2.1 INTRODUCTION

Dielectric materials are bad conductors of electricity. The most of electrons in these materials are bound with molecules, and there are no significant free electrons to conduct current. When these materials are placed in electric field, displacement of positive and negative charges in molecule takes place. The redistribution of charges may be such that effective centers of positive and negative charge distribution do not coincide. This positive and negative charge distribution separated by some distance can be treated as dipole. Applied electric field forces this molecular dipole to align in the direction of field. Alignment of molecular dipoles in the direction of field is called as polarization. Dielectric constant is a measure of ability of material to get polarizes in direction of applied electric field. That is dielectric constant gives ability of materials to store applied electrical energy in the form of polarization.

Dielectric materials can be classified in two categories as polar and non-polar, depending on the charge distribution in molecule. Non-polar dielectric consists of molecules with positive and negative charges such that their effective center of charge distribution coincides. Thus dipole moment of non-polar dielectric material is zero in absence of electric field. Polar dielectric materials are those in which centers of positive and negative charge distribution are separated by distance, forming a molecular dipole in absence of electric field. But since positive and negative charges are equal, the molecule is electrically neutral. The magnitude of molecular dipole moment depends on size and symmetry, such as Methane, Carbon tetrachloride, and benzene are non-polar while molecules having no center of symmetry such as Methanol, Ethanol, Acetone and water 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 charges ‘+q’ and ‘-q’ separated by a distance ‘d’, then dipole moment is ‘qd’. In molecular dipoles ‘q’ will be of 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. Thus the dipole moment ($\mu$) for the molecular dipoles is in the order of $10^{18}$ e. s. u. cm. The unit $10^{18}$ e. s. u. cm is called as Debye. The dipole moments of molecular dipoles are usually measured in Debye, abbreviated as D. Dielectric constant of material depends on dipole moment as well as on ability of these dipoles to align in direction of applied electric field.
When dielectric material is placed in electric field the total polarization is sum of contributions from three types of polarization. The polarization of molecular dipoles due to their orientation in the direction of applied field is known as orientation polarization ($P_o$). Applied electric field causes redistribution of charges in dielectric material. Polarization of dipoles created due to distortion in charge distribution of material is termed as distortion polarization ($P_D$). 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 direction of electric field is known as electronic polarization ($P_E$). Relative motion of atoms gives rise to polarization known as atomic polarization ($P_A$). The total polarization can be written as

$$P = P_o + P_D$$

But

$$P_D = P_E + P_A$$

Thus

$$P = P_o + P_E + P_A$$

The dipole moment per unit polarizing field is called as molecular polarizability ($\alpha$). Hence, total molecular polarizability ($\alpha$) is given as

$$\alpha = \alpha_o + \alpha_D = \alpha_o + \alpha_E + \alpha_A$$

Where $\alpha_D = \alpha_E + \alpha_A$ is called as distortion polarizability.

The insulators whose behaviour gets modified in the electric field are called as Dielectrics. When the change in the behaviour of dielectric is independent of the direction of the applied field, the dielectric is called as Isotropic. On the other hand, if the change in behaviour of the dielectric depends on the direction of applied field the dielectric is called as Anisotropic.

As molecule of any substance consists of atoms, group of atoms. Each group has a definite electric charge, either positive or negative. In the absence of external electric field, the net charge on molecule as a whole is zero, but the spatial arrangement of charges in a molecule may be different in different substances. According to spatial arrangement of charges in a molecule, the molecules are classified as polar or non-polar.
A polar molecule has permanent dipole moment. The dipole moment depends on the size and symmetry of the molecule. Although, the total numbers of positive and negative charges are equal, the distribution of two kinds of charges is different. The positive and negative charges are centered at points separated by a distance of molecular dimensions. e.g. Water, Ethanol. This forms an electric dipole. If the charge +q and -q are separated by a distance 'd', it forms a dipole moment given by -qd. In a molecule 'q' is of the order of electronic charge, $10^{-10}$ e.s.u., while the 'd' is of the order of $10^{-8}$ e.s.u. Therefore unit of dipole moment is $10^{-18}$ e.s.u., and is called a 'Debye', abbreviated as 'D'.

In the case of non polar molecules, the centers of positive and negative charges coincide with the centers of symmetry of the molecule, therefore have zero dipole moment. e.g. Benzene, Methane. Polar molecules always have a permanent dipole moment, even in the absence of an external electric field.

When the electric field is applied to dielectric, the molecular charges get displaced. The total charge passing through unit area within the dielectric, perpendicular to the direction of applied field is called polarization. The polarization are of three types-

a) **Electronic Polarization ($P_e$):** Electronic polarization is due to the displacement of electrons with respect to the atomic nucleons. This polarization occurs in all atoms, and can be observed in all dielectrics. It takes very small interval of time to occur. It is of the order of $10^{-15}$ sec., which is comparable with time period of ultraviolet light.

b) **Atomic Polarization ($P_a$):** Atomic polarization is due to mutual displacement of atoms or group of atoms. It takes a short time of the order of $10^{-13}$ to $10^{-12}$ sec., which corresponds to period of infrared light.

These two polarizations together called as Distortion polarization ($P_d$), because it is caused by displacement of charges in atom with respect to each other in the direction of applied field. As there is redistribution of charges in response to applied field, it posses dipole moment called induced dipole moment. The magnitude of induced dipole moment depends on the field strength and polarizability of the dielectric. The induced dipole moment, lasts so long as the electric field is present and do not depend on temperature of dielectric. The electrical energy required for distortion polarization is completely returned to the electric energy source after the removal of the voltage. For this reason it does not contribute to dielectric loss.
c) Orientation Polarization ($P_o$): Orientation polarization is property of the polar molecules. It is due to rotation of permanent dipoles of dielectric medium. The molecular dipoles orient in the direction of the applied field. It is function of molecule size, viscosity, temperature, and frequency of applied field. Orientation polarization takes a time of the order of $10^{-12}$ to $10^{-10}$ sec., corresponding to period of microwave frequency region.

