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1.1.1 Dielectric fundamentals

The measurement of dielectric properties of several agriculture, environmental, and food processes is needed for society. Microwave measurements and dielectric properties of materials are finding increasing applications, as new electro-technology is adapted for the use in the agriculture and food processing industries. The interest in dielectric properties of materials has previously been related with the design of electrical equipment, where different dielectrics can be used for insulating conductor and other components of electrical equipment. The measurement of dielectric properties is not an end unto itself. Rather, these properties are intermediary vehicle for understanding, explaining, and empirically rating certain physical-chemical properties of materials.

If we apply potential difference to a cross-piece of material, some or no electric current flows through it. If the material piece contains free electron as in case of copper, they move from one end to another and current generated in piece.

On the other hand if the material piece contains no free electrons as in case of ebonite, no electric current at result. Such material producing no current on application of potential difference is known as insulators. In an insulator the electrons are tightly bound to the atoms, therefore there are no free electrons or very less. In spite of non-conducting nature of insulators have an essential behavior in existence of electric field. In the presence of electric field the insulator piece develops a dipole property. The insulators such properties are called as dielectrics.

When two charges ‘+q’ and ‘-q’ are separated by distance ‘d’, then a dipole is formed and its dipole moment is ‘qd’. A piece of materials, dielectric does not process dipole moment as a whole under normal condition but gets the dipole moment when subjected to electric field. This may be the result of generation of new dipoles inside the piece or alignment of already existing dipoles in the piece due to the application of electric field. In this process the piece of dielectric develops net charge on two ends of piece. The process of development of net charges on the two ends of piece and acquiring dipole moment to the piece is known per unit volume.

The dielectrics are classified as polar and non-polar, depending on the separation existence of positive charge center from its negative charge center in molecule. Non-polar dielectric consists of molecules with charge distribution
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coincide. Thus dipole moment of non-polar dielectric material have center of positive and negative charge distribution in molecule separated by distance and form a molecular dipole even in absence of electric field. But since positive and negative charges are equal, the molecule is uncharged. The magnitude of molecular dipole moment depends upon size and similarities of molecule [1].

Dielectric study is the study of different dielectric properties and dependence of these properties on the composition and structure of substance on various external factors like temperature, humidity, intensity and frequency of change of an electric field.

The most common dielectric parameters are the dielectric permittivity, dielectric loss and relaxation time. The dielectric permittivity is defined as the ratio of the capacity of condenser with given substance as dielectric to the power of the same condenser with a vacuum as dielectric. The dielectric is function of temperature, frequency and it is written as complex quantity known as complex permittivity.

\[ \varepsilon^* (\omega) = \varepsilon' - j \varepsilon'' \]  

Where \( (\varepsilon') \) is dielectric permittivity and is called as real part, \( (\varepsilon'') \) is dielectric loss and is called as an imaginary factor.

Another important dielectric parameter is relaxation time \( (\tau) \), which is essentially a measure of time; the dipole would take to reach a random distribution on removal of the electric field. In a system, dipoles are oriented according to thermal distribution. An external field makes the thermal distribution disturbed and the dipoles are oriented in the direction of field [2].

The time required to reorient the dipoles after removal of electric field is called as relaxation time.

1.1.2 Applications of dielectric studies

The dielectric studies of materials give very important information about molecular interaction and dielectric parameters, which are of the direct technological importance. The knowledge of dielectric properties of materials, their temperature, and frequency dependence is of great importance in various areas in other applications that depend upon the dielectric properties of grain and seeds that include RF treatments of hard seeds to increase germination and electrical measurement of moisture content in grain.

The dielectric studies are useful for agriculture; it is found that the dielectric
permittivity increases with increasing moisture contents in the seeds and the dielectric permittivity with increasing moisture contents in the seeds and the dielectric permittivity decreases as the frequency increases. At large moisture level and lower frequency range, the magnitudes of variation in dielectric permittivity were large. This variation is used to get an idea of the moisture contents in seeds.

**Moisture measurement**

Accurate measurement of moisture content is of importance in many applications, including agricultural and the food processing industries. Because of the high relative permittivity of water, the dielectric properties of moist material are strongly dependent on their moisture content, these method rely on calibration curve relating relative permittivity to moisture content, which may be obtained by measuring a range of samples with known moisture level.

**Medicine**

Investigation of the dielectric properties of biological materials and their frequency and temperature dependence provide important information for the water state (free or bound), molecular structure, and hydration processes that are for primary importance in biochemistry and biophysics.

The interest of microwaves increased due to biological effects. Exposure to microwaves result in thermal stresses both deeps inside the body and also on the surface. Excessive exposure may cause damage but controlled exposure may result in therapy and human comfort. Controlled does of microwaves can be made useful for medical diagnosis, therapy and human comfort. Physical therapy of microwaves has been found effective in curing inflammation, piles and injury. Microwaves treatment of cancer has also been studied. Human comfort and physical health depend upon the energy exchange between man and surrounding. Normally heat is generated in the human body by metabolism in the body. Incident microwave energy can help the heat generation metabolism and keep human being at comfort even at low temperature.

**1.1.3 Dielectric techniques**

There are two basic techniques of dielectric study of solids and liquids, these are 1) Time domain technique. 2) Frequency domain technique.

1) **Time domain reflectometry technique**

Time domain reflectometry technique is useful for the measurement of dielectric properties (dielectric permittivity, relaxation time and excess parameters.)
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Time domain reflectometry had wide frequency spectrum.

