Chapter I

Introduction and objective of present thesis
Chapter I

**Introduction and objective of thesis**

1.1 Introduction

1.1.1 Dielectric fundamentals

The measurement of dielectric properties of several agriculture, environmental, and food processes is need for the society. Microwave measurements and dielectric properties of materials are finding increasing applications, as new electro-technology is adapted for the use in the agriculture and food processing industries. The interest in dielectric properties of materials has historically been associated with the design of electrical equipment, where various dielectrics are used for insulating conductor and other components of electrical equipment. The measurement of dielectric properties is not an end onto itself. Rather, these properties are intermediary vehicle for understanding, explaining, and empirically rating certain physical-chemical properties of materials.

If we apply potential difference across piece of material, some or no electric current flows through it. If the material piece contains free electron as in case of copper they move one end to another end and current generated in piece. On the other hand if the material piece contains no free electrons as in case of ebonite no electric current at result. Such material producing no current on application of potential difference is known as insulators. In an insulator the electrons are tightly bound to the atoms, therefore there are no free electrons or very less. In spite of non-conducting nature of insulators they have an important behavior in presence of electric field. In the presence of electric field the insulator
piece develops a dipole property. The insulators with such property are called as dielectrics.

When two charges ‘+q’ and ‘−q’ are separated by distance ‘d’, then a dipole is formed and its dipole moment is ‘qd’. A piece of materials, dielectric does not posses dipole moment as a whole under normal condition but gets the dipole moment when subjected to electric field. This may be the result of generation of new dipoles inside the piece or alignment of already existing dipoles in the piece due to the application of electric field. In this process the piece of dielectric develops net charge on two ends of piece. The process of development of net charges on the two ends of piece and acquiring dipole moment to the piece is known as polarization. The extent of polarization is measured by dipole moment per unit volume.

The dielectrics are classified as polar and non-polar, depending on the separation existence of positive charge center from its negative charge center in molecule. Non-polar dielectric consists of molecules with charge distribution such that their effective centers of positive and negative charge distributions coincide. Thus dipole moment of non-polar dielectric material have center of positive and negative charge distribution in molecule separated by distance and form a molecular dipole even in absence of electric field. But since positive and negative charges are equal, the molecule is electrically neutral. The magnitude of molecular dipole moment depends upon size and symmetry of molecule [1].

Dielectric study is the study of different dielectric properties and dependence of these properties on the composition and structure of substance on various external factors like temperature, humidity, intensity and frequency of change of an electric field.
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The most common dielectric parameters are the dielectric permittivity, dielectric loss and relaxation time. The dielectric permittivity is defined as the ratio of the capacity of condenser with given substance as dielectric to the capacity of the same condenser with a vacuum as dielectric. The dielectric is a function of temperature, frequency and it is written as complex quantity known as complex permittivity.

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

Where ($\varepsilon'$) is dielectric permittivity and is called as real part, ($\varepsilon''$) is dielectric loss and is called as an imaginary factor.

Another important dielectric parameter is relaxation time ($\tau$), which is essentially a measure of the time; the dipole would take to reach a random distribution on removal of the electric field. In a system, dipoles are oriented according to thermal distribution. An external field makes the thermal distribution disturbed and the dipoles are oriented in the direction of field [2].

The time required to reorient the dipoles after removal of electric field is called as relaxation time. The other dielectric parameters are excess permittivity ($\varepsilon^E$), excess inverse relaxation time ($1/\tau^E$), Kirkwood correlation factor ($g^f$ and $g^{ef}$), Bj coefficient and Thermodynamic parameters {$\Delta H$ and $\Delta S$}.

1.1.2 Importance’s of dielectric studies

The dielectric study of materials provides vital information about dielectric parameters and molecular interaction, which are of the direct technological importance. The knowledge of dielectric properties of materials and their frequency and temperature dependence is of great importance in various areas in
science and engineering in both basic and applied research. Dielectric properties obtain can be related to a physical parameter of interest. It has been demonstrated that properties such as moisture control, bacterial content, mechanical stress and other seemingly unrelated parameters are related to the dielectric properties or permittivity of the material.

