

SYNOPSIS OF THESIS WORK

The relaxation mechanism of polar molecules in nonpolar solvents under high frequency (hf) electric field is of special interest as it throws much light on various types of molecular associations like solute-solvent (monomer) and solute solute (dimer) formations in a given solvent. One may get an idea about the stability or unstability of the systems in the relaxation phenomena through the measured thermodynamic energy parameters. It also offers valuable information of size, shape and structure of a dipolar liquid molecule from the measured permittivities like real ϵ'_{ij} , imaginary ϵ''_{ij} parts of complex permittivity ϵ^*_{ij} under hf electric field, static ϵ_{oij} and infinite frequency permittivity $\epsilon_{\infty ij}$ at different weight fractions w_j of a dipolar liquid at a given temperature.

An extensive study is, therefore, made in this thesis to get relaxation time τ_j of a large number of polar liquids assuming the existence of single broad or two Debye type dispersions in order to arrive at the structural and associational aspects of them. τ_j 's are subsequently used to calculate the hf dipole moments μ_j 's of those polar molecules in terms of slope β of hf conductivity k_{ij} or σ_{ij} against w_j curve. τ_j 's are usually estimated from the ratio of the slopes of $k''_{ij}-w_j$ or $\sigma''_{ij}-w_j$ and $k'_{ij}-w_j$ or $\sigma'_{ij}-w_j$ curves at $w_j \rightarrow 0$ where k''_{ij} or σ''_{ij} and k'_{ij} or σ'_{ij} are the imaginary and real parts of the hf complex conductivity k^*_{ij} or σ^*_{ij} in c.g.s. and SI units. The variation of hf conductivity k_{ij} or σ_{ij} against w_j alongwith other measured parameters have been well displayed to get hf μ_j . The obtained τ_j 's from the methodology so far developed are finally compared with the existing methods of Murthy et al and Gopalakrishna. In the present method polar-polar interactions are thought to be fully eliminated.

The estimated hf μ_j 's are compared with the static dipole moment μ_s obtained from linear coefficient of $X_{ij}-w_j$ variation from the measured relaxation parameters under static or low frequency electric field within the frame work of Debye and Smyth model. The theoretical dipole moments μ_{theo} 's have conveniently

been obtained from available bond angles and bond moments of the substituent polar groups attached to the polar molecules. In almost all cases μ_{theo} 's are found to differ from experimental hf μ'_j 's and static μ_s 's suggesting the very existence of inductive and mesomeric moments of the substituent polar groups attached to the parent molecule.

The recent trend is to study the orientational polarisation of molecules in terms of measured orientational susceptibilities like real χ'_{ij} , imaginary χ''_{ij} and static χ_{0ij} rather than permittivities. $\epsilon_{\infty ij}$ includes the fast polarisation and appears frequently as a subtracted term in Bergmann's equation. The existence of double relaxation times τ_1 and τ_2 due to rotation of the flexible parts and the whole molecules themselves were also expressed in terms of measured susceptibilities.

To test the dielectric relaxation theories so far developed a rigorous study is, however, made on a number of dipolar molecules like long chain normal and octyl alcohols, anilines, aprotic polar liquids, para-compounds like parahydroxy propiophenone, parachloropropiophenone, paraacetamidobenzaldehyde, parabenzoyloxy benzaldehyde in dioxane, paraanisidine, paraphenitidine, orthochloroparanitroaniline and parabromonitrobenzene in C_6H_6 at various concentrations and temperatures in $^{\circ}C$. Different thermodynamic energy parameters like enthalpy ΔH_t , entropy ΔS_t and free energy ΔF_t of activation due to dielectric relaxation from Eyring's rate theory at different experimental temperatures in $^{\circ}C$ establish the structural and associational aspects of dielectropolar liquid molecules.

It is observed that in addition to displacement current, conduction current due to existence of free ions in the dipolar liquids is playing its role to yield rf conductivity under radio frequency (rf) electric field. But the displacement current alone gives rise to conduction under the microwave electric field. An attempt is, therefore, made to provide the feasibility of applying hf conductivity technique on some combinations of simpler dipolar molecules like alcohols in a suitable solvent or in pure states at a single or different experimental

temperatures in °C. The object of such study is to measure the dielectric relaxation parameters in order to yield the molecular dynamics of the systems under 1 MHz frequency of electric field. Some of the works of the author in c.g.s. units have been published in different journals of international repute. But nowadays the modern trend is to study the dielectric relaxation phenomena of polar molecules in nonpolar solvent in SI units because of its unified, coherent and rationalised nature. Later research works have been made in SI unit to get the interesting insight into the interactions of the dipolar molecules.

Thus the subject matter of this thesis is directed to get a concrete concept of structural and associational aspects of several dielectropolar molecules in liquid state from their measured relaxation parameters under GHz and rf electric fields. The new powerful theoretical approach enables one to test the adequacy or otherwise of the theories based on Debye-Smyth model which are usually found to deviate from the traditional dielectric theories prevailing elsewhere.