

CHAPTER 10

SUMMARY AND CONCLUSION OF THE THESIS WORKS

10. SUMMARY AND CONCLUSION OF THE THESIS WORKS

The subject matter of the thesis works has been divided into several CHAPTERS from 1 to 10. All the chapters are highly informative to shed more light on physico-chemical properties of the polar solvents under static and high frequency electric fields. The physico – chemical aspects of the solvents and solute liquids have been studied in detail and presented in terms of the variation of the measured relaxation parameters with weight fractions w_j 's of the polar solutes at a single or different temperatures to enhance the present knowledge of relaxation phenomena. Dielectric relaxation is one of the difficult unresolved problems of physics and chemistry today. The point which needs to be kept in mind is that all relaxation phenomena are of necessity connected with the presence in the systems under study of some form of disorder. There can be no relaxation in a perfectly ordered system, because nothing can relax from perfection. It is very interesting to note that many workers in this field of research do not know how to use the data of dielectric relaxation for the maximum effective utilisation. The First CHAPTER entitled "GENERAL INTRODUCTION AND REVIEW OF THE PREVIOUS WORKS" helps the reader to get a first hand information on the topic of correlation in the liquid solvents like polar and non polar liquids mixtures. The handy and new theories have been derived and presented in the SECOND CHAPTER having the heading "SCOPE AND OBJECTIVE OF THE PRESENT WORKS". The theories so far prescribed are widely used in different CHAPTERS of 3 to 9 in order to arrive at the conclusion of the works studied so far of the thesis of CHAPTER 10 called the "SUMMARY AND CONCLUSION OF THE THESIS WORKS". In which all the important findings are incorporated chapterwise from chapters 3 to 9 respectively.

The CHAPTER 3 entitled "STRUCTURAL ASPECTS AND PHYSICO-CHEMICAL PROPERTIES OF SOME AROMATIC POLAR NITRO COMPOUNDS IN SOLVENT BENZENE AT DIFFERENT TEMPERATURES UNDER GIGA HERTZ ELECTRIC FIELD" in which an interesting method based on complex orientational susceptibilities χ_{ij}^* s to study the dielectric relaxation

mechanism of some standard polar nitro compounds in non polar solvent benzene has been prescribed and applied successfully to arrive at their structural and physico-chemical properties. The dielectric orientational susceptibilities χ'_{ij} , the real and χ''_{ij} , the imaginary parts of χ^*_{ij} are involved with the measured relative permittivities ϵ'_{ij} and ϵ''_{ij} of ϵ^*_{ij} of Pant et al to measure the relaxation time τ_j of all the polar solutes from the ratio of the linear coefficients of individual variations of χ''_{ij} and χ'_{ij} with weight fractions w_j 's of the respective solute. They are further compared with τ_j 's obtained from the direct slope of the linear variations of χ''_{ij} and χ'_{ij} and Gopala Krishna's method measured by Pant et al. The temperature variation of τ_j 's from the former method helps one to get the thermodynamic energy parameters i.e. enthalpy of activation ΔH_τ , entropy of activation ΔS_τ and free energy of activation ΔF_τ of dielectric relaxation by using the rate process equation of Eyring et al to throw much light on their structural and physico chemical properties. The dimensionless parameter δ ($= \Delta H_\tau / \Delta H\eta_1$) which is the slope of the linear equation of $\ln\tau_j T = \ln a + \delta \ln \eta_1$, where η_1 the coefficient of viscosity of the solvent, is used to get Debye and Kalman factors. They reflect the associative nature along with the applicability of Debye-Smyth model of dielectric relaxation for such polar nitro molecules. The estimated dipole moments μ_j 's in terms of linear coefficient β 's of χ'_{ij} vs w_j like $\chi'_{ij} = \alpha + \beta w_j + \gamma w_j^2$ curves and dimensionless parameters b 's involved with measured τ_j 's are finally compared with theoretical dipole moments μ_{theo} 's, obtained from available bond angles and bond moment of the substituent polar groups of the molecules as well as with μ_j 's of Gopala Krishna's method used by Pant et al to shed more light on the conformations of the molecules, in addition to inductive, mesomeric and electromeric effects.

