CHAPTER V

DIELECTRICS
A REVIEW
5.1.1 A REVIEW:

The study of dielectrics of condensed matter is to understand its structure and also the molecular dynamics. The evaluation of these parameters, based on the properties of polarization, magnetization and conduction, is interpreted by the existing molecular theories. This approach connects both macroscopic and molecular behaviour of matter.

Under the varying external electric field, the motions of the particles of the dielectric material in characteristic times, build up an equilibrium polarization. When the effect of varying field continues, motions can have different polarizations, namely electronic and atomic polarizations concerned with the displacements of the electrons and the atoms, orientation and interfacial polarizations with respect to the permanent dipoles and moving charge carriers respectively of the dielectric material. Correspondingly, the properties of the dielectric materials at these polarizations are different from the equilibrium polarization. Hence, the total polarization is due to the sum of all the above said polarizations. The study of such different polarizations would be the study of displacements, orientations and distortion of the field of the molecules. For such study, the molecules need to be in either gaseous form or liquid state whereby the structures of molecules are obtained.

Under the effect of electric field, both gases and liquids and solids of condensed matter give rise to resonance
spectra consisting of electronic and vibrational frequencies greater than gigahertz\(10^{12}\ \text{Hz}\). The appearance of the spectral peaks is different in both cases. Peaks in condensed matter are slightly broadened not only due to the dispersion and absorption phenomena but also due to the electronic and atomic polarizations of the molecules in the condensed phase but not of individual molecules. Similarly, in the state of the condensed phase, rotational motions of dipolar molecules due to thermal energy associate themselves with orientational polarization. This gives rise to dielectric relaxation spectra. The characteristic times involved in relaxation spectra are normally greater than picoseconds\(10^{-12}\ \text{sec.}\). Hence, this results in a frequency-dependent polarization spectrum lying in the microwave, radio frequency regions. In this frequency range, conductivity may also contribute to the dielectric relaxation processes.

The analysis of the above spectra gives us the molecular parameters such as electric dipole moment \((\mu)\) and the dielectric relaxation time \((\tau)\) of any polar substance of interest. The former gives an idea of electronic structure and the molecular interactions whereas the latter is used for the construction of the molecular structure with the data obtainable by molecular and intra-molecular motions.

Perhaps Debye\(^{1-3}\) may be the first person to begin the study on the dielectric behaviour of the medium by introducing a complex dielectric constant \(\varepsilon^*\) through \(\tau\) the relaxation
time. This is related to the two macroscopic quantities namely $\varepsilon_s$ and $\varepsilon_\infty$ the static and optical permittivities respectively. The equation as given by Debye is as follows:

$$\varepsilon^* = \varepsilon_\infty + \left[ \frac{\varepsilon_s - \varepsilon_\infty}{1 + j\omega \tau} \right]$$

(5.1.1)

where, $\omega$ is the angular frequency of the applied electric field and the $\varepsilon_\infty$ corresponds to electric and atomic polarizations of the dielectric.

In the low frequency range, the deformation polarization contributes constant induced moments whereas $\varepsilon_s$ contributes fully to the orientation of the permanent dipole moments because orientational polarization gives only an average moment due to non-alignment in the field direction, the torque with applied field and randomising thermal agitation. The interfacial polarization due to heterogeneous media is negligible at very low frequencies.

Replacing the applied field by the Mosotti field in Debye’s theory and connecting molar complex permittivity $\rho^*$ to microscopic parameters such as $\alpha_e$ and $\alpha_\alpha$, the electronic and atomic polarizibilities respectively and $\mu$ and $\tau$ of the molecule, the equation takes the form

$$\rho^* = \frac{4}{3} \pi N \left[ \alpha_e + \alpha_\alpha + \left( \frac{\mu^2}{3\kappa T} \times \frac{1}{1 + j\omega \tau} \right) \right]$$

(5.1.2)
where, $N$ is Avogadro’s number.

According to Debye, $\tau$ is expressed as

$$\tau = \frac{4\pi n a^3}{kT} \quad (5.1.3)$$

where, $\eta$ is the viscosity of the medium and $a$ is the radius of the molecule assuming the molecules to be spherical, $\tau$ is usually of the order of a picosecond ($i.e., 10^{-12}$ sec.). For the estimation of $\tau$, measurements should be done with the applied electric field having a period nearer the relaxation time. For such measurements we need microwave signals in the GHz range where the evaluation of $\tau$ could be done.

For a non-conducting medium, dispersion, absorption and dielectric conductivity are obtained by separating out the real and imaginary parts of the complex permittivity $\varepsilon^*$ as given in an earlier equation 5.1.1 as follows:

Let $\varepsilon'$ and $\varepsilon''$ be the dielectric constant and dielectric loss factor pertaining to the real and imaginary parts of $\varepsilon^*$ and let $\tan \delta$ be the loss tangent.

The $\varepsilon'$, $\varepsilon''$ and $\tan \delta$ are given by the following expressions—

$$\varepsilon' = \varepsilon_\infty + \left[ \frac{\varepsilon_S - \varepsilon_\infty}{1 + \omega^2 \tau^2} \right] \quad (5.1.4)$$
\[ \varepsilon'' = \varepsilon_\infty + \left[ \frac{(\varepsilon_s - \varepsilon_\infty)\omega \tau}{1 + \omega^2 \tau^2} \right] \]  

(5.1.5)

\[ \tan \delta = \left[ \frac{\varepsilon''}{\varepsilon'} \right] \]  

(5.1.6)

The loss factor is maximum when \( \omega \tau = 1 \) and correspondingly \( \varepsilon''_{\text{max}} = \left( \varepsilon_s - \varepsilon_\infty \right)/2 \). The relaxation time and the contribution of the orientation polarization can be determined by the relations given above from the absorption characteristics of a dielectric as long as Debye theory is valid for the system under study. A typical dielectric spectrum is shown in Fig. 5.1.1.

