CHAPTER I

REVIEW OF THE PREVIOUS WORK

A. DIPOLE MOMENT OF POLAR MOLECULES FROM SOLUTION DATA

Debye's theory of the dielectric behaviour of polar molecules is the main basic proposition from which a vast amount of literature on the subject has grown up. One of the direct results of the theory is the development of the method to determine the dipole moment of polar molecules which is a useful parameter in understanding the molecular shape and structure, molecular interactions and bond lengths for atoms forming the molecules.

The first quantitative relation for the dielectric polarization of a substance in presence of an external field is given by the Clausius-Mosotti equation (1850, 1879)

$$P = \frac{\epsilon - 1}{\epsilon + 2} \frac{M}{d} = \frac{4\pi N}{3} \alpha_0$$

and the equation for molar refraction

$$\frac{n^2 - 1}{n^2 + 2} \frac{M}{d} = \frac{4\pi N}{3} \alpha_0$$

where ϵ is the dielectric constant, M is the molecular weight of the substance, d its density, N the number of molecules per mole, α_0 is the polarizability per molecule and n is the refractive index.

Debye assumed that when dipolar molecules are placed in a steady electric field, in addition to normal electronic and atomic polarization, a third polarization called orientational polarisation occurs due to permanent dipole moment μ of the polar molecule tending the molecules to align themselves in the direction of the field. In that case the total polarisation is given by Debye as

$$P = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} = \frac{4\pi N}{3}\left(\alpha + \frac{\mu^2}{3KT}\right) \quad (1.1)$$

where α is the polarizability by distortion and $\mu/3KT$ the polarizability by orientation, K is the Boltzmann constant, T is the absolute temperature and N is the Avogadro number. Thus Debye equation afforded the possibility of calculating molecular dipole moments from measurements of the dielectric constant which however did not arouse much interest until the middle of 1920. At that time understanding of the structure of molecules had advanced to such a degree that the value of the dipole moment could be connected with the geometrical arrangement of the atoms in the molecule. From then on, the significance of Debye's method was fully realized and an increasing number of determinations of permanent dipole moments were performed. But it is well known that Debye's equation is found to be experimentally valid for gases and for very dilute solutions of polar liquids in non-polar solvents and large deviations are observed for polar liquids and solids. These discrepancies are due to the following assumptions made by Debye:

1. No local directional forces due to neighbours act upon dipoles so that they are distributed according to Langevin's law.
2. The field due to molecule within the spherical region having radius larger than that of the molecules is zero.
3. The directing field was taken equal to the internal field.

Onsager (1936) was one of the first workers to examine the problem of internal field. In his treatment the molecule of a polar liquid is considered as a polarizable point dipole at the centre of a spherical cavity of molecular dimensions sorrounded by an unpolarized medium. He calculated the total field (F) on the spherical molecule as due to cavity field arising due to external charges and reaction field arising due to polarization of the environment medium by the field of the dipole. The internal field according to Onsager is

$$F = \frac{3\epsilon}{2\epsilon+1}E + \frac{2(\epsilon-1)}{(2\epsilon+1)a^3}m$$

where ϵ is the dielectric conetant of the sorrounding medium 'a' is the radius of the spherical cavity, E is the uniform macroscopic field outside the cavity and m is the dipole moment of the cavity. By applying this internal field instead of Lorentz field in Debye equation, Onsager obtained for molar polarization

$$\left(\frac{\epsilon-1}{\epsilon+2} - \frac{\epsilon_\infty-1}{\epsilon_\infty+2}\right)\cdot\frac{M}{d} = \frac{3\epsilon(\epsilon_\infty+2)}{(2\epsilon+\epsilon_\infty)(\epsilon+2)}\cdot\frac{4\pi N\mu^2}{9KT}$$

This equation differs from that of Debye by a

factor $\frac{3\epsilon(\epsilon_\infty+2)}{(2\epsilon+\epsilon_\infty)(\epsilon+2)}$ on the right hand side of equation (1.1). As ϵ approaches ϵ_∞, this factor approaches unity that is, the two equations lead to same results for infinitely dilute solutions of polar solute in nonpolar solvents or specially in case of gases where ϵ and ϵ_∞ are very close to unity at atmospheric pressure. Though Onsager's equation is approximately found to be valid in unassociated liquids, large discrepancies have been found in case of associated liquids. The discrepancies are due to:

1. Onsager did not consider the short range forces due to an ordered array of neighbouring molecules.
2. Onsager's treatment of polar molecules is limited to those which are spherical in form.
3. The environment of the molecule is treated as a homogeneous continuum and the local saturation effects are neglected.

The effect of short range forces was first considered by Kirkwood (1939). Unlike Onsager, Kirkwood does not assume the approximation of a uniform local dielectric constant identical with the macroscopic dielectric constant of the medium. By taking into account the sum of the molecular dipole moment and moment induced as a result of hindered rotation in the spherical region sorrounding the molecule, he derived the relation

$$\left(\frac{\epsilon-1}{\epsilon+2}-\frac{\epsilon_\infty-1}{\epsilon_\infty+2}\right)\cdot\frac{M}{d}=\left[\frac{3\epsilon(\epsilon_\infty+2)}{(2\epsilon+\epsilon_\infty)(\epsilon+2)}\right]\frac{4\pi N\mu^2 g}{9KT}$$

where g is the correlation parameter which characterises the intermolecular interaction and short range forces. The

equation becomes identical with Onsager's equation if $g = 1$. The departure of g from unity is a measure of hindered relative molecular rotation arising from short range intermolecular forces. For unassociated liquid the value of g is approximately unity while for associated liquid the value departs significantly from unity.

It is evident that Kirkwood equation represents a theoretical advance beyond Onsager equation, in that it taken into account the hindrance of molecular orientation by neighbouring molecules. In the absence of knowledge of liquid structure this factor is unknown and useful only as an empirical constant.

Fröhlich (1949) modified Kirkwood's theory by considering a dipolar dielectric with a number of polarizable units of same kind within a large spherical region. Each unit has various dipole moment $\bar{\mu}$ in different directions which occur in course of thermal fluctuations with a certain probability. The average moment $\bar{\mu}^*$ due to such unit within the spherical region is different from $\bar{\mu}$ because of short range interactions between the polarizable units and the deviation of the shape of the molecules from a sphere. On this basis an equation has been derived for low intensity fields as

$$\epsilon - 1 = \frac{3\epsilon}{2\epsilon + 1} \cdot \frac{4\pi N_0}{3} \cdot \frac{\bar{\mu}\bar{\mu}^*}{KT}$$

where N_0 is the number of units per unit volume. Fröhlich's theory has been extended to anisotropic molecules by Powle's (1955) and to the case of strong fields by O'Dwyer (1951).

The difficulties in Fröhlich's theory are associated with the evaluation of energy of interaction of the sample with the surrounding medium.

Thus from the different theories so far discussed above, it is clear that the dipole-dipole interaction plays an outstanding problem in the determination of dipole moment of polar liquids. Consequently a convenient method of dipole moment determination from solution data of polar solute in nonpolar solvents has been adopted as in this case the molecules are well separated from each other, the dipole-dipole interaction is consequently more or less absent and moreover the dipole moment value evaluated by this method comes in reasonable agreement with that obtained from gaseous state.

When a polar solute is dissolved in a nonpolar solvent, Debye has shown that the electric dipole moment μ of a solute molecule can be derived from the equations

$$\frac{\epsilon_{12}-1}{\epsilon_{12}+2}V_{12}=\frac{\epsilon_1-1}{\epsilon_1+2}V_1(1-x_2)+\frac{4\pi N}{3}\left(\gamma_{2e}+\gamma_{2a}+\mu^2/3KT\right)x_2 \quad \ldots \quad (1.2)$$

$$\frac{n_{12}^2-1}{n_{12}^2+2}V_{12}=\frac{n_1^2-1}{n_1^2+2}V_1(1-x_2)+\frac{4\pi N}{3}\gamma_{2e}x_2 \quad \ldots \quad (1.3)$$

where the suffix 12, 1 and 2 represent the solution, solvent and solute respectively, ϵ the dielectric constant, n the refractive index extrapolated from the visible part of the spectrum to infinite wavelength, γ_{2e} , γ_{2a} are the electronic and atomic constribution of polarizability of

solute of mole fraction x_2 respectively, N the Avogadro number, K the Boltzmann constant and T is the temperature in absolute scale. Equation (1.2) can be used directly to obtain the molar polarization of solute at infinite dilution and thus in turn the dipole moment of polar solute according to relation (Debye's method)

$$P_{2\infty} = \underset{x_2 \to 0}{\alpha t} \frac{[P_{12}] - (1-x_2)[P_1]}{x_2}$$

where $[P_{12}]$ = molar polarization of the solution

$$= \frac{\epsilon_{12} - 1}{\epsilon_{12} + 2} V_{12}$$

$[P_1]$ = molar polarisation of solvent

$$= \frac{\epsilon_1 - 1}{\epsilon_1 + 2} V_1$$

The value of $P_{2\infty}$ includes of course the contribution of electronic and atomic polarization which must be taken into consideration to evaluate the dipole moment of polar solute. If we neglect the contribution of electronic and atomic polarization of solute and solvent molecule, it can be shown from (1.2) and (1.3) assuming $\epsilon_1 = n_1^2$

$$\frac{\epsilon_{12} - 1}{\epsilon_{12} + 2} - \frac{n_{12}^2 - 1}{n_{12}^2 + 2} = \frac{4\pi n_1 \mu^2}{9KT} \qquad \cdots (1.4)$$

where n_1 is the number of solute molecules per c.c. But equation (1.4) when applied to same solute and solvent system in different concentration, gives different values of μ. This is due to the fact that Debye's equation is valid at infinite dilution only in restricted sense and partly due to the fact that the computation of μ depends

purely upon the theory of extrapolation of different physical quantities such as ϵ_{12} , n_{12} , d_{12} etc. since the extrapolation curve is not a straight line. Therefore several attempts have been made to improve the process of extrapolation by different authors.

Hedestrand (1929) pointed out that if ϵ_{12} and d_{12} vary linearly with x_2 , the mole fraction of the solute, then the value of total molar polarisation of the solute (P_2) can be calculated from eqn. (1.2) leading to

$$x_2 P_2 = x_2 \frac{\epsilon_{12}-1}{\epsilon_{12}+2} \cdot \frac{M_2}{d_{12}} + (1-x_2) M_1 \left[\frac{\epsilon_{12}-1}{\epsilon_{12}+2} \cdot \frac{1}{d_{12}} - \frac{\epsilon_1 - 1}{\epsilon_1 + 2} \cdot \frac{1}{d_1} \right] \quad \cdots (1.5)$$

Differentiating both sides of equation (1.5) with respect to x_2 and taking the limit $x_2 \longrightarrow 0$, we have $P_2 = P_{2\infty}$, the total molar polarisation of solute at infinite dilution, $\epsilon_{12} = \epsilon_1$, $d_{12} = d_1$, we get

$$P_{2\infty} = \frac{\epsilon_1 - 1}{\epsilon_1 + 2} \cdot \frac{M_2}{d_1} + \frac{3M_1}{d_1(\epsilon_1+2)^2} \left(\frac{\partial \epsilon_{12}}{\partial x_2} \right)_{x_2 \to 0} - \frac{\epsilon_1 - 1}{\epsilon_1 + 2} \cdot \frac{M_1}{d_1^2} \left(\frac{\partial d_{12}}{\partial x_2} \right)_{x_2 \to 0}$$

When the contribution of electronic and atomic polarisations are taken into consideration, $P_{2\infty}$ gives the orientational polarization ($P_{2\mu}$) of the solute molecule and thereby the value of μ . The advantage of Hedestrand's extrapolation

procedure is that it avoids the measurement of refractive index but the difficulty arises on the evaluation of $\left(\frac{\partial d_{12}}{\partial x_2}\right)_{x_2 \to 0}$. Cohen-Henriquez (1935) suggested an extrapolation procedure, the aim of which is to avoid the use of $\left(\frac{\partial d_{12}}{\partial x_2}\right)_{x_2 \to 0}$ and to use $\left(\frac{\partial n_{12}}{\partial x_2}\right)_{x_2 \to 0}$ instead. This can be achieved as equations (1.2) & (1.3) give

$$x_2 P_2 = \left[\frac{\epsilon_{12}-1}{\epsilon_{12}+2} - \frac{n_{12}^2-1}{n_{12}^2+2}\right] \cdot \frac{(1-x_2)M_1 + x_2 M_2}{d_{12}} - x_2\left[P_{2e}\right] - (1-x_2)\left[P_{1a}\right]$$

where $\left[P_{2e}\right]$ and $\left[P_{1a}\right]$ are the molar electronic and atomic polarization of solute and solvent respectively. Differentiating with respect to x_2 and taking the limit $x_2 \to 0$ and neglecting the contribution due to atomic polarization of the solvent, Cohen-Henriquez equation becomes

$$P_{2\infty} = \frac{3M_1}{(n_1^2+2)^2 d_1}\left[\left(\frac{\partial \epsilon_{12}}{\partial x_2}\right)_{x_2 \to 0} - 2n_1\left(\frac{\partial n_{12}}{\partial x_2}\right)_{x_2 \to 0}\right] + \left[P_{2e}\right]_{x_2 \to 0}$$

The modification of Cohen-Henriquez formula appeared to be rather suitable as it is not necessary to measure the density of the solution and particularly useful in those cases where atomic polarization of the solvent is very small. Böttcher (1952) has compared Debye, Hedestrand, Cohen-Henriquez and lastly the famour Guggenheim extrapolation techniques in case of phenol in benzene but unfortunately observed a notable

deviation in the value of μ as obtained by different methods. LeFèvre and Vine (1937) preferred to use the specific polarization instead of molar polarization and assumed that ϵ_{12} and d_{12} are linear function of weight fraction (ω_2) and calculated the specific polarization of a solute at infinite dilution as

$$P_{2\infty} = P_1(1-\beta) + c\alpha\epsilon_1 \qquad \cdots (1.6)$$

where

P_1 = specific polarization of the solvent

$$= \frac{\epsilon_1 - 1}{\epsilon_1 + 2} \cdot \frac{1}{d_1}$$

$$c = \frac{3}{(\epsilon_1+2)^2 d_1}$$

and α , β are constants which can be determined from the relation $\epsilon_{12} = \epsilon_1(1+\alpha\omega_2)$ and $d_{12} = d_1(1+\beta\omega_2)$. Halverstadt and Kumler (1942) have used specific volumes instead of densities and deduced that specific polarization at infinite dilution is given by the relation

$$P_{2\infty} = \frac{3\alpha v_1}{(\epsilon_1+2)^2} + (v_1+\beta)\frac{\epsilon_1-1}{\epsilon_1+2} \qquad \cdots (1.7)$$

where

$$\epsilon_{12} = \epsilon_1 + a\omega_2$$

$$v_{12} = v_1 + b\omega_2$$

But the value of μ calculated by using this relation by Halverstadt and Kumler was generally higher than those obtained

by usual methods and in some cases approximated to the values found from measurements on the vapours.

Higasi (1943) has suggested a very convenient but empirical relation for the quick determination of dipole moment. According to him, μ is given by

$$\mu = \beta\left(\frac{\Delta\epsilon}{x_2}\right)^{1/2} \quad \ldots \quad (1.8)$$

where $\Delta\epsilon = \epsilon_{12} - \epsilon_1$ is the difference in the values of dielectric constants of solution and solvent, β is a constant depending upon the intrinsic properties of the solvent and its value is found to be 0.90 D with a possible fluctuation of $\pm$ 0.10 e.s.u. Later on it has been shown by Krishna and Srivastava (1957) that equation (1.8) should be represented as

$$\mu = \beta\left(\frac{d\epsilon_{12}}{dx_2}\right)^{1/2} \quad \ldots \quad (1.9)$$

where $d\epsilon_{12}/dx_2$ is the slope of $\epsilon_{12} - x_2$ curve. They have established that equation (1.9) is valid for the straight portion of the $\epsilon_{12} - x_2$ curve with β as 0.828 D. In the same solvent Srivastava and Charandas (1959) have obtained different values of β for different solute molecules. This inturn, reflects the failure of Higasi's method in determining μ for liquid mixture. Jay Prakash (1973) has shown that equation (1.9) is a special case of Debye equation (1.4) under the assumption that ϵ_{12} is equal to or very close to unity. Therefore Higasi's equation and its modifications are valid for gases or for those

liquid mixtures of polar solute in nonpolar solvent which have dielectric constant close to unity. Since no such liquid mixture is known, Higasi's method, although a convenient approach, fails to be applicable in the case of a polar solute dissolved in nonpolar solvent.