Accurate measurement of these properties can be provides scientists and engineers with valuable information that allows them to properly incorporate the material into its intended applications or to monitor a process for improved quality control. The permittivity is the fundamental property of the material and is independent of the measurement technique.

The interpretation of dielectric behavior of a material in terms of its molecular structure is a scientific objective. The dielectric properties are essential and useful in a vast area of physical and biological sciences, engineering technologies. Applications of dielectric studies are Agriculture, Moisture measurement, Medicine, and Electrochemical super-capacitors, which are discussed below.

**Agriculture**

There are certain advancement in agricultural technology depends upon the availability of data on the dielectric behavior of agricultural products. For examples, data on frequency dependence of the dielectric properties of grain and insects were needed for determination of the optimum frequency range for selective dielectric heating of insects for the control of stored grain insects with radio frequency energy.
Other applications that depend upon the dielectric properties of grain and seeds that include RF treatments of hard seeds to increase germination and electrical measurement of moisture content in grain.

The dielectric studies are useful for agriculture; it is found that the dielectric permittivity increases with increasing moisture contents in the seeds and the dielectric permittivity decreases with increasing frequency. At high moisture level and low frequency range, the magnitudes of variation in dielectric permittivity were large. This variation is used to get an idea of the moisture contents in seeds.

**Moisture measurement**

Accurate measurement of moisture content is of importance in many applications, including agricultural and the food processing industries. Because of the high relative permittivity of water, the dielectric properties of moist material are strongly dependant on their moisture content, these method rely on calibration curve relating relative permittivity to moisture content, which may be obtained by measuring a range of samples with known moisture level.

**Medicine**

Investigation of the dielectric properties of biological substances and their frequency and temperature dependence give very valuable information about the state of water (free or bound), molecular structure, and hydration processes that are for primary importance in biochemistry and biophysics.

The interest of microwaves increased due to biological effects. Exposure to microwaves results in thermal stresses both deeps inside the body and also on the surface. Excessive exposure may cause damage but controlled exposure may results in therapy and human comfort. Controlled dose of microwaves can be
made useful for medical diagnosis, therapy and human comfort. Physical therapy of microwaves has been found effective in curing inflammation, piles and injury. Microwaves treatment of cancer has also been studied. Human comfort and physical health depend upon the energy exchange between man and surrounding. Normally heat is generated in the human body by metabolism in the body. Incident microwave energy can help the heat generation metabolism and keep human being at comfort even at low temperature.

**Electrochemical super-capacitors**

Recent advances in the electro-chemical capacitors [3] have resulted in new type of capacitors known as ‘super-capacitors’ or ‘ultra-capacitors’. These capacitors having capacitance (energy capable of being stored) of several hundred farads.

When a metal is brought in contact with solid or liquid ionic conductor, a charge accumulation is achieved electro-statically 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.

### 1.1.3 Dielectric techniques

There are two basic techniques of dielectric study of solids and liquids, these are

1. **Time domain technique**
2. **Frequency domain technique**
1.1.3 a Time domain technique

Time domain technique (TDS) is a technique of observing time dependant response of a system after the application of an electromagnetic field and finding the transfer function of the system when the input signal and the transient response, both as a function of time are known. The frequency response of the system is the ratio of Fourier transform of the transient response and the input signal. This method was restricted to low frequency dielectric response. However to obtain information in the microwave region, a fast rise time pulse (Pico second) with an equally fast detection system is required. A time domain system with a frequency response of 12.4GHz was introduced by Hewlett-Packard Co. U.S.A. in the mid 1960’s the system was initially used mainly for locating faults in the wide band transmission system such a coaxial lines, later on it had been modified to minimize errors in the measurements and to increase the frequency range in the dielectric studies [4]. Time domain technique in principle allows for the large range of frequencies to be covered without any change in the experimental set-up. At present time domain technique method has potential usefulness for broadband measurement of dielectric behaviors.

