
CHAPTER 11

SUMMARY AND CONCLUSION

The subject matter of the thesis works entitled “**High frequency absorptions, double relaxation times, dipole moments and molecular structures of some nonspherical polar and isotopomer molecules**” has been finally summarised chapterwise as presented earlier for convenience.

The Chapter I of this thesis entitled “**The general introduction and brief review of the previous works**” deals with the dielectric investigation of pure polar liquids and polar nonpolar liquid mixtures under static as well as high frequency electric field. This study enables one to realise the shapes, sizes and conformational structures of the nonspherical polar liquids under investigation. A brief survey work has also been added in the latter part of this chapter to observe the usual trend of the investigations in this line.

“**The scope and the objective of the present works**” in Chapter II contains the beautiful mathematical developments and elaborate discussions on the works. They have been widely used in the latter parts of the thesis. This includes the distribution of relaxation times between two limiting values as was done by Fröhlich (1949). Bergmann et al (1960) and Bhattacharyya *et al* (1970), however, devised different mathematical procedures to get molecular and intramolecular relaxation times τ_2 and τ_1 of pure polar liquids under high frequency electric field of Giga hertz range. The methods proposed by them involved with experimental measurements of dielectric relaxation parameters at different frequencies of the hf electric field. In order to eliminate experimental hazards of measurements at different hf electric field, we (1994) within the framework of Debye and Smyth model, however, developed a technique to get τ_2 and τ_1 of polar liquids in nonpolar solvents from the dielectric relaxation data measured under a single frequency electric field at a given temperature. The procedure is concerned with a derived straight line equation having certain intercept and slope to get τ_2 and τ_1 respectively. The dipole moments μ_1 and μ_2 could however, be estimated in terms of τ_1 of the flexible part attached to the parent molecule and τ_2 of the whole molecule itself together with slope β of the hf conductivity K_{ij} against ω_j curve of polar liquids at infinite dilution. The procedure is really very simple because the microwave conductivity is applicable to polar - nonpolar liquid mixture. Due to existence of distribution of relaxation times, polar molecules may possess either

symmetric or asymmetric distributions. They have been found out by using graphical technique for a polar - nonpolar liquid mixture. An experiment is performed to show whether aprotic polar liquids exhibit either double or monorelaxation behaviour using the theory mentioned above. In the last part of **Chapter II (Part B)** an approximate formulation is suggested to obtain dipole moment of isotopomer molecular ion like HD^+ using Morse - wave function because of the applicability of Morse - potential for nuclear vibration of such molecule.

The double relaxation times τ_2 and τ_1 of some highly nonspherical disubstituted benzene and aniline molecules in solvent benzene and carbon tetrachloride have been obtained from the single frequency measurements of the dielectric relaxation solution data under hf electric field at a given temperature. The weighted contributions c_1 and c_2 due to τ_1 and τ_2 are calculated from Fröhlich's equation as well as by new technique adopted here. The dipole moments μ_1 and μ_2 are computed from the slope β of ultra high frequency conductivity K_{ij} against the weight fraction ω_j of the respective solutes, in terms of estimated τ_1 and τ_2 . The conformational structures of polar molecules are obtained from the available bond moments and bond angles of molecules assuming the molecules to be planar. Again, the close agreement of μ_2 values from single frequency measurement technique with the existing methods immediately indicates that the approach suggested is a correct one. This has been presented in **Chapter III** under the heading **"Double relaxation times of nonspherical polar liquids in nonpolar solvent : A new approach based on single frequency measurement"**.

The **Chapter IV**, entitled **"Single frequency measurement of double relaxation times of monosubstituted anilines in benzene"**, however, reports the double relaxation times τ_2 (larger) and τ_1 (smaller) of some monosubstituted anilines in benzene at 35°C for 2.02, 3.86 and 22.06 GHz electric fields respectively from the single frequency measurement of dielectric relaxation parameters at different concentrations. The o- and m-anisidines like p-toluidines exhibit double relaxation phenomena at 3.86 and 22.06 GHz whereas o- and m-toluidines show the same effect at 2.02 and 3.86 GHz respectively. Only p-anisidine, however, shows the monorelaxation behaviour at all frequencies. The relative

contributions c_1 and c_2 towards dielectric relaxation for τ_1 and τ_2 are computed from Fröhlich's equations only for comparison with those of the graphical techniques. The dipole moments μ_1 and μ_2 in terms of τ_1 and τ_2 are then determined from the slope β of $K_{ij} - \omega_j$ curve for these compounds to establish their conformations.

