CHAPTER-2
PART-A

SECTION I

Theories of Dielectric and Thermodynamic parameters

SECTION II

Quantum Mechanical Calculations

PART-B

Experimental techniques for the determination of Dielectric permittivity of pure liquids and their binary mixtures
PART-A

SECTION I

THEORIES OF DIELECTRIC AND THERMODYNAMIC PARAMETERS

2.1 Introduction

A dielectric material increases the storage capacity of a condenser by neutralizing charges at the electrode surfaces which otherwise would contribute to the external field. Faraday was the first to recognize this phenomenon of dielectric polarization, which occurs due to the formation of dipole chains under the influence of the applied field.

Dielectric materials can be classified broadly into two categories as polar [46] and non-polar materials, depending on charge distribution in molecule. Non-polar dielectric materials consist of molecules with positive and negative charges such that their effective centers of charge distribution coincide. Thus dipole moment of non-polar dielectric materials is zero in the absence of electric field. Polar dielectric materials are those in which centers of positive and negative charge distribution are separated by a distance, forming a molecular dipole even in the absence of electric field. But since the positive and negative charges are equal, the molecule is electrically neutral. The magnitude of molecular dipole moment depends on the size and symmetry of the molecule. Molecules having a centre of symmetry, such as Methane (CH₄), Carbon tetrachloride (CCl₄) and Benzene (C₆H₆) are non-polar while molecules not having centre of symmetry such as Methanol (CH₃OH), Ethanol (C₂H₅OH), Acetone (CH₃-CO-CH₃) and Water (H₂O) are polar dielectrics.
Polar nature of dielectric materials is measured in terms of its permanent dipole moment. If we imagine a molecular dipole made up of charge $+q$ and $-q$ separated by a distance $d$, then the dipole moment is equal to $q \times d$. In the molecular dipoles, $q$ will be in the order of $10^{-10}$ e. s. u. i.e., magnitude of electronic charge and $d$ will be of the order of $10^{-8}$ cm (one Angstrom unit). Thus dipole moment ($\mu$) for molecular dipoles is in the order of $10^{-18}$ e. s. u. The unit $10^{-18}$ e. s. u. is called Debye. The dipole moments of molecular dipoles are usually measured in Debye, abbreviated as D. Dielectric constant of the material depends on dipole moment as well as on the ability of these dipoles to align in the direction of the applied electric field.

### 2.2 Polarization

When a dielectric is placed in an external electric field, the bound charges align in the direction of the field. This alignment is known as polarization ($P$). In many substances the polarization is proportional to the field ($E$). These materials are known as linear dielectrics.

$$P = \alpha E$$

(2.1)

where $\alpha$ is a constant of proportionality known as polarizability, which is a tensor in general.

The total polarization ($P$) produced in the material can be written as the sum of distortion polarization ($P_d$) and orientation polarization ($P_o$).

$$P = P_d + P_o$$

(2.2)

The polarization of dipoles created due to distortion in charge distribution of material is termed as distortion polarization. There are two types of distortions that can occur. Distortion in electron charge distribution relative to nucleus creates dipoles and
alignment of these dipoles in the direction of electric field is known as electronic polarization \((P_e)\). The relative motion of ions gives rise to polarization known as ionic polarization \((P_i)\). The polarization of molecular dipoles due to their orientation in the direction of applied field is known as orientation polarization.

Hence the total polarization can be written as,

\[
P = P_e + P_i + P_o
\]  

(2.3)

and the total molecular polarizability \((\alpha)\) is given by,

\[
\alpha = \alpha_e + \alpha_i + \alpha_o
\]  

(2.4)

where \(\alpha_e\): electronic polarizability (due to displacement of electron cloud with respect to positive nuclear cloud).

\(\alpha_i\): ionic polarizability (due to the displacement of anion and cations in opposite direction with respect to each other).

\(\alpha_o\): orientational polarizability (due to the rotation of the dipoles in the presence of external field).

Thus the polar molecules have permanent dipole moments even in the absences of an electric field. When an electric field is applied on the dielectric medium the dipoles try to align in the field direction.

### 2.3 Theories of dielectric relaxation

The theories of dielectric relaxation can be broadly divided into two parts as theories of static permittivity and theories of dynamic permittivity. The polar dielectric materials having a permanent dipole moment, can maintain equilibrium under all types of polarizations when placed in a steady electric field. The permittivity of material under these conditions is called static permittivity \((\varepsilon_0)\). When the dielectric material is
placed in the electric field varying with some frequency, then permittivity of material changes with the change in frequency of the applied field. This is because, molecular dipoles cannot orient faster to come-up with applied field when frequency is increased. Thus permittivity of material falls off with the increasing frequency of applied field.

The frequency dependent permittivity of the material is called as dynamic permittivity. Different theories of static and dynamic permittivity are given in the following sections.

2.3.1 Theories of static permittivity

Dielectric constant of the material is a measure of the extent to which the electric charge distribution in the material can be polarized by the application of an electric field. Theories of permittivity are based on the response of charge distribution to the applied electric field.

Let us consider a parallel plate capacitor in vacuum with surface area ‘A’ and distance between plates ‘d’. If this capacitor is charged such that charge on one plate is $+q$ e. s. u. and charge on other plate is $-q$ e. s. u., then the force between these charges is given by Coulomb’s law as

$$F = \frac{1}{4 \pi \varepsilon_0} \frac{q_1 q_2}{\varepsilon r^3} r$$

(2.5)

with $q_1, q_2$ in coulomb (C), $F$ in Newton, $r$ in metre. The vacuum permittivity $\varepsilon_0 = 8.85 \times 10^{-12}$ farad m$^{-1}$ and for an electrostatic system $4 \pi \varepsilon_0 = 1$. In the electrostatic system of units, which is still customary in the dielectric theory, $\varepsilon$ is a dimensionless quantity.
Considering the above conditions Coulomb’s law can be written as,

\[ F = \frac{q_1 q_2}{\varepsilon r^3} r \]  

(2.6)

and expressing the force \( F \) (dyne) of repulsion between two like charges \( q_1, q_2 \) (stat coulomb) separated by a distance \( r \) (cm) in a dielectric. When there is a vacuum between the plates, the electric field \( E \) is

\[ E = 4\pi q \]  

(2.7)

But, if the material of dielectric constant \( \varepsilon \) is placed between the plates, then the field is smaller by a factor \( \varepsilon \), because of polarization. Thus the electric field becomes

\[ E = \frac{4\pi q}{\varepsilon} \]  

(2.8)

The reduction in the apparent charge on plates is caused by the polarization of the medium. In fact, there is induced charge throughout the material but it annuls itself everywhere except on the surface. The amount of polarization charge can be written as

\[ P = \left(1 - \frac{1}{\varepsilon}\right) q \]  

(2.9)

The influence of the electric field on the dielectric is equivalent to charging of two surfaces of the dielectric with charges of opposite sign to those causing the field. The surface density of these opposite sign charges on the surface of dielectric is \( P \), and is known as polarization [47]. It is the total charge passing through any unit area within the dielectric (parallel) to the plates.

The electric displacement \( D \) is defined in terms of the original charge density (in vacuum) as

\[ D = 4\pi q \]  

(2.10)
From equation (2.8), we can write electric displacement in material with dielectric constant $\varepsilon$ as,

$$D = \varepsilon E = E + 4\pi P$$  \hspace{1cm} (2.11)

or

$$E(\varepsilon - I) = 4\pi P$$  \hspace{1cm} (2.12)

The capacitance of parallel plate capacitor $C$ is related to the charge $Q$ on the plates and the potential difference $V$ applied across the plates, by the equation

$$C = \frac{Q}{V}$$  \hspace{1cm} (2.13)

Neglecting edge effects, capacitance of parallel plate capacitor containing the material of dielectric constant $\varepsilon$ is

$$C = \frac{\varepsilon A}{4\pi d}$$  \hspace{1cm} (2.14)

A measurement of this capacitance leads to the knowledge of the static dielectric constant. This relationship is particularly useful in the measurement of permittivity by bridge techniques.

The surface charge $PA$ gives rise to total electric moment $M$ of the dielectric, given by

$$M = PA d = P V$$  \hspace{1cm} (2.15)

Thus, polarization can be regarded as dipole moment per unit volume in the dielectric material. The amount of polarization in the dielectric materials was calculated by using various theories as discussed in the following sections.

2.3.1.1 Clausius Mossotti equation

Consider a sphere of continuous isotropic dielectric of suitable size, which is large, compared to molecular dimensions but small as compared to the distance between
the plates. A homogeneous field is established in the dielectric when the plates are uniformly charged with surface charge density $\sigma$. If the actual intensity of the electric field acting on the single molecule is $F$ then under the influence of this force, molecules posses an electric moment which is given by

$$m = \alpha_0 F$$  \hspace{1cm} (2.16)

where $\alpha_0$ is polarizability of molecule.

The average moment in the direction of the field \( [48] \) is given by

$$\bar{m} = \frac{\mu^2 \cos^2 \theta}{kT} F + er$$  \hspace{1cm} (2.17)

where the first term indicates the moment due to permanent dipole moment of molecule and second term indicates the moment due to the displacement of the elastically bound charges. This equation shows that permanent dipole moment contributes to the polarization and hence the dielectric constant is temperature dependent, while moment induced by displacement is independent of temperature.

$F$, may be conveniently considered as the actual force by assuming unit positive charge in the medium to be enclosed by a small sphere. This force may be treated as consisting of three components.

1) Force due to charges of surface charge density $\sigma$ on the plates ($F_1$)
2) Force due to polarization of medium outside the small sphere ($F_2$)
3) Force due to medium contained in the small sphere ($F_3$)

$$F = F_1 + F_2 + F_3$$  \hspace{1cm} (2.18)

$$F_1 = 4 \pi \sigma$$  \hspace{1cm} (2.19)
and $F_2$ may be obtained by considering that the matter within the small sphere is to be removed. $F_2$ is made up of two parts, first the force due to layers of induced charges on the dielectric facing the conducting plates and second the layer of charge on surface of small spherical cavity.

$$F_2 = -4\pi P + \left( \frac{4\pi P}{3} \right)$$

(2.20)

where $P$ is the polarization of the medium i.e., the electric moment per unit volume set up in the dielectric.

A general expression for $F_3$ cannot be given but it may be evaluated in special cases. Lorentz [49] showed that for a cubic lattice of polarizable atoms, the dipoles inside the sphere produce zero field. This is true in gases and for those liquids in which molecules are moving totally independent of each other. By assuming $F_3 = 0$, the total force is given by

$$F = 4\pi \sigma - 4\pi P + \left( \frac{4\pi P}{3} \right)$$

(2.21)

But $D = 4\pi \sigma$ and $D = E + 4\pi P$

$$E(1-\varepsilon) = 4\pi P$$

(2.22)

$$F = E + \left( \frac{4\pi P}{3} \right)$$

(2.23)

$$F = E + E \left( \frac{1-\varepsilon}{3} \right)$$

(2.24)

$$F = E \left( \frac{\varepsilon + 2}{3} \right)$$

(2.25)

This is the relation existing between the actual force $F$ and electric field $E$. 

38
Let \( N_1 \) be the number of molecules per cubic centimeter, then by definition of polarization

\[
P = N_1 \mathbf{m} = N_1 \alpha_0 \mathbf{F}
\]  

(2.26)

Substituting \( \mathbf{F} \) from equation (2.25), we get

\[
P = N_1 \alpha_0 \left( \frac{\varepsilon + 2}{3} \right) \mathbf{E}
\]

(2.27)

By using equation (2.22) and (2.27), we get the relation between dielectric constant \( \varepsilon \) and molecular polarizability \( \alpha_0 \) as

\[
\frac{(\varepsilon - 1)}{(\varepsilon + 2)} = \frac{4\pi}{3} N_1 \alpha_0
\]

(2.28)

in pure substance, \( N_1 = N \frac{d}{M} \), where \( M \) is molecular weight, \( d \) is density and \( N \) is number of molecules per mole.

\[
\frac{(\varepsilon - 1) M}{(\varepsilon + 2) d} = \frac{4\pi}{3} N \alpha_0
\]

(2.29)

This equation is known as Clausius-Mossotti Equation.

**2.3.1.2 Debye theory of static permittivity**

Debye [46] has given his theory using dipolar polarizability using the method applied by Langevin to find the mean magnetic moment parallel to an applied field to gas molecules having permanent magnetic moments and adopted the expression for local field calculated by Lorentz. Debye put forward his theory on the following assumptions.

a) The molecule is considered as rigid system of charges

b) The external field is supposed to induce no charge at all.
The molecules are classified into two groups.

