CHAPTER: 2

DIELECTRIC RELAXATION THEORIES
2.1 INTRODUCTION

A dielectric is a nonconducting substance, i.e. an insulator. The term was coined by Whewell [1] in response to a request from Faraday. Whewell considered "dielectric", from the Greek "dia" meaning "through", since an electric field passes through the material but felt that "dielectric" was easier to pronounce. Although "dielectric" and "insulator" are generally considered synonymous, the term "dielectric" is more often used when considering the effect of alternating electric fields on the substance while "insulator" is more often used when the material is being used to withstand a high electric field. Von Hippel, in his seminal book [2] takes this definition further. He states,

"Dielectrics ... are not a narrow class of so-called insulators, but the broad expanse of nonmetals considered from the standpoint of their interaction with electric, magnetic fields, of electromagnetic fields. Thus we are concerned with gases as well as with liquids and solids, and with the storage of electric and magnetic energy as well as its dissipation."

Dielectrics are the study of dielectric materials and involve physical models to describe how an electric field behaves inside a material. It is characterized by how an electric field interacts with an atom and is therefore possible to approach from either a classical interpretation or a quantum one.

Many phenomena in electronics, solid state and optical physics can be described using the underlying assumptions of the dielectric model. This can mean that the same mathematical objects can go by many different names.

In the classical approach to the dielectric model, a material is made up of atoms. Each atom consists of a cloud of negative charge bound to and surrounding a positive point charge at its centre. Because of the comparatively huge distance between them, none of the atoms in the dielectric material interact with one another. Note that the model is not attempting to say anything about the structure of matter. It is only trying to describe the interaction between an electric field and matter. In the presence of an electric field the charge cloud is distorted.

Polarity refers to the dipole-dipole intermolecular forces between the slightly positively-charged end of one molecule to the negative end of another or the same molecule. Molecular polarity is dependent on the difference in electronegativity between
atoms in a compound and the asymmetry of the compound's structure. For example, water is thought to be polar because of the unequal sharing of its electrons. However, methane is considered non-polar because the carbon shares the hydrogen atoms uniformly.

Electrons are not always shared equally between two bonding atoms: one atom might exert more of a force on the electron cloud than the other. This "pull" is termed electronegativity and measures the attraction for electrons a particular atom has. The unequal sharing of electrons within a bond leads to the formation of an electric dipole: a separation of positive and negative electric charge.

Atoms with high electronegativities - such as fluorine, oxygen, and nitrogen - exert a greater pull on electrons than atoms with lower electronegativities. In a bonding situation this can lead to unequal sharing of electrons between atoms as electrons will spend more time closer to the atom with the higher electronegativity.

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 nonpolar. Polar molecules have slightly positive and slightly negatively charged ends.

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'.

A non-polar compound occurs when there is an equal sharing of electrons between two atoms. Examples of household non-polar compounds include fats, oil and petrol. Like dissolves like. Therefore, Most non-polar molecules are water insoluble (hydrophobic) at room temperature. However many non-polar organic solvents, such as
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turpentine, are able to dissolve non-polar substances. When comparing a polar and non-polar molecule with similar molar masses, the polar molecule generally has a higher boiling point, because of the dipole-dipole interaction between their molecules. The most common form of such an interaction is the Hydrogen Bond. Polar molecules always have a permanent dipole moment, even in the absence of an external electric field.

There are many dielectric theories, these theories depends on the applied field. In the development of these theories most contributions are due to Debye, Kirkwood, Frohlich, and Onsagar [3-6]. In this chapter only those dielectric theories are discussed which are needed to interpret the experimental results done in this work.

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 [7]. The polarization is 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 polarizibility 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 a 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:

$$P_t = P_e + P_a + P_o$$  \hspace{1cm} (2.1)

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

### 2.2 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. In general, permittivity isn't a constant, as it can vary with the position in the medium, the frequency of the field applied, humidity, temperature, and other parameters. In a nonlinear medium, the permittivity can depend on the strength of the electric field. Permittivity is a function of frequency, can take on real or complex values.

The polar dielectric materials having a permanent dipole moment, when placed in a steady electric field then that all types of polarization can maintain equilibrium with it, the permittivity of material under these conditions is called as static permittivity ($\varepsilon_s$). When dielectric material is placed in electric field varying with some frequency, then the permittivity of a material changes with change in frequency of applied field. This is because with increasing frequency molecular dipoles cannot orient faster to cope-up with applied field. Thus the permittivity of the material falls off with increasing frequency of applied field. The frequency dependent permittivity of material is called as dynamic permittivity. The different theories of static and dynamic permittivity are given in following sections.

### 2.3 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:

$$F = \frac{qq'}{er^2}$$  \hspace{1cm} (2.2)
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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-

\[
C = \frac{q}{V}
\]  
(2.3)

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

\[
C = \frac{\varepsilon A}{4\pi r}
\]  
(2.4)

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-

\[
\varepsilon = \frac{C}{C_0}
\]  
(2.5)

where \( C_0 \) is capacity with air of vacuum

The dielectric constant thus is dimensionless quantity.

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

\[
E_0 = 4\pi \sigma
\]  
(2.6)

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-

\[
E = \frac{4\pi \sigma}{\varepsilon}
\]  
(2.7)

The decrease in field strength is

\[
E_0 - E = 4\pi \sigma \left( 1 - \frac{1}{\varepsilon} \right) = 4\pi \sigma \left( \frac{\varepsilon - 1}{\varepsilon} \right)
\]  
(2.8)

The same decrease is possible by reducing the surface charge density from \( \sigma \) to
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 $P$.

\[
P = \sigma \left( \frac{\varepsilon - 1}{\varepsilon} \right) \quad (2.9)
\]

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-

\[
D = 4\pi \sigma \quad (2.10)
\]

from eq.(2.7)

\[
D = \varepsilon E \quad (2.11)
\]

Using eq.(2.7), (2.9), (2.10), (2.11), we get-

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

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

\[
(\varepsilon - 1) = \frac{4\pi P}{E} \quad (2.12)
\]

\[
\varepsilon = 1 + \frac{4\pi P}{E} \quad (2.13)
\]

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,

\[
m = P \ V \quad (2.14)
\]

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.
2.3.1 DEBYE THEORY OF STATIC PERMITTIVITY

Let us consider a sphere of homogeneous dielectric placed in parallel plates. The size of sphere be 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-

$$ m = \alpha_1 F $$

(2.15)

where $\alpha_1$ is total polarizability of the molecule. The average electric moment [7] is given by-

$$ \bar{m} = \frac{\mu^2 \cos^2 \theta}{kT} F + er $$

(2.16)

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 (2.16) 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

$$ F = F_1 + F_2 + F_3 $$

(2.17)

By definition

$$ F_1 = 4 \pi \sigma $$

(2.18)

$F_2$ 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.

\[ F_2 = -4\pi P + \left(\frac{4\pi P}{3}\right) \]  \hspace{1cm} (2.19)

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 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

\[ F = 4\pi \sigma - 4\pi P + \left(\frac{4\pi P}{3}\right) \]  \hspace{1cm} (2.20)

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

\[ F = E + 4\pi P - 4\pi P + \left(\frac{4\pi P}{3}\right) \]  \hspace{1cm} (2.21)

\[ F = E + \left(\frac{4\pi P}{3}\right) \]  \hspace{1cm} (2.22)

But

\[ \varepsilon E = E + 4\pi P \]  \hspace{1cm} (2.23)

\[ E(\varepsilon - 1) = 4\pi P \]  \hspace{1cm} (2.24)

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

\[ F = E \left(\frac{\varepsilon + 2}{3}\right) \]  \hspace{1cm} (2.25)

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

\[ P = N_1 m = N_1 \alpha_i F \]  \hspace{1cm} (2.26)

Substituting \( F \) from eq.(2.25), we get

\[ P = N_1 \alpha_i \left(\frac{\varepsilon + 2}{3}\right) E \]  \hspace{1cm} (2.27)

By using eq. (2.25) and substituting the value of \( P \) from eq. (2.27), we get the relation between dielectric constant \( \varepsilon \) and molecular polarizibility \( \alpha_i \) as -
\[
\frac{(\varepsilon - 1)}{(\varepsilon + 2)} = \frac{4\pi}{3} N_1 \alpha_1
\]  
(2.29)

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.(2.28) becomes-

\[
\frac{(\varepsilon - 1) M}{(\varepsilon + 2) \rho} = \frac{4\pi}{3} N \alpha_1
\]  
(2.29)

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

\[
P = \left(4 \frac{\pi}{3} \right) N \alpha_1
\]  
(2.30)

The molar polarization gives some information about electric properties of the molecule. From eq.(2.29) the molar polarization is given by-

\[
\overline{P} = \frac{(\varepsilon - 1) M}{(\varepsilon + 2) \rho}
\]  
(2.31)

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 [8] expression for local field. Langevin's method is used 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 \( \overline{m} \) will be expressed by -

\[
\overline{m} = \left[ \alpha + \frac{\mu^2}{3kT} \right] F
\]  
(2.32)
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 polarizibility is -

$$\alpha = \alpha_d + \mu^2 / 3kT$$

(2.33)

using this value in eq.(2.29), we get Debye equation as

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

(2.34)

This is Debye equation for permittivity.

Debye has given general equation in which $\alpha_i$ is expressed as the average of the three polarizibilities 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 polarizibility 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 polarizibility 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-

$$\frac{(\varepsilon - 1)}{(\varepsilon + 2)} \rho = \frac{4\pi N\mu^2}{9kT\rho}$$

(2.35)

and considering

$$\frac{4\pi N\mu^2}{9kT} = T_c$$

(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.

### 2.3.2 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 ferroelectricity is not common and certainly does not occur in water [9]. 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, 10] 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.

$$a = \sqrt[3]{\frac{3}{4\pi N_1}}$$

(2.38)

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 \( E \)

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

(2.39)

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

\( \varepsilon_0 \) is static dielectric constant.

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

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

(2.40)

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

The total internal field acting upon spherical polar molecule is -

\[
F = G + R
\]

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

(2.41)

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

(2.42)

From eq. (2.41) 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 induced moment \( \alpha_d F \) by the local field.

\[
m = \mu + \alpha_d F
\]

(2.43)

\[
m = \mu + \alpha_d \left[ gE + r \frac{m}{a^3} \right]
\]

(2.44)

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

(2.45)
Then mean moment parallel to the field is given by -

$$m = \frac{g \mu^2 E}{\left(1 - \frac{r \alpha_d}{a^3}\right) 3kT} + \frac{\alpha_d g}{\left(1 - \frac{r \alpha_d}{a^3}\right) 3kT}$$ \hspace{1cm} (2.46)

By using this equation in $P = N_1 \bar{m}$ we get -

$$\frac{(\varepsilon_o - 1)}{4\pi} = \frac{N_1 g}{\left(1 - \frac{r \alpha_d}{a^3}\right)} \left[ \alpha_d + \frac{1}{\left(1 - \frac{r \alpha_d}{a^3}\right) 3kT} \right] \mu^2$$ \hspace{1cm} (2.47)

But Onsager defined polarizibility $\alpha$ in terms of refractive index as

$$\alpha_d = \frac{n^2 - 1}{n^2 + 2} a^3$$ \hspace{1cm} (2.48)

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

$$\frac{(\varepsilon_o - n^2)(2\varepsilon_o + n^2)}{\varepsilon_o (n^2 + 2)} = \frac{4\pi N_1 \mu^2}{9kT}$$ \hspace{1cm} (2.49)

This is Onsager equation for static permittivity. In the Debye equation as the value of $\varepsilon_o$ increases, Lorentz field $F$ increases without limit, but in Onsager cavity field it tends to limit $\left(\frac{3E}{2}\right)$, while the reaction field tends to limit $\left(n^2 + 2/3\right)$. 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 $\varepsilon_o$ 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.
2.3.3 KIRKWOOD THEORY

The Onsager equation gives better result than Debye equation, but it doesn't take into account intermolecular interactions. It generally doesn't hold good for associated liquids such as carboxyl acids, alcohols etc. Kirkwood [4] introduced the orientation correlation of neighboring molecules due to short-range specific interaction as:

\[
\frac{(\varepsilon_0 - 1)(2\varepsilon_0 + 1)}{3\varepsilon_0} \frac{M}{\rho} = \frac{4\pi}{3} N \left[ \alpha_d + \frac{\mu \bar{\mu}}{3kT} \right]
\]  
(2.50)

or

\[
\frac{(\varepsilon_0 - 1)(2\varepsilon_0 + 1)}{3\varepsilon_0} \frac{M}{\rho} = \frac{4\pi}{3} N \left[ \alpha_d + \frac{g\mu^2}{3kT} \right]
\]  
(2.51)

where \( \mu \) is molecular dipole moment in the liquid and \( \bar{\mu} \) is the sum of the molecular dipole moment and the moment induced as the result of hindered rotation in the spherical region surrounding the molecule. The value of \( \bar{\mu} \) will be equal to \( \mu \) (the moment of the fixed dipole), if there is no local ordering. In general \( \bar{\mu} = g\mu \), where \( g \), the correlation parameter. The \( g \) is called as Kirkwood correlation parameter, which is a measure of local ordering in material. The value of \( g \) is one, if the average moment of the finite spherical region surrounding the molecule, which is held fixed, is equal to moment of fixed molecule. If the dipoles of neighboring molecules are oriented parallel to dipole of fixed molecule, then 'g' has value greater than one, whereas if dipoles of neighboring molecules are oriented anti parallel to dipole of fixed molecule, then the value of 'g' is less than one.

2.3.4 FROHLICH'S THEORY

Frohlich [5] 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 nonpolarizable dipoles is:

\[
\frac{(\varepsilon_0 - 1)(2\varepsilon_0 + 1)}{3\varepsilon_0} \frac{M}{\rho} = \frac{4\pi}{3} N \frac{\langle m_m^2 \rangle}{3kT}
\]  
(2.52)

where, \( \langle m_m^2 \rangle = \bar{\mu} \bar{\mu} = \mu \bar{\mu} = g\mu^2 \) and for molecule replacing \( \mu \) by its value -
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\[ \mu_0 = \frac{3}{\varepsilon_\infty + 2} \mu \]  

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 nonpolarizable dipole units to be embedded in polarizable continuum of permittivity \(n^2(\varepsilon_\infty)\).

The equation becomes -

\[
\frac{(\varepsilon_\infty - n^2)(2\varepsilon_\infty + n^2)}{\varepsilon_\infty (n^2 + 2)^2} \frac{M}{\rho} = 4\pi N \frac{g\mu^2_0}{9kT} 
\]

(2.54)

Except for interaction of correlation parameter \(g\), the equation is identical with Onsager’s equation. The correlation factor can be expressed as-

\[ g = 1 + z\langle \cos \theta_{ij} \rangle \]  

(2.55)

where \(\langle \cos \theta_{ij} \rangle\) 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, \(\langle \cos \theta_{ij} \rangle \neq 0\). i.e. when there is correlation between the orientation of neighbouring molecules. When the molecules tend to direct themselves with parallel dipole moments, \(\langle \cos \theta_{ij} \rangle\) will be positive and \(g\) will be larger than 1. When the molecules prefer an ordering with antiparallel dipoles, \(g\) will be smaller than 1.

**2.4 DIELECTRIC RELAXATION**

Dielectric relaxation is the momentary delay (or lag) in the dielectric constant of a material. This is usually caused by the delay in molecular polarization with respect to a changing electric field in a dielectric medium (e.g. inside capacitors or between two large conducting surfaces). Dielectric relaxation in changing electric fields could be considered analogous to hysteresis in changing magnetic fields (for inductors or transformers). Relaxation in general is a delay or lag in the response of a linear system, and therefore dielectric relaxation is measured relative to the expected linear steady state (equilibrium) dielectric values. The time lag between electrical field and polarization implies an irreversible degradation of free energy.
In physics, dielectric relaxation refers to the relaxation response of a dielectric medium to an external electric field of microwave frequencies. This relaxation is often described in terms of permittivity as a function of frequency, which can, for ideal systems, be described by the Debye equation. On the other hand, the distortion related to ionic and electronic polarization shows behavior of the resonance or oscillator type. The character of the distortion process depends on the structure, composition, and surroundings of the sample.

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 \(\mathbf{D} = \varepsilon' \mathbf{E} \). 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.

2.5 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 -

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

(2.56)

where $\tau$ is a constant which has the dimension of time and is called the macroscopic relaxation time. Rewriting this equation as

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

(2.57)

the solution of this equation is -

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

(2.58)

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. (2.58) gives-

$$C = \ln (P - P_1)$$
using this value of $C$ in eq.(2.58) and solving for $P_2$, we get -

$$P_2 = (P - P_1) \left(1 - e^{-\frac{t}{\tau}}\right)$$  \hspace{1cm} (2.59)

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-

$$P_2 = (P - P_1) e^{-\frac{t}{\tau}}$$  \hspace{1cm} (2.60)

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

$$E = E_0 e^{i\omega t}$$  \hspace{1cm} (2.61)

using eq.(2.11), static permittivity and refractive index are defined as-

$$4\pi P = E(\varepsilon_0 - 1)$$, as $\omega \to 0$;

i.e. $$P = \frac{(\varepsilon_0 - 1)E}{4\pi}$$  \hspace{1cm} (2.62)

$$4\pi P_1 = E(n^2 - 1)$$, as $\omega \to \infty$,

i.e. $$P_1 = \frac{(n^2 - 1)E}{4\pi}$$  \hspace{1cm} (2.63)

where $n$ is the refractive index. Using the values of $P$, $P_1$ in eq.(2.56), we get-

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

$$= \frac{(\varepsilon_0 - n^2)}{4\pi} E - \frac{P_2}{\tau}$$

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

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the solution of this equation is -

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

(2.64)

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 -

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

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

when polarization becomes complex, the permittivity must also become complex, and eq.(2.13) 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.(2.63) and eq.(2.64) we get -

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

(2.65)

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 \( \left[ \left( \varepsilon_0 - n^2 \right)/2 \right] \) 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 [3]. Where “n” is the refractive index and $n^2 = \varepsilon_{\infty}$.

### 2.5.1 THE DEBYE MODEL

The permittivity and dielectric loss are given by the Debye equation

$$\varepsilon^* = \varepsilon_{\infty} + \frac{(\varepsilon_0 - \varepsilon_{\infty})}{(1 + i\omega \tau)} \quad (2.66)$$

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

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

$$\varepsilon'' = \frac{(\varepsilon_0 - \varepsilon_{\infty}) \omega \tau}{(1 + \omega^2 \tau^2)} \quad (2.68)$$

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

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

$$\omega\tau = (1 + \omega^2 \tau^2) / 4$$

$$= 0.27 \text{ or } 3.73$$

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 (2.67) and (2.68) are the parametric equations of a circle. On eliminating and rearranging, we obtain

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

(2.69)

which is the equation of a circle, center $[(\varepsilon_0 + \varepsilon_{\infty}) / 2, 0]$, radius $(\varepsilon_0 - \varepsilon_{\infty}) / 2$. 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.

![Diagram of Dielectric Behaviour and Molecular Association](image)

**Fig. 2.1**: Variation of $\varepsilon'$ and $\varepsilon''$ with frequency $f$

**Fig. 2.2**: Debye semicircle associated with equation 2.69

### 2.5.2 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 [11].

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

(2.70)
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 

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

we obtain -

$$\frac{\varepsilon' - \varepsilon_{\infty}}{\varepsilon_0 - \varepsilon_{\infty}} = \frac{1 + (\omega \tau)^{(1-\alpha)} \sin(\pi \alpha / 2)}{1 + (\omega \tau)^{2(1-\alpha)} + 2(\omega \tau)^{(1-\alpha)} \sin(\pi \alpha / 2)}$$

(2.71)

$$\frac{\varepsilon''}{\varepsilon_0 - \varepsilon_{\infty}} = \frac{(\omega \tau)^{(1-\alpha)} \cos(\pi \alpha / 2)}{1 + (\omega \tau)^{2(1-\alpha)} + 2(\omega \tau)^{(1-\alpha)} \sin(\pi \alpha / 2)}$$

(2.72)

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

$$\frac{\varepsilon' - \varepsilon_{\infty}}{\varepsilon_0 - \varepsilon_{\infty}} = \frac{1}{2} \left[ 1 - \frac{1}{2} \left[ (\omega \tau)^{(1-\alpha)} - 1 \right] \right]$$

(2.73)

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

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

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

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

Similarly,
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\[
\frac{\varepsilon''}{\varepsilon_0 - \varepsilon_\infty} = \frac{1}{2} \frac{\cos(\pi \alpha / 2)}{\cos \theta + \sin(\pi \alpha / 2)}
\]

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

\[
\sin \alpha \theta = \frac{\varepsilon_0 + \varepsilon_\infty - 2\varepsilon'}{2\varepsilon''} \cos(\pi \alpha / 2)
\]
\[
\cos \alpha \theta = \frac{\varepsilon_0 - \varepsilon_\infty \cos(\pi \alpha / 2) - \sin(\pi \alpha / 2)}{2\varepsilon''}
\]

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

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

This is the equation of a circle with its center at -

\[
\left[\frac{1}{2}(\varepsilon_0 + \varepsilon_\infty), -\frac{1}{2}(\varepsilon_0 - \varepsilon_\infty) \tan(\pi \alpha / 2)\right]
\]
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.

