CHAPTER III

EXPERIMENTAL METHODS AND EVALUATION OF DIFFERENT PARAMETERS

This chapter has been divided in three sections. Section I reviews the experimental techniques of measuring the permittivity at different frequencies, section II describes the experimental set-up and measuring procedures used in the present investigations. The methods of evaluation of the various dielectric parameters has been described in section III.

SECTION - I

Brief Review

A macroscopic description of the electrical properties of a dielectric is provided by the complex permittivity. The significant external factors on which complex permittivity depends, are the frequency, the temperature, the pressure and the intensity of applied electric fields. The choice of method for measurement of complex permittivity depends mainly on the frequency. A variety of methods exist for the measurement of permittivity and dielectric loss, but the particular method adopted for the measurement is determined by the nature of the specimen and the frequency at which
the measurement is done. According to the frequency
experimental methods can be divided as follows:

3.1.1 Lumed Circuit Method:

Lumed circuit method, are used in the determination
of the complex permittivity of dielectrics over the
frequency range from zero to 200MHz\(^{1-5}\). Neither the
complex permittivity nor its rectangular components,
the dielectric constant and loss factor, are determined
directly. The working of these methods is based on
the impedance measurement with and without the dielec-
tric material in the circuit. According to frequency
this method can be subdivided as follows:
i) Direct current method (low frequency range, 0 to 10Hz)
ii) Bridge method (medium frequency range, 1Hz to 10MHz)
iii) (a) Resonance method (High frequency range)
    (b) Heléodyne beat method (100KHz to 200MHz

In the medium frequency range the capacitance
and the dissipation factor of a dielectric specimen
are obtained by a null method, involving some type
of capacitance bridge; dielectric constant and loss
factor are calculated therefrom. At higher frequencies,
where the errors of a capacitance bridge become exces-
sive, a resonant circuit is used. The capacitance
of the specimen is still measured by a substitution method, but the loss component is found from the width of the resonance curve.

The lumped circuit methods described above cannot be used at microwave frequencies, due to the skin effect and radiation losses. At higher frequencies when the sample extends to an appreciable part of wave length, the permittivity is measured by methods using distributed circuit.

3.1.2 Distributed Circuit Methods:

A large number of methods are used for measurement of complex permittivity of liquids at microwave frequencies. The following methods are widely used.

i) Microwave bridge method
ii) Cavity and cavity perturbation method
iii) Transmission line method
iv) Free space method

1) Microwave Bridge Method:

Microwave analogs of radio frequency impedance bridges have been constructed and used by several workers $^6$-$^8$ for measurement of complex permittivity
of liquids. However, these bridges are most useful for the region below 3GHz. The microwave bridges have the advantage that null detection is used and the uncertainty regarding the square law response of the detector is avoided. The main difficulty is construction of impedance standards, i.e., variable attenuators and phase shifters.

ii) Cavity and Cavity Perturbation Method:

Cavity and cavity perturbation methods\(^9\)-\(^{10}\) are highly sensitive and quite versatile with regard to the type of sample which can be measured by their use. It is very sensitive method so, very stable power sources and accurate frequency measuring equipment is necessary when these techniques are employed. Special, preferably high \(Q\), cavities must be constructed and, depending on the exact method, lengthy computations may have to be performed. Most often these methods are of the frequency variation type, although sometimes cavity length variation is used. The advantage of this method is that, it requires small amount of liquids and give accurate results.
iii) Transmission Line Method:

The basic requirement of transmission line method is to determine the phase factor $\beta$ and attenuation constant $\alpha$ of the electromagnetic wave propagating in the dielectric medium. In these methods the power from the microwave oscillator is transmitted through a co-axial line or through a waveguide before it is incident on the liquid sample confined in a cell of the same dimension as of the transmission line wave guide. When the electromagnetic wave is reflected from the short-circuited termination at the other end of the dielectric cell, there are two sets of travelling waves-incident and reflected-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 measurement of the dielectric constant and loss. The dielectric cell may have fixed lengths or there may be arrangement for varying the length of the liquid
column with the help of a movable plunger forming the short-circuited termination. The following alternative procedures are followed.

(a) By Impedance Measurement:

The first method utilizes the measurements of the terminal impedance of a shorted waveguide filled with a dielectric material. The standing wave ratio is measured in the air filled space of the wave guide 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 the co-axial line or wave guide 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 measurement of $\beta$ and $\alpha$ by following either the graphical method of Roberts and Von Hippel$^{11}$ or the analytical method of Cripwell and Sutherland$^{12}$.

