CHAPTER 2

EXPERIMENTAL
2.1 Experimental Techniques:

The present work involves measurement of phase transition temperatures, and then studied the dielectric parameters like dielectric constant ($\varepsilon'$), dielectric loss factor ($\varepsilon''$), temperature coefficient of dielectric constant, relaxation time ($\tau_\varepsilon$), activation energy ($E_a$), conductivity ($\sigma$), and confirm the presence of Fe$_3$O$_4$ nanoparticles in the interstitial sites of nano doped $p$-$n$- alkoxo benzoic acid lattices. The confirmation of transition temperatures for all the compounds through the dielectric, the techniques used to measure the above parameters are as given below. The details of different experimental techniques that are employed during the preparation, characterization and study of physical properties of the liquid crystals are presented in this chapter. The experimental methods and characterization techniques adopted in the present work are.

1. Determination of phase transition temperatures from the textural studies using polarized optical thermal microscopy (POM).
2. Glass slide and cell preparation
3. Characterization of phase transitions, involved liquid crystal phases with differential scanning calorimetry (DSC)
4. UV – Visible spectroscopy for confirmation of doped nanoparticles
5. Newton’s 4tht Ltd. LCR meter for dielectric measurements

2.1.1 Polarizing Optical Microscope

Textural and phase transition temperature measurements are made by the polarizing optical microscope (POM) of type Olympus BX50 with attached DP10 camera setup and computer controlled HCS 302 hot stage of Instec, USA. The samples are kept on a glass slide, heated to isotropic state, glass cover is placed over the heated sample and then cooled to room temperature at which the sample sticks to the glass plate. Such samples are placed in the sample holder of hot stage HCS 302 of Instec temperature controller and observed for textures of the prepared liquid crystals. The samples are heated and cooled at a rate of $5^\circ$C/min through a command “ramp to temperature ---$^\circ$C for --- min”. The phase transition studies are also carried out for confirmation by using Differential Scanning Calorimeter of TA instruments model DSC Q2000 V24.4 at a scan rate of $5^\circ$C/min.

A polarizing microscope is a special microscope that uses polarized light for investigating the optical properties of specimens. Although originally called a mineral
microscope because of its applications in petrographic and mineralogical research, in recent years it has now come to be used in such diverse fields as biology, medicine, polymer chemistry, liquid crystals, magnetic memory, and state-of-the-art materials.

There are two types of polarizing microscopes: transmitted light models and incident light models. Figure 2.1 shows the basic construction of a transmitted light polarizing microscope. As seen in Figure 2.2, compared to a typical microscope, a polarizing microscope has a new construction with the following added units: a polarizing condenser that includes a polarizer, a rotating stage that allows the position of the specimen to be set, a strain-free objective for polarized light, a centered revolving nose-piece that allows optical axis adjustment for the objective, an analyzer, a Bertrand lens for observing the pupil of the objective, a test plate, a compensator, and an eyepiece with crosshair.

![Figure 2.1 External view and construction of transmitted light polarizing microscope](image-url)
In polarized light microscopy, always perform the optical adjustments, e.g. centering of the rotatable stage, adjusting the optical axis of objective lens and vibration direction of a polarizer, before the observation. Among the observation methods of a polarizing microscope, the orthoscopic observation is the one in which only the roughly vertical light is exposed to the specimen surface and the optical properties are observed only in that direction. The most commonly used observation method in polarizing microscope is crossed nicols observation to inspect the double refractive structures in biology, rock minerals, liquid crystals, macromolecule materials, anisotropic properties such as emulsions, and stress strain [1].

2.1.2 Glass slide and cell preparation

A glass slide of dimension 75mmX25mm X1.35mm which is taken and rubbed with a paper in unidirection for a good number of times and the liquid crystalline compound is placed on it and the glass slide is heated until the substance on it completely melts. A small cover slip of thickness 18mm is placed on the melt and allowed to cool. When the cover slip is kept carefully on the substance, homogeneous uniform distribution of the substance is achieved. Now the glass slide is kept in the hot stage of POM to observe the texture changes with temperature. The prepared glass slide can be used for any number of thermal runs.