2) Frequency domain technique

Frequency domain technique is useful for the study dielectric parameters like dielectric permittivity, dielectric loss and \( \tan \delta \). Under frequency domain reflectometry technique there are number of experimental methods. At the frequencies below 1 GHz, commercially available measuring bridges and vector voltage meters are useful to determine the input impedance or transmission coefficient of specimen cell. At frequencies between 0.1 to 600 GHz, a traveling wave transmitted through the sample is probed interferometrically in the case of high loss liquids. At lower loss, standing wave patterns are frequently analyzed. In the frequency range 10 GHz \( \leq f \leq 100 \) GHz, however, due to unavoidable use of narrow band wave-guide devices, measurements are expensive and lengthy if the observations have to cover a large part of decade. Still time consuming, reclosed resonator techniques at microwaves frequencies. In this method cavity or part of it, is filled with the liquid and resulting shift in the resonant frequency and change of quality factor observed. Due to multiple reflections at the sample surface, the electromagnetic cavity field is extremely sensitive to the dielectric properties of the liquid. Cavity resonator method are capable of precise measurements on the sample available is small. Free space techniques, like quasi-optical interferometers and open reflectors arrangement are also used in dielectric studies of liquids having low loss. These methods avoid conduction loss due to wavelength or resonator walls. In most open system techniques, pollution of sample during measurement is severe problem. Atmospheric pressure for example, may strongly affect the dielectric low loss liquids.

At microwave frequencies 0.1 GHz to 100 GHz, a traveling wave method is widely used in measurement of lousy liquids. Transmission measurement techniques using microwave bridges have also been established for studies of small dielectric loss. Another convenient method of measuring the dielectric parameters of liquids consists in probing a standing electromagnetic wave either within the test liquid or in probing a standing electromagnetic wave either within the test liquid or in front of it. Recent improvement like sampling of standing wave pattern at regular intervals and accuracy. For that reason, precise data on large variety of liquids can now be obtained by standing waves observations. With closed resonator techniques designed for studies on lousy liquids at microwave frequencies. A thin glass capillary filled with the liquids under test is concentrically inserted in a circular cylindrical cavity.
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The experimental set up of frequency domain technique, which is given in chapter III. The experimental setup of microwave bench is routinely used for the measurement of dielectric properties [8] (dielectric permittivity, dielectric loss and $\tan \delta$). In this experimental work microwave X-band set up having frequency range 8.2 to 12.4 GHz is used. Dielectric parameters carried over 10.75 GHz. In this thesis systematic study has been done for five samples with increasing concentrations in mole per liter and observed the change in dielectric permittivity and dielectric loss etc. Dielectric loss is parameters, which describes the motion of the electric charge like conduction phenomena.

Specific dielectrics are found to display conduction which arises not only from the effect of polarization on the displacement current; but actual charge transport. Such conduction would normally be described by volume conductivity $\sigma$ (ohm$^{-1}$cm$^{-1}$) and the effect of it would be to add an additional term to the dielectric loss, which is inversely proportional to the frequency ($\omega$).

Depending upon the type of solutes and also on the concentrations of the solvents, various relaxation processes are observed, even in comparatively simple binary mixture. Due to the relaxation phenomena in biological tissue, it is almost impossible to look for the existence of the bound water by measurement on such complex systems. More reliable information can be derived from the study of simple binary solutions. There seems to be two situations. The dielectric properties of following binary systems have been reported for single frequency 10.75GHz.

1. Acetonitrile and methanol (CH$_3$OH)
2. Acetonitrile and ethanol (CH$_3$CH$_2$OH)
3. Acetonitrile and n-propyl alcohol (CH$_3$CH$_2$CH$_2$OH)
4. Acetonitrile and n-butyl alcohol (CH$_3$(CH$_2$)$_2$CH$_2$OH)
5. Acetonitrile and 1-pentanol (CH$_3$(CH$_2$)$_3$CH$_2$OH)

Comparison of TDR and FDR data

The time domain reflectometry had wide frequency spectrum. It require less samples, less time, to acquired data, however the frequency domain reflectometry had a limited frequency spectrum, it requires more samples and more time to acquire the data. The design of TDR instrument is hard and hard to manufacture, it has less power handling capability and more power losses. On the other hand FDR technique is easy to manufacture has more power handling capability and less power losses.
TDR

As per the sampling theorem the TDR technique is defined as “A band limited signal having no frequency component higher than ‘fm’ Hertz, may be completely recovered from the knowledge of its samples taken at the rate of at least ‘2fm’ samples per second.”

FDR

Frequency domain measurement with concentrations dependent systems have become popular due to simplicity and cost. This provide information regarding dipoles in the non-polar medium, however, the technique is also useful for pure polar or binary polar system. Frequency domain technique is more useful for pure polar or binary polar system.

Scope

Implementation of microwave processes, the availability of quantities data on dielectric properties of solvent systems or method for their prediction is essential. The dielectric relaxation behavior of liquid mixtures has gained increasing interest in recent years. Dielectric relaxation study is a very useful in ascertaining size and shape of the molecule; it also serves important properties of the solution such as activity and conductivity. It also suggests the presence of intermolecular interactions or association.

The dielectric constant of substance is one of the factors that determine how the material interacts with an electromagnetic field. It is a complex quantity consisting of real part and an imaginary part. The knowledge of dielectric properties of materials, their temperatures, frequency dependence is of great importance in various areas of science and engineering in both basic and applied research. Dielectric properties often can be related to physical parameter of interest. It has been demonstrated than properties such as moisture contents, Fruit ripeness, bacterial content, mechanical stress and other seemingly unrelated parameters are related to the dielectric properties or permittivity of the materials. Accurate measurement of these properties can provide scientists and engineers with valuable information that allows them to properly incorporate the materials into its intended application or to monitor a process for improved quality control. The permittivity is a fundamental property of the materials and is independent of the measurements technique. The researches of these binary liquids are useful for medical research, Agriculture, Medicine, Electrochemical super capacitors, Industrial and in a vast area of Physical, Biological,
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Sciences, Engineering Technology and more. Due to technical importance of this acetonitrile, methanol, ethanol, n-propyl alcohol, n-butyl alcohol, 1-pentanol liquids and their importance of dielectric properties and their use as biological solvent these liquids are used in recent years.

