2.1 Dielectric Relaxation Theories

Dielectric material is polarized by the external applied electric field due to this dielectric relaxation occurs. The decay in polarization is observed by removal of the electric field. This depends on the internal structure of a molecule and on molecular arrangement. [1] The orientation polarization decay exponentially with time; the characteristics time of this exponential decay is called relaxation time. This phenomenon may occur as; at low frequencies, the dipoles can “follow” the field and $\varepsilon'$ will be high. At high frequencies, the dipoles cannot follow the rapidly changing field - and $\varepsilon'$ falls off. The resonance character of the attenuation (the imaginary part of the complex permittivity) can be explained in a similar way. Before the resonance the loss is increasing because the dipoles still can totally orient when the electric field changes direction, so the loss is proportional to the frequency. After resonance the frequency is so high that the dipoles do not have enough time to orient, so there is less friction and less loss. The permittivity thus acquires a complex characteristic.

The complex permittivity $\varepsilon^*$ can be written as $\varepsilon'$-j$\varepsilon''$, where $\varepsilon'$ is a real part i.e. storage part of energy and $\varepsilon''$ is imaginary part and it is called dielectric loss.

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. Due to this, dipoles per unit volume decrease with increase in frequency and hence decrease in permittivity.

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

$$P = P_1 + P_2$$

(2.1)

Where $P_1$ is distortion and $P_2$ is dipolar polarization. When a field is applied to dielectric, the distortion polarization will establish very quickly, but the dipolar polarization takes some time to reach its equilibrium value.
Dielectric Relaxation Theories

\[ \frac{dP_2}{dt} = -\frac{P - P_1 - P_2}{\tau} \]  \hspace{1cm} (2.2)

where, \( \tau \) is constant called as macroscopic relaxation time. So rewriting above Eq. as

\[ \frac{dP_2}{P - P_1 - P_2} = -\frac{dt}{\tau} \]  \hspace{1cm} (2.3)

The solution of this Eq. is,

\[ \ln(P - P_1 - P_2) = -\frac{t}{\tau} + C \]  \hspace{1cm} (2.4)

where \( C \) is an arbitrary constant. If we assume that the field \( E \) is suddenly applied at \( t=0 \), then \( P_2=0 \), the Eq. gives

\[ C = \ln(P-P_1) \]  \hspace{1cm} (2.5)

Using this value of \( C \), for \( P_2 \) we get,

\[ P_2 = (P - P_1) \left(1 - e^{-\frac{t}{\tau}}\right) \]  \hspace{1cm} (2.6)

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

\[ \frac{dP_2}{dt} = -\frac{P_2}{\tau} \]  \hspace{1cm} (2.7)

the solution of this equation is

\[ P_2 = (P - P_1) e^{-\frac{t}{\tau}} \]  \hspace{1cm} (2.8)

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

\[ E = E_0 e^{j\omega t} \]  \hspace{1cm} (2.9)

Using Eq. (2.9), static permittivity and refractive index are defined as,

\[ 4\pi P = E(\varepsilon_0-1), \text{ as } \omega \rightarrow 0; \]
i.e. \[ P = \frac{(\varepsilon_0 - 1)E}{4\pi} \]

\[ 4\pi P_1 = E (n^2 - 1), \text{ as } \omega \rightarrow \infty \]

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

when n is the refractive index. Using the values of P and \( P_1 \) we get,

\[
\frac{dP_2}{dt} = -P \frac{P_1 - P_2}{\tau} \\
= \frac{(\varepsilon_0 - n^2)}{4\pi} E - P_2 \frac{P_2}{\tau} \\
= \frac{(\varepsilon_0 - n^2)}{4\pi} E_0 e^{j\omega t} - P_2 \frac{P_2}{\tau} \\
P_2 = \frac{(\varepsilon_0 - n^2)E}{4\pi (1 + j\omega \tau)}
\]  \hspace{1cm} (2.10)

\hspace{1cm} (2.11)

\hspace{1cm} (2.12)

In above equation, \( P_2 \) becomes 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,

\[ P' = p' - jp'' = P_1 + P_2 \]

\[ = \frac{(n^2 - 1)E}{4\pi} + \frac{(\varepsilon_0 - n^2)E}{4\pi (1 + j\omega \tau)} \]  \hspace{1cm} (2.13)

\hspace{1cm} (2.14)