Homeotropic alignment of indium tin oxide coated cells having area of 5mmX5mm with 6 micrometer spacing are obtained from M/s Instec Inc., USA.
Mesogens are injected in the liquid crystal cell by heating the sample in its isotropic state through capillary action. Better alignment of liquid crystal layer with few defects can be produced when the liquid crystal is allowed to flow into the cell towards the direction in which the surface is aligned. Now the prepared glass cell is ready for use in polarizing optical microscope. Both are shown in Figure 2.3

![Glass Slide](image)

![Cover Slip](image)

Figure 2.3 (a) Glass slide (b) Liquid crystal cell

2.1.3. Differential scanning calorimeter:

Differential scanning calorimeter (DSC) is a technique of recording the energy necessary to establish zero temperature difference between a substance and reference material against either time or temperature, as specimens are subjected to identical temperature regimes in an environment heated or cooled at a control rate. The temperature at which a peak is obtained at the first order phase transition represents a phase transition temperature. The DSC is sensitive enough not only to detect a first order phase transition but also a maximum specific heat in a second order phase transition. The area present in between the base line and the peak is a measure of the heat transition.
The Differential Scanning Calorimetry (DSC) was performed and Q20 V24.2 builds 107 universal V4.75TA instrument under nitrogen atmosphere at the heating/cooling rate of 1°C/min. This is shown in Figure 2.4.

Figure 2.4. Differential Scanning Calorimeter

2.1.4. UV – Visible Spectroscopy:

Ultraviolet – Visible spectroscopy refers to absorption spectroscopy or reflectance spectroscopy in the ultraviolet-visible spectral region. This means it uses light in the visible and adjacent (near-UV and near-infrared (NIR)) ranges. The absorption or reflectance in the visible range directly affects the perceived color of the chemicals involved.

Figure 2.5. UV – Visible spectrophotometer
In the region of the electromagnetic spectrum, molecules undergo electronic transitions. Molecules containing π-electrons or non-bonding electrons (n-electrons) can absorb the energy in the form of ultraviolet or visible light to excite these electrons to higher anti-bonding molecular orbital’s. The more easily excited the electrons (i.e. lower energy gap between the HOMO and the LUMO), the longer the wavelength of light it can absorb. UV/Vis spectroscopy is routinely used in analytical chemistry for the quantitative determination of different analytes, such as transition metal ions, highly conjugated organic compounds, and biological macromolecules. Hence the presence of added nano particles in alkyloxy benzoic acid samples (NnOBA, where n = 3 to 9 and 12) can be confirmed from UV-Visible Spectroscopy. The UV – Visible spectrophotometer of type Jasco make Japan, model No.V-670 was used.

2.1.5. L. C. R. Meter:

Dielectric constant and dielectric loss are measured in the frequency range of 1 Hz to 1 MHz at different temperatures by using Newton’s 4th Ltd., LCR meter model PSM1700. Homogeneously aligned Indium Tin Oxide (ITO) coated liquid crystal cells of 5mm X 5 mm X 6 μm supplied by M/s Instec. USA is used. The tanδ is obtained directly from the data of LCR meter. The accuracy of dielectric constant and loss are estimated to the error of 1% and 2% respectively and the temperature accuracy to ± 0.1°C. The data obtained from LCR meter is used to calculate relaxation time of the taken samples.
Figure 2.6 LCR meter in conjunction with Polarizing optical microscope
2 Theories of dielectric relaxation