Most of us are unaware of the properties and utilization of dielectric liquids in industry. Liquids, which are insulators, find large application in the industry of capacitors. The knowledge of properties such as dielectric constant, dielectric loss, loss factor, conductivity and thermodynamic parameters gives better understanding of the insulating liquids. Liquid dielectric serves mainly as impregnates for high voltage cables and capacitors. In some applications liquids have additional function such as heat transfer agent, in transformers. Synthetic hydrocarbons and halogenated aromatic hydrocarbons are also extensively used as liquid dielectrics. In this thesis our aim is to measure the dielectric parameters and relaxation time for the binary systems using X-band microwave setup.

1.2 Molecular Origins of Permittivity

Dielectric substances do not have free electrons, but their behavior is changed by the application of an external electric field. The electric field acts a force on each charged particle pushing positive charges in its own direction, while negative charges in opposite direction. Consequently centers of negative and positive charges of each molecules or atom move from their equilibrium positions in opposite direction, thus produces an electrical dipole and the dielectric substance is said to be polarized [1,4,5,6]. This phenomenon is called matter polarization which leads to induced dipole moment and gives contribution to the dielectric constant of the medium.

The term dielectric applies to the substance properties governing the interactions between matter and an electromagnetic field. A dielectric is a material having electrical conductivity low in comparison to that of a metal. It is characterized by its dielectric constant ($\varepsilon'$) and dielectric loss ($\varepsilon''$), both of which are functions of frequency and temperature. The dielectric constant is the ratio of the strength of an electric filed in a vacuum to that in the dielectric for the same distribution of charge.

\[ \varepsilon' = \frac{E}{E_0} = \frac{\text{field in vacuum}}{\text{field in dielectric}} \]

or

\[ \varepsilon'' = \frac{Q}{4\pi}\frac{1}{r^2} \]
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\[ \varepsilon_r = \frac{\varepsilon_0}{\varepsilon} \]  

(1.3)

Since \( E < E_0, \varepsilon > \varepsilon_0 \), so that \( \varepsilon_r > 1 \)

The dielectric constant may also be defined and measured as the ratio of the capacitance \( C \) of a capacitor filled with dielectric to the value \( C_0 \) of the same capacitor under vacuum.

\[ \therefore \varepsilon_r = \frac{C}{C_0} \]  

(1.4)

The capacitance of the condenser increase because the polarization of dielectric substance by the applied electric field. When a condenser is charged with an alternating current, loss may occur because of dissipation of part of the energy as heat. In vector notation the angle \( \delta \) between the vector for amplitude of charging current and the amplitude of the total current is the loss angle. Therefore dissipation factor or loss tangent is [7-10] given by

\[ \tan \delta = \frac{\text{loss current}}{\text{charging current}} = \frac{\varepsilon''}{\varepsilon'} \]  

(1.5)

Where \( (\varepsilon') \) is the loss factor of the dielectric in the condenser and is the measured dielectric constant of the material. At low frequencies of alternating field dielectric loss \( (\varepsilon'') \) is normally zero and \( (\varepsilon') \) is indistinguishable from the dielectric constant \( \varepsilon_{dc} \) measured with static field. \( \varepsilon' \) is associated with the ability of the dielectric material to store electric energy, while \( \varepsilon' \) is associated with the loss occurring in the dielectric.

1.3 Polarization Mechanisms

The separation of negative and positive charges under the influence of applied electric field and the resulting induced dipole moment is termed as “polarization”. Thus an atom is said to be polarized, if it possess an effective dipole moment. The induced dipole moment depends on the applied electric field \( E \). We define a quantity called polarizability [6-9] \( (\alpha) \) to relate the induced dipole moment \( (P) \) to the applied electric field \( E \).

\[ P = \alpha \cdot E \]  

(1.6)

The value of \( \alpha \) tells us how easily the atom can be polarized. In this case polarization of atom involves the displacement of electrons relative to the nucleus.
Hence $\alpha_e$ is called electronic polarization. In case of electronic polarization, the electron clouds within each atom become shifted by the applied field. As the electrons are pushed away by the applied field $E$, the coulomb attraction between the electrons and nuclear charge “pulls in” the electrons.

The force ($F_s$) on the electrons is,

$$F_s = (Ze)(E) \quad (1.7)$$

The restoring force ($F_r$) which is an attractive force between electrons and nucleus is given by

$$F_r = -\beta x \quad (1.8)$$

Where $x$ is the displacement of center of mass of the electrons w.r.t. nucleus $\beta$ is a constant and negative sign indicates restoring force ($F_r$) is always directed towards the nucleus.

In equilibrium, equating equations (1.7) an (1.8)

$$x = \frac{(Ze)(E)}{\beta} \quad (1.9)$$

($P_i$) is $P_i = (Ze)(x)$. Using equation (1.9).

We get,

$$P = \frac{(Ze^2)}{\beta} E \quad (1.10)$$

This equation gives electronic polarization. Comparing equation (1.10) and (1.6) we get

$$\alpha_e = \frac{(Ze^2)}{\beta} \quad (1.11)$$

If the applied electric field $E$ is removed suddenly, the restoring force $F_s = -\beta x$ pulls the electrons towards the nucleus. Thus the electronic charge could execute S.H.M. about the nucleus. The equation of motion of the negative charge center becomes

$$\frac{d^2x}{dt^2} + \omega^2 x = 0$$

Where $\omega^2 = \frac{\beta}{Ze}$

$$\omega$$ is the frequency of oscillation of center of mass of the electron cloud about the nucleus. From equations (1.12) and (1.11), we have
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\[
\alpha_e = \frac{(Ze^2)}{(m, \omega^2)} \tag{1.13}
\]

This equation gives static electronic polarizability.