The assumption of a single relaxation time fits satisfactorily the frequency response of a number of dielectrics, particularly, of dilute solutions of polar molecules in non-polar solvents. But the actual relaxation spectra of liquids and polymers are frequently characterized by a distribution of relaxation times spread around a most probable value which indicates a coupling of the dipole moments to their surroundings. We have to visualize the dipoles as statically jumping over potential wells, rather than smoothly rotating spheres, whenever the activation energy becomes available. In crystals, the permanent electric dipoles are, in general, completely immobilized, as far as any individual rotation is concerned.
Fig. 5.1.1: A typical dielectric relaxation spectrum.
A theory of distribution of relaxation times was first given by Von Schweilder\textsuperscript{3}, Wagner\textsuperscript{4} and Yager\textsuperscript{7}. In Yager’s theory the expressions for the distribution of relaxation time are based on Gaussian distribution in order to explain experimental curves. For long chain polymers, Kirkwood and Fuöss\textsuperscript{8} obtained a formula for distribution function which however, is found to be in agreement with experimental results. Given the loss-factor log frequency curve, Fuöss and Kirkwood\textsuperscript{9} showed as to how to derive the distribution function giving the best experimental fit. However there is no satisfactory general theory for the dependence of $\varepsilon'$ and $\varepsilon''$ on frequency as well as for the distribution function. Therefore, usually two empirical approaches are used in dealing with dielectric dispersion data on polar liquids. One of these is due to Cole and Cole\textsuperscript{10} who proposed a circular arc function and showed that in the case of a single relaxation time, the complex plane locus obtained by plotting $\varepsilon''$ versus $\varepsilon'$ at different frequencies is a semicircle with radius $[(\varepsilon_s-\varepsilon_\infty)/2]$ and centre at $[(\varepsilon_s+\varepsilon_\infty)/2]$ on $\varepsilon'$ axis as shown in Fig.5.1.2. However it is observed that all the molecules do not have the same type of Cole-Cole plots. To explain the various observed dielectric relaxation spectra, different empirical models have been proposed in the literature as discussed below.

The Cole-Cole Relaxation model:

It has been found from the measurements on a large number of compounds that $\varepsilon''$ against $\varepsilon'$ curve deviates
Fig. 5.1.2: Cole-Cole plot for Debye model
Fig. 5.1.3: Cole-Cole plot for Cole-Cole model ($\alpha > 0$).
considerably from the above predicted semicircular behaviour of Debye theory. Materials having long chain molecules or having a number of rotatable polar groups, show broader dispersion curves and lower maximum loss than obtained from Debye behaviour and in such cases $\varepsilon''$ against $\varepsilon'$ curve may be an arc of a circle which falls inside Debye semicircle. The curve is known as Cole-Cole arc as shown in Fig.5.1.3.

Cole\textsuperscript{11} suggested an empirical relation of the following form

$$\varepsilon^* = \varepsilon_\infty + \left[\frac{\varepsilon_S - \varepsilon_\infty}{1 + (j\omega t)^{1-\alpha}}\right]$$

(5.1.7)

where, $\alpha$ represents the symmetric distribution parameter of the relaxation time and lies between 0 and 1 \textit{i.e.} $0 < \alpha < 1$. In the limit when $\alpha=0$, then the Cole-Cole arc reduces to a Debye semicircle. The values of the parameter $\alpha$ increase with increasing internal degrees of freedom of molecules and decrease as the temperature increases.

The Cole-Davidson Relaxation model:

One cannot expect that, any dielectric medium complex plot of $\varepsilon''$ and $\varepsilon'$ should yield either a Cole-Cole arc or a semicircle with symmetry axis parallel to $\varepsilon''$ axis passing through the centre. Cole-Davidson\textsuperscript{12} have observed that complex plots for certain materials like 'glycerol' do not have this symmetry, instead, they have a skewed arc. To explain such observations they have suggested an empirical
Fig. 5.1.4: Cole–Cole plot for the Cole–Davidson model ($\beta < 1$).
model represented by the equation,

\[ \varepsilon^* = \varepsilon_\infty + \left[ \frac{\varepsilon_S - \varepsilon_\infty}{1 + j\omega \tau^\beta} \right] \]

(5.1.8)

where, \( \beta \) is an empirical parameter which lies between the limits 0 and 1. For \( \beta = 1 \) the equation 5.1.8 corresponds to Debye equation 5.1.1. As \( \beta \) decreases, the arc becomes progressively more symmetric as given in Fig.5.1.4.

The fact that experimental curves deviate from the normal Debye behaviour, is attributed to the distribution of relaxation times. The Cole-Cole, Cole-Davidson behaviour can be thought of as arising from a continuous spread of relaxation times each of which exhibits Debye behaviour. The distribution of relaxation times being symmetric in the case of Cole-Cole arc, while, Cole-Davidson arc is a result of series of relaxation processes of decreasing importance extending to the high frequency side of the main dispersion.

Havriliak-Negami Equation:

There are several dielectric systems where the two models discussed above fail to explain the observed dielectric spectra. Both the models contain only one empirical parameter to describe the shape of the complex plot. For this reason, a further generalization has been introduced by Havriliak and Negami, consisting of contribution of both Cole-Cole and Cole-Davidson expressions, thus the modified equation is -
\[ \varepsilon^* = \varepsilon_\infty + \left[ \frac{\varepsilon_S - \varepsilon_\infty}{1 + (j\omega \tau)^{1-\alpha}} \right]^\beta \]  

(5.1.9)

When \( \alpha = \beta = 0 \) the above equation reduces to Debye model. Similarly when \( \beta = 0 \) and \( 0 < \alpha < 1 \) and when \( \alpha = 0 \) and \( 0 < \beta < 1 \) the equation takes the form Cole-Cole model and Cole-Davidson model respectively.

The limitations of the above models are due to the absence of any particular physical significance which is capable of explaining the postulated forms of dependence, so that it amounts to an exercise of fitting the empirical parameters like \( \alpha \) and \( \beta \) hence do not elucidate the underlying physical reality.

Thermodynamic parameters:

The Debye model predicts strong dependence of the relaxation time \( \tau \) on the temperature. This indicates that at some stage in the relaxation process, a molecule needs certain amount of activation energy in excess of average thermal energy, to overcome the potential barrier. With this point in view, Eyring\(^4\) identifies the rate constant 'k' in his equation,

\[ k = \frac{KT}{h} e^{-\Delta G^*/RT} \]  

(5.1.10)

as the number of times per second a dipole acquires sufficient energy (activation energy \( \Delta G^* \)) to pass over the potential
barrier, and \( k = 1/\tau \), where \( \tau \) is the dielectric relaxation time.

Kauzmann\(^{13}\) is the first scientist to give a satisfactory interpretation of the dielectric relaxation process based on Eyring's rate process. He expressed relaxation time \( \tau \) by the equation,

\[
\tau = \frac{h}{kT} \exp \left( \frac{(\Delta H^* - T\Delta S^*)}{RT} \right) \tag{5.1.11}
\]

and activation energy is defined as \( \Delta G^* = \Delta H^* - T\Delta S^* \)

where \( \Delta H^* \) is the molar enthalpy of activation and \( \Delta S^* \) is the molar entropy of activation, the values of \( \Delta H^* \) and \( \Delta S^* \) may be determined from the slope and intercept of a linear plot of \( \ln(\tau T) \) versus \( 1/T \) respectively.

