CHAPTER III

ELECTRICAL CONDUCTIVITY OF ETHYL CELLULOSE
3.1 ELECTRICAL CONDUCTIVITY

Recently, polymers have attracted wide attention of scientists owing to their vital applications in microelectronics such as electrostatic recording, transducers, charge storage devices etc. Hence the understanding of the mechanism of electrical transport in thin polymeric films is of considerable importance. Interest in the mechanism of electrical conduction of polymers is due both to their technical importance as good insulators and to the fact that their conductivity is related to the physical structure as well as to their chemical nature.

Though much work on electrical behaviour of polymers has been reported in reviews and books \(^1\text{--}^{11}\) in past several years but still the mechanism of electrical transport is far from clear.

The knowledge of the following mechanisms is needed for a complete understanding of electrical conduction in any solid (semi conducting / semi insulating):

(i) Energy level diagram of the solid.
(ii) Carrier generation mechanism.
(iii) Carrier recombination and trapping, and
(iv) Mechanism of carrier transport.
3.1.1 Energy level diagram of the crystal

The molecules of organic solids are held together by weak Vander Waal forces. So the molecular properties are preserved to a high degree despite the binding of the molecules in a lattice. Consequently the weak, direct optical transitions between different molecules, or the energy bands, might well be obscured by the intra-molecular absorption, so the optical absorption spectra cannot yield a value for the band gap. The estimation of the value of the band gap in an organic solid is also not possible from the slope of \( \log \sigma \) Vs \( \frac{1}{T} \) plots. In fact the question whether intrinsic semi-conduction has ever been observed in an organic solid is itself not settled as yet.

However, from purely thermodynamic considerations, the estimates for the energies of the levels taking part in conduction in organic solids can still be obtained from a knowledge of the energies of the ionised states. According to this scheme, the energy \( E_C \) required to produce a pair of free carriers, where the electron is not attached to any molecule or to any hole, is given by:

\[
E_C = 2I_C - I_g
\]  

(3.1)

where \( I_C \) and \( I_g \) are the ionisation energies of the crystal and the gaseous molecules respectively. The state \( E_C \) has been
called by Lyons as the 'conduction band proper'. However, conduction levels should also be possible if a pair of positive and negative ions separated by large distance (\( \sim 120 \text{ A} \)) is created. As the electron, in this case, is bound to a molecule, the energy of such a state should be:

\[ E_c' = E_c - A_g \]

where \( A_g \) = electron affinity. Below \( E_c' \) level, there should be a series of states where the electron is electrostatically bound to the hole. The first of these states will arise where the hole and the electron are situated on the neighbouring molecules. Such states are known as charge transfer or Wannier excitation states. By photo injection experiments \(^{13,14}\) it has been established that the level \( E_c' \) rather than \( E_c \) should define the band gap.

3.1.2 Carrier generation mechanism

(A) In dark: Carrier generation in dark is possible by injection. Both holes and electrons can be injected into an organic solid. In Anthracene holes have been injected through iodine \(^{15}\) and O-Chloranil \(^{16}\) while Grancher and Adolp \(^{17}\) and Buchner and Mehl \(^{18}\) have reported electron injection in the same material.

Free carriers can also be generated by exciting an electron from the valence band to the conduction band of the
crystal. The conductivity relating the activation energy $E_{\text{act}}$ of solids is given by:

$$\sigma = \sigma_0 \cdot \exp \left( \frac{E_{\text{act}}}{2kT} \right) \quad \ldots \ldots (3.2)$$

One should therefore think that the activation energy may be related to the band gap of the crystal. However, such a correlation has been found to be conspicuously absent for organic solids.\(^{19}\)

Carriers injection into a crystal from an outside agency is also possible by using suitable electrodes. The energy required for injection is:

$$\phi_e + E_{\text{ext}} > I_c \quad \ldots \ldots (3.3)$$

where $\phi_e$ is the work function of the electrode material and $E_{\text{ext}}$ is the externally applied energy.

(B) Carrier generation in the light: The electrical conductivity of organic materials in the presence of light due to optical absorption has been investigated by various workers both theoretically\(^{20}\) and experimentally.\(^{21,22}\) The conclusions of these studies are: (i) the energy of longer wavelength absorption limit does not correspond to the band gap and is usually larger than it and (ii) the absorption of the light quantum by organic
semi-conductors results in the creation of Frenkel excitons within the crystal. These excitons are coupled hole electron pairs which are highly localised. Davydov, while investigating the absorption of light by complex molecular crystal, found that the peculiar feature of the absorption of light and luminescence in molecular crystals are connected with the process of migration of energy in the crystal. This migration is caused by resonance interaction between the molecular excited states. Such excited states are called excitons. These excitons are localised within a volume of space small enough to be identified with a particular molecule. Moreover, they interact very weakly and can, therefore, be treated as an approximately noninteracting gas of independent quasi particles. The excitons which are formed at the illuminated face of a molecular crystal are, therefore, capable of hopping from molecule to molecule and thereby diffusing through the crystal.

The generation of charge carriers on breaking of the excitons into an electron hole pair can occur by autoionisation of exciton induced by phonons, photoionisation induced by photons or by an interaction with a suitable electrode at the surface of the crystal. It has been suggested by experimental studies on the dissociation of excitons at the organic crystal-metal interfaces that the electron affinity, or any other similar property of the
electrode may affect the location of dissociation sites in the crystal.