1) Molecules with normal values of molar polarization and

2) Molecules with abnormally large values of polarization,

With these, in general the mean electric moment \( \bar{m} \) can be expressed as

\[
\bar{m} = \left[ \alpha_0 + \frac{\mu^2}{3kT} \right] F
\]  

(2.30)

where \( \alpha_0 \) indicates the polarizability due to distortion and \( \frac{\mu^2}{3kT} \) indicates the polarizability due to the orientation of dipoles in the field and it is added to the induced moment. Thus total polarizability is

\[
\alpha = \alpha_0 + \frac{\mu^2}{3kT}
\]  

(2.31)

Using this equation in equation (2.29), we get Debye equation as

\[
\frac{(\varepsilon - 1) M}{(\varepsilon + 2) d} = \frac{4\pi N}{3} \alpha = \frac{4\pi P}{3} \left[ \alpha_0 + \frac{\mu^2}{3kT} \right]
\]  

(2.32)

Debye has given somewhat more general derivation of this equation in which \( \alpha_0 \) is expressed as the average of the three polarizabilities along the three axes of the molecule treated as an ellipsoid of polarization.

The conclusions drawn from Debye theory are as follow

1) For nonpolar materials, the molar polarizability should be constant, independent of the temperature and pressure. An increase in the density of such a substance will lead to an increase in the permittivity.

2) For polar substances, the molar polarizability will fall with rising temperature, because the thermal agitation decreases the dipolar polarization.
The linear dependence of polarization upon the reciprocal of absolute temperature is taken for gases where molecular freedom occurs. But this is not the case with all polar liquids and polar solids. So for polar liquids, the Debye equation cannot be expected to hold. The application of Debye equation to dilute solutions is an approximation.

The application of Debye equation to polar liquids becomes evident by neglecting polarization due to distortion. Thus we can write

\[
\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi N\mu^2 d}{9kTM}
\]  

and considering

\[
\frac{4\pi N\mu^2 d}{9kM} = T_c
\]  

\[
\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{T_c}{T}
\]

when \( T_c = T \) then \( \varepsilon \to \infty \), that is \( T_c \) should be Curie temperature. When \( T \) is less than \( T_c \), the polarization becomes very high and causes such a large internal field, that the molecules will spontaneously align themselves parallel to one another, even in the absence of field.

2.3.1.3 Onsager theory

According to Debye theory, liquids act as ferroelectric material when \( T < T_c \), but the phenomenon of ferroelectricity is not common and certainly does not occur in water [50]. This failure of Debye equation is because of the assumption that \( F_3 = 0 \), which is almost certainly not valid. Because of this Onsager [6, 48, 51] has given his theory on
the following assumption. The molecule is polar molecule, which is spherical in form with molecular radius ‘a’ and is given by

\[ a^3 = \frac{3}{4\mu N_1} \]  

(2.36)

The sum of the volumes of spherical shaped molecules is equal to the total volume of material. There are no local directional forces due to their neighbours on the molecule. The internal field in the molecule consists of two parts,

1) The spherical cavity field \( G \), produced in the empty cavity by the external applied field

\[ G = \frac{3\varepsilon_0}{(2\varepsilon_0 + 1)} E = gE \]  

(2.37)

where \( g = \frac{3\varepsilon_0}{2\varepsilon_0 + 1} \)

2) The reaction field \( R \) setup in the cavity by polarization induced by dipoles in its surrounding is

\[ R = \frac{2(\varepsilon_0 - 1)}{2\varepsilon_0 + 1} \frac{m}{a^3} = r \frac{m}{a^3} \]  

(2.38)

where \( r = \frac{2(\varepsilon_0 - 1)}{(2\varepsilon_0 + 1)} \)

The total internal field acting upon spherical polar molecule is

\[ F = G + R \]

\[ F = \frac{3\varepsilon_0}{(2\varepsilon_0 + 1)} E + \frac{2(\varepsilon_0 - 1)}{2\varepsilon_0 + 1} \frac{m}{a^3} \]  

(2.39)

\[ F = gE + r \frac{m}{a^3} \]  

(2.40)

From equation (2.39), it can be observed that when \( \varepsilon_0 \to 0 \), Onsager’s internal field tends to finite value, while in Debye equation it tends to infinity.
The total moment \( m \) of the molecule is the vector sum of its permanent moment \( \mu \) and the induced moment \( \alpha F \) by the local field.

\[
M = \mu + \alpha F \tag{2.41}
\]

\[
m = \mu + \alpha \left[ g \mathbf{E} + (r \mathbf{m}) / a^3 \right] \tag{2.42}
\]

\[
m = \frac{\left( \frac{\mu + \alpha g \mathbf{E}}{1 - \frac{r \alpha}{a^3}} \right)}{1 - \frac{r \alpha}{a^3}} \tag{2.43}
\]

Then the mean moment parallel to the field is given by

\[
\bar{m} = \frac{g \mu^2 \mathbf{E}}{3kT} + \frac{\alpha g}{\left( 1 - \frac{r \alpha}{a^3} \right)} \tag{2.44}
\]

By using this equation in \( P = N_1 \bar{m} \) we get

\[
\frac{(\varepsilon_0 - 1)}{4\pi} = \frac{N_1 g}{\left( 1 - \frac{r \alpha}{a^3} \right)} \left[ \alpha + \frac{1}{\left( 1 - \frac{r \alpha}{a^3} \right)} \frac{\mu^2}{3kT} \right] \tag{2.45}
\]

But Onsager defined polarizability \( \alpha \) in terms of refractive index as

\[
\alpha = \frac{n^2 - 1}{n^2 + 2} \tag{2.46}
\]

By substituting for \( \alpha, a^3, g \) and \( r \) in the above equation, we get

\[
\frac{(\varepsilon_0 - n^2) \left( 2\varepsilon_0 + n^2 \right)}{\varepsilon_0 \left( n^2 + 2 \right)^2} = \frac{4\pi N_1 \mu^2}{9kT} \tag{2.47}
\]

This is Onsager equation for static permittivity. As the value of \( \varepsilon_0 \) increases, Lorentz field \( F \) increases without limit but in Onsager cavity field it tends to limit \( \frac{3E}{2} \),
while the reaction field tends to limit \( \frac{n^2 + 2}{3} \). Therefore Onsager equation does not predict the occurrence of ferroelectricity.

Debye’s theory and Onsager’s theory might be called semi statistical theories, in which the first uses statistical argument where as macroscopic arguments are used to obtain expression for local field in the second. Kirkwood and later Frohlich set out a rigorous expression to obtain static permittivity using statistical methods throughout.

### 2.3.1.4 Kirkwood Theory

Kirkwood [52] imagines a specimen of material containing \( N \) dipoles of moment \( \mu \) confined in spherical volume \( V \) and situated in an uniform external field. With this assumption, an equation for non polarizable dipoles is given by

\[
\frac{(\varepsilon_0 - 1)(2\varepsilon_0 + 1) M}{3 \varepsilon_0 d} = 4\pi N \frac{g \mu^2}{3kT}
\]  

(2.48)

where \( g \) is a correlation parameter which is a measure of local ordering in the material. The value of \( g \) is one, if the average moment of the finite spherical region about one molecule, which is held fixed, is equal to the moment of fixed molecule. If the dipoles of neighboring molecules are oriented parallel to the dipole of fixed molecule, then \( g \) has a value greater than one, whereas when dipoles of neighboring molecules orient antiparallel to the dipole of fixed molecule, then the value of \( g \) is less than one. Further, Kirkwood includes distortion polarization by attributing the polarizability \( \alpha \) to each dipole. Kirkwood has generalized the Onsager’s theory by eliminating the approximation of uniform local dielectric constant identical with macroscopic dielectric constant of the medium.
Thus the Kirkwood’s equation is written as

$$\frac{(\varepsilon_0 - 1)(2\varepsilon_0 + 1)}{3\varepsilon_0} \frac{M}{dN} = 4\pi N \left[ \alpha + \frac{\mu^2}{3kT} \right]$$ (2.49)

2.3.1.5 Frohlich’s Theory

Frohlich [53] considered a spherical region of macroscopic dimensions within an infinite specimen, which is treated as a continuous medium. He derived the expression for static permittivity using statistical method. According to Frohlich, the equation for non polarizable dipoles is

$$\frac{(\varepsilon_0 - 1)(2\varepsilon_0 + 1)}{3\varepsilon_0} \frac{M}{d} = 4\pi N \langle \bar{m} \bar{m} \rangle$$ (2.50)

It can be observed from this equation that if $m$ is identified as $\mu$ and $\bar{m}$ is written as $g\mu$, this equation is identical to Kirkwood’s equation (2.49).

Frohlich takes the distortion polarization into account by imagining non polarizable dipole units to be embedded in polarizable continuum of permittivity $n^2$. Thus Frohlich’s equation is

$$\frac{(\varepsilon_0 - n^2)(2\varepsilon_0 + n^2)}{\varepsilon_0(n^2 + 2)^2} \frac{M}{d} = 4\pi N \frac{g\mu^2}{9kT}$$ (2.51)

Except for interaction of correlation parameters, the equation is identical with Onsager’s equation (2.47).

2.3.2 Theories of Dynamic permittivity

An alternating electric field of appropriate frequency gives rise to dielectric dispersion. The characteristic orientational motions of the dipoles result in a frequency variation of the dielectric constant, and the appearance of ‘dielectric losses’ over a broad band of frequencies. When the direction of the field is changing sufficiently fast,
the molecular forces impeding the dipole orientation dominate and the dipole becomes unable to follow the changes at these frequencies and the orientation of permanent dipoles no longer contributes to the dielectric constant. Moreover, in a certain frequency band a phase lag between the field and dipole orientation develops and energy is drawn from the electrical source by the material, and is dissipated as heat. This phenomenon is described by a complex representation of the dielectric constant.

\[ \varepsilon^* = \varepsilon' - j\varepsilon'' \]  

(2.52)

where the real part \( \varepsilon' \) represents the dielectric constant and the imaginary part \( \varepsilon'' \) is known as the dielectric loss.

When a dielectric is placed in static electric field, all the three components of total polarization are in phase with the applied field. But as the frequency increases, dipoles owing to their bulky nature are unable to keep in phase with the applied electric field. This leads to a loss associated; hence the dielectric constant is treated as a complex quantity (\( \varepsilon' \)). When the external field is switched on or off, the rate of change of polarization is given by

Case-1: When the field is switched on

Let \( P = P_1 + P_2 \)

Where \( P = \) Total polarization

\( P_1 = \) Distortion polarization (in phase with the applied field)

\( P_2 = \) Dipolar polarization (the out of phase component)

Here

\[ \frac{dP_2}{dt} \alpha (P - P_1) \]

\[ \frac{d\left| (P - P_1 - P_2) \right|}{|P - P_1 - P_2|} = -\frac{dt}{\tau} \]  

(2.53)
where \( \tau \) is macroscopic relaxation time required for the polarization to reach a value equal to \( 1/e \) times of its value when the field is switched off.

