ABSTRACT

The Dielectric spectroscopy is a branch of spectroscopy where one gets information about structural changes and molecular interaction through dielectric relaxation data. The study of dielectric properties of liquid material is essential not only to understand the liquid structure but also to provide technical data for practical uses in electronics. The study is necessary to understand the physical phenomenon which occur in dielectrics placed in an electromagnetic field and the parameters of the dielectric which quantitatively determine to assess the applicability of the dielectric material, it is required to know not only their electrical properties such as thermal conductivity, stability to chemical reagents and solvents, thermodynamics parameters. The basics of molecular interaction are the hydrogen bonding. Hydrogen bonds are occurs between hydrogen containing dipoles and electronegative element. Electro-negativity provides us a relative ability of atom in molecule to attract bonding electrons.

Time Domain Spectroscopy developed by Prof. Cole in reflection mode is used for obtaining dielectric relaxation data. This technique is very useful, economic and fast compared to other techniques. TDR technique requires very small amount of sample and in single measurement we get permittivity and dielectric loss over wide range from range 10MHz to 20 GHz.

The basic TDR setup consists of step generator, sampling head, sample cell and broadband storage oscilloscope. A fast rising step pulse from generator propagates through coaxial transmission line and reaches dielectric sample placed in sample cell connected as open-ended load. It is partly transmitted and partly reflected at air dielectric interface. Both, reflected as well as transmitted step from sample contains information about dielectric behavior of sample. In the present work reflected step is used to evaluate.

Dielectric relaxation data. The time profile of reflected step with and without sample is recorded in the oscilloscope. This time domain data is transformed into frequency domain data using Fourier transformation. Frequency domain data is used to obtain complex reflection coefficient $\rho^*(\omega)$ over frequency range of 10 MHz to 20 GHz. Complex reflection Coefficient gives permittivity and dielectric loss in selected frequency range. But normally there occurs error in this data at higher frequencies due to fringing.
field, multiple reflections or due to quarter-wave resonance in case of high lossy liquids. The complex reflection data is called "RAW" data. An error in RAW data is corrected by bilinear calibration process. The corrected data is called "COR" data. The dielectric parameters obtained by fitting "COR" data to Havriliak-Negami equation,

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + \left(\frac{\gamma}{(j\omega\tau)}\right)^\alpha}$$

Where $\varepsilon'(\omega)$ is complex reflection coefficient, $\varepsilon_\infty$ is static permittivity, $\varepsilon_0$ is dielectric loss, $\omega$ is angular frequency, $\tau$ is relaxation time, $\alpha$ is relaxation time distribution parameter defined in Cole-Cole model, $\beta$ is relaxation time distribution parameter defined in Davison-Cole model. If we put $\alpha=0$ and $\beta=1$, above equation represents simple Debye model. A least squares fit method is used to obtain dielectric parameters.

Alcohols and ethers are versatile organic liquids used in chemical industries as solvents for oils, resins and an antifreeze for explosive. It is miscible with a number of organic solvents as well as water. The mixing properties of this liquids of alcohols and ethers have not been studied and hence it is decided to measure the static dielectric constant, $\varepsilon_s$, relaxation time $\tau$, in these mixtures at various temperature and composition. Dielectric relaxation studies of the binary mixtures have been particularly useful in understanding of intermolecular

The values of $\varepsilon_s$ and $\tau$, as a function of concentration of methanol, ethanol and 1-propanol in 2-Methoxyethanol, 2-Ethoxyethanol and 2-Butoxyethanol have been determined. It is interesting to note that the excess permittivity value for both systems are found to be negative and the negative values for both the system at higher concentration imply formation of multimeric structures. The inverse excess permittivity value for both system was also found negative and the negative value at higher concentration indicate slower rotations of the dipoles. This indicates that there is significant intermolecular interaction in the mixture.

The permittivity ($\varepsilon$) is related to square of molecular dipole moment, the value of permittivity ($\varepsilon$) is related to size of molecule in solution and temperature. The dielectric relaxation time $\tau$ is related to nature of intermolecular bonding, size of molecule, mobility of molecules in solution, molecular volume, viscosity and
temperature. Thus information at molecular level can be gained from a study of dielectric behavior. To understand structural changes in systems, excess permittivity ($\varepsilon^E$), excess inverse relaxation time ($1/\tau^E$) and Bruggeman factor ($I_{BR}$) are obtained. Thermodynamic parameters, i.e., activation energy in KJ/mole, change in enthalpy ($\Delta H$) and entropy ($\Delta S$) are calculated using Eyring's equation to understand molecular dynamics of the system.