Guggenheim (1949) has proposed an ingenious method which avoids the measurement of d_{12} accurately. In developing his method, he has incorporated the following assumptions:

1. The partial molar volume of the dipole compound (V_2) and partial molar volume of the solvent (V_1) are both independent of concentration and thus equal to V_2 and V_1 respectively which leads to

$$V_{12} = (1 - x_2) V_1 + x_2 V_2 \qquad \ldots (1.10)$$

2. A fictitious atomic polarizability $\left[\gamma'_{2a}\right]$ of the solute molecule has been assumed according to which the polarizabilities of the solute and solvent are in the ratio of their molar volumes.

3. The value of atomic polarizability of the solute molecule $\left[\gamma_{2a}\right]$ has been assumed equal to $\left[\gamma'_{2a}\right]$ This assumption leads to the elimination of the term corresponding to $\left[\gamma_{2a}\right]$.

Using (1.2), (1.3) and (1.10) it can be easily shown that

$$\left(\frac{\epsilon_{12}-1}{\epsilon_{12}+2} - \frac{n_{12}^2-1}{n_{12}^2+2}\right) = \left(\frac{\epsilon_1-1}{\epsilon_1+2} - \frac{n_1^2-1}{n_1^2+2}\right)$$

$$+ \frac{4\pi N}{3}\left(\gamma_{2a} - \gamma'_{2a} + \frac{\mu^2}{3KT}\right) c_2 \qquad \ldots (1.11)$$

where $C_2 = x_2/V_{12}$ = molar concentration in moles/cc. According to (1.11), if the experimental quantities

$$\frac{\epsilon_{12}-1}{\epsilon_{12}+2} - \frac{n_{12}^2-1}{n_{12}^2+2} = \frac{3(\epsilon_{12}-n_{12}^2)}{(\epsilon_{12}+2)(n_{12}^2+2)}$$

is plotted against C_2, the slope of the curve will give the value of μ when $\nu_{2a} = \nu'_{2a}$. As a further simplication he shows that if $\epsilon_{12}-n_{12}^2$ is plotted against C_2, the μ value can be obtained from the relation

$$\mu^2 = \frac{9KT}{4\pi N}\cdot\frac{3}{(\epsilon_1+2)(n_1^2+2)}\cdot\left(\frac{\Delta}{C_2}\right)_{C_2\to 0} \quad \cdots (1.12)$$

where

$$\Delta = \left(\epsilon_{12}-n_{12}^2\right) - \left(\epsilon_1 - n_1^2\right)$$

Smith (1950) has suggested a further simplication to Guggenheim's procedure by introducing the concept of weight fraction as a concentration unit instead of C_2. He shows that μ can be determined from the relation

$$P_{2\mu} = \frac{3M_2 v_1\left[\partial(\epsilon_{12}-n_{12}^2)/\partial\omega_2\right]_{\omega_2\to 0}}{(\epsilon_1+2)^2} \quad \cdots (1.13)$$

where v_1 is the specific volume of the pure solvent. Incorporating the ideas of Smith (1950) and LeFèvre (1950), Guggenheim (1951) modified his own equation for the evaluation of μ which can be written as

$$\mu^2 = \frac{9KT}{4\pi N}\cdot\frac{3}{(\epsilon_1+2)^2}\cdot\frac{M_2}{d_1}\cdot\left(\frac{\Delta}{\omega_2}\right)_{\omega_2\to 0} \quad \cdots (1.14)$$

where

$$\left(\frac{\Delta}{\omega_2}\right)_{\omega_2 \to 0} = \left[\left(\frac{\partial \epsilon_{12}}{\partial \omega_2}\right)_{\omega_2 \to 0} - 2n_1 \left(\frac{\partial n_1}{\partial \omega_2}\right)_{\omega_2 \to 0}\right]$$

Palit and Banerjee (1951) suggested to plot the specific polarisation of the solution

$$P_{12} = \frac{\epsilon_{12} - 1}{\epsilon_{12} + 2} \cdot \frac{1}{d_{12}}$$

against the weight fraction ω_2 and drew the tangent to this curve at $\omega_2 \to 0$ and extrapolate this tangent to pure solute. This gives $P_{2\infty}$, the partial specific polarisation of the solute at infinite dilution which multiplied by the molecular weight of the solute gives the true polarization of the solute $P_{2\infty}$. From extensive calculations with a large amount of published reliable data they found the validity of the theory. Based on the above concept, Palit (1952) developed a method according to which μ is given by

$$P_{2\mu} = \left[\frac{3(\epsilon_1 - n_1^2) M_2}{d_1(\epsilon_1 + 2)(n_1^2 + 2)}\left(1 - \frac{\beta_0}{d_1}\right)\right] + \left[\frac{3\alpha_0 M_2}{d_1(\epsilon_1 + 2)^2}\right] - \left[\frac{6 n_1 \gamma_0 M_2}{d_1(n_1^2 + 2)^2}\right] \quad \ldots \quad (1.15)$$

where

$$\alpha_0 = \left(\frac{\partial \epsilon_{12}}{\partial \omega_2}\right)_{\omega_2 \to 0}$$

$$\beta_0 = \left(\frac{\partial d_{12}}{\partial \omega_2}\right)_{\omega_2 \to 0}$$

$$\gamma_0 = \left(\frac{\partial n_{12}}{\partial \omega_2}\right)_{\omega_2 \to 0}$$

Equation (1.15) can be written as

$$P_{2\mu} = \frac{3(\epsilon_1 - n_1^2) M_2}{d_1(\epsilon_1+2)(n_1^2+2)}\left(1 - \frac{\beta_0}{d_1}\right) + \frac{3M_2}{d_1(\epsilon_1+2)^2}\left[\frac{\partial(\epsilon_{12} - K_1^2 n_{12}^2)}{\partial \omega_2}\right]_{\omega_2 \to 0} \quad \ldots (1.16)$$

where $K_1 = \frac{\epsilon_1 + 2}{n_1^2 + 2}$. If $\epsilon_1 = n_1^2$ (ie. $\beta_0 = d_1$)

the first term of (1.16) becomes equal to zero and hence

$$P_{2\mu} = \frac{3M_2}{d_1(\epsilon_1+2)^2}\left[\frac{\partial(\epsilon_{12} - n_{12}^2)}{\partial \omega_2}\right]_{\omega_2 \to 0}$$

which is nothing but the final modified Guggenheim equation of Smith (1.13). It is therefore, clear that Guggenheim-Smith procedure which in effect neglects the contribution of the first term of equation (1.15) or (1.16) may cause an error in the value of μ. Equation (1.15) has been successfully applied in a number of cases for the determination of dipole moment of polar solute and gives a reasonable value of μ even in the case of molecules having low dipole moment where Guggenheim's method fails to do so. Jay Prakash (1975) on the other hand shows that Debye's equation (1.4) can be re-arranged as

$$\mu^2 = \frac{27 M_2 KT}{4\pi N d_1}\left(\frac{\partial x}{\partial \omega_2}\right)_{\omega_2 \to 0}$$

where

$$\left(\frac{\partial x}{\partial \omega_2}\right)_{\omega_2 \to 0} = \left[\frac{1}{(\epsilon_1+2)^2}\left(\frac{\partial \epsilon_{12}}{\partial \omega_2}\right)_{\omega_2 \to 0} - \frac{2n_1}{(n_1^2+2)^2}\left(\frac{\partial n_{12}}{\partial \omega_2}\right)_{\omega_2 \to 0}\right]$$

When $\epsilon_1 = n_1^2$, the above equation reduces to well known Guggenheim equation (1.14) and hence it can be concluded that Guggenheim's procedure is simply a special case of Debye's method. But $\epsilon_1 = n_1^2$ for the solvent is not always satisfied which may introduce an error in the value of μ evaluated from Guggenheim's method as discussed earlier. However, the following points must be taken into account before applying Guggenheim's method for the evaluation of μ when a polar solute is dissolved in a nonpolar solvents.

1. The method will be less accurate when there is a considerable contraction or dilatation of the volume of the solution since equation (1.10) which has been applied in derivation of the theory will not be valid.
2. In case of molecules having low dipole moment it does not give accurate results.
3. The assumption $\epsilon_1 = n_1^2$ for the solvent is not always satisfied which introduces inaccuracy in the value of μ .

Though in a few cases Guggenheim's equation deviates slightly from the actual value of μ , the theory has been used by many workers (Murty, 1957; Purcell and Singer, 1965 etc)

due to its simplicity in comparison to other methods. Guha, Das and Acharyya (1977) obtained a physical parameter Y_{12} solely expressed interms of experimentally determined physical quantities ϵ_{12} and n_{12} of solutions of different weight fractions ω_2 of the solute which can represent the experimental facts at every stage of dilution.

Assuming

$$d_{12} = \frac{d_1}{1 - \beta\omega_2}$$

where

$$\beta = 1 - \frac{d_1}{d_2}$$

d_1 and d_2 are density of solvent and solute respectively and considering $Y_{12} = a_0 + a_1 \omega_2 + a_2 \omega_2^2 + \cdots$ they have calculated the dipole moment of several systems from reliable published data and found a good agreement with that of literature value.

Thus it is clear that the dipole moment of a polar solute dissolved in a nonpolar solvent totally depends upon the theory of extrapolation of different physical quantities such as ϵ_{12}, n_{12} etc. This process of extrapolation should be simple and straight forward and at the same time give an accurate value of μ which inturn provides us information regarding the structure of the molecule.

B. DIELECTRIC CONSTANT, LOSS, RELAXATION TIME AND RADIO FREQUENCY CONDUCTIVITY OF LIQUIDS.

In the case of static or low frequency dielectric constant, the dielectric is in equilibrium with applied field. When the frequency of the field is an alternating one, the permanent dipoles cannot follow the alterations of the field without measurable lag. This lag is commonly referred to as relaxation and the time in which the polarisation is reduced to 1/e times its original value is called the relaxation time. The polarization acquires a component out of phase with field and the displacement current acquires a conductance component in phase with the field resulting in thermal dissipation of energy. To have an idea, let us consider a parallel plate condenser, of geometrical capacitance C_o, connected to an alternating source of e.m.f. (E) = E_o exp. ($J\omega t$) of angular frequency $\omega = 2\pi f$ where f is the frequency.

The charge of the capacitor at any instant is $Q = C_o E$ and the charging current $I_c = dQ/dt$ which leads the applied voltage by a phase angle of 90°. If the space between the plates of the capacitor is now filled up with a dielectric liquid, the capacitor is increased to $C = \epsilon' C_o$ where ϵ' is the (real) dielectric constant of the liquid. Due to presence of dielectric the charge on the capacitor is increased to $Q = \epsilon' C_o E$ and the charging current is increased to

$$I_c = J\omega\epsilon' C_o E$$

It is known that no dielectric liquid is a perfect insulator so that in addition to I_c which leads by 90°, there is a loss current component I_l in phase with E of magnitude

$$I_l = G.E$$

where $G = 1/R$ is the equivalent conductance of the dielectric, R is the finite insulation resistance. Total current through the capacitor is therefore

$$I = I_c + I_l = J\omega\epsilon' C_o E + GE$$

$$= \left(J\omega C + G\right) E \qquad \cdots \quad (1.17)$$

This is shown in the vector diagram in Fig. (1.1 b). The current I leads E by a phase angle $\theta < 90^\circ$ where

$$\cos\theta = \left[\frac{I_l}{I}\right] = \frac{G}{\sqrt{G^2+\omega^2C^2}}$$

is the power factor. Alternatively the behaviour can be considered interms of loss angle δ and loss tangent $\tan\delta$ where $\delta = (90^\circ - \theta)$ and $\tan\delta = \frac{I_l}{I_c} = \frac{G}{\omega C}$. So it is observed that the loss current in a dielectric liquid is due to finite conductivity so that the capacitor can be represented as equivalent to a capacity C in parallel with resistance $R = 1/G$ as shown in Fig. (1.1 a).

In most materials, however the dielectric behaviour differs from this simple form, indicating the presence of other sources of dielectric loss. Without assuming the nature or origin of the dielectric loss, a complex dielectric constant can be defined as

$$\epsilon^* = \epsilon' - J\epsilon''$$

where ϵ'' is the dielectric loss factor

The total current thus

$$I = J\omega\epsilon^{*}C_0E$$
$$= J\omega(\epsilon' - J\epsilon'')C_0E$$
$$= J\omega\epsilon'C_0E + \omega\epsilon''C_0E \quad \ldots(1.18)$$

Its components being represented vectorially in Fig. (1.2). Now comparing equation (1.18) with (1.17), we get

$$G = \omega\epsilon''C_0 \quad \ldots \quad (1.19)$$
$$C = \epsilon'C_0$$

and loss tangent $\tan\delta = \frac{\omega\epsilon''C_0}{\omega\epsilon'C_0} = \frac{\epsilon''}{\epsilon'}$

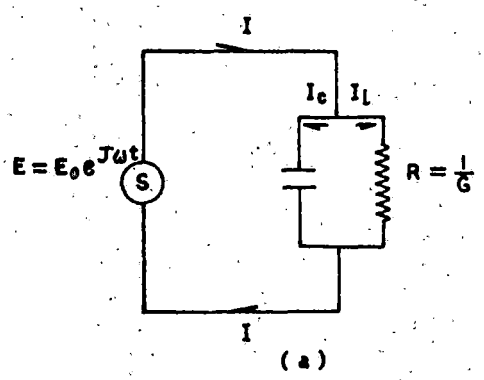
From equation (1.19)

$$\epsilon'' = \frac{G}{\omega C_0} = \frac{\text{specific conductivity} \times 4\pi}{\omega}$$

Therefore specific conductivity (real)

$$K' = \frac{\epsilon''\omega}{4\pi} \quad \ldots (1.20)$$

(For parallel plate capacitor, $C_0 = \frac{S}{4\pi l}$ in vacuum, and $G = 1/R$ where $R = \rho\frac{l}{S}$) Equation (1.20) directly gives us the relation between the a.c. conductivity and dielectric loss. In this connection, it will be interesting to examine the relation between the apparent conductivity to dielectric constant and loss in the light of analysis given by Murphy and Morgan (1939).



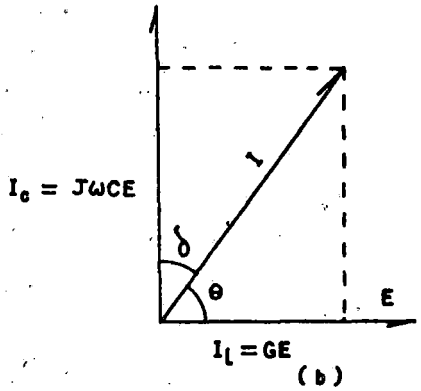


FIG. 1.1. EQUIVALENT CIRCUIT AND CHARGING CURRENT I_c & LOSS CURRENT I_L OF CAPACITOR WITH LOSSY DIELECTRIC.

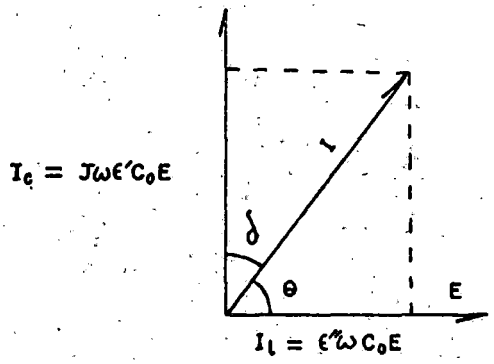


FIG. 1.2. COMPONENTS OF CURRENT THROUGH DIELECTRIC OF COMPLEX DIELECTRIC CONSTANT $\epsilon^* = \epsilon' - J\epsilon''$

For conductors, the conductivity (K) can be defined as the factor by which the voltage gradient E must be multiplied to give the current density (I)

$$I = KE$$

or as the factor by which the square of the voltage gradient must be multiplied to give heat (W) developed per second in a unit cube of material

$$W = IE = KE^2$$

for the heat developed by a given voltage is proportional to the current, no matter of what material the conductor is composed. However, the proportionality between the current and heat developed which is the characteristic of conductors does not hold in a dielectric material. When an alternating current flows in a dielectric it dissipates some energy as heat though the amount is generally much smaller than would be dissipated by an equal current flowing in a conductor. This heat which is developed in a dielectric by the polarization current is known as dielectric loss. In fact the complex conductivity represents the case of displacement of electric charge in a dielectric while its real part a-c conductivity is the factor which determines the rate of dissipation of electrical energy as heat in the material. In an ideal dielectric there should be no electron or free ion conduction but in actual practice there are some free ions or electrons and these produce Joule's heat as they drift towards the electrodes in the applied field. The total heat developed is the sum of the dielectric loss and Joule's heat and as the latter is proportional to the d-c or free ion

conductivity, the dielectric loss is proportional to the total a-c conductivity less the d-c conductivity.