Jortner has reviewed the photo carrier generation via exciton-exciton interaction. Triplet excitons may also interact to form an electron-hole pair. Alternatively, the carrier generation may proceed by the dissociation of singlet excitons formed in a triplet-triplet annihilation process. The corresponding probabilities of carrier generation by all these dissociations have been worked out by Kearns. The experimental evidence for photo carrier generation via the low probability mechanism of direct band to band transition in the region 2500-3000 Å was provided by Castro and Horning and Chaiken and Kearns. Silver and Sharma have worked out the theory for this process.

(C) Space charge limited currents: The surface charges on the interface of a micro-crystalline solid and electrode may give rise to an apparent volume space charge. The space charges are certainly present near the electrodes whenever a field is present and they decay when the field is switched off. Direct evidence for space charges in electrically stressed organic materials has been obtained by Forster and others.

The inhomogeneous distribution of lattice defects is among many other reasons of space charge generation. Since
these defects are likely to act as trapping centres, they cause their vicinity to have a charge density numerically different (even if not in sign) from that of the other regions of the solid.

The space charge limited currents (SCLC) depend only on the transport and trapping of the carriers within the crystals and they do not depend upon their source of generation. The character of the currents due to these injected charge carriers of one sign is defined by the density-distribution of the trap levels in the band gap. Rose and Lampert developed the theory of unipolar SCLC. The values of slope coefficient of current-voltage characteristics are typical of the continuous trap level distribution in the band gap of dielectrics.

The current $I_o$ that passes in a trap free solid due to carrier injection into either the conduction band or valence band (in Ohmic contact electrode system) is given by

$$I_o = 10^{-13} \mu \varepsilon AV^2/d^3$$

where $\mu$ is the mobility of carriers, $\varepsilon$ is the relative dielectric constant of the solid, $A$ is the area of the sample, $d$ the thickness of the sample and $V$ is the applied voltage. Taking trapping of carriers into account, the space charge
limited current \(^{51,52}\) is given by:

\[
I_t = 10^{-13} \left( \mu \frac{AV}{d^3} \right) \frac{N_c}{N_t} \exp \left( \frac{-E_t}{kT} \right)
\]  \(\text{(3.5)}\)

where \(N_c\) is the concentration of shallow traps lying \(E_t\) electron volt above the valence band, \(N_c\) is the effective density of states in valence band.

Müller \(^{53}\) solved the theory of SCLC without taking any assumptions of blocking electrodes. The existence of SCLC and influence of electrode material and that of temperature in many organic solids have been reported by Sworakowskii, \(^{54}\) Szymanski et al. \(^{55,56}\) Also other reports are available for existence of SCLC in sugar cane wax, \(^{57}\) Naphthalene, \(^{58}\) Xanthene, \(^{59}\) and photosensitive SCLC in Tetracene. \(^{60}\)

(D) Schottky Emission: R.S. effect is the high field emission of electrons from a metal into the conduction band of an insulator in contact with it. This process is identical with Richardson emission of thermions in vacuum. The specimen is a sandwiched system between two metal electrodes \(M_1\) and \(M_2\) of work function \(\phi_1\) and \(\phi_2\) with respect to insulator \(I\) respectively. On application of voltage between the electrodes, the actual potential experienced by an electron in passing from \(M_1\) to \(I\) is less than \(\phi_1\) and is shown by the broken line. It differs from conduction band level by virtue of the image forces between the electron in the insulator and metal. Image forces
Fig. 3.A: Showing the Schottky emission from the metal at negative potential into the conduction band of insulator.
are created because the abrupt changes in potential at the metal insulator interface are unrealistic, since abrupt changes in potential imply infinite fields. The actual fact is that the potential step changes smoothly as a result of the image forces. This arises as a result of the metal surfaces becoming polarized (positively charged) by an escaping electron which in turn exerts an attraction force on the electron. An electron in the metal with a forward energy greater than the potential maximum can enter the conduction band of the insulator and hence give rise to a conduction current.

Schottky Emission 61-64 is essentially thermionic emission from a metal electrode into the conduction band of a solid. The Schottky-Richardson current density is given by:

\[
J_{SR} = AT^2 \exp \left( -\frac{\phi}{kT} \right) \exp \left[ \frac{e^{3/2} E^{1/2}}{(4\pi\varepsilon\varepsilon_0)^{1/2} kT} \right] \quad \ldots (3.6)
\]

where \( A \) is Richardson constant, \( \phi \) is barrier height, \( \varepsilon \) the dielectric constant and \( E \) is the electric field strength at the electrode. It is clear from Equation (3.6) that the current density \( J_{SR} \) depends both on \( \exp \sqrt{\frac{E}{\varepsilon}} \) and temperature \( T \), \( [J_{SR} \sim T^2 \exp \left( -\frac{\phi}{kT} \right) ] \).

The barrier height \( \phi \) can be calculated from the slope of \( \log J/T^2 \) Vs \( 1/kT \) plots. The linearity on Schottky plot ( \( \log J \) Vs \( \sqrt{E} \) ) need not necessarily be assigned to
Schottky emission. This mechanism can be verified by determining the value of dielectric constant from Schottky slope $\beta_{SR}$ (from graph $\log J$ Vs $\sqrt{E}$) and that observed practically.

$$\beta_{SR} = \frac{1}{kT} \left( \frac{e^3}{4 \lambda \varepsilon \varepsilon_0} \right)^{1/2} \quad \ldots (3.7)$$

The observations of O'H Dwyer, 65 Lengyel, 66 Lilly and Mc Dowell 67 and Srivastava and Tomar 68 and others 69-72 have shown existence of this mechanism in their respective studies.