(b) Measurement with Variable Length of the Liquid Column:

The second method utilizes variable length of the liquid column with the help of a movable shorting plunger in the dielectric cell. The
value of the phase constant $\beta$ is evaluated by measuring the wavelength in the liquid sample and $\alpha$ by measuring either the amplitude of reflected wave or the standing wave ratio for different sample lengths.

For a liquid sample in a wave guide if the wavelength and attenuation constant in the dielectric sample are known, then the permittivity $\varepsilon^i$ and the loss factor $\varepsilon^{\|}$ is calculated from the following relations\textsuperscript{13}.

\[
\varepsilon^i = \left( \frac{\lambda_o}{\lambda_c} \right)^2 + \left( \frac{\lambda_o}{\lambda_d} \right)^2 \left[ 1 - \left( \frac{\alpha \lambda_d}{2\pi} \right)^2 \right]
\]

\[
\varepsilon^{\|} = \frac{1}{\pi} \left( \frac{\lambda_o}{\lambda_d} \right)^2 \alpha \lambda_d
\]

where $\lambda_o$ is the free space wave length, $\lambda_c$ is the cut-off wavelength, $\lambda_d$ is the wavelength in the dielectric sample in the cell and $\alpha$ is attenuation constant in it.

Thus the problem of finding the permittivity and dielectric loss reduces to the measurement of (i) wavelength in the sample and (ii) the amplitude of the reflected wave or voltage standing wave ratio from which $\alpha$ can be calculated. Both the procedures are briefly described 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 the micawindow. 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 into the liquid column and deflections are noted at suitable intervals till the plunger touches the micawindow. The plot of the reflected power against the liquid length exhibits a series of maxima and minima. Wavelength in the liquid, $\lambda_d$, and the attenuation per wave length $\propto \lambda_d$, can be calculated from the plot as suggested by Laquer and Smyth$^{14}$.

(ii) By Estimating V.S.W.R.:

The output 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 a V.S.W.R. meter. When the shorting plunger is moved in the liquid cell as described earlier, the V.S.W.R. meter shows maxima and minima. The average distance between consecutive minima gives $\frac{\lambda d}{2}$.

The attenuation constant for liquids with $\tan \delta > 0.1$ can be determined by Poley's method. 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. The V.S.W.R. can be determined directly when a V.S.W.R. meter is available. In the alternative, the width at twice minimum power points is determined and used to calculate the inverse V.S.W.R. $\xi_n$ from the simplified Robert and Von Hippel relation.

$$\xi_n = \frac{\sin \theta}{\sqrt{1 + \sin^2 \theta}}$$  \hspace{1cm} (3.2)

where $\theta = \frac{\pi \cdot \Delta x}{\lambda_g}$. Here $\Delta x$ is the distance between the points of twice minimum power.
If $s_m$, $s_n$ and $s_\infty$ 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 $s_m/s_n$ and $s_m/s_\infty$ can be given by the following relations suggested by Poley\textsuperscript{15}.

$$
\frac{s_m}{s_n} = \frac{\tanh \left[ m\pi \tan (\Delta/2) \right]}{\tanh \left[ n\pi \tan (\Delta/2) \right]} \\
\frac{s_m}{s_\infty} = \tan \left[ m\pi \tan (\Delta/2) \right]
$$

(3.3)

where $\pi \tan (\Delta/2) = \alpha \lambda_d/2$

For fixed values of $m$ and $n$ arbitrary values are assigned to $\pi \tan (\Delta/2)$ and two curves are drawn using (3.3). Next the value of $m$ and $n$ are changed and for each set of values of $m$ and $n$ arbitrary values to $\pi \tan (\Delta/2)$ are given and curves are drawn for each set as described earlier. Once curves for $s_m/s_n$ and $s_m/s_\infty$ are drawn corresponding to different values of $\pi \tan (\Delta/2)$, these curves can be used to read directly the value of $\pi \tan (\Delta/2)$ from the experimentally measured values of $s_n$, $s_m$ and $s_\infty$. Thus $\lambda_d$ and $\alpha \lambda_d$ being known, $\varepsilon'$ and $\varepsilon''$ can be calculated from the equation (3.1).
For liquids with low dielectric loss such as dilute solution of a polar substance in a non-polar solvent, $\lambda_d$ is determined by the method described earlier. But the method for determination of attenuation constant is different. Heston et al. pointed out that V.S.W.R. of low loss material is large and sensitive to small change in reflection co-efficient near unity which may be utilized to measure the attenuation constant of low loss dielectric.

