CHAPTER 1

INTRODUCTION

1.1 General

The study of dielectric relaxation of a substance is essentially the quantitative characterization of its interaction with the electromagnetic field. In the words of Professor C.P. Smyth[1] the pioneer worker in this field, the dielectric relaxation is an effective tool for the study of molecular and intramolecular motions and their relations to molecular structure - shape, size etc. in the liquid state or in solutions. In order to have a fair understanding about the present position of relaxation studies, a short account of the development of the theories of dielectric polarization, their uses in the analysis of the experimental data, together with a brief review of the previous works will be given in the following sections. The scope and the objects of the present investigations will be stated later.

1.2 Theories of Dielectric polarisation in polar molecules

1.2.1 Debye theory of dielectric polarisation

While studying the dielectric behaviour of different materials, early workers, Drude[2], Lampa[3], Lang[4] and others observed that the dielectric constant of certain dielectric materials decreased abruptly as the frequency of the applied field was increased. This abrupt diminution of the dielectric constant at higher frequencies of the field was termed 'anomalous dispersion' of the dielectric constant. The first successful explanation of the phenomenon of the anomalous dispersion was put forward by Debye[5], who pointed out that the characteristic property of the liquids responsible for anomalous dispersion was due to the polarity of the molecules constituting the dielectric. Debye explained that when a dielectric composed of polar molecules was placed in an electric field dielectric polarization composed of three parts - electronic, atomic and orientation polarization occurs. At lower frequencies of the field the total polarization remains in phase with the field, but at a higher frequencies, the polarization lags behind the field, as a result the polarization becomes complex. On removal of the field the polarization decays exponentially, given by the relation $P = P_0 e^{-t/\tau}$ The time in which the polarisation decays to $1/e$ th of the original value is called the dielectric relaxation time.

Debye[5] on applying the molecular diffusion theory and using the Lorentz expression for the internal field, deduced a relation connecting the polarisation with frequency of the applied field, given by

$$p^* = \frac{\epsilon^* - 1}{\epsilon^* + 2} \frac{M}{\rho} = \frac{4\pi N}{3} \left(\alpha_0 + \frac{\mu^2}{3KT} \frac{1}{1 + i\omega\tau} \right) \qquad (1.1)$$

where α_0 is the molar polarisability, M, N and ρ are the molecular weight, Avogadro's number and density respectively, μ the dipole moment and ϵ^* is the complex dielectric constant, given by the expression $\epsilon^* = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + ix}$ the real part of which gives the dielectric permittivity $\epsilon' = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + x^2}$ (1.2) and the imaginary part gives the dielectric loss

$$\epsilon'' = \frac{(\epsilon_0 - \epsilon_\infty)x}{1+x^2} \tag{1.3}$$

where $x = \frac{\epsilon_0+2}{\epsilon_\infty+2}\omega\tau_\mu$, τ_μ being the microscopic relaxation time. These equations (1.2) and (1.3) are called the Debye equations of dispersion for polar dielectrics. It is seen from the equation (1.2) that $\epsilon' \to \epsilon_0$ as $\omega \to 0$ and the value of ϵ' gradually decreases with the increase of frequency and when $\omega \to \infty$ at very high frequency $\epsilon' \to \epsilon_\infty$ This explains the phenomena of anomalous dispersion.

1.2.2 Frohlich treatment of dielectric polarisation

Frohlich[6] considered dielectric polarisation from the phenomenological or macroscopic point of view. He deduced a relation between a time dependent electric field E(t) and the corresponding electric displacement D(t). When a field E(u) is applied during a time interval u and u + du, then

$$D(t) = \epsilon_\infty E(t) + \int_{-\infty}^{t} E(u)\, f\,(t-u)\, du \tag{1.4}$$

The first term on the right hand side of the equation (1.4) is the instantaneous displacement, while the second is the absorptive term. Frolich assumed that the attainment of equilibrium is exponential with time and has the decay function

$$f(t) \propto e^{-t/\tau} \tag{1.5}$$

Differentiating the equations (1.4) and (1.5) with respect to time and combining the results, the following equation is obtained

$$\tau \frac{d}{dt}\left(D-\epsilon_{\infty}E\right)+\left(D-\epsilon_{\infty}E\right)=\left(\epsilon_0-\epsilon_{\infty}\right)E \qquad (1.6)$$

For a periodic field $E=E_0 \exp(i\omega\tau)$ where E_0 is independent of time (t) and ω the angular frequency.

$$\frac{d}{dt}E = i\omega E\ , \quad D=\epsilon^{*}E \quad \text{and} \quad \frac{d}{dt}D = i\omega\epsilon^{*}E \qquad (1.7)$$

Substituting the values in eqn.(1.6) and on rearrangement, the equation

$$\epsilon^{*}=\epsilon_{\infty}+\frac{\epsilon_0-\epsilon_{\infty}}{1+i\omega\tau} \qquad (1.8)$$

is obtained. Eqn.(1.8) is similar to Debye equation.

It should be noted here that the relaxation time derived by Frolich gives the macroscopic relaxation time τ_m.

The relation between the macroscopic relaxation time τ_m obtained by Frolich and the microscopic relaxation time τ_μ obtained by Debye is given by

$$\tau_m=\frac{\epsilon_0+2}{\epsilon_{\infty}+2}\tau_\mu \qquad (1.9)$$

Later on Powles[7] and Glarum[8] in a more rigorous manner obtained the relation between τ_m and τ_μ

$$\tau_m=\frac{3\epsilon_0}{2\epsilon_0+\epsilon_{\infty}}\tau_\mu \qquad (1.10)$$

It may be noted here that the Lorentz expression for internal field as used by Debye[5] was later modified by Onsager[9], Kirkwood[10] and others.

1.2.3 Kausmann's treatment of Dielectric polarization

Kausmann[11] considered the process of dielectric polarization from the view point of molecular rate process. He assumed that the molecular dipole orientation involves a passage over a potential barrier with a certain probability of jumping from one equilibrium position to another. With some simplifying assumptions he obtained a relation between the polarization P and the jumping rate K_0 given by

$$P(t) = P_0 e^{-K_0 t} \tag{1.11}$$

where t is such that $K_0 t = 1$ then

$$P(t) = P_0/e \tag{1.12}$$

This value of time t is called the relaxation time and is defined as $\tau = \frac{1}{K_0}$ Kausmann using Lorentz expression for internal field obtained an expression for polarization

$$P^* = N\alpha_0 \left(E_0 + 4\pi P_1/3\right) + \frac{N\mu^2/3KT}{1+i\omega/K_0'} \frac{\epsilon_0+2}{3} E_0 \tag{1.13}$$

where $P_1 = \frac{(\epsilon-1)E}{4\pi}$

and $K_0' = \frac{\epsilon_\alpha + 2}{\epsilon_0 + 2} K_0$

On simplification of eqn.(1.13) and separating real and imaginary parts equations for ϵ' and ϵ'' similar to Debye eqns.(1.2) and (1.3) are obtained.

Kausmann also postulated that the process of molecular orientation requires an activation energy to overcome the energy barrier separating the two equilibrium positions. Following

Eyring[12] rate equation, Kauzmann put forward the rate constant κ_0 given by

$$k_0 = \frac{1}{\tau} = \frac{kT}{h} e^{-\Delta F/RT} \tag{1.14}$$

$$\text{or} \quad \tau = \frac{h}{kT} e^{\Delta F/RT} = \frac{h}{kT} e^{\Delta H/RT - \Delta S/R} \tag{1.15}$$

where $\Delta F = \Delta H - T\Delta S$ is the molar free energy of activation for dipole orientation and ΔH, ΔS are the heat content and entropy change in the process of activation. The eqn.(1.15) can be written in the form

$$\tau = \frac{A}{T} e^{E_\tau/RT} \tag{1.16}$$

where E_τ is the activation energy for dipole orientation. According to Kauzmann this energy corresponds to intermolecular potential energy barrier and it has been used by large number of workers to determine the value of E_τ.

1.3 Debye's correlation of dielectric relaxation time with molecular structure

Debye assumed that when an electric field is applied to a molecular dipole placed in a viscous medium, the torque acting on the dipole orients it in the direction of the field with an angular velocity. The torque is counterbalanced by the internal friction ς of the medium, proportional to the angular velocity of the dipole. By the application of the stoke's formula he obtained a relation between the internal friction ς and internal viscosity η_{int} given by

$$\varsigma = 8\pi\eta_{int}a^3 \tag{1.17}$$

where a is the molecular radius.

The consideration of Brownian motion of dipole molecule in the liquid state, the relationship between ς and τ given by

$$\tau = \frac{\varsigma}{2KT} \tag{1.18}$$

where K is the Boltzmann constant.

Combining eqns.(1.17) and (1.18) the relationship

$$\tau = \frac{4\pi\eta_{int}a^3}{KT} \tag{1.19}$$

is obtained. Considering the picture of the molecule as a sphere, Debye considered the internal viscosity as macroscopic viscosity of the medium and the eqn.(1.19) becomes

$$\tau = \frac{4\pi\eta a^3}{KT} \tag{1.20}$$

The above equation shows that from the measured value of relaxation time τ and co-efficient of viscosity η at certain temperature, the size of the rotating polar molecules may be calculated.

1.3.1 Applicability of the Debye equation

The earlier works on the applicability of Debye equation (1.20) by different workers[13-19] were concerned in determining the molecular size and testing the linearity between τ and η at different temperature and at different solvents. But soon it was realised that the molecules in general, are neither spherical in shape nor the macroscopic viscosity represent the internal viscosity as required in Debye equation (1.20).

The Debye equation was therefore modified in two directions (1) to account for the deviation of the molecular shape from spherecal symmetry (2) to correlate the internal viscosity with the macroscopic viscosity.

(1) Perrin[20] treated the general case of rigid molecules of ellipsoidal shape and has shown that there would be three distinct relaxation times along the principal axes. Following Perrin, Fischer[21] obtained an expression for relaxation time for approximate ellipsoidal molecules in which dipole moment lies in any one of the axes, given by

$$\tau = \frac{4\pi \eta f abc}{kT} \qquad (1.21)$$

where a, b, c are the semi axes, f is a structure factor.

(2) To redefine internal viscosity : In order to take into account the interaction between the solvating medium and solute molecules, modifications of internal viscosity of Debye eqn.(1.20) were made by many workers, of which only the more important ones will be discussed here.

Wirtz and his coworkers[22] from consideration of solvent layer interaction deduced the following equations

$$\tau_\mu = \frac{4\pi}{KT} f_{rot}\, \eta\, r_2^3 \qquad (1.22)$$

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

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

Hill[23] suggested that the interaction between the solvent and solute would be best represented by a term called mutual viscosity η_{12}. The mutual viscosity η_{12} is related to macroscopic viscosities of the solution (η_m), solvent (η_1) and solute (η_2) given by the relation

$$\eta_m = x_1^2 \eta_1 \frac{\sigma_1}{\sigma_m} + x_2^2 \eta_2 \frac{\sigma_2}{\sigma_m} + 2 x_1 x_2 \eta_{12} \frac{\sigma_{12}}{\sigma_m} \qquad (1.23)$$

where σ_1 , σ_2 , σ_m are the intermolecular distances of the solvent, solute and solution respectively. σ_{12} is the mean distance between adjacent solute and solvent molecule. x_1 and x_2 are the mole fraction of the solvent and solute molecule.

For dilute solution of polar molecules in a non-polar solvents Hill's treatment gives

$$\tau_\mu = \frac{3}{KT} \eta\, k_{12}^2\, \sigma_{12} \qquad (1.24)$$

k_{12} is the radius of gyration, η_{12} mutual viscosity and σ_{12} is the mean distance between the adjacent solute and solvent molecule.

For pure dipolar liquid, Hill's equation is

$$\tau_\mu = \frac{A}{KT} \eta\, k^2 \sigma \qquad (1.25)$$

where A is a numerical constant, k is the mean radius of gyration, and σ is the intermolecular distance.

Besides modification of Debye equation (1.20) several empirical approaches to the problem of internal viscosity have been made.

Starting from Fischer equation (1.21) Hase[24] developed an expression for microscopic viscosity in terms of macroscopic viscosity

$$\eta_{micro} = \eta_1 \exp\left(-\frac{A V_2}{V_1}\right) \tag{1.26}$$

and are the molecular volume of polar solute and the non polar solvent and A is a numerical parameter.

Higasi[25] suggested that for highly viscous medium the relaxation time should be represented by

$$\tau = A \eta^{x} \tag{1.27}$$

where A is a constant, x is a parameter less than unity and the equation was valid for one temperature.

Halman[26] found that if the constant A is replaced by B/T then the eqn. (1.27) becomes valid over a small temperature range and the eqn. can be written in the form as

$$\tau = \frac{B}{T} \eta^{x} \tag{1.28}$$

Bhattacharyya et al.[27] and Sinha et al.[28] derived an expression

$$\eta_{int} = A \eta^{\gamma} \tag{1.29}$$

where $\gamma = \frac{\Delta H_\tau}{\Delta H_\eta}$

Equations (1.21) and (1.22) were examined by Pitt and Smyth[29] equation (1.24) were examined by Murty[30], Meakins[31], Pitt and Smyth[32] and others. Equation (1.26) was tested for high viscous solution by Kalman and Smyth[33]. It was found that if one equation was applicable for some molecule at some viscosities, for other molecules it fails. No single expression was found which is applicable for all molecules in solvent of different viscosities. It was found that Hill's equation is best suited to systems wgere the sizes of the solvent and the solute were not far from unity. Meakin[34] found that if the sise of the solute were three times as large as the solvent, the Debye equation is then applicable.

1.4 Distribution of Relaxation times

In the previous section the applicability of the Debye equation (1.20) which is concerned with rigid spherical molecule with a single relaxation time was discussed. But generally molecules are not spherical in shape, may be ellipsoidal or long chain. As mentioned earlier in Section (1.3.1), the ellipsoidal molecules having different relaxation times along three axes, would give rise to a distribution of relaxation times. Similarly in long chain molecules or molecules with flexible group a number of relaxation processes may simultaneously occur due to the orientation of different units about different segments. This may cause a distribution of relaxation times. Several types of distribution function have been developed and only the more important ones are discussed below.

1.4.1 Frohlich's distribution of relaxation times

Frohlich[6] considered a model in which each molecule has two equilibrium positions with opposite dipole orientations and has given an analysis for the continuous distribution of relaxation times between two limiting values τ_1 and τ_2. He assumed that if $y(\tau)d\tau$ is the contribution to static dielectric constant of the groups of dipoles having individual relaxation time in a range $\partial\tau$ near τ the total contribution of all the dipoles is

$$\epsilon_0 - \epsilon_\infty = \int_0^\infty y(\tau)\,d\tau \qquad (1.30)$$

Then following Debye eqns., (1.2) and (1.3)

$$\epsilon' = \epsilon_\infty + \int_0^\infty \frac{y(\tau)\,d\tau}{1+(\omega\tau)^2} \qquad (1.31)$$

$$\epsilon'' = \int_0^\infty \frac{y(\tau)\,\omega\tau\,d\tau}{1+(\omega\tau)^2} \qquad (1.32)$$

On simplification Frolich arrived at the expression for uniform distribution of potential barrier over a range v_0

$$\frac{\tau_1 - \tau_2}{\tau_2} = e^{v_0/KT} - 1 \qquad (1.33)$$

where v_0 is the potential barrier between the limit τ_1 and τ_2 The expression shows that the distribution should decrease with the increase of temperature, the truth of which is observed in most cases. Higasi et al.[35] used Frohlich's distribution for the analysis of dielectric data of alkyl bromides. The lowest τ_2 value was attributed to the rotation of the $-CH_2Br$ group and the highest τ_1 value was attributed to rotation of the whole molecule.

1.4.2 Cole Cole distribution of relaxation times

It was observed that the Debye equations (1.2) and (1.3) could be combined into a single equation

$$\left(\epsilon' - \frac{\epsilon_0 + \epsilon_\infty}{2}\right)^2 + \epsilon''^2 = \left(\frac{\epsilon_0 - \epsilon_\infty}{2}\right)^2 \qquad (1.34)$$

which is the equation of a circle. The plot of dielectric permittivity ϵ' and dielectric loss ϵ'' should be a semicircle (shown in Fig.1.1a) for the molecules which conforms to Debye equation as in the case of isobutyl bromide or halobenzenes.

Cole-Cole[36] observed that in a number of cases such plot is not semicircular but arc of a circle (shown in Fig.1.1b) intercepting the abscissa at values of ϵ_0 and ϵ_∞ with centre depressed below the abscissa axis. For these cases Cole and Cole put forward an empirical distribution function α given by a modified Debye equation

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{(1 + i\omega\tau_0)^{1-\alpha}} \qquad (1.35)$$

The value of α which lies between 0 and 1, gives a measure of distribution of relaxation times. α is obtained from the angle $\theta = \frac{\alpha\pi}{2}$ made by the diameter with the abscissa at ϵ_∞ point. The value of τ_0 which gives the most probable relaxation time is obtained from the relation

$$\frac{v}{u} = (\omega \tau_0)^{1-\alpha} \qquad (1.36)$$

where v is the distance of ϵ_0 to the experimental point on the Cole-Cole plot and u is the distance from the ϵ_∞ point to the same experimental point.

1.4.3 Davidson and Cole distribution

In a number of cases it was observed that the plot of ϵ' against ϵ'' was the form of a skewed arc (shown in Fig.1.1c). The result in these cases are better represented by Debye equation modified by Davidson and Cole[37] is given by

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{(1 + i\omega\tau_0)^\beta} \qquad (1.37)$$

where β is the constant lying between 0 and 1, when $\beta = 0$ the equation reduces to Debye equation. Skewed arc representation were observed by Mopsik and Cole[38] in pure haloethanes, by Higasi and co-workers[39] in Anthrones and in super cooled terphenyl solution, by Krishnaji et al.[40] in alkylthiols, Smyth and co-workers[41] in dibromoalkanes.

1.4.4 Distribution of more than one discrete relaxation times

The distribution in molecules having polar group or groups freely rotating with respect to each other and each carrying a invariant dipole moment was considered by Budo[42] and Kirkwood and Fuoss[43]. The dielectric behaviour in these cases was considered

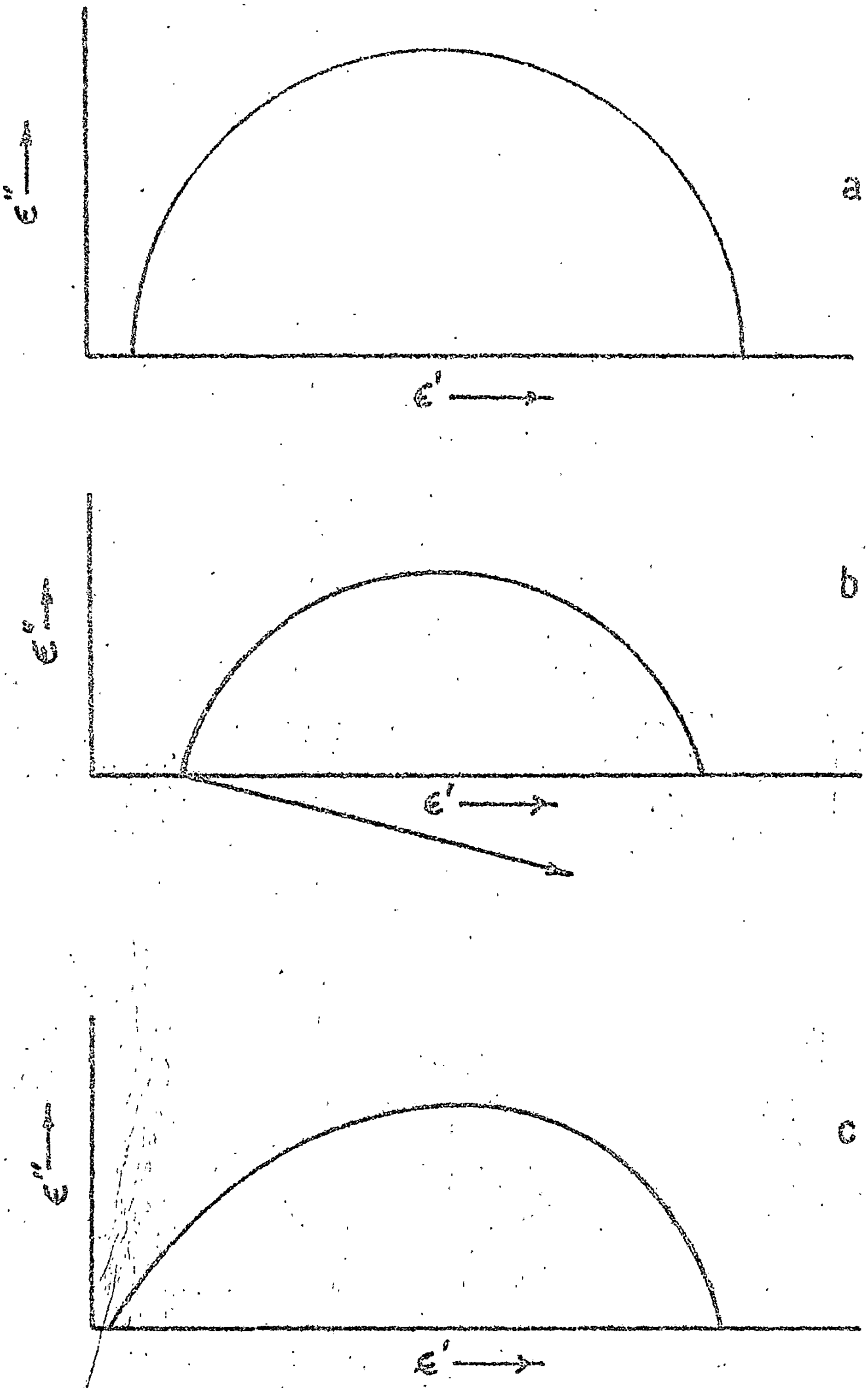

FIG.1.1

a) Debye semicircular arc plot

b) Cole-Cole arc plot

c) Davidson-Cole skewed arc plot

by Budo[42] as the superposition of the dispersions due to i) orientation of the molecule as a whole ii) orientation of different polar groups each obeying Debye equation with single relaxation time. The equations connecting ϵ' and ϵ'' were expressed by Budo as

$$\frac{\epsilon' - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \sum_i \frac{C_i}{1 + (\omega \tau_i)^2} \qquad (1.38)$$

$$\frac{\epsilon''}{\epsilon_0 - \epsilon_\infty} = \sum_i \frac{C_i \omega \tau_i}{1 + (\omega \tau_i)^2} \qquad (1.39)$$

where C_i's are the relative weight factors for different relaxation process, such that $\sum_i C_i = \frac{\sum \mu_i^2}{\mu^2} = 1$. The τ_i's are the relaxation times due to different orientating units associated with moments μ_i's and μ is the total moment of the molecule. The above equations are valid for molecules where there is no interaction between different orienting units. The analysis of dielectric data into a number of discrete relaxation times becomes too difficult and more so, if the relaxation times are too close. Different workers made different approaches for analysis of their data into two discrete relaxation processes. Vaughan et al.[44] found out a method for the determination of molecular and intramolecular relaxation by assuming superposition of the two Debye regions at a particular temperature.

Fong and Smyth[45] developed the double arc method in which they graphically analyse the data for two overlapping regions of the dielectric dispersion and found out the molecular and intramolecular relaxation times.

1.5 Method of analyses in two discrete relaxation times

1.5.1 Bergmann's method

Following Budo's equation (1.38) and (1.39), Bergmann et al.[46] put forward the following two equations for analyses of data into two discrete relaxation mechanisms.

$$\frac{\epsilon' - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{C_1}{1+(\omega\tau_1)^2} + \frac{C_2}{1+(\omega\tau_2)^2} \tag{1.40}$$

$$\frac{\epsilon''}{\epsilon_0 - \epsilon_\infty} = \frac{C_1\omega\tau_1}{1+(\omega\tau_1)^2} + \frac{C_2\omega\tau_2}{1+(\omega\tau_2)^2} \tag{1.41}$$

where τ_1 and τ_2 are two relaxation times and C_2 and C_2 their relative weight factors, such that $C_1 + C_2 = 1$ and $\frac{C_1}{C_2} = \frac{\mu_1^2}{\mu_2^2}$ μ_1 and μ_2 being the moments components responsible for respective relaxation processes. The Bergmann equations are widely used and have been used by many workers for analysis the data into two discrete relaxation processes by trial and error method.

1.5.2 Kastha's method

Bergmann's two equations having three unknown quantities τ_1, τ_2 and C_1 or C_2 can not be solved directly and different workers solved the equations (1.40) and (1.41) by trial and error method. Kastha[47] suggested an analytical method for straight forward calculations of τ_1 τ_2 and C_1

Combining the two equations of Bergmann and simplifying, equations

$$\frac{1-a}{b} = x_1 + x_2 - \frac{a}{b}x_1x_2 \tag{1.42}$$

and $$C_1 = \frac{(b - a x_2)(1 + x_1^2)}{x_1 - x_2} \qquad (1.43)$$

were obtained,

where $a = \frac{\epsilon' - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty}$, $b = \frac{\epsilon''}{\epsilon_0 - \epsilon_\infty}$

and $x_1 = \omega\tau_1$, $x_2 = \omega\tau_2$

The equation (1.42) is a equation of straight line, the slope of which gives $x_1 x_2$ and the intercept gives $x_1 + x_2$ for which τ_1 and τ_2 can be determined and from equation (1.43) C_1 can be determined. The equations (1.42) and (1.43) were successfully used by different workers[48-50].

1.6 Review of previous works

1.6.1 Rigid and Non rigid molecules with most probable relaxation times

Various workers used Cole-Cole method for the analysis of dielectric data in rigid and non rigid molecules of different shapes and sizes and reported the structural peculiarties of the molecules affected the relaxation times to a great extent.

Hennelley et al.[51] studied the dielectric behaviour of twenty seven organic polar molecules of different shapes, sizes and rigidity. Those which are spherical, conformed to Debye equation, for asymmetric molecules, distribution of relaxation times were found, the distribution increased with the increasing asymmetry, but decreased with rising of temperature.

Smyth and co-workers[52] observed that if the molecular shape and dipole direction of a set of molecules are closely similar, there exists a rough similarity between τ and η

But Miller and Smyth[53] reported that if the molecules have similar size, dipole moment and viscosity but different dipole direction their relaxation times are widely different.

In a number of haloethanes Crossley et al.[54] observed that the mean relaxation time and the distribution parameter increases with increase in size of the molecules.

In various aliphatic esters reported by various workers[55-58] the mean relaxation times as also the distribution increase with increase in size of the ester molecules.

Higasi and co-workers[59-61] studied a series of aliphatic alcohols in various solvents and obtained the principal relaxation time and Kirkwood g factor. Large molecules of triphenyl phosphine, triphenylarsine etc. were studied by Hassel et al.[62] who reported that the large relaxation time were in conformity with their sizes.

Formation of molecular complexes with solvents were reported by various workers[63-65] in substituted phenols from the lengthening of relaxation times.

The mean relaxation time in alkylcyanides and alkylthiols in the liquid state reported by Krishnaji and co-workers[66,40], was found to increase with increasing size of the molecules. The increase in the distribution parameter in alkylthiols at higher temperature was attributed to the orientation of various segments at higher temperature.

In a number of 1,2-disubstituted ethanes in the liquid state Hassan et al.[67-70] reported that the mean relaxation time increases with the increase in size of the molecules. They also pointed out that the dipolar activation energy in each case has got a parallelism with the lowering of the energy difference between the trans and gauche isomers from gaseous to the liquid state. They also observed that the dipolar activation energy was fairly equal to the electrostatic potential energy difference between the polar isomers in the liquid state.

1.6.2 Molecules with two discrete relaxation processes

Molecular and intramolecular relaxation processes in aromatic molecules having polar group such as $-OH$, $-SH$, NH_2, $-OCH_3$, $-N(CH_3)_2$, $-OCH_2Cl$, $-COCH_3$, $-CHO$, $-CH_2X$ (X = halogens, CN, SH, NH_2) etc. have been reported by many workers[71-82] mostly in dilute solution and in some cases in pure liquids. The molecular and group relaxation times in those cases were found consistent with their sizes. But the much lower relaxation time of the $-NH_2$ group compared to the $-OH$ group, was attributed to motion similar to the inversion of ammonia. It was interesting to note that in the disubstituted benzenes with similar substituents such as as $-OCH_3$, $-CH_2CN$, $-CH_2Br$, $-NH_2$ etc.[83,84] in the paraposition, the mean relaxation time was found to be much smaller than that when the same substituents are in the ortho and meta positions[72,79]. In the former case the relaxation was attributed to group rotation, while in the latter cases both the molecular and group rotation were present.

The surprisingly low relaxation time compared to the sizes of diphenyl ether[85], diphenyl methane and benzylether[86,87] and triphenylamine[88] was associated with some form of intramolecular motion in them.

Recently, Higasi and co-workers[89] reported that in the diphenyldioxide type of molecules, the small relaxation time might be due to butterfly motion of the two rings.

In some substituted phenols Magee and Walker[90] reported that both molecular and group rotation were present, but the group relaxation time was lengthened due to hydrogen bonding.

Has~~s~~an et al.[91,92] reported that while the esters of benzoic acid relax by molecular and group rotation, the monocarboxylic esters relax only by molecular reorientation.

It has been reported in primary amines[93] and ketones[94] that the dipole orientation takes place predominently by group rotation.

In the α, ω dihaloalkanes Garg and Smyth[41] and Suresh Chandra et al.[95] in pure liquid and dilute solution, the dipole orientations occurs by two mechanisms, the larger relaxation time was consistent with size of the molecules and the smaller relaxation time was consistent with the size of the end group $-CH_2X$.

Goulon et al.[96] reported a very small relaxation time due to intramolecular motion involving cis/trans transformation of the diacetyl molecule.

1.6.3 Poley absorption (absorption in submillimeter region)

While studying dielectric relaxation in various rigid molecules, Poley[97] observed a second dispersion in the submillimeter region, in addition to the normal dispersion in the cm. region due to molecular orientation. Confirmatory evidence of 'Poley absorption' in other molecules were reported by many workers[98-102]. From far infrared absorption in various polar and non polar molecules Davies et al.[103] concluded that the Poley absorption might be due to a fluctuating dipole element in polar liquids, while non polar absorption might be due to molecular collisions. Walker and co-workers[104,105] from similar studies in various molecules concluded that the Poley absorption can not be accounted for by simple rotational mechanism. Goulon et al.[106] from studies in submillimeter microwaves (112 GH_z) and in far infrared concluded that far infrared 'excess absorption' are complicated. Both resonance and non resonance absorption with some interaction of small group do occur. It appears that the situation is still not very clear.

1.6.4 Miscellaneous studies

a) Mixture of dipolar liquids

Relaxation studies of dipolar mixtures initiated by Alexandrov and Dzhian[107] and Schallamach[108] were followed by several workers. The more recent work of Forest and Smyth[109], Kadaba and co-workers[110-113] and others[114,115] showed that in the mixtures of non-associated liquids, the relaxation is the resultant of relaxation processes of individual compounds. In case of mixtures of associated liquids, the relaxation involves molecular clusters.

b) Associated liquids

In alcohols, the molecules are known to exist in a highly associated state. Relaxation studies in alcohols by different workers[116-123] indicate that there exist three distinct relaxation regions. The dispersion in the lowest frequency regions is associated with the relaxation of molecular clusters. The dispersion in highest frequency region arises due to the hydroxy group rotation and the dispersion in the intermediate frequency region is assigned to the rotation of free alcohol molecule arising out of frequent breaking of hydrogen bonds.

c) High polymers

Relaxation studies were also used in high polymers[124-128]. It is observed that in some cases polymeric chain exist as bent rods and in some other cases as flexible coils. The distribution parameter increases with increase in temperature, sometimes attains as high as 0.9.

d) Liquid crystals

Relaxation studies have been made by different workers[129-133] in various nematic and cholesteric liquid crystals. The magnitude and sign of the dielectric anisotropy are found to be frequency and temperature dependent. The relaxation time due to the respective rotation of the molecules perpendicular and parallel to the long axes are found to be different. The sign of the anisotropy and the relaxation time play important role in practical application of liquid crystals as display devices.

e) Biomolecules

Relaxation measurement have been made in biomolecules of amino acids, peptides and proteins in water solution in radio frequency region by various workers[134-136] and various molecular parameters were determined. The breaking and formation of N-H..O and O-H..O in amino acids and peptides respectively, takes place respectively as observed from the constancy in the values of free energy and enthalpy of the molecules. Three dispersion regions β γ and δ observed in protein molecules. The dispersion is concentration dependent and is attributed to bound water molecules.

1.7 Scope and Objects of the present investigations

A brief review of the studies of dielectric relaxation in various organic polar molecules in the liquid state and in solution was presented in the last sections. It is noted that much informations regarding the structural parameters of the molecules are obtained from such studies. It was also observed that though molecular and intramolecular motions in aromatic and aliphatic molecules with groups such as $-OH$, $-NH_2$, $-OCH_3$, $-COCH_3$, $-CHO$, $-N(CH_3)_2$ and $-CH_2X$ (X = halogens, $-NH_2$, $-CN$) etc have been reported by many workers but such studies in organic molecules having groups $-SH$, $-SCH_3$, $-NCO$, $-NCS$, $-NSO$, $-CH_2CH_2CH_2X$ (X = halogen, $-NH_2$, $-SH$) etc. are very few. It was therefore, thought worthwhile to select the following aromatic and aliphatic molecules in the liquid state and in some cases in solution for the present investigations.

Aromatic molecules : Benzene substituted molecules with groups $-SH$, SCH_3, $-NCO$, $-NCS$, $-NSO$, $CH_2CH_2CH_2X$ (X = halogen, $-SH$, $-NH_2$).

Aliphatic molecules : 2-halosubstituted propionates, 3-halosubstituted propionates, 4-halosubstituted butyrate, α,ω -dicyanoalkanes, 1,3-propanedithiol and 1,2,3-tribromopropane.

The object was to study -

1) The possibility of internal rotation in these molecules.

2) To apply the method of least squares instead of trial and error method and graphical methods used by other workers, for the analysis of the experimental data in terms of molecular and intramolecular relaxation times and their relative weight factors.

3) To determine the potential energy barrier for molecular orientation, group rotation and viscous flow.

4) To evaluate the dipole moment of the molecules.

5) To find out the existence of molecular conformations if any, and if so, to point out the possible conformation particularly in aliphatic molecules.

6) To find out if any, high frequency dispersion region of 'Poley type' is present.

The experimental technique for the measurements of dielectric data is given in Chapter 2.

The results and their interpretations are presented in Chapters 3 to 10. A summary of the results and conclusions are given in Chapter 11.

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