

INVESTIGATIONS ON THE DIELECTRIC PROPERTIES OF SOME POLAR LIQUIDS IN RADIO FREQUENCY REGION AND IN D . C. FIELDS

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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 polarization 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 polarization 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 surrounded 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 constant of the surrounding 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 surrounding 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 takes 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 (1948) 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 Fowle'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

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

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

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 contribution 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)

$$P_{2\infty} = \lim_{x_2 \rightarrow 0} \frac{[P_{12}] - (1-x_2)[P_1]}{x_2}$$

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

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

$[P_1]$ = molar polarization 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 $\epsilon_1 = n_1^2$

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

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 polarization of the solute (P_2) can be calculated from eqn. (1.2) leading to

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

Differentiating both sides of equation (1.5) with respect to

x_2 and taking the limit $x_2 \rightarrow 0$, we have $P_2 = P_{2\infty}$, the total molar polarization of solute at infinite dilution,

$\epsilon_{12} = \epsilon_1$, $d_{12} = d_1$, we get

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

When the contribution of electronic and atomic polarizations 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 $\left(\frac{\partial d_{12}}{\partial x_2}\right)_{x_2 \rightarrow 0}$. Cohen-Henriquez (1935) suggested an extrapolation procedure, the aim of which is to avoid the use of $\left(\frac{\partial d_{12}}{\partial x_2}\right)_{x_2 \rightarrow 0}$ and to use $\left(\frac{\partial n_{12}}{\partial x_2}\right)_{x_2 \rightarrow 0}$ instead. This can be achieved as equations (1.2) & (1.3) give

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

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

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

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 famous 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. LePèvre 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

$$p_{2\infty} = p_1(1-\beta) + c\alpha\epsilon_1 \quad \dots (1.6)$$

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

$$p_{2\infty} = \frac{3\alpha v_1}{(\epsilon_1 + 2)^2} + (v_1 + \beta) \frac{\epsilon_1 - 1}{\epsilon_1 + 2} \quad \dots (1.7)$$

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

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

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 ± 0.10 e.s.u. Later on it has been shown by Krishna and Srivastava (1957) that equation (1.8) should be represented as

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

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 in turn, 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

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

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

$$\left(\frac{\epsilon_{12} - 1}{\epsilon_{12} + 2} - \frac{n_{12}^2 - 1}{n_{12}^2 + 2} \right) = \left(\frac{\epsilon_1 - 1}{\epsilon_1 + 2} - \frac{n_1^2 - 1}{n_1^2 + 2} \right) + \frac{4\pi N}{3} \left(\gamma_{2a} - \gamma'_{2a} + \frac{\mu^2}{3KT} \right) C_2 \quad \dots (1.11)$$

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 $\gamma_{2a} = \gamma'_{2a}$. As a further simplification he shows that if $\epsilon_{12}-n_{12}^2$ is plotted against C_2 , the μ value can be obtained from the relation

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

where

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

Smith (1950) has suggested a further simplification 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

$$P_2\mu = \frac{3M_2V_1[\partial(\epsilon_{12}-n_{12}^2)/\partial\omega_2]_{\omega_2 \rightarrow 0}}{(\epsilon_1+2)^2} \dots (1.13)$$

where V_1 is the specific volume of the pure solvent. Incorporating the ideas of Smith (1950) and LeFevre (1950), Guggenheim (1951) modified his own equation for the evaluation of μ which can be written as

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

where

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

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 draw the tangent to this curve at $\omega_2 \rightarrow 0$ and extrapolate this tangent to pure solute. This gives $p_{2\infty}$, the partial specific polarization 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

$$P_{2\mu} = \left[\frac{3(\epsilon_1 - n_1^2)M_2}{d_1(\epsilon_1 + 2)(n_1^2 + 2)} \left(1 - \frac{\beta_0}{d_1}\right) \right] + \left[\frac{3d_0M_2}{d_1(\epsilon_1 + 2)^2} \right] - \left[\frac{6n_1\gamma_0M_2}{d_1(n_1^2 + 2)^2} \right] \quad (1.15)$$

where

$$d_0 = \left(\frac{\partial \epsilon_{12}}{\partial \omega_2}\right)_{\omega_2 \rightarrow 0}$$

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

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

Equation (1.15) can be written as

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

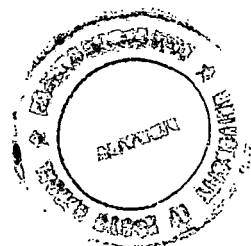
where $K_1 = \frac{\epsilon_1 + 2}{n_1^2 + 2}$. If $\epsilon_1 = n_1^2$ (i.e. $\beta_0 = d_1$)

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

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

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

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



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where

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

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 ^{to}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 in terms 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 $Y_{12} = a_0 + a_1 \omega_2 + a_2 \omega_2^2 + \dots$

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 in turn 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 polarization 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_0 , connected to an alternating source of e.m.f. $(E) = E_0 \exp. (j\omega t)$ of angular frequency $\omega = 2\pi f$ where f is the frequency.

The charge of the capacitor at any instant is $Q = C_0 E$ 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 $C = \epsilon' C_0$ where ϵ' is the (real) dielectric constant of the liquid. Due to presence of dielectric the charge on the capacitor is increased to $Q = \epsilon' C_0 E$ and the charging current is increased to

$$I_c = j\omega \epsilon' C_0 E$$

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

$$\begin{aligned} I &= I_c + I_l = j\omega\epsilon' C_0 E + GE \\ &= (j\omega C + G) E \end{aligned} \quad (1.17)$$

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

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

is the power factor. Alternatively the behaviour can be considered in terms 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

$$\begin{aligned} I &= J\omega\epsilon^*c_0E \\ &= J\omega(\epsilon' - J\epsilon'')c_0E \\ &= J\omega\epsilon'c_0E + \omega\epsilon''c_0E \quad \dots (1.18) \end{aligned}$$

Its components being represented vectorially in Fig. (1.2).

Now comparing equation (1.18) with (1.17), we get

$$\begin{aligned} G &= \omega\epsilon''c_0 \\ C &= \epsilon'c_0 \end{aligned} \quad \dots (1.19)$$

$$\text{and loss tangent } \tan \delta = \frac{\omega\epsilon''c_0}{\omega\epsilon'c_0} = \frac{\epsilon''}{\epsilon'}$$

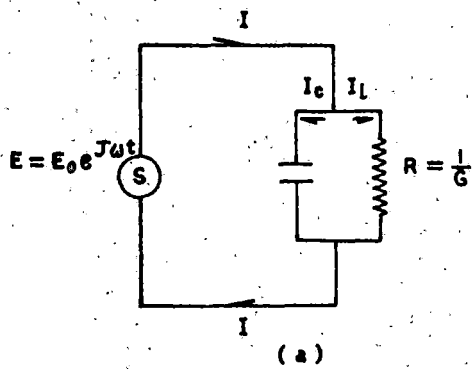
From equation (1.19)

$$\epsilon'' = \frac{G}{\omega c_0} = \frac{\text{specific conductivity} \times 4\pi}{\omega}$$

Therefore specific conductivity (real)

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

(For parallel plate capacitor, $C_0 = \frac{S}{4\pi l}$ in vacuum, and $G = 1/R$ where $R = e_1 \frac{l}{S}$) 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).



$$I_c = j\omega CE$$

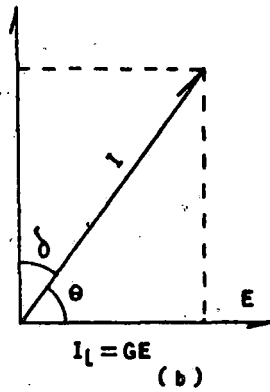


FIG. 1.1. EQUIVALENT CIRCUIT AND CHARGING CURRENT I_c & LOSS CURRENT I_l OF CAPACITOR WITH LOSSY DIELECTRIC.

$$I_c = j\omega \epsilon' C_0 E$$

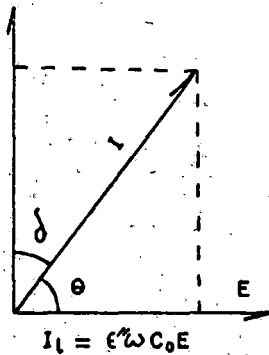


FIG. 1.2. COMPONENTS OF CURRENT THROUGH DIELECTRIC OF COMPLEX DIELECTRIC CONSTANT $\epsilon^* = \epsilon' - j\epsilon''$

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~~ 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 nuclear 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 ρ per unit area will appear on each plate and a polarization P will be created in the

dielectric. The displacement current flowing is $\frac{dQ}{dt}$ 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

$$K = \frac{1}{E} \cdot \frac{dQ}{dt}$$

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

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

$$\begin{aligned}
 I &= \frac{dq}{dt} = \frac{\epsilon' - j\epsilon''}{4\pi d} \frac{dV_0 e^{j\omega t}}{dt} \\
 &= \frac{\epsilon' - j\epsilon''}{4\pi d} j\omega V_0 e^{j\omega t} \\
 &= \left(\frac{j\omega\epsilon'}{4\pi} + \frac{\omega\epsilon''}{4\pi} \right) \frac{V_0 e^{j\omega t}}{d} \\
 &= \left(\frac{\omega\epsilon''}{4\pi} + \frac{j\omega\epsilon'}{4\pi} \right) \frac{V_0 e^{j\omega t}}{d} \\
 &= \left(\frac{\omega\epsilon''}{4\pi} + j \frac{\omega\epsilon'}{4\pi} \right) E_0 e^{j\omega t} \dots (1.21)
 \end{aligned}$$

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

$$I = \frac{dq}{dt} = (K' + jK'') E_0 e^{j\omega t}$$

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 terms of an equivalent parallel capacitance C_p and conductance

G_p so that an alternate expression for I is

$$\begin{aligned}
 I &= \frac{dq}{dt} \\
 &= \frac{0.9 \times 10^{12}}{A} (G_p + j\omega C_p) V_0 e^{j\omega t} \\
 &\dots (1.22)
 \end{aligned}$$

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

$$C_0 = \frac{\Lambda}{4\pi d \times 0.9 \times 10^{12}} \quad \dots (1.23)$$

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

$$\begin{aligned} K' &= \frac{\epsilon'' \omega}{4\pi \times 0.9 \times 10^{12}} \\ &= \frac{\epsilon'' f}{1.8 \times 10^{12}} \\ &= \frac{G_P \cdot f}{C_0 \cdot 2\pi f \cdot 1.8 \times 10^{12}} \\ &= \frac{8.85 \times 10^{-12} G_P}{C_0 \mu\mu f.} \end{aligned}$$

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

$$W = \frac{\omega}{2\pi} \int_0^{2\pi/\omega} I \cdot E \cdot dt \quad \dots (1.24)$$

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

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)

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

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

$$\begin{aligned} D &= D_0 \cos (\omega t - \delta) \\ &= D_0 \cos \omega t \cos \delta + D_0 \sin \omega t \sin \delta \end{aligned}$$

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 $D^* = \epsilon^* E$

$$\begin{aligned} \text{then } \epsilon^* &= \frac{D^*}{E} = \frac{D_0 e^{j(\omega t - \delta)}}{E_0 e^{j\omega t}} \\ &= \frac{D_0}{E_0} e^{-j\delta} \end{aligned}$$

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

$$\begin{aligned} W &= \frac{\omega}{8\pi} \cdot \frac{D_0}{E_0} \sin \delta \cdot E_0^2 \\ &= \frac{\epsilon'' \omega}{4\pi} \cdot \frac{E_0^2}{2} \\ &= \frac{K' E_0^2}{2} \end{aligned}$$

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

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

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

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

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

we get

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

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

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

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

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

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

$$= \frac{\epsilon_0 - \epsilon_\infty}{4\pi \times 0.9 \times 10^{12} \tau} \dots (1.29)$$

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

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

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

and

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

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.

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

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

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

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

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 $N_1 = CN = \frac{Nd_{12}}{M_2} \omega_2$

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

$$\epsilon' = \epsilon_{\infty 12} + \frac{4\pi Nd_{12}\omega_2\mu^2}{27M_2KT} \frac{(\epsilon_{12}+2)(\epsilon_{\infty 12}+2)}{1+\omega^2\tau^2}$$

$$\epsilon'' = \frac{4\pi Nd_{12}\omega_2\mu^2}{27M_2KT} \frac{(\epsilon_{12}+2)(\epsilon_{\infty 12}+2)}{1+\omega^2\tau^2} \omega\tau$$

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 imaginary part K'' of the radio frequency conductivity in case of dilute solutions

$$K' = \frac{4\pi^2 f^2 N\tau d_{12}\mu^2}{27M_2KT} \frac{(\epsilon_{12}+2)(\epsilon_{\infty 12}+2)}{1+4\pi^2 f^2 \tau^2} \omega_2$$

where $\omega = 2\pi f$ and

$$K'' = \frac{\omega}{4\pi} \left[\epsilon_{\infty 12} + \frac{4\pi Nd_{12}\omega_2\mu^2}{27M_2KT} \frac{(\epsilon_{12}+2)(\epsilon_{\infty 12}+2)}{1+\omega^2\tau^2} \right]$$

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 $B = \frac{n e^2}{6\pi a}$

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

$$K' = A + B f^2$$

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

$$\text{and } B = \frac{4\pi^2\mu^2 N \gamma d_{12}}{27M_2KT} (\epsilon_{12} + 2)(\epsilon_{\infty 12} + 2) \omega_2$$

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

$$\sigma = \sigma_0 \exp\left(-\Delta E / K T\right) \quad \dots (1.33)$$

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 $\log \sigma$ vs. $1/T$ plot according to the equation

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

Cheng 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

$$\mu = \mu_0 \exp\left(-W / K T\right)$$

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 Adamczewski'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 Adamczewski'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 $5 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$ 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.

Jackym (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 conductivity 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

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

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 $1/T$. Nicolson et al (1971) has measured electrical conductance (σ) of n-butyl, iso-butyl and amyl alcohols in the temperature range $0 - 97^{\circ}\text{C}$ using an alternating field ($f = 100 \text{ Hz}$). 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,

$$\tau = \left(\frac{A}{T} \right) \eta^{\alpha} \quad \dots (1.35)$$

where A is a constant for a given substance and $\chi = \frac{\Delta H_e}{\Delta H\eta}$ 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 et al 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)

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

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

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

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

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

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

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

where

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

Then

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

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

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

If only the conduction current is present

$$\begin{aligned} K' &= \frac{ne^2}{M} \cdot \frac{\gamma}{\gamma^2 + \omega^2} \\ &= \frac{ne^2}{M} \cdot \frac{6\pi a\eta / M}{(6\pi a\eta / M)^2 + \omega^2} \end{aligned}$$

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

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

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

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)

$$i \text{ (displacement)} = \frac{\omega}{4\pi} (\epsilon'' + j\epsilon') E_0 e^{j\omega t} \dots (1.38)$$

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

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

Thus

$$\begin{aligned} K' &= \frac{1}{4\pi} (\epsilon_0 - \epsilon_\infty) \omega^2 \tau + \frac{ne^2}{6\pi a\eta} \\ &= A + \frac{B}{\eta} \dots (1.39) \end{aligned}$$

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

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

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

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

where D is a constant and ΔE_{η} 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 $B = \frac{\pi e^2}{6\pi a}$ we have from (1.39) exp.

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

For a particular temperature

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

where

$$\beta = \frac{\pi e^2}{6\pi a K_0 D} \exp\left(\frac{-\Delta E_{\eta}}{KT}\right)$$

and

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

Then

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

which shows that ΔE_c will decrease with increase of frequency.

From equation (1.41)

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

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

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

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

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

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 criticised 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

Hocard predicts that

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

where C is constant.

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

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

For $C = 0$ equation (1.43) reduces to the expression of Ornstein and Zernike and for $d = 0$, to that of Hocard'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 Pickara. 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 consolute temperature. Arkhangelskii 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 Halliwell et al 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 similar to that of Fickars 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 et al (1966), Puls and Kirkaldy (1971), Gutschick and Pinga (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 Korina (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 isooctane-perfluoroheptane mixtures. The anomalous behaviour can be detected as far way as 10° from the critical temperature. However, other investigations 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

$$\eta_M = \eta_0 + \left(e \eta_2 \frac{\partial c_2}{\partial n_2} \right)^2 \left(\frac{a}{40\alpha} \right) k^{-1}$$

$$\eta_M - \eta_0 = \Delta \eta = \left(e \eta_2 \frac{\partial c_2}{\partial n_2} \right)^2 \left(\frac{a}{40\alpha k} \right) \dots (1.44)$$

where η_0 = local viscosity evaluated at the mean composition

e = 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 in terms of the diffusion constant D_{id} of an ideal mixture can be written as

$$D_{id} = \left(\frac{\alpha eRT}{m_1 m_2^2 n_1} \right) \left(\frac{\partial \ln x_2}{\partial n_2} \right) \dots (1.45)$$

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

$$\frac{\partial \ln x_2}{\partial n_2} = \left[v_1 n_2 (n_1 + n_2) \right]^{-1} \dots (1.46)$$

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

$$n_2 \left(\frac{\partial c_2}{\partial n_2} \right) = \frac{m_1 c_2}{e v_1} \dots (1.47)$$

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

$$\begin{aligned} \Delta \eta &= \eta_M - \eta_0 = \left[\frac{RT m_1 \Phi_2}{D_{id} e \Phi_1 v_1^2 v_2 (n_1 + n_2)} \right] \left[\frac{a}{40 R} \right] \\ &= \left[\frac{RT m_1 m_2 \Phi_2}{e v_1^2 D_{id} m_2 v_2 (n_1 + n_2) \Phi_1} \right] \left[\frac{a}{40 R} \right] \end{aligned}$$

$$= \left[\frac{\beta m_1 m_2 \Phi_2}{e v_1^2 v_2 (n_1 + n_2) \Phi_1} \right] \left[\frac{a}{40 R} \right]$$

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

$\Delta \eta$ can be rearranged as

$$\Delta \eta = \frac{m_1 m_2 \Phi_2}{e v_1^2 v_2 (n_1 + n_2) \Phi_1} \left(\frac{a^{1/2}}{R} \right) \frac{1}{40} \left(\beta a^{1/2} \right)$$

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

$$\left(\frac{a^{1/2}}{R} \right) = \left[\frac{v_1}{4\pi\Phi_2} \right]^{1/2} \left[\left\{ \Phi_1^{-1} - (1 - m^{-1}) - \frac{T_c}{T} (1 + m^{-1/2})^2 \Phi_2^{-1} \right\} - \frac{v_2}{v_1} \right]^{1/2}$$

where

$$v_1 = \frac{M_1}{e_1 N_0} = \text{volume per molecule of component I}$$

$$v_2 = \frac{M_2}{e_2 N_0} = \text{volume per molecule of component II}$$

$$m = \frac{v_2}{v_1} \quad T_c = \text{critical temperature}$$

$$\Phi_1 = v_1 n_1 \quad N_0 = \text{Avogadro's number}$$

$$\Phi_2 = v_2 n_2 \quad e_1 = \text{density of component I}$$

$$e_2 = \text{density of component II}$$

Taking the experimental data of Reed and Taylor on the mixture ($i - C_8 H_{18} - C_7 F_{16}$) and considering

$C_7 F_{16}$ as component II, Fixman shows from his theoretical model that viscosity rises sharply when binary liquid mixture is critically opalescent. He also calculated the

value of $\beta a^{1/2}$ 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 et al (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 Swanzing (1967) predict a strong divergence of the anomalous part of the shear viscosity as a power of $(T-T_c)$ 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 $(T - T_c)$ 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 et al (1969), Arcovita et al (1969), Huang and Webbs (1969) and Stein et al (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 increase 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, Marini and Tavetkov 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 quantization 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 $\hbar/2\pi$. 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.M. 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 χ with the electric field the polarization due to permanent dipoles will according to old quantum theory be $\left(3/2 \cos^2 \chi - 1/2\right)$ 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), Kest (1924), Friedel (1925) and Bauer (1926) show that the dielectric constants of certain "mesomorphic substances (anisotropic liquids) are perceptibly altered by magnetic fields. This nevertheless, 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

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

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

$$b = \gamma_0 + \frac{\gamma_1}{KT} + \frac{\gamma_2}{K^2T^2} + \frac{\gamma_3}{K^3T^3}$$

γ_0 is related to the molecular 'hyperpolarizability' and γ_1 is dependent upon the anisotropy in the polarizability tensor. The term in γ_2 is also dependent on the anisotropy but in addition is proportional to the square of the molecular dipole moment μ . γ_3 represents the dipole saturation term and is proportional to μ^4 . Buckingham considered that in a diamagnetic material ϵ can be

represented as

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

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 $2.3 \times 10^{-14} (3 \cos^2 \alpha - 1)$, α being the angle between electric field and magnetic field. For $\cos^2 \alpha = 1$ 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), Ortway (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 gives 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. Schweilddler (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 Jaffe (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 occurred 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 Dornste (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

$$I = AT^2 \exp \left[- \frac{\phi e}{KT} + \frac{1}{2.3KT} \left(\frac{e^3 E}{\epsilon} \right)^{1/2} \right] \dots (1.48)$$

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 deduced an equation in terms of specific conductivities

$$\sigma = \sigma_0 e^{-mE_0 t / a^2} + \sigma_f \quad \dots (1.49)$$

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

$$\frac{\sigma - \sigma_f}{\sigma_0} = \frac{m}{m + m'} e^{-mE_0 t / a^2} + \frac{m'}{m + m'} e^{-m'E_0 t / a^2} \quad \dots (1.50)$$

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 strength of the field. On this basis Plumley was able to give an expression for the current in terms 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

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

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 "hop^ping" 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

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

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 ($\tau = \tau_0 \exp(W/KT)$)] 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 cyclohexane 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 $10^{-3} \text{ cm}^2 \text{ sec}^{-1} \text{ volt}^{-1}$. 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 $4.2 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ Sec}^{-1}$ 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

$$\sigma = AJ^2 + BJL$$

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} $\Omega^{-1} \text{ cm}^{-1}$. (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 $7.2 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ to $5.8 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. 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 $2.4 \times 10^{-4} \text{ cm}^2/\text{volt}\cdot\text{sec}$. 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 in case 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 Kleinheins (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 Fredgold (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

$$\mu c v_c / a^2 \quad . \text{Consequently,}$$

$$\begin{aligned} c \cdot \frac{dv_c}{dt} &= \left[\frac{1}{R_0} - \frac{\mu c v_c}{a^2} \right] (V_0 - v_c) \\ &= \left[A_0 - b c v_c \right] (V_0 - v_c) \end{aligned}$$

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

$$\frac{1}{V_0 - \frac{A_0}{bc}} \log \frac{V_0 - v_c}{\frac{A_0}{bc} - v_c} = bt + \log C_1 \quad \dots (1.53)$$

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 simplification 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 $\lambda = b \left(V_0 - \frac{1}{\alpha} \right)$

If λ is assumed negative then $V_0 = V_0$ 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 $V_0 > \frac{a^2}{R_0 \mu c}$ and λ is positive quantity. Hence when t becomes infinity

$$V_c = \frac{V_0 [1 - e^{\lambda t}]}{[1 - \frac{V_0}{V_F} e^{\lambda t}]} \text{ where } V_F = \frac{1}{\alpha}$$

Since the intrinsic resistance R_0 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_0 , I_t and I_F where I_0 is the initial current, I_t the current at time t and I_F the final saturation current,

$$I_0 = \frac{V_0}{R_0} \dots (1.55)$$

$$I_t = \frac{V_0 - V_c}{R_0} = \left[V_0 - \frac{V_0 (1 - e^{\lambda t})}{1 - \frac{V_0}{V_F} e^{\lambda t}} \right] / R_0$$

$$= \frac{V_0 e^{\lambda t} \left[1 - \frac{V_0}{V_F} \right]}{R_0 \left[1 - \left(\frac{V_0}{V_F} \right) e^{\lambda t} \right]}$$

... (1.56)

$$\text{and } I_F = \frac{V_0 - V_F}{R_0} \dots (1.57)$$

From the above equations it can be shown that

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

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

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

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

$$V_F = \frac{1}{\alpha} = \frac{A_o}{bc} = \frac{nes a}{c}$$

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

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

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, 2δ is the vibrational frequency and δ is the jump distance and E is the electric field. The expression for conductivity has been given by

$$G = G_0 \left[\frac{2 + \cosh(\beta_F E^{1/2} / 2KT)}{3} \right] \left[\frac{2KT}{eE\delta} \sinh\left(\frac{eE\delta}{2KT}\right) \right] \quad (1.59)$$

where G_0 is the conductivity at low field strength given by

$$G_0 = \frac{Ne^2\delta^2}{6KT} \exp\left(-\frac{W_i + 2W_{\mu}}{2KT}\right)$$

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 permittivity of the dielectric, e is the elementary charge and ϵ_0 is the absolute permittivity of vacuum. In equation (1.59) the first term in brackets 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

$$\mu = 0.037 \exp(0.0352 n) \exp\left[\frac{(-624\sqrt{n} - 345)}{T}\right] \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$$

The formula though strictly valid in the range $5 \leq n \leq 9$ 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 $1.3 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$ and $4.5 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$ 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 in case 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. Dipole moment from measurements on solution of polar molecules in nonpolar solvents.

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

$$K' = \frac{4\pi^2 f^2 N \tau d_{12} \mu^2}{27 M_2 K T} \cdot \frac{(\epsilon_{12} + 2)(\epsilon_{\infty 12} + 2)}{1 + 4\pi^2 f^2 \tau^2} \omega_2$$

and

$$K'' = \frac{\omega}{4\pi} \left[\epsilon_{\infty 12} + \frac{4\pi N d_{12} \omega_2 \mu^2}{27 M_2 K T} \cdot \frac{(\epsilon_{12} + 2)(\epsilon_{\infty 12} + 2)}{1 + \omega^2 \tau^2} \right]$$

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

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

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 existence 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

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

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 $B = \pi e^2 / 6 \pi a$

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 Dyring, 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. Mobility and Free ion density from measurement of temporal variation of current in polar dielectrics.

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.

c. 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 molecules whereas 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 utilizing 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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CHAPTER II

EXPERIMENTAL SET UP.

A. THEORY OF MEASUREMENT OF RADIO FREQUENCY CONDUCTIVITY.

The block diagram of the experimental arrangement of radio frequency conductivity can be represented by a simple network, shown in figure (2.1).

Let Z_p be the equivalent impedance and for parallel combination

$$\begin{aligned} Z_p &= \frac{R}{1 + j\omega CR} \\ &= \frac{R(1 - j\omega CR)}{1 + \omega^2 C^2 R^2} \quad \dots (2.1) \end{aligned}$$

In case of series combination

$$Z_p = R' - \frac{j}{\omega C'} \quad \dots (2.2)$$

From equation (2.1) and (2.2)

$$R' = \frac{R}{1 + \omega^2 C^2 R^2} \quad \dots (2.3)$$

$$\frac{1}{\omega C'} = \frac{\omega CR^2}{1 + \omega^2 C^2 R^2} \quad \dots (2.4)$$

$$\text{As } \omega^2 C^2 R^2 > 1$$

$$C' = C$$

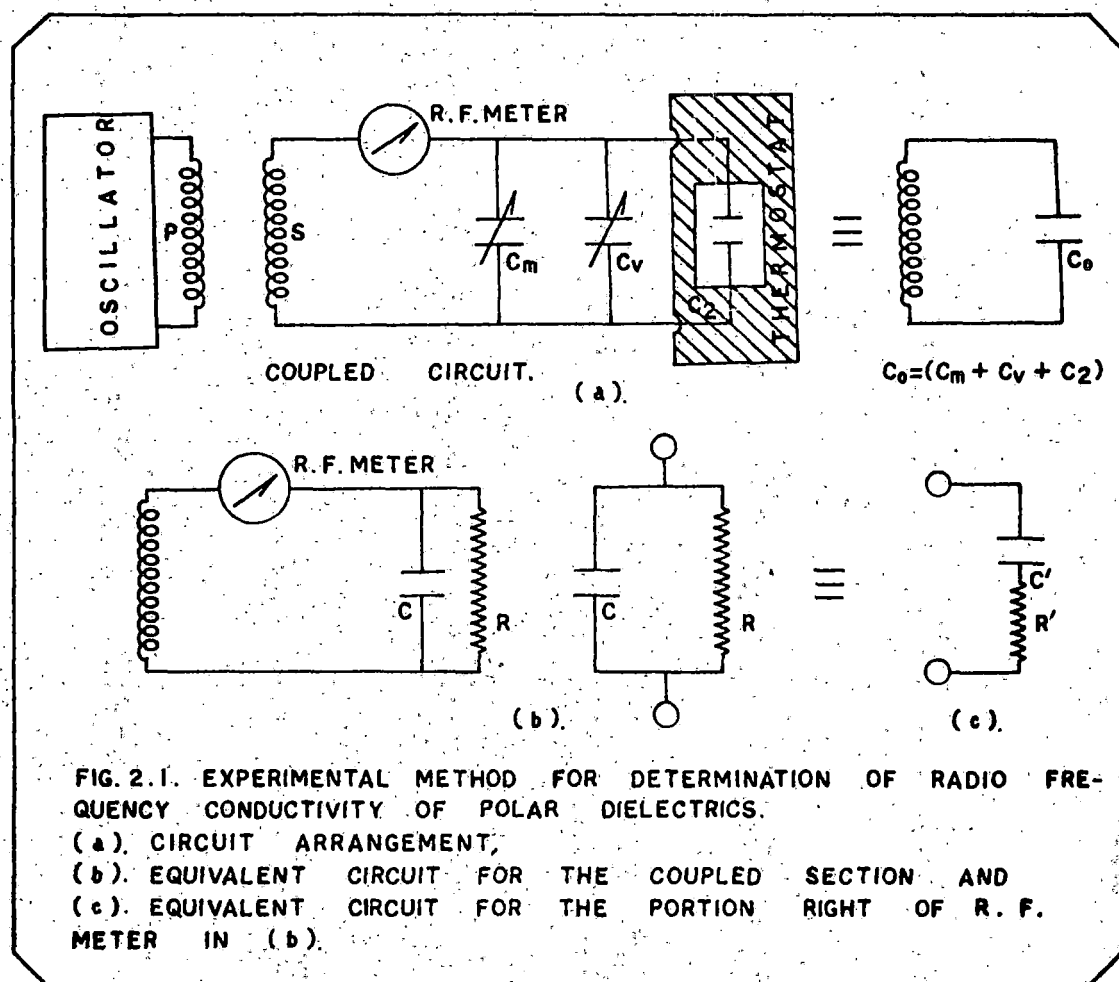


FIG. 2.1. EXPERIMENTAL METHOD FOR DETERMINATION OF RADIO FREQUENCY CONDUCTIVITY OF POLAR DIELECTRICS.
 (a). CIRCUIT ARRANGEMENT,
 (b). EQUIVALENT CIRCUIT FOR THE COUPLED SECTION AND
 (c). EQUIVALENT CIRCUIT FOR THE PORTION RIGHT OF R. F. METER IN (b).

Further the resonant current with the cell in the circuit but without liquid

$$I_0 = \frac{E}{R_0} \quad \dots (2.5)$$

where R_0 is the radio frequency resistance of the secondary tuning circuit and is given by

$$R_0 = \frac{C_2 - C_1}{2\omega C_2 C_1} \sqrt{\frac{I_1^2}{I_0^2 - I_1^2}}$$

where I_0 is the resonant current in the R.F. milliammeter and C_1 and C_2 are the capacitance for reducing the resonant current to a value I_1 which is equal to $\frac{1}{\sqrt{2}}$ of I_0 . The mathematical deduction of the value of radio frequency resistance R_0 has been given in the next section of this chapter.

Further the resonant current with cell filled with the liquid is given by

$$I_2 = \frac{E}{R_0 + R'} \quad \dots (2.6)$$

$$\text{Putting } \frac{I_1}{I_2} = \alpha \quad \dots (2.7)$$

and simplifying the equations (2.3), (2.5), (2.6) and (2.7)

$$\alpha - 1 = \frac{R}{R_0(1 + \omega^2 C^2 R^2)}$$

$$R = \frac{1 \pm \sqrt{1 - 4R_0^2(\alpha - 1)^2 \omega^2 C^2}}{2R_0(\alpha - 1)\omega^2 C^2}$$

In the present experimental set up $4R_o^2(\alpha-1)\omega^2C^2 \ll 1$

then

$$R = \frac{1}{R_o(\alpha-1)\omega^2C^2}$$

The radio frequency resistance of the polar liquid

$$R = e \cdot \frac{l}{S}$$

where e is the specific resistance, l is the length i.e. interelectrode spacing and ' S ' is the cross-sectional area of the electrodes. Since $e = \frac{1}{K'}$ where K' is the specific conductivity

$$K' = \frac{l}{SR}$$

The tuning condenser is a parallel plate condenser so the capacity of the tuning condenser

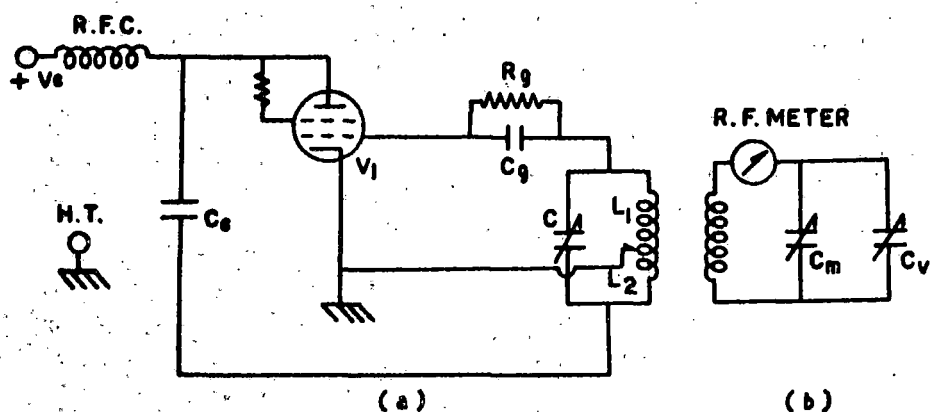
$$C_o = \frac{S}{4\pi l}$$

Therefore the radio frequency conductivity can be expressed as

$$K' = \frac{1}{4\pi R C_o} \dots (2.8)$$

B. MEASUREMENT OF RADIO FREQUENCY RESISTANCE OF
THE SECONDARY TUNING CIRCUIT AND ITS THEORY.

The method used here for determining radio frequency resistance may be stated as reactance variation method. The secondary tuning circuit consists of an inductance, a variable main and vernier condenser and a radio frequency milliammeter. The inductance, variable main condenser and the r.f. milliammeter are all connected in series whereas the vernier condenser is connected in parallel with the main condenser. The vernier condenser is fitted with vernier scale in order to note precisely the position of the condenser. The secondary tuning circuit is loosely coupled to the radio frequency oscillator (Hartley type) which is the driving oscillator of desired frequency shown in figure (2.2). The empty dielectric cell is fitted in parallel to the tuning condenser. The secondary tuning circuit is tuned to the desired frequency of the driving oscillator by proper adjustment of the tuning condensers both main and vernier. The resonant current in the radio frequency milliammeter and the capacitance of the tuning condensers are noted. Then the capacitance of the tuning condenser are adjusted to the value C_1 and C_2 on either side of the resonant value so that the current in the r.f. meter I_1 becomes $\frac{1}{\sqrt{2}}$ times of the resonant current i.e. 70.7% of I_0 . The reading for C_2 and C_1 are noted. When the tuning circuit is sharply tuned to desired frequency, the induced voltage in the secondary circuit becomes equal to E_0 . Therefore, $E_0 = I_0 R_0$ where R_0 is the radio frequency resistance of the circuit. When detuned, let the



List of components:

$V_1 = 6L6$

$R_g = 20K\Omega$

$C_g = 0.001 \mu F.$

$C_m \text{ \& } C = 0-500 \text{ P.F.}$

$C_s = 0.01 \mu F.$

$C_v = 0-60 \text{ P.F.}$

R.F.C. = RADIO FREQUENCY CHOKE

R.F. METER = RADIO FREQUENCY
MILLIAMMETER.

FIG. 2.2 (a). RADIO FREQUENCY OSCILLATOR
(b). SECONDARY TUNING CIRCUIT.

change in reactance value is ΔX . So the series impedance is

$R_0 + j\Delta X$ and hence

$$E_0 = I_1 \sqrt{R_0^2 + \Delta X^2}$$

Therefore

$$\begin{aligned} \frac{I_0}{I_1} &= \frac{E_0/R_0}{E_0/\sqrt{R_0^2 + \Delta X^2}} = \frac{\sqrt{R_0^2 + \Delta X^2}}{R_0} \\ \frac{I_0^2}{I_1^2} - 1 &= \frac{R_0^2 + \Delta X^2}{R_0^2} - 1 = \frac{\Delta X^2}{R_0^2} \\ R_0^2 &= \Delta X^2 \left(\frac{I_1^2}{I_0^2 - I_1^2} \right) \quad \dots (2.9) \end{aligned}$$

The slight change of reactance at the upper half and of the lower half power of maximum power respectively

$$\Delta X = \omega L - \frac{1}{\omega C_2} \quad \dots (2.10)$$

$$\Delta X = \frac{1}{\omega C_1} - \omega L \quad \dots (2.11)$$

where $\omega = 2\pi f_r$, f_r is the resonant frequency.

Adding (2.10) and (2.11)

$$2\Delta X = \frac{C_2 - C_1}{\omega C_2 C_1}$$

$$\Delta X = \frac{C_2 - C_1}{2\omega C_2 C_1}$$

Putting the value of ΔX in equation (2.9)

$$R_0^2 = \left(\frac{C_2 - C_1}{2 \omega C_1 C_2} \right)^2 \left(\frac{I_1^2}{I_0^2 - I_1^2} \right)$$

Thus the radio frequency resistance

$$R_0 = \frac{C_2 - C_1}{2 \omega C_1 C_2} \sqrt{\frac{I_1^2}{I_0^2 - I_1^2}} \dots (2.12)$$

So knowing the values of C_2 , C_1 , I_1 and I_0 , the radio frequency resistance R_0 of the circuit has been calculated by using the equation (2.12).

C.

APPARATUS USED.

The apparatus used for the measurement of radio frequency conductivity are (a) Radio frequency Oscillator, (b) Secondary tuned circuit (c) R.F. Milliammeter (d) Stabilized power supply, (e) Thermostat (f) Communication broadcasting receiver, wave meter and R.L.C. bridge, (g) Liquid purification arrangement (h) Dielectric cells (i) Ostwald's viscometer, (j) Chemical balance and weight box (k) Measuring cylinders, Beakers etc. (l) Arrangement for cleaning of the glass apparatus. The description of some of the important apparatus and their associated circuits is given.

Radio frequency Oscillator:-

The radio frequency oscillator used here is of Hartley type and the circuit diagram is shown in figure (2.2). The frequency range of the designed oscillator has been found to be from 300 KHz to 8.5 KHz. The inductance L of the tank circuit is divided into two parts L_1 and L_2 and their common point is connected to the cathode terminal of the vacuum tube 6L6. The end of L_2 is connected to the grid through R_g C_g , a parallel combination which is used for providing the grid bias voltage. The end of L_2 is connected to the plate of the oscillator valve 6L6 through the blocking condenser C_c . A condenser C is placed in parallel with the inductance thereby making a complete tank circuit. The amplified energy in the plate section is fed back to the grid circuit due to inductive coupling and the amount of coupling will depend upon the number of turns in L_1 and L_2 . The direct component of the plate current is supplied from a stabilized power supply through a radio frequency choke. The blocking capacitor C_c which has a small reactance compared with load impedance, allows a path to the a.c. component while the d.c. from the power supply is prevented. The gang condenser dial has been calibrated against frequency by the help of communication broadcasting receiver and also by an absorption wave meter.

Secondary tuned Circuit:-

The secondary tuning circuit consisting of inductance, a variable tuning main condenser, a radio frequency milliammeter are all connected in series. The circuit is loosely coupled to the Hartley oscillator's tank circuit. A variable vernier condenser is fitted parallel to the

main condenser of the secondary circuit in order to improve the accuracy of tuning the desired frequency. The dial of the tuning condensers both main and vernier has been calibrated in terms of capacitance with the help of R.L.C. bridge. The dial reading against capacitance of both the main and vernier condenser are shown in figure 2.3 (a) to 2.3 (d).

Calibration of the dial of the tuning condenser (Main) of the receiver circuit.

Table 2.1

Dial reading in degree	Capacitance in $\mu\mu F$	Dial reading in degree	Capacitance in $\mu\mu F$
0	490	19	128
1	470	20	115
2	447.5	21	103
3	426	22	91.5
4	405	23	81
5	384	24	71.5
6	363	25	63
7	340	26	55
8	320	27	48
9	299	28	41.5
10	280	29	36
11	260	30	31
12	241	31	27
13	222	32	23
14	205	33	20
15	188	34	18
16	171	35	17
17	155		
18	141		

Calibration of the dial of the tuning condenser (vernier)
of the receiver circuit.

Table 2.2

Dial reading in degree	Capacitance in $\mu\mu F$	Dial reading in degree	Capacitance in $\mu\mu F$
0	60.3	10	36
1	58	11	33.5
2	56.5	12	31.2
3.	53	13	28.8
4	50.6	14	26.4
5	48.1	15	24.2
6	45.6	16	22.6
7	43.2	17	21.4
8	40.8	18	20.7
9	38.5		

Radio frequency milliammeter:- The radio frequency milliammeter ranging from 0 to 200 m.a. is a thermocouple type and it is sensitive upto 30 KHz.

Stabilized power supply:- A stabilized power supply unit has been used to supply power to the oscillator. The basic circuit of the atabilized power supply of the degenerative type is shown in Figure (2.4) and actual circuit diagram shown in Figure (2.5).

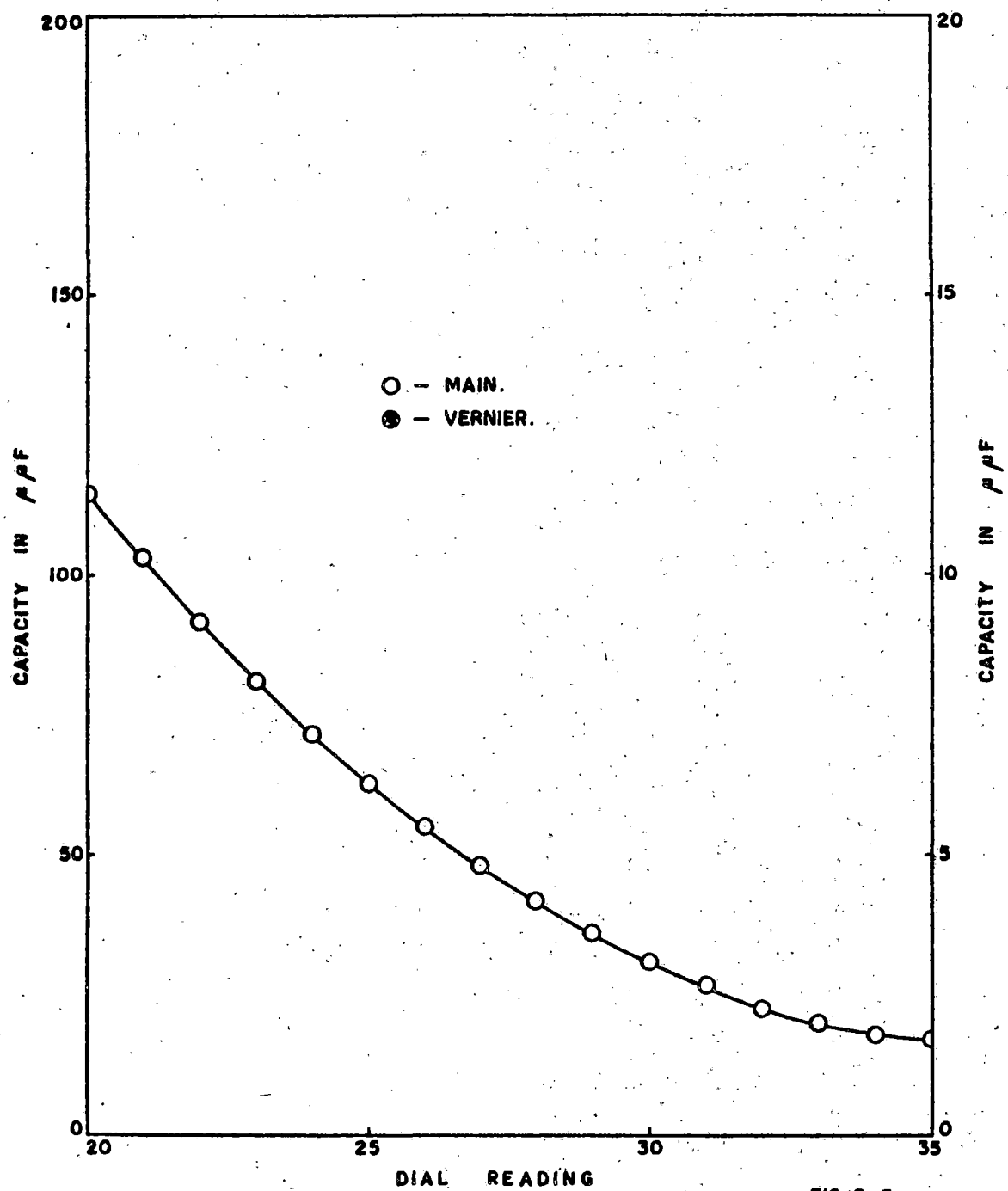


FIG. 2. 3a.

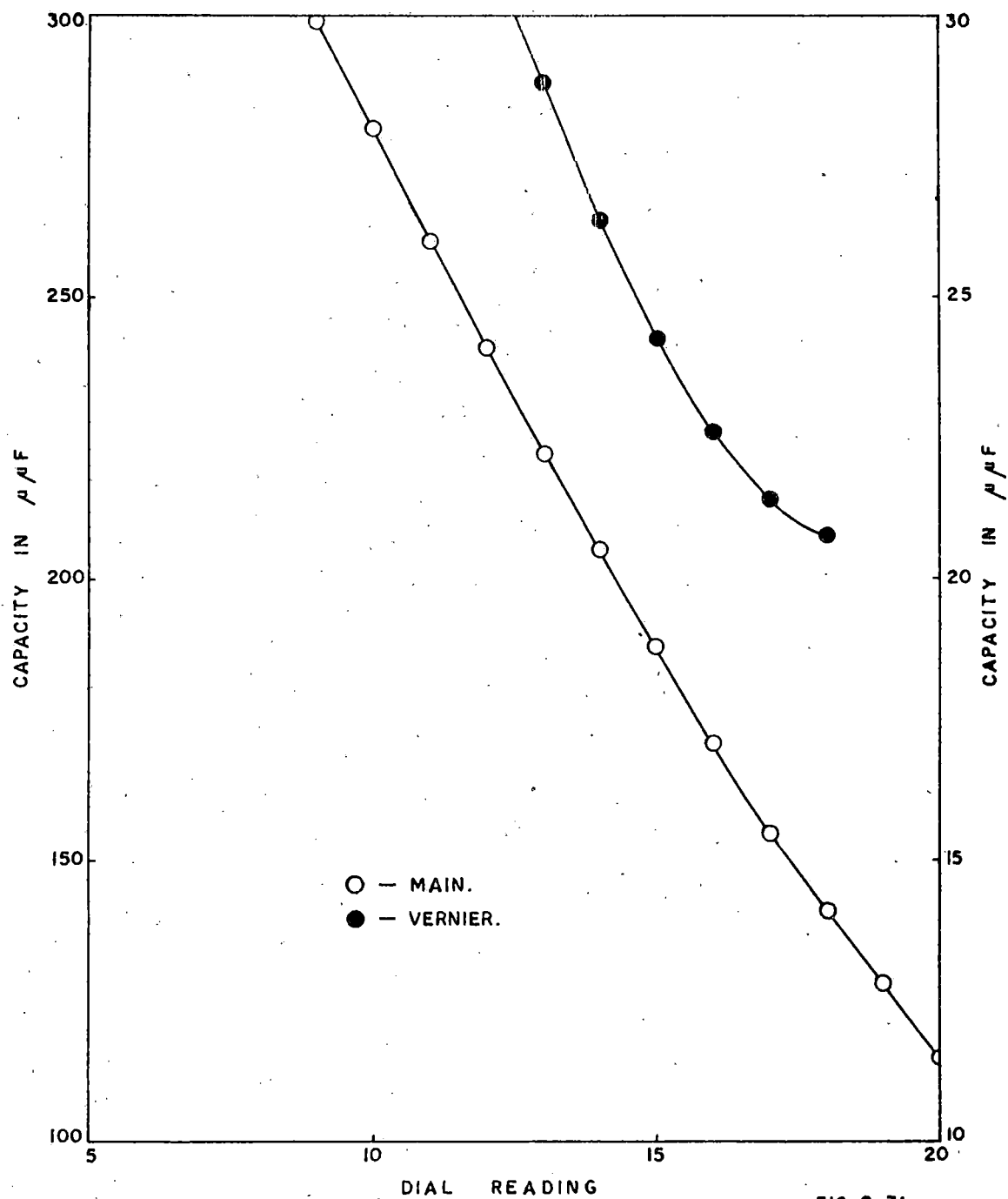


FIG. 2.3b.

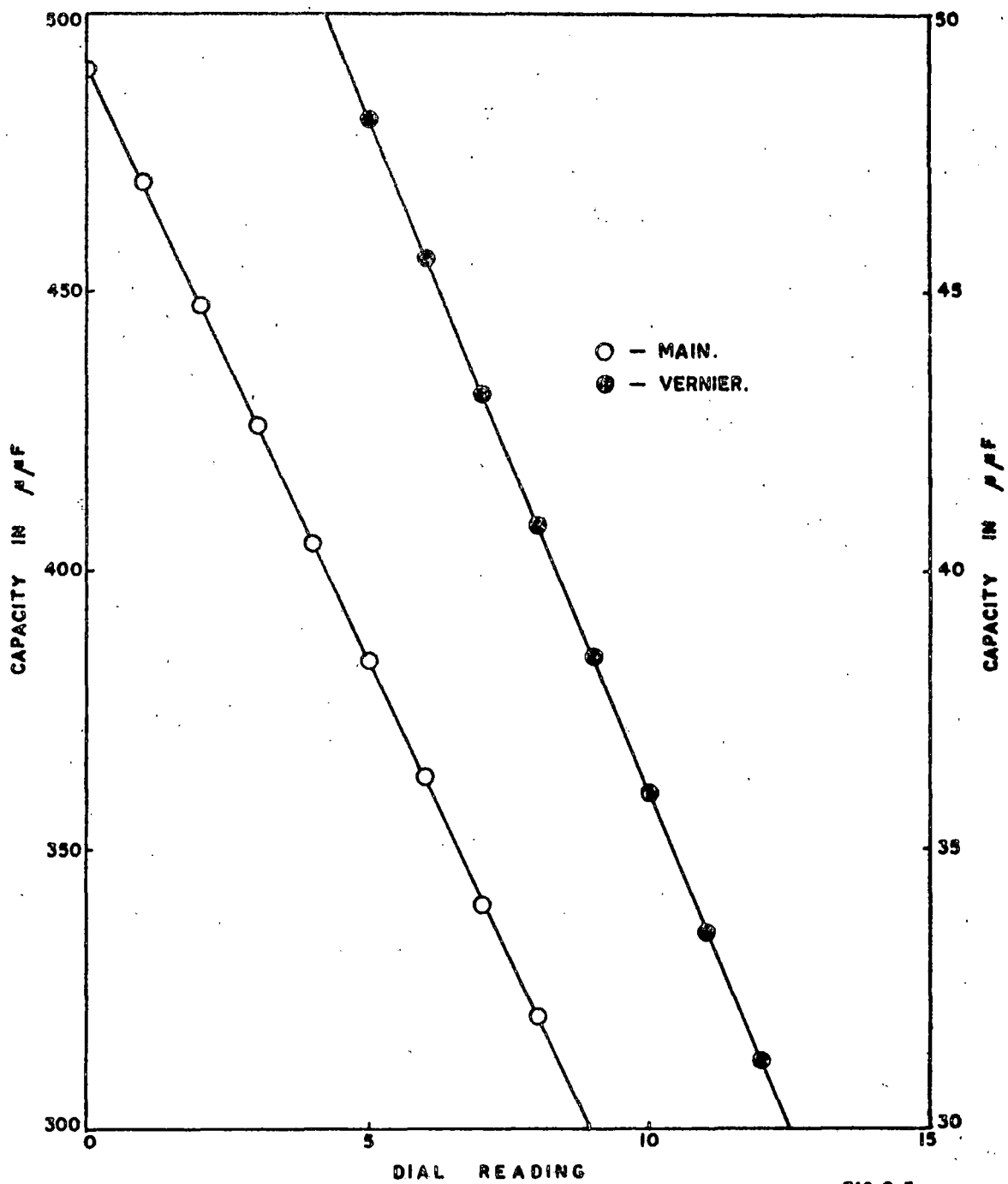


FIG. 2.3c.