As polarization is a complex term, the permittivity must also become a complex and therefore we can write as,

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

\[ = 1 + \frac{4\pi}{E} (p' - jp'') \]  \hspace{1cm} (2.15)

\hspace{1cm} (2.16)

\[ = 1 + \frac{4\pi}{E} (P_1 + P_2) \]  \hspace{1cm} (2.17)

Substituting the values of \( P_1 \) and \( P_2 \) in above Eq. we get,
Dielectric Relaxation Theories

\[ \varepsilon^* = \varepsilon' - j\varepsilon'' = n^2 + \frac{(\varepsilon_0 - n^2)}{(1 + j\omega\tau)} \quad (2.18) \]

where
\[ \varepsilon' = n^2 + \frac{\varepsilon_0 - n^2}{1 + \omega^2\tau^2} \quad (2.18.1) \]

and
\[ \varepsilon'' = \frac{\varepsilon_0 - n^2}{1 + \omega^2\tau^2} \omega\tau \quad (2.18.2) \]

The real part (\(\varepsilon'\)) is dielectric dispersion and imaginary part (\(\varepsilon''\)) is dielectric loss. The dielectric loss becomes maximum \([\varepsilon_0 - n^2]/2\) at a frequency \(\omega = 1/\tau\). The phase lag between polarization and the applied field leads to an absorption of energy in the dielectric. Also the maximum energy absorption occurs at \(\omega = 1/\tau\).

This Eq.(2.18) is called as Debye or Debye-Dude equation. Here ‘n’ is the refractive index and \(n^2 = \varepsilon_\infty\). To explain these dielectric relaxation phenomenons, a number of different models have been developed over time.

2.1.1 The Debye Model:

The permittivity and dielectric loss are given by the Debye equation [2]

\[ \varepsilon^* = \varepsilon_\infty + \frac{(\varepsilon_0 - \varepsilon_\infty)}{(1 + j\omega\tau)} \quad (2.19) \]

where \(\varepsilon_0\) static field dielectric, \(\varepsilon_\infty\) is the high frequency dielectric constant and \(\tau\) is the relaxation time. \(\varepsilon^* = \varepsilon' - j\varepsilon''\), \(\varepsilon'\) is known as dielectric dispersion and \(\varepsilon''\) is dielectric loss, and given by

\[ \varepsilon' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + \omega^2\tau^2} \quad (2.19.1) \]

\[ \varepsilon' = \frac{(\varepsilon_0 - \varepsilon_\infty)\omega\tau}{1 + \omega^2\tau^2} \quad (2.19.2) \]
The variation of $\varepsilon'$ and $\varepsilon''$ with frequency is shown in Fig. 2.1. Graphical representation of Debye model is obtained by plotting the imaginary part against the real part of complex permittivity shown in Fig. 2.2. The function can be obtained by elimination of $\omega$ from above Eqs. For simple dipole relaxation, a circle is obtained:

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

(2.20)

The dielectric permittivity is represented by semicircle of radius,

$$
\frac{\varepsilon_\infty - \varepsilon_0}{2}
$$

and centered at $\varepsilon' = \frac{\varepsilon_0 + \varepsilon_\infty}{2}$. The top of the semicircle corresponds to $\omega\tau=1$.

The frequency moves counter clockwise on the curve $\varepsilon_0, \varepsilon_\infty$.

$$
\varepsilon''_{\text{max}} = \frac{\varepsilon_0 - \varepsilon_\infty}{2}
$$

(2.21)
2.1.2 The Cole - Cole Model:

In certain liquids, such as long chain molecules for which the permanent dipole moment is not aligned with the long molecular axis and polymers have broader dispersion curves and lower maximum loss than would be expected from Debye equation. This deviation is usually explained by assuming there is not just one relaxation time but continuous distribution of relaxation time. If the molecule is aligned with the field, only the longitudinal component of the dipole moment is active during the relaxation process. The molecule tends to rotate about a short molecular axis with a long relaxation time because of inertial and viscous forces. In contrast, if the molecule is perpendicular to the field the transverse component of the dipole is active and the molecule relaxes by rotating rather quickly about its long axis, because inertial and viscous forces are smaller in this configuration. If the molecules are randomly oriented relative to the field, the corresponding relaxation time is distributed between these two extreme cases. If \( f(\tau) \) is the distribution function of the relaxation time between \( \tau \) and \( \tau + d\tau \), the corresponding Eq.

