

Synopsis

The dispersion and absorption phenomena of a polar non-polar liquid mixture consist of variation of ϵ_{ij}' , ϵ_{ij}'' and ϵ_{oij} with the angular frequency ω of the applied electric field. This phenomena of liquids and solids represent one of the greatest unresolved problems of physics today. The presence of dispersion and absorption phenomena in the systems under study are related to some form of disorder. There can be no absorption in a perfectly ordered system. Under the alternating electric field in a dipolar liquid molecule each type of polarisation takes some finite time to respond the applied electric field. Thus there exists a considerable lag in the attainment of the equilibrium. This lag in response to the alternation of the applied electric field is commonly known as dielectric relaxation. When the external electric field is withdrawn all types of polarisations decay exponentially with time. The time in which the orientational polarisation is reduced to $1/e$ times the initial value is called the relaxation time τ of a dipolar liquid. In case of static or low frequency electric field all the polarisations are operative. But as the frequency ω of the alternating electric field is very high, the polarisation is not able to attain equilibrium before the applied electric field is reversed.

Hence, to study the dielectric dispersion and absorption phenomena in terms of measured dielectric relative permittivities of polar nonpolar liquid mixture under low and high frequency electric fields have attracted the attention of a large number of workers for its wide application in different fields. Scientists are mainly interested to predict shape, size, structure and molecular interaction of the polar molecules. All the information are derived from the relaxation parameters like real ϵ_{ij}' , imaginary ϵ_{ij}'' , parts of complex relative permittivity ϵ_{ij}^* , static ϵ_{oij} and hf permittivity $\epsilon_{\infty ij}$ of a dipolar liquid molecule (j) in a nonpolar solvent (i) measured in the effective dispersive region of J-Band ($\sim 3\text{GHz}$), X-Band ($\sim 10\text{GHz}$) and K-Band ($\sim 24\text{GHz}$) electric fields.

These data are generally analysed on the basis of various models like Debye, Kirkwood, Fröhlich, Onsager etc. But Debye and Smyth model is very simpler, straightforward and topical one to apply to almost all rigid non-spherical polar liquid molecules in nonpolar solvents. In such case one polar unit is assumed to be far apart from

the other polar units and remains in the quasi-isolated state to eliminate polar-polar interactions almost completely.

Under the X-Band electric field of nearly 10GHz, the polar molecules are found to absorb electrical energy much more strongly to give rise to what is known as absorption phenomena. Saha et al and Sit et al had already studied the double relaxation phenomena of monosubstituted anilines and benzenes under 9.945 Ghz electric field by their formulations derived within the framework of Debye and Smyth model with the measured permittivities in CGS units to shed more light on the shape, size and structure of the polar molecules. Nowadays it is better to introduce the dielectric terminologies and parameters in terms of SI unit to have a deep insight on the shape, size and structure of the polar molecules. The modern concept to study the dielectric dispersion and absorption phenomena of a polar liquid is to use dimensionless complex relative permittivities. The complex high frequency electrical conductivity σ_{ij}^* of polar nonpolar liquid mixtures is related to σ_{ij}' and σ_{ij}'' called the real and imaginary parts of complex conductivity. σ_{ij}' and σ_{ij}'' are, however, related to ϵ_{ij}'' and ϵ_{ij}' by the relation $\sigma_{ij}' = \omega \epsilon_0 \epsilon_{ij}''$ and $\sigma_{ij}'' = \omega \epsilon_0 \epsilon_{ij}'$ where $\epsilon_0 =$ absolute permittivity of free space = $8.854 \times 10^{-12} \text{ F.m}^{-1}$. The dispersion and absorption phenomena under the heading of relaxation phenomena have already been studied for different polar molecules in terms of hf conductivity measurement to predict the conformational structures and molecular interactions in them.

The author had already applied the dielectric terminologies and parameters to some rigid aromatic molecules like anisidines and toluidines in benzene under X band [9.945 GHz] electric fields at 35°C. The relaxation times τ_j and the dipole moments μ_j due to rotation of the whole molecules exhibit the rigid nature of the molecules. The molecular associations are supported by the conformational structures of the molecules in which the presence of mesomeric, inductive and electromeric moments are found to play their vital role.