In the 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

$$Z(0) = \frac{g + j\tan\left(\frac{2\pi X_0}{\lambda_g}\right)}{1 + j\tan\left(\frac{2\pi X_0}{\lambda_g}\right)} Z_a$$

(3.4)

where $g = \frac{E_{min}}{E_{max}}$, $X_0$ is the distance of the first minima from the interface, $\lambda_g$ is the wavelength in the air filled wave guide and $Z_a$ is the characteristic impedance of the air medium.
If the length of the dielectric column is taken as integral multiple of \( \lambda_d/2 \) and terminated by a short circuit plunger as shown in Fig.3.1(a) or odd integral multiple of \( \lambda_d/4 \) in case of open circuited termination Fig.3.1(b), then the value of \( X_0 \) is zero and hence

\[
Z(0) = 0 \quad \text{since} \quad Z_\alpha = 1 \quad (3.5)
\]

we know that

\[
Z(0)_{sc} = Z_d \tanh \gamma_d \quad (3.6)
\]

therefore,

\[
\beta = Z_d \tanh \gamma_d \quad (3.7)
\]

where \( Z_d, \gamma \) and \( d \) are the characteristic impedance, propagation factor and length of the dielectric medium respectively.

\[
Z_d = \lambda_d / \lambda_g
\]

\[
d = n \lambda_d / 2
\]

where \( \lambda_g \) is the guide wave length.

Thus the equation (3.7) reduces to

\[
\beta = Z_d \left( \frac{n \alpha \lambda_d}{2} \right) = \frac{n \alpha \lambda_d^2}{2 \lambda_g} \quad (3.8)
\]

Equation (3.8) represent a straight line between
\( \lambda_d^2 \propto / 2 \lambda_g \)

Thus,

\[
\alpha = \frac{\alpha \lambda g}{\lambda_d^2} \left( \frac{d\phi}{d\eta} \right)
\]

(3.9)

substituting this value of attenuation constant \( \alpha \) in equation (3.1) and for low loss liquid \( (\alpha \lambda_d)^2 \) is very small compare to one so it can be neglected. Therefore, we can write the final equation for \( \varepsilon^1 \) and \( \varepsilon^{11} \) as follows:

\[
\varepsilon^1 = \left( \frac{\lambda_0}{\lambda_c} \right)^2 + \left( \frac{\lambda_0}{\lambda_d} \right)^2
\]

(3.10)

and

\[
\varepsilon^{11} = \frac{\alpha}{\pi} \left( \frac{\lambda_0}{\lambda_d} \right)^2 \left( \frac{\lambda g}{\lambda_d} \right) \left( \frac{d\phi}{d\eta} \right)
\]

(3.11)

Thus the values of dielectric permittivity \( \varepsilon^1 \) and dielectric loss \( \varepsilon^{11} \) for low loss dielectrics can be evaluated by measuring the quantities \( \lambda g , \lambda_d \) and \( \frac{d\phi}{d\eta} \).

The advantage of this method over other methods is that it eliminates the wave guide and plunger losses which sometimes are comparable to the losses in dielectric. We have, therefore, adopted this method for the short-circuited termination.
(iv) Free Space Method:

At higher microwave frequencies, i.e., millimeter wave region, where, waveguide methods become difficult due to small dimensions of waveguide and increased metallic losses, free space methods are employed. These methods were initially developed\textsuperscript{17-20} for determining the complex permittivity of dielectric material in sheet form. These methods have been extended to millimeter region by several workers\textsuperscript{21-26} for liquids.

SECTION - II
Experimental Set-up and Measurement Procedures

The experimental part of this investigation involves the measurements of the following characteristics of polar molecules and their binary mixtures in dilute solutions:

i) Permittivity and dielectric loss at microwave frequencies

ii) Static permittivity

iii) Refractive index

iv) IR absorption
3.2.1 Permittivity and Dielectric loss at Microwave Frequencies:

Microwave benches operating at frequencies 8.98GHz and 19.64GHz have been used for making the measurements of permittivity and dielectric loss. They are shown in Figs. 3.2 and 3.3. V.S.W.R. in each case has been measured by a slotted lines. The cell containing the experimental liquid is kept vertical and connected to the main line by an E-plane bend. In the microwave bench, 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 crystals used with X-band and K-band for detection are 1N23 and 1N26 respectively. The energy waves from the Klyston source enter the waveguide and pass through the liquid and are reflected back by a short-circuiting plunger. Thus a standing wave-pattern is set up.
**Fig. 3.2 X-band set-up**
Fig. 3.3 K-band set-up
With the liquid in the cell and the plunger at the cell window, 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 two successive minima is equal to $\frac{\lambda_d}{2}$. For low loss liquids $\varepsilon^l$ can be calculated by the equation.

$$\varepsilon^l = \left( \frac{\lambda_0}{\lambda_c} \right)^2 + \left( \frac{\lambda_0}{\lambda_d} \right)^2$$  (3.12)