Reflection method and transmission method are two methods for measurements in the time domain spectroscopy technique. Time domain reflectometry technique is a term of observing the time dependant electromagnetic field. For system with linear response characteristics, the two approaches are capable in principle of giving the same information differently expressed, with the relation between the two forms, a Laplace transforms and it’s inverse. An attractive feature of time domain technique measurement is that single record can give information developed in the last few years for generating and observing
rapidly changing waveform, notably tunnel diode pulse generator and sampling oscilloscope, now permits measurements ranging from a time resolution of a Pico second to times of several nano seconds or larger coverage of the corresponding frequency range from 10 MHz to 20 GHz. with complex instrumentation and data processing. As results, time domain measurements are an attractive for the study of system that has time dependant behavior of interest for this range.

In this thesis, the TDR technique is used to determine dielectric parameters of systems over wide frequency range, from 10 MHz to 20 GHz. Dielectric permittivity, Relaxation time, Excess parameters are studied for each system.

1.1.3 b Frequency domain technique

Frequency domain technique is useful for the study of dielectric parameters like dielectric permittivity, dielectric loss and tanδ. Under frequency domain reflectometry technique there are number of experimental methods. At the frequencies below 1GHz, commercially available measuring bridges and vector voltage meters are useful to determine the input impedance or transmission coefficient of specimen cell. At frequencies between 0.1 to 600 GHz., a traveling wave transmitted through the sample is probed interferometrically in the case of high loss liquids. At lower loss, standing wave patterns are frequently analyzed. In the frequency range 10 GHz ≤ f ≤ 100 GHz, however, due to unavoidable use of narrow band wave-guide devices, measurements are expensive and lengthy if the observations have to cover a large part of decade. Still time consuming, are closed resonator techniques at microwaves frequencies. In this method a cavity or part of it, is filled with the liquid and resulting shift in the resonant frequency and
change of quality factor are observed. Due to multiple reflections at the sample surface, the electromagnetic cavity field is extremely sensitive to the dielectric properties of the liquid. Cavity resonator methods are capable of precise measurements on the liquid with very low loss. These methods are also used if the volume of the sample available is small. Free space techniques, like quasi-optical interferometers and open reflectors arrangement are also used in dielectric studies of liquids having low loss. These methods avoid conduction loss due to wavelength or resonator walls. In most open system techniques, pollution of sample during measurement is a severe problem. Atmospheric pressure for example, may strongly affect the dielectric low loss liquids.

At microwave frequencies 0.1 GHz to 100 GHz, a traveling wave method is widely used in measurement of lossy liquids. Transmission measurement techniques using microwave bridges have also been established for studies of small dielectric loss. Another convenient method of measuring the dielectric parameters of liquids consists in probing a standing electromagnetic wave either within the test liquid or in front of it. Recent improvements like sampling of standing wave pattern at regular intervals and automated data processing essentially improved the experimental sensitivity and accuracy. For that reason, precise data on large variety of liquids can now be obtained by standing waves observations. With many closed resonator techniques designed for studies on lossy liquids at microwave frequencies. A thin glass capillary filled with the liquids under test is concentrically inserted in a circular cylindrical cavity. An account of frequency domain measurement of reflection and transmission at microwave frequency with circuit arrangement is given of Pandharipande V M [5]
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Frequency domain research laboratory of Dept. of Physics, Dr. Babasaheb Ambedkar Marathwada University group [6] has used many band setups to measure dielectric parameters. In this thesis the dielectric properties of amide group and glycol group has been reported by using X-band for four different frequencies i.e. 9,10,11,12 GHz and at room temperature. In this method the position of shorting plunger inside the cell with liquid is moved up at regular intervals and each time the standing wave power is recorded. This power profile of the standing wave pattern consist of a set of 100 equally spaced experimental data points which were used for least square fit to determine values of propagation permittivity in the liquid. The values of dielectric permittivity and dielectric loss can be obtained from propagation constant.
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1.1.4 Physical constant of formamide (FMD), n-methyl formamide (NMF), nn-dimethyl formamide (DMF), ethylene glycol (ELG), propylene glycol (PLG) and butylene glycol (BLG)

