Introduction

1. General :

The investigation of dielectric properties has provided an important approach to an understanding of the structure of matter. From the view point of molecular structure, the interaction of molecular system with microwave radiations provides an extremely sensitive tool for understanding the molecular behaviour.

In order to have a clear understanding of the subject of dielectric polarization and its relation with molecular structure, a brief historical survey of the development of various theories of dielectric polarization and their various modifications, together with a brief review of the previous works is given in the following sections. That will help us to ascertain the present position of knowledge obtainable from dielectric measurements. After that the aims and objects of the present investigation will be given.

1.1. History of early works :

The first quantitative relation treating the dielectric polarization of a substance in the presence of an external electric field is the famous 'Clausius-Mossotti equation[1].

$$\frac{\epsilon-1}{\epsilon+2} = \frac{\alpha_s}{a_s^3} \qquad \ldots (1.1)$$

where ϵ is the dielectric constant and α_s is the polarizability and a_s is the radius of the sphere of dielectric.

The equation was derived using the model of a conducting sphere in a non-conducting medium, without specifying any type of mechanism on the molecular scale. From the Clausius-Mossotti equation, the equation for molar polarization

$$P = \frac{\epsilon-1}{\epsilon+2}\frac{M}{\rho} = \frac{4\pi N}{3}\alpha_0 \qquad \ldots (1.2)$$

and the equation for molar refraction

$$\frac{n^2-1}{n^2+1}\frac{M}{\rho} = \frac{4\pi N}{3}\alpha_0 \qquad \ldots (1.1.3)$$

can be easily deduced, where n is the refractive index of the dielectric.

Many workers observed anomalous dispersion of refractive index of dielectric liquids at optical frequencies. Lorentz[2], Von Helmholtz[3], Drude[4] independently explained this phenomenon on the existence of vibrating charges with the characteristic frequencies. Subsequently the development of Cauchy formula and Sellmeyer formula were able to explain the anomalous dispersion of refractive index in a satisfactory manner.

Similar anomalous dispersion of dielectric constant at very high frequency electric field was first discovered by Drude[4].

The first successful explanation of this anomalous dispersion of dielectric constant was put forward by Debye[5] who postulated that the characteristic property of the liquid responsible for anomalous dispersion at radio frequency range was the polarity of their molecules.

2. Debye equation of polarization :

Debye assumed that when dipolar molecules are placed in a steady electric field, in addition to the normal electronic and atomic polarization, a third polarization called orientational polarization occurs due to polar molecules tending to align themselves in the direction of the field. Debye[5] calculated the total polarization including the orientational polarization as

$$P = \frac{\epsilon-1}{\epsilon+2}\,\frac{M}{\rho} = \frac{4\pi N}{3}\left(\alpha + \frac{\mu^2}{3KT}\right) \qquad \ldots (2.1)$$

Now if the field instead of being steady is a high frequency alternating field, the orientational polarization can not follow the changing electric field but lags behind the field or in other words the polarization and so the dielectric constant becomes complex

$$\epsilon^* = \epsilon' - j\epsilon'' \qquad \ldots (2.2)$$

where ϵ' is the dielectric constant at high frequency and ϵ'' is the loss of electrical energy dissipated in the form of heat. When the external electric field is removed, the polarization decays exponentially according to the relation

$$P = P_0\, e^{-t/\tau} \qquad \ldots (2.3)$$

The time $t = \tau$ in which the polarization reduces to $1/e$th the original value P_0 after the removal of the field is called the dielectric relaxation and is denoted by τ

Debye calculated the total molar polarization of the dipolar molecules in a high frequency field of angular frequency ω as

$$P^* = \frac{\epsilon^*-1}{\epsilon^*+2}\,\frac{M}{\rho} = \frac{4\pi N}{3}\left(\alpha + \frac{\mu^2}{3KT}\cdot\frac{1}{1+j\omega\tau}\right) \qquad \ldots (2.4)$$

where $\epsilon^* = \epsilon' - j\epsilon''$ which can explain well the behaviour of the dielectric as static field as well as at high frequency alternating field. If we put $\epsilon^* = \epsilon_0$ at $\omega = 0$ and $\epsilon^* = \epsilon_\infty$ at $\omega = \infty$, the equation (2.4) reduces to

$$\frac{\epsilon_0 - 1}{\epsilon_0 + 2}\frac{M}{\rho} = \frac{4\pi N}{3}\left(\alpha + \frac{\mu^2}{3KT}\right) \qquad \ldots (2.5)$$

and

$$\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2}\frac{M}{\rho} = \frac{4\pi N}{3}\alpha \qquad \ldots (2.6)$$

The dielectric constant ϵ_∞ denotes the value of the dielectric constant at very high frequencies and is called optical dielectric constant and the dielectric constant ϵ_0 at frequency $\omega = 0$ is called static dielectric constant.

From equations (2.2), (2.5) and (2.6) and separating the real and imaginary terms we get

$$\epsilon' = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + (\beta\omega\tau)^2} \qquad \ldots (2.7)$$

and

$$\epsilon'' = \frac{(\epsilon_0 - \epsilon_\infty)\beta\omega\tau}{1 + (\beta\omega\tau)^2} \qquad \ldots (2.8)$$

where $\beta = \frac{\epsilon_0 + 2}{\epsilon_\infty + 2}$

Equation (2.7) requires that ϵ' decreases from ϵ_0 at $\omega = 0$ to ϵ_∞ at $\omega = \infty$ which account for the dielectric dispersion in polar liquids and from equation (2.8) $\epsilon'' = 0$ both at $\omega = 0$ and $\omega = \infty$ and it is maximum at the critical frequency ω_m given by

$$\tau = \frac{\epsilon_\infty + 2}{\epsilon_0 + 2}\frac{1}{\omega_m} \qquad \ldots (2.9)$$

2.1. Derivation of Debye equation from somewhat different concepts:

2.1.1. Frohlichs phenomenological theory :

A convenient development of the Debye equation is given by Frohlich[6]. He gives it with slightly altered definition.