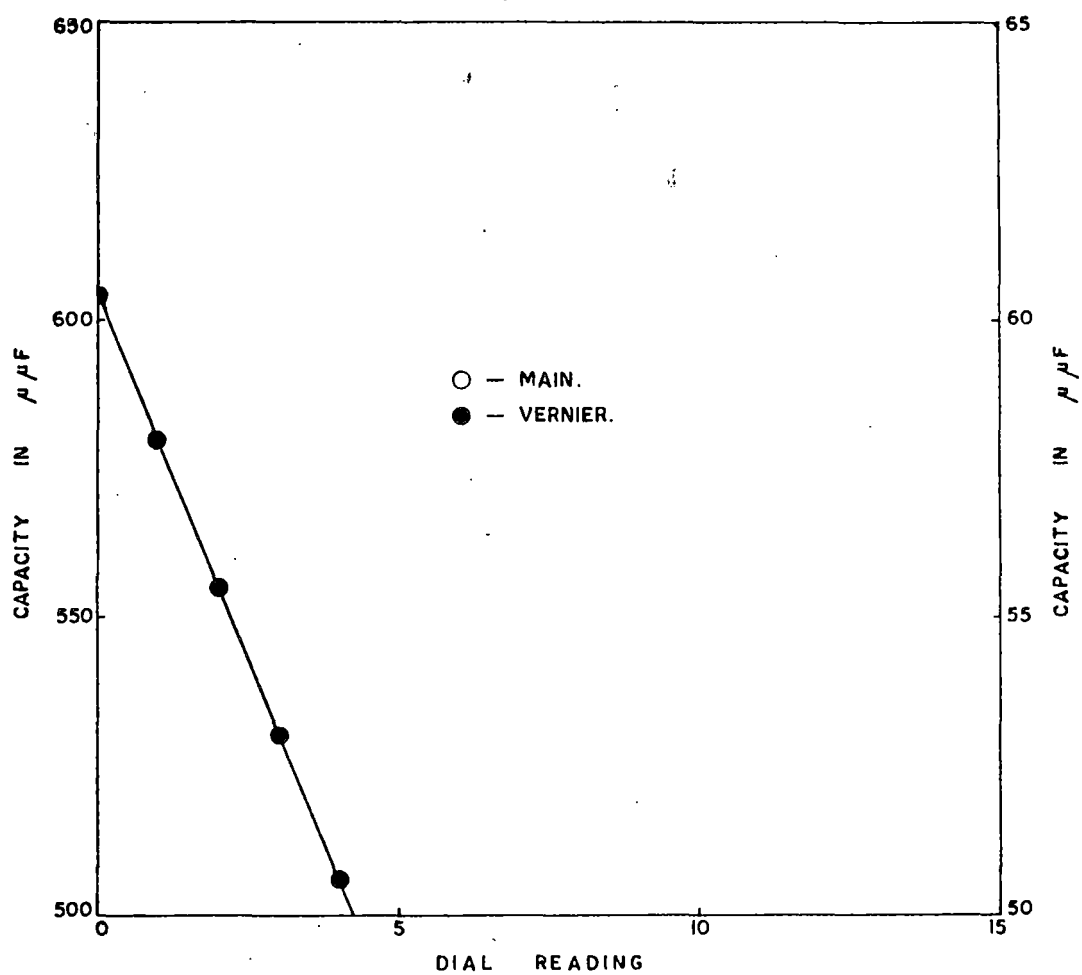


FIG. 2. 34.

The circuit of Figure (2.4) may be considered as conventional transformer-rectifier and filter (T.R.F.) circuit to obtain d.c. voltage from a.c. main supply. This unstabilized voltage is given to the regulator part consisting of series tube T_1 (i.e. pentode power tube) and an amplifier of gain G . A fixed reference voltage E_r (obtained from V.R. tube) and the difference amplifier of gain G is used to control T_1 , so as to afford degenerative compensation for any change in circuit conditions that tend to alter the existing output voltage. The reactance of the condenser C at ripple frequency may be made small compared with resistance in shunt with it. This condenser helps the stabilizer in reducing the ripple and it is not made large for avoiding undesirable transient oscillation in the out put voltage. In order to obtain a practically ripple free out put and almost perfect regulation a two stage d.c. amplification have been introduced in the circuit. The main supply line voltage is 220 volts, 50 c/s. Single phase is connected to the primary of the transformer and regulated d.c. voltage is obtained at output of the circuit whose range is 0 to 300 v. and current 200 mA. maximum.

A circuit arrangement is made along with the stabilized power supply to get -ve bias voltage supply. The negative bias supply is taken from a separate silicon rectifier IS95 regulated by a tube OA2. The variable negative bias voltage is obtained from 0 to 100V. by means of a potentiometer providing maximum load of 5 mA. only. The ripple

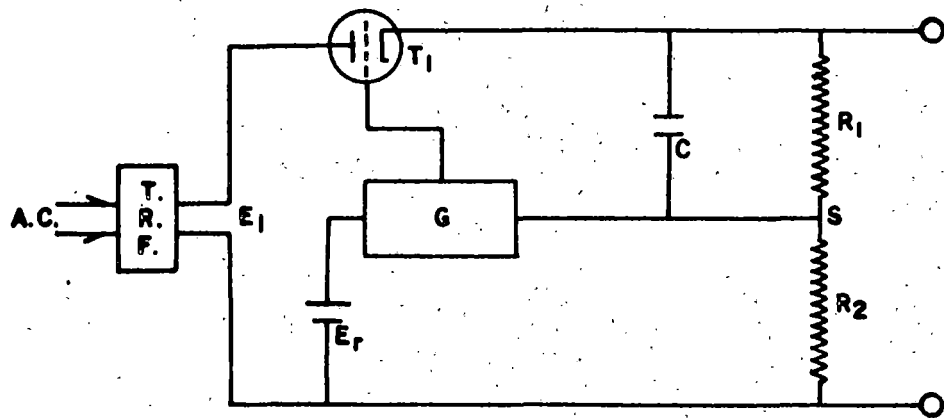


FIG. 2.4. BASIC CIRCUIT OF THE STABILIZED POWER SUPPLY OF THE DEGENERATIVE TYPE.

voltage output is less than 3 mV. in the positive supply and less than 10 mV. in the negative supply. A voltmeter calibrated from 0 to 300 volts is connected at the output terminal to read the d.c. output voltage. The practical circuit diagram of the regulated power supply unit is shown in Figure (2.5).

The components of power supply unit are given below:

1. Resistances:-

<u>Circuit Ref.No.</u>	<u>Description</u>	<u>Circuit Ref.No.</u>	<u>Description</u>
R ₁	5	R ₁₇	160 K
R ₂	8	R ₁₈	100 K
R ₃	1K	R ₁₉	15 K
R ₄ , R ₅	470 K	R ₂₀	68 K
R ₆	10 K	R ₂₁	47 K
R ₇ , R ₈ , R ₉	100 K	R ₂₂	470 K
R ₁₀	2.2 M	R ₂₃	470 K
R ₁₁	5 K	R ₂₄	220 K
R ₁₂ , R ₁₃ , R ₁₄	10 K	R ₂₅	470 K
R ₁₅	1 K	R ₂₆	200 K
R ₁₆	15 K	R ₂₇	100 K
		R ₂₈	1.5 K

II. Capacitor

C ₁	0.1 MFD
C ₂ , C ₄	16 MFD
C ₃ , C ₅	16 MFD
C ₆	8 MFD
C ₇ , C ₈	0.001 MFD
C ₉	0.042 MFD
C ₁₀	0.2 MFD

III. Potentiometer

P ₁	10K
P ₂	50 K

IV. Valves

V ₁ , V ₃ , V ₆	6X4
V ₂ , V ₄	6X5
V ₅	6X6

V. Diodes

D₁, D₂, D₃ IS 95

VI. Switches

S₁ DPDT (ON/OFF)

VII. Transformer

S₂ (A,B) DPDT (0-100V
and (100-300V)

TF 46 Mains
Transformer

S₃ DPDT (Meter
Selector)

VIII. Fuses

F₁ Main fuses
1 Amp.

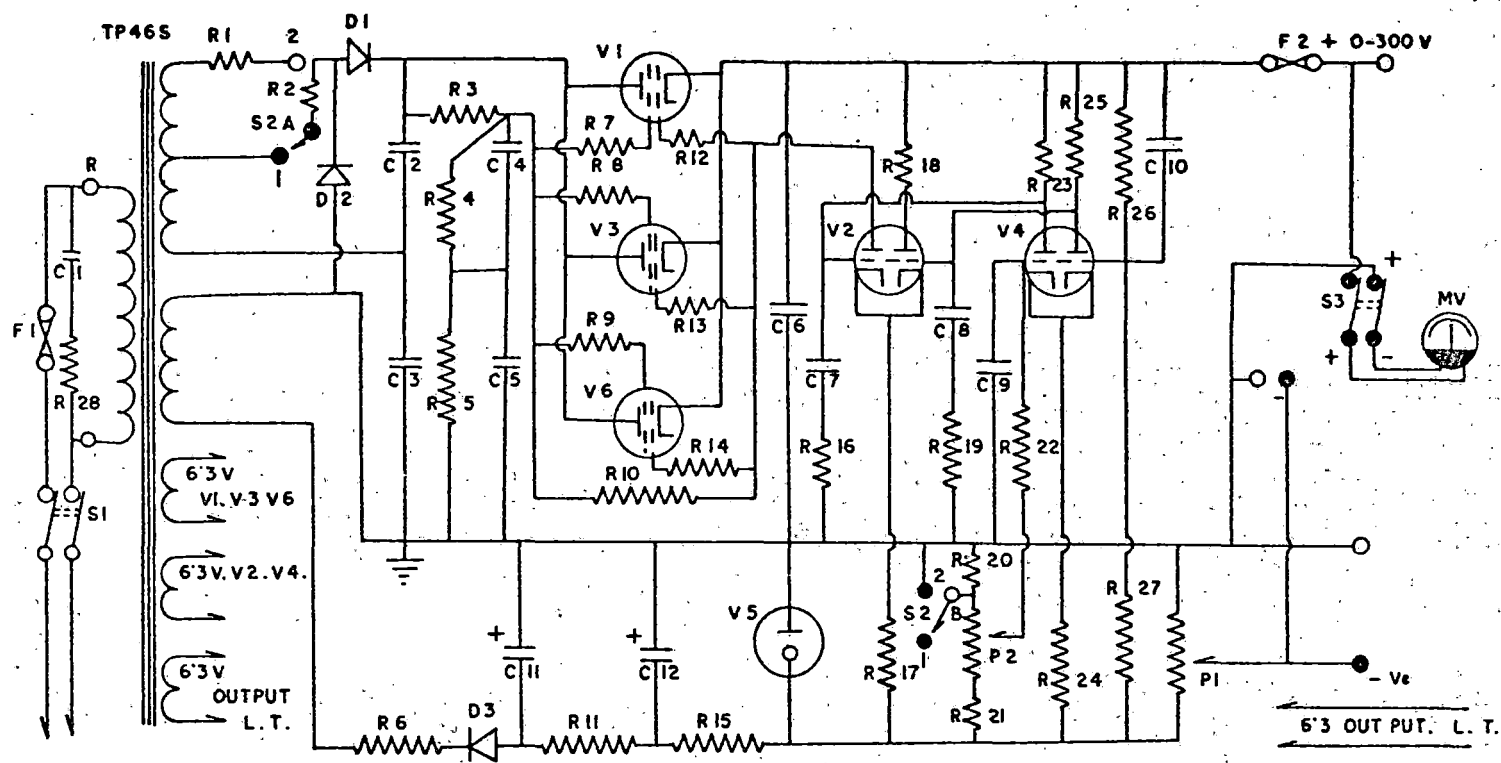
IX. Meter

Voltmeter (0 - 300 V)

F₂ H.T. Fuse 250 mA

Thermostat: A well temperature controlled thermostat has been utilized to maintain the constant temperature as well as for the variation of temperature of the dielectric cell. The dielectric cell introduced in the thermostat can be seen from outside by a glass window situated on the front side of the thermostat. It is operated by 220 V, 50 C/s. A.C. supply and can be controlled at any desired temperature, the maximum range of which is 150°C.

Dielectric Cell: Different types of dielectric cells as shown in figure 2.6 (a) to 2.6 (c) have been used throughout the conductivity measurement of organic liquids. Mainly a pyrex glass cell which is fitted with two parallel plate circular electrodes separated by a fixed distance have been utilized. The choice of material used in designing the

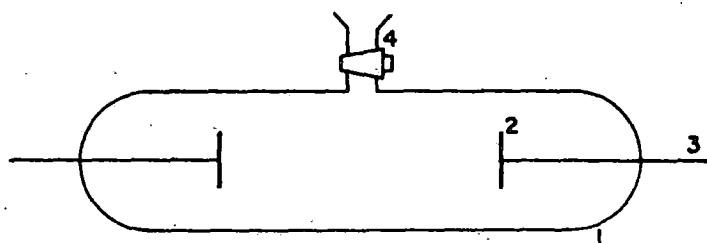


REGULATED POWER SUPPLY UNIT.

FIG- 2.5

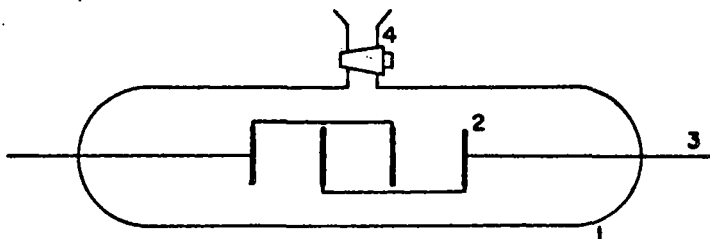
electrodes is an important factor in carrying out the experiments specially in conductivity measurement as an electrochemical reaction between electrodes and liquids may take place. The cell used during the radio frequency conductivity measurements of polar liquids as well as mixture of polar and nonpolar is a cylindrical glass tube of diameter 2.62 cm. fitted with two circular gold plates 1.08 cm. apart. (Figure 2.6 (a)). Each gold plate is connected with a platinum wire which is sealed with the glass tube whereas in d.c. conductivity measurement described in chapter VI, brass material has been used as electrodes with a gap 0.22 cm. fitted with tungsten wire in cylindrical glass tube of diameter 2.96 cm. (Figure 2.6 (c)). In order to find the effect of any electrochemical reactions between electrodes and liquid studied, the experiments have been repeated a number of times and in each case same results have been obtained. Brass electrodes have been used by many workers previously and more recently by Prabhakara Rao and Govinda Raju (1970) and Sen and Ghosh (1975).

In the other case i.e. to observe the change of dielectric constant of polar liquid in magnetic field whose experimental set up has been described in Section D of this chapter, two identical cells have been used in the measurement. Each cell consists of ^a cylindrical glass tube of diameter 2.75 cm. being fitted with four circular parallel electrodes made of silver. Two alternate plates are connected in parallel with a tungsten wire which is sealed with glass tube [Figure 2.6 (b)] .



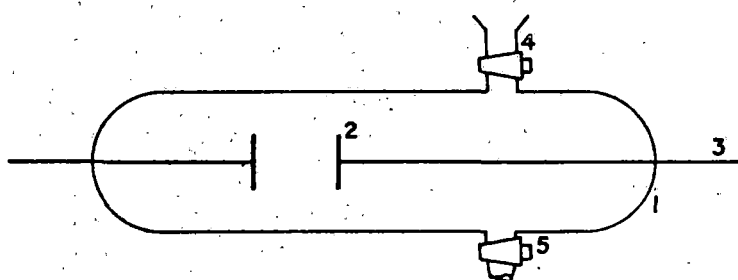
1. PYREX GLASS. 2. CIRCULAR HIGHLY POLISH GOLD ELECTRODE.
3. PLATINUM WIRE. 4. FILLING TUBE WITH GROUND GLASS
STOP COCK.

FIG.2.6(a).GOLD ELECTRODE CYLINDRICAL CELL.



1. PYREX GLASS. 2. CIRCULAR HIGHLY POLISH SILVER ELECTRODE.
3. TUNGSTEN WIRE. 4. FILLING TUBE WITH GROUND GLASS
STOP COCK.

FIG. 2.6(b). SILVER ELECTRODE CYLINDRICAL CELL.



1. PYREX GLASS. 2. CIRCULAR HIGHLY POLISH
BRASS ELECTRODE. 3. TUNGSTEN WIRE.
4. FILLING TUBE WITH GROUND GLASS STOP
COCK. 5. OUTLET TUBE WITH GROUND GLASS
STOP COCK.

FIG. 2.6(c). BRASS ELECTRODE CYLINDRICAL CELL.

Washing and Cleaning of the dielectric cell: The dielectric glass cells are thoroughly washed with chromic acid and care has been taken that no chemical reactions took place during washing particularly for brass electrode glass cell. After that cells are thoroughly washed with NaOH solution and washed several times with distilled water. To remove traces of water, the washed cells are kept inside a thermostat. The dried cells are again washed with dehydrated pure benzene and dried.

Other glass articles such as viscometer, beakers, pipet, measuring cylinder, specific gravity bottle etc. are washed and cleaned thoroughly in the same way as the dielectric cell.

Purification of liquids: The purity of liquid is a very important factor in the study of electrical conduction and breakdown in dielectric liquids. It is not possible to obtain reproducible results if the liquid is of insufficient purity and the characteristic properties of a liquid are often masked by phenomena arising due to presence of impurities. Traces of water and other electrolytic impurities are naturally the most important. The removal of these and small physical impurities such as dust particles is very important in all the purification method. In our present work, we have used the spectroscopic pure liquids of different reputed companies namely, E. Merck, British Drug House (B.D.H.) etc. All these chemicals were dried by dehydrating agents and then were distilled by fractional distillation. The proper fractions were distilled several times again under reduced pressure before use in the investigations.

Measurement of viscosity:-

The coefficient of viscosity

of the pure liquids and also of the solutions has been measured with the help of Ostwald type viscometer. If the time of fall of the experimental liquid and distilled water between two fixed marks in the viscometer which was placed inside the thermostat to maintain the constant temperature are t_1 and t then

$\eta_1 = \eta \frac{d_1 t_1}{d t}$ where η_1 and η are the coefficient of viscosity of the experimental liquids and water respectively and d_1 and d are their respective density at that temperature. The value of η and d of water are taken from international critical table. Thus by measuring d_1 , the value of η_1 has been calculated from the observed times of fall using the above expression. The measured coefficient of viscosity in the present investigation for different polar liquids is found to be in good agreement with the respective values reported in literature .

Measurement of static dielectric constant:-

The static die-

lectric constant of liquids at a particular temperature has been measured by resonance method using the same apparatus that has been utilized to measure the r.f. conductivity of different organic liquids (figure 2.1). The observation has been carried out at a frequency of 400 KHz. At any particular temperature which is maintained by thermostat, the dielectric constant is measured by comparing the capacity of the dielectric cell with liquid as dielectric to the capacity of the cell with air as dielectric. The capacity of the empty cell has been found out from the measurement of capacity of the cell filled with some standard liquids whose dielectric constant has been given in the literature. It is observed that the values of static

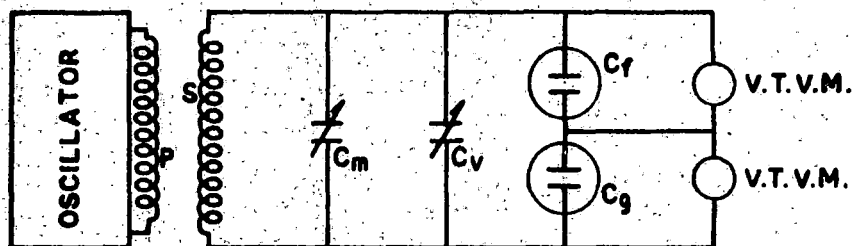
dielectric constant so obtained agrees well with those given in standard literature.

D. THEORY OF MEASUREMENT OF ϵ/ϵ_H

The block diagram of the experimental arrangement of measuring ϵ/ϵ_H where ϵ and ϵ_H are the dielectric constant of polar liquid in absence and presence of magnetic field respectively, can be represented by a simple network shown in figure (2.7).

The method used in the present study is almost similar to that utilized in measuring the dielectric constant of liquids by resonance method. Only the difference lies in the present circuit, is that instead of using a single dielectric cell, two dielectric cells C_F and C_G have been used and the detectors used are two valve tube voltmeters which are connected in parallel to the cells C_F and C_G as shown in figure (2.7). C_M and C_V are the main and vernier condensers. The detailed description of the cells [figure 2.6 (b)] have been described in Section C of this chapter. The experiment has been performed at a frequency of 800 KHz. and at a temperature of 30°C.

During the experiment the cell C_G is placed in the magnetic field whereas the cell C_F is placed outside the magnetic field. Both the cells are filled with experimental liquids. Keeping the oscillator adjusted at the desired frequency, resonance is obtained by adjusting the capacitance of the secondary tuning circuit until the voltage developed



P - PRIMARY COIL. S - SECONDARY COIL.
 C_m - MAIN CONDENSER. C_v - VERNIER CONDENSER.
 C_f & C_g - DIELECTRIC CELL. V.T.V.M. - VALVE TUBE
 V O L T M E T E R.

FIG. 2.7. BLOCK DIAGRAM FOR MEASUREMENT OF ϵ/ϵ_H

at the V.T.V.M. in the secondary tuning circuit reaches the maximum. Let at any particular value of C_m and C_v (say at resonance) the voltage developed at C_f and C_g are V_1 and V_2 respectively. If I_1 be the current flowing through the secondary circuit at this condition then we have

$$I_1 \times \frac{1}{\omega C_1} = V_1$$

and

$$I_2 \times \frac{1}{\omega C_2} = V_2$$

where C_1 and C_2 are the capacitance of the cell C_f and C_g respectively when filled with experimental liquids. Hence

$$\frac{C_2}{C_1} = \frac{V_1}{V_2}$$

$$\frac{C_2/\epsilon}{C_1/\epsilon} = \frac{V_1}{V_2}$$

$$\epsilon = \frac{V_1}{V_2} \cdot C_1/\epsilon \dots (2.13)$$

where ϵ is the dielectric constant of the liquid and C is the capacitance of the empty cell.

When the magnetic field is applied only to the cell C_g let the voltage developed are V_1' and V_2' across the two cells. Since only the capacitance in the cell C_g changes, let I_2 be the current flowing in the secondary circuit. Then in the similar way we have

$$I_2 \propto \frac{1}{\omega C_1} = V_1'$$

$$I_2 \propto \frac{1}{\omega C_2'} = V_2'$$

which gives

$$\frac{C_2'}{C_1} = \frac{V_1'}{V_2'}$$

$$\epsilon_H = \frac{V_1'}{V_2'} \cdot \frac{C_1}{C} \quad \dots (2.14)$$

where ϵ_H is the dielectric constant of the liquid in presence of magnetic field.

From equations (2.13) and (2.14)

$$\frac{\epsilon}{\epsilon_H} = \frac{V_1}{V_2} \cdot \frac{V_2'}{V_1'} \quad \dots (2.15)$$

Thus by observing only the voltages before and after application of the magnetic field, one can find directly the value of ϵ/ϵ_H .

Advantages of the Procedure: The procedure described above though does not give the absolute value of the change of dielectric constant of polar liquid in presence of magnetic field but it can be easily determined from equation (2.15) as ϵ value of pure liquid can be obtained from any standard literature. Only the voltage measured before and after application of the magnetic field is sufficient for the purpose which is the speciality of the procedure that has been adopted

here. Secondly it is well known that to measure the static dielectric constant by resonance method, it is required to calibrate accurately the capacitor of the secondary tuning circuit. But the method described here indicates that the calibration of the secondary tuning capacitor is not a primary factor, the experiment can be performed at any convenient position of the secondary tuning condenser.

E. APPARATUS USED FOR THE MEASUREMENT OF $\frac{\epsilon}{\epsilon_H}$

The apparatus used in this experiment are almost the same as that used in radio frequency conductivity measurement of dielectric liquids except V.T.V.M. and electromagnet. The dielectric cells, R.F. oscillator, secondary tuning circuit, stabilized power supply etc. are all described in Section C of this chapter. The description of the V.T.V.M. and an electromagnet are given below.

V.T.V.M. The two V.T.V.M. used as detectors are the vacuum tube voltmeter of Marconi Instruments Ltd. Model No. EF 10410.

Electromagnet: A large electromagnet (coil diameter 27.5 cm, resistance - 16 ohms per coil, number of turns - 800 per coil, distance adjustable of pole pieces - 7 cms.) has been used during the experiment. As it is evident from the theory that the effect of magnetic field on the change of dielectric constant is enhanced if the liquid is subjected to a magnetic field from all sides and in fact the effect is solely dependent

upon the ability of the applied magnetic field to compress the liquid. A simple configuration of the magnetic field such as either transverse or longitudinal magnetic field cannot produce the desired effect. Unless the liquid is compressed from all sides the effect would be negligible and hence a special design of the magnetic pole pieces has been made in order to obtain radial magnetic field.

Originally the pole pieces made of soft iron was cylindrical in nature and of diameter 8.3 cm. From each flat surface of the circular pole pieces, a portion of the material is cut-off in such a way that a cylindrical cavity of diameter 2.65 cm. is formed if the pole pieces are joined together along the axis which is radially perpendicular to the magnetic field. During the experiment the cell C_g is introduced totally inside the cylindrical cavity and the gap between the two middle points of the curvature is 3.0 cm. The remaining flat surface of the pole pieces was covered with thin mica sheet. This particular geometry of design produces a magnetic field which can compress the liquid from all sides. The sectional view of such a magnetic field arrangement is shown in figure (2.8). The field inside the cavity has been measured by a flux meter and is found to have maximum value at the centre of the cavity and gradually diminishes outwards. The main point is to compress the liquid from all sides and hence a slight deviation from uniform field has been tolerated. Thus an average value of magnetic field has been used during the calculation. The magnetic field for different currents

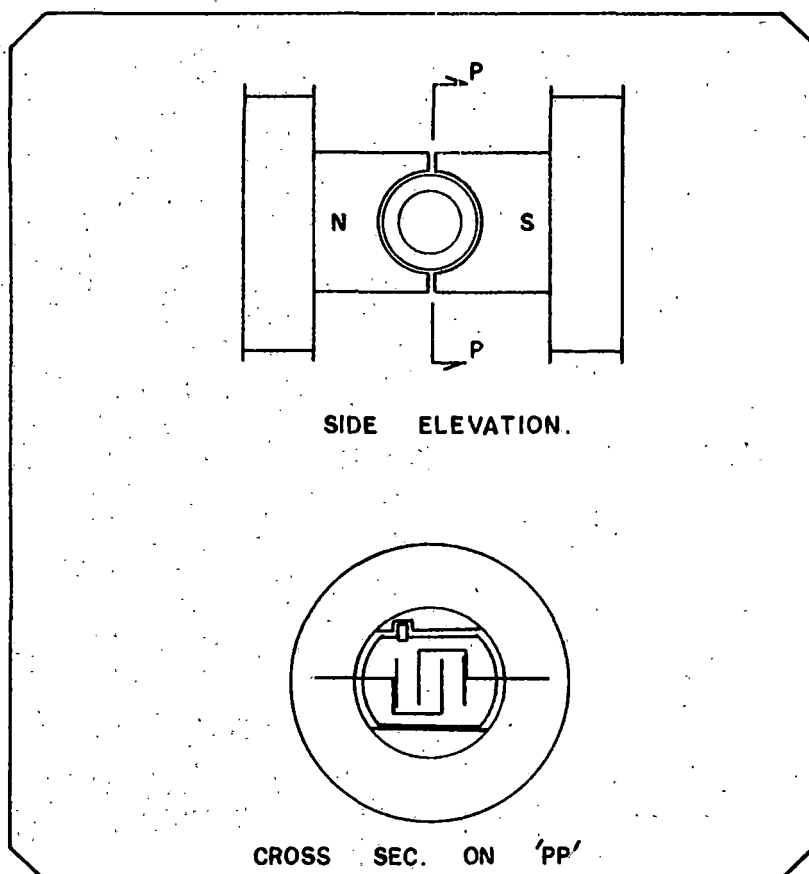


FIG. 2.8. SECTIONAL VIEW OF THE MAGNETIC FIELD ARRANGEMENT.

has been measured by a Gauss meter, Hall probe type, model No. GH 867 supplied by E.C.I.L., Hyderabad. A calibration curve drawn of the magnetic field against current in the coil of the electromagnet is shown in figure (2.9), keeping the pole pieces as it is after taking away the cell from cylindrical cavity of the pole pieces.

Calibration of electromagnet.

Table 2.3

Current in ampere through the coil of the magnet.	Average value of magnetic field in Gauss.
2	1500
3	2050
4	2550
5	3090
6.1	3450

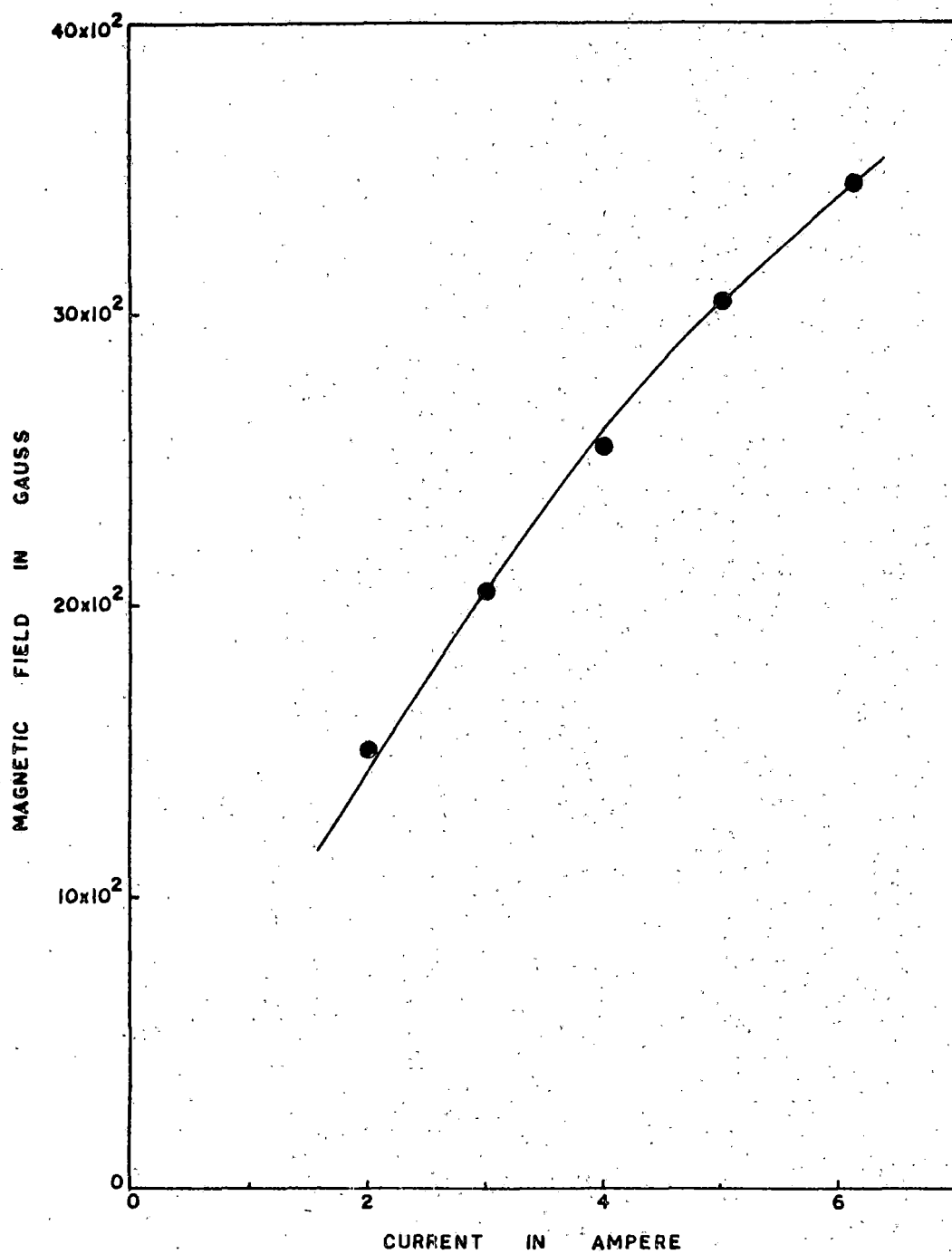


FIG. 2.9. CALIBRATION OF MAGNETIC FIELD.

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CHAPTER III

EVALUATION OF DIPOLE MOMENT FROM MEASUREMENTS ON SOLUTION OF POLAR MOLECULES IN NONPOLAR SOLVENTS

In the review of work for the evaluation of dipole moment of polar molecules from measurements carried out when a polar dielectric is dissolved in a nonpolar solvent it has been pointed out that various procedures adopted yield values of dipolemoment that differ from one another by a finite though small amount and the limitations of different methods have been discussed in detail. In this chapter it is proposed to present three different methods that yield results which are more consistent with the standard literature values.

(A) EXTRAPOLATION PROCEDURE IN COMPUTATION OF DIPOLE MOMENT OF POLAR LIQUIDS DISSOLVED IN NONPOLAR SOLVENTS

INTRODUCTION

There are several extrapolation procedures on ϵ_{12} , d_{12} and n_{12}^2 to compute the dipole moment μ of a polar liquid dissolved in a nonpolar solvent where ϵ_{12} , d_{12} and n_{12} are the dielectric constant, density and refractive index of the solution respectively. Guggenheim (1949, 1951) presented a formula to calculate the dipole moment of polar solutes dissolved in nonpolar solvent. Barelay, LeFevre and

Smythe (1950) calculated the μ value of triethylamine in benzene at 25°C and found the value to be 0.91 Debye. Later on, Guggenheim applied another extrapolation technique i.e. the variation of the ratio of finite difference between ϵ_{12} and n_{12}^2 against ω_2 and found the value of μ to be 0.87 Debye. The question of disagreement of the μ value arose due to different extrapolation techniques adopted by them. This point led us to recalculate μ of this system from more mathematical stand point by assuming ϵ_{12} and n_{12} as function of the concentration of the solution. As the solutions are usually made up by weights (Smith 1950) and it is easy to determine ω_2 than the concentration of solutes in moles per c.c., the simplest form in which to express the concentration is the weight fraction ω_2 of the solute and the best procedure is to represent ϵ_{12} and n_{12} as a function of ω_2 by

$$\epsilon_{12} = a_0 + a_1\omega_2 + a_2\omega_2^2 \dots (3.1)$$

$$n_{12} = b_0 + b_1\omega_2 + b_2\omega_2^2 \dots (3.2)$$

where a 's and b 's are constants. When $\omega_2 \rightarrow 0$, $\epsilon_1 = a_0$, $n_1 = b_0$,

$$\left(\frac{\partial \epsilon_{12}}{\partial \omega_2} \right)_{\omega_2 \rightarrow 0} = a_1 \text{ and } \left(\frac{\partial n_{12}}{\partial \omega_2} \right)_{\omega_2 \rightarrow 0} = b_1$$

i.e. a_0 , b_0 , a_1 and b_1 are the extrapolated values of

dielectric constant and refractive index of the solution and slopes of variation of ϵ_{12} and n_{12} against ω_2 respectively at infinite dilution. On the basis of the above mathematical standpoint, the calculated value of μ in case of triethylamine in benzene is found to be 0.864 Debye when

$\epsilon_1 = n_1^2$, which is slightly lower than the expected value. By applying a correction term based on $\epsilon_1 \neq n_1^2$, the μ value agrees with the Guggenheim's value. In order to check the applicability of our extrapolation procedure, we have selected five other systems i.e. aniline in benzene, methylaniline in benzene, dimethylaniline in benzene, phenol in benzene and diethyl ether in cyclohexane and the calculated μ values thus obtained are shown in table (3.1).

THEORY AND METHOD OF CALCULATION

The dielectric constant and the refractive index of solution can be represented by Debye equation (1929)

$$\frac{\epsilon_{12} - n_{12}^2}{(\epsilon_{12} + 2)(n_{12}^2 + 2)} = \frac{\epsilon_1 - n_1^2}{(\epsilon_1 + 2)(n_1^2 + 2)} + \frac{4\pi N \mu^2 d_{12}}{27 M_2 K T} \omega_2 \quad \dots(3.3)$$

where ϵ_1 , n_1 , N , d_{12} , M_2 and T represent the dielectric constant of solvent, refractive index of solvent, Avogadro number, density of solution, molecular weight of the solute and temperature in $^\circ K$ respectively. Since ϵ_1 and n_1 are constants, equation (3.3) on differentiation with respect to ω_2 yields after simplification when $\omega_2 \rightarrow 0$

and $d_{12} \longrightarrow d_1$

$$\mu^2 = \frac{27KT}{4\pi N} \cdot \frac{M_2}{d_1} \cdot \frac{1}{(\epsilon_1 + 2)^2} \left[\left(\frac{\partial \epsilon_{12}}{\partial \omega_2} \right)_{\omega_2 \rightarrow 0} - 2n_1 \left(\frac{\partial n_{12}}{\partial \omega_2} \right)_{\omega_2 \rightarrow 0} \left(\frac{\epsilon_1 + 2}{n_1^2 + 2} \right)^2 \right] \dots (3.4)$$

which is the general form of equation to evaluate the dipole moment of polar solute in nonpolar solvent. Now equation (3.4) can be written in terms of extrapolated values

$$\mu^2 = \frac{27KT}{4\pi N} \cdot \frac{M_2}{d_1} \cdot \frac{1}{(\alpha_0 + 2)^2} \left[a_1 - 2b_0 b_1 \left(\frac{\alpha_0 + 2}{b_0^2 + 2} \right)^2 \right] \dots (3.5)$$

Equation (3.5) has been utilized to calculate μ of the polar liquid.

The values of a_0 , a_1 , b_0 and b_1 have been calculated by least square method

i.e.

$$\begin{aligned} \sum \epsilon_{12} &= t a_0 + a_1 \sum \omega_2 + a_2 \sum \omega_2^2 \\ \sum \epsilon_{12} \omega_2 &= a_0 \sum \omega_2 + a_1 \sum \omega_2^2 + a_2 \sum \omega_2^3 \\ \sum \epsilon_{12} \omega_2^2 &= a_0 \sum \omega_2^2 + a_1 \sum \omega_2^3 + a_2 \sum \omega_2^4 \end{aligned}$$

and

$$\begin{aligned} \sum n_{12} &= t b_0 + b_1 \sum \omega_2 + b_2 \sum \omega_2^2 \\ \sum n_{12} \omega_2 &= b_0 \sum \omega_2 + b_1 \sum \omega_2^2 + b_2 \sum \omega_2^3 \\ \sum n_{12} \omega_2^2 &= b_0 \sum \omega_2^2 + b_1 \sum \omega_2^3 + b_2 \sum \omega_2^4 \end{aligned}$$

where t is the total number of experimental data measured at different weight fractions. Thus calculating a_0 , a_1 , b_0 and b_1 shown in table (3.1) from equations (3.1) and (3.2) against different systems by the least square method, the corresponding values of μ calculated from equation (3.5) are finally placed in table (3.2) together with reported μ values.

Table 3.1

Values of a_0 , a_1 , b_0 and b_1 obtained by least square method.

No.	System	Temp. in °C	a_0	a_1	b_0	b_1
1.	Triethylamine in benzene	25	2.3053	0.42216	1.5004	-0.13051
2.	Aniline in benzene	25	2.2702	3.12187	1.4981	0.08496
3.	Methylaniline in benzene	25	2.2730	2.99060	1.4983	0.06774
4.	Dimethylaniline in benzene	25	2.2730	2.51390	1.4981	0.07934
5.	Phenol in benzene	22	2.2799	3.31870	1.4997	0.04727
6.	Diethyl ether in cyclohexane	20	2.0311	1.96620	1.4259	-0.06245

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Table 3.2

Values of μ

No.	System	$\omega_2 \times 10^2$	ϵ_{12}	n_{12} (D-line of Sodium)	μ_{cal} (D)	μ_{lit} (D)
		0.000	2.2725	1.49332		
		2.200	2.2817	1.49050		
		2.860	2.2839	1.48963		
1.	Triethylamine in benzene	3.191	2.2849	1.48926	0.87	0.87 (Guggen- heim)
		4.030	2.2882	1.48788		
		5.724	2.2914	1.48617		
		6.517	2.2927	1.48513		
		8.308	2.2981	1.48280		
		0.0000	2.2725	1.4981		
		0.6341	2.2911	1.4987		1.505 (Few & Smith).
		0.7990	2.2962	1.4988		
		1.3396	2.3120	1.4992		
2.	Aniline in benzene	2.9740	2.3613	1.5004	1.57	1.50 - 1.60 (Smyth)
		4.4540	2.4066	1.5016		
		5.6711	2.4444	1.5026		
		6.9460	2.4849	1.5036		
		9.2304	2.5582	1.5054		

Table 3.2 (Contd.)

No.	System	$\omega_2 \times 10^2$	ϵ_{12}	n_{12} (D-line of Sodium)	$\mu_{cal.}$ (Debye)	$\mu_{lit.}$ (Debye)
		0.0000	2.2725	1.4982		
		0.7541	2.2953	1.4986		
		1.3651	2.3140	1.4992		
		2.7680	2.3571	1.4999		
3.	Methylaniline in benzene	4.0207	2.3960	1.5018	1.65	1.64 (Few & Smith)
		6.0396	2.4595	1.5023		
		7.9037	2.5185	1.5035		
		8.6875	2.5437	1.5040		
		10.6890	2.6086	1.5053		
		0.0000	2.2725	1.4982		
		1.0269	2.2976	1.4989		
		1.0915	2.2994	1.4989		
		1.7338	2.3154	1.4993		
4.	Dimethyl- aniline in benzene	3.2551	2.3535	1.5000	1.59	1.58 (Few & Smith)
		4.3015	2.3796	1.5006		
		5.8788	2.4194	1.5015		
		6.7394	2.4410	1.5019		
		9.2670	2.5049	1.5034		

Table 3.2 (Contd.)

No.	System	$\omega_2 \times 10^2$	ϵ_{12}	n_{12} (D-line of Sodium)	μ_{cal} (Debye)	$\mu_{lit.}$ (Debye)
		0.0000	2.280	1.49960		
		3.0311	2.382	1.50100		
		3.3827	2.394	1.50127		1.59
		3.7745	2.407	1.50127		(Debye)
5.	Phenol in benzene	4.1655	2.421	1.50148	1.64	1.59 - 1.62
		4.7249	2.442	1.50168		(Bottcher)
		5.9572	2.484	1.50208		
		6.6828	2.509	1.50258		
		0.0000	2.033	1.42630		
		4.1816	2.109	1.42285		
6.	Diethyl-ether in cyclohexane	7.8830	2.178	1.42006	1.35	1.29 (Glasstone)
		11.0190	2.246	1.41759		
		15.5700	2.317	1.41394		

CONCLUSIONS.

It is thus apparent that μ values calculated by the above procedure yield results consistent with the reported results in case of triethylamine, aniline, methylaniline and dimethylaniline.

In case of diethyl ether and phenol much reliance should not be given on computation of dipole moment as the experimental values of the refractive indices (n_{12}) of the solutions were not available. We, therefore, used the relation $n_{12} = x_1 n_1 + x_2 n_2$ (Glasstone, 1968) where x 's and n 's are the mole fraction and refractive indices of the pure solvent and solute respectively. The corresponding weight fraction of the solute ω_2 is related to x_2 by

$$\omega_2 = \frac{x_2 M_2}{x_1 M_1 + x_2 M_2}$$

Since the determination of accurate dipole moment of polar liquid in nonpolar solvent is difficult due to solvent effect though small (Smyth, 1955) and other effects (Böttcher, 1952) the problem should be attacked from the stand point of polar molecular structure in order to locate the more exactness in the value of μ . This proves the very soundness of the simple extrapolation technique which we have adopted in this paper.

(B) COMPUTATION OF DIPOLE MOMENT OF POLAR SOLUTES.

INTRODUCTION

The computation of electric dipole moment of polar liquids dissolved in nonpolar solvents is of much interest. But all the existing methods depend purely upon the theory of extrapolation of different physical quantities such as n_{12} the refractive indices, ϵ_{12} the dielectric constants of solution of different weight fraction ω_2 of solute, at infinite dilution (Ghosh and Acharyya, 1978). In a particular system i.e. triethylamine in benzene at 25°C, LeFèvre (1950) and Guggenheim (1951) used different extrapolation techniques and obtained different values of μ . Such results put the experimenters to a choice as to what method of extrapolation is needed to compute μ in a particular system.

In a recent paper Guha et al (1977) obtained a physical parameter Y_{12} expressed in terms of the experimental quantities ϵ_{12} and n_{12} of solutions of different weight fractions ω_2 of the solute and were able to represent the experimental facts at every stage of dilution for a large number of systems in which Y_{12} had been plotted against ω_2 . In this section the same principle has been adopted to evaluate the value of μ in case of three systems viz. aniline, methyl aniline and dimethyl aniline in benzene at 25°C at which ϵ_{12} and n_{12} are available (Few & Smith, 1949).

THEORY.

The well known Debye equation for polar and nonpolar liquid mixture of molar concentration C_2 of polar solute is given by Guggenheim (1949) assuming $\gamma_{2a} = \gamma'_{2a}$

as

$$\frac{\epsilon_{12}-1}{\epsilon_{12}+2} - \frac{n_{12}^2-1}{n_{12}^2+2} = \frac{\epsilon_1-1}{\epsilon_1+2} - \frac{n_1^2-1}{n_1^2+2} + \frac{4\pi N\mu^2}{9KT} C_2$$

... (3.6)

where the suffices 1, 2, and 12 represent solvent, solute and solution respectively and other symbols have their usual significance. Now C_2 , the molar concentration is related to

ω_2 the weight fraction of the solute by $C_2 = d_{12}\omega_2/M_2$ where d_{12} is the density of the solution which is also expressed as

$$\begin{aligned} d_{12} &= \frac{W_1 + W_2}{V_1 + V_2} = \frac{W_1 + W_2}{\frac{W_1}{d_1} + \frac{W_2}{d_2}} = \frac{d_1 d_2}{\frac{W_1}{W_1+W_2} d_2 + \frac{W_2}{W_1+W_2} d_1} \\ &= \frac{d_1 d_2}{\omega_1 d_2 + \omega_2 d_1} = \frac{d_1}{1 - \left(1 - \frac{d_1}{d_2}\right) \omega_2} \\ &= \frac{d_1}{1 - \beta \omega_2} \end{aligned}$$

where $\beta = 1 - \frac{d_1}{d_2}$ and $\omega_1 + \omega_2 = 1$, d_1 , d_2 are the densities of the pure solvent and solute respectively and W_1 , W_2 are the weights required to make a solution of weight fraction ω_2 of the solute.

Thus equation (3.6) can be put into the following form

$$\frac{\epsilon_{12} - n_{12}^2}{(\epsilon_{12} + 2)(n_{12}^2 + 2)} = \frac{\epsilon_1 - n_1^2}{(\epsilon_1 + 2)(n_1^2 + 2)} + \frac{4\pi N\mu^2}{27KT} \cdot \frac{d_1}{M_2} \cdot \frac{\omega_2}{1 - \beta\omega_2}$$

or

$$x_{12} = x_1 + \frac{4\pi N\mu^2}{27KT} \cdot \frac{d_1}{M_2} (1 + \beta\omega_2 + \beta^2\omega_2^2 + \dots)\omega_2$$

$$= x_1 + R\omega_2 + R\beta\omega_2^2 + \dots$$

... (3.7)

where $x_{12} = \frac{\epsilon_{12} - n_{12}^2}{(\epsilon_{12} + 2)(n_{12}^2 + 2)}$

$x_1 = \frac{\epsilon_1 - n_1^2}{(\epsilon_1 + 2)(n_1^2 + 2)}$

$R = \frac{4\pi N\mu^2 d_1}{27 M_2 K T}$

Thus the experimental quantity x_{12} can be expressed in a finite number of terms of the form

$$x_{12} = a_0' + a_1' \omega_2 + a_2' \omega_2^2 + \dots \quad (3.8)$$

as the higher powers of ω_2 are of no significance.

Comparing the coefficients of equal powers of ω_2 of equations (3.7) and (3.8) we have

$$R = \frac{4\pi N \mu^2}{27KT} \cdot \frac{d_1}{M_2} = a_1' \quad \dots (3.9)$$

$$R\beta = \frac{4\pi N \mu^2}{27KT} \cdot \frac{d_1}{M_2} \beta = a_2' \quad \dots (3.10)$$

We should expect that the value of μ can be calculated both from the given equations (3.9), (3.10) etc. But due to the presence of various effects to play their role in the value of a_2' , we are only left with the equation (3.9) which becomes

$$\mu = \sqrt{\left(\frac{27KT}{4\pi N} \cdot \frac{M_2}{d_1} a_1' \right)} \quad \dots (3.11)$$

Equation (3.11) has been utilized to compute the value of μ of polar solute when dissolved in nonpolar solvents.

METHOD OF CALCULATION

To evaluate the value of a_1' , an usual linear least square fitting has been performed on equation (3.8). The method has already been described in the previous section (Chapter III A). Thus calculating a_0' , a_1' , a_2' the normal equations have been arrived as

(i) Aniline in benzene at 25°C

$$x_{12} = 0.0015108 + 0.14936 \omega_2 - 0.030445 \omega_2^2$$

(ii) Methyl aniline in benzene at 25°C

$$x_{12} = 0.0015146 + 0.15357 \omega_2 - 0.040477 \omega_2^2$$

and

(iii) Dimethylaniline in benzene at 25°C

$$x_{12} = 0.001485 + 0.12749 \omega_2 - 0.060161 \omega_2^2$$

RESULTS AND CONCLUSION

The values of ϵ_{12} , n_{12} , ω_2 in case of three systems viz. aniline, Methylaniline and dimethylaniline in benzene have been placed in table (3.2) of the previous section (Chapter III A). The values of μ for these systems are calculated using equation (3.11) and are placed in table (3.3) along with data reported by Few and Smith (1949). It is found from table (3.3) that μ values of the systems are slightly higher than the reported ones. But in case of aniline, the dipole moment is within the range of 1.50 to 1.60 Debye (Smyth, 1955). Thus the close agreement between the calculated and reported values of μ suggests that in every system where there is no volume change due to mixing of solute and solvent, the accurate value of μ could be obtained without considering the case of infinite dilution. Moreover, the procedure is very simple because only a single extrapolation on x_{12} against ω_2 in any system is enough to find the value of a_1' and hence the dipole moment of polar liquid dissolved in nonpolar solvent.

Table 3.3

Dipole moment μ of solutes.

No.	Systems	Temp. in, °C.	$\mu_{cal.}$ (Debye)	$\mu_{lit.}$ (Debye)
1.	Aniline in benzene	25°C	1.53	1.505
2.	Methylaniline in benzene	25°C	1.66	1.64
3.	Dimethylaniline in benzene	25°C	1.61	1.58

* Few, A.V. and Smith, J. W. (1949), J. Chem. Soc.
Part I, 753.

(c) DIPOLE MOMENT OF POLAR SOLUTE FROM SOLUTION DATA

INTRODUCTION

The electric dipole moment μ of a substance can be determined by various methods, the most common of which are from dielectric constant measurement of pure liquids dissolved in nonpolar solvents, temperature variation of dielectric constant, microwave absorption in liquids etc. Out of these methods, determination of dipole moment from

$$\left[P_a \right]_d^0 + \left[P_o \right]_d^0 \quad \text{where} \quad \left[P_a \right]_d^0 \quad \text{and} \quad \left[P_o \right]_d^0$$

are the atomic and orientational polarization of dipole compound at infinite dilution respectively, by concentration variation of polar solute dissolved in nonpolar solvent is most convenient and gives a more accurate value of μ as in dilute solution the polar molecules are well separated from each other and consequently dipole-dipole interaction is almost absent.

Generally the dipole moment of polar solute dissolved in nonpolar solvent is determined from the well known Debye equation. But this equation when applied to same solute and solvent system in different concentrations gives different values of dipole moment. This is due to the fact that Debye's equation is valid at infinite dilution and partly due to the fact that the computation of $\left[P_a \right]_d^0 + \left[P_o \right]_d^0$ or simply $\left[P_o \right]_d^0$ and thus μ depends upon the method of extrapolation of different physical quantities ϵ_{12} n_{12} etc. as the extrapolation curve is not a

straight line. Therefore several attempts by different authors (Halverstad and Kumler, 1942; Higasi, 1943; Guggenheim, 1949, 1951; Smith, 1950; LePèvre, 1950; Palit, 1952; Jay Prakash, 1975) have been made to improve the process of extrapolation. Guggenheim's technique though simple is based on certain assumptions. He assumed $[P_a]_d^{\circ} = [P'_a]_d^{\circ}$ where $[P'_a]_d^{\circ}$ is the fictitious atomic polarizability of solute molecule according to which the ratio of atomic polarization of solute and solvent are in the ratio of their molar volumes. Secondly Guggenheim used an approximation $V_{12} = x_1 V_1 + x_2 V_2$ where V_{12} is the mean molar volume of the solution, x 's and v 's are the mole fraction and partial molar volume of solvent and solute respectively. This method will be definitely less accurate when there is considerable contraction or dilatation of the volume of the solution. Generally in all the methods, the contribution of atomic polarization has not been taken into consideration in evaluating the value of μ except by a few authors. This case has been presented by Böttcher (1952) where four extrapolation techniques of Debye, Hødestrand, Cohen-Henriquez and Guggenheim have been discussed in detail. The points that (i) as the solutions are usually made up of weights, it is easy to determine ω_2 than the mole fraction x_2 (ii) Guggenheim's approximation $V_{12} = x_1 V_1 + x_2 V_2$ which introduces much error in μ value when there is considerable contraction or dilatation in the volume of the solution (iii) specially and mainly the differences observed in

$[P_a]_d^{\circ} + [P_o]_d^{\circ}$ value of phenol in benzene by four extrapolation techniques as discussed by Böttcher made us

interested to recalculate $\left[P_a \right]_d^0 + \left[P_o \right]_d^0$ and hence $\left[P_o \right]_d^0$ or μ value of the same system from an extrapolation technique based on a more mathematical standpoint in terms of ω_2 and directly from Debye's equation. It is observed that the calculated μ value of phenol agrees well with that of Debye's and Guggenheim's method. In order to check the applicability of the extrapolation procedure, μ value has also been calculated in case of two other systems viz. aniline in benzene and dimethylaniline in benzene at 25°C.