The dielectric loss is measured by bringing the plunger down to the window and minimizing the power with the probe. Then the plunger is brought up to various minimum positions, i.e., liquid lengths equal to $n \frac{\lambda_d}{2}$, where $n$ is an integer and the inverse standing wave ratio $\xi$ is measured from the width at double minimum power points (Fig. 3.4). The value of $\xi_n$, thus found, is corrected because of the approximation involved in deriving the equation $\xi = \frac{\pi \cdot \Delta \chi}{\lambda_g}$. A curve showing subtraction factor for different values of $\frac{\pi \cdot \Delta \chi}{\lambda_g}$ is given in Fig. 3.5. To obtain the absolute value of $\xi_n$, correction has to be applied for wall losses and losses in bends and imperfections in the short.
STANDING WAVE PATTERN NEAR A MINIMUM

Fig. 3.4

CORRECTION CURVE FOR $\beta$

$\beta_{\text{meas}} = \frac{\pi \Delta x}{\lambda g} - \text{S.F.}$

Fig. 3.5
In the present case since the slope of the curve \( \sigma n \) vs \( n \) is used for calculating \( \varepsilon'' \), the correction is not necessary. The dielectric loss \( \varepsilon'' \) is given by

\[
\varepsilon'' = \frac{\sigma}{11} \left( \frac{\lambda_0}{\lambda_d} \right)^2 \left( \frac{\lambda_f}{\lambda_d} \right) \left( \frac{\partial \sigma}{\partial n} \right)
\] (3.13)

The estimated accuracy of the above measurements for \( \varepsilon' \) and \( \varepsilon'' \) is 1 per cent and 5 per cent respectively.

3.2.2 Measurement of Static Permittivity:

Static permittivity of solutions was measured by a type 1620A capacitance measuring assembly. It consists of the type 1615A capacitance bridge with the type 1311A audio oscillator and the type 1232A tuned amplifier and null detector. A elementary schematic diagram of the capacitance bridge is shown in Fig.3.6. It is essentially a transformer-ratio bridge of the type that uses a single decade of transformer voltage division and multiple, fixed standard capacitors to provide six decades of resolution in capacitance. The transformer ratio arms gives higher accuracy, resolution and stability in capacitance measurements at audio frequencies in comparison to resistive ratio arms. The measurements were made at 10KHz frequency.
and the accuracy of the measurement was ±0.01%.

The dielectric cell used in this investigation was fabricated in the workshop of Gujarat University and is shown in Fig.3.7. It is a co-axial cylindrical condenser. The distance between the two cylinders (about 1 mm) was kept constant by fixing quartz glass rods between the two co-axial cylinders. The cell is placed in a double walled pyrex glass container and water was circulated to maintain constant temperature. About 25 ml of the liquid completely immerse the two cylinders.

The cell is calibrated using liquids of known static permittivity. Let -

- $C_E$ be the capacity of the empty cell and leads
- $C_K$ be the capacity of connecting leads
- $C_C$ be the capacity of the empty cell
- $C_L$ be the capacity of the cell filled with the liquids

we can write

$$C_E = C_K + 1.C_C$$  \hspace{1cm} (3.14)

and

$$C_L = C_K + \varepsilon_0 C_C$$  \hspace{1cm} (3.15)

where $\varepsilon_0$ is the static permittivity of the liquid.
Fig. 3.6 Capacitance Bridge (Type 1615A)
Fig. 3.7 Dielectric cell

Quartz glass rod
Coaxial metal cylinders

Fig. 3.8 Temperature control unit

230V a.c.
Hence $\varepsilon_0 = \frac{C_L - C_E}{C_C} + 1$ \hspace{1cm} (3.16)

3.2.3 Description of Temperature Control Device:

The temperature of dielectric cells used for measurements of complex permittivity at microwave frequencies and static permittivity at 10 KHz was maintained at constant by a automatic temperature controlled device, developed in this laboratory (Figure 3.8). It consists of TRIAC and thermometer switch. TRIAC is controlled rectifier which can be switched on in both positive and negative half cycle of a.c. power. Thermometer switch consist of thermometer with mercury column and a set screw. One contact of the wire is taken from mercury column and other from set screw, which are connected between point A and point B. The desired temperature of the water bath can be adjusted by setting the screw in the mercury column. If the set temperature with the screw is more than the actual temperature (temperature of water bath), than there is no contact of mercury in column with the set screw. It provides high impedance and the device will works as "open switch". As the temperature increases, the height of mercury in column will increase. When set
temperature is equal to actual temperature (temperature of water bath), mercury will touch the set screw and device will work as "close switch".

