Chapter – VI

Alternating Current Conduction and Dielectric Studies
6.1 Introduction

Charge transport mechanism in conjugated polymers [1] and their related materials [2,3] have been of considerable interest recently because they can provide information about the electronic structure of these materials. The transport mechanisms in polymers are very much dependent on defects in polymer chains and the disorder/order created by dopant ions. The disorder, in atomic configuration and/or composition, is thought to cause localized electronic states or groups of states within the material. Since the charge carriers are localized, alternating current (ac) techniques are often employed to probe their behaviour [4]. A main distinguishing feature between ac conduction and dc conduction is that in the former it is necessary only to transfer a charge between a pair of states, whereas in the later a continuous percolation path between electrodes is necessary for the current to flow [5]. AC conductivity exhibits a common behaviour in many disparate materials [1-3], which can be represented as a power-law dependence of the conductivity on frequency,

\[ \sigma_{ac}(\omega, T) = A\omega^s \]

where \( \sigma_{ac} \) is the ac conductivity, \( A \) is a constant, \( \omega \) is the angular frequency \((=2\pi f)\), and 's' is the exponent of the frequency component generally less than or equal to unity.

From pair approximation to rate-equation theory, Miller and Abrahams have shown that \( \sigma_{ac}(\omega) \sim \omega^s \), with \( s = 0.8 \) [6,7]. However, 's' varies according to the material considered and with temperature. These variations can be partially accounted by assuming the validity of the pair approximation [8]. As an alternative approach, an empirical scaling law for \( \sigma_{ac}(\omega) \) is identified [9]. In this law \( \omega^s \) is apparent in finite ranges of frequency but 's' does not depend explicitly on the hopping mechanism. It depends only on the values of \( \sigma(\omega)/\sigma(0) \) in the range considered. Various theories developed for semiconductors and insulators to study the ac conductivity are found suitable for polymers [4-9].
Studies on frequency dependent transport add a great deal of knowledge about the nature of conduction in many systems. Immediately after the discovery of conducting polyacetylene [1], many works have been carried out on ac conduction studies for undoped and doped polyacetylene films to establish the behaviour of charges as function of frequency and temperature [10-12]. Frequency dependent conductivity measurements of partly protonated emeraldine [13] were proposed to support the presence of an interpolaron hopping mechanism similar to the intersoliton hopping mechanism proposed earlier by Kivelson [14]. A detailed study on ac conductivity [15] and microwave transport [16] in emeraldine form of polyaniline (PANI) support hopping of charge among polaron states and also describe the delicate role of temperature on dielectric constant and frequency dependent conductivity. The power law (index $s$ varies between 0.4 and 1) dependence of the ac conductivity on frequency in amorphous polyaniline prepared by plasma polymerization by Papathanassiou [17] suggested the multiple ac conductivity mechanism conflict with the predictions of the Austin and Mott model [18], which assumes a single mode of charge hopping in amorphous solids. Investigations on dielectric spectroscopy of doped PANI was systematically carried out by Singh et al. [19] in which they found that the activation energy obtained from DC, dipolar and modulus approach were nearly the same and support the thermally activated behaviour of polyaniline. Recent measurements on complex conductance of PANI composites as a function of PANI content, opened an alternative way of obtaining conducting organic composites at low cost [20]. Thermally activated conduction process at high temperature is recently reported for ac conductivity of Cr-doped polyaniline / poly (vinyl alcohol) blends [21].

6.2 Models for Alternating Current (AC) Conduction

The importance of alternating current (ac) conductivity and loss measurements in illuminating the physics of amorphous semiconductors arises because the ac conductivity is often dominated by electron states deep within the principal energy gap, in the region of the Fermi level. Such deep defect states are invariably associated with the irregularities and discontinuities of the amorphous atomic network, and have a strong influence on the properties of these materials. In order to interpret the experimental results of these materials many models have been proposed. It is
commonly assumed that the pair approximation holds well, namely, the dielectric loss occurs because of the localization of the carrier (electrons or polarons) motion within pairs of sites. It is well known that the ac conductivity of a system is governed by the relaxation mechanism generally assumed to be Debye-type, which is responsible for the electrical conduction [8]. The overall conductivity is then the summation of individual microscopic processes acting in parallel. However, two distinct models, namely quantum mechanical tunneling (QMT) and classical hopping over a barrier (CBH), or some combination or variant of the two have been proposed to account for the relaxation of dipoles. Here, the term 'hopping' is used for thermal activation of a charge carrier of a pair over the potential barrier between states, and the 'tunnelling' is for the process involving the direct coupling due to the overlap of the exponentially decaying wavefunctions of the two sites.