Let a dielectric material of dielectric constant ϵ fill the space between the parallel plates of a two plate condenser, which has a distance "d" cm. between the plates, each plate having an area "A" sq.cm. on each side. If a potential difference V is established between the plates, the electric field intensity

$$E = \frac{V}{d}$$

The effect of introducing a dielectric into the capacitor can be understood by considering the effect of the applied electric field on the bound charges in the dielectric. The very low conductivity of a dielectric material indicates that practically all the electronic charges are bound to their parent atoms or molecules by the electric fields due to the neuclear charges and they are not free to migrate under the action of an applied field. The action of the field E on the bound charges in the dielectric is to displace them slightly relative to one another, the positive charges being displaced in the direction of the field, the negative charges in the opposite direction. Each atom or molecule thus acquires an electric dipole moment parallel to and in the same direction as E. The effect is known as dielectric polarization, and an electric polarization vector P is defined as the electric dipole moment per unit volume. So if a potential difference V is established between the plates, a charge η per unit area will appear on each plate and a polarization P will be created in the

dielectric. The displacement current flowing is $A\,dq/dt$ and if we assume that the dielectric liquid is free from ions, so that the conductivity due to free ions may be neglected then the conductivity is

$$K = \frac{1}{E} \cdot dq/dt$$

$$\frac{dq}{dt} = KE$$

Since,

$$E = \frac{V}{d} = \frac{D}{\epsilon}$$

$$D = \frac{\epsilon V}{d}$$

$$\frac{dD}{dt} = \frac{\epsilon}{d} \cdot \frac{dV}{dt}$$

$$D = 4\pi q = E + 4\pi P$$

$$\frac{dD}{dt} = 4\pi \cdot \frac{dq}{dt}$$

$$\frac{dq}{dt} = \frac{1}{4\pi} \cdot \frac{dD}{dt} = \frac{\epsilon}{4\pi d} \cdot \frac{dV}{dt}$$

$$I = \frac{\epsilon}{4\pi d} \cdot \frac{dV}{dt}$$

where all the electrical quantities are expressed in electrostatic units. When the applied potential is alternating, V may be expressed as

$$V = V_0 e^{j\omega t}$$

where V_0 is the amplitude. The dielectric constant may then be written as the complex quantity. The current density

in the dielectric is then

$$I = \frac{dq}{dt} = \frac{\epsilon' - J\epsilon''}{4\pi d} \frac{dV_0 e^{J\omega t}}{dt}$$

$$= \frac{\epsilon' - J\epsilon''}{4\pi d} \cdot J\omega V_0 e^{J\omega t}$$

$$= \left(\frac{J\omega\epsilon'}{4\pi} + \frac{\omega\epsilon''}{4\pi}\right) \frac{V_0 e^{J\omega t}}{d}$$

$$= \left(\frac{\omega\epsilon''}{4\pi} + \frac{J\omega\epsilon'}{4\pi}\right) \frac{V_0 e^{J\omega t}}{d}$$

$$= \left(\frac{\omega\epsilon''}{4\pi} + J\frac{\omega\epsilon'}{4\pi}\right) E_0 e^{J\omega t} \quad \cdots (1.21)$$

If it is assumed that high frequency conductivity K is a complex quantity and is given by $K = K' + JK''$

$$I = \frac{dq}{dt} = \left(K' + JK''\right) E_0 e^{J\omega t}$$

where $K' = \frac{\omega\epsilon''}{4\pi}$ is the real part

and $K'' = \frac{\omega\epsilon'}{4\pi}$ is the imaginary part. For convenience in connection with a subsequent method of measurement, the admittance of the condenser may be expressed in term of an equivalent parallel capacitance C_p and conductance G_p so that an alternate expression for I in

$$I = \frac{dq}{dt}$$

$$= \frac{0.9 \times 10^{12}}{A} \left(G_p + J\omega C_p\right) V_0 e^{J\omega t}$$

$$\cdots (1.22)$$

where G_p is expressed in mhos, C_p in farads and 0.9×10^{12} is the ratio of the farad to the electrostatic unit of capacitance and also of the mho to the electrostatic unit of conductance. By using the

expression for the capacitance C_0 in farads of the empty condenser

$$C_0 = \frac{A}{4\pi d \times 0.9 \times 10^{12}} \qquad \cdots (1.23)$$

and using equations (1.21), (1.22) and (1.23)

$$\epsilon' = C_p/C_0$$

$$\epsilon'' = G_p/\omega C_0$$

$$K' = G_p/4\pi C_0 = \frac{\epsilon''\omega}{4\pi} = \frac{\epsilon'' f}{2}$$

$$K'' = \frac{1}{4\pi R C_0}$$

To obtain K' in ohms^{-1} cm^{-1}, we can write

$$K' = \frac{\epsilon''\omega}{4\pi \times 0.9 \times 10^{12}}$$

$$= \frac{\epsilon'' f}{1.8 \times 10^{12}}$$

$$= \frac{G_p \cdot f}{C_0 \cdot 2\pi f \cdot 1.8 \times 10^{12}}$$

$$= \frac{8.85 \times 10^{-12} G_p}{C_0 \mu\mu f.}$$

where $C_0 \mu\mu f$ is the capacitance in micro micro farads.

The dissipated energy per cc of the dielectric placed inside the parallel plates of the plane condenser and per second

$$W = \frac{\omega}{2\pi} \int_0^{2\pi/\omega} I.E.\, dt \qquad \cdots (1.24)$$

and also we have the equation $I = \frac{1}{4\pi} \cdot \frac{dD}{dt}$

We will first consider the case where D is in phase with E. Then we have

$$D = D_0 \cos \omega t$$

$$I = -\frac{\omega D_0}{4\pi} \sin \omega t$$

Thus the current density has phase difference $\pi/2$ with E. In this case no energy is dissipated in the dielectric and hence from equation (1.24)

$$W = -\frac{\omega^2}{8\pi^2} D_0 E_0 \int_0^{2\pi/\omega} \sin \omega t . \cos \omega t \, dt = 0$$

where there is a phase difference δ between D and E while $E = E_0 \cos \omega t$, we have

$$D = D_0 \cos (\omega t - \delta)$$

$$= D_0 \cos \omega t \cos \delta + D_0 \sin \omega t \sin \delta$$

Apparently $D_0 \cos \omega t$ is in phase with E where $D_0 \sin \delta$ has a phase difference of $\pi/2$ with E. The phase difference δ is generally called the loss angle.

$$I = -\frac{\omega}{4\pi} D_0 \sin \omega t \cos \delta + \frac{\omega}{4\pi} D_0 \cos \omega t \sin \delta$$

By this equation I is split into two parts. The first part has a phase difference of $\pi/2$ with E and thus it does not lead to a dissipation of energy. The second part, however, is in phase with E. The dissipated energy per c.c. of the

dielectric per second can be calculated as

$$W = \frac{\omega^2}{8\pi^2} D_0 E_0 \sin\delta \int_0^{2\pi/\omega} \cos^2\omega t \, dt$$

leading to $W = \frac{\omega}{8\pi} D_0 E_0 \sin\delta$

where the factor $\sin\delta$ is generally called the power factor.

If $D^* = D_0 \, e^{J(\omega t - \delta)}$

where D^* is the complex part of D_0 and $D^* = \epsilon^* E$

then $\epsilon^* = \frac{D^*}{E} = \frac{D_0 \, e^{J(\omega t - \delta)}}{E_0 \, e^{J\omega t}}$

$$= \frac{D_0}{E_0} e^{-J\delta}$$

But $\epsilon^* = \epsilon' - J\epsilon'' = \frac{D_0}{E_0}(\cos\delta - J\sin\delta)$

Then $\epsilon' = \frac{D_0}{E_0}\cos\delta$

and $\epsilon'' = \frac{D_0}{E_0}\sin\delta$

We find that the dissipated energy per c.c. of the dielectric and per second is given by

$$W = \frac{\omega}{8\pi} \cdot \frac{D_0}{E_0} \sin\delta \cdot E_0^2$$

$$= \frac{\epsilon''\omega}{4\pi} \cdot \frac{E_0^2}{2}$$

$$= \frac{K' E_0^2}{2}$$

The heat developed per cycle in the dielectric is evidently

$$W \text{ per cycle} = \frac{\epsilon'' E_0^2}{4} \text{ ergs per cycle.}$$

This demonstrates that K' is proportional to the heat developed per second and ϵ'' to that developed per cycle in the dielectric. In the above equation W is in ergs per second or per cycle when E_0, K' and ϵ'' are in e.s.u. These equations also show that the total current flowing in the dielectric has a dissipative and a non-dissipative part: ϵ' is proportional to non-dissipative part and ϵ'' to dissipative part. The loss tangent ϵ''/ϵ' may be interpreted as the ratio of the dissipative to the non.dissipative current and the power factor as the ratio of the dissipative current to the total current.

Under the influence of varying electric field each type of polarization takes some finite time to respond to applied field. This lag is known as relaxation. Considering Debye's expression for complex dielectric constant

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + J\omega\tau}$$

where ϵ_0 and ϵ_∞ are the static and high frequency dielectric constant and τ is the time of relaxation and separating real and imaginary part

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

$$\epsilon'' = \frac{(\epsilon_0 - \epsilon_\infty)\omega\tau}{1 + \omega^2\tau^2} \quad \cdots (1.25)$$

Substituting the value of ϵ'' and ϵ' in the expression of

$$K' = \frac{\epsilon'' \omega}{4\pi} \qquad \text{and} \qquad K'' = \frac{\epsilon' \omega}{4\pi}$$

we get

$$K' = \frac{1}{4\pi} \frac{(\epsilon_0 - \epsilon_\infty)\omega^2\tau}{1 + \omega^2\tau^2} \qquad \cdots (1.26)$$

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

Differentiation of equation (1.25) w.r. to ω shows that the dielectric loss factor has a maximum which occurs when $\omega\tau = 1$. The value ω_m of the angular frequency for which the loss factor is maximum, is called the critical frequency. In that case

$$\omega_m = \frac{1}{\tau} \qquad \cdots (1.27)$$

Equation (1.27) has been utilized by many workers in determining the value of relaxation time. On the otherhand, differentiation of equation (1.26) w.r. to ω shows that K' does not pass through a maximum as does ϵ'' but increases with ω, approaching a limiting value K_∞ the infinite frequency conductivity which is reached when 1 can be neglected in comparison with $\omega^2\tau^2$ so that

$$K'_\infty = \frac{\epsilon_0 - \epsilon_\infty}{4\pi\tau} \qquad \cdots (1.28)$$

$$= \frac{\epsilon_0 - \epsilon_\infty}{4\pi \times 0{\cdot}9 \times 10^{12}\tau} \qquad \cdots (1.29)$$

where equation (1.28) gives K'_{∞} in e.s.u. and (1.29) in ohms^{-1}cm^{-1}.

It is thus evident that from the measured value of radio frequency conductivity of pure polar liquid it is possible to calculate the time of relaxation which is a useful parameter in understanding the activation energy, intermolecular field and the structure of the molecule concerned.

We have assumed in calculating the above expressions that there is no free ions or electrons in the dielectric liquids. In this case displacement current is the only factor contributing to the conductivity as has been tacitly assumed by Murphy and Morgan. In practice all dielectrics fall far short of this ideal requirement. The evidence for the existence of free ions and electrons has been shown by many workers in recent years such as Standhammer and Seyer (1957), Adamczewski (1969), Loheneysen and Nageral (1971), Sen and Ghosh (1974) etc. However, it has been found that in polar dielectric liquids, the percentage of ions is large in comparison to nonpolar liquids. As the ion conduction produces Joule's heat, in an actual dielectric when an electric field is applied the total heat produced is due to the combined effect of dielectric loss and Joule's heating. Thus the radio frequency conductivity measurement provides us information regarding the displacement current and conduction current in a dielectric liquid which will be further discussed in section D.

C. RELAXATION TIME AND ION CONCENTRATION FROM RADIO FREQUENCY CONDUCTIVITY OF POLAR SOLUTE IN NON-POLAR SOLVENTS.

Most of the earlier works centered around the studies of the applicability of Debye equation for the determination of molecular radii from the measurement of relaxation times and macroscopic viscosity and experiments were done mainly by the microwave techniques on pure polar liquids as well as on polar liquids dissolved in nonpolar solvents. In case of dilute solutions of polar solute dissolved in nonpolar solvent, the system is in a quasi-isolated state and polar molecules are well separated to affect each other and consequently dipole-dipole interaction forces are absent. The theory for the formulation of time of relaxation from the radio frequency conductivity measurement of polar liquid in nonpolar solvent is discussed here for which we start from well known Debye equation (1.1)

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi N_1}{3}\left(\alpha + \frac{\mu^2}{3KT}\right)$$

where N_1 is the number of dipoles per c.c. Now if the field instead of being steady is a high frequency alternating one, the orientational polarization cannot follow the changing electric field but lags behind the field or in other words the polarization and so the dielectric constant becomes complex and Debye's equation is given by

$$\frac{\epsilon^* - 1}{\epsilon^* + 2} = \frac{4\pi N_1}{3}\left(\alpha + \frac{\mu^2}{3KT}\frac{1}{1 + J\omega\tau^*}\right) \quad (1.30)$$

where $\epsilon^* = \epsilon' - J\epsilon''$ can explain well the behaviour of dielectric in static field as well as in alternating field. If we put $\epsilon^* = \epsilon_0$ at an angular frequency $\omega = 0$ and $\epsilon^* = \epsilon_\infty$ at $\omega = \infty$, equation (1.30) reduces to

$$\frac{\epsilon_0 - 1}{\epsilon_0 + 2} = \frac{4\pi N_1}{3}\left(\alpha + \frac{\mu^2}{3KT}\right) \quad \cdots (1.31)$$

and

$$\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} = \frac{4\pi N_1}{3}\cdot\alpha \quad \cdots (1.32)$$

In eqn. (1.30) τ^* is known as intrinsic relaxation time which is related to τ by the relation

$$\tau^* = \frac{\epsilon_\infty + 2}{\epsilon_0 + 2}\,\tau$$

For very dilute solution since $\epsilon_0 \simeq \epsilon_\infty$, τ^* may be replaced by τ.

A convenient development of Debye's equation has been given by Frölich who investigated the properties of dielectric substances in an alternating field by considering that the attainment of equilibrium in a dielectric is exponential with time and has the decay function $f(t)$ which is proportional to $e^{-t/\tau}$ where τ is independent of time, but dependent upon temperature. He has obtained the relation

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + J\omega\tau}$$

Since ϵ^* is a complex quantity, separating real and imaginary parts we get the well known equations

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

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

These two are the basic equations which are used in determining the value of ϵ' and ϵ'' of a polar solute when dissolved in nonpolar solvent.

From (1.31) and (1.32)

$$\frac{\epsilon_0 - 1}{\epsilon_0 + 2} - \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} = \frac{4\pi N_1}{3} \cdot \frac{\mu^2}{3KT}$$

i.e.

$$\epsilon_0 - \epsilon_\infty = \frac{4\pi N_1 \mu^2 (\epsilon_0 + 2)(\epsilon_\infty + 2)}{27\,KT(1 + \omega^2\tau^2)}$$

Substituting this value in ϵ' and ϵ'', we get

$$\epsilon' = \epsilon_\infty + \frac{4\pi N_1 \mu^2}{27\,KT} \cdot \frac{(\epsilon_0 + 2)(\epsilon_\infty + 2)}{1 + \omega^2\tau^2}$$

$$\epsilon'' = \frac{4\pi N_1 \mu^2}{27\,KT} \cdot \frac{(\epsilon_0 + 2)(\epsilon_\infty + 2)\,\omega\tau}{1 + \omega^2\tau^2}$$

When a polar solute (2) is dissolved in a nonpolar solvent (1) to make a solution (12) of concentration C moles per c.c.