\[
\varepsilon^* (\omega) = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty) \int_0^\infty \frac{f(\tau)d\tau}{1 + j \omega \tau}
\]

Because this leads to circular arc centered below the axis, K.S. Cole and R. H. Cole have proposed a modified form of Debye’s equation with a term ‘\( \alpha \)’ characterizing the flattening of the diagram. The Cole –Cole equation is [3]

\[
\varepsilon^* (\omega) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + (j \omega \tau)^{1-\alpha}} \text{ with } 0 \leq \alpha \leq 1.
\]

The value of ‘\( \alpha \)’ has a tendency to increase with increasing number of internal degrees of freedom in the molecules and with decreasing temperature [2-3]. The value of ‘\( \alpha \)’ increases with decreasing chain length, i.e. the distribution of relaxation time tends toward symmetric distribution with decreasing chain length. Cole-Cole plot with different values of symmetric
distribution parameter ($\alpha$) is shown in fig. 2.4 The Cole-Cole equation can be solved for dielectric dispersion and absorption as,

$$
\varepsilon'(\omega) = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty) \frac{1 + (\omega \tau_0)^{1-\alpha} \sin \frac{1}{2} \alpha \pi}{1 + 2(\omega \tau_0)^{1-\alpha} \sin \frac{1}{2} \alpha \pi + (\omega \tau_0)^{2(1-\alpha)}} \quad (2.23.1)
$$

$$
\varepsilon''(\omega) = (\varepsilon_0 - \varepsilon_\infty) \frac{(\omega \tau_0)^{1-\alpha} \cos \frac{1}{2} \alpha \pi}{1 + 2(\omega \tau_0)^{1-\alpha} \sin \frac{1}{2} \alpha \pi + (\omega \tau_0)^{2(1-\alpha)}} \quad (2.23.2)
$$

Fig. 2.3 a) shows the how Complex permittivity differs from Debye type in Cole-Cole behavior and fig. 2.3 b) shows the Cole-Cole plot for this Cole-Cole model.

![Fig. 2.3 a) Complex Permittivity for Debye (----) & Cole-Cole ($\alpha = 0.5$) model,](image)

b) Cole-Cole plot for Cole-Cole model
2.1.3 The Cole-Davidson Model:

Cole–Davidson model describes the asymmetric distribution of relaxation times. The proposed Cole-Davidson equation is [3]

\[ \varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{[1 + j\omega\tau]^\beta} \quad \text{with} \quad 0 \leq \beta \leq 1. \tag{2.24} \]

which corresponds to relaxation time and gives rise to a skewed arc \( \varepsilon' (\varepsilon'') \). When \( \beta \) is close to unity this reduces to Debye’s model and for \( \beta \) less than unity an asymmetric distribution of relaxation time is obtained. Skewed arc behavior in liquids has been reported by many workers and has been explained in terms of cooperative phenomenon and multiple relaxation processes. The molecule becomes less rigid with increasing chain length and can relax in more than one way. The different groups may rotate the whole molecule. The relaxation time for the former process is smaller than that for the latter. The intramolecular process has similar effects to the intermolecular cooperative phenomenon observed in pure...
polar liquids. In Fig. 2.5 the complex permittivity and Cole-Cole plot for CD type behavior is shown also Cole-Cole plot for Cole-Davidson model at different \( \beta \) values is shown in Fig 2.6.

This expression reduces to the Debye equation for \( \beta = 1 \). Since

\[
1 + i\omega \tau = e^{i\varphi} \sqrt{1 + (\omega \tau)^2} = e^{i\varphi} / \cos \varphi
\]

where \( \varphi = \tan^{-1} \omega \tau \), separation of the real and imaginary parts is easy, leading to the following expressions for \( \varepsilon' \) and \( \varepsilon'' \):

\[
\varepsilon'(\omega) = \varepsilon_{\infty} + (\varepsilon_s - \varepsilon_{\infty}) \cos \varphi^\beta \cos \beta \varphi \quad (2.24.1)
\]

\[
\varepsilon''(\omega) = (\varepsilon_s - \varepsilon_{\infty}) \cos \varphi^\beta \sin \beta \varphi \quad (2.24.2)
\]
2.1.4 The Havriliak-Negami Model:

More recently Havriliak-Negami found that none of the above dielectric functions was successful in giving the spectral response they had measured in a number of polymetric materials. There are many examples of dielectric behaviors which cannot be explained by Cole-Cole and Davidson–Cole expressions,[4] both of which contain only one adjustable parameter to describe the shape of the plot ($\varepsilon''$ vs. $\varepsilon'$). Havriliak-Negami generalized the expression, consisting in a contribution of both Cole-Cole and Davidson–Cole expression as given below [4-5]. Fig 2.7 shows the complex permittivity of HN behavior and b) Cole-Cole plot to it.