The "DIELECTRIC RELAXATION PHENOMENA OF SOME APROTIC LIQUIDS UNDER GIGA HERTZ ELECTRIC FIELD" in CHAPTER 4 presents the double 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-dimethylsulphoxide (DMSO); N,N-dimethylformamide (DMF), N,N-

dimethylacetamide (DMA) and N, N-diethylformamide (DEF) in benzene (i) 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 solute at various experimental temperatures. 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 $\chi'_{ij} - w_j$ curves are compared with those τ 's from ratio of individual slope of $(d\chi''_{ij}/dw_j)w_j \rightarrow 0$ and $(d\chi'_{ij}/dw_j)w_j \rightarrow 0$, linear slope of $\chi''_{ij} - \chi'_{ij}$, conductivity measurement technique along with those of Gopala krishna's method. The estimated μ_1 's agree with the measured and reported μ 's to indicate that a part of the molecule is rotating under GHz electric field. The theoretical dipole moment μ_{theo} 's are obtained in terms of available bond angles and 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 were obtained for DMSO only assuming dielectric relaxation as a rate process to know the molecular dynamics of the system. The plot of $\ln(\tau_1 T)$ against $1/T$ of DMSO reveals that it obeys Eyring rate theory unlike $\ln(\tau_2 T) - 1/T$ curve.

The straight line 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 some dipolar long straight chain alcohols (j) in n-heptane (i) derived from the available relative permittivities ϵ'_{ij} , ϵ''_{ij} , ϵ_{oij} and $\epsilon_{\alpha ij}$ at 25°C under nearly 24 GHz electric field. The intercepts and slopes of the above equation. are used to get relaxation times τ_1 and τ_2 of the rotation of flexible part and the whole molecules. $\chi'_{ij} (= \epsilon'_{ij} - \epsilon_{\alpha ij})$ and $\chi''_{ij} (= \epsilon''_{ij})$ are the real and imaginary parts of hf dimensionless complex dielectric

orientational susceptibility χ_{ij}^* and χ_{oij} ($=\epsilon_{oij} - \epsilon_{\infty ij}$) is the low frequency dielectric susceptibility which is real. τ_j 's of such alcohols are also measured from the ratio of the slopes of the individual variations of χ'_{ij} and χ''_{ij} with ω_j 's at $\omega_j \rightarrow 0$ and the direct slope of χ''_{ij} versus χ'_{ij} equations of Muthy et al . These τ_j 's are finally compared with the reported τ_j 's of Gopala Krishna and τ_1, τ_2 by double relaxation method to see that the flexible part of the molecule is only rotating under the most effective dispersive region of 24 GHz electric field. The weighted contributions c_1 and c_2 towards dielectric relaxations for estimated τ_1, τ_2 are, however, obtained from Fröhlich's theoretical formulations of χ'_{ij} / χ_{oij} and χ''_{ij} / χ_{oij} to compare them with those of graphical ones of $(\chi'_{ij} / \chi_{oij})\omega_j \rightarrow 0$ and $(\chi''_{ij} / \chi_{oij})\omega_j \rightarrow 0$. The latter ones are employed to get symmetric distribution parameter γ to have the symmetric relaxation times τ_s . The arbitrary curve of $(1/\phi) \log \cos\phi$ against ϕ in degree together with $(\chi'_{ij} / \chi_{oij}) \omega_j \rightarrow 0$ and $(\chi''_{ij} / \chi_{oij}) \omega_j \rightarrow 0$ experimentally obtained, gives the asymmetric distribution parameter δ to get the characteristic relaxation time τ_{cs} . All these findings finally establish the symmetric relaxation behaviour for such compounds. The dipole moments μ_1 and μ_2 for the flexible part and the whole molecule are determined from τ_1 and τ_2 and the linear coefficient β of χ'_{ij} versus ω_j 's curves . All the measured μ_j 's are compared with the reported μ_j 's and μ_{theo} 's derived from the bond angles and bond moments of the substituted polar groups of the compounds to arrive at the physico chemical properties by the conformations sketched in this chapter The slight disagreement of estimated μ_j 's and μ_{theo} 's is , however, explained with the consideration of inductive and mesomeric moments in addition to strong hydrogen bonding of the flexible polar groups attached to the parent molecule. All these findings are presented in CHAPTER 5 having title "THE PHYSICO-CHEMICAL ASPECTS OF SOME LONG STRAIGHT CHAIN ALCOHOLS FROM SUSCEPTIBILITY MEASUREMENT UNDER A 24 GHz ELECTRIC FIELD AT 25⁰C"