The properties of dielectric substances in an alternating field was considered by Frohlich on the assumption of an exponental decay function $\alpha(t)$ which is proportional to $e^{-t/\tau}$ where τ is independent of time and depends upon temperature.

He deduced the relation between the electric field $E(t)$ which is dependent on time and the corresponding electric displacement $D(t)$ A field $E(u)$ is applied during a time between u and $u+du$

Then

$$D(t) = \epsilon_\infty E(t) + \int_{-\infty}^{t} E(u)\,\alpha(t-u)\,du \qquad \ldots (2.1.1.1)$$

The first term of equation (2.111.1) is the instantaneous displacement while the second is the absorptive term.

The equation (2.1.1.1) is transformed into a differential equation

$$\tau \frac{d}{dt} D(t) = \epsilon_\infty \tau \frac{d}{dt} E(t) + \int_{-\infty}^{t} E(t)\,\alpha(t-u)\,du + \tau\alpha(0)E(t) \quad (2.1.1.2)$$

Since $\quad \frac{d}{dt}\alpha(t) = \frac{1}{\tau}\alpha(t)$

on simplification

$$\tau \frac{d}{dt}(D - \epsilon_\infty E) + (D - \epsilon_\infty E) = \tau\alpha(0)E \qquad \ldots (2.1.1.3)$$

In a constant electric field, equation (2.1.1.3) becomes

$$\tau \frac{d}{dt}(D - \epsilon_\infty E) + (D - \epsilon_\infty E) = (\epsilon_0 - \epsilon_\infty)E \qquad \ldots (2.1.1.4)$$

So far, the field is assumed constant. Now for a periodic field

$$E \propto \exp(j\omega\tau)$$

then

$$\frac{d}{dt}E = j\omega E, \quad D = \epsilon^{*}E, \quad \frac{d}{dt}D = j\omega\epsilon^{*}E \qquad (2.1.1.5)$$

Putting these values and separating the real and imaginary terms

$$\epsilon' = \epsilon_{\infty} + \frac{\epsilon_0 - \epsilon_{\infty}}{1 + (\omega\tau)^2} \qquad (2.1.1.6)$$

and

$$\epsilon'' = \frac{(\epsilon_0 - \epsilon_{\infty})\,\omega\tau}{1 + (\omega\tau)^2} \qquad (2.1.1.7)$$

Examination of eqn.(2.1.1.7) shows that ϵ'' approaches zero both for small and large values of $\omega\tau$, while it is maximum for $\omega\tau = 1$

2.1.2. Kauzmann's theory :

Kauzmann[7] has given an extensive analysis of dipole orientation as rate phenomenon. He developed the theory of dielectric relaxation on the basis of rotational jumps of dipoles across the potential barriers and obtains the Debye equation both when these jumps are large and small. He also showed the probability of jumping across the potential barrier is smaller than in presence of an external field.

With the aid of simplifying assumptions he obtains the polarization $P(t)$ due to dipole orientation as

$$P(t) = P_0 e^{-k_0 t} \qquad (2.1.2.1)$$

where P_0 is the orientation polarization at $t = 0$ and k_0 is the rate constant for the activation of dipole i.e. the mean rate of jumping. When t has such a value that

$$k_0 t = 1 \qquad (2.1.2.2)$$

$P(t)$ must decayed to P_o/e This value of t is a relaxation time which may be defined as

$$\tau = 1/K_o \tag{2.1.2.3}$$

Kauzmann used Lorentz expression for the internal field and obtained the total polarization of the dipole under an external periodic field.

$$P_{OT} = \frac{N_o \alpha_\mu}{1 + j\omega/K_o}\left(\frac{\epsilon_o+2}{3}\right)E_o + \alpha_{el}\left(E_o + \frac{4\pi}{3}P_{OT}\right) \tag{2.1.2.4}$$

Putting $P_{OT} = \left(\frac{\epsilon - 1}{4\pi}\right)E$ and $\alpha_\mu = \frac{\mu^2}{3KT}$

and $\epsilon = \epsilon' - j\epsilon''$

On simplification and separating the real and imaginary terms

$$\epsilon' = \epsilon_\infty + \frac{\epsilon_o - \epsilon_\infty}{1 + x^2} \tag{2.1.2.5}$$

and

$$\epsilon'' = \frac{(\epsilon_o - \epsilon_\infty)x}{1 + x^2} \tag{2.1.2.6}$$

where $x = \frac{\omega}{K_o'}$ and $K_o' = \frac{\epsilon_\infty + 2}{\epsilon_o + 2} K_o$

which are familiar Debye's equation.

2.2. Modifications of the internal field in the Debye equation :

From the appreciable difference between the moment values calculated from gas dielectric constant and from solution dielectric constant it is clear that the application of Debye equation to dilute solution is an approximation. Of course, for polar liquids, the Debye equation can not be expected to hold for considerable dipole-dipole interaction which is of the order of 10 KT (Debye[8], Fowler[9]).

Modification of Debye equation by Von Vleck[10], Arkel and Snoek[11], Muller[12], White[13] and others are of theoretical interpret. While the modification by Onsager[14], Kirkwood[15] and Powles[16] are of practical importance and are discussed below.

