I N T R O D U C T I O N

The study of dielectrics in the three states of matter, solid, liquid and gaseous is a topic of great interest in modern scientific research. The subject of the ionization and conductivity in polar and non polar liquid dielectrics has been studied for a long time and has acquired great interest in recent times. The subject, is far from being exhausted and several aspects of the phenomena have received intensive attention in recent years and significant progress has been made in this field. However much more investigation is necessary to understand completely the phenomena of ionization and conductivity of dielectric liquids, specially by radio frequency electric field. The subject of the present work is to study some of the salient features of ionization and conductivity of polar liquid dielectrics and it is expected that this will enable us to postulate a theory regarding the mechanism of ionization and electrical conductivity in dielectric liquids.

CHAPTER I

REVIEW OF THE PREVIOUS WORK.

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

The earliest detailed investigation of conduction current in a liquid was done by Quincke in 1895. He used a static generator of 30 KV and employing an inter-electrode gap width of 1 to 3 mm showed that the current depends upon voltage, gap width, and nature of the liquid. Quincke concluded that the current is non ohmic and probably electrolytic in origin. Curie (1902) observed that the electrical conductivity of petroleum ether, carbon tetrachloride, carbon disulphide and benzene was increased by exposure to gamma rays or x-rays. Schweildler (1907) showed experimentally that the conductivity of saturated hydrocarbons 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 result shows 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 sec. Similar result was obtained for heptane and petroleum ether.

But Jaffé (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 γ-rays, and he concluded that for field of less than 100V/cm, a large part of the current is caused by external ionising radiation. Hikuradse (1932) studied the current in dielectric liquids over 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 independent of pressure. When all 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. The residual conductivity of a supposedly pure insulating liquid has been reduced by a factor of a thousand or more by treating it in such a way as to remove traces of water. When a reasonable low limiting value of the conductivity has been reached, the next problem is to find out, how it originates. However there is no general agreement as to it characteristics.

Baker and Boltz (1937) and Dornte (1940) interpreted their investigation to mean that the conductivity is due to thermionic emission from the cathode combined with a Schottky effect. That has been criticised by Lepage and DuBridge (1940) and they observed that Log I is a linear function of $\sqrt{E}$ and later concluded that the current is due to field-enhanced thermionic emission and derived the

following relation

$$J = AT^2 \exp\left[-\frac{\phi e}{RT} + \frac{1}{2.3\,RT}\left(\frac{e^3 E}{K'}\right)^{\frac{1}{2}}\right]$$

where K' is the dielectric constant 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 their views there are even in purest hydrocarbon 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. Ruhle (1943) developed the idea of induced conduction and McK (1949) showed that variation of current strength with time can be represented by the equation $I - I_\infty = \left(I_0 - I_\infty\right) e^{-KT}$ where I_0 is the initial current, I_∞ is the limiting current and K is the constant which contains the ionic mobilities. The effect is assumed to be due to initial existence of ionic clusters in the body of liquid which gradually disperse. He performed experiments on acetone, nitrobenzene and acetone substituted compounds. Ruhle (1943), 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 $J = AE^2 \exp(-\frac{b}{E})$. Jaffe' and Lellay (1953) studied time dependent currents in hexane for wide gaps and low voltages and concluded that the currents are ionic. The break down in dielectric liquid gives additional information concerning the conduction current in dielectric liquid. Goodwin and Macfadyen (1953) demonstrated that the time lag to break down is determined by positive ion mobility. Green (1955) has studied the conduction and break down in hexane and 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 neutralisation. The ions then set up a local field across the surface layer that tend to produce electron emission. The size of the local field depends upon the magnitude of the ionic current and probability of neutralisation of the ions. Standhammer and Beyer (1957) have obtained evidence for the formation of pure ions in cyclohexane and cyclohexane saturated with water.

Riehl (1955) and Keepler (1960) observed that the level of conduction of some polynuclear aromatic compounds, such as naphthalene and anthracene increases by a factor 10^3 to 10^6 on melting. The mechanism by which these liquids conduct has been subjected to only a few investigations and the only conclusion that has been reached is that, no long range order is necessary for conduction

and higher conduction in the molten form is due to higher mobility of the charge carrier. Hart and Mungall (1957) observed that the conduction current in chlorobenzene continued to decrease even after continuous distillation for as long as three months. From studies of drift mobility, LeBlanc (1959) suggested that electrons exist in n-hexane in quasi-trapped state. Forster (1962) 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. This relation suggests that conduction depends upon the probability that an electron will be transfered from one benzene molecule to another is a function of the number of molecules located between the electrodes and capable of sustaining the electron jump. So he reasonably assumed that only electron migration rather than diffusion is valid in the conduction process. The increase of conduction due to increase of temperature of the liquid would be the result of enhanced transfer probabilities resulting from an increase of molecular collision leading to electron transfer. Again Forster (1964) showed that conduction in aliphatic hydrocarbons is most probably related to the presence of polar impurities or trapped electrons present in the liquid or generated at the electrode surface. In unsaturated hydrocarbons experimental evidence suggested the existence of electronic conduction. In addition to the hopping process, he suggested that at ordinary temperatures a small but possibly potentially significant fraction of the molecules in a

hydrocarbon liquid will be in lowest excited state. The interaction of excited molecules is believed to lead to the formation of positive and negative ions. In the first process, the electron transfer step was visualised to occur by an overlap of orbital constituting peripheral π-bonds on two adjacent molecules. He suggested an emperical relation for the activation energy of the quasi-trapped mechanism $\epsilon a = 0.067\ p.ev$ in which p is the number of peripheral π-electron. For nitrobenzene $p = 8$ which gives an activation energy of 0.54 ev, agreeing remarkably well with observed value of 0.53 ev observed by Rao and Raju (1970). This is another confirmation of the electronic nature of the conduction current. In proposing the theory for conduction current in insulting liquid, Silver (1965) assumed a slow generation rate of carriers, regardless of generation mechanism, and the electrodes were non injecting, only acting to balance the positive and negative charges. Further, it was assumed that the electrodes did not block the discharge of ions reaching them. One consequence of Silver's theory is that the conductivity is a function of the electrode spacing and of the form

$$V = AJ^2 + BJ.l.$$

where A and B are constants, V is the applied voltage, J the current density and l, the gap length. This theory explained successfully the variation of conductivity with electrode spacing at various constant voltage in benzene, but in the case of nitrobenzene,

material of the electrodes plays an important role, the cathode appears to be the likely injector of electrons as suggested by Felici (1959). Felici observed that the conductivity of pure nitrobenzene increased within minutes of bringing metallic electrodes in contact with liquid and ascribed this to the dissolution of metal in the liquid. The role of dispersed conducting particles in the dielectric in enhancing the conductivity is 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 possible due to absorption of gases and moisture present in room air. Adamczewski and Jachym (1968) investigated on the group of saturated hydrocarbons which are characterised by the conductivities of two order of magnitudes lower than those of other liquids. They concluded that the natural conductivity values of organic liquids is a function of $\frac{1}{T}$. Where T is the temperature. They further observed that among all investigated organic compounds which occur in liquid state, the lowest conductivity values are those of non-polar liquids; Gaspard and Gosse (1970) gave a clear evidence of ionic conduction in polar dielectrics. They used membrane electrodes and gave evidence for three distinct regions of conduction and in each case conduction is ionic in nature. It is due to impurities at low and medium fields and injection of ions at high field. They observed considerable

erratic variation of current with time under permanent electric field. H.V.Löhneysen and H.Nägerl (1971) also 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.

Considering all the experimental evidences and assumptions taken by various authors, we may summerize that (a) the classical purification technique of impurities in organic polar liquids was not sufficient, so it can be assumed that the conduction in the organic polar liquid was due to ionic impurities, which already exist in the liquid. Due to the application of electric field between the metallic electrodes the impurities (positive ions and negative ions) move towards the electrodes and thereby conduction current was observed. The time dependence of the conduction current also has been observed.

(b) High apparent resistivity is obtainable in solvents by ion-exchange or electrolytic elimination of strongly dissociated impurities and if care is taken to avoid charge injection during the application of slowly increasing field. According to Briére and Gaspard (1968), the residual conduction results from bulk generation of ions by ionic dissociation of weak electrolytes. Each species of impurity gives a well defined saturation plateau in agreement with field displacement of a dissociation recombination equilibrium.

(c) There are experimental evidences that various electrochemical mechanism i.e. dissolution of electrode gives rise to large injection of electron in the pure nitrobenzene. Most of the investigators have assumed that ionic carriers are responsible for the electrical conduction and they obtained the value of mobility between electrodes as quite high and comparable to ionic mobility. So in general, when describing bulk conductivity as well as injected currents in the polar liquid, an important distinction must be made between residual and natural conduction by taking into account the physico-chemical state of the liquid sample and electrochemical properties of the electrode-liquid interface.

Bulk conductivity may be stated to be of natural type when the process of generation of charge carrier becomes an intrinsic property of the liquid. This is the general case of organic polar liquids, whatever the actual degree of ionic impurity may be. Similar distinction can be made in the case of charge carrier injection in the liquid. Another simplest method of production of ions is the electrochemical oxidation or reduction of self dissociated liquids. The molecular loss or capture of an electron at the electrodes leading to the production of radical cation or anion may be valid in case of non-dissociated liquids. This possibility is the most 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. Also we know, 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. Finally, it is also observed that some electrode themselves are chemically active, and it happened through anodic dissolution. All these possibilities, have been reviewed recently by Gaspard and Gosse (1970).

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

The dielectric properties have provided an important approach to an understanding of the structure of the matter. Consider a parallel plate capacitor, of geometrical capacitance C_o, 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 $Q_o = C_o E$ and the charging current $I_c = \frac{dQ}{dt} = j\omega C_o E$ which leads the applied voltage by a phase angle of 90^o.

If the space between the plates of the capacitor is now filled up with a dielectric liquid, the capacitance is increased to

$$C = \frac{k'}{\epsilon_o} C_o = \epsilon' C_o$$

where k' and ϵ_o are the (real) permitivities of the dielectric and of vacuum respectively, and their ratio ϵ' is the (real) dielectric constant of the liquid. In the c.g.s. system of unit $\epsilon_o = 1$. Due to the presence of the dielectric, the charge on the capacitor is increased to $Q = \epsilon' C_o E$ and the charging current is increased to

$$I_c = j\omega C E$$
$$= j\omega \epsilon' C_o E$$

It is known that no dielectric liquid is a perfect insulator so that in addition to I_c, which leads E by 90^o, there is a loss current

component I_l in phase with E and of magnitude

$$I_l = G.E$$

where $G = \frac{1}{R}$ is the equivalent conductance of the dielectric. R is the finite insulation resistance.

Total current through the capacitor is therefore

$$I = I_c + I_l = \left(j\omega \epsilon' C_o E + G E\right)$$
$$= \left(j\omega C + G\right) E \qquad (1.1)$$

This is shown in the vector diagram in Fig. (1.1 b). The current I leads E by a phase angle $\theta < 90^0$ 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 term of loss angle δ

$\delta = (90 - \theta)$, where the loss tangent

$$\tan\delta = \frac{I_l}{I_c} = \frac{G}{\omega C}$$

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 $R = \frac{1}{G}$ shown in Fig. (1.1).

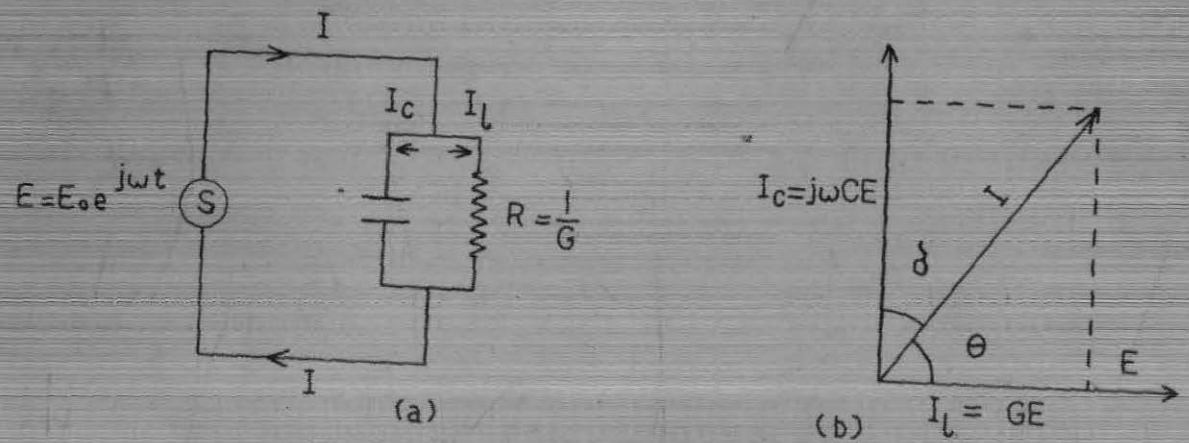

Fig. 1.1. Equivalent circuit, and (a) charging current I_c and loss curret I_t, of capacitor with lossy dielectric.

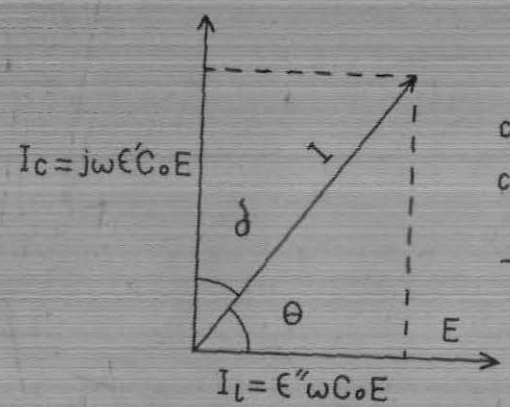

Fig. 1.2. Components of current through dielectric of complex dielectric constant $\epsilon^* = \epsilon' - j\epsilon''$

In most materials, however the dielectric behaviour differs from this simple form, indicating the presence of other source of dielectric loss. To give a general description, 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, which for a perfect dielectric with no loss would be equal to zero.

The total current

$$\begin{aligned} I &= j\omega\epsilon^{*}C_{o}E \\ &= j\omega(\epsilon' - j\epsilon'')C_{o}E \\ &= (j\omega\epsilon' + \omega\epsilon'')C_{o}E \\ &= j\omega\epsilon' C_{o}E + \omega\epsilon'' C_{o}E \end{aligned} \qquad (1.2)$$

its components being represented vectorially in fig. (1.2). Now comparing equation (1.2) with equation (1.1), we get

$$G = \omega\epsilon'' C_{o}$$

and

$$C = \epsilon' C_{o}$$

and loss tangent $\tan\delta = \dfrac{\omega\epsilon'' C_{o}}{\omega\epsilon' C_{o}} = \dfrac{\epsilon''}{\epsilon'}$

from $G = \omega\epsilon'' C_{o}$

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

Therefore specific conductivity (real) $= \frac{\epsilon'' \omega}{4\pi} = K'$

[∵for parallel plate capacitor, $C_o = \frac{S}{4\pi l}$ in vacuum and $G = \frac{1}{R}$ where $R = \rho \frac{l}{S}$]

The dielectric loss is made evident in the loss current which results from the dissipation of part of the energy of the field as heat. So the idea of finite ohmic conductivity existing in the dielectric liquid which when placed inside the capacitor may be considered. In this connection, it will be interesting to examine the relation of the apparent conductivity to dielectric constant and loss in the light of the analysis given by Murphy and Morgan (1939).

For conductors, the conductivity K is given by

$$K = \frac{I}{E} = \frac{I \times E}{E^2} = \frac{W}{E^2}$$

where I is the current density, E the voltage gradient, and W the heat developed per second in a unit cube of the material. This proportionality between current and heat developed in the conductor does not hold in a dielectric material, for, in a dielectric, the ratio of heat developed to current flowing varies with the material. In an ideal dielectric there would be no free ion conduction, but, in actual insulating materials, Joule's heat may be produced by the drift of electrons or free ions in the applied field. The total heat

developed is the sum of the dielectric loss and the Joule's heat. The dielectric loss is thus proportional to the total measured a.c. conductivity minus 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" square cm on each side. If a potential difference V is established between the plates the electric field intensity

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

The effect of introducing a dielectric into the capacitor can be understood by considering the effect of the applied electric field on the bound charges in the dielectric. The very low conductivity of a dielectric material indicates that practically all the electronic charges are bound to their parent atoms or molecules by the electric fields due to the neuclear charges, and they are not free to migrate under the action of an applied field. The action of the field E on the bound charges in the dielectric is to displace them slightly, relative to one another, the positive charges being displaced in the direction of the field, the negative charges in the opposite direction. Each atom or molecule thus acquires an electric dipolemoment 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 q per unit area will appear on each plate and a polarization P will be created in the dielectric. The displacement current flowing in the leads to the condenser is $\frac{Adq}{dt}$ 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

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

$$dq/dt = KE.$$

since the following familiar relations hold,

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

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

or, $$\frac{dD}{dt} = \frac{\epsilon}{d} \cdot \frac{dv}{dt}$$

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

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

or, $$\frac{dq}{dt} = \frac{1}{4\pi} \cdot \frac{dD}{dt} = \frac{\epsilon}{4\pi d} \cdot \frac{dv}{dt}$$

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

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

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

and the dielectric constant is complex the current density in the dielectric is then

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

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

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

as, $\frac{V_0}{d} = E_0$

then, $$I = \left(\frac{j\omega\epsilon'}{4\pi} + \frac{\omega\epsilon''}{4\pi}\right) E_0 e^{j\omega t}$$

$$I = \left(\frac{\omega\epsilon''}{4\pi} + j\,\frac{\omega\epsilon'}{4\pi}\right) E_0 e^{j\omega t}$$

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

$$I = \frac{dq}{dt} = \left(K' + jK''\right) E_0 e^{j\omega t} \qquad (1.3)$$

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

and $K'' = \frac{\omega\epsilon'}{4\pi}$ imaginary part

For convenience in connection with a subsequent account of the methods of measurement, the admittance of the condenser may be expressed in term of an equivalent parallel capacitance C_p and conductance G_p. So that,

$$I = \frac{dq}{dt} = \frac{0.9 \times 10^{12}}{A}\left(G_p + j\omega C_p\right) V_0 e^{j\omega t} \qquad (1.4)$$

where G_p is in mhos, C_p is in Farads and 0.9×10^{12} is the ratio of the farad to the electrostatic unit of capacitance and of the mho to the electrostatic unit of conductance. By using the expression for the capacitance C_0 in farads of the empty condenser

$$C_0 = \frac{A}{4\pi d \times 0.9 \times 10^{12}}$$

and comparing equation (1.3) and (1.4) we obtain

$$\epsilon' = \frac{C_p}{C_0}$$

$$\epsilon'' = \frac{G_p}{\omega C_0}$$

$$K' = \frac{G_p}{4\pi C_0}$$

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

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

$$K' = \frac{\epsilon'' \omega}{4\pi \times 9 \times 10^{12}}$$

$$K' = \frac{\epsilon'' . f}{1.8 \times 10^{12}} = \frac{G_p . f}{C_0 . 2\pi f . 1.8 \times 10^{12}}$$

$$K' = \frac{8.85 \times 10^{-2} G_p}{C_0 \ \mu\mu F}$$

where C_0 is the capacitance in micro micro farads.

The dissipated energy per cm^3 of the dielectric placed inside the parallel plates of the plane condenser and per second

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

and from equation $I = \frac{1}{4\pi} \cdot \frac{dD}{dt}$

We will consider first the case where D is in phase with E

Then we have $D = D_0 \cos\omega t$

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

Thus the current density has phase difference $\pi/2$ with E.

In this case no energy is dissipated in the dielectric, since according to (A3) we have

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

when there is a phase difference δ between D and E, while $E = E_0 \cos\omega t$.

We have

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

or $D = D_0 \cos\omega t.\cos\delta + D_0 \sin\omega t \cdot \sin\delta$

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

$$I = -\frac{\omega}{4\pi} D_o \sin\omega t.\cos\delta - \frac{\omega}{4\pi} D_o \cos\omega t.\sin\delta.$$

By this equation I is split into two parts.

This part again has a phase difference of $\frac{\pi}{2}$ 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 cm^3 of the dielectric per second can be calculated as

$$W = \frac{\omega^2}{8\pi^2} D_o E_o . \sin\delta \int_o^{2\pi/\omega} \cos^2\omega t . dt.$$

leading to

$$W = \frac{\omega}{8\pi} D_o E_o \sin\delta .$$

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

If

$$D^* = D_o e^{j(\omega t - \delta)}$$

where D^* is the complex part of D_o

and

$$D^* = \epsilon^* E^*$$

then

$$\epsilon^* = \frac{D^*}{E^*} = \frac{D_o e^{j(\omega t - \delta)}}{E_o e^{j\omega t}}$$

$$\epsilon^* = \frac{D_o}{E_o} e^{-j\delta}.$$

But

$$\epsilon^* = \epsilon' - j\epsilon'' = \frac{D_o}{E_o}(\cos\delta - j\sin\delta)$$

Then

$$\epsilon' = \frac{D_o}{E_o} \cos\delta.$$

and

$$\epsilon'' = \frac{D_o}{E_o} \sin\delta$$

We find that the dissipated energy per cm^3 of the dielectric and per second is given by

$$W = \frac{\omega}{8\pi} \cdot \frac{D_o}{E_o} \cdot \sin\delta E_o^2$$

$$W = \frac{\epsilon'' \omega E_o^2}{4\pi \cdot 2.}$$

$$W = K' \frac{E_o^2}{2}$$

$W = K' \frac{E_o^2}{2}$ ergs per sec. where $\frac{\epsilon'' \omega}{4\pi} = K'$

The heat developed per cycle in the dielectric is evidently

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

These equations show that K' (r.f. conductivity) is proportional to the heat developed per second and ϵ'' to that developed per cycle.

Considering Debye's expression for complex dielectric constant

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

and separating the real and imaginary part

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

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

where ϵ_o represent the static dielectric constant, ϵ_∞ is the dielectric constant at infinite frequency i.e. $\epsilon_\infty = n^2$ where n is the

refractive index, τ being the relaxation time and ω the angular frequency of r.f. field.

Substituting the value of ϵ'' and ϵ' in the expression $K' = \frac{\epsilon''\omega}{4\pi}$. and $K'' = \frac{\epsilon'\omega}{4\pi}$ we get,

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

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

This shows that the real part of conductivity 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

$$K'_\infty = \frac{(\epsilon_0 - \epsilon_\infty)\,\omega^2\tau}{4\pi\,\omega^2\tau^2} \qquad (1.5)$$

$$K'_\infty = \frac{(\epsilon_0 - \epsilon_\infty)}{4\pi\tau}. \qquad (1.6)$$

Assuming the dipolar molecules to be a sphere of radius 'a' rotating in a continuous viscous fluid possessing a coefficient of internal friction η, Debye obtained for the process of molecular relaxation the relationship,

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

It has been customary to use for η the experimentally measured macroscopic viscosity instead of the unknown microscopic internal friction coefficient or viscosity. It is evident from the calculated values of molecular radius of various solutes by Müller (1938) that the equation $\tau = \frac{4\pi a^3 \eta}{KT}$ does not adequately represent the relation between relaxation time, molecular radius, and macroscopic viscosity of the medium.

Instead of Debye equation, Fischer (1939) calculated the relaxation time of an ellipsoidal molecule using the expression,

$$\tau = \frac{4\pi \eta^* f\ a.\ b.\ c.}{K.T}$$

in which f is a molecular structor factor, a,b and c are the semi-major and semi minor axes of the molecular ellipsoid, and η^* is an empirical viscosity value,

$$\eta^* = 0.36\eta$$

The empirical factor 0.36 was obtained as the value necessary to bring agreement between relaxation time calculated from loss measurements and that calculated from molecular dimensions.

It is thus evident that from the measured values of radio frequency conductivity of pure polar liquids, it is possible to calculate the time of relaxation and the radius of the rotating unit.

Dielectric constants, losses and conductivity of solutions in Non polar Solvents.

To obtain the expression for ϵ' and ϵ'' for dilute solutions of polar molecules in a non-polar solvent the expression of total polarization per cubic centimeter is given by

$$P_1 = N_1 \alpha_0 \left(E_0 + \frac{4\pi P_1}{3}\right) + \frac{N_1 \mu^2/3KT}{1 + j\,\omega/k_0} \left(\frac{\epsilon_0 + 2}{3}\right) E_0$$

where N_1 is the Avogadro number (79) and C is the concentration of Polar solute in moles per cm^3, neglecting the small difference between ϵ_0 and ϵ_∞ for the dilute solution gives

$$P_m = \frac{c N_1 \mu^2/3KT}{1 + j\omega\tau} \cdot \frac{\epsilon_0 + 2}{3} E_0$$

We then get, if ϵ^* is the complex dielectric constant of the solution,

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

and thus, separating the real and imaginary parts

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

and

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

Putting the values of ϵ' and ϵ'', we get the expression of real part K' and imaginary part K" of the r.f. conductivity,

$$K' = \frac{N_1 c \mu^2 (\epsilon_0 + 2)(\epsilon_\infty + 2) \omega^2 \tau}{27 KT (1 + \omega^2 \tau^2)} \quad (1.7)$$

and

$$K'' = \frac{\omega}{4\pi} \left[\epsilon_\infty + \frac{4\pi N_1 c \mu^2 (\epsilon_0 + 2)(\epsilon_\infty + 2)}{27 KT (1 + \omega^2 \tau^2)} \right] \quad (1.8)$$

where K and T are Botlzman constant and the temperature respectively. So it is evident that, by measuring the r.f. conductivity of the solution of polar solutes in a non-polar solvent, 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 we have good number of experimental evidences that in almost all dielectric liquids there are certain percentage of ions. In polar dielectric liquid the percentage of ions is large in comparison to the non-polar liquids which are often called as liquid organic semi-conductors. So if we take a parallel plate condenser type cell, containing polar dielectric liquid and the cell is placed in series to a electrical circuit, where the electric field intensity changes with time, then a conduction current appears, along with a displacement current component. The radio frequency conductivity

measurement however provides information regarding both the displacement and conduction current in a dielectric liquids.

C. THE PHENOMENA OF CRITICAL OPALESCENCE

The existence of critical points was discovered by Andrews (1869) in connection with his classical investigation of the 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. It was realised that critical points have a certain anomalous nature, they prove rather elusive to routine thermodynamic investigations. Equilibria under critical conditions are extremely slow to establish themselves and prove very sensitive to the minutest perturbances.

Perhaps the most spectacular among critical phenomena is the enormous amount of light scattering, the so called critical opalescence. Smoluchowski (1908) have his famous interpretation of this phenomenon, tracing it to abnormally large molecular fluctuations. This was at the same time the key to the above mentioned peculiarities of the critical point. The standard method of Statistical Mechanics of computing fluctuations make use of the method of canonical ensembles. By applying this to critical point one arrives at the result that the fluctuations tend to infinity. In reality the fluctuations are usually large, but obviously finite. This means that at the critical point both thermodynamics and statistical methods reach their limits of applicability.

Klein and Tisza (1949) have generalised the concept of canonical ensemble by introducing the "cellular method". Instead of concentrating attention on the system as a whole the whole system is divided into cubic cells. These cells are chosen as identical in size and shape and arranged in a simple cubic array.

It was assumed in the old theory that the cells are statistically independent, where as in the new theory an interaction depending on the instantaneous states of contiguous cells has been introduced. By the application of the new idea it became possible to give a simple analytical expression to the conservation of extensive quantities. It leads also to the correlation between fluctuations of various cells. This correlation may extend to distant cells, particularly at the critical point, so the theory leads to finite value of the critical fluctuations.

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

$$\frac{I}{I_0} \propto \frac{1}{\lambda^4}\left(1+\cos^2\theta\right)\left(\gamma\right)^{\frac{1}{2}} \qquad (1.9)$$

where I and I_0 are the intensity of scattered and incident radiation of wave length λ observed in the direction θ, β is the compressibility,

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

and $\gamma = \partial^3 V / \partial \rho^3$ the expression is valid at the critical point; Ornstein and Zernike (1914) modified the Smoluchowski's theory and obtained

$$\frac{I}{I_o} \propto \frac{1}{\lambda^4}\left(1+\cos\theta^2\right) \frac{1}{\left\{\frac{1}{\beta} + d^2\left(\frac{\sin\theta/2}{\lambda}\right)^2\right\}} \qquad (1.10)$$

The constant d^2 is a measure of the radius of the intermolecular forces and is proportional to E defined in equation $\left[E = \frac{1}{3}\int r^2 f(r) d\tau\right.$, where f(r) is short range isotropic function. $\left.\right]$

The additional term in the dinomenator arises from the correlation of fluctuation in different volume elements giving rise to a $\frac{1}{\lambda^2}$ dependence and an enhancement of the forward scattering at critical point. The result is not quite complete as it stands, since it makes I/I_o infinite for $\theta = 0$ at the critical point. Placzek (1930) has shown that taking the finite volume of the scattering medium into account a factor is introduced which preserves finiteness without modifying the experimentally realizable situations.

The theory presented by Rocard (1935) predicts that

$$\frac{I}{I_o} \propto \frac{1}{\lambda^4}\left(1+\cos^2\theta\right) \frac{1}{\left(\frac{1}{\beta}+C\right)} \qquad (1.11)$$

where C is a constant arising from the additional term in the pressure.

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

$$\frac{I}{I_o} \propto \frac{1}{\lambda^4}\left(1+\cos^2\theta\right)\left(\frac{1}{\beta}+C+d^2\frac{\sin^2\theta/2}{\lambda^2}\right)^{-1} \qquad (1.12)$$

For C = 0, the equation (1.12) reduces to the expression of Ornstein and Zernike and for d = 0, to that of the Rocard's expression.

The prediction of the Ornstein-Zernike and Rocard theories differ in two ways, the wave length dependence, which becomes $\frac{1}{\lambda^2}$ at the critical point in the former theory, and the angular distribution, which is preferentially forward at the critical point. The measurement of dependence of critical opalescence on the wave length and angle of scattering could throw some light on this problem. The experimental work on critical opalescence has not settled the question in clear fashion. The result of Andant (1924) and Bhattacharyya (1923), indicated a change in wave length dependence in the immediate vicinity of the critical point. Both find dependence of $\frac{1}{\lambda^2}$ at the critical point. It is generally recoguised that near critical point, large fluctuations of some of the properties of the system occur. If these fluctuations are accompanied by changes in the refractive index, the system is no longer optically uniform andthe amount of light scattered will be large.

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. 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 wave length of light.

Piekara (1932) has observed that at the critical temperature the static dielectric constant of dissolved nitrobenzene in hexane at the critical concentration rises sharply. He also studied the fluctuation of density, and the 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.

Viscosity of critical Mixture:

The history of measurements on binary mixtures in the critical region extends over a considerable period. It was early postulated that the great increase in viscosity of the mixture as the critical temperature and composition are approached is in some way connected with inhomogeneties extending over small distances. The analogy with the large viscosities of colloidal solutions was the main basis of this hypothesis.

The sharp rise in the value of the coefficient of viscosity and ultrasonic absorption at the critical region have also been measured by a number of workers (Reed and Taylor; Chynoweth and Schneider; Schmidt, Jura, and Hildebrand).

Fixman (1962) provided a theory for the increase in coefficient of viscosity in the critical region, by assuming that the density fluctuation causes a velocity gradient which produces distortion in the long wave length part of the spectrum in the density fluctuation. The restoration to uniform density through diffusion dissipates energy and this loss has been interpreted as the increase of viscosity.

A straight foreword calculation of the viscosity of the mixture would require a rather accurate knowledge of both intermolecular potential and radial distribution functions at small intermolecular distances, and also the perturbation induced in the latter by the velocity gradient. Fixman has developed his theory in two stages.

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

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

$$\eta_M = \eta_0 + \left(\rho n_2 \frac{\partial c_2}{\partial n_2}\right)^2 \left(\frac{a}{40\alpha}\right) k^{-1} \qquad (1.13a)$$

$$\left(\eta_M - \eta_0\right) = \Delta\eta = \left(\rho n_2 \frac{\partial c_2}{\partial n_2}\right)^2 \left(\frac{a}{40\alpha k}\right) \qquad (1.13b)$$

Here η_0 = local viscosity evaluated at the mean composition

ρ = density of the mixture

c_2 = mass of component 2 in unit mass of mixture

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

α = diffusion constant

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

The equation (1.13b) 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, the expression for α in term of the diffusion constant D_{id} of an ideal mixture can be written as

$$D_{id} = \left(\frac{\alpha \rho R T}{m_1 m_2^2 n_1}\right)\left(\frac{\partial \ln x_2}{\partial n_2}\right) \qquad (1.14)$$

where n_1 = number of molecules of component 1/c.c.
m_1 = mass per molecules of component I
m_2 = mass per molecules of component II
x_2 = mole fraction of component II

it can be readily verified that,

$$\frac{\partial \ln x_2}{\partial n_2} = \left[V_1 n_2 \left(n_1 + n_2\right)\right]^{-1} \qquad (1.15)$$

when the dependence of V_1 and V_2 on composition is neglected.

Also $\frac{\partial c_2}{\partial n_2}$ in equation (1.13b) can be written as

$$n_2\left(\frac{\partial c_2}{\partial n_2}\right) = \frac{m_1 c_1}{\rho V_1} \qquad (1.16)$$

Putting the equations (1.14), (1.15) and (1.16) in eq. (1.13b) the viscosity increment expression becomes

$$\Delta\eta = \left(\eta_M - \eta_0\right) = \left[\frac{kT m_1 \Phi_2}{D_{id}\, \rho\, \Phi_1 V_1^2 V_2 (n_1+n_2)}\right]\left(\frac{a}{40k}\right)$$

or,

$$\Delta\eta = \left[\frac{kT m_1 m_2 \Phi_2}{D_{id}\, m_2 \rho\, V_1^2 V_2 (n_1+n_2)\, \Phi_1}\right]\left(\frac{a}{40k}\right)$$

or,

$$\Delta\eta = \left(\frac{\beta m_1 m_2 \Phi_2}{\rho V_1^2 V_2 (n_1+n_2)\, \Phi_1}\right)\left(\frac{a}{40k}\right)$$

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

$$\Delta\eta = \frac{m_1 m_2 \Phi_2}{\rho V_1^2 V_2 (n_1+n_2)\Phi_1}\left(\frac{a^{\frac{1}{2}}}{R}\right)\frac{1}{40}\left(\beta a^{\frac{1}{2}}\right) \qquad (1.17)$$

Where,

$$\left(\frac{a^{\frac{1}{2}}}{R}\right) = \left[\frac{V_1}{4\pi\Phi_2}\right]^{\frac{1}{2}}\left[\left\{\Phi_1^{-1} - \left(1-m^{-1}\right) - \frac{T_c}{T}\left(1+m^{-\frac{1}{2}}\right)^2\Phi_2\right\}^{-1} - \frac{V_2}{V_1}\right]^{\frac{1}{2}}$$

$\left(\frac{a}{k}\right)$ may be evaluated from the expression

$$\frac{4\pi a}{k^2} = -\frac{V_1}{\Phi_2}\left[\frac{kT}{\left(\partial\mu_1/\partial\Phi_2\right)_{P,T}} + \frac{V_2}{V_1}\right]$$

and using Flory-Huggins Formula

$$\left(\frac{\partial\mu_1}{\partial\Phi_2}\right)_{P,T} = -kT\left[\Phi_1^{-1} - \left(1-m^{-1}\right) - 2\left(\frac{\mu_0}{T}\right)\Phi_2\right]$$

where

$$\mu_0 = \frac{1}{2}T_c\left(1+m^{-\frac{1}{2}}\right)^2$$

and,

$$\Phi_2^c = \left(1+m^{\frac{1}{2}}\right)^{-1}$$

$$\Phi_1 = V_1 n_1 = \left(\frac{M_1}{\rho_1 N_0}\right) n_1$$

and

$$\Phi_2 = V_2 n_2 = \left(\frac{M_2}{\rho_2 N_0}\right) n_2$$

$m = \frac{V_2}{V_1}$ and T_c = critical temperature

N_0 = Avogadro's number.

Fixman has considered the experimental data of Reed and Taylor on the mixture (i-C_8H_{18}-C_7F_{16}) and considered C_7F_{16} as species 2.

Then the mixture has the properties

$T_c = 296.8^{\circ}K$ $\qquad$ $m = 1.353$

$V_1 = 165.9\ No^{-1}$ $\qquad$ $V_2 = 224.6\ No^{-1}$

$\Phi_2^c = 0.462$ $\qquad x_2^c = 0.387$

and $\rho^c = 1.135$ gm/c.c

Putting these datas in the equation (14)[1.17] he obtained the viscosity increment $\Delta\nu$ in centistokes

$$\Delta\nu = \left(\frac{10^2}{\rho}\right)\Delta\eta$$

or. $$\Delta\nu = 2.25\times10^{-6}\beta\left(\frac{a}{R}\right)$$

$$\left(\frac{a^{\frac{1}{2}}}{R}\right) = 6.89\left[\left(\Phi^{-1} - 0.2609 - 1026.6T^{-1}\Phi_2\right)^{-1} - 1.353\right]^{\frac{1}{2}}$$

He plotted the viscosity in centistokes ν versus, the volume fraction Φ_1 of i-C_8H_{18} in the mixture C_7H_{16} - i-C_8H_{18} at

(a) $T-T_c = 6.36^0$c (b) $T-T_c = 1.3^0$c (c) $T-T_c \cong 0^0$c

and obtained a curve which shows the viscosity rises sharply when the binary liquid mixture is critically opalescent.

He also calculated the friction constant β . Since the friction constant β is expected to be in the vicinity of 10^{12}-10^{13} Sec^{-1} and the constant "a" should be of the order of 1.Å he obtained $\beta(a^{\frac{1}{2}}) = 3.55 \times 10^{12}$ ($Å^{\frac{1}{2}}$ Sec^{-1}) a quite reasonable value.

Fixman has concluded that the comparison of the theory with

the experiment is not completely conclusive. What is needed evidently, is more viscosity data very near the critical temperature to minimize the first difficulty and an experimental determination of $\frac{\partial \mu}{\partial \Phi_2}$ in the same region.

It has not however been conclusively proved whether the intense density fluctuation is due to the formation of groups of molecules in the critical opalescent state. 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 wave length of light.

A general theory which can explain all the experimentally observed facts such as sharp rise in dielectric constant and loss, increase in viscosity and ultrasonic absorption, fluctuation of molecular polarization and density, depolarization and large increase of intensity of scattered light has not yet been provided.

D. TEMPERATURE DEPENDENCE OF ELECTRICAL CONDUCTIVITY IN LIQUIDS.

In making a wide survey of the various properties of ions in the solution, we generally meet three types of problem.
(a) Comparing different species of ions in the same solvent.
(b) dealing with the same species of ions in different solvents
(c) dealing with ions in same solvent at different temperature.
In electrolytes as well as in dielectric liquids the electrical conductivity has been attributed mainly due to the presence of ions. In order to understand the nature of the ionic conduction a large number of experiments have been performed regarding the variation of ionic conductivity with temperature. It has been observed that an increase of temperature results in an increase of ionic conduction at infinite dilution and this variation of conduction with temperature may be expressed with a fair degree of accuracy by means of the equation

$$\overset{\circ}{K}_t = \overset{\circ}{K}_{25}\left[1 + \alpha\left(t - 25\right) + \beta\left(t - 25\right)^2\right]$$

where K_t° is the ion conduction at infinite dilution at the temperature t, and K_{25}° is the value at 25°C. The factors α and β are constants for a given ion in the particular solvent.

(Walden's rule) Ionic conduction and Viscosity Temperature effect.

From a series of experiments it was observed by many workers that the activation energy for electrolytic conductance was almost identical with that of the viscous flow; hence it was presumed that ionic conductance was related to the viscosity of the medium.

Quite apart from any question of actual mechanism however, equality of the so called activation energies for both the processes means that the positive temperature coefficient of ion conductance is roughly equal to the negative temperature coefficient of viscosity. The experimental results helped to predict that the product of the ionic conductance and viscosity at a series of temperature should be approximately constant. Table 1.1 below shows the values of $K_o\eta_o$ at temperatures between 0^oC to 156^oC, where K_o is the ionic conductance of acetate ion at infinite dilution and η_o the viscosity of water.

Table 1.1

(Conductance Viscosity product of acetate ion)

Temperature	0^oC	18^oC	25^oC	59^oC	75^oC	100^oC	128^oC	156^oC
$K_o\eta_o$	0.366	0.368	0.366	0.368	0.369	0.368	0.369	0.369

The data for non-aqueous media are less complete, but it appears that in general the product of ionic conductance and viscosity in such media is also approximately constant over a range of temperature. Walden noted that the product of the equivalent conductance at infinite dilution and viscosity of the solvent was approximately constant and independent of the nature of the latter, and the conclusion is known as Walden's rule, which may be expressed as

$$\lambda_0 \eta_0 \approx \text{Constant}$$

for a given electrolyte in any solvent.

Table 1.2 shows the result obtained by Walden and others in a variety of media. The viscosities are expressed in poises.

Table 1.2

For Tetraethylammonium Iodide in various solvents at 25°C

Solvent	C_6H_5OH	CH_3OH	CH_3COCH_3	CH_3CN	$C_2H_4Cl_2$	CH_3NO_2	$C_6H_5NO_2$
$\lambda_0 \eta_0$	.63	.63	.66	.64	.60	.69	.67

The above results are utilized to formulate a rule which states that the product of ionic conductance at infinite dilution and viscosity is constant, for all temperatures and this formula is known as Walden's rule.

Debye-Hückel theory: (Interionic attraction; the ionic Atmosphere).

There may be a possibility that attractive forces between ions might have some influence on electrolytic conductance and in this regard, Debye and Hückel (1923) postulated a theory that every ion may be considered as being surrounded by an ionic atmosphere of opposite sign. They considered a positive ion situated at a distance r from a small volume element dv. The distance r is supposed to be of the order of less than about 100 times the diameter of an ion. As a result of the thermal movement of the ions, there will be at a certain instant an excess of negative ion in the volume element. If a time average is taken, however, it will be found to have, as a consequence of electrostatic attraction by a positive charge at a certain point a negative charge density. Every ion may thus be regarded as being associated with an ionic atmosphere of opposite sign. The net charge of the atmosphere is of course, equal in magnitude, but opposite in sign to that of the central ion; the charge density will obviously be greater in the immediate vicinity of the later and will fall off with increasing distance. Suppose the time average of the electrical potential in the centre of the volume element dv is ψ; then the work required to bring a positive ion from infinity up

to this point is $(z_+ e\psi)$ and to bring up a negative ion, it is $(-z_- e\psi)$, where z_+ and z_- are numerical values of the valences of the positive and negative ions respectively, and e is the electronic charge. If the Boltzmann law of the distribution of the particles in a field of varying potential energy is applicable to ions, the time average numbers of positive ions (dn_+) and of negative ions (dn_-) present in the volume element dv are given by

$$dn_+ = n_+ e^{-\left(z_+ \frac{e\psi}{KT}\right)} d\vartheta.$$

and

$$dn_- = n_- e^{-\left(-z_- \frac{e\psi}{KT}\right)} d\vartheta.$$

where n_+ and n_- are the total numbers of positive and negative ions respectively, in unit volume of the solution; K is the Boltzmann constant, i.e. the gas constant per single molecule, and T is the absolute temperature. The electrical density ρ i.e. the net charge per unit volume, in the given volume element is therefore given by

$$\rho = \frac{e\left(z_+ dn_+ - z_- dn_-\right)}{d\vartheta}$$

$$\rho = e\left[n_+ z_+ \exp\left(z_+ \frac{e\psi}{KT}\right) - n_- z_- \exp\left(z_- \frac{e\psi}{KT}\right)\right] \qquad (1\cdot18)$$

for a uni-univalent electrolyte z_+ and z_- are unity, and n_+ and n_- must be equal, because of electrical neutrality. Hence equation

(1.18) becomes

$$\rho = ne\left[\exp\left(-\frac{e\psi}{KT}\right) - \exp\left(\frac{e\psi}{KT}\right)\right] \qquad (1.19)$$

where n is the number of either kind of ion in unit volume. Expanding the two exponential series, and writing x in place of $\frac{e\psi}{KT}$, the equation (1.19) becomes

$$\rho = -\frac{e^2\psi}{KT}\,2n\left(1 + \frac{x^2}{3!} + \frac{x^4}{5!} + \cdots\right)$$

and if it is assumed that x i.e. $\frac{e\psi}{KT}$, is small in comparison with unity, all terms beyond the first in the parenthesis may be neglected, so that

$$\rho = -\frac{e^2\psi}{KT}\,2n \qquad (1.20)$$

In the general case, when z_+ and z_- are not necessarily unity, if the assumption is made that $\left(\frac{Ze\psi}{KT}\right)$ is much less than unity in each case, so that

$$\rho = -\frac{e^2\psi}{KT}\sum_i n_i z_i^2 \qquad (1.21)$$

where n_i and z_i represent the number (per unit volume) and valence of the ions of the ith kind. The summation is taken over all the types of ions present in the solution, and equation (1.21) is

applicable irrespective of the number of different kinds of ions.

In order to solve for ψ it is necessary to have another relationship between ρ and ψ and this may be obtained by introducing poisson's equation, which is equivalent to assuming the Coulomb's law of force between electrostatic charges holds good for ions. This equation in rectangular co-ordinate is

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} = -\frac{4\pi\rho}{\epsilon} \qquad (1.22)$$

x, y and z are the co-ordinates of the point in the given volume element, and ϵ is the dielectric constant of the medium converting to polar co-ordinates, and making use of the fact that the terms containing $\frac{\partial\psi}{\partial\theta}$ and $\frac{\partial\psi}{\partial\phi}$ will be zero, since the distribution of potential about any point in the electrolyte must be spherically symmetrical, and consequently independent of the angle θ and ϕ ; equation (1.22) becomes

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) = -\frac{4\pi\rho}{\epsilon} \qquad (1.23)$$

If the values of ρ given by equation (1.21) is inserted, this becomes

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) = \frac{4\pi e^2}{\epsilon KT}\psi\sum_i n_i z_i^2 = k^2\psi \qquad (1.24)$$

where the quantity k is defined by

$$k = \left[\frac{4\pi e^2}{\epsilon KT} \sum_i n_i Z_i^2 \right]^{\frac{1}{2}} \qquad (1.25)$$

The differential equation (1.24) can be solved, and the solution has the general form

$$\psi = \frac{A \exp(-kr)}{r} + \frac{A' \exp(kr)}{r} \qquad (1.26)$$

where A and A' are constants which can be evaluated in the following manner. Since ψ must approach zero as r increases because potential at an infinite distance from a given point in the solution must be zero, it follows that the constant A' must be zero, equation (1.26) consequently becomes

$$\psi = \frac{A \exp(-kr)}{r} \qquad (1.27)$$

For a very dilute solution $\sum_i n_i z_i^2$ is almost zero, and hence so also is k, as may be seen from equation (1.25); the value of the potential at the point under consideration will then be $\frac{A}{r}$, according to equation (1.27). In such a dilute solution the potential in the neighbourhood of any ion will be due to that ion alone, since other ions are too far away to have any influence: further, if the ion is regarded as being a point charge, the potential at small

distances will be $Z_i e/\epsilon r$. It follows, therefore, that

$$\frac{A}{r} = \frac{z_i e}{\epsilon r}$$

$$A = \frac{z_i e}{\epsilon}$$

and insertion of this result in equation (1.27) gives

$$\psi = \frac{z_i e}{\epsilon} \exp\left(-kr\right)/r \qquad (1.28)$$

This equation may be written in the form

$$\psi = \frac{z_i e}{\epsilon r} - \frac{z_i e}{\epsilon r}\left\{1 - \exp\left(-kr\right)\right\}$$

and if the solution is dilute, so that k is small and $\left[1 - \exp(-kr)\right]$ is practically equal to kr, this becomes

$$\psi = \frac{z_i e}{\epsilon r} - \frac{z_i e k}{\epsilon} \qquad (1.29)$$

The first term on the right of the equation (1.29) is the potential at a distance r due to a given point ion when there are no surrounding ions; the second term must, therefore, represent the potential arising from the ionic atmosphere. It is seen, therefore, that ψ_i the potential due to the ionic atmosphere, is given by

$$\psi_i = -\frac{z_i e k}{\epsilon} \qquad (1.30)$$

for a dilute solution. Since this expression is independent of r, it may be assumed to hold when r is zero, so that the potential on the ion itself, due to its surrounding atmosphere which is $-z_i e$ since it is equal in magnitude and opposite in sign to that of the central ion itself, were placed at a distance $\frac{1}{K}$ from the ion the potential produced at, it would be $-\frac{z_i e K}{\epsilon}$, which is identical with the value given by equation (1.30). It is seen, therefore, that the effect of the ion atmosphere is equivalent to that of a single charge, of the same magnitude, placed at a distance $\frac{1}{K}$ from the ion; the quantity $\frac{1}{K}$ can thus be regarded as a measure of the thickness of the ion atmosphere in a given solution. The thickness of the ionic atmosphere will depend on the number of ions of each kind present in unit volume and on their valence. If C_i is the concentration of the ions of the ith kind expressed in moles (gram-ions) per litre, then

$$n_i = C_i \frac{N}{1000}$$

where N is the Avogadro number, hence, from equation (1.25) after making slight rearrangement

$$\frac{1}{K} = \left(\frac{\epsilon T}{\sum C_i z_i^2} \times \frac{1000 k}{4\pi e^2 N} \right)^{\frac{1}{2}} \qquad (1.31)$$

The value of the universal constants are as follows: K is 1.38×10^{-16} erg per degree, e is 4.802×10^{-10} e.s. unit and N is 6.025×10^{23}, hence

$$\frac{1}{K} = 2.81 \times 10^{-10} \left(\frac{\epsilon T}{\sum c_i z_i^2} \right)^{\frac{1}{2}} \text{ cm.}$$

The thickness of the ionic atmosphere is thus seen to be of the order of 10^{-8} cm; it decreases with increasing concentration and increasing valence of the ions present in the electrolyte, and increases with increasing dielectric constant of the solvent and with increasing temperature.

Time of Relaxation of Ionic Atmosphere:-

As long as the ionic atmosphere is 'stationary' that is to say, it is not exposed to an applied electrical field or to a shearing force tending to cause movement of the ion with respect to the solvent, it has spherical symmetry. When the ion is made to move under the influence of an external force, however e.g. by the application of an electrical field, the symmetry of the ionic atmosphere is disturbed. If a particular kind of ion moves to the right, for example, each ion will constantly have to build up its ionic atmosphere to the right, while the charge density to the left gradually decays. The rate at which the atmosphere tothe right fomrs and that to the left dies away is expressed in terms of a quantity

called time of relaxation of the ionic atmosphere. The decay of the ionic atmosphere occurs exponentially, so the return to random distribution is asymptotic in nature; it follows, therefore, that the time required for the ionic atmosphere to fall actually to zero is, theoretically, infinite. It has been shown, however, that, after the removal of the central ion, the surrounding atmosphere falls virtually to zero in the time $4q\theta$ where θ is the time of relaxation of the ionic atmosphere and q is defined by

$$q \equiv \frac{Z_+ Z_-}{Z_+ + Z_-} \times \frac{K_+' + K_-'}{Z_+ K_-' + Z_- K_+'} \qquad (1.32)$$

Z is the valence, excluding the sign and K is the ion conductance of the respective ions. For a binary electrolyte, i.e. one yielding only two ions, Z_+ and Z_- are equal and q is 0.5; the time for ionic atmosphere to decay virtually to zero is then 2θ.

When an ion of valence Z is moving with a steady velocity through a solution, under the influence of an electrical force eZV where V is the applied potential gradient, this force must balance the force due to resistance represented by fu, where f is the resultant coefficient of frictional resistance and u is the steady velocity of the ion. It follows, therefore, that

$$eZV = fu$$
$$f = eZV/u$$

If the potential gradient is 1 volt per cm. then V is $\frac{1}{300}$ e.s. unit; further the velocity u is then given by

$$\overset{\circ}{K}'_{+} = F\overset{\circ}{u}_{+} \quad \text{and} \quad \overset{\circ}{K}'_{-} = F\overset{\circ}{u}_{-}$$

$$f = \frac{ezF}{300K} = 15{\cdot}4\times10^{-8}\frac{z}{K'} \qquad (1.33)$$

where F is Faraday = 96,500. Since $e = 4.802 \times 10^{-10}$ e.s. unit. It has been shown by Debye and Falkenhagen that the relaxation time is related to the frictional coefficients f_+ and f_- of the two ions constituting a binary electrolyte by the expression

$$\tau = \frac{2f_+ f_-}{f_+ + f_-} \cdot \frac{1}{KTR^2} \text{ Sec.} \qquad (1.34)$$

The R has the same significance as before. Utilizing equation (1.33) and remembering that z_+ is equal to z_- for a binary electrolyte and that K'_+ and K'_- is equal to K', the equivalent conductance of the electrolyte, the equation (1.34) becomes

$$\tau = 30{\cdot}8\times10^{-8}\frac{z}{K'}\cdot\frac{1}{KTR^2} \text{ Sec.} \qquad (1.35)$$

Mechanism of Electrolytic conductance
(The Debye-Huckel-Onsager conductance equation)

The existence of a finite time of relaxation means that the

ionic atmosphere surrounding a moving ion is not symmetrical, the charge density being greater behind than infront; since the net charge of the atmosphere is opposite to that of the central ion, there will be an excess charge of the opposite sign behind the moving ion. The asymmetry of the ionic atmosphere, due to the time of relaxation will thus result in a retardation of the ion moving under the influence of an applied field. This influence on the speed of an ion is called the relaxation effect or assymmetry effect.

Another factor which tends to retard the motion of an ion in solution is the tendency of the applied potential to move the ionic atmosphere with its associated solvent molecules, in a direction opposite to that in which central ion, with its solvent molecules is moving. An additional retarding influence, equivalent to an increase in the viscous resistance of the solvent is thus exerted on the moving ion, this is known as the electrophoretic effect, since it is analogous to the resistance acting against the movement of a Colloidal particle in an electrical field.

An attempt to calculate the magnitude of the forces opposing the motion of an ion through a solution was made by Debye and Huckel: they assumed the applicability of Stokes's law and derived the following expression for the electrophoretic force on an ion of the ith kind:

$$\text{Electrophoretic Force} = \frac{e z_i k}{6\pi\eta} f_i v \qquad (1.36)$$

where $e z_i$ and κ have their usual significance, the latter being taken as equal to the reciprocal of the thickness of the ionic atmosphere; η is the viscosity of the medium; f_i is the coefficient of frictional resistance of the solvent opposing the motion of the ion of the ith kind, and V is the applied potential gradient. The same result was derived in an alternative manner by Onsager, who showed that it is not necessary for Stokes's law to be strictly applicable in the immediate vicinity of an ion.

In the first derivation of the relaxation force Debye and Huckel did not take into account the natural Brownian movement of the ions; allowance for this was made by Onsager who deduced the equation

$$\text{Relaxation Force} = \frac{e^3 z_i \kappa}{6\epsilon KT}\omega V \qquad (1.37)$$

where ϵ is the dielectric constant of the medium and ω is defined by

$$\omega \equiv z_+ z_- \cdot \frac{2q}{1+q^{\frac{1}{2}}} \qquad (1.38)$$

the value of q being given by equation (1.32).

It is now possible to equate the forces acting on an ion of the ith kind when it is moving through a solution with a steady velocity u_i; the driving force due to the applied electrical field is $e z_i V$; and this is opposed by the frictional force of the solvent,

equal to $K_i u_i$, together electrophoretic and relaxation forces; hence

$$ez_i V = f_i u_i + \frac{e z_i k}{6\pi\eta} f_i V + \frac{e^3 z_i k}{6\epsilon k T} \omega V \qquad (1.39)$$

On dividing throughout by $f_i V$ and rearranging, this becomes

$$\frac{u_i}{V} = \frac{ez_i}{f_i} - \frac{ez_i k}{6\pi\eta} - \frac{e^3 z_i k}{6\epsilon k T} \cdot \frac{\omega}{f_i}$$

If the field strength and potential gradient, is taken as 1 volt per cem, i.e. V is 1/300, then

$$u_i = \frac{e z_i}{300 f_i} - \frac{ek}{300}\left(\frac{z_i}{6\pi\eta} + \frac{e^2 z_i}{6\epsilon k T} \cdot \frac{\omega}{f_i}\right) \qquad (1.40)$$

At infinite dilution k is zero, and so under this conditions this equation becomes

$$\frac{K_i'}{\alpha F} = \frac{k_i^{o\prime}}{F} - \frac{eR}{300}\left(\frac{z_i}{6\pi\eta} + \frac{e}{6\epsilon k T} \cdot \frac{e z_i}{f_i} \cdot \omega\right) \qquad (1.41)$$

For simplicity, the assumption is now made that the electrolyte is completely dissociated, that is to say, α is assumed to be unity; this, as will be evident shortly, is true for solution of strong electrolytes at quite appreciable concentrations. Equation (1.41) can then be put in the form

$$K_i' = k_i^{o\prime} - \frac{eR}{300}\left(\frac{z_i}{6\pi\eta} F + \frac{300 e}{6\epsilon k T} k_i^{o\prime} \omega\right) \qquad (1.42)$$

replacing $\frac{ez_i}{f_i}$ by (300 K_i^o/F). Introducing the expression for k given by equation (1.25), and utilizing the standard values of e.k and N, equation (1.42) becomes

$$K_i' = K_i^{o\prime} - \left[\frac{29.15 z_i}{(\epsilon T)^{1/2}\eta} + \frac{9.90\times 10^5}{(\epsilon T)^{3/2}} K_i^{o\prime}\omega\right]\sqrt{C_+ z_+^2 + C_- z_-^2} \qquad (1.43)$$

The quantities C_+ and C_- represent the concentrations of the ions in moles per liter; these may be replaced by the corresponding concentrations C in equivalents per liter, where C which is the same for both ions, is equal to $C_- z_i$ hence

$$K_i' = K_i^{o\prime} - \left[\frac{29.15 z_i}{(\epsilon T)^{1/2}\eta} + \frac{9.9\times 10^5}{(\epsilon T)^{3/2}} K_i^{o\prime}\omega\right]\sqrt{C(z_+ + z_-)}$$

$$K_i' = K_i^{o\prime} - \left[\frac{29.15(z_+ + z_-)}{(\epsilon T)^{1/2}\eta} + \frac{9.9\times 10^5}{(\epsilon T)^{3/2}} K_i^{o\prime}\omega\right]\sqrt{C(z_+ + z_-)} \qquad (1.44)$$

The above equation represents forms of the Debye-Hückel-Onsager conductance equation; these relationships, based on the assumption that dissociation of the electrolyte is complete, attempt to account for the falling off of the equivalent conductance at appreciable concentrations in terms of a decrease in ionic velocity resulting

from interionic forces. The decrease of conductance due to these forces is represented by the quantities in the square brackets; the first term in the brackets gives the effect due to the electrophoretic force and the second term represents the influence of the relaxation, or assymmetry force. It will be apparent from equation (1.44) that for a given solvent at a definite temperature, the magnitude of the interionic forces increases, as is to be anticipated, with increasing the valence of the ions and with increasing concentration of the electrolyte.

Pao (1943) conducted a long series of measurements of current-voltage characteristic under different temperatures in Iso-octane and liquid air, both of which were ionised by γ-rays from a radium source and observed that the current increases systematically with an increase in temperature but the slopes of straight lines remain constant in the saturation region and no difference was found as a result of changing the direction of applied voltage.

He explained the phenomena qualitatively by the fact that viscosity decreases with the increase of temperature and hence the ions in the column are more readily separated from each other. Jaffee developed a formula expressing the value of the current at any field in terms of the mobility, diffusion and recombination coefficient of the ions and is represented by

$$\frac{1}{I_A} = \frac{1}{I_\infty}\left[1 + \frac{\alpha N}{7{\cdot}85 b\omega} \times \frac{1}{E} \times F\left(\frac{b^2\omega^2E^2}{2D^2}\right)\right] \qquad (1.45)$$

where I_A is the current per unit area at a field E, I_∞ the saturation current at infinite field, N the number of ion pairs produced per cm length of a column; b, the initial diameter of the column within which the ions are found and α, ω and D are the recombination, mobility and diffusion coefficient respectively of the ion. Having examined Jaffee's theory of columnar ionization, Pao arrived at the following relationship

$$\frac{1}{I_A} = \frac{1}{I_\infty}\left(1 + S\frac{1}{E}\right) \qquad (1.46)$$

where $$S = \frac{\alpha N}{7.85\, b\omega}$$

An interesting fact observed from the nature of the curve, $\frac{1}{I_A}$ against $\frac{1}{E}$ in iso-octane irradiated by γ-rays at 313.3°K, 273°K, 260.6°K, 230°K, and at 191°K is that all the straight lines intersect at one point (the same I_∞ value). This indicated that the number of ions produced by the ionising agent is independent of the temperature of the liquid. On the basis of his experimental results, he obtained an emperical relation between S and T

$$S = \frac{\text{Constant}}{T^{1.28}} \qquad (1.47)$$

Pao also investigated, the variation of induced and natural conductivity of iso-octane and liquid oxygen with temperature.

Plumley (1941) applied potential dissociation theory to explain residual conductivity of the dielectric liquid and stated that even those molecules of the liquid whose dielectric constant is very low (2-4) are likely to dissociate in higher electric field. According to his theory, the neutral molecules generally form pairs of positive and negative ions which may dissociate into two ions in an electric field. Thus for heptane

$$2C_7H_{16} \rightleftharpoons C_7H_{15}^{-} + C_7H_{17}^{+}$$

He was able to give an expression for the current in term of temperature T and the field E, applicable to number of dissociated molecules

$$I_A = C \exp\left(\frac{2q}{KT}\right)\left(\frac{qE}{300\epsilon}\right)^{1/2} \qquad (1.48)$$

where C is a constant and is proportional to the number of dissociated molecules at zero field. K is Boltzmann constant, q the unit charge and ϵ , the dielectric constant.

The expression (1.48) could be represented as

$$\ln I_A = AE^{\frac{1}{2}} \qquad (1.49)$$

This is an important conclusion of Plumley's theory.

Reiss and Pao have compared the Plumley's relationship with their own results and observed the dependence of the current on both temperature and dielectric constant.

Frenkel's Theory. Frenkel (1947) based his theory of electrical conduction in dielectric liquids on his own general theory of liquids. According to this theory the molecules of a liquid are bound together by the forces of cohesion but owing to thermal motion they widely oscillate around their position of equilibrium. There is a distinct probability that in the course of oscillation a molecule might acquire such a kinetic energy that it would be able to separate itself from its neighbouring molecule and travel at a distance equivalent to its dimensions and then stop in a new position of equilibrium. The number of travelling molecules is determined by the difference u_o between the potential energy u_2 of a molecule in an excited state and the potential energy U_1 of a molecule in a normal state ($U_o = U_2 - U_1$). The number of molecules also depends on the kinetic energy of a molecule in its random thermal motion i.e. it depends on the temperature T of the liquid. When an ion is influenced by an external force, their potential energy is reduced as it moves towards the direction of the action of the force. The frequency of the molecule's free vibration when in a static position is denoted by ν (frequency is the number of possible jumps over the wall of the potential U_o). The number n of molecules which surmount the

wall in unit time and in a given direction is

$$n = \frac{n_0}{6} \nu \exp\left(-\frac{U_0}{KT}\right) \qquad (1.50)$$

The numerical 6 is in the denominator because one-third of the molecules moves in one of the three perpendicular directions and a half of this third turns in one direction. In the absence of external forces the activated molecules of the liquid move at random in various directions and surmount the potential wall arriving at new positions of equilibrium. This description of thermal motion in liquids explains various phenomena including the effect of temperature on the viscosity of the liquid.

After application of an electric field, the ions acquire additional velocity towards the field and thus gain extra kinetic energy $\Delta u = q E \delta/2$ (q denotes the ion charge, E, the electric field strength and δ, the length of the free path of an ion) Δu is thus the work of the electric field along half of the length of the free path. The additional number of ions crossing over the potential wall as a result of the action of an electric field was

$$\Delta n = \frac{n_0}{6} \nu \left[\exp\left(-\frac{U_0 - \Delta u}{KT}\right) - \exp\left(-\frac{U_0 + \Delta u}{KT}\right)\right] \qquad (1.51)$$

The following expression was obtained for lower field $\Delta U \ll KT$; when

the functions $\exp\left(-\frac{\Delta u}{KT}\right)$ and $\exp\left(\frac{\Delta u}{KT}\right)$ were expanded

$$\Delta n = \frac{n_0}{3}\,\delta\,\exp\left(-\frac{u_0}{KT}\right)\frac{\Delta u}{KT} \qquad (1.52)$$

$$\Delta n = \frac{n_0 q E \delta}{6KT}\,\exp\left(-\frac{u_0}{KT}\right) \qquad (1.53)$$

The number of additional jumps made by one ion per second towards the field was determined by the expression

$$\frac{\Delta n}{n_0} = \left(\frac{q\delta}{6KT}\right) E\,\exp\left(-\frac{u_0}{KT}\right) \qquad (1.54)$$

The velocity of the transfer of ions towards the field was

$$v_E = \frac{\Delta n}{n_0}\,\delta = \frac{q\delta^2}{6KT} E\,\exp\left(-\frac{u_0}{KT}\right) \qquad (1.55)$$

$$v_E = \frac{\Delta u \delta}{3KT}\,\exp\left(-\frac{u_0}{KT}\right) \qquad (1.56)$$

and the mobility of ions in the liquid

$$u = \frac{v_E}{E} = \frac{q\delta^2}{6KT}\,\exp\left(-\frac{u_0}{KT}\right) \qquad (1.57)$$

$$u = \frac{\Delta u\, \delta\nu}{3KTE} \exp\left(-\frac{U_0}{KT}\right) \qquad (1.58)$$

The mobility of ions depends on the length of the 'free' path of an ion, the temperature of the liquid and so on the work necessary to separate an ion from its neighbouring molecules. In the weak fields ($E \ll KT$) this mobility does not depend on the field strength.

The intensity of the ion current in the region below saturation point was formulated as follows,

$$i = n_0 q v_E = n_0 q u E \qquad (1.59)$$

or
$$i = \frac{n_0 q^2 \delta^2 \nu}{6KT} \exp\left(-\frac{U_0}{KT}\right) E \qquad (1.60)$$

the electrical conductivity of the liquid was

$$\sigma = \frac{i}{E} = n_0 q u$$

$$\sigma = \frac{n_0 q^2 \delta^2 \nu}{6KT} \exp\left(-\frac{U_0}{KT}\right) \qquad (1.61)$$

where n_0 denotes the number of ions per c.c.

According to Frenkel the mechanism of electrical conduction in dielectric liquid interpreted by Adamczewski is as follows; an ion produced by an external agent attaches itself to a molecule thus forming an entity. As a result of thermal motion, however, the ion

is able to separate itself from the molecule. In this process the ion loses energy when overcoming the coupling forces, i.e. when generating activation energy. After separation from the molecule the ion travels along a certain free path, whose length is comparable to the dimension of the molecule, and attaches itself to another molecule. The mean free path δ depends both on the structure of the molecule and on the moving ion.

The ions in a liquid may be surrounded by neutral molecules (this is characteristic for polar liquids). For this reason the ions in a liquid have similar values of mobility 10^{-4} $cm^2 sec^{-1} V^{-1}$. Where as the mobility of gaseous ions may be of different order of magnitude.

The equation (1.61) may be written as

$$\sigma = A \exp\left(-\frac{\Delta E}{KT}\right) \qquad (1.62)$$

where $A = \frac{n_0 q^2 \delta^2 \nu}{6KT}$ and $U_0 = (U_2 - U_1) = \Delta E$

It follows from the above formula that the conductivity of ions in a liquid should increase rapidly with an increase in temperature. In comparison with the term $\exp\left(-\frac{\Delta E}{KT}\right)$, the value A charges very slowly with increasing temperature. To a first approximation, therefore, it can be assumed that relationship $\ln\sigma = f\left(\frac{\Delta E}{KT}\right)$ should be linear and this is generally consistant with experimental

data. Standhammer and Seyer (1957) attempted to measure the conductivity of cyclohexane saturated with water as a function of temperature, and also calculated the number of ions per cubic centimeter per second produced in cyclohexane with the change of water content and temperature. The result obtained clearly showed that the logarithm of the conductivity of the cyclohexane, saturated with water, was inversely proportional to the absolute temperature.

Forster (1962) published the results of his research on electric conduction in benzene under normal condition i.e. when the liquid was saturated with air, the self conductivity in benzene was of the order 10^{-14} ohm^{-1} cm^{-1}; while after the de-aeration of the freshly purified liquid, it was about 10^{-16} ohm^{-1} cm^{-1}. He observed that the temperature dependence of the conductance of benzene was in all cases a straight line, *i.e.* when log of conductance or log of specific conductance was plotted against $\frac{1}{T}$. He obtained the following relationship for the dependence of conductivity on temperature at the various separations of the electrodes,

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

where σ_0 and ΔE are material constants. The value of activation energy ΔE was determined by least-square analysis. Within experimental error of ± 0.04 ev the values of activation energy obtained was $\Delta E = 0.42$ ev. The value of σ_0 was 5×10^{-6} ohm^{-1} cm^{-1} for distilled and degassed benzene and its value was found to increase with decreasing purity of benzene.