(E) Poole-Frenkel Effect : Poole-Frenkel effect 73-78

is similar to Schottky emission. The only difference is that the electrons are excited thermally from traps in the conduction band of the insulator. Due to immobility of the positive charges associated with the trap, barrier lowering in Poole-Frenkel effect is twice that in case of Schottky effect. The current density in this case is given by:

$$J_{PF} = CE \exp \left( -\varphi/kT \right) \exp \left[ \frac{1}{kT} \left( \frac{E \cdot e^3}{\lambda \varepsilon \varepsilon_0} \right)^{1/2} \right] \quad \ldots (3.8)$$

where $C$ is a constant independent of field and temperature and other parameters have their usual meanings. PF mechanism is a bulk process and would be expected to exhibit symmetric I-V characteristics. The values of dielectric constant are
calculated from the slopes $\beta_{PF}$ of PF plots.

$$\beta_{PF} = \frac{1}{kT} \left( \frac{e^3}{\pi \varepsilon \varepsilon_0} \right)^{1/2} \quad \ldots \quad (3.9)$$

The PF effect is more pronounced when donor-like traps (electron liberating) are present in abundance in the bulk of the insulator which are neutral when occupied by an electron. Even if some holes are liberated from acceptor like centres, their contribution to the total current is usually very small owing to their much lower mobility and greater mass. These centres bind their carriers by long range coulomb forces and the resulting lowering of the potential barrier under the influence of an external electric field from the initial value $W_0$ to $\Delta W$ is given by:

$$\Delta W = \gamma E^{1/2} \quad \text{where} \quad \gamma = \left( \frac{e^3}{\pi \varepsilon \varepsilon_0} \right)^{1/2} \quad \ldots \quad (3.10)$$

Jonscher and Ansari\(^7\) point out that the proper distinction to draw between the Poole-Frenkel and Richardson-Schottky mechanism is whether the effect is bulk or electrode dominated; there is no compelling reason to judge this from the magnitude of a factor in the exponent of the temperature dependent term.

In principle, there are some additional points of distinction between the two effects\(^6\):

(1) It appears that the Poole-Frenkel effect [Eqn. (3.8)] differs from Richardson-Schottky effect [Eqn. (3.6)] in that a plot of $\log \sigma$ vs. $E^{1/2}$ at constant temperature...
is linear for Poole-Frenkel effect while for R.S. effect the log J Vs E^1/2 plot is linear.

(ii) Dielectric constant of the material may be tested from the slopes of the two equations to establish the correct mechanism.

3.1.3 Carrier Recombination and Trapping : In most semi-insulators of wide band gap, carrier loss via direct recombination of holes and electrons has to compete with other recombination processes and is significant only at high carrier densities. Carrier recombination in organic materials has been studied by variety of methods including fluorescence, electroluminescence, pulsed X-rays, field dependence of carrier generation and ionization by high energy particles. The hole-electron recombination cross section in anthracene found from fluorescence due to the recombination of simultaneously injected holes and electrons came out to be much too higher than in say Ge. In Sano's experiment carrier pair generation was attributed to injection and subsequent acceleration of electrons which in turn caused ionization of neutral molecules. Kepler and Coppage studied recombination of carriers generated by pulsed X-rays and deduced the mean free paths of holes and electrons to be much less than 120 Å. If an electron gets closer to a hole than this critical distance, the possibility of its getting trapped and eventually recombining with the hole increases markedly.
Any discrete state present between conducting bands can trap the carriers and thus reduce the number of free carriers. Hoesterey and Letson found anthraquinone and anthrone to trap electrons in anthracene substantially even when present at a concentration of 10 ppm only. Effect on holes was not so pronounced but with tetracene the trapping of holes was very severe, which was explained to be due to multiple trapping in the shallow trap of depth 0.43 eV. Weisz et al. observed, in unintentionally doped anthracene crystals from various sources, two types of trapping processes. The faster process was removable by annealing and hence attributed to the crystal defects, whereas the slower process was not affected by annealing and was due to chemical impurities. Thomas et al. have evaluated trap densities in crystals prepared by different procedures. Sworakowsky has successfully calculated trap depths for holes and electrons in anthracene crystal doped with anthraquinone and tetracene. Barbe and Wastegate and Cox and Knight have calculated experimentally electron trapping levels and their densities in \( \beta \)-metal free Phthalocyanine single crystals. Literature regarding discrete and experimentally distributed trapping levels is also present.

3.1.4 Mechanism of Carrier Transport: Theoretical approaches to explain the mechanism of carrier transport in organic solids
have been progressing and to date three models on the basis of the mobility of carriers have been proposed.

(A) **Tunnel model of conduction**

Tunneling is a quantum mechanical approach in which (say) an electron passes through a potential energy barrier without acquiring enough energy to pass over the top of the barrier. Eley and Parfitt \(^9\) were the first to suggest this model and later on Eley et al. \(^92-94\) proposed semiconduction mechanism in molecular crystals.

Organic solids other than free radicals have two electrons in the highest occupied molecular orbital, while the orbital just above it is totally empty. Thermal or photo excitation may elevate one electron from former to the latter orbital leaving a hole in the former. With free radicals no such excitation is necessary. Under the influence of an external electric field, the potential barrier between the molecules is lowered through which the electrons and/or the holes can then tunnel to occupy the corresponding orbitals in the adjacent molecules. Since the model involves the tunneling of a charge carrier away from an oppositely charged site, the tunneling particle remains bound to hole until the coulombic energy between them has reduced to a value \(\sim kT\). This situation will be obtained after the electron has tunneled over a distance of several lattice spacings.
The use of a band model, however, implies a periodicity in the potential extending conveniently throughout the crystal. If the potential varies irregularly, the transparency of the larger barriers will then determine the charge transfer.