The total polarization is:

$$P_t = P_e + P_a + P_o$$

Thus the polar materials have greater permittivity than the non polar, because of additional polarization due to orientation.

2.2 THEORIES OF STATIC PERMITTIVITY:

The dielectric constant may be expressed in terms of the force between two point charges $q$ and $q'$, separated by distance $r'$ in a homogeneous dielectric as:

$$F = \frac{qq'}{\varepsilon r'^2} \quad (2.1)$$

where $\varepsilon$ is the static dielectric constant, a characteristic of the medium between the two charges. It is also defined as the ratio of the field strength in vacuum to that in the material for the same distribution of charge. In MKS system the dielectric constant of free space is $8.854 \times 10^{-12}$ farad/meter.

The capacitor, charged to $q$ at potential $V$ is said to have a capacity of:

$$C = \frac{q}{V} \quad (2.2)$$

If $A$ is the area of each parallel plate with $r'$ distance between them, filled by dielectric of '$\varepsilon$', the capacity is given by:

$$C = \frac{\varepsilon A}{4\pi r} \quad (2.3)$$

where $\varepsilon$ is the ratio of the dielectric constant of the medium between the plates to that of free space. Often, it is referred as a measure of the ability of a fluid, (or solid) to decrease the force of attraction and repulsion between the charged particles. Also, $\varepsilon$ is given by-
\[ \varepsilon = \frac{C}{C_0} \] (2.4)

The dielectric constant thus is dimensionless quantity.

The electric field between the plates of charged capacitor in vacuum is

\[ E_0 = 4\pi\sigma \] (2.5)

where, \( \sigma \) is the surface charge density. If the space between the plates is filled with a homogeneous dielectric material of dielectric constant \( \varepsilon \), the field strength decreases to-

\[ E = \frac{4\pi\sigma}{\varepsilon} \] (2.6)

The decrease in field strength is

\[ E_0 - E = 4\pi\sigma \left( 1 - \frac{1}{\varepsilon} \right) = 4\pi\sigma \left( \frac{\varepsilon - 1}{\varepsilon} \right) \] (2.7)

The same decrease is possible by reducing the surface charge density from \( \sigma \) to \( \sigma \left( \frac{\varepsilon - 1}{\varepsilon} \right) \) by charging the surface of the dielectric opposite to each plates with a charge of opposite sign to that on the plate. Let this surface density be \( P \).

\[ P = \sigma \left( \frac{\varepsilon - 1}{\varepsilon} \right) \] (2.8)

It is produced by an induced charge shift through the dielectric. This is called polarization, which can be expressed as an electric moment per unit volume.

The dielectric displacement is defined as-

\[ D = 4\pi\sigma \] (2.9)

from eq. (3.6)

\[ D = \varepsilon E \] (2.10)

Using eq.(3.6), (3.8), (3.9), (3.10), we get-

\[ D = E + 4\pi P \]

\[ \varepsilon E = E + 4\pi P \]
\[
(\varepsilon - 1) = \frac{4\pi p}{E} \tag{2.11}
\]

\[
\varepsilon = 1 + \frac{4\pi p}{E} \tag{2.12}
\]

This equation gives relation between applied electric field, polarization and permittivity.

The charge +PA on one surface of the dielectric material and -PA on the opposite surface, resulting from a displacement of charge throughout the dielectric, gives an electric moment \((PA)(r)\), where 'r' being the thickness.

\[M = PA r\]

Let \(A r = V\), volume of the slab.

\[M = PV \tag{2.13}\]

Thus polarization \(P\) can be defined as electric moment per unit volume. The polarized slab behaves like an assembly of electric dipoles parallel to one another.

2.2.1 DEBYE THEORY OF STATIC PERMITTIVITY:

Let us consider a sphere of homogeneous dielectric placed in parallel plates. The size of sphere is larger than molecular dimensions but smaller than the spacing between the plates. Let the plates are uniformly charged with surface charge density \(\sigma\). If \(F\) is intensity of electric field acting on single molecule, then electric moment of molecule is given by-

\[m = \alpha_t F \tag{2.14}\]

where \(\alpha_t\) is total polarizability of the molecule. The average electric moment \(^1\) is given by-

\[\bar{m} = \frac{\mu^2 \cos^2 \theta}{KT} F + e r \tag{2.15}\]

The first term in this equation represents the contribution due to permanent dipole moment of molecule and the second one, represents due to displacement of elastically bound charges. It is obvious from equation (2.15) that the moment due to permanent dipole is temperature dependent.
F may be conveniently considered as actual force by assuming unit positive charge in a medium enclosed by a small sphere. This force may be treated as consisting of three components, $F_1$, $F_2$, and $F_3$ defined as

1) The force $F_1$ due to charges of surface density $\sigma$ on plates.

2) The force $F_2$ due to polarization of medium outside the small sphere.

3) The force $F_3$ due to medium contained in the small sphere.

Thus

$$F = F_1 + F_2 + F_3$$

(2.16)

By definition

$$F_1 = 4 \pi \sigma$$

(2.17)

$F_2$ may be obtained by considering that the matter within the small sphere is to be removed. $F_2$ is made up of two parts, the first one due to layers of induced charges on dielectric facing the conducting plates, and the second one of the layer of charge on surface of small spherical cavity.

$$F_2 = -4 \pi P + \frac{4 \pi P}{3}$$

(2.18)

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 showed that for a cubic lattice of polarizable atoms the dipoles inside sphere produce zero fields.

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

$$F = 4 \pi \sigma - 4 \pi P + \frac{4 \pi P}{3}$$

(2.19)

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

$$F = E + 4\pi P - 4\pi P + \frac{4\pi P}{3}$$

(2.20)

$$F = E + \frac{4 \pi P}{3}$$

(2.21)
But  

\[ \varepsilon E = E + 4\pi P \quad (2.22) \]

\[ E(\varepsilon - 1) = 4\pi P \quad (2.23) \]

\[ F = E + E(\varepsilon - 1)/3 \]

\[ F = E(\varepsilon + 2)/3 \quad (2.24) \]

This is the relation existing between the actual force \( F \) and electric field \( E \).

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

\[ P = N_1 m = N_1 \alpha F \quad (2.25) \]

Substituting \( F \) from eq.(2.24), we get

\[ P = N_1\alpha\left(\frac{\varepsilon + 2}{3}\right)E \quad (2.26) \]

By using eq.(3.23) and substituting the value of \( P \) from eq.(3.26), we get the relation between dielectric constant \( \varepsilon \) and molecular polarizability \( \alpha \) as -

\[ \frac{(\varepsilon - 1)}{(\varepsilon + 2)} = \frac{4\pi}{3}N_1\alpha_i \quad (2.27) \]

In pure substance \( N_1 = N\rho / M \), where \( M \) is molecular weight, \( \rho \) is density and \( N \) is number of molecules per mole. The eq.(3.27) becomes-

\[ \frac{(\varepsilon - 1) M}{(\varepsilon + 2) \rho} = \frac{4\pi}{3}N\alpha_i \quad (2.28) \]

This equation is known as Clausius-Mossotti Equation. The right hand side of equation gives the molar polarization given by-

\[ P = (4\pi/3)N\alpha_i \quad (2.29) \]

The molar polarization gives some information about electric properties of the molecule. From eq.(3.28) the molar polarization is given by-

\[ \overline{p} = \frac{(\varepsilon - 1) M}{(\varepsilon + 2) \rho} \quad (2.30) \]

This molar polarization is different from the \( P \) used to denote the electric moment per unit volume. Debye proposed his theory using Langevin's method and Lorentz's expression for local field. Langevin's is the method to determine the mean magnetic
moments of gas molecules having permanent magnetic moment. Debye put forth his theory on the basis of following assumptions.

1) The molecule is considered as rigid system of charges.

2) The external field is supposed to induce no change at all.

The molecules are classified into two groups as-

a) Molecules with normal values of molar polarization and

b) Molecules with abnormally large values of polarization, with these, in general the mean electric moment $\bar{m}$ will be expressed by -

$$
\bar{m} = \left[ \alpha_d + \frac{\mu^2}{3KT} \right] F
$$

(2.31)

where $\alpha_d$ is the polarizability due to distortion and $\mu^2/3KT$ indicates the polarizability due to orientation of dipoles in the field and it is added to the induced moment. Thus total polarizability is -

$$
\alpha = \alpha_d + \frac{\mu^2}{3KT}
$$

(2.32)

using this value in eq.(2.28), we get Debye equation as

$$
\frac{(\varepsilon - 1) M}{(\varepsilon + 2) \rho} = \frac{4\pi N}{3} \alpha_t = \frac{4\pi N}{3} \left[ \alpha_d + \frac{\mu^2}{3KT} \right]
$$

(2.33)

This is Debye equation for permittivity.

Debye has given general equation in which $\alpha_t$ is expressed as the average of the three polarizabilities along the three axes of molecule treated as an ellipsoid of polarization. It follows from Debye theory that-

1) For non polar materials, the molar polarizability should be constant, independent of 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 Debye equation can be used for calculating the molecular dipole moment from measured static permittivity in the gaseous phase and in the dilute solutions of polar compounds in non-polar solvents. Of course, for pure polar liquids, the Debye equation can't be used because of dipolar interaction between the molecules.

However, Debye equation can be applied to polar liquids by neglecting polarization due to distortion. In that case the Debye equation becomes:

\[
\frac{(\varepsilon - 1)}{(\varepsilon + 2)} = \frac{4\pi N \mu^2 \rho}{9KTM}
\]

and considering

\[
\frac{4\pi N \mu^2 \rho}{9KM} = T_c
\]  \hspace{1cm} (2.35)

\[
\frac{(\varepsilon - 1)}{(\varepsilon + 2)} = \frac{T_c}{T}
\]  \hspace{1cm} (2.36)

At temperature below \( T_c \), the polarization becomes so intense and causes large internal field that the molecules will spontaneously align themselves parallel to one another, even in absence of an external field, and the material becomes ferroelectric. Hence Debye equation can't be applied for pure polar liquids.

2.2.2 ONSAGER THEORY:

The validity of Debye equation is restricted to fluids only, because of first assumption. Hence not applicable to crystalline materials. Similarly, second assumption limits its validity to the cases of gases at moderately low densities and possibly of dilute solutions of polar molecules in non-polar solvents. Also, according to Debye theory liquids act as ferroelectric material when \( T < T_c \), but the phenomenon of ferro-electricity is not common and certainly does not occur in water\(^7\). This failure of Debye equation is attributed to the assumption that \( F_3 = 0 \). i.e. He didn't account the force due to medium in the spherical cavity, which is almost certainly not valid.

Onsager\(^6,8\) considered the local field at molecule and gives a model for permittivity. He treated a molecule as a polarizable point at the center of a spherical
cavity of molecular dimension in a homogenous medium. The radius 'a' of the molecule is defined by assuming -

\[ \frac{4}{3} \pi a^3 N_1 = 1 \]

i.e. the sum of the volumes of the spherical cavities is equal to total volume of the material.

\[ a = \sqrt[3]{\frac{3}{4\pi N_1}} \quad (2.37) \]

This assumption that the cavity in which the molecule lies can be treated as sphere in a homogeneous medium limits the validity of the theory to materials in which there are no strong local forces due to neighbors.

The internal field in the molecule consists of two parts -

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

\[ G = \frac{3\varepsilon_0}{2\varepsilon_0 + 1} E = gE \quad (2.38) \]

where, \( g = (3 \varepsilon_0) / (2 \varepsilon_0 + 1) \);

\( \varepsilon_0 \) is static dielectric constant.

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

\[ R = \frac{2(\varepsilon_0 - 1)m}{(2\varepsilon_0 + 1)a^3} = r \frac{m}{a^3} \quad (2.39) \]

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

The total internal field acting upon spherical polar molecule is -

\[ F = G + R \]

\[ F = \frac{3\varepsilon_0}{2\varepsilon_0 + 1} E + \frac{2(\varepsilon_0 - 1)m}{(2\varepsilon_0 + 1)a^3} \quad (2.40) \]
\[ F = gE + r \frac{m}{a^3} \]  \hspace{1cm} (2.41)

From eq.(3.40) it can be observed that when \( \varepsilon_0 \rightarrow 0 \), 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 induced moment \( \alpha_dF \) by the local field.

\[ m = \mu + \alpha_d F \]  \hspace{1cm} (2.42)

\[ m = \mu + \alpha_d [ gE + (r \alpha m) / a^3 ] \]  \hspace{1cm} (2.43)

\[ m = \frac{(\mu + \alpha_d gE)}{\left(1 - \frac{r \alpha_d}{a^3}\right)} \]  \hspace{1cm} (2.44)

Then mean moment parallel to the field is given by -

\[ \bar{m} = \frac{g \mu^2 E}{(1 - \frac{r \alpha_d}{a^3})3KT} + \frac{\alpha_d g}{(1 - \frac{r \alpha_d}{a^3})} \]  \hspace{1cm} (2.45)

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

\[ \frac{(\varepsilon_0 - 1)}{4\pi} = \frac{N_i g}{\left(1 - \frac{r \alpha_d}{a^3}\right)} \left[ \alpha_d + \frac{1}{\left(1 - \frac{r \alpha_d}{a^3}\right)} \frac{\mu^2}{3KT} \right] \]  \hspace{1cm} (2.46)

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

\[ \alpha_d = \frac{n^2 - 1}{n^2 + 2} a^3 \]  \hspace{1cm} (2.47)

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

\[ \frac{(\varepsilon_0 - n^2)(2\varepsilon_0 + n^2)}{\varepsilon_0 (n^2 + 2)^2} = \frac{4\pi N_i \mu^2}{9KT} \]  \hspace{1cm} (2.48)

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

This equation makes it possible, to compute the permanent dipole moment of the molecule from the measurement of permittivity of pure liquid, if the density and $\varepsilon_\infty$ are known. Onsager avoids one of the assumptions, which limits the validity of the Debye equation, namely, the component of local field due to molecules inside the sphere. However, he adopted the other assumption, that there are no local directional forces due to their neighbours on the molecules, so that the dipole moments are distributed according to Langevin’s law. Hence, there is considerable discrepancy in case of those liquids in which there is strong intermolecular interaction\(^9\).

2.2.3 FROHLICH’S THEORY:

Frohlich\(^{10}\) using statistical method obtained a more general expression. He considered a spherical region of macroscopic dimensions within an infinite specimen, which is treated as a continuous medium. According to Frohlich, the equation for non-polarizable dipoles is-

$$\frac{(\varepsilon_0 - 1)(2\varepsilon_0 + 1) M}{3\varepsilon_0} = \frac{4\pi N \langle m^2 \rangle}{3KT}$$  \hspace{1cm} (2.51)

where, $\langle m^2 \rangle = \mu^2 = \mu_0^2 = g\mu^2$ and for molecule replacing $\mu$ by its value -

$$\mu_0 = \frac{3}{\varepsilon_\infty + 2}\mu$$  \hspace{1cm} (2.52)

which is the moment in vacuum($\mu_0$) of a spherical molecule cavity of a material of dielectric constant $\varepsilon_\infty$ having a dipole moment $\mu$ at its center. The Frohlich takes the distortion polarization into account by imagining non-polarizable dipole units to be embedded in polarizable continuum of permittivity $n^2(\varepsilon_\infty)$.

The equation becomes -

$$\frac{(\varepsilon_0 - n^2)(2\varepsilon_0 + n^2) M}{\varepsilon_0(n^2 + 2)^2} = \frac{4\pi N g\mu_0^2}{9KT}$$  \hspace{1cm} (2.53)
Except for interaction of correlation parameter $g$, the equation is identical with Onsager’s equation. The correlation factor can be expressed as:

$$g = 1 + z\langle \cos \theta \rangle$$  \hspace{1cm} (2.54)$$

where $\langle \cos \theta \rangle$ depends only on the orientation of the two molecules i.e. $i^{th}$ and $j^{th}$ molecules. It can be seen that $g$ will be different from 1 when $\langle \cos \theta \rangle \neq 0$, i.e. when there is correlation between the orientation of neighboring molecules. When the molecules tend to direct themselves with parallel dipole moments, $\langle \cos \theta \rangle$ will be positive and $g$ will be larger than 1. When the molecules prefer an ordering with anti-parallel dipoles, $g$ will be smaller than 1.

2.3 DIELECTRIC RELAXATION:

Dielectric relaxation occurs when, a dielectric material is polarized by the externally applied alternating field. The decay in polarization is observed on removal of the field. The decay in polarization occurs due to orientation of electric dipoles in an electric field. This depends on the internal structure of a molecule and on molecular arrangement. The orientation polarization decays exponentially with time; the characteristic time of this exponential decay is called relaxation time. It is defined as the time in which this polarization reduces to $(1/e)^{th}$ times the original value. Dielectric relaxation is the cause of anomalous dispersion in which permittivity decreases with increasing frequency.

Under the influence of an ac electric field, the polar molecules of a material orient themselves and attain an equilibrium distribution in molecular orientation. When the polar molecules are of large size or frequency of ac field is very high or the viscosity of the medium is very large, the orientation of molecules is not fast enough for the attainment of equilibrium with the applied field. The polarization then acquires a component out of phase with the field and the displacement current acquires a conductance component in phase with field, resulting in thermal dissipation of energy. The permittivity thus acquires a complex characteristic.
In such cases it is used to relate the displacement $\vec{D} = \varepsilon' \vec{E}$. The complex permittivity $\varepsilon'$ can be written as $\varepsilon' - i \varepsilon''$, where $\varepsilon'$ is real part proportional to stored energy and $\varepsilon''$ is imaginary part and it is dielectric loss.

Several theories are available in the literature regarding the relaxation mechanism and its relation to the molecular structure. These may be broadly classified into two groups. One is based on the application of Stoke’s law of a sphere rotating in a viscous medium of macroscopic measurable viscosity. Another approach is by considering dielectric relaxation as a rate phenomenon like one for viscosity and diffusion, and is based on the concept of transition of a dipole over certain potential barrier. A dipole in a liquid may have two equilibrium positions, which are separated by a barrier of definite height. The dipole must acquire sufficient energy in excess over the average thermal energy in order to be able to jump to the next equilibrium position.

2.4 THE DYNAMIC PERMITTIVITY:

When an alternating field of high frequency is applied to a dielectric material, the dipolar polarization can’t reach its equilibrium value fast enough or follow the polarizing field. Because of this, dipoles per unit volume decreases with increase in frequency and hence there is decrease in permittivity.

Let $P$ be the total equilibrium polarization given by -

$$P = P_1 + P_2$$

where, $P_1$ is the distortion polarization and $P_2$ is dipolar polarization.

When a field $E$ is applied to a dielectric, the distortion polarization ($P_1$) will establish very quickly, but the dipolar polarization ($P_2$) takes some time to reach its equilibrium value. If we assume that $P_2$ increases at a rate proportional to its departure from its equilibrium value -

$$\frac{dP_2}{dt} = - \frac{P - P_1 - P_2}{\tau}$$

where $\tau$ is a constant which has the dimension of time and is called the macroscopic relaxation time. Rewriting this equation as
\[ \frac{dP_2}{P - P_1 - P_2} = -\frac{dt}{\tau} \]  

the solution of this equation is -

\[ \ln (P - P_1 - P_2) = \frac{-t}{\tau} + C \]  

where C is constant. If we assume the field E is suddenly applied at \( t = 0 \), then \( P_2 = 0 \) at \( t = 0 \), then eq. (3.57) gives:

\[ C = \ln (P - P_1) \]

using this value of C in eq. (3.57) and solving for \( P_2 \), we get -

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

Similarly, if a polarization \( P \) is established by a steady field \( E \) and then field is switched off at \( t = 0 \), distortion polarization \( P_1 \) falls immediately to zero and \( P_2 \) decreases exponentially with characteristic time constant \( \tau \) as-

\[ \frac{dP_2}{dt} = -\frac{P_2}{\tau} \]

The solution of this equation is-

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

Suppose the applied field alternates with angular frequency \( \omega \), can be expressed as-

\[ E = E_0 e^{i\omega t} \]  

using eq. (3.11), static permittivity and refractive index are defined as-

\[ 4\pi\varepsilon P = E(\varepsilon_0 - 1), \text{ as } \omega \to 0; \]

i.e. \[ P = \frac{(\varepsilon_0 - 1)E}{4\pi} \]  

\[ 4\pi\varepsilon_1 P_1 = E(n^2 - 1), \text{ as } \omega \to \infty, \]
i.e. \[ P_1 = \frac{(n^2 - 1)E}{4\pi} \] (2.62)

Where \( n \) is the refractive index. Using the values of \( P, P_1 \) in eq.(3.55), we get-

\[
\frac{dP_2}{dt} = -\frac{P - P_1 - P_2}{\tau}
\]

\[
= \frac{\left(\varepsilon_0 - n^2\right)}{4\pi} E - \frac{P_2}{\tau}
\]

\[
= \frac{\left(\varepsilon_0 - n^2\right)}{4\pi} E_0 e^{i\omega t} - \frac{P_2}{\tau}
\]

The solution of this equation is -

\[ P_2 = \frac{\left(\varepsilon_0 - n^2\right)E}{4\pi(1 + i\omega\tau)} \] (2.63)

In this equation, \( P_2 \) has become a complex quantity. This means that dipolar part of the polarization is not in phase with the applied field \( E \). We can express polarization as -

\[ P^* = p' - i p'' = P_1 + P_2 \]

\[ = \frac{(n^2 - 1)E}{4\pi} + \frac{\left(\varepsilon_0 - n^2\right)E}{4\pi(1 + i\omega\tau)} \]

when polarization becomes complex, the permittivity must also become complex, and eq.(2.12) can written as -

\[ \varepsilon^* = \varepsilon' - i \varepsilon'' = 1 + \frac{4\pi}{E} P' \]

\[ \varepsilon^* = 1 + \frac{4\pi}{E} (p' - ip'') \]

\[ \varepsilon^* = 1 + \frac{4\pi}{E} (P_1 + P_2) \]

substituting the values of \( P_1 \) and \( P_2 \) from eq.(2.62) and eq.(2.63) we get -

\[ \varepsilon^* = \varepsilon' - i \varepsilon'' = n^2 + \frac{\left(\varepsilon_0 - n^2\right)}{(1 + i\omega\tau)} \] (2.64)
where \( \varepsilon' = n^2 + \frac{\varepsilon_0 - n^2}{1 + \omega^2 \tau^2} \),

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

The real part is called as dielectric dispersion and imaginary part is called as dielectric loss. The dielectric loss becomes maximum \( \left[ (\varepsilon_0 - n^2)/2 \right] \) at a frequency \( \omega = 1/\tau \). The phase lag between the polarization and the applied field leads to an

Absorption of energy in the dielectric. The maximum energy absorption occurs at \( \omega = 1/\tau \).

These are known as the Debye or the Debye-Drude equations\(^2\). Where “n” is the refractive index and \( n^2 = \varepsilon_\infty \).

2.4.1 THE DEBYE MODEL:

The permittivity and dielectric loss are given by the Debye equation

\[
\varepsilon^* = \varepsilon_\infty + \frac{(\varepsilon_0 - \varepsilon_\infty)}{(1 + i \omega \tau)} \tag{2.65}
\]

where \( \varepsilon^* = \varepsilon' - i \varepsilon'' \), \( \varepsilon' \) is known as dielectric dispersion and \( \varepsilon'' \) is known as dielectric loss which are given by -

\[
\varepsilon' = \varepsilon_\infty + \frac{(\varepsilon_0 - \varepsilon_\infty)}{(1 + \omega^2 \tau^2)} \tag{2.66}
\]

\[
\varepsilon'' = \frac{(\varepsilon_0 - \varepsilon_\infty) \omega \tau}{(1 + \omega^2 \tau^2)} \tag{2.67}
\]

The variation of \( \varepsilon' \) and \( \varepsilon'' \) with frequency is shown in Figure (2.1). The frequency is displayed on a logarithmic scale. The dielectric loss reaches its maximum

\[
\varepsilon''_{\text{max}} = \frac{\varepsilon_0 - \varepsilon_\infty}{2}, \text{ at a frequency } \omega = 1/\tau, \text{ and falls to half its maximum when}
\]

\[
\omega \tau = (1 + \omega^2 \tau^2)/4
\]
The dielectric loss is thus considerable over frequencies varying in value by a factor of more than 10.

Another way to represent the experimental results is to construct Argand diagram by plotting \( \varepsilon'' \) against \( \varepsilon' \) at the same frequency. The equation (2.66) and (2.67) are the parametric equations of a circle. On eliminating and rearranging, we obtain

\[
\left( \varepsilon' - \frac{\varepsilon_0 + \varepsilon_\infty}{2} \right)^2 + \varepsilon''^2 = \left( \frac{\varepsilon_0 - \varepsilon_\infty}{2} \right)^2 \tag{2.68}
\]

which is the equation of a circle, center \( \left( \frac{\varepsilon_0 + \varepsilon_\infty}{2}, 0 \right) \), radius \( \frac{\varepsilon_0 - \varepsilon_\infty}{2} \). Thus by plotting \( \varepsilon'' \) against \( \varepsilon' \) a semicircle is obtained as shown in Figure (2.2). For many simple liquids the experimental points do indeed lie on a semicircle. The method has the disadvantage that the frequency, which is the independent variable and the one whose value is most accurately known, is not explicitly shown.

Fig. 2.1: Variation of \( \varepsilon' \) and \( \varepsilon'' \) with frequency \( f \)
2.4.2 THE COLE-COLE MODEL:

For many materials, particularly long-chain molecules and polymers, \( \varepsilon'' \) against \( \varepsilon' \) curve is not a semicircle. Such molecule shows a broader dispersion curve and has a lower maximum loss than that expected from Debye relations. The Cole-Cole has suggested an empirical relation to represent the permittivity of the following form\(^{12}\):

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

(2.69)

where \( \alpha \) represents the symmetric distribution parameter of the relaxation time and lies between 0 and 1, i.e. \( 0 < \alpha < 1 \). Rationalizing this expression and using -

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

we obtain -
\[
\frac{\varepsilon' - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \frac{1 + (\omega \tau)^{2(1-\alpha)} \sin(\pi \alpha / 2)}{1 + (\omega \tau)^{2(1-\alpha)} + 2(\omega \tau)^{2(1-\alpha)} \sin(\pi \alpha / 2)}
\] (2.70)

\[
\frac{\varepsilon''}{\varepsilon_0 - \varepsilon_\infty} = \frac{(\omega \tau)^{2(1-\alpha)} \cos(\pi \alpha / 2)}{1 + (\omega \tau)^{2(1-\alpha)} + 2(\omega \tau)^{2(1-\alpha)} \sin(\pi \alpha / 2)}
\] (2.71)
To find locus in the complex plane, of which these arcs are the parametric equations, we have to eliminate $\omega \tau$. We can do this by solving for $\omega \tau$ and then substituting its value back into the equation. We rewrite the equations

$$
\frac{\varepsilon' - \varepsilon''}{\varepsilon_0 - \varepsilon_w} = \frac{1}{2} \left[ 1 - \frac{1}{2} \left[ \frac{1}{1 + (\omega \tau)^{2(1-\alpha)} + (\omega \tau)^{(1-\alpha)} \sin(\pi \alpha/2)} \right] \right]
$$

$$
= \frac{1}{2} \left[ 1 - \frac{1}{2} \left[ \frac{(\omega \tau)^{(1-\alpha)} - (\omega \tau)^{-(1-\alpha)}}{(\omega \tau)^{(1-\alpha)} + (\omega \tau)^{-(1-\alpha)} + \sin(\pi \alpha/2)} \right] \right]
$$

$$
= \frac{1}{2} \left[ 1 - \frac{\sin \alpha \theta}{\cos \alpha \theta + \sin(\pi \alpha/2)} \right]
$$

where $(\omega \tau)^{(1-\alpha)} = \exp(\theta)$, or $\theta = (1-\alpha) \ln(\omega \tau)$.

Similarly,

$$
\frac{\varepsilon''}{\varepsilon_0 - \varepsilon_w} = \frac{1}{2 \cos \alpha \theta + \sin(\pi \alpha/2)} \cos(\pi \alpha/2)
$$

Solving these equations for $\sin(\alpha \theta)$ and $\cos(\alpha \theta)$ gives

$$
\sin \alpha \theta = \frac{\varepsilon_0 + \varepsilon_w - 2\varepsilon'}{2\varepsilon''} \cos(\pi \alpha/2)
$$

$$
\cos \alpha \theta = \frac{\varepsilon_0 - \varepsilon_w \cos(\pi \alpha/2) - \sin(\pi \alpha/2)}{2\varepsilon''}
$$

We can now eliminate $\theta$ (hence $\omega \tau$) by using $\cos^2 \theta - \sin^2 \theta = 1$. The equation obtained in this way can be rearranged in the form

$$
\left[ \frac{1}{2} (\varepsilon_0 + \varepsilon_w) - \varepsilon' \right]^2 + \left[ \frac{\varepsilon'' + \frac{1}{2} (\varepsilon_0 - \varepsilon_w) \tan(\pi \alpha/2)}{2} \right]^2 = \frac{1}{4} (\varepsilon_0 - \varepsilon_w)^2 \sec^2(\pi \alpha/2) \quad (2.72)
$$

This is the equation of a circle with its center at -
\[
\left[ \frac{1}{2} (\varepsilon_0 + \varepsilon_\infty) - \frac{1}{2} (\varepsilon_0 - \varepsilon_\infty) \tan(\pi \alpha/2) \right] \text{ and radius } \frac{1}{2} (\varepsilon_0 - \varepsilon_\infty) \sec(\pi \alpha/2).
\]

The values of \( \alpha \) found experimentally, show a tendency to increase with increasing number of internal degree of freedom in the molecules, and with decreasing temperature. In limit \( \alpha = 0 \), of course, the Cole-Cole curve reduces to the Debye semicircle.

2.4.3 THE DAVIDSON-COLE RELAXATION MODEL

The Cole-Cole arc is symmetrical about a line through the center, parallel to the \( \varepsilon'' \) axis. Cole and Davidson found that the experimental results for certain materials do not have this symmetry, the \( \varepsilon''-\varepsilon' \) plot being a skewed arc. They suggested that behaviour of this kind could be represented by the expression -

\[
\varepsilon^* = \varepsilon_\infty + \frac{(\varepsilon_0 - \varepsilon_\infty)}{(1 + i \omega \tau )^\beta} \tag{2.74}
\]

Rearranging

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

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

Rationalizing to find \( \varepsilon' \) and \( \varepsilon'' \) yields

\[
\frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \frac{(1 - i \omega \tau )^\beta}{(1 + \omega^2 \tau^2)^{\beta/2}} = \frac{(\cos \phi - i \sin \phi)^\beta}{(1 + \omega^2 \tau^2)^{\beta/2}} = \frac{\exp(-i\beta\phi)}{(1 + \tan^2 \phi)^{\beta/2}}
\]

where \( \tan \phi = \omega \tau \). Therefore

\[
\frac{\varepsilon' - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \cos \beta \phi \cdot \cos \beta \phi \tag{2.76}
\]

\[
\frac{\varepsilon''}{\varepsilon_0 - \varepsilon_\infty} = \cos \beta \phi \cdot \sin \beta \phi \tag{2.77}
\]
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

$$\frac{d\varepsilon''}{d\varepsilon'} = \frac{d\varepsilon''}{d\phi} / \frac{d\varepsilon'}{d\phi} = -\cot(\beta + 1)\phi$$

In the high-frequency limit, $\omega \tau \to \infty$, $\phi = \tan^{-1}(\omega \tau) = \pi / 2$,

$$\frac{d\varepsilon''}{d\varepsilon'} = \tan(\pi \beta / 2)$$

This equation seems to be 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.

2.4.4 THE HAVRILIAK-NEGAMI MODEL:

It was found that none of the above dielectric functions was successful in giving the spectral response they had measured in a number of polymeric materials. There are many examples of dielectric behaviour, which can not be explained by Cole-Cole\textsuperscript{11} and Davidson-Cole\textsuperscript{12} expressions, both of which contain only one adjustable parameter to describe the shape of the plot $\varepsilon''$ versus $\varepsilon'$. Havriliak-Negami\textsuperscript{13} generalized the expression, consisting in a contribution of both Cole-Cole and Davidson-Cole expression as given below

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

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.

2.5 DIELECTRIC PARAMETERS RELATED TO MOLE BEHAVIOUR:

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

2.5.1 BRUGGEMAN FACTOR:

The static permittivity of two component mixture must lie somewhere between two extremes corresponding to static permittivity of two liquids. In order to understand the dipole interaction in the mixture of two liquids, a various mixture formulae have been propose\textsuperscript{7,14}.

Bruggeman mixture formulae\textsuperscript{14} can be used as first evidence of molecular interactions in binary mixture. These formula states that static permittivity of binary mixture ($\varepsilon_{om}$), solute ($\varepsilon_{os}$) and solvent ($\varepsilon_{ow}$) can be related to volume fraction of solvent ($V_{ow}$) in mixture as

$$f_B = \left( \frac{\varepsilon_{om} - \varepsilon_{ow}}{\varepsilon_{os} - \varepsilon_{ow}} \right) \left( \frac{\varepsilon_{os}}{\varepsilon_{om}} \right)^{1/3} = 1 - V_{ow}$$ \hspace{1cm} (2.79)

According to above equation linear relationship is expected in Bruggeman factor $f_B$ and $V$. Any deviation from this linear relation indicated molecular interactions. It is practically observed that in our experimental data for binary mixtures do not fit well with equation 3.79. The modified Bruggeman mixture formula, given below, is used to fit experimental data.

$$f_B = \left( \frac{\varepsilon_{om} - \varepsilon_{ow}}{\varepsilon_{os} - \varepsilon_{ow}} \right) \left( \frac{\varepsilon_{os}}{\varepsilon_{om}} \right)^{1/3} = 1 - [a-(a-1) * V] = 1-f(V)$$ \hspace{1cm} (2.80)

With “$a$” as a fitting parameter and ‘$f$’ can be interpreted as fraction of effective volume $V$. The relative change in value of “$a$” reveals amount of interaction between solute and solvent, as follows:

1. $a > 1$, indicates that the effective microscopic volume of solvent gets more than actual volume. The solute exerts a repulsive force in the system.

2. $a < 1$, indicated that the effective microscopic volume of solvent gets less than actual volume. The solute exerts an attractive macroscopic force in the system.

3. $a = 1$, indicated no change in effective microscopic volume of the system and corresponds to the ideal Bruggeman mixture factor.
2.5.2 EXCESS PARAMETERS:

Studying excess dielectric properties\(^6,15,16\) can access the useful information regarding structural changes in binary mixture. Let A and B are two molecular systems with measurable macroscopic properties PA and PB. If we prepare the mixture of A and B having mole fraction \(X_A\) and \(X_B\) \((X_B = 1 - X_A)\), then the excess macroscopic property \(P_E\) corresponding to mixture is defined as

\[
P_E = P_{AB} - (P_A * X_A + P_B * X_B)  \tag{2.81}
\]

Where \(P_{AB}\) is measured value of property P for mixture. The values of \(P_E\) provide information regarding interactions between A and B. The \(P_E = 0\) indicates no significant interaction between A and B. The \(P_E > 0\) indicated that interaction between A and B leads to increase in the value of property P. Similarly, \(P_E < 0\) indicates decreases in macroscopic property P.

The quantitative picture can be visualized by fitting \(P_E\) to the Redlich-Kister equation\(^22,23\).

\[
P_E = X_A X_B \sum_{n=0}^{\infty} B_n (X_A - X_B)^n  \tag{2.82}
\]

The coefficients \(B_n\)’s provide information regarding molecular interactions. E.g., \(B_0\) 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 work excess dielectric prosperities 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\(^17,18\). The broadening of two levels are additive for two energy levels. The analogy is taken here in dielectric spectroscopy. The excess permittivity \((\varepsilon)^E\) and excess inverse relaxation time \((1/\tau)^E\) are defined as

\[
\varepsilon^E = (\varepsilon_o - \varepsilon_\infty)_m - \left[ (\varepsilon_o - \varepsilon_\infty)_A X_A + (\varepsilon_o - \varepsilon_\infty)_B X_B \right]  \tag{2.83}
\]

\[
(1/\tau)^E = (1/\tau)_m \left[ (1/\tau)_A X_A + (1/\tau)_B X_B \right]  \tag{2.84}
\]

Where X is mole fraction and subscripts m, A and B represent mixture, solvent and solute respectively. The excess permittivity \((\varepsilon)^E\) may provide quantitative information about multimers formation in the mixtures as follows:

1. \(\varepsilon^E = 0\) indicates the liquid A and B do not interact at all.
2. $\varepsilon^E < 0$ indicates the liquid A and B interaction in such a way that the total effective dipoles get reduced. The liquid A and B may form multimers leading to the less effective dipoles. In general, the negative excess permittivity indicates the formation of multimers in the binary mixtures.

3. $\varepsilon^E > 0$ indicates the liquid A and B interaction in such a way that the total effective dipole moment increases. There is a tendency to form multimers, dipole aligned in parallel direction.

The information regarding the dynamics of liquid A and B interaction can be retrieved from this excess inverse relaxation time $(1/\tau)^E$ as follows:

1. $(1/\tau)^E = 0$ indicates there is no change in the dynamics of liquid A and B interaction.
2. $(1/\tau)^E < 0$ indicates the liquid A and B interaction produces a field such that the effective dipoles rotate slowly.
3. $(1/\tau)^E > 0$ indicates the liquid A and B interaction produces a field such that the effective dipoles rotate faster i.e., the field will co-operate in rotation of dipoles.

2.5.3 THERMODYNAMIC PARAMETERS:

Kauzmann\textsuperscript{19} has given an extensive analysis of dipole orientation as a rate phenomenon. Eyring\textsuperscript{20} considered that dipole orientation involves passage over a potential energy barrier with a certain probability of jumping from one orientation to another. He obtained the polarization $P(t)$, as a function of time as -

$$P(t) = P_0 e^{-k_0 t}$$

where $P_0$ is orientation polarization at $t = 0$;

$k_0$ is the rate constant for the activation of dipole, i.e. mean number of jumps made by a dipole in unit time.

When $t$ is such that $k_0 t = 1$, $P(t)$ must have decayed to $P_0/e$. This value of $t$ is a relaxation time, which may be defined as $\tau = 1/k_0$.

The process of molecular orientation requires activation energy sufficient to overcome the energy barrier separating the two mean equilibrium positions. The number of times such a rotation will occur per second is given by the rate expression-
\[ k_0 = \frac{1}{\tau} = \frac{KT}{h} \; e^{-\Delta F/RT} \]  

(2.86)

where \( h \) is Planck's constant;

\[ \Delta F \text{ is molar free energy of activation for dipole relaxation.} \]

Since \( \Delta F = \Delta H - T\Delta S \),

\[ \tau = \frac{h}{KT} e^{\Delta H/RT} e^{-\Delta S/R} \]

(2.87)

where \( \Delta H \) is the enthalpy(heat) of activation for dipole relaxation and \( \Delta S \) is the entropy of activation for dipole relaxation.

The entropy of activation \( \Delta S \) may be calculated since \( \Delta F \) is now known from eq.(2.31), and \( \Delta H \) is obtained from the slope of the curve for \( \ln(\tau T) \) plotted against \( 1/T \).

Eq.(2.87) can be rewritten as -

\[ \ln(\tau T) = \frac{\Delta H}{RT} + A \]

(2.88)

where \( A = \ln\left(\frac{h}{k}\right) - \left(\frac{\Delta S}{R}\right) \)

In eq.(3.87), \( \Delta H / R \), is the slope of \( \ln(\tau T) \) v/s \( 1/T \). If \( \Delta H \) and \( \Delta S \) are independent of temperature, then plot of \( \ln(\tau T) \) v/s \( 1/T \) is linear. The slope \( \Delta H / R \) gives the height of potential barrier. Differentiating eq.(3.86) gives -

\[ \Delta H = R \frac{d[\ln(\tau T)]}{d[1/T]} - RT \]

(2.89)

Thermodynamic properties may be used to access the dipole under the influence of applied field. The activation energy for every compound increases as the temperature increases, whereas the relaxation time decreases. This may be due to decreased viscosity of medium. With increase in temperature the thermal agitation increases and dipole requires more energy in order to attain the equilibrium with the applied field. The molar free energy of activation is greater than the molar enthalpy of activation, which results into negative values of enthalpy. This indicates that the activated state is more ordered than the normal state, which is true as in the activated state, and the dipoles try to align with the applied field.
REFERENCES