The CHAPTER 6 "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” in which double relaxations of some normal aliphatic alcohols have been studied to get relaxation times τ_1 and τ_2 due to rotation of flexible part and end over end rotation of the whole molecule from the intercept and slope of a linear equation of $(\chi_{oij} - \chi'_{ij}) / \chi'_{ij}$ against χ''_{ij}/χ'_{ij} for different weight fractions w_j 's of solute in n-heptane at 25°C under electric field frequencies of 24.33, 9.25 and 3.00 GHz. Alcohols like 1-butanol, 1-hexanol, 1-heptanol and 1-decanol are long straight chain hydrogen bonded polymer type molecules having -OH groups which may bend twist or rotate internally about C-C bond under GHz electric field exhibiting characteristic τ . Estimated τ_j obtained from ratio of slopes of individual variation of χ''_{ij} and χ'_{ij} against w_j at $w_j \rightarrow 0$ are compared with those of Murthy et al, Gopala krishna (reported data) and τ_1 , τ_2 by double relaxation method. Relative contributions c_1 and c_2 due to τ_1 and τ_2 towards dielectric relaxations estimated from Fröhlich's equations are compared with the experimental ones obtained by graphical technique. Graphical variations of χ'_{ij} / χ_{oij} and χ''_{ij} / χ_{oij} with w_j at $w_j=0$ together with arbitrary curve of $(1/\phi) \log(\cos\phi)$ against ϕ in degree have been utilised to get symmetric γ and asymmetric δ distribution parameters. The symmetric relaxation time τ_s by γ and characteristic relaxation time τ_{cs} by δ and ϕ are computed to suggest symmetric relaxation behaviour of the molecules. Linear coefficient β 's of $\chi'_{ij} - w_j$ curves and dimensionless parameters b_1 and b_2 involved with estimated τ_1 and τ_2 are used to get dipole moments μ_1 and μ_2 due to rotation of flexible part and the whole molecule which are compared with reported μ 's (Gopalakrishna) and μ_{theo} 's. The slight disagreement between μ_1 and μ_{theo} obtained from available bond angles and reduced bond moments of substituent polar groups attached to parent molecules arises due to strong internal hydrogen bonds present among the -OH groups of dipolar liquid molecules.

The ratio of the linear coefficients of the fitted individual equations of $\chi''_{ij} - w_j$ and $\chi'_{ij} - w_j$ 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 $^{\circ}\text{C}$. 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_r , entropy of activation ΔS_r and free energy of activation ΔF_r 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_i} , 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 p-compounds. Debye–Pellat's equations are, therefore, used to obtain static as well as infinitely hf permittivities ϵ_{0ij} and $\epsilon_{\infty ij}$ 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 $\chi'_{ij} - w_j$ equations to yield hf μ_j 's in terms 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 electrometric effects in them. All these facts are given in CHAPTER 7 called "DIELECTRIC RELAXATION OF AROMATIC PARA SUBSTITUTED DERIVATIVE POLAR LIQUIDS FROM DISPERSION AND ABSORPTION PHENOMENA UNDER GHz ELECTRIC FIELD"