We have $N_1 = CN = \frac{N d_{12}}{M_2} \omega_2$

where N is the Avogadro number, d_{12} is the density of the solution, ω_2 and M_2 are the weight fraction and molecular weight of the solute respectively.

Hence

$$\epsilon' = \epsilon_{\infty 12} + \frac{4\pi N d_{12} \omega_2 \mu^2}{27 M_2 KT} \frac{(\epsilon_{12}+2)(\epsilon_{\infty 12}+2)}{1+\omega^2\tau^2}$$

$$\epsilon'' = \frac{4\pi N d_{12} \omega_2 \mu^2}{27 M_2 KT} \frac{(\epsilon_{12}+2)(\epsilon_{\infty 12}+2)}{1+\omega^2\tau^2} \omega\tau$$

Putting the values of ϵ'' and ϵ' in $K' = \frac{\epsilon'' \omega}{4\pi}$ and $K'' = \frac{\epsilon' \omega}{4\pi}$, we get the real part K' and imaginery part K'' of the radio frequency conductivity in case of dilute solutions

$$K' = \frac{4\pi^2 f^2 N \tau d_{12} \mu^2}{27 M_2 KT} \frac{(\epsilon_{12}+2)(\epsilon_{\infty 12}+2)}{1+4\pi^2 f^2 \tau^2} \omega_2$$

where $\omega = 2\pi f$ and

$$K'' = \frac{\omega}{4\pi}\left[\epsilon_{\infty 12} + \frac{4\pi N d_{12} \omega_2 \mu^2}{27 M_2 KT} \frac{(\epsilon_{12}+2)(\epsilon_{\infty 12}+2)}{1+\omega^2\tau^2}\right]$$

So it is evident that by measuring the radio frequency conductivity of solutions of polar solute in nonpolar solvents it is possible to calculate the value of

relaxation time.

We have assumed in calculating the above expressions that there is no existence of free ions or electrons in the dielectric liquids. But as discussed in earlier section, in an actual dielectric when an electric field is applied the total heat is produced due to combined effect of dielectric as well as Joule's heat due to conduction of ions. In that case for pure polar liquids Sen and Ghosh (1974) deduced a mathematical relation for the r.f. conductivity which is of the form

$$K' = A + \frac{B}{\eta}$$

where $A = \frac{1}{4\pi}(\epsilon_0 - \epsilon_\infty)$

and $B = \frac{ne^2}{6\pi a}$

n is the number of ions per c.c. of the polar solute, e is the electronic charge, η is the viscosity of the liquid and 'a' is the radius of the rotating unit. From the slope of $K' - \frac{1}{\eta}$ curve the number of ions per c.c. of the liquid such nitrobenzene, n-propyl alcohol and acetone has been calculated and in all the three liquids the value becomes ~~is~~ of the order of 10^{13}. But when a polar solute is dissolved in a non-polar solvent it has been shown by Sen and Ghosh (1980) that K' can be written in the form

$$K' = A + Bf^2$$

where $A = \frac{ne^2}{6\pi a \eta_{12}}$

and $B = \frac{4\pi^2 \mu^2 N \gamma d_{12}}{27 M_2 KT} (\epsilon_{12}+2)(\epsilon_{\infty 12}+2)\omega_2$

where η_{12} is the viscosity of the solution and other symbols have their usual significance. From the above expressions it is thus possible to find the relaxation time as well as free ion concentration.

D. ACTIVATION ENERGY FOR CONDUCTIVITY AND VISCOSITY.

In investigations on the conduction mechanism of liquid dielectrics both in natural state and when excited by ionization, an important role is played by the activation energy. The activation energy ΔE for electric conduction is determined in the simplest form from the formula

$$\sigma = \sigma_0 \exp\left(-\Delta E/KT\right) \quad \cdots (1.33)$$

where K is the Boltzmann constant, T is the absolute temperature, σ_0 is a constant having the dimensions of the conductivity σ. Experimentally ΔE can be determined from the slope of log σ Vs. 1/T plot according to the equation

$$\Delta E = -K \frac{\partial(\ln \sigma/\sigma_0)}{\partial(1/T)}$$

Chong and Imushi (1960) measured the mobilities of negative charge carriers in hexane and benzene as a function of temperature and found that the experimental results could be represented by

$$u = u_0 \exp\left(-W/KT\right)$$

where the activation energy W in hexane was 0.16 eV (3.7 KCal mol^{-1}). Gzowski (1961) conducted a series of experiments at a temperature ranging from 8°c to 51°c using saturated hydrocarbons and determined the values of activation energy for the viscosity and mobility of ions from the

relation

$$\eta = A \exp\left(W_1/RT\right)$$

$$u = B \exp\left(-W_2/RT\right)$$

In order to examine the dependence of ion mobility on the viscosity of the liquid, Gzowski drew two plots. The first one corresponds to the Stokes-Walden law $u = f(\eta^{-1})$ while the second was with Adamczweski's formula $u = f(\eta^{-3/2})$. It has been found that the negative ion mobility follows Walden's law whereas the mobilities of positive ions obey Adamczweski's formula. Forster (1962) observed that the temperature dependence of conductance of benzene was in all the cases a straight line when log of conductance or log of specific conductance was plotted against 1/T. He obtained the relationship of the form given by equation (1.33) for the dependence of conductivity on temperature at the various separation of electrodes and found the value of ΔE as 0.42 eV. The value of σ_0 was 5×10^{-6} ohm^{-1} cm^{-1} for distilled and degassed benzene and its value was found to increase with decreasing purity of benzene. The values of activation energy obtained by Forster for aromatic hydrocarbons were about 0.4-1 eV.

Jachym (1963 - 64) conducted a series of experiments on the dependence of conductivity of liquid on temperature. The dependence of both natural and ionization conductivity

(by means of X-ray and γ -radiation) was simultaneously measured in cyclohexane. These experiments showed that an increase in the ionization current was less dependent than the natural current on the increase of temperature. The activation energy for natural conductivity was almost four times greater than that for ionization conductivity. Measurements taken in saturated hydrocarbons (from hexane to hexadecane) of natural and ionization currents in a wider range of temperatures showed another important difference in the dependence of natural and ionization conductivity on temperature. Ionization coductivity is characterized by straight lines which are almost parallel to each other when $\ln I$ is plotted against $1/T$ but in the case of self conductivity, however, an abrupt change takes place at a certain temperature, above which a further increase in the natural current is connected with an increase in activation energy. A number of experiments on the electrical conductivity as a function of temperature in various liquids were conducted by Bassler and Riehl (1964 - 65). They have shown that at higher temperature, organic liquids show an intrinsic conductivity with an activation energy which is characteristic for each substance and they have obtained a relation connecting the conductivity and activation energy given by

$$K' = K_0 \exp\left(-\frac{\Delta E_c}{2KT}\right) \cdots (1.34)$$

Organische, Halbleiter (1966) justified the validity of the above equation under the condition when the size of the molecule is small. Adamczewski and Jachym (1968) in their paper have given a comparison of results by various research workers for the conductivity of different dielectric liquids and concluded that the natural conductivity values of organic liquids is a function of 1/T. Nicolau et al (1971) has measured electrical conductance (σ) of n-butyl, iso-butyl and amyl alcohols in the temperature range 0 - 97°C using an alternating field (f = 100 Hz). The variation of σ with temperature for these aliphatic alcohols has been explained by assuming that the intermolecular hydrogen bonds play an important role in the mechanism of electric conduction. They have also determined the activation energy of these alcohols using the same relation given by equation (1.34). Regarding the nature of internal frictional coefficient which opposes the rotation of polar molecules in a high frequency field much work has been done. Srivastava et al (1972) investigated the relaxation mechanism of some polar liquids in a mixture of benzene and paraffin as a solvent at microwave frequencies and found that static viscosity is not suitable for explaining the experimental results obtained by them in the Debye equation represented by

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

Krishnaji and Man Singh (1964) derived an equation using the theory of rate processes,

$$\tau = \left(\frac{A}{T}\right)\eta^x \qquad \cdots (1.35)$$

where A is a constant for a given substance and $x = \frac{\Delta H_\epsilon}{\Delta H_\eta}$ the ratio of two enthalpies. But the experimental data obtained by Srivastava et al shows that neither Debye equation nor equation (1.35) can explain the results satisfactorily. The linear nature of the curve as required by the above two equations between $\log \tau$ Vs. $\log \eta$ or τ Vs. η deviates when the viscosity becomes high. The deviation from linearity starts from a lower value of viscosity at higher frequencies. Dina Nath (1968) has also reported a considerable deviation from the linearity curve in the high viscosity region. This discrepancy at high viscosity region has been explained by Srivastava et al on the basis of viscoelastic effect. They explained that the viscosity which is directly measured is the d.c. viscosity and this is different from the viscosity at microwave frequencies. This has also been shown by Trevena (1968). Hence they suggested that it is desirable to use the dynamical viscosity $\eta_{dyn.}$ in place of static viscosity. Barlow and Lamb (1959) have shown a relation connecting the two viscosities as

$$\frac{\eta_{stat}}{\eta_{dyn.}} = 1 + (\omega \tau_s)^2$$

where τ_s is the viscoelastic relaxation time which represents a time constant that governs the return to equilibrium of the system following a sudden disturbance. Barlow and Lamb's expression has been tested by Srivastava etal but unfortunately found to be unsuitable to explain the observed experimental facts.

The frequency dependence of viscosity has been investigated by Sen and Ghosh (1978) who have determined the activation energy of conductivity and viscosity of some polar liquids such as acetone, nitrobenzene and normal propyl alcohol from the experimentally measured values of radio frequency conductivity at different temperature from room temperature to boiling point of liquid and at different frequencies in the range 0.4 to 8 MHz. It has been shown that the activation energy for electrical conductivity and that for viscosity are related to one another, both being functions of frequency and gradually decrease almost linearly with increase of frequency. The generalised theory put forward by Sen and Ghosh (1974, 1978) is based on the assumption of the existence of free ions in polar dielectrics so that when a radio frequency field is applied to a polar liquid, displacement current is not only the factor contributing to the conductivity as has been assumed by Murphy and Morgan (1939) but the conduction current due to natural plays a ionization plays a dominant role. Murphy and Morgan's expression assuming the absence of free ions for the conductivity is given by

$$K' = \frac{\epsilon'' \omega}{4\pi} = \frac{1}{4\pi} \frac{\epsilon_0 - \epsilon_\infty}{1 + \omega^2\tau^2} \omega^2 \tau \quad (1.36)$$

where the symbols have their usual significance. Substituting Debye's expression for the relaxation time $\tau = \frac{4\pi\eta a^3}{KT}$ in (1.36)

$$K' = \frac{(\epsilon_0 - \epsilon_\infty)\, \omega^2 a^3 \eta / KT}{1 + \frac{16\pi^2\eta^2 a^6 \omega^2}{K^2T^2}}$$

As in the case of most common dielectric liquids $\tau = 10^{-11}$ s and considering the frequency range in the r.f. region so that $\omega^2\tau^2 \ll 1$

$$K' = \frac{(\epsilon_0 - \epsilon_\infty)\omega^2 a^3 \eta}{KT}$$

Thus it is evident that if measurements of radio frequency conductivity are made at gradually higher and higher temperatures then as $\epsilon_0 - \epsilon_\infty$ and η/T are both decreasing functions of temperature, K' should decrease with the increase of temperature. But the experimental results show that radio frequency conductivity increases with the increase of temperature. It is well known that in-case of electrolytes where the conduction is mainly due to ions, Walden's rule is valid which states that the product of equivalent conductance at infinite dilution and the viscosity of the solvent is approximately constant and independent of the nature of the later. To find out whether a similar relationship holds in case of radio frequency conductivity of polar dielectrics, K' has been plotted against $1/\eta$ and it has been observed that the variation is almost linear for all the frequencies investigated and can be well explained by assuming the presence of free ions in polar dielectrics.

Taking the analogy from the motion of an electron in an ionized gas when the degree of ionization is small and assuming the resistive force as due to viscosity, the

equation of motion of the ion is given by

$$M.\frac{dv}{dt} = eE_0 e^{j\omega t} - 6\pi a\eta v$$

where 'a' is the radius of the molecule, η the coefficient of viscosity of liquid. Then

$$v = \frac{eE_0 e^{j\omega t}}{M(\nu + j\omega)}$$

where

$$\nu = 6\pi a\eta/M$$

Then

$$v = \frac{eE_0}{M}\left[\frac{\nu}{\nu^2+\omega^2} - j.\frac{\omega}{\nu^2+\omega^2}\right]e^{j\omega t}$$

If n denotes the number of free ions produced per unit volume then the current

$$i\,(\text{conduction}) = \frac{ne^2}{M}\left[\frac{\nu}{\nu^2+\omega^2} - j.\frac{\omega}{\nu^2+\omega^2}\right]E_0 e^{j\omega t}$$

If only the conduction current is present

$$K' = \frac{ne^2}{M}.\frac{\nu}{\nu^2+\omega^2}$$

$$= \frac{ne^2}{M}.\frac{6\pi a\eta/M}{(6\pi a\eta/M)^2+\omega^2}$$

As $a \simeq 10^{-8}$ cm., $\eta = 10^{-3}$ poise and $M = 10^{-24}$ gm.

$6\pi a\eta/M \gg \omega$

$$K' = \frac{ne^2}{6\pi a\eta} \qquad \ldots (1.37)$$

where K' is the real part of the radio frequency conductivity. Further as the applied field is alternating, from Murphy and Morgan equation (1.21)

$$i \text{ (displacement)} = \frac{\omega}{4\pi}\left(\epsilon'' + J\epsilon'\right) E_0 e^{J\omega t} \qquad \ldots (1.38)$$

Remembering $\omega^2\tau^2 \ll 1$ from (1.36), (1.37) & (1.38)

$$i \text{ (total)} = \left[\frac{1}{4\pi}\left(\epsilon_0 - \epsilon_\infty\right)\omega^2\tau + \frac{ne^2}{6\pi a\eta}\right] E_0 e^{J\omega t}$$

Thus

$$K' = \frac{1}{4\pi}\left(\epsilon_0 - \epsilon_\infty\right)\omega^2\tau + \frac{ne^2}{6\pi a\eta}$$

$$= A + \frac{B}{\eta} \qquad \ldots (1.39)$$

where $A = \frac{1}{4\pi}\left(\epsilon_0 - \epsilon_\infty\right)\omega^2\tau = \pi f^2\left(\epsilon_0 - \epsilon_\infty\right)\tau$

and $B = \frac{ne^2}{6\pi a}$ where $\omega = 2\pi f$

It is thus observed that in $K' - \frac{1}{\eta}$ curve, 'A' is the

intercept made by the straight line with K' axis and is a function of frequency while 'B' denotes the slope of the curve. The above theoretical deduction can explain very satisfactorily the observed experimental results with regard to dependence of radio frequency conductivity on viscosity as well as the variation of 'A' on frequency and enables us to calculate the number of ions per c.c. of the polar dielectric. The experimental results by Sen and Ghosh (1974) also shows that there is a similarity between equation (1.39) and Walden's rule.

Again the best representative empirical formula regarding the variation of viscosity of a liquid with temperature is given by

$$\eta = D \exp\left(\frac{\Delta E_v}{KT}\right) \quad \cdots (1.40)$$

where D is a constant and ΔE_v is the activation energy for viscous flow.