Current density for tunneling is described by Fowler Nordheim equation:

\[ J = AV^2 \exp \left( -\frac{\phi}{N} \right) \] \hspace{1cm} (3.11)

where symbols have their usual meaning.

(B) Hopping Model

If two molecules are separated by a potential barrier, a carrier on one can move to the other either by tunneling through the barrier or by moving over the barrier via an activated state. The latter process is called hopping. Such a mechanism is well known in 3-d transition metal oxides which have a very low mobility that increases exponentially with temperature. Due to small overlap of 3-d orbitals, the charge carriers spend an amount of time on a particular cation which is long compared to the vibrational frequency of the lattice, and this allows the ions surrounding a charge carrier to be displaced by its electric field. This displacement creates a field which tends to prevent the charge carrier from leaving its lattice site, and so the charge carrier gets trapped itself. Under this condition, the charge transfer can only occur when
random lattice movement causes the energy levels of the carrier site and a neighbouring cation to be equal.

The intermolecular coupling in an organic solid is weak and the observed mobilities small which suggests the application of hopping model to explain charge transport in these crystals. The most important consequence of the hopping mechanism is a temperature activated mobility. But whatever meagre data is available for organic solids, it shows a decrease in mobility with the increase in temperature. Le Blanc found the hole mobility in liquid pyrene to be smaller by three order of magnitude than in the crystal. Also the liquid mobility showed a positive activation energy unlike the negative temperature co-efficient of solid mobility. This led Le Blanc to suggest that the transport would be described by hopping model in the poly crystalline and/or amorphous organic materials whereas conventional band theory should apply to pure solids in the single crystalline form. Munn and Siebrand have developed charge transport theory for organic solids.

(C) Electronic band Model

Before discussing charge transport mechanism it is useful to develop, at least, a rough sketch of energy level diagram of a high molecular weight polymer. Structurally, the length and the spatial arrangement of molecular chains change from one polymer to another and depend upon many factors
like molecular weight, presence of side groups, degree of crystallinity etc. However, for our benefit we may exploit their common features. Each polymer has very large molecules or macromolecules which have a large number of recurring structural units called 'monomers' that are tightly bound together by strong covalent bonds. The molecules of a polymer (macromolecules) are in the form of long chains and can change their relative orientations easily, because relatively much weak Vander wall's type of forces hold them together. Thus there are two types of bonds in a polymer namely, strong intramolecular bond with an activation energy of 4 to 9 eV and weak intermolecular bonds with very low activation energy. The intermolecular bonds give rise to a valence band that is full of electrons in the absence of an electron acceptor and a normally empty conduction band. Both these bands are expected to be wide, more than 1 eV in view of strong overlap of the wave functions corresponding to intramolecular bonds. The much weaker intermolecular bonds must result in very narrow bands which need not be either completely empty or full, the separation of which is also much smaller than intermolecular band gap. In addition, the structural disorders resulting from chain folding, chain termination and from amorphous matrix between crystallites will produce localised states $^{64(a)}$ which may be distributed in space and energy and which may be occupied by electrons.
The much popular way of explaining the observed electrical conductivity is in terms of a modified electronic band model. Though this model one can calculate the width of energy bands by overlap integrals between electron molecular wave functions on adjacent molecules. The weak intermolecular attraction in molecular crystals results in narrow conduction band and low carrier mobilities.

Small electrical conductivity and high activation energy of organic solid suggest that some kind of intermolecular interaction takes place, which, in an electric field, gives rise to electronic conduction. It is suggested \(^9\) that this interaction is molecular orbital overlap. The extent of orbital overlap is a function of molecular structure and hence, if semiconduction arises from such overlap, it is not surprising that semiconduction activation energy correlate with the properties which are also a function of molecular structure, such as the molecular ionization energy, electron affinity and excitation energy of the ground triplet state-transition. \(^99,100\)

One of the entities which influences these properties is the number of more easily polarizable \(\pi\)-electrons. As the number of these increases in a conjugated system, there is a trend toward smaller activation energies of conduction, indicating that the probability of achieving overlap is enhanced by the presence of a large number of \(\pi\)-electrons. However, if the overlapping of molecular orbitals gives rise to semiconduction, then some
other factors which contribute to such overlapping should also encourage semiconduction, even if only few $\pi$ - electrons are present in the individual molecule. Since intermolecular hydrogen bonds may provide such overlap, it might be expected that the activation energy in hydrogen bonded compounds should be lower than anticipated solely on the basis of the number of $\pi$ - electrons.

3.2 Dependence of Dark Electrical Conductivity on various factors

A brief review of factors which affect the electrical conductivity of polymers is given below:

3.2.1 Field A number of mechanisms $^{101,102}$ have been employed to explain the increase of conductivity with field. Poole $^{103}$ has reported exponential variation of conductivity with field while Joffe $^{104}$ states that it is only the steady state conductivity which increases with field and the true conductivity is independent of field. Exactly opposite to Joffe, Boran and Quittner $^{105}$ have emphasized that steady state conductivity increases with applied field and approaches the true conductivity at high fields. Wenderowitsch and Drisina $^{106}$ have produced similar results in line with Joffe maintaining independency of conductivity with field. The variation of current through the sample with applied voltage has been generally found to be:

$$I \propto V^n$$

......... (3.12)
for \( m = 1 \), the behaviour is termed Ohmic, for \( m = 2 \) a SCILC flows through a trap-free insulator. However, Riehl \(^{107}\) have claimed that in organic substances electrical conductivity is proportional to \( \exp \left( - \frac{B}{T} \right) \) where \( T \) is absolute temperature and \( B \) lies between 0.4 to 0.7 eV. Electrical conductivity was found to increase with high fields but not the value of \( B \). Many others \(^{108,109}\) have proposed theories to explain the variation of conductivity with field. Srivastava et al. \(^{110}\) have emphasized that at high field \( I-V \) characteristics show departure from Ohm's law.