RESULTS AND DISCUSSION

Considering a solution of polar solute in nonpolar solvent, we have from Debye's equation

$$\frac{\epsilon_{12} - 1}{\epsilon_{12} + 2} V_{12} = \frac{\epsilon_1 - 1}{\epsilon_1 + 2} V_1 (1 - x_2) + \frac{4\pi N}{3} \left(\gamma_{2e} + \gamma_{2a} + \frac{\mu^2}{3KT} \right) x_2 \quad \dots (3.12)$$

and

$$\frac{n_{12}^2 - 1}{n_{12}^2 + 2} V_{12} = \frac{n_1^2 - 1}{n_1^2 + 2} V_1 (1 - x_2) + \frac{4\pi N}{3} \gamma_{2e} x_2 \quad \dots (3.13)$$

where subscripts 12, 1, 2, represent solution, solvent and solute respectively, n 's the refractive index extrapolated from the visible part of the spectrum to infinite wavelength

γ_{2e} and γ_{2a} are the electronic and atomic contribution of polarizability of solute molecule respectively and the other symbols have their usual meaning.

$$\text{Putting } x'_{12} = \frac{\epsilon_{12} - 1}{\epsilon_{12} + 2} - \frac{n_{12}^2 - 1}{n_{12}^2 + 2}$$

$$\text{and } \frac{4\pi N}{3} \gamma_{1a} = \left(\frac{\epsilon_1 - 1}{\epsilon_1 + 2} - \frac{n_1^2 - 1}{n_1^2 + 2} \right) V_1$$

we get from equations (3.12) and (3.13)

$$x'_{12} V_{12} = \frac{4\pi N}{3} \gamma_{1a} (1 - x_2) + \frac{4\pi N}{3} \left(\gamma_{2a} + \frac{\mu^2}{3KT} \right) x_2 \quad \dots (3.14)$$

$$\text{Again putting } V_{12} = \frac{M_{12}}{d_{12}} = \frac{x_1 M_1 + x_2 M_2}{d_{12}}$$

where d_{12} is the density of the solution and expressing mole fraction of the solute x_2 to weight fraction ω_2 by the relation

$$x_2 = \frac{\omega_2 M_1}{\omega_1 M_2 + \omega_2 M_1}$$

equation (3.14) after simplification yields

$$x''_{12} = \frac{4\pi N}{3} \gamma_{1a} \frac{1}{M_1} + \frac{4\pi N}{3} \left\{ \left(\gamma_{2a} + \frac{\mu^2}{3KT} \right) \frac{1}{M_2} - \gamma_{1a} \frac{1}{M_1} \right\} \omega_2 \quad \dots (3.15)$$

where $x''_{12} = \frac{x'_{12}}{d_{12}}$. Since Debye's equation is valid at infinite dilution, equation (3.15) shows that if a graph is plotted between x''_{12} and ω_2 the curve should be a

straight line atleast at infinite dilution with an initial height $\frac{4\pi N}{3} \gamma_{1a} \frac{1}{M_1}$ and a slope equal to

$\frac{4\pi N}{3} \left\{ \left(\gamma_{2a} + \frac{\mu^2}{3KT} \right) \frac{1}{M_2} - \gamma_{1a} \frac{1}{M_1} \right\}$ from which the value of $[P_a]_s$ and $[P_a]_d^0 + [P_o]_d^0$ can be easily determined where

$[P_a]_s = \frac{4\pi N}{3} \gamma_{1a} =$ molar atomic polarization of pure solvent

$[P_a]_d^0 = \frac{4\pi N}{3} \gamma_{2a} =$ molar atomic polarization of solute at infinite dilution.

$[P_o]_d^0 = \frac{4\pi N}{3} \cdot \frac{\mu^2}{3KT} =$ molar orientation polarization of solute at infinite dilution

As an application of this formula we choose the same system as taken by Bötcher (1952) i.e. phenol in benzene at 22°C where the measured values of ϵ_{12} , n_{12} and d_{12} etc. are given along with two other systems from Few and Smith's (1949) measurements viz. aniline in benzene and dimethylaniline in benzene at 25°C. All the values are placed in table (3.5). In the later two systems instead of n_{12} (at infinite wave length), n_{12} (D-line of sodium) are supplied. It has been found that when x_{12}'' is plotted against ω_2 , the curve is almost a straight line with a slight curvature in nature (Fig. 3.1). Hence the best one is to represent x_{12}'' as a

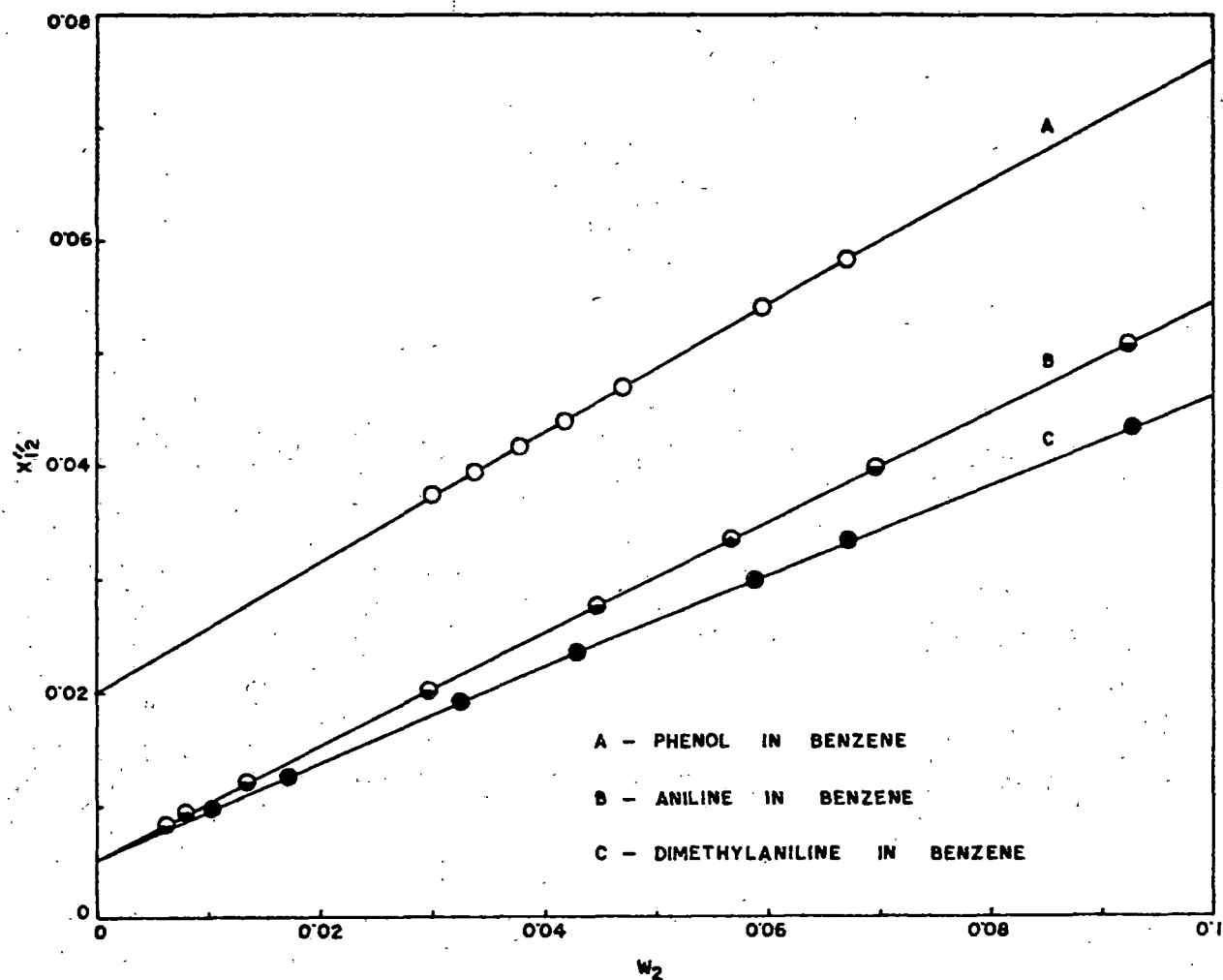


FIG. 3.1. VARIATION OF $x'_{12} = \left[\left(\frac{\epsilon_{12}-1}{\epsilon_{12}+2} - \frac{2}{n_{12}^2+2} \right) / d_{12} \right]$ WITH w_2

function of ω_2 by

$$x_{12}'' = a_0'' + a_1'' \omega_2 + a_2'' \omega_2^2 \dots (3.16)$$

where a_0'' , a_1'' and a_2'' are constants which are evaluated by the method of least square fitting and are placed in table (3.6). The method of least square fitting has already been discussed in a previous section (Chapter III A). In figure (3.1) the solid lines represent the fitting curve together with the experimental points placed upon them. It is seen that the fitted curves are in excellent agreement with the experimental points which justify the assumption made in equation (3.16). At infinite dilution the initial height is given by a_0'' and the slope becomes

$$\left(\frac{\partial x_{12}''}{\partial \omega_2} \right)_{\omega_2 \rightarrow 0} = a_1''$$

Hence from equation (3.15) at infinite dilution

$$\left[P_a \right]_S = a_0'' M_1 \dots (3.17)$$

and

$$\left[P_a \right]_d^0 + \left[P_o \right]_d^0 = (a_0'' + a_1'') M_2 \dots (3.18)$$

Equation (3.17) and (3.18) have been utilized in determining the value of $\left[P_a \right]_S$ and $\left[P_a \right]_d^0 + \left[P_o \right]_d^0$ when a polar solute is dissolved in nonpolar solvent. In case of phenol in benzene, since $a_0'' = 0.0200058$ and $M_1 = 78.11$, from equation (3.17) $\left[P_a \right]_S = 1.56$ cc which is in good

agreement with the value 1.54 as obtained from Debye's method i.e.

$$[P_a]_s = [P]_s - [P_e]_s \quad \dots(3.19)$$

where $[P]_s$ = molar polarization of pure solvent

$$= \frac{\epsilon_1 - 1}{\epsilon_1 + 2} \cdot \frac{M_1}{d_1} = 26.65 \text{ cc.}$$

and $[P_e]_s$ = molar electronic polarization of pure solvent

$$= \frac{n_1^2 - 1}{n_1^2 + 2} \cdot \frac{M_1}{d_1}$$

$$= 25.11 \text{ cc}$$

Putting again the value of a_0'' , a_1'' and M_2 in equation (3.18)

$$[P_a]_d^0 + [P_o]_d^0 = 56.79 \text{ cc}$$

To calculate $[P_o]_d^0$ and hence the dipole moment, we have to estimate the value of $[P_a]_d^0$. In case of polar molecules, it is very difficult to determine atomic polarization with required accuracy. Theoretically it seems that when $[P]_d^0$ is plotted against $1/T$ of the equation

$$[P]_d^0 = \frac{4\pi N}{3} \left(\sqrt{2}e + \sqrt{2}a + \frac{\mu^2}{3KT} \right)$$

the initial height and slope will give respectively the value

of $[P_e]_d^0 + [P_a]_d^0$ and $\frac{4\pi N \mu^2}{9K}$. Since

$[P_e]_d^0$ can be easily determined, $[P_a]_d^0$ thus may be calculated. In practice, however, this method is very inaccurate. It often, happens that the atomic polarization and

dipole moment of polar molecule is slightly dependent upon temperature so that the linear dependency mentioned above is disturbed. This leads to important deviations in the calculated values of atomic polarization and dipole moment of the substance. Thus in the present case only a rough estimation of $\left[P_a \right]_d^{\circ}$ is possible. The molar atomic polarization of simple polar compounds consisting only of carbon, hydrogen and oxygen is generally between 10 - 20% of molar electronic polarization. Since

$$\left[P \right]_d^{\circ} = \left[P_e \right]_d^{\circ} + \left[P_a \right]_d^{\circ} + \left[P_o \right]_d^{\circ} \dots (3.20)$$

we have from equations (3.18) and (3.20)

$$\left[P_e \right]_d^{\circ} = \left[P \right]_d^{\circ} - (a''_0 + a''_1) M_2 \dots (3.21)$$

The value $\left[P \right]_d^{\circ}$ has been determined by many authors using different extrapolation techniques but at present taking the same value of $\left[P \right]_d^{\circ}$ i.e. 83.1 as taken by Böttcher (1952) from Debye's method, the value of $\left[P_e \right]_d^{\circ}$ from equation (3.21) becomes, 26.31 cc where as from Debye's extrapolation technique it has been found to have the value 26.6 cc. It should be pointed out that in some cases if the ratio of molar atomic polarization of solute and solvent are in the ratio of their molar volumes i.e.

$$\text{if } \frac{\left[P_a \right]_d^{\circ}}{\left[P_a \right]_s^{\circ}} = \frac{V_2}{V_1} = \frac{M_2 d_1}{M_1 d_2}$$

then we can calculate easily the value of $\left[P_a \right]_d^{\circ}$ which

was called by Guggenheim "the fictitious atomic polarizability" of solute. Particularly in this condition since $\left[P_a \right]_d^{\circ}$ is known, $\left[P_o \right]_d^{\circ}$ and hence μ can be accurately determined using equation (3.18). But in practice this is not so and fortunately since a small inaccuracy in $\left[P_a \right]_d^{\circ}$ has only a small influence upon $\left[P_o \right]_d^{\circ}$, we estimate $\left[P_a \right]_d^{\circ}$ to 15% of $\left[P_e \right]_d^{\circ}$ i.e. the same value 4 cc (approx.) as taken by Böttcher. Hence $\left[P_o \right]_d^{\circ}$ in our case becomes $(56.79 - 4) \text{ cc} = 52.79 \text{ cc}$. Taking again the same value $K = 1.37 \times 10^{-16}$, $N = 6.02 \times 10^{23}$ and $T = 295^{\circ}\text{K}$ in order to compare with the four extrapolation techniques, the value of μ has been calculated with the aid of the equation

$$\left[P_o \right]_d^{\circ} = \frac{4\pi N}{3} \cdot \frac{\mu^2}{3KT}$$

and becomes equal to 1.59 D. The value of $\left[P_a \right]_d^{\circ} + \left[P_o \right]_d^{\circ}$, $\left[P_o \right]_d^{\circ}$ and μ obtained from different methods are listed below.

Table 3.4

Method	$\left[P_a \right]_d^{\circ} + \left[P_o \right]_d^{\circ}$ cc	$\left[P_o \right]_d^{\circ}$ cc	μ (D)
Debye	56.5	52.5	1.59
Hedestrand	57.5	53.5	1.60
Cohen-Henriquez	58.6	54.6	1.62
Guggenheim	56.3	52.3	1.59
Present case	56.79	52.79	1.59

It is seen from table (3.4) that though $\left[P_a \right]_d^\circ + \left[P_o \right]_d^\circ$ and $\left[P_o \right]_d^\circ$ value in our case slightly differs with the reported values but μ agrees very well with that of Debye and Guggenheim's method.

In case of aniline in benzene and dimethylaniline in benzene, all the calculations have been made as in the case of phenol in benzene. The values of $\left[P_a \right]_s$ from equations (3.17) and (3.19) are placed in table (3.6) along with a_0'' , a_1'' and a_2'' whereas in table (3.7) the calculated values of $\left[P \right]_d^\circ$, $\left[P_a \right]_d^\circ + \left[P_o \right]_d^\circ$, $\left[P_e \right]_d^\circ$, $\left[P_a \right]_d^\circ$, $\left[P_a \right]_d^\circ + \left[P_e \right]_d^\circ$, $\left[P_o \right]_d^\circ$

and μ value have been placed along with the available values of the same mentioned in Few and Smith's (1949) paper. It is to be noted that in case of aniline in benzene and dimethylaniline in benzene $\left[P_a \right]_s$ being much smaller than $\left[P_a \right]_s$ of phenol in benzene which is due to the refractive index measured in terms of nd_{12} and hence the value of $\left[P_a \right]_d^\circ$ in case of aniline and dimethylaniline in benzene is taken 5% of $\left[P_e \right]_d^\circ$ as has been rightly suggested by J.W. Smith for the calculation of μ where nd_{12} are available. From table (3.6) it is also observed that $\left[P_a \right]_s$ of phenol in benzene should be 1.54 instead of 1.56. This difference is due to the fact that Debye's equation is valid at infinite dilution only in a restricted sense and may be also due to inaccuracy in evaluating the value of refractive index at infinite wavelength from the visible part of the spectrum. When the dipole moment of phenol is calculated

taking $[P_a]_S = 1.54$ from eqn. (3.17), no change in dipole moment has been observed. However table (3.4) and (3.7) which shows a consistent calculated results of μ with the reported ones suggests that it is possible to determine a more accurate value of $[P_a]_d^\circ + [P_o]_d^\circ$ and hence $[P_o]_d^\circ$ or μ value of a polar solute when dissolved in a nonpolar solvent from this extrapolation procedure which we have discussed in this paper.

Table 3.5

No.	System	$\omega_2 \times 10^2$	ϵ_{12}	n_{12} (At infinite wavelength)	d_{12}
		0.0000	2.280	1.47500	0.87646
		3.0311	2.382	1.47640	0.88182
		3.3827	2.394	1.47670	0.88220
1.	Phenol in benzene	3.7745	2.407	1.47680	0.88288
		4.1655	2.421	1.47710	0.88368
		4.7249	2.442	1.47730	0.88452
		5.9572	2.484	1.47780	0.88638
		6.6828	2.509	1.47810	0.88760

Table 3.5(Contd.)

No.	System	$\omega_2 \times 10^2$	ϵ_{12}	n_{12} (D-line of sodium)	$1/a_{12}$
		0.0000	2.2725	1.4981	1.14457
		0.6341	2.2911	1.4987	1.14362
		0.7990	2.2962	1.4988	1.14292
		1.3396	2.3120	1.4992	1.14228
2.	Aniline in benzene	2.9740	2.3613	1.5004	1.13948
		4.4540	2.4066	1.5016	1.13691
		5.6711	2.4444	1.5026	1.13483
		6.9460	2.4849	1.5036	1.13266
		9.2304	2.5582	1.5054	1.12873
		0.0000	2.2725	1.4982	1.14456
		1.0269	2.2976	1.4989	1.14360
		1.0915	2.2994	1.4989	1.14350
		1.7338	2.3154	1.4993	1.14286
3.	Dimethyl aniline in benzene	3.2551	2.3535	1.5000	1.14145
		4.3015	2.3796	1.5006	1.14046
		5.8788	2.4194	1.5015	1.13895
		6.7394	2.4410	1.5019	1.13813
		9.2670	2.5049	1.5034	1.13574

1. Böttcher, C.J.F. (1952), Theory of Electric Polarization, Elsevier Publishing Co.

2-3. Few, A.V. and Smith, J.W.(1949), J.Chem.Soc., Part-I, 753.

Table 3.6

Values of a_0'' , a_1'' , a_2'' and $[P_a]_s$

System	Temp. , in °C,	a_0''	a_1''	a_2''	$[P_a]_s$ from eqn. (3.17) cc	$[P_a]_s$ from eqn. (3.19) cc
Phenol in benzene	22	0.0200058	0.58342	-0.19138	1.56	1.54
Aniline in benzene	25	0.00521068	0.50825	-0.13743	0.407	0.409
Dimethyl- aniline in benzene	25	0.00508585	0.43863	-0.25992	0.397	0.405

Table 3.7

Values of $[P]_d^{\circ}$, $[P_a]_d^{\circ} + [P_o]_d^{\circ}$, $[P_e]_d^{\circ}$, $[P_a]_d^{\circ}$, $[P_e]_d^{\circ} + [P_o]_d^{\circ}$, and μ .

System	Observer	Temp. in °C	$[P]_d^{\circ}$ (cc)	$[P_a]_d^{\circ} + [P_o]_d^{\circ}$ (cc)	$[P_e]_d^{\circ}$ (cc)	$[P_a]_d^{\circ}$ (cc)	$[P_e]_d^{\circ} + [P_o]_d^{\circ}$ (cc)	$[P_o]_d^{\circ}$ (cc)	μ (D)
Aniline in benzene	Hojendahl*	25	76.0	-	29.0	-	29.0	47.0	1.51
	LeFevre & LeFevre*	25	78.4	-	31.0	-	31.0	47.4	1.51
	Higasi*	25	80.0	-	30.6	-	30.6	49.4	1.54
	Few & Smith*	25	78.35	-	-	-	32.23	46.12	1.505
	Present case	25	78.40	47.808	30.592	1.53	32.122	46.278	1.505
Dimethyl aniline in benzene	Fogelberg & Williams*	25	94	-	41	-	41	53.0	1.58
	Few & Smith*	25	94.06	-	-	-	43.23	50.83	1.577
	Present case	25	94.10	53.689	40.411	2.021	42.432	51.668	1.59

*Few, A.V. and Smith, J.W. (1949), J.Chem.Soc. Part-I, 753.

Comparison of three extrapolation techniques.

In this chapter the three extrapolation techniques so far described have been utilized in Debye's equation to evaluate the dipole moment of polar solute dissolved in nonpolar solvents. In order to compare them, the calculated values of dipole moment of some systems using the three extrapolation techniques are placed in table (3.8).

Table 3.8.

System	$\mu_{cal.}$ from eqn. (3.5)	$\mu_{cal.}$ from eqn. (3.11)	$\mu_{cal.}$ from eqn. (3.15)	$\mu_{lit.}$ (D)
Aniline in benzene	1.57	1.53	1.505	1.505 ^a
Methylaniline in benzene	1.65	1.66		1.64 ^a
Dimethylaniline in benzene	1.59	1.61	1.59	1.58 ^a
Phenol in benzene	1.64	1.61	1.59	1.59 ^b

a. Few, A.V. and Smith, J.W. (1949), J.Chem.Soc.Part-I, 753.

b. Böttcher, C.J.F. (1952), Theory of Electric Polarization, Elsevier Publishing Co.

It is seen that there is close agreement between the calculated values of μ from equations (3.5) and (3.11) where the contribution due to atomic polarization has not been taken into consideration but differs when calculated from equation (3.15). This is due to the fact that in equation (3.15) the contribution due to atomic polarization has been taken into

consideration and thus the value obtained from equation (3.15) is much nearer to the reported ones. It is to be noted that equation (3.11) can be obtained from the slope of $x'_{12}/3 - \omega_2$ curve at infinite dilution instead of $x''_{12} - \omega_2$ and by neglecting the contribution of atomic polarization of solvent and solute molecule. Thus the μ value obtained without considering the infinite dilution as demanded earlier from (3.11)

(Ghosh et al, 1977) will not be feasible as a_1' which was used to compute the value of μ is nothing but simply the slope of $\frac{x'_{12}}{3} - \omega_2$ curve at infinite dilution. When the density of the solution is not available, μ can also be determined in a similar way as in equation (3.15) except that the slope should be obtained from $x'_{12} - \omega_2$ curve instead of $x''_{12} - \omega_2$ curve at infinite dilution. Finally the close agreement between the μ values by three extrapolation techniques suggest that it is possible to calculate dipole moment of polar solute by applying any of three extrapolation techniques. Since the dipole moment value from equations (3.5) and (3.15) requires to some extent more mathematical calculation, it can be concluded that for quick as well as an accurate value of dipole moment determination from solution data, equation (3.11) is sufficient to tackle the problem as this procedure is very simple and only a single extrapolation on x_{12} against ω_2 in any system is enough to find the value of a_1' and hence the dipole moment of polar liquid. But when more accurate value of dipole moment is required, the correction due to atomic polarization must be taken into consideration and then equation (3.15) plays a useful role to evaluate the dipole moment of polar solute when dissolved in nonpolar solvents.

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Extrapolation procedure in computation of dipole moment of polar liquid in nonpolar solvent

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There are several extrapolation procedures on ϵ_{012} , d_{12} and n_{012}^2 to compute the dipole moment μ of polar liquid dissolved in nonpolar solvent. As the solutions are usually made up by weights (Smith 1960) and easy to determine ω_2 than the concentration of solutes in moles per cc, the simplest form in which to express the concentration is the weight fraction ω_2 of the solute and the best one is to represent ϵ_{012} and n_{012} as a function of ω_2 by

$$\epsilon_{012} = a_0 + a_1\omega_2 + a_2\omega_2^2 \quad \dots (1)$$

$$n_{012} = b_0 + b_1\omega_2 + b_2\omega_2^2 \quad \dots (2)$$

where a 's and b 's are constants, ϵ_{012} and n_{012} are the dielectric constant and refractive index of solution of weight fraction ω_2 of the solute.

When,

$$\omega_2 \rightarrow 0, \epsilon_{01} = a_0, n_{01} = b_0, \left(\frac{\partial \epsilon_{012}}{\partial \omega_2} \right)_{\omega_2 \rightarrow 0} = a_1 \text{ and } \left(\frac{\partial n_{012}}{\partial \omega_2} \right)_{\omega_2 \rightarrow 0} = b_1$$

i.e. a_0 , b_0 , a_1 and b_1 are the extrapolated values of the dielectric constant and refractive index of the solution and slopes of variation of ϵ_{012} and n_{012} against ω_2 respectively at infinite dilution.

Guggenheim (1949, 1951) presented a formula to calculate μ of polar liquid in nonpolar solvents. Based on this formula Le-Fevre (1950) and Guggenheim (1951) applied different extrapolation techniques i.e. the ratio of finite difference on ϵ_{012} and n_{012}^2 against ω_2 to compute μ in case of triethylamine in benzene at 25°C and obtained different values i.e. 0.91 and 0.87 Debye respectively. This point made us interested to recalculate μ of that system from the more mathematical standpoint as stated above, and the calculated value of μ is found to be 0.864 Debye (when $\epsilon_{01} = n_{01}^2$) slightly lower than the expected value. By applying a correction term based on $\epsilon_{01} \neq n_{01}^2$, the μ agrees with the Guggenheim's value. In order to check the applicability of our extrapolation procedure, we have calculated μ of other five systems and are shown in Table 1.

The dielectric constant and the refractive index of a solution can be represented by Debye equation (1929),

Table 1. Values of a_0 , a_1 , b_0 , b_1 , $\mu_{cal.}$ and $\mu_{rept.}$

No.	Systems	Temp. in °C	a_0	a_1	b_0	b_1	$\mu_{cal.}$ (Debye)	$\mu_{rept.}$ (Debye)
1.	Triethylamine in benzene ¹	25	2.3053	0.42216	1.5004	-0.13051	0.87	0.87
2.	Aniline in benzene ²	25	2.2702	3.12187	1.4981	0.08496	1.57	1.50-1.60
3.	Methylaniline in benzene ³	25	2.2730	2.99060	1.4983	0.06774	1.65	1.64
4.	Dimethylaniline in benzene ⁴	25	2.2730	2.51390	1.4981	0.07934	1.59	1.58
5.	Phenol in benzene ⁵	22	2.2799	3.31870	1.4997	0.04727	1.64	1.62
6.	Diethylether in cyclohexane ⁶	20	2.0311	1.96620	1.4259	-0.06245	1.35	1.29

¹ Guggenheim E. A. *Trans. Faraday Soc.* **46**, 573 (1951).

²⁻⁴ Few A. V. & Smith J. W. *J. Chem. Soc.* P-I, 753 (1949).

⁵ Guggenheim E. A. *Trans. Faraday Soc.* **45**, 714 (1949).

⁶ Glasstone S. *Physical Chem.* Macmillan & Co. Limited, Second Edition (1968).

$$\frac{\epsilon_{012} - n_{012}^2}{(\epsilon_{012} + 2)(n_{012}^2 + 2)} = \frac{4\pi N \mu^2}{27 M_2 k T} \omega_2, \quad \dots (3)$$

where N , d_{12} , M_2 and T are Avogadro number, density of the solution, molecular weight of the solute and temperature in °K respectively. Eq. (3) on differentiation with respect to ω_2 yields when $\omega_2 \rightarrow 0$ and $d_{12} \rightarrow d_1$

$$\mu^2 = \frac{27kT}{4\pi N} \cdot \frac{M_2}{d_1} \cdot \frac{1}{(\epsilon_{01} + 2)^2} \left[\left(\frac{\partial \epsilon_{012}}{\partial \omega_2} \right)_{\omega_2 \rightarrow 0} - 2n_{01} \left(\frac{\partial n_{012}}{\partial \omega_2} \right)_{\omega_2 \rightarrow 0} \left(\frac{\epsilon_{01} + 2}{n_{01}^2 + 2} \right)^2 \right] \dots (4)$$

when $\epsilon_{01} = n_{01}^2$, eq. (4) can be converted into a well known Guggenheim formula as shown by Jayprakash (1975). Now eq. (4) can be written in terms of the extrapolated values

$$\mu^2 = \frac{27kT}{4\pi N} \cdot \frac{M_2}{d_1} \cdot \frac{1}{(a_0 + 2)^2} \left[a_1 - 2b_0 b_1 \left(\frac{a_0 + 2}{b_0^2 + 2} \right)^2 \right] \dots (5)$$

The values of a_0 , b_0 , a_1 and b_1 have been calculated from eqs. (1) and (2) against different systems by the usual least square method and the corresponding values of μ calculated from eq. (5) are finally placed in Table 1 with reported μ values.

In case of diethyl ether and phenol much reliance should not be given on computation of dipole moment as the experimental values of the refractive indices of the solutions were not available. We, therefore, used the relation $n_{012} = x_1 n_{01} + x_2 n_{02}$ (Glasstone 1968) where x 's and n 's are the mole fraction and refractive indices of the pure solvent and solute respectively. The corresponding weight fraction of the solute ω_2 is related to x_2 by

$$\omega_2 = \frac{x_2 M_2}{x_1 M_1 + x_2 M_2}.$$

Since the determination of accurate dipole moment of polar liquid in non-polar solvent is difficult due to solvent though it is small (Smyth 1952) and other effects (Böttcher 1952) the problem should be attacked from the standpoint of polar molecular structure in order to locate the more exactness in the value of μ . However, Table 1 shows a consistent calculated results of μ which are more or less equal to the reported ones. This proves the very soundness of the simple extrapolation technique which we have adopted in this note.

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ON COMPUTATION OF DIPOLE MOMENT OF POLAR SOLUTES

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Abstract

Recently a simple and straight forward procedure has been derived from Debye equation to compute the dipole moment of polar liquids in nonpolar solvents. The computed results of μ in three different systems, are compared with reported ones to suggest the basic soundness of the procedure adopted.

Introduction

The computation of electric dipole moment of polar liquids dissolved in nonpolar solvents is of much interest. But all the existing methods depend purely upon the theory of extrapolation of different physical quantities such as η_f , the refractive indices n_f , the dielectric constants of solution of different weight fractions ω_f of solute, at infinite dilution [1]. In a particular system, i.e. triethyl amine in benzene at

25° C. Le-Ferve and Smyth [2] and Guggenheim [3] used different extrapolation techniques i.e. the ratio of finite differences on ϵ_f and η_f against ω_f and thus found two values of μ . Such affairs put the experimenters to choose as to what method of extrapolation is needed to compute μ in a particular system.

In one of our recent papers [4], we obtained a physical parameter X_f solely expressed in terms of the experimental

quantities ϵ_{ij} and η_{ij} of solutions of different weight fractions ω_j of the solute and were to represent the experimental facts at every stage of dilution for a large number of system in which X_{ij} had been plotted against ω_j elsewhere.

In this note, we, therefore, have thought to utilise three systems (i) aniline, (ii) methyl aniline and (iii) dimethyl aniline in benzene at 25° C at which ϵ_{ij} and η_{ij} are available [5].

Theory

The well known Debye equation [6] for polar and nonpolar liquid mixture of molar concentration c_j of polar solute is given by

$$\left(\frac{\epsilon_{ij}-1}{\epsilon_{ij}+2} - \frac{\eta_{ij}-1}{\eta_{ij}+2} \right) = \left(\frac{\epsilon_i-1}{\epsilon_i+2} - \frac{\eta_i-1}{\eta_i+2} \right) + \frac{4\pi N \mu^2 c_j}{9kT} \quad \dots(1)$$

where the suffices i, j and ij represent solvents, solute and solution respectively, and other symbols have their usual meanings. Now c_j the molar concentration is related to ω_j the weight fractions of the solute

by $c_j = \frac{d_{ij} \omega_j}{M_j}$ where d_{ij} is the density of the solution which is also expressed as

$$d_{ij} = \frac{W_i + W_j}{V_i + V_j} = \frac{W_i + W_j}{\frac{W_i}{d_i} + \frac{W_j}{d_j}} = \frac{d_i d_j}{\frac{W_i}{W_i + W_j} d_j + \frac{W_j}{W_i + W_j} d_i}$$

$$= \frac{d_i d_j}{\omega_j d_j + \omega_i d_i} = \frac{d_i}{1 - \left(1 - \frac{d_i}{d_j}\right) \omega_j} = \frac{d_i}{1 - \beta \omega_j}$$

$$\text{since } \beta = 1 - \frac{d_i}{d_j} \text{ and } \omega_i + \omega_j = 1$$

where d_i, d_j are the densities of the pure solvent and solute respectively and W_i, W_j are the weights required to make a solution of weight fractions ω_j .

Thus eqn. (1) is put into the following form

$$\frac{\epsilon_{ij}-\eta_{ij}}{(\epsilon_{ij}+2)(\eta_{ij}+2)} = \frac{\epsilon_i-\eta_i}{(\epsilon_i+2)(\eta_i+2)} + \frac{4\pi N \mu^2}{27kT} \cdot \frac{d_i}{M_j} \cdot \frac{\omega_j}{1-\beta \omega_j}$$

$$\text{or } X_{ij} = X_i + \frac{4\pi N \mu^2}{27kT} \cdot \frac{d_i}{M_j} \cdot \omega_j (1-\beta \omega_j)^{-1}$$

$$= X_i + \frac{4\pi N \mu^2}{27kT} \cdot \frac{d_i}{M_j} \cdot \omega_j (1+\beta \omega_j + \beta^2 \omega_j^2 + \dots)$$

$$= X_i + R \omega_j + R \beta \omega_j^2 + \dots \quad \dots(2)$$

where $R = \frac{4\pi N \mu^2}{27kT} \cdot \frac{d_i}{M_j}$. Thus the experimental quantity X_{ij} can be expressed in a finite number of terms of the form

$$X_{ij} = a_0 + a_1 \omega_j + a_2 \omega_j^2 + \dots \quad \dots(3)$$

as the higher powers of ω_j is of significance. Comparing the co-efficients of equal powers of ω_j of eqns. (2) and (3) we have,

$$R = \frac{4\pi N \mu^2}{27kT} \cdot \frac{d_i}{M_j} = a_1 \quad \dots(4)$$

$$R \beta = \frac{4\pi N \mu^2}{27kT} \cdot \frac{d_i}{M_j} \cdot \beta = a_2 \quad \dots(5) \text{ etc.}$$

We should expect the value of μ from the given equations (4), (5) etc. But due to presence of various effects to play their role in the value of a_2 , we are only left with the eqn. (4), which becomes,

$$\mu = \sqrt{\left(\frac{27kT}{4\pi N} \cdot \frac{M_j}{d_i} \cdot a_1 \right)} \quad \dots(6)$$

to compute the value of μ of polar solute.

Method of calculation

To evaluate the value of a_1 , an usual linear least square fitting has been performed on equation (3) when we have,

$$\sum X_{ij} = i a_0 + a_1 \sum \omega_j + a_2 \sum \omega_j^2$$

$$\sum X_{ij} \omega_j = a_0 \sum \omega_j + a_1 \sum \omega_j^2 + a_2 \sum \omega_j^3$$

$$\sum X_{ij} \omega_j^2 = a_0 \sum \omega_j^2 + a_1 \sum \omega_j^3 + a_2 \sum \omega_j^4$$

the values of the constants a_0, a_1 and a_2 are obtained. i = number of experimental data under

consideration. Thus three normal equations have been arrived at

(i) Aniline in benzene at 25°C
 $X_{1j} = 0.0015108 + 0.14936 \omega_j - 0.030445 \omega_j^2$

(ii) Methyl aniline in benzene at 25°C
 $X_{1j} = 0.0015146 + 0.15357 \omega_j - 0.040477 \omega_j^2$

and (iii) Dimethyl aniline in benzene at 25°C
 $X_{1j} = 0.001483 + 0.12749 \omega_j - 0.060161 \omega_j^2$

Conclusions

The values of μ have thus obtained from eqn. (6) and are placed in table 1, along with the data of μ reported by Ghosh and Acharyya [1] and Few and Smith [5]. It is found from the table 1, the μ values of

systems ^{Aniline} i.e., methyl aniline and dimethyl aniline in benzene are slightly higher than the reported ones. But in the case of aniline, its dipole moment is within the range of 1.50 to 1.60 Debye. Thus the close agreement between the calculated and reported values of μ suggests that in every system where is no volume change due to mixing, the accurate value of μ could be obtained without considering the case of infinite dilution. Moreover, the procedure is very simple because only a single extrapolation on X_{1j} against ω_j in any system is enough to find the value of a_1 and hence the dipole moment of polar liquid dissolved in nonpolar solvent.

Table 1
Dipole moment μ of solutes at 25°C

Systems	Molecular weight of solute M_j	μ cal. (D)	μ rept. (D)	μ rept. (D)
1. Aniline in Benzene	93.11	1.53	1.50	1.57
2. Methyl aniline in Benzene	107.0	1.66	1.64	1.65
3. Dimethyl aniline in Benzene	121.0	1.61	1.58	1.59

**Ref. [5]

*Ref. [1]

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CHAPTER IV

DETERMINATION OF RELAXATION TIME OF POLAR MOLECULES DISSOLVED IN NONPOLAR SOLVENTS BY RADIO FREQUENCY CONDUCTIVITY MEASUREMENTS.

INTRODUCTION

The experimental determination of the dielectric relaxation time of polar liquids is of much interest as it gives information regarding the role of internal field acting inside the dielectric, the free energy of activation and the structure of the molecule concerned. Determination of relaxation time has been made by measuring the dielectric constant and loss factor either in the microwave or in the radio frequency region where the basic assumption is that the medium is a perfect dielectric. In an ideal dielectric there should be no free ion or ion conduction which seems to be quite doubtful as in practice all dielectrics fall far short of the ideal requirement. As the ion conduction produces Joule's heat in actual dielectrics when an electric field is applied, the total heat is produced due to the combined effect of dielectric loss and Joule's heating. The evidence for the existence of free ions has been shown by many workers in recent years such as Standhammer and Seyer (1957), Adamczewski and Jachym (1968), Lohneysen and Nagerl (1971) etc. Though the cause of generation of ions in both polar and nonpolar

liquids has been attributed to various causes such as cosmic rays, natural radioactivity, thermal dissociation etc. Still no specific reason has yet been advanced for the formation of free ions and electrons. Assuming the presence of free ions which contribute to conduction current and the existence of usual displacement current, Sen and Ghosh (1974) have deduced a mathematical expression for the radio frequency conductivity which has satisfactorily explained the observed experimental facts and it has been possible to calculate the number density of free ions in some pure polar liquids. The purpose of the present paper is to show that measurement of radio frequency conductivity of a polar solute in a nonpolar solvent not only enables us to compute the relaxation time at infinite dilution but it also helps us to estimate the concentration of free ions that exist in real dielectrics. The determination of τ from solution data will give an accurate value of τ as in dilute solution the polar molecules are well separated from each other and consequently dipole-dipole interaction forces are absent. The measurement of radio frequency conductivity has been carried out in case of ethyl and methyl alcohol in benzene at 30°C under the application of a radio frequency field within the frequency range of 400 KHz to 800 KHz.

EXPERIMENTAL ARRANGEMENT.

The method that has been used here is the same as the variation of resonance method of measuring dielectric constant. The block diagram of experimental arrangement is shown in figure (2.1) of chapter II. The theory of the method of

measurement of radio frequency conductivity has also been described in chapter II.

The dielectric cell used here is a cylindrical glass tube of diameter 2.62 cm. fitted with two circular gold electrodes, 1.08 cm. apart. Each gold plate is connected with a platinum wire which is sealed with the glass tube. The dielectric cell is fitted in parallel to the tuning condenser of the secondary circuit. The resonant current I_1 and I_2 in the r.f. meter and the corresponding tuning capacitances C_1 and C_2 are noted. I_1 being the r.f. current when the cell is empty and I_2 being the r.f. current when the cell is filled with the liquid. The capacitances of the tuning condenser corresponding to $\frac{1}{\sqrt{2}}$ i.e. 70.7% of I_1 (on either side of resonance value) are also noted. From these measurements the real part of radio frequency conductivity K' of ethyl alcohol and methyl alcohol dissolved in nonpolar solvent benzene has been calculated for a wide range of concentration at 400 KHz, 500 KHz, 600 KHz and 800 KHz and at a temperature of 30°C. The values are placed in table (4.1) and the variation of K' with weight fraction of the solute are shown in figure (4.1) and (4.2). The dielectric constants of the solution at different concentrations have been measured by the same apparatus by utilizing the resonance method. The viscosity of the solution has been measured with the help of Ostwald's viscometer. The principle of measurement of dielectric constant and viscosity has been described earlier in chapter II.

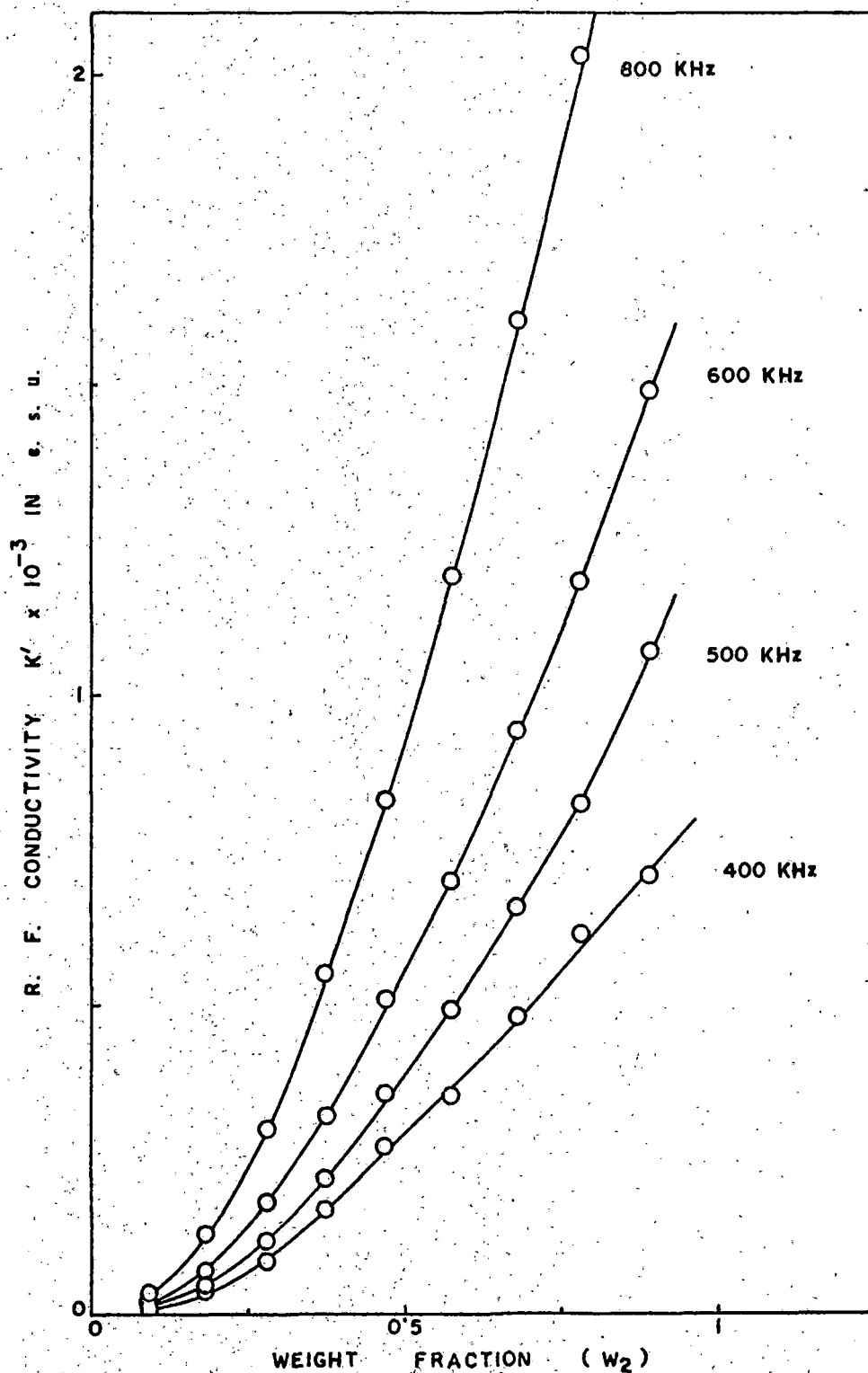


FIG. 4.1. VARIATION OF R. F. CONDUCTIVITY WITH CONCENTRATION. (ETHYL ALCOHOL IN BENZENE).

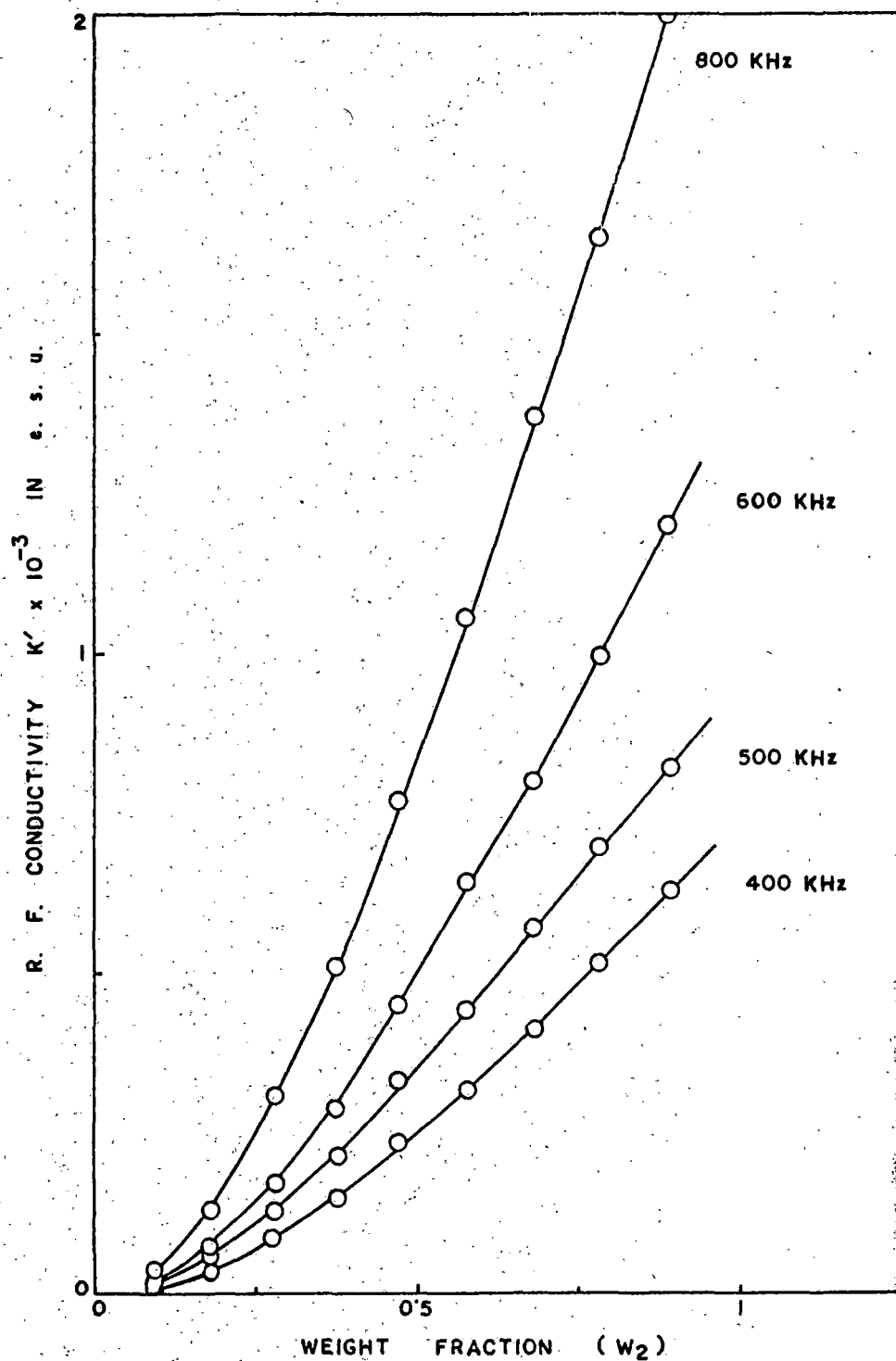


FIG. 4.2. VARIATION OF R. F. CONDUCTIVITY WITH CONCENTRATION. (METHYL ALCOHOL IN BENZENE).

RESULTS AND DISCUSSION

(a) Concentration Variation Method.

According to Murphy and Morgan (1939), the high frequency conductivity of the dielectric is given by

$$K = K' + j\omega K''$$

where K' is the real part of the conductivity and K'' the imaginary part. Assuming further that no free electrons and ions are present, Murphy and Morgan deduced that K' and K'' are related to ϵ' and ϵ'' by

$$\begin{aligned} K' &= \frac{\epsilon'' \omega}{4\pi} \quad \dots (4.1) \\ K'' &= \frac{\epsilon' \omega}{4\pi} \end{aligned}$$

where ϵ' and ϵ'' are the real and imaginary part of the complex dielectric constant, ω is the angular frequency of the applied field. In case of polar-nonpolar liquid mixture having N_2 number of polar solutes per cc where $N_2 = \frac{N d_{12}}{M_2} \omega_2$, loss factor ϵ'' is given by Smyth (1955) as

$$\epsilon'' = \frac{4\pi N d_{12} \mu^2 \omega_2 (\epsilon_{12} + 2)(\epsilon_{\infty 12} + 2)}{27 M_2 K T (1 + \omega^2 \tau^2)} \omega \tau \quad \dots (4.2)$$

where d_{12} is the density of the solution of weight fraction ω_2 of polar solute having its molecular weight M_2 and dipole moment μ . ϵ_{12} is the static dielectric constant, $\epsilon_{\infty 12}$ is the high frequency dielectric constant of the

solution and $\epsilon_{\infty 12} = n_{12}^2$ where n_{12} is the refractive index of the solution. τ is the relaxation time, N the Avogadro number and T is the temperature in absolute scale.

As the frequency at which the radio frequency conductivity has been measured is 400 KHz to 800 KHz., $\omega^2 \tau^2 \ll 1$ and hence from equations (4.1) and (4.2)

$$K' = \frac{4\pi^2 f^2 N \tau \mu^2 d_{12} (\epsilon_{12} + 2)(n_{12}^2 + 2)}{27 M_2 K T} \omega_2 \dots (4.3)$$

where $\omega = 2\pi f$. Equation (4.3) can be used directly for the determination of time of relaxation at infinite dilution and the method has been described in detail in a previous communication by Sen and Ghosh (1972).

Since equation (4.3) based on Debye's equation is valid at very dilute solution and as it is very difficult to measure the radio frequency conductivity accurately at such dilutions, the value of τ has been determined from equation

(4.3) by introducing the concept of local field. By defining local field $F = \frac{(\epsilon_{12} + 2)(n_{12}^2 + 2)}{9}$ and $d_{12} = \frac{d_1}{1 - \beta \omega_2}$ where $\beta = \left(1 - \frac{d_1}{d_2}\right)$ and d_2 are the density of the solvent and solute respectively, we have

$$\begin{aligned} \frac{K'}{F \omega_2} &= \frac{4\pi^2 f^2 N \tau \mu^2}{3 M_2 K T} \cdot \frac{d_1}{1 - \beta \omega_2} \\ &= \frac{4\pi^2 f^2 N \tau \mu^2 d_1}{3 M_2 K T} \left(1 + \beta \omega_2 + \beta^2 \omega_2^2 + \dots\right) \end{aligned} \dots (4.4)$$

which is again expressed in the quadratic form such as

$$\frac{K'}{F\omega_2} = a_0 + a_1\omega_2 + a_2\omega_2^2 + \dots \quad \dots(4.5)$$

where a_0 , a_1 and a_2 are constants. As the various effects (Smyth, 1955) are present in a_1 and a_2 , equating only the first term of equations (4.4) and (4.5) or at infinite dilution

$$\left[\frac{K'}{F\omega_2} \right]_{\omega_2 \rightarrow 0} = \frac{4\pi^2 f^2 N \gamma \mu^2 d_1}{3 M_2 K T} = a_0 \quad \dots (4.6)$$

Equation (4.6) has been utilized in determining the value of time of relaxation at infinite dilution where the assumption of free ions or electrons has not been taken into consideration. Refractive indices of the solution have been calculated by using the relation

$$n_{12} = x_1 n_1 + x_2 n_2 \quad (\text{Glasstone, 1968})$$

where x 's and n 's are the mole fraction and refractive indices of the pure solvent and solute respectively. The mole fraction x_2 of the solute is related to ω_2 by

$$x_2 = \frac{\omega_2 M_1}{\omega_1 M_2 + \omega_2 M_1}$$

The values of ϵ_{12} and n_{12} are placed in table (4.2) for both the alcohols at different weight fractions ω_2 .

