3.1 Introduction

The dielectric relaxation spectroscopy has become a helpful tool for extracting significant information related to the structure, dynamics and to the quality-status of various materials. In this regard, relevant scientific efforts have been mainly devoted to the dielectric spectroscopy of liquids [1–5], since numerous industrial applications require an on-line continuous monitoring of the processing quality status.

The dielectric relaxation time of glycol solutions ranges from picoseconds to nanoseconds [6]. This corresponds to the microwave and radio frequency (RF) region (0.001 ≤ ν/GHz ≤ 100) of the electromagnetic spectrum. In such cases neither the conventional methods like the a. c. bridge technique nor lumped circuits, (few hundred MHz) nor the infrared optics covering high frequencies be used [7]. Therefore, for aqueous solutions of biomaterials special technique or combinations of techniques are required. These methods form basically a reflection/transmission type spectroscopy and provide frequency coverage up to several GHz. The gain of that measurement can be carried out for samples which have high and low dielectric loss [8-10]. The present work deals with methodology adopted for the study including principle of time domain reflectometry, establishment and development of TDR, and data analysis is used for the purpose of high frequency permittivity of binary mixture, bio-molecules and polymers.

Dielectric relaxation studies involve measurement of dielectric permittivity and dielectric loss at microwave frequencies. The response of a dielectric material to a microwave frequency is expressed by its complex permittivity $\varepsilon^*(\omega) = \varepsilon'(\omega) - j\varepsilon''(\omega)$ which determines the storage and dissipation of electric energy [11, 12]. The measurement of complex permittivity of a liquid involves measurement of permittivity ($\varepsilon'$) and dielectric loss ($\varepsilon''$) of the liquid sample at a single frequency. Thus the selection of a method for measurement of complex permittivity...
depends mainly on the frequency. The schematic chart of frequency dependent dielectric techniques is shown in Fig. 3.1. Many experimental results relating to the dielectric behavior of liquid have been published in past few years.

![Schematic chart of experimental techniques](image)

**Fig. 3.1** Schematic chart of experimental techniques.

### 3.2 Basic Principle of TDR

Time domain reflectometry (TDR) measurements are based on the generation of a step-like electrical signal propagating through a coaxial cable that connects the TDR-generator with the probe and, subsequently, on the analysis of the deriving reflected signal [13]. The presence of impedance mismatching (e.g. due to sample under test), creates a reflected signal and the related reflection coefficient is associated to the dielectric properties of the samples under test. TDR-based techniques can measure at the same time both the level and the static dielectric
constant of different liquids. However, in order to improve the measurement accuracy, the evaluation of frequency dependent dielectric permittivity of liquids is a key issue.

TDR dielectric measurement system consists of step generator which produces fast rising pulse of the order of picoseconds. A train of suitable fast rising pulses is applied to a transmission line, usually a co-axial line with characteristic impedance 50Ω. A co-axial line is connected to sampling device i.e. sample holder. The schematic block diagram of the experimental setup of TDR [14-15] is shown in Fig.3.2.

![Block Diagram of Time Domain Reflectometry](image-url)
When this line is terminated to different load conditions the following waveform is observed as shown in fig

i) \( Z = 50\Omega \) means line is terminated by characteristic impedance (matched load), no reflection of the transmitted wave.

ii) \( Z = \infty \) means line is terminated by infinite impedance (Open load), no current after sample section.

iii) \( Z = 0 \) means line terminated by zero impedance (Short circuited), no potential difference at the terminal end. Fig. 3.3 shows circuit diagram of a) matched load termination, b) Open circuit termination and c) Short circuit termination.

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**Fig.3.3** Circuit diagram of load termination.
Fig. 3.4 TDR Waveforms - Open, Short and 50Ω termination. The short circuit is measured as $-1 \rho$ (rho) and the open circuit (infinite rho) results in a $\rho$ of +1.

3.3 DSA 8200 Digital Serial Analyzer Sampling Oscilloscope

It is a modular high performance mainframe that contains digitizer, time base and display circuit. The Tektronix DSA8200 is the state-of-art Sampling Oscilloscope for communication signal analysis, TDR/TDT/Serial data network Analysis, acquisition and measurement of repetitive ultra fast signals with 80E08 TDR sampling module having user selectable bandwidth, CDROM and USB port. The DSA8200 is the industry’s highest performance fully integrated time domain reflectometry (TDR) measurement system. Offering true differential TDR measurements up to 50 GHz bandwidth with 15 ps reflected rise time and 12 ps incident rise time. The DSA8200 Sampling oscilloscope accommodating up to four dual channel true differential TDR modules for fast accurate multi-lane impedance characterization. The MS-Window XP operating system, advanced connectivity to third party software and necessary ports is provided with the oscilloscope [16-17].
3.4 Plug-in 80E08 TDR/Sampling Module

The 80E08 TDR/Sampling module provides two accurate oscilloscope measurement channels (CH1 & CH2) with user selectable bandwidth of 20 GHz and 30 GHz. The high bandwidth mode gives high fidelity display and measurement of high-speed waveforms. It is capable to performing both single ended TDR/TDT measurements. The TDR rate can be selected automatically and manually for repetition rate of TDR step.

In single ended TDR measurement, a fast rising step voltage pulse of 200 mV with 18 ps incident and 20 ps reflected time. In differential TDR measurement a positive going step is launched on channel and an effective negative going step is launched on channel 2. The response controls are provided which shows the single ended or differential mode response of a TDR system under test. The actual photograph of experimental set up is shown in Fig. 3.5., it consists of Tektronix DSA8200 Sampling Oscilloscope, TDR module 80E08, a transmission line and sample cell.
Fig. 3.5 TDR setup with Temperature controller system.
3.5 Sample Cell

The sample cell holds the liquid under study. The physical dimensions of the cell are very important, so one must be careful while designing the sample cell. The impedance of the cell should be matched with coaxial transmission line to which cell is attached. If there is impedance mismatch, unwanted reflections may disturb the wave in this manner some errors in the measurements. The proper design of cell includes the inner conductor and outer conductor diameters. The sample length must be enough to avoid unwanted reflections. In total reflection method, the sample length must be long enough to produce an ample difference signal but short enough to keep less complication of resonance effects at frequencies above the range of significance. The semi rigid co-axial cable of flat end, copper, from Huber + Suhner Electronics Pvt. Ltd. was used as a sample cell. The flat end sample cell is touched on the sample to evaluate the dielectric relaxation without any damages of the sample shown in Fig.3.7 (a, b). This kind of cell is widely use to investigate the dielectric properties of biological materials and tissues [18-21], petroleum products [22], constructive materials [22], and numerous other nondestructive permeability and permittivity measurements.

![Coaxial cable with open ended Sample cell and End point of sample cell](image)

**Fig. 3.6** a) Coaxial cable with open ended Sample cell. b) End point of sample cell.
3.6 Choice of Time Window

The proper selection of time window is related to the frequency range of interest. The minimum frequency observable is given as,

\[ f_{\text{min}} = \frac{1}{\text{time window}}, \]  

and maximum frequency observable is

\[ f_{\text{max}} = \frac{N}{2} \times \text{time window}, \]

where \( N \) is the number of points used to sample and digitize the signal. The smaller time window causes loss of signal while larger time window includes unwanted reflections. Thus selection of proper time window is important to minimize these effects.

In the TDR technique, two pulses are measured, first the reflected pulse without sample and second reflected pulse with sample \( R_1(t) \) and \( R_X(t) \) respectively. These pulses averaged 100 times and digitized with 2000 points per waveform.

3.7 Data Analysis

The reflected pulses without \( R_1(t) \) and with \( R_X(t) \) sample, respectively as shown Fig.3.7. The pulses were subtracted \( p(t) = [R_1(t) - R_X(t)] \) and added \( q(t) = [R_1(t) + R_X(t)] \) by using software. The time domain data is converted into frequency domain data using Fourier transform, the distortion of the pulse upon the reflection can be understand by Fourier analysis. According to this analysis, pulse is considered as an infinite series of sine and cosine terms, each of which is a harmonic of the basic fundamental frequency of the pulse. Since each term of the series has a different frequency, each views a different reflection coefficient at the air-liquid interface, results in the distortion of the pulse shape. The objective of the TDR system is
to observe the shape and size of the input and output pulses from which reflection coefficient is obtained, which is the complex quantity and is the function of frequency. Fourier transform is obtained by a summation method using following equation [23]

\[ p(\omega) = T \sum_{n=0}^{N} \exp(-j\omega nT) p(nT) \] (3.11)

where \( T \) is the sampling interval or time difference between two adjacent points, \( \omega \) is the angular frequency and \( n \) the number of points. The Fourier transformation using summation methods have some limitations that for all the sampling intervals, the nature of pulse as shown in Fig. 3.8 a.

![Graph](image)

**Fig. 3.7** Reflected pulses without \( R_1(t) \) and with sample \( R_x(t) \) for pure water.
Fig. 3.8 a Sample pulse of $R_1(t) + R_x(t)$ for pure water.

Fig. 3.8 b Sample pulse of $R_1(t) - R_x(t)$ for pure water.
The pulse of q(t) as shown in Fig. 3.8 b is not known exactly. The q(t) rises monotonically to a long time limit. Therefore summation method of Fourier transformation cannot be used for q(t) curve. The Fourier transform of such type of curves can be obtained with the samulon method [24] as follows:

\[
q(\omega) = \frac{T}{1 - \exp(-j\omega T)} \left[ \sum_{n=0}^{N} (q(nT) - q((n-1)T)) \exp(-j\omega nT) \right] \quad (3.12)
\]

In our experiment n is 2000 points and (T) depends on time window and number of points per waveform (N). For example, if time window is 2ns then T is 1ps for 2000 points per waveform. Thus the time domain data is converted into the frequency domain data in the frequency range of 10 MHz to 30 GHz.

The frequency dependent data obtained from Fourier transform is further used to calculate frequency dependent complex reflection coefficient ρ*(ω) given by equation follows [25-27].

\[
\rho^*(\omega) = \frac{c}{j\omega d} \frac{p(\omega)}{q(\omega)} \quad (3.13)
\]

where c is the speed of light in mm/ps, ω is the angular frequency, d is an effective pin length, p(ω) and q(ω) are the Fourier transformations of p(t) and q(t) respectively. The complex reflection coefficient spectrum is called as ‘raw’ data, using this ‘raw’ data complex permittivity can be determined as follows.

From the transmission line theory, the basic equation for determining relative complex permittivity spectra ε* can be written as,
\[ \varepsilon^*(\omega) = \frac{c}{j\omega d} \frac{r_0 - r_x}{r_0 + r_x} Z \cot(Z) \]  

(3.14)

where \( Z = \frac{(\omega d/C)}{\varepsilon^*} \) and \( r_0 \) and \( r_x \) are the Fourier transform of the pulses from the cell without sample \( R_1(t) \) and with sample \( R_X(t) \), respectively. If we consider single reflection then \( Z \cot(Z) = 1 \) and above equation becomes,

\[ \varepsilon^*(\omega) = \frac{c}{j\omega d} \frac{r_0 - r_x}{r_0 + r_x} \]  

(3.15)

Eq.(3.15) indicates that the dielectric constants of unknown sample can be found if the time profile of the incidents \( r_0 \) and \( r_x \) pulses are recorded with in a frequency range determined by the time limits of \( r_0 \) and \( r_x \).

The above equation can be rearranged as,

\[ r_0 = \left[ \frac{\varepsilon^* + \frac{C}{j\omega d}}{\frac{C}{j\omega d} - \varepsilon^*} \right] r_x \]  

(3.16)

If the sample cell is without any liquid i.e. with air is considered the \( \varepsilon^* = 1 \) and we get,

\[ r_0 = \left[ 1 + \frac{C}{i\omega d} \right] r_i \]  

(3.17)

where \( r_i \) is reflected pulse for air with \( \varepsilon^* = 1 \). By using Eq. (3.17) and (3.18) the term \( r_0 \) can be eliminate as,

\[ \frac{r_i}{r_x} = \left[ \frac{\varepsilon^* + \frac{C}{i\omega d}}{\frac{C}{i\omega d} - \varepsilon^*} \right] \times \left[ \frac{\frac{C}{i\omega d} - 1}{1 + \frac{C}{i\omega d}} \right] \]  

(3.18)
The equation can be rearranged to get,

\[ \varepsilon^* - 1 = \frac{1 + \left(\frac{\omega d}{C}\right)^2 \rho^*}{1 - \left(\frac{\omega d}{C}\right)^2 \rho^*} \]  

(3.19)

or

\[ \varepsilon^* - 1 = \frac{(1 + A) \rho^*}{1 - B \rho^*} \]  

(3.20)

where \( A = B = \left(\frac{\omega d}{C}\right)^2 \)

Thus using Eq. (3.19) one can obtain the complex permittivity spectrum in desired frequency range.

The problem in TDR experiments arises from the fact that the characteristic impedance of the transmission line connecting the measuring plane of the cell is generally not uniform along the propagation axis. This fact introduces reflections of the travelling pulses superimposed on the reflection from the cell. In ideal case, \( A = B = \left(\frac{\omega d}{C}\right)^2 \) but under experimental conditions transmission line cannot be ideal i.e. \( A \neq B \neq \left(\frac{\omega d}{C}\right)^2 \). To minimize the effect of unwanted reflections, Cole et.al [28] has described bilinear calibration method in low frequency limit.

\[ \lim_{\omega \to 0} \rho^* = \varepsilon^* - 1 \]  

(3.21)

So, the permittivity at low frequency can be obtained directly by determining \( \rho^* \). Corrections in ‘raw’ data are necessary to get accurate values at high frequencies. The unwanted reflections also depend on pin length of the sample used. For different pin lengths the position of randomness of data shifts either to low frequency side or high frequency side in the spectrum.
The calibration process suggested by Cole et.al. involves experimental determination of A* and B* values for getting reliable ε* at higher frequencies. The experimental permittivity is obtained by

\[ \varepsilon^* - 1 = \frac{(1 + A^*) \rho^*}{1 - B^* \rho^*} \]  

where, \( A^* = A' - jA'' \) and \( B^* = B' - jB'' \). The frequency dependent values of A* and B* are determined by using two or more standard liquids. Using Eq. (3.22) for two standard liquids we get four linear equations which can be solved to obtain unknown the complex values \( A', A'', B' \) and \( B'' \).

It is also important to used proper calibrating liquids because the accuracy of the calculated permittivity depends on the choice of the calibrating liquids. To improve accuracy in ‘raw’ spectra of calibrating liquid should be closer to that of liquid under investigation. An example complex permittivity spectra with respect to frequency for aqueous solutions of polar liquids (water, alcohols, acetone, Dimethyleformamide (DMF), 1,4-dioxane and Glycerol), is shown in Fig. 3.9 (a, b, c, d, e, f).

This corrected data can be fitted using non linear least square fit method with suitable model to obtain the dielectric parameters such as static dielectric constant \( (\varepsilon_0) \), relaxation time \( (\tau) \) and high frequency permittivity \( (\varepsilon_\infty) \).
Fig. 3.9a Frequency dependence dielectric permittivity ($\varepsilon'$) and dielectric loss ($\varepsilon''$) for water at $25^\circ$C.

Fig. 3.9b Frequency dependence dielectric permittivity ($\varepsilon'$) and dielectric loss ($\varepsilon''$) for alcohols at $25^\circ$C.
**Fig. 3.9c** Complex permittivity spectra for acetone at 25°C.

**Fig. 3.9d** Complex permittivity spectra for Dimethylformamide at 25°C.
**Fig. 3.9e** Complex permittivity spectra for 1,4-Dioxane at 25°C.

**Fig. 3.9f** Complex permittivity spectra for Glycerol at 25°C.
The complex permittivity spectra were fitted to Havriliak-Negami equation using least square fit method [30].

\[
\varepsilon^*(\omega) = \varepsilon_\infty + \frac{(\varepsilon_0 - \varepsilon_\infty)}{[1 + (j\omega\tau)^{-\alpha}]} \beta
\]

where \(\varepsilon_0\) is the static dielectric constant, \(\varepsilon_\infty\) is the permittivity at high frequency, \(\tau\) is the relaxation time. \(\alpha\) and \(\beta\) are symmetric and asymmetric distribution parameters of relaxation times, respectively. The Havriliak-Negami equation includes three relaxation models as limiting forms,

i) If \(\alpha = 0\) and \(\beta = 1\) then single Debye relaxation.

ii) \(0 \leq \alpha \leq 1\) then it would be a Cole-Cole model of symmetric distribution of relaxation time and

iii) \(\alpha = 0\) and \(\beta\) varied such that \(0 \leq \beta \leq 1\), this behavior is identified as Cole-Davidson (CD) asymmetric distribution of relaxation time.
References


[16] Tektronix DSA8200 Sampling Oscilloscope user’s guide.

[17] 80E08 TDR Plug-in Modules user and programmer’s guide.


