SUMMARY AND CONCLUSION

The subject matter of the thesis work titled "*Relaxation phenomena of dielectropolar liquid molecules under low and high frequency electric fields*" has been divided into a large number of chapters. All the chapters are highly informative to shed more light on the relaxation phenomena of dipolar liquid molecules in non-polar solvents under low and high frequency (hf) electric fields.

A brief account of early works on dielectric relaxation of liquids (DRL) by different groups of workers has been presented in Chapter 1. The fundamental theories to explain the relaxation phenomena of polar molecules both in pure state and in suitable non-polar solvents have been well discussed in this chapter in C.G.S. units. An extensive review of polarisation is included at the end of this chapter in order to get a chronological development of the subject.

The theoretical formulations recently derived and used by the present author to estimate hf relaxation time τ_j, static or low frequency dipole moments μ_s, hf dipole moment μ_j, double relaxation times and dipole moments τ_1, τ_2 and μ_1, μ_2 under hf electric fields of GHz range are presented in Chapter 2. The aim of this chapter is to provide a comprehensive theoretical formulation in SI units in order to study the relaxation phenomena of polar-nonpolar liquid mixtures in terms of the measured relative permittivities under low and hf electric fields. The concept of relaxation mechanism of polar molecules in non-polar solvents is, however, gained through μ_s, μ_j, μ_1 and μ_2 based on Smyth's model. The different thermodynamic energy parameters of enthalpy of activation ΔH_τ, entropy of activation ΔS_τ and free energy of activation ΔF_τ can, however, be obtained from the temperature variation of measured τ_j's of polar molecules in non-polar solvents to throw much light on the concept of rigid phase rotators of the molecules in a given solvent. The Chapter 2 approaches with different objects in view: It provides an archetypal example of the application of dielectric relaxation, to help and elucidate the shape, size and structure of dielectropolar molecules in liquid states.

The theoretical formulations, so far derived in Chapter 2, were tested by an experimental measurement as shown in Chapter 3 to support the applicability of the method based on Debye-Smyth model. The block diagram of the experimental set up of HP 4192A Impedance Analyser has been sketched along with a brief description of measurements of ε_{ij}', ε_{ij}'' ε_{oij} and $\varepsilon_{\alpha ij}$ at various concentrations and temperatures of aprotic polar liquids like dimethylsulphoxide (DMSO), N,N-diethylformamide (DEF), N,N-dimethylformamide (DMF) and N,N-dimethylacetamide (DMA) all in C_6H_6. From the linear curve of $(\varepsilon_{oij}-\varepsilon_{ij}')/(\varepsilon_{ij}'-\varepsilon_{\alpha ij})$ against $\varepsilon_{ij}''/(\varepsilon_{ij}'-\varepsilon_{\alpha ij})$ it was observed that all the systems show double relaxation times τ_2 and τ_1 due to end over end rotation of the whole molecules as well as the flexible parts attached to the parent molecules. The τ_1, in agreement with reported τ, signifies that a part of the molecules is rotating under 10 GHz electric field. The support of this fact came from the measured thermodynamic energy parameters ΔH_τ, ΔS_τ and ΔF_τ from

$\ln(\tau_j T)$ against $1/T$ for DMSO. The theoretical values c_1 and c_2 of weighted contributions towards dielectric relaxations for the measured τ_1 and τ_2 were ascertained from Fröhlich theoretical equations. They are compared with the experimental c_1 and c_2 as obtained by the graphical technique. The corresponding dipole moments μ_2 and μ_1 were obtained from τ_2 and τ_1 in order to compare with the static μ_s's, reported μ and theoretical dipole moments μ_{theo}'s from the available bond angles and bond moments of the substituent polar groups attached to the parent molecules in Debye units. The molecular conformations are, however, sketched by μ_{cal} from μ_s / μ_{theo} which takes into account of the existence of mesomeric and inductive effects of different polar groups of such molecules.

Chapter 4 presents a beautiful study of the relaxation phenomena of some polysubstituted benzenes in C_6H_6 through hf conductivity σ_{ij}'s measurements. τ_j's measured from the ratio of the slopes of the individual variations of imaginary part σ_{ij}'' and real part σ_{ij}' of complex hf conductivity σ_{ij}^* with w_j's in the limit $w_j=0$ at a given temperature is more reliable in comparison to the direct slope of the variation of $\sigma_{ij}''-\sigma_{ij}'$ at different w_j's. τ_j's were found in close agreement with the reported values. ΔH_τ, ΔS_τ and ΔF_τ were computed by applying Eyring's rate theory with the measured τ in order to get solvent environment. The estimated values of γ and ΔH_η show the solid phase rotators of the molecule in a solvent. ΔH_η is involved with the translation and the rotational energies. The comparison of the Kalman factor $\tau_j T/\eta^\gamma$ and Debye factor $\tau_j T/\eta$ suggests the applicability of Debye model of dielectric relaxation for such dipolar liquid molecules. The excellent agreement of the measured μ_j's in terms of measured τ_j's and slope β's of $\sigma_{ij}-w_j$ curves with the reported μ's establishes the basic soundness of the conductivity measurement technique used. The slight disagreement between μ_j's and μ_{theo}'s reveals the existence of mesomeric, inductive and electromeric effects within the polar groups attached to the parent benzene ring. The temperature dependence of τ_j's and μ_j's is much more significant to conceive the solvent environment of the polar molecules and the molecular dynamics of the systems. It sheds more light on their structural conformations.