### 3.2.2 Temperature

The behaviour of electrical conductivity depends very much on the temperature state of the polymer. A rise in temperature tends to increase the current and conductivity. The electrical conductivity at various temperatures obeys the exponential relation \(^{111(a)}\)

\[ \sigma = \sigma_0 \exp \left( - \frac{E}{kT} \right) \tag{3.13} \]

where \( \sigma \) is the conductivity, \( E \) the activation energy of conduction, \( \sigma_0 \) the pre-exponential factor, \( k \) the Boltzmann's constant and \( T \) is the absolute temperature of the substance.

If the \( \log \sigma \) is plotted against \( \frac{1}{T} \), two or more regions (a high temperature region and the other low temperature region) depending strongly upon the past history of the material,
are generally seen. The complete conductivity curve is a
superposition of two or more curves\textsuperscript{112} given by:

\[ \sigma = \sigma_1 \exp\left(-\frac{E_1}{kT}\right) + \sigma_2 \exp\left(-\frac{E_2}{kT}\right) \quad \ldots (3.14) \]

where \( \sigma_1 \) and \( \sigma_2 \) are pre-exponential terms. Out of the two
terms in Eqn. (3.14) the first has a small coefficient and small
activation energy and predominate at lower temperatures while
the other has a larger coefficient and larger activation energy
and is predominant at higher temperatures.

The study of conductivity dependence on field and
temperature sometimes reveals that current-temperature and
current-field curves obtained on increasing and decreasing of
temperature or field are quite different and distinct, resulting
into a sort of hysteresis loop. Hysteresis effect has been
observed in case of paraffin wax,\textsuperscript{113} carnauba wax,\textsuperscript{114}
polyethylene,\textsuperscript{115} naphthalene,\textsuperscript{116} sugarcane wax,\textsuperscript{117}
\( \beta \)-naphthol,\textsuperscript{118} xanthene,\textsuperscript{119} p-chloroaniline\textsuperscript{120} and pyrene.\textsuperscript{121}

3.2.3 Pressure: Eley et al.\textsuperscript{91,122} and Akamotu and
Inokuchi\textsuperscript{123} implied the existence
of limiting pressure above which the electrical conductivity
does not change. Akamotu and Inokuchi\textsuperscript{123} found that
conductivity increases with pressure and remains constant
approximately above 80 atmospheres.
The pressure dependence of apparent dark conductivity has been observed by many workers. Materials studied include quarternyle, 124 pentacene, 125,126 anthracene, violanthrone, pyranthrene, 127,128 ferrocene, 129 benzophenone 130 and many others. 131-140 The increase in conductivity has been followed by a lowering of activation energy. Eley et al. 91,122 attributed it to packing effects on powder specimen. Brown and Aftergut 141 state that macroscopic voids are removed due to pressure. Activation energies at the highest pressure studies were found decreasing to about one sixth of that of atmospheric value. 1

3.2.4 Thickness: There are considerable evidences regarding the dependence of electrical conductivity on sample thickness. According to Wright 144 the current varies as the inverse cube of thickness. Sharma 145 has found a linear relationship between conductivity and thickness in sealing wax. Bashara and Dotty 146 have found that the SCLC increases with thickness. Thomas et al. 147 are in agreement with the findings of Wright.

3.2.5 Impurity Content: The electrical conductivity of organic compounds is extremely sensitive to the presence of impurities. The conductivity itself could be used as a measure of purity provided the absolute value for a given material is known. Effect of purification on
the semi-conduction of imidazole was carried out by Brown and Aftergut 148 and it was found that the presence of two slopes in \( \log \sigma \) Vs \( \frac{1}{T} \) plots is indicative of an impure specimen since further purification gives rise to single slope. Recently similar results for 1-8 diamino naphthalene has been reported by Srivastava et al. 149 Pick and Wissmann 150 showed for naphthalene that the activation energy depends on the presence of impurities. Effect of known impurities on electrical properties of hydrocarbons have been investigated by Northrop and Simpson. 151 Recently impurity incorporation in polystyrene has been the subject of many workers. 152-154 All of them have reported increase in conductivity with dopant.

3.2.6 Humidity: Numerous workers 101,102,155 have found that humidity and also impurities cause the conductivity to increase with field strengths. Moisture affects 156 the conductivity in two ways:

(1) It increases the dielectric constant and therefore, the concentration of ions by reducing the effective dissociation energy, and

(2) It brings about the departure from Ohm's law in high fields as a result of activation perturbation even in the absence of thermal and chemical effects. Manthia et al. 157 have concluded the increase in conductivity with humidity.
3.2.7 Electrode Material: Reucroft studied the conductivity of anthracene monocrystals with different electrodes (Na, Ag, In) and found the identical results with respect to the magnitude of the conduction current and therefore concluded that the observed electrode barriers are independent of the work function of the electrode material. Eley et al. measured the conductivity of bovine plasma albumen with four electrode metals Cu, Pt, Al and In. Closely similar results were obtained in all cases. Recently Kulshrestha et al. have reported no variation in electrical conductivity of polystyrene doped with chloranil as regards different materials of the electrodes. Though Bhatnagar and Srivastava have reported a measurable influence of the electrode materials of Zn, Cu and Al on the conductivity of Indian sugarcane wax at 35°C. Srivastava et al. have also noted considerable effect of electrode materials in the conductivity of copper phthalocyanene doped polystyrene.