Putting the value of K' and η from (1.34) and (1.40) respectively and remembering $A = \pi f^2 (\epsilon_0 - \epsilon_\infty)\tau$ and $B = \frac{ne^2}{6\pi a}$ we have from (1.39)

exp.

$$\exp\left(\frac{-\Delta E_c}{2KT}\right) = \frac{f^2(\epsilon_0 - \epsilon_\infty)\pi\tau}{K_0} + \frac{ne^2}{6\pi a D K_0} \exp\left(\frac{-\Delta E_v}{KT}\right) \quad (1.41)$$

For a particular temperature

$$\Delta E_c = 2KT \log\left(\frac{1}{\beta + \alpha f^2}\right)$$

where $$\beta = \frac{ne^2}{6\pi a K_0 D} \exp\left(\frac{-\Delta E_v}{KT}\right)$$

and

$$\alpha = \frac{(\epsilon_0 - \epsilon_\infty)\pi\gamma}{K_0}$$

Then

$$\frac{d}{df}(\Delta E_c) = - \frac{4\alpha KTf}{[\beta + \alpha f^2]}$$

which shows that ΔE_c will decrease with increase of frequency.

From equation (1.41)

$$\exp\left(\frac{-\Delta E_c}{2KT}\right) = \frac{A}{K_0} + \frac{B}{K_0 D} \exp\left(\frac{-\Delta E_v}{KT}\right) \quad \ldots (1.42)$$

Thus it is possible to find the value of activation energy for viscosity from equation (1.42) if we know the values of K_0 and ΔE_c of equation (1.34) and A and B of equation (1.39).

As the process of electrical conductivity and that of viscosity are now considered in terms of activation energy it is worthwhile to measure this quantity and study its variation which will enable us to investigate the processes further.

E. OPALESCENT BINARY LIQUID MIXTURE.

It is well known that certain binary liquid mixtures such as aniline and n-hexane, methyl alcohol and cyclohexane, nitrobenzene and n-hexane etc. exhibit a marked opalescence or turbidity at a temperature known as critical solution temperature. This phenomenon of opalescence in liquid mixtures has been studied by many investigators both theoretically and experimentally from different angles such as light scattering phenomena, change of dielectric constant, viscosity, ultrasonic absorption etc.

The existence of critical points was discovered by Andrews (1869) in connection with his classical investigation of carbon dioxide isothermal. His main conclusion was that there is only a single fluid condition of matter which can split into coexisting forms of different density provided the temperature is below a certain critical value. Smoluchowski (1908) and Einstein (1910) were the first to propose a theoretical explanation of opalescence in liquid mixtures in the immediate neighbourhood of the critical solution temperature. These authors regarded opalescence in liquid mixtures as due to local fluctuations in composition and consequent optical inhomogeneity. The theory of Smoluchowski and Einstein predicts an infinite intensity of scattered light and also complete polarization.

Regarding the theory of light scattering Smoluchowski's theory (1908) predicts

$$\frac{I}{I_0} \propto \frac{1}{\lambda^4}\left(1 + \cos^2\theta\right)\gamma^{1/2}$$

where I and I_0 are the intensity of scattered and incident radiation of wavelength λ observed in the direction θ and $\gamma = \frac{\partial^3 V}{\partial P^3}$. Ornstein and Zernike (1914 - 1926) quantitatively studied the intensity of light scattering in opalescent binary liquid mixtures and put forward a modified theory which takes into account the mutual influence of fluctuations in density in neighbouring small elements of volume in the fluid. According to them, modified Smoluchowski's equation becomes

$$\frac{I}{I_0} \propto \frac{1}{\lambda^4}\left(1 + \cos^2\theta\right)\frac{1}{\left\{\frac{1}{\beta} + d^2\left(\frac{\sin\theta/2}{\lambda}\right)^2\right\}}$$

where the constant d^2 is a measure of the range of the intermolecular forces and β is the compressibility given by

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

Rocard and Ponte (1928) adversely critised the Ornstein - Zernike theory and have shown that some of the conclusions derived from Ornstein - Zernike theory do not agree with the observed results. An attempt has been made by Rocard himself (1933) to explain the finite value of the depolarization of the opalescent scattering. He takes into consideration the scattering arising from the fluctuations in the molecular field which according to him become appreciable at the critical solution temperature. The theory presented by

Rocard predicts that

$$\frac{I}{I_0} \propto \frac{1}{\lambda^4}\left(1 + \cos^2\theta\right)\frac{1}{\left(1/\beta + C\right)}$$

where C is constant.

Hence the general expression for the light scattering at the critical points can be written in the form

$$\frac{I}{I_0} \propto \frac{1}{\lambda^4}\left(1 + \cos^2\theta\right)\left(\frac{1}{\beta} + C + d^2\frac{\sin^2\theta/2}{\lambda^2}\right)^{-1} \quad (1.43)$$

For C = 0 equation (1.43) reduces to the expression of Ornstein and Zernike and for d = 0, to that of Rocard's expression. Though the measurement of dependence of critical opalescence on the wavelength and angle of scattering could throw some light on this problem, the experimental work has not settled the problem in clear fashion so far.

It was pointed out by Krishnan (1935) that it is important to make comparative studies of the state of polarization of the transversely scattered light with the incident light in different states of polarization in order to get a correct idea of the state of dispersion of the scattering elements in the medium. The depolarization factor observed by him in the light scattered transversely by opalescent binary liquid mixture is different from unity although in case of clear solutions the value is unity. The discrepancy was explained by Krishnan on the hypothesis that in case of clear solution the scattering is due to single molecules whereas in case of opalescent mixture it is due to cluster of molecules. Whether the intense density

fluctuation is due to formation of groups of molecules in the critical state has not however been conclusively proved. No information regarding the actual composition of elementary volumes or groups of molecules can however be obtained from the light scattering data except the fact that scattering is due to ellipsoidal particles of size not very small in comparison with the wavelength of light.

So far as the change of dielectric constant of binary liquid mixtures near the critical temperature is concerned, Piekara (1932) observed that in case of nitrobenzene-hexane system at the critical temperature, dielectric constant ϵ' increased with decreasing temperature and the derivative $\frac{d\epsilon'}{dT}$ was not constant but decreased near the critical temperature. He also studied the density and molecular polarization of the mixture. Considerable fluctuation of density took place as the critical point is approached which manifests itself by the appearance of critical opalescence. It is obvious that the density fluctuations are responsible for such considerable decrease of polarization of nitrobenzene. Semenchenko (1951) examined a number of polar nonpolar systems and found that there are maxima in both dielectric constant ϵ' and dielectric loss ϵ''. He formulated that in general, the primary process of the formation of a dispersed system at the critical point consists in the transition of the system into a microheterogeneous state and under the critical condition a maximum possible microheterogeneity can be realized for a given system.

When these conditions are disturbed, there occurs a sudden fusion of the molecular aggregates and a transition of the microdispersed system into an ordinary dispersed system having a milky cloudiness as its characteristic. Using these principles and a thermodynamic argument, Semenchenko has been able to explain the existence of maximum of the dielectric constant and other physical properties. Although Semenchenko's treatment predicts a large increase in ϵ' at critical temperature, the experimental evidence is meager and frequently contradictory. Lomova and Shakhparonov (1960) studied the nitrobenzene-hexane system and observed similar results for the change of dielectric constant at the critical temperature as that obtained earlier by Piekara. Quinn and Smyth (1963) examined the nitrobenzene - 2,2,4 trimethylpentane at a single concentration of nitrobenzene, namely 25% by weight at frequencies 0.5, 3.0×10^3, 9.3×10^3 and 2.4×10^4 M.Hz. A pronounced maximum was found in ϵ' at a temperature about 2°C above the consulate temperature. Arkhangelskei and Semenchenko (1967) examined a number of polar nonpolar systems and found that dielectric constant ϵ' and dielectric loss ϵ'' show a maximum at the critical temperature region. Lubezky and McIntosh (1974) studied the aniline - cyclohexane system and found no anomalous large values of ϵ' and ϵ'' at the critical temperature. They have suggested that the approach to the system to phase separation involves only the density fluctuations and no evidence was found for the sudden formation of molecular clusters when approached to critical point.

A re-examination of the thermodynamical arguments led by Walliwell etal also predicts that there should be no anomalous value of ϵ' at the critical temperature. Recently Konecki (1978) investigated a large number of systems viz. nitrobenzene in 2,2,4-trimethyl pentane, hexane, cyclohexane and cyclopentane purely from experimental point of view and observed no maxima in ϵ' value at critical point but the derivative $d\epsilon'/dT$ decreased with decreasing temperature near the critical temperature. The results are similer to that of Piekara obtained earlier in case of nitrobenzene-hexane system.

Although there are some contradictory results regarding the sharp increase in ϵ' in the opalescent state it is however conclusively proved that there is a sharp rise in the coefficient of viscosity and ultrasonic absorption near the critical temperature. The large values of anomalous ultrasonic absorption near the critical region have been reported by different workers such as Chynoweth and Schneider (1951), Fixman (1962), Anantaraman etal (1966), Pule and Kirkaldy (1971), Gutschick and Pings (1971), Aggarwal and Gupta (1975), Nishigaki (1978) and also reviewed by C.W. Garland (1970) and K. Kawasaki (1976).

The anomalous increase in viscosity of binary liquid mixtures near the critical temperature has long been a matter of interest. Mondain - Monval and Quiquerez (1944 - 1945) investigated the viscosity and opalescence of binary and ternary systems such as water - aniline - ethanol,

water-benzene-ethanol, water-toluene-ethanol, aniline-cyclohexane, nitrobenzene-hexane and observed an increase in viscosity near the critical temperature. The systems showing abnormal viscosity are believed to possess a colloidal structure in the critical region. Semenchenko and Morina (1950) investigated the viscosity of nitrobenzene-hexane mixture. The results showed that the peak of viscosity in the critical region was atleast 20% in excess of the value that would correspond to a linear increase. Reed and Taylor (1959) have observed the anomalous increase in the viscosity of isooc - tane-perfluoroheptane mixtures. The anomalous behaviour can be detected as far way as 10° from the critical temperature. However, other investigatbrs found that for these systems the anomaly occurs only at temperatures much closer to the critical point.

Fixman (1962) on the basis of density fluctuation near the critical region treated theoretically the increase of viscosity of critical mixtures. His method involves calculation of the entropy production through diffusion which results when a mixture in a state of composition fluctuation is caused to have a velocity gradient. The long wavelength part of the spectrum of composition fluctuation is intense and very easily distorted by a velocity gradient in the critical region. The return to uniform composition through diffusion dissipates energy, and the loss is interpreted as an excess viscosity. Fixman has developed his theory in two

stages. In the first stage, he has considered the local equation of motion and diffusion in a mixture in the critical region, a parallel plate flow and in the second stage, a calculation of the entropy production. The calculation shows that the frictional resistance of diffusion induced by the velocity gradient is really responsible for enormous entropy production.

Considering the above mentioned stages, the final expression of the macroscopically observed viscosity is

$$\eta_M = \eta_0 + \left(\rho n_2 \frac{\partial c_2}{\partial n_2}\right)^2 \left(\frac{a}{40\alpha}\right) k^{-1}$$

$$\eta_M - \eta_0 = \Delta\eta = \left(\rho n_2 \frac{\partial c_2}{\partial n_2}\right)^2 \left(\frac{a}{40\alpha k}\right) \qquad \cdots (1.44)$$

where η_0 = local viscosity evaluated at the mean composition

ρ = density of the mixture

c_2 = mass of component 2 in unit mass of mixture

a = distance through which shearing force acts and generally expressed in angstroms

α = diffusion constant

n_2 = number of molecules in component 2/c.c.

The equation (1.44) has to be put in a form suitable for comparison with experiment and for the use of approximate theories of the thermodynamic properties of the solution.

Considering Gibbs-Duhem relation and the theory of rate process by Glasstone, Laidler and Eyring (1941), the expression for α interms of the diffusion constant D_{id} of an ideal mixture can be written as

$$D_{id} = \left(\frac{\alpha e RT}{m_1 m_2^2 n_1}\right)\left(\frac{\partial \ln x_2}{\partial n_2}\right) \qquad \cdots (1.45)$$

where,

n_1 = number of molecules of component I/cc

n_2 = number of molecules of component II/cc

m_1 = mass per molecule of component I

m_2 = mass per molecule of component II

x_2 = mole fraction of component II

and it can be readily verified that

$$\frac{\partial \ln x_2}{\partial n_2} = \left[V_1 n_2 (n_1 + n_2) \right]^{-1} \qquad \cdots (1.46)$$

Also $n_2 \frac{\partial c_2}{\partial n_2}$ in equation (1.44) can be written as

$$n_2\left(\frac{\partial c_2}{\partial n_2}\right) = \frac{m_1 c_2}{e V_1} \qquad \cdots (1.47)$$

From equations (1.44), (1.45), (1.46) and (1.47) the viscosity increment expression becomes

$$\Delta\eta = \eta_M - \eta_0 = \left[\frac{RT m_1 \varphi_2}{D_{id}\, e \varphi_1 V_1^2 V_2 (n_1+n_2)}\right]\left[\frac{a}{40R}\right]$$

$$= \left[\frac{RT m_1 m_2 \varphi_2}{e V_1^2 D_{id} m_2 V_2 (n_1+n_2)\varphi_1}\right]\left[\frac{a}{40R}\right]$$

$$= \left[\frac{\beta m_1 m_2 \varphi_2}{e V_1^2 V_2 (n_1 + n_2) \varphi_1} \right] \left[\frac{a}{40 R} \right]$$

where friction constant $\beta = \frac{KT}{m_2 D_{id}}$

$\Delta\eta$ can be rearranged as

$$\Delta\eta = \frac{m_1 m_2 \varphi_2}{e V_1^2 V_2 (n_1 + n_2) \varphi_1} \left(\frac{a^{1/2}}{R} \right) \frac{1}{40} \left(\beta a^{1/2} \right)$$

where $\frac{a^{1/2}}{R}$ has been evaluated by Fixman as

$$\left(\frac{a^{1/2}}{R} \right) = \left[\frac{V_1}{4\pi\varphi_2} \right]^{1/2} \left[\left\{ \varphi_1^{-1} - \left(1 - m^{-1}\right) - \frac{T_c}{T} \left(1 + m^{-1/2}\right)^2 \varphi_2 \right\}^{-1} - \frac{V_2}{V_1} \right]^{1/2}$$

where

$V_1 = \frac{M_1}{e_1 N_0}$ = volume per molecule of component I

$V_2 = \frac{M_2}{e_2 N_0}$ = volume per molecule of component II

$m = V_2/V_1$ $\quad T_c$ = critical temperature

$\varphi_1 = V_1 n_1$ $\quad N_0$ = Avogadro's number

$\varphi_2 = V_2 n_2$ $\quad e_1$ = density of component I

e_2 = density of component II

Taking the experimental data of Reed and Taylor on the mixture ($i - C_8H_{18} - C_7F_{16}$) and considering C_7F_{16} as component II, Fixman showe from his theoretical model that viscosity rises sharply when binary liquid mixture is critically opalescent. He also calculated the

value of $\beta \alpha^{1/2}$ and concluded that the comparison of the theory with the experiment is not completely conclusive and what is needed for this, is more viscosity data near the critical temperature.

Campbell etal (1968) have studied aniline-hexane system and observed anomalously high viscosity over a temperature range of 2.4°C above the critical solution temperature. Brunet and Gubbins (1969) reported the increase in viscosity that occurs for a binary mixture close to the critical temperature in case of phenol - water, aniline-cyclohexane, methanol-n-hexane, methanol-cyclohexane. Viscosities have been measured for the above systems at several temperatures and over the entire composition range. Comparison of the experimental results with the predictions of Fixman's theory reveals that the temperature dependence of the excess viscosity is well described by the theory. However, the theory is less successful in predicting the effect of composition on excess viscosity. Yang and Meeks (1971) observed the increase in viscosity in case of cyclohexane-aniline binary liquid mixture near the critical temperature for three compositions 0.430, 0.445, and 0.460 mole fractions of aniline. Neither logarithmic nor exponential behaviour of the viscosity is followed for the full range of temperatures investigated.

The pioneering theoretical work of Fixman as well as the later treatment of Kawasaki (1966) and Deutch and Zwanzing (1967) predict a strong divergence of the anomalous part of the shear viscosity as a power of (T-Tc) near critical temperature.