The values of activation energy obtained by Forster for aromatic hydrocarbons were about 0.4 - 1ev and for benzene, toluene, and xylenes about 0.41 e.v. He found similar values of activation energy for self-conductivity in cyclohexane ($\sim$ 0.42 ev).

Jachym conducted a long 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 ionisation current on the increase in temperature. That is, the activation energy for natural conductivity was almost four times greater than that for ionization conduction. Adamczewski measured the natural and ionisation currents in wider range of temperature for hexane to hexadecane and showed another important difference in the dependence of natural and ionisation conductivity on temperature. Ionisation conductivity is characterised by straight lines, which are almost parallel to each other when $\ln I$ is plotted against $\frac{1}{T}$, but in the case of self conductivity, however, a sudden change takes place at a certain temperature, above which a further increase in the natural current was 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 his colleagues. They determined the activation energy for these processes and established the following general relationship for

natural conductivity.

$$\sigma = \sigma_1 + \sigma_2 = \sigma_{01} \exp\left(-\frac{\Delta E_1}{KT}\right) + \sigma_{02} \exp\left(-\frac{\Delta E_2}{KT}\right) \qquad (1.63)$$

where $\sigma_{01} = (2 \pm 1)10^{-2}$ ohm^{-1} cm^{-1} was independent of the chemical structure of the molecules, and σ_{02} was characteristic for each substances.

Bassler and his colleagues discovered that in several liquids there were changes of slope in the curves. This indicated that at a certain temperature, a change occurs in the activation energy of the conduction process, which shows that the second term of the equation (1.62) begins to prevail.

Organische, Halbleiter (1966), justified the validity of the relationship

$$\sigma = \sigma_0 \exp\left(-\frac{\Delta E}{2KT}\right) \qquad (1.64)$$

in case of organic substance having a small molecular size.

Adamczewski, and Jachym (1963) in their paper have given a comparison of results by various research workers for the conductivity of different dielectric liquids as a function of temperature, $(\frac{1}{T})$.

SCOPE AND OBJECT OF THE PRESENT WORK.

It is evident from the review of the work done both in theoretical and experimental aspects on the electrical conductivity of dielectric liquids that it is possible to obtain some definite information regarding the state, the degree of dissociation and the presence of free electrons and ions in liquids. The prevalent theories regarding the mechanism of electrical conduction in liquids as presented by different authors have been discussed in detail and the models that have been built up to explain the electrical conductivity in liquids both polar and non-polar have helped us to gain some knowledge regarding the nature of the liquid state. The theory of conduction in electrolytes has been established on a solid foundation by Debye and Hückel and later on the theory has been improved by the work of Onsager, Kirkwood, Debye and Falkenhagen. The experimental results however definitely indicate that all dielectric liquids both polar and non-polar exhibit a finite conductivity. No general theory regarding the mechanism of conduction in the dielectric liquids has however been advanced so far. The main object of the present investigation is to obtain experimental data regarding the nature of electrical conduction in dielectric liquids and to present a consistent theory with the aid of the data thus obtained. It is evident from the review of literature in this field that almost all the work on the electrical conductivity of dielectrics has been carried out in d.c. fields and mostly on non-polar dielectrics. It is thus thought worthwhile to carry out measurements in

the radiofrequency region because these types of measurements will provide us with data for both the conduction and displacement currents as well. The measurements have been particularly restricted to a number of polar molecules. It is thus proposed to undertake the following lines of investigation in the present work.

A. Radiofrequency conductivity of a number of polar liquids dissolved in different non polar solvents.

Almost all calculations of dielectric relaxation time in liquids have been made from the measurement of dielectric constant and loss in polar liquids and utilizing the well known expressions of Debye,

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

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

the relaxation time τ has been calculated. It has been shown by Murphy and Morgan that the radiofrequency conductivity of a polar dielectric is a complex quantity and is related with the real and imaginary parts of dielectric constants by the equations

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

and

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

In these deductions it is assumed however that no free electronic or ionic conduction is present and the total current is the displacement current.

It is thus apparent that the measurement of the radio frequency conductivity of a polar liquid enables us to calculate the relaxation time of the molecules in the dielectric and offers an alternative method to dielectric constant measurement. The relaxation time τ is given according to Debye by the relation

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

where η is the coefficient of macroscopic viscosity and 'a' is the radius of the rotating unit. Thus the measurement of τ will enable us to obtain information regarding the nature of the intermolecular field and the structure of the molecule. As in the case of dielectric constant and loss measurements, experiments are to be performed with polar molecules dissolved in non polar solvents in order to minimise the dipole-dipole, dipole induced dipole interaction. The problem of representing the internal force which opposes the rotational movement of the molecule under the action of field applied, by viscous force is a subject of speculation and no definite conclusion has been reached though a number of empirical representations have been suggested. The measurement of radio frequency conductivity of polar molecules in different non polar solvents will

enable us to get an idea regarding the nature of this internal force because the presence of different non polar solvent molecules will have different effect on the magnitude of this internal force.

B. Nature of Opalescent binary mixtures.

It is well known that in the region of critical opalescence of two binary liquid mixtures abrupt changes of some of the physical properties of the mixture occur. A sharp rise in the value of the dielectric constant and loss, coefficient of viscosity, ultrasonic attenuation occurs as the critical temperature is approached. In the 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 that in case of clear solution the scattering is due to single molecules where as 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 light scattering experiments. Fixman has 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 wave length 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. The object of this part of the investigation is to measure the change of viscosity from the radiofrequency conductivity measurements as the mixture approaches the critical stage and compare the results with Fixman's theory. Further it will also enable us to calculate the volume of the rotating unit and which in turn will give a measure of the volume of scatterers in the critical opalescent stage. No general theory which can explain all the observed experimental results has been developed and it is expected that this study may provide some data which will be helpful in developing such a theory.

C. Relationship of viscosity with Radiofrequency conductivity in case of polar liquids.

In Sections A and B, it has been assumed after Murphy and Morgan that no free electron or ion conduction takes place in a dielectric and only the displacement current prevails. To test the validity of this assumption the work in the present section is proposed to be undertaken. From the expression for radio frequency conductivity as deduced by Murphy and Morgan and assuming $\tau = \frac{4\pi a^3 \eta}{KT}$ we get,

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

As in the most common dielectrics $\tau = 10^{-11}$ Sec. and the frequency of the applied voltage varies from 400 Kc/Sec. to 6 MC/Sec, $\omega^2\tau^2$ is $\ll 1$

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

Thus if measurement of radio frequency conductivity is made at gradually higher and higher temperatures then as $(\epsilon_o - \epsilon_\infty)$ and η/T are both decreasing functions of temperature, K' should decrease with the increase of temperature. The experimental results will thus indicate whether the assumption of the absence of free ions and 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 non polar dielectrics. Based on the experimental results it is proposed to modify the expression for the total radio frequency current that flows in a dielectric when placed in an external electric field.

It is further known that in case of d.c. field the product of 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 can be established in case of polar dielectrics with regard to radio frequency conductivity and viscosity.

D. Activation Energy for Viscosity of Polar dielectrics.

The presence of free ions and electrons in polar and non polar dielectrics has been demonstrated by recent measurements of electrical conductivity in these liquids by a large number of workers. An expression in the form has been deduced by Sen and Ghosh

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

(1974) Where $A = \pi f^2 \left(\epsilon_o - \epsilon_\infty\right) \tau$ and $B = \frac{ne^2}{6\pi a}$. Where 'a' is the radius of the molecule and ion and η is the coefficient of viscosity and f is the frequency of the applied r.f. field.

It has further been suggested that the dependence of conductivity of organic liquids on temperature is similar to that of specific conductivity in case of intrinsic semi conductors. Bassler and Riehl (1965) have suggested that in case of organic liquids the variation of conductivity with temperature can be represented by an equation

$$K' = K_o \exp\left(-\frac{\Delta E_c}{2kT}\right)$$

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

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

where ΔE_η is the activation energy for viscous flow. According to the assumptions of hole theory ΔE_η should be equal to 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_η no definite and clear picture is at present available and since an expression has been deduced incorporating radio frequency conductivity and viscosity an attempt can be made to correlate the activation energy for viscosity with the characteristic energy of activation for conductivity.

It is presumed that the information thus obtained for the factor responsible for viscosity in liquids may help in clarifying the idea regarding the nature of the internal intermolecular force which opposes the rotation of a molecular dipole placed in an external electric field.

E. Effect of a transverse magnetic field on the radio frequency conductivity of polar dielectrics.

Assuming the presence of free ions and electrons in a polar dielectric it has been possible to deduce an expression relating the conductivity of a polar dielectric and its viscosity. To provide an indirect evidence for the presence of free ions; it is proposed to study the variation of radio frequency current in a number of polar dielectrics when a variable transverse magnetic field is

applied to the dielectric. It is expected that if a sufficiently strong magnetic field is applied it may affect the motion of the ions and thereby cause a change in the magnitude of the current flowing through the dielectric. If the magnetic field is not sufficiently strong another effect may be expected. It has been shown by Kimura (1943) that the viscosity of a polar liquid is changed when placed in a transverse magnetic field and as the radio frequency conductivity is related to viscosity a change in r.f. conductivity is also expected. A systematic study of the nature of the variation of viscosity with magnetic field may throw some light on the nature of the viscous forces operating in a liquid.

F. Temporal variation of current in polar dielectrics.

It has been a general observation that when 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 electrode. These observed experimental facts obviously suggest that in dielectrics free ions do exist. It is thus proposed to make a systematic investigation of the phenomena in a number of polar dielectrics as regards the change of current with time. No detailed theory regarding the mechanism of the decrease of current with time has been established so far. The detailed theory will obviously have to take into consideration the motion of the ions in the field applied. The theory may also enable us to calculate the

mobility and number density of the ions.

The proposed experiments are supposed to provide us with information regarding the nature of the current that flows in dielectrics which are supposed to be ideal insulators. The results will also show the imperfection in natural dielectrics. With these experimental results it may be possible to develop a systematic theory regarding conduction processes in dielectrics.

R E F E R E N C E S

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