Solving this, with the boundary condition that at \( t = 0 \), \( P_2 = 0 \) we get

\[
P_2 = (P_1 - P) \left( 1 - e^{\frac{t}{\tau}} \right)
\]

which can be represented graphically as shown in Figure 2.1

![Figure 2.1: Growth of polarization with respect to \( t/\tau \)](image)

**Case -2:** When field is switched off

\[
\frac{dP_2}{dt} = \frac{P - P_1 - P_3}{\tau}
\]

when \( t = 0 \), \( P_2 = P - P_1 \) from which we obtain

\[
P_2 = (P - P_1) \left( 1 - e^{-\frac{t}{\tau}} \right)
\]

which can be represented graphically as shown in Figure 2.2
At low frequency, \( 4\pi P = \varepsilon(\varepsilon_\infty - 1) E \) as \( \omega \to 0 \) \hspace{1cm} (2.57)

since \( P = P_1 + P_2 \),

the contribution due to both exists only at very low frequencies

but at high frequencies, \( 4\pi P_1 = (\varepsilon_\infty - 1) E \) as \( \omega \to \infty \) & \( \varepsilon_\infty = n^2 \) \hspace{1cm} (2.58)

because at high frequency \( P_2 = 0 \)

From the rate equation-2.55, \[
\frac{dP_2}{dt} = -\frac{P - P_1 - P_2}{\tau} = \frac{\varepsilon}{4\tau}(\varepsilon_\infty - n^2)E_0\exp(j\omega t) \frac{-P_2}{\tau} \hspace{1cm} (2.59)
\]

In steady state the solution to above equation is given by,

\[
P_2 = \frac{\varepsilon(\varepsilon_\infty - n^2)}{4\pi(1+j\omega \tau)} E \hspace{1cm} (2.60)
\]

\[
P_1 + P_2 = P' - jP''
= \frac{\varepsilon}{4\pi}(n^2 - 1)E + \frac{\varepsilon(\varepsilon_\infty - n^2)}{4\pi(1+j\omega \tau)} E \hspace{1cm} (2.61)
\]

where \( P' \) and \( P'' \) are real
\[ \varepsilon^* = \varepsilon' - j\varepsilon'' \]

\[ 1 + \frac{4\pi}{\varepsilon E} (P' - jP'') = n^2 + \frac{\varepsilon_0 - n^2}{1 + j\omega \tau} \]

\[ \varepsilon' \text{ and } \varepsilon'' \text{ are given by } \]

\[ \varepsilon' = n^2 + \frac{\varepsilon_0 - n^2}{1 + \omega^2 \tau^2} \] (2.62)

\[ \varepsilon'' = \frac{\varepsilon_0 - n^2}{1 + \omega^2 \tau^2} \] (2.63)

and the loss tangent

\[ \tan \phi = \frac{\varepsilon''}{\varepsilon'} \]

The dielectric constant is strictly not a constant but varies with various physical parameters of which frequency and temperature are of prime importance. The variation of \( \varepsilon' \) and \( \varepsilon'' \) with frequency can be represented graphically as shown in Figure 2.3.

\[ \text{Figure 2.3: Variation of } \varepsilon' \text{ and } \varepsilon'' \text{ with } \omega \tau \]
2.3.2.1 Debye model

The frequency dependence of the dielectric constant at any angular frequency \( \omega \) represented by the familiar Debye equation [6, 48] is

\[
\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + j\omega \tau}
\]

(2.64)

where \( \varepsilon_\infty \) is the high frequency dielectric constant closely related to the refractive index \( (\varepsilon_\infty = n^2) \) and \( \varepsilon_0 \) is the dielectric constant, measured for static electric field. The real and imaginary parts of the complex dielectric constant are then given by

\[
\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + j\omega \tau}
\]

(2.65)

\[
\varepsilon'' = \frac{(\varepsilon_0 - \varepsilon_\infty) \omega \tau}{1 + j\omega \tau}
\]

(2.66)

\( \tau \) is called the macroscopic relaxation time and corresponds to the time required for the polarization of the dielectric to decrease or to relax \( \frac{1}{e} \) of its value after the removal of the field. This relaxation time, which decreases with temperature, is related to the physical properties of the polar molecule and their environments. It may also be seen from these equations that \( \varepsilon' \) (dielectric loss factor) reaches its maximum,

\[
\varepsilon''_{\text{max}} = \frac{(\varepsilon_0 - \varepsilon_\infty)}{2}
\]

(2.67)

when the frequency \( \omega = \frac{1}{\tau} \).

The two equations for \( \varepsilon' \) and \( \varepsilon'' \) above, may be rearranged and written as

\[
\left( \frac{\varepsilon' - \varepsilon_\infty}{\varepsilon_0 + \varepsilon_\infty} \right)^2 + \varepsilon''^2 = \left( \frac{\varepsilon_0 - \varepsilon_\infty}{2} \right)^2
\]

(2.68)
This is the equation of a circle in the \( \varepsilon', \varepsilon'' \) plane with centre at \( \left( \frac{\varepsilon_\infty + \varepsilon_\infty}{2}, 0 \right) \) and radius equal to \( \frac{\varepsilon_\infty - \varepsilon_\infty}{2} \).

The results of dielectric measurements are represented by plotting \( \varepsilon'' \) against \( \varepsilon' \) in an Argand diagram, on a semicircle lying above the \( \varepsilon' \) axis (Figure 2.4).

![Figure 2.4: Debye semi circle](image)

### 2.3.2.2 Cole-Cole model

Cole and Cole [54] observed that in many materials, the locus of \( \varepsilon' \) and \( \varepsilon'' \) is an arc of a semi-circle following the empirical equation

\[
\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_\infty - \varepsilon_\infty}{(1 + j\omega \tau)^{1-\alpha}} ; \quad 0 \leq \alpha \leq 1
\]  

(2.69)

where \( \alpha \) is a constant, called the distribution parameter and is a measure of the deviation of the dispersion from the normal Debye type.

The real and imaginary parts are obtained by rationalizing this expression and using

\[
j^{(1-\alpha)} = \exp \left\{ \frac{j\pi(1-\alpha)}{2} \right\}
\]  

(2.70)
\[ \frac{\varepsilon' - \varepsilon_c}{\varepsilon_c - \varepsilon_\infty} = \frac{1 + (\omega \tau)^{1-\alpha} \sin\left(\frac{\pi \alpha}{2}\right)}{1 + (\omega \tau)^{2(1-\alpha)} + 2(\omega \tau)^{1-\alpha} \sin\left(\frac{\pi \alpha}{2}\right)} \] (2.71)

\[ \frac{\varepsilon''}{\varepsilon_c - \varepsilon_\infty} = \frac{(\omega \tau)^{1-\alpha} \cos\left(\frac{\pi \alpha}{2}\right)}{1 + (\omega \tau)^{2(1-\alpha)} + 2(\omega \tau)^{1-\alpha} \sin\left(\frac{\pi \alpha}{2}\right)} \] (2.72)

The locus of these parametric equations in the complex plane can be obtained as

\[ \left\{ \frac{1}{2} (\varepsilon_c + \varepsilon_\infty) - \varepsilon' \right\}^2 + \left\{ \varepsilon'' + \frac{1}{2} (\varepsilon_c - \varepsilon_\infty) \tan\left(\frac{\pi \alpha}{2}\right) \right\}^2 = \frac{1}{4} (\varepsilon_c - \varepsilon_\infty)^2 \operatorname{sec}^2\left(\frac{\pi \alpha}{2}\right) \]

This is the equation of a circle with its centre at

\[ \left\{ \frac{1}{2} (\varepsilon_c + \varepsilon_\infty), -\frac{1}{2} (\varepsilon_c - \varepsilon_\infty) \tan\left(\frac{\pi \alpha}{2}\right) \right\} \] and radius \( \frac{1}{2} (\varepsilon_c - \varepsilon_\infty) \operatorname{sec}\left(\frac{\pi \alpha}{2}\right) \)

The Debye dispersion and Cole-Cole arc dispersion are shown in Fig. 2.5 and from the Fig. 2.5., \( \theta \) is given by the following relation [55].

\[ \theta = \left(\frac{\pi \alpha}{2}\right) \]

\[ \tan \theta = \frac{\sinh[(1-\alpha)Y]}{\cos(\pi \alpha/2)} \]

and \( Y = \log\left(\frac{\lambda}{\lambda_c}\right) \)

The relaxation time \( \tau \) can be found [3, 6, 54] from the arc plot by using

\[ \omega \tau = \left(\frac{v}{u}\right)^{1-\alpha} \] (2.73)

where \( u \) and \( v \) are shown in Figures 2.4 and 2.5.
The value of $\alpha$ generally decreases as the temperature is increased. In the limit when $\alpha = 0$, the Cole-Cole arc reduces to the Debye semicircle. Later an attempt is made by Kastha [56] to provide a physical basis for the use of Cole-Cole relation.

![Cole-Cole plot](image)

**Figure 2.5: Cole-Cole depressed arc**

### 2.3.2.3 Davidson-Cole relaxation model

The Cole-Cole arc is symmetrical about a line through the centre, parallel to the $\varepsilon''$ axis. Davidson and Cole [57] found that the experimental results for certain materials do not have this symmetry, the $\varepsilon'$ Vs $\varepsilon''$ plot being a skewed arc. They suggested that behaviour of this kind could be represented by the expression
\[ \varepsilon^* = \varepsilon_\infty + \frac{(\varepsilon_0 - \varepsilon_\infty)}{(1 + j\omega\tau)^\beta} \quad (2.74) \]

Rearranging
\[ \frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \frac{1}{(1 + j\omega\tau)^\beta} \quad (2.75) \]

where \( \beta \) is again a constant, \( 0 < \beta \leq 1 \).

Rationalizing to find \( \varepsilon' \) and \( \varepsilon'' \) yields
\[ \frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \frac{(1 - j\omega\tau)^\beta}{(1 + \omega^2\tau^2)^\beta} \]
\[ = \frac{(\cos \phi - j\sin \phi)^\beta}{(1 + \omega^2\tau^2)^{\beta/2}} \]
\[ = \exp(-j\beta\phi) \]
\[ = \frac{\exp(-j\beta\phi)}{(1 + \tan^2 \phi)^{\beta/2}} \]

where \( \tan \phi = \omega \tau \). Therefore
\[ \frac{\varepsilon' - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \cos^\beta \phi \cdot \cos \beta \phi \quad (2.76) \]
\[ \frac{\varepsilon''}{\varepsilon_0 - \varepsilon_\infty} = \cos^\beta \phi \cdot \sin \beta \phi \quad (2.77) \]

The value of \( \beta \) determines the angle at which the arc cuts the \( \varepsilon' \) axis at the high frequency end. Differentiating the above two equations with respect to \( \phi \) gives
\[ \frac{d\varepsilon''}{d\varepsilon'} = \left( \frac{d\varepsilon''}{d\phi} / \frac{d\varepsilon'}{d\phi} \right) = -\cot(\beta + 1)\phi \]

In the high frequency limit, \( \omega \tau \to \infty \), \( \phi = \tan^{-1}(\omega \tau) = \pi / 2 \),
\[ \frac{d\varepsilon''}{d\varepsilon'} = \tan(\pi\beta / 2) \quad (2.78) \]

This equation is very successful in representing the behaviour of substances at
low temperatures. As the temperature is raised, $\beta \to 1$, so that the arc tends to Debye semicircle.

**2.3.2.4 Havriliak - Negami model**

It was found that none of the above dielectric functions was successful in giving the spectral response in case of polymeric materials. There are many examples of dielectric behaviour, which cannot be explained by Cole-Cole and Davidson-Cole expressions, both of which contain only one adjustable parameter to describe the shape of the plot $\varepsilon'$ Vs $\varepsilon''$. Havriliak-Negami [58] generalized the expression, in contribution of both Cole-Cole and Davidson-Cole expression as given below

$$
\varepsilon^* = \varepsilon_\infty + \frac{(\varepsilon_0 - \varepsilon_\infty)}{\left[1 + (\omega \tau)^{(1-\alpha)}\right]^\beta} \quad (2.79)
$$

which includes Cole-Cole model if $\beta = 1$, the Davidson-Cole model if $\alpha = 0$ and for $\alpha = 0, \beta = 1$ it gives the Debye model.

**2.4 Dipole Moment**

The frequency dependence of dielectric constant is due to the dipolar polarization, as discussed above. Also the polarization ($P = \alpha E$) is proportional to the applied field $E$, which is a function of frequency.

The temperature dependence may be understood as follows. When a field is applied, the dipoles align themselves in the direction or opposite to that of the field. But at any given temperature above 0 K, the system has thermal energy, which tends to randomize the system. Hence, there is a variation in potential difference and so in $\varepsilon$. Also, as the temperature is changed, the density of the material changes and from Clausius-Mosotti’s equation $\varepsilon$ is proportional to $\rho$ and hence $\varepsilon$ changes with
temperature. Thus the dipole moment can be determined by studying either the
can be determined by studying either the
frequency or the temperature variation of dielectric constant. Another way to determine
dipole moments, especially suitable for polar liquids is to measure dielectric constant as
a function of a non-polar solvent concentration. By this, the individual dipoles are
separated from one another.

