

PART - A

Chapter 1

**GENERAL INTRODUCTION AND
REVIEW OF THE PREVIOUS WORKS**

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1.1 POLARISATION

The theory of dielectric relaxation phenomena of polar molecules and polar-nonpolar liquid mixtures goes back to the time when Debye¹ published a monograph entitled "Polar molecules" in 1929. When a dielectric material is placed under a static electric field different types of polarisation occur. The centre of gravity of negative charges due to the electrons and that of positive charges for the nucleus of the molecules get displaced in opposite directions thereby causing the local dipole. This process of creation of induced dipoles in non-polar molecules is called the electronic polarisation. The external field may also cause displacement of the atoms or ions within the molecules and thereby changes the interatomic or interionic distances. An induced dipole moment is thus created to yield the atomic polarisation. The electronic and atomic polarisation per unit local field is known as electronic polarisability α_e and atomic polarisability α_a respectively. α_a is, however, of the order of 10% to 15% of α_e . The sum of them is called distortion polarisability α_d . When the dielectric molecules are asymmetric in nature they possess a permanent dipole moment μ due to the asymmetric distribution of charges in them. Under static electric field, in addition to the distortion polarisation, the polar dielectrics also suffer from the orientational polarisability α_o where

$$\alpha_o = \mu^2 / 3kT \quad \dots\dots\dots (1.1)$$

Here k is the Boltzmann constant and T is the temperature in Kelvin. In this case the permanent dipole tend to orient along the electric field direction. The alignment is, however, opposed by the thermal motions of molecules. Thus the

total polarisability in case of a dielectropolar molecule is :

$$\alpha_e + \alpha_a + \alpha_0 = \alpha_d + \mu^2/3kT \quad \dots\dots\dots (1.2)$$

Now, under the application of the alternating electric field each type of polarisation takes some finite time to respond to the applied electric field. Thus there exists a considerable lag in the attainment of the equilibrium. This lag in response to the alternation of the applied electric field is commonly known as dielectric relaxation. When the external electric field is switched off, all types of polarisation decay exponentially with time. The time in which the polarisation is reduced to 1/e times the original value is called the relaxation time. In the case of static or low-frequency electric field all the polarisation are operative. But as the frequency 'f' of the alternating electric field is very much greater than the relaxation time — the polarisation is not able to attain the equilibrium before the applied electric field is reversed. Dielectric dispersion thus arises as a result of decay in the polarisation. In different regions of the frequencies of the applied electric field, different polarisabilities occur. For example the electronic polarisation is very much effective under the electric fields of optical frequencies.

When the frequency of the applied electric field exceeds certain critical value, the permanent dipoles can not follow the exact alternation of the electric field. The critical value of the frequency depends on the chemical composition, structure, shape and size of the dielectric molecules and on the temperature. The critical value of the applied electric field, in most cases, is higher than $3 \times 10^6 \text{ Sec}^{-1}$.

The polarisation acquires a component out of phase with the electric field and the displacement vector acquires a conductance-component in phase with the applied electric field resulting in thermal dissipation of energy. In such cases, it is used to connect the displacement vector \vec{D} and the applied electric field vector \vec{E} by

$$\vec{D} = \epsilon^* \vec{E} = (\epsilon' - j\epsilon'') \vec{E}, \quad \dots\dots\dots (1.3)$$

where $\epsilon^* = \epsilon' - j\epsilon''$ (1.4)

ϵ' and ϵ'' being the real and the imaginary parts of the complex dielectric constant ϵ^* . ϵ'' is often called the dielectric loss and j is a complex number, $j = \sqrt{-1}$. The loss tangent $\tan \delta$ is defined as

$$\tan \delta = \frac{\epsilon''}{\epsilon'} \text{ (1.5)}$$

1.2. CLAUSIUS MOSSOTTI EQUATION

The investigation of dielectric material started from the work of Clausius and Mossotti² for nonpolar gases when they are subjected to a strong electric field. The Clausius and Mossotti² equation for a nonpolar gas is :

$$\frac{\epsilon - 1}{\epsilon + 2} \frac{M}{\rho} = \frac{4\pi N\alpha}{3} \text{ (1.6)}$$

where ϵ is the dielectric constant, M is the molecular weight, ρ is the density of the dielectric material, N is the Avogadro's number and α is the total molecular polarisability except orientational polarisability of a molecule.

1.3. DEBYE EQUATION

Debye¹, extended the above eq: (1.6) for a polar dielectric. When the polar gas is subjected to a static electric field eq: (1.6) becomes :

$$\frac{\epsilon - 1}{\epsilon + 2} \frac{M}{\rho} = \frac{4\pi N}{3} \left(\alpha + \frac{\mu^2}{3kT} \right) \text{ (1.7)}$$

The eq: (1.7) is, however, used to estimate the dipole moment μ of a polar gas by plotting molar polarisation P_m where

$P_m = \frac{\epsilon - 1}{\epsilon + 2} \frac{M}{\rho}$ against the reciprocal of the temperature T in K. In case of a dilute solution of polar - nonpolar liquid mixture Debye's equation (eq: 1.7) can, however, be applied to determine the permanent dipole moment of the polar liquid. In such case, one polar unit is separated from the other by large number

of nonpolar molecules. It is, however, well known that Debye's equation (eq.1.7), in general, does not hold good for a pure polar liquid.

1.4. DEBYE EQUATION FOR POLAR - NONPOLAR LIQUID MIXTURE

The method to calculate dipole moment μ_j associated with each polar molecule behaving as a unit is to dissolve the polar liquid in a suitable nonpolar solvent in order to reduce the polar-polar interactions. This is only possible if the concentration of the solution is made extremely low.

Let us assume that we have two substances — one of the i th type which is nonpolar and the other of the j th type which is polar, mixed together to form a solution. Here n_i = the number of molecules of the i th liquid per c.c. and n_j = the number of molecules of the j th liquid per c.c., α_i and α_j are the deformational polarisabilities of the i th and j th liquids of molecular weights M_i and M_j respectively. They are mixed together to form a solution of a certain concentration. If ϵ_{ij} = the dielectric constant of a given solution we have from Debye's eq. (1.7):

$$\begin{aligned} \frac{\epsilon_{ij} - 1}{\epsilon_{ij} + 2} \frac{M_i x_i + M_j x_j}{\rho_{ij}} &= \frac{4\pi N}{3} \left[\alpha_i x_i + \alpha_j x_j + \frac{\mu_j^2}{3kT} x_j \right] \\ &= \frac{4\pi N}{3} \left[\alpha_i (1 - x_j) + \alpha_j x_j + \frac{\mu_j^2}{3kT} x_j \right] \\ &= \frac{4\pi N}{3} \alpha_i + \frac{4\pi N}{3} \left[(\alpha_j - \alpha_i) x_j + \frac{\mu_j^2}{3kT} x_j \right] \\ &= \frac{4\pi N}{3} \alpha_i + \frac{4\pi N}{3} \cdot \frac{\mu_j^2}{3kT} x_j \quad \dots\dots (1.8) \end{aligned}$$

[$\because \alpha_i = \alpha_j$ = distortion polarisability of the solute as well as solvent]

where x_i and x_j are the mole fractions of the solvent and solute defined by

$x_i = \frac{n_i}{n_i + n_j}$; $x_j = \frac{n_j}{n_i + n_j}$. Since $\alpha_j = \alpha_d + \mu_j^2 / 3kT$ and $\alpha_i = \alpha_d$ where α_d is the distortion polarisability of the solute as well as the solvent molecules. The above eq. (1.8) is also written as

$$\frac{\epsilon_{ij}-1}{\epsilon_{ij}+2} V_{ij} = \frac{\epsilon_i-1}{\epsilon_i+2} V_i + \frac{4\pi N \mu_j^2}{9kT} x_j, \quad \text{..... (1.9)}$$

where V_{ij} and V_i are the specific volumes of the solution and solvent respectively. In conformity with neutral dielectrics, taking $\epsilon = n_D^2$ where n_D is the refractive index, the eq. (1.9) may also be presented in another form :

$$\frac{n_{Dij}^2 - 1}{n_{Dij}^2 + 2} V_{ij} = \frac{n_{Di}^2 - 1}{n_{Di}^2 + 2} V_i \quad \text{..... (1.10)}$$

It is evident from eqs. (1.9) and (1.10) that μ_j of any dielectropolar liquid treated as a solute in a solution could, however, be measured.

From eqs. (1.9) and (1.10) one gets

$$\left(\frac{\epsilon_{ij}-1}{\epsilon_{ij}+2} - \frac{n_{Dij}^2 - 1}{n_{Dij}^2 + 2} \right) = \left(\frac{\epsilon_i-1}{\epsilon_i+2} - \frac{n_{Di}^2 - 1}{n_{Di}^2 + 2} \right) \frac{V_i}{V_{ij}} + \frac{4\pi N \mu_j^2}{3 \cdot 3kT} \frac{x_j}{V_{ij}}$$

$$\begin{aligned} \text{or,} \quad & \left(\frac{\epsilon_{ij}-1}{\epsilon_{ij}+2} - \frac{n_{Dij}^2 - 1}{n_{Dij}^2 + 2} \right) \\ & = \left(\frac{\epsilon_i-1}{\epsilon_i+2} - \frac{n_{Di}^2 - 1}{n_{Di}^2 + 2} \right) + \frac{4\pi N \mu_j^2}{9kT} c_j \quad \text{..... (1.11)} \end{aligned}$$

defining c_j as the molar concentration per unit volume i.e. $c_j = x_j / V_{ij}$ and $V_i / V_{ij} \rightarrow 1$ for extremely dilute solution.

Equation (1.11) apparently seems to be simple to yield μ_j of polar solute. But eq. (1.11) has not been used to measure μ_j because of its different values at different molar concentration. But Debye equation can only be applicable in

solution of extremely dilute concentration and hence the different parameters such as $\epsilon_{ij}, n_{Dij}, \rho_{ij}$ in eq. (1.11) would have to be determined at infinite dilution only by extrapolation.

1.5. EXTRAPOLATION TECHNIQUE

The extrapolation technique is, however, accompanied by errors for measurement. The difficulty in extrapolation technique arises due to the fact that the parameters involved in eq. (1.11) in most cases are not always linear.

Hedestrand³, Cohen Henrique⁴ and others^{5,6} suggested various types of extrapolation techniques to evaluate dielectric parameters and the total polarisation at infinite dilution. But all the methods are not free from some inherent difficulties to locate the exact magnitudes of the quantities required to be measured. The difficulties arise out of the calculation of $(\frac{\partial \rho_{ij}}{\partial x_j})_{x_j \rightarrow 0}$ and $(\frac{\partial n_{Dij}}{\partial x_j})_{x_j \rightarrow 0}$ by graphical extrapolation techniques. Bottcher⁶, however, calculated μ_j of a large number of polar solutes in different solvents by using different extrapolation methods. She found marked differences in the values of μ_j for phenol in benzene as a result of different extrapolation techniques. Higasi⁷ put forward the following empirical formula :

$$\mu_j = \beta (\Delta \epsilon / x_j)^{1/2} \quad \dots\dots\dots (1.12)$$

for the direct evaluation of the dipole moment. Here β is a constant which depends entirely on the physical properties of the solvent. For benzene as solvent $\beta = (0.9 \pm 0.1) D$ and $\Delta \epsilon = \epsilon_{ij} - \epsilon_i$ respectively. Later on, Krishna and Srivastava⁸ used the following relation :

$$\mu_j = \beta (d\epsilon_{ij} / dx_j)^{1/2} \quad \dots\dots\dots (1.13)$$

to calculate μ_j of some polar solutes in liquid state. The term $(d\epsilon_{ij} / dx_j)$ in eq. (1.13) represents the slope of ϵ_{ij} against x_j curve at $x_j \rightarrow 0$. In their calculations the value of β came out to be 0.828 D. Again, some workers⁹ found the different values of β for different polar liquids. A question, therefore, arises regarding the validity of Higasi-method.

Prakash¹⁰, however showed that eq. (1.13) is a special case of Debye's equation (eq. 1.11) when ϵ_{ij} is very nearly equal to unity. Since no such polar liquid mixture is available in practice for which $\epsilon_{ij} \simeq 1$, Higasi's method can not be regarded as a universal one to compute μ_j at all concentrations of the polar liquid.

1.6. GUGGENHEIM EQUATION AND EXTRAPOLATION TECHNIQUE

Guggenheim¹¹, later on, introduced a new concept of fictitious atomic polarisability in order to make the solution free from atomic polarisation. From eq. (1.11), a curve may be drawn with the measurable quantity $3(\epsilon_{ij} - n_{Dij}^2) / (\epsilon_{ij} + 2)(n_{Dij}^2 + 2)$ or simply $(\epsilon_{ij} - n_{Dij}^2)$ against c_j ; the slope of the resulting curve may be used to obtain μ_j of a polar solute (j) in nonpolar solvent (i). Writing $\Delta = (\epsilon_{ij} - n_{Dij}^2) - (\epsilon_i - n_{Di}^2)$ in eq. (1.11) we find an expression for μ_j of a polar liquid in nonpolar solvent like

$$\mu_j^2 = \frac{9kT}{4\pi N} \frac{3}{(\epsilon_i + 2)(n_{Di}^2 + 2)} \left(\frac{\Delta}{c_j} \right)_{c_j \rightarrow 0} \quad \dots\dots (1.14)$$

The above equation is, however, deduced on the basis of the fact that $\epsilon_i = n_{Di}^2$ according to Maxwell's electromagnetic theory¹². Smith¹³ subsequently introduced the idea of weight fraction w_j in place of c_j where

$$c_j = (\rho_{ij} / M_j) w_j \quad \dots\dots (1.15)$$

Guggenheim¹⁴, later on, modified the equation (eq. 1.14) for μ_j of a polar solute in terms of w_j

$$\mu_j^2 = \frac{9kT}{4\pi N} \frac{3}{(\epsilon_i + 2)^2} \frac{M_j}{\rho_i} \left(\frac{\Delta}{w_j} \right)_{w_j \rightarrow 0} \quad \dots\dots (1.16)$$

$$\text{where } \left(\frac{\Delta}{w_j} \right)_{w_j \rightarrow 0} = \left[\left(\frac{\partial \epsilon_{ij}}{\partial w_j} \right)_{w_j \rightarrow 0} - 2n_{Di} \left(\frac{\partial n_{Di}}{\partial w_j} \right)_{w_j \rightarrow 0} \right] \dots\dots (1.17)$$

M_j is the molecular weight of the polar solute and ρ_i is the density of the solvent used. In the above equations i.e. eqs. (1.16) and (1.17), it is necessary to get the required values by extrapolation of ϵ_{ij} and n_{Dij} against w_j to yield μ_j of a given polar liquid. Hence a large number of data of ϵ_{ij} and n_{Dij} for different weight fractions w_j 's for a given solute – solvent mixture were to be experimentally measured. Jai Prakash¹⁰ started from eq. (1.14) and deduced the following relation :

$$\mu_j^2 = \frac{27M_j kT}{4\pi N \rho_i} \left(\frac{\partial x_{ij}}{\partial w_j} \right)_{w_j \rightarrow 0} \dots\dots (1.18)$$

where the value of $\partial x_{ij} / \partial w_j$ in the limit $w_j = 0$ is given by :

$$\left(\frac{\partial x_{ij}}{\partial w_j} \right)_{w_j \rightarrow 0} = \left[\frac{1}{(\epsilon_i + 2)^2} \left(\frac{\partial \epsilon_{ij}}{\partial w_j} \right)_{w_j \rightarrow 0} - \frac{2n_i}{(n_i^2 + 2)^2} \left(\frac{\partial n_{ij}}{\partial w_j} \right)_{w_j \rightarrow 0} \right]$$

to obtain μ_j of a polar liquid. The eq. (1.18) reduces to the famous Guggenheim equation (1.16) if we put $\epsilon_i = n_{Di}^2$. Thus a conclusion may be reached that Guggenheim's formula is a special case of Debye formula when $\epsilon_i = n_{Di}^2$. Therefore, certain limitations always exist in all these processes of determining the dipole moments of a polar solute in nonpolar solvent. The limitations include that the polar solutes should be of high dipole moment and the solutions under measurement should be of low concentration. It is, therefore, obvious that the evaluation of μ_j depends on the theory of extrapolation of different physical parameters like ϵ_{ij} , n_{Dij} and ρ_{ij} of the solutions of different w_j 's of the polar solutes. As for example, in the case of trimethyl amine in benzene at 25°C, Le Fevre and Smyth⁵ and Guggenheim¹⁴ obtained two values of μ_j i.e. 0.91D and 0.83D by using different extrapolation techniques. Such affairs usually put the experimentalists to choose as to what method of extrapolation is needed to compute μ_j in a given system.

Acharyya et. al¹⁵ tried to develop the dielectric theory of polar-nonpolar liquid mixtures within the frame work of Debye's theory¹ because the Guggenheim-

equation (eq. 1.16) can be derived from Debye's equation¹, This was shown by Jai Prakash¹⁷. In the eq. (1.11) when c_j is replaced by w_j in $c_j = \rho_{ij} w_j / M_j$, the measurable quantities of the left hand side of eq. (1.11) is an implicit functions of ρ_{ij} and w_j . But ρ_{ij} , the density of the solution is a function of w_j also. We can thus define ρ_{ij} as :

$$\begin{aligned} \rho_{ij} &= (W_i + W_j) / (V_i + V_j) = \frac{W_i + W_j}{\frac{W_i}{\rho_i} + \frac{W_j}{\rho_j}} \\ &= \frac{\rho_i \rho_j}{\frac{W_i}{W_i + W_j} \rho_j + \frac{W_j}{W_i + W_j} \rho_i} = \frac{\rho_i \rho_j}{w_i \rho_j + w_j \rho_i} \\ &= \frac{\rho_i}{1 - \left(1 - \frac{\rho_i}{\rho_j}\right) w_j} = \frac{\rho_i}{1 - \gamma w_j}, \end{aligned}$$

since $w_i + w_j = 1$ and let γ is a constant for the given solvent and solute of densities ρ_i and ρ_j respectively i.e. $\gamma = \left(1 - \frac{\rho_i}{\rho_j}\right)$. W_i and W_j are the respective weights

of the solvent and solute of volumes V_i and V_j to make a solution of weight fraction w_j of the polar solute. Hence the eq. (1.11) can now be written as :

$$\frac{\epsilon_{ij} - n_{Dij}^2}{(\epsilon_{ij} + 2)(n_{Dij}^2 + 2)} = \frac{\epsilon_i - n_{Di}^2}{(\epsilon_i + 2)(n_{Di}^2 + 2)} + \frac{4\pi N \mu_s^2}{27kT} \cdot \frac{\rho_i}{M_j} \cdot \frac{w_j}{(1 - \gamma w_j)}$$

$$\text{or, } X_{ij} = X_i + \frac{4\pi N \mu_s^2}{27M_j kT} \rho_i w_j (1 + \gamma w_j + \gamma^2 w_j^2 + \dots)$$

$$= X_i + \frac{4\pi N \mu_s^2 \rho_i}{27M_j kT} (w_j + \gamma w_j^2 + \dots)$$

$$= X_i + R w_j + R \gamma w_j^2 + \dots \dots \dots (1.19)$$

where $R = (4\pi N\mu_s^2\rho_i) / 27M_jkT$ and μ_s = static dipole moment under static electric field. The eq. (1.19) as derived, is of highly converging in nature for the low concentration of the solution of polar-nonpolar liquid mixture under investigation. Thus the eq. (1.19) can be expressed in finite number of terms like:

$$X_{ij} = a + bw_j + cw_j^2 \quad \text{..... (1.20)}$$

for w_j lying between $0 < w_j < 1$. Thus eq. (1.20) may be a linear one if we calculate the correlation coefficient r lying between $-1 \leq r \leq 1$ only to conclude that the parameters lie almost on the straight line. For $r < 0.95$, the experimentalist could apply the polynomial equations as given by the eqs. (1.19) or (1.20). The error in the regression equation of the type of eq. (1.20) could also be computed to shed light of the functional dependence of the evaluated μ_s of a single polar solute in a given nonpolar solvent. Equating the coefficients of equal powers of w_j from eq. (1.19) and (1.20) one gets:

$$(4\pi N\mu_s^2\rho_i) / (27M_jkT) = b$$

$$\text{or, } \mu_s = [(27M_jkTb) / (4\pi N\rho_i)]^{1/2} \quad \text{..... (1.21)}$$

$$\text{and } \mu_s = [(27M_jkTc) / (4\pi N\rho_i(1 - \rho_i/\rho_j))]^{1/2} \quad \text{..... (1.22)}$$

etc. to estimate the dipole moment of a polar solute in a nonpolar solvent.

To evaluate the values of the coefficients a , b & c etc. in eq. (1.20) two or three normal equations are usually formed for X_{ij} by fitting the available experimental data of $\epsilon_{ij}s'$ and n_{Dij}^2s' of a polar-nonpolar liquid mixture for different w_j 's.

They are :

$$\Sigma X_{ij} = ta + b\Sigma w_j + c\Sigma w_j^2$$

$$\Sigma X_{ij} \cdot w_j = a\Sigma w_j + b\Sigma w_j^2 + c\Sigma w_j^3 \text{ and}$$

$$\Sigma X_{ij} \cdot w_j^2 = a\Sigma w_j^2 + b\Sigma w_j^3 + c\Sigma w_j^4, \text{ where } t \text{ is the number of the experimental data available for a given system.}$$

The usual procedure for extrapolation for ϵ_{ij} & n_{Dij}^2 was to take the advantage of

calculus only to estimate the ratio of dependent and independent variables according to Le Fevre⁵. Moreover, the present extrapolation technique is a single one which seems undoubtedly a better simplification over the usual treatments where at least two least square fittings¹¹ were necessary in order to compute μ_s of a polar liquid. Although, the value of μ_s , if computed from eq. (1.22), is expected to be the same one as obtained from eq. (1.21). However, no rigorous explanation could at present be offered.

This theory so far developed, has already been tested for a large number of polar-nonpolar liquid mixtures¹⁵⁻¹⁷ to compute μ_s 's. This sort of procedure as stated above, has been widely used in this thesis.

The technique has been utilised to frame the normal equations of hf conductivities K_{ij} or K_{ijk} to get μ_j or μ_{jk} for a single or binary polar-mixture in a non-polar solvent at different w_j 's or w_{jk} 's at an experimental temperature. This could, however, predict the very nature of K_{ij} or K_{ijk} in the form :

$$K_{ijk} = \alpha + \beta w_{jk} + \gamma w_{jk}^2 \quad \dots\dots\dots (1.23)$$

where i denotes the solvent, j or k indicates solutes. α , β , and γ are the coefficients to be determined. The very nature of K_{ij} , K_{ik} or K_{ijk} as a function of w_j , w_k or w_{jk} is shown graphically elsewhere³⁶. Recently Suryavanshi and Mehrotra¹⁸ suggested the least square fit method to determine the molecular properties viz. the dipole moment and the relaxation time in dilute liquid systems using Debye and Smyth model of dielectric relaxation data. The above mentioned authors¹⁸ were, however, inspired by our works¹⁹. They¹⁸ applied this technique in five important liquids like nitrobenzene, ethyl benzoate, methyl acetate, benzophenone and acetone. They¹⁸ found that the fit methods are in excellent agreement with those of graphical methods due to Gopala Krishna²⁰ and Smyth²¹. A conclusion is, therefore, reached that the present fit method is not only an accurate one, but it also gives an estimation of the % of errors in terms of the correlation coefficient 'r' in the values to be determined.

In this thesis, we have tried to apply such a universal powerful technique based on rigorous mathematical basis to obtain μ_j , μ_k , or μ_{jk} of a large number of single (j or k) or binary (jk) liquids specially, amides, only to avoid personal judgement to locate the exact magnitudes¹¹ of the measured parameters.

1.7. REAL AND IMAGINARY PARTS OF DIELECTRIC CONSTANTS AND LOSS TANGENT

When a dielectric material medium is subjected to an alternating electric field of a certain frequency, two cases may arise. In one case, there exists no measurable phase difference between \vec{D} and \vec{E} which usually occurs in low frequency electric field. For this case we can use the relation $\vec{D} = \epsilon \vec{E}$. But in other case i.e. for hf electric field there is a considerable phase difference between the displacement vector \vec{D} and the applied electric field \vec{E} . Then the simple relation $\vec{D} = \epsilon \vec{E}$ does not hold good at different temperatures and for different dielectrics. The essential and important difference between the two cases, as mentioned above, is that in the second case there is a considerable absorption of electrical energy by the dielectric material at a given temperature from the applied electric field of a suitable frequency unlike in the first case. This sort of absorption of electrical energy from the applied electric field $\vec{E}(t) = \vec{E}_0 e^{j\omega t}$, where ω is the angular frequency of the applied electric field constitutes a phenomenon of "dielectric loss". The phase difference between \vec{D} and \vec{E} can, however, occur for a dielectric material due to (i) electrical conduction due to transport of charge which gives rise to the electrical conductivity, (ii) relaxation effect for the permanent dipoles and (iii) resonance effect for the rotational or the vibrational motions of the molecules, molecular ions or electrons present in the dielectric liquids.

In order to account for the phase difference between \vec{D} and \vec{E} let us consider $\vec{E}^* = \vec{E}_0 e^{j\omega t}$ and $\vec{D}^* = \vec{D}_0 e^{j(\omega t - \delta)}$. Here, δ is the required phase difference and $\omega = 2\pi f$, f being the frequency of the alternating electric field in kilo Hertz or Giga Hertz.

$$\text{Now, we can write } \epsilon = \vec{D}^* / \vec{E}^* = (D_0 / E_0) e^{-j\delta} = (D_0 / E_0) (\cos\delta - j \sin\delta) \dots (1.24)$$

only to show that the dielectric constant is a complex one in hf electric field. The complex dielectric constant ϵ^* consists of a real ϵ' and a imaginary part ϵ'' such that

$$\epsilon^* = \epsilon' - j\epsilon'' \dots (1.25)$$

Thus $\epsilon' = (D_0 / E_0) \cos \delta$ and $\epsilon'' = (D_0 / E_0) \sin \delta$. The dielectric loss can also be expressed in terms of $\tan \delta$ by :

$$\epsilon'' = \epsilon' \tan \delta \quad \text{..... (1.26)}$$

where $\tan \delta$ is the loss tangent.

1.8. DIELECTRIC LOSS AND HIGH FREQUENCY CONDUCTIVITY

When a polar dielectric is subjected to an alternating electric field of the type $E = E_0 e^{j\omega t}$, the conductivity K , due to displacement current alone is given by

$$K = (1/E) (dq/dt) \quad \text{..... (1.27)}$$

Again, $D = 4\pi q = E + 4\pi\rho$ and $E = V/d = D/\epsilon$, we have

$$\frac{dq}{dt} = \frac{1}{4\pi} \frac{dD}{dt} = \frac{\epsilon}{4\pi d} \frac{dV}{dt} = I \text{ (say)}$$

The applied potential difference V is also alternating like $V = V_0 e^{j\omega t}$, where V_0 is the amplitude, the expression for the displacement current I is given by,

$$I = \frac{dq}{dt} = \frac{\epsilon^*}{4\pi d} \frac{dV}{dt}$$

Introducing $\epsilon^* = \epsilon' - j\epsilon''$ and $V = V_0 e^{j\omega t}$ in the above equation, I is then given by:

$$\begin{aligned} I &= \frac{\epsilon' - j\epsilon''}{4\pi d} j\omega V_0 e^{j\omega t} \\ &= \left(j \frac{\omega\epsilon'}{4\pi} + \frac{\omega\epsilon''}{4\pi} \right) \frac{V_0}{d} e^{j\omega t} \\ &= \left(\frac{\omega\epsilon''}{4\pi} + j \frac{\omega\epsilon'}{4\pi} \right) E_0 e^{j\omega t} \quad \text{..... (1.28)} \end{aligned}$$

According to Ohm's law we have

$$I = K E_0 e^{j\omega t} \quad \text{..... (1.29)}$$

where K is called the total hf complex conductivity being given by

$$K = K' + jK'' \quad \text{.....(1.30)}$$

Thus K' = the real part of the hf conductivity = $\omega \epsilon'' / 4\pi$ and

K'' = the imaginary part of the hf conductivity = $\omega \epsilon' / 4\pi$.

In the deductions, it was, however, assumed that the conduction current due to free molecular ions and electrons in impure liquids, is neglected. The magnitude of the total hf - conductivity is now written as :

$$K = (\omega/4\pi) (\epsilon'^2 + \epsilon''^2)^{1/2} \quad \text{..... (1.31)}$$

1.9. DEBYE EQUATION AND CONDUCTIVITY UNDER HIGH FREQUENCY ELECTRIC FIELD

Again, Debye - equation for the complex dielectric constant ϵ^* is

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + j\omega\tau} \quad \text{..... (1.32)}$$

where ϵ_0 , ϵ_∞ are the static and high frequency dielectric constants and τ is the relaxation time. Equating the real and imaginary parts from the right hand sides of the eqs. (1.25) and (1.32) we get

$$\epsilon' = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + \omega^2\tau^2} \quad \text{and}$$

$$\epsilon'' = \frac{\epsilon_0 - \epsilon_\infty}{1 + \omega^2\tau^2} \omega\tau \quad \text{..... (1.33)}$$

The expressions for conductivities are, therefore, written as

$$K' = \frac{1}{4\pi} \frac{\epsilon_0 - \epsilon_\infty}{1 + \omega^2\tau^2} \omega^2\tau \quad \text{and} \quad \text{..... (1.34)}$$

$$K'' = \frac{\omega}{4\pi} \left(\epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + \omega^2\tau^2} \right) \quad \text{..... (1.35)}$$

The variation of ϵ'' with respect to the angular frequency ω of the applied electric

field can be judged if we differentiate eq. (1.33) with respect to ω . The maximum value of ϵ'' is found when $\omega\tau = 1$. The frequency corresponding to the maximum value of ϵ'' is known as the critical frequency $f_0 = 1/2\pi\tau$. Thus the value of f_0 experimentally determined, seems to provide a method to estimate τ . But the situation is different in the case of variation of K' as shown in eq. (1.34) with respect to ω . Differentiation of K' in eq. (1.34) w.r.to ω shows that K' increases with ω and K' approaches a limiting value of K'_∞ at an infinite frequency. Since $\omega^2\tau^2 \gg 1$ when ω is very large K'_∞ is

$$K'_\infty = \frac{\epsilon_0 - \epsilon_\infty}{4\pi\tau} \dots\dots\dots (1.36)$$

Equation (1.36), therefore, suggests a method of measuring τ from the knowledge of the hf conductivity of a dielectric material. It is needless to mention that τ of a dielectric material is the most useful parameter in understanding the nature of the intermolecular field, the structure and the activation energy of a molecule. In all the above considerations, it is assumed that there are no free ions or electrons in the dielectrics and the displacement current is the only factor to contribute to the total conductivity as assumed by Murphy and Morgan²².

But this fact is far from reality. A large number of workers²³⁻²⁵ had detected the very existence of free ions and electrons in the dielectrics available in the purest form. Sen and Ghosh²⁶, however, indicated that the existence of free ions or electrons in a dielectric is due to the presence of trace impurity in the dielectric. The percentage of ions in polar dielectrics is greater than those in nonpolar dielectrics. When an electric field is set up across a dielectric, the total heat produced in the dielectric is not only due to dielectric loss ϵ'' , but due to Joule's heating also. The dielectric parameters measured in terms of hf - conductivity conclusively establish a fact that the conduction through the polar dielectrics is due to the combined effect of the displacement current and the conduction current.

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1.10. DIELECTRIC LOSS, RELAXATION TIME AND THE DISTRIBUTION OF RELAXATION TIME

The conception of the complex dielectric-constant ϵ^* in the form of $\epsilon^* = \epsilon' - j\epsilon''$ helps us to deduce the expression of ultra high frequency conductivity of a dielectric under the action of the alternating electric field in the range of frequencies of 10^6 to 10^9 Hz. The polarisation of a dielectric material substance under the static electric field is $\vec{P}_s = (\epsilon_s - 1) \vec{E}/4\pi$. But we know that $\vec{P}_s = \vec{P}_D + (\vec{P}_s)_{dip}$, where $(\vec{P}_s)_{dipole}$ signifies that part of the polarisation due to parmanent dipole associated with each polar molecule and \vec{P}_D is the polarisation due to deformation of the molecule, given by $\vec{P}_D = (\epsilon_D - 1) \vec{E}/4\pi$. After a certain time t during the application of the electric field $\vec{P}_s \rightarrow \vec{P}_t$. Hence we can write :

$$\vec{P}_t = \vec{P}_D + \vec{P}_{dip} \quad \dots\dots (1.37)$$

Let us assume that the rate of increase of \vec{P}_{dip} with respect to t is proportional to the difference of values of $(\vec{P}_s)_{dip}$ and the \vec{P}_{dip} . Thus we have

$$\frac{d\vec{P}_{dip}}{dt} = \frac{1}{\tau} [(\vec{P}_s)_{dip} - \vec{P}_{dip}] \quad \dots\dots (1.38)$$

where τ is a constant known as the relaxation time. Equation (1.38) on intègration with respect to time t yields that

$$\vec{P}_{dip} = (\vec{P}_s)_{dip} (1 - e^{-t/\tau}) \quad \dots\dots\dots (1.39)$$

For alternating field at any time t

$$(\vec{P}_s^*)_{dip} = \frac{\epsilon_s - 1}{4\pi} E_t^* - \frac{\epsilon_\infty - 1}{4\pi} E_t^* \quad \dots\dots\dots (1.40)$$

$$\text{or, } (\vec{P}_s^*)_{dip} = \left(\frac{\epsilon_s - \epsilon_\infty}{4\pi} \right) E_t^* = \left(\frac{\epsilon_s - \epsilon_\infty}{4\pi} \right) E_0 e^{j\omega t} \quad \dots\dots\dots (1.41)$$

Eq. (1.38) can now be written as :

$$\frac{d(\vec{P}_{dip}^*)}{dt} = \frac{1}{\tau} \left[\frac{\epsilon_s - \epsilon_\infty}{4\pi} E_0 e^{j\omega t} - \vec{P}_{dip}^* \right]$$

which after integration yields :

$$\vec{P}_{\text{dip}}^* = C e^{-t/\tau} + \frac{1}{4\pi} \frac{\epsilon_s - \epsilon_\infty}{1+j\omega\tau} E_0 e^{j\omega t} \quad \dots\dots\dots (1.42)$$

The total polarisation after sufficient time t is given by

$$\begin{aligned} \vec{P}^* &= \vec{P}_\infty^* + \vec{P}_{\text{dip}}^* \\ &= \left[\frac{\epsilon_\infty - 1}{4\pi} + \frac{1}{4\pi} \frac{\epsilon_s - \epsilon_\infty}{1+j\omega\tau} \right] \vec{E}_0 e^{j\omega t} \quad \dots\dots\dots (1.43) \end{aligned}$$

This formula indicates that P* is a sinusoidal function of the time with same frequency of the applied field. Now, the dielectric displacement can be written as $\vec{D}^* = \epsilon^* \vec{E}^*$

$$\text{or, } \vec{D}^* = \vec{E}^* + 4\pi \vec{P}^*$$

$$\text{or, } \vec{D}^* = \vec{E}^* + \left[(\epsilon_\infty - 1) + \frac{\epsilon_s - \epsilon_\infty}{1+j\omega\tau} \right] \vec{E}^*$$

$$\text{or, } \epsilon^* \vec{E}^* = \vec{E}^* + \left[\frac{(\epsilon_\infty - 1)(1+j\omega\tau) + (\epsilon_s - \epsilon_\infty)}{1+j\omega\tau} \right] \vec{E}^*$$

$$\text{or, } \epsilon^* \vec{E}^* = \vec{E}^* + \left[\frac{(\epsilon_s - 1) + j\omega\tau (\epsilon_\infty - 1)}{1+j\omega\tau} \right] \vec{E}^*$$

$$\text{or, } \epsilon^* \vec{E}^* = \left(\epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1+j\omega\tau} \right) \vec{E}^*$$

$$\text{or, } \epsilon^* \vec{E}^* = \left[\epsilon_\infty + \frac{(\epsilon_s - \epsilon_\infty)(1-j\omega\tau)}{1+\omega^2\tau^2} \right] \vec{E}^*$$

$$\text{or, } \epsilon^* = \left[\epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1+\omega^2\tau^2} - j \frac{\epsilon_s - \epsilon_\infty}{1+\omega^2\tau^2} \omega\tau \right] \quad \dots\dots\dots (1.44)$$

The real part, ϵ' and the imaginary part, ϵ'' of eq. (1.39) are, therefore, given by:

$$\epsilon' = \epsilon_{\infty} + \frac{\epsilon_s - \epsilon_{\infty}}{1 + \omega^2 \tau^2} \quad \dots\dots\dots (1.45)$$

and $\epsilon'' = \frac{\epsilon_s - \epsilon_{\infty}}{1 + \omega^2 \tau^2} \omega \tau \quad \dots\dots\dots (1.46)$

which are similar with eqs. (1.33) if we put $\epsilon_s = \epsilon_o$.

Now, from eqs. (1.45) and (1.46) we can again write

$$\frac{\epsilon' - \epsilon_{\infty}}{\epsilon_s - \epsilon_{\infty}} = \frac{1}{1 + \omega^2 \tau^2} \quad \dots\dots\dots (1.47)$$

and $\frac{\epsilon''}{\epsilon_s - \epsilon_{\infty}} = \frac{\omega \tau}{1 + \omega^2 \tau^2} \quad \dots\dots\dots (1.48)$

In order to check the validity of the above two eqs. (1.47) & (1.48), the experimentally observed results are usually represented graphically by plotting ϵ' and ϵ'' against $\omega \tau$ in Figs 1.1 and 1.2 respectively. The plot of ϵ' and ϵ'' against the logarithm of frequencies, ω ($= 2\pi f$) or wave lengths λ ($= 2\pi c/\omega$) of the applied electric fields could have been done. The resulting curves of ϵ' against $\log \omega$ and ϵ'' against $\log \omega$ are called the dispersion and absorption curves respectively as shown in Figs. (1.3) and (1.4).

Another method of critically examining the above two eqs. (1.47) and (1.48) has been proposed by Cole-Cole²⁷. Their method is to construct an Argand diagram in a complex plane in which the imaginary part ϵ'' of ϵ^* is plotted against the real part ϵ' , provided each point corresponds to one frequency. Thus combining the eqs. (1.47) and (1.48) one gets

$$\left(\epsilon' - \frac{\epsilon_s + \epsilon_{\infty}}{2} \right)^2 + \epsilon''^2 = \left(\frac{\epsilon_s - \epsilon_{\infty}}{2} \right)^2 \quad \dots\dots\dots (1.49)$$

to represent the semicircle with radius $(\epsilon_s - \epsilon_{\infty})/2$, and centre lying on the

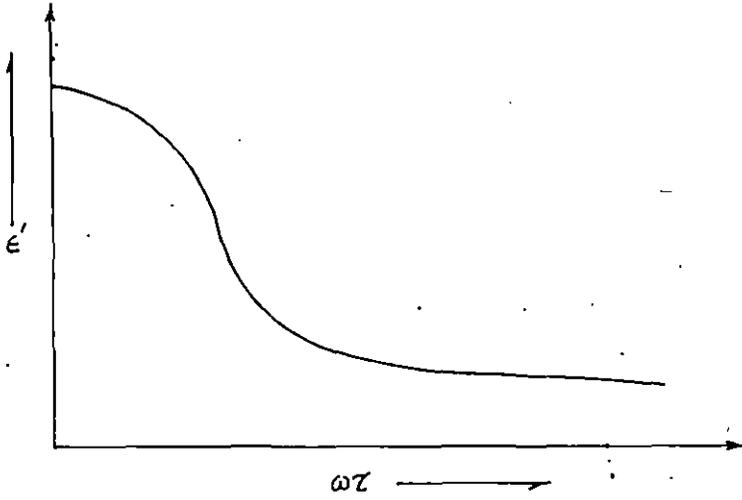


Fig. 1.1. Variation of real parts of dielectric constant with $\omega\tau$.

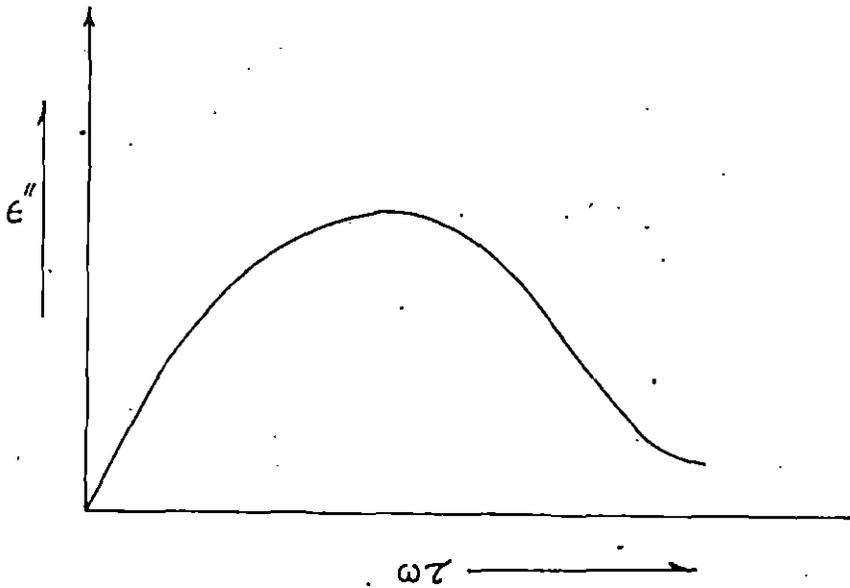


Fig. 1.2. Variation of imaginary parts of dielectric constant with $\omega\tau$.

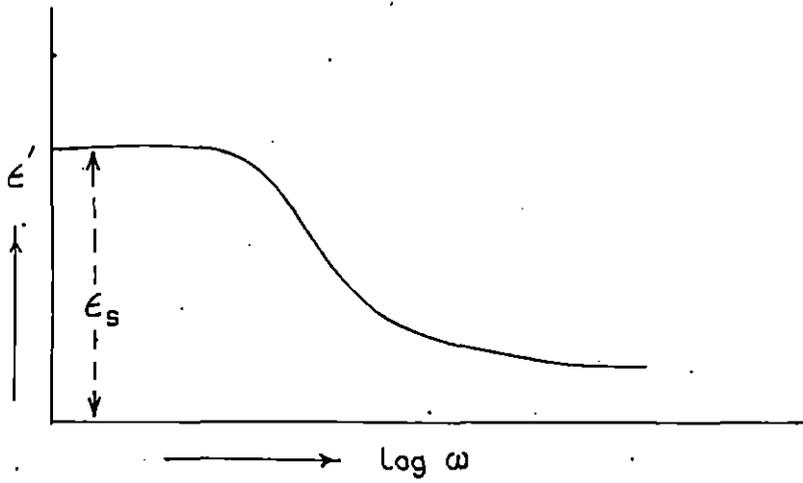


Fig. 1.3. Frequency dependence of real part of dielectric constant.

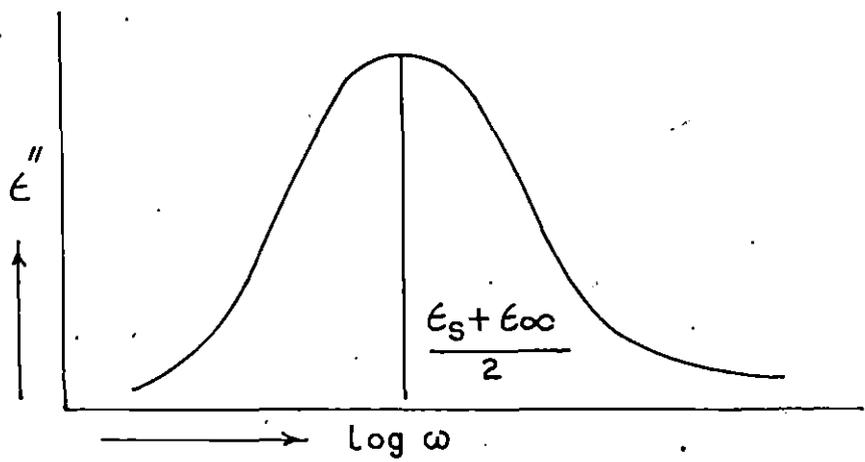


Fig. 1.4. Frequency dependence of imaginary part of dielectric constant.

abscissa at a distance $(\epsilon_s + \epsilon_\infty)/2$ from the origin. This is achieved by plotting ϵ'' against ϵ' measured for a large number of frequencies "f" of the applied electric field and is shown in Fig. 1.5. The intersection points with the abscissa, as shown in Fig. 1.5, are given by $\epsilon' = \epsilon_\infty$ and $\epsilon' = \epsilon_s$.

It has been found experimentally that almost all liquids even the lipid molecules such as glyceroltriacetate, glyceroltributrate, glyceroltripropionate etc.²⁸ satisfy the above eq. (1.44). Of course, there are some exception for disubstituted and polysubstituted benzenes. The dispersion curve is found to be flatter and extends over a wide range of frequencies while the absorption curve is broader and the maximum value of ϵ'' is smaller than the value given by $\epsilon''_m = (\epsilon_s + \epsilon_\infty)/2$. But still, the curves with the experimental points are found to be symmetrical as observed in Fig. 1.5. This is because of the fact that the behaviour of dielectrics can not be described by a single relaxation time. Cole and Cole²⁷ observed for a number of liquids and solids that the experimental curve is almost a circular arc, but with its centre lying under the abscissa. Cole and Cole²⁷ showed that the Debye semicircle as shown in Fig. 1.5, has its centre depressed below the abscissa axis as illustrated in Fig. 1.6. The radius drawn through the point $\epsilon' = \epsilon_\infty$ makes an angle α where $\alpha < 90^\circ$ with the abscissa axis of Fig. 1.6. The angle α is a measure of distribution of relaxation time which varies with temperature, but not with frequency. For such a distribution of relaxation time the Debye equation becomes

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

which may be extended to :

$$\epsilon^* = \epsilon_\infty + (\epsilon_s - \epsilon_\infty) \int_0^\infty \frac{G(\tau)}{1 + j\omega\tau} d\tau \quad \dots\dots\dots (1.50)$$

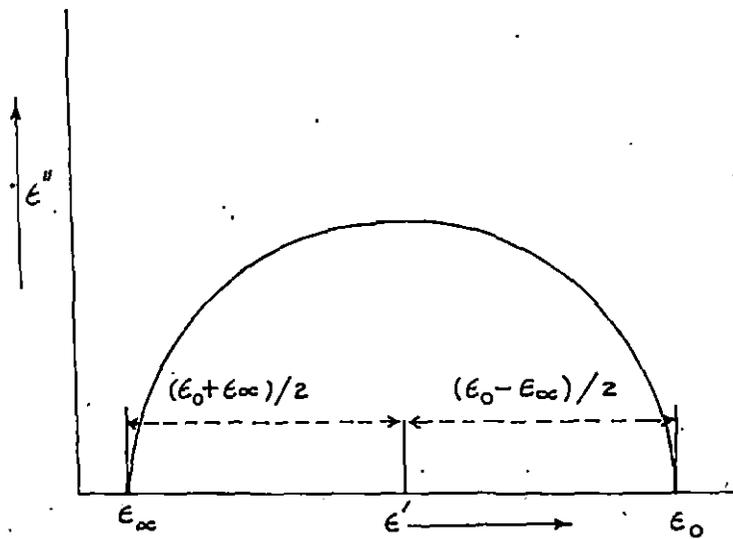


Fig. 1.5. Debye semi circle plote of ϵ'' against ϵ'

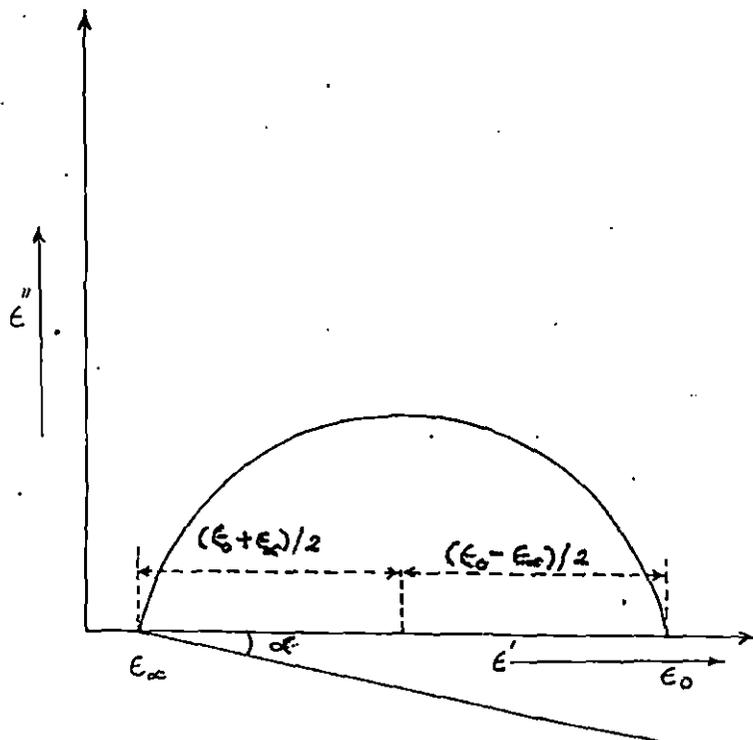


Fig. 1.6. Cole-Cole plot of ϵ'' vs ϵ' .

with the most probable relaxation time τ_0 . τ_0 can, however, be calculated from the relation :

$$\frac{v}{u} = (\omega\tau_0)^{1-\alpha} \quad \dots\dots\dots (1.51)$$

where v and u are the distances from ϵ_s and ϵ_α to any experimental point on the Cole-Cole plot. v/u becomes equal to $\omega\tau_0$ for $\alpha = 0$ only to yield Debye equation.

In eq. (1.50), $G(\tau)$ is the distribution function. $G(\tau) d\tau$ indicates the fraction of the molecules associated at a given instant with relaxation times τ and $\tau + d\tau$.

But $G(\tau)$ satisfies

$$\int_0^\infty G(\tau) d\tau = 1 \quad \dots\dots\dots (1.52)$$

which is the normalisation condition. But the original equations for ϵ' and ϵ'' could, however, be given by :

$$\epsilon' = \epsilon_\alpha + (\epsilon_s - \epsilon_\alpha) \int_0^\infty \frac{G(\tau)}{1 + \omega^2\tau^2} d\tau \quad \text{and}$$

$$\epsilon'' = (\epsilon_s - \epsilon_\alpha) \int_0^\infty \frac{G(\tau)}{1 + \omega^2\tau^2} \omega\tau d\tau.$$

1.11. DIELECTRIC RELAXATION IN DILUTE SOLUTION OF POLAR MOLECULES IN NON POLAR SOLVENT

The real part ϵ'_{ij} and the imaginary part ϵ''_{ij} for solutions of different concentrations are measured at a certain frequency of the applied electric field to estimate the relaxation time τ_s of a polar solute in a given solvent.

Let α_i be the polarisability of a nonpolar molecule of the solvent and α_j that of a polar molecule behaving as the solute. Let us, further, suppose that n_i and n_j represent the number of non - polar and polar molecules present in unit volume of the solution respectively, then

$$\frac{\epsilon_{oij} - 1}{\epsilon_{oij} + 2} \frac{f_i M_i + f_j M_j}{\rho_{ij}} = \frac{4\pi}{3} N f_i \alpha_i + \frac{4\pi}{3} N f_j \alpha_j + \frac{4\pi}{3} N f_j \frac{\mu^2}{3kT} \quad \dots (1.53)$$

$$\text{and } \frac{\epsilon_{\infty ij} - 1}{\epsilon_{\infty ij} + 2} \frac{f_i M_i + f_j M_j}{\rho_{ij}} = \frac{4\pi}{3} N f_i \alpha_i + \frac{4\pi}{3} N f_j \alpha_j \quad \dots\dots\dots (1.54)$$

$\epsilon_{\infty ij}$ and ϵ_{oij} are the dielectric constants of the solution at infinite or optical frequency and the static field respectively. M_i and M_j are the molecular weights of the solvent and solute molecules. ρ_{ij} is the density of the solution. f_i and f_j are the mole fractions of the solvent and solute which are defined by :

$$f_i = n_i / (n_i + n_j) \text{ and } f_j = n_j / (n_i + n_j) \text{ respectively.}$$

Now, from eqs. (1.53) and (1.54) it can be written as

$$\epsilon_{oij} - \epsilon_{aij} = \frac{4\pi N c_j \mu_j^2}{27kT} (\epsilon_{aij} + 2) (\epsilon_{oij} + 2) \quad \dots\dots\dots (1.55)$$

where c_j is the concentration of the solute molecules per c.c. Hence from eq. (1.46) with the help of eq. (1.55) we have,

$$\epsilon_{ij}'' = \frac{4\pi N c_j \mu_j^2 (\epsilon_{aij} + 2) (\epsilon_{oij} + 2)}{27kT} \frac{\omega\tau}{1 + \omega^2\tau^2} \quad \dots\dots\dots (1.56)$$

In case of dilute solution of a polar solute it is assumed that $\epsilon_{oij} \approx \epsilon_{aij} \approx \epsilon'_{ij}$: the above eq. (1.56) becomes

$$\epsilon_{ij}'' = \left(\frac{\epsilon'_{ij} + 2}{3}\right)^2 \frac{4\pi N c_j \mu_j^2}{3kT} \left(\frac{\omega\tau}{1 + \omega^2\tau^2}\right) \quad \dots\dots\dots (1.57)$$

Again, c_j , the concentration of the solute molecules per unit volume is given by: $c_j = (\rho_{ij}/M_j) w_j$ where w_j is the weight fraction of the solute of molecular weight M_j in a solution of density ρ_{ij} . The eq. (1.57) is then written as :

$$\epsilon_{ij}'' = \frac{4\pi N \rho_{ij} \mu_j^2}{3M_j kT} \left(\frac{\epsilon'_{ij} + 2}{3}\right)^2 \left(\frac{\omega\tau}{1 + \omega^2\tau^2}\right) w_j \quad \dots\dots\dots (1.58)$$

Equation (1.58) shows that the ϵ_{ij}'' of a solution is linear function of w_j of the polar liquid dissolved in a non-polar solvent, provided the concentration of the solution is very low. In that case ϵ'_{ij} may be replaced by ϵ'_i alone and ρ_{ij} becomes ρ_i in eq. (1.58).

1.12. ULTRA HIGH AND RADIO FREQUENCY CONDUCTIVITIES, RELAXATION TIMES AND DIPOLE MOMENTS OF POLAR SOLUTES IN NON-POLAR SOLVENTS

From the above discussions, it is evident that ϵ''_{ij} for a given polar-nonpolar liquid mixture, depends linearly on w_j of the polar liquid as indicated by eq. (1.58). The real part K'_{ij} of the complex hf conductivity K^*_{ij} is according to eq. (1.30) : $K'_{ij} = (\omega/4\pi) \epsilon''_{ij}$, which with the help of eq. (1.58) becomes

$$K'_{ij} = \frac{\omega}{4\pi} \frac{4\pi N \rho_{ij} \mu_j^2}{3M_j kT} \left(\frac{\epsilon'_{ij} + 2}{3} \right)^2 \left(\frac{\omega \tau}{1 + \omega^2 \tau^2} \right) w_j$$

$$= \frac{N \rho_{ij} \mu_j^2}{3M_j kT} \left(\frac{\epsilon'_{ij} + 2}{3} \right)^2 \left(\frac{\omega^2 \tau}{1 + \omega^2 \tau^2} \right) w_j \quad \dots\dots\dots (1.59)$$

The imaginary part K''_{ij} of hf-conductivity is also realised by using the eqs. (1.30) and (1.35) the latter is, however, written as :

$$K''_{ij} = \frac{\omega}{4\pi} \left(\epsilon_{\alpha ij} + \frac{\epsilon_{\alpha ij} - \epsilon_{\alpha ij}}{1 + \omega^2 \tau^2} \right)$$

which with the help of eq. (1.55) becomes :

$$K''_{ij} = \frac{\omega}{4\pi} \left[\epsilon_{\alpha ij} + \frac{4\pi N c_j \mu_j^2}{27kT} (\epsilon'_{ij} + 2)^2 \frac{1}{(1 + \omega^2 \tau^2)} \right]$$

$$= \frac{\omega}{4\pi} \left[\epsilon'_{ij} + \frac{4\pi N \rho_{ij} \mu_j^2}{27M_j kT} (\epsilon'_{ij} + 2)^2 \frac{w_j}{1 + \omega^2 \tau^2} \right] \quad \dots\dots\dots (1.60)$$

If ω is very large $\omega^2 \tau^2$ can not be neglected in comparison to 1 in the denominator of eqs. (1.59) and (1.60) respectively. But in the rf electric field $\omega \simeq 10^6$ c.p.s. and hence $\omega^2 \tau^2 \ll 1$, the real as well as the imaginary parts of conductivities become

$$K'_{ij} = \frac{N \rho_{ij} \mu_j^2}{3M_j kT} \left(\frac{\epsilon'_{ij} + 2}{3} \right)^2 \omega^2 \tau w_j \quad \dots\dots\dots (1.61)$$

and

$$K''_{ij} = \frac{\omega}{4\pi} \left[\epsilon'_{ij} + \frac{4\pi N \mu_j \rho_{ij}}{27 M_j kT} (\epsilon'_{ij} + 2)^2 w_j \right] \quad \dots\dots\dots (1.62)$$

respectively. Both ϵ'_{ij} , ϵ''_{ij} and K'_{ij} , K''_{ij} could, however, be expressed in terms of τ of the polar solute.

1.13. EYRING'S RATE THEORY

The study of dielectric relaxation from the stand point of chemical rate process has been first pointed out by Eyring²⁹ and has been discussed in detail by Kauzmann³⁰. They considered that the dipole orientation involves the passage over a potential barrier with a probability of jumping of the molecular dipole from one equilibrium position to another. Several attempts have been made by various workers to give a molecular theory of τ leading to a relation between τ and molecular parameters. In Debye theory, τ is connected with the inner friction of the medium. The rotation of the polar molecule is hindered with the inner friction of the medium in which the polar molecules are embedded. The turning couple on the dipolar molecule caused by the applied electric field is opposed by a torque proportional to the angular velocity of rotation of the dipole. If the dipole is regarded as a sphere of radius "a" immersed in a medium with internal viscosity coefficient η_{int} , the constant ξ which depends on surrounding medium is given by Stock's formula as :

$$\xi = 8\pi\eta_{int} a^3 \quad \dots\dots\dots (1.63)$$

The relaxation time τ is obtained as

$$\tau = \xi / 2kT \quad \dots\dots\dots (1.64)$$

Equations (1.63) and (1.64) when combined gives that

$$\tau = \frac{4\pi a^3}{kT} \eta_{int} \quad \dots\dots\dots (1.65)$$

η_{int} is a measure of microscopic property of the liquid. η_{int} is related with macroscopic viscosity η of a liquid by $\eta_{int} = \eta / \rho$. Hence, the Debye relation

can be written as :

$$\tau = 4\pi\eta a^3 / \rho kT \quad \dots\dots\dots (1.66)$$

The above equation (eq. 1.66) can be used to measure the size of the rotating unit at a given temperature in terms of the measured τ and η . Thus the relaxation time τ_s offers a unique method to obtain η_{int} of the solvent medium. The molecular volume or the radius of the rotor could thus be calculated from eq. (1.66) and were found very much less than that calculated from the other sources in most cases. Such deviations from the Debye's relation are due to the fact that the method used is very simple one.