Following systems were studied in present work listed below;

Using TDR
1) FMD+PLG
2) FMD+BLG
3) NMF+PLG
4) NMF+BLG
5) DMF+PLG
6) DMF+BLG

Using FDR
1) FMD+ELG
2) FMD+PLG
3) DMF+ELG
4) DMF+PLG

Table 1.1 Physical constant for compounds

<table>
<thead>
<tr>
<th>Sr. no.</th>
<th>Name</th>
<th>Molecular Formula</th>
<th>M.W.</th>
<th>M.P. in °C</th>
<th>B.P. in °C</th>
<th>Density gm/cc</th>
<th>Dipole Moment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Formamide</td>
<td>HCONH₂</td>
<td>45.04</td>
<td>215.0</td>
<td>210.5</td>
<td>1.1292</td>
<td>3.4</td>
</tr>
<tr>
<td>2</td>
<td>N-Methyl Formamide</td>
<td>HCONHCH₃</td>
<td>59.07</td>
<td>178.0</td>
<td>182.0</td>
<td>0.9988</td>
<td>3.8</td>
</tr>
<tr>
<td>3</td>
<td>NN-Dimethyl Formamide</td>
<td>(CH₃)₂NCHO</td>
<td>73.10</td>
<td>92.60</td>
<td>153.0</td>
<td>0.9445</td>
<td>3.8</td>
</tr>
<tr>
<td>4</td>
<td>Ethylene glycol</td>
<td>HOCH₂CH₂OH</td>
<td>62.07</td>
<td>181.4</td>
<td>193.7</td>
<td>1.1097</td>
<td>2.2</td>
</tr>
<tr>
<td>5</td>
<td>Propylene glycol</td>
<td>HOCH₂CH₂CH₂OH</td>
<td>76.10</td>
<td>79.00</td>
<td>105.0</td>
<td>1.0530</td>
<td>2.4</td>
</tr>
<tr>
<td>6</td>
<td>Butylene glycol</td>
<td>HOCH₂CH₂CH₂OH</td>
<td>90.12</td>
<td>15.50</td>
<td>231.0</td>
<td>0.9655</td>
<td>2.5</td>
</tr>
</tbody>
</table>
1.1.5 Molecular structure of formamide, n-methyl formamide, nn-dimethyl formamide, ethylene glycol, propylene glycol and butylene glycol

Formamide (FMD)

O

\[ \text{H -- C -- NH}_2 \]

N-Methyl Formamide (NMF)

O

\[ \text{H -- C -- NHCH}_3 \]

NN-Dimethyl Formamide (DMF)

O

\[ \text{H -- C -- N(CH}_3)_2 \]

Ethylene Glycol (ELG)

H \quad H

\[ \text{OH -- C -- OH} \]

H \quad H

Propylene Glycol (PLG)

H \quad H \quad H

\[ \text{OH -- C -- C -- OH} \]

H \quad H \quad H

Butylene Glycol (BLG)

H \quad H \quad H \quad H

\[ \text{OH -- C -- C -- C -- OH} \]

H \quad H \quad H \quad H
1.2 Objective of the present thesis

The main objective of this thesis is to study the interaction of amide group and with the dihydroxyl group liquids. These liquids are useful for medical research and in a vast area of physical and biological sciences engineering technology.

Recently, dielectric relaxation behavior of mixtures of polar molecules under varying conditions of complexation, temperature and environment factors has evoked considerable interest. Based on the results, models of relaxation processes in liquid mixtures have been formulated. The study of association of two polar molecules due to hydrogen bonding from the dielectric location measurements at microwave frequencies is scarce. Pajdowska and Sobezyk [13] have studied the complex dielectric constant $\varepsilon^*(\omega)$ over the dispersion frequency range for mixtures of propionic acid tri-n-butyl amine of varying compositions. Purcell and Smyth [14] were the first to detect solute solvent interactions through measurements of relaxation time. The dielectric relaxation data for N, N-disubstituted amides showed that these liquids in dilute non-polar solvents obey the simple Debye equation [15]. The hydrogen bonding ability of these amides with phenols and alcohols is well known. Sharma and Sharma [16] studied the dielectric relaxation behavior of DMF + methanol in benzene solution. They showed that the dielectric relaxation time is maximum at equimolar concentration.

The permittivity of material is one of the factors that determine how the material interacts with an electromagnetic field. It is a complex quantity consisting of real part and an imaginary part. The knowledge of dielectric properties of materials and their frequency and temperatures dependence is of great importance in various areas of science and engineering in both basic and applied research. Dielectric properties often can be related to a physical parameter
of interest. It has been demonstrated than properties such as moisture contents, fruit ripeness, bacterial content, mechanical stress and other seemingly unrelated parameters are related to the dielectric properties or permittivity of the materials. Accurate measurements of these properties can provide scientists and engineers with valuable information that allows them to properly incorporate the materials into its intended application or to monitor a process for improved quality control. The permittivity is a fundamental property of the materials and is independent of the measurements technique.

The studies of dielectric properties of liquid samples consist of measurement of dielectric permittivity, dielectric loss, and relaxation time and excess parameters. Using TDR and FDR techniques carries out these measurements.

**Time domain reflectometry technique**

The experimental setup of time domain technique, which are shown in chapter third, which is useful for the measurement of dielectric properties (dielectric permittivity, relaxation time and excess parameters). Frequency range of spectrum is 10MHz to 10GHz [7]. In this thesis the measurement of dielectric properties of Form amide, N-Methyl formamide, NN-Dimethyl formamide, Propylene glycol and Butylene glycol liquids are carried out at 20°C, 30°C and 40°C temperature due to their medical applications and microwave remote sensing. All the work carried out for this thesis is done under time domain research lab, Department of Physics, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad.
Frequency domain reflectometry technique

The experimental set up of frequency domain technique, which is given in Chapter five. The experimental setup of microwave bench is routinely used for the measurement of dielectric properties [8] (Dielectric permittivity, dielectric loss and tan δ). In this experimental work microwave X-band set up having frequency range 8.2 to 12.4 GHz is used. Dielectric parameters carried over 9,10,11,12 GHz. In this thesis systematic study has been done for four samples with increasing concentrations in mole per liter and observed the change in dielectric permittivity and dielectric loss. Dielectric loss is parameters, which describes the motion of the electric charge like conduction phenomena.

Certain dielectrics are found to display conduction which arise not only from the effect of polarization on the displacement current; but actual charge transport, i.e. ionic conduction in electrolytes. Such conduction would normally be described by volume conductivity $\sigma$ (ohm$^{-1}$cm$^{-1}$) and the effect of it would be to add an additional term to the dielectric loss, which is inversely proportional to the frequency ($\omega$) [9,10,11].

Depending upon the type of solutes and also on the concentrations of the solvents, various relaxation processes are observed, even in comparatively simple binary mixture. Due to the relaxation phenomena in biological tissue, it is almost impossible to look for the existence of the bound water by measurement on such complex systems. More reliable information can be derived from the study of simple binary solutions. There seems to be two situations.

The dielectric property of Formamide, NN-Dimethyl formamide, Ethylene glycol and Propylene glycol liquids has been reported for four different
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frequencies. All the work carried out for this thesis is done under frequency domain research lab, Department of Physics, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad.
References


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