CHAPTER 3

ELECTRICAL CONDUCTION
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3.1. Introduction

The study of electrical properties of solids are of considerable significance from two major points of view: firstly for its own sake, since conducting, insulating and semi-conducting materials are of fundamental consequence for the major functions of energy storage and transmission and of communication; and secondly for the information such study can provide on the dynamic processes proceeding within the solid and at its surface and to develop understanding of those processes and their control for specific purposes. The interest in energy transmission and communication applies not only to industry and everyday life but also to biological processes.

The electrical charge carriers in solids are generally divided into two classes: ions and electrons. Ions are relatively massive, and ion transfer is often described by a "hopping" mechanism. On the other hand, electron motion in metals and broad band semi-conductors are described quantum mechanically, (though a "hopping" process, is invoked for electrons in narrow-band semi-conductors where they have large
effective masses). The proton, small but massive compared with electron lies between these extremes.

The electrical properties of organic solids are of increasing interest, both due to their technical importance and to the interesting relation between such properties and their physical structures (1-4). In 1946, Szent-Györgyi (5,6) suggested that proteins may have an electronic structure similar to that of semi-conductors. Based on his ideas, Evans and Gergly (7) conducted the experiments and reported that such conditions may exist in proteins.

In 1953, Eley et al. (8) reported semi conductivity in albumin, fibrinogen and edestin and found that water present in the molecules could decrease the energy gap for the movement of electrons. Later Cardew and Eley (9) showed that hemoglobin and globin exhibit electrical conductance. Electrical conduction phenomena were also investigated by Rosenberg (10) and Postov and Rosenberg (11) confirming that electrical conduction and semi conduction exist in a number of proteins and in general in biopolymers and biological molecules. Electrical conduction in collagen has been reported by Eley and Spivey (12) and by Bardelmayer (13,14). Baxter (15) from his experimental observations, suggested that the observed conduction in biomolecules is due to the jumping of electrons over water molecules adsorbed on the macro molecule surface. In
recent years research has also been done in variety of materials and reported elsewhere (15-25).

To conduct the TSD measurements on an electret, it is customary to have electrode contacts at its surfaces and the observed depolarization current may depend strongly on the nature of electrodes (26-30).

The electrode contacts can be divided into three classes. They are ohmic, neutral and blocking contacts (31). If the metal electrode work function is less than that of insulator, electrons are injected from electrode into the conduction band of insulator giving rise to a space charge in the insulator. On the other hand if the work function of metal electrode is greater than that of insulator the electrons flow from the insulator into the metal and a space charge region of positive charge, the depletion region, is created in the insulator and an equal negative charge resides on electrode. Neutral contacts are those in which the work function of the metal electrode and the insulator are same (32). The effect of the electrode material in the depolarization current of an electret can not be interpreted as the basic properties of the electret forming materials. Therefore, the
knowledge of the nature of electrical contacts is essential to draw some definite conclusions about the charge storage and transfer characteristics of bioelectret and the study of dc conduction characteristics provide a convenient method to investigate the nature of electrical contacts and to understand the conduction mechanism. Results of dc conduction studies on Dextrin and Folic acid are being presented in this chapter.

3.2. dc Conduction Mechanisms

In the bulk material, the conduction occurs due to the drift of defects under the influence of an applied electric field and may be called as ionic conduction. The large number of defects known to exists in amorphous materials suggest that the mechanism might be important in these materials. Ionic conduction can also occur due to the moisture present in the material.

Another important model of charge transport is the tunnelling of the charge carriers. The tunnelling model has been proposed and discussed by Eley(33). This model assumes that an electron in a molecular orbit on one molecule can
tunnel through a potential barrier to nonoccupied site of a neighbouring molecule with energy conserved in the tunnelling processes. This may return back to its ground state but its probability is less. In the band model nothing is mentioned about the potential barrier between the molecules. However, in the tunnelling model, charge carriers are expected to tunnel over a distance of many molecules.

The charge transport can also be described in terms of hopping model which is more applicable than the band model. In this model charge carriers are excited and are jumping from one molecule to another molecule.

In fact there are only a very few number of charge carriers generated in the bulk of the polymers. Thus in most cases the conduction is explained in terms of charge injection from the contacts.

In case of organic solids, where the conductivity due to electrons excited from valence band to the conduction band is not adequate, the complex conductivity can be explained in terms of the electron emission from cathode,
which is called Schottky-Richardson mechanism (34-37). The electrons liberated from the traps of the bulk may also be the source of conductivity (Poole-Frenkel effect) (38).

When the injection current from the cathode is larger than the bulk current at the same field, homo polar space charge is formed in front of the electrode, resulting in the bulk space charge limited current. But when the injection current is smaller than the bulk current the electrode limited current flows with heteropolar space charge and depletion layer formation in front of the electrode.

\[ \text{173}\text{,}\text{)} \]

The theoretical aspects of different modes of conduction and the method to identify the conduction mechanism are summarized below.

3.2.1 Schottky-Richardson Mechanism

Schottky emission of electrons may occur from the metal contact of the negative potential into the conduction band of the dielectric. The fact that the electrons are emitted
into a dielectric instead of vacuum is taken care of by minor modification of Richardson's formula for thermionic emission of electrons. At very low voltage the conduction is due to the field assisted-thermionic emission of electrons from negative biased electrode or the migration of electrons to the positively biased electrode. The presence of electric field at the barrier modifies the emission current as it reduces the work function separating the two materials and is known as Schottky effect. For a trap free insulator the current density \( j \) is given by

\[
j = A T^2 \exp\left(-\frac{\phi_s}{kT} + \beta_{SR} E^{1/2}/kT\right)
\]  

(3.1)

where \( \beta_{SR} = (e^3/4\varepsilon_0 \varepsilon_d)^{1/2} \) and is known as Schottky coefficient, \( d \) is the thickness, \( \varepsilon_0 \) is the permittivity of the free space, \( \varepsilon \) is the dielectric constant, \( e \) is the electronic charge, \( A \) is constant, \( T \) is the absolute temperature and \( \phi_s \) is the metal-dielectric potential barrier height and \( E \) is the applied field potential.

The above equation predicts a linear relationship between \( \ln(j) \) and \( E^{1/2} \) of slope \( \beta_{SR}/kT \) at constant temperature. At constant voltage, a plot of \( \log(j/T^2) \) and \( 1/T \)
can yield \( \phi \) the barrier height. This behaviour has been reported by several workers (39-48).

3.2.2 Poole - Frenkel Effect.

Poole-Frenkel effect describes the electron transfer by field enhanced thermal excitation of trapped electrons into the conduction band of the dielectric. To experience this effect, a trap is required to be positively charged when empty and uncharged when filled. So a trap which is neutral when empty and charged when filled will not manifest the P-F effect. The interaction between the positively charged trap and the electron gives a coulombic barrier. (49,50) P-F effect is the lowering of this coulombic potential barrier when it interacts with an electric field. The current-voltage relationship for Poole-Frenkel effect is given by the equation (51-54)

\[
j = B \exp(-\phi_{PF}/kT + \beta_{PF}E^{1/2}/kT)
\]

(3.2)

where \( \phi_{PF} \) is the barrier associated with the promotion of an electron from a donor level to the conduction state, or alternatively with the promotion of an electron from a valence
state to an accepter level and the factor \((\frac{p}{PF}E^{1.2})\) is the amount by which the coulombic barrier is lowered due to its interaction with the field. This field lowering of the barrier is known as the Poole-Frenkel effect and predicts a field dependence for the conductivity expressed as

\[ \sigma = \sigma_0 \exp\left(-\frac{p}{PF}E^{1.2}/2kT\right) \tag{3.3} \]

and the Poole-Frenkel mechanism is characterized by the linearity of \(\log(\sigma)\) vs \(E^{1.2}\) plots i.e. Poole-Frenkel plots as predicted by equation (3.3). A similar behaviour has been reported in case of different materials by different authors.

(55-62)

### 3.2.3 Fowler-Nordheim plots.

These plots may be used to characterize the tunnelling currents. The voltage-current relationship for Fowler-Nordheim (63) is given by the equation

\[ j = AV^2 \exp(-\varphi/V) \tag{3.4} \]
and predicts a linear relationship between $\log(J/V^2)$ and $(1/V)$.
The straight lines with negative slopes on Fowler-Nordheim plots characterize tunnelling(64-66).

3.2.4 Space Charge Limited Current.

Whenever an electric field is applied across a dielectric, space charges build up near the electrodes and decays instantaneously when the field is switched off(67). Wisdom and Forster(68,69) have observed direct evidence for space charge in electrically stressed organic materials. It has been also observed that the space charge limited current (SCLC) depends only on the transport and trapping of the carriers within the crystal(70,71) and they do not depend on their source of generation. The existence of space charge limited current and the influence of electrode material and that of temperature have been reported by many workers(72-74).

Lampert and Rose(75,76) derived an equation for SCLC given by
\[ I_0 = I_0 \frac{N_e}{N_t} \exp\left(-\frac{E}{kT}\right) \]  \hspace{1cm} (3.5)

where \( N_e \) is the concentration of shallow traps lying \( E \) electron volt above the valence band, \( N_t \) is the effective density of states in the valence band and \( I_0 \) is the number of carriers injected to the dielectric given by the equation

\[ I_0 = 10^{-19} \mu \varepsilon AV^2/d^3 \]  \hspace{1cm} (3.6)

where \( \mu \) is the mobility of carriers, \( \varepsilon \) is the relative dielectric constant, \( A \) is the area, \( d \) the thickness of the sample and \( V \) is the applied voltage

3.3 Experimental Set up

To investigate the mode of conduction and to find out the type of electrode contacts, the D.C. conductivity measurements of the samples are made with the help of an experimental set up designed and developed at I.I.T Delhi. The block diagram of the experimental setup is given in fig (3.1).
The finely powdered samples of Dextrin and Polic acid are compressed by applying a pressure of 12N/cm² and pellets of diameters 13 mm and thickness 0.51 mm and 0.33 mm respectively are made to measure the steady state current. Both the surfaces of the pellets are coated with silver paint and are sandwiched between two aluminium blocks, which are connected to an electrometer (Keithley's electrometer model no. 610 C). To apply the DC field a power supply (Aplab Medium Voltage Power Supply, model no. 7332) with a maximum capacity of 600V, is used. The sample holder is housed in a thermostat in which the temperature can be controlled with an accuracy of ±0.5K. The crosssectional view of the sample holder is shown in fig (3.2).
FIG. 3.1: EXPERIMENTAL SET-UP: DC CONDUCTIVITY MEASUREMENTS

- Relay
- Variac
- Sample
- Heater
- DC Power Supply
- Electrometer
FIG. 3.2: SAMPLE HOLDING ASSEMBLY:
DC CONDUCTIVITY MEASUREMENTS
3.4. Results.

When an external dc voltage is applied in metal insulator metal system, the current rises rapidly and then approaches to a constant value. This steady state conduction current has been recorded at room temperature (303K) by increasing the applied voltage from 100V to 600V thereby increasing the applied field from 2 kV/cm to 12 kV/cm. The experiment is repeated at seven thermostatically controlled temperatures i.e. from 303K to 373K with an interval of 10K. The results of observed I-V-T measurements are analyzed in terms of different conduction mechanism described in section 3.2. The results are divided into two parts as part A and part B. The part A includes results of measurements on Dextrin shows the different plots in fig (3.3) to fig (3.9). The part B includes the results of measurements on Folic acid shown in fig (3.10) to fig (3.16), depicting different plots. These are used to find the possible conduction mechanism that may be operative in case of Dextrin and Folic acid in the following section.
3.5 Discussion.

Part A - Results of Studies on Dextrin.

A1 I-V Characteristics

The current-voltage characteristics of Dextrin is presented in the form of ln (I) vs ln(V) in fig (3.3). From the figure it is observed that the current increases non-linearly with respect to the applied voltage. This non-linearity rules out any possibility of ohmic conduction in the voltage range studied. It can also be noted that the plots do not obey the power law \( I = kV^m \) where \( k \) and \( m \) are constants. The value of \( m \) is estimated from the graph and is found to be less than 2 i.e \( m < 2 \). This characteristics rules out ohmic as well as space charge limited current(77-78).

The results based on these isothermal I-V characteristics also indicate thermally activated conduction over the entire temperature range. Hence the possibility of tunnelling mechanism being operative in the present case can also be ruled out. A similar behaviour is observed in different polymers(79,80).
A.2 Poole-Frenkel plots.

The $\ln(\phi)$ is plotted against $E^{1/2}$ in fig (3.4). As discussed earlier, the Poole-Frenkel mechanism is characterized by the linearity of Poole-Frenkel plots (55-82). But in the present case of Dextrin the plots are found to be almost parallel to the axis corresponding to the voltage, showing no dependence on field. This behaviour indicates the possibility of Poole-Frenkel mechanism not being operative in case of Dextrin, since this mechanism predicts a field dependence for the conductivity.

A.3 Fowler-Nordheim plots

Fowler-Nordheim plots can be used to characterize the tunnelling currents and predict a linear relationship between $\ln(J/V^2)$ and $1/V$ (64-66). The straight lines with negative slopes indicate the tunnelling mechanism. In the present case the Fowler-Nordheim plots (fig. 3.5) are not found to be linear. This behaviour indicates the possibility of tunnelling mechanism being absent in general in case of Dextrin. But the negative slope observed for higher values of
voltage indicate a little contribution of tunnelling mechanism at higher fields.

A.4 Schottky plots.

The Schottky plots [ln (J) vs \( E^{1/2} \)] of Dextrin is shown in fig (3.6) According to the Schottky-Richardson mechanism the emission of electrons are due to the combined effect of thermal activation and the applied voltage and predicts a linear relationship between the current density and square root of the applied field. In the present case of Dextrin the Schottky plots are found to be linear with positive slopes and suggests the possibility of Schottky emission in case of Dextrin. This possibility can be further investigated with the help of current density vs temperature plots, Richardson plots and Arhehenius plots.

A.5. Current density vs temperature plots.

In fig. (3.7) the plots of ln(J) vs temperature show the temperature dependence of current density. In the present investigation the current density is found to
strongly depend on temperature which can be considered as an
evidence for Schottky-Richardson mechanism. Further straight
lines with single slopes in all the fields studied rules out
any thermodynamic transition in the temperature range studied

A.6. Richardson plots.

For further confirming the applicability of
Schottky-Richardson mechanism $\ln(J/T^2)$ is plotted against $(1/T)$
and is shown in fig (3.8). These plots (Richardson plots) are
found to be linear and support the mode of conductivity as the
Schottky-Richardson mechanism in case of Dextrin. A similar
behaviour is reported in several research in different organic
polymers(80-83). The effective metal-insulator potential
barrier has been calculated from the slope of these plots and
the value is found to be near about 0.32eV in all the cases and
is given in table (3.1)

A.7. Arrehenius plots.

Arrehenius plots which show the relation
between log of conductivity ($\sigma$) and inverse absolute
temperature (1/T) are shown in fig (3.9) where as the points corresponding to the different fields are so close that only a representative plot is shown. The activation energy for the conduction process have been calculated from the slopes of the plots and are found to be in good agreement with the calculated metal-insulator potential barrier (table 3.1). This good agreement further indicates the operation of the Schottky-Richardson mechanism in case of Dextrin.
Figure 3.3
Current-Voltage Plots (Dextrin)
Figure 3.4
Poole-Frenkel Plots (Dextrin)

In(Cond.)

373
363
353
343
333
323
313
303

sqrt E

1.2 1.7 2.2 2.7 3.2 3.7
Figure 3.5
Fowler-Nordheim Plots (Dextrin)

\[ \ln \left( \frac{j}{\sqrt{2}} \right) \]

\[ 1000/V \]

-23
-24
-25
-26
-27
-28

373
363
353
343
333
323
313
303

Figure 3.6
Schottky Plots (Dextrin)
Figure 3.7
Current density vs Temp. Plots (Dextrin)
Figure 3.8
Richardson Plots (Dextrin)

High Field

Low Field

\( \ln \left( \frac{j}{T^2} \right) \)

1000/T

2.5 2.7 2.9 3.1 3.3 3.5
Figure 3.9
Arrehenius Plots (Dextrin)

In(cond)

1000/T

High Field
Low Field
<table>
<thead>
<tr>
<th>Voltage applied (volts)</th>
<th>Potential barrier ($\phi$) (eV)</th>
<th>Activation energy (E) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.31</td>
<td>0.31</td>
</tr>
<tr>
<td>200</td>
<td>0.31</td>
<td>0.31</td>
</tr>
<tr>
<td>300</td>
<td>0.31</td>
<td>0.31</td>
</tr>
<tr>
<td>400</td>
<td>0.37</td>
<td>0.32</td>
</tr>
<tr>
<td>500</td>
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<td>0.32</td>
</tr>
<tr>
<td>600</td>
<td>0.32</td>
<td>0.32</td>
</tr>
</tbody>
</table>
Part B

B.1. I-V Characteristics

The observed current-voltage relationship for Folic acid is presented in the form of ln(I) vs ln(V) plots in fig (3.10). The current is found to increase nonlinearily with respect to the applied voltage and rules out any possibility of ohmic conduction in the voltage range studied. The power law \( I = kV^m \) where \( k \) and \( m \) are constants does not seem to be obeyed and the calculated value of \( m \) found to be less than 2 and rule out the possibility of space charge limited current in the conduction processes (77,78).

A thermally activated conduction over the entire temperature range is also indicated on the basis of the results based on these isothermal I-V characteristics and the possibility of tunnelling mechanism not being operative in the present case is indicated.
B.2. Poole-Frenkel plots

The Poole-Frenkel mechanism is characterized by the linearity of Poole-Frenkel plots \((\ln (\nu) vs \ E^{1/2})\). In the present case of Folic acid the plots as shown in fig (3.11) are found to be almost parallel to the square root of field axis and suggest the possibility of Poole-Frenkel mechanism being not operative in case of Folic acid.

B.3. Fowler-Nordheim plots

Fowler-Nordheim plots can be used to characterize the tunnelling currents and predict a linear relationship between \(\ln (J/V^2)\) and \((1/V)\). The straight lines with negative slopes indicate the tunnelling mechanism(64-65). In the present case, the Fowler-Nordheim plots shown in fig (3.12) are not found to be linear and the slopes are also positive. This behaviour rules out the possibility of tunnelling mechanism being operative in case of Folic acid.
B.4. Schottky plots

The Schottky plots [ln (J) vs \(E^{1/2}\)] for Folic acid are shown in fig (3.13). In the Schottky-Richardson mechanism, the emission of electrons are due to the combined effect of thermal activation and the applied voltage and a linear relationship between the current density and square root of the applied field is predicted. In the present case of Folic acid the Schottky plots are found to be linear with positive slopes and suggests the possibility of Schottky emission.

B.5. Current density vs temperature plots

The temperature dependence of the current density is plotted in fig. (3.14) in the form of ln(J) vs temperature and show a strong temperature dependence of current density which can be considered as an evidence for Schottky-Richardson mechanism. The straight lines with single slopes for all the fields studied is an indication of absence of thermodynamic transition in the temperature range studied in the case of Folic acid.
B.6. Richardson plots

The ln(J/T^2) plotted against (1/T) may be used as an additional evidence of the applicability of Schottky-Richardson mechanism. In fig (3.15) the linearity of the plots (Richardson plots) supports the Schottky-Richardson mechanism as the mode of conduction in case of Folic acid. The slope of the plots have been used to calculate effective metal-insulator potential barrier which is found to be near about 0.34eV in all the cases and is given in table (3.2).

B.7. Arrhenius plots

The activation energy of the conduction mechanism have been calculated using the slopes of Arrhenius plots showing the relation between log of conductivity [ln (σ)] and inverse absolute temperature (1/T) depicted in fig (3.16). The activation energy for the conduction processes is found to be slightly greater than the calculated metal-insulator potential barrier. This behaviour further confirms the applicability of Schottky-Richardson mechanism in case of Folic acid. But the possibility of trapping the charge carriers in
the shallow traps can not be ruled out because of the difference in the activation energy and metal-insulator potential barrier.
Figure 3.10
Current-Voltage Plots (Folic acid)
Figure 3.11
Poole-Frenkel Plots (Folic Acid)
Figure 3.12
Fowler-Nordheim Plots (Folic acid)
Figure 3.13
Schottky Plots (Folic acid)
Figure 3.14
Current density vs Temp Plots (Folic acid)
Figure 3.15
Richardson Plots (Folic acid)
Figure 3.16
Arrehnius Plots (Folic acid)

\[ \text{In}(\text{cond}) \]

High Field

Low Field

1000/T

2.5  2.7  2.9  3.1  3.3  3.5

-20  -19  -18  -17  -16
<table>
<thead>
<tr>
<th>Voltage Applied (Volts)</th>
<th>Potential Barrier ($\phi$) (eV)</th>
<th>Activation Energy (E) (eV)</th>
</tr>
</thead>
<tbody>
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<td>100</td>
<td>0.34</td>
<td>0.42</td>
</tr>
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</tr>
<tr>
<td>600</td>
<td>0.35</td>
<td>0.42</td>
</tr>
</tbody>
</table>
3.6 Conclusion

The observed results of dc conduction studies of Dextrin and Folic acid, lead to the conclusion that the conduction mechanism being operative is primarily the Schottky-Richardson mechanism. However some of the charge carriers may get trapped in shallow traps and the subsequent release is controlled by the Poole-Frenkel mechanism(84). From the analysis it can also be concluded that the electrode contacts are blocking in nature. A similar behaviour is observed in case of all the biological materials studied in our lab so far(85,86) and in case of majority of biopolymers studied by different researchers in this field(77,79). These blocking contacts are found to be highly suitable specially for the study of the thermally stimulated depolarization current (TSDC) in case biopolymers at low temperature because of its independent nature in the absence of any applied field.
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