“Double relaxations of monosubstituted anilines in benzene under effective dispersive region” in the Chapter V deals with the mono or disubstituted anilines in benzene at 35°C under 9.945 GHz electric field to show some interesting property by those liquids from single frequency measurement technique. The mono or disubstituted benzenes and anilines are thought to absorb energy much more strongly in the effective dispersive region of nearly 10 GHz electric field. The dielectric relaxation data of the monosubstituted anilines measured at different frequencies (Sit et al 1994) showed either double or monorelaxation behaviour. When the same data are extended to 9.945 GHz (\cong 3 cm. wavelength) electric field, each of them, on the other hand ; exhibits the double relaxation phenomenon by showing the reasonable relaxation times τ_1 (smaller) and τ_2 (larger) for the flexible part as well as the whole molecule itself for their rotations in hf electric field. τ_1 and τ_2 are, however, obtained from the slopes and intercepts of a derived equation involved with dielectric relaxation data for different weight fractions ω_j 's measured under a single frequency electric field. The relative contributions c_1 and c_2 in terms of τ_1 and τ_2 towards relaxation are calculated from Fröhlich equations and the graphical technique. The values of symmetric and asymmetric distribution parameter γ and δ are also calculated to test the rigidity of the molecules under investigation. The dipole moments μ_1 and μ_2 in terms of τ_1 and τ_2 are finally estimated from the slope β of hf conductivity K_{ij} as a function of ω_j 's in order to support their conformations.

The Chapter VI of **“Double relaxation of straight chain alcohols under high frequency electric field”** is concerned with some interesting property of a few normal alcohols under different hf electric fields at a given temperature. Alcohols like 1-butanol, 1-hexanol, 1-heptanol and 1-decanol are long straight chain polar molecules almost like polymers. In these alcohols as well as in methanol and ethanol there exist many possibilities of having internal rotations, bending and twisting each with a characteristic

relaxation time under high frequency electric field. An attempt is, therefore, made to detect the double relaxation phenomena by the new approach suggested earlier. It involves single frequency measurements of the dielectric relaxation data of those compounds in solvent n-heptane at 25°C under three different frequencies of 24.33, 9.25 and 3.00 GHz electric field as well as those of methanol and ethanol in benzene at 9.84 GHz, respectively to get τ_1 and τ_2 of their flexible part and the whole molecules. The alcohols under investigation, always exhibit the double relaxation behaviours at all frequencies except methanol at 9.84 GHz, indicating separate broad dispersions in them. The relative contributions c_1 and c_2 towards dielectric relaxations due to τ_1 and τ_2 are calculated from Fröhlich's equations to compare with those as obtained by graphical method. The dipole moments μ 's are also estimated in terms of the relaxation times τ_1 and τ_2 , obtained from the slopes and intercepts of straight line equation and in terms of slopes β 's of the hf conductivities K_{ij} 's of the solutions against the weight fraction ω_j 's of the solutes in order to support their usual conformations.

Some isomeric octyl alcohols in n-heptane at 25°C under the electric field frequencies of 24.33, 9.25 and 3.00 GHz as straight chain alcohols are also studied to detect the double relaxation times τ_1 and τ_2 for their flexible parts and whole molecules by the single frequency measurement of dielectric relaxation parameters. This has been given in Chapter VII of **"Double relaxations of some isomeric octyl alcohols by high frequency absorption in nonpolar solvent"** of this thesis. The isomers of alcohols are long chain, hydrogen bonded, polymer type molecules having methyl and hydroxyl groups attached to their C-atoms which may bend, twist or rotate internally under hf electric field each with a characteristic relaxation time. The relative contributions c_1 and c_2 towards dielectric relaxations due to τ_1 and τ_2 are also estimated by using Fröhlich's equations and the graphical technique. The dipole moments μ_1 and μ_2 in terms of τ_1 and τ_2 are again found out from the slope β of the total hf conductivity K_{ij} as a function of weight fractions ω_j 's of the solutes indicating μ_1 for the rotation of -OH groups about - C - O bonds only. μ_1 and μ_2 are finally compared with the theoretical dipole moments μ_{theo} 's arising out of

their structures with bond angles and bond moments of their substituent groups to establish their conformations which are justified like normal alcohols as observed earlier.

The **Chapter VIII** under the title of “**Structural and associational aspects of binary and single polar liquids in nonpolar solvents under high frequency electric field**” deals with the structural and associational aspects of binary (jk) 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 solvents (i). They, however, studied in terms of their high frequency (hf) conductivities. The relaxation times τ 's and dipole moments μ 's of respective solutes under hf electric field of Giga hertz range at various temperatures are estimated from the measured real and imaginary parts of hf complex dielectric constants at different weight fractions of polar solutes. The variation of τ_{jk} 's 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 in DMF. The solute - solvent molecular association i.e the rupture of dimers begins at and around 50 mole % of DMSO in DMF and continues up to 100 mole % DMSO. The concentration and temperature variation of τ_{jk} of these aprotic liquids are in accord with the information of variation of τ_{jk} of jk polar mixtures with x_k 's of DMSO. Thermodynamic energy parameters are also obtained from Eyring's rate process equation with the estimated τ 's to support the molecular associations. The slight disagreement between the theoretical dipole moment μ_{theo} from the bond angles and bond moments is noticed with the measured τ 's in terms of slopes of concentration variation of hf conductivity curves at infinite dilutions and τ 's. This indicates the temperature dependence of mesomeric and inductive moments of different substituent groups in such polar molecules.