Perrin³¹ later on modified Debye's relation by considering the rotor as the ellipsoid which is a better approximation for a real molecule. The permanent dipole moment μ , for such molecules, has three components μ_a , μ_b and μ_c along the three principal axes, a, b and c. The corresponding relaxation times τ_a , τ_b and τ_c are now given by in terms of P^*

$$P^* = \frac{\epsilon^* - 1}{\epsilon^* + 2} \frac{M}{\rho} = 4\pi N \left[\alpha + \frac{1}{3kT} \left(\frac{\mu_a^2}{1 + j\omega\tau_a} + \frac{\mu_b^2}{1 + j\omega\tau_b} + \frac{\mu_c^2}{1 + j\omega\tau_c} \right) \right] \quad \dots\dots(1.67)$$

and the dipole moment components along the axes. In many cases of the rigid rotors of ellipsoidal shape could yield dipole moment in one of the axes of consideration. Fischer³² on the basis of the Perrin's theory derived the following equation:

$$\tau = (4\pi\eta_{int}/kT)f_{abc} \quad \dots\dots\dots (1.68)$$

where f_{abc} is a molecular structure factor, a, b and c are the semi axes of the ellipsoid. The numerical values of ' f_{abc} ' has been tabulated by Budo et. al³². η_{int} is known from the macroscopic viscosity and by $\eta_{int} = K\eta$ (1.69)

The constant K is less than 1. Such emperical value of viscosity is required to bring agreement between τ calculated from the loss measurement and the molecular dimensions. Fischer³² reported the value of K as 0.36 in solutions of

benzene where as Aihara and Davies³³, however, used 0.23 for K for benzene and Xylene. This at once suggests that K is not a universal constant, but depends on the nature of the solute and solvent.

Now, according to the theory of absolute rate process, based on statistical mechanics, the dielectric relaxation mechanism may be explained by treating the dipole orientation as a rate process in which the polar molecule rotates from one equilibrium position to another. This process of rotation requires an activation energy sufficient to overcome the energy barrier separating the two mean equilibrium positions as shown in Fig. (1.6). The average time required for a single rotation is equivalent to what is known as the relaxation time τ_s such that $\tau_s T = (h/k) \exp (\Delta F_\tau / RT)$ and since from thermodynamics $\Delta F_\tau = \Delta H_\tau - T\Delta S_\tau$ we have $\tau_s T = (h/k) \exp (-\Delta S_\tau / R) \exp (\Delta H_\tau / RT)$ (1.70)

where ΔF_τ is defined as the free energy of activation, ΔH_τ is the heat change due to activation and ΔS_τ indicates the difference of entropy of activation respectively. The similar theory of viscous flow leads to a relation :

$$\begin{aligned} \eta &= (Nh / V) \exp (\Delta F_\eta / RT) \\ &= (Nh / V) \exp (-\Delta S_\eta / R) \exp (\Delta H_\eta / RT) \end{aligned} \quad \text{..... (1.71)}$$

where V is the molar volume, ΔF_η is the free energy of activation per mole for viscous process, ΔH_η is enthalpy of activation and ΔS_η is the entropy of activation for the viscous process respectively.

The approximate linearity of the plot of $\ln (\tau_s T)$ against $1/T$ as predicted by the eq. (1.70) has been used in this thesis, in several places to estimate the thermodynamic parameters like ΔF_τ , ΔH_τ and ΔS_τ of a polar rotor in a given solvent only to get a deep insight into the molecular dynamics of the systems under consideration.

When a radio frequency electric field $E = E_0 e^{j\omega t}$ is applied across the condenser plates containing a polar-non polar liquid mixture, the total heat produced in the dielectric is due to the dielectric loss for displacement of charges and Joule's

heating. The conductivity of dielectric is K' where $K' = \omega \epsilon''_{ij} / 4\pi$. There is also the ohmic conductivity, σ_{ij} which arises due to migration of charge carriers. Sen and Ghosh³⁴⁻³⁵ put forward a theory on conductivity based on the assumption of existence of free ions in a polar dielectric. When a rf-electric field is applied upon a polar liquid, in addition to the dielectric displacement current contributing to the conductivity as assumed by Murphy and Morgan²², there is obviously a conductivity due to conduction current for the free ions present in the liquid. Thus using Murphy-Morgan equation (1.30) Debye's dielectric loss equation (1.58) of the section (1.11) the generale quation for the hf-dielectric conductivity K' has been deduced.

$$\text{Thus } K' \text{ is } K' = \frac{1}{4\pi} \frac{(\epsilon_s - \epsilon_\infty)\omega^2\tau}{1 + \omega^2\tau^2}$$

Again, from eq. (1.66) of section (1.13) e.g. $\tau = 4\pi\eta a^3 / kT$, the hf K'

$$\text{is } K' = \frac{\epsilon_s - \epsilon_\infty}{kT(1 + \omega^2\tau^2)} \omega^2\eta a^3 \quad \dots\dots\dots (1.72)$$

which under rf-electric field for which $\omega^2\tau^2 \ll 1$ gives rise to what is known as the rf K' as

$$K' = \frac{\epsilon_s - \epsilon_\infty}{kT} \omega^2\eta a^3 \quad \dots\dots\dots (1.73)$$

Now, both $(\epsilon_s - \epsilon_\infty)$ as well as η/T decreases as the temperature T of the liquid increases. The K' from eq. (1.73), is expected to decrease gradually with the increase of temperature. But the experimental observation goes against this prediction. Like electrolytic conduction where Walden's rule is valid, the rf- K' increases as the temperature of the dielectropolar liquid or liquid mixture increases. A relation like $K'\eta = \text{a constant}$ is beautifully obeyed by a large number of polar liquids. If we consider the motion of an ion of mass M in a dielectric medium of coefficient of viscosity η , the equation of motion of the ion through the dielectric is given by :

$$M \frac{dv}{dt} = eE_0 e^{j\omega t} - 6\pi\eta a v \quad \dots\dots\dots (1.74)$$

where a = radius of the molecular ion, then $v = \frac{eE_0 e^{j\omega t}}{M(\gamma + j\omega)}$,

where $\gamma = 6\pi\eta a/M$. Thus

$$v = \frac{eE_0}{M} \left[\frac{\gamma}{\gamma^2 + \omega^2} - j \frac{\omega}{\gamma^2 + \omega^2} \right] e^{j\omega t} \quad \dots\dots\dots (1.75)$$

If we further consider that n represents the number of ions per unit volume of the liquid, the ionic current i_c is $i_c = nev$ (1.76)

where e = charge associated with each ion. Hence from eqs. (1.75) and (1.76) the final expression of i_c is

$$i_c = \frac{ne^2}{M} \left[\frac{\gamma}{\gamma^2 + \omega^2} - j \frac{\omega}{\gamma^2 + \omega^2} \right] E_0 e^{j\omega t} \quad \dots\dots\dots (1.77)$$

Taking the real part of eq. (1.77) the dc-conductivity σ due to free ions is :

$$\begin{aligned} \sigma &= \frac{ne^2\gamma}{M(\gamma^2 + \omega^2)} = \frac{ne^2}{M} \frac{6\pi\eta a/M}{\left(\frac{6\pi\eta a}{M}\right)^2 + \omega^2} \\ &\cong \frac{ne^2}{6\pi\eta a} \quad \dots\dots\dots (1.78) \end{aligned}$$

This is valid for the approximate values of $a \cong 10^{-8}$ cm, $\eta = 10^{-3}$ poise and $M \sim 10^{-24}$ gm. The value of $(6\pi\eta a/M)$ is much greater than ω . Hence the total conductivity K is given by :

$$K = K' + \sigma = \frac{(\epsilon_s - \epsilon_\infty)\omega^2\tau}{4\pi} + \left(\frac{ne^2}{6\pi a}\right) \frac{1}{\eta} \quad \dots\dots\dots (1.79)$$

which can be compared to the equation

$$K = A + B/\eta \quad \dots\dots\dots (1.80)$$

Thus eq. (1.79) or eq. (1.80) is a fundamental equation representing a straight

line of the total conductivity K against $1/\eta$. The intercept A and the slope B of the straight line through the measured values of K and η respectively measures the rf-dielectric conductivity K' where

$$K' = \frac{1}{4\pi} (\epsilon_s - \epsilon_\infty) \omega^2 \tau$$
 and ionic conductivity σ where $\sigma = (ne^2 / 6\pi a)$ respectively.

In this thesis, last chapter deals with the rf- K' of some interesting polar-nonpolar liquid mixtures, measured under one-megaHertz electric field in order to throw much light on the relaxation mechanism of those compounds chosen. But the first six chapters are concerned with the hf conductivities to serve the same role for binary and ternary mixtures of dielectric polar liquids.

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