3.3. Experimental Techniques for Conductivity Measurement:

There are three important features in the measurement of conductivity: (i) preparation of sample, (ii) choice of electrode materials and (iii) measuring instrument of suitable range.

Preparation of the sample depends upon the nature of
materials. For example, alkali halides can be taken in crystal forms while the substances in powder form may be taken in the shape of pressed discs/pellets. But the probable chances of occurring internal cracks and granular effects in pellets introduce serious effects in the conductivity. Reports show that there is no agreement between the results of the same material used in single crystals and compressed pellets form and therefore loss tangent measurements must be approached with extreme caution. Polycrystalline and aromatic compounds are used in the form of films evaporated on a glass substrate which has been coated in advance with a metal film used as electrode. Solution cast films in semi-insulating materials are being used these days. They are preferred of all because of low probability of voids, pinholes and other like defects in them.

So far as the discussion of electrode material is concerned it has already been discussed in article 3.2.7.

There are number of instruments available to measure dark current. The use of an instrument depends upon its sensitivity and the conductivity of the material under probe.

3.4 Present Experimental Technique

The study of steady state dark conductivity has been undertaken in the present investigation. Electrical conductivity of the material can be measured to any degree of
accuracy by measuring current, voltage and dimensions of the specimen under test provided (i) the sample has uniform properties, (ii) it has sufficiently large number of carriers to make the effect of temperature variation on charge carrier density.

The thin film sample, sample holder, electrometer used here are all that described in Chapter II.

After making proper electrical connections as shown in Fig. 3.0, the sandwiched sample of EC mounted on electrode assembly was placed inside the thermostat and allowed to attain required temperature. It took about 3-4 hours. When the sample attained the desired temperature, a DC voltage was applied with the help of a Keithley 245 high voltage DC supply. A sudden burst of current observed in the beginning decreases with time. Its final steady state value was recorded. At lower voltages and lower temperature region it took about 5 to 6 hours to reach the steady state while at higher voltages and higher temperatures, steady state was obtained in considerably low period. The effect of voltage variation in current was noted by increasing the voltage in steps of 20 volts at fixed temperatures while temperature variation was measured keeping voltage constant and increasing the temperature in steps of 10°C. Measurements were taken in the voltage and temperature ranges of 100-240 volts and 40-100°C respectively. A fresh sample was used for each set of observation. The following variations were attempted :-
I. (a) voltage variation at fixed temperatures.
    (b) temperature variation at fixed voltages.

II. thickness variation at fixed temperature and varying voltages.

III. electrode variation at fixed temperature and varying voltages.

3.5 Results:

(i) The isothermal I-V characteristics, plotted in the form of \( \log I - \log V \) curves (Fig. 3.1) exhibit almost similar nature for all temperatures from 40-100\(^o\)C. The curves show two distinct parts, one at low field region (100-160 volts \( \approx 2.3 \times 10^3 \) V/cm field) and the other at high field region (160-240 volts \( \approx 3.2-4.8 \times 10^5 \) V/cm field). In these two regions, the curves exhibit approximate linear relationship, separately. These two straight line curves with different slopes have a knee at a point. This knee appearing between the two regions is not very sharp but can be seen clearly which appears to lie nearly at 160 volts. The increase of current between 60\(^o\) to 70\(^o\)C is higher than that at lower temperatures. At 80\(^o\)C, I-V characteristics lie below 70\(^o\)C. Above 80\(^o\)C, the increase in current is higher than at lower temperatures.
FIG 31 LOG I - LOG V PLOTS IN PURE EC.
(ii) Variation in the thickness of BC films develop noteworthy changes in the conductivity (Fig. 3.2). Thinnest film (3 µm) exhibits more conductivity than thick films. It shows a curve like increasing nature in the low field range which becomes nearly constant at higher fields. Thick films (4 µm) show intermediate conductivity which increases slowly with voltage. But the conductivity values for 5 µm thick films showing lowest conductivity exhibit only a slight change in conductivity with voltage in the same manner. All curves of Fig. 3.2 represent conductivity at 100°C.

(iii) The Schottky plots of BC samples show the variation of current density with field in the form of \( \log J \text{ Vs } E^{1/2} \) (Fig. 3.3). These plots show perfect linearity in higher field region. While Poole-Frenkel plots in the form of \( \log \sigma \text{ Vs } E^{1/2} \) (Fig. 3.4) show some deviations of points.

(iv) Fig. 3.5 shows \( \log J \text{ Vs } E^{1/2} \) isotherms for three metal electrodes Ag, Au and Al, all taken at 100°C. With Ag electrode minimum current while with Al electrode intermediate current in the beginning and higher current in high field region is obtained. Highest and intermediate currents in the lower and higher field region respectively are obtained with Au electrodes. All the plots show perfect linearity for almost full region of root of field (\( E^{1/2} \)).
FIG 32 LOG $\sigma$ vs LOG V PLOTS IN PURE ETHYLCELLULOSE FOR DIFFERENT THICKNESSES
FIG. 3.3 LOG J vs $E^{1/2}$ (SCHOTTKY PLOTS) FOR PURE EC.
FIG. 3.4 LOG $\sigma$ VS $\sqrt{E}$ PLOTS FOR PURE EC (POOLE-FRENKEL PLOTS)
FIG. 3.5 LOG J vs $E^{1/2}$ PLOTS FOR DIFFERENT ELECTRODE MATERIALS IN PURE EC. (AT 373°K)
(v) Fowler Nordheim plots \( \log J/V^2 \) vs \( 1/V \) are shown in Fig. 3.6. All the curves display similar nature showing a decreasing trend in the beginning and increasing afterwards. They do not yield linear portions in high field (low values of \( 1/V \)) region.