According to Kauzmann, the activation energy may be interpreted as the energy required to make possible, the reorientation of a molecule, or the energy required for the molecule to jump from one equilibrium state to the other. The activation energy \( \Delta G^* \) increases with decrease in relaxation time \( (\tau) \). The decrease in the relaxation time \( (\tau) \) may be due to the decrease in viscosity \( (\eta) \) of the medium.

A study of these thermodynamic parameters may be useful in assessing the states of the dipole under the influence of the applied field. The magnitude of \( \Delta H^* \) may give an idea of the structure, e.g., for long chain alcohols, \( \Delta H^* \) is high,
predicting linear long chain structure of the molecules through 'hydrogen bonding'.

Normally, as the temperature increases, $\Delta G^*$ increases whereas $\tau$ decreases. The decrease in the relaxation time due to the decreasing viscosity of the medium and the increase in the activation energy ($\Delta G^*$), may be due to the increase in the thermal agitation, whereby the dipole requires more energy in order to attain the equilibrium with the applied field. In most of the cases, $\Delta G^* > \Delta H^*$, resulting in negative values of entropy of activation ($\Delta S^*$) indicating the more ordered state of dipoles in the activated state. However, as noticed by Hill et al. not much significance can be attached to these values of $\Delta S^*$ in the absence of higher accuracy.
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TIME DOMAIN SPECTROSCOPY
5.2.1 INTRODUCTION:

The development of time domain spectroscopy (TDS) in the past few decades has turned out to be the best tool for the study of dielectric behaviour of materials over a wide range of frequencies. Essentially, it is a technique of observing the time dependent response of a sample after the application of a time dependent electromagnetic field. The response characteristics measured in terms of any observable quantity like current, charge or voltage as a function of real time, make this technique "a real time analysis". In frequency domain technique, response of the sample to an applied alternating sinusoidal field of some specific frequency, is measured in terms of steady state quantities like amplitude and phase which are later used to evaluate complex permittivity \( \varepsilon^*(\omega) = \varepsilon' - j\varepsilon'' \).

One of the important features of the time domain technique is that a single record can give information over a considerable range of time or frequency. Until recently, this technique was limited for times greater than a few microseconds but the potential application of time domain spectroscopy to the dielectric studies has developed in the last two decades due to the developments in the fast pulse generator and sampling oscilloscope. Such devices permit the measurements ranging from a time resolution of a few picoseconds to times of several nanoseconds or even longer corresponding to frequency range from a few MHz to several
GHz. For the coverage of the same frequency range in conventional frequency domain techniques one requires a considerable amount of complex instrumentation and data processing. As a result, the time domain measurement technique has become an attractive alternative to the study of the systems that have time dependent behaviour in the frequency range of interest.

Fellner - Feldegg\textsuperscript{1,2} introduced time domain spectroscopy (TDS) technique into the field of dielectric study of liquids and solids in 1969. Since then fruitful attempts have been made to modify the equipment\textsuperscript{3-8} as well as computational methods to increase the frequency coverage and accuracy of the measurements. With such modifications, people could use this technique for measuring dielectric parameters by using various chemicals such as alcohols\textsuperscript{7-11}, organic liquids\textsuperscript{12}, electrolyte/aqueous solutions\textsuperscript{13,14}, polymer solutions\textsuperscript{15} and solids\textsuperscript{16}. Kent\textsuperscript{17}, Iskander and Stuchly\textsuperscript{18} could apply this technique to study the dielectric behaviour of biological samples.

Based on monitoring the response pulse, either reflected or transmitted through the sample under study time domain spectroscopy may conveniently be classified into two categories such as:

1. Time Domain Reflectometry (TDR) technique and
2. Time Domain Transmission (TDT) technique.
Gestblom et al.\textsuperscript{10-21} employed the transmission technique for the study of low loss liquids, whereas Cole\textsuperscript{7} could use reflectometry technique (TDR) for the study of several liquids, electrolyte, polymer and aqueous solutions.

Suggett\textsuperscript{22} used this technique for the study of the complex permittivity of aminoacids and Finer\textsuperscript{23} \textit{et al.} for the peptides. Many reviews regarding the improvements in the instrumentation and data analysis\textsuperscript{24-27} are available in the literature. A detailed account of TDS technique and its applicability in respect of the study of dielectric behaviour, has been given by Cole\textsuperscript{7,24}.

5.2.2 BASIC PRINCIPLES AND EQUATIONS IN TDS:

The study of reflected or transmitted signals when a fast rising voltage pulse is applied to a sample under test placed in the coaxial line, has led to the development of a variety of methods for determining dielectric response of the sample under study\textsuperscript{27}. The most commonly used experimental arrangements and relevant equations used in TDS are discussed in brief.

Generally in the TDS system a train of suitably generated fast rising pulses, is applied to a coaxial transmission line (usually with 50Ω characteristic impedance). The sample under test is either inserted in or attached to the coaxial line with some form of termination. This causes
Fig. 5.2.1: Experimental arrangement for the Time Domain measurements.
change in the transient waveform which is a measure of the response properties of the sample. Such a response waveform in the line may be observed at some point in the transmission line by a voltage probe connected to a sampling oscilloscope or any other data acquisition system as shown in Fig. 5.2.1.

The most common arrangements for observation are -
1. reflected waveform from the sample in the line terminated by a matched section of 50 $\Omega$ impedance for no reflection of the transmitted wave,
2. reflected waveform from a sample used as the termination i.e., with an open circuit and for no current after the sample section,
3. reflected waveform from a short-circuited sample with no potential difference at the terminal end and
4. transmitted waveform in the section of the line behind the sample terminated by 50 $\Omega$ to eliminate reflection from the end of the line.

The forms of response observed in the above four arrangements are schematically represented in Fig. 5.2.2, where dashed line indicates the responses for no sample present in the coaxial line setup.

In an ideal coaxial line, the resultant voltage $V(t)$ at the front surface of the sample is the sum of the forward travelling initial pulse $V_o(t)$ and reflected part of the pulse
from the sample $R(t)$ i.e., $V(t) = V_q(t) - R(t)$, with a transmitted part $T(t)$ behind the sample. The relation amongst $V_q(t)$, $R(t)$ and $T(t)$ is decided by the response characteristics of the sample.