An experiment is, therefore, made to measure the dielectric relaxation parameters like real ϵ'_{ij} , imaginary ϵ''_{ij} parts of complex dielectric constant ϵ^*_{ij} , static dielectric constant ϵ_{0ij} and dielectric constant at infinite frequency $\epsilon_{\infty ij}$ ($= n^2_{Dij}$) of some aprotic polar liquids (j) dissolved in benzene (i) at different temperatures under nearly 10 GHz electric field as a function of weight fraction ω_j of polar solutes. The aprotic liquids like dimethyl sulphoxide (DMSO), N,N-diethyl formamide (DEF), N, N-dimethyl formamide (DMF)

and N, N-dimethyl acetamide (DMA) are chosen because of their wide biological applications and importance in medicine and industry. The measured data at nearly 10 GHz are seen to predict the double relaxation times τ_1 and τ_2 , except DMA, due to rotations of their flexible parts and the whole molecules by the method of single frequency measurement. τ_1 agrees well with the reported τ signifying the fact that under hf electric field of 10 GHz a part of the molecule is rotating. The relative weighted contributions c_1 and c_2 towards dielectric relaxations due to τ_1 and τ_2 are also ascertained from Fröhlich's equations and graphical technique. The corresponding dipole moments μ_2 and μ_1 in terms of τ_2 and τ_1 and slope β of hf conductivity K_{ij} against ω_j at $\omega_j \rightarrow 0$ are compared with reported μ_j . μ_1 's, however, agree well with μ_j 's and static μ_s . The molecular conformational structures are obtained by μ_{cal} from μ_s and μ_{theo} from available bond angles and bond moments by considering mesomeric and inductive moments of the substituent groups. The comparison of μ_1 , μ_2 and μ_j with μ_s shows that μ 's are very little affected by hf electric field. The energy parameters like enthalpy of activation ΔH_τ , entropy of activation ΔS_τ and activation energy ΔF_τ from $\ln(\tau T)$ against $\frac{1}{T}$ equations of DMSO seem to establish that unlike the rotation of the whole molecule, the flexible part satisfies the Eyring rate theory. These observations have been included in the **IXth Chapter** of the thesis, entitled **“Double relaxation times, dipole moments and molecular structures of some nonspherical aprotic polar liquids in benzene from high frequency absorption measurement”**.

Part B of the thesis containing the single **Chapter X** under the heading **“Dipole moment of isotopomer molecule”** deals with an approximate formulation to calculate the dipole moments of isotopomer molecular ions like HD^+ , HT^+ etc. in the ground state for the vibrational quantum number $v = 0$ using Morse wave function because of the applicability of Morse potential for nuclear vibration of such molecular ions. It also provides one with the finite number of bound vibrational level as seen in practice. The computed value is little larger than the literature one probably due to the approximate nature of the potential used, although it gives accurate dissociation energy D_e and

vibrational frequency ν_0 of ionic molecules unlike Fues vibrator type potential yielding ν_0 only.

The summary and a concluding remark at the end of all the chapters of this thesis is presented in the **Chapter XI**.

Thus, the first part of the thesis (i.e Part A) contains beautiful, systematically developed theoretical formulations to estimate the double relaxation times τ_1 and τ_2 of polar solutes dissolved in nonpolar solvents from the measured dielectric relaxation parameters at a given temperature under a high frequency (microwave) electric field as a function of weight fractions of polar solutes. The theories are tested for a large number of nonspherical or chain like polar molecules of different shapes and sizes presented in Chapters III to IX. They reveal interesting information on their structures in terms of estimated τ 's and μ 's from hf absorption studies of solution data. So, it can be concluded that the study of nonspherical type polar liquids in nonpolar solvents has opened a new and vast scope for the future works. The different models of Onsager, Kirkwood, Fröhlich etc may be expected to be the better choice for the polymer type long chain polar liquids or liquid crystals in nonpolar solvents like benzene, dioxane, carbon tetrachloride, n-heptane, paraxylene etc. in addition to Debye - Smyth model which is supposed to be successful in predicting dielectric relaxations of nearly spherical type of polar liquids of simpler configurations.

The Part B of the thesis presents a quantum mechanical approach to suggest an approximate formulation of dipole moment of isotopomer molecular ions like HD^+ , HT^+ etc. for $v = 0$ vibrational level assuming Morse - potential for nuclear vibration of such molecules. The technique is very simple and straightforward. This may be extended to $v = 1$ and $v = 2$ vibration levels too. Further, dipole moment calculation may be made assuming rotation - vibration wave function of molecular ions.