The 230 a.c. voltage is applied between $MT_2$ and $MT_1$ of TRIAC through heater coil and neon lamp is connected across the heater. Thermometer switch is connected between gate and $MT_1$ terminal of TRIAC. Here resistance $R_G$ is used to trigger the TRIAC. Triggering is synchronized with a.c. voltage waveform and by selecting the proper value of $R_G$, the a.c. power through the coil can be controlled. The RC circuit is a protector circuit for TRIAC known as snubber circuit.

When the thermometer switch is open, the TRIAC will be fired through the coil. It remains ON, till the voltage between $MT_2$ and $MT_1$ becomes zero, i.e., up to end of cycle. Due to current passes through heater, the heater starts its heating process and the temperature of water bath go on increasing. When temperature of water bath will be equal to set temperature, the thermometer switch will close and the potential of the gate and $MT_1$ will be equal. The TRIAC
will offer a very high impedance. Now, the current will not pass through the heater coil and the heating action will be stopped by heater.

In short, when the temperature switch (Ts) is open, TRIAC is in ON mode, heater is ON and neon lamp lights. When temperature switch is close TRIAC is in OFF mode, heater is OFF and neon turns OFF.

3.2.4 Measurement of Refractive Index:

Refractive index of solution for sodium D-line has been measured by a direct reading Abbe's refractometer having an accuracy of 0.1 percent.

3.2.5 Infrared Absorption:

Infrared spectroscopy is one of the most powerful analytical techniques, which offers the possibility of chemical identification. One of the most important advantages of IR spectroscopy over the other usual methods of structural analysis is that it provides useful information about the structure of molecules quickly. This method can solve many problems in organic
chemistry and co-ordination chemistry, while in some other problems, infrared data advantageously complement the results obtained by other methods.

The technique is based upon the simple fact that a chemical substance shows marked selective absorption in the infrared region. After absorption of IR radiations, the molecules of a chemical substance vibrate at many rates of vibration, giving rise to close packed absorption bands, called an IR absorption spectrum, which may extend over a wavelength range. Various bands will be present in IR spectrum which will correspond to the characteristic functional groups and bonds present in a chemical substance. Thus, an IR spectrum of a chemical substance is a fingerprint for its identification.

The infrared radiation refers broadly to that region of electromagnetic spectrum which lies between the visible and microwave region. However, this region may be divided into three regions.
(1) The very near infrared region, 1.2 - 2.5 \( \mu m \).
(2) The near infrared region, 2.5 - 25 \( \mu m \).
(3) The far infrared region, 25 \( \mu m \) to 300-400 \( \mu m \).
But, mostly the IR spectra is taken in the range from 2.5 to 25 μm or 4000 to 400 wave number (waves per cm), because this range gives the important information about the vibration of a molecule.

The IR absorption of the substances is usually studied by a spectrophotometer. Various types of spectrophotometers are prepared by different companies. In the present study the infrared spectrum of the samples were recorded using double beam spectrophotometer (Perkin-Elmer Model 180). The basic components of an infrared spectrophotometer is shown in Fig.3.9.

A source provides radiation over the whole range of the infrared spectrum, the monochromator disperses the light and then select a narrow wave number range, the energy is measured by a detector and the latter transforms it into an electrical signal, which is then amplified and registered by a recorder.

The various popular sources of IR radiations are:
Fig. 3.9 Block diagram of Spectrophotometer
In the present work Globar source was used for IR studies. It is a rod of silicon carbide (carborundum) which is about 50mm in length and 4mm in diameter. When it is heated to a temperature between 1300 and 1700°C, it strongly emits radiation in the IR region.

The radiation source emits radiations of various frequencies. As the sample in IR spectroscopy absorbs only at certain frequencies, it therefore becomes necessary to select desired frequencies from the radiation source and reject the radiation of other frequencies. This selection has been achieved by means of monochromators. The monochromator performs three functions which are basic to the operation of the instrument (a) it disperses the radiation into its wave number components (b) it restricts the radiation arriving at the detector to a narrow wave number band (c) it maintains the energy incident at the detector at an approximately constant level, when no sample is present throughout the wave number range of the
The energy content of infrared radiation is very low, thus requires a very sensitive means of detection. The function of a detector is to produce an electrical signal which is proportional to the incident radiation intensity over to whole spectral range of the instrument. The various types of detectors used in IR spectroscopy are (i) Bolometers (ii) Thermocouples (iii) Thermistors (iv) Golay cell (v) Photoconductivity cell. The instrument uses thermocouples as detector. It is made by welding together at each end of two wires of different semiconductors materials of high thermoelectric efficiency. If two welded joints are kept at different temperatures, a small electrical potential is developed between two junction which is proportional to the temperature difference of the junctions. The one welded joints (called cold junction) is kept at a constant temperature and is not exposed to IR radiation, but the other welded joint (called hot junction) is exposed to the IR radiation, which increases the temperature of the junction. The temperature difference between two junction generates potential
differences, which depends on how much IR radiation falls on the hot junction.