**Dielectrics:**
A dielectric material increases the storage capacity of a condenser by neutralizing charges at the electrode surfaces which otherwise would contribute to the external field. Faraday was the first to recognize this phenomenon of dielectric polarization, which occurs due to the formation of dipole chains under the influence of the applied field. Dielectric materials can be classified broadly into two categories as polar and non-polar materials, depending on charge distribution in molecule. Non-polar dielectric materials consist of molecules with positive and negative charges such that their effective centers of charge distribution coincide. Thus dipole moment of non-polar dielectric materials is zero in the absence of electric field. Polar dielectric materials are those in which centers of positive and negative charge distribution are separated by a distance, forming a molecular dipole even in the absence of electric field. But since the positive and negative charges are equal, the molecule is electrically neutral. The magnitude of molecular dipole moment depends on the size and symmetry of the molecule. Molecules having a centre of symmetry, such as Methane (CH₄), Carbon tetrachloride (CCl₄) and Benzene (C₆H₆) are non-polar while molecules not having centre of symmetry such as Methanol (CH₃OH), Ethanol (C₂H₅OH), Acetone (CH₃-CO-CH₃) and Water (H₂O) are polar dielectrics.

Polar nature of dielectric materials is measured in terms of its permanent dipole moment. If we imagine a molecular dipole made up of charge \( +q \) and \( -q \) separated by a distance ‘\( d \)’, then the dipole moment is equal to \( q \times d \). In the molecular dipoles, \( q \) will be in the order of \( 10^{-10} \) e. s. u. i.e., magnitude of electronic charge and ‘\( d \)’ will be of the order of \( 10^{-8} \) cm (one Angstrom unit). Thus dipole moment (\( \mu \)) for molecular dipoles is in the order of \( 10^{-18} \) e. s. u. The unit \( 10^{-18} \) e. s. u. is called Debye. The dipole moments of molecular dipoles are usually measured in Debye, abbreviated as D. Dielectric constant of the material depends on dipole moment as well as on the ability of these dipoles to align in the direction of the applied electric field.

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

\[ P = \alpha E \]  \hspace{1cm} (2.1)

Where \( \alpha \) is a constant of proportionality known as polarizability.

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

\[ P = P_d + P_o \]  \hspace{1cm} (2.2)

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

Hence the total polarization can be written as,

\[ P = P_e + P_i + P_o \]  \hspace{1cm} (2.3)

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

\[ \alpha = \alpha_e + \alpha_i + \alpha_o \]  \hspace{1cm} (2.4)

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

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

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

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

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

2.2.1 Theories of static permittivity

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

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

$$F = \frac{1}{4 \pi \varepsilon_0} \frac{q_1 q_2}{r^2}$$  \hspace{1cm} (2.5)

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

Considering the above conditions Coulomb’s law can be written as,

$$F = \left[ \frac{q_1 q_2}{\varepsilon r^3} \right] r$$  \hspace{1cm} (2.6)

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

$$E = 4\pi q$$  \hspace{1cm} (2.7)

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

$$E = \frac{4\pi q}{\varepsilon}$$  \hspace{1cm} (2.8)
The reduction in the apparent charge on plates is caused by the polarization of the medium. In fact, there is induced charge throughout the material but it annuls itself everywhere except on the surface. The amount of polarization charge can be written as

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

(2.9)

The influence of the electric field on the dielectric is equivalent to charging of two surfaces of the dielectric with charges of opposite sign to those causing the field. The surface density of these opposite sign charges on the surface of dielectric is \( P \), and is known as polarization [4]. It is the total charge passing through any unit area within the dielectric (parallel) to the plates.

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

\[ D = 4\pi q \]  

(2.10)

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

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

(2.11)

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

(2.12)

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

\[ C = \frac{Q}{V} \]  

(2.13)

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

\[ C = \frac{\varepsilon A}{4\pi d} \]  

(2.14)

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

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

\[ M = P A d = P V \]  

(2.15)
Thus, polarization can be regarded as dipole moment per unit volume in the dielectric material. The amount of polarization in the dielectric materials was calculated by using various theories as discussed in the following sections.

2.2.1.1 Clausius Mossotti equation

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

$$m = \alpha_0 F$$

(2.16)

Where $\alpha_0$ is polarizability of molecule.