Another report of Kadanoff and Swift (1968) and Swift (1968) on the other hand, suggests that the singular part of the viscosity does not diverge as a power of (T - Tc) in the critical region, but atmost shows a weak divergence. A decision based on experiments as to which of the two theoretical approaches describes more accurately the shear viscosity coefficient near the critical temperature has been difficult to make. The early work of Reed and Taylor (1959), Woermann and Sarholz (1965) and Barber and Champion (1969) lend support to the view that the singularity is strongly divergent. The experimental results presented by Leister etal (1969), Arnovita etal (1969), Huang and Webbs (1969) and Stein etal (1971) support at least in the sense that there is apparently no strong power law divergence. The measurement of viscosity by Ballaro et al (1972) shows that an anomalous behaviour of viscosity appears closer to the critical point. It has been found that the singular behaviour of the viscosity cannot be fitted by a simple power law nor by a logarithmic one in the entire range of temperature. The asymptotic behaviour, however, tends to become logarithmic as the critical temperature is approached.

Sen and Ghosh (1972) have measured the radio frequency conductivity in case of two opalescent mixtures (nitrobenzene - n-hexane, aniline-cyclohexane) and found a large increase of radio frequency conductivity at critical temperature. From the calculated value of time of relaxation and radius of the

rotating unit, it has been shown that the intense density fluctuation at critical stage is not due to formation of cluster of molecules as proposed by Krishnan. Utilizing Fixman's theory they have calculated the increase of viscosity and hence the values of frictional constant β which are found to be in close agreement as regards the order of magnitude incase of a liquid. They have also suggested an alternative method of calculating the value of β and finally concluded that as assumed by Fixman, there is an intense density fluctuation in the critical state and return to normal density fluctuation through diffusion dissipates energy which appears as a sharp increase of viscosity.

F. DIELECTRIC CONSTANT OF POLAR LIQUIDS IN MAGNETIC FIELD.

The problem of the effect of magnetic field on the dielectric constant of a substance has not received much attention either by experimentalists or by theoreticians. It is due to the fact that so far experimentally investigated, the change in the dielectric constant is normally very small. However in liquid crystals large changes have been observed (Kast 1924, Bauer 1926, Marinin and Tsvetkov 1939) and appreciable effects have been found in some solids (McMahon 1956).

The phenomenon of spatial quantization is one of the best known and most characteristic feature of the quantum theory. By this is meant the fact that according to the quantum conditions the molecule can only assume certain particular orientations in space. The particular condition responsible for the spatial quantisation is usually the requirement that the angular momentum of the molecule along some direction fixed in space be an integral or half integral multiple M of $h/2\pi$. Here M is called the magnetic quantum number. A direct experimental confirmation of spatial quantization is furnished by the well known experiment of Stern and Gerlach (1924) on the deflection of atoms in a nonhomogeneous magnetic field. Since the technical difficulties of this experiment are so great, Ruark and Breit (1925) have proposed to devise other means of testing the space quantization. According to the suggestions made by Ruark and Breit as well as some theoretical calculations

made by Debye (1926) the possible change in the dielectric constant of gases viz. helium, oxygen and air in magnetic field due to space quantization were undertaken experimentally due by Weatherby and Wolf (1926) using heterodyne beat method and the results show that for helium (20 cm. pressure) air (76 cm) and oxygen (76 cm) at room temperature, there is no change in dielectric constant to 1 part in 500,000. The magnetic field was of the order of 7000 - 8000 gauss while the electric field was estimated at 5000 - 10,000 volts/cm. Experiments were carried out with the direction of the electric field both parallel and normal to the direction of the magnetic field. Since none of these gases helium, oxygen or air are of so called polar class, naturally it seems that lack of effect of magnetic field in the above gases is due to their small permanent electric polarization. L.H. Mott-Smith and Daily (1926) have made an experiment to test the change of dielectric constant in presence of magnetic field of the system Hcl and NO gases which have certainly a strong permanent electric dipole moment, but no change was detected. The magnetic field strength was 4800 gauss and the apparatus was capable of detecting a change in dielectric constant of one part in 100,000. The gases were tested at pressures of about 2 to 40 cm. of mercury at room temperature and with the magnetic field both parallel and perpendicular to the electric field.

Pauling (1927) investigated theoretically the motion of a diatomic dipole molecule in crossed magnetic and electric fields and showed that according to old quantum theory there will be spatial quantization particularly with respect to the direction of the magnetic field for experimentally realizable values of field strengths. He proved mathematically that in presence of strong magnetic field making an angle ψ with the electric field the polarization due to permanent dipoles will according to old quantum theory be $\left(3/2\ \cos^2\psi - 1/2\right)$ times its value in the absence of the magnetic field. On the other hand according to new quantum mechanics, the theory of dielectric constant of diatomic dipole gas requires the dielectric constant not to depend upon the direction characterizing the spatial quantization so that a magnetic field should not influence the dielectric constant of a gas such as hydrogen chloride. Assuming certain conditions Van Vleck (1927) deduced the Debye formula

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi N}{3}\left(\alpha + \frac{\mu^2}{3KT}\right)$$

with the help of new quantum mechanics and confirms the idea of Pauling that unless the magnetic field is exceedingly larger than those ordinarily considered, a magnetic field should according to new quantum mechanics be without effect on the dielectric constant of gases. He also concluded that it must not, however, be inferred that the dielectric constants of all substances are not influenced by magnetic field.

For instance, the experiments of Jezewski (1924), Kast (1924), Friedel (1925) and Bauer (1926) show that the dielectric constants of certain "mesomorphic substances (anisotropic liquids) are perceptibly altered by magnetic fields. This neverthless, must not be regarded as disproving the existing theory, as liquid crystals are likely to be built out of large complexes (elementary crystals) rather than out of ordinary free molecules such as were assumed by Van Vleck in deducing the Langevin-Debye theory intended primarily for gases.

Buckingham (1957) investigated the effect of a strong magnetic field on the static dielectric constant of a diamagnetic fluid theoretically using statistical mechanics. In a strong uniform electric field E, ϵ can be written as a power series in E^2

$$\epsilon = \epsilon_0 + bE^2 + cE^4 + \cdots$$

where b and c are characteristic of the specimen and it has been shown (Van Vleck 1932, Buckingham 1956) that

$$b = q_0 + \frac{q_1}{KT} + \frac{q_2}{K^2T^2} + \frac{q_3}{K^3T^3}$$

q_0 is related to the molecular 'hyperpolarizability' and q_1 is dependent upon the anisotropy in the polarizability tensor. The term in q_2 is also dependent on the anisotropy but in addition is proportional to the square of the molecular dipole moment μ . q_3 represents the dipole saturation term and is proportional to μ^4. Buckingham considered that in a diamagnetic material ϵ can be

represented as

$$\epsilon = \epsilon_0 + BH^2 + CH^4 + \cdots$$

where $B = B_D + B_V$, B_V being magnetostriction term given by

$$B_V = - \frac{(\epsilon_0 - 1)(\epsilon_0 + 2)\, V_H}{3V}$$

If B is measured at constant volume then $B_V = 0$ and hence $B = B_D$. Using statistical mechanics Buckingham calculated the value of B_D in case of non-polar molecules, spherical molecules and polar anisotropic molecules. Utilizing this theory in case of nitrobenzene, Buckingham found that B_D becomes equal to 2.3×10^{-14} $(3\cos^2\Omega - 1)$, Ω being the angle between electric field and magnetic field. For $\cos^2\Omega = 1$ and $H = 20400$ oersteds, the change of dielectric constant $\Delta\epsilon = 2.0 \times 10^{-5}$ which is only one thirtieth of Piekara's observed (1936) experimental value $\Delta\epsilon = 6 \times 10^{-4}$ in case of nitrobenzene for the same field strength. Piekara and Chelkowski (1963) have detected experimentally an increase of dielectric constant of nitrobenzene by an amount 3.9×10^{-6} when a strong magnetic field from 0 to 40 kilo Gauss is applied with a circuit capable of detecting $\Delta\epsilon \simeq 10^{-6}$. The measurements were carried out by the method of magnetic field strength differences in order to reduce heating of the condenser by eddy currents. The variation of $\Delta\epsilon$ thus found was in very good agreement with the theoretical calculations for a

local electric field of Onsager type.

In the above discussion the magnetic field applied is horizontal so that the volume of the liquid may be taken as constant. The effect of magnetic field can be looked upon as producing a mechanical stress in the liquid. As a result the volume and hence the density of the liquid will change and a change in dielectric constant may be expected. In fact the effect of pressure on the dielectric constant of a liquid has been investigated by many workers such as Roentgen (1894), Ortvay (1911), Falkenberg (1920), Kyropoulos (1926), DanForth Jr. (1931), Jacobs and Lawson (1952) Gilchrist, Early and Cole (1957), Johari and Dannhauser (1968) and more recently by Franck and Deul (1978). It has been observed that the dielectric constant increases with the increase of pressure. When a dielectric is placed in a magnetic field it is subjected to a mechanical stress which is equivalent to pressure and it is expected that if a sensitive arrangement can be made, the small change of dielectric constant can be detected.

G. ELECTRICAL CONDUCTIVITY OF LIQUIDS IN D.C. FIELDS.

The conduction of electricity is one of the most fundamental problems in liquid dielectrics as it given the information regarding ionic concentration, mobility of ions and activation energy. The earliest investigation of conduction current in a liquid was done by Quincke in 1895. He concluded that the current is non-ohmic and probably electrolytic in origin. Curie (1902) observed that the electrical conductivity of petroleum ether, carbon tetrachloride, carbon disulphide and benzene was increased by exposure to gamma rays or x-rays. Schweildler (1907) showed experimentally that the conductivity of saturated hydrocarbon decreased with increased purification. Jaffe (1906, 1908) studied the current voltage characteristic of hexane when irradiated by gamma rays and considered the current as sum of two separate currents, one rising to a saturation value like the current in the gas while the second is an ohmic current. In 1909 he succeeded in measuring the small current that developed when a voltage was impressed on highly purified hexane in a brass conductivity cell. His results show that in the pure state the conductivity of hexane was due to cosmic radiation and that about 146 ions were produced per cm^3 per second. But Jafee (1913) himself discarded this view of separate currents in favour of a theory according to which the ions are produced in very densely packed columns

isolated from each other. These columns are the tracks of the photo electrons ejected by the gamma rays and he concluded that for a field of less than 100 V/cm, a large part of the current is caused by external ionizing radiation. Nikuradse (1932) studied the current in dielectric liquids over a wide range of field strength and gap width. He observed that current depends on the purification of the liquid, electrode geometry and electrode material, but is independent of pressure. When all the ionizing agents such as x-rays and other radio active sources were removed, it was found that there still exists a residual or natural conductivity in these liquids. Many theories have been advanced to explain the mechanism of current conduction in liquid dielectrics.

Earlier investigators (Nikuradse 1932) obtained some evidence that ionization by collision in analogy to gaseous conduction occured in liquids. It is assumed that ions are initially present in the liquid which are the current carriers at low field strengths. These are supposed to be formed by some ionizing agents such as x-rays or cosmic rays or from electrolytic dissociation. At intermediate field strength this ion current saturates and becomes independent of field until a value is reached such that the ions attain sufficient velocity to form new ions by collision at a rate that the current becomes an exponential function of the voltage. Inge and Walther (1935) rejected this view on the ground that the electronic free path in a liquid would be insufficient for an electron to acquire the energy needed for ionization.

Reiss (1936, 1937) applied the Onsager theory of weak electrolytic dissociation to explain the conductivity phenomena. His supposition is that even the most chemically pure dielectrics contain traces of polar impurities whose ionization is sufficiently enhanced at high fields to explain the observed conductivities. Baker and Boltz (1937) and Dornte (1940) interpreted their investigation to mean that the conductivity is due to thermionic emission from the cathode combined with a Schottky effect. According to them, current - voltage relation is given by

$$\log I = \frac{e^{3/2}(E\epsilon)^{1/2}}{KT}$$

where ϵ is the dielectric constant of the liquid, E is the field strength. This has been criticised by Lepage and Dubridge (1940) who showed that the current - voltage relation is of the form

$$\log I = \frac{e^{3/2}(E/\epsilon)^{1/2}}{KT}$$

Later on they concluded that current is due to field enhanced thermionic emission and derived the relation

$$I = AT^2 \exp\left[-\frac{\varphi e}{KT} + \frac{1}{2\cdot 3KT}\left(\frac{e^3E}{\epsilon}\right)^{1/2}\right] \quad \cdots(1.48)$$

where ϵ is the dielectric constant of the liquid.

Gemant (1940) suggested a method for the determination of ionic mobilities in insulating liquids from the current - time curve obtained after application of a d-c potential.

The ionic radii and the concentration of the charge carriers have been computed from the mobilities thus obtained. Assuming that the decay of current passing through an insulating liquid after the application of a d-c potential is, partly at least, caused by the removal or accumulation of ions present near the electrodes, Gemant deducedan equation interms of specific conductivities

$$\sigma = \sigma_0 e^{-mE_0t/a^2} + \sigma_f \quad \cdots (1.49)$$

where m = mobility of an ion, E_0 = Applied field a = Interelectrode distance of the condenser of cross sectional area 1sq.cm, σ_f = specific conductivity corresponding to saturation value. If m and m' are the mobilities of positive and negative ions then equation (1.49) can be rearranged to

$$\frac{\sigma - \sigma_f}{\sigma_0} = \frac{m}{m+m'} e^{-mE_0t/a^2} + \frac{m'}{m+m'} e^{-m'E_0t/a^2} \quad \cdots (1.50)$$

Equation (1.50) is the final form from which ionic mobilities have been computed. The ionic radii and number of particles have been evaluated from the equations

$$r = \frac{en}{6\pi\eta m} \quad \text{and} \quad n' = \frac{\sigma_0}{en(m+m')}$$

where e is the electronic charge, n is the valency of ion and η is the viscosity of the liquid.

Plumley (1941) and Pao (1943) interpreted with experimental support, the potential dissociation theory originally proposed by Onsager (1934) for very weak electrolytes. According to this theory there are present in purest hydrocarbons such as hexane, a very small number of ions resulting from spontaneous dissociation of molecules. A favourable orientation of the molecules with respect to the field increases dissociation and the number increases rapidly with the st strength of the field. On this basis Plumley was able to give an expression for the current interms of temperature T and field E, applicable to a number of dissociated molecules

$$I_A = C \exp\left(\frac{2q}{KT}\right)\left(\frac{qE}{300\epsilon}\right)^{1/2}$$

where C is a constant and is proportional to the number of dissociated molecules at zero field, K is the Boltzmann constant, q the unit charge and ϵ is the dielectric constant. The above expression can be represented as

$$\ln I_A = A E^{1/2}$$

which is an important conclusion of Plumley's theory. Eck (1949) showed that variation of current strength with time can be represented by the equation

$$I - I_\infty = (I_0 - I_\infty) e^{-KT}$$

where I_0 is the initial current, I_∞ is the limiting value of current and K is a constant which contains ionic mobilities. The effect is assumed to be due to initial existence of ionic clusters in the body of the liquid which

gradually disperse. He performed experiments on acetone, nitrobenzene and acetone substituted compounds. Goodwin and Macfadyen (1953) measured the current as a function of electrode gap width and field strength. Extrapolation to zero gap width showed the existence of a zero gap width current that obeys a field emission relation of the form

$$I = AE^2 \exp(-b/E) \quad \ldots (1.51)$$

Jaffe and LeMay (1953) studied the time dependent currents in hexane for wide electrode gaps and low voltages and concluded that the currents are ionic. Green (1955) studied the conduction and breakdown in n-hexane and concluded that the magnitude of the conduction current depends on the nature of the cathode and a significant current would remain for zero gap width. A more important conclusion made by him is that field emission relation or field enhanced thermionic emission theory represented by the equation (1.48) or (1.51) is not able to explain the observed experimental facts. On the other hand he assumed that positive ions are always present in the liquid because of external radiation or dissociation of impurity molecules. When an external field is applied these ions drift towards the cathode but a cathode surface layer impedes their immediate neutralization. The ions then set up a local field across the surface layer that tends to produce electron emission. The size of the local field depends upon the magnitude of the ionic current and the probability

of neutralization of the ions. Crowe (1956) put forward the hypothesis of the "hopping" electron. This was later discussed by LeBlanc (1959) on the basis of experimental results. According to this hypothesis, the electron in the liquid travels as a free electron the distance λ and is then captured by a molecule (trap). It remains in the trap in a bound state for the time τ and then leaves the trap as a free electron to travel the distance λ until the next capture. Thus the drift mobility of the ion in the electric field can be formulated as

$$u = \frac{u_0 \lambda}{c(\tau + \lambda/c)} \qquad \cdots \quad (1.52)$$

where u_0 denotes the ion mobility in the absence of traps and c is the mean velocity of the electron in its thermal motion. If the influence of temperature on the time τ [the length of time in which the electron remains in the trap $\left(\tau = \tau_0 \exp(W/KT)\right]$ is taken into consideration equation (1.52) can be written as $c = 10^7$ cm/sec. and $\tau \gg c$

$$u = \frac{u_0 \lambda}{c \tau_0} \exp\left(-\frac{W}{KT}\right)$$

where W denotes the mean energy with which the electron is captured. Standhammer and Seyer (1957) have obtained evidence for the formation of ions in cyclohexane and cyclohexene saturated with water. Hart and Mungall (1957) observed that the conduction current in chlorobenzene continued to decrease even after continuous distillation for as long as three months.