The measured data of ϵ_{ij}' , ϵ_{ij}'' , ϵ_{0ij} and $\epsilon_{\infty ij}$ of some straight chain alcohols in solvent benzene at 25°C under 24 GHz electric field were utilised by the author to study the various intra and inter molecular relaxation phenomena. The τ of the alcohol molecules were estimated by the slope of the variations $\sigma_{ij}'' - \sigma_{ij}'$ and also with the ratio of the slopes of the

individual variations of $\sigma_{ij}''-w_j$ and $\sigma_{ij}'-w_j$ curves at $w_j \rightarrow 0$. In the latter method the polar-polar interactions are fully avoided because here the single polar molecule is surrounded by a large number of solvent molecules. τ_j 's from the ratio of the individual slopes at $w_j \rightarrow 0$ are much more reliable than those of the linear slopes of σ_{ij}'' against σ_{ij}' as they are in close agreement with the reported data. The excellent agreement of the measured dipole moment μ_j 's in terms of measured τ_j and slope β of $\sigma_{ij}-w_j$ with the reported μ 's suggest the basic soundness of the technique of the conductivity measurement used. The polar liquid in a given non-polar solvent behaves as a bound charged species due to polarisation under GHz electric field in order to have very large conductivity σ_{ij} in $\Omega^{-1}m^{-1}$ for different w_j 's although they are insulators. The slight disagreement between μ_j 's and the theoretical dipole moments μ_{theo} 's from the conformational structures reveals the existence of mesomeric, inductive and electromeric effects within the free polar groups attached to the parent molecules. The methodology so far developed is, however, involved with the transfer of bound molecular charges of dipolar molecules in a given solvent.

The author measured the dielectric relaxation time τ_j and the hf dipole moment μ_j of some dipolar methyl benzenes like toluene; 1,3,5- trimethyl benzene; 1,2,3,4- tetra methyl benzene; 1,2,4,5- tetra methyl benzene; 1,2,3,5- tetra methyl benzene; pentamethyl benzene; trifluoro toluene and p-fluoro toluene in benzene at 25 °C under 9.585 GHz electric field by the conductivity measurement in SI unit. A comparison is made between the hf μ_j 's and μ_{theo} 's from the available bond angles and bond moments to see the frequency effect on the measured data.

The recent trend is to study the relaxation mechanism of dipolar liquid molecules through hf dielectric orientational susceptibility χ_{ij}^* rather than the permittivity ϵ_{ij}^* or hf conductivity σ_{ij}^* . The susceptibility parameter is directly linked with the orientational polarisation of the molecule whereas hf or ac conductivity is concerned with the transport of bound molecular charges of the polar species in a non-polar solvent. The susceptibility derived from the measured permittivities of polar non-polar liquid mixtures provides one with only three parameters which are sufficient to predict the relaxation phenomena. The terms are real $\chi_{ij}' = \epsilon_{ij}' - \epsilon_{\infty ij}$, imaginary $\chi_{ij}'' = \epsilon_{ij}''$ parts of complex orientational dielectric susceptibility χ_{ij}^* and $\chi_{oij} = \epsilon_{oij} - \epsilon_{\infty ij}$ is the low frequency dielectric susceptibility which is real.

The simplification in the relaxation formulations could, however, be achieved if the fast polarisation process is excluded. This can be done by working in terms of the orientational hf complex susceptibility χ_{ij}^* rather than hf complex permittivity ϵ_{ij}^* because, ϵ_{ij}^* includes within it all the polarisation processes. The algebra becomes clumsy if the analysis is made in terms of ϵ_{ij}^* because $\epsilon_{\infty ij}$ frequently appears as the subtracted term in the formulations.

Terms corresponding to $(\epsilon_{ij}' - \epsilon_{\infty ij}) / (\epsilon_{0ij} - \epsilon_{\infty ij})$ and $\epsilon_{ij}'' / (\epsilon_{0ij} - \epsilon_{\infty ij})$ in Bergmann equations can be replaced by χ_{ij}' / χ_{0ij} and χ_{ij}'' / χ_{0ij} where χ_{0ij} is the low frequency susceptibility which is real, appears frequently. The use of χ 's forms would simplify the theory considerably. The inclusion of new physical parameters like χ_{ij} and its very nature of variations with w_j 's gives a new insight into the dielectric mechanism involved in the polar liquids.