The average moment in the direction of the field [5] is given by

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

(2.17)

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

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

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

$$F = F_1 + F_2 + F_3$$

(2.18)

$$F_1 = 4 \pi \sigma$$

(2.19)

and $F_2$ may be obtained by considering that the matter within the small sphere is to be removed. $F_2$ is made up of two parts, first the force due to layers of induced charges on the dielectric facing the conducting plates and second the layer of charge on surface of small spherical cavity.
\[ \mathbf{F}_2 = -4\pi \mathbf{P} + \left( \frac{4\pi \mathbf{P}}{3} \right) \]  

(2.20)

where \( \mathbf{P} \) is the polarization of the medium i.e., the electric moment per unit volume set up in the dielectric.

A general expression for \( \mathbf{F}_3 \) cannot be given but it may be evaluated in special cases. Lorentz [6] showed that for a cubic lattice of polarizable atoms, the dipoles inside the sphere produce zero field. This is true in gases and for those liquids in which molecules are moving totally independent of each other. By assuming \( \mathbf{F}_3 = 0 \), the total force is given by

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

(2.21)

But \( \mathbf{D} = 4\pi \sigma \) and \( \mathbf{D} = \mathbf{E} + 4\pi \mathbf{P} \)

\[ \mathbf{E} \left( 1- \varepsilon \right) = 4\pi \mathbf{P} \]  

(2.22)

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

(2.23)

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

(2.24)

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

(2.25)

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

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

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

(2.26)

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

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

(2.27)

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

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

(2.28)

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

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

(2.29)
This equation is known as Clausius-Mossotti Equation. The right hand side of equation indicates the molar polarization and is given by

\[ P = \left( \frac{4\pi}{3} \right) N\alpha_0 \]  

(2.30)

The molar polarization is purely a molecular quantity giving some information about electric properties of the molecule. By using equation (2.29) and (2.30), we can write equation for molar polarization as

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

(2.31)

Thus molar polarization is different from the \( P \) used to denote the electric moment per unit volume.

### 2.2.1.2 Debye theory of static permittivity

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

a) The molecule is considered as rigid system of charges  
b) The external field is supposed to induce no charge at all.

The molecules are classified into two groups.

1) Molecules with normal values of molar polarization and  
2) Molecules with abnormally large values of polarization.

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

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

(2.32)

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

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

(2.33)

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

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

(2.34)
Debye has given somewhat more general derivation of this equation in which \( \alpha_0 \) is expressed as the average of the three polarizabilities along the three axes of the molecule treated as an ellipsoid of polarization.

The conclusions drawn from Debye theory are as follow:

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

2) For polar substances, the molar polarizability will fall with rising temperature, because the thermal agitation decreases the dipolar polarization.

The linear dependence of polarization upon the reciprocal of absolute temperature is taken for gases where molecular freedom occurs. But this is not the case with all polar liquids and polar solids. So for polar liquids, the Debye equation cannot be expected to hold. The application of Debye equation to dilute solutions is an approximation.

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

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

and considering

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

\[
\frac{(\epsilon - 1)}{(\epsilon + 2)} = \frac{T_c}{T}
\]

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

2.2.1.3 Onsager theory

According to Debye theory, liquids act as ferroelectric material when \( T < T_c \), but the phenomenon of ferroelectricity is not common and certainly does not occur in water [7]. This failure of Debye equation is because of the assumption that \( F_3 = 0 \), which is almost certainly not valid. Because of this Onsager [5, 8, 9] has given his
theory on the following assumption. The molecule is polar molecule, which is spherical in form with molecular radius ‘a’ and is given by
\[ a^3 = \frac{3}{4\mu N_1} \] (2.38)

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

1) The spherical cavity field \( G \), produced in the empty cavity by the external applied field
\[ G = \frac{3e_0}{(2e_0 + 1)} E = gE \] (2.39)
where \( g = (3e_0) / (2e_0 + 1) \)

2) The reaction field \( R \) setup in the cavity by polarization induced by dipoles in its surrounding is
\[ R = \frac{2(e_0 - 1)}{2e_0 + 1} \frac{m}{a^3} = r \frac{m}{a^3} \] (2.40)
where \( r = \frac{2(e_0 - 1)}{(2e_0 + 1)} \)

The total internal field acting upon spherical polar molecule is
\[ F = G + R \]
\[ F = \frac{3e_0}{(2e_0 + 1)} E + \frac{2(e_0 - 1) m}{2e_0 + 1} \frac{m}{a^3} \] (2.41)
\[ F = gE + r \frac{m}{a^3} \] (2.42)

From equation (2.41), it can be observed that when \( e_0 \rightarrow 0 \), 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 the induced moment \( \alpha F \) by the local field.
\[ M = \mu + \alpha F \] (2.43)
\[ m = \mu + \alpha \left[ gE + (r \frac{m}{a^3}) \right] \] (2.44)
\[ m = \frac{(\mu + \alpha gE)}{\left(1 - \frac{ra}{a^3}\right)} \] (2.45)
Then the mean moment parallel to the field is given by

$$\bar{m} = \frac{g}{3kT} \frac{\mu^2 E}{1 - \frac{r \alpha}{a^2}} + \frac{\alpha g}{3kT} \frac{1}{1 - \frac{r \alpha}{a^2}}$$

(2.46)

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

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

(2.47)

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

$$\alpha = \frac{n^2 - 1}{n^2 + 2} a^3$$

(2.48)

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

$$\frac{(\varepsilon_0 - n^2)(2\varepsilon_0 + n^2)}{\varepsilon_0(n^2 + 2)^2} = \frac{4\pi N_1 \mu^2}{9kT}$$

(2.49)

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

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

### 2.2.1.4 Kirkwood Theory

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

$$\frac{(\varepsilon_0 - 1)(2\varepsilon_0 + 1)}{3\varepsilon_0} \frac{M}{\varepsilon} = 4\pi N_1 \frac{g \mu^2}{3kT}$$

(2.50)

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

Thus the Kirkwood’s equation is written as

$$\frac{(\varepsilon_0 - 1)(2\varepsilon_0 + 1)}{3\varepsilon_0} \frac{M}{d} = 4\pi N \frac{\alpha + g\mu^2}{3kT}$$  \hspace{1cm} (2.51)

### 2.2.1.5 Frohlich’s Theory

Frohlich [11] considered a spherical region of macroscopic dimensions within an infinite specimen, which is treated as a continuous medium. He derived the expression for static permittivity using statistical method. According to Frohlich, the equation for non polarizable dipoles is

$$\frac{(\varepsilon_0 - 1)(2\varepsilon_0 + 1)}{3\varepsilon_0} \frac{M}{d} = 4\pi N \frac{\langle m\bar{m}\rangle}{3kT}$$ \hspace{1cm} (2.52)

It can be observed from this equation that if $m$ is identified as $\mu$ and $\bar{m}$ is written as $g\mu$, this equation is identical to Kirkwood’s equation (2.51).

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

$$\frac{(\varepsilon_0 - n^2)(2\varepsilon_0 + n^2)}{\varepsilon_0 (n^2 + 2)^2} \frac{M}{d} = 4\pi N \frac{g\mu^2}{9kT}$$ \hspace{1cm} (2.53)

Except for interaction of correlation parameters, the equation is identical with Onsager’s equation (2.49).

### 2.2.2 Theories of Dynamic permittivity

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

\[ \varepsilon^* = \varepsilon' - j\varepsilon'' \tag{2.54} \]

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

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

**Case-1:** When the field is switched on

Let \( \mathbf{P} = \mathbf{P}_1 + \mathbf{P}_2 \)

Where \( \mathbf{P} = \) Total polarization

\( \mathbf{P}_1 = \) Distortion polarization (in phase with the applied field)

\( \mathbf{P}_2 = \) Dipolar polarization (the out of phase component)

Here

\[ \frac{d\mathbf{P}_2}{dt} = \alpha (\mathbf{P} - \mathbf{P}_1) \]

\[ \frac{d(\mathbf{P} - \mathbf{P}_1 - \mathbf{P}_2)}{\mathbf{P} - \mathbf{P}_1 - \mathbf{P}_2} = \frac{dt}{\tau} \tag{2.55} \]

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

Solving this, with the boundary condition that at \( t = 0, \mathbf{P}_2 = 0 \) we get

\[ \mathbf{P}_2 = (\mathbf{P} - \mathbf{P}_1) (1 - e^{-\frac{t}{\tau}}) \tag{2.56} \]

which can be represented graphically as shown in Figure 2.7.
Case -2: When field is switched off

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

(2.57)

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

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

(2.58)

which can be represented graphically as shown in Figure 2.8

Let the applied field be of the form

\[ E = E_0 \exp(j\omega t) \]  

(2.59)

At low frequency, \( 4\pi P = \varepsilon(\varepsilon_0 - 1) E \) as \( \omega \to 0 \)

since \( P = P_1 + P_2 \)

the contribution due to both exists only at very low frequencies
but at high frequencies, \(4\pi \mathbf{P}_1 = (\varepsilon - 1) \mathbf{E}\) as \(\omega \to \infty\) & \(\varepsilon = n^2\)
because at high frequency \(\mathbf{P}_2 = 0\)

From the rate equation-2.57, 
\[
\frac{d\mathbf{P}_2}{dt} = \frac{-\mathbf{P}_1 \cdot \mathbf{P}_2}{\tau}
\]
\[
= \frac{\varepsilon}{4\tau}\left(\varepsilon_0 - n^2\right) E_0 \exp(j\omega t) \cdot \frac{\mathbf{P}_2}{\tau}
\]

In steady state the solution to above equation is of the form
\[
\mathbf{P}_2 = A \exp(j\omega t)
\]

where
\[
A = \frac{\varepsilon (\varepsilon_0 - n^2) E_0}{4\pi (1+j\omega \tau)}
\]

By substitution of above equations into the rate equation
\[
\mathbf{P}_2 = \frac{\varepsilon (\varepsilon_0 - n^2) E_0}{4\pi (1+j\omega \tau)}
\]

(2.61)

From the above equation, we see that \(\frac{\mathbf{P}_2}{E_0}\) is complex which means that the dipolar part of the polarizability is out of phase with respect to the applied field.

\[
\mathbf{P}_1 + \mathbf{P}_2 = \mathbf{P}' - j\mathbf{P}''
\]
\[
= \frac{\varepsilon}{4\pi} (n^2 - 1) \mathbf{E} + \frac{\varepsilon (\varepsilon_0 - n^2)}{4\pi (1+j\omega \tau)} \mathbf{E}
\]

where \(\mathbf{P}'\) and \(\mathbf{P}''\) are real

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

\(\varepsilon'\) and \(\varepsilon''\) are given by

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

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

and the loss tangent
\[
\tan \phi = \frac{\varepsilon''}{\varepsilon'}
\]

The dielectric constant is strictly not a constant but varies with various physical parameters of which frequency and temperature are of prime importance. The variation of \(\varepsilon'\) and \(\varepsilon''\) with frequency can be represented graphically as shown in
Figure 2.9 Variation Dielectric constant and dielectric loss with ω

2.2.2.1 Debye model

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

$$\varepsilon' = \varepsilon_{\infty} + \frac{\varepsilon_0 - \varepsilon_{\infty}}{1 + j\omega \tau} \quad (2.64)$$

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

$$\varepsilon' = \varepsilon_{\infty} + \frac{\varepsilon_0 - \varepsilon_{\infty}}{1 + j\omega \tau} \quad (2.65)$$

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

\( \tau \) is called the macroscopic relaxation time and corresponds to the time required for the polarization of the dielectric to decrease or to relax \( \frac{1}{e} \) of its value after the removal of the field. This relaxation time, which decreases with temperature, is related to the physical properties of the polar molecule and their environments. It may also be seen from these equations that \( \varepsilon'' \) (dielectric loss factor) reaches its maximum,
\[ \varepsilon''_{\text{max}} = \frac{(\varepsilon_\infty - \varepsilon_s)}{2} \]  

(2.67)

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

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

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

(2.68)

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

The results of dielectric measurements are represented by plotting \( \varepsilon' \) against \( \varepsilon'' \) in an Argand diagram, on a semicircle lying above the \( \varepsilon' \) axis (Figure 2.10).

![Figure 2.10 Debye semi circle](image)

**Figure 2.10 Debye semi circle**

### 2.2.2.2 Cole-Cole model

Cole and Cole [12] observed that in many materials, the locus of \( \varepsilon' \) and \( \varepsilon'' \) is an arc of a semi-circle following the empirical equation

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

(2.69)

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

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

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

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

(2.71)

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

(2.72)

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

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

This is the equation of a circle with its centre at

\[
\left\{ \frac{1}{2}(\varepsilon_o + \varepsilon_c) - \varepsilon' \right\} \quad \text{and radius} \quad \frac{1}{2}(\varepsilon_o - \varepsilon_c) \sec\left(\frac{\pi\alpha}{2}\right)
\]

The Debye dispersion and Cole-Cole arc dispersion are shown in Fig. 2.5 and from the Fig. 2.5., \(\theta\) is given by the following relation [13].

\[
\theta = \frac{\pi\alpha}{2}
\]

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

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

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

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

(2.73)

where \(u\) and \(v\) are shown in Figures 2.10 and 2.11.

The value of \(\alpha\) generally decreases as the temperature is increased. In the limit when \(\alpha = 0\), the Cole-Cole arc reduces to the Debye semicircle. Later an attempt is made by Kastha [14] to provide a physical basis for the use of Cole-Cole relation.
2.2.2.3 Davidson-Cole relaxation model

The Cole-Cole arc is symmetrical about a line through the centre, parallel to the \( \varepsilon' \) axis. Davidson and Cole [15] found that the experimental results for certain materials do not have this symmetry, the \( \varepsilon' \) Vs \( \varepsilon'' \) plot being a skewed arc. They suggested that behaviour of this kind could be represented by the expression

\[
\varepsilon^* = \varepsilon_\infty + \left(\varepsilon_0 - \varepsilon_\infty\right) \left(1 + j\omega\tau\right)^\beta
\]  
(2.74)

Rearranging

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

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

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

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

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

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

\[
\frac{\varepsilon''}{\varepsilon_0 - \varepsilon_\infty} = \cos\beta \phi \cdot \sin\beta \phi
\]  
(2.77)
The value of $\beta$ determines the angle at which the arc cuts the $\epsilon'$ axis at the high frequency end. Differentiating the above two equations with respect to $\phi$ gives

$$\frac{d\epsilon''}{d\epsilon'} = \left(\frac{d\epsilon''}{d\phi}\right) = -\cot(\beta + 1)\phi$$

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

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

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

2.2.2.4 Havriliak - Negami model

It was found that none of the above dielectric functions was successful in giving the spectral response in case of polymeric materials. There are many examples of dielectric behavior, which cannot be explained by Cole-Cole and Davidson-Cole expressions, both of which contain only one adjustable parameter to describe the shape of the plot $\epsilon'$ Vs $\epsilon'$. Havriliak-Negami [16] generalized the expression, in contribution of both Cole-Cole and Davidson-Cole expression as given below

$$\epsilon'^* = \epsilon'_\infty + \frac{(\epsilon_0 - \epsilon'_\infty)}{1 + (j\omega \tau)^{(1-\alpha)}]}$$

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.

2.3 Thermodynamic parameters

i) Dielectric constant

The dielectric constant of a material is numerically the ratio of the capacitance of a capacitor containing that material to the capacitance of the same electrode system with vacuum.

Using the following equation the dielectric constant, ($\epsilon^1$) for series of pure and nano alkyloxy benzoic acids are calculated.

$$\epsilon^1 = \left(\frac{C_p - C_o}{\epsilon_o A}\right) + 1$$

(2.80)
Where \( A \) = area of the cell, \( d \) = thickness of the cell, \( \varepsilon_0 \) = permittivity of free space \( 8.85 \times 10^{-12} \) \( \text{Fm}^{-1} \), \( C_p \) = capacitance with sample and \( C_o \) = capacitance without sample.

**ii) Temperature coefficient of dielectric constant**

Through dielectric constant the temperature coefficient of dielectric constant (\( \tau_\varepsilon \)) is calculated using equation (2). Values of \( \tau_\varepsilon \) can be positive or negative, indicating an increasing or decreasing dielectric constant, respectively, with an increasing temperature [17]. As these are thermotropic liquid crystals their temperature stability with respect to other materials is low [17]. In determining \( \tau_\varepsilon \), the measured dielectric constant at isotropic temperature as reference temperature is compared with that obtained at initial and final temperature range of LC phase studied.

\[
\tau_\varepsilon = \frac{\varepsilon (T_{\text{final}}) - \varepsilon (T_{\text{initial}})}{\varepsilon (T_{\text{ref}}) - \varepsilon (T_{\text{ref}})} * 10^6 \left( \frac{\text{ppm}}{\text{oC}} \right)
\]

(2.81)

Where \( T_{\text{initial}} \) = starting LC phase temperature value, \( T_{\text{final}} \) = ending LC phase temperature value, \( \varepsilon (T_{\text{initial}}) \); \( \varepsilon (T_{\text{final}}) \) are the corresponding dielectric constant respectively and \( \varepsilon (T_{\text{ref}}) \) = dielectric constant at some reference temperature (50\(^\circ\)C). The \( \tau_\varepsilon \) value has units of parts per million per degree Celsius [ppm/\(^\circ\)C].

**iii) Dielectric loss**

The simplest model for a capacitor with a lossy dielectric is as a capacitor with a perfect dielectric in parallel with a resistor giving the power dissipation. The dielectric loss angle (\( \tan \delta \)) values are directly measured from the experimental technique, and the imaginary part of permittivity (dielectric loss, \( \varepsilon^{\text{11}} \)) is calculated using the equation (3) for the series of compounds studied.

\[
\varepsilon^{\text{11}} = \varepsilon^{\text{1}} \tan \delta
\]

(2.82)

**iv) conductivity**

Based on \( \varepsilon^{\text{11}} \) data the sample conductivity \( \sigma \) (siemens per meter) was estimated using equation (4). The changes in the electrical conductivity are measured from 1 KHz to 1MHz frequencies.
\[ \sigma_{ac} = 2\pi \varepsilon_0 \varepsilon'^{11} f \]  

(2.83)

Where \( \varepsilon_0 = \) permittivity of free space \( 8.85 \times 10^{-12} \) Fm\(^{-1} \), \( f = \) corresponding frequency in Hz and \( \varepsilon'^{11} = \) dielectric loss.

v) Activation energy

Most widely adopted form of the Arrhenius equation [18] for the effect of temperature on conductivity is shown in equation (2.84). The activation energy is viewed as an energetic threshold for a fruitful electric field production generated by the LC molecules orientation. It is possible to calculate activation energy with the Arrhenius equation by just using the conductivity at two temperatures. It would be more realistic and reliable if more data of conductivity is taken at different temperatures. Hence by using the ac conductivity values measured from equation (2.83) in the LC temperature region at 1 KHz to 1MHz, the activation energy (W) is calculated by using equation (2.84).

\[ \sigma_{ac} = \sigma_o \exp \left( \frac{-W}{KT} \right) \]  

(2.84)

Where \( W = \) activation energy KJ/mol, \( K = \) Boltzmann constant in eV/K, \( T = \) temperature relative to the conductivity value calculated using a reference temperature and the considering temperature values of corresponding phases, \( \sigma_{ac} = \) conductivity in LC phase and \( \sigma_o = \) conductivity in the isotropic phase at different frequencies.

vi) Relaxation time

By using the dielectric data (dielectric constant and loss) from LCR meter, the Cole Cole plots are drawn for different temperatures. The relaxation time \( \tau \) (Sec) can be found [19] from the arc plot by using the equation (2.85)

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

(2.85)

Where \( \alpha = \theta / 90 \) (distribution parameter), \( \omega = 2\pi f \) (angular frequency, Hz) and \( u, v \) values are determined from the drawn Cole Cole plots.
References: