which the present author is involved. But the latter two methods are very lengthy and often needs the tedious computer simulation technique unlike σ_{ij} and χ_{ij} measurements. The latter appear to be simple, straight forward 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 the latter methods are not so simple like Debye - Smyth and Hill model used in this thesis. Further work can be carried out to predict the relaxation phenomena by assuming moment of inertia of the polar molecules under ultra high frequency (uhf) electric field. Numerical calculation on relaxation parameters of polar molecules in nonpolar

solvents may be carried out on the basis of Newton Raphson method to arrive at the results.

The discussion made above on the thesis entitled 'Structural and associational aspects of some dielectropolar liquid molecules in nonpolar solvents from relaxation phenomena' thus summarised ultimately provides the future workers in this field of liquid dielectrics to open a new and vast scope to work further in the investigation of structural and associational aspects of interesting dielectropolar liquids in nonpolar solvents like benzene, n-hexane, n-heptane, para-xylene, carbon tetrachloride, dioxane etc. under hf electric field. It can thus be concluded that the study of highly nonspherical polar liquid molecules in nonpolar solvents is, however, explained by the Debye-Smyth model which was supposed to be applicable to the nearly spherical molecules of simpler configuration in different nonpolar solvents.