The values of $\frac{K'}{F\omega_2}$ are then calculated. It is possible to calculate a_0 of equation (4.6) by extrapolating the curve of $\frac{K'}{F\omega_2}$ against ω_2 upto infinite dilution and then γ may be determined. In order to observe the validity of equation (4.5), values of a_0 , a_1 and a_2 have been calculated by performing the usual linear least square fitting upon equation (4.5) and the values have been listed in table (4.3) at different frequencies. The method of least square fitting has already been described in chapter III A. The fitted curves of $\frac{K'}{F\omega_2}$ against ω_2 are shown in figure (4.3) and (4.4) for different frequencies by solid lines together with the experimental points placed upon them. It is seen that the fitted curves are in excellent agreement with the experimental points particularly at lower dilutions except a small deviation in case of ethyl alcohol at 800 KHz. Further from figures (4.3) and (4.4) it is seen that $\frac{K'}{F\omega_2}$ increases with ω_2 at lower concentration and then decreases slightly with ω_2 at higher concentration. Since a_0 , a_1 and a_2 have been calculated from the experimental values, one of them must have a negative value in order to satisfy the nature of variation of $\frac{K'}{F\omega_2}$ against ω_2 and as a_0 the intercept of the curve is positive, a_1 the slope of the curve is also a positive quantity then a_2 must a negative value. Further Debye's equation is strictly valid for infinite dilution, the precise value of a_0 is necessary to calculate γ . The value of a_0 may be obtained both from least square method as well as from extrapolation method but here it is

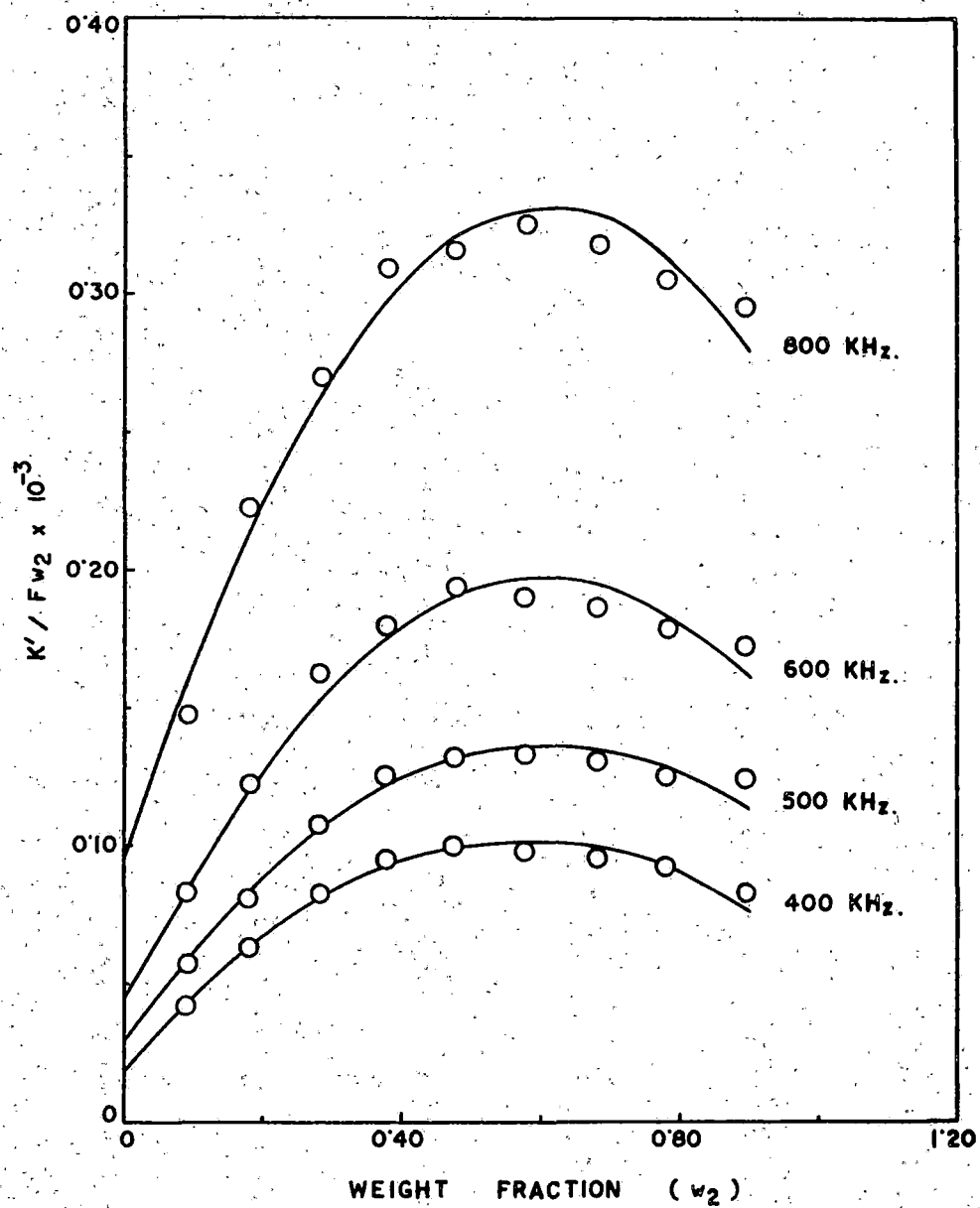


FIG. 4.3. VARIATION OF K' / Fw_2 WITH CONCENTRATION.

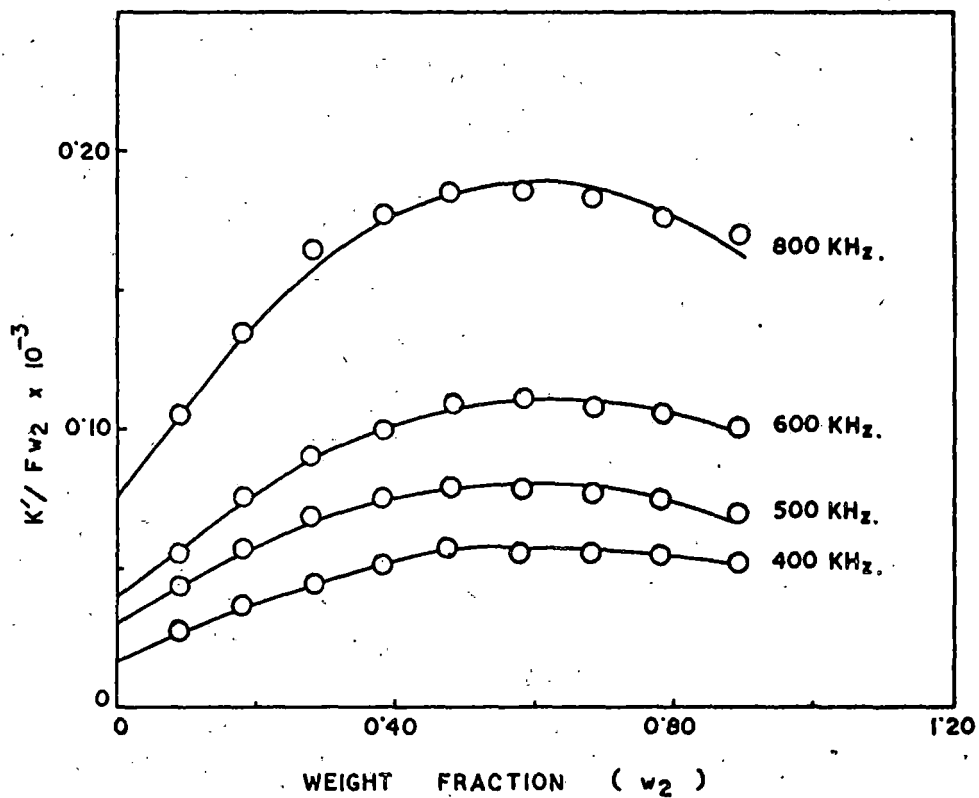


FIG. 4.4. VARIATION OF K' / Fw_2 WITH CONCENTRATION.

found that there is an excellent agreement between the two values which justifies definitely the assumption made in equation (4.5). From the values of a_0 thus calculated by least square method, τ 's have been calculated from equation (4.6) for both the alcohols and the values have been entered in table (4.3). In our calculation we have utilized μ values of polar solute in vapour state and consequently a correction has been made for the solvent effect by utilizing the relation given by Müller (1934)

$$\mu_s = \mu_o \left[1 - C(\epsilon - 1)^2 \right]$$

where μ_s is the dipole moment in solution and μ_o is the dipole moment of pure solute, ϵ is the dielectric constant of the solvent. C is an empirical constant for which Müller gave a value 0.038. It has been claimed that this value holds for a large number of liquids and consequently the modified relaxation time τ^* can be obtained from equation (4.3)

$$\tau^* = \frac{\tau}{\left[1 - C(\epsilon - 1)^2 \right]}$$

The value of τ^* for both the alcohols has been calculated and are placed in table (4.3). It is observed from table (4.3) that without considering the existence of free ions or electrons, τ^* is almost constant and independent of frequency which is in good agreement with the previous results obtained by different workers that the relaxation

time is independent of frequency. A slight change in the value of relaxation time has been noticed here with the change of frequency in case of both the alcohols. According to the Debye equation $\tau = \frac{4\pi\eta a^3}{kT}$ where η is the viscosity of the solvent and 'a' is the molecular radius of the solute,

τ should be independent of frequency but it has been shown by Sen and Ghosh (1978) that the activation energy and hence the viscosity of a polar substance changes with the increase of frequency.

(b) Frequency Variation Method.

From equation (4.3) it is also observed that if a graph is plotted between K' and f^2 , the curve should be a straight line passing through the origin. To find out the nature of the graph, the experimental values of K' from lower to highest possible concentration have been plotted against the square of the frequency and the results are shown in figure (4.5) and (4.6). Both the figures clearly show that dielectric loss is not the only contributing factor to the radio frequency conductivity but the presence of free ions and electrons should be taken into account. Assuming that free ions are present in polar liquid, it has been deduced by Sen and Ghosh (1974) that when only the conduction current is present

$$K' = \frac{ne^2}{M} \cdot \frac{6\pi a\eta/M}{\left[\left(\frac{6\pi a\eta}{M}\right)^2 + \omega^2\right]}$$

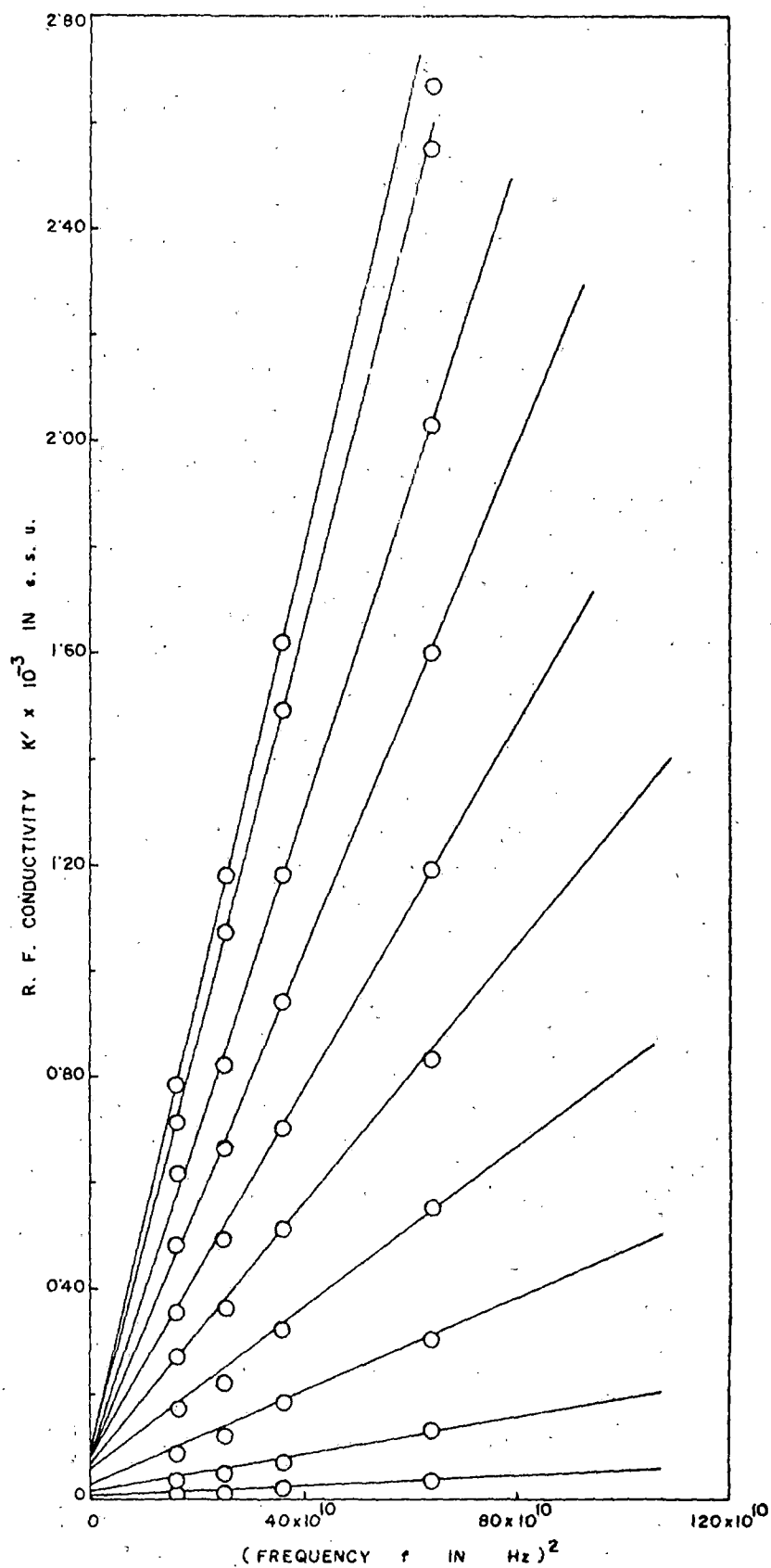


FIG. 4.5. VARIATION OF R. F. CONDUCTIVITY WITH $(\text{FREQUENCY})^2$. (ETHYL ALCOHOL IN BENZENE).

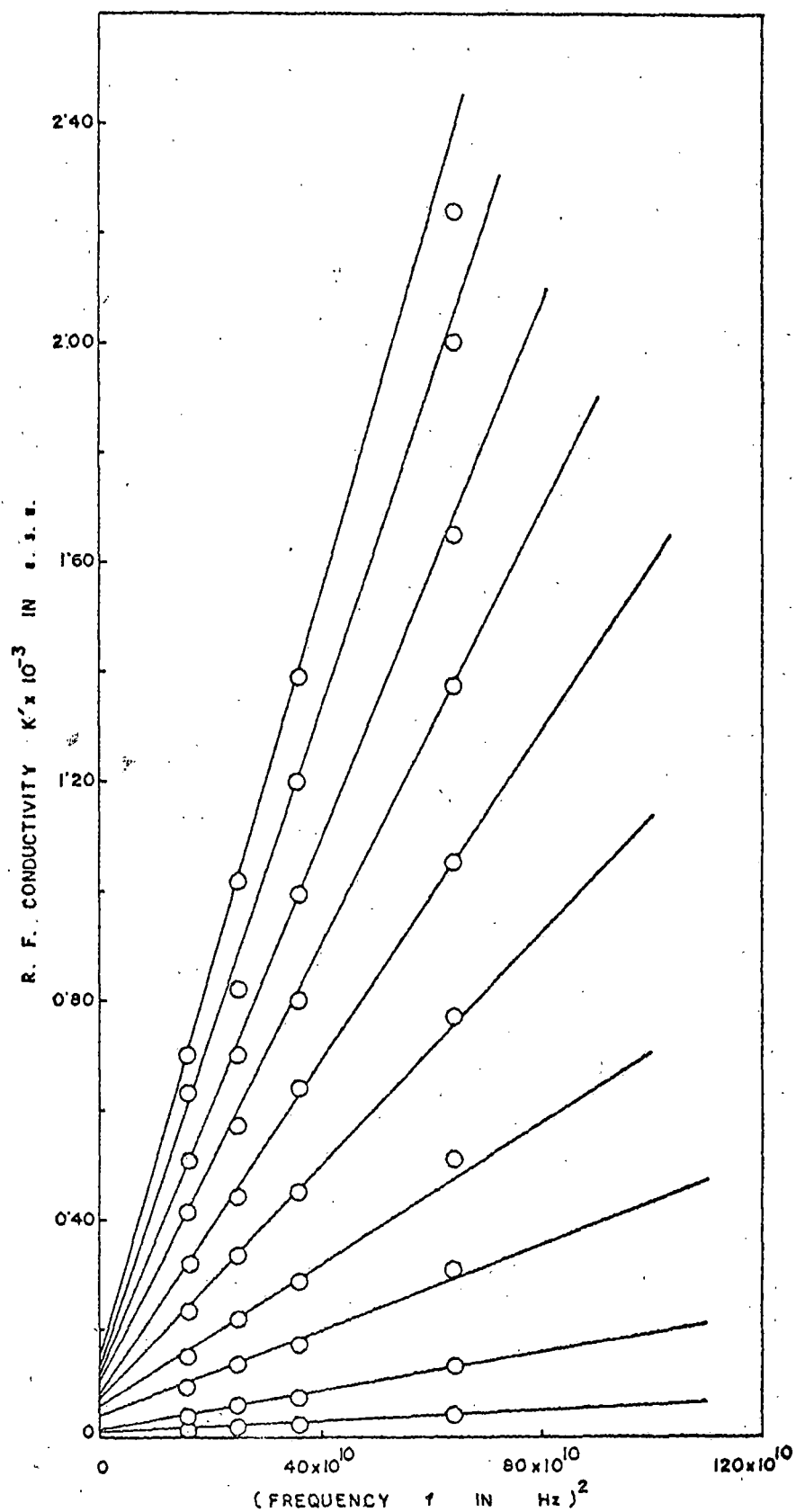


FIG. 4.6. VARIATION OF R. F. CONDUCTIVITY WITH (FREQUENCY)² (METHYL ALCOHOL IN BENZENE).

and if n_s is the number of ions per c.c. and η_{12} is the viscosity of the solution and M is the mass of the ion

$$K' = \frac{n_s e^2}{M} \frac{6\pi a \eta_{12} / M}{\left[\left(\frac{6\pi a \eta_{12}}{M} \right)^2 + \omega^2 \right]}$$

As 'a' the molecular radius of the ion $\approx 10^{-8}$ cm.,
 $\eta_{12} \approx 10^{-3}$ poise, $M \approx 10^{-24}$ gms.

$$\frac{6\pi a \eta_{12}}{M} \gg \omega$$

Hence

$$K' = \frac{n_s e^2}{6\pi a \eta_{12}} \quad \dots (4.7)$$

where K' is the real part of the conductivity. Further as the field is alternating, from Murphy and Morgan (1939)

$$i \text{ (displacement)} = \frac{\omega}{4\pi} (\epsilon' + j\epsilon'') E_0 e^{j\omega t} \quad \dots (4.8)$$

Remembering $\omega^2 \tau^2 \ll 1$, from equations (4.2), (4.7) and (4.8)

$$i_{\text{total}} = \left[\frac{n_s e^2}{6\pi a \eta_{12}} + \frac{4\pi^2 f^2 N \tau \mu^2 d_{12} (\epsilon_{12} + 2) (\eta_{12}^2 + 2)}{27 M_2 K T} \omega_2 \right] E_0 e^{j\omega t}$$

Thus

$$K' = \frac{n_s e^2}{6\pi a \eta_{12}} + \frac{4\pi^2 f^2 N \tau \mu^2 d_{12} (\epsilon_{12} + 2) (\eta_{12}^2 + 2)}{27 M_2 K T} \omega_2$$

$$= A + B f^2 \quad \dots (4.9)$$

where

$$A = \frac{n_s e^2}{6 \pi a \eta_{12}} \quad \dots (4.10)$$

$$B = \frac{4 \pi^2 f^2 N \gamma \mu^2 d_{12} (\epsilon_{12} + 2) (\eta_{12}^2 + 2)}{27 M_2 K T} \omega_2$$

It is thus observed that at a particular weight fraction, from the slope and intercept of the $K' - f^2$ curve the value of relaxation time and the number density of the ions can be calculated. It is to be noted that the second term on the right hand side of equation (4.9) is valid for a dilute solution whereas the first term is valid for all concentrations. Consequently though measurements have been made for a wide range of concentrations, the value of γ have been reported for four concentrations only (for very dilute solutions). The results are entered in table (4.4) and γ values are plotted against corresponding weight fractions. Extrapolating the curve, γ value for infinite dilution and hence γ^* has been calculated and entered in table (4.4). As γ varies with concentration even for very dilute solution it is evident that at such a low concentration interaction between solute molecules cannot be totally neglected.

From tables (4.3) and (4.4), it is seen that the value of γ at infinite dilution or γ^* for methyl alcohol is less than that of ethyl alcohol. This result is also consistent with results obtained by previous workers. It is

further observed that τ value for both the alcohols derived from the frequency variation method is about 15 to 20% lower than that from concentration variation method at a single frequency. This may be due to the fact that in case of concentration variation method, the total loss has been assumed to be due to dielectric loss alone but actually the real dielectric loss is less by the contribution of the conductivity loss due to presence of free ions and electrons. It is evident from equation (4.3) that the dielectric loss which is $\frac{2K'}{f}$ is proportional to τ . Hence if ϵ_c'' is the dielectric loss and τ_c is the relaxation time and ϵ_f'' the dielectric loss when presence of ions is taken into consideration and τ_f is the corresponding relaxation time.

$$\frac{\epsilon_c''}{\epsilon_f''} = \frac{\tau_c}{\tau_f}$$

As $\epsilon_c'' > \epsilon_f''$

τ_f will be $< \tau_c$

Further from the intercept of the curves, the number of ions per c.c. of the solution (n_s) has been calculated and are placed in table (4.4). The value of 'a' the radius of the ions is taken equal to that of alcohol molecule and from the kinetic theory it comes out to be 2.8454×10^{-8} cm. in case of ethyl alcohol and 2.5319×10^{-8} cm. in case of methyl alcohol. This value of 'a' has been taken constant

throughout the calculation of n_s at different concentrations. From the values of n_s at different concentrations the number of ions per c.c. of the polar solute has been computed from the relation

$$n = \frac{n_s v_1}{v_2}$$

where v_1 and v_2 are respectively the total volume of the solution and solute at a particular weight fraction ω_2 . The calculated values of n_s and n have been placed in table (4.4) at different concentrations. From table (4.4), it is observed that the value of n_s gradually increases with the increase of concentration as it should be. The value of n is almost constant for a particular liquid for higher concentration which shows that effect of free ions and hence of conduction current becomes predominant at this stage. The value of n in pure liquid agrees well with the result obtained by Sen and Ghosh (1974) viz. in case of propyl alcohol, $n = 9.11 \times 10^{13}$, in case of nitrobenzene $n = 4.556 \times 10^{13}$ and in case of acetone $n = 1.139 \times 10^{13}$ ions/cc.

The value of η_{12} where η_{12} is the viscosity of the solution which will try to retard the motion of the ions as in the case of electrolytes, will depend upon η_1 (solvent) and that of η_2 (solute) and the resultant viscosity may increase or decrease depending upon the relative values of viscosity of the solvent and the solute. Our viscosity

values are of course experimentally obtained by direct measurement. From equation (4.10)

$$A = \frac{n_s e^2}{6 \pi a \eta_{12}}$$

the intercept A is inversely proportional to η_{12} only if n_s is constant but since n_s is a function of ω_2 such a simple relation may not be valid.

The present work thus shows that an accurate measurement of the relaxation time can be made by measurement of the radio frequency conductivity of a polar solute dissolved in a nonpolar solvent. The results for concentration variation method at a fixed frequency and the frequency variation method at one or more concentrations are compared. It is however, preferable to employ the frequency variation method because this takes into account the presence of free ions and electrons which are always present in a polar dielectric. The method also provides us a procedure by which it is possible to calculate the number of free ions in a dielectric and this can be taken as a measure of impurity or free ion charge carriers.

Table 4.1

Ethyl alcohol in benzene.

Values of $K' \times 10^{-3}$ in e.s.u.

Temp. = 30°C.

ω_2	400 KHz.	500 KHz.	600 KHz.	800 KHz.
0.090839	0.0098017	0.0134151	0.019418	0.0343168
0.18355	0.03621	0.04747	0.06883	0.13017
0.27819	0.08621	0.12057	0.18138	0.30158
0.37480	0.16917	0.22305	0.31906	0.54988
0.47347	0.27101	0.35790	0.51162	0.83163
0.57428	0.35437	0.48840	0.69692	1.18868
0.67726	0.48166	0.65630	0.93906	1.60309
0.78246	0.61639	0.82465	1.17770	2.03163
0.89001	0.71217	1.06636	1.48990	2.55055
1	0.78521	1.17835	1.61968	2.68525

Methyl alcohol in benzene

Values of $K' \times 10^{-3}$ e.s.u.

Temp. = 30°C

ω_2	400 KHz.	500 KHz.	600 KHz.	800 KHz.
0.09093	0.0094457	0.0150035	0.0211086	0.0371208
0.18370	0.03584	0.05556	0.07337	0.13037
0.27841	0.08456	0.13004	0.17195	0.31286
0.37507	0.14675	0.21632	0.28635	0.50821
0.47373	0.23429	0.33400	0.44974	0.76731
0.57454	0.31651	0.44286	0.63951	1.0547
0.67752	0.41307	0.57205	0.80271	1.37432
0.78267	0.51446	0.69555	0.99652	1.65001
0.89013	0.62632	0.82331	1.20047	2.00169
1	0.69761	1.02037	1.39016	2.24268

Table 4.2
Ethyl Alcohol in Benzene

ω_2	ϵ_{12}	n_{12}	d_{12}	η_{12} (Poise)
0.090839	3.65	1.47544	0.8598	0.005618
0.18355	4.93	1.45774	0.8511	0.005759
0.27819	6.80	1.44154	0.8423	0.006125
0.37480	8.53	1.42666	0.8336	0.006392
0.47347	10.53	1.41294	0.8250	0.006890
0.57428	12.48	1.40025	0.8161	0.007330
0.67726	15.07	1.38848	0.8073	0.008063
0.78246	17.60	1.37754	0.7986	0.008574
0.89001	20.53	1.36734	0.7901	0.009598
1	24.26	1.35780	0.7810	0.01040

Methyl Alcohol in Benzene

ω_2	ϵ_{12}	n_{12}	d_{12}	η_{12} (Poise)
0.09093	6.51	1.46322	0.8599	0.005693
0.18370	9.07	1.43744	0.8513	0.005546
0.27841	13.31	1.41603	0.8426	0.005523
0.37507	15.47	1.39797	0.8338	0.005499
0.47373	18.00	1.38354	0.8254	0.005444
0.57454	21.07	1.36918	0.8165	0.005391
0.67752	24.00	1.35752	0.8076	0.005343
0.78267	26.21	1.34726	0.7992	0.005294
0.89013	29.49	1.33814	0.7906	0.005250
1	32.00	1.3300	0.7818	0.005196

Table 4.3

Ethyl Alcohol in Benzene

Frequency in KHz.	$a_0 \times 10^{-3}$	$a_1 \times 10^{-3}$	$a_2 \times 10^{-3}$	$\gamma \times 10^{11}$	$\gamma^* \times 10^{11}$
400	0.018231	0.028393	-0.24115	1.12	1.28
500	0.029437	0.34936	-0.28255	1.16	1.33
600	0.044904	0.50504	-0.41697	1.19	1.36
800	0.093938	0.78302	-0.64054	1.42	1.63

Methyl Alcohol in Benzene

Frequency in KHz.	$a_0 \times 10^{-3}$	$a_1 \times 10^{-3}$	$a_2 \times 10^{-3}$	$\gamma \times 10^{11}$	$\gamma^* \times 10^{11}$
400	0.01680	0.12610	-0.098084	0.72	0.83
500	0.030079	0.17120	-0.14541	0.82	0.94
600	0.041188	0.22245	-0.17617	0.78	0.89
800	0.077246	0.37337	-0.31014	0.82	0.94

Table 4.4

Ethyl Alcohol in Benzene

ω_2	$\gamma \times 10^{11}$	$\gamma \times 10^{11}$ (γ_{∞} finite dilution)	$\gamma^* \times 10^{11}$	$\eta_s \times 10^{-12}$	$\eta \times 10^{-12}$
0.090839	1.92			0.1308	1.31
0.18355	2.96			0.2681	1.34
0.27819	4.00			0.4277	1.52
0.37480	4.38			0.8926	2.23
0.47347		0.98	1.12	1.1226	2.24
0.57428				1.3648	2.27
0.67726				1.5013	2.14
0.78246				1.7961	2.25
0.89001				2.0106	2.23
1				2.1241	2.12

ω_2	$\gamma \times 10^{11}$	$\gamma \times 10^{11}$ (γ_{∞} finite dilution)	$\gamma^* \times 10^{11}$	$\eta_s \times 10^{-12}$	$\eta \times 10^{-12}$
0.09093	1.10			0.1171	1.17
0.18370	1.35			0.1722	1.32
0.27841	1.46			0.4574	1.52
0.37507	1.61			0.6262	1.57
0.47373		0.70	0.80	0.7890	1.58
0.57454				0.9487	1.58
0.67752				1.1062	1.58
0.78267				1.2605	1.58
0.89013				1.4130	1.57
1				1.5598	1.56

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**Determination of Relaxation Time of Polar Molecules
Dissolved in Nonpolar Solvents
by Radio-Frequency Conductivity Measurements**

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Determination of Relaxation Time of Polar Molecules Dissolved in Nonpolar Solvents by Radio Frequency Conductivity Measurements

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Molecular relaxation time in case of Methanol and Ethanol dissolved in benzene has been obtained by measuring the radio frequency conductivity of the solution at different concentrations utilizing Murphy and Morgan⁶⁾ equation and also at different frequencies of the measuring field utilizing the expression deduced by Sen and Ghosh⁴⁾ which assumes the presence of free ions. It is observed that τ value for both the alcohols obtained from frequency variation method is slightly lower than that obtained by the concentration variation method which suggests that actual dielectric loss is less due to finite conductivity of the solution due to the presence of the free ions whose concentration has also been obtained in both the alcohols.

§1. Introduction

The experimental determination of the dielectric relaxation time of polar liquids is of much interest as it gives information regarding the role of internal field acting inside the dielectric, the free energy of activation and the structure of the molecule concerned. Determination of relaxation time has been made by measuring the dielectric constant and loss factor either in the microwave or in the radio frequency region where the basic assumption is that the medium is a perfect dielectric. In an ideal dielectric there should be no free ion or ion conduction which seems to be quite doubtful as in practice all dielectrics fall far short of the ideal requirement. As the ion conduction produces Joule's heat in actual dielectrics when an electric field is applied the total heat is produced due to the combined effect of dielectric loss and Joule's heating. The evidence for the existence of free ions has been shown by many workers in recent years such as Ständhammer and Seyer,¹⁾ Loheneysen and Nageral,²⁾ Adamczewski and Jachym.³⁾ Though the cause of generation of ions in both polar and nonpolar liquids has been attributed to various causes such as cosmic rays, natural radioactivity, thermal dissociation etc. still no specific reason has yet been advanced for the formation of free ions and electrons. Assuming the presence of free ions which contribute to

conduction current and the existence of usual displacement current, Sen and Ghosh⁴⁾ have deduced a mathematical expression for the radio frequency conductivity which has satisfactorily explained the observed experimental facts and it has been possible to calculate the number density of free ions in some pure polar liquids. The purpose of the present paper is to show that measurement of radio frequency conductivity of a polar solute in a nonpolar solvent not only enables us to compute the relaxation time at infinite dilution, but also helps us to estimate the contribution of free ions that exist in real dielectrics. The determination of τ from solution data will give an accurate value of τ as in a dilute solution where the polar molecules are well separated from each other and consequently dipole-dipole interaction forces are absent. The measurement of radio frequency conductivity has been carried out in case of Ethanol and Methanol in benzene at 30°C under the application of a radio frequency field within the frequency range of 400 kHz to 800 kHz.

§2. Experimental Arrangement

The method of determining the radio frequency conductivity has been described in detail in a previous communication by Sen and Ghosh.⁵⁾ The dielectric cell used is a cylindrical glass tube of diameter 2.62 cm fitted with two circular gold electrodes, 1.08 cm apart. Each

gold plate is connected with a platinum wire which is sealed with the glass tube. The real part of radio frequency conductivity k' of Ethanol and Methanol dissolved in nonpolar solvent benzene has been measured for a wide range of concentration at 400 kHz, 500 kHz, 600 kHz, and 800 kHz and at a temperature of 30°C. The dielectric constants of the solution at different concentrations have been measured by the same apparatus by utilizing the resonance method.

§3. Results and Discussion

(a) Concentration variation method

According to Murphy and Morgan,⁶⁾ the high frequency conductivity of the dielectric is given by

$$k = k' + Jk'',$$

where k' is the real part of the conductivity and k'' the imaginary part. Assuming further that no free electrons and ions are present, Murphy and Morgan⁶⁾ deduced that k' and k'' are related to ϵ' and ϵ'' by

$$k' = \frac{\epsilon''\omega}{4\pi}, \quad k'' = \frac{\epsilon'\omega}{4\pi}, \quad (1)$$

where ϵ' and ϵ'' are the real and imaginary part of the complex dielectric constant, ω is the angular frequency of the applied field. In case of polar-nonpolar liquid mixture having N_2 number of polar solutes per c.c. where $N_2 = N(d_{12}/M_2)\omega_2$ loss factor ϵ'' is given by Smyth⁷⁾ as

$$\epsilon'' = \frac{4\pi N d_{12} \omega_2 \mu^2 (\epsilon_{12} + 2)(\epsilon_{\infty 12} + 2)}{27 M_2 K T (1 + \omega^2 \tau^2)}, \quad (2)$$

where d_{12} is the density of the solution of weight fraction ω_2 of polar solute having its molecular weight M_2 and dipole moment μ . ϵ_{12} is the static dielectric constant and $\epsilon_{\infty 12}$ is the high frequency dielectric constant of the solution and $\epsilon_{\infty 12} = n_{12}^2$ where n_{12} is the refractive index of the solution, τ is the relaxation time, N the Avogadro number and T is the temperature in absolute scale.

As the frequency at which the radio frequency conductivity has been measured is 400 kHz to 800 kHz, $\omega^2 \tau^2 \ll 1$ and hence from eqs. (1) and (2)

$$k' = \frac{4\pi^2 f^2 N \tau \mu^2 d_{12} (\epsilon_{12} + 2)(n_{12}^2 + 2)}{27 M_2 K T} \omega_2, \quad (3)$$

where $\omega = 2\pi f$. Equation (3) can be used directly for the determination of time of relaxation at infinite dilution and the method has been described in detail in a previous communication by Sen and Ghosh.⁸⁾

Since eq. (3) based on Debye's equation is valid only at very dilute solution and as it is very difficult to measure the radio frequency conductivity accurately at such dilutions, the value of τ has been determined from eq. (3) by introducing the concept of local field after Ghosh and Acharyya.⁹⁾ By defining local field

$$F = \frac{(\epsilon_{12} + 2)(n_{12}^2 + 2)}{9},$$

and

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

where

$$\beta = \left(1 - \frac{d_1}{d_2}\right),$$

where d_1 is the density of the solvent and d_2 is the density of the solute. We have

$$\frac{k'}{F \omega_2} = \frac{4\pi^2 f^2 N \tau \mu^2 d_1}{3 M_2 K T} [1 + \beta \omega_2 + \beta^2 \omega_2^2 + \dots], \quad (4)$$

which is again expressed in the quadratic form such as

$$\frac{k'}{F \omega_2} = a_0 + a_1 \omega_2 + a_2 \omega_2^2 + \dots, \quad (5)$$

where a_0 , a_1 and a_2 are the constants. As the various effects (Smyth⁷⁾) are present in a_1 and a_2 , equating only the first term of eqs. (4) and (5) at infinite dilution

$$\left| \frac{k'}{F \omega_2} \right|_{\omega_2 \rightarrow 0} = \frac{4\pi^2 f^2 N \tau \mu^2 d_1}{3 M_2 K T} = a_0. \quad (6)$$

Equation (6) has been utilized in determining the value of time of relaxation at infinite dilution where the assumption of free ions or electrons has not been taken into consideration. Refractive indices of the solution have been calculated by using the relation

$$n_{12} = x_1 n_1 + x_2 n_2,$$

(Glasstone¹⁰⁾) where x 's and n 's are the mole fraction and refractive indices of the pure solvent and solute respectively. The mole

fraction x_2 of the solute is related to ω_2 by

$$x_2 = \frac{\omega_2 M_1}{\omega_1 M_2 + \omega_2 M_1}.$$

The values of ϵ_{12} and n_{12} are placed in Table I for both alcohols at different weight fraction ω_2 . The values of $k'/F\omega_2$ are then calculated. It is possible to calculate a_0 of eq. (6) by extrapolating the curve of $k'/F\omega_2$ against ω_2 upto infinite dilution and then τ may be deter-

Table I. Ethanol in Benzene.

ω_2	ϵ_{12}	n_{12}	d_{12}	η_{12}
0.090839	3.65	1.47544	0.8598	0.005618
0.18355	4.93	1.45774	0.8511	0.005759
0.27819	6.80	1.44154	0.8423	0.006125
0.37480	8.53	1.42666	0.8336	0.006392
0.47347	10.53	1.41294	0.8250	0.006890
0.57428	12.48	1.40025	0.8161	0.007330
0.67726	15.07	1.38848	0.8073	0.008063
0.78246	17.60	1.37754	0.7986	0.008574
0.89001	20.53	1.36734	0.7901	0.009598
1	24.26	1.35780	0.7810	0.01040

Methanol in Benzene

ω_2	ϵ_{12}	n_{12}	d_{12}	η_{12}
0.09093	6.51	1.46322	0.8599	0.005693
0.18370	9.07	1.43744	0.8513	0.005546
0.27841	13.31	1.41603	0.8426	0.005523
0.37507	15.47	1.39797	0.8338	0.005499
0.47373	18.00	1.38354	0.8254	0.005444
0.57454	21.07	1.36918	0.8165	0.005391
0.67752	24.00	1.35752	0.8076	0.005343
0.78267	26.21	1.34726	0.7992	0.005294
0.89013	29.49	1.33814	0.7906	0.005250
1	32.00	1.3300	0.7818	0.005196

mined. In order to observe the validity of eq. (5), values of a_0 , a_1 and a_2 of eq. (5) have been calculated by performing the usual linear least square fitting upon eq. (5) and the values have been listed in Table II at different frequencies. The fitted curves of $k'/F\omega_2$ against ω_2 are shown in Figs. (1) and (2) for different frequencies by solid lines together with the experimental points placed upon them. It is seen that the fitted curves are in excellent agreement with the experimental points particularly at lower dilutions except a small deviation in case of Ethanol at 800 kHz. Further from Figs. (1) and (2) it is seen that $k'/F\omega_2$ increases

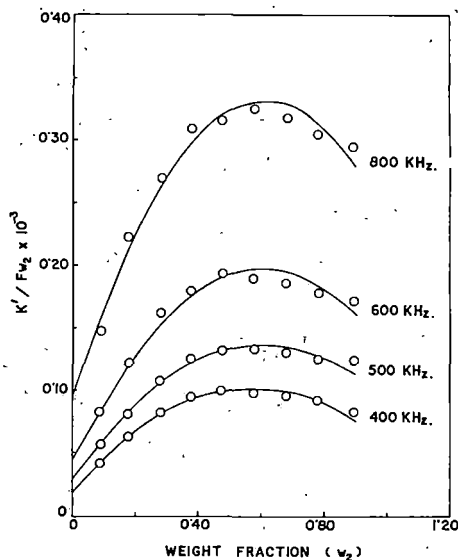


Fig. 1. Variation of $k'/F\omega_2$ with ω_2 (Ethanol in Benzene).

Table II. Ethanol in Benzene.

Frequency kHz	$a_0 \times 10^{-3}$	$a_1 \times 10^{-3}$	$a_2 \times 10^{-3}$	$\tau \times 10^{11}$	$\tau^* \times 10^{11}$
400	0.018231	0.028393	-0.24115	1.12	1.28
500	0.029437	0.34936	-0.28255	1.16	1.33
600	0.044904	0.50504	-0.41697	1.19	1.36
800	0.093938	0.78302	-0.64054	1.42	1.63

Methanol in Benzene

Frequency kHz	$a_0 \times 10^{-3}$	$a_1 \times 10^{-3}$	$a_2 \times 10^{-3}$	$\tau \times 10^{11}$	$\tau^* \times 10^{11}$
400	0.01680	0.12610	-0.098084	0.72	0.83
500	0.030079	0.17120	-0.14541	0.82	0.94
600	0.041188	0.22245	-0.17617	0.78	0.89
800	0.077246	0.37337	-0.31014	0.82	0.94

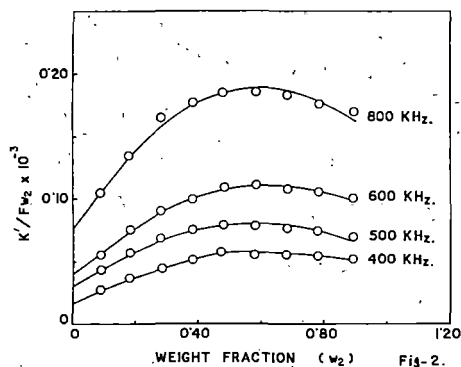


Fig. 2. Variation of $k'/F\omega_2$ with ω_2 (Methanol in Benzene).

with ω_2 at lower concentration and then decreases slightly with ω_2 at higher concentration, since a_0 , a_1 , and a_2 have been calculated from the experimental values using eq. (5) one of them must have a negative value in order to satisfy the nature of variation of $k'/F\omega_2$ against ω_2 ; as a_0 the intercept of the curve is positive, a_1 the slope of the curve is also a positive quantity then a_2 must have a negative value. Further Debye's equation is strictly valid for infinite dilution and the precise value of a_0 is necessary to calculate τ . The value of a_0 has been obtained both from least square method as well as from extrapolation method and there is excellent agreement between the two values. From the values of a_0 , τ has been calculated from eq. (6) for both the alcohols and have been entered in Table II. In our calculation we have utilized μ values of polar solute in vapour state and consequently a correction has been made for the solvent effect by utilizing the relation given by Muller¹¹⁾

$$\mu_s = \mu_0[1 - C(\epsilon - 1)^2],$$

where μ_s is the dipole moment in solution and μ_0 is the dipole moment of pure solute, ϵ is the dielectric constant of the solvent. C is an empirical constant for which Muller gave a value 0.038. It has been claimed that this value holds for a large number of liquids and consequently the modified relaxation time τ^* can be obtained from eq. (3),

$$\tau^* = \frac{\tau}{[1 - C(\epsilon - 1)^2]^2}.$$

The value of τ^* for both the alcohols has been calculated and are placed in Table II. It is

observed from Table II that without considering the existence of free ions or electrons, τ^* is almost constant and independent of frequency which is in good agreement with the previous results obtained by workers that the relaxation time is independent of frequency. A slight change in the value of relaxation time has been noticed here with the change of frequency in case of both the alcohols. According to the Debye equation

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

where η is the viscosity of the solvent, and a is the molecular radius of the solute and hence τ should be independent of frequency, but it has been shown by Sen and Ghosh¹²⁾ that the activation energy and hence the viscosity of a polar substance changes with the increase of frequency.

(b) Frequency variation method

From eq. (3) it is also observed that if a graph is plotted between k' and f^2 , the curve should be a straight line passing through the origin. To find out the nature of the graph, the experimental values of k' from lower to highest possible concentration have been plotted against the square of the frequency and the results are shown in Figs. 3 and 4. Both the figures clearly show that dielectric loss is not the only contributing factor to the radio frequency conductivity but the presence of free ions and electrons should be taken into account. Assuming that free ions are present in polar liquid, it has been deduced by Sen and Ghosh⁴⁾ that when only the conduction current is present,

$$k' = \frac{ne^2 6\pi a \eta / M}{M \left[\left(\frac{6\pi a \eta}{M} \right)^2 + \omega^2 \right]},$$

and if n_s is the number of ions per c.c. and η_{12} is the viscosity of the solution and M is the mass of the ion

$$k' = \frac{n_s e^2 6\pi a \eta_{12} / M}{M \left[\left(\frac{6\pi a \eta_{12}}{M} \right)^2 + \omega^2 \right]},$$

as a the molecular radius of the ion $a \approx 10^{-8}$ cm $\eta_{12} \approx 10^{-3}$ poise, $M \approx 10^{-24}$ gms

$$\frac{6\pi a \eta_{12}}{M} \gg \omega.$$

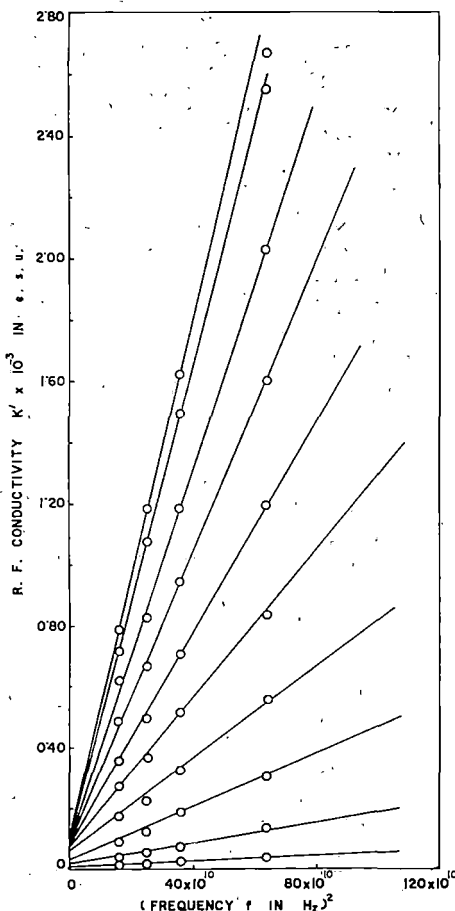


Fig. 3. Variation of r.f. conductivity with f^2 (Ethanol in Benzene).

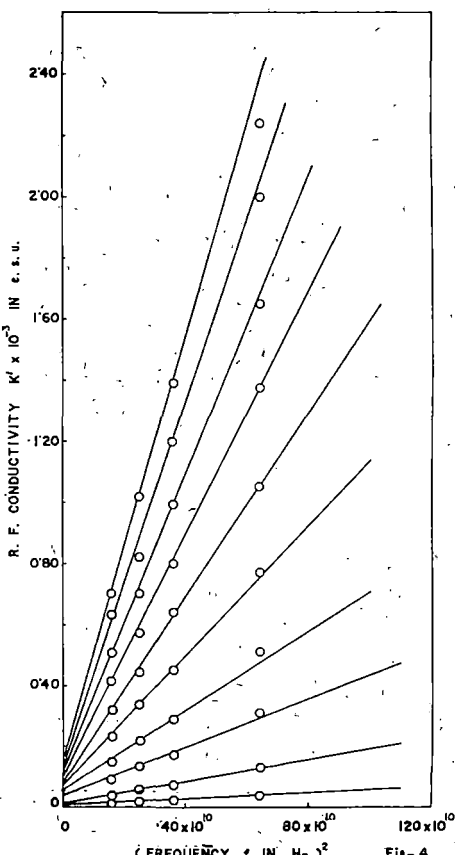


Fig. 4. Variation of r.f. conductivity with f^2 (Methanol in Benzene).

Further as the field is alternating, from Murphy and Morgan⁶⁾

$$k' = \frac{n_s e^2}{6\pi a \eta_{12}}, \tag{7}$$

$$i_{(\text{displacement})} = \frac{\omega}{4\pi} (\epsilon' - J\epsilon'') E_0 e^{J\omega t}. \tag{8}$$

Remembering $\omega^2 \tau^2 \ll 1$ from eqs. (2), (7) and (8)

$$i_{\text{total}} = \left[\frac{n_s e^2}{6\pi a \eta_{12}} + \frac{4\pi^2 f^2 N \tau \mu^2 d_{12} (\epsilon_{12} + 2) (n_{12}^2 + 2)}{27 M_2 K T} \right] \omega_2 E_0 e^{J\omega t}.$$

Thus

$$k' = \frac{n_s e^2}{6\pi a \eta_{12}} + \frac{4\pi^2 f^2 N \tau \mu^2 d_{12} (\epsilon_{12} + 2) (n_{12}^2 + 2)}{27 M_2 K T} \omega_2 = A + B f^2, \tag{9}$$

where

$$A = \frac{n_s e^2}{6\pi a \eta_{12}},$$

and

$$B = \frac{4\pi^2 N \tau \mu^2 d_{12} (\epsilon_{12} + 2) (n_{12}^2 + 2)}{27 M_2 K T} \omega_2. \tag{10}$$

It is thus observed that at a particular weight fraction from the slope and intercept of the $k'-f^2$ curve the value of relaxation time and the number density of the ions can be calculated. It is to be noted that the second term on the right hand side of eq. (9) is valid for a dilute solution whereas the first term is

valid for all concentrations. Consequently though measurements have been made for a wide range of concentrations the values of τ have been reported for four concentrations only (for very dilute solutions). The results are entered in Table III and τ values are plotted against corresponding weight fractions. Extrapolating the curve τ value for infinite dilution and hence τ^* has been calculated and entered in Table III. As τ varies with concentration even for very dilute solution it is evident that even at such a low concentration interaction between solute molecules cannot be totally neglected.

From Tables II and III, it is seen that the value of τ at infinite dilution or τ^* for Methanol is less than that of Ethanol. This result is also consistent with results obtained by previous workers. It is further observed that τ value for both alcohols derived from the frequency variation method is about 15 to 20% lower than that from concentration variation method at a single frequency. This may be due to the fact that in case of concentration variation method the total loss has been assumed to be

due to dielectric loss alone but actually the real dielectric loss is less by the contribution of the conductivity loss due to presence of free ions and electrons. It is evident from eq. (3) that the dielectric loss which is $2k''/f$ is proportional to τ . Hence if ϵ_c'' is the dielectric loss and τ_c is the relaxation time and ϵ_f'' the dielectric loss when presence of ions is taken into consideration and τ_f is the corresponding relaxation time

$$\frac{\epsilon_c''}{\epsilon_f''} = \frac{\tau_c}{\tau_f},$$

as

$$\epsilon_c'' > \epsilon_f'', \quad \tau_f \text{ will be } < \tau_c.$$

Further from the intercept of the curves, the number of ions per c.c. of the solution (n_s) has been calculated and are placed in Table III. The value of a the radius of the ions is taken equal to that of alcohol molecule and from the kinetic theory it comes out to be 2.8464×10^{-8} cm in case of Ethanol and 2.5319×10^{-8} cm in case of Methanol. This value of ' a ' has been taken constant throughout the calculation of n_s at different concentrations. From the values of n_s at different concentrations the number of ions per c.c. of the polar solute has been computed from the relation

$$n_s = n v_2 / v_1,$$

where v_1 and v_2 are respectively the total volume of the solution and solute at a particular weight fraction ω_2 . The calculated values of n_s and n have been placed in Table III, at different concentrations. From Table III, it is observed that the value of n_s gradually increases with the increase of concentration as it should be. The value of n is almost constant for a particular liquid for higher concentration which shows that effect of free ions and hence of conduction current becomes predominant at this stage. The value of n in pure liquid agrees well with the result obtained by Sen and Ghosh,⁽⁴⁾ viz. in case of propyl alcohol, $n = 9.11 \times 10^{13}$; in case of nitrobenzene, $n = 4.556 \times 10^{13}$ and in case of acetone $n = 1.139 \times 10^{13}$ ions/c.c.

The value of η_{12} where η_{12} is the viscosity of the solution which will try to retard the motion of the ions as in the case of electrolytes will depend upon η_1 (solvent) and that of η_2 (solute) and the resultant viscosity may increase or decrease depending upon the relative values of viscosity of the solvent and the solute. Our

Table III. Ethanol in Benzene.

ω_2	$\tau \times 10^{11}$	$\tau \times 10^{11}$ infinite dilution	$\tau^* \times 10^{11}$	$n_s \times 10^{-12}$	$n \times 10^{-12}$
0.090839	1.92			0.1308	1.31
0.18355	2.96			0.2681	1.34
0.27819	4.00			0.4277	1.52
0.37480	4.38			0.8926	2.23
0.47347				1.1226	2.24
0.57428		0.98	1.12	1.3648	2.27
0.67726				1.5013	2.14
0.78246				1.7961	2.25
0.89001				2.0106	2.23
1				2.1241	2.12

Methanol in Benzene

ω_2	$\tau \times 10^{11}$	$\tau \times 10^{11}$	$\tau^* \times 10^{11}$	$n_s \times 10^{-12}$	$n \times 10^{-12}$
0.09093	1.10			0.1171	1.17
0.18370	1.35			0.1722	1.32
0.27841	1.46			0.4574	1.52
0.37507	1.61			0.6262	1.57
0.47373				0.7890	1.58
0.57454		0.70	0.80	0.9487	1.58
0.67752				1.1062	1.58
0.78267				1.2605	1.58
0.89013				1.4130	1.57
1				1.5598	1.56

viscosity values are of course experimental obtained by direct measurement. From eq. (9)

$$A = \frac{n_s e^2}{6\pi a \eta_{12}},$$

the intercept A is inversely proportional to η_{12} only if n_s is constant but since n_s is a function of ω_2 such a simple relation may not be valid.

The present work thus shows that an accurate measurement of the relaxation time can be made by measurement of the radio frequency conductivity of a polar solute dissolved in a non-polar solvent. The results for concentration variation method at a fixed frequency and the frequency variation method at one or more concentrations are compared. It is however, preferable to employ the frequency variation method because this takes into account the presence of free ions and electrons which are always present in a polar dielectric. The method also provides us a procedure by which it is possible to calculate the number of free ions in a dielectric and this can be taken as a measure

of impurity or free ion charge carriers.

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CHAPTER V

RELAXATION TIME AND ACTIVATION ENERGY FOR VISCOSITY FROM RADIO FREQUENCY CONDUCTIVITY MEASUREMENT.

INTRODUCTION

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 solvents has evoked considerable interest as it provides a method for 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 (τ) gives us information regarding the activation energy, intermolecular field and structure of the molecule concerned. In an ideal dielectric there should be present no free ions or electrons. In this case displacement current is the only factor contributing to the conductivity as has been assumed by Murphy and Morgan (1939). But in practice all dielectrics fall far short of this ideal due to the existence of free ions and electrons. The evidence for the existence of free ions and electrons has been shown by many workers such as Standhammer and Seyer (1957), Adamczewski and Jachym (1968) and Lohneysen and Nagerl (1971). Assuming the existence of

free ions, Sen and Ghosh (1974) have deduced a mathematical expression for the radio frequency conductivity of polar dielectrics which has satisfactorily explained the observed experimental results and it has been shown that it is possible to calculate the number of free ions per unit volume in some pure polar liquids. In a recent paper Sen and Ghosh (1980) have shown that by utilizing the expression for radio frequency conductivity, it is possible to calculate the time of relaxation accurately when the polar molecule is dissolved in non-polar solvents and also to determine the free ion concentration in the liquid. The generation of free ions in both polar and nonpolar liquids has been attributed to various factors such as cosmic rays, natural radioactivity, thermal dissociation etc. Thus when a radio frequency field is applied to a polar liquid, the total heat produced is due to the combined effect of displacement current and conduction current. The object of the present study is to extend the investigations to a number of polar liquids in order to establish the general validity of the expression deduced by Sen and Ghosh (1974). Considering the existence of free ions Sen and Ghosh (1978) have shown recently 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 the increase of frequency. The results are similar to those observed by Andrade and Dodd (1946) where it has been found that viscosity decreases upto a certain frequency which they termed as critical frequency.

Again it is now generally accepted that η which has been assumed to be the coefficient of macroscopic viscosity in the Debye expression $\tau = \frac{4\pi\eta\alpha^3}{KT}$ cannot adequately represent the internal friction term. The observation that the activation energy for viscosity varies with frequency should be taken into consideration to examine the nature of the internal force and this may help to develop a theory whose origin lies with some process closely connected with the charge distribution in molecules. Though the activation energy for electrical conductivity and that for viscosity have been calculated by Sen and Ghosh (1978) in case of only three polar liquids viz. nitrobenzene, n-propyl alcohol and acetone, it will be worthwhile to observe whether the same result is valid for other polar liquids as well. In the present investigation, the variation of activation energy with frequency of the applied field will also be investigated by measuring the radio frequency conductivity of a number of polar molecules over a range of frequencies.

EXPERIMENTAL ARRANGEMENT

The method that has been used here is the same as the variation of resonance method of measuring the dielectric constant. The block diagram of the experimental arrangement is shown in figure (2.1) of chapter II.

The dielectric cell used is a cylindrical glass tube of diameter 2.62 cm. fitted with two circular gold electrodes 1.08 cm. apart. Each gold plate is connected with a

platinum wire which is sealed with the glass tube. The dielectric cell is fitted in parallel to the tuning condenser of the secondary circuit. The resonant current I_1 and I_2 in the r.f. meter and the corresponding tuning capacitances, C_1 and C_2 are noted. I_1 and I_2 are the r.f. current when the cell is empty and filled with the liquid respectively. The capacitances of the tuning condenser corresponding to $\frac{1}{\sqrt{2}}$ i.e. 70.7% of I_1 (on either side of the resonance value) are also noted. From these measurements the real part of the radio frequency conductivity of the investigated liquids has been calculated. The theory of measurement of radio frequency conductivity has been described in detail in chapter II. The liquids investigated are methyl alcohol, ethyl alcohol, benzyl alcohol, aniline and benzyl chloride and measurements have been made for a wide range of temperatures and the frequency of the applied radio frequency field has been varied from 400 KHz. to 800 KHz. A well controlled regulated thermostat has been used to measure the radio frequency conductivity at different temperatures.

RESULTS AND DISCUSSION

The real part of the radio frequency conductivity (K') has been measured in case of ethyl, methyl and benzyl alcohol from 25°C to 60°C and in case of aniline and benzyl chloride from 30°C to 80°C under the application of a radio frequency field whose frequency is varied from 400 KHz to 800 KHz.

The values of K' are placed in table (5.1). It is observed that the radio frequency conductivity increases with the increase of temperature in contrary to the expectation due to Murphy and Morgan equation which indicates that K' should decrease with the increase of temperature. This evidently shows that dielectric loss is not the only contributing factor to radio frequency conductivity but the presence of free ions and electrons have to be taken into consideration to explain the observed results. The experimental values of K' are plotted against the corresponding values of $1/\eta$ where η is the coefficient of viscosity at the corresponding temperature and the results are shown in figure (5.1) to (5.5). It is observed that curves are straight lines with different intercepts for different frequencies for the liquids studied and this shows that the equation deduced by Sen and Ghosh (1974) namely

$$\begin{aligned} K' &= \frac{1}{4\pi} (\epsilon_0 - \epsilon_\infty) \omega^2 \tau + \frac{n e^2}{6 \pi a \eta} \\ &= A + \frac{B}{\eta} \end{aligned} \quad \dots (5.1)$$

is valid where ϵ_0 and ϵ_∞ are the static and high frequency dielectric constant of the liquid respectively, n is the number of ions per c.c., e is the electronic charge, 'a' is the radius of the molecule and η is the viscosity of the polar liquid. Equation (5.1) also establish the fact observed earlier by Sen and Ghosh (1974) that there is a

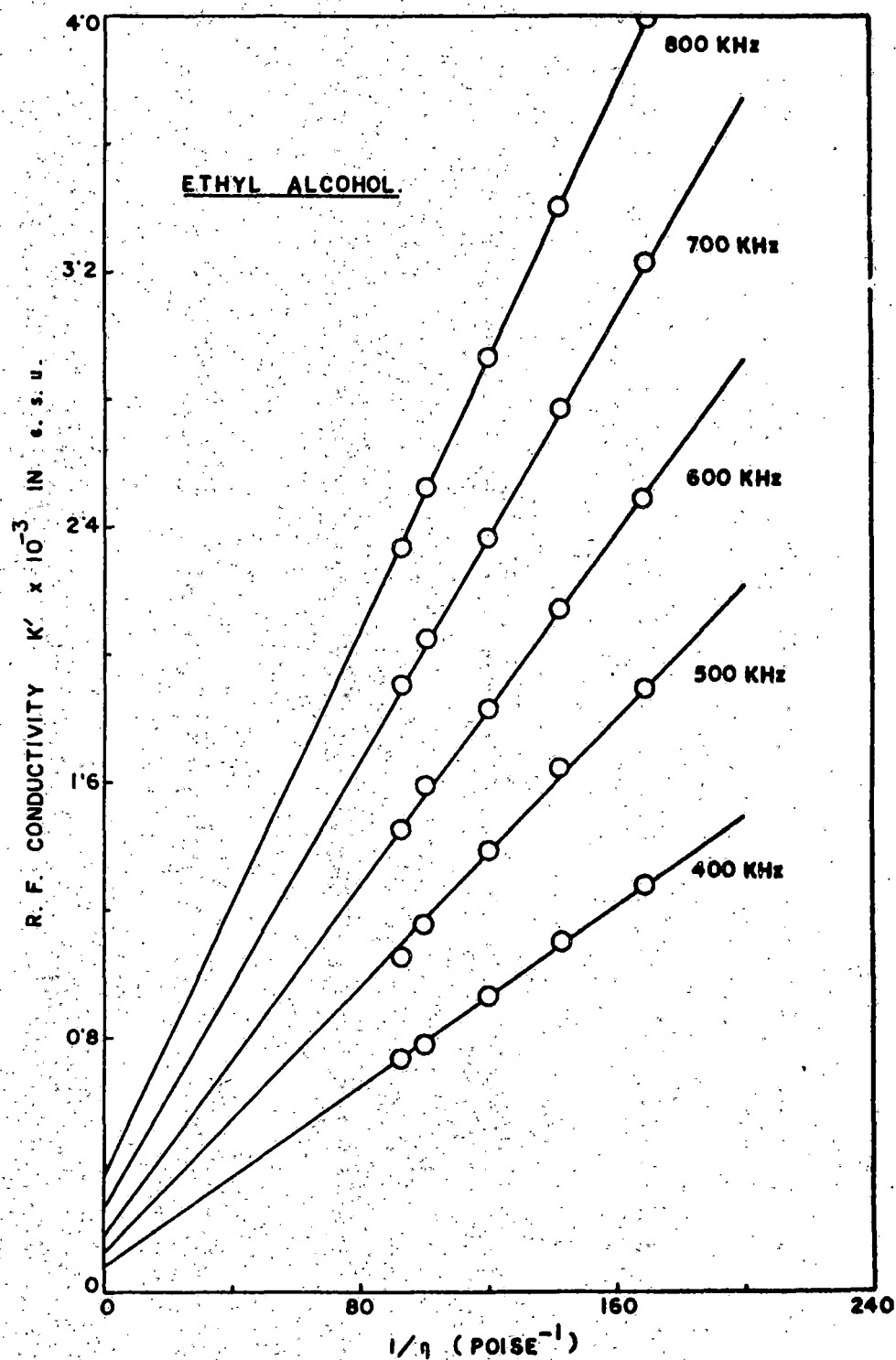


FIG. 5.1. VARIATION OF R. F. CONDUCTIVITY WITH $1/\eta$

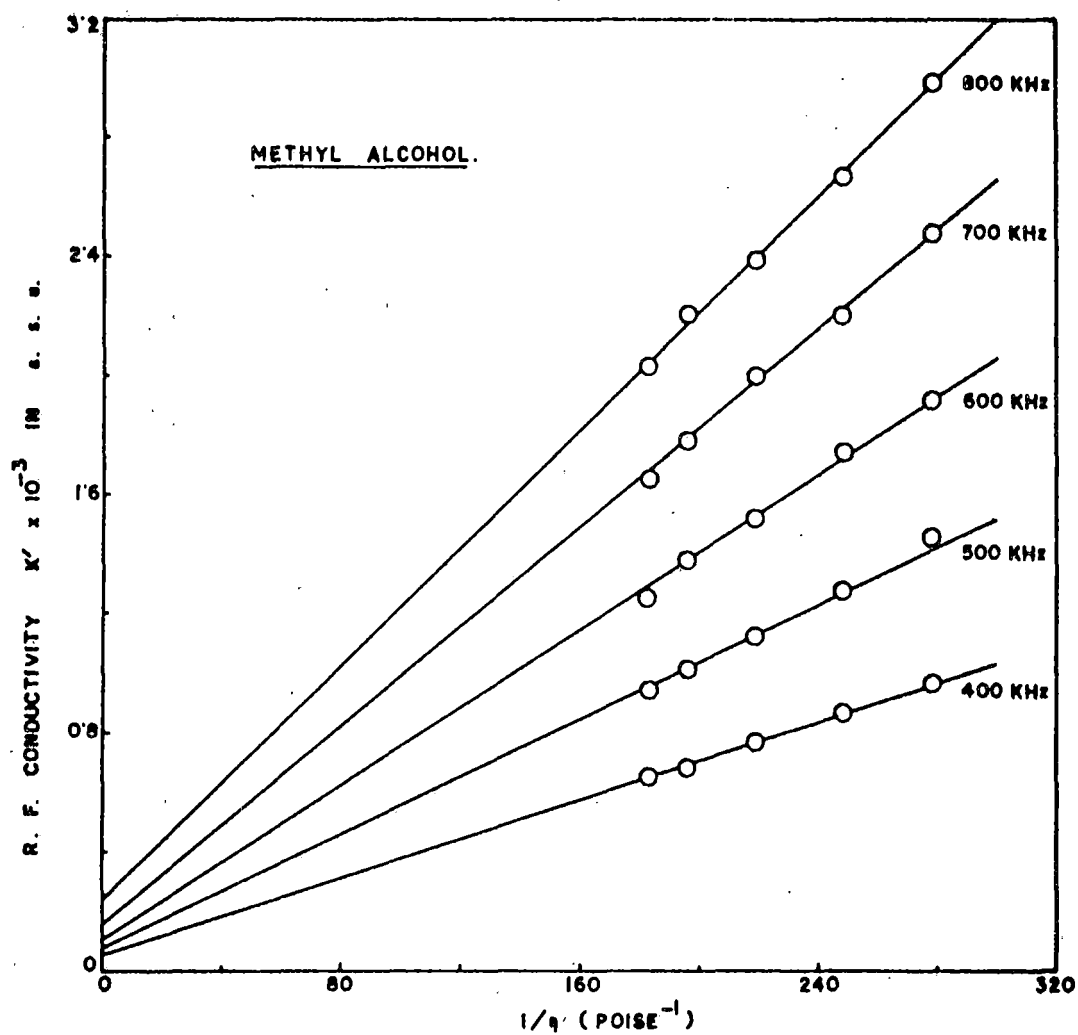


FIG. 5. 2. VARIATION OF R. F. CONDUCTIVITY WITH $1/\eta$

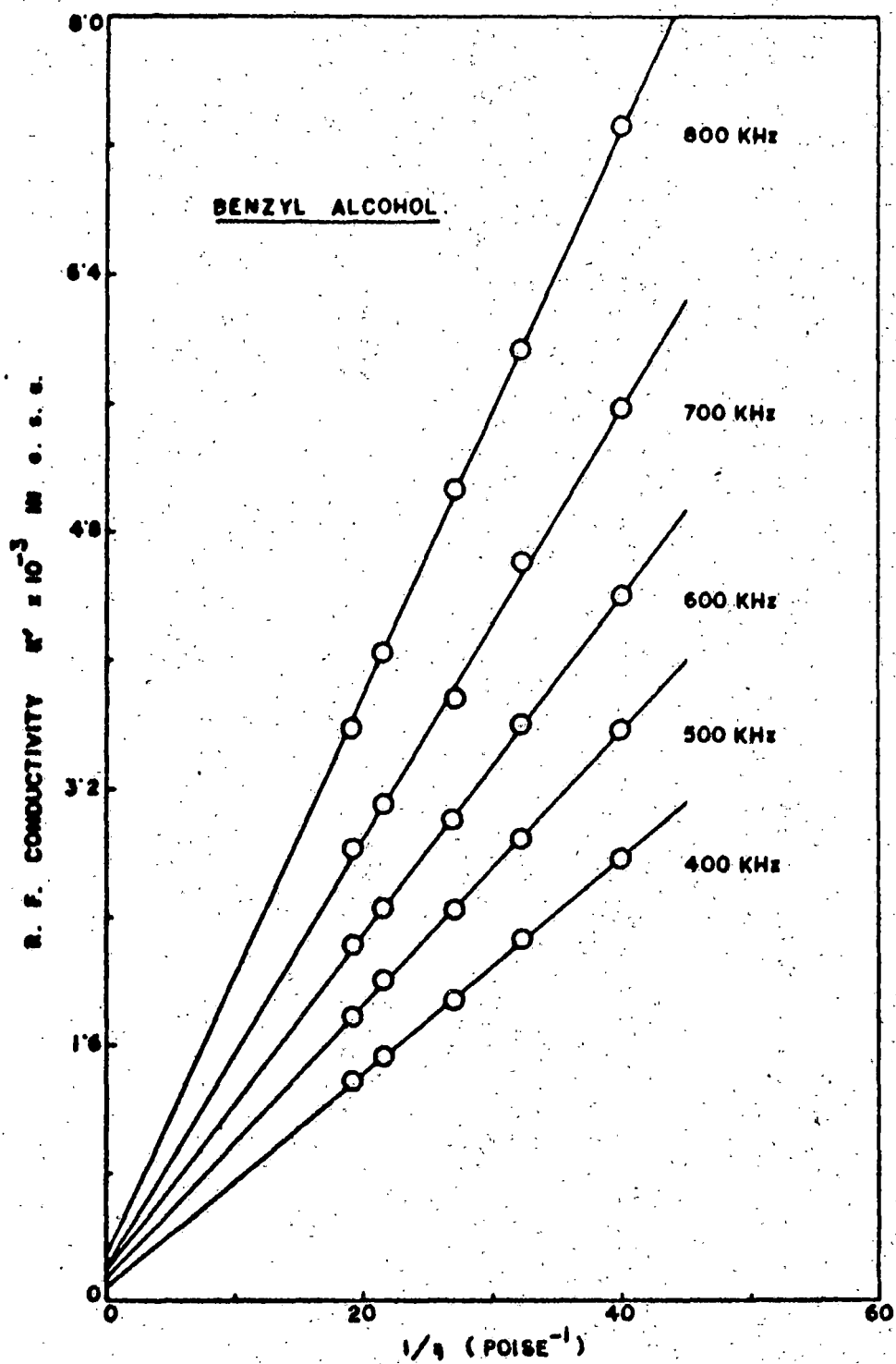


FIG. 5.3. VARIATION OF R. F. CONDUCTIVITY WITH $1/\eta$

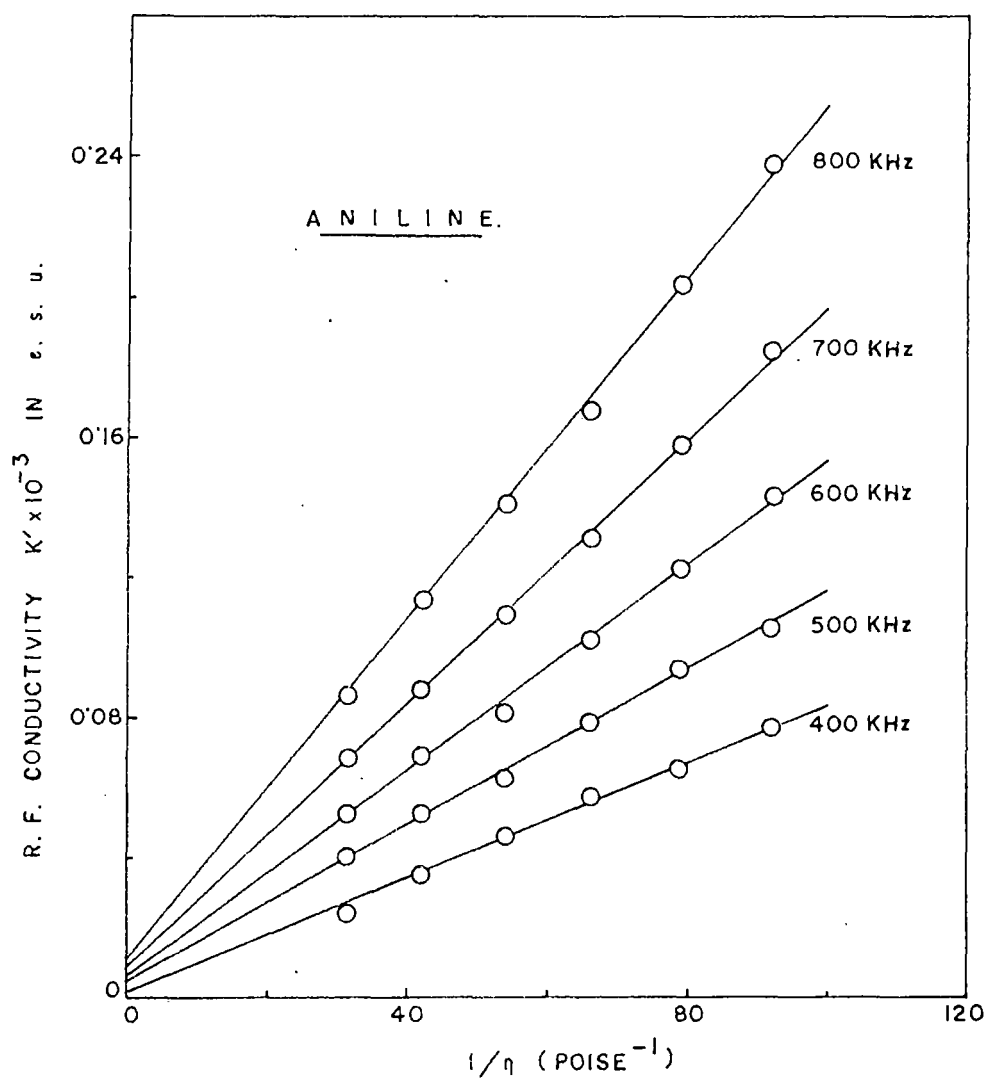


FIG. 5.4. VARIATION OF R.F. CONDUCTIVITY WITH $1/\eta$

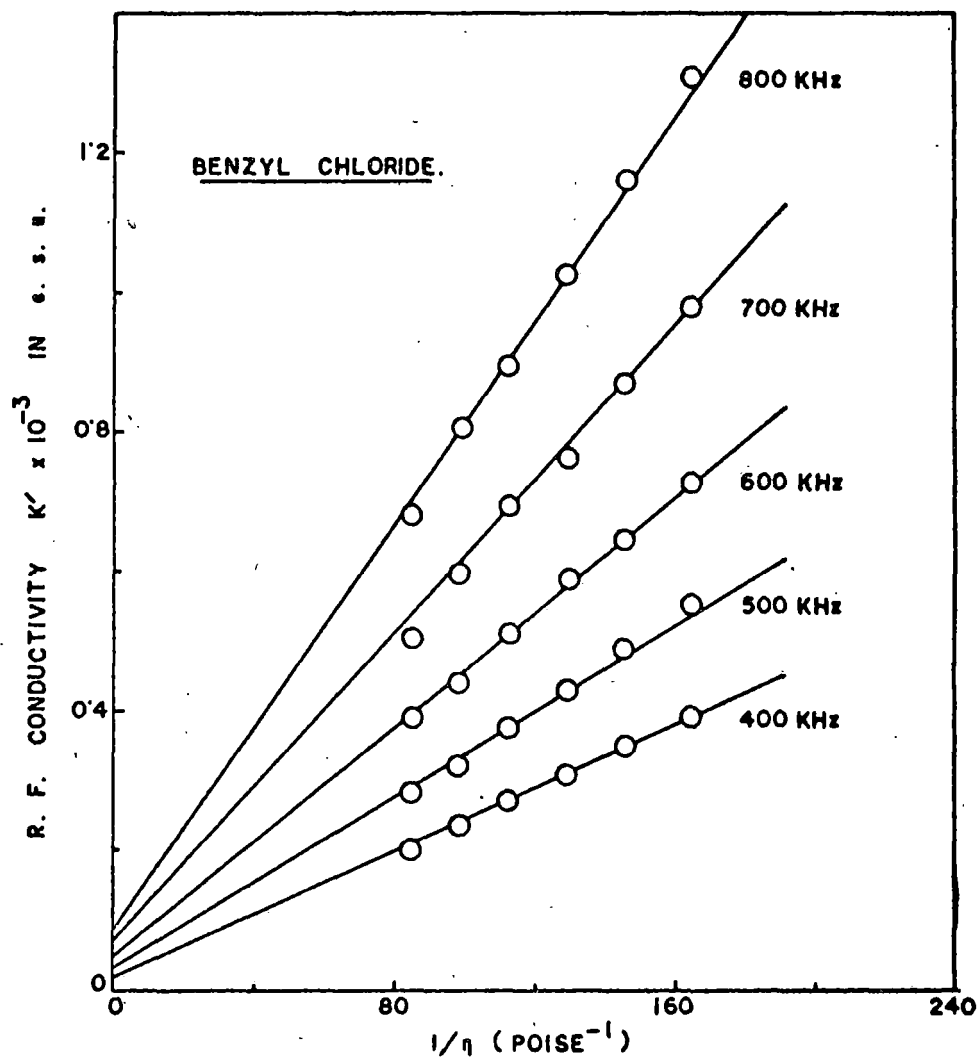


FIG. 5.5. VARIATION OF R. F. CONDUCTIVITY WITH $1/\eta$

similarity between equation (5.1) and Walden's rule which states that in case of electrolytes the product of equivalent conductance at infinite dilution and the viscosity of the solvent is approximately constant and independent of the nature of the medium. The values of A in equation (5.1) for different frequencies for the liquids are entered in the third column in table (5.2) and from the fourth column it is noted that A/f^2 where f is frequency of the applied radio frequency field, is almost constant for a particular liquid. This shows the quantitative validity of equation (5.1). Taking the mean average value of A/f^2 for each liquid, the value of γ has been calculated and the results are entered in the sixth column of table (5.2). The average slope of the curves for each liquid and the value of 'a', the molecular radius calculated from the kinetic theory has also been entered in the sixth column of table (5.2). Utilizing these values, the value of n , the free ion concentration has been calculated for each liquid and the results are entered as the last entry column six of table (5.2).

It is observed from table (5.2) that the number of ions per c.c. in case of liquids studied here is of the order of 10^{12} to 10^{14} . It is minimum (of the order of 10^{12}) in case of aniline and is maximum (of the order of 10^{14}) in case of benzyl alcohol. The value of free-charge carrier density in case of benzyl alcohol has been found to 2.8×10^{16} per c.c. by Lohneysen and Nagel (1971) which shows that free

charge density depends upon the state of purity of the liquid. In the case of nitrobenzene, acetone and propyl alcohol as previously studied by Sen and Ghosh (1974) the charge carrier density is of the order of 10^{13} per c.c. In case of alcohols, it is seen that the time of relaxation increases with the increasing molecular size. Such behaviour has been noted before by many workers such as Cole and Cole (1941) on the measurements of Slevogt (1939) and B  z (1939) particularly in case of alcohols and that of Smyth and Collaborators (1948, 1960, 1961) in case of other series of compounds. The actual value of τ for the liquids calculated here though of the same order of magnitude as reported in the literature will be different with that ~~≡~~ from dielectric constant measurements, because the value of τ here corresponds to a state of the liquid in which $\eta \rightarrow \infty$ (infinity) and Murphy & Morgan equation will lose its validity long before this stage is reached.

It has been shown by Sen and Ghosh (1978) that as $K' = K_0 \exp. (-\Delta E_c / 2KT)$, the activation energy for electrical conductivity (ΔE_c) and K_0 can be obtained by plotting $\log K'$ against $1/T$ [Figure (5.6) to (5.10)]. Further it has been deduced by Sen and Ghosh (1978) that

$$e^{-\Delta E_c / 2KT} = \frac{A}{K_0} + \frac{B}{K_0 D} e^{-\Delta E_v / KT} \quad \dots (5.2)$$

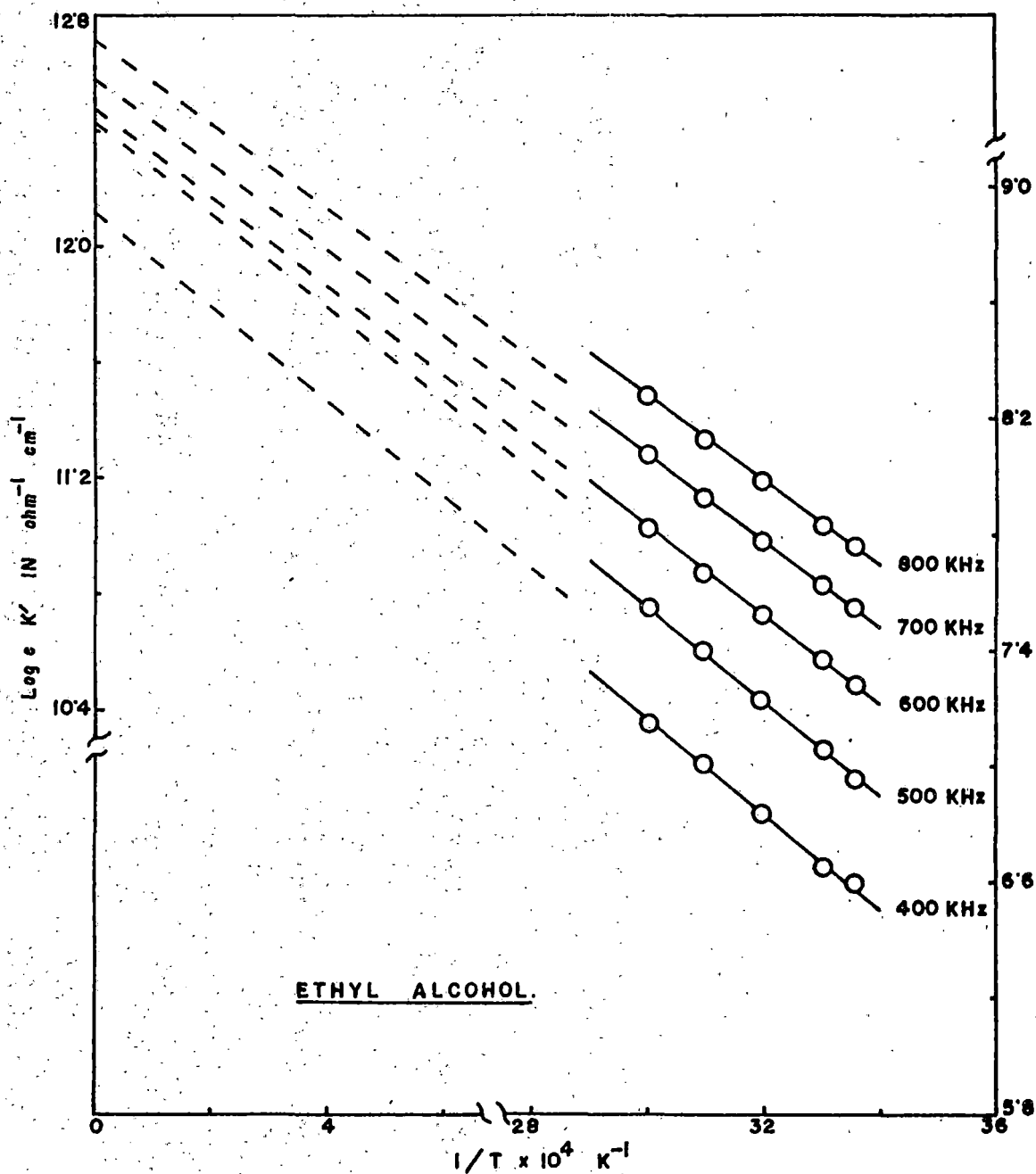


FIG. 5.6. VARIATION OF $\log \epsilon K'$ WITH $1/T$.

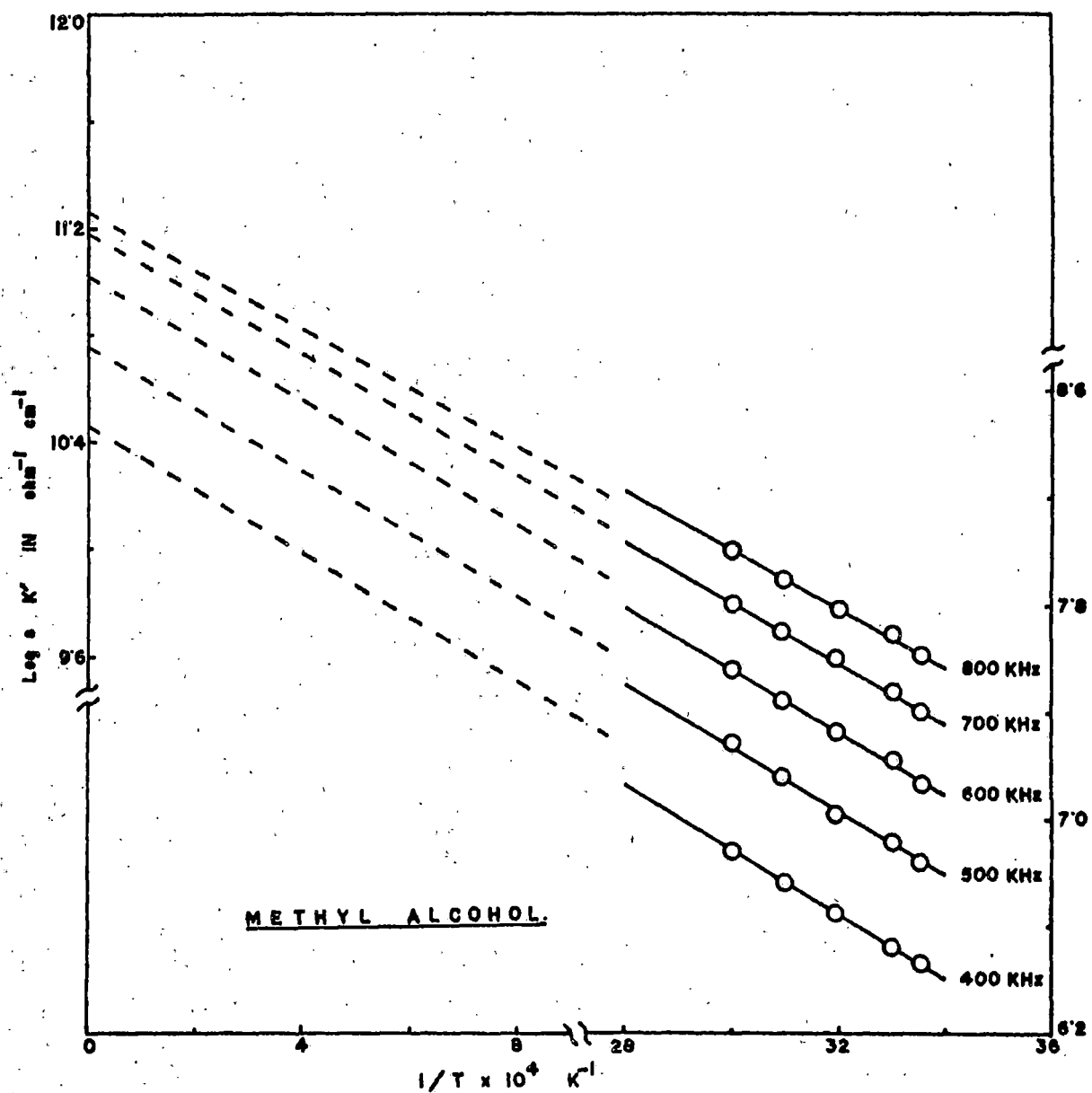


FIG. 5.7. VARIATION OF $\text{Log } \epsilon K'$ WITH $1/T$.

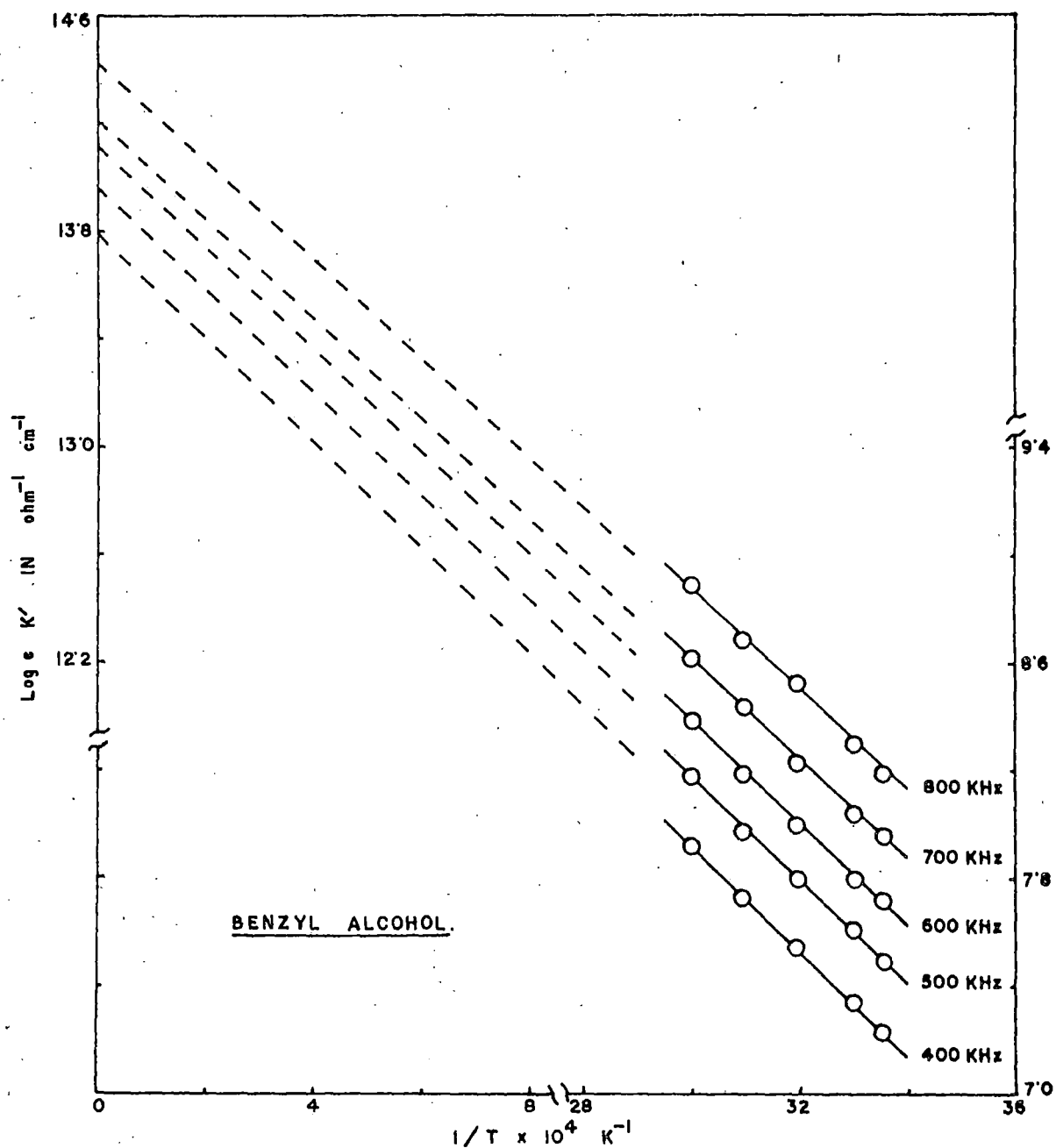


FIG. 5.8. VARIATION OF $\log e K'$ WITH $1/T$

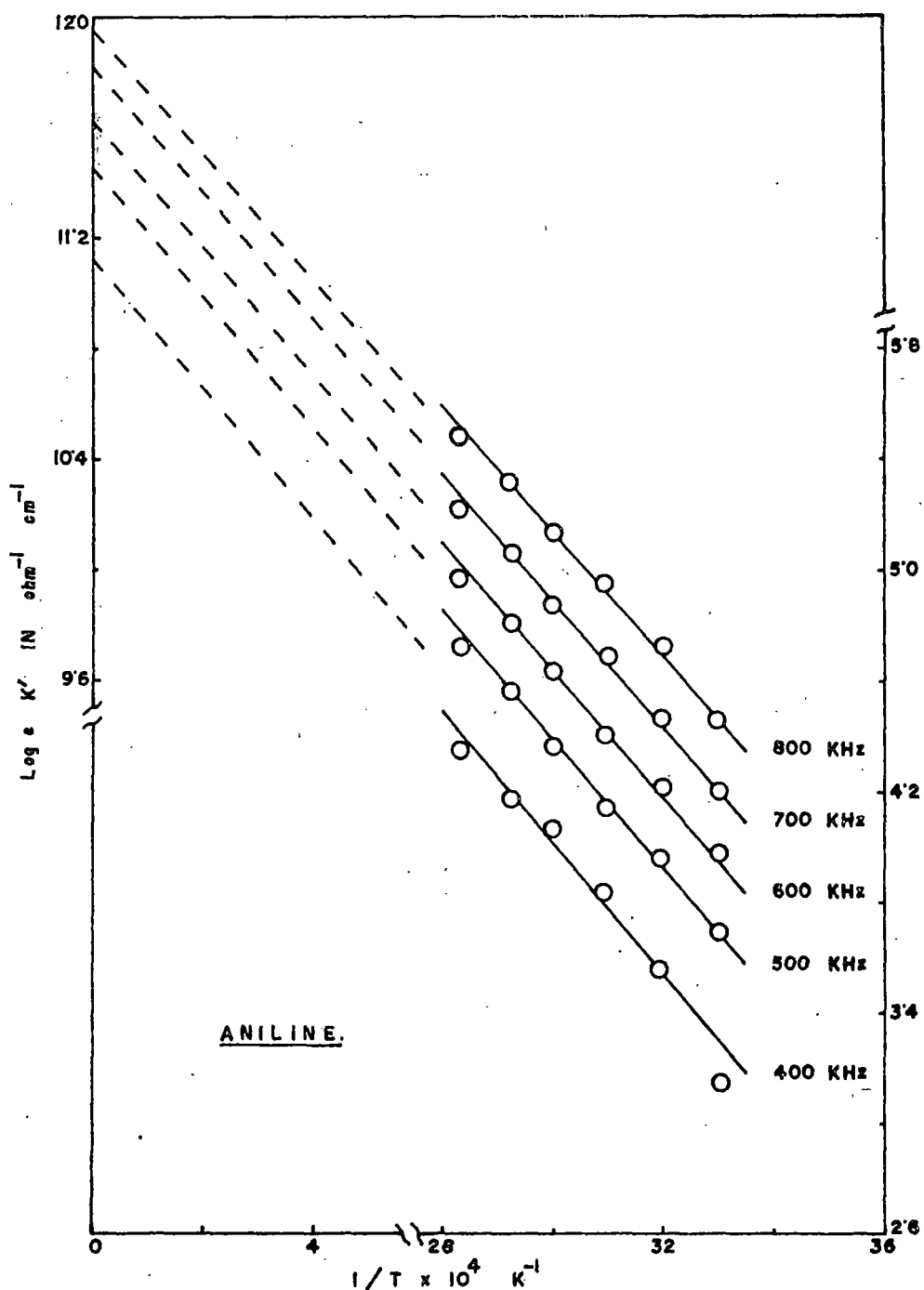


FIG. 5.9. VARIATION OF $\text{Log } \epsilon K'$ WITH $1/T$.

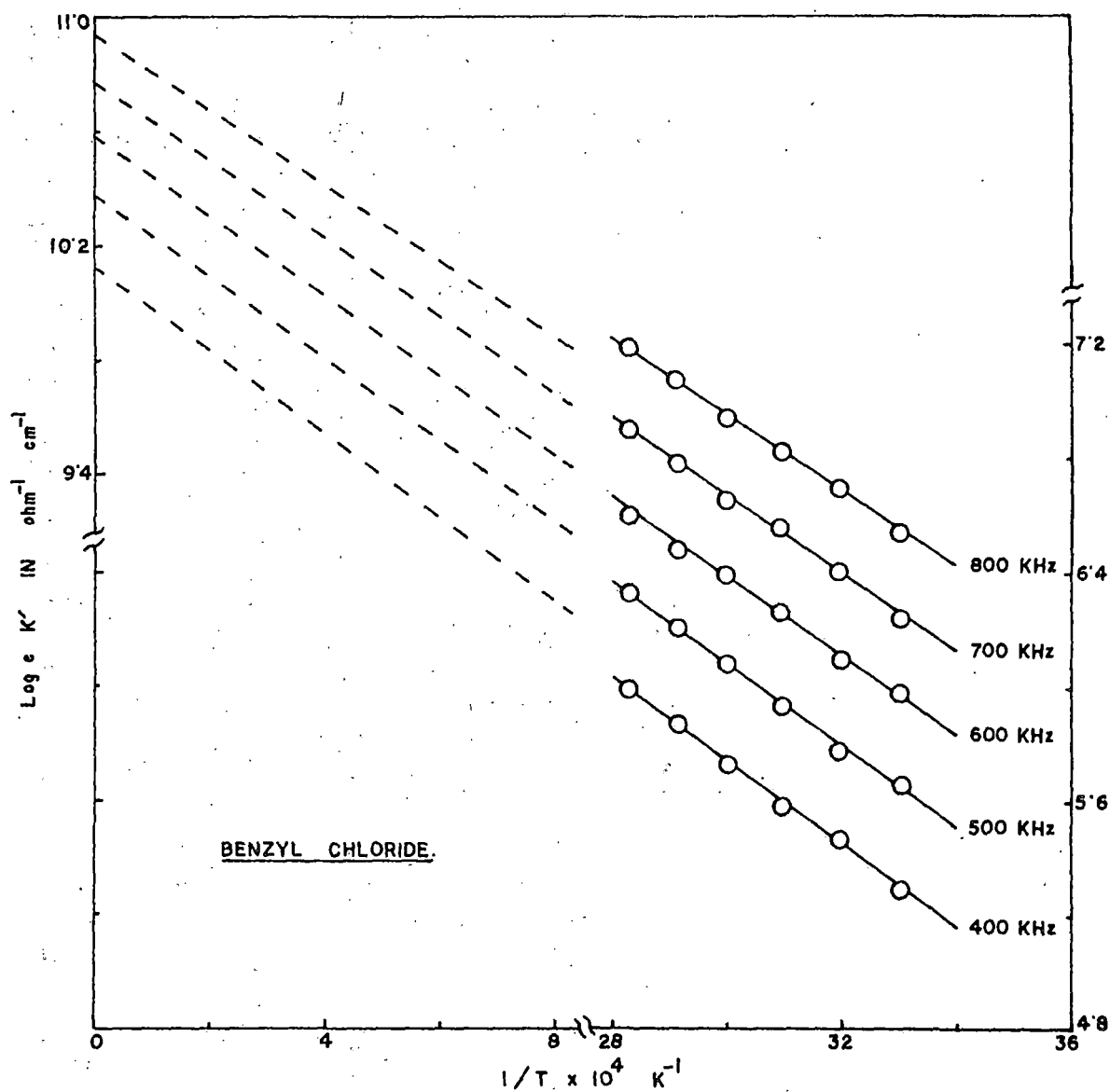


FIG. 5.10. VARIATION OF $\text{Log } \epsilon K'$ WITH $1/T$

where A and B are the same constants as in equation (5.1) and D is the constant in the equation

$$\eta = D e^{\Delta E_v / KT}$$

The values of D for the liquids have been obtained by plotting curves of $\log \eta$ against $1/T$ [Figure (5.11)].

The values of ΔE_v for different frequencies for the liquids investigated have been calculated and entered in the last ^{but one} column of table (5.3). From the table, it is seen that the activation energy for electrical conductivity and that for viscosity become a function of frequency, both gradually decrease with the increase of frequency. The results are plotted in figure (5.12) and it is observed that there is a tendency of saturation towards higher frequencies as was reported earlier by Andrade and Dodd (1946). It is further observed that in case of alcohols both ΔE_c and

ΔE_v increase with the molecular size. Though there is a general tendency for τ and ΔE_v to increase with the increasing molecular size or weight, the results for aniline and benzyl chloride indicate that a definite conclusion cannot be drawn regarding the variation of time of relaxation and activation energy with the size, shape and nature of the molecules. Such behaviour of τ has been observed by LeFèvre and Sullivan (1954) where measurements of τ have been made in order to observe the variation of τ with molecular size or weight for 32 different solutes mainly

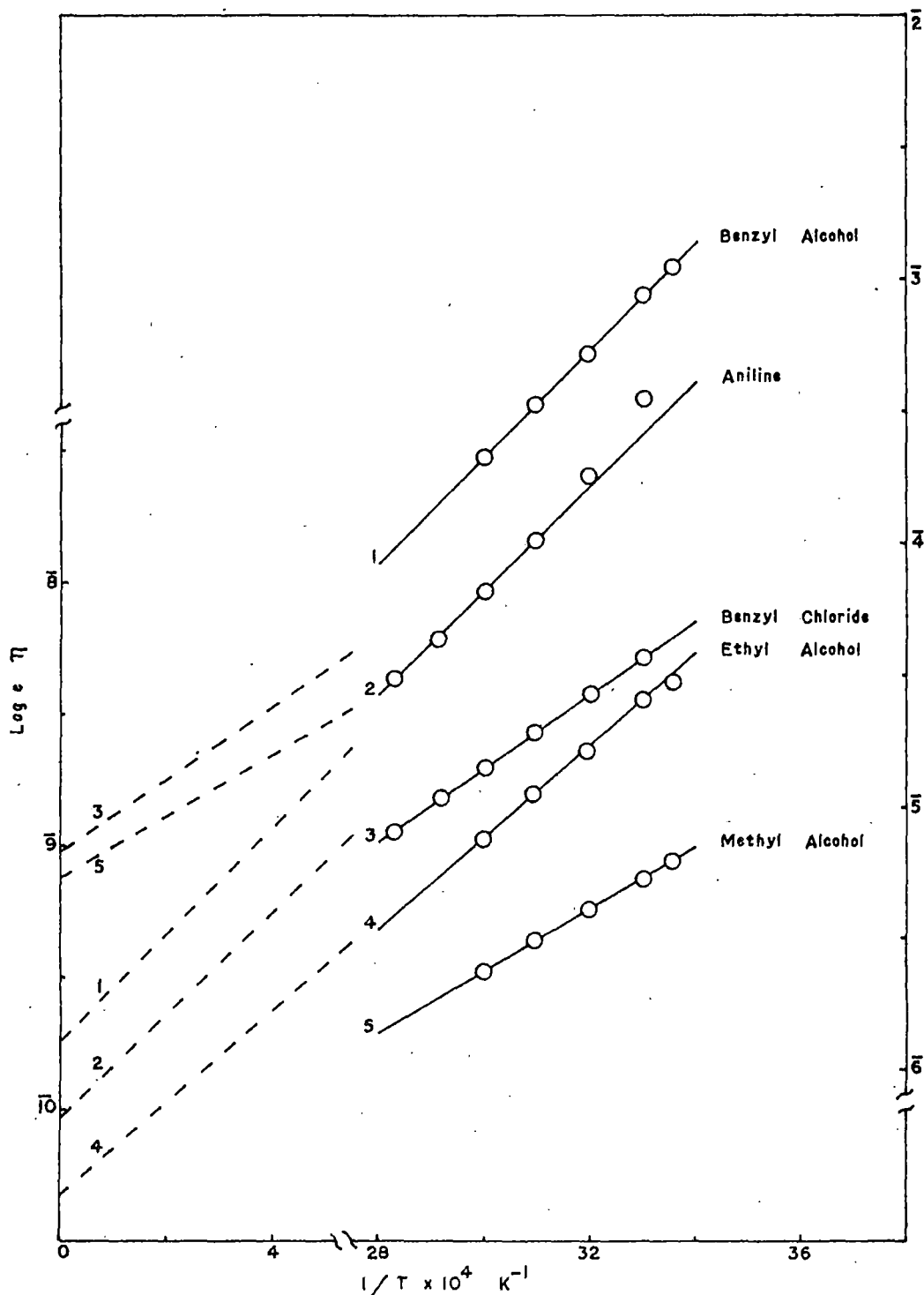


FIG. 5. II. VARIATION OF $\text{Log } e \eta$ WITH $1/T$.

in carbon tetrachloride solvent and they found that γ value at infinite dilution shows no smooth variation with the size or shape of the molecule. When the activation energy for viscosity is plotted against frequency (figure 5.12), it is found that the curve is almost linear and by extrapolation to zero frequency, the value of activation energy obtained agrees well ^{with} ~~to~~ that found in literature.

We can thus conclude that the expression for radio frequency conductivity deduced by Sen and Ghosh (1974) has general validity for a large number of polar molecules and the equation can be utilized for calculating the time of relaxation and the number of free-charge carriers in polar liquids. Though the number of free ions is very small (percentage of ionization of the order of 10^{-6}), it gives a measure of the imperfection in pure liquid dielectric. Another point that emerges is that viscosity of a polar dielectric becomes a function of the frequency of the applied radio frequency field and must have some bearing on the experimental results of Andrade and Dodd regarding the effect of electric field on viscosity. 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 result that activation energy for viscosity become a function of the frequency of the applied radio frequency field.

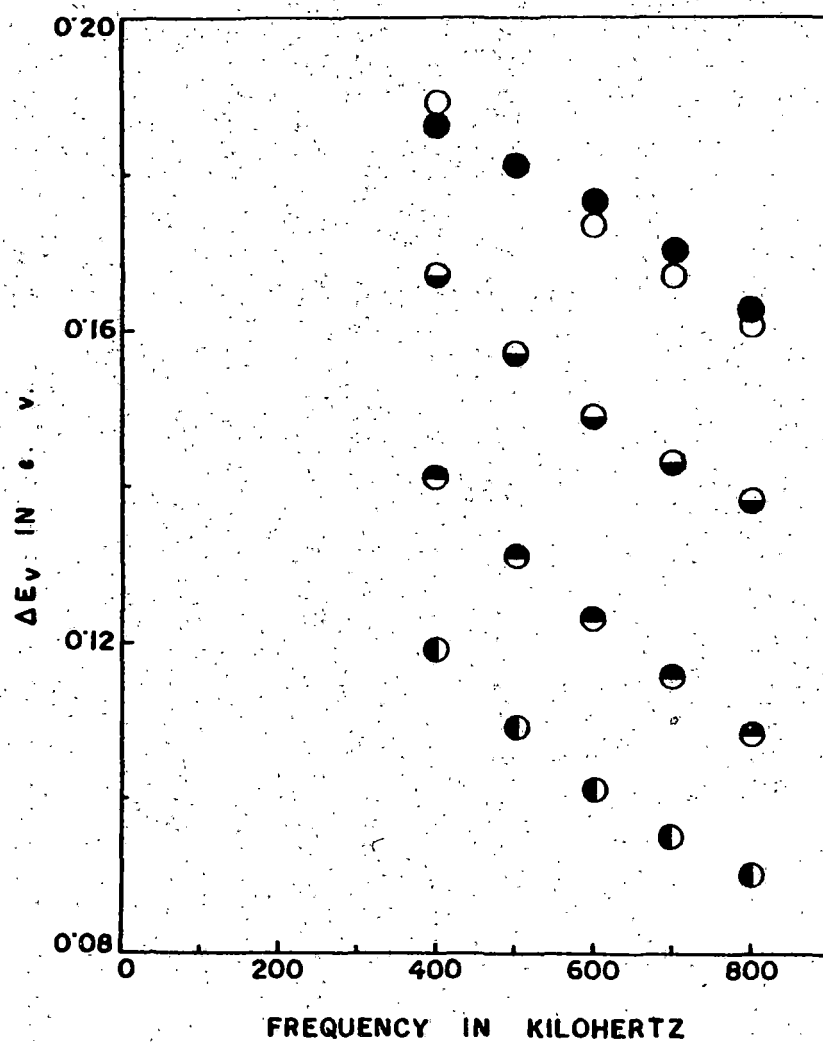


FIG.5.12.VARIATION OF ΔE_v WITH FREQUENCY
 ● BENZYL ALCOHOL, ○ ANILINE, ◐ ETHYL
 ALCOHOL, ◑ BENZYL CHLORIDE, ◒ METHYL
 ALCOHOL.

Table 5.1

Values of $K' \times 10^{-3}$ in c.s.u. at different temperatures.

System	Freq- uency in KHz.	25°C	30°C	40°C	50°C	60°C
Ethyl alcohol	400	0.73389	0.77153	0.93127	1.10490	1.27210
	500	1.04615	1.15346	1.38837	1.64173	1.89299
	600	1.44525	1.59088	1.83108	2.13809	2.47784
	700	1.90345	2.04816	2.35906	2.77113	3.23012
	800	2.33409	2.52149	2.92894	3.39789	4.00332
Methyl alcohol	400	0.64790	0.68265	0.77320	0.86923	0.97127
	500	0.93771	1.01247	1.11510	1.28032	1.46135
	600	1.24871	1.38046	1.51962	1.74927	1.91499
	700	1.64742	1.77052	2.00411	2.20479	2.47563
	800	2.03417	2.20895	2.38545	2.66762	2.99451
Benzyl alcohol	400	1.39781	1.53646	1.87619	2.27667	2.7565
	500	1.78559	2.01496	2.4432	2.90663	3.55803
	600	2.24656	2.44408	3.00259	3.59857	4.39323
	700	2.85035	3.11178	3.76121	4.61955	5.56828
	800	3.58662	4.03688	5.05596	5.94665	7.30901

Table 5.1 (Contd.)

Values of $K' \times 10^{-3}$ in c.g.s. at different temperatures.

System	Freq- uency in KHz	30°C	40°C	50°C	60°C	70°C	80°C
Aniline	400	0.02502	0.03468	0.04647	0.05841	0.06444	0.07651
	500	0.04002	0.05257	0.06210	0.07812	0.09428	0.11051
	600	0.05227	0.06862	0.08116	0.10198	0.12316	0.14430
	700	0.06679	0.08773	0.10920	0.13057	0.15785	0.18512
	800	0.08600	0.11301	0.14088	0.16848	0.20395	0.23931
Benzyl chloride	400	0.19587	0.23588	0.26337	0.30558	0.34898	0.39349
	500	0.28161	0.31794	0.37422	0.43263	0.49296	0.55546
	600	0.39025	0.43835	0.51255	0.59153	0.64570	0.72843
	700	0.50221	0.59769	0.69656	0.76374	0.86878	0.97836
	800	0.68003	0.80708	0.89446	1.02577	1.16593	1.31474

Table 5.2

Values of A , A/f^2 , B , a , τ and n at Different Temperatures.