1.3.1 Dipole Moment

Dipole moment originates from the asymmetry of the positive and negative charge densities of the system. Positive charges arise from the nuclei, they are localized. Changes in the positive charge density results from structural transformations of the molecule. Negative charge density arises from the electronic system, which is delocalized. The extent of delocalization depends on the chemical structure. An important concept in dielectric theory is that of an electric dipole moment \( \mathbf{P} \) which is a measure of the electrostatic effect of a pair of opposite charges \((+Q)\) and \((-Q)\) separated by a finite distance \(x\), is so that dipole moment \( \mathbf{P} \) is defined by \( \mathbf{P} = Qx \). Although the net charge is zero, this entity gives an electric field in space and also interacts with electric field from other sources. In a molecule \( Q \) will be of the order of \( 10^{-10} \) e.s.u., while \( x \) will be of the order \( 10^{-8} \) cm. Thus the order of the dipole moment \( P \) is \( 10^{-18} \) e.s.u. The unit \( 10^{-18} \) e.s.u. is called Debye and dipole moments are commonly measured in Debye \( (D) \). The magnitude of the dipole moment depends on the size and similarities of the molecule. Molecules having no center of symmetry such as water \((\text{H}_2\text{O})\), \((\text{CH}_3\text{OH})\), \((\text{C}_2\text{H}_5\text{OH})\), \((\text{CH}_3\text{CO CH}_3)\) etc. have permanent dipole moments is known as polar molecules \([7-8]\). While molecules having center of symmetry, such as Methane \((\text{CH}_4)\), Carbon tetrachloride \((\text{CCl}_4)\), \((\text{C}_6\text{H}_6)\), \((\text{C}_4\text{H}_8\text{O}_2)\), \((\text{C}_6\text{H}_{14})\) etc. have no dipole moments are called non polar molecules \([7-8]\). The dipole moment of the molecules of a substance influences its permittivity and studies of permittivity can be used to measure the dipole moment of molecule.

1.3.2 Clausius Mossotti Equation

Polarization \( P \) of a medium by a defined as the dipole moment per unit volume.

\[
\therefore \quad P = \frac{(p_1 + p_2 + p_3 + \ldots + p_N)}{\text{Volume}}
\]

Where \( P = p_1 + p_2 + \ldots + p_N \) are the dipole moment induced at \( N \) molecules in unit volume. If \( P_i \) gives the average induced dipole moment per molecule then it can be as,
\[ P = N P_i \]  
\[ \text{Using equation (1.6) we get } P = N (\alpha E) \]  

Now to express the dependence of \( P \) on the field \( E \) we define a quantity called susceptibility \( \chi_e \) by \[ P = \chi_e \varepsilon \varepsilon_0 E \]  

Equation (1.15) and (1.16) gives \[ \chi_e = \frac{N\alpha_e}{\varepsilon_0} \]  

or \[ \varepsilon_r - 1 = \frac{N\alpha_e}{\varepsilon_0} \]  
\[ \therefore \chi_e = \varepsilon_r - 1 \]  

or \[ \varepsilon_r = 1 + \frac{(N\alpha_e)}{(\varepsilon_0)} \]  

(1.17)

The equation gives relative permittivity \( \varepsilon_r \) in terms of electronic polarization. The importance of this equation is that it relates the microscopic polarization mechanism that determines (\( \alpha_e \)) to the microscopic property (\( \varepsilon_r \)). The equation (1.17) is only approximate because we consider that, the field is acting on individual atom or molecule is \( E \). However the induced polarization (\( P_i \)) depends upon the real field experienced by the molecule. When the dielectric becomes polarized, then at some point inside the dielectric, the field depends on not only on the charges present on the plates but also depends on the orientation of all the other dipoles around this point in the dielectric. The actual field experienced by a molecule in a dielectric is given by [1-4].

\[ E_{loc} = E + \frac{P}{3\varepsilon} \]  

(1.18)

The induced polarization in the molecule depends on this field (\( E_{loc} \)) rather than the average field \( E \). Therefore we write

\[ P_i = \alpha E_{loc} \]  

(1.19)

Substituting in equation (1.4) we get

\[ P = N\alpha E_{loc} \]  

(1.20)

Using equations (1.16) and (1.20), equation (1.18) gives

\[ \frac{(\varepsilon_r - 1)}{(\varepsilon_r + 2)} = \left( \frac{N\alpha_e}{3\varepsilon_0} \right) \]  

(1.21)
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This is the Clausius Mossotti equation. This equation allows the calculation of the microscopic property \((\varepsilon_r)\) from microscopic polarization phenomenon namely. \((\alpha_e)\)

From electromagnetic we know that, refractive index \(\mu = \sqrt{\varepsilon_r}\), then

\[
\frac{(\mu^2 - 1)}{(\mu^2 + 2)} = \frac{(N\alpha_e)}{(3\varepsilon_0)}
\]

(1.22)

This relation is known as Lorentz formula and is valid only as long as \(\varepsilon_r\) is frequency independent. Now multiplying equation (1.21) by \((M/d)\) on both sides, we get

\[
\frac{(\varepsilon_r - 1)}{(\varepsilon_r + 2)} \times \frac{M}{d} = \frac{(N\alpha_e)}{(3\varepsilon_0)} \times \frac{M}{d}
\]

Where M is the molecular weight of the dielectric and ‘d’ is its density.

But we have \(\frac{NM}{d} = N_A\), Avogadro’s number

\[
\therefore \frac{(\varepsilon_r - 1)}{(\varepsilon_r + 2)} \times \frac{M}{d} = \frac{(N_A\alpha_e)}{(3\varepsilon_0)}
\]

(1.23)

\(N_A\alpha_e\) is called molar polarizability.

1.3.3 Atomic Polarization (Ionic Polarization)

This type of polarization occurs in ionic crystals as shown in Figure 1.1(a). Consider one-dimensional NaCl crystal in which a chain of alternate \(Na^+\) and \(Cl^-\) ions are shown. In the absence of an electric field \(E\) the crystal has no net polarization because the dipole moments of equal magnitude are lined up head to head and tail to tail. Due to this, the net dipole moment is zero.

The dipole moment \((P_+\) in the positive X-direction has the same magnitude as \((P_-)\) in the negative X-direction.

\[
\therefore \text{Net dipole moment } P_{net} = P_+ - P_- = 0
\]

In the presence of a field \(E\) along X-direction the \(Cl^-\) ions are pushed in the (-x) direction and \(Na^+\) ions are pushed in the (+x) direction about their equilibrium positions. Due to this the dipole moment \(P_+\) in the x direction increases to \(P_+\) and the dipole moment \(P_-\) decrease to \(P_-\) as shown in Figure 1.1 (b).

Therefore the net dipole moment in this case will not be zero. The net dipole moment per ion pair becomes \((P_+ - P_-)\) which depends on the applied field \(E\).
The induced dipole moment \( (P) \) in this case, in terms of the local field \( (E_{loc}) \) experienced by the ion is given by [6].

\[
P_i = \alpha_i E_{loc}
\]  

(1.24)

\( \alpha_i \) is the ionic polarizability. Generally \( \alpha_i \) is ten times more than \( \alpha_e \). Hence due to these ionic solids have large dielectric constant. The polarization \( P \) exhibited by the ionic substance is given by

\[
P = N_i P_i
\]  

(1.25)

From equation (1.24) and (1.25) we get

\[
P = N_i \alpha_i E_{loc}
\]  

(1.26)

or

\[
E_{loc} = \frac{P}{N_i \alpha_i}
\]

Where \( N_i \) gives number of ion pairs per unit volume. The actual field experienced by the ion is given by [1-4]

\[
E_{ae} = \frac{E + P}{3\varepsilon_0}
\]

Using equation (1.25) and (1.16) we get

\[
\frac{(\varepsilon_r - 1)}{(\varepsilon_r + 2)} = \frac{(N_i \alpha_i)}{(3\varepsilon_0)}
\]  

(1.27)

Equation (1.27) is called Clausius-Mossotti equation. The electronic polarization simply adds to the ionic polarization. However its magnitude is much smaller than the ionic polarization in the solids.

**FIGURE 1.1 (a) and (b)**

(a) A NaCl chain in the NaCl crystal without an applied field.

(b) In the presence of an applied field, the ions become slightly displaced, which leads to a net average dipole moment per ion
1.3.4 Orientation Polarization

A molecule having permanent electric dipole moment is called a polar molecule [6-8] the molecule is electrically neutral even though the distributions of the two kinds of charges are different. Molecules having permanent dipole moment oriented randomly in the material, in the absence of electric field due to thermal agitation. Consider a molecule, which has a permanent dipole moment $P_0$. When the field $E$ is applied the dipole tries to align in the direction of the field. The charges (-Q) and (+Q) experience a force $F=QE$ in opposite directions. Therefore a torque $\tau = p_0 E \sin \theta$ acts on the dipole. This torque rotates the dipole to align $P_0$ with the field $E$. If all the molecules in the substance rotate and align with the field then the polarization would be given by

$$P = N p_0$$

(1.28)

Where $N$ gives number of molecules per unit volume. However due to thermal energy the molecules move randomly and collide with each other. These collisions destroy the dipole alignments. Thus the thermal energy tries to randomize the orientations of the dipole moments.

To find average induced dipole moment $P_i$ and $E$, one must know the average potential energy of a dipole in the field $E$. The average potential energy represents the average external work done by the field in aligning the dipoles with the field. The work done (dw) by the field in rotating the dipole by $d\theta$ is $dw = \tau d\theta$. For maximum work the torque has to rotate the dipole from $\theta = 0^\circ$ to $\theta = 180^\circ$.

Therefore $\text{Max. P.E.} = \int_0^\pi \tau d\theta$

or

$\text{Max. P.E.} = \int_0^\pi p_0 E \sin \theta \, d\theta$

or $\text{Max. P.E.} = 2p_0 E$  \hspace{1cm} (1.29)

But the average dipole $\text{P.E.} = \frac{1}{2} \text{Max. P.E.}$

or average dipole $\text{P.E.} = \frac{1}{2}(2p_0 E) = p_0 E$ \hspace{1cm} (1.30)

This energy must be greater than the thermal energy $(5/2) KT$ per molecule.

If $(5/2) KT >> \text{P.E.}$ then the thermal energy of collision prevents dipole alignment with the field $E$. If $(5/2) KT << \text{P.E.}$ then the thermal energy is insufficient to destroy the dipole alignments.
The average induced dipole moment along E is directly proportional to the magnitude of \( p_0 \) itself and also proportional to the ratio of average dipole energy to average thermal energy that is

\[
P_\alpha = \frac{p_0 (p_0 E)}{(5/2)(KT)}
\]

Calculation using Boltzmann statistics for the distribution of dipole energies among the molecules that is, the probability that the dipole has an energy E which is proportional to \( \exp (-E/KT) \), then we have, when P.E. \( < KT \).

\[
P_i = \frac{p_0^2 E}{3KT}
\] (1.31)

Replacing E by \( E_{\text{loc}} \), we get

\[
\alpha_d = \frac{p_0^2}{3KT}
\] (1.32)

From equation (1.32) it is clear that, in contrast to the electronic and ionic polarization, orientation polarization is strongly depend on temperature. \( \alpha_d \) Decrease with increase of temperature and therefore obviously relative permittivity \( (\varepsilon') \) also decrease with temperature. Orientation polarization is normally exhibited by polar liquid e.g. water, alcohol, acetone, amines and various electrolytes and also polar gases e.g. steam, HCl gas, it can also occur in solids if there are permanent dipoles, even if polar rotation involves a discrete jump of an iron from one site to another, such as in various glasses. In the presence of electronic, ionic and orientation polarization mechanisms, the average induced dipole moment per molecule will be given by the addition of all the contributions in terms of the local field \( E_{\text{loc}} \).

\[
p_{av} = \alpha_e E_{\text{loc}} + \alpha_i E_{\text{loc}} + \alpha_d E_{\text{loc}}
\]

Each effect adds linearly to the net dipole moment per molecule. This can be verified experimentally. The dielectric constant \( (\varepsilon_r) \) under electronic, ionic and orientation polarization is the given by

\[
\frac{(\varepsilon_r - 1)}{(\varepsilon_r + 2)} = \frac{N}{3\varepsilon_0} \left[ \alpha_e + \alpha_i + \alpha_d \right]
\] (1.33)

The equation (1.32) can be used in Clausius-Mossotti equation. This modification is called Debye modification. Thus Clausius-Mossotti equation becomes
(1.34)

Equation (1.34) is the form of \( Y = mx + C \) with

\[
Y = \left( \frac{\varepsilon - 1}{\varepsilon + 2} \right), \quad m = \left( \frac{N P_0^2 / 9 \varepsilon_0 K}{N \alpha / 3 \varepsilon_0} \right), \quad x = \left( \frac{1}{T} \right) \quad \text{and} \quad C = \left( \frac{N \alpha / 3 \varepsilon_0}{3} \right)
\]

Study of molecular structure can be made using above equation (1.34). This equation predicts that polarizability of polar molecule is temperature dependent. The plot of \( (\varepsilon - 1)/(\varepsilon + 2) \) against \( 1/T \) gives information regarding the arrangement of atoms in a molecule. If the line of the plot obtained is horizontal along \( x \)-axis then it implies that molecules are non-polar and atoms are symmetrically placed. On the other hand if the line of the plot obtained is inclined to the \( X \)-axis then it shows that molecules are polar and atoms are not symmetrically placed. The polarity arises due to charge asymmetry of the molecule.

**1.3.5 Dielectric in Alternating Field**

The static dielectric constant is an effect of polarization under dc conditions. When the applied field is a sinusoidal then the polarization of the medium under ac condition leads to an ac dielectric constant that is generally different that the static case. The sinusoidal varying field changes magnitude and direction continuously and it try to line up the dipoles one-way and then the other way and so on. If the instantaneous induced dipole moment per molecule can instantaneously pursue the field changes, then at any instant we have

\[
P = \alpha_d E
\]

And the polarizability \( \alpha_d \) has its maximum value from dc conditions that is

\[
\alpha_d = \frac{P_0^2}{3KT}
\]

There are two factors opposing the instant alignment of the dipoles with the field first is that, the thermal agitation tries to randomize the dipole orientations and second is that, the molecules rotate in a viscous medium by virtue of their interactions with neighbor, which is particularly strong in the liquids and solids. This means that the dipoles cannot respond instantaneously to the change in the applied field. The
dipoles cannot follow the field. If the applied field changes too quickly, and therefore remains randomly oriented. Hence at high frequencies $\alpha_d$ will be zero, as the field cannot induce a dipole moment. However at low frequencies the dipoles can respond quickly to follow the field and $\alpha_d$ has its maximum values. Thus it is clear that $\alpha_d$ changes from its maximum value to zero as the frequency of the field is increased. Now we need to find the behavior of $\alpha_d$ as functions of frequency ($\omega$) so that we can determine the dielectric constant ($\varepsilon_r$), by the Clausius-Mossotti equation.

Suppose that the field across the dipolar medium is suddenly decreased from $E_0$ to $E$ at a time we define as zero. The field $E$ is smaller than $E_0$ so that the induced dc dipole moment per molecule should be smaller and is given by $\alpha_d(0)E$ where $\alpha_d$ at $\omega = 0$ Thus, the induced dipole moment per molecule has to decrease from $\alpha_d(0)E_0$ to $\alpha_d(0)E$. The relaxation process, in the induced dipole moment is achieved by random collisions with each other and with the walls of the container. Assuming that ($\tau$) is the average time, between molecular collisions, then this is the mean time it takes per molecule to randomize the induced dipole moment. If $p$ is the instant induced dipole moment, then $p - \alpha_d(0)E$ is the excess dipole moment, which must go to zero through random collisions as $\tau \to \infty$. The rate at which the induced dipole moment is changing is $-\left[\frac{p - \alpha_d(0)E}{\tau}\right]$ where the negative sign represents a decrease. Thus we have

$$\frac{dp}{dt} = -\left[\frac{p - \alpha_d(0)E}{\tau}\right]$$

(1.37)

This is a dipolar relaxation equation, and can be used to obtain the dipolar polarizability under alternating condition. For Alternating current field we write $E = E_0 \exp(j\omega t)$ and solving the equation (1.37) we get

$$p = \alpha_d(\omega)E_0\exp(j\omega \tau); \text{ Where } \alpha_d(\omega) \text{ is given by}$$

$$\alpha_d(\omega) = \frac{\alpha_d(0)}{1 + j\omega \tau}$$

(1.38)

This equation represents the orientation polarizability under ac field conditions. Polarizability $\alpha_d(\omega)$ is a complex quantity and indicates that $\rho$ and $E$ is
out of phase. At low frequencies, $\omega \tau \ll 1$, $\alpha_d(\omega)$ is nearly equal to $\alpha_d(0)$. Hence $p$ is in phase with $E$. We can easily obtain the dielectric constant $\varepsilon_r$ from $\alpha_d(\omega)$ with the help of Clausius-Mossotti equation, which then leads to a complex number for $\varepsilon_r$. By convention, we generally write the complex dielectric constant as:

$$\varepsilon_r = \varepsilon'_r - j\varepsilon''_r$$  \hspace{1cm} (1.39)

Where $\varepsilon'_r$ is the real part and $\varepsilon''_r$ is the imaginary part. Figure 1.2 shows that $\varepsilon'_r$ and $\varepsilon''_r$ are frequency dependent. The real part $\varepsilon'_r$ decreases from its maximum value $\varepsilon'_r(0)$ to 1 at high frequencies. The unreal part $\varepsilon''(\omega)$ is zero at low and high frequencies but peaks when $\omega \tau = 1$ or $\omega = 1/\tau$. The real part $\varepsilon'_r$ can be used to calculate the capacitance ($C = \varepsilon_r \varepsilon_0 A / d$). The imaginary part $\varepsilon''(\omega)$ represents the energy lost in the dielectric medium, as the dipoles are oriented in opposition to arbitrary collisions one way and then the other way and so on by the field.

![Diagram](image)

**FIGURE 1.2 (a and b)**

(a) An ac field applied to a dipolar medium. The polarization $p(p = Np)$ is out of phase with the alternating current field.

(b) The relative permittivity with real ($\varepsilon'_r$) and imaginary ($\varepsilon''_r$) parts that exhibit relaxation at $\omega = 1/\tau$.

The power dissipated in the dielectric medium is related to $\varepsilon''_r$ and peaks when $\omega = 1/\tau$. This occurs, when the period is $1/\omega$ to rotate a dipole and do one cycle of work by the field. The two processes, that is energy storage by the field and energy transfer to random collisions, occur at the same rate, and hence energy is being
transferred to heat most efficiently. The energy loss is determined by \( \varepsilon_r^* \) in engineering applications of dielectrics in various electrical devices we would like to minimize \( \varepsilon_r^* \) for a given \( \varepsilon_r^* \). We define the relative magnitude of \( \varepsilon_r^* \) with respect to \( \varepsilon_r^* \) through a quantity, tan\( \delta \) called the loss tangent or loss factor which is defined by

\[
tan \delta = \frac{\varepsilon_r^*}{\varepsilon_r^*}
\]  

(1.40)

It is frequency dependent and peaks just beyond \( \omega = 1/\tau \). The actual value of \( 1/\tau \) depends on the material, but typically for liquids and solids it is in the GHz range. From Maxwell’s theory of e. waves it follows that the relative permittivity \( \varepsilon_r^* \) of a material is identical to the square of its refractive index calculated at the very similar frequency. The square of refractive index \( n_D^2 \) measured at the frequency of D-lines of sodium gives a mean of finding what proportion of the polarizability is still effective at this frequency. This will be approximately the electronic polarizability. In polar molecules the difference between the static permittivity and \( n_D^2 \) is mainly due to the permanent dipole moment.

**Debye Equations**

The dielectric constant and orientation polarizability are related through the equation \( \varepsilon_r = 1 + (N\alpha_d)/\varepsilon_0 \). We can substitute for \( \alpha_d \) from equation (1.38) and for \( \varepsilon_r \) from equation (1.39) therefore we get

\[
\varepsilon_r^* - j\varepsilon_r^* = 1 + \frac{N}{\varepsilon_0} \left( \frac{\alpha_d(o)}{1 + j\omega\tau} \right)
\]

or

\[
\varepsilon_r^* - j\varepsilon_r^* = 1 + \frac{N\alpha_d(o)}{\varepsilon_0} \times \frac{1 - j\omega\tau}{1 + (\omega\tau)^2}
\]

We can now equate real and imaginary parts. However \( N\alpha_d(o) \) determines the static dielectric constant.

\[
\varepsilon_r(0) - 1 = \frac{N\alpha_d(0)}{\varepsilon_0} \text{ then}
\]

\[
\varepsilon_r = 1 + \frac{[\varepsilon_r(0) - 1]}{1 + (\omega\tau)^2}
\]

(1.41)
These equations are called Debye equations. They reflect the behavior of $\varepsilon_r'$ and $\varepsilon_r''$ as a function of frequency as shown in Figure (1.2). The imaginary part $\varepsilon_r''$ exhibit a peak at $\omega=1/\tau$ which is called Debye loss peak. Many gases and some liquids with dipolar molecules exhibit this type of behavior. In case of solids, the peak is much broader due to large spread of relaxation times.

1.4 Excess Dielectric Parameters

The excess dielectric properties such as excess permittivity ($\Delta \varepsilon'$), excess loss factor ($\Delta \varepsilon''$), excess activation energy ($\Delta E_a$) etc. can be obtained by using the relations of the form

$$\Delta Y = Y_m - (X_A Y_1 + X_B Y_2)$$

(1.43)

When $\Delta Y$ any excess parameter and $Y$ is refers to the above mentioned quantities, i.e. permittivity ($\varepsilon'$), loss factor ($\varepsilon''$), activation energy ($E_a$), relaxation time ($\tau$) etc. The subscripts m, 1 and 2 used in the above equation are respectively for the mixture, liquid (1) and liquid (2). $X_A$ and $X_B$ are the mole fractions of the two components in the liquid mixtures.

The equation (1.43) for the excess permittivity ($\Delta \varepsilon'$) can be written as

$$\Delta \varepsilon' = \varepsilon'_m - (X_A \varepsilon'_1 + X_B \varepsilon'_2)$$

(1.44)

We have three cases, if

1. $\Delta \varepsilon'=0$ : This indicates the solute and solvent do not interact at all.

2. $\Delta \varepsilon'<0$ : This means that solute and solvent interact in such a way that the total effective dipoles reduced. The mixture of solutes and solvents might form multimers leading to the less effective dipoles. The excess permittivity ($\Delta \varepsilon'$) is associated with the polarization.

3. $\Delta \varepsilon'>0$ : The solute and solvent interact in such a way that the effective dipoles tend to be more. The excess loss factor ($\Delta \varepsilon''$) given by

$$\Delta \varepsilon'' = \varepsilon''_m - (X_A \varepsilon''_1 + X_B \varepsilon''_2)$$

(1.45)

The excess loss may be regarded as a parameter which reflects the entropy
Dielectric behavior of some binary liquid mixtures at microwave frequencies

Chapter-1: Introduction

Dielectric behavior of a binary system. The loss factor is regarded due to the molecular motions which are governed by the complex forces of molecules interactions. Similarly we can find the excess parameter for activation energy $(\Delta E_\eta)$, square of refractive index $(\Delta n_\eta)^2$ and viscosity $(\Delta \eta)$. These parameters help to explain the dielectric behavior of the binary or ternary mixtures of organic compounds.

1.5 Relaxation time and energy parameters

The average time taken by the dipoles to reorient in the field direction is known as the relaxation time $(\tau)$.

Measurement of thermodynamic parameters of a liquid is done from the measurement of dielectric constant $(\varepsilon')$ and dielectric loss $(\varepsilon'')$ for different concentrations and temperatures. The values of dielectric constant $(\varepsilon')$ and loss $(\varepsilon'')$ obtained are further utilized to evaluate the relaxation time $(\tau)$ by employing the following expression [12].

\[
X = \frac{(\varepsilon'' + \varepsilon' + \varepsilon'^2 - 2)}{(\varepsilon' + 2)^2 + \varepsilon'^2}
\]

\[
Y = \frac{3\varepsilon''}{(\varepsilon' + 2)^2 + \varepsilon'^2}
\]

and

\[
\tau = \left(\frac{\lambda_0}{2\pi C}\right) \left(\frac{dy}{dx}\right)
\]

(1.46)

Where $C$ is the velocity of electromagnetic waves and other have their usual meaning. Factors X and Y can be computed from the measured values of $(\varepsilon')$ and $(\varepsilon'')$. The slope of the line drawn between X and Y can be used to determine the value of relaxation time $(\tau)$.

The energy parameters, free energy $(\Delta F_\eta)$, enthalpy $(\Delta H_\eta)$ and entropy of activation $(\Delta S_\eta)$ for the dielectric relaxation process and corresponding parameters for the viscous flow $(\Delta F_\eta), (\Delta H_\eta) and (\Delta S_\eta)$ can be calculated by using Eyring’s equation [11] for the rate process.

According to Eyring’s theory [4-11] of rate process the temperature dependence of relaxation time is given by the equation.

\[
P = \left(\frac{KT}{h}\right) \exp \left(\frac{-\Delta F}{RT}\right)
\]

(1.47)
Where $\Delta F$ is the free energy of activation and is the difference between the free energies of activated and inactivated states, excluding that part of activation energy. $P$ represents the number of times per second that a dipole acquires sufficient energy to pass over the potential barrier from one equilibrium position to the other.

The microscopic relaxation time ($\tau$) is related to $P$, by $P = \left(\frac{1}{\tau}\right)$, where, $h$ is plank’s constant and $R$ is gas constant. From the principle of thermodynamics, we have $\Delta F = \Delta H - T\Delta S$ where $\Delta H$ molar enthalpy of activation is, $\Delta S$ is molar entropy of activation. $T$ is absolute degree temperature. Therefore equation (1.47) can be written as:

$$\left(\frac{1}{\tau}\right) = \left(\frac{K T}{h}\right) \exp \left[-\frac{(\Delta H - T\Delta S)}{R T}\right]$$

$$\tau = \left(\frac{h}{K T}\right) \exp \left(\frac{\Delta H}{R T}\right) \exp \left(-\frac{\Delta S}{R}\right)$$

(1.48)

This expression can be written as,

$$\ln \left(\tau T\right) = \left(\frac{\Delta H}{R T}\right) + A$$

Where

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

(1.49)

In this equation $\left(\frac{\Delta H}{R}\right)$ gives the slope of $\ln(\tau T)$ versus $(T)^{-1}$ plot. If the $\Delta H$ and $\Delta S$ are independent of temperature, then the plot of $\ln(\tau T)$ versus $(T)^{-1}$ is linear. The slope $\left(\frac{\Delta H}{R}\right)$ provides the height of potential barrier.

Hence $\left(\frac{\Delta H}{R}\right) = \frac{d[\ln(\tau T)]}{d\left(\frac{1}{T}\right)} = \text{slope}$

(1.50)

For every compound the activation energy is found to increases as the temperature increases, while as the relaxation time decreases. This may be due to the decrease in viscosity of medium with rise in temperature. Thermal agitation increases as temperature increases and dipole requires more energy in order to reach the equilibrium with the applied field.