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

(2.25)

It includes Cole-Cole model if $\beta = 1$, the Davidson–Cole model if $\alpha=0$ and if $\alpha=0$ and $\beta = 1$ it gives the Debye model. Separation of the real and the imaginary parts gives rather intricate expressions for $\varepsilon'$ and $\varepsilon''$:

![Cole-Cole plot for Cole-Davidson model at different \(\beta\) Values](image)
Dielectric Relaxation Theories

\[ \varepsilon'(\omega) = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty) \frac{1 + (\omega \tau_0)^{1-\alpha} \sin \frac{1}{2} \alpha \pi}{1 + 2(\omega \tau_0)^{1-\alpha} \sin \frac{1}{2} \alpha \pi + (\omega \tau_0)^{2(1-\alpha)}} \]  

(2.25.1)

\[ \varepsilon''(\omega) = (\varepsilon_0 - \varepsilon_\infty) \frac{\sin \beta \varphi}{\{1 + 2(\omega \tau_0)^{1-\alpha} \sin \frac{1}{2} \alpha \pi + (\omega \tau_0)^{2(1-\alpha)}\}^{3/2}} \]  

(2.25.2)

where

\[ \varphi = \frac{\text{arctg}((\omega \tau_0)^{1-\alpha} \cos \frac{1}{2} \pi \alpha)}{1 + (\omega \tau_0)^{1-\alpha} \sin \frac{1}{2} \pi \alpha} \]  

(2.25.3)

**Fig. 2.7** (a) Complex permittivity spectra of Harvilik-Nigemi behavior and (b) Cole-Cole plot analogous to it.
2.2 Dielectric parameters related to molecular behavior

2.2.1 Static permittivity:

Suppose that a charge ‘q’ e.s.u. per unit area is applied to a parallel plate having area ‘A’ and separated by a distance ‘d’. If vacuum is present between the two plates then electric field intensity ‘E’ is given by

\[ E_{\text{vacuum}} = 4\pi q \]  

(2.26)

If dielectric material of dielectric constant ‘ε’ is introduced between the plates then the field is smaller by factor ‘ε’ because of the polarization so it becomes

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

(2.27)

The same drop in field strength might have been attributed to a reduction of the surface charge density by the amount;

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

(2.28)

The surface charge density of these opposite sign charges on the surface of the dielectrics is P and is known as the polarization; it is the total charge passing through any unit area within the dielectric (parallel) to the plates.

The electric displacement D is defined in terms of the original applied charge density:

\[ D = 4\pi q \]  

(2.29)

\[ D = \varepsilon E \]  

(2.30)

If Eqn. (2.27) and (2.28) rearranged and simplified as,

From Eq. (2.27) \( q = \varepsilon E / 4\pi \), if we put this value in Eq. (2.28) we get,

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

(2.31)

And also we can write it as;
Dielectric Relaxation Theories

\[ \varepsilon - 1 = \frac{4\pi P}{E} \]  \hspace{1cm} (2.32)

The potential difference ‘V’ between the plates is simply

\[ V = \frac{E}{d} \]  \hspace{1cm} (2.33)

and the total charge ‘Q’ is related to the capacitance C of the system by

\[ Q = CV \]  \hspace{1cm} (2.34)

Neglecting edge effects, the capacitance of a pair of parallel plates, each of area A and containing materials of dielectric constant ‘\( \varepsilon \)’ is

\[ C = \frac{A\varepsilon}{4\pi d} \]  \hspace{1cm} (2.35)

A measurement of this capacitance leads to a knowledge of the static dielectric constant For a given substance the static dielectric constant is the ratio of capacity of a condenser with that substance as the dielectric medium to the capacity of the same condenser with a vacuum as the dielectric medium

\[ \varepsilon_0 = \frac{C}{C_0} \]  \hspace{1cm} (2.36)

The dielectric constant is a function of temperature and is a dimensionless quantity.

The polarization can therefore be regarded as the dipole moment per unit volume.

\[ P = \frac{\mu}{V} \quad \text{or} \quad \mu = P V \]  \hspace{1cm} (2.37)

The inner field ‘F’ is by considering a microscopic spherical region surrounding the molecule, but large compared with it. Electrostatic calculation [6] shows it to be equal to

\[ E + \frac{4\pi P}{3} \]  

and therefore using Eq. 2.32

\[ F = \frac{(\varepsilon + 2)}{3} E \]  \hspace{1cm} (2.38)
This is the total internal field arises from the external contribution, which is the external field inside the spherical region due to all sources except the polarization inside this region.

### 2.2.2 Relaxation time ($\tau$)

Relaxation time describes the time required for dipoles to become oriented in an electric field or the time needed for thermal agitation to disorient the dipoles after the electric field is removed. Relaxation times Debye [1,7] suggested that a spherical or nearly spherical molecule could be treated as a sphere (radius $r$) rotating in a continuous viscous medium of bulk viscosity $\eta$. The relaxation time is given by the given equation,

$$\tau = \frac{8\pi\eta r^3}{2kT}$$

The relaxation time evaluated from experimental measurements is the effective time constant for the process observed in the medium studied, even for solutions. Because of the incidence of the internal field factor, this is not the value of the molecular dipole relaxation. Depending upon the internal field assumption a variety of relationships between theoretical and effective relaxation times has been defined. Relaxation times for dipole orientation at room temperature are between $10^{-10}$s for small dipoles diluted in a solvent of low viscosity and more than $10^{-4}$s for large dipoles in a viscous medium such as polymers (polyethylene) or dipole relaxations in crystals (the relaxation associated with pairs of lattice vacancies).

The relaxation times of ordinary organic molecules are close to a few picoseconds. Fig. 2.8 gives relaxation frequency range for classical organic functions: alkanes [8], alcohols [9], alcohol ether [10-11], esters [12], acid chlorides [13], aliphatic and aromatic halogens [14-15], aliphatic and aromatic ketones [16-17], nitriles [18], and aliphatic and aromatic amines [19-20].
2.2.3 Kirkwood Model:

The dielectric constant is sensitive about the forces between neighboring dipoles. The first attempt to explain the dielectric constant by taking account of these forces is made by Kirkwood [22]. He considered a spherical specimen of the material, containing dipoles. The field inside the specimen is smaller than that outside by factor $3/(\epsilon+2)$. Each fixed configuration of these dipoles between which there is assumed to be a strongly directional coupling is denoted by X. Their relative probabilities are weighted by Boltzmann statistics. In the absence of an applied electric field, the system is in the state X, have a dipole moment $M(X)$. When the field is applied in direction $e$, then the average component of moment $\mu_i$ of the $i^{th}$ molecule in the direction ‘$e$’ can be shown by

\[
\langle \mu_i \cdot e \rangle = \frac{1}{\epsilon+2} \mu_i \cdot e
\]
<\mu_i e> = <(\mu_i e) (M(X)e)> \frac{E}{kT} \quad (2.39)

When E=0, the average on the right-hand side of the above equation is made. Allowing all configurations at random, it turns out to be

<\mu e> = <\mu \overline{M}> \frac{E}{3kT} \quad (2.40)

The moment $\overline{M}$ is that of the whole specimen when one molecule is in a fixed orientation, but the others are allowed to take up all possible configurations at random. Part of this moment is

(i) Induced by the molecule

(ii) Local ordering associated with a structural model.

$$\overline{M} = \int Pdv + \mu^* \quad (2.41)$$

Where the integral is taken over the whole specimen except spherical part. Calculation of ‘P’ in terms of a radial expansion of potential yields.

$$\overline{M} = \frac{9\varepsilon_0\mu^*}{(\varepsilon_0 + 2)(2\varepsilon_0 + 1)} \quad (2.42)$$

The permittivity is related to $\overline{M}$ by

$$\varepsilon_0 - 1 = \frac{4\pi \overline{M}}{VE} \quad (2.43)$$

Substitutions yield eventually

$$\frac{(\varepsilon_0 - 1)(2\varepsilon_0 + 1)}{3\varepsilon_0} = \frac{4\pi N_0 \mu \mu^*}{3VkT} \quad (2.44)$$

$$= \frac{4\pi N_0 g \mu^2}{3VkT} \quad (2.45)$$
where \( V \) is the molar volume. The moment \( \mu^* \) is that of a sphere when the central molecule is held in a fixed alignment, and structural forces partially align the other molecules in the sphere. Normally only a few layers of molecules are considered in the structural calculation of \( \mu^* \). The Kirkwood correlation parameter ‘\( g \)’ is the usual means by which the ratio \( \mu^*/\mu \) is expressed. It is a valuable measure of intermolecular angular correlation in a material. In this model an unpolarizable point dipole molecule is assumed which of course is unknown in nature. It is necessary to take some account of the induced dipole moment, not the permanent dipole moment \( \mu_g \) of the free (gas) molecule, but a value calculated from an addition of the permanent moment and the moment induced by neighboring dipoles. Thus it is necessary to know the polarizability ‘\( \alpha \)’ of the permanent dipole molecule.

If the field acting on the polarizable molecule is taken to be the Onsager cavity field ‘\( G \)’ then

\[
\mu = \mu_g \left( \frac{(2\varepsilon_0 + 1)(n^2 + 2)}{3(2\varepsilon_0 + n^2)} \right) \tag{2.46}
\]

The Kirkwood equation becomes

\[
\frac{(\varepsilon_0 - 1)(2\varepsilon_0 + 1)}{3\varepsilon_0} = \frac{4\pi N_0}{V} \left( \alpha + \frac{g \mu^2}{3kT} \right) \tag{2.47}
\]

which is an inaccurate form because it does not reduce to Onsager’s solution when \( g = 1 \).

If the total local field ‘\( F \)’ is taken to be acting on the polarizable molecule, then it can be shown that a different expression is obtained for ‘\( \varepsilon \)’.

\[
\frac{(\varepsilon_0 - n^2)(2\varepsilon_0 + n^2)}{\varepsilon_0 (n^2 + 2)^2} = \frac{4\pi N_0 g \mu^2}{9kTV} \tag{2.48}
\]

This is the Kirkwood–Frohlich equation [23-24].

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 molecule are oriented parallel to dipole of fixed molecule, then ‘g’ has value greater than one, whereas if dipoles of neighboring molecule are oriented anti parallel to dipole of fixed molecule, then ‘g’ has value less than one.

2.2.4 Effective Kirkwood Correlation factor

For binary mixture of liquids above equation needs some modification. One of the models can be given for the mixture as [23]

\[
\frac{4\pi N}{9kT} \left[ \frac{\mu_A^2 \rho_A X_A}{M_A} + \frac{\mu_B^2 \rho_B X_B}{M_B} \right] g_{\text{eff}} = \frac{(\varepsilon_{0m} - \varepsilon_{\text{sm}})(2\varepsilon_{0m} + \varepsilon_{\text{sm}})}{\varepsilon_{0m}(\varepsilon_{\text{sm}} + 2)^2}
\]

(2.49)

where \(X_A\) and \(X_B\) volume fraction of liquids A and B respectively and \(g_{\text{eff}}\) is the effective Kirkwood correlation factor, \(m\) – indicates the binary mixture of A and B. The \(g_{\text{eff}}\) will be different from 1 when there is correlation between the orientations of neighboring molecules. The effective correlation provides information in the mixture as follows

\(g_{\text{eff}} > 1\) : Indicates parallel orientation of electric dipoles.

\(g_{\text{eff}} < 1\) : Indicates anti-parallel orientation of electric dipoles.

\(g_{\text{eff}} = 1\) : Indicates that there is no interaction between the molecules in liquid

2.2.5 Bruggeman Model:

The static permittivity of mixture of two polar dielectrics can be found out by a useful model known as Bruggeman [25] mixture formula. The static permittivity of mixture with volume fraction of solute by

\[
f_B = \left[ \frac{(\varepsilon_{0m} - \varepsilon_{01})}{(\varepsilon_{01} - \varepsilon_{02})} \right] \left( \frac{\varepsilon_{01}}{\varepsilon_{0m}} \right) = 1 - V
\]

(2.50)

where \((f_B)\) is the Bruggeman dielectric factor. The \(\varepsilon_{0m}\), \(\varepsilon_{01}\) and \(\varepsilon_{02}\) are the static dielectric constant corresponding to mixture, solute and solvent respectively; \(V\) - is the volume
fraction of solvent. From above equation, the linear relation is expected from a plot ($f_B$) Vs Vol. fract. of solvent. But in binary liquids, there is non-linear relationship is observed shown in Fig. 2.9. To explain non-linear relationship of the plot, above equation has been modified as [26],

$$f_B = \left[ \frac{(\varepsilon_{0m} - \varepsilon_{02})}{(\varepsilon_{01} - \varepsilon_{02})} \right]^{\frac{1}{3}} \left( \frac{\varepsilon_{01})}{\varepsilon_{0m})} \right)^{1} = 1 - \left[ a - (a - 1) V \right] V \quad (2.51)$$

In this equation, volume fraction ($V$) is changed by a factor ‘a-(a-1) V’ of the mixture, a=1corresponds to Bruggeman’s equation.

The value of ‘a’ can be determined by least square fit method and deviation from unity indicates the molecular interaction in the mixture [27].

![Fig. 2.9 Bruggeman factor($f_B$) vs. Vol. fraction of solvent](image)
2.2.6 Excess dielectric Model:

There is no appropriate molecular theory available in the literature, which correlates the dielectric parameters to solute-solvent interaction. The solute-solvent interaction may provide the structural information of binary liquids. In the absence of such a theory, excess dielectric constant parameters [28-29]. The excess permittivity \( \left( \varepsilon_0^E \right) \) may also provide structural information is as follows [30-31].

\[
\left( \varepsilon_0^E \right) = \left( \varepsilon_0 \right)_{\text{m}} - \left[ \left( \varepsilon_0 \right)_A X_A + \left( \varepsilon_0 \right)_B \left( 1 - X_A \right) \right]
\]

(2.52)

where \( \left( \varepsilon_0 \right)_{\text{m}} \), \( \left( \varepsilon_0 \right)_A \) and \( \left( \varepsilon_0 \right)_B \) represent values static dielectric constant corresponding to mixture, solvent and solute, respectively and ‘\( X_A \)’ is the mole fraction of solvent, The excess dielectric constant \( \varepsilon_0^E \) may provide qualitative information about multimers formation in the mixtures as follows:

i) \( \varepsilon_0^E = 0 \) indicates that mixture constituents do not interact.

ii) \( \varepsilon_0^E < 0 \) indicates that mixture constituents interact such that the total number of effective dipoles contributed in the mixture \( \varepsilon_0 \) values get reduced.

iii) \( \varepsilon_0^E > 0 \) indicates that the constituents of a mixture interact such that there is an increase in number of effective dipoles contributed in the mixture \( \varepsilon_0^E \) values.

iv) Higher the magnitude of \( \varepsilon_0^E \) represents the stronger and long-range H-bond interaction between unlike molecules and vice versa.
2.2.7 Eyring Model:

Relaxation processes in dielectrics may be considered as the passing of a dipole across a potential barrier that separates the minima of energy. Let $\Delta G$ denote the difference in free enthalpy per mole of molecules, i.e. the difference of free enthalpy between the excited and ground state. According to Eyring [30], $k$ represents the number of times per unit time a dipole acquires sufficient energy to pass across the potential barrier from one equilibrium position to another. In such a case,

$$k = \frac{kT}{\hbar} \exp\left(\frac{-\Delta G}{RT}\right)$$

(2.53)

The microscopic relaxation time $\tau$ is related to $k$ by $k = 1/\tau$. In accordance with the principles of thermodynamics [31] $\Delta G = \Delta H - T\Delta S$. Therefore the relaxation process is as analogous to chemical rate process [32]. The temperature variation of the inverse microscopic relaxation time will then be approximately exponential, according to the equation:

$$\tau = \frac{kT}{\hbar} \exp\left(\frac{\Delta H}{RT}\right)\exp\left(-\frac{\Delta S}{RT}\right)$$

(2.54)

where $\Delta H$ is molar enthalpy of activation, and $\Delta S$ is the molar entropy of activation. Recasting the above equation we get

$$\ln(\tau T) = \frac{\Delta H}{RT} - \frac{\Delta S}{RT} + \ln \frac{h}{k} = \frac{\Delta H}{RT} + A$$

(2.55)

It follows from the equation that if $\Delta H$ and $\Delta S$ are independent of the temperature, the plot of $\ln(\tau T)$ vs. $1/T$ is linear with negative slope. Using the tangent of the slope of this function we can determine the height of the potential barrier $\Delta H$. 
References:


