PREFACE OF THE THESIS

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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-dinitrocholorobenzene, 3,4-dinitro chlorobenzene, p-hydroxypropiophenone, p-chloropropiophenone, p-acetamidobenzal-dehyde, 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, $\Delta H\tau$, $\Delta S\tau$ and $\Delta F\tau$ 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 lnA which contains the entropy of activation and the slope ΔH_τ / 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 μ_{exp} / μ_{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}, $\varepsilon_{\infty ij}$, etc and presented in this thesis in chapter seven. The close agreement of μ_s with μ_1 from the double relaxation method interms of τ_1 of the same method and μ_j's from the measured τ_j's of the ratio of $\{(d\chi_{ij}''/d\omega_j) / (d\chi_{ij}'/d\omega_j)\}_{\omega_j \to 0}$ 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-dinitrocholorobenzene, 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^{0}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'_js in terms of estimated $\tau_j's$. of the polar compounds are, however, compared with the theoretical $\mu_{theo}'s$ 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-nitroailine, p-bromonitrobenzene are given in chapter 7 having title "*DIELECTRIC RELAXATION OF AROMATIC PARA SUBSTITUTED DERIVATIVE POLAR LIQUIDS FROM DISPERSION AND ABSORBTION 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 25^0C. (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 absorbtion 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)