(vi) Variation of conductivity with temperature at different fields \( \log \sigma \) vs \( 10^3/T \) is shown in Fig. 3.7. Their slopes give the corresponding values of activation energy. All curves are of similar nature with nearly similar slopes.

(vii) The variation of activation energy with field has been traced in Fig. 3.8 for EC thin film samples. Activation energy decreases with field.

3.6 Discussion

The isothermal I-V curves (Fig. 3.1) show an Ohmic nature up to a field range of \( 3.2 \times 10^5 \) volts/cm and beyond it the slope of current-voltage curves changes. Abrupt rise in current between 60°-70°C shows possibility of some phase transition in the polymer matrix. The lower glass transition of EC lies between 60°-75°C. The polymeric chains may undergo some transitional changes between these temperatures and the current therefore, show abrupt increase. The reason of getting down of 80°C isothermal curve is very obvious. The polymer matrix undergo glass like to rubber like transition and therefore
FIG. 3.6 LOG (J/V²) vs 1/V PLOTS FOR PURE EC.
(FOWLER–NORDHEIM PLOTS)
FIG. 3.7 LOG $\sigma$ vs $\frac{1}{T}$ PLOTS FOR PURE ETHYL CELLULOSE
(ARRHENIUS PLOTS)
FIG. 3.8 PLOT OF ACTIVATION ENERGY
vs $E^{1/2}$ FOR PURE EC.
the macromolecules start losing their preferred orientation during transition of phase. The initial stage of change in phase is very sensitive of course. Above 80°C, currents again show increasing trend. Once the chains are mobilised the current will certainly show greater increment. And that is what is happening above 80°C.

Now for the confirmation of the different natures of conduction mechanism, values of $m$ from $I \propto V^m$ were calculated and are collected in Table 3.1. The values of $m$ in the lower region of field (below $3.2 \times 10^3$ V/cm = 160 volts) lie between 1 to 1.5 for all temperatures except that nearby room temperature ($\approx 40^\circ$C) for which it is 1.9. This shows that in lower fields, Ohm’s law is obeyed with certain deviation at room temperature. Above 160 volts ($\approx 3.2 \times 10^3$ V/cm) the value of $m$ is always greater than 2. This recommends the probability of space charge limited conduction strongly. The current is also thickness dependent as exhibited in Fig. 3.2. These are sufficient grounds to believe the existence of space charge limited conduction.

The other likely processes of conduction at high fields are tunneling, field emission and field enhanced thermionic emission either over an interfacial barrier (Richardson-Schotky RS mechanism) or from localised coulombic traps within the polymer matrix (Poole-Frenkel PF mechanism).
At first hand, let us subject RS and PF mechanisms on trial. The log J Vs E \(1/2\) plots (Fig. 3.3) of pure EC show perfect linearity above \(3.2 \times 10^5\) V/cm field region. This follows that in high field region the conduction process is being governed by either Richardson-Schottky (RS) or Poole-Frenkel (PF) effect as both processes bear a current field relationship of the form \(J \propto \exp (\beta E^{1/2})\). The coefficient \(\beta\) in the case of RS mechanism is:

\[
\beta_{RS} = \frac{1}{kT} \left( \frac{e^3}{4 \pi \varepsilon \varepsilon_0} \right)^{1/2}
\]

where \(\varepsilon\) is the high frequency dielectric constant of the insulator (3.2 for EC), \(k\) is Boltzmann's constant (\(k = 8.615 \times 10^{-5}\) eV/\(^\circ\)K), \(\varepsilon_0\) is the permittivity of free space (\(= 8.86 \times 10^{-12}\) m.k.s. unit) and \(e\) is the electronic charge. The value of \(\beta\) in PF mechanism is:

\[
\beta_{PF} = \frac{1}{kT} \left( \frac{e^3}{\pi \varepsilon \varepsilon_0} \right)^{1/2}
\]

i.e. \(\beta_{PF} = 2\beta_{RS}\)

Table 3.2 gives the theoretical values of \(\beta_{RS}\) and \(\beta_{PF}\) at different temperatures along with their experimental values calculated out from the slopes of Figs. 3.3 and 3.4 respectively. Theoretical and experimentally calculated values of \(\beta_{RS}\) are in fair agreement. Some reports \(96,167\) suggest that the relation \(\beta_{PF} = 2\beta_{RS}\) is approximate and in some cases may hold good validity.
However, Lilly et al. 67 have shown that $\beta$ values remain the same for both mechanisms. Therefore it is not sufficient to explain the results on the basis of the comparison of the theoretical and experimental values of $\beta$ only. The linearity on Schottky plots need not necessarily be assigned to Schottky emission. Hence Poole-Frenkel plots (Fig. 3.4) were also tested. These graphs are also linear in high field region within experimental error. But their linearity is comparatively thinner with respect to Schottky plots.