The Chapter 5 reports the measured τ_j and μ_j of some methyl benzenes and ketones in C_6H_6 at 25^0C under 9.585 GHz electric field from the measured ε_{ij}' and ε_{ij}'' at various w_j's. The methodology to get τ_j from the ratio of the individual slopes of σ_{ij}'' and σ_{ij}' against w_j seems to be a significant improvement over the existing one of the linear slope of $\sigma_{ij}''-\sigma_{ij}'$ curve. The variation of $\sigma_{ij}-w_j$ like $\sigma_{ij}''-w_j$ curve is often convex in nature indicating the probable occurrence of phase change of the liquid state after a certain concentration. The estimated μ_j by using τ_j from both the methods are compared with those of Gopalakrishna and theoretical ones to establish the applicability of the method.

The double relaxation phenomena in apparently rigid aliphatic polar liquids like chloral and ethyltrichloroacetate in non-polar solvents benzene, n-heptane and n-hexane under 4.2, 9.8 and 24.6 GHz electric field at 30^0C have been extensively studied in Chapter 6. Five systems of polar-nonpolar liquid mixtures show τ_1, τ_2 and μ_1, μ_2 due to rotation of their flexible parts and the whole molecules. The probability of showing double relaxation phenomena is greater in aliphatic solvents at 9.8 and 24.6 GHz electric fields indicating their non rigidity. This is also supported by the symmetric and asymmetric distribution parameters γ and δ estimated from the values of x [$=(\varepsilon_{ij}'-\varepsilon_{\alpha ij})/(\varepsilon_{oij}-\varepsilon_{\alpha ij})$] and y [$=\varepsilon_{ij}''/(\varepsilon_{oij}-\varepsilon_{\alpha ij})$] at $w_j \rightarrow 0$. The unusual variations of x and y with w_j's predict their probable solute-solute and solute-solvent molecular associations under hf electric field. μ_{theo}'s in terms of the available bond angles and bond moments conform the estimated μ_j's only to establish the existence of mesomeric, inductive and electromeric effects in them.

In Chapter 7, the relaxation phenomena of some disubstituted benzenes and anilines in C_6H_6 and CCl_4 through hf susceptibility χ_{ij} measurement technique have been presented. The main advantage of this method is that it is directly linked with the orientation polarisation and excluded the fast polarisation process. τ_2 and τ_1 were obtained from the intercept and slope of a linear equation of $(\chi_{oij}-\chi_{ij}')/\chi_{ij}'$ against χ_{ij}''/χ_{ij}' for different w_j's. τ_j's were calculated from the ratio of the individual slopes of χ_{ij}'' and χ_{ij}' with w_j's at $w_j \rightarrow 0$ assuming single Debye like dispersion and compared with those of Murthy et al and Gopalakrishna. The relative contributions c_1 and c_2 towards dielectric relaxations for τ_1 and τ_2 can, however, be obtained from the Fröhlich 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 $(\chi_{ij}''/\chi_{oij})_{wj \rightarrow 0}$ graphically. The symmetric and characteristic relaxation times τ_s and τ_{cs} were determined in order to establish the different relaxation behaviours for such polar molecules. μ_2 and μ_1 for the rotations of the whole molecules as well as the flexible parts were ascertained from τ_2 and τ_1 and the linear coefficient β of $\chi_{ij}'-w_j$ curve. μ_j's were finally compared with the reported μ and μ_{theo} to conclude that for disubstituted anilines a part of the molecule is rotating while the whole molecular rotation occurs for disubstituted benzenes.

Chloral and ethyltrichloroacetate showed double relaxation phenomena in aliphatic solvents through chi-squares minimization of the measured data. High frequency susceptibility χ_{ij} measurement under 4.2, 9.8 and 24.6 GHz electric fields at 30^0C has been applied. The findings were . . . displayed in Chapter 8. The measured τ_2, τ_1 and μ_2, μ_1 were found to be little deviated from hf σ_{ij} measurement technique. The hf χ_{ij} measurement, although is very simple, it does not include any approximation in the calculation of μ_j. Nevertheless, the variation of χ_{ij}'/χ_{oij} and χ_{ij}''/χ_{oij} with w_j's remain almost unaltered with respect to σ_{ij} measurement technique. The measured μ_j's when compared with μ_{theo}'s established the associational aspects of the polar

molecules with solvents and solutes. The mesomeric and inductive moments of the molecules could, however, be studied. The existence of fractional +ve charge δ^+ on C-atom and −ve charge δ^- on O-atom of C$\Leftarrow$O group in both the polar liquids showed the electromeric effect to form π–complex with the π–delocalised electron clouds of benzene ring.