5.2.3 PROPAGATION IN THE SAMPLE AND BOUNDARY CONDITIONS:

a. Reflection from Sample in a matched line:

The conventional solution by standard methods\textsuperscript{28} gives an expression for the reflection coefficient $S_{11}(i\omega)$, defined as the ratio of transform $r(i\omega)$ and $v_{o}(i\omega)$ of the reflected pulse, $R(t)$ and incident pulse, $V(t)$ respectively.

$$S_{11}(i\omega) = \frac{r(i\omega)}{v_{o}(i\omega)} = \rho^* \frac{1 - \exp\left(\frac{2i\omega d}{c} \sqrt{\varepsilon^*}\right)}{1 - \rho^* \exp\left(-\frac{2i\omega d}{c} \sqrt{\varepsilon^*}\right)}$$  \text{(5.2.1)}

where $\rho^* = \frac{(\sqrt{\varepsilon^*} - 1)}{(\sqrt{\varepsilon^*} + 1)}$ is the complex reflection coefficient and $'d'$ is the sample length. The exponential terms in this expression are the results due to successive reflections at the two sample surfaces. This is easily seen by series expansion of the denominator. The fact is that for a non dispersive dielectric with $\varepsilon^*$ real, the quantity $[(2d/c)\sqrt{\varepsilon^*}]$ is the time for a round trip in the sample with speed $c/\sqrt{\varepsilon^*}$, in which case the exponential is simply the transform of an impulse delayed by this time. This formulation is useful for recognizing the accumulated effects of reflection; at the same time one has the problems in solving for $\varepsilon^*$, a complex quantity in general, given by
$S_{11}(i\omega)$. One simplification is to omit the exponentials, thereby restricting the range to times, before the arrival of the first reflection from the back of the sample, i.e., times less than $(2d/c)\sqrt{|\varepsilon|}$. To the extent this direct or single reflection method is valid, one has merely,

$$\varepsilon^* = \left[ \frac{(1+S_{11})}{(1-S_{11})} \right]^2 \quad (5.2.1a)$$

The limitations in the approximation are quite severe, in the case of excessively long samples which may be required to obtain sufficiently long times or low frequencies. In the simplification, one will have to take into account the error in 'truncating' the integral transform of $R(t)$, when $R(t)$ is known over finite time rather than the proper upper limit of $t = \infty$, but which is not being done in practice, in the following transform equation:

$$f(i\omega) = \mathcal{Z} F(t) = \int_0^\infty dt \exp(-i\omega t) F(t)$$

By judicious rearrangement of the terms in equation 5.2.1a one can have a more advantageous form of equation,

$$\varepsilon^* - 1 = (2c/d) \left[ \frac{(r/i\omega\sigma)}{1 - i\omega(r/i\omega\sigma)} \right] (xcotx + i\omega d/c) \quad (5.2.2)$$

where $x= \frac{\omega d/\sqrt{\varepsilon^*}}{c}$. 
The first bracket takes the account of the fact that the voltage at the sample input is not \( v_0 \) but \( (v_0 - r) \), while the term \( xcotx \) in the second bracket accounts for propagation effect in the sample section of length \( 'd' \) and the term \( (i\omega d/c) \) accounts for termination by \( G_C \), the characteristic conductance of the coaxial line. The simplicity in the evaluation, arises from the fact that the complicating factor \( xcotx \) has the limiting value unity for \( x \ll 1 \) and the series expansion,

\[
xcotx = 1 - (\omega d/c)^2 \frac{2}{3} - (\omega d/c)^4 \frac{2}{45} + \ldots \quad (5.2.3)
\]

is valid for \( |x| < \pi \) and rapidly converges for \( |x| < 1 \). Hence, eqn.5.2.2 is solved by iteration.

The formulae 5.2.1 and 5.2.2 also indicate clearly an upper frequency limit on the usefulness of the method, as for \( \varepsilon^* \), real \( xcotx \) is zero at \( x = \omega d / \sqrt{\varepsilon/c} = \pi / 2 \), corresponding to a sample having one-quarter wavelength long, and \( xcotx \) changes rapidly near this point, by making calculated values of \( \varepsilon^* \) extremely sensitive to small errors in the evaluation of \( r(i\omega)/i\omega v_o(i\omega) \). These were the observations made independently by Gestblom and Noreland through detailed calculations regarding the behaviour of the reflection coefficient \( S_{11}(i\omega) \) or its equivalent.
Fig. 5.2.2

Observed responses for a dielectric sample for various terminations. The dashed curves are for no sample. The time $T_s$ is the time of arrival of the incident pulse at the front surface of the sample.
b. Reflection from open circuited sample:

In this arrangement, a sample in a length 'd' terminates the coaxial line. As shown in Fig.5.2.2, the observed voltage pulse rises to a value $2V_0$, i.e., the voltage doubling effect arises from reflection at an open circuit. The difference signal is a measure of the current needed to charge the sample to $2V_0$ and at low frequency, the arrangement corresponds to the simple steady state procedure for measuring permittivity by placing a sample in a cell at the end of a coaxial line. Neglecting end effects at the back face, the transform $p(i\omega)$ of the difference signal $P(t)$ shown in Fig.5.2.2 is related to the transform $v_0(i\omega)$ of the incident pulse by

$$\frac{p(i\omega)}{v_0(i\omega)} = (1 + \rho^*) \left\{ \frac{1 - \exp(-2i\omega d\varepsilon^*/c)}{1 - \rho^* \exp(-2i\omega d\varepsilon^*/c)} \right\} \quad (5.2.4)$$

In this explicit solution for $p(i\omega)$ by the usual method, the relation of $\varepsilon^*$ to the observed ratio is not readily apparent. But in this case, network admittance analysis directly yields the following very simple result.

$$\varepsilon^* = \frac{(p/2i\omega v_0)}{(c/d) \frac{(p/2i\omega v_0)}{1 - i\omega(p/2i\omega v_0)}} \frac{xcotx}{1} \quad (5.2.5)$$

The advantages of the sample termination method are that in many cases simpler thermostatted cells are more readily available because the sample can be placed at the end of the coaxial line rather than inserting in it. Disadvantages are
that an ideal open circuit is impossible to realise its exactness, because if the permittivity of the sample is very large water or aqueous solutions with $\varepsilon \approx 80$), the maximum length for satisfactory results at high frequencies (1 GHz or more) becomes so small (1-2mm) that a satisfactory cell design becomes difficult. But, however, corrections for finite stray capacitance at the end of the line or an increased effective electrical length could be thought in a quite simple way.

c. Reflection from Short-Circuited Sample:

This arrangement is superficially attractive as an ideal short circuit is closely approximated by simply closing off the coaxial line with a metal disk. The transform $S(i\omega)$ of the difference $S(t)$ between the signals for short circuit in front and behind the sample is related to the transform $v_o(i\omega)$ by,

$$\frac{S(i\omega)}{v_o(i\omega)} = (1 - \rho^*) \left[ \frac{1 - \exp(-2i\omega d\varepsilon^*/c)}{1 + \rho^* \exp(-2i\omega d\varepsilon^*/c)} \right]$$

with judicious arrangement of the above equation one can obtain the useful form of the equation similar to equations 5.2.2 and 5.2.5,

$$1 = (c/d) \left[ \frac{(s/2i\omega v_o)}{1 - i\omega(s/2i\omega v_o)} \right] xcotx$$

where, propagation constant $x = \omega d\varepsilon^*/c$. The expression becomes independent of $\varepsilon^*$ for $xcotx = 1$. However, the results
of this kind are not without information. So for it is assumed that the sample is nonmagnetic with relative permeability $\mu^* = 1$. If it differs from unity the sample inductance is $\mu^* L_0 d$, the propagation constant becomes $x = \sqrt{\varepsilon \mu^* / c}$ and then eqn.5.2.7 takes the form,

$$
\mu^* = (c/d) \left[ \frac{(s/2i\omega_0)}{1 - i\omega(s/2i\omega_0)} \right] x\cot x \quad (5.2.8)
$$

The possibility of using short-circuit TDR measurements for the study of magnetic behaviour has been found some application, for example, Nicolson and Ross have combined short- and open-circuit measurements of the same sample to obtain both $\mu^*$ and $\varepsilon^*$ by using the modified form of eqn.5.2.5 and 5.2.8. The use of short-circuit methods for the study of dielectric and conductance behaviour is rather severely restricted by the requirements on $x = d/\sqrt{\varepsilon^* / c}$, which requires the frequency to be large enough for $x\cot x$ to differ appreciably from unity but not in the vicinity of $\pi/2$ or odd-multiple of $\pi/2$ (quarter wave resonance) in which $x\cot x$ is so small that the sample itself is nearly a short-circuit.

d Transmission Method:

The title indicates, that one uses the signal emerging from the sample into the coaxial line rather than that reflected towards the generator. Gestblom and Noreland have pointed out that the transmission method has two distinct potential advantages over the reflection method. One of the
advantages is that, the expression for the ratio of transmitted to incident pulse transforms, from which permittivity or other information is to be extracted, varies considerably more smoothly with $\varepsilon^*$ in ranges where the propagation factor $\beta \cot \beta$ in the reflection equation is near zero or infinity. The second is that, the delay in arrival of the transmitted signal which is a measure of $\sqrt{\varepsilon^* - 1}$, should be large enough for reasonable sample lengths. This makes uncertainties in the zero of time less serious. In frequency domain language, the phase shifts are large compared to those from the timing error in a realizable marker pulse.

The conventional expression for the ratio of the transform $t(i\omega)$ of the total transmitted pulse $T(t)$ to the transform $v_o(i\omega)$ of the pulse for no sample is;

$$\frac{t(i\omega)}{v_o(i\omega)} = (1 - \rho^2) \left[ \frac{\exp[-i\omega \varepsilon^* - 1/c]}{1 - \rho^2 \exp(-2i\omega \varepsilon^*/c)} \right]$$  \hspace{1cm} (5.2.9)

5.2.4 TIME DOMAIN REFLECTOMETRY (TDR):

As discussed earlier, the term TDR refers to a technique of observing time dependent reflection response of a sample of interest after the application of a fast-rising voltage pulse.

In TDR, a train of suitably generated fast-rising pulses, about 25 ps. rise time, is applied to a transmission line, usually coaxial line with 50 ohms characteristic impedance. The pulse propagates unchanged along the line as
long as the electric properties of the line remain the same. To the coaxial line a sampling device is connected. This sampler measures the voltage which is passing through the sampling gate in conjunction with a TDR sampler plug-in. The sampler is capable of converting a very fast signal into a slower one, the fast signal being repetitive. This signal is displayed on an oscilloscope screen.

5.2.5 USE OF TRANSMISSION LINE THEORY IN TDR:

Consider a section of uniform transmission line of length 'd' filled with a dielectric of complex permittivity $\varepsilon^*$. It may be regarded as a symmetrical four-terminal network, having an input admittance $Y_{in}$ given by:

$$Y_{in} = \frac{Y_o + Y_d}{1 + z_s Y_d}$$

(5.2.10)

where $Y_o$ is the open circuit admittance of the section, $z_s$ is its short circuit impedance and $Y_d$ the input admittance of the line or network used to terminate the section. If the geometric capacitance and inductance per unit length of the line are $C_c$ and $L_c$, then from transmission line theory, $Y_o$ and $z_s$ are given by:

$$Y_o = i \omega C_c \varepsilon^* \left[ \frac{\tanh x}{x} \right]$$

(5.2.11)

$$z_s = i \omega L_c \left[ \frac{\tanh x}{x} \right]$$
where, \( x = i\omega \sqrt{L_C C} \sqrt{\varepsilon^*} \). The speed, \( c \) of propagation in vacuo is, \( c = (L_C C)^{-1/2} \). These expressions are for a nonmagnetic sample with relative permeability \( \mu^* = 1 \).

For an ideal coaxial line and for dielectric permittivity \( \varepsilon^* \), the admittance \( y_d \) relative to the characteristic conductance \( G_c \) is given by \( (C_L / L) \). The input admittance of dielectric section and termination, is given by,

\[
y_{\text{in}} = \frac{i(\omega)}{V(\omega)}
\]

where, "i" and "v" denote the current and voltage respectively and \( \omega = 2\pi f \). The Laplace transforms of \( V(t) \) and \( I(t) \) are given by,

\[
V(\omega) = \mathcal{L}_{\omega} V(t) = \int_0^\infty \exp(-i\omega t) V(t) \, dt
\]

\[
i(\omega) = \mathcal{L}_{\omega} I(t) = \int_0^\infty \exp(-i\omega t) I(t) \, dt
\]

From the transmission line theory, the current \( i \) and voltage \( v \) in coaxial line with characteristic admittance \( G_c \) are related to incident \( v_0(\omega) \) and reflected voltage \( r_x(\omega) \) by
\[ i(\omega) = G_c [v_0(\omega) - r_x(\omega)] \]

\[ v(\omega) = [v_0(\omega) + r_x(\omega)] \]

Hence, equation 5.2.12 becomes,

\[ Y_{in} = G_c \left[ \frac{[v_0(\omega) - r_x(\omega)]}{[v_0(\omega) + r_x(\omega)]} \right] \]  
(5.2.14)