The third mentioned method has been used in the present case. Hence it is
discussed in detail. Assuming spherical shape of solute molecules and the solvent to
form a continuous medium, Guggenheim [59] showed that the dipole moment is given
by

\[
\mu^2 = \frac{27kT}{4\pi N(\varepsilon \_{1} + 2)(n_1^2 + 2)} C \Delta
\]

(2.80)

where \( \Delta = (\varepsilon_{12} - n_{12}^2) - (\varepsilon_{\text{solvent}} - n_{\text{solvent}}^2) \)  subscript 1 → solvent, 12 → solution

\[ C = \text{concentration of solute in solvent in moles/cc} \]

\[ \varepsilon_1 = \text{dielectric constant of solvent} \]

\((\varepsilon - n^2)\) is a measure of the dipolar polarization because \(\varepsilon\) is a function of \((P_e + P_i + P_d)\) and \(n^2\) is a function of \(P_e\). Generally \(P_i\) is assumed to be 5 to 20% of \(P_e\) and

calculations are made because it is very difficult to measure \(P_i\). But the advantage of

Guggenheim’s equation lies in that, \(P_i\) does not come into picture owing to the

assumption that the solute molecules are spherical in nature. The contributions of \(P_i\), to

the two terms in the expression for \(\Delta\) cancel each other.

The values of \(\mu\) found from this expression are less than those determined from

other equations, but \(\mu\) vary much from solvent to solvent.
**Higasi’s Method**

The dipole moment of the binary systems has been computed using Higasi’s method as proposed by Higasi *et al.* [60], using the following equation

\[
\mu^2 = \frac{27 k T M_2 (a_0 - a_\infty)}{4 \pi N d_1 (\varepsilon_i + 2)^2}
\]

where \( M_2 \) is molecular weight of solute, \( d_1 \) is density of solvent, \( a_0 \) and \( a_\infty \) are respectively the slopes of \( \varepsilon_0 \) and \( \varepsilon_\infty \) with respect to the concentration. The other constants have their usual meaning.

In general the dipole moment found in solution state is lower than that determined from the gaseous phase. This can be attributed to solvent effects. The solvent effect may be understood as follows. In the gaseous phase the dipoles are separated from one another and hence interactions between dipoles are excluded. But in liquids there is an interaction between dipoles and the dipole moment determined is more authentic. This can be analyzed from microwave absorption spectroscopy.

In solution, each dipole of the polar solute is surrounded by non-polar solvent molecules. Every polar molecule induces a polarization (and hence dipole moment) in the neighbouring non-polar molecules. This induced polarization in the non-polar molecules may be either in the direction of dipole of the solute or in an opposite way. In the former case, the dipole moment in solution form has a higher value than in the gaseous state which is not seen very often experimentally. In the latter case the dipole moment has a lower value than in the gaseous phase.

In the experimental investigations on pure liquids, it is generally found that the observed dipole moments are lower than those reported from experiments on gaseous
samples. More accurate method of determining the dipole moment is from the microwave absorption spectroscopy of gaseous samples as all other interactions are lower.

The excessive dipole moment ($\Delta \mu$) of the system as given by Debecker and Huyskens [61]

$$\Delta \mu = \mu_{ab} - \mu_a - \mu_b$$

(2.82)

where $\mu_a$ and $\mu_b$ is the dipole moment of the individual solute system and $\mu_{ab}$ is the dipole moment of the binary system.

2.5 Dielectric parameters related to molecular behaviour

There are different formulae with which one can correlate dielectric parameters with molecular activities in liquid. The correlation between dielectric parameters and molecular interactions as well as the structural changes in mixture can be explored to some extent by using various theories. In the absence of exact theory exploring these quantities, available theories with some assumptions can provide the trend regarding interactions and the structural changes.

2.5.1 Kirkwood correlation factor

The molecular interactions between a polar solute and a non-polar solvent can be described by the modified Kirkwood-Frohlich correlation factor. The Kirkwood-Frohlich theory [6] takes into account the short-range interactions through the introduction of the dimensionless correlation factor $\mathcal{g}$, which gives information regarding the orientation of the electric dipoles in polar liquids. The Kirkwood correlation factor ($\mathcal{g}$) for the pure liquids is given [62] by the expression,
\[
\frac{4\pi N_A \mu^2 \rho}{9kTM} g = \frac{(\varepsilon - \varepsilon_\infty)(2\varepsilon + \varepsilon_\infty)}{\varepsilon (\varepsilon_\infty + 2)^2}
\]  
(2.83)

where \( N_A \) is the Avogadro’s number, \( \mu \) is the dipole moment in the gaseous phase, \( \rho \) is the density, \( k \) is the Boltzmann constant, \( T \) is the temperature in Kelvin, \( M \) is the molecular weight, \( \varepsilon \) is the dielectric permittivity at static frequency and \( \varepsilon_\infty \) is the permittivity at optical frequency.

For a mixture of two polar liquids, say 1 and 2 the equation (2.83) could be modified [63], as under.

1) Assuming that \( g_{eff} \) is the effective correlation factor for the mixture, the Kirkwood equation for the mixture can be expressed as

\[
\frac{4\pi N_A}{9kT} \left( \frac{\mu_1^2 \rho_1}{M_1} x_1 + \frac{\mu_2^2 \rho_2}{M_2} x_2 \right) g_{eff} = \frac{(\varepsilon_m - \varepsilon_{\infty m})(2\varepsilon_m + \varepsilon_{\infty m})}{\varepsilon_m (\varepsilon_{\infty m} + 2)^2}
\]  
(2.84)

2) Assuming that the dipole moments of both the liquids are affected by the same amount \( g_f \), the Kirkwood equation for the mixture is modified as

\[
\frac{4\pi N_A}{9kT} \left( \frac{\mu_1^2 \rho_1 g_1}{M_1} x_1 + \frac{\mu_2^2 \rho_2 g_2}{M_2} x_2 \right) g_f = \frac{(\varepsilon_m - \varepsilon_{\infty m})(2\varepsilon_m + \varepsilon_{\infty m})}{\varepsilon_m (\varepsilon_{\infty m} + 2)^2}
\]  
(2.85)

where \( x_1 \) and \( x_2 \) are the mole fractions of liquids 1 and 2 in the mixture respectively and the suffixes 1, 2 and \( m \) represent liquid 1, liquid 2 and mixture respectively.

The Kirkwood correlation factor \( g \) is a measure of the molecular association of a reference molecule with its nearest neighbours. The departure of \( g \) from unity is an indication for the molecular association.

1. \( g=1 \) represents equilibrium state between the multimers or non-association among the dipoles.
2. $g > 1$ indicates the parallel orientation among the dipoles.

3. $g < 1$ indicates the anti-parallel orientation among the dipoles of the liquid.

Here the value of $g_{\text{eff}}$ in equation (2.84) varies from $g_1$ to $g_2$, in case of associative and non-associative mixtures, as the concentration (mole fraction) of liquid 2 increases from 0 to 100% and the value of $g_r$ in equation (2.85) is unity for pure polar liquids and close to unity if there is no interaction. The deviation of $g_r$ value from unity indicates the interaction between liquids 1 and 2.

### 2.5.2 Bruggeman factor

The static permittivity of two component mixture must lie somewhere between two extremes corresponding to static permittivity of the two liquids. In order to understand the dipole interaction in the mixture of two liquids, a various mixture formulae have been proposed [64, 65].

Bruggeman formula [65, 66] can be used as the first evidence of molecular interactions in binary mixture and it is given by

$$f_B = \left( \frac{\varepsilon_m - \varepsilon_2}{\varepsilon_1 - \varepsilon_2} \right) \left( \frac{\varepsilon_1}{\varepsilon_m} \right)^{\frac{1}{3}} = (1 - \phi_2)$$

(2.86)

where $\phi_2$ is the volume fraction of liquid 2 in liquid 1. If there is no interaction between the components in the mixture then the Bruggeman factor ($f_B$) should vary linearly with volume fraction $\phi_2$, but if there is interaction between the components then $f_B$ varies non-linearly with $\phi_2$.

1. $f_B = 1$ indicates that no change in effective microscopic volume of the system and corresponds to the ideal Bruggeman mixture factor.
2. $f_B > 1$ indicates that the effective microscopic volume of solvent gets more than actual volume. The solute exerts a repulsive force in the system.

3. $f_B < 1$ indicates that the effective microscopic volume of solvent gets less than actual volume. The solvent exerts an attractive macroscopic force in the system.

### 2.5.3 Excess properties

Information regarding the structural changes in binary mixture can be accessed by studying the excess dielectric properties [50, 67, 68]. Let A and B be two molecular systems with measurable macroscopic properties $P_A$ and $P_B$. If we prepare the mixture of A and B having mole fraction $x_A$ and $x_B$ respectively such that $x_B = (1- x_A)$, the excess macroscopic property $P^E$ corresponding to mixture is defined as

$$P^E = P_{AB} - (P_A \cdot x_A + P_B \cdot x_B)$$  \hspace{1cm} (2.87)

where $P_{AB}$ is the measured value of property P for the mixture. The values of $P^E$ provide information regarding interactions between A and B.

1. $P^E = 0$ indicates no significant interaction between A and B.
2. $P^E > 0$ indicates that interactions between A and B leads to increase in the macroscopic property $P$.
3. $P^E < 0$ indicates decrease in the macroscopic property $P$.

The quantitative picture can be visualized by fitting $P^E$ to the Redlich-Kister equation [69, 70]

$$P^E = x_A x_B \sum_{n=0}^{\infty} B_n (x_A - x_B)^n$$  \hspace{1cm} (2.88)

The coefficients $B_n$ provide information regarding molecular interactions for example, $B_0$ corresponds to the effective interaction between one molecule of system A
and another molecule of system B. $B_1$ corresponds to interaction between two molecules of A and one molecule of B and so on.

In the present study, excess dielectric properties are determined corresponding to static permittivity and inverse relaxation time. The inverse relaxation time is taken instead of relaxation time, as inverse relaxation time corresponds to broadening of spectral lines in resonant spectroscopy [71]. The broadening of two levels are additive for two energy levels. The analogy is taken here in the dielectric spectroscopy. The excess permittivity ($\varepsilon^E$) and excess inverse relaxation time ($\frac{1}{\tau}^E$) are defined as

$$
\varepsilon^E = (\varepsilon_m - \varepsilon_{\infty m}) - \left[ (\varepsilon_1 - \varepsilon_{\infty 1})x_1 + (\varepsilon_2 - \varepsilon_{\infty 2})x_2 \right] 
$$

(2.89)

$$
\left(\frac{1}{\tau}\right)^E = \left(\frac{1}{\tau}\right)_m - \left[ \left(\frac{1}{\tau}\right)_1 x_1 + \left(\frac{1}{\tau}\right)_2 x_2 \right] 
$$

(2.90)

where $x$ is mole fraction and the suffixes 1, 2 and m represent liquid 1, liquid 2 and mixture respectively.

The excess permittivity ($\varepsilon^E$) may provide qualitative information about the multimers formation in the mixtures as follows,

[i] $\varepsilon^E = 0$ indicates that liquids 1 and 2 do not interact at all.

[ii] $\varepsilon^E > 0$ indicates that liquids 1 and 2 interact in a way that the total effective dipole moment increases.

[iii] $\varepsilon^E < 0$ indicates that liquids 1 and 2 interaction in such a way that the total effective dipoles moment decreases.
Information regarding the interaction dynamics of liquids 1 and 2 can be retrieved from this excess inverse relaxation time \( \left( \frac{1}{\tau} \right)^E \) as follows,

[i] \( \left( \frac{1}{\tau} \right)^E = 0 \) indicates there is no change in the dynamics.

[ii] \( \left( \frac{1}{\tau} \right)^E > 0 \) indicates that interaction of liquids 1 and 2 produces a field such that the effective dipoles rotate faster.

[iii] \( \left( \frac{1}{\tau} \right)^E < 0 \) indicates that interaction of liquids 1 and 2 produces a field such that the effective dipoles rotate slowly.

2.5.4 Determination of excess Helmholtz free energy due to dipolar interaction

The thermodynamic excess functions on addition of an inert solvent to hydrogen-bonded molecules are often measured by calorimetric methods and the results are interpreted on the basis of H-bond breaking mechanism leaving the dipolar component altogether. Further, the dipole-dipole interaction energy also contributes to H-bond energy. Hence even theoretical treatments [72] that are useful in the interpretation of the structure and thermodynamic properties of weak interactions give inaccurate results in associated liquids. The best approach in the present situation is to segregate the contribution due to dipolar interactions by experimental studies of the concentration dependence of dielectric polarization of the associated liquids in inert solvents.
The dipolar cohesive energy is given by

$$W^r = -\left(\frac{4\pi N_A^2}{3V}\right)\left(\frac{\varepsilon - 1}{2\varepsilon + n_D^2}\right)\left(\frac{n_D^2 + 2}{3}\right)\mu^2$$

(2.91)

The Helmholtz free energy is given by

$$F = -kT \ln z$$

(2.92)

where $z$ is the canonical partition function. Hence, dipolar energy change ($\Delta F$) on mixing can be obtained by a proper choice of the partition function. Wüster et al. [73] obtained the electrostatic part of the free energy of mixing and excess entropy on mixing, from Barker’s [74] thermodynamic relations. However, the method is cumbersome. Haskell [75] developed a still elegant method by factorizing out the partition function corresponding to the interaction energy of the dipole from the experimental values of molar polarizations of the mixture. However, the partition functions used are by no means complete. The manifestations of short range correlations were not considered.