2.2.1. Modification of internal field of Debye equation by Onsager:

The re-examination by Onsager[14] of the problem of internal field led to a considerable advance in dielectric theory. Onsager limits his treatment to polar molecules to those which are spherical in form. He considered a rigid dipole of moment (m) into a cavity of radius (a) in an unpolarized medium and the spherical cavity in the polarized medium.

He calculated the total field on the spherical molecule as a reaction field which acts upon the dipole as a result of electric displacement

$$F' = \frac{3\epsilon}{2\epsilon+1} E + \frac{2(\epsilon-1)}{(2\epsilon+1)} m \qquad (2.2.1\text{-}1)$$

where E is the external field.

By applying this internal field instead of Lorentz field in Debye equation, Onsager obtained for molar polarization

$$\left(\frac{\epsilon-1}{\epsilon+2} - \frac{\epsilon_\infty-1}{\epsilon_\infty+2}\right)\frac{M}{\rho} = \frac{3\epsilon(\epsilon_\infty+2)}{(2\epsilon+\epsilon_\infty)(\epsilon+2)} \quad \frac{4\pi N\mu^2}{9kT} \qquad (2.2.1.2)$$

The Onsager equation differs from that of Debye equation only by the factor $\frac{3\epsilon(\epsilon_\infty+2)}{(2\epsilon+\epsilon_\infty)(\epsilon+2)}$ on the right hand side of Debye equation.

Onsager pointed out that his assumption for spherical molecule could cause errors.

2.2.2. Modification of Onsager equation by Kirkwood :

Kirkwood[15] has modified the Onsager equation by considering hindering rotation that would play a part in the dielectric polarization of polar liquids. He has generalized the Onsager theory by eliminating the approximation of uniform local dielectric constant identical with macroscopic dielectric constant of the medium obtaining

$$\frac{(\epsilon-1)(2\epsilon+1)}{9\epsilon}\,\frac{M}{\rho} = \frac{4\pi N}{3}\left(\alpha_0 + \frac{\mu\bar{\mu}}{3KT}\right) \qquad (2.2.2.1)$$

where μ is the molecular dipole moment in the liquid and $\bar{\mu}$ is the sum of the molecular dipole moment and the moment induced as a result of hindering rotation in the spherical region surrounding the molecule. $\mu\bar{\mu}$ may be replaced by

$$\mu\bar{\mu} = g\mu^2 \qquad (2.2.2.2)$$

where g is the correlation parameter.

The equation (2.2.2.1) then becomes

$$\frac{(\epsilon-1)(2\epsilon+1)}{9\epsilon}\,\frac{M}{\rho} = \frac{4\pi N}{3}\left(\alpha_0 + \frac{g\mu^2}{3KT}\right) \qquad (2.2.2.3)$$

By statistical reasoning Frohlich[6] has obtained a more general expression

$$\left(\frac{\epsilon-1}{\epsilon+2} - \frac{\epsilon_\infty-1}{\epsilon_\infty+2}\right)\frac{M}{\rho} = \frac{3\epsilon(\epsilon_\infty+2)}{(2\epsilon+\epsilon_\infty)(\epsilon+2)}\;\frac{4\pi N g\mu^2}{9KT} \qquad (2.2.2.4$$

which becomes identical with Onsager equation (2.2.1.2) if $g = 1$

It is evident that Kirkwood equation represents a theoretical advance beyond Onsager equation in that it takes into account the hindrance of molecular orientation by neighbouring molecule. In the absence of knowledge of liquid structure this factor is unknown and useful only as an emperical constant. For dipole moment measurement in polar liquids Onsager equation is the best one.

2.2.3. Modification of internal field of Debye equation by Powles :

Powles^{16} has given an analysis of the form of the internal field necessary to yield for a molecular process with a single molecular relaxation time τ_{μ} a exponential decay of macroscopic relaxation time is then obtained as

$$\tau_M = \frac{3\epsilon_0}{2\epsilon_0 + \epsilon_\infty}\tau_\mu \tag{2.2.3.1}$$

Equation (2.2.3.1) indicates that the difference between the macroscopic relaxation time and the molecular relaxation time is small, the ratio never being greater than a limiting value of $3/2$. The difference between two relaxation times is small for most polar liquids and negligible for solutions in non-polar solvents.

2.3. Debye's formulation of relaxation time with molecular radius :

In his original treatment Debye assumed that the torque applied to a dipole molecule by the electric field is counter balanced by frictional forces which are proportional to the angular velocity of the dipolar molecule at steady state condition

$$M = \varphi \frac{d}{dt} v \tag{2.3.1}$$

where φ is frictional coefficient.

Debye showed that if the dipoles are regarded as sphere of radius a immersed in a medium of internal viscosity η the frictional coefficient φ is given by the Stoke's formula

$$\varphi = 8\pi\eta a^3 \qquad (2.3.2)$$

The consideration of Brownian motion of dipole molecule in the liquid state leads to the relationship between φ and τ

$$\tau = \varphi/2KT \qquad (2.3.3)$$

From equation (2.3.2) and equation (2.3.3) the relation

$$\tau = \frac{4\pi\eta a^3}{KT} \qquad (2.3.4)$$

is obtained.

The relation (2.3.4) can be used to obtain the radius 'a' of any molecule from measurement of relaxation time and microscopic viscosity at any temperature.

2.4. Modification of internal viscosity and the derivation of the molecular shape from spherical symmetry in the Debye equation :

It has been observed that except in a very few cases the molecular radius determined from equation $\tau = \frac{4\pi\eta a^3}{KT}$ are found to be much smaller than the radius measured from other methods. Also the ratio τ/η does not remain constant with increasing viscosities. So it is clear that the Debye equation does not represent correctly the behaviour of the dielectric relaxation process. Hence the equation has been modified in two salient directions i) to account for the derivation of moleculer shape from spherical symmetry and

ii) to re-define the internal viscosity.

