

## Preface

The proposed thesis is aimed at to study the relaxation phenomena of some interesting dielectropolar liquid molecules in non-polar solvents under low and high frequency electric field at various experimental temperatures.

The relaxation phenomena in liquids and solids represent one of the most difficult unresolved problems of physics today. The presence of all relaxation phenomena in liquids under study or even for solids are related to some form of disorder. There can be no relaxation in a perfectly ordered system, because nothing can relax from perfection. Under the application of the alternating electric field in a dielectropolar liquid molecule each type of polarisations takes some time to respond the applied electric field. The lag in response to the alternation of the applied electric field is commonly known as dielectric relaxation.

The dipolar liquid molecules in non-polar solvents under low and *hf* electric fields attracted the attention of a large number of workers for its wide applications in different fields. All the information are derived from the measured relaxation parameters like real  $\epsilon_{ij}'$ , imaginary  $\epsilon_{ij}''$  parts of complex relative permittivity  $\epsilon_{ij}^*$ , static relative permittivity  $\epsilon_{0ij}$  and high frequency relative permittivity  $\epsilon_{\infty ij}$  of a polar liquid molecule (j) dissolved in a non polar solvent (i) measured under any suitable experimental arrangement of the effective dispersive region of J-Band (~3 GHz), X-Band (~10 GHz) and K-Band (~24 GHz) electric fields. These data are analysed on the basis of various models like Debye, Kirkwood, Fröhlich, Onsager etc.

Out of the above models, Debye and Smyth model is very simple, straightforward and applicable to almost all rigid spherical polar liquid molecules in non-polar solvents. In such case one polar unit is assumed to be far apart from the others and remains in quasi-isolated state to eliminate polar-polar interactions almost completely.

We have therefore, become selective to chose some apparently rigid aliphatic polar molecules like chloral and ethyltrichloroacetate in non polar aromatic solvent benzene and alicyclic aliphatic solvents *n*-hexane and *n*-heptane to study their conformations under three different frequencies in GHz range. Chloral and ethyltrichloroacetate in a variety of non polar solvents under single frequency electric field show the double relaxation phenomena due to rotation of the whole molecule as well as the flexible parts attached to the parent molecules exhibiting the non-rigid nature of the molecules. The static and *hf* dipole moments for the above systems were also estimated. This investigation also includes polar liquid molecules like trifluoroethanol, trifluoroacetic acid and octanoyl chloride dissolved in benzene too.

$\tau_j$ 's and  $\mu_j$ 's of some polysubstituted benzenes like meta-diisopropylbenzene, para-methyl benzoylchloride and ortho-chloroacetophenone in benzene at different experimental temperatures

under GHz electric field frequency were investigated to get new information about molecular environment of the polar molecules and shed more light on their structural conformations and associational behaviour. Various energy parameters like enthalpy of activation  $\Delta H_v$ , entropy of activation  $\Delta S_v$  and free energy of activation  $\Delta F_v$  were proposed from the standpoint of dielectric relaxation of the polar molecules. The molecules are complicated in nature and one of them is para compound in which peculiar behaviours are quite expected. With these facts, we are very much tempted to make a rigorous study by our well-known conductivity measurement technique.

The author also measured the relaxation parameters  $\epsilon_{ij}'$ ,  $\epsilon_{ij}''$ ,  $\epsilon_{oij}$  and  $\epsilon_{\infty ij}$  of some aprotic polar liquids like DMSO, DEF, DMF and DMA in benzene by HP 4192A impedance analyser at Dept. of Spectroscopy, IACS, Kolkata for different concentrations and at different experimental temperatures to test the theories newly developed.

Relaxation mechanism have been studied for some methyl benzenes and ketones in benzene through high frequency conductivity measurement technique to get structural and associational aspect of the molecules.

The recent trend is to study the relaxation mechanism of dielectropolar liquid molecules through  $hf$  dielectric orientation susceptibility  $\chi_{ij}^*$  rather than permittivity  $\epsilon_{ij}^*$  or conductivity  $\sigma_{ij}^*$ . The dimensionless  $\chi_{ij}^*$  are directly linked with the orientation polarisation of the molecules while  $hf$  conductivity  $\sigma_{ij}$  is concerned with the transport of bound molecular charge of the polar-nonpolar liquids and  $\epsilon_{ij}^*$  includes all the polarisations.

Relaxation phenomena in terms of dielectric orientation susceptibility measurement technique were studied for chloral and ethyltrichloroacetate in benzene, *n*-hexane and *n*-heptane and a number of disubstituted benzenes and anilines in benzene and carbon tetrachloride under  $hf$  electric field. The molecules are supposed to absorb electric energy much more strongly nearly 10 GHz (~X-Band) electric field to show the interesting behaviour of the molecule from relaxation phenomena.

Double relaxation phenomena seems to be the material property of some dipolar liquids in non-polar solvents. It had been extensively studied by the author for a number of alcohols in *n*-heptane under three different  $hf$  electric fields.

Thus the entire object of the thesis is to study the relaxation phenomena of polar liquid molecules in various non-polar solvents under high and low frequency electric field at a single or different temperatures in order to arrive at their conformational structures from the derived present formalisms on the basis of Debye and Smyth model. The correlation between the conformational structures of the compounds under investigation with the observed results enhances the scientific contents of the thesis as it adds a better understanding to the existing knowledge of dielectric relaxation phenomena so far achieved.