An improved calculation based on Kirkwood theory was made [76] which utilizes the concept of correlation in the statistical theory of Ramshaw [77] and the Wertheim’s mean spherical model [78] includes mutual correlation between like and unlike polar molecules.

According to this relation, the excess Helmholtz free energy ($\Delta F^E$) is a good dielectric parameter to evaluate the interaction between the components in the mixture through breaking mechanism of hydrogen bond and is expressed [79] as

$$\Delta F^E = \Delta F_{or}^E + \Delta F_{rr}^E + \Delta F_{12}^E$$

(2.93)

where $\Delta F_{or}^E$ represents the excess dipolar energy due to long range electrostatic
interaction.

\( \Delta F_{rr}^E \) represents the excess dipolar energy due to the short range interaction between identical molecules.

\( \Delta F_{12}^E \) represents the excess free energy due to short-range interaction between dissimilar molecules.

The above terms are given in detail in equation (2.94)

\[
\Delta F^E = \frac{-N_A}{2} \left\{ \sum_{r=1,2} x_r^2 \mu_r^2 \left[ R_{fr} - R_{fr}^0 \right] + \sum_{r=1,2} x_r^2 \mu_r^2 \left[ g_{rr} - I \right] \right\} 
+ x_1 x_2 \mu_1 \mu_2 \left[ R_{f_1} + R_{f_2} - R_{f_1}^0 - R_{f_2}^0 \right] \right\} 
\]

(2.94)

where \( R_{fr}^0 = \left( \frac{8\pi N_A}{9V_r} \right) \left( \frac{\varepsilon_r - I}{2\varepsilon_r + \varepsilon_{\infty}} \right) \),

\( R_{fr} = \left( \frac{8\pi N_A}{9V_r} \right) \left( \frac{\varepsilon_m - I}{2\varepsilon_m + \varepsilon_{\infty}} \right) \),

\( \varepsilon_{\infty} = \varepsilon_{\infty} \), \( V_r \) is the molar volume of the components and \( \varepsilon_r, \varepsilon_{\infty} \) are the dielectric permittivity values at static and optic frequencies of the pure liquids respectively.

2.5.5 Thermodynamic parameters

According to Eyring the relaxation process in dielectrics may be considered as, passing of a dipole across a potential barrier that separates the minima of energy \([80, 81]\). In order to determine the activation enthalpy, from the theory of rate process, Kauzmann \([82]\) obtained from the relaxation time,

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

(2.95)
Here $\Delta G^*$ is the activation free energy, $\Delta H^*$ is the molar enthalpy of activation and $\Delta S^*$ is the molar entropy of activation for the dipole reorientation process. $\Delta H^*$ is obtained from the slope of log $(\tau T)$ Vs $(1 / T)$. It follows from this equation that, if $\Delta H^*$ and $\Delta S^*$ are independent of temperature, the plot of log $(\tau T)$ Vs $(1 / T)$ is linear. Using the tangent of the slope of this function, we can determine the height of the potential barrier $\Delta H^*$.

$$\Delta H^* = R \frac{d(\log \tau T)}{d(1/T)} = R \frac{d(\log \tau)}{d(1/T)} - RT \quad (2.96)$$

No absolute significance can be attached to $\Delta S^*$ calculated, but the order of magnitude of the enthalpy of activation can give some clue to the molecular energy in the relaxation process. A study of the thermodynamic parameters for the polar compounds may be useful in assessing the states of dipole under the influence of the applied field. A qualitative approach is possible as several complicated functions are involved in the relaxation process, but the discussion has its own utility in that. It gives a better representation of the dielectric behaviour of the molecule.

For every compound, the activation energy is found to increase as the temperature increases while the relaxation time decreases. This may be due to the decreasing viscosity of the medium [83]. With increase in temperature, the thermal agitation increases and the dipole requires more energy in order to attain the equilibrium with the applied field and the molar free energy of activation, results in negative entropy values. This indicates that the activated state is more ordered than the normal state, which is true as in the activated state; the dipoles try to align with the applied field.
The excess thermodynamic parameters like excess activation free energy \((\Delta G^*)_E\), excess molar enthalpy of activation \((\Delta H^*)_E\) and excess molar entropy of activation \((\Delta S^*)_E\) at different mole fractions can be determined by fitting the Eyring rate equation with the help of equation (2.88).
SECTION-II
QUANTUM MECHANICAL CALCULATIONS

2.6 Introduction

Quantum mechanics is essential to understand the behavior of energy and matter at the atomic and subatomic scales. Quantum mechanics gives a mathematical description of the behavior of the electrons that has never been found to be wrong. However, the quantum mechanical calculations have never been solved exactly for any chemical system other than the hydrogen atom. There are a number of simplifying assumptions in \textit{ab-initio} theory, but the calculations are more complete and more time expensive. Obtaining accurate results require powerful computer workstations. Semiempirical calculation uses experimental data in the place of time expensive integrals. The analysis of energies can predict what molecular processes are likely to occur. The system with the lowest energy is the most stable configuration. The starting geometry of the molecule must be given in the program. Once the energy and gradients of energy are computed, then there are a number of different algorithms available for \textit{ab-initio} and semiempirical calculations.

Geometry optimization methods start with an initial geometry and then change that geometry to find a lower energy shape. This results in a local minimum closest to the starting geometry. In order to find the most stable conformer (a global minimum of the energy), many different geometries were tried to find the one with the lowest energy. The lowest energy conformer will have the largest weight in the ensemble of energetically accessible conformers. The accuracy in the computation of molecular geometries depends on the level of theory being used to compute the energy. The choice
of computational methods must be based on a clear understanding of both the chemical system and the information to be computed.

2.7 *Ab-initio* calculations

*Ab-initio* is a Latin term which means "from the beginning". The term is applied to calculations of atomic and molecular structure directly from the first principles of quantum mechanics, without using quantities derived from experiment (such as ionization energies found by spectroscopy) as parameters. These calculations use no input other than the Schrödinger equation and the values of the fundamental constants such as $e$, $m_e$, $\hbar$ and the atomic numbers of the atoms present.

The term “computational chemistry” is generally used when mathematical methods are automated and implemented on a computer to solve the quantum mechanical wave equations for atoms and molecules. This field is entirely built upon solving and getting approximate solutions. Some of these solutions are very ambiguous and some are more accurate than any experimental result. Obtaining accurate results require extremely powerful computers and a large investment of time. *Ab-initio* predictions are true for properties that depend on the behavior of isolated molecules. The amount of computing time required, in *ab-initio* calculations, increases rapidly as the size of the atom or molecule increases. These *ab-initio* calculations can, for example, be used to determine the bond lengths and bond angles of molecules by calculating the total energy of the molecule for a variety of molecular geometries and finding which conformation has the lowest energy.

The most common type of *ab-initio* calculation is called a Hartree-Fock calculation (abbreviated HF), in which the primary approximation is the central field
approximation. Additional approximations may be invoked into HF theory to go for semiempirical methods or additional determinants can be added for generating solutions, which can be made to converge towards the exact solution of Schrödinger equation. The Hartree-Fock equations form a set of pseudo-eigen value equations, as the Fock operator depends on all the occupied molecular orbitals through the coulomb and exchange operators. A specific Fock orbital can only be determined if all the other occupied orbitals are known. Therefore, Self-Consistent Field (SCF procedure) iterative methods must be employed for determining the orbitals. The HF method treats each electron as if it were independent but acting under the influence of a potential due to the atomic nuclei and an average due to the other electrons.

Molecular orbital theory says that each electron can be described by an orbital and according to the Pauli principle, each orbital can accommodate a maximum of two electrons, one of either spin. The Linear Combination of Atomic Orbital (LCAO) approximation of HF theory expresses each of the HF orbitals in terms of the atomic orbitals centred on each nucleus. In other words, N molecular orbitals can be created from a superposition of N atomic orbitals. The accuracy of the representation of true molecular orbital as a LCAO, increases with the size of the basis set.

2.8 Semiempirical calculations

Semiempirical quantum chemistry attempts to address two limitations, namely slow speed and low accuracy, of the Hartree-Fock calculation by omitting or parameterizing certain integrals based on experimental data. As a result, semiempirical methods are very fast, applicable to large molecules and may give accurate results when applied to molecules that are similar to the molecules used for parameterization.
The fundamental difference between the \textit{ab-initio} and semiempirical calculation is shown in Figure 2.6. The time required for performing an HF calculation scales as the fourth power of the number of basis functions. This arises from the number of two electron integrals necessary for constructing the Fock matrix. Semiempirical methods reduce the computational cost by reducing the number of these integrals.

Semiempirical methods are parameterized to reproduce various results such as geometry, energy, dipole moments, heat of formation, ionization potential etc. A few methods have been parameterized to reproduce a specific property such as electronic spectra or NMR chemical shifts. They are used to compute properties other than those in the parameterization set. Semiempirical calculations are set up with the same general structure as a HF calculation in that they have a Hamiltonian and a wave function. Within this framework, certain pieces of information are approximated or completely omitted.

Only a minimal basis set is used and the core electrons are not included. Some of the two electron integrals are omitted. In order to correct for the errors introduced by omitting part of the calculation, the method is parameterized. Parameters to estimate the omitted values are obtained by fitting the results to experimental data or \textit{ab-initio} calculations. These parameters replace some of the integrals that are excluded. The advantage of semiempirical calculations is that they are much faster than \textit{ab-initio} calculations. Modern semiempirical models are based on the Neglect of Diatomic Differential Overlap (NDDO) method in which the overlap matrix $S$ is replaced by the unit matrix. This allows one to replace the Hartree-Fock secular equation $|H-ES| = 0$ with a simpler equation $|H-E| = 0$. 
Figure 2.6: Flowchart of ab-initio and semiempirical calculation
Existing semiempirical models differ by the further approximations that are made when evaluating one- and two-electron integrals and also by the parameterization philosophy. The different types of semiempirical NDDO Models are explained below.

2.8.1 MNDO (Modified Neglect of Diatomic Overlap)

This is the oldest NDDO based model that parameterizes one-center two-electron integrals based on spectroscopic data for isolated atoms, and evaluates other two-electron integrals using the idea of multipole-multipole interactions from classical electrostatics. A classical MNDO model uses only s and p orbital basis sets while more recent MNDO/d adds d-orbitals that are especially important for the description of hypervalent sulphur species and transition metals. MNDO has a number of known deficiencies, such as inability to describe the hydrogen bond due to a strong intermolecular repulsion. The MNDO method is characterized by a generally poor reliability in predicting heats of formation. For example, highly substituted stereoisomers are predicted to be too unstable compared to linear isomers due to overestimation of repulsion is sterically crowded systems.

2.8.2 AM1 (Austin Model 1):

This method takes a similar approach to MNDO in approximating two-electron integrals but uses a modified expression for nuclear-nuclear core repulsion. The modified expression results in non-physical attractive forces that mimic van der Waals interactions. The modification also necessitated reparameterization of the model, which was carried out with a particular emphasis on dipole moments, ionization potentials and geometries of molecules. This allows for some description of the hydrogen bond and
other deficiencies such as systematic over-estimates of basicities. On the other hand, AM1 improves nicely some properties, such as heats of formation, over MNDO.

2.8.3 PM3 (Parametric Method 3)

This method uses a Hamiltonian that is very similar to the AM1 Hamiltonian but the parameterization strategy is different. While AM1 was parameterized largely based on a small number of atomic data, PM3 is parameterized to reproduce a large number of molecular properties. Different parameterization and slightly different treatment of nuclear repulsion allow PM3 to treat hydrogen bonds rather well but it amplifies non-physical hydrogen-hydrogen attractions in other cases. This results in serious problems when analyzing intermolecular interactions (methane is predicted to be a strongly-bound dimer) or conformations of flexible molecules (OH is strongly attracted to CH₃ in 1-pentanol). The accuracy of thermo chemical predictions with PM3 is slightly better than that of AM1. The PM3 model has been widely used for rapid estimation of molecular properties and has been recently extended to include many elements, including some transition metals.