Chong et al (1958 - 60) while studying the Kerr effect in nitrobenzene found that the movement of positive ions are responsible for the field distortion and the mobility of the ions is estimated to be of the order of 10^{-3} cm^2 sec^{-1} $volt^{-1}$. While conducting the experiment of temperature variation of mobilities of negative charge carriers in hexane and benzene, they found the numerical values of ion mobility at room temperature to be 8.5×10^{-4} and 4.2×10^{-4} cm^2 V^{-1} Sec^{-1} respectively. Blank et al (1961) studied the current time characteristic curve and found that rate of decay of current depends upon the amount of impurity present in the liquid and decreased with repeated purification of liquid, Forster (1962, 1964) studied the nature of conduction in pure benzene and also at different concentrations in n-hexane and obtained a relation $\sigma_S = \sigma_H e^{CK}$ where σ_H is the conduction of n-hexane, K is constant and C is the concentration. He showed that the conduction in aliphatic liquids is most probably related to the presence of polar impurities or trapped electrons present in the liquid or generated at the electrode surface. According to Forster's theory, self conduction consists of two different processes: electronic conduction σ_e and conduction σ_d caused by excited molecules. In the former process a free electron jumps from one molecule to a neighbouring molecule where it is held up for a short time (this is called trap conduction model). The latter process is based on the hypothesis that a liquid at room temperature contains a small but strictly defined number of molecules which are excited to the lowest degree of

excitation. The interaction of excited molecules is believed to lead to the formation of positive and negative ions. He obtained the following relationship for the dependence of conductivity on temperature at the various separations of the electrode

$$\sigma = \sigma_0 \exp\left(-\frac{W}{KT}\right)$$

where the activation energy (W) obtained by Forster for aromatic hydrocarbons was about 0.4 - 1 eV. and for benzene, toluene and xylene about 0.41 eV.

Jachym (1963) measured the mobility of negative and positive ions in cyclohexane. Briere (1964) has studied the conductivity of water and organic liquids using varying gap and different electrodes and found that the apparent conductivity increased more rapidly with applied voltage for polar rather than for nonpolar liquids, but the current decreases with time in both the cases. He concluded that the electric behaviour of liquids submitted to high stresses is strongly controlled by secondary processes due to the accumulation of non-discharged ions at the electrodes. Utilizing some calculations of J.J. Thomson (1928), Silver (1965) has developed a theoretical model for the conduction of current in insulating liquids which shows that it is possible to calculate from the measurement of potential distribution the rate of formation and motion of charges. A consequence of Silver's theory is that the conductivity is a function of electrode spacing of the form

$$V = AJ^2 + BJl$$

where A and B are constants, V is the applied voltage J is the current density and l the gap length. While this theory explained successfully the variation of conductivity with electrode spacing at various constant voltages in benzene, the results in nitrobenzene suggest that the electrodes play an important role; the cathode appears to be the injector of electrons. The role of dispersed conducting particles due to the dissolution of metal in the liquid dielectrics in enhancing the conductivity has been explained by Felsenthan and Vonne Gut (1967). It was further observed that when the liquid is allowed to remain in the cell which was kept open to the atmosphere, the conductivity increases. This is possibly due to absorption of gases and moisture present in the atmosphere. Kao et al (1967) observed that for low electric field, dark conduction in n-hexane obeys ohms law which is associated with the irremovable impurities. Adamczewski and Jachym (1968) published a paper which gives a short summary of results concerning electrical conductivity of dielectric liquids obtained by them as well as by different workers. They concluded that (1) the natural conductivity values of organic liquids is a function of 1/T where T is the absolute temperature (2) among all investigated organic compounds which occur in liquid state, the lowest conductivity values are those of nonpolar liquids (3) there are great differences between the lowest values of natural conductivities reported by various authors. The differences depend

most often on the degree of purity and in particular on the presence of traces of admixtures of water and electrolytes (4) in a certain group of dielectric liquids (e.g. in the group of aromatic hydrocarbons) a considerable role is played by π - electrons which bring about an increase in conductivity by several orders of magnitude (5) the lowest value of natural electric conductivity in best liquid insulators is of the order of 10^{-19} to 10^{-20} Ω^{-1} cm^{-1}. (6) ionization and conductivity excited by x-rays or gamma rays may be million times greater (depending on source strength) than natural conductivity for the same liquids (7) there is a considerable difference between activation energy values for natural and excited conduction.

While carrying out a series of measurements on the variation of current with time in case of number of liquids, Adamczewski and his co-workers (1969) provided an expression to explain the nature of the current decay as

$$I = I_0 \exp. (-\lambda t)$$

where I_0 denotes the initial current and λ is a constant containing mobility factor. The ionic mobilities in pure non-polar liquids such as hexane, heptane, nonane and their mixtures have been measured by Adamczewski (1969) and the value in all the cases is of the order of $7.2 \times 10^{-4} cm^2 V^{-1} S^{-1}$ to $5.8 \times 10^{-4} cm^2 V^{-1} S^{-1}$. Briere and Gaspard (1970) studied the photoconduction in case of highly purified nitrobenzene.

Gaspard and Gosse (1970) gave clear evidence of ionic conduction in polar dielectrics. They used membrane electrodes and gave evidence for three distinct regions of conduction and in each conduction is ionic in nature. The value of μ^+ in case of nitrobenzene has been found to be 2.4×10^{-4} cm^2/volt.sec. Prabhakar Rao and Govinda Raju (1969, 1970) studied the natural conduction in chlorobenzene, bromobenzene and nitrobenzene. They found that the electrode material, dissolved air and degree of purification have a pronounced influence on the conductivity of polar liquids. The conduction current is found to be caused mainly by injection of electrons from cathode into the liquid. Lohneysen and Nageral (1971) assumed the existence of natural charge carriers of two kinds having mobilities μ_1 and μ_2 for developing a satisfactory theory for time dependent current density. They have obtained the value of number of ions present incase of benzyl alcohol as 2.8×10^{16} per c.c. Although the mechanism of charge transport in dielectric liquids has been investigated for many years, it is only during the last ten years, that significant progress has been achieved in the study of the behaviour of fast charge carriers and electronic mobility specially in nonpolar dielectrics with some results reported in case of polar liquids as well. Some of the references which may be mentioned are those of Kleinhoins (1970), Schmidt and Allen (1970), Holroyd and Allen (1971), Davis et al (1971), Dodelet and Freeman (1972), Wollers (1973), Bakale and Schmidt (1973), Allen and Holroyd (1974), Blair and Tredgold (1974), Krause (1974, 1976), Bickert et al (1976), Adamczewski and Calderwood (1976, 1977), Admec and Calderwood (1978).

Sen and Ghosh (1975) studied the current - time characteristic curve in polar dielectrics such as acetone, nitrobenzene, n-propyl, iso-butyl and iso-amyl alcohol and found that initially the current falls very rapidly and then slowly and finally approaches a saturation value. Assuming the existence of free ions in the liquid, the quantitative theory advanced by Gemant (1940) has been further developed which has satisfactorily explained the observed experimental facts and enables us to calculate mobility and ion density in the liquids. When there is no applied external voltage, the free ions which have been assumed to be present in the liquid, are moving in a random manner and the dielectric shows an intrinsic resistance. When the external voltage is applied the positive ions begin to move towards the negative electrode and thereby form a condenser. As charges accumulate on this condenser a voltage develops which opposes the externally applied voltage and the current falls. As more and more charges accumulate in the condenser, the opposing voltage increases though not linearly and current gradually decreases. Ultimately when all the free ions have accumulated on the condenser thus formed, a saturation voltage is developed which makes the current approach the saturation value gradually.

Let R_0 represent the ohmic resistance of the liquid and V_0 the applied voltage and let the ions accumulate near the electrode thereby forming a capacitance C. If V_c represents the voltage developed across the condenser after a time t then the amount of charge removed from the liquid is CV_c and the loss of charge concentration per c.c. is CV_c/aS where S represents the cross-sectional area and "a" the distance between the two

plates. This corresponds to a loss of $\frac{\mu c V_c}{a s}$ in specific conductivity where μ is the mobility of ions. Hence the removal of ion results in the loss of conductance equivalent to $\mu c V_c / a^2$. Consequently,

$$c \cdot \frac{dV_c}{dt} = \left[\frac{1}{R_0} - \frac{\mu c V_c}{a^2}\right](V_0 - V_c)$$

$$= \left[A_0 - bcV_c\right](V_0 - V_c)$$

where $A_0 = 1/R_0$ and $b = \mu/a^2$

Thus,

$$\frac{dV_c}{dt} = b(K_1 - V_c)(K_2 - V_c)$$

where

$$K_1 = A_0/bc \quad \text{and} \quad K_2 = V_0$$

Integrating we get

$$\frac{1}{V_0 - \frac{A_0}{bc}} \log \frac{V_0 - V_c}{\frac{A_0}{bc} - V_c} = bt + \log C_1 \qquad \ldots \quad (1.53)$$

where C_1 is constant. When $t = 0$ and $V_c = 0$

$$\log C_1 = \frac{1}{V_0 - \frac{1}{\alpha}} \log \frac{V_0}{1/\alpha} \quad \text{where } \alpha = \frac{bc}{A_0}$$

Putting the value of $\log C_1$ in equation (1.53) and after simplication we get,

$$V_c = \frac{V_0(1 - e^{\lambda t})}{1 - \alpha V_0 e^{\lambda t}} = \frac{V_0(e^{-\lambda t} - 1)}{e^{-\lambda t} - \alpha V_0}$$

... (1.54)

where $\lambda = b\left(V_o - \frac{1}{\alpha}\right)$

If λ is assumed negative then $V_o = V_o$ at $t = \infty$ which means that the final current would then become equal to zero which is contrary to the experimental observations as shown by Sen and Ghosh (1975) and other previous workers. This leads them to assume that $V_o > \frac{a^2}{R_o \mu c}$ and λ is positive quantity. Hence when t becomes infinity

$$V_c = \frac{V_o\left[1 - e^{\lambda t}\right]}{\left[1 - \frac{V_o}{V_F} e^{\lambda t}\right]} \quad \text{where} \quad V_F = \frac{1}{\alpha}$$

Since the intrinsic resistance R_o of the liquid is not changed because the ions are not discharged as it has been found that when the d.c. potential is removed the original conductivity is restored. We thus have three currents I_o, I_t and I_F where I_o is the initial current, I_t the current at time t and I_F the final saturation current,

$$I_o = \frac{V_o}{R_o} \quad \text{.... (1.55)}$$

$$I_t = \frac{V_o - V_c}{R_o} = \left[V_o - \frac{V_o\left(1 - e^{\lambda t}\right)}{1 - \frac{V_o}{V_F} e^{\lambda t}}\right] \Big/ R_o$$

$$= \frac{V_o e^{\lambda t}\left[1 - \frac{V_o}{V_F}\right]}{R_o\left[1 - \left(\frac{V_o}{V_F}\right)^2 e^{\lambda t}\right]}$$

... (1.56)

and $I_F = \frac{V_o - V_F}{R_o}$ ... (1.57)

From the above equations it can be shown that

$$\log_e \frac{I_t(I_o - I_F)}{I_o(I_t - I_F)} = \lambda t \qquad \cdots (1.58)$$

From equation (1.58) it is thus possible to calculate the value λ and hence from (1.54), (1.55) and (1.57) it is also possible to calculate also the value of b. As $\mu = ba^2$ knowing the interelectrode distance 'a', the mobility of ions μ may thus be calculated.

As V_F is the final voltage across the condenser and if it is assumed that all the free ions in the dielectric have accumulated on the surface of the condenser formed then

$$V_F = \frac{Q}{C} \quad \text{where} \quad Q = nesa$$

where n is the number of ions per unit volume, S is the cross sectional area of the electrodes and e is the charge carried by an ion. Thus

$$V_F = \frac{1}{\alpha} = \frac{A_o}{bc} = \frac{nesa}{C}$$

Since

$$A_o = \frac{1}{R_o} \quad \text{and} \quad b = \mu/a^2$$

$$n = \frac{a}{R_o \mu e s}$$

which gives the number of ions per cc present in the liquid.

Adamec and Calderwood (1975) proposed a conduction mechanism in polymer insulating materials. Here the conduction is supposed to be caused by the generation of charge carriers by

ionization of neutral centres in the bulk of the dielectric due to thermal activation process which may be modified by the electric field. Thereafter, the carriers are trapped in neutral potential wells and occasionally jump from one equilibrium position to another on being thermally activated. Assuming that all directions for charge carrier movement are equally probable for both thermal ionization and thermal detrapping processes and further assuming the jumping in dielectric is small i.e. comparable to or smaller than the range of coulombic force, the mobility of the charge carriers has been given by

$$\mu = \frac{\nu \delta}{3E} \exp\left(-\frac{W_\mu}{KT}\right) \operatorname{Sinh}\left(\frac{eE\delta}{2KT}\right)$$

where the contribution to the current is made only by those carriers which jump over a potential barrier W_μ along and against the field direction between the two equilibrium positions, ν is the vibrational frequency and δ is the jump distance and E is the electric field. The expression for conductivity has been given by

$$\sigma = \sigma_0 \left[\frac{2 + \operatorname{Cosh}\left(\beta_F E^{1/2}/2KT\right)}{3}\right]\left[\frac{2KT}{eE\delta} \operatorname{Sinh}\left(\frac{eE\delta}{2KT}\right)\right] \quad \ldots (1.59)$$

where σ_0 is the conductivity at low field strength given by

$$\sigma_0 = \frac{N e^2 \nu \delta^2}{6KT} \exp\left(-\frac{W_i + 2W_\mu}{2KT}\right)$$

where $\beta_F = \left(e^3/\pi \epsilon_0 \epsilon\right)^{1/2}$ is the Frenkel parameter,

N is the concentration of ionizable centres, W_i is the ionization energy, ϵ is the relative static permitivity of the dielectric, e is the elementary charge and ϵ_0 is the absolute permitivity of vacuum. In equation (1.59) the first term in brakkets represents the field dependence of the charge carrier concentration, the second one the field dependence of mobility. Both the terms approach to unity with a slope tending to zero at low fields, thus expressing the tendency towards ohmic behaviour of the material at low field strength.

From the study of the published experimental results, Adamczewski and Calderwood (1975) found that it is possible to develop a formula relating the mobility of ions of the saturated hydrocarbon series with the number of carbon atoms n which is given by

$$\mu = 0{\cdot}037 \exp(0{\cdot}0352\, n) \exp[(-624\sqrt{n} - 345)/T]\ \mathrm{cm^2 V^{-1} s^{-1}}.$$

The formula though strictly valid in the range $5 \leqslant n \leqslant 9$ has been found to explain the experimental results in close agreement even for $n = 1$. Adamec and Calderwood (1977) showed that their conductivity equation represented by equation (1.59) yields an almost identical field dependence of conductivity to that of Onsager (1934) over the whole range of field strength starting from ohmic region to breakdown of dielectrics.

Recently while studying the electroviscous effect of tetra-butyl ammonium bromide in benzene and Silver perchlorate in benzene, Honda et al (1979) found that the mean ionic mobility in the solution becomes 1.3×10^{-4} cm^2 V^{-1} S^{-1} and 4.5×10^{-4} cm^2 V^{-1} S^{-1} respectively.

