Chapter 2

GENERAL SURVEY OF WORK ON DIELECTRICS

2.1 INTRODUCTION

Michael Faraday in 1831 was introduced the concept of a dielectric\(^1\), defined as a medium in which electric induction can take place. Dielectric or dielectric material is an insulator whose behavior changes when subjected to an external electric field. When change in behavior is independent of direction of applied field, then the dielectric is called isotropic. On the other hand, if the change in behavior of dielectrics depends on direction of applied field, then the dielectric is called anisotropic. Dielectric have played important role as materials in device fabrication used in industry. In fact large variety of materials including ceramics, polymers, liquid crystals and other organic and inorganic compounds, all undergo change under applied electric field and can be investigated as a dielectric. With the development of new materials, study of such substances has attracted interest of scientists and engineers alike.

The study of dielectric properties of materials is of great assistance in exploring the molecular structure and dynamics of condensed matter. The development and application of high frequency current technology increased the demand for dielectric materials. The dielectric relaxation phenomenon has been applied extensively in understanding the molecular structure and in the preparation of new dielectric materials used for special purposes such as in fiber optics, pollution control and converters of energy, memory cells and microelectronic thin film technology. This method has also been applied to study the biological and non-biological macromolecules such as plastic fibers, polymers, rubber wool and cellulose. The recent application of dielectric studies on biological molecules has shown the possibility of treating malignant diseases by studying the response of diseased cells of the body to the radiation used and then localizing the heat in the area of interest.

The information such as molecular flexibility or rigidity, shape and size etc. obtained using dielectric relaxation as the probe which serves the basis for
determining its carcinogenic or anti-carcinogenic action, is of vital importance for investigation of cancer.

The dependence of dielectric relaxation on the frequency, temperature, pressure and other external factors has been used to investigate the correlation between the morphology and electrical properties of macromolecules.

2.2 DIELECTRIC POLARIZATION

The common feature of dielectric materials\(^1,4\) is their ability to store electric energy. This is accomplished by the displacement of positive and negative charges under the effect of the applied electric fields and against the force of atomic and molecular attraction. The mechanism of charge displacement (i.e., polarization) depends on the type of dielectric material and the frequency of the applied field. There are four main types of dielectric polarization. They have very similar qualitative effects but appear at very different frequencies. The microscopic elements that are involved in this are at the level of a complete zone of the material, the molecule, the ion, and the atom, respectively. In all cases, the electric equilibrium is disturbed because the applied field causes the spatial separation of charges of opposite sign. With an alternating field, the frequency determines the dominant type of polarization.

Space charge polarization gives rise to low-frequency response. It occurs when the material contains free electrons whose displacements are restricted by obstacles, such as grain boundaries. When an electric field is applied, the electrons accumulate on the obstacle, and the resulting charge separation polarizes the material. Entire regions of the material become either positive or negative. This type of polarization is fundamental in semiconductor electronics.

Polarization by dipole alignment occurs at higher frequencies (HF, Microwaves) and also at molecular level. It lies at the basic of dielectric heating.

Ionic polarization takes place at infrared frequencies; it is due to the separation of positive and negative ions in the molecule.

Electronic polarization occurs at very high frequencies close to the ultraviolet region. The atomic nucleus is positive and fixed in the matrix of the dielectric material. The negative electronic cloud surrounding it is displaced in the direction of the applied field.
In practice, these phenomena may overlap and it is not always easy to establish strict barriers between them.

When a molecular system is placed in an electric field, there is always the tendency for the electrically charged species to move along the field in the appropriate direction, causing the atom to develop an induced dipole moment. This induced moment has all the characteristics of an assembly of dipole produced by an elastic displacement of electrons. This polarization mechanism is known as electronic or optical polarization.