Despite their limitations, these semiempirical methods are often used in computational chemistry because they allow the study of systems that are out of reach of more accurate methods. For example, modern semiempirical programs allow study of molecules consisting of thousands of atoms while *ab-initio* calculations that produce similar thermo chemical accuracy are feasible on molecules consisting of less than 50-70 atoms.
Semiempirical calculations can be useful in many situations, such as

- Computational modeling of structure-activity relationships to gain insight about reactivity or property trends for a group of similar compounds.
- Design of chemical synthesis or process scale-up, especially in industrial settings where getting a qualitatively correct answer today is more important than getting highly accurate answer next week.
- Development and testing of new methodologies and algorithms, for example development of hybrid quantum mechanics / molecular mechanics (QM/MM) methods for modeling of biochemical processes.
- Checking for gross errors in experimental thermo chemical (e.g. heat of formation) data.
- Preliminary optimization of geometries of unusual molecules and transition states that cannot be optimized with molecular mechanics methods.
- In many applications where qualitative insight about electronic structure and properties is sufficient.

The limitations of semiempirical methods should be kept in mind when deciding if these are suitable tools for the task. For large systems, either molecular mechanics or semiempirical quantum mechanics could be used for optimization and calculation of conformational energies. The molecular mechanics approach is faster and in most cases produces more accurate conformational energies and geometries. Some molecular mechanics methods, such as MM3 and MM4, can also predict thermo chemistry of stable species reasonably well. On the other hand, if there is no suitable force field for
the system (e.g. in case of reactive intermediates or transition states), semiempirical methods may be the only choice.

For small system, the compromise must be made between the semiempirical approach and the more reliable but much more time-consuming ab-initio calculations. In general, semiempirical results can be trusted only in situations when they are known to work well (e.g. systems similar to molecules in the parameterization set) and strong caution should be exercised in cases where semiempirical methods are known to fail (e.g. prediction of activation barriers).

2.9 Basis Set

One of the approximations inherent in essentially all ab-initio methods is the introduction of a basis set. Molecular orbitals can be expressed by a set of known functions called basis functions, which constitute a basis set. The basic functions commonly used in electronic structure calculations are Slater Type Orbitals (STO) and Gaussian Type Orbitals (GTO). The first step in obtaining a molecular wave function is to select a set of single particle wave functions to be used in constructing the wave function. This is termed as choosing the basis set.

One choice of a basis set for the initial orbitals is Slater atomic orbital (STO). The STO has the general form

\[
\chi_{\zeta,n,m}(r,\theta,\phi) = N r^{n-1} e^{-\zeta r} Y_{l}^{m}(\theta,\phi)
\]  

(2.97)

where effective nuclear charge \(\zeta = (Z-s)/n^*\)

\[Z = \text{atomic number}\]

\[s = \text{shielding constant}\]

\[n^* = n \text{ for } n \leq 3\]
= 3.7 for n=4
= 4.0 for n=5
= 4.2 for n=6

N is the normalization constant and $Y_{l}^{m}(\theta,\phi)$ are spherical harmonic functions.

The calculations of three and four centred integrals cannot be performed analytically with STOs. STOs have no radial nodes and hence are not mutually orthogonal. STOs are used for atomic and diatomic systems where high accuracy is required. The major time consuming aspect of molecular structure calculations is the number and complexity of the electron interaction integrals that must be evaluated. Boys has suggested that the atomic orbitals can be expressed in terms of Gaussian Type Orbitals (GTO) which are functions of the form

$$G_{n,l,m}(r,\theta,\phi) = N r^{n-1} e^{-\varsigma r^2} Y_{l}^{m}(\theta,\phi)$$ (2.98)

One of the most expensive calculations is the evaluation of electron-electron interaction integrals (for N orbital basis set, $N^4$ integrals have to be evaluated). Calculations of multi centred integrals are extremely complex with STOs. Hence, GTOs are preferred. An STO can be written in terms of GTOs as

$$\chi_{n,l,m}(r,\theta,\phi) = \sum_{i=1}^{3} a_{i}^{n,l,m} G_{i}(n, l, m)$$ (2.99)

STO-3G         Minimal basis set
6-31G (d)      Split-Valence basis set

The volume over which an electron can move is increased by increasing the number of basis functions per atom. Inner shell represented by a single orbital is made up of a set of Gaussians. Valence shell orbitals are split into two – inner valence and outer valence region. The advantage of replacing exponential functions by Gaussians
stems from the property $\theta, \phi$ that the product of two Gaussians based on different centers in itself is a Gaussian based on a point lying between the centers. Therefore a complicated three or four centred integral can be expressed as a relatively simple equivalent to two centred integral which can be evaluated faster. The disadvantage of the method lies in the fact that an atomic orbital is not well represented by a simple Gaussian function and so each atomic orbital has to be expressed as a sum of several Gaussians. The smallest number of possible basis functions is known as minimum basis set. In STO-3G basis set, three gaussians are used to represent one Slater type orbital.

2.10 Molecular Orbital Theory

Molecular orbital theory is the most widely applied theoretical tool for the examination of molecular electronic structure. A molecular orbital is the wave function of an electron that can occupy an orbital, which spreads throughout the molecule. The square of the amplitude of the orbital at any point is proportional to the electron density there. Molecular orbital is expressed as a sum of atomic orbitals centered on each nucleus. An assembly of $n$ electrons with $N$ nuclei is described by the Schrödinger equation as

$$H(N, Q, n, q, t)\psi(N, Q, n, q, t) = -\frac{\hbar}{2\pi^2} \frac{\delta}{\delta t} \psi(N, Q, n, q, t)$$

$H(N, Q, n, q, t)$ represents the Hamiltonian operator and is a function of $3N$ nuclear spatial coordinates symbolized $N$; $3n$ spatial coordinates for the $n$ electrons denoted $n$; $3N$ momentum coordinates for the nuclei represented by the symbol $Q$; $3n$ momentum coordinates for the $n$ electrons represented by the symbol $q$, and the time $t$. $\psi(N, Q, n, q, t)$ represents a wave function for $(N + n)$ particle system. Complete behavior of the system can be deduced from the wave function $\psi(N, Q, n, q, t)$ throughout time.
Energies, dipole moments, bond lengths, angles and charge distribution are derivable from Schrödinger’s wave equation.

Using Born-Oppenheimer approximation, Hamiltonian is written as

\[ H_i = \sum_i^N - \frac{\hbar^2}{8 \pi^2 m} \nabla_i^2 - \sum_i^N \frac{Z_i}{r_{i\alpha}} + \sum_{j>i} e^{2} \frac{1}{r_{ij}} \] (2.100)

The majority of wave functions used today are of the independent particle type or simply a superposition of two or more terms of this type. Hamiltonian can be written as a sum of N terms i.e.,

\[ H(1,2,...N) = \sum_{i=1}^{N} H_i(i) \] (2.101)

The wave function is simply a product of N single-particle wave functions (orbitals) \( \phi_i(i) \).

The associated N-particle distribution function is then

\[ \psi(1,2,...N) = [\phi_1(1)\phi_2(2),...,\phi_N(N)] \] (2.102)

Assuming that the system of particles is non-interacting, the cross interference terms vanish, \( \phi_i^* \phi_j = 0 \) for \( i \neq j \), Therefore

\[ \psi^*(1,2,...N)\psi(1,2,...,N) = \phi_1^* \phi_1 + \phi_2^* \phi_2 + ... + \phi_N^* \phi_N \\
+ \phi_1^* \phi_2 + \phi_2^* \phi_3 + ... + \phi_1^* \phi_N \\
+ \phi_2^* \phi_1 + \phi_3^* \phi_3 + ... + \phi_2^* \phi_N + ... + \phi_N^* \phi_1 + \phi_N^* \phi_2 + \phi_N^* \phi_{N-1} \] (2.103)

The Schrödinger wave equation reduces to

\[ H(1,2,...N) \psi(1,2,...N) = E \psi(1,2,...N) \] or

\[ [H_1(1) + H_2(2),..., H_N(N)] f_1(1) f_2(2),..., f_N(N)=E [f_1(1) f_2(2)... f_N(N)] \] (2.104)

The above equation is of variable separable form and can be decomposed to N single particle equations

\[ H_i(i) f_i(i)= e_i f_i(i) \] (2.105)
If the interactions between electrons are taken into account, then Schrödinger equation is reduced to a set of coupled differential equations by modifying the Hamiltonian.

The wave function $\psi(1, 2, \ldots N) = f_1(1) f_2(2) \ldots f_N(N)$ is expressed as antisymmetrized product of single particle wave function in order to satisfy Pauli’s exclusion principle.

$$\psi(1, 2, \ldots, N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(1) & \phi_1(2) & \ldots & \phi_1(N) \\ & \ddots & \vdots & \end{vmatrix}$$  \hspace{1cm} (2.106)

This determinant is called Slater determinant. The single particle wave function constitute an orthonormal set

$$\int \phi_i^*(1) \phi_j(1) \, dt = \left\{ \begin{array}{cl} 1 & i = j \\ 0 & i \neq j \end{array} \right. \hspace{1cm} (2.107)$$

We wish to vary the set of orbitals $f$ and minimize the energy of the system, subject to the constraint that the orbitals be an orthonormal set. That is achieved by the Fock operator $F$

$$F_i = - \frac{1}{2} \Delta_i - \sum_{a} \frac{Z_{ia}}{r_{ia}} + \sum_{j} (2J_{ij} - K_{ij})$$

$$F_i \phi_i = \sum_{j} \lambda_{ij} \phi_j^{HF} \hspace{1cm} (2.108)$$

This HF equation is solved by Roothaan method or Analytical SCF method. The total HF wave function can now be written as

$$\phi_{HF} = \phi_1^{HF}(1) \phi_2^{HF}(2) \ldots \phi_N^{HF}(N) \hspace{1cm} (2.109)$$
The single-particle functions $\phi^{HF}_i(i)$ are termed as Hartree-Fock orbitals for the system.

The SCF method begins with a set of approximate orbitals for all the electrons in the system $\chi_1(r)\chi_2(r), \ldots \chi_n(r)$. One electron is then selected and the potential in which it moves is calculated by freezing the distribution of all other electrons and treating their averaged distribution as a centrosymmetric source of potential. The Schrödinger equation for the electron is solved for this potential, which gives a new orbital for it (new set of LCAO coefficients). This procedure is repeated for all the other electrons in the system using the electrons in the frozen orbitals as the source of potential. This process is iterated till self-consistency of the set of orbitals is obtained.

For a given molecular geometry, the SCF procedure involves the following steps.

1. Calculate all one and two electron integrals.
2. Generate a suitable start guess for the MO coefficients.
3. Form the initial density matrix.
4. Form the Fock matrix as the core (one-electron) integrals + the density matrix times the two-electron integrals.
5. Diagonalize the Fock matrix. The eigenvectors contain the new MO coefficients.
6. Form the new density matrix. If it is sufficiently close to the previous density matrix, SCF procedure is completed, otherwise go to step 4.

The SCF iterative scheme often converges for geometries near equilibrium and uses small basis sets. Distorted geometries and large basis sets containing diffuse functions rarely converge.
SCF is most commonly employed due to the following reasons:

1. This model has a well-defined end point in terms of the approximate eigen values obtained. It leads to energetically best possible single determinant wave function.

2. The expectation values of all one-electron operators are correctly predicted.

### 2.11 Limits of HF-SCF theory

1. Electron correlation neglected (Neglect of the local distortion of the distribution of electrons)

2. Neglect of relativistic effects (Calculated molecular potential energy differs from the true energy)

3. Inaccurate predictions of molecular dissociation energies. (Shape of the molecular potential energy curve differs.)

   In spite of neglecting correlation effects, the equilibrium geometries are reasonably well predicted. Molecular force constants and hence vibration frequencies are slightly exaggerated. The molecular potential energy curve is shown in Figure 2.7.