The CHAPTER 8 titled "STRUCTURAL AND PHYSICO-CHEMICAL PROPERTIES OF POLYSUBSTITUTED BENZENES IN BENZENE FROM RELAXATION PHENOMENA" in which a brief report on the physico-chemical properties and structural aspects of some polysubstituted benzenes in benzene

at different experimental temperatures under 10 GHz electric field is made to estimate relaxation times τ_j 's, dipole moments μ_j and thermodynamic energy parameters like enthalpy ΔH_τ , entropy ΔS_τ and free energy of activation ΔF_τ due to dielectric relaxation with formulations derived from orientational susceptibilities χ_{ij} 's. τ_j 's of the polar solutes obtained from the slope of the linear equation of χ''_{ij} and χ'_{ij} are, however, compared with those obtained from the ratio of the linear coefficients of individual variations of χ''_{ij} and χ'_{ij} with weight fractions w_j 's of the solute. τ_j 's from the later method are used to get thermodynamic energy parameters from the Eyring's rate process equation to shed more light on the physico-chemical properties of the polar liquid molecules concerned. The estimated μ_j 's in terms of linear coefficients β 's of $\chi'_{ij} - w_j$ curves and dimensionless parameters b 's involved with measured τ_j 's are finally compared with theoretical dipole moments μ_{theo} 's obtained from vector addition of available bond angles and bond moments of substituted polar groups. The estimated μ_{theo} gives valuable information regarding structures of the molecules. The slight disagreement between high frequency μ_j 's and μ_{theo} 's provides an interesting insight on the inductive, mesomeric and electromeric effects of the substituted polar groups attached to the parent molecules.

Finally, the CHAPTER 9 of "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) in a nonpolar solvent benzene C_6H_6 (i) are studied in terms of the ternary(ijk) high frequency (hf) orientational susceptibilities χ_{ijk} 's at different experimental temperatures in $^{\circ}C$ to arrive at the structural and associational aspects of those polar liquids. The estimation of binary relaxation time τ_{jk} and dipole moment μ_{jk} and several thermodynamic energy parameters like the enthalpy of activation $(\Delta H_\tau)_{jk}$, the entropy of activation $(\Delta S_\tau)_{jk}$, the free energy of activation $(\Delta F_\tau)_{jk}$ of the binary solutes are, however, obtained in order to reach

the conclusion. The dimensionless parameter $\delta = (\Delta H_{\tau})_{jk} / \Delta H_{\eta_i}$ estimated from the slope of the linear equation of $\ln \tau_{jk} T$ against $\ln \eta_i$ where η_i is the coefficient of viscosity of the solvent used, provides one with the information of the solute-solute and solute-solvent molecular associations among the molecules concerned. Almost constant values of Debye factor $\tau_{jk} T / \eta_i$ unlike Kalman factors $\tau_{jk} T / \eta_i^{\delta}$ indicate the Debye relaxation mechanism obeyed by the solutions of binary associated molecules in C_6H_6 . The measured hf binary dipole moment μ_{jk} in terms of estimated binary relaxation time τ_{jk} are compared with the theoretical dipole moments μ_{theo} 's obtained from the bond moments of the substituent polar groups attached to the parent molecules only to support their conformations of associations. The disagreement between μ_{jk} 's and μ_{theo} 's indicates the inductive, mesomeric and electromeric effects of the substituent polar groups in addition to their H-bonding in a gigahertz electric field.

The theoretical formulations so far derived in S.I. units with internationally accepted symbols of dielectric terminologies and parameters are found out to be simple, straight forward and unique one to measure the dielectric relaxation parameters of several polar liquid molecules in non polar solvents under hf electric fields. All the curves satisfied by experimental points in many Figures of different CHAPTERS show the correctness of the theoretical formulations so far presented within the frame work of Debye-Smyth and Hill model of dielectric theories. Although, there exists different models like Kirkwood, Fröhlich and Onsagar. But they are not so simple like the new direct method so far suggested. The methods like thermally stimulated depolarization current density (TSDC) and isothermal frequency domain of AC spectroscopy (IFDS) may give a firm answer to the problem of dielectric relaxation with which the present author is involved. But the weak point of these methods are that they are comparatively very lengthy and often need tedious computer simulation technique. A sound theoretical formulations with the help of Newton – Raphson method may be developed for molecules of high molecular weights by considering their moments of inertia about the central axes. Future workers are, therefore, advised in this field of research of dielectrics and liquid crystals to deal

with this problem. Finally it can be concluded that the CHAPTERS 3,4,5,6,8 and 9 published in the reputed Indian and foreign journals establish the correctness of the present theoretical formulations to predict the physico – chemical problems of some simple polar liquid molecules in non polar solvents under high frequency electric field.