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4.1 INTRODUCTION:

Electrical conductivity of the material is an important factor while studying the electrical properties. Since the discovery of conducting polyacetylene at the end of the 1970s, charge-transport mechanisms in semiconducting and conducting polymers have been of great interest. As in polyvinyl acetate, a transition from insulating (zero dc conductance for temperature T going to zero) to metallic state (nonzero dc conductance in the limit of zero Kelvin) occurs by increasing the doping level and metallic polypyrrole (Martens et al, 2001), among highly doped conducting polymers, is one of the most widely studied due to its environmental stability, which makes it attractive for technological applications. In the recent years, there has been a great deal of increasing interest in the synthesis and characterization of conducting polymers because of their electrical, electrochemical, electrochromic devices, optical, switching devices, optical properties (Chiang et al 1977) and their possible application to organic batteries, sensors, microelectronic devices and electrocatalysis (Martens et al, 2001). Among the other members, polypyrrole has been extensively studied because monomer pyrrole is easily oxidized, water-soluble, commercially available, and possesses environmental stability, good redox properties and high electrical conductivity, which make it a good candidate for many applica-
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tions e.g. sensor, biosensor, modified electrodes, actuators and electronic devices (Jasne, 1988 and Palmisano et al, 1997). However, it has poor mechanical properties and poor stability at ambient conditions.

Since the properties of the polypyrrole films depend on a number of parameters, such as the type of counter-ion and solvent and their concentrations, and on other synthesis conditions, research on the preparation and characterization of conducting polymers is still continuing.

There are two techniques used to measure electrical conductivity. i) AC conductivity measurement:

This technique is used to identify good ionic conductors. Complex impedance, admittance, permittivity and modulus, are the four basic functions to analyzed the ac data.

ii) DC conductivity measurements:

This technique is used to identify good ionic as well as electronic conductors. The contribution of ionic or electronic components to the conductivity depends on the temperature range. Polypyrrole is a mixed conducting polymer, where a electronic as well as ionic conductivity is present. Due to the good intrinsic properties, polypyrrole appears promising for use in batteries. Hence study of ionic conductivity becomes most useful parameter.
4.2 THEORETICAL ASPECTS FOR AC CONDUCTIVITY:

4.2.1 Frequency dependence of ac conductivity:

There are three mechanisms of charge transport that can contribute to a direct current in amorphous semiconductors. They all can contribute to the ac conductivity as follows.

(a) Transport by carriers excited to the extended states near Ec or Ev. For these \( \sigma(\omega) \) would be given a formula of Drude type,

\[
\sigma(\omega) = \sigma(0) \left( \frac{1}{1 + \omega^2 \tau^2} \right)
\]

Where \( \tau \) is the relaxation time and the value of \( \tau \) is very small.

(b) Transport by carriers excited into the localized states at the edges of the valence or conduction band. No complete theoretical treatments of \( \sigma(\omega) \) for hopping under condition of non-degenerate state are known, but a similar dependence of frequency under degenerate conditions is given by Mott et al (1979) as,

\[
\omega \left[ \ln \nu_{ph}/\omega \right]^i
\]

(c) If energy density of states \( N(E_f) \) is finite, hopping transport occurs by electrons with energies near the Fermi level. The exponential dependence of conductivity \( \sigma(\omega) \) should be proportional to \( \tau \), if \( kT \) is small as compared to the energy range over which \( N(E_f) \) may be taken as constant and independent of \( \tau \) if \( kT \) is larger than the width of same well defined defect band in which \( E_f \) lies. Observed results have
been given by Davis and Mott et al (1970) using the formula for ac conductivity \( \sigma(\omega) \) given by Austin et al (1969)

\[
\sigma(\omega) = \frac{1}{3} \pi e^2 kT \{N(E_F)\}^2 \alpha^{-1} \omega \{\ln(v_{ph}/\omega)\}^4
\]  

Assumptions involved in this formula have been discussed by Pollak (1971) and Pollak et al (1969) and Butcher (1974).

1) Hoping should be between independent pairs of centres i.e. multiple hoping can be neglected.

2) There should be no correlation between the hop energy and the hop distance.

The frequency dependence of conductivity is given as \( \sigma(\omega) \propto \omega^s \). Where 's' is a weak function of frequency, if \( \omega \ll v_{ph} \). A plot of \( \ln \sigma(\omega) \) versus \( \ln \omega \) is therefore approximately linear and slope 's' is given by

\[
s = 1 - \frac{4}{\ln (v_{ph}/\omega)}
\]  

Alternating current conductivity is very interesting. In every amorphous conductor e.g. pyrrole monomer, the conductivity follows the equation,

\[
\sigma(\omega) = A\omega^s
\]  

Where 'A' is constant, depend on temperature and 's' is the frequency exponent, and is nearly unity or <1 and may be weakly temperature dependence.
4.2.2 Quantum Mechanical Tunneling Model (QMT):

Austin et al (1969) have suggested for single electron motion undergoing quantum mechanical tunneling, the expression for ac conductivity is

\[ \sigma(\omega) = \frac{\pi/e}{3} e^{2kT} \left\{ N(E_F) \right\}^{1/2} \alpha^{-5} \omega \left\{ \ln(\nu_{ph}/\omega) \right\}^4 \]  \hspace{1cm} (4.6)

Where \( \frac{\pi}{3} \) is the numerical constant,

\( \alpha \) is the electron wave function decay constant,

\( \nu_{ph} \) is the phonon frequency and

\( N(E_F) \) is the energy density of states near the Fermi level.

The hopping distance \( R \) at frequency \( \omega \) is given by,

\[ R = (1/2\alpha) \ln (\nu_{ph}/\omega) \]  \hspace{1cm} (4.7)

\[ R = (1/2\alpha) \ln (1/\omega \tau_0) \]  \hspace{1cm} (4.8)

Where \( \tau_0 \) is the characteristic relaxation time.

The frequency exponent \( s \) is given by

\[ s = 1 - \frac{4}{\ln (1/\omega \tau_0)} \]  \hspace{1cm} (4.9)

In this model \( s \) should be temperature independent but frequency dependent. Quantum mechanical treatment (QMT) of a carrier through the potential barrier between the sites separated by a distance \( R \) demands that, i) ac conductivity should be dependent on temperature and ii) Exponent \( s \) should be frequency dependent. Equation (4.6) is derived by
assuming that the multiple hopping is neglected means the hopping is considered only between independent pair of charge centres and no corelation between hop energy and hopping distance. However, Pollak (1976) has replaced the numerical factor $\pi/3 = (1.047)$ in equation (4.6) by $\pi^3/96 = (0.322)$. Similarly, Bucher et al (1971) have replaced the same factor by $3.66\pi^2/6 = (6.020)$

### 4.2.3 Hopping of Charge Carrier over the Barrier (HOB) model:

Pike (1971), Springelt (1974) and Elliott (1977) have suggested that the ac conductivity is a phenomenon due to hopping of charge carriers over the barrier, called HOB. The HOB model discussed the temperature and frequency dependence of conductivity and the exponent’s is determined from the relation

$$s = 1 - 6kT/W_m$$  \hspace{1cm} (4.10)

Where $W_m$ is the binding energy of the carrier in its localized site, which is assumed to be band gap, ‘$k$’ is the Boltzman’s constant. The values of ‘$s$’ obtained from equation (4.10) are the theoretical values.
4.3: EXPERIMENTAL SETUP REQUIRED FOR MEASUREMENT OF AC CONDUCTIVITY:

AC electrical conductivity of polypyrrole sample was measured (Hernandez et al 2001) by finding out the resistance from impedance $Z$ and phase $\theta$ data, by using equation,

$$R = |Z| \cos \theta \quad (4.11)$$

![Experimental set up for measurement of ac conductivity]

The impedance measurements were carried out by WK 4230 impedance analyzer (Wayne Karr Electronics, USA) with test leads at Department of Physics, Government Vidarbha Institute of Science and Humanities, Amravati. The analyzer is fully automatic, high performance instrument designed to measured a wide range of impedance parameters as well as phase gain and delay. The WK 4230 analyzer improves efficiency and quality of development and production of many type of com-
plex components of semiconductors and metals.

The two measurement display sections such as primary display A and secondary display B directly read out the parameters along with the appropriate units. The impedance and phase angle can be measured as a function of frequency with the help of WK 4230 impedance analyzer in laboratory in the frequency range 100Hz to 200 KHz.

A good ohmic contacts were established between silver electrodes of sample holder and polypyrrole film by applying conducting silver paint on both surfaces of the films, before loading the films between silver electrodes. The diameter of electrodes is same as that of the diameter of film, so as to reduce the surface losses at high frequencies.

A sample holder along with a film was kept in the furnace and is connected to the test leads of WK 4230 impedance analyzer as shown in figure (4.1). The primary parameter $Z$ and secondary parameter $\theta$ were measured for various frequencies in the frequency range of 100Hz to 200 KHz for temperatures 312, 333, 348, 373 and 398K.

4.4 THEORY OF DC CONDUCTIVITY:

A mechanism very often proposed to explain the dc conductivity in disordered and amorphous materials is Mott's Variable-Range Hopping (VRH) (Mott et al 1979). This mechanism describes a phonon-
assisted quantum-mechanical transport process in which a balance is obtained between the thermodynamic constraint on a charge carrier moving to a nearby localized state of different energy, and the quantum mechanical restraint on a carrier moving to a localized state of similar energy, but spatially separated. The VRH description is equally applicable to charge carriers such as electrons, holes, polarons or bipolarons provided that the appropriate wave function is incorporated. The temperature dependence of the dc conductivity according to Austin et al (1969) and Mott (1968) is given by

\[
\sigma = n e \mu = (v_0 N e^2 R/kT) C(1-C) \exp(-2\alpha R) \exp(-W/kT) \quad (4.12)
\]

Where \(N\) is the number of metal ions sites per unit volume and \(C\) is the ratio of ion concentration in low valance state to total concentration of metal ion; the term \(\exp(-2\alpha R)\) represents electron overlap integral between sites. \(R\) is the hopping distance and \(W\) is activation energy. Assuming that a strong electron lattice interaction exists, the activation energy \(W\) is the result of polaron formation with binding energy \(W_p\), and any energy difference \(W_d\) which might exists between the initial and final sites due to variation of the local arrangements of ions. Austin et al (1969) have shown that

\[
W = W_H = (1/2) W_d \quad \text{for } T > \theta_d / 2
\]
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\[ W_p = W_D \quad \text{for } T < \frac{\theta_D}{4} \quad (4.13) \]

Where \( W_H \) is the polaron hopping energy, \( W_D \) is the disorder energy arising from the energy difference between two neighboring hopping sites and \( \theta_D \) is Debye temperature. The polaron hopping energy \( W_H \) is given by

\[ W_H = \frac{W_p}{2} \quad (4.14) \]

Where \( W_p \) is polaron binding energy. The polaron hopping energy \( W_H \) calculated from the theory of Austin et al (1969) and is given by

\[ W_H = \left( \frac{e^2}{4\varepsilon_p} \right) \left( \frac{1}{r_p} - \frac{1}{R} \right) \quad (4.15) \]

Where \( \frac{1}{\varepsilon_p} = \frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_s} \)

Where \( \varepsilon_s \) and \( \varepsilon_\infty \) are the static and high frequency dielectric constants of the material respectively, \( \varepsilon_p \) is the effective dielectric constant (Bogomolov et al, 1967), \( r_p \) is the polaron radius estimated from the site spacing \( R \) (for crystal like solids) (Austin et al, 1968) and is given as

\[ r_p = \left( \frac{1}{2} \right) \left( \frac{\pi}{6N} \right)^{1/3} \]

\[ = \frac{R}{2} \left( \frac{\pi}{6} \right)^{1/3} \quad (4.16) \]

Two methods have been suggested to calculate the polaron binding energy. The most general expression was given by Holstein (1959);

\[ W_p = \frac{1}{2N} \sum_q \left| v_q \right|^2 \omega_q \quad (4.17) \]
Where \(|v_q|^2\) is the electron-phonon coupling constant, \(\omega_q\) is the frequency of optical phonons of wave number \(q\) and \(N\) is the site density.

Another method has been given by Mott (1969) which gives a direct estimate (for polar lattices, if the distance \(R\) through which the electron must be transferred is not large compared to \(r_p\))

\[
W_p = \frac{\varepsilon^2}{\varepsilon_p r_p} \ (4.18)
\]

In generalized polaron model, the activation energy is

\[
W = W_H - J \ (4.19)
\]

Where \(J\) is polaron band width which is related to the electron wave function overlap on adjacent sites.

To check the nature of the hopping conduction mechanism (adiabatic or nonadiabatic) three methods have been suggested.

1. Freidman et al. (1963) derived an expression for the mobility in the case of nonadiabatic hopping:

\[
\mu = \frac{3}{2} \frac{e^2 R^2}{kT} (\frac{\pi}{kT W_H})^{1/2} \exp \left( -\frac{W_H}{kT} \right) \ (4.20)
\]

While Emin et al. (1969) derived an expression for mobility in case of adiabatic hopping:

\[
\mu = \frac{4}{3} \frac{e^2 R^2}{kT} \exp \left( \frac{J - W_H}{kT} \right) \ (4.21)
\]

2. In the second method, the polaron band width \(J\) should satisfy the
inequality suggested by Holstein (1959):

\[ J > \left[ \frac{2kT \omega_H}{\pi} \right] \frac{\hbar \omega_0}{\pi} \] for adiabatic hopping \hspace{1cm} (4.22)

\[ J < J^* \] For non-adiabatic hopping

Where \( J^* = \left( \frac{2kT \omega_H}{\pi} \right)^{1/4} \left( \frac{\hbar \omega_0}{\pi} \right)^{1/2} \) \hspace{1cm} (4.23)

The polaron band width \( J \) can be estimated from

\[ J \approx e^3 \{ N(E_F) \}^{1/2} \omega \rho^{3/2} \] \hspace{1cm} (4.24)

Where \( N(E_F) \) is the density of states at the Fermi level. \( J \) can be estimated from

\[ J \propto \exp (-\alpha R) \]

or \[ J = J_0 \exp (-\alpha R) \] \hspace{1cm} (4.25)

3. The third method has been suggested by Sayer et al. (1972) and Murawski et al. (1979). When an overlap integral between sites \( J_0 \exp (-\alpha R) \) approaches \( J_0 \), i.e. \( \exp (-\alpha R) \rightarrow 1 \), the hopping is adiabatic and it is mainly controlled by the activation energy. The dc conductivity is given by:

\[ \sigma = (\nu N e^2 R/kT) C(1-C) \exp (-W/kT) \] \hspace{1cm} (4.26)

To explore the nature of hopping conduction, a graph of \( \log \sigma \) against activation energy \( W \) at a fixed temperature for the polypyrrole of different weight percentage is to be plotted. If this plot shows straight line nature, then it indicates that equation (4.26) is valid. The plot gives
slop equal to $1/kT$ and the intercept on log$\sigma$–axis gives the value of constant $A'$, where

$$A = \log \left[ (\nu N e^2 R / k T) C (1-C) \right]$$

From the slope of the plot of log$\sigma$ versus activation energy $W$, $1/kT$, the value of the temperature is estimated. If the estimated temperature is found to be nearly equal to the observed temperature, then the hopping conduction is adiabatic in nature and it is mainly controlled by the activation energy. If the equation (4.26) is not valid, the value of estimated temperature observed will be very different, this will then suggest that the nature of hopping conduction is nonadiabatic.

Recently, Triberies et al (1985), Triberies (1985) have applied percolation theory to the small polaron hopping regime and evaluated the conductivity in disordered systems. Hernandez et al (2001) and Kaur et al (2004) have applied the above theory to conducting polypyrrole composite to evaluate electrical conductivity. Considering the co-relation due to energy of common sites in the percolation cluster the following expression for the conductivity has been obtained.

$$\sigma = \sigma'_0 \exp\left[-(T'_0 / T)\right]^{1/4} \quad (4.27)$$

Where $\sigma'_0$ and $T'_0$ are constant and $T'_0$ is given by

$$T'_0 = 13.5 \alpha^2 / k N_0 \quad (4.28)$$

The conductivity (Mott, 1969) for the variable range hopping is predicted to be
\[ \sigma = \sigma_0 \exp\left[-\left(\frac{T_0}{T}\right)^{1/4}\right] \] (4.29)

Where \( T_0 \) is given by \( T_0 = \frac{19.44a^3}{k N(E_F)} \) (4.30)

Where \( N(E_F) \) is the density of state at Fermi level of energy \( E_F \).

### 4.5: EXPERIMENTAL SETUP REQUIRED FOR MEASUREMENT OF DC CONDUCTIVITY:

The dc conductivity of all polypyrrole thin films under study was measured by ohms law method.

The circuit (Fig.:4.2) consists of an electronically regulated power supply (Systronic 425) of 20 Volts and a digital picoameter (Scientific, Roorkee) having input impedance 10 M\( \Omega \). Knowing the currents and applied voltage, the I-V characteristics are plotted at temperature 308, 323, 348, 373, 398, 423 and 473K. As the trap square law region is observed between 2V to 10V, the dc conductivity is calculated by using the dimensions of polypyrrole thin films.
4.8 RESULTS AND DISCUSSION:

The transport mechanism, in semiconducting polymers and their
derivatives has been of great interest since 1974 (Ito et al/1974). Since
then new efforts have been made to improve and understand the charge
transport characteristics of these quasi-one-dimensional electric dis­
ordered materials, offering new concept and mechanism for conductiv­
ity (Conwell,1997). Both ac and dc conductivities are considered di­
rectly in relation to the electronic structure and therefore they have been
used to study the mechanism of charge transport.

Looking the industrial applications of polypyrrole, it is worth to
study the density and molar volume of polypyrrole films. The density
and molar volume of 1, 5, 8,10 and 40 Wt.%, polypyrrole films are
tabulated in table (4.1). Density of the films is calculated using the re­
lation

\[
d = \frac{M}{V}
\]  \hspace{1cm} (4.32)

Where M is the mass of the film, and

\[ V \text{ is the Volume of film} = \pi r^2 \times \text{thickness} \]

Similarly, molar volume of the sample is calculated using the relation

\[
\overline{V} = \frac{\overline{M}}{d}
\]  \hspace{1cm} (4.33)

Where \( \overline{M} \) is the Average molecular weight of the film.

The other values of physical parameters such as number of ions
per cubic cm (N), polaron radius (r_p) and hopping distance (R) are re-
ported in table (4.1). The values are found to be of the order of polypyrrole composite as reported by Hernandz et al (2001). The value of hopping distance is found to in the range 0.94 to 3.02 Å. Polaron radius varies from 0.38 to 1.22 Å. For small polaron, the reported value of polaron radius is about 1.6 Å. The values of number of ions per cubic cm is found to be in the range 3.69 x 10^{22} to 5.44 x 10^{22} cubic centimeter. These values are in agreement with the values reported by Singh et al (1996).

Table 4.1: Physical parameters of polypyrrole films

<table>
<thead>
<tr>
<th>PPY sample Wt.%</th>
<th>Density (d) (gm/cc.)</th>
<th>Molar Volume (V)</th>
<th>Hopping distance (R_{hop}) in Å</th>
<th>Polaron radius (r_p) in Å</th>
<th>No. of ions per cc (N) 10^{22}cc</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.15</td>
<td>60.9</td>
<td>3.02</td>
<td>1.22</td>
<td>3.69</td>
</tr>
<tr>
<td>5</td>
<td>6.59</td>
<td>59.2</td>
<td>2.46</td>
<td>0.99</td>
<td>3.95</td>
</tr>
<tr>
<td>8</td>
<td>19.95</td>
<td>23.4</td>
<td>1.25</td>
<td>0.50</td>
<td>4.95</td>
</tr>
<tr>
<td>10</td>
<td>14.93</td>
<td>34.8</td>
<td>1.57</td>
<td>0.63</td>
<td>4.59</td>
</tr>
<tr>
<td>40</td>
<td>50.61</td>
<td>25.6</td>
<td>0.94</td>
<td>0.38</td>
<td>5.44</td>
</tr>
</tbody>
</table>

4.8.1 AC electrical conductivity:

The dispersion of real part of frequency dependent ac conductivity σ(ω) for polypyrrole films over the temperatures 313, 333, 348, 373 and 398K is depicted in figure (4.3a) to (4.3e). The increase of σ(ω) with frequency is due to the presence of various kinds of inhomogeneity present in the material. As can be seen, at lower temperatures
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Fig. 4.3a Plot of log $\sigma_{ac}$ against log$ f$ for 1 Wt. % of polypyrrole sample
Fig. 4.3b Plot of log $\sigma_{ac}$ against log$ f$ for 5 Wt. % of polypyrrole sample
Fig. 4.3c Plot of log $\sigma_{ac}$ against log$ f$ for 8 Wt. % of polypyrrole sample

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Table 4.2 : Values of exponent 's' calculated from fig.(4.3a) to (4.3 e) of polypyrrole files

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Polypyrrole weight percent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>311</td>
<td>0.1153</td>
</tr>
<tr>
<td>333</td>
<td>0.0689</td>
</tr>
<tr>
<td>348</td>
<td>0.0555</td>
</tr>
<tr>
<td>373</td>
<td>0.047</td>
</tr>
<tr>
<td>398</td>
<td>0.0498</td>
</tr>
</tbody>
</table>

Fig. : 4.3d Plot of log $\sigma_\infty$ against log $f$ for 10 Wt. % of polypyrrole sample
Fig. : 4.3e Plot of log $\sigma_\infty$ against log $f$ for 40 Wt. % of polypyrrole sample
\( \sigma_{ac} \) increases with frequency, whereas at 348, 373 and 398 K a plateau is observed. This shows that \( \sigma_{ac} \) is approximately independent of frequency in a frequency region which extend to the higher frequencies with increase in temperature. The conductivity values at the plateau increases with increasing temperature. This is due to the distribution of dopped material throughout the polymer matrix will change the local electric field (Roth et al., 1983) and hence the local electrical properties (Fahamy et al., 2001). At low frequencies the applied electric field forces the charge carriers to drift over large distances. When the frequency is increased the mean displacement of the charge carriers is reduced and real part of conductivity follows \( \sigma(\omega) \propto \omega^s \) law, characterizing hopping conduction (McDonald, 1987). It was found that at most of the temperatures \( \sigma(\omega) \) shows simple power law dispersion, particularly in higher frequency region, which may be described by well-known relation (4.5) (Elliot, 1987). The behavior representing by equation (4.5), termed as universal dynamic response, has been widely observed in disordered materials (Elliot, 1988). From the graph shown by figure (4.3a) to (4.3e) values of \( s \) have been evaluated at different temperatures for 1, 5, 8, 10 and 40 Wt.% polypyrrole films, and are listed in table (4.2).

Equation (4.5) could not be fitted sucessfully to the experimental data of figures (4.3a) to (4.3e) over the whole frequency range as \( s \)
values are less for different Wt.% of the polypyrrole samples. This may be due to the contribution to the conductivity, from the carrier moment at different temperature is different, thereby resulting in decrease of 's' with increase of temperature. In addition, the decrease of exponent 's' with increasing temperature is due to the measured conductivity values at lower frequencies increases more rapidly with temperature (Fahmy, 2001). From table (4.2) it is found that the values of 's' for 1Wt.% at room temperature is 0.1153 whereas the values of 's' for 40Wt.% at room temperature is 0.0273. The low value of 's' is due to the hopping of localized charge carriers (Paquin et al, 1982) and high values of 's' indicates the localized hopping of ions, in random or non-periodic potentials, especially at low temperatures (Polak et al, 1972). The variation of exponent 's' reflects the change in the nature of the conduction process with change in temperature and composition. Frequency dependent plots shown in figure (4.3a) to (4.3e) are linear up to some extent. This leads us to believe that the conduction is governed either by (a) transport by charge carriers excited into localized states at the edge of valence or conduction band or (b) hopping transport by carriers with energy close to Fermi level (Mott et al, 1979). At low temperature the $\sigma(\omega)$ is independent of temperature indicates that the conduction is due to hopping of charge carriers. This support the find-
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ing of polaron formation in these polypyrrole films and also suggested that the conduction takes place through these polarons.

Several authors (Mott et al, 1979 and Austin et al, 1969) discussed the treatment of conduction by polarons. The polaron formation in the polymers may be categorized as large and small polarons. In large polaronic model the conductivity is by band mechanism at all temperatures and the ac conductivity decreases with frequency. The small polarons conduct in band like manner upto a certain temperature, the conductivity showing an increase with frequency.

Following mechanisms of charge transport are suggested.

(a) Transport by carriers excited to the extended states near Ec or Ev, for these the $\sigma(\omega)$ would be given by the formula of Drude type (Equation 4.1). The relaxation time $\tau$ will be very short of the order of $10^{-15}$ sec, and a decrease in $\sigma(\omega)$ as $\omega^{-2}$ is not expected until a frequency of the order of Hz is reached. This corresponds to an energy quantum line above the fundamental optical absorption edge in the materials. The Drude formula is hardly applicable for such small values of $\tau$. It is expected that the range of frequencies (upto say $10^7$ Hz) show no frequency dependence of the conductivity associated with the carriers in the extended states.

(b) Transport by carriers excited into the localized states at the ...
edges of the valance or conduction band. No complete theoretical treat-
ment of \( \sigma(\omega) \) for hopping under the condition of non-degenerate statist-
tics are known but might be expected a similar dependence of frequency
to that derived under degenerate conditions as \( \omega \left\{ \ln \left( \frac{\nu_{ph}}{\omega} \right) \right\}^4 \). This
varies approximately as \( \omega^5 \), where \( s<1 \) when \( \omega<\nu_{ph} \). The temperature
dependence of ac conductivity should be the same as that of the carrier
concentration at the band edges.

(c) Hopping transport by electrons with energies near the Fermi
level, provided \( N(E_F) \) finite. In this case \( \sigma(\omega) \) should increase with fre-
quency in the manner similar to that for the process described in (b).
However, the exponential dependence on the temperature will be absent
and \( \sigma(\omega) \) should be proportional to \( T \), if \( kT \) is small as compared with
the energy range over which \( N(E_F) \) may be taken as constant, and inde-
dependent of \( T \) if \( kT \) is larger than the width of some well defined defect
band in which Fermi energy \( E_F \) lies.

4.8.2 DC electrical conductivity:

A mechanism very often proposed to explain the dc conductivity
in disordered and amorphous materials is Mott’s variable range hopping
(VRH) (Mott et al, 1979). This mechanism describes a phonon-assist
quantum mechanical transport process in which a balance is obtained
between a thermodynamic constraint on a charge carrier moving to a nearby localized state of different energy,

$$\sigma_{dc} = \sigma_0 \exp \left[ - \left( \frac{T_0}{T} \right)^\gamma \right]$$  \hspace{1cm} (4.34)

Where $\sigma_0$ is the conductivity at infinite temperature and $T_0$ is the characteristic temperature that determines the thermally activated hopping among localized state at different energies. In conventional VRH, which assumes exponentially localized state, $\gamma = 1/(1+d)$, where $d$ is the dimensionality of the system, i.e. $d = 1,2,3$. The corresponding expression for $\sigma_0$ and $T_0$ vary according to the dimensionally of the transport process (Mott et al., 1979).

The VRH model and its field of applications has been extensively reviewed by various authors (Mott et al., 1990). The value of exponent in equation (4.34) is considered to provide the information on the conduction mechanism and is related to the dimensionality of the process. The experimental results are generally plotted as $\log \sigma_{dc} T^{1/2}$ against $T^{-\gamma}$, as established by Mott et al., (1979), and remarked upon by Epstein et al. (1983), under the consideration that VRH is a multiphonon process. When exponent is equals a quarter, i.e. $d = 3$, it evident three-dimensional transport process, which is that most often observed in conducting polymers. However, when plotting a data for $d = 1$ for temperature range 308 to 473K a better fit is obtained as shown in figure (4.4), indi-
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cating in this way that the transport mechanism in polypyrrole films corresponds to a one dimensional process.

For the case of one dimensional hopping transport, $T_0$ is given by,

$$T_0 = \frac{8\alpha}{kN(E_F)Z} \quad (4.35)$$

Where $N(E_F) = 7.23 \times 10^{21} \text{ eV}^{-1} \text{ cm}^{-3}$ (Hernandez 2001), assumed constant, over the range $kT$ at the Fermi energy $E_F$, $\alpha$ is the delocalization length of the electron wave function to decay to $1/e$ of its initial value (considered to be between 3 to 10 Å, depending upon the disorder of polymer), $k$ is Boltzman constant and $Z$ is number of nearest-neighbour chains. The value of $T_0$ has been estimated from the slope of fitted straight line in figure (4.4) and is tabulated in table (4.3). Different values of this parameter have been found in the literature for different

![Figure 4.4: Dependence of dc conductivity according to equation (4.3) with $d = 1$](image)

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semiconducting polymer composite. Depending on the kind of polymer blend, the values of $T_0$ are ranging from $T_0 \approx 2500$ for highly conducting blend to $T_0 > 25000$ for lightly conducting polymer (Pinto et al, 1996). For the case, $d = 2$, two-dimensional behavior is predicted; whereas for $d = 1$, the most commonly invoked descriptions are the charge energy limited tunnelling (CELT) (Sheng et al, 1973), the fluctuation-induced tunneling (FIT) (Abeles et al, 1975) or the quasi-one-dimensional VRH models (Mott et al, 1979 and Joo et al, 1994). For the application of any of these models the following must be considered.

(a) When the polymer is made up of metallic regions embedded into non-conducting-amorphous regions, and considering that the insulating barriers between two conducting regions are sufficiently thin (in the range of few angstroms) (Paash et al, 1994), electron tunnelling can occurs between small surface areas. A tunnel junction can be approximated by a parallel plate capacitor, $C$, and a resistance, $R$. When the conducting segments are large, the total capacitance, $C_0$, between the segments is large. Therefore the charging energy $e^2/2C_0$ becomes negligible and the conduction is due to FIT (Abeles et al 1975). When the size of conducting segment is small, between 20-50 Å, and the isolated

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metallic grains are dispersed in a dielectric matrix, the charging energy plays an important role. Charge carriers are transported from one isolated metallic grains to the next by tunnelling described by the CELT model. The effects of changing energy are seen in both temperature and electric field dependence of the conductivity. The low field charging energy limited conductivity is in the form of (Sheng et al, 1973)

\[ \sigma_{dc} = \sigma_0 \exp \left[ -\left( \frac{D}{kT} \right)^{-1/2} \right] \]  

(4.36)

where \( D \) is a constant equal to \( kT_0 \)

(b) For the quasi-one-dimensional case, the VRH model predicts a temperature conductivity dependence given by the same analytical form as equation (4.34), with \( \gamma = 1/2 \), as

\[ \sigma_{dc} = \sigma_0 \exp \left[ -\left( \frac{T_0}{T} \right)^{-1/2} \right] \]  

(4.37)

It is also possible to define the Mott's parameters for this quasi-one-dimensional case, \( T_0 \) according to equation (4.35) and \( \sigma_0 \) by,

\[ \sigma_0 = \frac{e^2 v_{ph}}{k\alpha TA} \]  

(4.38)

where \( k \) is the Boltzmann constant,

e is electronic charge,

\( v_{ph} \) is the hopping frequency, taking the value of about \( 10^{13} \) s\(^{-1} \) (Hernandez et al, 2001),

\( A \) is the cross-sectional area of chain.
When experimental data are plotted as $\log \sigma_{dc} T^{1/2}$ against $T^{-1/2}$ an excellent fit to a straight line is obtained, as shown in figure (4.4). The fact that $\sigma_{dc}$ was fitted to $T^{-1/2}$ (fig.4.4) indicates that the charge transport mechanism can be explained using any of the aforementioned theoretical approximation, i.e. either quasi-one-dimensional VRH or the three-dimensional CELT model.

As reported in literature (Omastova et al, 1996), many synthesized polypyrrole as well as polypyrrole composites can be built in such a way as that considered in the CELT model. If the dopant are not distributed homogeneously to electron donor sites, partial ionization and heterogeneity is caused, which originate the formation of small semiconducting domains separated by some insulating regions of undoped polymer. In such a system conduction occurs by carrier transfer or tunneling between conducting areas rather than by hopping between localized states. This description could be also applicable to composite materials in which conducting areas embedded in an insulating matrix. The CELT transport mechanism considers that the predominant component in the blend is insulating one, which consist the matrix, filling most of the volume of the sample, and that the charge transport depends on the size of conducting island. According to Zuo et al (1987), the dimensions of conducting areas can be estimated by using the equation (4.38).
The values of ‘d’ are listed in table (4.3).

\[ d = \frac{(kT_0)}{4eE_0} \]  \hspace{1cm} (3.38)

where \( T_0 \) is the slope of straight line plot \( \log \sigma_{dc} T^{1/2} \) against \( T^{-1/2} \) (fig. 4.4)

e is the electronic charge of carrier,

\( E_0 \) is intensity of electric field in the sample.

Typical value of in \( E_0 \) in the polymer composites ranges from 10 to 100 kV cm\(^{-1}\) (Zuo et al, 1987). Considering the intermediate and typical average value of \( E_0 = 50 \) kV cm\(^{-1}\) (Hernandez et al, 2001) inside the polypyrrole thin films and \( T_0 \) listed in table (4.3), after a list square fit, the size or dimension of semiconducting areas was found as listed in table (4.3). These values lies among those reported for semiconducting areas in other polypyrrole composites (Omastova et al, 1996).

Min et al (1994) shows that quasi one dimensional VRH model as well as the condition of synthesis and the insulating polymer used for preparation blend plays an vital role in the conduction mechanism of polymer blend. (Potje et al, 1989) shows that, in polyoxiphynilene-polypyrrole composite, polyoxiphynilene build the high insulating matrix, which avoid any transport of charge carriers through their own chain and enhances the void space between the semiconducting polymer chains. Hence the hopping probability of the charge carriers between these con-
ducting polypyrrole chains and total conductivity of the sample are reduced. Because of the low probability for the charge carriers to undergo interchain hopping, another charge transport process should exist which allow the charge carriers to flow through conducting path in order to contribute to the conductivity. One of the most probable chain formations which allow the charge carriers to flow through the conducting paths and contribute to the conductivity is that in which the polymer blend consist either of a large number of parallel or mixed chain of finite length aligned in the preferred direction. This kind of chain arrangement has been found in other composite system (Wang et al, 1991). There, it has been shown that such an arrangement constitutes a lightly disordered system, in which the wavefunctions of weakly localized electronic states in one chain overlap with those of the neighboring chains, allowing in this way the hopping of charge carriers. Moreover, Nakhmedov et al (1989) have shown that the connection to the adjacent aligned chains are successively interrupted and the end of the single chain are connected to the end of only few, one or two, aligned neighboring chain, the dynamics of charge carriers should cross over from a three dimensional transport process to the quasi-one-dimensional transport mechanism, and equation (4.34) hold with $d = 1$ ($\gamma = 1/2$). Based on
these ideas it can be believed that this is the most probable chain formation in polypyrrole thin films, which allow to explain the transport mechanism based on the quasi-one-dimensional hopping process.

As above already mentioned, the fitting of the experimental values of figure (4.4) to the theoretical model of equation (4.34), gives rise to a value of parameter $T_o$. Joo et al (1994) shows that $kT_o$ can be considered that as the effective energy separation between localized states and that this value represent a measure of the degree of disorder in an amorphous region. The lower $kT_o$ means the more coherently the polymers chains are organized. The activation energy is calculated by using the equation $\sigma_{dc} = \sigma_o \exp \left[ - \frac{W}{kT} \right]$ and the slope of the plot shown in figure (4.5). The values of activation energy for different polypyrrole films are tabulated in table (4.3).

The adiabatic or non-adiabatic nature of hopping conduction is examined using the condition given by Holstein. According to Holstein the polaron bandwidth $J$ should satisfy the inequality of the equation ($J<J^*$). The values of $J$ are calculated form equation (4.24) and the values of $J^*$ are calculated form equation (4.23) and listed in table (4.3). The values of $J$ for all polypyrrole samples under study are found to less than $J^*$ suggesting that the nature of hopping conduction is non-adiabatic. Similarly to confirm the nature of hopping conduction, an-
other method suggested by Sayer et al. (1972) and Murawski et al. (1979) is applied. Exploration of equation $\sigma_{dc} = \sigma_0 \exp \left[ - \frac{W}{kT} \right]$ is done by plotting $\log \sigma_{dc}$ versus activation energy $W$ at fixed temperature 373K as shown in figure (4.6). This plot shows a straight line nature, whose slope gives the temperature 91.35K. This temperature is not close agreement with the fixed temperature 373K chosen for plotting a straight line except 40 wt %. This indicates that the hopping conduction is non-adiabatic in nature.

The dc conductivity is plotted against various wt. % of polypyrrole samples as shown in figure (4.7). It is found that the conductivity increases up to 10 Wt % of sample and for 40 wt % of sample it decreased.

![Fig. 4.5 Variation of log $\sigma_{dc}$ with inverse of temperature](image)

![Fig. 4.6 Variation of log $\sigma_{dc}$ with activation energy $W$](image)
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Fig. : 4.7 Variation of $\sigma_\epsilon$ with Wt.% of polypyrrole

Table 4.3: Transport properties of polypyrrole (PPY) files

<table>
<thead>
<tr>
<th>PPY sample Wt.%</th>
<th>Polaron hopping energy $W_{\text{hop}}$ (eV)</th>
<th>Polaron binding energy $W_{\text{b}}$ (eV)</th>
<th>Polaron band width at $T=398$ K</th>
<th>Characteristic temp. $(T_0)$K</th>
<th>Dimension of conducting area $d$ (nm)</th>
<th>Activation energy in eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0030</td>
<td>0.00606</td>
<td>0.0098</td>
<td>0.0128</td>
<td>3411</td>
<td>735</td>
</tr>
<tr>
<td>5</td>
<td>0.0011</td>
<td>0.00218</td>
<td>0.0021</td>
<td>0.008</td>
<td>3694</td>
<td>797</td>
</tr>
<tr>
<td>8</td>
<td>0.0029</td>
<td>0.00576</td>
<td>0.009</td>
<td>0.0102</td>
<td>3941</td>
<td>850</td>
</tr>
<tr>
<td>10</td>
<td>0.0137</td>
<td>0.0274</td>
<td>0.0912</td>
<td>0.0945</td>
<td>4188</td>
<td>903</td>
</tr>
<tr>
<td>40</td>
<td>0.0225</td>
<td>0.045</td>
<td>0.198</td>
<td>0.0955</td>
<td>3479</td>
<td>750</td>
</tr>
</tbody>
</table>

Armes et al (1990) has reported the polymerization of polypyrrole monomer with FeCl$_3$ as dopant. The approximate stoichiometric reaction thought to proceed as shown in scheme -(4.1).

$3 \times \text{C}_5\text{H}_4\text{NH} + 7 \times \text{FeCl}_3 \rightarrow \left( \text{C}_5\text{H}_4\text{N}^+ \text{Cl}^- \right) + 7 \times \text{FeCl}_3 + 6 \text{HCl}$

Scheme -(4.1)
The variation of electrical conductivity with time has been taken as a measure of ionic conductivity. These graph indicates fast exponential type decrease in electrical conductivity initially, saturating later to almost constant values which could be separated as electronic and ionic part by extrapolating the linear part to zero time for electronic and pointwise subtraction for ionic conduction. It is evident that mobile ions are present in the samples. The polymetric backbone might have acquired some polar character due to the presence of lone pair of electron on pendent groups as a result of which some proton might have released under the influence of an external field showing ionic conduction (Maulik et al, 2002).

4.8 CONCLUSION:

AC conductivity of polypyrrole thin films have been investigated in the range of frequency 100 Hz to 200 KHz and for temperatures 313, 333, 348, 373 and 398K. It was observed that ac conductivity of these films is frequency and temperature dependent and it generally follows the law $\sigma_{ac} \propto \omega^{\alpha}$, particularly in high frequency range.

DC conductivity of polypyrrole thin films have been investigated in the temperature range 308, 333, 348, 373, 398, 425 and 473K. The conductivity values are in good agreement with the values already re-
ported for other conducting polymer composites. The fitting of experimental temperature dependent data indicates a quasi-one-dimensional mechanism for polypyrrole thin films. From Mott's VRH model the realistic values for different parameters were calculated. The small polaron hopping conduction is observed to be non-adiabatic in nature.
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