### 2.12 Geometry Optimization

Optimization is a process of finding stationary points of a multidimensional function. Stationary points are points where the first derivative is zero or minimum and the second derivative should be negative. The gradient $\mathbf{g}$ has the first derivatives of the function with respect to all variables and can be calculated analytically. The Hessian $\mathbf{H}$ is the second derivative matrix. Force constants are eigen values of the Hessian matrix. If all the force constants are positive on the potential energy surface of the molecule, then it indicates a stationary point on the function or a potential well on the potential energy surface.
Figure 2.7: Molecular potential energy curve
One negative force constant indicates a saddle point on the potential energy surface. Negative force constants give rise to imaginary frequencies. If we represent $U$ for the energy and $X_1, X_2, \ldots X_n$ for these variables, representing the bond lengths, bond angles and dihedral angles, then the gradient $g$ and the Hessian $H$ are represented as

$$
g = \begin{bmatrix}
\frac{\partial U}{\partial x_1} \\
\frac{\partial U}{\partial x_2} \\
\vdots \\
\frac{\partial U}{\partial x_n}
\end{bmatrix} \quad \text{and} \quad H = \begin{bmatrix}
\frac{\partial^2 U}{\partial x_1^2} & \frac{\partial^2 U}{\partial x_1 \partial x_2} & \ldots & \frac{\partial^2 U}{\partial x_1 \partial x_n} \\
\frac{\partial^2 U}{\partial x_2 \partial x_1} & \frac{\partial^2 U}{\partial x_2^2} & \ldots & \frac{\partial^2 U}{\partial x_2 \partial x_n} \\
\vdots & \vdots & \ddots & \vdots \\
\frac{\partial^2 U}{\partial x_n \partial x_1} & \frac{\partial^2 U}{\partial x_n \partial x_2} & \ldots & \frac{\partial^2 U}{\partial x_n^2}
\end{bmatrix}
$$

The negative of the gradient when evaluated at a point on the potential energy surface points in the direction of steepest descent down the potential energy surface. The new set of variables are calculated using $X_{\text{new}} = X_{\text{old}} - H^{-1}g$.

The function to be optimized and its derivatives are calculated with a finite precision, which depends upon the computational implementation. Therefore, a stationary point cannot be located exactly and the gradient can only be reduced to a certain value. The optimization is considered to be converged if the gradient is reduced below a suitable cut-off value.
Figure 2.8: Grid searching
Optimization process starts with an initial geometry and then changes that geometry to find a lower energy shape. This usually results in a local minimum that is closest to the starting geometry. The lowest energy conformers will have the largest weight in the ensemble of energetically accessible conformers.

For a polyatomic molecule with \( N \) atoms, there are \( 3N-6 \) force constants. Out of these, six force constants are zero or negligibly small and these correspond to translation and rotation. These force constants have to be calculated for every stationary point to check the presence of any negative values. A larger molecule will have many minima, one of which is the global minimum as shown in Figure 2.8. To locate the global minimum, the simplest way to search the conformation space is by choosing a set of conformers, each of which is different by a set number of degrees from the previous one. This process is called grid searching (Figure 2.8). If a small step size is used, then, it is extremely time consuming but this is the only way to completely ensure that the absolute global minimum has been found.
PART-B

EXPERIMENTAL TECHNIQUES FOR THE DETERMINATION OF DIELECTRIC PERMITTIVITY OF PURE LIQUIDS AND THEIR BINARY MIXTURES

2.13 Introduction

There is no single experimental method for measuring the dielectric constant and the loss factor of the polar liquids at all frequencies. It was necessary to employ different techniques to investigate the dielectric properties of liquids over the available frequency ranges. Moreover, at a single frequency, different methods depending upon loss factor of the liquids are being used. These methods are applied at different frequencies (radio frequencies, microwave frequencies and optical frequency) as well. The interpretation of dielectric data in pure liquids is usually complicated due to the viscosity and the dipolar interaction effects. Also, the form of the internal field has been a subject of controversy in drawing conclusions from dielectric absorption data on pure liquids.

In a polar liquid, the large electrostatic interactions between molecules modify their rotational freedom and alter the reaction fields in the medium to a large extent. In pure liquids the interactions between neighbouring molecules tend to be somewhat specific. So usually they are used as solutes in dilute solutions in a polar or non-polar solvent, particularly, if the results are extrapolated towards zero concentration to eliminate solute-solute interactions [84]. Also to avoid the much disputed ambiguity concerning the internal field correction, the dielectric relaxation time is preferably measured in dilute solutions of a non-polar solvent [85]. In such studies, the solute molecules will be isolated from each other depending on the concentration used, which
means that the solute molecules will be in a quasi-isolated state. Further, the dipole-dipole interaction effects will be minimized. The resulting dipole moment value will be close to the gaseous value and the relaxation time will be microscopic type.

The accuracy of measurement of dielectric constant \( (\varepsilon') \) and the dielectric loss \( (\varepsilon'') \) in dilute solutions is of primary importance in deriving molecular parameters. Two most widely used methods are of Von Hippel [86] and Heston et al. [87] for dilute solution measurements involving mathematical expressions derived with approximations of the theoretical formula, apart from the time-consuming standing wave ratio measurements. Although curve fitting methods have been reported for the evaluation of \( \varepsilon' \) and \( \varepsilon'' \) in pure liquids, reports of similar techniques are not available for dilute solution measurements. The present chapter deals with the different experimental techniques and related theories.

2.14 Determination of density

The mass measurements are performed on a digital electronic balance (Mettler Toledo AB 135, Switzerland) with an uncertainty of ± 0.00001 g. The densities of the pure liquids are measured at corresponding temperatures by using a 10 ml specific gravity bottle [88]. The experimental values of densities for pure liquids at temperatures (303 to 323) K are given in Table 2.1.

2.15 Dielectric measurements at radio frequencies (LF-impedance analyzer)

The dielectric measurements in the present investigation are taken on LF Impedance analyzer in the frequency range 1 kHz to 10 MHz [89] (as shown in PLATE 2.1) in the temperature range 303 K-323 K.
PLATE 2.1: LF-IMPEDEANCE ANALYZER WITH TEMPERATURE CONTROLLER
Table 2.1: Densities (kg-m\(^{-3}\)) for pure liquids at temperatures (303 to 323) K

<table>
<thead>
<tr>
<th>Temperature K</th>
<th>Propan-1-ol</th>
<th>Propan-2-ol</th>
<th>Methyl benzoate</th>
<th>Ethyl benzoate</th>
<th>Benzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>303</td>
<td>0.7955</td>
<td>0.7762</td>
<td>1.0788</td>
<td>1.0421</td>
<td>0.8684</td>
</tr>
<tr>
<td>308</td>
<td>0.7915</td>
<td>0.7716</td>
<td>1.0739</td>
<td>1.0381</td>
<td>0.8632</td>
</tr>
<tr>
<td>313</td>
<td>0.7874</td>
<td>0.7669</td>
<td>1.0690</td>
<td>1.0342</td>
<td>0.8581</td>
</tr>
<tr>
<td>318</td>
<td>0.7829</td>
<td>0.7627</td>
<td>1.0642</td>
<td>1.0303</td>
<td>0.8520</td>
</tr>
<tr>
<td>323</td>
<td>0.7789</td>
<td>0.7528</td>
<td>1.0594</td>
<td>1.0265</td>
<td>0.8475</td>
</tr>
</tbody>
</table>

Capacitance measurements are made with LF impedance analyzer. HP 4192A meter is a fully automatic high performance test instrument used to measure a wide range of parameters. The measurement speed of the instrument is 29 ms\(^{-1}\). This analyzer is test quick recovery and has a built in comparator. It can measure the capacitance to a high accuracy and wide measurement range, which allows it to make precise measurements at the spot frequencies 1 kHz, 10 kHz, 100 kHz, 1 MHz and 10 MHz. The two measurement display sections, capacitance and dissipation factor provide the direct read out of the parameters. The instrument has got two modes of measurement viz. normal mode and average mode. In normal mode operation, the instrument performs measurements at high speed where as in the average mode it has short, medium or long range rate to average the measurement results. The second mode has been adopted in the present measurements to have a high reliable and repeatable value than in the normal mode of the measurement.
2.16 Dielectric permittivity at micro wave frequency (Plunger technique)

This method has been proposed by Heston et al. [87]. The methods used for measuring the high dielectric loss, made use of the large variation in the reflection coefficient as the sample length is changed. The absolute magnitude of the reflection coefficient for low-loss dielectrics is very close to unity, since power absorption by the dielectric filled waveguide section is relatively small. Because the variation in reflection coefficient with sample length is very small and difficult to measure with any degree of reliability, an alternative approach has been adopted. The Voltage Standing Wave Ratio, VSWR, is quite sensitive to small changes in dielectric loss since for low-loss dielectric the VSWR is large (The standing Wave ratio is very sensitive to small changes in the reflection coefficient). This sensitivity of the standing wave ratio, to small changes in the reflection coefficient near unity, is used to measure the dielectric absorption of low-loss systems, i.e. dilute solutions.

Since the values of $\varepsilon''$ measured in the solution study are small, the dielectric constant $\varepsilon'$ may be obtained by the measurement of the difference between successive minima in the dielectric filled cell (plunger) by varying the thickness of the sample. So, the expression for $\varepsilon'$ becomes

$$\varepsilon' = \lambda_o^2 \left( \frac{1}{\lambda_d^2} + \frac{1}{\lambda^2} \right)$$

(2.111)

where $\lambda_o$ is the free space wavelength, $\lambda_c$ the cut-off wavelength and $\lambda_d$ is the wavelength in the dielectric filled wave guide of the plunger. Hence, it is assumed that $\varepsilon'$ is unaffected appreciably by $\varepsilon''$.

The dielectric loss is evaluated from the measurement of the inverse standing
wave ratio $\rho_n$ at each minimum (n). $\rho_n$ is determined by the “width at twice minimum” method. So, the inverse standing wave ratio is given as

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

(2.112)

where $\lambda_g$ is the guide wavelength and $\Delta x = \text{distance between half-power positions from one } \sqrt{2}E_{\text{min}} \text{ position to the other } \sqrt{2}E_{\text{min}} \text{ position. Here it is assumed that } \Delta x \text{ is small relative to } \lambda_g$. This assumption is important and places a limit on the highest value of $\varepsilon^\prime$ which can be measured by this method. So, the final expression for $\varepsilon^\prime$ is given as

$$\varepsilon^\prime = \frac{2\lambda_o^2}{\pi \lambda_g} \left( \frac{\partial \rho_n}{\partial n} \right)$$

(2.113)

Therefore, the slope of $\rho_n$ Vs n, when multiplied by $\frac{2\lambda_o^2}{\pi \lambda_g^2}$ will yield $\varepsilon^\prime$.

**Disadvantages of this method**

The entire standing wave profile is not used in the calculations. Measurements are made only at the various minima. In this method, due to the assumption that $\Delta x$ is smaller than the guide wavelength, there is a limit on the $\varepsilon^\prime$ value. Another assumption which limits the use of this method is that $\varepsilon^\prime$ value is unaffected appreciably by $\varepsilon^\prime.$

**2.16.1 Theory of simplified plunger technique**

The dielectric filled waveguide of the plunger is separated from the remaining waveguide components by a thin mica sheet ($z=0$). Let the incident electromagnetic wave at the air-dielectric interface ($z=0$) be represented by $A_0 e^{j\omega t}$.

The wave is transmitted through the sample of length $d$ and is reflected at the shorting plunger ($z=d$). The wave is transmitted through the sample of length $d$ and is
reflected at the shorting plunger \((z=d, \text{ Figure 2.9})\).

\[ \text{Figure 2.9: Block diagram of Plunger with Mica sheet} \]

The returning wave at \(z=0\) is then represented by, \(A_0 e^{j\omega t-2\gamma x}\)

where \(\gamma = \alpha + j \beta\)

\(\gamma = \text{Propagation constant}\)

\(\alpha = \text{Attenuation constant}\)

\(\beta = \frac{2\pi}{\lambda_g} \text{Phase constant}\)

Amplitude of the resultant standing wave given by

\[ A = A_0 e^{j\omega t} + A_0 e^{j\omega t-2\gamma x} \quad \text{(2.114)} \]

Intensity of the standing wave is given by

\[ I \propto |A|^2 \quad \text{(2.115)} \]

Substituting (3.4) in (3.5) and \(\gamma = \alpha + j\beta\), we get
\[ I = |A_0|^2 \left( 1 + e^{-4\alpha x} - 2e^{-2\alpha x} \cos 2\beta x \right) \]  

(2.116)

The experimental data is fitted to the equation (2.116).