One is, therefore, bound to test them on the basis of fundamental difference between them. RS mechanism is electrode limited while FF is not. 79 Hence to distinguish real mechanism of operation between them, a graph between $\log J$ Vs $E^{1/2}$ (Fig. 3.5) has been plotted with three different electrode materials (Ag, Al and Au) at 373°K, the other electrode being Al in each case and which was assigned positive polarity always. Three different straight lines were obtained. This reason is sufficient to cast doubt on the applicability of FF mechanism in the conduction process. Further the values of $\varepsilon$ calculated from the slopes of Schottky and Poole-Frenkel plots (collected in Table 3.2) also go in favour of RS mechanism. Hence the probability of prevailing of RS mechanism in high field conduction is very high.

Tunneling is the next mechanism of conduction to be tested.
Tunneling current is described approximately by Fowler-Nordheim equation:

\[ J = AV^2 \exp \left( -\frac{\phi}{V} \right) \]

where \( \phi \) is the barrier height. If current is due to tunneling, a straight line of negative slope must appear in \( \log J/V^2 \) Vs 1/V plots (Fig. 3.6). But the graphs do not give straight lines at low 1/V values. Hence tunneling possibilities are also disconnected in the present case.

It has been reported that conduction in organic solids is greatly determined by the localised levels. "Cellulose derivatives are prominent species among high polymers containing lot of structural disorders and impurities within them." The values of slope coefficient \( m > 2 \) of I-V characteristics are the typical proofs for the continuous trap level distribution in the band gap of semi-insulating Ethyl Cellulose. These defects and impurities can govern the conduction mechanism and also act as trapping centres and get populated by injected charge carriers from the electrodes. Charge carriers from these localised levels are thermally excited to their respective transport bands causing thermally activated Ohmic conduction. Depending upon the population of these levels and their respective transport bands, the conduction may change from Ohmic to Schottky emission.

To view the effect of thermal activation on these trapping
sites, activation energies have been calculated from the
slopes of log $\sigma$ Vs $10^3/T$ graphs (Fig. 3.7) and collected
in Table 3.3.

Plot of activation energy Vs $E^{1/2}$ (Fig. 3.8) shows
linearity and decrease in activation energy with increasing
root of field. This indicates hopping like action among these
localised levels. Intercept of this straight line at zero
field yield a value of $W_0 = 1.12 \times 10^{-19}$ joules ($= 0.7$ eV)
and its slope gives the value of $r = 1.42 \times 10^{-22}$ J. $V - 1/2$
M $^{1/2}$ which is not in agreement with its theoretical value
$6.7 \times 10^{-24}$ J. M $^{1/2} V - 1/2$ calculated from the formula
$r = (e^3/\kappa \epsilon \epsilon_0)$. Hence hopping like motion among these
localised levels is also ruled out.

Now the only mechanism left for trial is ionic conduction.
Fig. 3.8 shows decrease in activation energy with $\sqrt{E}$. For
ionic conduction special features are:

(i) Activation energy is very large in comparison to electronic
activation energy which is almost unity or less than it.

(ii) Polarisation effects are found under DC field.

(iii) Transport of material from one electrode to other electrode,
and

(iv) The large transit time for the ions, are probable.

But none of the above features have been observed.
Hence this sort of conduction is also less probable.
3.7 Conclusions:

On the basis of preceding discussion, the following conclusions may be drawn:

(i) At lower values of fields Ohmic conduction prevails but due to structural disorders trap level charges present in the bulk of the insulator develop minute deviations from Ohmic conduction.

(ii) Space charges build up at high fields ($> 3.2 \times 10^5 \text{ V/cm}$) is the associating factor for the conduction of current.

(iii) For EC film a two fold mechanism explain the high field conduction. Besides space charges injected from electrodes, Schottky emission is the dominant process responsible for the transport of these charge carriers.
<table>
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<tr>
<th>Temp. (°K)</th>
<th>&quot; m &quot; (100-160 V)</th>
<th>&quot; m &quot; (160-240 V)</th>
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### Table 3.2

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<tr>
<th>Temp. °K</th>
<th>$B_{RS}$ (Theo.)</th>
<th>$B_{RS}$ (Exptl.)</th>
<th>$B_{PF}$ (Theo.)</th>
<th>$B_{PF}$ (Exptl.)</th>
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<th>$\epsilon_{RS}$</th>
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### Table 3.3

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REFERENCES


61 (l) Schottky, W.; Z. Physik 15, 972 (1914)


76 Schenkel, F.W.; Electronics 38, 67 (1965).


79 Jonscher, A.K. and Ansari, A.A.; Phil. Mag. 23, 205 (1971);
Jonscher, A.K.; Int. Meeting on E.S. Charging, Frankfurt,
Germany (29 March, 1974) p. 29.

80 Helfrich, W. and Schneider, W.G.; Phys. Rev. Lett. 14,
229 (1965).

81 Batt, R.H., Braun, C.L. and Horning, J.F.; J. Chem. Phys. 49,


1609 (1963).

84 Weiss, S.Z., Jarnagin, R.C., Silver, M. and Balberg, J.;


Hartshorn, L. and Rushton, J.; IEE 75, 631 (1934); 77, 723 (1935); 83, 315 (1938).


Poole, H.; Phil. Mag. 12, 112 (1916); 34, 195 (1917); 42, 488 (1921).


Boran, O. and Quittner, F.; Zeits. F. Physik 64, 760 (1930).


142 Guntherschulze, A. and Betz, H.; Zeits. F. Physik 91, 70 (1934); 92, 357 (1934).
145 Sharma, B.L.; Ph.D. Thesis, Saugar Univ. (India), (1965).