The present author was, therefore, interested to study some disubstituted benzenes and anilines like o-chloro nitrobenzene; 4-chloro 3 nitro benzotrifluoride; 4-chloro 3-nitro toluene; o-nitro benzo trifluoride; m-nitro benzo trifluoride; 2-chloro 6-methyl aniline; 3-chloro 2-methyl aniline; 3-chloro 4-methyl aniline; 4-chloro 2-methyl aniline and 5-chloro 2-methyl aniline in solvent benzene and carbon tetrachloride at 35 °C under a single high frequency 9.945 GHz electric field. Aniline as well as benzene derivatives are expected to absorb electric energy much more strongly in hf electric field for the presence of their flexible parts such as methyl or other groups attached to the parent molecules. Therefore, they exhibit double relaxation times τ_2 and τ_1 . The dipole moments μ_2 and μ_1 due to rotations of the whole molecules and the flexible parts were found out. The relaxation time τ_j 's are measured from the linear slope of $\chi_{ij}'' - \chi_{ij}'$ curve as well as from the ratio of the individual slopes of $\chi_{ij}'' - w_j$ and $\chi_{ij}' - w_j$ curves at $w_j \rightarrow 0$. The hf μ 's are then compared with the theoretical dipole moment μ_{theo} 's from the conformational structures.

The corresponding dipole moments μ_2 and μ_1 of the whole and the flexible part of the molecule are estimated to compare with the static μ_s measured under low frequency electric field and reported μ 's. The theoretical dipole moments μ_{theo} is calculated by

applying the vector addition method to the bond moments of the substituent polar groups of the molecules in order to predict their conformational structures.

Thus the subject matter of the thesis is aimed at to study the dispersion and absorption phenomena of polar liquid molecules in different nonpolar solvents under high and low frequency electric field at a single or different temperatures in $^{\circ}\text{C}$ to predict their conformational structures.

Moreover, the present study through the hf σ_{ij} measurement in terms of modern concept of dielectric terminology and parameter yields the average microscopic τ whereas double relaxation phenomena of the molecules offer a better understanding of microscopic as well as macroscopic molecular τ . The existence of a double relaxation phenomena reflects the material property of the chemical systems under investigation and is not dependent on the measurement frequency. Likewise, although permittivity and dielectric absorption vary with the frequency, the fundamental dielectric parameters such as dielectric decrement and relaxation time which describe the relaxation properties of the system do not.

Further study of several polar molecules like N,N-dimethyl sulphoxide (DMSO); N,N-dimethyl formamide (DMF); N,N-dimethyl acetamide (DMA) and N,N-diethyl formamide (DEF) in benzene under most effective dispersive region of nearly 10 GHz electric field at 25, 30, 35 and 40 $^{\circ}\text{C}$ for DMSO; 25 $^{\circ}\text{C}$ for DMA and DMF and 30 $^{\circ}\text{C}$ for DEF in terms of orientational susceptibilities χ_{ij} 's measured under single frequency electric fields reveals that double relaxation phenomena occurs in them. Also the hf μ_j and μ_1 due to τ_1 differs from μ_{theo} either by elongation or reduction of bond moments of the substituted polar groups by μ_1/μ_{theo} in agreement with the measured μ 's to take into account of inductive, mesomeric and electromeric effects. Thus the correlation between conformational structures with the observed results increases the scientific contents.

The measured data in terms of ϵ_{ij}' and ϵ_{ij}'' of the complex permittivity ϵ_{ij}^* by Dhar et al and Somvanshi et al for some para substituted derivative polar liquid molecules in solvents dioxane and benzene in the temperature range of 17 – 40 $^{\circ}\text{C}$ have been made in terms of modern established symbols of dielectric orientational susceptibilities χ_{ij}' and χ_{ij}''

with weight fraction w_j in the present study. The Debye-Pellat's equation have been used to find out static ϵ_{0ij} and hf $\epsilon_{\infty ij}$. They are used in the formulations developed by us to get static dipole moments μ_s in order to compare with the μ_1 and μ_2 derived from the τ_1 and τ_2 by the susceptibility measurements. The information so far gathered is finally compared with μ_{theo} 's in para compounds under considerations.

The analysis of measured data of the polar molecules in terms of dielectric susceptibility χ_{ij}^* gives a new dimension and insight into the meaning of the dielectric equations. The errors in estimated τ 's and μ 's are found to be correct up to $\pm 10\%$ and $\pm 5\%$ respectively. A little disagreement between the estimated μ 's and the μ_{theo} 's from available bond angles and bond moments suggests the existence of mesomeric, inductive and electromeric effects of the substituent polar groups of the molecules under high and low frequency electric fields.