Chapter 1

Introduction
1. Introduction

Microwaves are the electromagnetic waves roughly in the frequency range of 1 GHz to 300 GHz. The corresponding wavelength range is 30 cm to 0.1 cm [1]. The developments in electronics, computers made possible to study interaction of electromagnetic waves with aqueous, non-aqueous materials by applying dielectric theory [2]. According to dielectric spectroscopy, the dielectric properties of a material are sensitive to electromagnetic waves.

The dielectric properties are usually expressed in terms of complex permittivity as a function of frequency:

\[ \varepsilon^*(\omega) = \varepsilon'(\omega) - j\varepsilon''(\omega) \]  \hspace{1cm} (1.1)

where the real part (\(\varepsilon'\)) measures the dielectric permittivity, the imaginary part (\(\varepsilon''\)) measures the dielectric loss or absorption, \(j\) is an imaginary number equal to \(\sqrt{-1}\).

The dielectric permittivity of a material is related with its ability to interact with electromagnetic waves. Debye established that the dielectric dispersion of the real permittivity (\(\varepsilon'\)) and the dielectric absorption (\(\varepsilon''\)) occur in the dipolar liquids and solids due to dipole relaxation arising from reorientational motion of molecular dipoles. The dielectric properties of a material depends upon its molecular structure and changes with it.

The characterization of materials properties includes the measurement of complex permittivity as a function of frequency and it is an important field in microwave electronics. The study of material properties at microwave frequencies plays very important role in the various fields of sciences and engineering. It is also helpful for agriculture, food engineering, medical treatments and bioengineering [3].
Microwave dielectric spectroscopy is suitable even for opaque and white materials as it is not an optical technique.

Dielectric relaxation spectroscopy is a proven tool for the investigation of molecular dynamics, co-operative processes and intermolecular interactions and relaxation phenomena of hydrogen bonded systems [4-16]. The time domain reflectometry (TDR) technique has been widely used to obtain dielectric spectra to measure dielectric properties of hydrogen bonded systems [17-25]. This technique covers a broad range of frequencies in a single measurement. For time domain reflectometry, a fast rising repetitive step pulse generated by step generator is propagated through a coaxial line which is terminated by the sample under study (Fig. 1.1). A reflected pulse travels through the same coaxial line. The shape of the reflected pulse remains unchanged as long as there is no mismatch in the impedance of coaxial line. A sampling oscilloscope monitors the changes in the reflected step pulses.

![Fig.1.1. Block diagram of TDR [26]](image-url)
Sugar alcohols are hydrogen bonded sweeteners which occur in nature or can be derived from corresponding saccharides by catalytic hydrogenation. Hydrogenation is a process in which carbonyl group is reduced to –OH group, also called as hydroxyl group. Sugar alcohols are commonly referred as polyols or polyhydric alcohols since their molecules contain more than one –OH groups. A sugar alcohol molecule is composed of linear backbone chain of carbon atoms and an –OH group is attached to each carbon atom and the number of carbon atoms (N_c) is equal to the number of –OH groups (N_{OH}). The general formula of sugar alcohols is C_{n}H_{n+2}O_{2}. Sugar alcohols are sweet in taste but they do not raise that much blood sugar level as sucrose dose. Also, they don’t develop dental decay. Hence, sugar alcohols are generally used in food, confectionary, and pharmaceutical products.

The dielectric relaxations in various polyhydric alcohols such as Glycerol, Threitol, Xylitol and Sorbitol have been studied extensively, mostly in the super cooled region, using dielectric spectroscopy [4-10,12-16].

The sugar alcohols used in the present study are Erythritol (C_{4}H_{10}O_{4}), Xylitol (C_{5}H_{12}O_{5}) and Mannitol (C_{6}H_{14}O_{6}) which are generally used in various food and pharmaceutical products. The number of –OH groups in Erythritol, Xylitol, Mannitol are 4, 5 and 6 respectively.

Water (H_{2}O) is a good organic, polar and hydrogen bonded solvent. Fig. 1.2 shows structure of water molecule. It has hydrogen bond donor and acceptor site. The oxygen atom is more electronegative than hydrogen atom (Fig.1.3) hence a water molecule acts as an electric dipole and has a permanent dipole moment.
When an electric field is applied to water, polarization of the water molecules takes place by the reorientation of the dipoles. Water is essential for all living things. It is involved in many manufacturing processes which are used in chemical, medical, pharmaceutical engineering etc. Dielectric spectroscopy is non-destructive technique which can be used to measure water contents in solid and liquid materials [10,11].

When a sugar alcohol is added in water, the existing hydrogen bonded structure of the sugar alcohol and water gets broken and new hydrogen bonds are formed between the sugar alcohol and water molecules and the intermolecular association takes place.

Dimethyl Sulfoxide (DMSO) with structural formula (CH$_3$)$_2$SO is a highly polar, aprotic solvent i.e. no hydrogen bonding between pure DMSO molecules.
exists. However, it can act as a hydrogen bond acceptor. DMSO is incorporated into a number of products for healthcare and drug delivery applications due to its ability to act as a carrier for transferring other drugs through the cell membrane [27, 28]. This property creates an interest to study its structural behaviour with other pharmaceutically useful systems such as polyhydric sugar alcohols.

The main objectives of the present study are:

1. To measure the complex permittivity spectra of the aqueous and non-aqueous (in DMSO) binary mixtures of sugar alcohols (Erythritol, Xylitol and Mannitol) at different temperatures using TDR.

2. To evaluate dielectric parameters such as dielectric permittivity, relaxation time and relaxation time distribution parameters from the complex permittivity spectra.

3. To compute Kirkwood correlation factor and thermodynamic parameter such as enthalpy from the dielectric parameters.

4. To study the intermolecular interactions in the form of hydrogen bonding within the aqueous and non-aqueous binary mixtures of the sugar alcohols.

In the present study, the measurements have been carried out in the frequency range of 10 MHz to 30 GHz by using the Tektronix DSA8200 Digital Serial Analyzer sampling mainframe along with the sampling module Tektronix 80E08. A pulse of 18 ps rise time has been propagated through the open ended coaxial line which is terminated by the sample under study. The reflected pulses of 20 ps rise time without sample $R_1(t)$ and with sample $R_X(t)$ have been recorded.
There are total seven chapters in the present thesis. They are as below:

**First chapter** presents general introduction on microwave dielectric dispersion, sugar alcohols, water molecule, DMSO and hydrogen bonding.

**Second chapter** includes different dielectric theories such as Debye relaxation theory, Cole-Cole relaxation theory, Cole-Davidson relaxation theory, Havriliak-Negami relaxation theory, Onsager theory, Kirkwood dielectric theory, thermodynamic parameters etc.

**Third chapter** deals with the methodology adopted for the dielectric measurements. Basic principles of Time Domain Reflectometry is discussed. The measurement of complex permittivity spectra and data analysis is also discussed.

**Fourth chapter** contains Thermodynamic and dielectric relaxation study of Erythritol-Water binary mixture using time domain reflectometry. The dielectric permittivity measurements were done in the temperature range of 5 °C to 25 °C for different weight fractions of erythritol in water from 10 MHz to 30 GHz. The dielectric parameters have been evaluated. The interaction between erythritol and water molecules is discussed using the Kirkwood correlation factor and Thermodynamic parameters.

**In Fifth chapter** Dielectric Relaxation and Hydrogen Bonding Interaction in Xylitol-Water Mixtures Using Time Domain Reflectometry is discussed. The measurement of complex dielectric permittivity has been carried out at temperatures from 0 °C to 25 °C for different weight fractions of xylitol \((0 < W_X \leq 0.7)\) in water. The dielectric relaxation behaviour of the binary mixtures is described by Cole-Davidson model. The dielectric parameters such as static dielectric constant and
relaxation time for the mixtures have been evaluated. The molecular interaction is discussed using the Kirkwood correlation factor ($g^{\text{eff}}$) and thermodynamic parameter.

**Sixth chapter** deals with Dielectric dispersion and hydrogen bonding interactions study of aqueous D-mannitol using time domain reflectometry. The complex dielectric permittivity have been measured at different temperatures for different weight fractions of D-mannitol in water. The dielectric relaxation behaviour of these mixtures is explained using Cole-Davidson model. Kirkwood correlation factor and Thermodynamic parameters are used to explain the molecular interaction between D-mannitol and water molecules.

**Seventh chapter** contains Microwave dielectric relaxation study of polyhydric sugar alcohols in non aqueous solutions using TDR technique. The dielectric measurements for the binary mixtures of Erythritol-DMSO, Xylitol-DMSO and Mannitol-DMSO have been carried out in the frequency range of 10 MHz to 30 MHz using TDR technique at different temperatures. The dielectric parameters such as static dielectric constant ($\varepsilon_0$), relaxation time (\(\tau\)), asymmetric distribution of relaxation time (\(\beta\)) have been evaluated in each case. The molecular interaction is studied using the Kirkwood correlation factor and thermodynamic parameters. Also, the effect of number of –OH groups in the sugar alcohol molecules on the different parameters is discussed.

**Eighth chapter** includes the Summary & Conclusions.