System	Freq- uency in KHz	$A \times 10^{-3}$	$A/f^2 \times 10^7$	Ave. value of $A/f^2 \times 10^7$	Values of B , a , τ and n .
Ethyl alcohol	400	0.08	0.0050		$B = 4.063$
	500	0.13	0.0052		$a = 2.8537 \times 10^{-8} \text{ cm.}$
	600	0.18	0.0050	0.00526	$\tau = 0.75 \times 10^{-11} \text{ sec.}$
	700	0.27	0.0055		$n = 3.28 \times 10^{13}$
	800	0.36	0.0056		
Methyl alcohol	400	0.05	0.0031		$B = 6.551$
	500	0.08	0.0032		$a = 2.5266 \times 10^{-8} \text{ cm.}$
	600	0.10	0.0028	0.00324	$\tau = 0.33 \times 10^{-11} \text{ sec.}$
	700	0.16	0.0033		$n = 1.35 \times 10^{13}$
	800	0.24	0.0037		
Benzyl alcohol	400	0.08	0.0050		$B = 113.10$
	500	0.14	0.0056		$a = 3.4516 \times 10^{-8} \text{ cm.}$
	600	0.20	0.0056	0.00522	$\tau = 1.66 \times 10^{-11} \text{ sec.}$
	700	0.24	0.0049		$n = 3.19 \times 10^{14}$
	800	0.32	0.0050		

Table 5.2 (Contd.)

System	Freq- uency, $\lambda \times 10^{-3}$ in KHz.	$\lambda/f^2 \times 10^7$	Ave. value of $\lambda/f^2 \times$ 10^7	Value of B, a, γ and n.
Aniline	400	0.002	0.00017	B = 1.554
	500	0.005	0.00020	a = 3.3141×10^{-8} cm.
	600	0.006	0.00017	γ = 1.31×10^{-11} sec.
	700	0.009	0.00018	n = 4.21×10^{12}
	800	0.011	0.00017	
Benzyl chloride	400	0.020	0.0013	B = 4.443
	500	0.035	0.0014	a = 3.5838×10^{-8} cm.
	600	0.050	0.0014	γ = 1.17×10^{-11} sec.
	700	0.075	0.0015	n = 1.30×10^{13}
	800	0.090	0.0014	

Table 5.3.

Values of $\frac{A}{K_0}$, $\frac{B}{K_0 D}$, ΔE_c and ΔE_v for Different
Frequencies at 30°C.

System	Freq. 'in KHz.	$\frac{A}{K_0} \times 10^3$	$\frac{B}{K_0 D}$	ΔE_c (ev)	ΔE_v (ev)	ΔE_v (ev) at zero frequency.
Ethyl alcohol	400	0.4356	2.3246	0.285	0.167	
	500	0.5192	1.7034	0.281	0.157	
	600	0.6844	1.6218	0.267	0.149	0.188
	700	0.9283	1.4673	0.259	0.143	
	800	1.0769	1.2759	0.255	0.138	
Methyl alcohol	400	1.4327	1.7158	0.206	0.119	
	500	1.6985	1.2714	0.201	0.109	
	600	1.6367	0.9801	0.200	0.101	0.141
	700	2.2321	0.8351	0.194	0.095	
	800	3.0900	0.7709	0.187	0.090	
Benzyl alcohol	400	0.0821	1.9703	0.337	0.186	
	500	0.1212	1.6631	0.332	0.181	
	600	0.1489	1.4303	0.330	0.177	0.206
	700	0.1634	1.3076	0.322	0.170	
	800	0.1749	1.0500	0.319	0.163	

Table 5.3 (Contd.)

Values of $\frac{A}{K_0}$, $\frac{B}{K_0 D}$, ΔE_c and ΔE_v for Different
Frequencies at 30°C

System	Freq- quency in KHz,	$\frac{A}{K_0} \times 10^3$	$\frac{B}{K_0 D}$	ΔE_c (ev)	ΔE_v (ev)	ΔE_v (ev) at zero frequency
Aniline	400	0.0296	0.5224	0.409	0.189	
	500	0.0538	0.3794	0.407	0.182	
	600	0.0534	0.3138	0.402	0.174	0.215
	700	0.0662	0.2593	0.397	0.167	
	800	0.0703	0.2255	0.392	0.161	
Benzyl chloride	400	0.8055	1.4949	0.252	0.141	
	500	1.0866	1.1524	0.248	0.131	
	600	1.2710	0.9435	0.242	0.123	0.169
	700	1.5766	0.7803	0.236	0.115	
	800	1.5960	0.6582	0.230	0.108	

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Relaxation Time & Activation Energy for Viscosity from Radiofrequency Conductivity Measurements

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From the measurement of radiofrequency conductivity of a number of polar molecules such as methyl alcohol, ethyl alcohol, benzyl alcohol, aniline and benzyl chloride at different temperatures and over a frequency range 400-800 kHz, the relaxation time, the number of free ions per unit volume and the variation of activation energy of viscosity with frequency have been obtained. The results prove the validity of the equation deduced earlier by S N Sen and R Ghosh [*J. phys. Soc. Japan*, 36 (1974), 743] and give a quantitative estimate of the imperfection in liquid polar dielectrics. The variation of activation energy of viscosity with frequency of the applied field indicates that viscosity is connected with the nature of charge distribution in a molecule and it is pointed out this should be taken into account to find the nature of internal frictional force acting in a liquid.

1. Introduction

The experimental determination of radio frequency conductivity of polar liquids and its variation with temperature and also when the polar liquid is dissolved in non-polar solvents has evoked considerable interest as it provides a method for the determination of dipole moment and the time of relaxation (τ) of the polar molecule. 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 structure of the molecule concerned. In an ideal dielectric, there should be present no free ions or electrons. In this case, displacement current is the only factor contributing to the conductivity as has been assumed by Murphy and Morgan.¹ But in practice, all dielectrics fall far short of this ideal due to the existence of free ions and electrons. The evidence for the existence of free ions and electrons has been shown by many workers such as Standhammer and Seyer,² Lohneyson and Nagel,³ and Adamczewski and Jachym.⁴ Assuming the existence of free ions, Sen and Ghosh⁵ have deduced a mathematical expression for the radio frequency conductivity of polar dielectrics which has satisfactorily explained the observed experimental results and it has been shown that it is possible to calculate the number of free ions per unit volume in some pure polar liquids. In a recent paper Sen and Ghosh⁶ have shown that by utilizing the expression

for radio frequency conductivity, it is possible to calculate the time of relaxation accurately when the polar molecule is dissolved in non-polar solvents and also to determine the free ion concentration in the liquid. The generation of free ions in both polar and non-polar liquids has been attributed to various factors such as cosmic rays, natural conductivity, thermal dissociation, etc. Thus when a radio frequency field is applied to a polar liquid, the total heat produced is due to the combined effect of displacement current and conduction current. The object of the present study is to extend the investigations to a number of pure polar liquids in order to establish the general validity of the expression deduced by Sen and Ghosh.⁵ Considering the existence of free ions, Sen and Ghosh⁷ have shown recently that the activation energy for electrical conductivity and that for viscosity are related to one another, both being functions of frequency and gradually decreasing almost linearly with the increase of frequency. The results are similar to those observed by Andrade and Dodd⁸ where it has been found that viscosity decreases upto a certain frequency which they termed as critical frequency. Again it is now generally accepted that η which has been assumed to be the coefficient of macroscopic viscosity in the Debye expression $\tau = 4\pi\eta a^3/kT$ cannot adequately represent the internal friction term. The observation by Sen and Ghosh⁷ that the activation energy for viscosity varies with frequency should be taken into consideration to examine the nature of

the internal force and this may help to develop a theory whose origin lies with some process closely connected with the charge distribution in molecules. Though the activation energy for electrical conductivity and that for viscosity have been calculated by Sen and Ghosh⁷ in case of only three polar liquids, viz. nitrobenzene, *n*-propyl alcohol and acetone, it will be worthwhile to observe whether the same result is valid for other polar liquids as well. In the present investigation, the variation of activation energy with frequency of the applied field will also be investigated by measuring the radio frequency conductivity of a number of polar molecules over a range of frequencies.

2. Experimental Arrangement

The method of determining the radio frequency conductivity has been described in detail in a previous communication by Sen and Ghosh.⁹ The dielectric cell used is a cylindrical glass tube of a diameter 2.62 cm fitted with two circular gold electrodes 1.08 cm apart. Each gold plate is connected with a platinum wire which is sealed with the glass tube. The liquids investigated are methyl alcohol, ethyl alcohol, benzyl alcohol, aniline and benzyl chloride and measurements have been made for a wide range of temperatures and the frequency of the applied radio frequency field has been varied from 400 kHz to 800 kHz.

3. Results and Discussion

The real part of the radio frequency conductivity (K') has been measured in case of ethyl, methyl and benzyl alcohol from 25 to 60°C and in case of aniline

and benzyl chloride from 30 to 80°C under the application of a radio frequency field whose frequency is varied from 400 kHz to 800 kHz. The experimental values of K' where K' is the radio frequency conductivity at different temperatures are plotted against the corresponding values of $1/\eta$ where η is the coefficient of viscosity at the corresponding temperature and the results are shown in Fig. 1. for different frequencies. It is observed that curves are straight lines with different intercepts for different frequencies for the liquids studied and this shows that the equation deduced by Sen and Ghosh⁵ namely

$$K' = \frac{1}{4\pi} (\epsilon_0 - \epsilon_\infty) \omega^2 \tau + \frac{n e^2}{6\pi a \eta} \quad \dots(1)$$

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

is generally valid. The values of A for different frequencies for the liquids are entered in the second column in Table I and from the third column it is noted that A/f^2 , where f is the frequency of the applied radio frequency field, is almost a constant for a particular liquid. This shows the quantitative validity of Eq. (1). Taking the mean average value of A/f^2 for each liquid, the value of τ has been calculated and the results are entered in the 4th column of Table I. The average slope of the curves for each liquid has also been entered in the 4th column of Table I and the value of a the molecular radius calculated from the kinetic theory has also been entered in the 4th column of Table I. Utilizing these values, the value of n the free ion concentration has been calculated for each liquid and the results are entered as the last entry in column 4 of Table I.

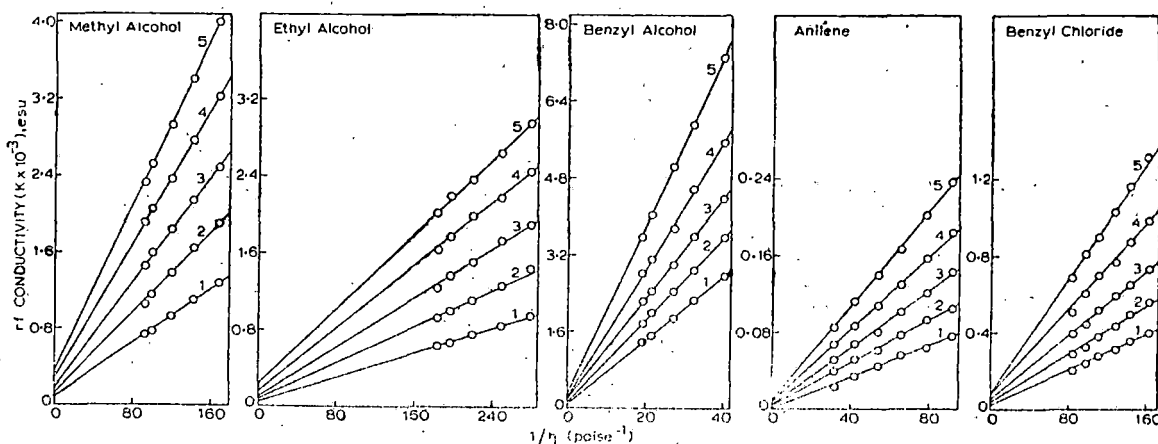


Fig. 1—Variation of K' with $1/\eta$ for ethyl alcohol, methyl alcohol, benzyl alcohol, aniline and benzyl chloride

It is observed from Table I that the number of ions per cc in case of liquids studied here is of the order of 10^{12} to 10^{14} . It is minimum (of the order of 10^{12}) in case of aniline and is maximum (of the order of 10^{14}) in case of benzyl alcohol. The value of free-charge carrier density in case of benzyl alcohol has been found to be 2.8×10^{10} per cc by

Loheneysen and Nageral³ which shows that free-charge density depends upon the state of purity of the liquid. In the case of nitrobenzene, acetone and propyl alcohol as previously studied by Sen and Ghosh,⁵ the charge carrier density is of the order of 10^{12} to 10^{13} /cc. In case of alcohols, it is seen that the time of relaxation increases with the increasing molecular size. Such a behaviour has been noted before by many workers such as Cole and Cole¹⁰ on

Table 1—Values of A , A/f^2 , B , a , τ and n at Different Temperatures for the Polar Molecules Studied

Frequency in kHz	Value of $A \times 10^{-3}$	$A \times 10^7/f^2$	Values of B , a , τ and n
Ethyl alcohol			
400	0.08	0.0050	$B = 4.063$
500	0.13	0.0052	$a = 2.8537 \times 10^{-8}$
600	0.18	0.0050	$\tau = 0.75 \times 10^{-11}$ sec
700	0.27	0.0055	$n = 3.28 \times 10^{13}$
800	0.36	0.0056	
		Ave: 0.00526	
Methyl alcohol			
400	0.05	0.0031	$B = 6.551$
500	0.08	0.0032	$a = 2.5266 \times 10^{-8}$
600	0.10	0.0028	$\tau = 0.33 \times 10^{-11}$ sec
700	0.16	0.0033	$n = 1.35 \times 10^{13}$
800	0.24	0.0037	
		Ave: 0.00324	
Benzyl alcohol			
400	0.08	0.0050	$B = 113.10$
500	0.14	0.0056	$a = 3.4516 \times 10^{-8}$
600	0.20	0.0056	$\tau = 1.66 \times 10^{-11}$ sec
700	0.24	0.0049	$n = 3.19 \times 10^{13}$
800	0.32	0.0050	
		Ave: 0.00522	
Aniline			
400	0.002	0.00017	$B = 1.554$
500	0.005	0.00020	$a = 3.3141 \times 10^{-8}$
600	0.006	0.00017	$\tau = 1.31 \times 10^{-11}$ sec
700	0.009	0.00018	$n = 4.21 \times 10^{12}$
800	0.011	0.00017	
		Ave: 0.00018	
Benzyl chloride			
400	0.020	0.0013	$B = 4.443$
500	0.035	0.0014	$a = 3.5838 \times 10^{-8}$
600	0.050	0.0014	$\tau = 1.17 \times 10^{-11}$ sec
700	0.075	0.0015	$\eta = 1.30 \times 10^{13}$
800	0.090	0.0014	
		Ave: 0.0014	

Table 2—Values of A/K_0 , B/K_0D , ΔE_c and ΔE_v for Different Frequencies at 30 °C

Frequency in kHz	$A \times 10^3 / K_0$	B / K_0D	ΔE_c eV	ΔE_v eV	ΔE_v (eV) at zero frequency
Ethyl alcohol					
400	0.4356	2.3246	0.285	0.167	
500	0.5192	1.7034	0.281	0.157	
600	0.6844	1.6218	0.267	0.149	0.188
700	0.9288	1.4673	0.259	0.143	
800	1.0769	1.2759	0.255	0.138	
Methyl alcohol					
400	1.4327	1.7158	0.206	0.119	
500	1.6985	1.2714	0.201	0.109	
600	1.6367	0.9801	0.200	0.101	0.141
700	2.2321	0.8351	0.194	0.095	
800	3.0900	0.7709	0.187	0.090	
Benzyl alcohol					
400	0.0821	1.9703	0.337	0.186	
500	0.1212	1.6631	0.332	0.181	
600	0.1489	1.4303	0.330	0.177	0.206
700	0.1634	1.3076	0.322	0.170	
800	0.1749	1.0500	0.319	0.163	
Aniline					
400	0.0296	0.5224	0.409	0.189	
500	0.0538	0.3794	0.407	0.182	
600	0.0534	0.3138	0.402	0.174	0.215
700	0.0662	0.2593	0.397	0.167	
800	0.0703	0.2255	0.392	0.161	
Benzyl chloride					
400	0.8055	1.4949	0.252	0.141	
500	1.0866	1.1524	0.248	0.131	
600	1.2710	0.9435	0.242	0.123	0.169
700	1.5766	0.7803	0.236	0.115	
800	1.5960	0.6582	0.230	0.108	

the measurements of Slevogt¹¹ and Baz¹² particularly in case of alcohols and that of Smyth and collaborators¹³⁻¹⁵ in case of other series of compounds. The actual value of τ calculated for the liquids presently studied though of the same order of magnitude as reported in the literature, will be different from that calculated from dielectric constant measurements, because the value of τ here corresponds to a state of the liquid in which $\eta \rightarrow \infty$ (infinity) and Murphy-Morgan equation will lose its validity long before this stage is reached.

It has been shown by Sen and Ghosh⁷ that as $K' = K_0 \exp \{-\Delta E_c/2kT\}$, the activation energy for electrical conductivity can be obtained by plotting $\log K'$ against $1/T$. Further, it has been deduced (Sen and Ghosh⁷) that

$$\exp \{-\Delta E_c/2kT\} = \frac{A}{K_0} + \frac{B}{K_0 D} \exp \{-\Delta E_v/kT\} \quad (2)$$

where A and B are the same constants as in Eq. (1) and D is the constant in the equation

$$\eta = D \exp \{\Delta E_v/kT\}$$

The values of ΔE_v for different frequencies for the liquids investigated have thus been calculated and entered in the last ^{but one} column of Table 2. From Table 2, it is seen that the activation energy for electrical conductivity and that for viscosity become a function of frequency, both gradually decrease with the increase of frequency. The results are plotted in Fig. 2 and it is observed that there is a tendency of saturation towards higher frequencies as was reported earlier by Andrade and Dodd.⁸ It is further observed that in case of alcohols both ΔE_c and ΔE_v increase with the increase of molecular size. Though there is a general tendency for τ and ΔE_v to increase with the increasing molecular size or weight, the results for aniline and benzyl chloride indicate that a definite conclusion cannot be drawn regarding the variation of time of relaxation and activation energy with the size, shape and nature of the molecules. Such a behaviour of τ has been observed by LeFevre and Sullivan¹⁶ where measurements of τ have been made in order to observe the variation of τ with molecular size or weight for 32 different solutes mainly in carbon tetrachloride solvent and they found that τ value at infinite dilution shows no smooth variation with the size or shape of the molecule. When the activation energy for viscosity is plotted against the frequency (Fig. 2), it is found that the curve is almost linear and by extrapolation to zero frequency, the value of activation energy obtained agrees well with that found in literature.

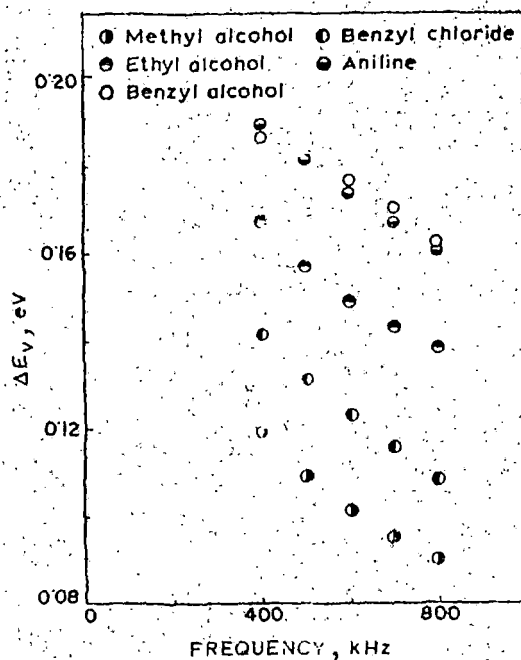


Fig. 2—Variation of ΔE_v with frequency

We can thus conclude that the expression for radio frequency conductivity deduced by Sen and Ghosh⁵ has general validity for a large number of polar molecules and the equation can be utilized for calculating the time of relaxation and the number of free-charge carriers in polar liquids. Though the number of free ions is very small (percentage of ionization of the order of 10^{-6}), it gives a measure of the imperfection in pure liquid dielectrics. Another point that emerges is that viscosity of a polar dielectric becomes a function of the frequency of the applied radio frequency field and must have some bearing on the experimental results of Andrade and Dodd regarding the effect of electric field on viscosity. 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 result that activation energy for viscosity becomes a function of the frequency of the applied radio frequency field.

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CHAPTER VI

MOBILITY AND FREE ION DENSITY FROM MEASUREMENT OF TEMPORAL VARIATION OF CURRENT IN POLAR DIELECTRICS.

INTRODUCTION

In an ideal dielectric there should be present no free ions or electrons but the experimental determination of radio frequency conductivity of polar liquids by Sen and Ghosh (1974, 1978, 1980 a) and other workers by different methods have shown the presence of free ions in polar dielectrics. Assuming the existence of free ions, Sen and Ghosh (1980 b) have shown that from radio frequency conductivity measurement of a polar solute in nonpolar solvent it is possible not only to calculate the number of ions per c.c. in solution but also in pure liquid but also the relaxation time of the polar solute molecule. Nicolau et al (1971) have studied the electrical conductance in case of aliphatic alcohols under the application of alternating current field of 50 - 600 V/cm. and frequency of 100 Hz. in the temperature range 0 - 97°C. and have shown that in case of alcohols a finite conductivity exists even if extreme care is taken to purify the liquids.

When a d.c. field is applied to a dielectric liquid which has been carefully purified it is known that initially the current falls rapidly with time and then decreases slowly

and later shows generally a tendency of saturation. The decay of current passing through an insulating liquid is assumed to be due to removal or accumulation of ions near the electrodes. Though the cause of generation of ions in both polar and nonpolar liquids has been attributed due to various causes such as cosmic rays, natural radio activity, thermal dissociation etc. yet no specific reason has been established regarding the mechanism by which these are produced.

In polar dielectrics natural conduction has been attributed to generation of ions by electrolytic dissociation of impurities. Nikuradse (1932) observed that the conduction current depends upon the measure of purification of the liquid and electrode material. The observation is consistent with that of Hart and Mungall (1957), Zaky et al (1963), Prabhakara Rao and Govinda Raju (1970) and other workers. Blanck et al (1961) found that the rate of decay of current depends upon the impurity present in the liquid and decreased with repeated purification of the liquid. Apart from conductivity due to ions, the polar dielectrics have an intrinsic conductivity which may be as suggested by Forster (1964) due to presence of polar impurities or trapped electrons present in the liquid or generated at the electrode surface. Nikuradse (1932) observed that in case of highly purified liquid when all ionizing agents such as x-rays, radio active sources etc. were removed it was found that there still exists a residual conductivity. As the

conductivity of the liquid has been found to depend on the nature of electrodes it can be presumed that electrons are emitted from the electrode surface and contribute to residual conductivity. Baker and Boltz (1937) interpreted their results as due to thermionic emission from cathode combined with Schottkey effect. This has been criticised by LePage and Dubridge (1940) and they concluded that the current is due to field-enhanced thermionic emission. Eek (1949) showed that in case of a d-c field, variation of current 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 current and K is a constant which consists the ionic mobility term and he assumed that the decay of current was due to initial existence of large ionic clusters in the body of the liquid which gradually disperse. 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. Further it has been observed by Adamczewski and his Co-workers (1969) that in case of saturated hydrocarbons which are nonpolar the variation of current with time could be represented by

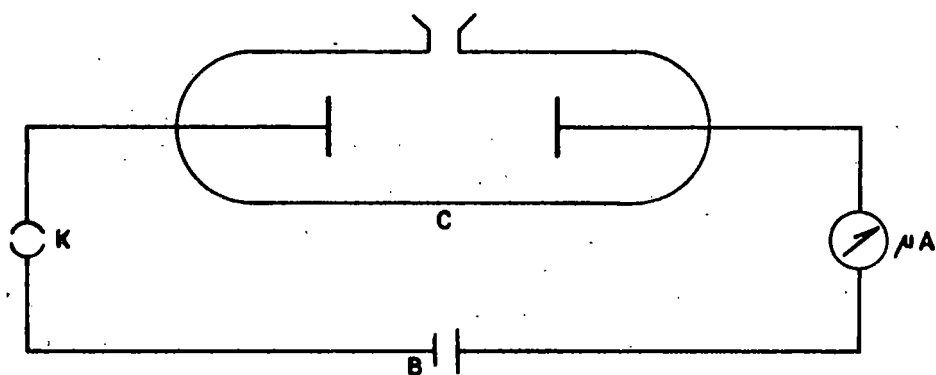
$$I = I_0 \exp. (-\lambda t)$$

where I_0 denotes the initial current and λ is a constant containing mobility factor. Gaspard and Gosse (1970) gave clear evidence of ionic conduction in polar dielectrics. Similar effect has been observed by Standhammer and Seyer (1957) who investigated the problem in cyclohexane and cyclohexane saturated with water. Bohneysen and Nagerl (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. 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; the remarkable of which are due to Kleinheins (1970), Schmidt and Allen (1970), Wollers (1973), Bakale and Schmidt (1973), Allen and Holroyd (1974), Blair and Tredgold (1974), Bickert et al (1976), Krause (1976), Adamczewski and Calderwood (1976, 1977), Adamec and Calderwood (1975, 1978) in the study of the behaviour of fast charge carriers and electronic mobility specially in nonpolar dielectrics with the exception of few work in polar liquids by other authors. Considering all the experimental evidences and assumptions taken by various authors we may conclude that liquids whether polar or nonpolar are never free of ions or electrons which may be due to (i) impurities present in liquid (ii) electrolytic dissociation of impurities (iii) thermionic emission from cathode or field-enhanced thermionic emission (iv) electrochemical dissociation i.e. dissolution of electrode in liquid

which may give rise to injections of electrons and (v) other various factors such as thermal dissociation, cosmic rays, natural radio activity etc. Based on the assumption of the existence of free ions, the time-current curve has been analysed by a number of workers and certain conclusions have been drawn regarding the ionic mobilities and free ion concentrations. Sen and Ghosh (1975) have extended the quantitative theory of Gemant (1940) and explained very satisfactorily the observed variation of current with time which enables us in conjunction with the experimental results to calculate the mobility and charge density of ions. Though the theory has been applied only in case of five polar liquids where the variation of current has been noted for a long time, it will be worthwhile to observe whether the same is valid for other polar liquids as well particularly for a small interval of time. The purpose of the present paper is thus to observe the general validity of the theory developed by Sen and Ghosh (1975) in order to establish the existence of free ions in polar liquids supported earlier from radio frequency conductivity measurements by Sen and Ghosh (1974, 1978, 1980) and to calculate the mobility and free charge density of ions.

EXPERIMENTAL ARRANGEMENT

The schematic diagram of the experimental arrangement is shown in figure (6.1). The conductivity cell used is a cylindrical glass tube of diameter 2.96 cm. fitted with two



C - DIELECTRIC CELL. B. - DRY STORAGE BATTERY.

μA - D. C. MICROAMMETER. K - KEY.

FIG. 6.1. CIRCUIT DIAGRAM OF THE EXPERIMENTAL ARRANGEMENT.

circular brass disc of diameter 2.5 cm and separated by a distance 0.22 cm. The design of the cell has already been described in chapter II. In order to find the effect of any electrochemical reactions between electrodes and liquid studied, the experiments have been repeated a number of times and in each case same results have been obtained. Brass electrodes have been used by many workers previously and more recently by Prabhakara Rao and Govinda Raju (1970) and Sen and Ghosh (1975). Before filling the dielectric cell with the liquid, the glass cell was cleaned with chromic acid and repeatedly washed with distilled water and lastly with benzene and finally dried under vacuum. All the liquids used were spectroscopically pure grade and purified by repeated vacuum distillation. Traces of moisture present in the liquid were all also removed. The liquids were directly introduced into the cell under vacuum distillation in order to avoid any contamination.

A dry cell has been used as the current source and the current flowing through the dielectric liquid has been measured by a D.C. microammeter. The liquids investigated are ethyl alcohol, methyl alcohol, iso-propyl alcohol, aniline and benzyl chloride at room temperature.

RESULTS AND DISCUSSION

The variation of current with time has been measured in case of ethyl alcohol, aniline and benzyl chloride for applied voltage of 2.5 volts, 2.0 volts and 1.0 volt, in case of methyl alcohol and iso-propyl alcohol for applied voltage of 1.5 volts, 1.0 volt and 0.5 volt respectively. The results are plotted in figure (6.2) to (6.6). The nature of variation of current with time and rate of decay of current with applied voltage are in close agreement with the results of previous workers. The applied voltage has been kept low so that current voltage characteristics obeys ohms law and in order to prevent dissociation of molecules. 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 the 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.

If V_0 is the applied voltage, R_0 is the ohmic resistances of the liquid then the initial current is given by

$$I_0 = \frac{V_0}{R_0} \quad \dots (6.1)$$

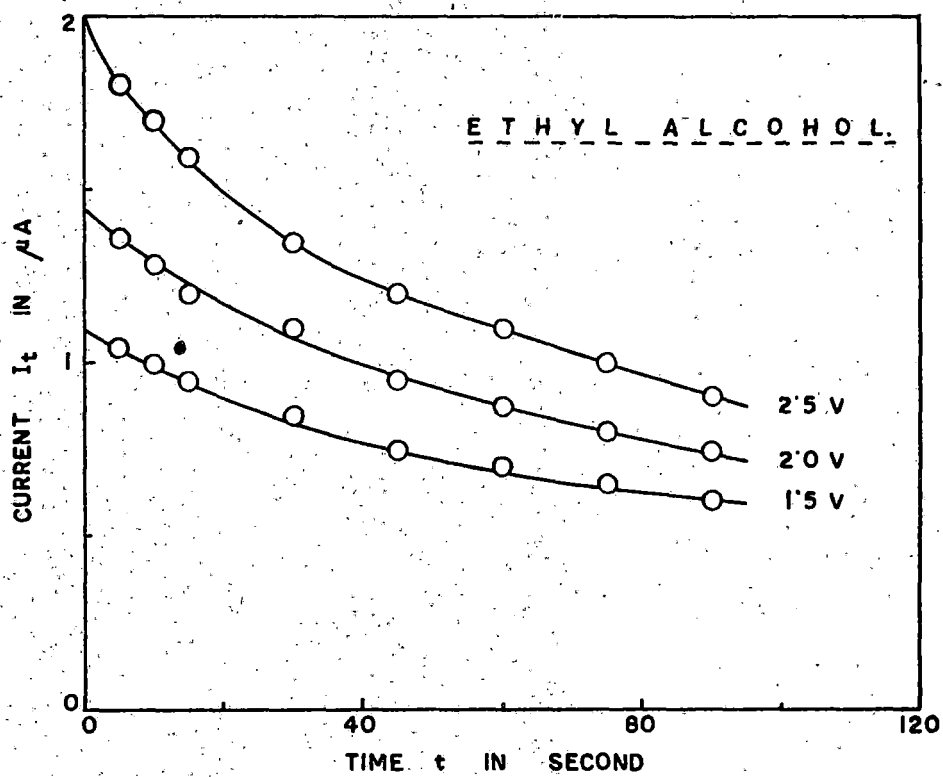


FIG. 6.2. VARIATION OF CURRENT WITH TIME.

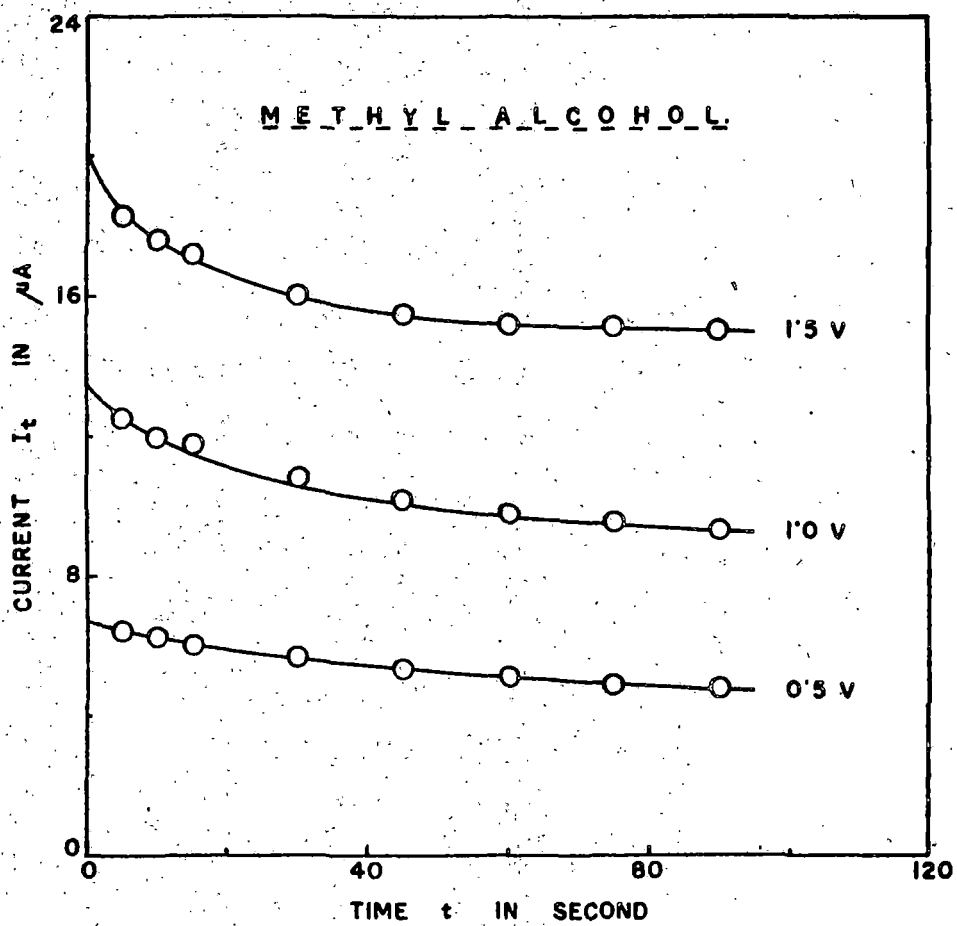


FIG. 6.3. VARIATION OF CURRENT WITH TIME.

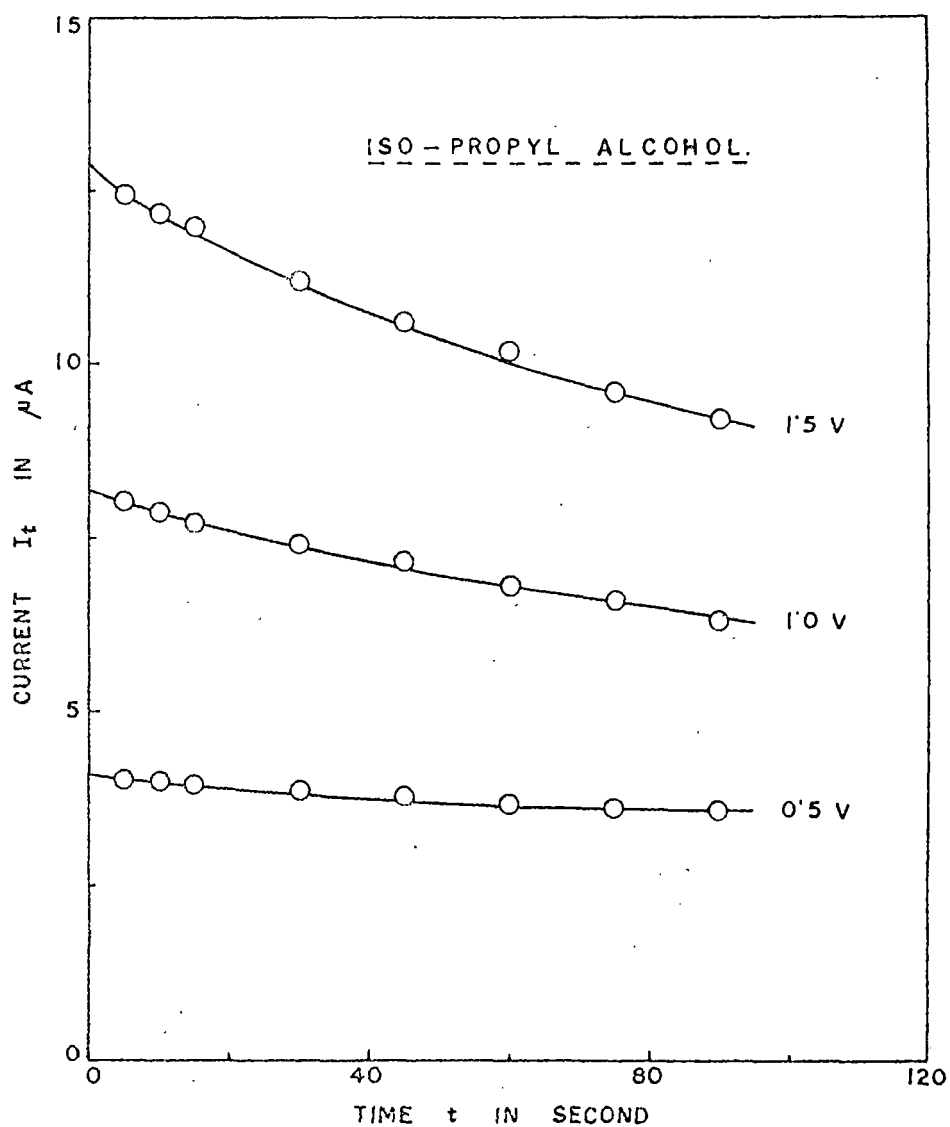


FIG. 6.4. VARIATION OF CURRENT WITH TIME.

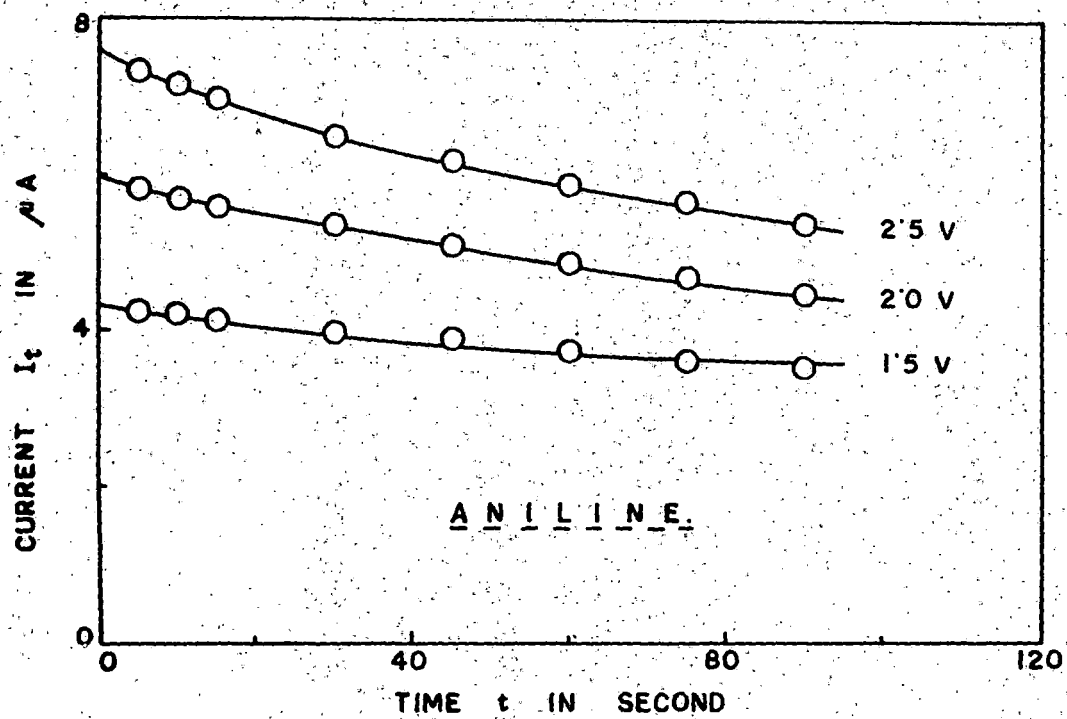


FIG. 6. 5. VARIATION OF CURRENT WITH TIME.

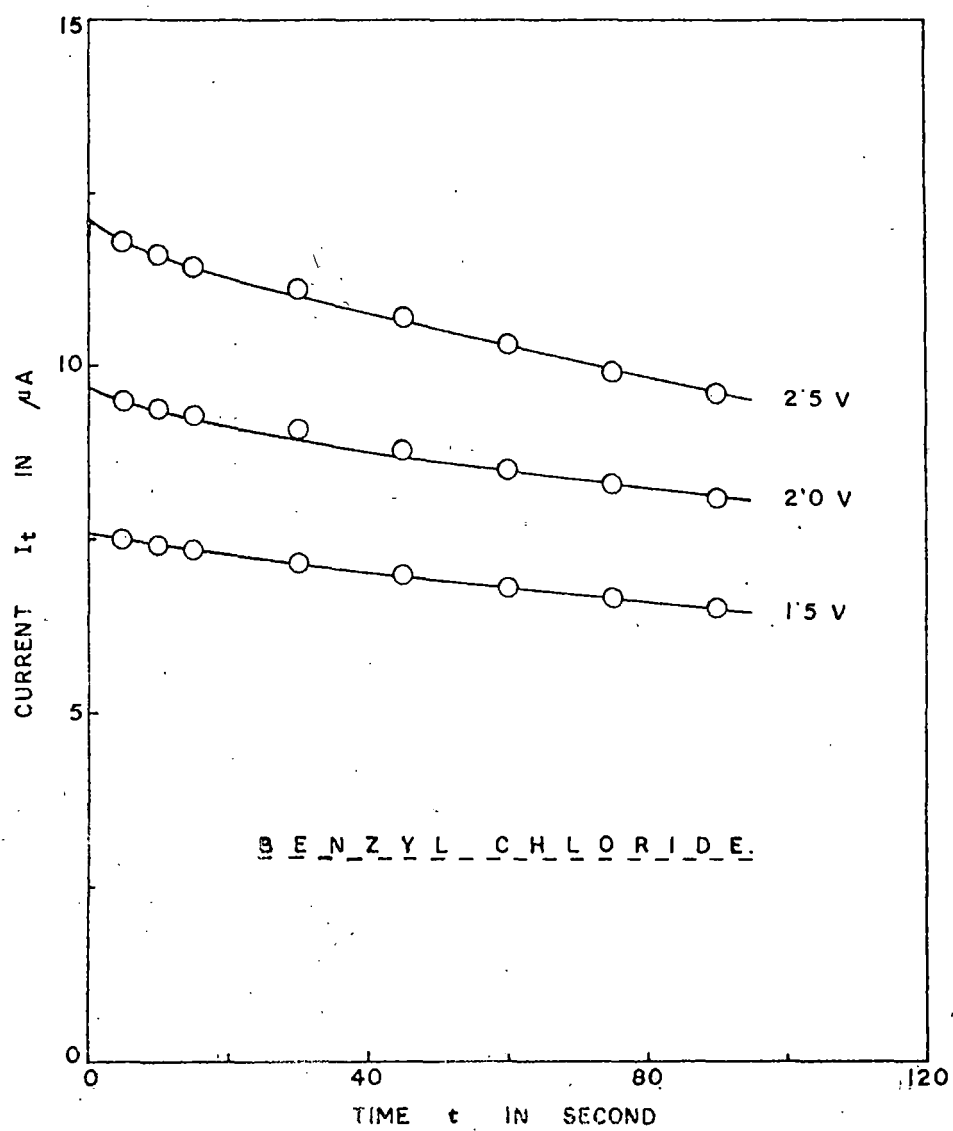


FIG. 6.6. VARIATION OF CURRENT WITH TIME.

I_0 has been found out from the current time curve extrapolating the curve to $t = 0$. The value of R_0 has been calculated and are entered in the third column of table (6.1). The value is of the same order of magnitude as found in literature and further for each liquid the ohmic resistance is almost the same for different applied voltages thereby showing that ohms law is valid for these polar liquids specially for low applied voltages.

Due to application of external voltage V_0 as the ions accumulate near the electrode, a capacitance say C will be formed and if V_0 and V_f represent the voltage developed across the condenser at time t and its saturation value respectively then the final saturation current I_F is given by

$$I_F = \frac{V_0 - V_F}{R_0} \quad \dots (6.2)$$

and it has been deduced by Sen and Ghosh (1975) that

$$\log_e \frac{I_t [I_0 - I_F]}{I_0 [I_t - I_F]} = \lambda t \quad \dots (6.3)$$

I_t is the current at time t , λ is given by the relation

$$\lambda = b \left[V_0 - \frac{1}{\alpha} \right] \quad \dots (6.4)$$

where $b = \frac{\mu}{a^2}$ and $\frac{1}{\alpha} = V_F$, μ being the ionic mobility in the liquid and 'a' is the distance between the electrodes. In order to determine I_F in equation (6.2), the values of current I_t have been plotted against some values of $1/t$ when the current appears to approach the saturation value and the intercept of the curve for $1/t = 0$ is taken as I_F . The value of $V_0 - V_F$ has been calculated from equation (6.2) and are placed in the fourth column of the table. From equation (6.3) it is observed that when $\log_e \frac{I_t [I_0 - I_F]}{I_0 [I_t - I_F]}$ is plotted against t , the curve should be a straight line passing through the origin and with a slope equal to λ . Figure (6.7) to (6.11) shows such curves for each liquid studied and for different initial applied voltages which definitely established the validity of equation (6.3). The value of λ has been calculated and are entered in the fifth column of the table. As $(V_0 - 1/\alpha)$ i.e. $(V_0 - V_F)$ is known, the value of b and hence μ has also been calculated for each liquid and for different initial applied voltages and are placed in sixth and seventh columns of the table. Lastly the number of ions per c.c. 'n' present in the liquid has been evaluated from the relation $n = \frac{a}{R_0 \mu e S}$ as deduced by Sen and Ghosh (1975) where e is the electronic charge, S is the cross-sectional area of the electrode. The values are placed in the last column of the table. It is observed from the table that though the number of free ions varies in different liquids, the order of mobility of the liquids is the same and is of the same order as that of weak

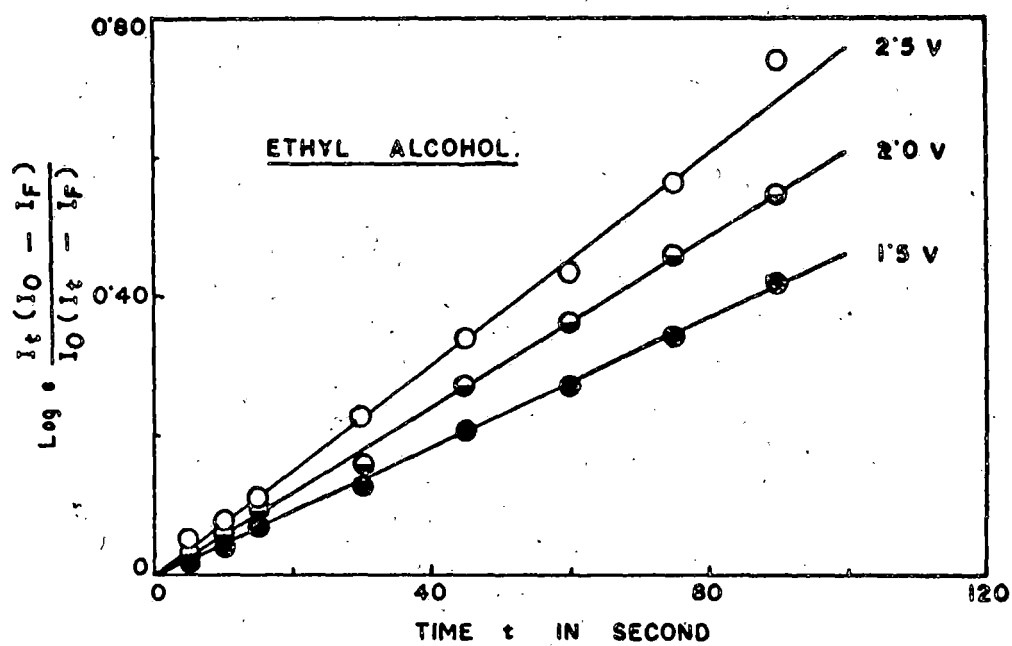


FIG. 6.7. VARIATION OF $\text{Log } \frac{I_t(I_0 - I_F)}{I_0(I_t - I_F)}$ WITH TIME.

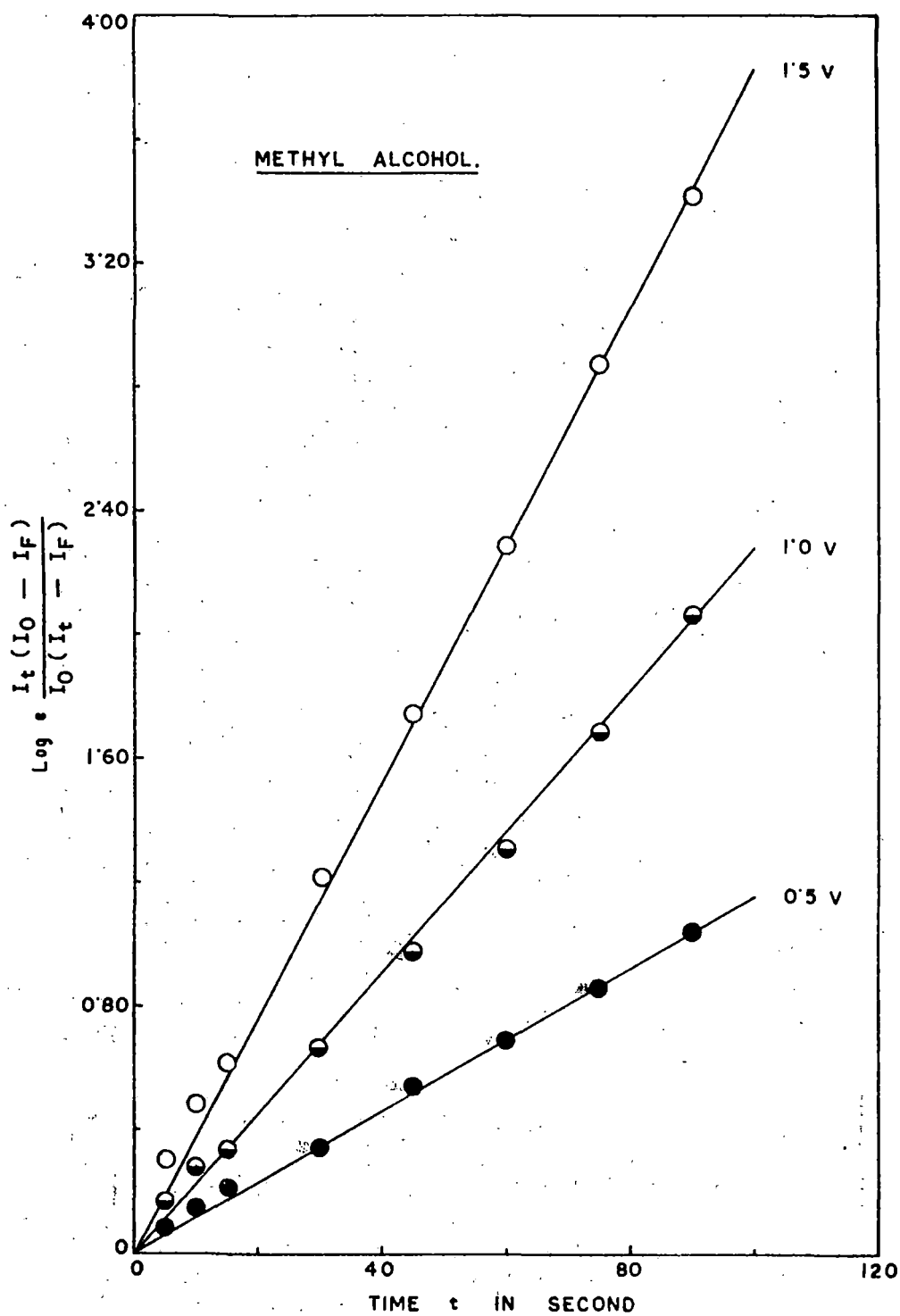


FIG. 6.8. VARIATION OF $\text{Log} * \frac{I_t (I_0 - I_F)}{I_0 (I_t - I_F)}$ WITH TIME.

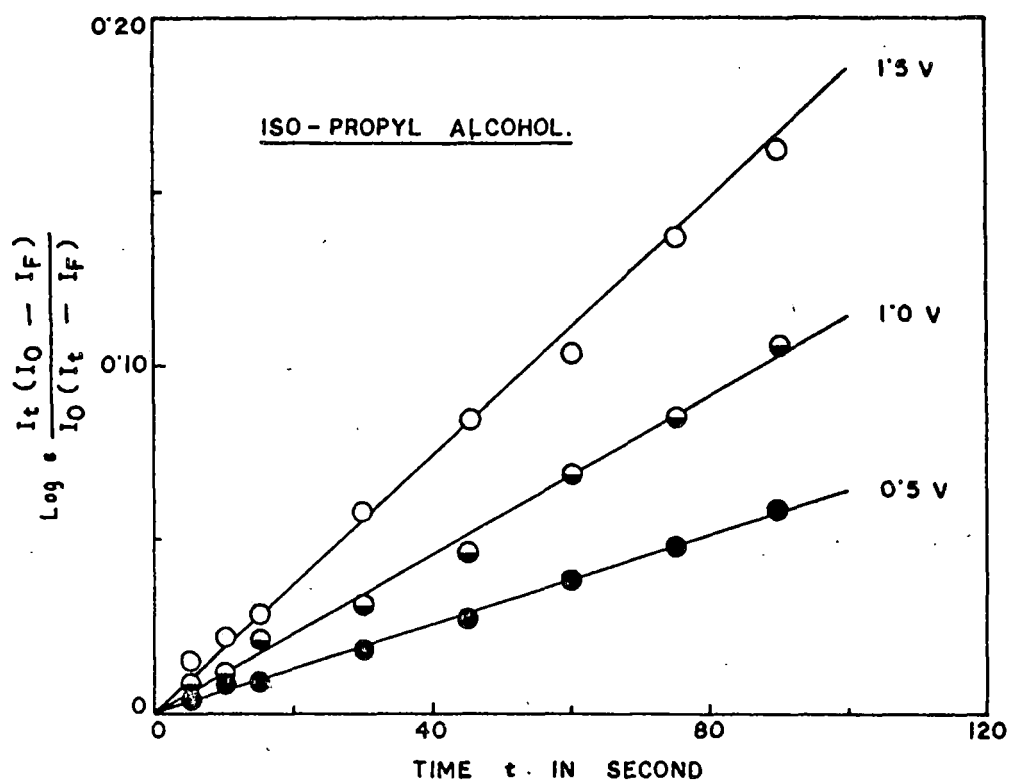


FIG. 6.9. VARIATION OF $\text{Log} \cdot \frac{I_t(I_0 - I_F)}{I_0(I_t - I_F)}$ WITH TIME.