The electrical potential developed across detector is amplified by the amplifier circuit. This amplified signal is recorded by recorder on a chart.

SECTION - III

3.3(A) Methods for Evaluation of Relaxation Time and Distribution Parameters:

The measured values of dielectric constant \( \varepsilon' \) and dielectric loss \( \varepsilon'' \) is used to evaluate dielectric relaxation time \( \tau \) and distribution parameter \( \alpha \). There are several methods available in literature for this, they can be broadly classified in following categories.

i) Frequency variation method using single concentration

ii) Concentration variation method along with frequency variation

iii) Concentration variation method at single frequency
Since, the present study was carried out in dilute solutions the last two methods were used for evaluation of relaxation time and distribution parameter and will be described here.

(i) Concentration Variation Method along with Frequency Variation:

To avoid dipole-dipole interaction the dielectric relaxation studies are frequently carried out in dilute solutions of polar substance in non-polar solvent. In this method solutions of polar solute in a non-polar solvent is prepared. The permittivity $\varepsilon^1$ and dielectric loss $\varepsilon^{\prime\prime}$ so obtained are plotted against concentration. The plots are linear and can be represented by the following equations:

\[
\begin{align*}
\varepsilon^1 &= \varepsilon_1^{\prime\prime} + a^{\prime\prime}W_2 \\
\varepsilon^{\prime\prime} &= a^{\prime\prime}W_2 \\
\varepsilon_0 &= \varepsilon_{10} + a_0W_2 \\
\varepsilon_\infty &= \varepsilon_{1\infty} + a_\inftyW_2
\end{align*}
\]

(3.17) subscript 1 refers to the pure solvent, $W_2$ is the concentration of the solute in weight fraction and a's are the slopes of the straight lines.
The slopes $a'$ and $a''$ so obtained are plotted to obtain a complex plane plot. Plots of different shapes are obtained from which $\tau$ and $\omega$ or $\beta$ can be calculated.

For rigid molecules obeying Debye equation, the locus of complex plane plot is a semicircle with its centre on real axis, and cuts the real axis at $a_0$ and $a_\infty$. Thus $a_0$ and $a_\infty$ are determined but the value of $\tau$ is not accurately determined. It may be estimated with fair accuracy from the interpolated frequency of the mid-point of the semicircle. An alternative graphical or analytical method for such cases is given by Cole\textsuperscript{27} which is extremely useful and convenient. Debye equation can be written as

$$a^* = a_\infty + \frac{a_0 - a_\infty}{1 + \frac{j}{\omega \tau}} \quad (3.18)$$

Separating real and imaginary parts one gets,

$$a' = a_0 - \tau (\omega a'') \quad (3.19)$$

$$a'' = a_\infty + \frac{1}{\omega} \left( \frac{a''}{\omega} \right) \quad (3.20)$$

The advantage of these equations is that they are linear relations in measured quantities like $a'$, $a''$, and $a''/\omega$ hence, $a_0$, $a_\infty$ and $\tau$ can be obtained.
In general liquid do not conform to Debye behaviour. The complex plane plot falls inside the Debye semicircle having the centre below the real axis. The Cole-Cole equation for dilute solutions becomes,

\[ a^* = a_\infty + \frac{a_0 - a_\infty}{1 + (\frac{\omega \tau_0}{\epsilon})^{1-\xi}} \]  

(3.21)

where \( \xi \) is constant having value between 0 and 1 and is called distribution parameter. The diameter drawn through the centre from \( a_\infty \) makes an angle \( \xi \pi/2 \) with the \( a' \)-axis. The tangent of this angle can be found out from the plot, whence \( \xi \) can be calculated. The most probable relaxation time \( \tau_0 \) can be found out from the relation,

\[ \frac{V}{U} = (\omega \tau_0)^{1-\xi} \]  

(3.22)

where \( V \) and \( U \) are the distance of the experimental point, corresponding to an angular frequency \( \omega \), from \( a_\omega \) and \( a_\infty \) respectively (Fig.3.10).

An alternative method for determining \( \tau_0 \) and \( \xi \) is as follow,
\[ \log\left(\frac{V}{\omega}\right) = (1-\alpha)\log\omega + (1-\alpha)\log \tau_0 \]  

(3.23)

A plot of \( \log\left(\frac{V}{\omega}\right) \) against \( \log\omega \) gives a straight line whose slope is \( (1-\alpha) \) and intercept is \( (1-\alpha)\log \tau_0 \), from which \( \alpha \) and \( \tau_0 \) can be evaluated.

Data for considerable variety of dielectrics are consistent with the logarithmically symmetrical dispersion and absorption dependence on frequency. However, in some cases asymmetric frequency dependence may occur. The complex plane plot in such cases is a skewed arc (Fig.3.11). Cole-Davidson equation for such a distribution may be written as,

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

(3.24)

putting \( a^* = a' - ja'' \) and separating real and imaginary parts, the following relations are obtained.

\[ a' = a_\infty + (a_0 - a_\infty)(\cos\phi)^\beta \cos\beta\phi \]  

(3.25)

\[ a'' = (a_0 - a_\infty)(\cos\phi)^\beta \sin\beta\phi \]  

(3.26)

and \( \tan\phi = \omega\tau_0 \)

Hence, \( \omega\tau_0 = \tan \left[ \frac{1}{\beta} \tan^{-1}\left(\frac{a''}{a' - a_\infty}\right) \right] \)  

(3.27)
Fig. 3.10 Distances of the experimental point 'P'.
An approximate value of $\beta$ can be obtained from the skewed arc in which high frequency side approaches asymptotically a line making an angle $\beta \frac{\pi}{2}$ with the real axis of $a^1$. $\mathcal{Z}_0$ can be calculated from equation (3.27) by substituting the measured values of $a^{\prime\prime}/a^{\prime} - a_\infty$ at a given frequency. The value of $\beta$ is then adjusted within the experimental range for getting constant value of $\mathcal{Z}_0$ from different frequency data. Knowing $\mathcal{Z}_0$ and $\beta$, $T_{av}$ can be calculated as,

$$T_{av} = \mathcal{Z}_0 \beta \tag{3.28}$$

A better method would be to draw normalised curve between $a^{\prime} - a_\infty /a_\infty - a_\infty$ and $a^{\prime\prime} /a_\infty - a_\infty$ for different known values of $\beta$ by varying $\phi$ by fixed amounts. The values of these quantities obtained experimentally are also plotted on the same graph. The value of $\beta$ can be found out from the curve which fits the experimental values the best. Knowing $\beta$, $\mathcal{Z}_0$ can be calculated from equation (3.27) by substituting the calculated values of $a^{\prime\prime}/a^{\prime} - a_\infty$ at a given frequency. The value of $\mathcal{Z}_0$ found for different frequency data will come out to be practically constant.

(ii) 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 at a single frequency are suggested by Gopal Krishna and Higasi.

Gopal Krishna's method:

In this method the relaxation time and dipole moment are determined. The advantage of this method over other 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. The method is based on Debye equation. For dilute solutions complex permittivity \( \varepsilon^* \) (as a function of frequency) can be written as:

\[
\frac{\varepsilon^* - 1}{\varepsilon^* + 2} = \frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} + \frac{4\pi N \mu^2}{3 k T} \cdot \frac{1}{1 + j \omega \tau}
\]  

(3.29)

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 one obtains,

$$\frac{\varepsilon' + \varepsilon''^2 - 2}{(\varepsilon' + 2)^2 + \varepsilon''^2} = \frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} + \frac{4\pi \eta \mu^2}{q k T} \cdot \frac{1}{1 + \omega^2 \tau^2} \quad (3.30)$$

$$\frac{3 \varepsilon''}{(\varepsilon' + 2)^2 + \varepsilon''^2} = \frac{4\pi \eta \mu^2}{q k T} \cdot \frac{\omega \tau}{1 + \omega^2 \tau^2} \quad (3.31)$$

substituting

$$X = \frac{\varepsilon''^2}{(\varepsilon' + 2)^2 + \varepsilon''^2}$$

and

$$Y = \frac{3 \varepsilon''}{(\varepsilon' + 2)^2 + \varepsilon''^2}$$

in equation (3.30) and putting $P = (\varepsilon_\infty - 1)/(\varepsilon_\infty + 2)$, one gets,

$$X = P + \frac{1}{\omega \tau} \cdot Y \quad (3.32)$$

$p$ may be regarded as fairly constant at low concentrations, its variation with concentration will be negligible in comparison to the error in the values of $X$. 

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and $Y$ due to experimental error in $\varepsilon_1$ and $\varepsilon_{\|}$ at a microwave frequency. Hence if $X$ is plotted against $Y$ the reciprocal of the slope of the 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. For estimating $\mu$ one can write equation (3.30) as,

$$X = P + Kw d_{12}$$

(3.33)

in which

$$K = \frac{4 \pi N \mu^2}{9 kT m} \frac{1}{1 + \omega^2 \tau^2}$$

in terms of $N$, the Avagadros number ($N = \frac{n m}{A}$), 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

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

(3.34)

where $d_0$ is the density of the solvent. From the graph between $X$ and $W$ the slope $(dX/dW)_{W \to 0}$ gives $Kd_0$. Whence $\mu$ can be calculated using equation (3.33).