The structure of molecules has strong influence on polarization processes. Due to its asymmetrical structure when a polar molecule or dipole is put in an electromagnetic field, the two opposite charges in the molecule attempt to migrate in the field thus applying a couple to the molecule. This tends to align the dipole along the field. This is called orientation polarization and this leads to the phenomenon of dielectric relaxation. If the electric field strength varies very fast, the polarization will lag behind the changing field. Therefore, the dielectric properties of materials in time dependent field will deviate characteristically from the corresponding equilibrium properties of steady fields. The lag in the electric polarization behind the field results in a complex dielectric constant, defined as

$$\varepsilon^*(\omega) = \varepsilon' - j\varepsilon''$$

Where $\varepsilon'$ is the real part that determines the displacement current also called as dielectric constant and $\varepsilon''$ is the dielectric absorption called as dielectric loss factor. Static dielectric constant ($\varepsilon_0$ or $\varepsilon_\infty$) is the dielectric constant at $\omega$ tends to zero, where as the $\varepsilon_\infty$ is dielectric constant $\omega$ at tends to $\infty$ which is generally assumed to be square of the refractive index.

The complex permittivity is sufficient to describe dielectric behavior of molecular system. Several methods have been developed for the determination of $\varepsilon'$ and $\varepsilon''$ or $\varepsilon'$ and $\tan\delta$. Some employ transmission lines and others use resonant cavities into which the sample is introduced and the resulting perturbation measured.

2.3 DIELECTRIC RELAXATION

Dielectric relaxation\textsuperscript{1,2} occurs when the electric field that induces polarization in a dielectric is removed. The material takes a certain time to return to molecular
disorder, and the polarization subsides exponentially with time constant $\tau$, or relaxation time. This constant is the time necessary for the polarization of the material to fall by a factor of $1/e$ (to 36.79% of its value in the field).

There are two relaxation regions that correspond to two distinct mechanisms, namely $\alpha$ relaxation that occurs at low frequencies and is due to microbrownian motion within the chain, and $\beta$ relaxation that occurs at higher frequencies and is due to dipole orientation, as well as torsional movement of the chains.

Decay of orientation polarization has long been recognized as an exponential process. Orientation polarization involving rotation of dipolar molecules is the process requiring usually $10^{-12}$ to $10^{-10}$ sec. But for very large molecules or for very viscous medium, the time required may be much higher. When a field applied to a dielectric is removed, the decay of polarization with time is called "Dielectric relaxation". Relaxation time measures the time of dipoles to become randomly oriented again when the applied field is suddenly removed.

The dependence of the relaxation time on the temperature has led to another approach in explaining the phenomenon. Eyring explained it as the rate process, which was extensively analyzed by Kauzman and Frohlich. In rate process, the molecular dipole orientation involves passage over a potential energy barrier with a certain probability of jumping one orientation to another. Such a process is governed by an activation energy dependent upon the inter molecular forces. The variation in the local environment of the molecules leads to the distribution of activation energy and this gives rise to the distribution of relaxation time. Analysis of relaxation time ($\tau$) as a function of temperature was carried out using Eyring relation to yield enthalpy of activation $H$, free energy of activation $G$, and entropy of activation $S$.

2.4 ELECTRICAL CONDUCTIVITY

The dielectric investigations provide a fundamental method for studying the structural changes, the rotational process involved and heat energies associated in the materials. The electrical properties of the materials depend not only on chemical composition and structural features but also on the degree of molecular order. The dielectric investigations account for the dispersion behavior associated with molecular configuration and it's ordering, and these, in turn, affect the conductivity behavior of
the system. Hence it is interesting to study the conductivity changes with temperature and frequency in different systems. The results were discussed in terms of various models such as quantum mechanical tunneling, correlated barrier hopping, overlapping large polaron tunneling and hopping over barrier\(^7\).

2.5 AREAS OF DIELECTRIC STUDY

2.5.1 AGRICULTURAL

Knowledge of dielectric properties of grains and seeds becomes increasingly significant as agricultural technology becomes more sophisticated, new applications for electric energy are developed and as new methods, processes and devices come into being, which utilize or are influenced by the electrical nature of the materials.

The dielectric properties of grain and insect are key factors determining degree of differential heating that can be achieved in radio frequency dielectric heating for stored grain insect control\(^8\). Dielectric absorption properties are also important when microwave or dielectric heating applications are being considered for materials because the design of the equipment and power absorption by materials are dependent upon the dielectric properties. The high correlation between dielectric constant and moisture content has made possible the development of electronic instruments for rapidly measuring moisture content\(^9\). The dielectric properties of grains have also been studied in order to determine usefulness of electronic moisture monitoring equipment for flowering grains, in drying of grain and in milling industries. Modern electrical moisture meters use either conductivity or dielectric properties depending upon their design. Many of them sense dielectric constant and use frequency of measurement in the range 1 MHz and 50 MHz. Holladay\(^10\) detected successfully the heat damage in artificially dried corns through measurement of moisture distribution in corn kernel. Hunt et al. developed methods for measuring oil contents of soyabean using dielectric measurement technique. Oil contents of sunflower seeds have also been successfully measured using similar technique for designing equipments for all these applications, data on dielectric properties of these materials are necessary. Therefore investigations were undertaken to generate basic dielectric data on various kinds of seeds of Indian origin. A large number of grain species of different varieties e.g.-pulses (Lentil, Black gram, Green gram, Gram, Pigeon pea), Oil seeds (Groundnut, Yellow sarson, Toria, Sesame, Linseed), Vegetable seeds (Tomato,
Radish, Lady’s finger, Spinach), Seeds of aromatic and medicinal plants (Isabgol, Opium puppy, Ashwagandha, Pal marosa) were taken for investigating the dielectric behavior for varying moisture levels, over a wide range of frequencies (10 KHz-30 MHz and 10 GHz), and temperature range from 15°C to 45°C and for two bulk density levels.

In general, it was found that dielectric constant increased with increasing moisture content and decreased with increasing frequency. At high moisture levels and low frequency range, the magnitudes of variations in dielectric constants were large.

2.5.2 DISPLAY DEVICES

Liquid crystals and their mixtures have become extremely important because of their increasing application in modern technology. Polymer dispersed liquid crystals form a relatively new class of a wide variety of materials, which have use in many types of displays, switchable windows and the light shutter devices. Cholesteric liquid crystals are used frequently in electro-optic displays and also in thermographic applications. When a crystalline solid is heated, it transforms into an isotropic liquid at its melting point. Isotropic liquid does not have a long-range order. Similarly on cooling, isotropic liquid gets converted into a crystalline solid. However, there are certain substances like 4-n-penty-4'-cyano-biphenyl (PCB) and N- (4-methoxoy-benzylidene)-4-n-butylaniline (MBBA) which do not directly pass from crystalline solid to isotropic liquid and vice-versa but adopt an intermediate structure which flows like a liquid but still possesses the anisotropic physical properties similar to crystalline solid. This type of phase is termed liquid crystal. Liquid crystalline molecules are organic in nature and many of them are elongated in shape. The core of the liquid crystal molecules is usually composed of ring systems (aromatic, heterocyclic or alicyclic). The dielectric date of cholesteryl oleyl carbonate\textsuperscript{11,12}, cholesteryl stearate liquid crystals and their mixtures have been obtained using an HP impedance /gain phase analyzer. The values of $\varepsilon'$ increase with decrease in temperature from which it may be concluded that there is considerable freedom for dipole orientation even in solid phase of mesogen and their mixtures. The variation of $\varepsilon'$ with temperature is smaller in solid phase. However in the cholesteric phase $\varepsilon'$ decreases rapidly with increase in temperature. The values of $\varepsilon''$ increase with
temperature in cholesteric phase but it is almost constant in isotropic phase. Dielectric parameters clearly indicate sharp discontinuities at transition temperatures exhibiting solid-cholesteric and cholesteric-isotropic phase transition. In the mixtures the transition temperatures for both solid-cholesteric and cholesteric-isotropic transition vary with concentration of cholesteryl stearate and show almost a linear behavior. Therefore, investigations on phase transition behavior of cholesteryl oleyl carbonate; measuring dielectric parameters, percentage optical transmittance, birefringence, order parameter and density in the temperature range of $15^\circ C-85^\circ C$ have made cholesteryl stearate and their mixtures.