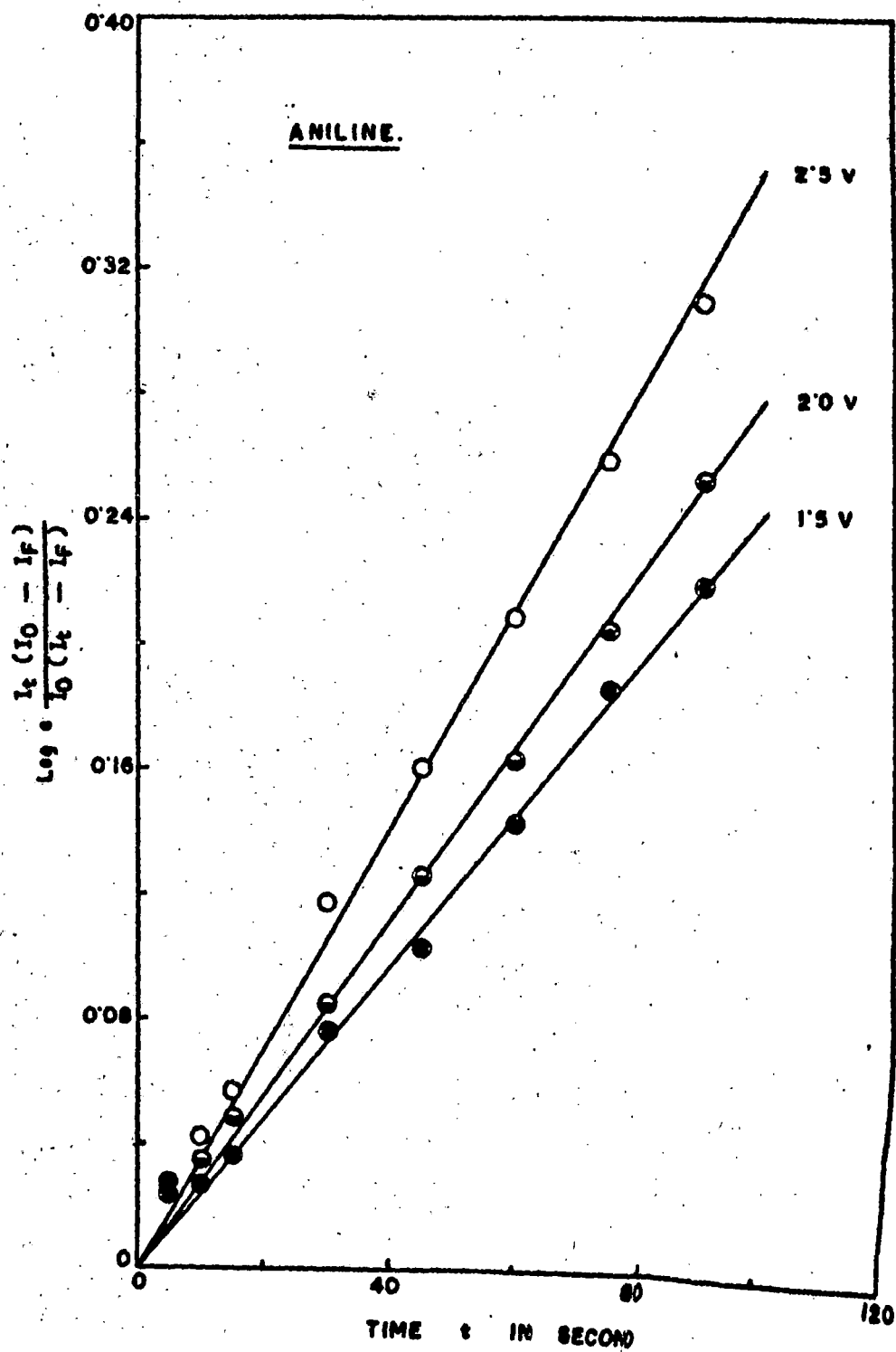


FIG. 6.10. VARIATION OF $\text{Log} \frac{I_t(I_0 - I_F)}{I_0(I_t - I_F)}$ WITH TIME.

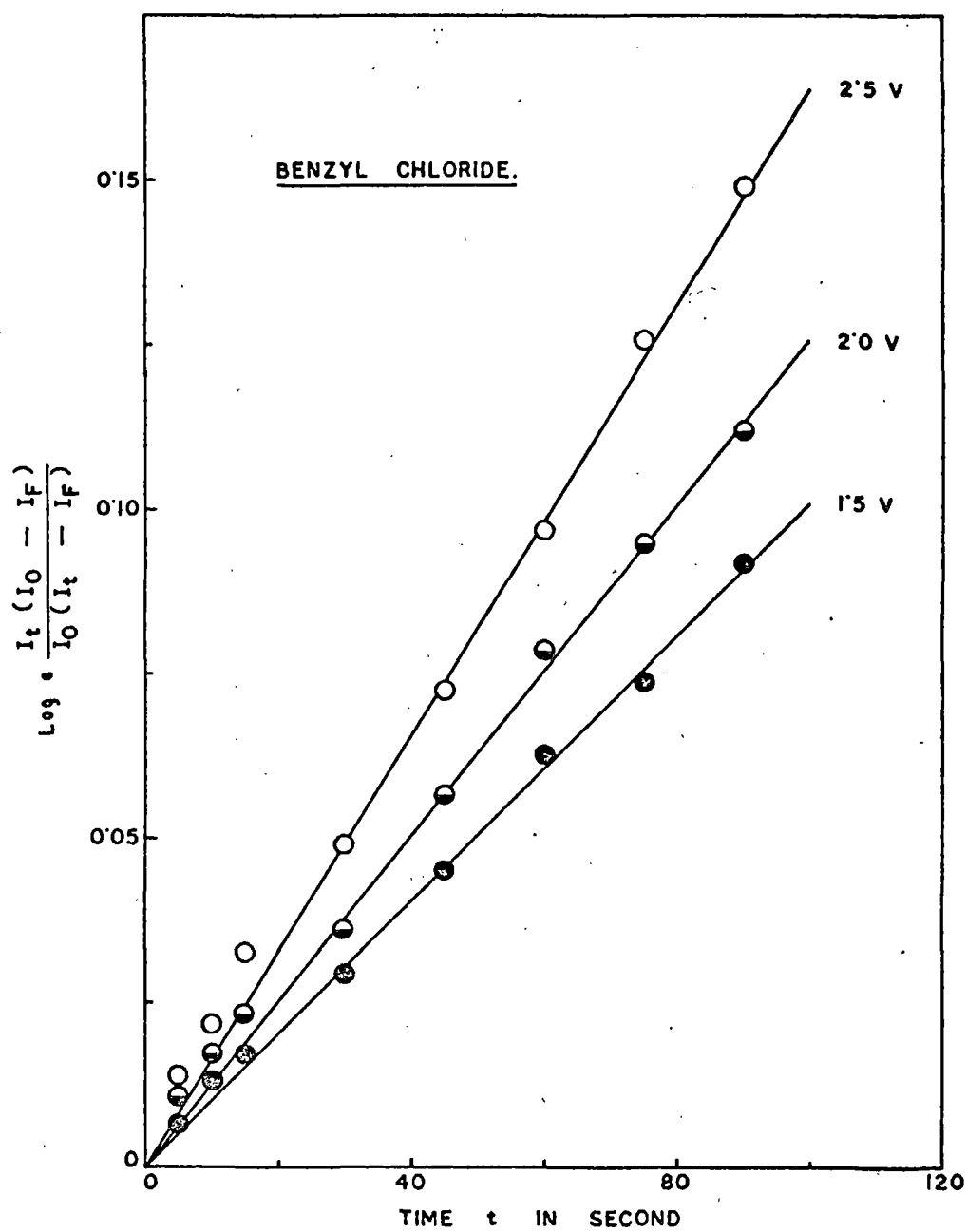


FIG. 6.11. VARIATION OF $\text{Log } \frac{I_t(I_0 - I_F)}{I_0(I_t - I_F)}$ WITH TIME.

electrolytes (Glasstone, 1942). Adamczewski (1969) has reported the ionic mobilities in pure nonpolar liquids such as hexane, heptane, nonane and their mixtures and the value in all the cases is of the order of $7.2 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ to $5.8 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The value of μ^+ in case of nitrobenzene has been previously reported by Gaspard and Gosse (1970) as $2.4 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. In liquid anthracene, it has been reported by Krause (1976) that the electric current is mainly caused by ions which have mobilities $12 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 22°C . Wollers (1973) has reported the mobility of negative charge carriers in benzene as $5 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ whereas Kleinheins (1970) found that positive charge carriers could be injected into liquid benzene the mobility of which is about $7 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature. Recently while studying the electroviscous effect of tetra-butyl ammonium bromide in benzene and Silver perchlorate in benzene, Monda et al (1979) found that the mean ionic mobility in the solution becomes $1.3 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $4.5 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ respectively. Thus it is evident that in case of weak electrolytes or non-polar or polar liquids though the number of ions varies, the order of mobility is the same. Of course Allen and Holroyd (1974) have found the electronic mobility of pentane and hexane of the order of $10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ respectively at room temperature whereas Bakale and Schmidt (1973) have found the ionic mobility of methane at 137°K as

$4.3 \times 10^{-3} \text{ cm}^2 \text{ v}^{-1} \text{ s}^{-1}$. While studying the Kerr effect in nitrobenzene it has been found by Chong et al (1958) that assuming the movement of positive ions to be responsible for field distortion the mobility of the ions is found to be of the order of $10^{-3} \text{ cm}^2 \text{ v}^{-1} \text{ s}^{-1}$. It is also observed from the table that the value of n varies from 10^{14} to 10^{16} per c.c. which is in close agreement with the results obtained by Sen and Ghosh (1975) and also with that of Lohneysen and Nagerl (1971) who obtained the value of n as 2.8×10^{16} per c.c. in case of benzyl alcohol.

It is thus evident that radio frequency conductivity measurements as well as temporal variation of d.c. current in polar liquids definitely indicate that free ions are present in these liquids and it has been possible by the development of a theoretical analysis to calculate the mobility as well as the free ion density. The results thus provide us with data regarding the measurement of imperfection in these polar dielectrics.

Table 6.1

Temp. = 28.9°C

Liquid	App- lied vol- tage in Volts	Resis- tance R ₀ in ohms x 10 ⁻⁶	V ₀ -V _F in volts	λ	b	Mobility	
			μ in cm ² V ⁻¹ S ⁻¹ x 10 ⁴			Ions/cc n	
	2.5	1.2500	0.7500	7.60×10^{-3}	1.013×10^{-2}	4.902	4.572×10^{14}
Ethyl Alcohol	2.0	1.3793	0.6207	6.10×10^{-3}	0.983×10^{-2}	4.757	4.265×10^{14}
	1.5	1.3636	0.4364	4.60×10^{-3}	1.054×10^{-2}	5.101	4.027×10^{14}
Methyl Alcohol	1.5	0.0750	1.1100	3.82×10^{-2}	3.441×10^{-2}	16.650	2.243×10^{15}
	1.0	0.0741	0.6592	2.30×10^{-2}	3.489×10^{-2}	16.890	2.239×10^{15}
	0.5	0.0741	0.3037	1.16×10^{-2}	3.820×10^{-2}	18.490	2.045×10^{15}
Iso-propyl Alcohol	1.5	0.1163	0.4071	1.86×10^{-3}	4.569×10^{-3}	2.221	1.090×10^{16}
	1.0	0.1220	0.2440	1.14×10^{-3}	4.672×10^{-3}	2.261	1.016×10^{16}
	0.5	0.1220	0.1281	0.64×10^{-3}	4.996×10^{-3}	2.418	0.949×10^{16}
Aniline	2.5	0.3289	0.9867	3.52×10^{-3}	3.567×10^{-3}	1.726	4.922×10^{15}
	2.0	0.3333	0.7999	2.79×10^{-3}	3.488×10^{-3}	1.688	4.972×10^{15}
	1.5	0.3409	0.6477	2.42×10^{-3}	3.736×10^{-3}	1.808	4.539×10^{15}
Benzyl Chloride	2.5	0.2066	0.8677	1.64×10^{-3}	1.890×10^{-3}	0.914	1.483×10^{16}
	2.0	0.2062	0.7011	1.26×10^{-3}	1.797×10^{-3}	0.869	1.560×10^{16}
	1.5	0.1974	0.5132	1.01×10^{-3}	1.968×10^{-3}	0.952	1.490×10^{16}

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Mobility and Free Ion Density from Measurement of Temporal Variation of Current in Polar Dielectrics

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Abstract : The temporal variation of current in polar dielectrics such as ethyl alcohol, methyl alcohol, iso-propyl alcohol, aniline and benzyl chloride has been studied over a small interval of time until the saturation current is reached in each case. Assuming the existence of free ions, the results have been analysed quantitatively utilizing the expression deduced by Sen and Ghosh (1975) and it has been possible to calculate the mobility as well as the number density of free ions. The results provide definite evidence regarding the spontaneous generation of free ions in polar dielectrics.

Introduction : In an ideal dielectric there should be present no free ions or electrons but the experimental determination of radio frequency conductivity of polar liquids by Sen and Ghosh (1974, 1978, 1980 b) and other workers by different methods have shown the presence of free ions in polar dielectrics. Assuming the existence of free ions, Sen and Ghosh (1980 a) have shown that from radio frequency conductivity measurement of a polar solute in nonpolar solvent it is possible not only to calculate the number of ions per c. c. in pure liquid but also the relaxation time of the polar solute molecule. Nico Lau et al (1971) have studied the electrical conductance increase of aliphatic alcohols under the application of alternating current field of 50-600 V/cm. and frequency of 100Hz. in the temperature range 0-97°C. and have shown that increase of alcohols a finite conductivity exists even if extreme care is taken to purify the liquids. When a d-c field is applied to a dielectric liquid which has been carefully purified it is known that initially the current falls rapidly with time and then decreases slowly and later shows generally a tendency of saturation. The decay of current passing through an insulating liquid is assumed to be due to removal or accumulation of ions near the electrodes. Though the cause of generation of ions in both polar and nonpolar liquids has been attributed to various causes, such as cosmic rays, natural radio-activity,

thermal dissociation etc. yet no specific reason has been established regarding the mechanism by which these are produced.

In polar dielectrics natural conduction has been attributed to generation of ions by electrolytic dissociation of impurities. Nikuradse (1932) observed that the conduction current depends upon the purification of the liquid and electrode material. This observation is consistent with that of Hart and Mungall, (1957); Zaky et al (1963), Pravakar Rao and Govinda Raju (1970) and other workers. Blanc et al (1961) found that the rate of decay of current depends upon the impurity present in the liquid and decreased with repeated purification of the liquid. Apart from conductivity due to ions the polar dielectrics have an intrinsic conductivity which may be as suggested by Forster (1964) due to presence of polar impurities or trapped electrons present in the liquid or generated at the electrode surface. Nikuradse (1932) observed that increase of highly purified liquid when all ionizing agents such as X-rays, radio active sources etc. were removed it was found that there still exists a residual conductivity. As the conductivity of the liquid has been found to depend on the nature of electrodes it can be presumed that electrons are emitted from the electrode surface and contribute to residual conductivity. Baker and Boltz (1937) interpreted their

results as due to thermionic emission from cathode combined with Schottky effect. This has been criticised by LePage and Dubridge (1940) who concluded that the current is due to field-enhanced thermionic emission. Eck (1949) showed that in case of a d. c. field, variation of current 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 current and k is a constant which contains the ionic mobility term and he assumed that the decay of current was due to initial existence of large ionic clusters in the body of the liquid which gradually disperse. Utilising 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. Further it has been observed by Adamczewski and his co-workers (1969) that in case of saturated hydrocarbon which are nonpolar the variation of current with time could be represented by

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

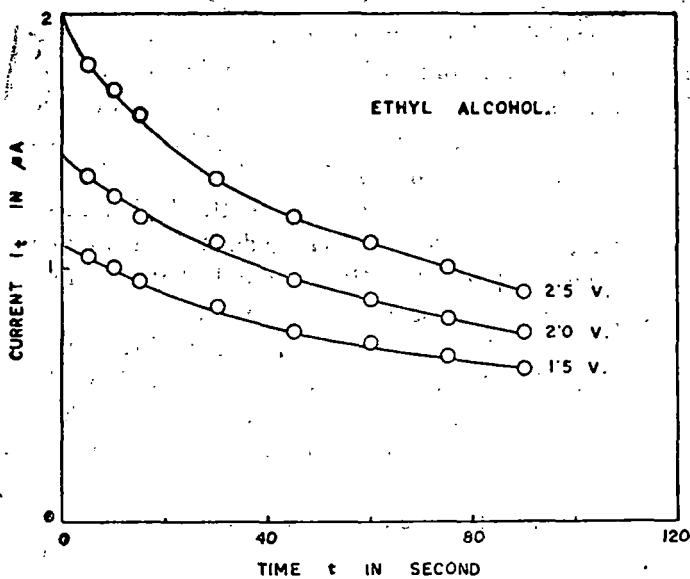


FIG. 1.

Variation of current with time (Ethyl Alcohol)

where I_0 denotes the initial current and λ is a constant containing mobility factor. Gaspard and Goose (1970) gave clear evidence of ionic conduction in polar dielectrics. Similar effect has been observed by Standhammer

and Seyer (1957) who investigated the problem in cyclohexane and in cyclohexane saturated with water.

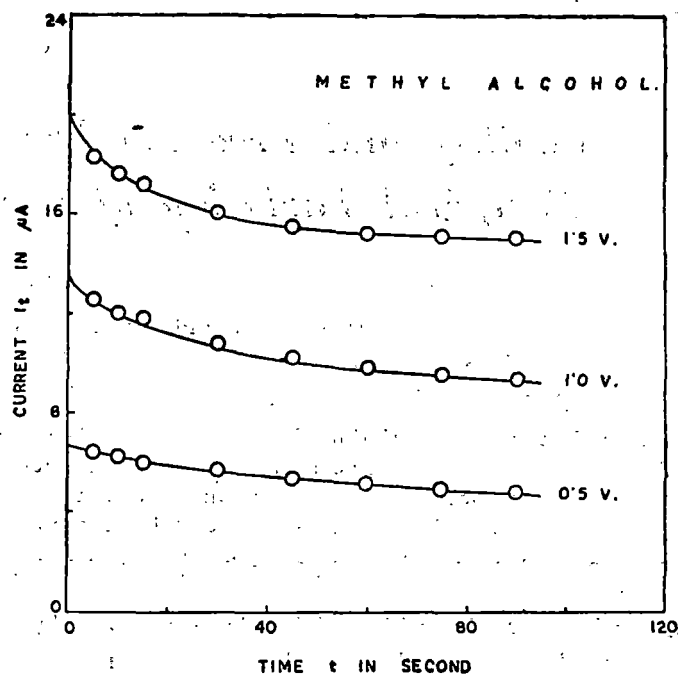


FIG. 2.

Variation of current with time (Methyl Alcohol)

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. Although the mechanism of charge transport in dielectric liquids has been investigated for many years, it is only during about last ten years that significant progress has been achieved, the remarkable of which are due to Kleinheins (1970), Schmidt and Allen (1970), Wollers (1973), Bakale and Schmidt (1973), Allen and Holryd (1974), Blair and Tredgold (1974), Bickert et al (1976), Krause (1976), Adamczewski and Calderwood (1976, 1977), Adamec and Calderwood (1978) in the study of the behaviour of fast charge carriers and electronic mobility specially in non-polar dielectrics with the exception of a few works in polar liquids by other authors. Considering all the experimental evidences and assumptions taken by various authors we may conclude that liquids whether polar or nonpolar are never free of ions or electrons which may be due to (i) impurities present in liquid (ii) electrolytic dissociation of impurities (iii) thermionic emission from cathode or field-enhanced thermionic emission.

ssion (iv) electro chemical dissociation i.e. dissolution of electrode in liquid which may give rise to injection of electrons and (v) other various factors such as thermal dissociation, cosmic rays, natural conductivity etc. Based on the assumption of the existence of free ions, the time-current curve has been analysed by a number of workers and certain conclusions have been drawn regarding the ionic mobilities and free ion concentrations. Sen and Ghosh (1975) has extended the quantitative theory of Gemant (1940) and explained very satisfactorily the observed variation of current with time which enables us in conjunction with the experimental results to calculate the mobility and charge density of ions. Though the theory has been applied only in case

ral validity of the theory developed by Sen and Ghosh (1975) in order to establish the existence of free ions in polar liquids supported earlier from radio frequency conductivity measurements, (1974, 1978, 1980) and to calculate the mobility and free charge density of ions.

Experimental Arrangement : The schematic diagram of the experimental arrangement, the procedure and the other relevant informations, have been discussed in detail in the previous communication by Sen and Ghosh (1975). The conductivity cell used is a cylindrical glass tube of diameter 2.96 cm. fitted with two circular brass disc of diameter 2.5 cm. and separated by a distance 0.22 cm. The liquids investigated are ethyl alcohol, methyl alcohol, iso-propyl alcohol, aniline and benzyl chloride at room temperature.

Results and Discussion : The variation of current with time has been measured in case of ethyl alcohol, aniline and benzyl chloride for applied voltage of 2.5 volts, 2.0 volts and 1.0 volt, in case of methyl alcohol

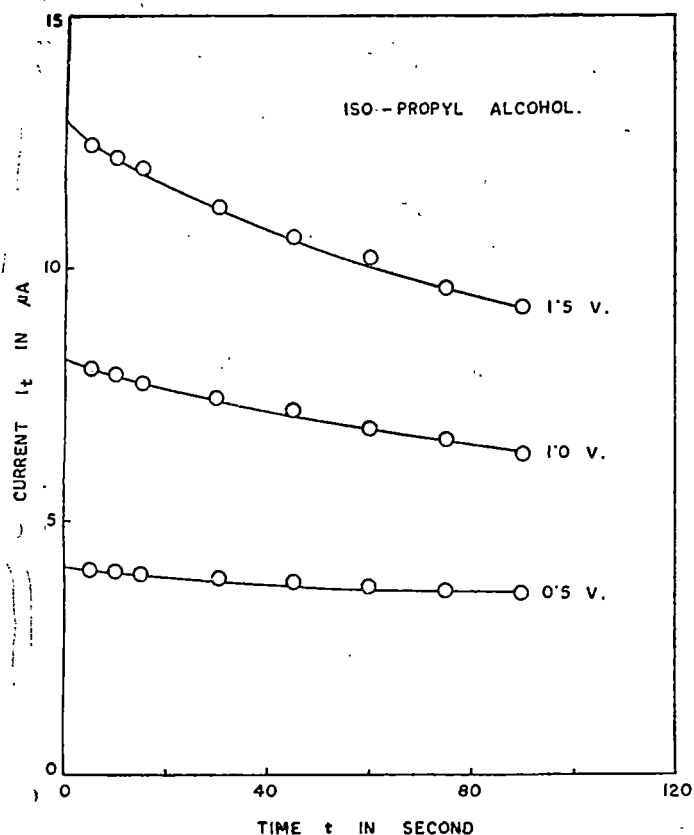


FIG. 3.

Variation of current with time (Iso-propyl Alcohol)

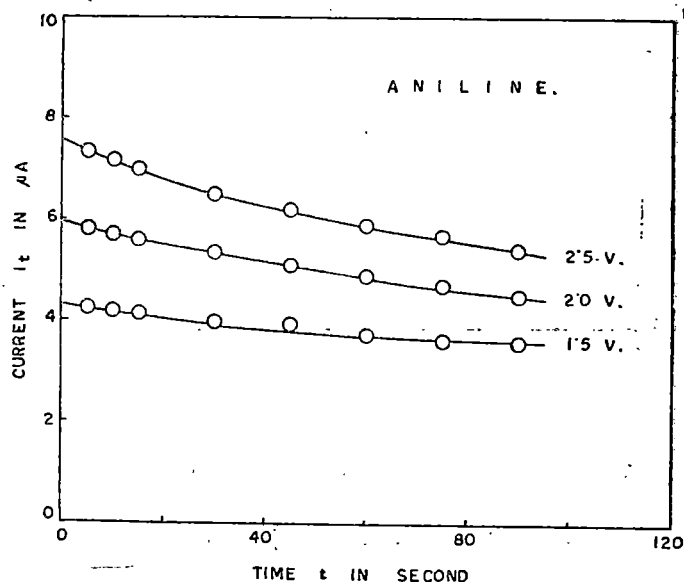


FIG. 4.

Variation of current with time (Aniline)

of five polar liquids where the variation of current has been noted for a long time, it will be worthwhile to observe whether the same is valid for other polar liquids as well particularly for a small interval of time. The purpose of the present paper is thus to observe the gene-

and iso-propyl alcohol for applied voltage of 1.5 volts, 1.0 volt and 0.5 volt respectively. The results are plotted in figs 1 to 5. The nature of variation of current with time and rate of decay of current with applied voltage are in close agreement with the results of previous

workers. The applied voltage has been kept low so that current-voltage characteristics obeys ohms law and in order to prevent dissociation of molecules. 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 char-

I_0 has been found out from the current-time curve extrapolating the curve to $t=0$. The value of R_0 has been calculated and are entered in the third column of the table 1. The value is of the same order of magnitude as found in literature and further for each liquid the ohmic resistance is almost the same for different applied voltages thereby showing that ohms law is valid for these polar liquid specially for low applied voltages.

Due to application of external voltage V_0 as the ions accumulate near the electrode, a capacitance say C will be formed and if V_0 and V_f represent the voltage developed across the condenser at time t and its saturation value respectively then the final saturation current I_f is given by

$$I_f = \frac{V_0 - V_f}{R_0} \quad (2)$$

and it has been deduced by Sen and Ghosh (1975) that

$$\log_e \frac{I_t [I_0 - I_f]}{I_0 [I_t - I_f]} = \lambda t \quad (3)$$

I_t is the current at time t , λ is given by relation

$$\lambda = b \left[V_0 - \frac{1}{\alpha} \right] \quad (4)$$

where $b = \mu/a^2$ and $1/\alpha = V_f$, μ being the ionic mobility in the liquid and 'a' is the distance between the elec-

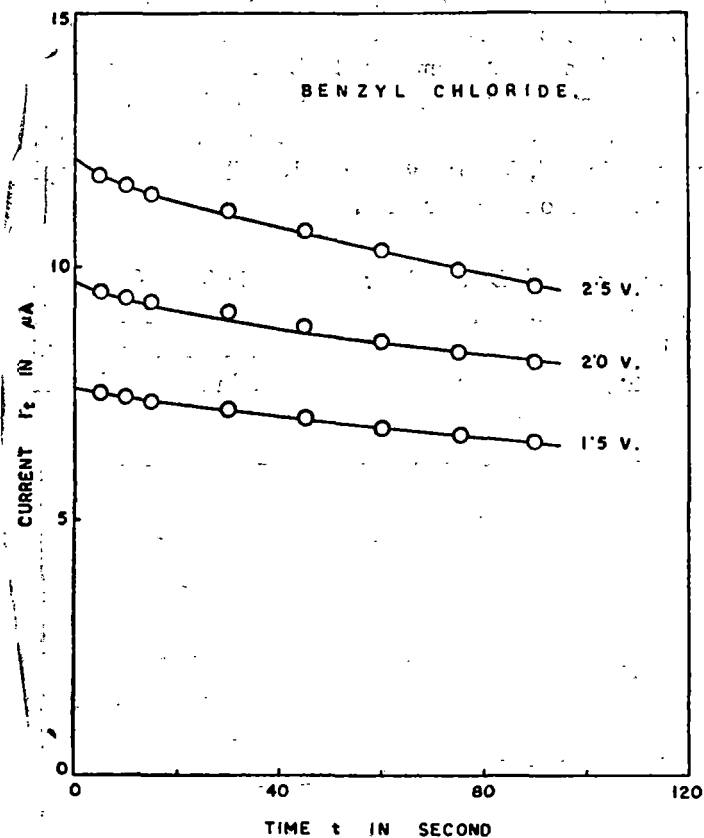


FIG. 5.

Variation of current with time (Benzyl Chloride)

ges accumulate in the condenser the opposing voltage increases though not linearly and the 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.

If V_0 is the applied voltage, R_0 is the ohmic resistance of the liquid then the initial current I_0 is given by

$$I_0 = \frac{V_0}{R_0} \quad (1)$$

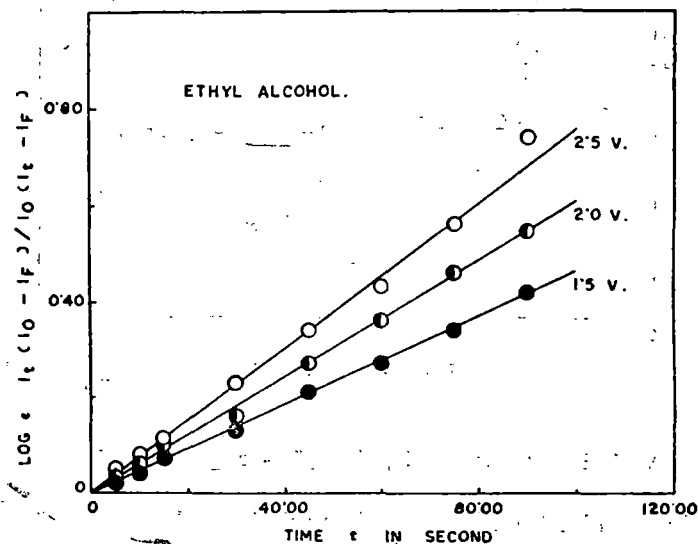


FIG. 6.

 Variation of $\log_e \frac{I_t [I_0 - I_f]}{I_0 [I_t - I_f]}$ with time (Ethyl Alcohol)

trodes. In order to determine I_f in eqn. (2) the values of current I_t have been plotted against some values of $1/t$ when the current appears to approach the saturation value and the intercept of the curve for $1/t=0$ is taken as I_f . The value of $V_o - V_f$ has been calculated from eqn. (2) and are placed in the fourth column of the table. From eqn. (3) it is observed that when $\log_e \frac{I_t [I_o - I_f]}{I_o [I_t - I_f]}$ is plotted against t , the curve should be a straight line passing through the origin and with a slope equal to λ . Fig. 6 to 10 shows such curves for each liquid studied and for different initial applied voltages which definitely established the validity of eqn. (3). The value of λ has been calculated and are entered

in the fifth column of the table. As $(V_o - 1/\alpha)$ i. e. $(V_o - V_f)$ is known, the value of b and hence μ has also been calculated for each liquid and for different initial applied voltage and are placed in sixth and seventh columns of the table. Lastly the number of ions per c.c. 'n' present in the liquid has been evaluated from the relation $n = \frac{a}{R_o \mu e s}$ as deduced by Sen and Ghosh (1975 where e is the electronic charge, S is the cross-sectional area of the electrode. The values are placed in the last column of the table. It is observed from the table though the number of free ions varies in different liquids, the order of mobility of the liquids is the same and is of the same order as that of weak electrolytes (Glasstone, 1942). Adamczewski (1969) has reported the ionic mobilities in pure nonpolar liquids such as hexane, heptane, nonane and their mixtures and the value in all the cases is of the order of $7.2 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$ to $5.8 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$. The value of μ^+ in case of nitrobenzene has been previously reported by Gaspard and Gosse (1970) as $2.4 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$. In liquid anthracene, it has been reported by Krause (1976) that the electric current is mainly caused by ions which have mobilities $1.2 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$ at 220°C . Wollers (1973) has reported the mobility of negative charge carriers in benzene as $5 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$ whereas Kleinheins (1970) found that positive charge carriers could be injected into liquid

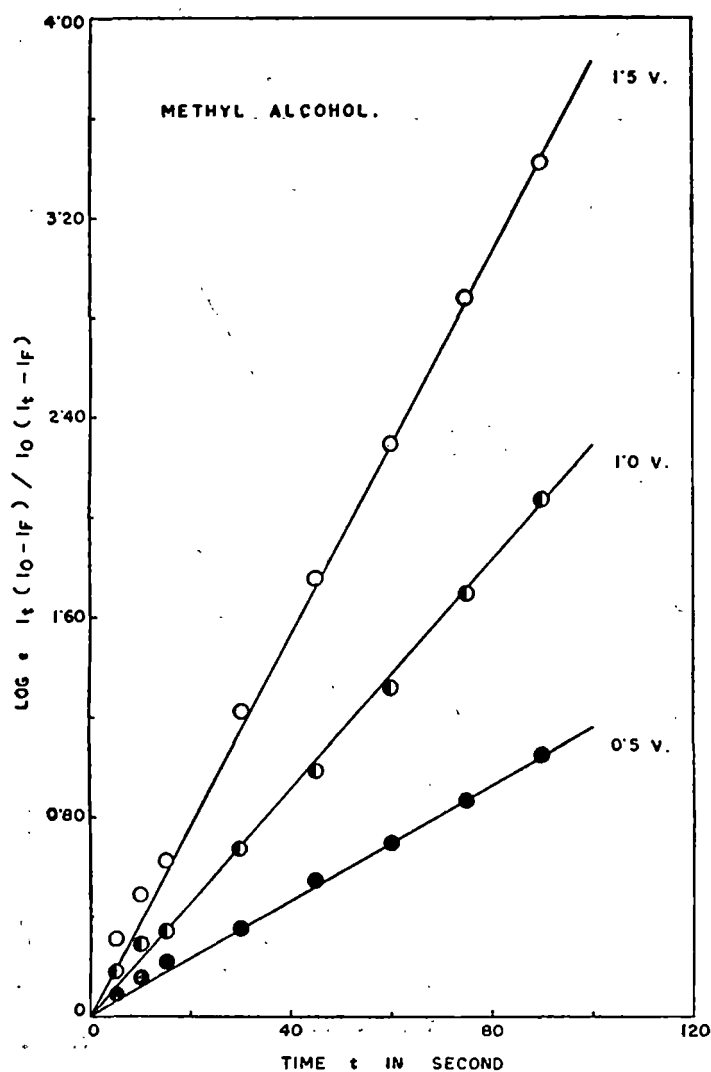


FIG. 7.

Variation of $\log_e \frac{I_t [I_o - I_f]}{I_o [I_t - I_f]}$ with time (Methyl Alcohol)

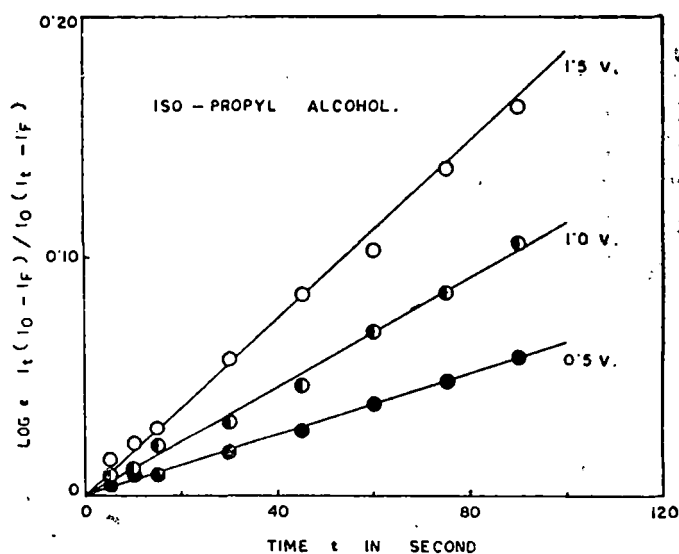


FIG. 8.

Variation of $\log_e \frac{I_t [I_o - I_f]}{I_o [I_t - I_f]}$ with time (Iso-propyl Alcohol)

benzene the mobility of which is about $7 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$ at room temperature. 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 $1.3 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$ and $4.5 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$ respectively. Thus it is evident that in case of weak electrolytes or nonpolar or polar liquids though the number of ions varies, the order of mobility is the same. Of course Allen and Holroyd (1974) have found the electronic mobility of pentane and hexane of the order of $10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$ and $10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$ respectively at room temperature whereas Bakale and Schmidt (1973) have found the ionic mobility of methane at 137°K as $4.3 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$. While studying the Kerr effect in nitrobenzene it has been found by Ch-

ong et al (1958) that assuming the movement of positive ions to be responsible for field distortion the mobility of the ions is found to be of the order of $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$. It is also observed from the table that the value of n varies from 10^{14} to 10^{16} per c.c. which is in close agreement with results obtained by Sen and Ghosh (1975) and also with that of Lohneysen and Nageral (1971) who obtained the value of n 2.8×10^{16} per c.c. in case of benzyl alcohol.

It is thus evident that radio frequency conductivity measurements as well as the temporal variation of d.c. current in polar molecules definitely indicate that free ions are present in these liquids and it has been possible by the development of a theoretical analysis to calculate the mobility as well as the free ion density. The results thus provide us with data regarding the measure of imperfection in these polar dielectrics.

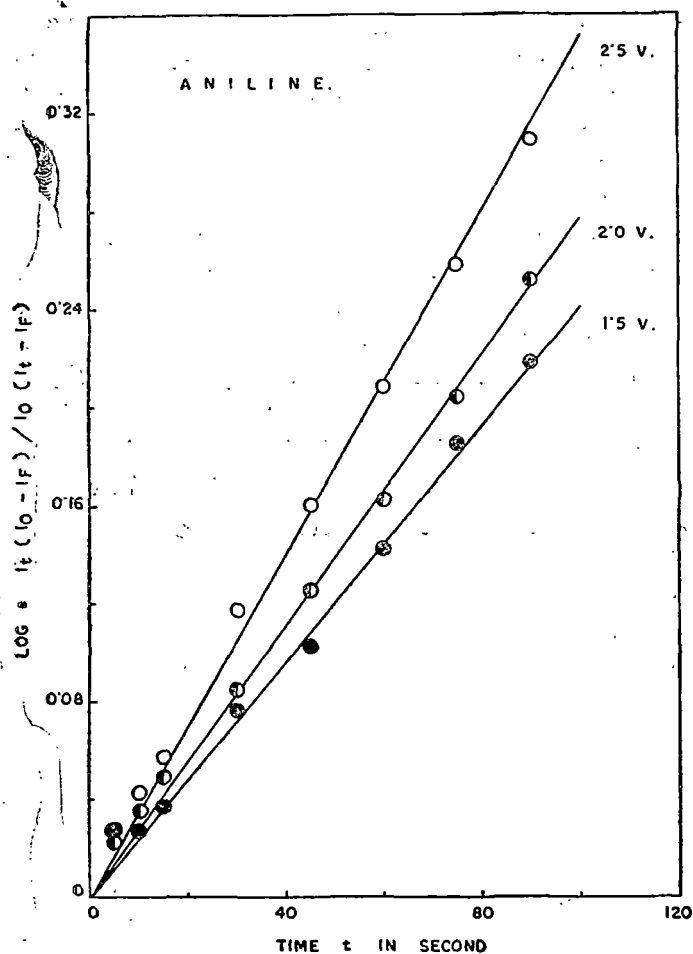


FIG. 9.

Variation of $\log e \frac{I_t [I_0 - I_F]}{I_0 [I_t - I_F]}$ with time (Aniline)

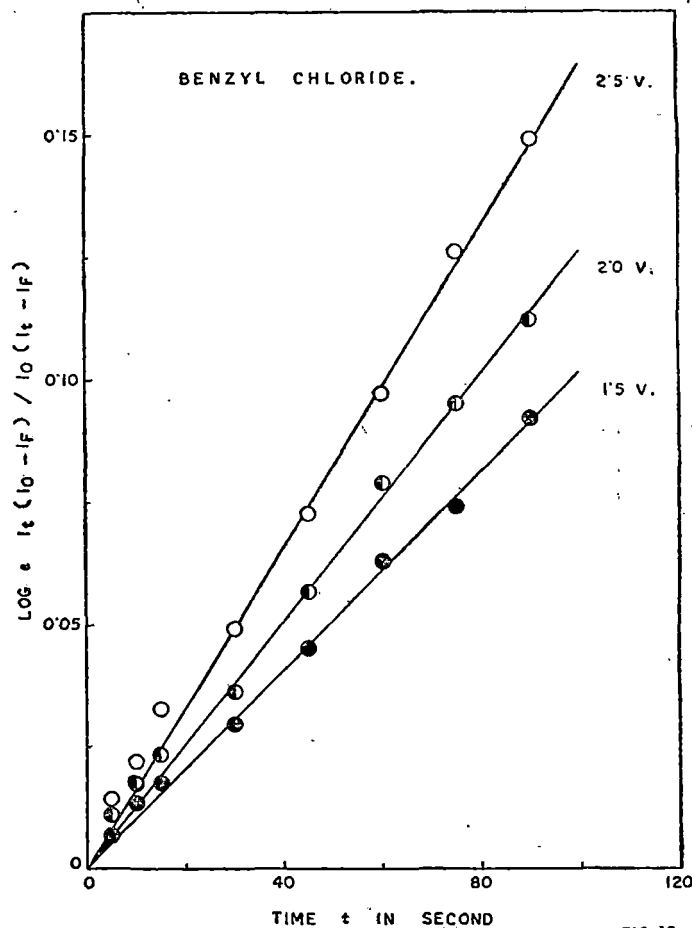


FIG. 10.

Variation of $\log e \frac{I_t [I_0 - I_F]}{I_0 [I_t - I_F]}$ with time (Benzyl Chloride)

Knowledge : The author is indebted to Prof. S. N. Sen, Senior Professor and Head of the Department Physics, NBU for his kind interest and guidance during the progress of the work.

TABLE I

Temperature 28.9°C.

Liquid	Applied voltage in volts	Resistance R_0 in ohms $\times 10^{-6}$	$V_0 - V_f$ in volts	λ	b	Mobility μ $\text{cm}^2\text{V}^{-1}\text{Sec}^{-1} \times 10^4$	Ions/cc n
Ethyl Alcohol	2.5	1.2500	0.7500	7.60×10^{-8}	1.013×10^{-3}	4.902	4.572×10^{14}
	2.0	1.3793	0.6207	6.10×10^{-8}	0.983×10^{-3}	4.757	4.265×10^{14}
	1.5	1.3636	0.4364	4.60×10^{-8}	1.054×10^{-3}	5.101	4.027×10^{14}
Methyl Alcohol	1.5	0.0750	1.1100	3.82×10^{-8}	3.441×10^{-3}	16.650	2.243×10^{15}
	1.0	0.0741	0.6592	2.30×10^{-8}	3.489×10^{-3}	16.890	2.239×10^{15}
	0.5	0.0741	0.3037	1.16×10^{-8}	3.820×10^{-3}	18.490	2.045×10^{15}
Iso-propyl Alcohol	1.5	0.1163	0.4071	1.86×10^{-8}	4.569×10^{-3}	2.221	1.090×10^{16}
	1.0	0.1220	0.2440	1.14×10^{-8}	4.672×10^{-3}	2.261	1.016×10^{16}
	0.5	0.1220	0.1281	0.64×10^{-8}	4.996×10^{-3}	2.418	0.949×10^{16}
Aniline	2.5	0.3289	0.9867	3.52×10^{-8}	3.567×10^{-3}	1.726	4.922×10^{15}
	2.0	0.3333	0.7999	2.79×10^{-8}	3.488×10^{-3}	1.688	4.972×10^{15}
	1.5	0.3409	0.6477	2.42×10^{-8}	3.736×10^{-3}	1.808	4.539×10^{15}
Benzyl chloride	2.5	0.2066	0.8677	1.64×10^{-8}	1.890×10^{-3}	0.914	1.483×10^{16}
	2.0	0.2062	0.7011	1.26×10^{-8}	1.797×10^{-3}	0.869	1.560×10^{16}
	1.5	0.1974	0.5132	1.01×10^{-8}	1.968×10^{-3}	0.952	1.490×10^{16}

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CHAPTER VII

RADIO FREQUENCY CONDUCTIVITY OF OPALESCENT BINARY LIQUID MIXTURES.

INTRODUCTION

Recently much effort has been made both theoretically and experimentally to study the dielectrical behaviour such as relaxation process and transport phenomena near the critical temperature of binary liquid mixtures. Although Semenchenko's treatment (1951) on the basis of thermodynamical considerations predicts a large increase of ϵ' , the real part of the dielectric constant at the critical solution temperature, the experimental evidence is meager and frequently contradictory. Arkhangelskii 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. Similar results have been reported by Quinn and Smyth (1963). Piekara (1932) observed that in case of nitrobenzene - hexane system at the critical temperature ϵ' increased with decreasing temperature and the derivative $\frac{d\epsilon'}{dt}$ was not constant near the critical temperature. Similar results have been reported by Konecki (1978) recently. Although there are some contradictory results regarding the sharp increase of ϵ' in the opalescent state it has however been conclusively shown by different workers (Reed and Taylor, 1959; Chynoweth and Schenieder, 1951; Schmidt et al 1959; Yang and Weeks 1971) experimentally that there is a sharp rise in the

coefficient of viscosity and ultrasonic absorption near the critical temperature. 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. It was shown by Krishnan (1935) that the depolarization factor observed in the light scattered transversely by opalescent binary liquid mixtures 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 the clear solution the scattering is due to single molecules whereas in case of opalescent mixtures it is due to cluster of molecules. 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 the 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 the critical stage is not due to formation of cluster of molecules as

proposed by Krishnan. The same conclusion has been arrived by Lubezky and McInlosh (1974) though on different grounds. Sen and Ghosh (1972) have also applied Fixman's theory in order to calculate the internal frictional constant β and found a good agreement with the literature value. Though Fixman's theory has been applied only in two systems by Sen and Ghosh (1972) more investigation is necessary to verify the theory in explaining the experimental results in the radio frequency conductivity measurement. The object of the present work is to extend the investigations to a number of other binary opalescent mixtures.

- (a) to observe whether the intense density fluctuation is due to formation of clusters of molecules in the critical state
- (b) to verify Fixman's theory in case of other opalescent mixtures and
- (c) to observe whether the internal frictional term β changes for a particular polar solute in different nonpolar solvents, which may throw some light regarding the nature of β , the internal friction constant introduced by Fixman. For this purpose the measurement of radio frequency conductivity has been carried out in case of three opalescent binary mixtures viz. methyl alcohol + n-hexane, methyl alcohol + carbon disulphide and methyl alcohol + cyclohexane under the application of a radio frequency field of 400 KHz.

EXPERIMENTAL ARRANGEMENT

The method that has been used here is the same as the variation of resonance method of measuring dielectric constant which has been described earlier in chapter II. The block diagram of the experimental arrangement and the theory of the method of measurement has been described in detail. The dielectric cell used is a cylindrical glass tube of diameter 2.62 cm. fitted with two circular gold electrodes 1.08 cm. apart. Each gold plate is connected with a platinum wire which is sealed with the glass tube. The dielectric cell is fitted in parallel to the tuning condenser of the secondary circuit. The resonant currents I_1 and I_2 in the r.f. meter and the corresponding tuning capacitances C_1 and C_2 are noted. I_1 being the r.f. current when the cell is empty and I_2 being the r.f. current when the cell is filled with the liquid. The capacitances of the tuning condenser corresponding to $\frac{1}{\sqrt{2}}$ i.e. 70.7% of I_1 (on either side of the resonance value) are also noted. From these measurements, the real part of radio frequency conductivity of the investigated liquids has been calculated. The mixture studied here are methyl alcohol + n-hexane, methyl alcohol + carbon disulphide and methyl alcohol + cyclohexane which shows opalescence at 29.5°C, 40.5°C and 45°C respectively. In the three mixtures, methyl alcohol contains 30%, 20% and 26.14% by weight respectively. A well controlled regulated thermostat has been used to keep these mixtures at the temperature of opalescence.

During the experiment, at first the empty cell is placed in the thermostat and the resonant current in the r.f. meter and the corresponding tuning capacity are noted. Next the cell is filled with pure polar liquid and the resonant current and the corresponding capacity are noted at the temperature at which the mixture becomes opalescent. Again the clear solution of the mixture is taken in the cell containing appropriate proportion of polar nonpolar components as is necessary for opalescent mixture and placed in the thermostat at a temperature slightly higher than the temperature of opalescence and resonant current with corresponding capacity are noted. Lastly the resonant current and the corresponding capacity are noted when the mixture becomes opalescent. The same procedure has been followed in all the three mixtures. So as a whole, three sets of separate measurements are made in case of mixtures:

- (a) Measurement of K' for the pure polar liquid at a temperature at which the mixture becomes opalescent.
- (b) Measurement of K' of the clear solution of the mixture containing appropriate proportion of polar-nonpolar components as is necessary to make an opalescent mixture at critical temperature but at a temperature slightly higher than the temperature of opalescence.
- (c) Measurement of K' when the mixture is opalescent.

Following the theory of Murphy and Morgan (1939)

we have

$$K' = \frac{\epsilon'' \omega}{4\pi} \dots (7.1)$$

where K' is the real part of the radio frequency conductivity, ϵ'' the loss factor and ω is the angular frequency of the applied field. In case of polar liquid K' is given by

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

where ϵ_0 and ϵ_∞ are the static and high frequency dielectric constant of the liquid and τ is the time of relaxation. As the frequency at which the radio frequency conductivity has been measured is 400 KHz, $\omega^2 \tau^2 \ll 1$ and hence

$$K' = \frac{1}{4\pi} (\epsilon_0 - \epsilon_\infty) \omega^2 \tau \dots (7.2)$$

In case of polar-nonpolar liquid mixture having

N_2 number of polar solutes per c.c. where $N_2 = \frac{N d_{12}}{M_2} \omega_2$ loss factor ϵ'' is given by Smyth (1955)

$$\epsilon'' = \frac{4\pi N d_{12} \omega_2 \mu^2 (\epsilon_{12} + 2)(\epsilon_{\infty 12} + 2)}{27 M_2 K T (1 + \omega^2 \tau^2)} \omega \tau \dots (7.3)$$

where d_{12} is the density of the solution of weight fraction ω_2 of polar solute having its molecular weight M_2 and dipole moment μ . ϵ_{12} and $\epsilon_{\infty 12}$ are the static and high frequency dielectric constant of the mixture,

τ is the time of relaxation, N the Avogadro number and T is the temperature in absolute scale. ϵ_{∞} may be taken as the square of the refractive index (n_{12}). Considering $\omega^2 \tau^2 \ll 1$, we have from equation (7.1) and (7.3)

$$K' = \frac{4\pi^2 f^2 N \tau \mu^2 d_{12} (\epsilon_{12} + 2)(n_{12}^2 + 2)}{27 M_2 K T} \omega_2 \quad \dots (7.4)$$

Equations (7.2) and (7.4) have been utilized for the determination of time of relaxation in case of polar liquid and the solution respectively.

RESULTS AND DISCUSSION

The experimental values of K' measured at different stage have been entered in the third column of Table (7.1). The time of relaxation calculated from eqns. (7.2) and (7.4) are placed in fourth column of the table. The dielectric constant of the pure liquid and the mixture have been measured by the same apparatus by resonance method. The refractive indices of the solution have been calculated from the relation

$$n_{12} = x_1 n_1 + x_2 n_2$$

where x 's and n 's are the mole fraction and refractive indices of the pure solvent and solute respectively. The mole fraction x_2 of the solute is related to ω_2 by

$$x_2 = \frac{\omega_2 M_1}{\omega_1 M_2 + \omega_2 M_1}$$

The value of η_{12} , the viscosity of the clear solution of the binary mixture have been calculated from the relation $\log \eta_{12} = x_1 \log \eta_1 + x_2 \log \eta_2$ where x 's and n 's are the mole fraction and coefficient of viscosity of the solvent and solute respectively.

It is known that the equation $\tau = \frac{4\pi\eta a^3}{KT}$ can be utilized for calculating the radius of the rotating unit where τ is the relaxation time extrapolated to infinite dilution. However relative change in the value of 'a' can be estimated if we measure τ at two different concentrations. As in this case we have calculated τ from experimental determination of radio frequency conductivity in case of pure liquid as well as when methyl alcohol is dissolved in different nonpolar solvents in the same proportion as is necessary in case of opalescent mixture but at a temperature 1°C above the critical temperature we get

$$\frac{a^3}{a_{12}^3} = \frac{\tau}{\tau+1} \cdot \frac{\eta_{12}}{\eta} \cdot \frac{\tau}{\tau_{12}}$$

where a and a_{12} are the radii of the rotating unit for polar solute and solution respectively. Putting the values in the right hand side we get in case of methyl alcohol and methyl alcohol - n-hexane mixture

$$\frac{a}{a_{12}} = 1.001$$

In case of methyl alcohol - Cs_2 mixture, the ratio $\frac{a}{a_{12}}$ is of the order of 1.303 and methyl alcohol-cyclohexane mixture the ratio is 1.202. Hence it is clear that there is a slight change in the value of the radius of the rotating unit and even at a temperature 1°C higher than that at which opalescence takes place there is no evidence of cluster formation. If it is further assumed that for a change of temperature of 1°C the viscosity of the mixture is the same as that in the critical state even then from the relation

$$\frac{\tau_{\text{clear}}}{\tau_{\text{crit.}}} = \frac{a^3 \cdot T}{a_c^3 (T+1)}$$

it is found putting the value of τ_{clear} and $\tau_{\text{crit.}}$

$$\frac{a}{a_c} = 0.8433$$

where a and a_c are the radius of the rotating unit when the solution is clear and opalescent respectively.

Hence it can be argued that there is no appreciable change in the radius of the rotating unit; otherwise there is no evidence of cluster formation as the temperature for critical opalescence is approached. Similar results have been reported earlier by Sen and Ghosh (1972) in case of nitrobenzene + n-hexane and aniline + cyclohexane mixtures. As the abrupt change of relaxation time when the mixture passes into opalescent stage cannot be explained by the change in the value of radius of the rotating unit, we have to assume that there is a sudden change of viscosity. We have then from the ratio of relaxation times

$$\frac{\eta_c}{\eta_{12}} = \frac{\tau_c \cdot T}{\tau_{12} (T+1)}$$

where η_c and η_{12} are the viscosity at the critical opalescent state and that of mixture which is not opalescent but at a temperature higher by 1°C respectively, τ_c and τ_{12} are the time of relaxation under similar conditions as mentioned above. The value of $\frac{\eta_c}{\eta_{12}}$ have been listed in the sixth column of the table (7.1) which shows that in case of all the mixtures there is an abrupt change of viscosity as the critical temperature is approached. From the theory of Fixman (1962), the increase in viscosity is given by

$$\Delta\eta = \left\{ \frac{m_1 m_2 \Phi_2}{\rho v_1^2 v_2 \Phi_1 (\eta_1 + \eta_2)} \right\} \left\{ \frac{a^{1/2}}{K} \right\} \frac{1}{40} (\beta a^{1/2})$$

where the symbols have been described earlier in chapter I and

$$\left(\frac{\alpha^{1/2}}{R}\right) = \left\{ \frac{V_1}{4\pi\Phi_2} \right\}^{1/2} \left[\left\{ \Phi_1^{-1} - (1 - \bar{m}^{-1}) - \frac{T_c}{T} (1 + \bar{m}^{-1/2})^2 \Phi_2 \right\}^{-1} - \frac{V_2}{V_1} \right]^{1/2}$$

The values of $\frac{m_1 m_2 \Phi_2}{e V_1^2 V_2 \Phi_1 (\eta_1 + \eta_2)}$ and $\frac{\alpha^{1/2}}{R}$ have been calculated and are placed in seventh and eighth column of the table. Since

$$\frac{\Delta\eta}{\eta_{12}} = \frac{\eta_c}{\eta_{12}} - 1$$

putting the experimental values of $\frac{\eta_c}{\eta_{12}}$, the value of $\Delta\eta$ has been calculated and finally assuming $\alpha = 1^\circ\text{A}$ as in Fixman's paper, the internal frictional term β has been calculated and entered in the 9th. column of the table.