Considering all the experimental evidences and assumptions taken by various author we may summarize that

a) the classical purification technique of impurities in organic polar liquids is not sufficient, so it can be assumed that the conduction in the organic liquid is due to ionic impurities which already exist in the liquid. Due to the application of the electric field between the metallic electrodes the impurities (positive and negative ions) move towards the electrodes and thereby conduction current is observed. The time dependence of conduction current has also been observed.

b) There are experimental evidences that various electrochemical mechanism i.e. dissolution of electrode gives rise to large injection of electron in pure nitrobenzene. Most of the investigators have assumed that ionic carriers are responsible for the electrical conduction.

c) The electron emission from the cathode may be one of the causes for self conduction in dielectric liquids. The molecular loss or capture of an electron at the electrodes leading to the production of radical cation or anion may be valid incase of non-dissociated liquids. This is suitable to describe the so called electronic conductivity of nitrobenzene, since the nitrobenzene anion has been detected by electron spin resonance during conduction by space charge

injection in highly pure nitrobenzene with platinum electrodes.

d) In most liquids a number of electro-active species are always present (impurities such as oxygen, water and various organic compound) and consequently simultaneous different electro-chemical reaction can give rise to complicated behaviour characteristic of residual injection into an impure liquid.

e) Dissociation of molecules into ions as a result of the application of electric field may produce the electrical conduction in the dielectrics. This is specially true in high fields.

f) Ionizing influence of radioactive impurities present naturally or artificially in both the walls of the vessel or in the air may also be responsible for the electrical conduction in liquids.

g) It has been experimentally observed that there is an ionizing effect of cosmic rays or cosmic ray cascades or showers upon the formation of ion pairs in liquids.

Thus it may be concluded that though the mechanism of formation of ions may be attributed to various causes, the free ions are definitely present specially in organic polar liquids. Several theories of conduction mechanism in polar liquids have been postulated and a general review of the work done in this field has been presented here.

SCOPE AND OBJECT OF THE PRESENT WORK

In the previous section a review of the work that has been carried out so far regarding the various properties of polar and nonpolar dielectrics has been presented. The object of the present work is to extend these investigations so as to collect new data specially in case of polar molecules and propound a theory to explain the results so that the general properties of these dielectrics can be better understood.

The computation of dipole moment from solution data of polar molecules in nonpolar solvents is most convenient since in this case the dipole-dipole interaction is more or less absent and moreover the value evaluated by this method comes in reasonable agreement with that obtained from gaseous state. But Debye's equation which is the main basic equation for the evaluation of dipole moment from solution data when applied to same solute and solvent system in different concentrations is found to give different values of μ . This is due to the fact that Debye's equation is valid at infinite dilution only in a restricted sense and partly due to the fact that the computation of μ depends upon the theory of extrapolation of different physical quantities such as dielectric constant, refractive index, density of the solution etc. since the extrapolation curve is not a straight line. Keeping this in view an attempt has been made in the present work to describe several extrapolation techniques based purely from mathematical stand point which enables us to calculate the value of dipole moment of polar solute when dissolved in nonpolar solvents.

It has been pointed out that the measurement of electrical conductivity of dielectric liquids enables us to obtain some definite information regarding the degree of dissociation and the presence of free ions and electrons in liquids. From the review of the work it is noted that dielectrics specially polar dielectrics are not perfect insulators but even after repeated processes of purification show a finite conductivity which may be ascribed to the presence of free ions. Though several theories of conduction mechanism in polar liquid have been postulated, it has been found that all observed experimental results cannot be explained satisfactorily. It is thus thought worthwhile to carry out the measurement of conductivity both in the d.c. field and in radio frequency field with a view to obtain a clear idea of conduction mechanism in polar dielectrics. The measurement in the radio frequency region will provide us with data for both the conduction and displacement currents which when measured incase of polar molecule in nonpolar solvents will help us not only to estimate the density of free ions but also the value of relaxation time, a useful parameter in understanding the nature of activation energy, intermolecular field and structure of the molecule concerned.

The case of opalescent binary liquid mixture is an example where the polar and nonpolar dielectrics interact to produce a state of matter whose property requires a thorough investigation. Among other properties it has been observed that viscosity of the mixture rises abruptly near the critical temperature which can be well explained by the

theory advanced by Fixman (1962). It is also observed from the review that although Fixman's theory has been utilized to explain the anomalous increase in viscosity near the critical temperature no attempt has been made to find whether the internal frictional term introduced by Fixman changes for a particular solute in different nonpolar solvents. It will be thus interesting to observe the nature of variation of β, the frictional coefficient which may throw some light in the molecular configuration.

Further very little work has been reported experimentally regarding the change of dielectric constant of a polar liquid in a superimposed magnetic field. The object of the present work is to observe the effect of radial magnetic field on the dielectric constant of polar liquids and to explain the experimental results by a suitable theory. Considering all the aspects mentioned above, it is proposed to undertake the following lines of investigations in the present work.

a. <u>Dipole moment from measurements on solution of polar molecules in nonpolar solvents.</u>

It is well known that Debye's equation for calculation of dipole moment of polar solute in nonpolar solvents is valid at infinite dilution only in a restricted sense. This is partly due to the fact that the assumption concerning the validity of Debye equation is approximate and partly by the inaccuracy of the extrapolation procedure which becomes complicated by the fact that the extrapolation curve is

not a straight line. Therefore several attempts have been made to improve the process of extrapolation by different authors. But almost all the existing procedures for computing the electric dipole moment of a polar solute in nonpolar solvent involve either numerical complications or personal judgements regarding extrapolation and curve fitting. The object of the present work is to describe an extrapolation technique based solely on mathematical grounds by assuming that

$$\epsilon_{12} = a_0 + a_1 \omega_2 + a_2 \omega_2^2$$

$$n_{12} = b_0 + b_1 \omega_2 + b_2 \omega_2^2$$

where a's and b's are constants, ϵ_{12} and n_{12} are the dielectric constant and refractive indices of the solution of weight fraction ω_2 of the solute. Though the above method based on the extrapolation of dielectric constant and refractive indices of the solution applied in Debye's equation, a much simpler method based on Guggenheim's equation (discussed in details in section A) has also been discussed and it is found that a single extrapolation upon some physical parameters is enough to find the value of dipole moment of polar liquid when dissolved in nonpolar solvents.

It has been discussed in section A that though Guggenheim's equation for the evaluation of dipole moment is simple still it is less accurate when there is considerable contraction or dilatation of the volume of the solution. A method to determine the dipole moment of polar solute directly from Debye's equation has been described taking into consideration the correction for atomic polarization.

b. Relaxation time of polar molecules dissolved in nonpolar solvents by radio frequency conductivity measurements.

The experimental determination of radio frequency conductivity of polar liquids and its variation with temperature and also when the polar liquid is dissolved in nonpolar solvent is a useful tool which provides the determination of dipole moment and the time of relaxation of the polar molecules. Determination of dipole moment can give an insight into the properties like distinguishing functional groups whereas the relaxation time gives us information regarding the activation energy, intermolecular field and the structure of the molecule concerned. The time of relaxation is usually evaluated by measuring the dielectric constant and the loss factor either in the microwave or in the radio frequency region where the basic assumption is that the medium is a perfect dielectric. The expressions for the real part of the dielectric constant (ϵ') and loss factor (ϵ'') according to Debye are

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

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

where the symbols have their usual significance. It has been shown by Murphy and Morgan that the radio frequency conductivity of a polar dielectric is a complex quantity and is related with the real and imaginary part of dielectric constant by the

equation

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

and

$$K'' = \frac{\omega}{4\pi}\left[\epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1+\omega^2\tau^2}\right]$$

But when a polar solute is dissolved in nonpolar solvents, the expression for K' and K'' are given by

$$K' = \frac{4\pi^2 f^2 N \tau d_{12} \mu^2}{27 M_2 KT} \cdot \frac{(\epsilon_{12}+2)(\epsilon_{\infty 12}+2)}{1+4\pi^2 f^2 \tau^2} \omega_2$$

and

$$K'' = \frac{\omega}{4\pi}\left[\epsilon_{\infty 12} + \frac{4\pi N d_{12} \omega_2 \mu^2}{27 M_2 KT} \cdot \frac{(\epsilon_{12}+2)(\epsilon_{\infty 12}+2)}{1+\omega^2\tau^2}\right]$$

It is thus evident that the measurement of the radio frequency conductivity of polar liquid or polar liquid dissolved in nonpolar solvents enables us to calculate the relaxation time and offers an alternative method to dielectric constant measurement. Again the relaxation time is given according to Debye by the relation

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

where η is the coefficient of macroscopic viscosity and 'a' is the radius of the rotating unit. Thus the measurement of τ will enable us to obtain information regarding the nature of the intermolecular field and structure of the molecule.

In the deduction of Murphy and Morgan it is assumed however that no free electronic or ionic conduction is present and the total current is the displacement current. But it is evident from the review of the work that there is ample of evidence for the existance of free ions and electrons specially in polar dielectrics. So under the application of radio frequency field in polar dielectrics, displacement current is not only the contributing factor, the total heat developed is due to the combined effect of displacement current and conduction current. Thus the radio frequency conductivity measurement provides us the information of both displacement and conduction current in a dielectric liquid. The purpose of the present work is to show that measurement of radio frequency conductivity not only enables us to compute the relaxation time at infinite dilution when the measurement is carried out by dissolving polar solute in nonpolar solvents but also to estimate the ionic concentration which measures the imperfection that exists in real dielectrics.

c. Relaxation time and activation energy for viscosity from radio frequency conductivity measurements.

It has been assumed by Murphy and Morgan that no free electrons or ion conduction takes place in a dielectric and only displacement current prevails. From the expression of radio frequency conductivity as deduced by Murphy and Morgan and assuming $\tau = \frac{4\pi\eta a^3}{KT}$ we get

$$K' = \frac{(\epsilon_0 - \epsilon_\infty)\,\omega^2 a^3 (\eta/KT)}{1 + \frac{16\pi^2\eta^2\omega^2 a^6}{K^2T^2}}$$

As in most common dielectrics $\tau = 10^{-11}$S and frequency of the applied voltage are in the radio frequency region, $\omega^2\tau^2 \ll 1$ and hence

$$K' = \frac{(\epsilon_0 - \epsilon_\infty)\omega^2 a^3 \eta}{KT}$$

Thus if the measurement of radio frequency conductivity is made at gradually higher and higher temperature then as $(\epsilon_0 - \epsilon_\infty)$ and η/KT are both decreasing function of temperature, K' should decrease with increase of temperature. The experimental results will thus indicate whether the assumption of the absence of free ions or electrons in the liquid can be regarded as valid.

In recent years considerable evidence has accumulated which clearly indicates the presence of free ions and electrons in the dielectric and there is a wide difference in the number density of ions in polar and nonpolar dielectrics. Based on the experimental results and assuming the existence of free ions in liquid, Sen and Ghosh (1974) deduced the expression of radio frequency conductivity which is given by

$$K' = A + B/\eta$$

where $A = \pi f^2(\epsilon_0 - \epsilon_\infty)\tau$ and $B = ne^2/6\pi a$ where 'a' is the radius of the rotating unit, η is the coefficient of viscosity, τ is the relaxation time, and ϵ_0 and ϵ_∞ are the static and high frequency dielectric constant, f is the frequency of the applied field. Thus the measurement of radio frequency conductivity of polar liquid at different temperature enables us to calculate the

relaxation time and the number of free charge carriers in polar liquids. Though the number of free ions is very small, it gives a measure of the imperfection in pure liquid dielectrics.

Bassler and Riehl (1965) have suggested that incase of organic liquids the variation of conductivity with temperature can be represented by the equation

$$K' = K_0 \exp. \left(\frac{-\Delta E_c}{2KT} \right)$$

where ΔE_c is the activation energy for conductivity which is characteristic for each liquid. From the hole theory of viscosity as proposed by Eyring, the variation of viscosity with temperature can be represented by the equation

$$\eta = D \exp. \left(\frac{\Delta E_v}{KT} \right)$$

where ΔE_v is the activation energy for viscous flow. According to the assumption of hole theory ΔE_v should be equal to the energy of vaporization of the liquid but actually the experimental results indicate that it is smaller than the energy of vaporization and varies from liquid to liquid by a factor which varies from 3 to 4. Regarding the physical significance of the term ΔE_v, no definite and clear picture is at present available, only an attempt has been made by Sen and Ghosh (1978) to correlate the activation energy for viscosity with the characteristic energy of activation for conductivity. As it has been experimentally shown that the activation energy for viscosity varies with

frequency, this must have some bearing on the experimental results of Andrade and Dodd (1946) where it has been found that viscosity decreases upto a certain frequency which they termed as critical frequency.

Thus the information that the activation energy for electrical conductivity and that for viscosity are related to one another, both being functions of frequency and gradually decreases almost linearly with the increase of frequency may help to develop a theory whose origin lies with some process closely connected with the charge distribution in molecules. The nature of the internal frictional force which has been taken to be analogous to viscous force in Debye's expression for relaxation time can be reviewed in the light of the present experimental results.

It is further known that in case of d.c. field the product of the equivalent conductivity and viscosity of the liquid is a constant and the formulation is known as Walden's rule. It will be interesting to see whether a similar relationship as observed by Sen and Ghosh (1974) can be established in general in case of polar dielectrics with regard to radio frequency conductivity and viscosity.

d. <u>Mobility and Free ion density from measurement of temporal variation of current in polar dielectrics.</u>

It has been a general observation that when a d.c. electric field is applied to a dielectric, the current decreases rapidly with time initially and then slowly to a certain minimum value. The decay of current is supposed to be

due to removal or accumulation of ions near the electrodes. The observed experimental facts, obviously suggest that in dielectrics, free ions do exist. A general theory regarding the mechanism of the decrease of current with time has been provided by Sen and Ghosh (1975) which has satisfactorily explained the observed experimental facts and enables us to calculate the mobility and density of ions. The object of the present work is to observe the general validity of the theory by extending the observation to other polar molecules and thereby prove the existence of free ions and electrons specially in case of polar dielectrics.

e. Radio frequency conductivity of opalescent binary liquid mixtures.

It is well known that in the region of critical opalescence of two binary liquid mixtures, an abrupt change of some physical properties of the mixture occur. Though there is some contradictory opinion about the change of dielectric constant near the critical region, the change in the coefficient of viscosity, ultrasonic absorption and radio frequency conductivity occurs as the critical temperature is approached. In case of light scattering it has been observed that the depolarization factor in case of opalescent binary mixture is different from unity although in the case of clear solution the value is unity. It has been suggested by Krishnan (1935) that in case of clear solution the scattering is due to single moleculeswhereas in case of opalescent binary mixtures the scattering is due to cluster of molecules. However, no

definite information regarding the composition and size of the clusters can be obtained from the data on the light scattering experiments. Sen and Ghosh (1972) have shown from radio frequency conductivity measurements that no evidence for the formation of cluster of molecules in the opalescent state can be obtained. Fixman (1962) however, provided a theory regarding the increase of viscosity in the region of critical opalescence utilising the principle of Statistical mechanics. The increase in viscosity is explained by Fixman on the assumption that the density fluctuation causes a velocity gradient which produces a distortion in the long wavelength part of the spectrum of density fluctuation. The restoration to uniform density through diffusion dissipates energy and this appears in the form of increased viscosity. However, Fixman does not provide any information in his theory regarding the internal friction term β . The object of this part of investigation is to measure the change of viscosity from the radio frequency conductivity measurement as the mixture approaches the critical stage and compare the results with Fixman's theory. The other object is to observe whether the intense density fluctuation is due to formation of cluster of molecules in the critical state and also to observe whether the internal friction term β changes for a particular solute in different nonpolar solvents which may throw some light on the screening effect of the surrounding molecules of a polar solute. No general theory which can explain all the observed results has been developed and it is expected that this study may provide

some data which will be helpful in developing such a theory.

f. Dielectric constant of polar liquids in magnetic field.

From the review of the previous work it is evident that few work has been performed on the effect of magnetic field on the dielectric constant of pure polar liquids. The effect is almost absent in presence of transverse magnetic field. The object of the present work is to investigate the change of dielectric constant of polar liquid in presence of radial magnetic field. In this case the liquid is subjected to a magnetic field from all sides so that it may be compressed and infact a detectable change in dielectric constant has been found. In order to explain the observed results two theories have been advanced, one considering the compresibility of liquid and the other from gas kinetics. The results indicate that gas kinetic equation is not actually valid because the strong interaction between individual molecules plays a dominant part in case of liquids.

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