In Chapter 9, the static or low frequency μ_s of some aliphatic polar liquids in different non-polar solvents were studied in terms of static experimental parameter X_{ij}. X_{ij}'s are related with ε_{oij} and $\varepsilon_{\infty ij}$ of polar-nonpolar liquid mixtures at different w_j's. A comparison is, however, made with the hf μ_j from hf σ_{ij} measurement technique and μ_{theo}. A little disagreement is caused by the permanent polarisation of different substituent polar groups acting as pusher or puller of electrons towards or away from C-atom of the compounds. The reduction in bond moments evidently occur in all the polar liquids by a factor μ_s/μ_{theo} to conform to the exact μ_s or μ_j.

With all these discussions made above, a conclusion regarding the relaxation phenomena can, however, be reached by other and our groups. The findings are presented in Chapter 10. In course of our prolonged studies on relaxation phenomena of polar-nonpolar liquid mixtures it reveals that the existence of double relaxation phenomena reflects the material property of the chemical system under investigation and is not dependent on the measurement frequency. Although relative permittivities ε_{ij}' and $\varepsilon_{\infty ij}$, dielectric loss ε_{ij}'' vary with frequency, the fundamental dielectric parameters such as dielectric decrement and relaxation time which describe the relaxation properties of the system, do not. The theoretical consideration in the chapters 6 and 8 appears to be sound in getting τ_1 and τ_2. But chloral in C_6H_6 in Chapter 6 exhibited double relaxation behaviour at 9.8 GHz. This should be reflected at all the frequencies. The analysis is expected to produce the same τ_1 and τ_2 at all the three frequencies. We then applied the chi-squares minimisation on the data set in Chapter 8 to predict τ_1 and τ_2 of chloral and ethyltrichloroacetate in aliphatic solvents. Under such context we, therefore, decided to restudy a number of normal and isomeric octyl alcohols in n-heptane at 25°C under 3.00, 9.25 and 24.33 GHz electric fields through hf susceptibility χ_{ij}'s measurements. Three graphs of $f(\omega_k)$ against $\ln\omega_k$ were drawn at those frequencies for a number of arbitrary angular frequencies ω_k's. $\ln\omega_2$ and $\ln\omega_1$ for a fixed value of $f(\omega_k)$ of $f(\omega_k)$–$\ln\omega_k$ curve, however yield the same τ_2 and τ_1 for a system from the intersection points of $\ln\omega_1$ against $\ln\omega_2$ curve for three different frequencies. τ_2 and τ_1 were then compared with the average τ's of our single frequency measurement technique stated elsewhere. The estimated μ_2 and μ_1 in terms of the linear coefficients β's of χ_{ij}'–w_j curves and the measured τ_2 and τ_1 by different methods showed that μ's were slightly different in different frequencies because rotation of the whole molecule as well as the flexible parts are probably affected by the frequency of the applied alternating electric field. The measured μ_j's were then compared with μ_{theo}'s of almost all the alcohols.

The dielectric theories are presented in SI units in some chapters. SI units used are of unified, coherent and rationalised nature. The curves with the available experimental points in all the figures of different chapters show the validity of the theoretical formulations so far derived. The correlation coefficient r's, % of errors and chi-squares minimisation testing computed on the various data at a given experimental temperature go to support the reliability of the derived formulations. 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 orientation susceptibility χ_{ij}'s in SI units as seen in Chapters 7, 8 and 10 of this thesis. 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. But Thermally Stimulated Depolarisation Current Density (TSDCD) and Isothermal Frequency Domain AC Spectroscopy (IFDS) can recently be used to study the dielectric relaxation phenomena. These may give a firm answer to the problem of polar-nonpolar liquid mixtures with which the present author is concerned. But the latter two methods consist of a tedious computer simulated calculation unlike σ_{ij} or χ_{ij} measurement quoted above. Thus 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. Further work can be carried out to predict the relaxation phenomena by assuming moment of inertia of the polar molecules under uhf electric field. Numerical calculation on relaxation parameters may be carried out on the basis of Newton-Raphson method to arrive at the results.

The thesis thus provides the future workers in liquid dielectrics to open a new and vast scope to work further on the interesting dielectropolar liquids in non-polar solvents under hf electric field. It can thus be concluded that the relaxation phenomena of highly non-spherical polar liquid molecules in non-polar solvents could, in fact, be explained by the Debye-Smyth model which was supposed to be applicable to the nearly spherical molecules of simpler configuration. 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 dielectric relaxation phenomena.