The case (i) has been treated by Perrin[17] who considered the molecule as ellipsoids which will be discussed in section 3.3.

2.4.2. Redefining of internal viscosity :

In order to redefine the internal viscosity various workers have derived different equations.

Writz[18] from considerations of solvent layer interaction developed an expression

$$\tau_r = \frac{4\pi}{KT} f_{rot}\, \eta\, r_2^3 \qquad (2.4.2.1)$$

with $f_{rot} = \left[\left(6 r_1 / r_2 \right) + \left(1 + r_1 / r_2 \right)^{-3} \right]^{-1}$

where r_1 and r_2 are the mean radii of the solvent and solute molecules respectively.

Hase[19] has developed an expression which employs an exponential functional relation between the microscopic viscosity and the macroscopic viscosity η_1 i.e.

$$\eta(\text{micro}) = \eta_1 \exp(-A\, v_2 / v_1) \qquad (2.4.2.2)$$

where v_2 and v_1 are the molar volumes of the polar solute and non-polar solvent respectively and A is a numerical parameter.

Hill[20] introduce a term of mutual viscosity η_{12} which is related to the macroscopic viscosity of solution η_m solvent η_1 and solute η_2 given by

$$\eta_m = x_1^2 \eta_1 \frac{\sigma_1}{\sigma_m} + x^2 \eta_2 \frac{\sigma_{12}}{\sigma_m} \qquad (2.4.2.3)$$

where σ is the intermolecular distance. For dilute solution

$$\tau_r = \frac{3}{KT}\eta_{12}K_{12}^2\sigma_{12} \qquad (2.4.2.4)$$

and for liquid

$$\tau_r = \frac{A}{KT}\eta K^2\sigma \qquad (2.4.2.5)$$

where K is the mean radius of gyration of the molecule about any axis perpendicular to the axis of dipole and A is a numerical constant.

Vaughan and Smyth[21] introduced a term "properly averaged viscosity" given by

$$\eta_m = x_A^2\eta_A + x_B^2\eta_B + 2x_Ax_B\eta_{AB} \qquad (2.4.2.6)$$

where η_m, η_A and η_B refers to the viscosity of the solution, solvent and solute and x_A and x_B are molar fraction of solute and solvent respectively.

Higasi[22] derived an equation for τ-value in a highly viscous medium

$$\tau = A\eta^x \qquad (2.4.2.7)$$

where A is a constant and x is a parameter which is less than unity. When $x = 1$, we have the Debye equation.

Le-Fevre and Sullivan[23] suggested the equation

$$\tau = \frac{\pi}{2KT}\eta_1 ABC(\exp\Delta_1)(\epsilon+2)^{-1} \qquad (2.4.2.8)$$

where A, B, C are mutually perpendicular axial lengths, Δ_1 is depolarization factor of the solvent and ϵ is the dielectric constant of the solvent.

The above expressions for internal viscosity were tried by many workers on different molecules. They found that if one equation is applicable for some molecules, for other it fails. No single expression has been found which is applicable for all molecules.

However, it has been found that Hill's equation is best suited to system where solute and solvent sizes are not far from unity.

Meakins[24] found that if the size of the solute is at least three times as large as the solvent molecule, the Debye equation is applicable.

3. Distribution of Relaxation times :

If the interaction between the solute molecules surrounded by other solute or solvent molecules were completely uniform, a single relaxation mechanism as envisaged in the original Debye equation would be obtained. But the non-uniformity in such interactions is expected owing to the fact that the entire system is composed of a statistical assembly of individual absorbing molecule experiencing varying solute or solvent environments. So the use of symmetrical distribution functions have been developed of which more important ones are discussed in the following sections.

3.1. Cole Cole distribution :

The arc dispersion function of Cole Cole[25] has been applied to the analysis of experimental dielectric data most frequently because of the attractively simple graphical form by which data of $\epsilon'(\omega)$ and $\epsilon''(\omega)$ can be analysed in its terms.

Cole-Cole have shown that the Debye equations (2.7) and (2.8) can be combined in the form of the equation

$$\left(\epsilon' - \frac{\epsilon_0-\epsilon_\infty}{2}\right)^2 + \epsilon''^2 = \left(\frac{\epsilon_0-\epsilon_\infty}{2}\right)^2 \qquad (3.1.1)$$

which is the equation of a circle. The plot of ϵ' and ϵ'' in a complex plane gives a semicircle. Such plots in the case of rigid polar molecules are semicircles which mean that the dielectric data conforms to Debye equation. Cole and Cole have found that for a considerable number of liquids such ϵ' vs ϵ'' plots represent arc of a circle intersecting the abscissa axis at the values of ϵ_∞ and ϵ_0. The center of the circle of which this arc is a part is depressed below the abscissa axis and the diameter drawn through the center through the ϵ_∞ point makes an angle $\alpha\pi/2$, with the abscissa axis. The value of α gives a measure of distribution of relaxation times, which may vary with temperature but not with frequency. Values of α lies between 0 and 1, and except for polymer are commonly less than 0.3. The Debye equation is modified by them as

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_0-\epsilon_\infty}{1+(j\omega\tau_0)^{1-\alpha}} \qquad (3.1.2)$$

With the most probable relaxation time τ_0 which can be calculated from the relation

$$\frac{\vartheta}{U} = (\omega\tau_0)^{1-\alpha} \qquad (3.1.3)$$

where ϑ is the distance on the Cole-Cole plot from ϵ_0 point to the experimental point and U is the distance from the same experimental point to the ϵ_∞ point. If α is zero, $\frac{\vartheta}{U}$ becomes equal to $\omega\tau_0$ which is true for Debye equation.

3.1.1. Davidson and Cole skewed arc method :

A number of cases have been observed in which the arc is skewed. These are representable by Debye equation modified by Davidson and Cole[26]

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{(1 + j\omega\tau_0)^\beta} \tag{3.1.1.1}$$

where β is an emperical constant with a value between 0 and 1, when $\beta = 1$, the equation reduced to Debye equation.

3.2. Frohlich distribution of relaxation times :

A distribution of relaxation time between two limiting values τ_1 and τ_2 has been given by Fröhlich[6]. He showed that if $y(\tau)d\tau$ is the contribution to the static dielectric constant of the group of dipoles having individual relaxation time in a range $\delta\tau$ near τ the total contribution of all the dipole is

$$\epsilon_0 - \epsilon_\infty = \int_0^\infty y(\tau)\, d\tau \tag{3.2.1}$$

then

$$\epsilon' = \epsilon_\infty + \int_0^\infty \frac{y(\tau) d\tau}{1 + (\omega\tau)^2} \tag{3.2.2}$$

and

$$\epsilon'' = \int_0^\infty \frac{y(\tau)\omega\tau d\tau}{1 + (\omega\tau)^2} \tag{3.2.3}$$

On simplification he arrived at the equation

$$\frac{\tau_1 - \tau_0}{\tau_0} = e^{v_0/kT} - 1 \tag{3.2.4}$$

The equation shows that the relative width of the distribution should decrease with rising temperature. The maximum absorption occurs at the critical frequency

$$\omega_c = (\tau_0 \tau_1)^{-1/2} \tag{3.2.5}$$

3.3. Perrin distribution of relaxation time :

To account for the deviation from spherical symmetry of the molecule Perrin[17] has extended the Debye theory to the case of ellipsoidal molecule with semi-axes a, b and c and has thus replaced $\mu^2/1+j\omega\tau$ in Debye equation by

$$\mu_a^2/1+j\omega\tau_a + \mu_b^2/1+j\omega\tau_b + \mu_c^2/1+j\omega\tau_c$$

where μ_a, μ_b and μ_c are the components of μ along these axes and τ_a, τ_b and τ_c are the corresponding relaxation times.

In the ellipsoidal molecule, where a dipole lie along one of the axes Fischer[75] has shown that

$$\tau = (4\pi\eta^* f abc)/kT \tag{3.3.1}$$

where a, b and c are semi-axes of the ellipsoid, f is a structure factor and $\eta^* = 0.36\,\eta$ where η is the macroscopic viscosity.

3.4. Non-rigid molecule containing more than one relaxation mechanism :

Now we consider a molecule into which is incorporated a segment possessing a dipole moment component perpendicular to the direction of the bond axis which joints it to the rest of the molecule. If the intramolecular potential energy $V(\theta)$ is constant for all values of angle θ the segment is freely rotating and only rotation of the segment of the molecule in the intermolecular force field leads to dielectric absorption. This case of molecules have been treated by Budó[27], Bergmann et al[28], and Kastha[29]. The The behaviour is then characterised essentially by a superposition of relaxation dispersion of the various segments against the intermolecular potential energy surface.

3.4.1. Budó's method :

Budó has extended the theory for free rotation to include restricted rotation for the case where the molecule consists of two groups of equal size with a common rotational axis.

Following Debye, Budó calculated the distribution function of the molecule of a liquid having rotatable polar group on the basis of rotational Brownian motion due to thermal agitation and obtained the mean moment as

$$\overline{m} = \frac{F_0 e^{j\omega t}}{3KT}\left(\mu_a^2/_{1+j\omega\tau_a} + \mu_b^2/_{1+j\omega\tau_b} + \mu_c^2/_{1+j\omega\tau_c}\right) \quad \cdots (3.411)$$

where μ_a is the total dipole moment in the direction of the axis of rotation of the polar group, μ_b and μ_c are the components of the fixed dipole moments of the whole molecule and of the part of the polar group in a direction perpendicular to the axis of rotation respectively. τ_a, τ_b and τ_c are the relaxation times corresponding to μ_a, μ_b and μ_c respectively.

If the molecule contains a number polar groups with components $\mu_1, \mu_2, \cdots \mu_n$ perpendicular to the axis of rotation. Budó showed that the expression for average moment should be written as

$$\overline{m} = \frac{F_0 e^{j\omega t}}{3KT} \left\{ \frac{\mu_a^2}{1+j\omega\tau_a} + \frac{\mu_b^2}{1+j\omega\tau_b} + \frac{\mu_1^2}{1+j\omega\tau_1} + \cdots\cdots + \frac{\mu_n^2}{1+j\omega\tau_n} \right] \quad (3.4.1.2)$$

In the case of static field, this reduced to

$$\overline{m} = \frac{F_0}{3KT} \left[\mu_a^2 + \mu_b^2 + \mu_1^2 + \cdots\cdots + \mu_n^2 \right] \quad (3.4.1.5)$$

i.e. the expression is arising from the interaction of the invarient components of the dipole moments with the electric field.

3.4.2. Bergmann's method :

If two distinct relaxation processes occur simultaneously, their effect on the dielectric behaviour can be added together and the observed behaviour can be used to calculate the relaxation time for each process.

Bergmann et al. have shown that molecules having two mutually perpendicular relaxation times the dielectric data could be analysed by two equations

$$\frac{\epsilon' - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{C_1}{1+(\omega\tau_1)^2} + \frac{C_2}{1+(\omega\tau_2)^2} \quad (3.4.2.1)$$

and

$$\frac{\epsilon''}{\epsilon_0 - \epsilon_\infty} = \frac{C_1\omega\tau_1}{1+(\omega\tau_1)^2} + \frac{C_2\omega\tau_2}{1+(\omega\tau_2)^2} \quad (3.4.2.2)$$

where τ_1 and τ_2 are the two relaxation times, C_1 and C_2

are the relative weights of each relaxation term and $C_1 + C_2 = 1$. If the probability of occurence of the two processes are equal, then

$$\frac{C_1}{C_2} = \frac{\mu_1^2}{\mu_2^2} \qquad (3.4.2.3)$$

where μ_1 and μ_2 are the effective dipole moment which are relaxing.

Bergmann's equations have been frequently used by many workers for analysis of the data in terms of two relaxation processes.

If the two relaxation processes are very close together, it is difficult to distinguish them from the above equation.

3.4.3. Kastha's method :

Kastha[29] has given a straight forward analytical method of analysis of the dielectric data in terms of two relaxation processes.

Kastha pointed out that though the equation due to Bergmann et al.

$$\frac{\epsilon' - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{C_1}{1+(\omega\tau_1)^2} + \frac{C_2}{1+(\omega\tau_2)^2}$$

and

$$\frac{\epsilon''}{\epsilon_0 - \epsilon_\infty} = \frac{C_1\omega\tau_1}{1+(\omega\tau_1)^2} + \frac{C_2\omega\tau_2}{1+(\omega\tau_2)^2}$$

are valid in dilute solutions, in the case of polar liquids, these equations are not applicable. He has given the following functional relationship among the ϵ', ϵ'', τ_1 and τ_2 in the case of polar liquids.

$$\frac{(\epsilon_0+2)[(\epsilon'-\epsilon_\infty)(\epsilon'+2)+\epsilon''^2]}{(\epsilon_0-\epsilon_\infty)[(\epsilon'+2)^2+\epsilon''^2]} = \frac{C_1}{1+(\omega\tau_1)^2} + \frac{C_2}{1+(\omega\tau_2)^2} \quad \cdot\cdot(3.4.3.1)$$

and

$$\frac{(\epsilon_\infty+2)(\epsilon_0+2)\,\epsilon''}{(\epsilon_0-\epsilon_\infty)[(\epsilon'+2)^2+\epsilon''^2]} = \frac{C_1\omega\tau_1}{1+(\omega\tau_1)^2} + \frac{C_2\omega\tau_2}{1+(\omega\tau_2)^2} \quad \cdot\cdot(3.4.3.2$$

with $C_1+C_2=1$

and ϵ_0, ϵ', ϵ'' and ϵ_∞ have usual significance. Denoting the expressions on L.H.S. of equations (3.4.3.1) and (3.4.3.2) by 'a' and 'b' and putting $\omega\tau_1 = x_1$ and $\omega\tau_2 = x_2$ then

$$a = \frac{C_1}{1+(\omega\tau_1)^2} + \frac{C_2}{1+(\omega\tau_2)^2} \qquad (3.4.3.3)$$

and

$$b = \frac{C_1\omega\tau_1}{1+(\omega\tau_1)^2} + \frac{C_2\omega\tau_2}{1+(\omega\tau_2)^2} \qquad (3.4.3.4)$$

From these relations

$$C_1 = \frac{(b-ax_2)(1+x_1^2)}{x_1-x_2} \qquad (3.4.3.5)$$

and

$$C_2 = \frac{(a-bx_1)(1+x_2^2)}{x_1-x_2} \qquad (3.4.3.6$$

$$a(1-a)-b^2 = \frac{C_1C_2(x_1-x_2)^2}{(1+x_1^2)(1+x_2^2)} \qquad (3.4.3.7$$

The existence of two relaxation processes requires the condition that $a(1-a)-b^2>0$

Putting $C_1+C_2=0$ the equation (3.4.3.7) reduces to

$$\frac{1-a}{b} = x_1+x_2-\frac{a}{b}x_1x_2 \qquad (3.4.3.8)$$

dividing the equation (3.4.3.8) by ω

$$\frac{1-a}{b\omega} = \tau_1+\tau_2-\frac{a\omega}{b}\tau_1\tau_2$$

From the equation (3.4.3.9) obtained at two different frequencies ω_1 and ω_2 the values of τ_1 and τ_2 can be evaluated directly, knowing the value of a and b.

This method of straight forward calculation to find out the molecular and intramolecular relaxation times have been used with success by Bhattacharya et al.[30], Sinha[31], Kastha et al.[32], Hasan et al.[33,34,35] and others.

4. A brief review of the previous works :

Most of the earlier works centered round the studies of the applicability of the Debye equation in the determination of molecular radii from the measurement of relaxation times and macroscopic viscosity and the experiments were done mainly on the polar rigid and non-rigid molecules in non-polar solvents. But due to various forces (London force, dipole induced dipole forces and dipole-dipole forces) acting among the molecules in the liquid state. Such works in pure liquid state are rather fewer compared to those in dilute solution of non-polar solvents.

In general, the liquid system, in which microwave absorption has been studied may be classified into two main catagories :

i) solution of polar rigid and non-rigid molecules in non polar solvents and ii) pure polar liquids.

4.1. Solution of polar rigid molecules in non-polar solvents :

The first quantitative verification of Debye theory was attempted by Mizushima[36]. He measured the dielectric constant and absorption coefficient of several alcohol at constant wave length of λ = 3.08 meter and 50 meter within a temperature range from -68°C to + 65°C employing resonance method. He verified Debye theory quantitatively in the case of alcohol by calculating the molecular radius and found them to be almost of the right order of magnitude, but there was large departure in case of glycerine which in fact gave too small a value for a molecular radius.

Following Mizushima, many workers began to study the dispersion and absorption in polar liquids in dilute solution of non polar solvents.

Muller[37] from measurements of dielectric loss at different frequencies calculated the critical wave lengths and τ - values for a number of molecules such as nitrobenzene, chlorobenzene, o- and m-dichlorobenzene etc. at different viscous media. He found that the molecular radii calculated from Debye equation are too low compared to value determined by other methods. He also observed that the molecular radii become still lower the higher is the viscosity of the medium.

Whiffen and Thompson[38] from studies of some organic molecules in non-polar solvents obtained value of relaxation times which in low viscous medium arranged among themselves as regards magnitude in accordance with their sizes. But they obtained the τ - values of any solute in different viscous media and found that the value only increased by 4-7 fold for an increase in viscosity of eighty fold.

Similar results were obtained by Jackson and Powles[39] from the measurements of τ - values of benzophenon in benzene and paraffin solution. They observed that for viscosity ratio 300. the corresponding ratio of τ - value was only 18.

Curtis et al.[40] observed that although the viscosity of the liquid was the same, τ - value was different in solutions and in liquid state. Smyth[41] also observed the same thing.

Sinha et al.[42] studied the influence of viscosity on relaxation time and their conclusion was that the macroscopic viscosity did not correctly represent the internal viscosity as required by Debye equation.

Sovanadri[43] assumed that this might be due to dipole-dipole interactions in the liquid state.

It has already been discussed in section (1.4.2) the various equation developed by many workers redefining the internal viscosity of the medium. It was observed that if one equation is applicable for some molecule, it fails for other.

4.2. Non-rigid molecules in non-polar solvents :

Fischer and Frank[44] using a thermal method of measuring dielectric loss at 4.3 meter obtained relative value of relaxation times of some aromatic halides. They observed that the relaxation of p-xylene chloride and p-xylene bromide were about half as large as the τ -value of o-dichloro and o-dibromobenzene respectively. The shorter relaxation times in large molecules were explained by them as being associated with the orientation of $-CH_2X$ group rotation around their bonds to the ring. From similar measurements Fischer[45] obtained the τ -value of p-phenylene diamine and 4-4 diamin diphenyl in dilute benzene solution were less than 0.15×10^{11} sec. which are much smaller to be associated to molecular rotation. So they concluded that these lower values of τ might arise simply from rotation of the $-NH_2$ group, they also considered the possibility of inversion of molecules as observed in NH_3 molecule.

The small τ- value of diphenyl ether led Fischer to suggest that the τ- value might be due to orientation of internal rotation of the molecule, in particular the oxygen atom, which might occur in the thers as well.

Since after the development of Budó's theory (discussed in section 3.4.1) considering molecular and intramolecular rotations and subsequently the equation developed by Bergmann et al.[28], molecular and intramolecular rotations have been observed in large number of molecules like $-OCH_3$, $-NH_2$, $-CH_2Cl$, $-CH_2Br$, $-CH_2CN$, $-OH$, $COCH_3$ and others[46,47,48,49,50] by many workers.

It is interesting to note that the molecules like p-xylene halides, p-xylene cyanide, p-dimethoxy benzene, p-diaminobenzene etc. give so small values of relaxation time which could be associated with group rotation, indicating molecular orientation being almost negligible in these cases.

Very recently some works on aliphatic molecules like bromoalkanes[51], aliphatic amines[52], ketones[53] and α,ω-dichloro-alkanes[54] in dilute solution have been reported. In bromoalkanes and ketones data have been analysed in terms of rotation of the molecule as a whole but in amines the $-NH_2$ group rotation have been attributed to be responsible for dielectric relaxation.

It has been observed that while the molecular relaxation time is very sensitive to viscosity of the medium and temperature, the group rotation τ_2 is rather less sensitive of both viscosity and temperature.

4.3. Pure liquid state :

The intractibility of the liquid state severely limiting the exactness attainable by theoretical treatments, recommends the alternative approach which makes the use of molecular probes whose probable behaviour is well enough understood in its correlation to that of others. So that conclusions may be drawn from a series of compansions. The earlier studies of molecular shape and dielectric relaxation have been reviewed comprehensively by Smyth.

Whiffen and Thompson[55] from dielectric measurements in toluene, o-xylene, p-cyamine etc. in pure liquid state obtained the

the τ -values which are according to the sizes of the molecules. Petro and Smyth[56] also observed the same.

Smyth and his coworkers[57] examined the effects of the direction of the dipole moment with respect to the molecular plane on the relaxation behaviour of the molecules of different shapes and sizes in the liquid state. They observed that though the molecules 2,4,6-trimethyl pyridine and 2,4,6 trimethyl - 1,3,5 trioxane are of equal size, dipole moment and viscosity in the liquid state, the two molecules have quite different values of critical wave length i.e. the τ -values, because of the direction of the dipole moment were parallel and perpendicular respectively to the spheroidal molecular plane. Similar results were also obtained in isoquinolene and quinolene in the liquid state, the former having a larger τ- value than the latter though both are of same shape, size and viscosity but the dipole direction was different. Results of 1-methyl and 2-methyl naphthalene[58] in the liquid state show similar behaviour.

From dielectric loss measurement of some rigid molecules of mono substituted benzene in the liquid state, Poley[59] obtained the relaxation times which increases with the molecular sizes. He also observed that the value of high dielectric constant ϵ_∞ was much higher than the corresponding value of n_D^2 (n_D=refractive index) and noted that the difference between $\epsilon_\infty - n_D^2$ was temperature dependent. He suggested that in addition to the dispersion region due to molecular orientation, there is another region of dipolar absorption in the neighbourhood of 1 mm region.

Petro and Smyth[60] from the investigations in substituted benzene and pyridines in the liquid state observed a regular increase in the τ-values with increase in sizes of the substituents. They also observed a high frequency dispersion region of 'Poley type'. Similar investigations were carried out by Rampolla and Smyth[58] to the case of substituted naphthalene and quinolenes in the liquid state.

From all these studies, Smyth and his coworkers[57] concluded that a change in the direction of the dipole vector for similarly shaped non-spherical molecule has marked value on relaxation time but not on viscosity.

Higasi et al.[61] reanalysed the experimental data of n-alkyl bromides in the liquid state in terms of distribution between two limits given by Frohlich[6]. The τ-value in the lower limit was associated with the relaxation time of internal rotation of the $-CH_2Br$ group, while the upper limit to the orientation of the whole molecule. The numerical value obtained for the two limits, one small increasing slowly with molecular size and the other large and increasing rapidly with the molecular size were consistent with the physical picture of the relaxation process indicating approximating correctness of Frohlich. Similar results were also observed by many workers such as Heston, Hennelly and Smyth[62]; Laquer and Smyth[63] and Branin and Smyth[64].

Krishnaji and Mansingh[65] have reported the dielectric relaxation in some alkyl cyanides[65] and in alkylthiols[66] in the liquid state. In alkyl cyanides the relaxation time was in the order of increasing size of the molecules. In the alkylthiols they observed that the plot of ϵ' vs ϵ'' gave a skewed arc indicating more than two relaxation behaviour.

Bhattacharyya et al[67] reported that in polar liquids with rigid dipoles having moment ($\approx$ 1.5 D or less), the effect of dipolar interaction was negligible.

Relaxation times (τ) and viscosities (η) had been experimentally determined by Bhanumati[68] at different temperatures for a few liquids such as α-chloronaphthalenes, butyl phthalate and isoamyl phthalate and τ alone for ethyl benzoate, o-chloro phenetole and β-chlorophenetole. The value of potential barrier heights for dipole relaxation (H_τ) and that for viscous flow (H_η) were evaluated from linear plots of $\mathrm{Log}\, T\tau$ vs $1/T$ and $\mathrm{Log}\, \eta$ vs $1/T$ respectively. The calculated values of H_η were found to be greater than those of H_τ as the phenomenon of viscous flow considered the process of translation as well as of rotation but only rotational process was considered in the dipole relaxation and this leading to the greater value of H_η with respect to H_τ.

Garg and Smyth[69] reanalysed the dielectric data of anisole and aniline in the liquid state, combining the data at 2 mm microwave region. They obtained τ_2 value for methoxy group rotation as 3.2 p.sec and its weight factor as 0.2, while these values in dilute solution are about 8 and 0.8 respectively.

Recently Anderson and Smyth[70] reported dielectric relaxation in some dibromobutanes in pure liquid state and reported that the rate of transformation of rotamer into another did not contribute much to dielectric relaxation process while Garg and Smyth[71] reported the dielectric behaviour in α,ω - bromoalkanes in terms of molecular and CH_2Br group relaxation process.

4.4. Associated liquids :

Molecular association may be expected to influence dielectric relaxation by modifying the structure of the liquid in the direction greater near range order as the molecular interaction become increasingly energetic and by providing variety of molecular aggregates, stabilized by intermolecular forces, each of which might exhibit distinctive mechanisms for absorption of energy from a external point.

The investigation of dielectric relaxation of alcohols, one of the first molecular system to be studied in this connection has continued to be persued actively in recent years.

Dielectric measurements of Garg and Smyth[72] on the normal alcohols from propyl to dodecyl in the pure liquid state have shown three dispersion regions as was previously reported by other workers. Relaxation time for first dispersion region was about $1 - 2.2 \times 10^{-10}$ sec, for the second region it lay between $1.7 - 5 \times 10^{-11}$ sec and for the third region it was $1.7 - 4 \times 10^{-12}$ sec. The long relaxation times were associated with polymeric clustors resulting from strong hydrogen bonding between OH groups. The shortest relaxation time was ascribed to the orientation of the OH group. The intermediate relaxation time was attributed to the rotation of free alcohol molecules.

Cole and Davidson[73] brought the dispersion of n-propyl alcohol into the region of audio and radio frequencies. In addition to the usual primary dispersion region, two dispersion regions were found which made small but significant contribution to the dielectric constant. The relaxation times for intermediate dispersion were 200 times smaller than those for the primary ones. Brot[74] made similar conclusions from his measurements on straight chain alcohol $CH_3(CH_2)_nOH$ with n = 5 - 9 and 11. In second dispersion region, the principle of superposition of relaxation time did not hold good. A third dispersion region near $\lambda = 1$ cm was assigned to the orientation of the dipoles in the interior of polymeric species.

5. Scope and objects of present investigations :

From the brief review of the previous works on dielectric studies as made in last section, it was observed that the amount of such works in pure liquids is much smaller than that in dilute solutions and also the amount of such works on aliphatic molecules in pure liquids is still smaller. There seems to be little studies reported so far, on 1,2-disubstituted ethanes, which have two or more isomeric forms, having different values of dipole moments. So the behaviour of these isomeric molecules to dielectric relaxation are expected to be different. Therefore, a programme was undertaken to study the dielectric relaxation in a number of such 1,2-disubstituted ethanes in the liquid state, the results of which constitute the first part of the thesis.

It was also observed in the section (4.3) that intramolecular rotation in molecules containing small groups like -OH, $-NH_2$, $-OCH_3$, $-CH_2X$ ($X = CH_3$, C_2H_5 ... etc) have been reported extensively. Few such group rotation have been reported so far in molecules having large polar groups as in esters. The second part of the thesis constitute the results of investigation of some ester molecules with large polar groups.

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