2.5.3 ELECTRONICS

Microelectronic thin film technology and memory cells: Integrated circuits$^{13}$ are a combination of active and passive elements that are manufactured by successive diffusion or ion implantation process on a semiconductor substrate. The active elements are generally silicon planer chip. The passive elements are either thin or thick film components. In thin film; a thin film of conducting (resistor) or nonconducting (capacitor) material is deposited on a passive insulated substrate, such as ceramic, glass or silicon dioxide, by vacuum deposition. The basic materials for monolithic microwave integrated circuits are, substrate materials (alumina, GaAs, glass, ferrite/garnet), conductor materials (aluminium, copper, gold, silver), dielectric films ($Al_2O_3$, SiO, $SiO_2$, $Si_3N_4$, $Ta_2O_5$) and resistive film (Cr, Cr-SiO, NiCr Ta, Ti). The substrate materials have high dielectric constant (9 or higher), and dielectric strength $(10^7)$. The larger the dielectric constant the greater is the coupling with microwaves.

Supercapacitors$^{14}$; the principle components of a battery are two dissimilar electrodes located in a conductive medium. A capacitor, on the other hand, is based on two identical electrodes and a sandwiched non-conducting dielectric medium. Recent advances in the electro-chemical capacitors have resulted in new type of capacitors known as ‘supercapacitors’ or ‘ultra-capacitors’. These have capacitance (energy capable of being stored) of several hundred farads (generally, the capacitance of normal capacitors is in the range of fractions of a farad).

When a metal is brought in contact with a solid or liquid ionic conductor, a charge accumulation is achieved electrostatically on either side of the interface, leading to development of an electrical double layer, which is essentially a molecular
dielectric. No charge transfer takes place across the interface and the current observed during this process is a displacement current due to the rearrangement of charges. The capacitance \( C \) of supercapacitor is given by

\[
C = C_{\text{dl}} + C_{\phi}
\]

Where \( C_{\text{dl}} \) is electrical double layer capacitance and \( C_{\phi} \) is its pseudocapacitance.

This is a new class of reversible electrochemical energy storage systems that use: (a) The capacitance associated with charging and discharging of the electrical double-layer at the electrode-electrolyte interface and are hence called as electrical double-layer capacitors (EDLCs), given by

\[
C_{\text{dl}} = \varepsilon A / 4 \pi t
\]

Where \( \varepsilon \) (6500 to 10000) is the dielectric constant of the electric double-layer region, \( A \) (2000 \( \text{m}^2/\text{g} \)) is the surface area of the electrode, and \( t \) (10\( \text{nm} \)) is the electrical double-layer thickness. (b) The pseudocapacitance with electrosorption or surface redox reactions, which are referred as pseudocapacitors.

While EDLCs with capacitance of many tens of farads per gram of the electrode material have been achieved employing high surface-area carbon powders, fibers, or felts, much higher capacitance values are accomplished with pseudocapacitors employing certain high surface-area oxides or conducting polymers. Theses electrochemical capacitors are being envisaged for several applications to complement the storage batteries. In fact, these supercapacitors are said to have enabled applications for which neither a battery nor a capacitor could provide the required power and energy, such as for load leveling in switching power supplies, turbochargers for batteries, etc. In certain capacitor- battery hybrid power packs for telecom applications for example, in digital cellular phones, pagers, etc., the supercapacitor is used resulting in minimizing voltage loss and battery drain; longer run time, high pulse power application is also thereby achieved. Thus there is a substantial scope for technology development in this newly emerging area, where materials science and polymer technology will have a pivotal role in conjunction with electrochemistry.

2.5.4 CERAMIC INDUSTRY

Ceramic materials play a vital role in space-related systems such as satellites, space-borne weapons. The conductivity properties being closely associated with
dielectric dispersion are one of the important parameters describing the electrical behavior of ceramics. The behavior of ac conductivity of BaTiO₃ and AlN ceramics were examined for frequency and temperature variations. The effect of doping on conductivity behavior has been examined. The results obtained have been discussed in terms of various models.

The analysis of conductivity data in both the ceramics, BaTiO₃ and AlN shows that conductivity exhibits linear variation with frequency except in the case of 0.5 mole% CaO additive in AlN which exhibits a deviation from linearity. It is observed that the conductivity depends on frequency as characterized by the relation of the type $\sigma=A (\omega)^S$ with $S$ having values $< 1.0$. The results obtained are found to be in good agreement with earlier studies on several systems. BaTiO₃ shows a change of phase at 120°C. On doping of BaTiO₃ ceramic with La, the transition temperature shifts towards lower temperature shifts towards lower temperature 117.9°C. The occurrence of peak shows a change of phase probably from ferroelectric to paraelectric.

The smart structures, known as micro-system technology, essentially exploit various physical properties of ceramic dielectrics such as ferro-electric, piezo-electric, electrostrictive and magnetostrictive, etc. The driving force for some of these dielectric is the electric field. The application of ferro-electric ceramic in the electronic industry has been constantly growing. Until today lead zirconate titanate (PZT) ceramics dominate in the piezo-electric field and barium titanate ceramic prevail for dielectric and semiconducting application. PZT ceramics are mainly used as piezo-electric transducers. Ceramic-polymer composites find extensive application such as hydrostatic pressure sensor and hydrophone, acoustic imaging, medical ultrasonic imaging, pulse-echo applications and pyroelectric applications such as infrared detectors. PZT-polymer composite in the form of wire is used as hydrophone probe for measuring ultrasonic field in water and blood pressure sensor. Similarly BaTiO₃-polymer composites are used for self-controlled heating elements and multiplayer capacitors, thermo compensated capacitors and dielectric memory devices. The SiC fiber reinforced is used an important material for aerospace applications. These applications have lead to the laboratory processing and examining materials for their dielectric, and piezo-electric properties. The high
electromechanical coupling and large mechanical quality factor offered by these materials provide for such a dominant role in the device application in the market.

Employing additives may alter the desired properties of these materials. AIN ceramic has drawn attention from scientists and engineers due to its excellent thermal, mechanical and electrical properties. Additives, for example CaO, MgO, SrO and Y₂O₃, can suitably alter the density of the AIN ceramic. It has been found that CaO can be used as an efficient additive to obtain highly dense samples of AIN without affecting the oxidation resistance. Various workers have studied the kinetics of densitification, mechanical and electrical properties of AIN. Investigations have been made on the effect of CaO additive on the dielectric behavior of hot pressed AIN ceramic. The measurements have been made on the annealed samples in order to avoid effect on moisture absorption. The study has shown that CaO doping affects the dielectric behavior of hot pressed AIN ceramic appreciably.

2.5.5 POLYMER INDUSTRY

Molecules which have flexible group attached to an aromatic ring have been widely by dielectric techniques. Usually the dielectric studies of pure liquids or their dilute solutions in nonpolar solvent have been analyzed using Budo’s relation. Numerous studies of large number of molecules by Davies and Edward, Davies and Swain, McLellan and Walker have demonstrated that it is possible to separate completely the absorption due to the molecular and group process by dispersing the solute in a polymer matrix. The enthalpies of activation for the group process have compared well with those from the other direct method of NMR and ultrasonic. The methods which provides for separation of the molecular and group processes in most of the systems, was utilized for studying the energy barriers and other relaxation parameters of several amides, esters, benzyl cyanide and polymers.

The matrix solutions were prepared using Davies and Swain procedure by dissolving weighted quantities of polystyrene pellets and the desired solute in a non-polar solvent, trans-1, 2-dichloroethylene. The concentration of the solute (in mole/liter) in the matrix was calculated using the formula of Tay and Walker. To obtain the relaxation time, Fuoss-Kirkwood equation was used:

\[ \cosh^{-1} \left( \frac{\varepsilon''}{\varepsilon''_{\infty}} \right) = \beta \ln \left( \frac{f_{\infty}}{f} \right) \]

\[ \tau = \frac{1}{2\pi f_m} \]
Where ε", β, τ and f_m are dielectric loss, distribution function, relaxation time and frequency maxima respectively. On analyzing the Eyring plot, chloromethyl formate yielded enthalpy of activation of 91.4 and 34.4 kJ/mol. The higher value of enthalpy seems to be arising due to the cooperative motion of molecules taking the polymer segments along with the motion of molecules. The lower value of enthalpy of 34.4 kJ/mol has been found to be in good agreement with the enthalpy obtained for ester group rotation.

The polystyrene matrix technique has also been applied to some other materials to study absorption due to molecular and group processes separately and the results obtained using this technique have been found to be quite satisfactory. Various hydrogen-bonded complexes of the type NH–N within a polystyrene matrix have been characterized by means of Eyring energy of activation parameters. The dielectric absorption of the complex was completely separated from that of the parent molecules and this enabled a much more accurate determination of the activation parameters that would be feasible by the study of such systems in the liquid states, where overlap of the dielectric absorption processes normally occurs. Dielectric relaxation processes of some aromatic –CH2X molecules where X = Cl, Br and I, aromatic –COCI molecules and parasubstituted benzenes19,20 have also been studied using this technique and it was observed that the group relaxation process could be completely separated from the molecular process. The enthalpy of activation for the group rotation of these molecules has been found to be almost identical with those obtained using NMR technique and also from molecular orbital calculations theoretically.

The polymers offer substantial resistance to the flow of electricity; and being widely used for electrical insulation purposes. In usual carbon-based polymers, the sp³ carbons form sigma bonds; as a result the electrons are in bound state. The electrical conduction mainly occurs in inorganic systems like Cu, Si, etc. due to the presence of delocalized electron sea; where as, in organic and biological systems the electrons are localized by covalent bonding, hence they not really conductive. It is known that in a linear chain of sp² carbon atoms, consisting of alternating single and double bonds, the delocalized π-electron could can attribute special features to the electrical and optical properties in organic systems. An insulating polymer [polysulfurnitrile, (SN)_x, poly paraphenylenethylenevinylene, (ppv)] can be made to be metallic and conduct electricity
if alternating single and double bonds link the carbon atoms in a chain, and the electrons are either removed via oxidation (p-type doping) or introduced via reduction (n-type doping). These extra charge carriers created by doping move along chain, making them conduct electricity, and metallic.

The A.C. conductivity decreases and the dielectric constant increases as the percentage of ferroelectric and ferromagnetic materials in conducting polymer (polyaniline, polypyrrole) increases. The observed change in A. C. conductivity may be due to presence of Polarons and Bipolarons and the polarization mechanisms is responsible for the variation of the dielectric constant in these composites.

The interesting applications of conducting polymers are; light emitting diodes, solar cells, transistors, diodes, holographic storage, chemical and biological sensors, capacitors, batteries, antistatic coatings, electromagnetic interference shielding, anticorrosive coatings, gas and liquid separation membranes, artificial muscles, lithography and metallization, photoelectrochromic devices, xerographic photoreceptors, all-polymer electronic circuits, etc.

2.5.6 MEDICAL

Cancer is associated with rapidly growing and proliferating cells. If a cell cannot make thymidine, it cannot synthesize DNA. Inhibiting dihydrofolate reductase also prevents the synthesis of thymidine because cells have a limited amount of tetrahydrofolate. If they cannot convert dihydrofolate back to tetrahydrofolate, they cannot continue to synthesize thymidine.

The recent application of dielectric studies on biological molecules has shown the possibility of treating malignant diseases by studying the response of diseased cells of the body to the radiation used and then localizing the heat in the area of interest. The energy necessary for hyperthermia is not excessive: 1.5W is theoretically sufficient to raise the temperature of a 20-mm diameter tumor by 5°C in one minute, if energy is efficiently transmitted to the tumor. Neoplastic tissue has a higher dielectric loss factor than healthy tissue because of its higher water content. For example, skin carcinoma contains 81.6% water as compared with 60.9% in normal epidermis; hepatoma contains 81.9% as compared with 71.4% in liver. These differences are to be sufficient to enable us to discriminate between different types of carcinoma by diagnostic radio-frequency imaging.
The information such as molecular flexibility or rigidity, shape and size etc. obtained using dielectric relaxation as the probe which serves the basis for determining its carcinogenic or anti-carcinogenic action, is of vital importance for investigation of cancer.

The values of dielectric constant and dielectric relaxation time for mouth cancer patient’s saliva are ($\varepsilon_0 = 81.68$, $\tau = 13.29$ps) larger than normal person’s saliva ($\varepsilon_0 = 76.57$, $\tau = 11.38$ps).

2.6 DIELECTRIC SPECTROSCOPY

The study of structural changes in liquids is the subject of interest for many people in field of Physics, Chemistry and Biological Sciences. The dielectric spectroscopy is the nice probe to access information at molecular level. One can understand the structural changes in liquid due to change in amount of hydrogen bonding by using Dielectric Spectroscopy. This method is based on frequency dependant changes in dielectric properties of material. Dielectric relaxation study deals with ability of material to store electrical energy in the form of polarization. Applied electrical energy causes charge redistribution in dielectric material, which will build-up induced polarization.

Dielectric spectroscopy has two main branches namely Frequency Domain dielectric spectroscopy (FDS) and Time Domain dielectric spectroscopy (TDS). FDS needs number of experimental setups to cover entire frequency range of interest (say 10MHz to 20 GHz), while TDS provides similar information with single experimental setup. As TDS provides us information in single measurement, degradation of sample with time can be avoided in case of biological samples. The amount of sample needed in TDS is very less as compared to FDS. The measurements in TDS are very fast than in FDS. Normally in FDS the dielectric parameters are measured at less than 10 frequency points. But in TDS one can get information at more than 200 frequency points in single measurement. In FDS the absolute values of dielectric parameters are more precise as that in TDS, but access to structural changes in liquids is through relative change in dielectric parameters and not through absolute values. Thus relative changes in dielectric parameters are more important to predict structural changes in liquid. The relative change in dielectric parameters over wide range of frequencies
and wide range of concentrations at various temperatures can be very systematically measured in TDS. Thus we can more closely investigate molecular interactions with TDS.

TDS provides an effective approach to explore structure of matter, dielectric relaxation mechanisms and molecular interactions. An experimental method used to determine the dielectric characteristics of a system, by monitoring its response to fast rising step pulse, is termed as Time Domain Spectroscopy (TDS). The part of incident step pulse is reflected back from sample and some part is transmitted through the sample. The reflected as well as transmitted step pulse from sample holds information about dielectric behavior of sample. Time Domain Reflectometry (TDR) technique uses reflected pulse whereas Time Domain Transmission (TDT) method deals with transmitted pulse through sample.

In the present work TDR technique is used to determine dielectric parameters of systems studied. This technique provides dielectric spectra of sample over wide frequency range, from 10 MHz to 20 GHz, in a single measurement. The amount of sample required for one measurement is less than 0.5 ml. As measurements are taken simultaneously over entire frequency range of interest, the method is most suitable for study of biological systems. This technique is very useful, economical and fast as compared to other techniques.

2.7 LITERATURE SURVEY

Many research groups to study molecular interactions in liquids have used TDR method. Microwave group at Physics Dept. of Dr.B.A.M. University, Aurangabad, has developed experimental setup and computer programs required to study dielectric properties of pure liquids as well as binary mixtures using TDR method. Our group to study interactions between various functional groups in organic compounds and biological samples has very effectively used this method. The molecular interactions in aqueous solutions of associative compounds such as Ethylene Glycol\textsuperscript{24}, Hexamethylphosphoramidate \textsuperscript{25}, Dimethylsulfoxide \textsuperscript{26}, tetra Butyl alcohol\textsuperscript{27}, Acetone and Tetrahydrofuran\textsuperscript{28}, N, N Dimethylformamide\textsuperscript{29}, N Methylformamide\textsuperscript{30}, Primary alcohols \textsuperscript{31-34} was reported earlier. Similarly an aqueous solution of non associative solute Acetonitrile was reported by Helambe et. al. The solute solvent interactions between long chain polymeric structures in alcohols with
nonpolar molecules such as Benzene and n-Octane\textsuperscript{35} and non-associative polar solutes such as Aniline\textsuperscript{36,37}, n-nitrides\textsuperscript{38}, p-Flourophenylacetonitrile\textsuperscript{39} was studied previously. The dielectric relaxation study of binary mixtures of primary alcohols and polar solutes such as Dimethylformamide\textsuperscript{40}, Dimethylsulfoxide\textsuperscript{41}, Tetrahydrofuran\textsuperscript{42} and 2-Nitroacetoephonone\textsuperscript{43} was reported earlier. The binary mixture of Ethanol, with one –OH group, and Ethylene Glycol, with two –OH groups was reported by S.M. Puranik et. al.\textsuperscript{45}. The binary mixtures of biological samples such as Methanol-Algae\textsuperscript{46}, Honey-Water\textsuperscript{47}, Glucose-Water\textsuperscript{48}, Glycine and Valine-Water\textsuperscript{49} were studied by many research workers. Pure biological samples such as Albumin and Yolk of avian egg\textsuperscript{50} and mammalian milk\textsuperscript{51} were studied by Lokhande et. al. using TDR technique. The dielectric relaxation study of electrolyte Ca (NO\textsubscript{3})\textsubscript{2}4H\textsubscript{2}O in aqueous solution of Urea was reported by S.C. Mehrotra et.al.\textsuperscript{52}. Many other research workers\textsuperscript{53-58} in various fields carried out structural dynamics in different type of pure liquids and binary mixtures by using different experimental techniques.

2.8 INTRODUCTION TO PROBLEM

The Ayurvedic medicines are becoming popular worldwide. The scientific interactions of these with the human body are important in medical applications. Dielectric spectroscopy is an important tool to get information about structural changes and molecular interactions through dielectric relaxation data. In the present work interaction of –NH- amino, >C=O carbonyl, -OH hydroxyl, -CN cyanide and –COOH carboxyl groups, which are most common groups in ASAVA of Ayurvedic medicines, with ethanol at 10\textdegree{}C, 20\textdegree{}C, 30\textdegree{}C and 40\textdegree{}C is studied. No work has been reported on these systems using TDR technique. The systems studied in the present work are listed below-

1. Arvindasava + Ethanol
2. Karpooarsava + Ethanol
3. Chandanasava + Ethanol
4. Chavikasava + Ethanol
5. Drakshasava + Ethanol
6. Kanakasava + Ethanol
7. Panchasava + Ethanol
8. Lodhrasava + Ethanol
9. Lohasava + Ethanol
10. Pippalyasava + Ethanol
11. Punarnavasava + Ethanol
12. Ushirasava + Ethanol

The systems presented in this thesis are studied using TDR method. All above systems are studied by preparing 11 concentrations by volume fraction ‘X’ of solute with 0 ≤ X ≤ 1 and two pure liquids. Temperature dependent variations in dielectric and thermodynamic parameters for all systems are reported.
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