For the nonconducting sample, the equation 5.2.14 gives28,

\[ Y_{in}(\omega) = i\omega C_g \varepsilon^* \]  
(5.2.15)

where, \( C_g \) is the geometrical capacitance of the sample and \( \varepsilon^* \) is its frequency-dependent complex dielectric constant. From the above equation, the permittivity can be defined as,

\[ \varepsilon^* = \frac{G_c}{i\omega C_g} \left[ \frac{[v_0(\omega) - r_x(\omega)]}{[v_0(\omega) + r_x(\omega)]} \right] \text{xcotx} \]  
(5.2.16)

or

\[ \varepsilon^* = \frac{c}{i\omega d} \left[ \frac{[v_0(\omega) - r_x(\omega)]}{[v_0(\omega) + r_x(\omega)]} \right] \text{xcotx} \]  
(5.2.17)

where, \( c \) is speed of electromagnetic radiation in air and \( d \) is the length of coaxial line section filled with the dielectric. Here, function \( x(\omega d/c) \varepsilon^{1/2} \) accounts for propagation, multiple reflection in the sample and coaxial line and it is given by3,
\[ \cot x = 1 - \left( \frac{1}{3} \right) (\omega d/c)^2 \varepsilon^* - \left( \frac{1}{45} \right) (\omega d/c)^4 \varepsilon^*^2 + \ldots \]  

\[ \text{the series expansion being valid for } |x| < \pi. \]  

The condition \(|x| < 1\), corresponding to a maximum frequency \(\omega\), is given by,

\[ \omega < \frac{c}{d} \left| \varepsilon^{1/2} \right| \]  

\[ (5.2.19) \]

and it is not a necessary upper limit but is the one above which the solution rapidly becomes sensitive to small errors, especially near \(x = \pi/2\) for which \(\cot x = 0\). Therefore, one has to take equation (5.2.19) as a restriction on cell design and possible frequency range of interest.

For this experimental setup, \(x=1\) was considered in equation (5.2.17) and by rearranging the terms in that equation, we have,

\[ V_0 = r_x \frac{[1 + i\omega d/c \varepsilon^*]}{[1 - i\omega d/c \varepsilon^*]} \]  

\[ (5.2.20) \]

For air (\(\varepsilon^* = 1\)), equation (5.2.20) gives,

\[ V_0 = r_1 \frac{[1+i\omega d/c]}{[1-i\omega d/c]} \]  

\[ (5.2.21) \]
where, $r_1$ is the reflected pulse in case $\varepsilon^*=1$ and $r_x$ is reflected pulse when sample is inside the cell. From equations 5.2.20 and 5.2.21, we have,

$$r_x = \frac{1-i\omega d/c}{1+i\omega d/c} \times \frac{1+i\omega d/c}{1-i\omega d/c} r_1$$

(5.2.22)

or

$$\frac{c}{i\omega d} \left( \frac{r_1 - r_x}{r_1 + r_x} \right) = \left[ \frac{\varepsilon^* - 1}{1 + \left( \frac{\omega^2 d^2/c^2}{\varepsilon^*} \right)} \right]$$

(5.2.23)

The quantities $(r_1 - r_x)$ and $(r_1 + r_x)$ will be called $p$ and $q$ respectively. Since $p(t) = R_1(t) - R_x(t)$ and $q(t) = R_1(t) + R_x(t)$, we can also write reflection coefficient as,

$$\rho^* = \frac{c}{i\omega d} \frac{p}{q} = \varepsilon^* - 1.$$  

(5.2.24)

5.2.5 EXPERIMENTAL SET UP:

The block diagram of the experimental set up used in the present work is shown in Fig.5.2.3 and plate 1 shows the actual experimental set up. The Tektronix 7854 oscilloscope is the heart of the instrumental set up. It is essentially a sampling oscilloscope (plate 2) with a 7S12 special TDR unit. The 7S12 TDR unit consists of a S-52 pulse generator and S-6 sampling head. The pulse generator consists of a tunnel diode producing a fast-rising step-voltage pulse of 200mV and 25ps rise time with a repetitive frequency of 1kHz. Such a pulse
Fig. 5.2.3: The block diagram of experimental setup for the Time Domain Reflectometry.

1. 7S12 TDR Unit.
2. S-52 pulse generator.
3. S-6 sampling head.
4. Tektronix 7854 oscilloscope.
5. Sample under test (cell).
6. PC/XT (data recorder).
7. LEEE-488 GPIB.
8. 50Ω impedance co-axial line (45 cm).
9. 50Ω impedance co-axial line (131 cm).
Plate-1: Actual experimental set-up used for TDR measurements
Plate-2: Tektronix-7854 oscilloscope with co-axial line system for TDR measurements
is transmitted to sampling head through a coaxial line of characteristic impedance 50 Ω. Through another coaxial line, the pulse travels from the sample head to the specially designed sample cell and reflected part of the signal retraces back to the sampling head. The length of the transmission line(6) (Fig.5.2.3) is about double the transmission line(7) (Fig.5.2.3), so that the incident pulse is well separated from the reflected pulse.

When the incident step reaches the open end of coaxial cell, virtually all the energy is reflected in phase with the incident step, so the reflection adds to the incident step. This signal is immediately reflected towards the sampling gate. The remaining part will be absorbed into the cell and according to dielectric behaviour of the cell, this voltage will be returned gradually with some delay towards the sampling gate. The reflection is a second step in the same direction (positive going) as incident step and having the same amplitude as that of incident step. Figure 5.2.4a shows the incident and reflected waves from the empty cell. The time between the two steps is proportional to the round-trip distance between the sampling head and open end of coaxial cell.

If the cell is filled with dielectric material, the characteristic impedance of transmission line will change and gives the reflection. These reflections will be subtracted
Fig. 5.2.4a: Incident and reflected pulses without sample in a time window of 10 ns.
Fig. 5.2.4b: Incident and reflected pulses with sample in a time window of 10 ns.
from the incident step, producing a negative going reflection for a positive going incident step. A schematic build-up of reflection pattern is shown in Figure 5.2.4b.

Sample Cell:

The sample liquid under test is placed in the sample cell attached at the end of the coaxial line (Fig 5.2.3). Proper designing of the cell is essential such that the characteristic impedance of the cell should match with the coaxial transmission line. Any mismatch in this regard causes serious errors in the measurements due to unwanted reflections. The proper design of the cell depends on the proper choice of diameters of the inner and outer conductors and the length of the inner conductor called pin length which is one of the important dimensions of the cell used in the analysis of the data. The cell filled with the sample till the central pin is immersed in the sample. In the total reflection method the sample must be long enough to produce an adequate difference signal but short enough to keep away the complications of resonance in the frequency range of our interest. The cell is in the form of coaxial cylinders as inner and outer conductors with its characteristic impedance,

$$Z_C = \frac{1.38}{\varepsilon^{1/2}} \log (b/a)$$

and the capacitance $C$ is given by

$$C = 2\varepsilon^{1/2} / \log(b/a)$$
Fig. 5.2.5a: SMA coaxial cell

Fig. 5.2.5b: Dimensions of the SMA cell and fringing field
where, $a$ and $b$ are outer diameter of the inner conductor and inner diameter of the outer conductor respectively, $\epsilon_v$ permittivity of free space and $\epsilon$ is the dielectric constant of air or teflon.

Using the above equation with $Z_c = 50 \, \Omega$, either $a$ or $b$ may be calculated assuming the other one.

In the present work, SMA (Standard Military Application) connector itself is used as a cell. Its Hexanut acts as an outer conductor having $a = 3.5 \, \text{mm}$ and the inner axial conductor of the connector is considered as inner conductor of the cell. As the SMA connectors are already suitably designed to have $50 \, \Omega$ impedance, there is no mismatching of impedance with the rest of coaxial transmission line. Therefore, SMA cells are considered to be the best for dielectric measurements of the liquid samples. The height of the outer conductor (i.e., Hexanut) is extended by hollow metallic cylinder (threaded into the hexa nut) for some practical purposes (Fig. 5.2.5a).

When the cell is filled with the sample above the inner conductor, then its pin length cannot be taken as the sample length $d$ because of the fringing field as shown in Fig. 5.2.5b.
Fig. 5.2.6: Constant temperature bath.

1. Brass container with hollow cylinder at the center
2. Thermocole cover
3. SMA cell
4. Transmission line
5. To digital Thermometer
6. Thermocouple
Due to this fringing effect, the effective pin length will be greater than its physical length. Therefore, exact information about this effective pin length is essential in the evaluation of dielectric behaviour. A simple experiment is discussed separately in appendix regarding the determination of the pin-length. The effective pin length of the SMA cell used in the present work was found to be 1.35 mm.

The presence of the sample cell at the end of the coaxial line has an advantage in controlling the temperature of the sample. This is done by keeping a temperature bath over the sample cell as shown in Fig.5.2.6.

Temperature of the water in the bath is electronically controlled to be between 20°C and 60°C and the actual temperature of the sample is measured by placing a thermocouple right near the sample cell. A digital temperature indicator/controller model CT-806 supplied by Century Ltd., India, is used and the temperature measured with an error not exceeding ±0.2°C.

**Time Window:**

In the present experimental set up, one can view the reflected part of the signal on the CRT screen of the sampling oscilloscope. The noise associated with the signal can be minimised by averaging the signal provided, the time window is very stable with respect to the desired part of the signal.
Fig. 5.2.7: Reflected pulse with sample in a smaller time window (2 ns).
Reflected pulse with sample in a larger time window (10 ns).

Fig. 5.2.8: Reflected pulse with sample in a larger time window (10 ns).
Fig. 5.2.9: Reflected pulse with sample in a right time window (5 ns).
The time window is the time during which a part of the signal can be observed.

According to equation 5.2.24,

\[ \rho^*(\omega) = \frac{C}{\omega d} \times \frac{p(\omega)}{q(\omega)} \]

two reflected parts of the pulses \( R_1(t) \) and \( R_X(t) \) without and with sample in the cell respectively are to be observed/recorded over certain time window. Using the system controls of time window/ Y-shift, the interested region of the reflected part of the signal can be positioned on the screen. Choice of the time window has to be very judicious for obtaining correct values of frequency-dependent permittivity spectrum. If the time window is too small, then some important part of the signal is going to be lost (Fig.5.2.7), and corresponding reflection coefficients, \( \rho^*(\omega) \) cannot be error-free and results become misleading. If the time window is too large, then unwanted reflections due to connectors etc. will be included in the reflected part of the pulse as shown in Fig.5.2.8 which leads to an error in \( \rho^*(\omega) \) values. To minimize these errors a time window should be long enough not to lose the information and short enough to keep off the unwanted reflections as shown in Fig.5.2.9.

5.2.6 EXPERIMENTAL PROCEDURE :

The reflected pulses \( R_1(t) \) and \( R_X(t) \) without and with sample respectively are recorded with appropriate time window
Fig. 5.2.10: Reflected pulses without sample $R_1(t)$ and with sample $R_X(t)$. 

Voltage in arbitrary unit

Time (ms)
Plate-3: p(t) and q(t) pulses as observed on the screen of the oscilloscope
Fig. 5.2.11: $p(t)$ (subtracted) and $q(t)$ (added) pulses.
and averaging the signals for 100 times. The time window thus selected in the present work is 5 ns. Two waveforms $R_1(t)$ and $R_x(t)$ (Fig. 5.2.10 & plate 3) were digitized into 1024 points and stored in the memory of the oscilloscope. Then they were transferred to PC/XT through GPIB (General Purpose Interface Bus). This information is stored in the computer in two different files which we have called them as 'DAT' files. Addition and subtraction of the two waveforms where, $p(t) = R_1(t) - R_x(t)$ and $q(t) = R_1(t) + R_x(t)$ were performed in the computer and file containing information of $p$ and $q$ as a function of time is called 'TDR' file.

A typical graph of $p(t)$ and $q(t)$ is shown in Fig. 5.2.11. In making 'TDR' files, each data point is multiplied by a factor of 10000, thus TDR file contains arrays of data points of $p(t)$ and $q(t)$ for $2^{10} = 1024$ digitized points spread over the selected time window. This information in the time domain has to be converted into frequency domain using Fourier Transformation in order to obtain the frequency-dependent dielectric behaviour of the sample.

Analytical approximations to the pulse and their transforms are required for understanding the methods and their use, but several discrete Fourier Transformation algorithms are usually adopted to make the full use of available discrete information.
In general, the Fourier transform $F(\omega)$ of $F(t)$ is given by,

$$F(\omega) = \int_{-\infty}^{\infty} F(t) e^{-i\omega t} dt$$

limits of integration being 0 and $\infty$ in our case. In practice the pulses are sampled at regular time intervals $T$ and then discrete Fourier transform is performed,

$$F(\omega) = T \sum_{n=0}^{N} F(nT) e^{-i\omega nT}$$

where, $N$ represents maximum number of digitized points. Such a summation necessarily has errors due to terminating the summation at a finite $N$ (truncation errors) and due to a finite value of $T$ (aliasing errors).

While performing Fourier transform one should be careful about the nature of the curve of which transform is to be obtained. Since the nature of curves of $p(t)$ and $q(t)$ is different as shown in Fig.5.2.11, hence different methods of Fourier transform are to be used.

The Fourier transform of $p(t)$ is obtained by a summation method using equation.

$$p(\omega) = T \sum_{n=0}^{N} \exp(-i\omega nT) \ p(nT)$$
The Fourier transformation using summation method has some limitations viz., for all the sampling intervals $T$, the nature of the pulse form, must be known. Further, the transform $p(\omega)$ is simply the area under the curve $p(t)$ which has an initial peak followed by a decay to zero or a finite limiting value strictly to infinite time.

$p(t) \rightarrow 0$ or constant as $t \rightarrow \infty$ in such cases truncation error is minimum (Fig. 5.2.7).

The Samulon method was used to get Fourier transform of added pulse, $q(t)$, as follows,

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

(5.2.28)

In the above equations $T$ is the distance between two nearest cursors in the $p(t)$ and $q(t)$ curves. $N$ is the total number of points.

A natural question may arise, as to why two different methods of Fourier transformation were used for $p(t)$ and $q(t)$ curves. The reason is as follows:

In the summation method, the major restriction is that "pulse form must be known" for all values of $T$, time interval between successive digitized sample points at regular
intervals. Further, the transform $p(\omega) = R_1(t) - R_x(t)$ is simply the area under the curve $p(t)$ which has an initial peak followed by a decay to zero or a finite limiting value strictly to infinite time. This clearly indicates that the transformation with summation method is quite simple.

But the summation method cannot be valid for added pulse $q(t)$, because in this case, pulse form is not known exactly. Here, $q(t)$ rises monotonically to a long time limit. Therefore Samulon method is preferred to be used for the $q(t)$ curve. In this case the difference $[q(nT) - q(n-1)T]$ is an approximation to the derivative $dq/dt$. Further, for a function $q(t)$ approaching a constant $q(\infty)$ the difference goes to zero and the sum remains finite with $1/i\omega$, which is divergence of $q(i\omega)$. But it has been observed that the Samulon formula is very sensitive to noise, resulting in fluctuating difference but, the summation method is a smoothing process and a signal-averaging one. This makes the very method unimportant.

The Fourier transform $p(\omega)$ and $q(\omega)$ can then be used to determine complex reflection coefficient, using eq.5.2.24, as follows,

\[ \rho^*(\omega) = \frac{c}{i\omega d} \frac{p(\omega)}{q(\omega)} \quad (5.2.29) \]

where, $p(\omega)$ and $q(\omega)$ are the Fourier transforms as described
Fig. 5.2.12: A typical raw spectrum.
above, \(d\) is an effective pin length, \(c\) and \(\omega\) have their usual meaning. The reflection coefficient \((\rho^*)\) may be the first approximation to the complex permittivity.

The complex reflection coefficient spectra, called raw data (Fig.5.2.12), is used for the determination of complex permittivity as follows.

The basic equation for determining relative complex permittivity \(\varepsilon^*\) of the sample, derived from transmission line theory, is conveniently written as,

\[
\varepsilon^*(\omega) - 1 = \frac{c}{i\omega d} \left[ \frac{r_0 - r_x}{r_0 + r_x} \right] \times \cot x \tag{5.2.30}
\]

By considering only a single reflection, then for \(\cot x = 1\) and the above equation is written as,

\[
\varepsilon^*(\omega) = \frac{c}{i\omega d} \left[ \frac{r_0 - r_x}{r_0 + r_x} \right] \tag{5.2.31}
\]

From the above equation,

\[
r_0 = \frac{\left[ \varepsilon^* + \frac{c}{i\omega d} \right]}{\left[ \frac{c}{i\omega d} - \varepsilon^* \right]} r_x \tag{5.2.32}
\]

for air as medium \(\varepsilon^* = 1\) then,
Eliminating $r_0$ from equations 5.2.32 and 5.2.33,

$$
\frac{r_1}{r_x} = \left[ \frac{\varepsilon^* + \frac{C}{\omega d}}{\frac{C}{\omega d} - \varepsilon^*} \right] \left[ \frac{\frac{C}{\omega d} - 1}{1 + \frac{C}{\omega d}} \right] \quad (5.2.34)
$$

Rearranging the above equation, in terms of $\rho^*$ as,

$$
\varepsilon^* - 1 = \frac{(1 + A)\rho^*}{(1 - B\rho^*)} \quad (5.2.35)
$$

where, $A$ and $B$ are two complex quantities. For an ideal transmission line $A = B = (\omega d/c)^2$.

5.2.7 BILINEAR CALIBRATION:

As discussed in the previous sections, $\rho^*(\omega)$ (Raw spectra) may be treated as the first approximation of $\varepsilon^*(\omega)$ at lower frequencies. But, the raw spectra need some corrections to be done for obtaining reliable values of $\varepsilon^*(\omega)$ at higher frequencies. Based on equation 5.2.35 Cole has suggested bilinear calibration method for correcting the raw spectra. Two parameters $A$ and $B$ in eqn. 5.2.35 are the constants for an ideal transmission line, whereas in practice it is not ($A \neq B$) due to several unwanted reflections of different origin viz., pulse generator, sampling head, mismatching of impedance of
coaxial line, connector reflections etc. Hence, for the application of Cole method it is very much wanted that exact values of A and B be known for the given experimental setup, at all frequencies of interest. They can very well be determined by solving eqn.5.2.35 knowing raw spectra of two standard liquids of which dielectric data are reliably known. Cole et al. have suggested some standard liquids like acetone, chlorobenzene, 1,2-dichloroethane etc. However, even with this approach this bilinear calibration method is not going to be free from defects, because one of the major requirements is that dielectric spectra of the unknown liquids and standard liquids must be similar; otherwise results may be misleading in sense, calibrated liquids themselves may dominate the dielectric parameters of the unknown system. For this reason we have not used the above said method of calibration in the present work as the results were found to be unreliable.

5.2.8 CALIBRATION BY LEAST SQUARES FIT METHOD:

With a different approach Bartolini et al. have suggested a method of calibrating raw spectra to minimise the unwanted reflections at higher frequency end. In the experimental procedure as adopted by Cole, empty cell was considered as reference. However, Bertolini could point out that it would be better to use some standard known liquid as reference instead of empty cell(\(i.e.,\)air). Though this method is found to yield better results, some shortcomings do exist.
A new method of calibration based on Bertolini et al. has been developed by Mehrotra and his group specially being designed for the study of binary mixtures. In the present work, the same method we have adopted.
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