This method is suitable for medium and high loss liquids because the variation in $P$ are negligible as compared to those in $X$ and $Y$ and hence it can be
considered as constant. In low loss liquids the variation of $P$ are comparable to those in $X$ and $Y$ and hence results obtained are not accurate.

**Higasi Method:**

Higasi\(^{31}\) has proposed that value of the relaxation time $\tau_0$ and distribution parameter $\alpha$ can be found out from the measured values of $a^1$ and $a^{11}$ at a single frequency in the dispersion region. The Cole-Cole equation expressed in terms of slopes is,

\[
\frac{a^* - a_\infty}{a_0 - a_\infty} = \frac{1}{\left(1 + j\omega \tau_0\right)^{1-\alpha}} \tag{3.35}
\]

Putting $a^* = a^1 - ja^{11}$ and separating into real and imaginary parts one gets

\[
\tau_0 = \frac{1}{\omega} \left( \frac{A^2 + B^2}{C^2} \right)^{\frac{1}{2}} \left(1 - \alpha\right) \tag{3.36}
\]

\[
(1 - \alpha) = \frac{\alpha}{\pi} \tan^{-1} \frac{A}{B} \tag{3.37}
\]
where
\[ A = a^1 (a_\nu - a_\infty) \]  
\[ B = (a_\nu - a^1) (a^1 - a_\infty) - a^{11} \]  
\[ C = (a^1 - a_\infty)^2 + a^{11} \]  

For a system with single relaxation time (\( \chi = 0 \)), the Cole-Cole equation reduces to Debye equation which may be written as,
\[ \frac{a^* - a_\infty}{a_\nu - a_\infty} = \frac{1}{1 + j\omega \tau} \]  

putting \( a^* = a^1 - ja^{11} \) and separating into real and imaginary parts one obtain,
\[ \frac{a^1 - a_\infty}{a_\nu - a_\infty} = \frac{1}{1 + \omega^2 \tau^2} \]  
\[ \frac{a^{11}}{a_\nu - a_\infty} = \frac{\omega \tau}{1 + \omega^2 \tau^2} \]
\[ a^1 = a_\infty + \frac{1}{\tau} \left( \frac{a^{11}}{\omega} \right) \]

and
\[ a^1 = a_\nu - \tau \left( a^{11} \omega \right) \]

Hence
\[ \tau = \frac{1}{\omega} \sqrt{\frac{a_\nu - a^1}{a^1 - a_\infty}} \]
or \[ \tau = \frac{1}{\omega} \left[ A \pm \sqrt{A^2 - 1} \right] \] (3.47)

where \( A = \frac{a_0 - a_\infty}{2a^{\|1}} \) (3.48)

From equation (3.44)
\[ \tau = \frac{1}{\omega} \cdot \frac{a^{\|1}}{a^{\|} - a_\infty} \] (3.49)

and from equation (3.45)
\[ \tau = \frac{1}{\omega} \cdot \frac{a_0 - a^{\|}}{a^{\|1}} \] (3.50)

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

3.3(B) Evaluation of Thermodynamical Parameters:

The thermodynamical quantities viz., free energy of activation \( \Delta F_0^* \), enthalpy \( \Delta H_0^* \) and entropy of activation \( \Delta S_0^* \) can be obtained by determining the relaxation time at different temperatures using Eyring's rate equation\(^\text{32} \). The expression for free energy of activation is given by
\[ \Delta F_0^* = R T \ln \left( \frac{K}{\hbar} \varpi_0 \right) \] (3.51)

knowing \( \varpi_0 \) and the value of other constants, \( \Delta F_0^* \) can be calculated. Substituting the thermodynamic relation \( \Delta F_0^* = \Delta H_0^* - \Delta S_0^* \) in the above expression and differentiating with respect to \( \frac{1}{T} \), one gets,

\[ \Delta H_0^* = R \frac{d \ln (T \varpi_0)}{d (1/T)} \] (3.52)

\[ \ln (T \varpi_0) \] is plotted against the reciprocal of absolute temperature. The slope of the straight line, when multiplied by \( R \), gives \( \Delta H_0^* \), the most probable enthalpy of activation.

Finally, the most probable entropy of activation is determined from the relation

\[ \Delta F_0^* = \Delta H_0^* - T \Delta S_0^* \] (3.53)
REFERENCES:


