CHAPTER I

INTRODUCTION
Introduction

Dielectrics occur in different states of aggregation. They interact with electric, magnetic and electromagnetic fields. These materials may be gases, liquids or solids and they are found to have the ability of storing/dissipating electric and magnetic energy.

The investigation of dielectric properties has provided an important approach to an understanding of the structure of the matter. In other words, the results of the study of molecular systems can be understood by dielectric methods, namely, by the non-quantal response of dielectric materials to electric fields ranging from the static field to those of frequencies up to $10^{12}$ Hz.

The phenomenological electric properties of matter can be described in terms of polarization, magnetisation and conduction and these can be interpreted from the stand-point of molecular theory. For example, the polarization and magnetisation vectors can be interpreted as the electric and magnetic dipole moment per unit volume of the dielectric. Assuming that these moments express the additive action of a host of elementary moments, a connection can be obtained between the macroscopic constants of the dielectric and its molecular parameters. The total polarization is contributed by different types of polarizations, namely, electronic, atomic, orientation and interfacial. These are due to the formation of induced moments by the displacements of the electrons and nuclei; the moments resulting from the orientation of permanent dipoles; and finally, field distortions brought about by moving charge carriers (space charge or interfacial polarization). By applying these considerations to molecules
in the gaseous or liquid state the structures of molecules can be obtained.

The general type of response of gases to alternating electric fields gives rise to a sequence of resonance states and consequence resonance spectra. In the case of liquid and solid dielectrics the resonance spectra of electronic and vibrational excitation are found but they are characteristic of the condensed phase but do not belong to individual molecules. The rather sharp spectral lines of gases are greatly broadened in the case of condensed phase. The rotational states in the condensed phase are, however, entirely altered. To turn molecules or molecular groups requires space, which is at a premium in liquids and solids. Simultaneously, the permanent dipole moments of molecular groups are the characteristic building elements in the formation of the condensed phases. Therefore, free rotation as in gases will no longer be possible and the quantised rotation spectra, which consequently disappear, are replaced by relaxation spectra.

Following Maxwell (1) a dielectric medium may be specified in terms of a permittivity (or dielectric constant) $\varepsilon$, a permeability $\mu$, and an effective conductivity $\sigma$. The permeability of all dielectric materials, except ferromagnetic, will in general be equal to $\mu_0$ of free space. When such a dielectric is placed in a periodic electromagnetic field $E = Re^{j\omega t}$, it carries an electric current density, given by

$$I = \sigma E + \frac{\varepsilon \partial E}{\partial t}$$

$$= (\sigma + j\omega\varepsilon) E e^{j\omega t} \quad -(1.1)$$

The first term denotes a conduction current in time phase with
the applied field, and the second, a displacement current density in phase quadrature. The resultant current density leads \( \mathbf{E} \) by an angle \( \phi \) and \( \cos \phi \) is called the power factor of the dielectric. The complement of the phase angle \( \phi \) is usually denoted by an angle \( \delta \), known as the loss angle and \( \tan \delta = \sigma / \omega \varepsilon \) is referred to as loss tangent. For small values of \( \delta \), the loss \( \tan \delta \) is indistinguishable from the power factor. The resultant current \( I \) is expressed in the form,

\[
I = (\sigma + j \omega \varepsilon) \mathbf{E} e^{jct}
\]

\[
= j \omega (\varepsilon + \sigma / j \omega) \mathbf{E} e^{j\omega t}
\]

\[
= j \omega (\varepsilon - \sigma / j \omega) \mathbf{E} e^{j\omega t}
\]

\[
= j \omega (\varepsilon' - j \varepsilon'') \mathbf{E} e^{j\omega t}
\]

\[
= j \omega \varepsilon^* \mathbf{E} e^{j\omega t} \text{ (say) and } \varepsilon^* \text{ may be taken as an equivalent dielectric constant of the conducting medium and } \tan \delta = \frac{\sigma}{\omega \varepsilon} = \varepsilon''/\varepsilon' \text{; the quantities } \varepsilon' \text{ and } \varepsilon'' \text{ are both functions of frequency.}
\]

It was Debye (2,3) who first illuminated the molecular aspects of the theory of dielectric polarization and his concepts are still used in interpreting the results. Debye's treatment for the motion of dipoles in condensed phases subjected to an alternating electric field deals with the fact that the polar molecules rotate in a medium of friction. He introduced a molecular parameter \( \tau \) called relaxation time, and the dielectric behaviour of the medium is described in terms of the complex dielectric constant \( \varepsilon^* \) and this in turn is related to the two macroscopic parameters, the static \( (\varepsilon_0) \) and optical \( (\varepsilon_\infty = \varepsilon_D) \), permittivities, by the equation
Where, $\omega$ is the angular frequency of the applied alternating field. The quantity $\varepsilon_\infty$ corresponds to the electronic and resonance polarization of the dielectric. In the low frequency range of the relaxation polarization, this deformation polarization contributes constant induced moments. The parameter $\varepsilon_0$ contains in addition, the full contribution resulting from the orientation of the permanent moments which only contribute an average moment because they can not align themselves in the field direction as a result of the opposing forces, the torque due to the applied electric field and the randomising thermal agitation. The interfacial polarization which arises only in heterogenous media and will be significant at very low frequencies is usually negligible.

In the case of gases and vapours at low pressures the dielectric medium is supposed to be acted by the local field, the applied field itself or by the Mosotti (4) field (this only changes interpretation but not the shape of the relaxation spectra) and the complex permittivity $\varepsilon^*$ is connected with the microscopic molecular parameters, namely, the electronic and atomic polarizabilities ($\alpha_e, \alpha_a$), the electric dipole moment ($\mu$) and the relaxation time ($\tau$) of the molecules of the dielectric, as shown by the relation,

$$p^* = \frac{4}{3}\pi N_A \left\{ \alpha + \alpha + \frac{\mu^2}{3kT} \frac{1}{1+j\omega\tau} \right\}$$

Where $p^*$ is the complex molar polarization, $N_A$ is the Avogadro's number, $K$ is the Boltzmann's constant and $T$ is the absolute temperature. The relaxation time $\tau$ is shown by Debye to be equal to $4\pi n a^3/KT$ where, $n$ (in cp) is the macroscopic viscosity of the medium assuming the molecules
to be spherical with radius 'a' and thus τ is usually of the order of picoseconds.

It is seen from equation (1.2) that the real (ε'), and imaginary (ε'') parts of ε* and the loss tangent tanδ can be expressed as

\[ ε' = ε_0 + \frac{(ε_0 - ε_∞)}{2(1 + \frac{2}{ωτ})}, \quad ε'' = \frac{(ε_0 - ε_∞)ωτ}{2(1 + \frac{2}{ωτ})} \]

and \[ tan δ = \frac{ε''}{ε′} \]

These relations show that if ε'' is plotted against ωτ, the loss factor ε'' is maximum when ωτ=1. Similarly a plot between the dielectric conductivity σ (= ωε'') and ωτ also gives a dispersion curve as above but is a mirror image of it. Further, the maximum value of ε''(= \( \frac{ε_0 - ε_∞}{2} \)) permits one to determine the value of τ. To be specific for a dielectric medium (gas/dilute solution) to which Debye equation is valid the loss tangent, as a fair approximation can be expressed by a relation of the form (5).

\[ tan δ = A \cdot \frac{ωτ}{(1 + \frac{ω^2τ^2}{2})} \]

Where A is given by,

\[ \frac{(ε' + 2)ε'}{ε'} = \frac{4πN_A W_{12} d_{sol.} \mu^2}{2πKT M_{sol.}} \]

with W, d, M representing weight fraction, density, and molecular weight. This relation in conjunction with the Debye equation for τ (=4πn a^3/KT) indicates that if dielectric measurements are carried-out on a liquid or on an arbitrary concentration of it in a non-polar medium (6,7) as a function of i) frequency, ii) temperature and iii) viscosity, the loss
tangent reaches a maximum for $\omega \tau = 1$ so that $\tau$ and $\nu$ can be determined with a preknowledge of other quantities appearing in these equations.

The assumption of a single relaxation time fits satisfactorily the frequency response of a number of dielectrics, particularly, of dilute solutions of polar materials in non-polar solvents. But, the actual relaxation spectra of liquids, associated liquids in non-polar solvents, non-rigid molecules, molecules departing from spherical shape, and polymers etc; are frequently characterized by a distribution of relaxation times spread around a most probable value which indicates a coupling of the dipole-moments to their surroundings, a fixation in certain prescribed positions. Instead of smoothly rotating spheres we have to visualise the dipoles as statistically jumping over potential walls, whenever the activation energy becomes available. In crystals, the permanent electric dipole-moments are, in general, completely immobilised, as far as any individual rotation is concerned.

A theory for the distribution of relaxation times was first given by Von Schweiler (8), Wagner (9) and Yager (10) gave expressions based on a Gaussian distribution to explain experimental curves. Further, Kirkwood and Fuoss (11) obtained a formula for the distribution function in the case of polymers. However, no general theory is available yet for the dependence of $\varepsilon'$ and $\varepsilon''$ on frequency nor for the distribution function. Therefore, usually, two empirical approaches are used in dealing with dispersion data on polar liquids.

In Cole-Cole (12) approach, if the medium is associated with a single relaxation time the complex plane locus obtained by plotting $\varepsilon''$ versus $\varepsilon'$ is a semi-circle with radius $(\varepsilon_0 - \varepsilon_\infty)/2$ and centre at $(\varepsilon_0 + \varepsilon_\infty)/2$
on the $\varepsilon'$-axis; whereas, if there is a distribution of relaxation times, the locus is generally a circular arc with centre depressed below the $\varepsilon'$-axis. They showed that this means that the Debye equation for the complex dielectric constant, $\varepsilon^*$ must be modified to

$$
\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{(1 + j \omega \tau_0)^{1-a}}
$$

\[ \text{---(1.6)} \]

Where $a$ is a parameter, which would be equal to zero in the case of a single relaxation time. For distribution of relaxation times, $a$ varies between 0 and 1 and for this case $\tau_0$ is the most probable relaxation time. However, this relation is found to be valid in many simple molecules but deviation from the usual circular shape of the Cole-Cole plot is found in the case of certain other dielectric systems such as associated liquids, (eg. glycerol, alcohols etc.), non-spherical molecular media etc. In these dielectrics the dispersion is not symmetric but is represented by a skewed arc. Davidson and Cole (13) interpreted the results by means of an empirical expression for the complex dielectric constant as function of the frequency, given by,

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

\[ \text{---(1.7)} \]

Where the parameter 'b' may assume a value between 0 and 1 and $\tau^b$ is the relaxation time different from $\tau_0$ in equation (1.6). But it is doubtful if this new empirical formula has any advantage over the Cole-Cole relation.

In the Fuoss and Kirkwood (14) approach a different empirical relation is suggested and the experimental data could be analysed in the light of this empirical relation, namely,
\[ \varepsilon'' = \varepsilon''_{\text{max}} \cdot \text{Sech} \beta \log \left( \omega / \omega_{\text{max}} \right) \quad \text{--(1.8)} \]

Where \( \beta \) is a parameter varying from 0 for an infinitely broad dispersion to 1 for a Debye dispersion. For the variation of \( \varepsilon' \) versus \( \log \omega \), however, no general expression has been given by them but they have computed analytical expressions for two specific values of the parameter, \( \beta \). Later Macdonald (15) obtained analytical equations for \( \varepsilon' \) which will provide a method for a complete comparison with experiment and enable the determination of the dependence of \( \varepsilon' \) on frequency, for any value of \( \beta \) from 0 to 1.

From what is said above, it is seen that Debye’s model for dielectric relaxation is too simple particularly because of the fact that the relaxation rate as indicated by the equation for \( \tau = 4\pi n a^3 / kT \) depends strongly on the temperature which indicates that at some stage in the relaxation process a molecule needs a certain amount of energy (activation energy) in excess of the average thermal energy to overcome a potential barrier. This points to the possibility of the dielectric relaxation being treated like viscosity as a rate process, as has been done by Eyring (16). This interpretation of dielectric relaxation implies that the accompanying conversion of electrical energy into heat is similar to the conversion of chemical energy into heat during a chemical reaction, whereas in the Debye's theory it would be a result of inner friction. Thus, in this interpretation the expression obtained for the relaxation time by Eyring may be expressed as

\[ \tau = \frac{h}{kT} \exp \frac{\Delta G^a_\tau}{RT} \quad \text{--(1.9)} \]

which is just similar to the expression for viscosity, treated also as a rate process.
Where $A G^*=A h^* - T A s^*$ is the molar free energy of activation, $A h^*$ is the molar enthalpy of activation, and $A s^*$ is the molar entropy of activation and the suffixes $\tau$, $\eta$ indicate 'for relaxation process' and 'for viscous flow process'.

The activation energies for the two phenomena are different, the one for dielectric relaxation being less than that for viscosity as the latter involves in addition to rotational motion, the translational motion of the molecules too. An extension of Eyring's theory due to Kauzmann (17) shows that a distribution of relaxation times according to the Cole-Cole relation (eqn. 1.6) can easily be understood by this theory.

From the above discussion of the phenomenon of dielectric relaxation it is seen that the two molecular parameters $\mu$ and $\tau$ can be determined by experimentally determining the real and imaginary ($\varepsilon'$, $\varepsilon''$) parts of the complex dielectric constant $\varepsilon^*$ from dielectric measurements carried out on dilute solutions of the specimen in non-polar solvents, to which Debye's theory, which assumes a single relaxation time, is applicable. The dipole moment only can be determined from the measurement of $\varepsilon_0$ in dilute solutions in non-polar solvents. By carrying out dielectric measurements in the pure liquid state to which the Cole-Cole representation may be applied, the relaxation time $\tau (\alpha =0)$ or the distribution of it ($\alpha \neq 0$) may be obtained. However, a crude estimation of the distribution of $\tau$ can be made from the dilute solution measurements at a single frequency in the microwave region as suggested by Higasi (32). By determining $\varepsilon_0$, density and refractive index (optical permittivity) of the pure liquids, the dipole moment in the pure liquid state can be determined using several equations reported in the literature (18-29).
The relaxation time of a molecule in the pure liquid is larger than that in the solution of the same viscosity. Smyth, Higasi, and their collaborators (30,31,32) have attributed this difference to the hindrance of molecular rotation by dipole-dipole interaction which is present in the pure liquid and largely absent in the dilute solution. Thus, if the dielectric properties of a medium could be studied both in dilute solution and in the pure liquid state, such studies, in conjunction with Eyring's rate process equation would give considerable information about the dielectric behaviour of the medium.

If one is interested in knowing whether the dielectric medium is characterised by a single relaxation time or a distribution of it, one usually carries out dielectric measurements in the pure liquid state at different frequencies. Such studies do not give any information regarding the other molecular parameter, $\mu$, the determination of which necessitates another separate set of dielectric measurements. This is because no theory using the right internal field such as Onsager's (18) internal field for D.C. applied fields, has yet been available at high frequencies, as far as the author is aware and because consequently there is no method available yet. Unlike in the pure liquid case, for dilute solutions a well-tested Debye's theory, dealing with dielectric dispersion and absorption, according to which a dilute solution of a polar solute in a non-polar solvent characterised by a single relaxation time, is available and the dielectric measurements on the single set of these dilute solutions permit one to obtain both $\mu$ and $\tau$. Further, although from both types of measurements it is possible to study the variation of $\tau$ with temperature, from which the activation energy, free energy of activation and enthalpies for dielectric relaxation can be determined, it is not possible to study
variation of $\tau$ with viscosity from dielectric measurements in the pure liquid state, for which purpose one has to take recourse only to the dilute solution measurements.

From what is said above, there are some additional considerations in favour of dilute solution measurements. However, the dielectric studies pertaining to both pure liquid and dilute solution measurements have proved to be much useful in relation to molecular structure and in the understanding of the dielectric behaviour of polar molecules and the results of such measurements on a variety of polar substances is extensively discussed and reported in the literature (33-36).

A search of the literature indicates that whereas the dipole moment of a polar molecule in the ground state can be determined from the methods briefly indicated above, it is also possible to obtain the dipole moment of a molecule in an excited electronic state from the solvatochromic shifts of different solvents (37, 38, 39). The method involves recording of the absorption spectrum of a polar molecule in a series of polar and non-polar solvents. These studies can also be used to determine the shape parameter (40) of the polar molecule under study. It is found that such studies lead to make certain quantitative conclusions about the structure of the molecule, and the nature of the spectral transition involved.

Liquid crystalline materials form an interesting group of materials amongst dielectrics. A typical liquid crystal can exhibit dual nature i.e., rheological properties of the liquids and anisotropic properties of the crystals. These materials are gaining increasing technical importance because of their wide variety of applications in several areas. But not
much work seems to have been done on the physical properties of these materials in the liquid crystalline phase. The experimental results of the studies pertaining to the determination of order parameter using dielectric-, optical-, diamagnetic-, volumetric-, and ultrasonic- methods in these materials can lead to useful and important information regarding their molecular structure, the nature of the phase transitions involved, and pretransition effects.

However, in view of what is stated above, despite the huge amount of work done in this field in the last few decades, the author is inclined to think that the phenomena of electric polarization, dielectric relaxation and so on, do not seem to be as well-understood as might be wished. Therefore, he has felt that it might be worthwhile to investigate these phenomena experimentally in some more molecules, including those of liquid crystals with the hope that the results obtained may lead to a somewhat better understanding of them. Further, as indicated before dielectric measurements on dilute solutions of a polar molecule in a non-polar solvent have the advantage that the dependence of dielectric relaxation upon the viscosity of the medium can be studied. With these considerations in mind he has carried-out dielectric measurements on a single weight fraction of a polar solute in a non-polar solvent as a function of frequency (two frequencies), temperature, and the medium viscosity. Similar measurements on some of their mixtures are also carried out. The excited state electric dipole moment and shape parameters of some liquid crystals and sound and thermodynamic parameters are determined in the case of certain other molecules. The results of all these experimental investigations are reported on the pages to follow in this thesis.
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