3.1 Introduction

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 [1–2]. The complex permittivity depends on some external factors like frequency, temperature, intensity of applied electric field and pressure [3]. The measurement of complex permittivity of any sample involves the measurement of dielectric permittivity ($\varepsilon'$) and dielectric loss ($\varepsilon''$) as a function of frequency. Thus the choice of a method for measurement of complex permittivity depends mainly on the frequency.

In the last few years, Time Domain Reflectometry (TDR) [4] is used for measurement of complex permittivity because in TDR, a single measurement covers a wide frequency range. The following sections of this chapter describe the experimental set up, technique and different methods to measure permittivity at various frequencies used in present investigations.

3.2 Methods for measurement of permittivity

(i) Complex permittivity at microwave frequency

(ii) Static permittivity

(iii) Measurement of refractive index

3.2.1 Complex permittivity at microwave frequency

In present thesis complex permittivity of polar liquids and their mixtures is measured in dilute solutions of non polar solvents using standard microwave test bench operating at spot frequency 9.1 GHz (Chapter VI). The methods adopted for measurement of complex permittivity of polar–non-polar solution at spot frequency is described in section 3.2.1.1.

Apart from this complex permittivity of polar liquids in pure form is also measured using Time Domain Reflectometry (TDR) at microwave frequencies. The detail of this method adopted is described in detail in section 3.2.1.2.
3.2.1.1 Complex permittivity at spot microwave frequencies

There are varieties of methods to measure the complex permittivity of solutions of polar liquids in non-polar solvents in frequency domain. In the present investigations, transmission line technique was used and thus only this technique is described here. Basically in this technique, there is determination of attenuation constant $\alpha$ and phase factor $\beta$ of the electromagnetic wave propagating in the dielectric medium. In this technique, the power from the microwave oscillator is transmitted through a waveguide or through a coaxial line before it is incident on the liquid sample confined in a cell of the same dimension as of the waveguide or transmission line. When the electromagnetic wave is reflected from the short circuit termination at the other end of the dielectric cell, there are two sets of travelling waves reflected and incident moving in opposite directions in the air filled space above the dielectric. These two sets of travelling waves produce stationary waves. The study of the characteristic of the standing wave in the air filled space above the dielectric is utilized for the measurement of dielectric constant and loss. The dielectric cell may be of the fixed lengths or there may be arrangement of varying the length of the liquid column with the help of the movable plunger forming the short circuited termination.

The first method utilizes the measurement of the terminal impedance of a short waveguide filled with a dielectric material. The standing wave ratio can be measured in the air filled space of the waveguide above the dielectric medium when the input signal is reflected at a short circuited termination placed immediately behind the dielectric. The dielectric is inserted in the closed end of waveguide or coaxial line opposite to the oscillator end, filling the volume to a height $d$. Above the dielectric, the standing wave pattern is studied by moving a probe in the slotted section and used for the measurement of $\alpha$ and $\beta$ by following either the graphical method of Roberts and Von Hippel [5] or the analytical method of Cripwell and Sutherland [6]. The second method utilizes variable length of the liquid column with the help of movable shorting plunger in the dielectric cell. The phase constant $\beta$ is calculated by measuring the wavelength in the liquid sample and $\alpha$ by measuring either the standing wave ratio or the amplitude of reflected wave for different sample lengths.

For liquid sample in waveguide if the attenuation constant and the wavelength in the dielectric sample are known, then the permittivity $\varepsilon'$ and loss $\varepsilon''$ is calculated from the following equations [2],

\[ \varepsilon' = \frac{\beta}{2\pi d}, \quad \varepsilon'' = \frac{\alpha}{2\pi d}. \]
Where \( \lambda_c \) is the cutoff wavelength, \( \lambda_0 \) is the free space wavelength; \( \lambda_d \) is the wavelength of the dielectric sample in the cell and \( \alpha \) is the attenuation constant in it. Thus, the problem of finding the permittivity and dielectric loss reduces to the measurement of,

(i) The voltage standing wave ratio or the amplitude of reflected wave from which \( \alpha \) can be calculated.

(ii) Wavelength in the sample

The descriptions of both the procedures are explained below:

(i) **By measuring reflection coefficient**

The liquid is put in the cell and the plunger is kept at the uppermost position so that the maximum amount of liquid is between the plunger and mica window. The reflected power through a unidirectional coupler is fed to a galvanometer via a crystal detector and the deflection is noted. Now the plunger is moved slowly in to the liquid column and the deflections are noted at suitable intervals till the plunger touches the mica window. The plot of the reflected power against the liquid length exhibits a series of maxima and minima. The attenuation per wavelength \( \alpha \lambda_d \), wavelength in the liquid \( \lambda_d \) can be calculated from the plot as suggested by Laquer and Smyth [7].

(ii) **By Estimation of V.S.W.R.**

The o/p from the probe in the slotted section is fed to a galvanometer or to a V.S.W.R. meter via a crystal detector. The microwave oscillator output is also modulated by an audio signal if the V.S.W.R. is determined by V.S.W.R. meter. When the shorting plunger is moved in liquid cell as described earlier, the V.S.W.R. meter shows maxima and minima. The average distance between consecutive minima gives \( \lambda_d/2 \). The attenuation constant for liquids with \( \tan \delta > 0.1 \) can be determined by Poley’s method [8]. For liquid lengths equal to \( m \lambda_d/2 \), \( n \lambda_d/2 \) and infinite respectively, the standing wave ratio in the waveguide is determined by moving the probe in the slotted section. When V.S.W.R. meter is available then V.S.W.R. can be determined directly. In the alternative, the width at twice minimum power points is determined.
and used to calculate the inverse V.S.W.R. $\rho_n$ from the simplified Von Hippel relation and Robert,

$$\rho_n = \frac{\sin \theta}{\sqrt{1+\sin^2 \theta}}$$  \hspace{1cm} (3.3)

Where,

$$\theta = \frac{\pi \Delta x}{\lambda_g}$$

Here $\Delta x$ is the distance between the points of twice minimum power. If $\rho_m$, $\rho_n$ and $\rho_\infty$ be the inverse voltage standing wave ratio for liquid lengths equal to $m\lambda_d/2$, $n\lambda_d/2$ and infinite respectively, then their ratios $\rho_m/\rho_n$ and $\rho_m/\rho_\infty$ can be given by the following relations suggested by Poley [8],

$$\frac{\rho_m}{\rho_n} = \frac{\tanh \left[m\pi\tan \left(\frac{\lambda_d}{2}\right)\right]}{\tanh \left[n\pi\tan \left(\frac{\lambda_d}{2}\right)\right]}$$ \hspace{1cm} (3.4)

$$\frac{\rho_m}{\rho_\infty} = \tanh \left[m\pi\tan \left(\frac{\lambda_d}{2}\right)\right]$$ \hspace{1cm} (3.5)

Where,

$$\pi\tan \left(\frac{\lambda_d}{2}\right) = \frac{\alpha\lambda_d}{2}$$

For fixed values of $m$ and $n$, arbitrary values are assigned to $\pi\tan \left(\frac{\lambda_d}{2}\right)$ and two curves are drawn using equation (3.4) and (3.5). Now the values of $m$ and $n$ are changed and for each set of values of $m$ and $n$ arbitrary values to $\pi\tan \left(\frac{\lambda_d}{2}\right)$ are given and curves are drawn for each set as described earlier. Once curve for $\rho_m/\rho_n$ and $\rho_m/\rho_\infty$ are drawn corresponding to different values of $\pi\tan \left(\frac{\lambda_d}{2}\right)$, these curves can be used to read directly the value of $\pi\tan \left(\frac{\lambda_d}{2}\right)$ from the experimentally measured values of $\rho_m$, $\rho_n$ and $\rho_\infty$. Thus if $\lambda_d$ and $\omega\lambda_d$ being known then $\varepsilon'$ and $\varepsilon''$ can be calculated from equations (3.1) and (3.2) respectively.

For the liquids with the low dielectric loss such as dilute solution of a polar molecule in non polar solvent, $\lambda_d$ is determined by the method described earlier. But the method of determining attenuation constant is different. Heston et al [9] suggested that V.S.W.R. of low loss material is large and sensitive to small change in reflection coefficient near unity which may be utilized to measure the attenuation constant of low loss dielectric. In present investigations Heston’s method has been adopted for short circuited termination was used.

The input impedance of the dielectric medium at the interface is,
\[ Z(0) = \frac{\rho + j\tan \left( \frac{\pi x_0}{\lambda_g} \right)}{1 + j\tan \left( \frac{\pi x_0}{\lambda_g} \right)} Z_a \]  

(3.6)

Where, \( \rho = \frac{E_{\text{min}}}{E_{\text{max}}} \)

\( \lambda_g \) is the wavelength in the air filled waveguide, \( x_0 \) is the distance of the first minima from the interface and \( Z_a \) is the characteristic impedance of the air medium. If the length of the dielectric column is taken as an integral multiple of \( \frac{\lambda_d}{2} \) and terminated by a short circuit plunger as shown in Figure 3.1 (a) or odd integral multiple of \( \frac{\lambda_d}{4} \) in case of open circuited termination Figure 3.1 (b). Then the value of \( x_0 \) is zero and hence, \( Z(0) = \rho \), since \( Z_a = 1 \) (3.7)

Now we know that,

\[ Z(0)_{\text{sc}} = Z_d \tanh V_d \]  

(3.8)

Therefore,

\[ \rho = Z_d \tanh V_d \]  

(3.9)

Where, \( Z_d, V \) and \( d \) are the characteristic impedance, propagation factor and length of the dielectric medium respectively,

\[ Z_d = \frac{\lambda_d}{\lambda_g} \]

\[ d = \frac{n\lambda_d}{2} \]

Here, \( \lambda_g = \text{Guide wavelength} \)

Equation (3.9) reduces to,

\[ \rho = Z_d \left( \frac{n\alpha_d}{2} \right) = \frac{n\alpha_d^2}{2\lambda_d} \]  

(3.10)

Equation (3.10) represents a straight line between \( \rho \) and \( n \) with a slope, \( \frac{\lambda_d^2}{2\lambda_g} \)

Thus,

\[ \alpha = \frac{2\lambda_g}{\lambda_d^2} \left( \frac{d\rho}{dn} \right) \]  

(3.11)

Substituting this value of attenuation constant \( \alpha \) in the equation (3.1) and (3.2) and for low loss liquid \( \left( \frac{\alpha \lambda_d}{2\pi} \right)^2 \) is very small compare to one so it can be neglected. Therefore, the final equation of \( \varepsilon' \) and \( \varepsilon'' \) are as follows,
\[ \varepsilon' = \left( \frac{\lambda_0}{\lambda_c} \right)^2 + \left( \frac{\lambda_0}{\lambda_d} \right)^2 \]  
(3.12)

And

\[ \varepsilon'' = \frac{2}{\pi} \left( \frac{\lambda_0}{\lambda_d} \right)^2 \left( \frac{\lambda_s}{\lambda_d} \right) \left( \frac{\partial \rho}{\partial n} \right) \]  
(3.13)

Thus the values of dielectric permittivity \( \varepsilon' \) and dielectric loss \( \varepsilon'' \) for low loss dielectrics can be evaluated by measuring the quantities \( \lambda_{ds}, \lambda_s \) and \( \frac{\partial \rho}{\partial n} \). The advantage of this method over other methods is that it eliminates the plunger and waveguide losses, which sometimes are comparable to the losses in dielectric. Therefore in
present thesis of Chapter VI, this method was adopted for short circuited termination. Microwave bench operating at frequency 9.1 GHz (X-band) have been used for carrying out measurements of permittivity and dielectric loss. It is shown in Figure 3.2.

V.S.W.R. in each case has been measured by a slotted line. The cell containing the experimental liquid is kept vertical and connected to the main line by an E-plane bend. In the microwave bench set up, the liquid filled section of the cell is separated from the rest of the microwave line by a thin sheet of mica. A short-circuiting reflecting plunger is used to vary the length of the liquid column. The length of the liquid column can be adjusted to an accuracy of 0.001 cm. The temperature of the cell is maintained constant within ± 0.5°C by circulating water in the jacket surrounding the cell. The crystal used for detection of microwaves at X-band was IN23. The energy waves from the klystron source enter the waveguide and pass through the liquid and are reflected back by a short circuiting plunger. Thus the standing wave pattern is set up.

The plunger at cell window and with the liquid in the cell, the probe is set to a minimum power position. Then the plunger is turned upwards, increasing the depth of the liquid until another power minimum is obtained. The length of the liquid column is adjusted by moving the plunger for a series of minima. The distance between the

![Figure 3.2 X-band Microwave bench set up](image-url)
two successive minima is equal to $\lambda_d/2$. For low loss liquid $\varepsilon'$ can be calculated by the following equation,

$$
\varepsilon' = \left(\frac{\lambda_0}{\lambda_c}\right)^2 + \left(\frac{\lambda_0}{\lambda_d}\right)^2
$$

(3.14)

The dielectric loss is measured by bringing the plunger down to the window and minimizing the plunger with the probe. Then the plunger is brought up to the different minimum positions, i.e. liquid lengths equal to $n\lambda_d/2$, where $n$ is the integer and the inverse standing wave ratio $\rho$ is measured from the width at double minimum points as shown in Figure 3.3. The value of $\rho_n$, thus found is corrected because of the approximation involved in deriving the equation, $\rho = \frac{\pi \Delta x}{\lambda_g}$.

![Standing wave patterns near minima.](image)

**Figure 3.3** Standing wave patterns near minima.

A curve showing subtraction factor for different values of $\frac{\pi \Delta x}{\lambda_g}$ is given in Figure 3.4. To obtain the absolute value of $\rho_n$, correction has to be applied for wall losses and losses in bends and imperfections in the short. In the present case since the slope of the curve $\rho_n$ versus $n$ is used for calculating $\varepsilon''$, the correction is not necessary. The dielectric loss $\varepsilon''$ is given by,
The term “Time Domain Reflectometry (TDR)” is used as a technique of observation of time dependent reflection response of sample under study, after application of time dependent electromagnetic field. TDR is basically depending on transmission line theory in the time domain which allows studying heterogeneities in the coaxial lines as a function of the shape of test signal. If the line is homogeneous, the shape of this pulse will not change and in case of heterogeneous occurs in the line i.e. if the sample is inserted then the signal is partly reflected and partly passes through it. Dielectric measurements are carried out along coaxial transmission line with the sample mounted in sample cell that terminates the line. The measurement of loss and permittivity at very high frequency range was first developed by H Fellner–Feldegg [10]. 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 it is a coaxial line with characteristic
impedance 50 Ω. A coaxial line is connected to a sampling device (sample holder). The schematic block diagram of the experimental set up for TDR [11–12] is shown in Figure 3.5.

![Schematic block diagram of TDR set up.](image)

**Figure 3.5** Schematic block diagram of TDR set up.

### 3.2.1.2.2 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 sampling oscilloscope for TDR/TDT/Serial data network analysis, Communication signal analysis, Acquisition and
Measurement of repetitive ultrafast signals with 80E08 TDR sampling module, CD ROM and USB port. The DSA8200 is the industry’s highest performance fully integrated time domain reflectometry measurement system. This measurement system offers 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 multiple impedance characterization. The MS Window XP Operating system, advanced connectivity to third party software and necessary ports is provided with the oscilloscope [13–14].

3.2.1.2.3 Plug-in 80E08 TDR/ sampling module

The 80E08 TDR/sampling module gives two accurate oscilloscope measurement channels (CH1 and CH2) with user selectable bandwidth of 20 GHz and 30 GHz. The high bandwidth mode provides measurement of very high speed waveforms and high fidelity display. It is capable to performing both single ended TDR / TDT measurements. The TDR rate can be selected automatically or manually for repetition rate of TDR step. In single ended TDR measurement a positive going step with 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 1 and 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 snapshot of actual experimental set up is as shown in Figure 3.6. It consists of TDR module 80E08, Tektronix DSA8200 Sampling oscilloscope, a transmission line and sample cell.

3.2.1.2.4 Sample cell

The sample cell holds the liquid which is under consideration. While designing the sample cell, its physical dimensions are very important. The impedance of the cell should be matched with co axial transmission line to which cell is connected. If there is impedance mismatched then there may be disturbance in wave occur by some unwanted reflections thereby causing some errors in the measurements. The proper design of cell includes the inner conductor and outer conductor diameters. The length of the inner conductor is known as “Pin length” of the cell and it is very important factor in dielectric analysis. The sample length must be enough to avoid unwanted reflections.
In total reflection method, the sample length short enough to keep less complication of resonance effects while long enough sample length to produce an adequate difference signal at frequencies above the range of interest. Flat end of coaxial cable copper, semi rigid from Hubert Suhner Electronics Pvt. Ltd. was used as a sample cell.

The flat end sample cell is touched on the sample to measure the dielectric relaxation without any damages of the sample as shown in Figure 3.7. This kind of cell is widely used now for studying the dielectric properties of pharmaceutical and biological useful materials [15–18], Petroleum products [19], Constructive materials [20] and number of other non destructive permittivity and permeability measurements.

**3.2.1.2.5 Choice of time window**

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

$$ f_{\text{min}} = \frac{1}{\text{time window}} $$
Maximum frequency observable is,

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

Where, N is the number of points used for sample and digitized the signal. The larger time window causes unwanted reflections and smaller time window includes loss of signals. So selection of proper time window is important to minimize these effects. In Chapter V of present thesis, dielectric relaxation study of binary mixtures of picolines and alcohols have been carried out over entire concentration range at different temperatures using TDR technique and time window of 2 ns is used. In the TDR technique, two pulses are considered, first the reflected pulse without sample \( R_1(t) \) and second reflected pulse with sample \( R_x(t) \). These pulses digitized with 2000 points and averaged 100 times per waveform.

**3.2.1.2.6 Data Analysis**

The reflected pulses without sample \( R_1(t) \) and with sample \( R_x(t) \) were subtracted \( p(t) = [R_1(t) - R_x(t)] \) and added \( q(t) = [R_1(t) + R_x(t)] \) by using computer software. The time domain data is converted in to frequency domain data by using Fourier transform. The distortion shown in the pulse upon the reflection can be understood by Fourier analysis. According to the Fourier 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. Each term of the series has a different frequency; each views a different reflection coefficient at the air liquid interface, resulting the distortion of the pulse shape. The main 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 [21] using the following formula,

$$p(\omega) = T \sum_{n=0}^{N} \exp(-j\omega n T)p(nT)$$  \hspace{1cm} (3.16)

Here $\omega$ is the angular frequency, $T$ is the time difference between two adjacent points or sampling interval. The Fourier transformation using summation methods have some limitations. Fourier transformation of $q(t)$ curves can be obtained with the sanulon method [21] as follows,

$$q(\omega) = \frac{T}{1-\exp(-j\omega T)} \left[ \sum_{n=0}^{N} (q(nT) - q(n-1)T)\exp(-j\omega n T) \right]$$  \hspace{1cm} (3.17)

Here, $\omega$ is the angular frequency. $T$ is the sampling interval. In present work $n$ is the 2000 points and $(T)$ depends on time window and number of points per waveform $(N)$. For example, if time window is 2 ns then $T$ is 1 ps 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 25 GHz. The frequency dependent data obtained from the Fourier transform is used to calculate frequency dependent complex reflection coefficient $\rho^*(\omega)$ which is given by equation [22–24],

$$\rho^*(\omega) = \frac{c}{\omega d} \frac{p(\omega)}{q(\omega)}$$  \hspace{1cm} (3.18)

Where, $\omega$ is the angular frequency, $d$ is the pin length, $c$ is the speed of light. $p(\omega)$ and $q(\omega)$ are the fourier transformations of $p(t)$ and $q(t)$ respectively. The complex reflection coefficient spectra are the "raw" data and using this "raw" data complex permittivity can be determined.

### 3.2.2 Measurement of static permittivity

The values of static permittivity of the studied liquid samples and mixtures in pure form as well as their dilute solutions were determined by using "Capacitive Measurement Method" at 2 MHz. Agilent E4980A precision LCR meter with Agilent 16452A liquid test fixture was used for determination of accurate values of static permittivity of the liquid samples. The capacitances of the liquid dielectric test fixture with and without samples were measured. The test fixture correction coefficient was also considered to cancel the stray capacitance during the determination of the $\varepsilon_0$ values. The static permittivity is then determined from the relation [25],

$$\varepsilon_0 = \alpha \frac{C_p}{C_0}$$  \hspace{1cm} (3.19)
Where, \( c_0 \) and \( c_p \) are the capacitances of the free space and with sample respectively. \( \alpha \) is the correction coefficient of the cell. The snapshot of the actual experimental set up of precision LCR meter is as shown in Figure 3.8. The temperature was maintained constant with constant temperature water bath as shown in Figure 3.9. The measurement accuracy of static permittivity is \( \pm 0.3\% \), which was estimated by the calibration of the cell with the standard liquids by using their literature values.

![Figure 3.8 Actual snapshot of LCR meter which was used for measurement.](image)

![Figure 3.9 Constant temperature water bath.](image)
3.2.3 Refractive index

The refractive index is a very important optical constant used to determine molar refraction and purity of sample. The small change in molar refraction affects the molecular packing and molecular interaction [26 –29].

The speed of the light in a vacuum is always same but when light travels through and other medium it travels more slowly as it is reemitted by the atoms in the material and constantly being absorbed. The ratio of the speed of light (c) in a vacuum to the speed of light (v) in another material is defined as the refractive index (n) of the material.

\[
\text{Refractive index of material } n = \frac{c}{v}
\]  

(3.20)

When a beam of light crosses a boundary from one medium into another its direction of travel as well as its speed changes i.e. it is refracted. (Except the light travel is perpendicular to the boundary of two medium then there is no change in direction). The relationship between the angle of incidence (\(\theta_A\)), speed of light in the two mediums \((V_A \text{ and } V_B)\), angle of refraction (\(\theta_B\)) and the refractive indexes of the two mediums \((n_A \text{ and } n_B)\) is given as,

\[
\frac{V_A}{V_B} = \frac{\sin \theta_A}{\sin \theta_B} = \frac{n_B}{n_A}
\]  

(3.21)

So it is possible to measure the refractive index of the sample by measuring the angle of refraction and knowing the refractive index of the layer that is in contact with the sample, instead of measuring the speed of light in a sample. Refractive index is normally measured by the refractometer using above principle but may be differ in their optical design. In present work of this thesis, Abbe’s refractometer was used for measuring refractive index of the samples.

An Abbe’s refractometer is a bench top refractometer with the highest precision of the different types of refractometer. In the Abbe’s refractometer, the liquid sample is sandwiched in to a thin layer between a refracting prism and an illuminating prism. The refracting prism is made by glass with a high refractive index (e.g. 1.75). It must be cleared that the refractive index of the liquid should be smaller than that of refracting prism so as to allow for the critical angle phenomenon. A beam of light from the sodium source is reflected by mirror and passed through the illuminating prism. In illuminating prism the bottom surface of which is ground (i.e. rough ended like a ground glass joint). So each point on this surface can be thought of...
as generating light rays travelling in all directions and scattered in liquid film at
different angle of incidence.

The photograph of used Abbe’s refractometer set up is shown in Figure 3.10.
The surface of the refractometer prism was cleaned using acetone and this ensured
that no stains or air bubbles were left on the prism surface. The lower prism was lifted
and locked with the upper prism. Moreover, it should be special care was taken to
avoid water absorption in the chemicals because this contamination has an important
effect on refractive index measurement. For getting the maximum illumination
through the telescope, the bottom reflecting mirror was adjusted. The milled drum
was rotated till sharp critical line (boundary line) coincides with the junction of the
crossed graticule index line. By keeping the telescope in the above mentioned position
the corresponding reading of the scale was taken against the index mark. This gives
the refractive index of specimen within accuracy of ±0.0001 in present experimental
set up. Then measurement of refractive index of pure liquids and their binary mixture
at different temperature were taken.

![Figure 3.10 Experimental set up of Abbe’s refractometer.](image)

3.3 Measurement of density

The density of any sample is given by the ratio of its mass to its volume
(kg/m³). The fluid density is a major key in the control of most industrial process
because it gives accurate determination of the quantity and quality of the product. Density is widely used in the characterization of material for both pure and mixtures. The density of liquids is very important to study the specific acoustic impedance, the excess molar volume, viscosity, isentropic compressibility etc.

Density can be measured using several measuring instruments, such as pyknometer, vibration type density meters, hydrometers and also using the method of hydrostatic weighing. In present investigation, density of the pure liquids and liquid mixtures was determined by using a double-arm pyknometer by relative measurement method. The pyknometer having a volume of 10 ml was calibrated with double distilled water and gave an estimated reproducibility of ±0.0001 gm/cm³. The actual snapshot of double-arm pyknometer is shown in Figure 3.11. A digital single pan balance (REPTECH, RA 323, Class 1; Reputed Microsystems, Ahmedabad) having an accuracy of ±0.1 mg was used for the weight measurements. By using the following relation the density of the unknown mixture at any experimental temperature can be determined. The density of water at different temperatures was taken from literature.

\[ \rho = \frac{m \rho_w}{m_w} \text{ gm/ml} \tag{3.22} \]

Where, \( m \) = mass of liquid, \( \rho_w \) = density of water and \( m_w \) = mass of water

![Figure 3.11 Actual snapshot of double-arm pyknometer.](image)
3.4 Measurement of viscosity

In present investigation, an Ostwald’s viscometer of 10 ml capacity was used for the viscosity measurement of pure liquids and liquid mixtures. The viscometer was calibrated with double distilled water immersed in the water bath which was kept at constant experimental temperature. Using a suitable arrangement, the water was sucked above the marked level and then it was allowed to flow freely. The time taken for the flow of water is noted. The water is replaced with a mixture, whose viscosity is to be determined. The time flow of water ($t_w$) and time flow ($t_s$) of solution was measured with digital stop clock having an accuracy of ±0.1 s. The photograph of Ostwald’s viscometer is as shown in Figure 3.12. The temperature of the samples was maintained within ±0.1 K in an electronically controlled thermostatic water bath. The viscosity of the unknown mixture is determined using the relation,

$$\eta = \frac{(p\cdot t_s)}{(p_w, t_w)} \eta_w$$

(3.23)

Where, $\eta_m$, $\rho$, and $t_w$ are respectively the viscosity, density and time of flow of water. $p$ and $t_s$ are respectively density and time of flow of mixture.

![Ostwald's viscometer](image)

Figure 3.12 Ostwald’s viscometer

3.5 Measurement of ultrasonic velocity

The speed of sound waves were measured by using digital pulse echo velocity meter [Model no. VCT-70A, Vi Microsystems Pvt. Ltd., Chennai (India)] at a fixed frequency of 2 MHz with an accuracy of ±2 m/s. electronically operated digital constant temperature bath for ultrasonic [Supplied by Vi Microsystems Pvt. Ltd., Chennai (India)] was used to circulate water through the double walled measuring cell.
made up of steel containing the experimental solution at the desired temperature. The snapshot of the photograph of the ultrasonic velocity meter is as shown in Figure 3.13.

![Figure 3.13 Snapshot of Ultrasonic velocity meter.](image)

3.6 Evaluation of relaxation time, dipole moment and distribution parameters

The measured values of dielectric constant ($\varepsilon'$) and dielectric loss ($\varepsilon''$) is used to evaluate the dielectric relaxation time ($\tau_0$), distribution parameter ($\alpha$) and dipole moment ($\mu$). There are several methods available in literature to determine these parameters. The methods used for evaluation of these parameters used in Chapter VI are described here:

3.6.1 Concentration variation method at a single frequency

The difficulty with frequency variation method is that for accurate determination of relaxation time and distribution parameter nearly a complete band of microwave frequencies is required which is rarely available in laboratories. To overcome this difficulty a concentration variation method [30–31] at a single frequency are suggested by Gopal Krishna [32] and Higasi [33].

3.6.1.1 Gopal Krishna’s method

In this method the relaxation time and dipole moment are determined. The main advantage of this method over other method consists in eliminating the determination of density of the solution and further when the value of relaxation time alone is required even the concentration of the solute in the non polar solvent need not be determined. This method is based on Debye equation.
For dilute solutions, complex permittivity $\varepsilon^*$ (as a function of frequency) can be,

$$\frac{\varepsilon^*-1}{\varepsilon^*+2} = \frac{\varepsilon_\infty-1}{\varepsilon_\infty+2} + \frac{4\pi\mu^2}{9KTV \left(1+j\omega\tau\right)}$$

(3.24)

Where $n$ is the number of polar molecules per c.c.

Putting $\varepsilon^* = \varepsilon' - j\varepsilon''$ and splitting the above equation into real and imaginary parts,

$$\frac{\varepsilon'+\varepsilon'^2+\varepsilon''^2-2}{(\varepsilon'+2)^2+\varepsilon''^2} = \frac{\varepsilon_\infty-1}{\varepsilon_\infty+2} + \frac{4\pi\mu^2}{9KTV \left(1+\omega^2\tau^2\right)}$$

(3.25)

$$\frac{3\varepsilon''}{(\varepsilon'+2)^2+\varepsilon''^2} = \frac{4\pi\mu^2}{9KTV \left(1+\omega^2\tau^2\right)} \omega\tau$$

(3.26)

Substituting,

$$X = \frac{\varepsilon'+\varepsilon'^2+\varepsilon''^2-2}{(\varepsilon'+2)^2+\varepsilon''^2} \quad \text{and} \quad Y = \frac{3\varepsilon''}{(\varepsilon'+2)^2+\varepsilon''^2}$$

in equation (3.23) and putting $P = \frac{(\varepsilon_\infty-1)}{(\varepsilon_\infty+2)}$.

It can be gets

$$X = P + \frac{1}{\omega\tau} Y$$

(3.27)

$P$ may be known as fairly constant at low concentrations, its variation with concentration will be negligible in comparison to the error in values of $X$ and $Y$ due to experimental error in $\varepsilon'$ and $\varepsilon''$ at a microwave frequency. Hence if $X$ is plotted against $Y$ then the reciprocal of the slope of straight line so obtained will be equal to $\omega\tau$ from which $\tau$, the relaxation time of the solute molecule in solution can be calculated from the following equation,

$$\tau_G = \frac{1}{2\pi f} \left(\frac{dY}{dX}\right)$$

For estimation of $\mu$, it can write the equation (3.23) as,

$$X = P + kWd_{12}$$

(3.28)

In which

$$k = \frac{4\pi N\mu^2}{9KTM \left(1+\omega^2\tau^2\right)}$$

$N = \text{Avogadro's constant (} N = nM/ d_{12}W)$

Where, $M$ is the molecular weight of the polar substance, $W$ is the weight fraction of the solute and $d_{12}$ is the density of the solution. At low concentration $d_{12}$ varies linearly with $W$ and may be written as,

$$d_{12} = d_0 (1 + \alpha W)$$

(3.29)
Where, \( d_0 \) is the density of the solvent.

From the graph between \( X \) and \( W \), the slope \( \left( \frac{dX}{dW} \right)_{W \to 0} \) gives \( kd_0 \).

\( M \) can be calculated using equation (3.26).

This method is more suitable for medium and high loss liquids because the variations in \( P \) are negligible as compared to \( X \) and \( Y \) and hence it can be considered as constant. For low loss liquids the variation of \( P \) are comparable to those in \( X \) and \( Y \), so results obtained are not accurate.

**3.6.1.2 Higasi's method**

Higasi [33] has suggested that the value of relaxation time \( \tau_0 \) and distribution parameter \( \alpha \) can be found by measured values of \( a' \) and \( a'' \) at a single frequency in the dispersion region.

The Cole–Cole equation can be written in terms of slopes as,

\[
\frac{a' - a_\infty}{a_0 - a_\infty} = \frac{1}{(1 + j\omega \tau_0)^{1-\alpha}}
\]

Substitute the value of \( a^* = a' - ja'' \) and separating into real and imaginary parts,

One gets,

\[
\tau_0 = \frac{1}{\omega} \left( \frac{A^2 + B^2}{C^2} \right)^{1/(1-\alpha)}
\]

\[
1 - \alpha = \frac{2}{\pi} \tan^{-1} \frac{A}{B}
\]

Where,

\[
A = a''(a_0 - a_\infty)
\]

\[
B = (a_0 - a')(a' - a_\infty) - a''^2
\]

\[
C = (a' - a_\infty)^2 + a''^2
\]

For a system of single relaxation time (\( \alpha = 0 \)), the Cole–Cole equation reduces to Debye equation and it may be written as,

\[
\frac{a' - a_\infty}{a_0 - a_\infty} = \frac{1}{(1 + j\omega \tau_0)}
\]

Putting \( a^* = a' - ja'' \) and separating in to real and imaginary parts,

\[
\frac{a' - a_\infty}{a_0 - a_\infty} = \frac{1}{(1 + \omega^2 \tau^2)}
\]

\[
\frac{a}{a_0 - a_\infty} = \frac{\omega \tau}{(1 + \omega^2 \tau^2)}
\]

\[
a = a_0 - \tau \left( \omega a' \right)
\]
\[ a^* = a_\infty + \frac{i}{\tau} \left( \frac{a'}{a_\infty} \right) \tag{3.40} \]

Hence,
\[ \tau = \frac{1}{\omega} \sqrt{\frac{a_0 - a}{a - a_\infty}} \tag{3.41} \]

or \[ \tau = \frac{1}{\omega} [A \pm \sqrt{A^2 - 1}] \tag{3.42} \]

Where,
\[ A = \frac{a_0 - a_\infty}{2a^*} \tag{3.43} \]

From equation (3.37),
\[ \tau = \frac{1}{\omega} \left[ \frac{a^*}{a_0 - a_\infty} \right] \tag{3.44} \]

and from equation (3.38),
\[ \tau = \frac{1}{\omega} \left[ \frac{a_0 - a}{a} \right] \tag{3.45} \]

If Debye equation for single relaxation time is valid for the system under the consideration and further the measurements are sufficiently accurate \( \tau \) can be evaluated using any of the above equations.

The values of dipole moment (\( \mu \)) calculated by Higasi’s equation [34] as,
\[ \mu_H = \left[ \left( \frac{27kT}{4\pi N} \right) \left( \frac{M}{(\epsilon_1 + 2)^2 \delta} \right) \right]^{\frac{1}{2}} \left( a_0 - a_\infty \right)^{\frac{1}{2}} \tag{3.46} \]

Where, \( \epsilon_1 \) and \( \delta_1 \) are the values of permittivity and density of non-polar solvent, respectively. \( T \) is the absolute temperature, \( N \) is Avogadro’s constant and \( M \) is the molecular weight of solute.

\( M \) is given by the relation,
\[ M = \frac{(X_1 M_1 m)}{[(1-X_1)m_1]} \tag{3.47} \]

Where, \( X_1 \) is mole fraction of non-polar solvent, \( M_1 \) is molecular weight of non-polar solvent; \( m \) and \( m_1 \) are the weights of the polar solute and non-polar solvent, respectively in the solution.

The dipole moment (\( \mu \)) value calculated using Guggenheim’s equation [35],
\[ \mu_G = \left[ \left( \frac{27kT}{4\pi N} \right) / (\epsilon_1 + 2) (n_2^2 + 2) \right] \left( \frac{\Delta}{C \rightarrow 0} \right)^{\frac{1}{2}} \tag{3.48} \]

Where, \( \Delta = (\epsilon_{12} - n_{12}^2) - (\epsilon_1^2 - n_1^2) \)

Subscript 1 indicates non-polar solvent, 12 is the solution, \( C \) is the concentration of solute in mole/cc and \( n \) is the refractive index.
\( \frac{\Delta}{C} \) is the slope of the \( \Delta \) versus \( C \) plot for the concentration of \( C=0 \).

For the binary mixture of solute \( C \) is determined by the relation, \( C = \left( \frac{m_{d12}}{M_{m12}} \right) \).

### 3.7 Evaluation of Physico–Chemical parameters

Physico–Chemical properties derived from the measurement of speed of sound, density and viscosity of liquid and their mixtures are useful in understanding the nature of intermolecular interaction and provide important information with which to speculate the molecular liquid structure. From these measured parameters following parameters can be calculated:

#### 3.7.1 Acoustic impedance (\( Z \))

Sound travels through materials under the influence of sound pressure, because molecules or atoms of a liquid are bound elastically to one another. The specific acoustic impedance \( Z \) is related to the density and ultrasonic velocity by the relation is [36],

\[
Z = U \rho \text{ kgm}^{-2} \text{s}^{-1}
\]

(3.49)

Acoustic impedance is important (i) in determination of acoustic transmission and reflection at the boundary of two materials having different acoustic impedance (ii) in design of ultrasonic transducers and (iii) for assessing absorption of sound in a medium.

#### 3.7.2 Effective molecular weight (\( M_{\text{eff}} \))

The effective molecular weight is calculated by using the equation (Ravinder Reddy and Linga Reddy 1999),

\[
M_{\text{eff}} = X_1 M_1 + X_2 M_2
\]

(3.50)

Where \( M_1 \) and \( X_1 \) are molecular weight and the mole fraction of solute and \( M_2 \) and \( X_2 \) are the corresponding quantities of the solvent respectively.

#### 3.7.3 Adiabatic compressibility (\( \beta \))

It is a measure of intermolecular association or dissociation repulsion. Singh and Kalsh [37] showed that adiabatic compressibility is a independent of temperature and pressure for unassociated and weakly associated molecules. The structural change of the molecules in the mixture takes place due to the existence of electrostatic field between the interacting molecules. Thus, the structural arrangement of the molecules results in a considerable change in adiabatic compressibility.

The adiabatic compressibility in a liquid mixture can be calculated by employing ultrasonic velocity and density using the relation [38],

\[
\beta = \frac{1}{\rho} \left( \frac{d\rho}{dP} \right)
\]
3.7.4 Intermolecular free length \( (L_f) \)

The free length is the distance between the surfaces of the neighboring molecules. Generally, when the ultrasonic velocity increases, the values of intermolecular free length are decreases. The decrease in intermolecular free length indicates the interaction between the solute and solvent molecules due to the structural arrangement in the neighborhood of constituent ions or molecules gets affected considerably. The adiabatic compressibility can be calculated using the Jacobson’s empirical relation [39],

\[
L_f = K(\beta)^{1/2} \times 10^{-10} \text{ m}
\]

Where, \( K \) is temperature dependent Jacobson constant.

3.7.5 Acoustic relaxation time \( (\tau) \)

Relaxation time and absorption coefficient are directly correlated. The absorption coefficient of a sound wave is the result of the time lag between the passing of the ultrasonic wave and the return of the molecule, to their equilibrium position. It is calculated using the relation [40],

\[
\tau = \frac{4\eta}{3U^2\rho} \text{ sec}
\]

3.7.6 Internal pressure \( (\pi_i) \)

The internal pressure is a energy-volume coefficient and it is a measure of the resultant force of attraction and force of repulsion between the interacting components in the mixture. Its measurement is significant in the evaluation of thermodynamic properties of liquids because it is closely related to ultrasonic velocity, free volume, viscosity, latent heat of vaporization and compressibility in the liquid phase. By considering the validity of the internal pressure, a simple relation using easily measurable parameters were given by Suryanarayana [41] as,

\[
\pi_i = bRT \left[ \frac{\eta}{U} \right]^{1/2} \left[ \frac{\rho^3}{M_{\text{eff}}^2} \right] \text{ Pa}
\]

Where \( b \) is the cubic packing factor which is assumed to be 2 for all the liquids and solutions, \( K \) is the temperature dependent constant, \( R \) is the gas constant, \( T \) is the absolute temperature, \( \eta \) is the viscosity in Ns/m\(^2\), \( U \) is the ultrasonic velocity in m/s and \( \rho \) is the density in kg/m\(^3\) of the liquid mixture.
3.7.7 Molar Volume ($V_m$)

The molar volume can be calculated using the following formula [42]

$$V_m = \frac{M_{\text{eff}}}{\rho} \text{ m}^3 \text{ mol}^{-1} \quad (3.55)$$

Where $M$ is the effective molecular weight and $\rho$ is the density of the solution.

3.7.8 Free volume ($V_f$)

Free volume is defined as the average volume in which the centre of the molecules can move inside the hypothetical cell due to the repulsion of surrounding molecules. Free volume can be calculated by different methods. Suryanarayana and Kuppusamy [43] on the basis of dimensional analysis, obtained an expression for free volume in terms of experimentally measurable parameters like ultrasonic velocity and viscosity and is given by,

$$V_f = \left[ \frac{M_{\text{eff}} U}{K\eta} \right]^\frac{3}{2} \text{ m}^3 \text{ mol}^{-1} \quad (3.56)$$

Where $M_{\text{eff}}$ is the effective molecular weight, $K$ is the temperature dependent constant and its value is $4.28 \times 10^9$.

3.7.9 Gibb’s free energy ($\Delta G$)

The acoustic relaxation time ($\tau$) for a given transition is related to the activation energy. The variation of acoustic relaxation time ($\tau$) with temperature ($T$) can be expressed in the form of Eyring’s rate process theory [44],

$$\frac{1}{\tau} = \left[ \frac{kT}{h} \right] \exp \left[ - \frac{\Delta G}{kT} \right]$$

The above equation can be rearranged as,

$$\Delta G = (kT) \ln \left[ \frac{kT\tau}{h} \right] \quad (3.57)$$

Where, $k$ is Boltzmann’s constant ($1.38 \times 10^{-23}$ J/K), $h$ is plank’s constant ($6.6 \times 10^{-34}$ Js), $T$ is absolute temperature and $\tau$ is the acoustic relaxation time.

3.7.10 Excess parameters

For studying the non ideality of the liquid mixtures the difference between the experimental and ideal mixture values, namely excess parameters of all the acoustical parameters were determined [45]. The excess values have been obtained by subtracting the ideal value from the experimental value. The excess values for all the parameters were calculated using the equation,

$$A^E = A_{\text{mix}} - \left( \sum x_i A_i \right) \quad (3.58)$$
References


13. Tektronix DSA8200 Sampling Oscilloscope user’s guide.

14. 80E08 TDR Plug-in Modules user and Programmer’s guide.