When β is calculated from the alternative formula

$\beta = \frac{e}{\mu m_2}$ as has been suggested by Sen and Ghosh (1972), the value becomes equal to 4.407×10^{15} where μ the mobility of hydroxyl ion and in this case is taken as $20.5 \times 10^{-4} \text{ cm/sec.}$ (Glasstone 1962) and $m_2 = M_2/N$ where N is the Avogadro's number. It is observed that the value of β calculated by an independent procedure is of the same order of magnitude as obtained by Fixman's calculation from the experimental results obtained in the previous investigation.

It is observed from table (7.1) column (9) that β varies with the nature of the nonpolar solvent and we get different values of β when the opalescent mixture is made with methyl alcohol as one of the components and hexane, carbon disulphide and cyclohexane as nonpolar components. Fixman in his paper has introduced β as a measure of internal frictional constant. From column (11) of the table it is however noted that the product $\beta \times \frac{\eta_c}{\eta_{12}}$ is almost constant for all the three opalescent mixture studied in the present investigation. Evidently $\frac{\eta_c}{\eta_{12}}$ can be taken as a measure of the screening effect of the surrounding molecules on the resultant internal friction constant.

This method of measuring the radio frequency conductivity enables us to calculate the sharp increase of viscosity when the critical temperature is approached as has been observed by direct experimental measurement of Reed and Taylor (1959) in case of iso-octane perfluorooheptane and that of Yang and Meeks (1971) in case of cyclohexane-Aniline binary liquid systems.

The analysis of the experimental results thus indicates that there is a sharp increase of viscosity as the critical temperature is approached and there is no evidence of cluster formation in the critical opalescent state. The experimental results thus lend support to the theory of Fixman (1962) regarding the sudden increase of viscosity in the critical state.

Table 7.1

Sl. No.	Nature of the liquid state	R.P. conductivity in e.s.u. $\times 10^{-3}$	Relaxation time τ in 10^{11} (sec)	Viscosity of the mixture η_{12} above opalescent temp. (°C)	Value of $\frac{\eta_c}{\eta_{12}}$	Value of $\frac{m_1 m_2 \phi_1}{e v_1^2 v_2 \phi_1 (n_1 + n_2)}$	Value of $\frac{a^{1/2}}{R} \times 10^{12}$	Value of $\beta \times 10^{-15}$	Value of $\beta = \frac{e}{\mu m_2} \beta \times \frac{\eta_c}{\eta_{12}}$	Value of $\beta \times 10^{-15}$
1.	Methyl alcohol at 29.5°C	0.6376	4.159							
	Methyl alcohol at 30% by wt. + n-hexane 70% by wt. at 30.5°C	0.0821	2.727	0.38469	1.6725	0.1695	4.8325	1.264		2.114
	Opalescent mixture at 29.5°C	0.1373	4.561							
	Methyl alcohol at 40.5°C	0.7778	5.073							
2.	Methyl alcohol 20% by wt. + carbon disulphide 80% by wt. at 41.5°C	0.0667	1.829	0.35978	2.4220	0.3066	6.8019	0.981	4.407	2.376
	Opalescent mixture at 40.5°C	0.1616	4.429							
	Methyl alcohol at 45°C	0.8287	5.506							
3.	Methyl alcohol 26.14% by wt. + cyclohexane 73.86% by wt. at 46°C	0.0903	3.862	0.53865	1.6181	0.1895	5.3135	1.323		2.141
	Opalescent mixture at 45°C	0.1462	6.249							

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Radio Frequency Conductivity of Opalescent Binary Liquid Mixtures

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The radio frequency conductivity of three opalescent binary mixtures (methyl alcohol + n-hexane, methyl alcohol + carbondisulphide, methyl alcohol + cyclohexane) have been measured under a radio frequency field of 400 kHz. It has been shown from the simultaneous measurement of rf conductivity of the polar component and that of the binary mixture in the same proportion as is necessary to make an opalescent mixture but at a temperature slightly above the critical temperature, that there is no evidence of cluster formation in the critical state. From the abrupt increase of relaxation time at the critical temperature, the increase of viscosity has been obtained and the value of internal friction constant has been calculated utilizing Fisman's theory. It is shown that the internal friction constant depends upon the nature of the non-polar component of the opalescent mixture.

SEN & GHOSH : rf CONDUCTIVITY OF BINARY LIQUID MIXTURES
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1. Introduction

Recently much effort has been made, both theoretically and experimentally to study such dielectric behaviour as the relaxation process and transport phenomena near the critical temperature of binary liquid mixtures. Although Semenchenko's treatment on the basis of thermodynamical considerations predicts a large increase of ϵ' , the real part of the dielectric constant at the critical solution temperature, the experimental evidence is meager and frequently contradictory. Arkhangelskii and Semenchenko¹ examined a number of polar-non polar systems and found that dielectric constant ϵ' and dielectric loss ϵ'' show a maximum at the critical temperature region. Similar results have been reported by Quinn and Smyth.² Piekara³ observed that in case of nitrobenzene-hexane system at the critical temperature, ϵ' increased with decreasing temperature and the derivative $d\epsilon'/dT$ was not constant near the critical temperature. Similar results have been reported by Konecki⁴ recently. Although there are some contradictory results regarding the sharp increase of ϵ' in the opalescent state it has, however, been conclusively shown by different workers⁵⁻⁹ experimentally that there is a sharp rise in the coefficient of viscosity and ultrasonic absorption near the critical temperature. Fixman¹⁰ explained theoretically the increase of viscosity of critical mixtures near the critical region on the basis of density fluctuations. 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. It was shown by Krishnan¹¹ that the depolarization factor observed in the light scattered transversely by opalescent binary liquid mixtures 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 the clear solution the scattering is due to single molecules whereas in case of opalescent mixtures it is due to cluster of molecules. Sen and Ghosh¹² have measured the rf conductivity in case of two opalescent mixtures (nitrobenzene + n-hexane, aniline + cyclohexane) and found a large increase of rf conductivity at the 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 the critical stage is not due to formation of cluster of molecules as proposed by Krishnan. The same conclusion has been arrived at by Lubazky and McIntosh¹³ though on different grounds. Sen and Ghosh¹² have also applied Fixman's theory in order to calculate the internal frictional constant β and found a good agreement with the literature value. Though Fixman's theory has been applied only in two systems by Sen and Ghosh, more investigation is necessary to verify the theory in explaining the experimental results in the rf conductivity measurement. Hence it was considered desirable to extend the investigations to a number of other binary opalescent mixtures with the following aims in view:

- (a) To observe whether the intense density fluctuation is due to formation of clusters of molecules in the critical state,
- (b) To verify Fixman's theory in case of other opalescent mixtures and
- (c) To observe whether the internal frictional term β changes for a particular polar solute in different non-polar solvents, since this may throw some light regarding the nature of β , the internal friction constant introduced by Fixman.

For this purpose, the measurement of rf conduc-

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study was carried out in case of three opalescent binary mixtures, viz. methyl alcohol + n-hexane, methyl alcohol + carbon disulphide and methyl alcohol + cyclohexane under the application of a rf field of 400 kHz.

1. Experimental Arrangement

The method of determining the rf conductivity has been described in detail in a previous communication by Sen and Ghosh.¹² The dielectric cell used is a cylindrical glass tube of diameter 2.62 cm fitted with two circular gold electrodes 1.08 cm apart. Each gold plate is connected with a platinum wire which is sealed with the glass tube. A constant temperature bath was used to keep the mixtures at the desired temperatures. Following the theory of Murphy and Morgan¹⁴, we have

$$K' = \frac{\epsilon'' \omega}{4\pi} \quad \dots(1)$$

where K' the real part of the rf conductivity, ϵ'' the loss factor and ω the angular frequency of the applied field. In case of polar liquid K' is given by

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

where ϵ_0 and ϵ_∞ are the static and high frequency dielectric constants of the liquid and τ is the time of relaxation. As the frequency at which the rf conductivity has been measured is 400 kHz, $\omega^2 \tau^2 \ll 1$ and hence

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

case of a polar-non-polar liquid mixture having N_1 number of polar solute per cc where $N_1 = (N d_{12} / M_2) \mu_2$, loss factor ϵ'' is given by Smyth¹⁵

$$\epsilon'' = \frac{4\pi N d_{12} \mu_2}{27 M_2 k T} \frac{(\epsilon_0 + 2)(\epsilon_\infty + 2)}{(1 + \omega^2 \tau^2)} \omega \tau \quad \dots(3)$$

where d_{12} is the density of the solution of weight fraction w_2 of polar solute having its molecular weight M_2 and dipole moment μ_2 . The terms ϵ_0 and ϵ_∞ represent the static and high frequency dielectric constants of the mixture, τ is the time of relaxation, N is the Avogadro's number, k the Boltzmann's constant and T the temperature in absolute scale. Value

of ϵ_∞ may be taken as the square of the refractive index (n). Considering $\omega^2 \tau^2 \ll 1$ we have from Eqs. (1) and (3)

$$K' = \frac{4\pi^2 f^2 N \tau n^2 d_{12} (\epsilon_0 + 2)(n^2 + 2)}{2f \cdot M_2 kT} n_2 \quad \dots (4)$$

where $\omega = 2\pi f$. Eqs. (2) and (4) have been utilized for the determination of time of relaxation in case of pure polar liquid and the solution respectively.

Results and Discussions

Three sets of measurements were made in case of mixtures as follows:

- (a) Measurement of K' for the pure polar liquid at a temperature at which the mixture becomes opalescent.
- (b) Measurement of K' of the clear solution of the mixture containing appropriate proportion of polar-non-polar components necessary to make an opalescent mixture at the critical temperature, but at a temperature slightly higher than the temperature of opalescence.
- (c) Measurement of K' when the mixture is opalescent.

The experimental values of K' thus measured are given in the third column of Table I. The time of relaxation for pure liquid and clear solution of the mixture in appropriate proportion but at a temperature 1°C above the opalescent temperature, has been calculated from Eqs. (2) and (4) respectively. The dielectric constant of the pure liquid and the mixture have been measured by the same apparatus by the resonance method. The refractive indices of the solutions have been calculated from the relation

$$n = x_1 n_{01} + x_2 n_{02} \text{ (Glasstone}^{10}\text{)}$$

where x 's and n 's are the mole fraction and refractive indices of the pure solvent and solute res-

pectively. The mole fraction x_2 of the solute is related to w_2 by

$$x_2 = \frac{w_2 M_1}{w_2 M_1 + w_1 M_2}$$

The value of η_{12} , the viscosity of the clear solution of the binary mixture has been calculated from the relation $\log \eta_{12} = x_1 \log \eta_1 + x_2 \log \eta_2$ where x_i s and η_i s are the mole fraction and the coefficient of viscosity of the solvent and solute respectively.

It is known that the equation $\tau = 4\pi\eta a^3/kT$ can be utilized for calculating the radius of the rotating unit when the value of τ is extrapolated to infinite dilution. However, the relative change in the value of a can be estimated if we measure τ at two different concentrations. As in this case, we have calculated τ from experimental determination of rf conductivity in case of the pure liquid as well as when methyl alcohol is dissolved in different non-polar solvents in the same proportion as is necessary in case of opalescent mixture but at a temperature 1°C above the critical temperature we get

$$\frac{a^3}{a_{12}^3} = \frac{T}{T+1} \cdot \frac{\eta_{12}}{\eta} \cdot \frac{\tau}{\tau_{12}}$$

where a and a_{12} are the radii of the rotating unit for the polar solute and solution respectively.

Substituting the values in the right hand side of the above equation, we get in case of methyl alcohol and methyl alcohol-n-hexane mixture $a/a_{12} = 1.001$.

In case of methyl alcohol- CS_2 mixture, the ratio a/a_{12} is of the order of 1.305 and for methyl alcohol-cyclohexane, the ratio is 1.202. Hence it is clear that there is slight change in the value of the radius of the rotating unit and even at a temperature 1°C higher than that at which opalescence takes place there is no evidence of cluster formation. If it is further assumed that for a change of temperature of 1°C , the velocity of the mixture is the same as that in the critical state, from the relation:

$$\frac{\tau_{\text{clear}}}{\tau_{\text{crit}}} = \frac{a^3 T}{a_c^3 (T+1)}$$

It is found by substituting the value of τ_{clear} and τ_{crit}

$$a/a_c = 0.8423$$

where a and a_c are the radius of the rotating unit when the solution is clear and opalescent respectively.

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Hence it can be argued that there is no appreciable change in the radius of the rotating unit; otherwise, there is no evidence of cluster formation as the temperature of critical opalescence is approached. Similar results have been reported earlier by Sen and Ghosh¹¹ in case of nitrobenzene + n-hexane and aniline + cyclohexane mixtures. As the abrupt change of relaxation time when the mixture passes into opalescent stage cannot be explained by the change in the value of radius of the rotating unit, we have to assume that there is a sudden change of viscosity.

We have then from the ratio of relaxation times

$$\frac{\eta_c}{\eta_{12}} = \frac{\tau_c T}{\tau_{12} (T+1)}$$

where η_c and η_{12} are the viscosity at the critical opalescent state and that of mixture which is not opalescent but at a temperature higher by 1°C respectively, τ_c and τ_{12} are the time of relaxation under similar conditions as mentioned above. The values of η_c/η_{12} are listed in the sixth column of Table I. From the Table I col. 6 it is evident that in case of all the mixtures there is an abrupt change of viscosity as the critical temperature is approached. From the theory of Fixman,¹² the increase in viscosity is given by

$$\Delta \eta = \left\{ \frac{n_1 m_2 \phi_2}{c V_1 V_2 \phi_1 (n_1 + n_2)} \right\} \left\{ \frac{d^{1/2}}{K} \right\} \frac{1}{40} \left(\frac{d^{1/2}}{K} \right)$$

where the symbols have the same significance as in Fixman's paper and

$$\frac{\sigma^{1/2}}{K} = \left\{ \frac{V_1}{4\pi\phi_1} \right\}^{1/2} \left[\left\{ \phi_1^2 - (1-n^2) \right\} - \frac{\epsilon_0}{T} \right. \\ \left. (1+n^{-1/2}) \left\{ \frac{1}{\phi_1} - \frac{V_1}{V_2} \right\}^{1/2} \right]$$

The values of $\frac{n_1 n_2 \phi_1}{e V_2 V_1 \phi_1 (n_1 + n_2)}$ and $\sigma^{1/2}/K$ have been calculated and are given in 7th and 8th columns of Table I. Since $\frac{\Delta \eta}{\eta_{12}} = \left[\frac{\eta_0}{\eta_{12}} - 1 \right]$ putting the experimental values of η_0/η_{12} the value of $\Delta \eta$ has been calculated and finally assuming $a=1$ Å as in Fixman's paper, the internal frictional term β has been calculated and entered in the 9th column of Table I. When β is calculated from the alternative formula $\beta = e/\mu_1 n_1$ as has been suggested by Sen and Ghosh,¹² the value becomes equal to 4.407×10^{15} where μ_1 is the mobility of the hydroxyl ion and in this case is taken as 20.5×10^{-6} cm/sec. (Glasstone¹⁰) and $n_1 = M_1/N$ where N is the Avogadro's number. It is observed that the value of β calculated by an independent procedure is of the same order of magnitude as obtained from Fixman's calculation from the experimental results obtained in the present investigation.

It is observed from Table I column 9 that β varies with the nature of the non-polar solvent and we get different values of β when the opalescent mixture is made with methyl alcohol as one of the components and hexane, carbon disulphide and cyclohexane as non-polar components. Fixman in his paper has introduced β as a measure of internal frictional constant. From column 11 of Table I it is, however, noted that the product $\beta \times \eta_0/\eta_{12}$ is almost a constant for all the three opalescent mixtures studied in the present investigation. Evidently η_0/η_{12} can be taken as a measure of the screening effect of the surrounding molecules on the resultant internal friction constant.

This method of measuring the rf conductivity enables us to calculate the sharp increase of viscosity when the critical temperature is approached as has been observed by direct experimental measurement of Reed and Taylor⁶ in case of iso octane perfluorohex-

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tane and that of Yang and Meeks⁹ in case of cyclohexane-aniline binary liquid system.

The analysis of the experimental results thus indicates that there is a sharp increase of viscosity as the critical temperature is approached and there is no evidence of cluster formation in the critical opalescent state. The experimental results thus lend support to the theory of Fixman regarding the sudden increase of viscosity in the critical state.

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Table 1—Values of Parameters Calculated for Binary Liquid Mixtures

Sl. no.	Liquid mixture system	rf conduc- tivity 10^{-3} esu	Relaxa- tion time 10^{-12} sec	Viscosity of the mixture (η_2) 1°C above opalescent temperature $^\circ\text{C}$	Value of $\frac{1-\phi_2}{\eta_2/\eta_1}$	Value of $\frac{n_1 m_2 \phi_2}{(n_1 + n_2)}$	Value of $\alpha^{1/2}/K$ $\times 10^{12}$	Value of $\beta \times 10^{12}$	Value of $\beta \times \tau_{\text{relax}}$ of $\beta = \frac{C_p m_2}{C_p m_1}$ $\times 10^{-13}$
1.	Methyl alcohol at 29.5°C	0.6376	4.159						
	Methyl alcohol 36% by wt + n-hexane 70% by wt at 30.5°C	0.0821	2.727	0.38469	1.6725	0.1695	4.8323	1.264	2.114
	Opalescent mixture at 29.5°C	0.1373	4.561						
2.	Methyl alcohol at 40.5°C	0.7778	5.073						
	Methyl alcohol 20% by wt + carbon disulphide 80% by wt at 41.5°C	0.0667	1.829	0.35978	2.4220	0.3066	6.8019	0.981	4.407
	Opalescent mixture at 40.5°C	0.1616	4.429						
3.	Methyl alcohol at 45°C	0.8287	5.506						
	Methyl alcohol at 26.14% by wt + cyclohexane 73.86% by wt at 46°C	0.0903	3.862	0.53865	1.6181	0.1895	5.3135	1.323	2.110
	Opalescent mixture at 45°C	0.1462	6.249						

CHAPTER VIII

DIELECTRIC CONSTANT OF POLAR LIQUIDS IN MAGNETIC FIELD.

INTRODUCTION.

The theoretical investigations by Debye (1926), Ruark and Breit (1925) aroused interest to look for a change in the dielectric constant of a gas when a strong magnetic field is applied to it. Experiments in search of this effect on helium, oxygen, HCl and NO have been performed by Weatherby and Wolf (1926), MOTZ-Smith and Daily (1926) by using heterodyne beat method. But no change was detected under any conditions upto 10000 gauss where the apparatus was capable of detecting a change in the dielectric constant of one part in 5,00,000. The tests were carried out with the direction of the electric field both parallel and normal to the direction of the magnetic field.

Piekara and Chelkowski (1963) have calculated theoretically and detected experimentally an increase in the dielectric constant of nitrobenzene by an amount of 3.9×10^{-6} when a strong magnetic field from 0 to 40 kilogauss is applied with a circuit capable of detecting $\Delta\epsilon = 10^{-6}$. But no systematic investigation of other liquids has been found in the literature; the effect is extremely difficult to detect either in an ordinary longitudinal or a

transverse magnetic field. Our calculations show that the effect is enhanced if the liquid is subjected to magnetic field from all sides so that it may be compressed. In fact the present paper shows the effect of such a radial magnetic field on the dielectric constant of a number of liquids. As the expected change is extremely small an arrangement has been devised that can be used to detect a small change if any in the dielectric constant of liquids.

THEORY.

From the well known Debye equation we have

$$\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{\rho_0} = \frac{4\pi N}{3} \left(\alpha_0 + \frac{\mu^2}{3KT} \right) \quad \dots(8.1)$$

where ϵ , M , ρ_0 and α_0 are the dielectric constant, molecular weight, density and distortion polarizability of the liquid respectively, N the Avogadro number, K is the Boltzmann constant and T is the absolute temperature. It is assumed that when the dielectric is subjected to a magnetic field a mechanical stress is set up whose effect is to compress the dielectric and change the density of the liquid. When the magnetic field is applied, right hand side of equation (8.1) is unaffected. So

$$\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{\rho_0} = \frac{\epsilon_H - 1}{\epsilon_H + 2} \cdot \frac{M}{\rho_H} \quad \dots (8.2)$$

where ϵ_H and ρ_H are the dielectric constant and density of the liquid in presence of magnetic field. From equation (8.2)

$$\epsilon_H = \frac{1 + 2 \cdot \frac{\rho_H}{\epsilon_0} \cdot \frac{\epsilon - 1}{\epsilon + 2}}{1 - \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{\rho_H}{\epsilon_0}} \quad \dots (8.3)$$

Case I (Considering compressibility factor)

If β represents the compressibility factor then

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

Here the Maxwell's stress $\partial P = \frac{\mu H^2}{8\pi}$

$$\beta = \frac{v_0 - v_H}{v_0} \cdot \frac{8\pi}{\mu H^2}$$

where μ is the permeability of the liquid and H is the magnetic field.

$$\beta = \frac{\epsilon_H - \epsilon_0}{\epsilon_H} \cdot \frac{8\pi}{\mu H^2}$$

Therefore,

$$1 - \frac{\epsilon_0}{\epsilon_H} = \frac{\beta \mu H^2}{8\pi}$$

$$\frac{\epsilon_H}{\epsilon_0} = \frac{1}{1 - \frac{\beta \mu H^2}{8\pi}} = \frac{1}{1 - \alpha H^2}$$

where

$$\alpha = \frac{\beta \mu}{8\pi} = \frac{\beta}{8\pi} \quad (\text{since } \mu = 1) \dots (8.4)$$

Putting the value $\frac{e_H}{e_0}$ in equation (8.3), we get after simplification

$$\epsilon_H = \frac{3\epsilon - \alpha H^2 (\epsilon + 2)}{3 - \alpha H^2 (\epsilon + 2)} \dots (8.5)$$

Case II (Considering Gas Kinetics)

If it is assumed that the liquid behaves like a gas then in absence of magnetic field

$$P = n_0 K T$$

where n_0 = number of molecules/cc

$$P = \frac{e_0}{M m} K T$$

where K = Boltzman constant

T = absolute temperature

M = Molecular weight of liquid

m = mass of hydrogen atom.

When magnetic field is applied, the above equation becomes

$$P_H = \frac{e_H}{M m} K T = \frac{e_0}{M m} K T + \frac{\mu H^2}{8\pi}$$

$$\frac{e_H}{e_0} = 1 + \frac{\mu H^2 M m}{8\pi e_0 K T} = 1 + \alpha' H^2$$

where

$$\alpha' = \frac{\mu M m}{8 \pi K T e_0} = \frac{M m}{8 \pi K T e_0} \quad (\text{Since } \mu = 1) \quad \dots (8.6)$$

Putting the value of $\frac{e_H}{e_0}$ in equation (8.2) we get after simplification

$$\epsilon_H = \frac{3\epsilon + 2(\epsilon - 1)\alpha' H^2}{3 - (\epsilon - 1)\alpha' H^2} \quad \dots (8.7)$$

Thus from both the equations (8.5) and (8.7) it is evident that there should be a change in the dielectric constant of the liquid when subjected to a strong magnetic field.

EXPERIMENTAL ARRANGEMENT

The method used in the present study is almost similar to that utilized in measuring the dielectric constant of liquids by resonance method. The block diagram of the experimental arrangement is shown in figure (2.7) of chapter II.

Two identical dielectric cells have been used in the experiment. Each cell consists of a cylindrical glass tube of diameter 2.75 cm. being fitted with four circular parallel electrodes made of silver. Two alternate plates are connected in parallel with a tungsten wire which is sealed with the glass tube. One of the cells is placed inside the cylindrical cavity made by the two pole pieces of

the large electromagnet i.e. placed in the magnetic field whereas the other cell is placed outside the magnetic field. The cells are connected in parallel to the tuning condenser of the secondary circuit. The detectors used are two V.T.V.M. which are connected in parallel to the cells as shown in figure (2.7). The experiment has been performed at a frequency of 800 KHz. and at a temperature of 30°C.

The theory of measurement of $\frac{\epsilon}{\epsilon_H}$ has been described in detail in chapter II where ϵ and ϵ_H are the dielectric constant of the liquid in absence and presence of magnetic field respectively. At any particular value of tuning condenser (say at resonance) the voltage developed V_1 and V_2 at two V.T.V.M. in absence of magnetic field are noted. Noting again the voltage developed V_1' and V_2' after the application of the magnetic field $\frac{\epsilon}{\epsilon_H}$ value has be determined from the relation

$$\frac{\epsilon}{\epsilon_H} = \frac{V_1}{V_2} \cdot \frac{V_2'}{V_1'} \quad \dots (8.8)$$

Thus by observing only the voltages before and after the application of the magnetic field, one can find directly the value of $\frac{\epsilon}{\epsilon_H}$ which is the speciality of the procedure that has been adopted here. The other advantage is that the calibration of the tuning condenser is not a primary factor. The experiment has been performed in case of nitrobenzene, ethyl alcohol and methyl alcohol.

From the theory developed it is evident that the effect sought is solely dependent upon the ability of the applied magnetic field to compress the liquid. A simple configuration of the magnetic field such as either a transverse or a longitudinal magnetic field cannot produce the desired effect. Unless the liquid is compressed from all sides the effect would be negligible and hence a special design of the magnetic field has been made which has been described in detail in chapter II. From each flat surface of the circular pole pieces of diameter 8.3 cm., a portion of the material is cut-off in such a way that a cylindrical cavity of diameter 2.85 cm. is formed if the pole pieces are joined together along the axis which is radially perpendicular to the field. During the experiment one of the cells is introduced inside this cylindrical cavity. The sectional view of such a magnetic field arrangement is shown in figure (2.8) of chapter II. This particular geometry of design produces a magnetic field which can compress the liquid from all sides. The field inside the cavity has been measured by a flux meter and is found to have maximum value at the centre of the cavity and gradually diminishes outwards. The main point is to compress the liquid from all sides and hence a slight deviation from uniform field has been tolerated. An average value of magnetic field has been used for calculation, the calibration of which with the current flowing through the electromagnet is shown figure (2.9) of chapter II, keeping the pole pieces as it is after taking away the cell from cylindrical cavity of the pole pieces.

RESULTS AND DISCUSSION.

The ratio of the dielectric constant of the liquid with and without magnetic field has been measured at a temperature of 30°C , in case of purified nitrobenzene, ethyl alcohol and methyl alcohol using equation (8.8). The results are shown in table (8.1) at two different magnetic fields along with the calculated theoretical values by considering the compressibility factor and gas kinetics from equations (8.5) and (8.7) respectively. The value of α and the literature value of dielectric constants are also placed in table (8.1). It is observed from the table that dielectric constant in case of nitrobenzene, ethyl alcohol and methyl alcohol increases slightly with the increase of magnetic field but no change has been clearly detected below the magnetic field of strength 3050 gauss. The increase of dielectric constant cannot be due to rise of temperature as the dielectric constant in the above three cases decreases with the increase of temperature. The effect has been, sought to be observed by applying a uniform transverse magnetic field upto 8000 gauss but no change could be detected. It is observed from the table that the value of α' as deduced from gas kinetics is maximum in case of nitrobenzene and minimum in case of methyl alcohol where the molecular weight plays the dominant role but the opposite case is found when deduced by considering the compressibility factor. It is also observed from the table that the experimental results are closely in agreement with the value calculated by

considering the compressibility factor which clearly established that the effect of magnetic field is some what like pressure which compresses the liquid inside the cell. The effect of pressure on the dielectric constant of liquids has been found by Dan Forth Jr. (1931) where the same evidence has been found i.e. dielectric constant of the liquid increases with the increase of pressure. The effect is evidently due to magnetostriction.

In order to test how our theoretical calculations will predict the change of dielectric constant of gases in a superimposed magnetic field, the value of ϵ_H in case of hydrogen, oxygen and nitrogen has been calculated utilizing both the equations (8.5) and (8.7) and it has been found that the change is extremely small and occurs in the fourth place of decimal and unless an extremely sensitive arrangement is made it is impossible to detect this change even for the highest magnetic field used in the present investigation.

It is further concluded that the change in dielectric constant calculated from the compressibility equation is much nearer to experimental values. This indicates that gas kinetic equation are not actually valid in case of liquids because the strong interaction between individual molecules plays a dominant part in case of liquids.

Table 8.1

Liquid	Temp. 'in °C , (t) , at t°C	Litera- ture 'value of ϵ '	Compre- ssibility , factor in sq.cm/ dynes x 10 ¹¹	'Value of α from eqn.(8.4) , x 10 ¹²	'Value of α from eqn. (8.6) , x 10 ¹¹	'Magnetic field H , in gauss	'Theoreti- cal value of ϵ/ϵ_H 'from eqn. (8.5)	'Theore- tical value of ϵ/ϵ_H 'from eqn. (8.7)	'Expt. value of ϵ/ϵ_H 'from eqn. (8.8)
Nitrobenzene	30	33.97	5.23	2.0820	15.828	3450	0.99970	0.97810	0.99762
						3050	0.99977	0.98288	0.99811
Ethyl Alcohol	30	23.52	11.91	4.7413	9.0378	3450	0.99954	0.99124	0.99840
						3050	0.99964	0.99316	0.99909
Methyl Alcohol	30	31.55	12.93	5.1473	6.2803	3450	0.99934	0.99191	0.99444
						3050	0.99948	0.99368	0.99533

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Dielectric Constant of Polar Liquids in Magnetic Field

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Assuming that when a dielectric is placed in a magnetic field a mechanical stress $\mu H^2/8\pi$ where μ is the permeability and H is the magnetic field develops on the surface of a dielectric, a theoretical expression for the change of dielectric constant of the medium has been derived when placed in an external magnetic field. As the expected change is extremely small a specially designed magnetic field and a very sensitive system of dielectric constant measurement have been utilized in the present investigation. The results are reported for nitrobenzene, ethyl and methyl alcohol for a radial magnetic field upto 4000 gauss and the experimental results are in close agreement with theoretical predictions.

§1. Introduction

The theoretical investigations by Debye,¹⁾ Ruark and Breit²⁾ aroused interest to look for a change in the dielectric constant of a gas when a strong magnetic field is applied to it. Experiments in search of this effect on helium, oxygen, HCl and NO have been performed by Weatherby and Wolf,³⁾ Lewiss, MOTT-Smith and Daily⁴⁾ by using the heterodyne beat method. But no change was detected under any conditions upto 10000 gauss where the apparatus was capable of detecting a change in the dielectric constant of one part in 500000.

Piekara and Chelkowski⁵⁾ have calculated theoretically and detected experimentally an increase in the dielectric constant of nitrobenzene by an amount of 3.9×10^{-6} when a strong magnetic field from 30 to 40 kilogauss is applied with a circuit capable of detecting $\Delta\epsilon \approx 10^{-6}$. But no systematic investigation of other liquids has been found in the literature; the effect is extremely difficult to detect either in an ordinary longitudinal or a transverse magnetic field. Our calculations show that the effect is enhanced if the liquid is subjected to magnetic field from all sides so that it may be compressed. In fact the present paper shows the effect of such a radial magnetic field on the dielectric constant of a number of liquids. As the expected change is extremely small an arrangement has been devised that can be used to detect a small change if any in the dielectric constant of liquids.

§2. Theory

From the well known Debye equation we have,

$$\frac{(\epsilon - 1)}{(\epsilon + 2)} \frac{M}{\rho_0} = \frac{4\pi N}{3} \left(\alpha_0 + \frac{\mu^2}{3kT} \right), \quad (1)$$

where ϵ , M , ρ_0 and α_0 are the dielectric constant, molecular weight, density and distortion polarisability of the liquid respectively, N the Avogadro number, k is the Boltzmann constant and T is the absolute temperature. It is assumed that when the dielectric is subjected to a magnetic field a mechanical stress is set up whose effect is to compress the dielectric and change the density of the liquid. When magnetic field is applied, right hand side of eq. (1) is unaffected.

So

$$\frac{(\epsilon - 1)}{(\epsilon + 2)} \cdot \frac{M}{\rho_0} = \frac{(\epsilon_H - 1)}{(\epsilon_H + 2)} \cdot \frac{M}{\rho_H}, \quad (2)$$

where ϵ_H and ρ_H are the dielectric constant and density of the liquid in presence of magnetic field. From eq. (2)

$$\epsilon_H = \frac{1 + 2 \frac{\rho_H}{\rho_0} \cdot \frac{(\epsilon - 1)}{(\epsilon + 2)}}{1 - \frac{(\epsilon - 1)}{(\epsilon + 2)} \cdot \frac{\rho_H}{\rho_0}}, \quad (3)$$

Case I (Considering compressibility factor)
If β represents the compressibility factor then

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

Here the Maxwell's stress $\partial P = \mu H^2 / 8\pi$.

$$\beta = \frac{(v_0 - v_H)}{v_0} \cdot \frac{8\pi}{\mu H^2},$$

where μ is the permeability of the liquid and H is the magnetic field.

$$\beta = \frac{(\rho_H - \rho_0)}{\rho_H} \cdot \frac{8\pi}{\mu H^2}.$$

Therefore,

$$1 - \frac{\rho_0}{\rho_H} = \frac{\beta \mu H^2}{8\pi},$$

$$\frac{\rho_H}{\rho_0} = \frac{1}{1 - \frac{\beta \mu H^2}{8\pi}} = \frac{1}{1 - \alpha H^2}.$$

where

$$\alpha = \frac{\beta \mu}{8\pi} = \frac{\beta}{8\pi} \quad (\text{since } \mu = 1). \quad (4)$$

Putting the value ρ_H / ρ_0 in eq. (3), we get after simplification

$$\epsilon_H = \frac{3\epsilon - \alpha H^2(\epsilon + 2)}{3 - \alpha H^2(\epsilon + 2)}. \quad (5)$$

Case II (Considering Gas kinetics)

If it is assumed that the liquid behaves like a gas then in absence of magnetic field,

$$P = n_0 k T,$$

where n_0 = number of molecules/cc

$$P = \frac{\rho_0}{Mm} k T,$$

k = Boltzmann constant

T = absolute temperature.

M = Molecular weight of liquid

m = mass of hydrogen atom.

when magnetic field is applied, the above equation becomes

$$P_H = \frac{\rho_H}{Mm} k T = \frac{\rho_0}{Mm} k T + \frac{\mu H^2}{8\pi},$$

$$\frac{\rho_H}{\rho_0} = 1 + \frac{\mu H^2 M m}{8\pi \rho_0 k T} = 1 + \alpha' H^2,$$

where

$$\alpha' = \frac{\mu M m}{8\pi k T \rho_0} = \frac{M m}{8\pi \rho_0 k T} \quad \text{since } \mu = 1. \quad (6)$$

Putting the value of ρ_H / ρ_0 in eq. (2), we get after simplification

$$\epsilon_H = \frac{3\epsilon + 2(\epsilon - 1)\alpha' H^2}{3 - (\epsilon - 1)\alpha' H^2}. \quad (7)$$

Thus from both the eqs. (5) and (7) it is evident that there should be a change in the dielectric constant of the liquid when subjected to a strong magnetic field.

§3. Experimental Arrangement

The method used in the present study is almost similar to that utilised in measuring the dielectric constant of liquids by resonance method. The block diagram of the experimental arrangement is shown in Fig. 1.

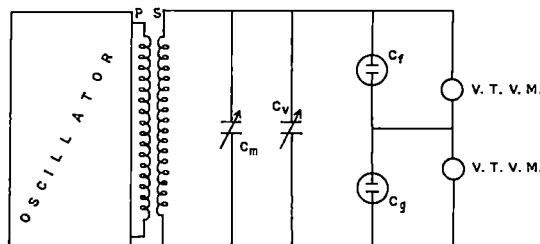
Two identical dielectric cells have been used in the experiment. Each cell consists of a cylindrical glass tube of diameter 2.75 cm, being fitted with four circular parallel electrodes made of silver. Two alternate plates are connected in parallel with a tungsten wire which is sealed with the glass tube. The cell C_g is placed in the magnetic field whereas the cell C_f is placed outside the magnetic field. The cells are connected in parallel to the main condenser C_m and vernier C_v of the secondary circuit. The detectors used are two valve tube voltmeters which are connected in parallel to the cells as shown in the figure. The experiment has been performed at a frequency of 800 Kc/sec and at a temperature of 30°C.

At any particular value of C_m and C_v (say at resonance), the voltages, V_1 and V_2 at C_f and C_g are noted. If I_1 be the current flowing through the secondary circuit at this condition; then we have

$$I_1 \times \frac{1}{\omega C_1} = V_1,$$

$$I_1 \times \frac{1}{\omega C_2} = V_2.$$

where C_1 and C_2 are the capacitance of the cell



BLOCK DIAGRAM FOR MEASUREMENT OF ϵ / ϵ_H

Fig. 1. Block diagram for measurement of ϵ / ϵ_H .

C_f and C_g respectively when filled with the liquid. Hence

$$\begin{aligned}\frac{C_2}{C_1} &= \frac{V_1}{V_2}, \\ \epsilon/C_1/C &= \frac{V_1}{V_2}, \\ \epsilon &= \frac{V_1}{V_2} \cdot \frac{C_1}{C}.\end{aligned}\quad (8)$$

where ϵ is the dielectric constant of the liquid and C is the capacitance of the empty cell.

When magnetic field is applied only to the cell C_g let the voltage developed are V'_1 and V'_2 across the two cells. Since only the capacitance in the cell C_g changes, let I_2 be the current flowing in the secondary circuit. Then in the similar way we have

$$\begin{aligned}I_2 \times \frac{1}{\omega C_1} &= V'_1, \\ I_2 \times \frac{1}{\omega C_2} &= V'_2,\end{aligned}$$

or

$$\begin{aligned}\frac{C'_2}{C_1} &= \frac{V'_1}{V'_2}, \\ \epsilon_H &= \frac{V'_1}{V'_2} \cdot \frac{C_1}{C},\end{aligned}\quad (9)$$

where ϵ_H is the dielectric constant of the liquid in presence of magnetic field.

From (8) and (9) we get

$$\frac{\epsilon}{\epsilon_H} = \frac{V_1}{V_2} \cdot \frac{V'_2}{V'_1}, \quad (10)$$

Thus by observing only the voltages before and after the applications of the magnetic field one can find directly the value of ϵ/ϵ_H which is the speciality of the procedure that has been adopted here. The other advantage is that the calibration of the condensers is not a primary factor. Equation (10) has been utilised in measuring the value of ϵ/ϵ_H in case of nitrobenzene, ethyl alcohol and methyl alcohol.

From the theory developed it is evident that the effect sought is solely dependent upon the ability of the applied magnetic field to compress the liquid. A simple configuration of the magnetic field such as either a transverse or a longitudinal magnetic field cannot produce the desired effect. Unless the liquid is compressed from all sides the effect would be negligible and

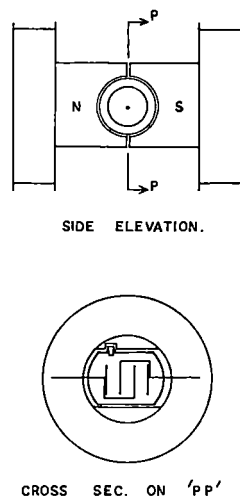


Fig. 2. Sectional view of the magnetic field arrangement.

hence a special design of the magnetic field has been made.

The magnetic field is produced by a large electromagnet having specially designed pole pieces (Fig. 2). From each flat surface of the circular pole pieces of diameter 8.3 cm, a portion of the material is cut-off in such a way that a cylindrical cavity of diameter 2.85 cm is formed if the pole pieces are joined together along the axis which is radially perpendicular to the field. During the experiment the cell C_g is introduced totally inside this cylindrical cavity and the gap between the two middle points of the curvature is 3.0 cm. The remaining flat surface of the pole pieces was covered with thin mica sheet. This particular geometry of design produces a magnetic field which can compress the liquid from all sides. The field inside the cavity has been measured by a flux meter and is found to have maximum value at the centre of the cavity and gradually diminishes outwards. The main point is to compress the liquid from all sides and hence a slight deviation from uniform field has been tolerated. An average value of magnetic field has been used for calculation.

§4. Results and Discussion

The ratio of the dielectric constant of the liquid with and without magnetic field has been measured at a temperature of 30°C, in case of purified nitrobenzene, ethyl alcohol and methyl alcohol using eq. (10). The results are shown in

Table I.

Liquid	Temp. in °C	Literature value of ϵ at $t^\circ\text{C}$	Compressi- bility factor in $\text{Sq. cm}/$ dynes $\times 10^{11}$	Value of α from eq. (4) $\times 10^{12}$	Value of α' from eq. (6) $\times 10^{11}$	Magnetic field H in gauss	Theoreti- cal value of ϵ/ϵ_H from eq. (5)	Theoreti- cal value of ϵ/ϵ_H from eq. (7)	Expt. value ϵ/ϵ_H from eq. (10)
Nitrobenzene	30	33.97	5.23	2.0820	15.828	3450	0.99970	0.97810	0.99762
						3050	0.99977	0.98288	0.99811
Ethyl alcohol	30	23.52	11.91	4.7413	9.0378	3450	0.99954	0.99124	0.99840
						3050	0.99964	0.99316	0.99909
Methyl alcohol	30	31.55	12.93	5.1473	6.2803	3450	0.99934	0.99191	0.99444
						3050	0.99948	0.99368	0.99533

Table I at two different magnetic fields along with the calculated theoretical values by considering the compressibility factor and gas kinetics from eqs. (5) and (7) respectively. The value of α and the literature value of dielectric constants are also placed in Table I. It is observed from the table that dielectric constant in case of nitrobenzene, ethyl alcohol and methyl alcohol increases slightly with the increase of magnetic field but no change has been clearly detected below the magnetic field of strength 3050 gauss. The increase of dielectric constant cannot be due to rise of temperature as the dielectric constants in the above three cases decreases with the increase of temperature. The effect has been, sought to be observed by applying a uniform transverse magnetic field upto 8000 gauss but no change could be detected. It is observed from the table that the values of α' as deduced from gas kinetics is maximum in case of nitrobenzene and minimum in case of methyl alcohol where the molecular weight plays the dominant role but the opposite case is found when deduced by considering the compressibility factor. It is also observed from Table I that experimental results are closely in agreement with the values calculated by considering the compressibility factor which clearly established that the effect of magnetic field is somewhat like pressure which compresses the liquid inside the cell. The effect of pressure on the dielectric constant of liquids has been found by Dan Forth Jr.⁶⁾ where the same evidence has been found i.e. dielectric constant

of the liquid increases with the increase of pressure. The effect is evidently due to magnetostriction.

In order to test how our theoretical calculations will predict the change of dielectric constant of gases in a superimposed magnetic field, the value of ϵ_H in case of hydrogen, oxygen and nitrogen has been calculated utilizing both the eqs. (5) and (7) and it has been found that the change is extremely small and occurs in the fourth place of the decimal and unless an extremely sensitive arrangement is made it is impossible to detect this change even for the highest magnetic field used in the present investigation.

It is further concluded that the change in dielectric constant calculated from the compressibility equation is much nearer to experimental values. This indicates that gas kinetic equations are not actually valid in case of liquids because the strong interaction between individual molecules plays a dominant part in case of liquids.

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SUMMARY AND CONCLUSION.

The following lines of investigation has been undertaken in the present work and a general summary and conclusion is presented.

(A) Extrapolation procedure in computation of dipole moment of polar liquid in nonpolar solvent.

The evaluation of dipole moment from Debye's equation depends partly upon the theory of extrapolation of different physical quantities such as dielectric constant (ϵ_{12}), refractive index (n_{12}) density (d_{12}) of the solution. In order to observe the suitability of the extrapolation techniques, μ values of some systems have been calculated assuming

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

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

where a 's and b 's are constants and ω_2 is the weight fraction of the polar solute. When $\omega_2 \rightarrow 0$

$$\epsilon_1 = a_0, n_1 = b_0, \left(\frac{\partial \epsilon_{12}}{\partial \omega_2} \right)_{\omega_2 \rightarrow 0} = a_1 \text{ and } \left(\frac{\partial n_{12}}{\partial \omega_2} \right)_{\omega_2 \rightarrow 0} = b_1$$

In case of mixture (12) of polar solute (2) in

nonpolar solvent (1), Debye's equation is given by

$$\frac{\epsilon_{12} - n_{12}^2}{(\epsilon_{12} + 2)(n_{12}^2 + 2)} = \frac{\epsilon_1 - n_1^2}{(\epsilon_1 + 2)(n_1^2 + 2)} + \frac{4\pi N \mu^2 d_{12}}{27 M_2 K T} \omega_2$$

which on differentiation with respect to ω_2 yields after simplification in terms of a_0 , a_1 , b_0 and b_1 in the form

$$\mu^2 = \frac{27 K T}{4 \pi N} \cdot \frac{M_2}{d_1} \cdot \frac{1}{(a_0 + 2)^2} \left[a_1 - 2 b_0 b_1 \left(\frac{a_0 + 2}{b_0^2 + 2} \right)^2 \right]$$

The values of a_0 , a_1 , b_0 and b_1 have been calculated by usual least square method and the corresponding μ values thus calculated are in good agreement with the literature values.

(b) Computation of dipole moment of polar solutes.

The well known Debye equation of polar nonpolar liquid mixture of molar concentration C_2 of polar solute is given by Guggenheim assuming $\gamma_{2a} = \gamma'_{2a}$ as

$$\frac{\epsilon_{12} - 1}{\epsilon_{12} + 2} - \frac{n_{12}^2 - 1}{n_{12}^2 + 2} = \left(\frac{\epsilon_1 - 1}{\epsilon_1 + 2} - \frac{n_1^2 - 1}{n_1^2 + 2} \right) + \frac{4\pi N \mu^2}{9 K T} C_2$$

where the symbols have been described in Chapter III. As

$$c_2 = \frac{d_{12} \omega_2}{M_2} \quad \text{and} \quad d_{12} = \frac{d_1}{1 - \beta \omega_2}$$

where $\beta = 1 - \frac{d_1}{d_2}$, d_1 and d_2 are the density of the solvent and solute respectively, ω_2 and M_2 are the weight fraction and molecular weight of solute. Guggenheim's equation can be written as

$$\begin{aligned} X_{12} &= X_1 + R \omega_2 + R \beta \omega_2^2 + \dots \\ &= a'_0 + a'_1 \omega_2 + a'_2 \omega_2^2 \end{aligned}$$

where a'_0 , a'_1 and a'_2 are constants and

$$X_{12} = \frac{\epsilon_{12} - n_{12}^2}{(\epsilon_{12} + 2)(n_{12}^2 + 2)}, \quad X_1 = \frac{\epsilon_1 - n_1^2}{(\epsilon_1 + 2)(n_1^2 + 2)}$$

$$R = \frac{4\pi N \mu^2}{27KT} \cdot \frac{d_1}{M_2}$$

Equating the coefficient of ω_2 from both sides of the above expression, gives after simplification

$$\mu = \sqrt{\frac{27KT M_2 a'_1}{4\pi N d_1}}$$

which has been utilized to compute the value of μ for three different systems after evaluating a'_1 by usual linear least square fitting. The procedure is very simple because only a single extrapolation on X_{12} against ω_2

in any system is enough to find the value of a_1' and hence the dipole moment of polar liquid dissolved in nonpolar solvent.

(c) Dipole moment of polar solute from solution data.

Guggenheims' method (1949, 1951) for the determination of dipole moment of a polar solute in nonpolar solvent is widely used because it is very simple and also avoids the measurement of density of different dilute solutions. But the approximation which has been used by Guggenheim himself introduces some error in μ value when there is considerable contraction or dilatation of the volume of the solution. Hence a method of determination of μ value from solution data has been described obtained directly from Debye's expressions which can be written as

$$\chi_{12}'' = \frac{4\pi N}{3} \gamma_{1a} \frac{1}{M_1} + \frac{4\pi N}{3} \left\{ \left(\gamma_{2a} + \frac{\mu^2}{3KT} \right) \frac{1}{M_2} - \gamma_{1a} \frac{1}{M_1} \right\} \omega_2$$

where the symbols have been described in Chapter III. From the intercept and slope of $\chi_{12}'' - \omega_2$ curve, the value of $[P_a]_s$ and $[P_a]_d^0 + [P_o]_d^0$ have been determined where

$$[P_a]_s = \frac{4\pi N}{3} \gamma_{1a} = \text{molar atomic polarization of pure solvent.}$$

$$[P_a]_d^0 = \frac{4\pi N}{3} \gamma_{2a} = \text{molar atomic polarization of solute at infinite dilution}$$

$$[P_o]_d^0 = \frac{4\pi N}{3} \cdot \frac{\mu^2}{3KT} = \text{molar orientation polarization of solute at infinite dilution.}$$

To determine mathematically the intercept and slope of the $X_{12}'' - \omega_2$ curve, the experimental quantity X_{12}'' has been expressed in a finite number of terms of form

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

where a_0'' , a_1'' and a_2'' are constants and evaluated by usual least square methods. Thus

$$[P_a]_s = a_0'' M_1$$

$$[P_a]_d^0 + [P_o]_d^0 = (a_0'' + a_1'') M_2$$

Estimating $[P_a]_d^0$, the value of $[P_o]_d^0$ and hence μ value has been evaluated and compared with results obtained by different extrapolation techniques.

(a) Determination of relaxation time of polar molecules dissolved in nonpolar solvents by radio frequency conductivity measurements.

Molecular relaxation time in case of methyl and ethyl alcohol dissolved in benzene has been obtained by measuring the radio frequency conductivity of the solution at different concentrations utilizing Murphy and Morgan (1939) equation and also at different frequencies of the measuring field utilizing the expression deduced by Sen and Ghosh (1974)

which assumed the presence of free ions. It is observed that γ value for both the alcohols obtained from frequency variation method is slightly lower than that obtained by concentration variation method which suggests that actual dielectric loss is less due to finite conductivity of the solution due to the presence of free ions whose concentration has also been obtained in both the alcohols.

(e) Relaxation time and activation energy for viscosity from radio frequency conductivity measurements.

From the measurement of radio frequency conductivity of a number of polar molecules such as methyl alcohol, ethyl alcohol, benzyl alcohol, aniline and benzyl chloride, at different temperatures and over a frequency range of 400 to 800 KHz. the relaxation time, the number of free ions per unit volume and the variation of activation energy with frequency have been obtained. The results prove the validity of the equation deduced earlier by Sen and Ghosh (1974) and gave a quantitative estimate of the imperfection in liquid polar dielectrics. The variation of the activation energy of η viscosity with frequency of the applied field indicates that viscosity is connected with the nature of the charge distribution in a molecule and it is pointed out that this should be taken into account to find the nature of the internal frictional force acting in a liquid.

(f) Measurement of mobility of ions and free ion density from temporal variation of current in polar dielectrics.

In order to prove further the existence of free ions it has been proposed to study the temporal variation of current in polar dielectrics such as ethyl alcohol, methyl alcohol, iso-propyl alcohol, aniline and benzyl chloride which has been described in detail in chapter VI. It has been experimentally observed that when a d.c. field is applied across dielectric liquids which has been distilled a number of times, the initial current usually decreases rapidly with time and then decreases slowly and later shows generally a tendency of saturation. The decay of current passing through dielectric liquids is assumed to be due to removal or accumulation of ions near the electrodes. Assuming the existence of free ions in the liquids, a quantitative theory has been developed by Sen and Ghosh (1975) which can explain the variation of current with time in satisfactory agreement with experimental results.

The results obtained in this chapter lend additional support to the idea leading to the equation of Sen and Ghosh (1975). From the analysis of the results it has been possible to calculate the mobility and free ion density in each of these liquids, which are consistent with the results reported earlier.

(g) Radio frequency conductivity of opalescent binary liquid mixtures.

The radio frequency conductivity of three opalescent binary mixtures (methyl alcohol + n -hexane, methyl alcohol + carbon disulphide, methyl alcohol + cyclohexane) have been measured under a radio frequency field of 400 KHz and results reported in chapter VII. It has been shown from the simultaneous measurement of r.f. conductivity of the polar component and that of binary mixture in the same proportion as is necessary to make an opalescent mixture but at a temperature slightly above the critical temperature that there is no evidence for cluster formation in the critical state. From the abrupt increase of relaxation time at the critical temperature the increase in viscosity has been obtained and the value of the internal frictional constant has been calculated utilizing Fixman's theory. It is shown that the internal friction constant depends upon the nature of the nonpolar component of the opalescent mixture.

(h) Dielectric constant of polar liquids in magnetic field.

Assuming that when a dielectric is placed in a magnetic field a mechanical stress $\frac{\mu H^2}{8\pi}$ where μ is the permeability and H is the magnetic field developed on the surface of a dielectric, a theoretical expression for the change of dielectric constant of the medium has been derived.

As the expected change is extremely small a specially designed magnetic field and a very sensitive system of dielectric constant measurement have been utilized in the present investigation. The results are reported for nitrobenzene, methyl and ethyl alcohol for a radial magnetic field upto 4000 gauss and experimental results are in close agreement with theoretical predictions.

In the present investigation some properties of polar dielectric liquids have been investigated. Three different methods for the determination of dipole moment of polar molecules have been presented and results calculated on this basis are in good agreement with the literature values. The measurement of radio frequency conductivity of the polar dielectrics when dissolved in nonpolar solvents and at different temperatures and with the variation of frequency of the applied field have enabled us to compute the relaxation time, free ion density and activation energy for viscosity. Some useful information regarding the nature of the liquid state at the critical opalescent mixture has also been obtained. Finally the effect of a super imposed magnetic field on the dielectric constant of polar molecules has also been investigated.