At \( x=\left( \frac{n+1}{2} \right) \lambda_g \), Intensity is maximum \( y= (y_{\text{max}})_n \)

\[ y_n \propto A_0^2 \left( 1 + e^{-4\alpha \left( \frac{n+1}{2} \right) \lambda_g} - 2e^{-2\alpha \left( \frac{n+1}{2} \right) \lambda_g} \cos 2\beta \left( \frac{n+1}{2} \right) \lambda_g \right) \]

\[ y_n = KA_0^2 \left( 1 + e^{-2\alpha \left( \frac{n+1}{2} \right) \lambda_g} \right)^2 \]

(2.117)

As \( n \to \infty \), \( (y_n)_\infty = y_\infty = KA_0^2 \)

\[ y_n = y_\infty \left( 1 + e^{-2\alpha \left( \frac{n+1}{2} \right) \lambda_g} \right)^2 \]

(2.118)

\[ \ln \left( \sqrt{\frac{y_n}{y_\infty}} - 1 \right) = -n\alpha \lambda_g - \frac{\alpha \lambda_g}{2} \]

(2.119)

A graph is plotted between \( n \) and \( \ln \left( \sqrt{\frac{y_n}{y_\infty}} - 1 \right) \) where slope gives the value of \( \alpha \lambda_g \)

\( \lambda_0 \) = Free space wavelength,

\( \lambda_c \) is the cutoff wavelength for given node numbers \( n \) and \( m \).

\[ \frac{1}{\lambda_c^2} = \left( \frac{m}{2a} \right)^2 + \left( \frac{n}{2b} \right)^2 \]

(2.120)

For TE_{10} mode, \( \lambda_c = 2a \), \( a \) being the breadth and \( b \) the height of the waveguide.

Using the optimized values of \( \alpha \) and \( \beta \), the complex dielectric permittivity of the sample is computed from the relations

\[ \varepsilon' = \lambda_o^2 \left( \frac{1}{\lambda_c^2} + \left( \frac{\beta^2 - \alpha^2}{4\pi^2} \right) \right) \]

(2.121)
\[ \varepsilon'' = \frac{\varepsilon_0^2}{2\pi^2} \]  

(2.122)

A small offset correction function can be added to all the thickness of the sample to get an improved overall fitting of the theoretical curve with respect to the experimentally obtained profile. This compensates for the effect on the reflected power profile due to the Teflon sheet used as an isolator to isolate the liquid from the rest of the microwave bench. However it is not used in the present study as the author is satisfied by the experimental profile. The error in the estimation of \( \varepsilon' \) and \( \varepsilon'' \) is \( \pm 1\% \) and \( \pm 2\% \) respectively.

2.16.2 Experimental set up for microwave studies at X-band

The block diagram of microwave bench (X-band) is shown in Figure 2.10 and the basic setup of X-band test bench with temperature controller is shown in PLATE 2.2.

(i) Klystron & Power supply

The klystron is a vacuum tube that can be used either as a generator or as an amplifier of power at microwave frequencies. It supplies the required electric energy (regulated) to the klystron. Here a klystron is basically a velocity modulated tube which produces frequencies of 250 MHz-100 GHz with a power output of 10 KW-500 KW with 58% efficiency. Klystron power supply (ALP 160 D) manufactured by A. Lakhanpal Delhi was used. The power supply is connected to a klystron (2K225) mounted on klystron mount (ALP-X-06).

(ii) Variable attenuator

Attenuator is used for varying microwave power completely without any reflection, without any change in its frequency. It is used for isolation between instruments for reducing the power input to a particular stage to prevent overloading. The
attenuator constructed here is of the variable flap type with a metallised glass strip as the dissipative element and consists of a piece of wave guide 6” long. It has a narrow 1/16” slot on the broad face to take in the glass plate of 1/32” thickness. The glass plate is fixed between metal strips and the curved surfaces passes through the slot. The metal strips are cut out of a single rod fixed to the top of the guide with hinge so that it can move upwards and downwards by means of a spring and screw which, moves against the top surface thus enabling the glass plate to move into or out of the slot in the guide and controlling the depth of penetration. It has an approximate attenuation of 20 dB.

(iii) Coupler

Directional coupler is a device, which can sample a small amount of microwave power for measurement purposes. It gives two or more paths for the incoming energy.

(iv) Frequency meter

The frequency meter is an instrument, which gives the frequency value of input wave by using the principle of resonant cavity.

(v) Slotted section

A coupling probe moving along the wave guide can be used to detect the standing wave pattern present inside the wave guide. It consists of a slotted section and facility for attaching the detecting instruments. The slot is made at the centre of the microwave guide parallel to the axis. A small probe is inserted through the slot, senses the relative field strength of the standing wave pattern inside the wave guide. Here the probe is connected to a crystal detector to study the pattern.
Fig. 2: Block diagram of apparatus for determination of complex dielectric constant for liquids.
(vi) Tunable Detector

This tunable detector helps to detect the microwaves, which uses crystals to detect. We can tune these detectors to match the microwave transmission system and the detector.

(vii) VSWR meter (Voltage standing wave Ratio meter)

A standing wave indicator is a highly sensitive fixed frequency electronic meter, calibrated to indicate directly both voltage and power, standing wave ratios, when used with square law detectors such as crystal diodes and barrettes. The maximum sensitivity of the instrument is 0.1 µV for full scale meter deflection. The noise level is less than 0.03 µV as referred to a signal obtained to the input jack. Here a multimeter can also be adopted to measure the voltage readings.

(viii) Dielectric cell

The dielectric cell is connected to the bench through a 90° E-bend. Liquid dielectric medium is contained in the cell. A reflecting plunger inside the cell reflects the microwave power from the dielectric and the field due to this interfere with the field due to incoming microwave power from the klystron to form standing waves within the slotted line wave guide. The resultant microwave power due to these standing waves within the slotted line can be sensed by the probe penetrating the slot and the corresponding potential difference developed across the crystal detector. This is proportional to the net microwave power.
2.16.3 Fabrication of dielectric cell

The dielectric cell is fabricated in the laboratory. It consists of rectangular wave-guide of dimensions 0.9” × 0.4”. The length of the wave-guide was 16 cm. The cell has been silvered inside to avoid any possible contamination of liquid.

A mica window is used for separating the dielectric cell from the setup. Dielectric thickness can be varied with precision by the movement of plunger inside the dielectric medium. The movement of the plunger is done using screw brass rod threaded with 1 mm pitch and passes through a nut in the centre of brass disc of 30 mm diameter. The cross sectional diagram of dielectric cell is given in Figure. 2.11. The short circuit plunger can be moved up and down in the cell by rotating the brass disc in the clockwise and anticlockwise directions respectively with the help of the marking present on it. Thus for each rotation of the brass disc the plunger moves by 1 mm.

The rotating disc is prevented from raising or lowering. The short-circuit plunger is fixed to one end by means of two bent brass guide pieces that engage into a continuous groove on the vertical side of the disc. The movement can be measured with an accuracy of 0.025 cm. The cell is internally silvered to prevent the chemical attack and to reduce the wall losses. Initially the plunger is brought very close to the mica sheet thereby reducing the dielectric thickness to zero.
Figure 2.11: Dielectric cell
The probe within the slotted line is moved along the slot and kept at a position where the crystal output is Minimum. Dielectric thickness is increased in small steps by slowly withdrawing plunger and the corresponding output from the crystal is recorded. Before going to the present study, plunger was tested for non-polar liquids like benzene, carbon tetrachloride and hexane. Those values are in agreement with the reported values.

2.17 Refractometry studies

Refractive index of any material is a measure of the electronic polarization of the material. Maxwell equation gives the relation between the refractive index and the high frequency (optical frequency) dielectric constant.

\[ n_D^2 = \varepsilon_\infty \]  

(2.123)

Although the refractive index is ideally the value measured at very high frequency \( n_\infty \), it is found to be sufficient to use refractive index measured at the Sodium D line (\( n_D \)).

The direction of an obliquely incident ray of light changes when it passes from one medium to the other. The change in direction, towards or away from the normal depends on the density of the medium. The denser the second medium, the more change towards the normal. Refractive index is normally defined as \( n = \frac{\sin i}{\sin r} \), where \( i \) and \( r \) are the angles of incidence and reflection respectively.

For an ideal experiment to determine the refractive index of a material, medium 1 has to be vacuum, but air is used for practical purposes. The difference in \( n \) determined by the two methods is found to be less than 0.03%.

2.17.1 Abbe refractometer

A refractometer, measures the extent to which light is bent (i.e., refracted) when it moves from air into a sample and is typically used to determine the index of a liquid
sample. A refractive index is a unit less number, between 1.30 and 1.70 for most of the compounds and is normally determined to three digit precession. Since the index of refraction depends on both the temperature of the sample and the wavelength of light (yellow) used, both these are indicated reporting the refractive index

\[ n_D^{27} = 1.49 \]

where \( n \) denotes refractive index, the superscript indicates the temperature in °C and the subscript denotes the wavelength of light (In this case D indicates the sodium D light at 589 nm).

The refractive index of a liquid can be measured using Abbe type refractometer. The instrument used was supplied by ASCO AS-17760 and is shown in PLATE 2.3. Sodium vapour lamp is used as the source of light. The liquid sample whose refractive index is to be determined is sandwiched into a thin layer between an illuminating prism and a refracting prism (Figure 2.12). The refracting prism is made of glass with a high refractive index (e.g. 1.70) and the refractometer is designed to be used with samples having a refractive index smaller than that of the refracting prism.

Figure 2.12: Refractometer Prism
The Illumination of the Prism

It is a dense flint prism with $60^0$ angle. One of its faces is around upper (illuminating prism) surface. The second face is polished and fitted with a window which can be opened or closed by a cover plate. This is carried by a metal sector hanged to the side plate of instrument. This can be drawn on to the measuring prism and clamped there firmly with a locking knob so that the ground face rests on the polished surface. Light enters through the window and gets diffused at the matt surface, thus allowing some rays to incident on the medium just grazing.

The Measuring Prism

This is an essential part of the instrument. The refracting edge of the Abbe’s refractometer prism is $60^0$. It is made of dense flint whose refractive index is just greater than the maximum extent of the scale. The vertical section of the prism is shown in the diagram. The top horizontal surface is polished and the surface B has a window which can be either opened or closed with a hinged mirror. This face B is ground matt and serves to find the refractive indices in reflected light. The face C is also polished. The frame of instrument is inclined to the face for the convenience of observation as well as to see that the measuring face A is horizontal.

The polished face C rests in contact with the hole in the body and the emergent light passes through this hole on to the mirror. A small mirror is attached to the metal sector. A light source is projected through the illuminating prism, so each point on this surface can be thought of as generating light rays traveling in all directions. As shown in Figure 2.12, light travelling from point A to point B will have the largest angle of incidence ($\theta_i$) and hence the largest possible angle of refraction ($\theta_r$) for that sample. All
other rays of light entering the refracting prism will have smaller \( \theta_r \) and hence lie to the left of point C. Thus, on the back side of the refracting prism, a light region to the left and a dark region to the right is observed. Samples with different refractive indices will produce different angles of refraction and this will be reflected in a change in the position of the borderline between the light and dark regions. By the appropriately calibrated scale, the position of the borderline can be used to determine the refractive index of any sample. The refractive index of any given material is a test for the purity of the material. The error in the estimation of \( \varepsilon_{\infty} \) by this method is \( \pm 0.04 \% \).

2.18 Fourier Transform Infrared Spectrometer (FT-IR)

Infrared (IR) radiation refers broadly to the part of electromagnetic spectrum between the visible and microwave regions. The limited portion of IR spectrum from 400 cm\(^{-1}\) to 4000 cm\(^{-1}\) is of greatest practical use in determining bond formation in organic compounds. Although the IR spectrum is characteristic of the entire molecule, it is true that certain groups of atoms give rise to bands at or near the same frequency regardless of the structure of the rest of the molecule.

Infrared radiation of frequencies less than 100 cm\(^{-1}\) is absorbed and converted by an organic molecule into energy of molecular rotation. Infrared radiation in the range from 10000 cm\(^{-1}\) to 100 cm\(^{-1}\) is absorbed and converted by an organic molecule into energy of molecular vibration. This absorption is also quantized. A single vibrational energy is accompanied by a number of rotational energy changes. Due to this vibrational spectra appear as bands rather than as lines. The frequency or wavelength of absorption depends on the relative masses of the atoms, the force constants of the bonds and the geometry of the atoms. Particularly we consider the
vibrational – rotational bands which occur between 4000 cm\(^{-1}\) to 400 cm\(^{-1}\). The band positions in IR spectra are represented in wave number \(\nu\), which is equal to reciprocal of wavelength, and its unit is cm\(^{-1}\). In the present study, FTIR 5300 model spectrometer of JASCO (Japan) instrument is used and is shown in PLATE 2.4.