2.5.3 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 behavior of this kind could be represented by the expression -
Rearranging
\[
\frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \frac{1}{(1 + i\omega\tau)^\beta}
\]

(2.76)

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

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

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

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

(2.78)

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

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.
2.5.4 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 behavior, which cannot be explained by Cole-Cole [11] and Davidson-Cole [12] expressions, both of which contain only one adjustable parameter to describe the shape of the plot $\varepsilon''$ versus $\varepsilon'$. Havriliak-Negami [13] generalized the expression, consisting in a contribution of both Cole-Cole and Davidson-Cole expression as given below

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

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.

2.6 DIELECTRIC PARAMETERS RELATED TO MOLECULAR BEHAVIOR

There are different formulas with which one can correlate dielectric parameters with molecular activities in liquids. 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. 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, various mixture formulae have been proposed [14, 18]

2.6.1. 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, various mixture formulae have been proposed [14, 15].
Bruggeman mixture formulae [15-17] can be used as first evidence of molecular interactions in binary mixture. This formula states that static permittivity of binary mixture (\(\varepsilon_{sm}\)), solute A (\(\varepsilon_{sA}\)) and solvent B (\(\varepsilon_{sB}\)) can be related to volume fraction of solvent (V) in mixture as

\[
f_B = \left( \frac{\varepsilon_{sm} - \varepsilon_{sB}}{\varepsilon_{sA} - \varepsilon_{sB}} \right) \left( \frac{\varepsilon_{sA}}{\varepsilon_{sm}} \right)^{1/3} = 1 - V
\]  

(2.80)

According to above equation linear relationship is expected in Bruggeman factor \(f_B\) and (V). Any deviation from this linear relation indicates molecular interactions.

### 2.6.2 EXCESS PROPERTIES

The information regarding interaction of liquids A and B may be obtained from excess dielectric properties [9, 18-26] like excess permittivity and excess relaxation time in the mixture. Let A and B are 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 \(X_B\) [where \(X_B = (1- X_A)\)], the excess macroscopic property \(P^E\) corresponding to mixture is defined as

\[
P^E = P_{AB} - (P_A * X_A + P_B * X_B)
\]

where \(P_{AB}\) is measured value of property \(P\) for mixture.

The values of \(P^E\) provides information regarding interactions between A and B. \(P^E = 0\) indicates no significant interaction between A and B. \(P^E > 0\) indicates that interactions between A and B leads to increase in the value of property \(P\). Similarly, \(P^E < 0\) indicates decrease in macroscopic property \(P\).

In the present work 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 [27]. The broadening of two levels are additive for two energy levels. The analogy is taken from dielectric spectroscopy.

The excess permittivity (\(\varepsilon_{sE}\)) is defined as

\[
\varepsilon_{sE} = (\varepsilon_{s})_m - [(\varepsilon_s)_A * x_A + (\varepsilon_s)_B * x_B]
\]  

(2.81)
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where x mole fraction and suffices m, A, B represents mixtures, liquid A (Alkoxyalkanol) and liquid B (Aromatic compound) respectively.

The excess permittivity may provide qualitative information about structure formation in the mixture as follows

i) $\varepsilon_E^s=0$ indicates the liquid A and B do not interact and do not change their individual structural properties in the presence of other liquid.

ii) $\varepsilon_E^s < 0$ indicates the liquid A and B interact 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.

iii) $\varepsilon_E^s > 0$ indicates the liquid A and B interact in such a way that the total effective dipole moment increases. This may be due to breaking of multimer structure into monomer structure due to presence of other molecule.

Similarly the excess inverse relaxation time $(1/\tau)^E$ may be defined as

$$(1/\tau)^E = (1/\tau)_m - \left[ (1/\tau)_A x_A + (1/\tau)_B x_B \right]$$  \hspace{1cm} (2.82)

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

i) $(1/\tau)^E = 0$: There is no change in the dynamics of liquid A and B.

ii) $(1/\tau)^E < 0$: The liquid A and B interaction produces a field such that the effective dipoles rotate slowly.

iii) $(1/\tau)^E > 0$: The liquid A and B interaction produces a field such that the effective dipoles rotate rapidly i.e. the field will co-operate in rotation of dipoles.

The experimental values of both the excess parameters were fitted to the Redlich – Kister [28-29] equation.

$$P^E = x_A x_B \sum_{j=0}^{n} B_j (x_A - x_B)^j$$  \hspace{1cm} (2.83)

where $P^E$ is either $\varepsilon^E$ or $(1/\tau)^E$, $x_A$ and $x_B$ are mole fractions of A and B respectively, using these $B_j$ values excess parameters at various concentration were calculated and used to draw the smooth curves. The coefficients $B_j$’s provide information
regarding molecular interactions. e. g. $B_0$ corresponds to 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.

### 2.6.3 KIRKWOOD CORRELATION FACTOR

The Kirkwood correlation factor ‘$g$’ [2-3] is also a parameter containing information regarding orientation of electric dipoles in polar liquids. The $g$ for the pure liquid is given by the following expression

$$g = \frac{4\pi N \mu^2 \rho}{9kT M} = \frac{(\varepsilon_s - \varepsilon_x)(2\varepsilon_s + \varepsilon_x)}{\varepsilon_s(\varepsilon_x + 2)^2} \quad (2.84)$$

where $\mu$ is dipole moment in gas phase, $\rho$ is density at temperature $T$, $M$ is molecular weight, $k$ is Boltzman constant and $N$ is Avogadro’s number. The corresponding equation for binary mixtures is not available in literature. However, for mixture of two polar liquids say A and B above equation can be modified using some assumptions.

Assume that ($g$) for mixture is expressed by an effective averaged correlation factor ($g_{eff}$) such that Kirkwood equation for the mixture can be expressed as

$$g_{eff} = \frac{4\pi N \left( \frac{\mu_A^2 \rho_A X_A}{M_A} + \frac{\mu_B^2 \rho_B X_B}{M_B} \right)}{9kT} \frac{\left( \varepsilon_{sm} - \varepsilon_{xm} \right)(2\varepsilon_{sm} + \varepsilon_{xm})}{\varepsilon_{sm}(\varepsilon_{xm} + 2)^2} \quad (2.85)$$

where $X_A$ and $X_B$ the volume fractions of liquids A and B respectively.

The another way to visualize variation in Kirkwood correlation factor is to assume that correlation factors for molecules A and B in mixture contribute to effective ($g$) in proportion to their pure liquid values $g_A$ and $g_B$. Under this assumption Kirkwood equation for the mixture can be written as

$$g_f = \frac{4\pi N \left( \frac{\mu_A^2 \rho_A g_A X_A}{M_A} + \frac{\mu_B^2 \rho_B g_B X_B}{M_B} \right)}{9kT} \frac{\left( \varepsilon_{sm} - \varepsilon_{xm} \right)(2\varepsilon_{sm} + \varepsilon_{xm})}{\varepsilon_{sm}(\varepsilon_{xm} + 2)^2} \quad (2.86)$$

Where, $g_f$ is correlation factor for mixture. The values of $g_{eff}$ in equation (2.85) will change from $g_A$ to $g_B$ as the fraction of component B increases from zero to unity. In equation (2.86), $g_f$ is unity for pure liquids and will remain close to unity if there is no interaction between A and B.
2.6.4 THERMODYNAMIC PARAMETERS

Kauzmann [30] has given an extensive analysis of dipole orientation as a rate phenomenon [31-33]. Eyring [31, 34] considered that dipole orientation involves passage over a potential energy barrier with a certain probability of jumping from one orientation to another. They obtained the polarization $P(t)$, as a function of time as -

$$P(t) = P_0 e^{-k_0 t}$$  \hspace{1cm} (2.87)

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 [30, 34] -

$$k_0 = 1/\tau = \frac{kT}{h} e^{-\Delta F/RT}$$ \hspace{1cm} (2.88)

where $h$ is Plank's constant;

$\Delta F$ is molar free energy of activation for dipole relaxation.

Since $\Delta F = \Delta H - T \Delta S$,

$$\tau = \frac{h}{kT} e^{\Delta H/RT} e^{-\Delta S/R}$$ \hspace{1cm} (2.89)

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.(2.88), and $\Delta H$ is obtained from the slope of the curve for $\ln(\tau T)$ plotted against $1/T$.

Eq. (2.89) can be rewritten as -

$$\ln(\tau T) = \frac{\Delta H}{RT} + A$$ \hspace{1cm} (2.90)
where \[ A = \ln \left( \frac{h}{k} \right) - \left( \frac{\Delta S}{R} \right) \]

In eq. (2.90), \( \Delta H / R \), 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. (2.89) gives:

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

(2.91)

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 [35-36]. 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