6.2.1 Quantum mechanical tunnelling model

The charge transition rates for coupling of a pair of states are given by the eqn.

$$\tau = 2\tau_0 \exp(2\alpha R_{12})$$

(6.2)

where $\tau_0$ is an inverse optic phonon frequency, $\alpha^{-1}$ is the spatial extent of the localized state wave function, $R_{12}$ is the distance between the pair of states. The ac conductivity within the pair approximation for this model was first derived by Austin and Mott [18] has been expressed as,

$$\sigma_{ac} = \frac{\pi^4 e^2 N(E_F)^2 k_B T}{12 \alpha} \omega R_{12}^4$$

(6.3)

where $e$ is the electronic charge, $N(E_F)$ is the density of the localized states, $k_B$ is the Boltzmann constant. According to this model, within the pair approximation, the exponent 's' is given by

$$s = 1 + \frac{4}{\ln(\omega \tau_0)}$$

(6.4)

Note that for this model 's' is independent of $T$. As per Mott, if we assume that $\tau_0 \approx 10^{-13}$ s, for a typical audio frequency ($\omega \approx 10^4$ s$^{-1}$) we obtain the value $s \approx 0.81$, which was first observed for impurity states in crystalline semiconductors by Pollak and Geballe [6].
6.2.2 Polaron tunnelling model

A further class of frequency dependent losses arises when an electron tunnels between states close to the Fermi level, but where the energy states is lowered after arrival of the electron by relaxation of the lattice round it. The combined excitation is known as the polaron; there is an extensive literature about polarons in crystalline materials, and their role in the amorphous state has been reviewed and summarized by Mott and Davis [22]. Following this work, they showed physically that the process of electron transfer between a pair of degenerate states would generally involve activation energy \( W_H = W_P / 2 \), where \( W_P \) is the polaron energy associated with the lattice deformation at an occupied site.

Long has considered two separate mechanisms leading to polaron formation. In the small or molecular polaron [23] \( W_P \) arises from the local bonding changes. Hence the distortions round two sites do not overlap and the activation energy for particle transfer will be independent of the separation of the sites. This type of polaron has been extensively analyzed using the molecular model of Holstein [23]. The probability of transfer between the two sites is expressible at high temperatures in the form [24]

\[
\tau = \tau_0 \exp \left( \frac{W_H}{k_B T} \right) \exp(2\alpha R) \tag{6.5}
\]

At low temperatures [25], where the distorted lattice is in its ground state at each site, the activation term becomes independent of temperature giving

\[
\tau = \tau_0 \exp \left( \frac{W_H}{\frac{1}{4}h\omega_0} \right) \exp(2\alpha R) \tag{6.6}
\]

Here \( \omega_0 \) is the characteristic vibrational frequency for the lattice distortion. The transition between high and low temperature regimes occurs at \( k_B T = \frac{1}{4} h \omega_0 \).

To calculate the expected ac loss by molecular polaron tunnelling, the Long has noted that the temperature term in the Eqn. (6.5) does not involve the separation of the states. Hence, the standard tunnelling formalism can be used with the transition time \( \tau_0 \) replaced by a temperature dependent parameter \( \tau_0 \exp\left(W_H/k_B T\right) \). The resultant loss is given by the following Eqn. (6.3) with a revised \( R_m \).
and a frequency exponent

\[ s = 1 + \frac{4}{\ln(\omega \tau_0) + \frac{W_H}{k_B T}} \]  \hspace{1cm} (6.8)

This describes an exponent, which increases with temperature. In principle, ‘s’ can decrease to zero as T drops. However a more likely behaviour is that the temperature will decrease below \( \hbar \omega_0 / 4k_B \) before this occurs, leading to a temperature independent ‘s’ less than 1.

The ac conductivity due to small polaron at high temperature is of hopping type and frequency independent but at low temperature it depends upon frequency according to the expression [26]

\[ \sigma_{ac} = \frac{\omega^2 \tau_0}{1 + \omega^2 \tau_0^2} \]  \hspace{1cm} (6.9)

Since \( \tau_0 \) is small (~10^{-13} s), at frequencies \( \omega < 10^{12} \text{ Hz} \), \( \omega^2 \tau_0^2 \ll 1 \) and hence it can be neglected from the denominator of eqn.(6.9). Thus a plot of \( \log(\sigma_{ac}) \) vs \( \log \omega^2 \) should be a straight line, indicates the prevalent of small polaron tunnelling conduction mechanism.

The second case of interest is where the polaron energy is derived from polarization changes in the deformed lattice, as in ionic crystals. The resultant excitation is called a large or dielectric polaron, and as its name implies, because of the long range of the coulomb interaction, its well will extend over many interatomic distances. Long [8] proposed that if the spatial extent of the polaron or polaron radius is large when compared with the interatomic spacing, an appreciable overlap of the polaron distortion clouds occurs because of the long-range nature of the dominant coulomb interaction, with a result of reduced polaron-hopping energy according to the equation [18,22]

\[ W_H = W_{HO} \left( 1 - \frac{r_p}{R} \right) \]  \hspace{1cm} (6.10)
where \( r_p \) is the polaron radius, \( R \) the intersite separation and \( W_{HO} \) is the barrier height for infinite site separation given by

\[
W_{HO} = \frac{e^2}{4\varepsilon_p r_p^2}
\]  

(6.11)

where \( \varepsilon_p \) is the effective dielectric constant. It is assumed that \( W_{HO} \) is constant for all sites, whereas the intersite separation \( R \) is a random variable. The ac conductivity for the overlapping-large-polaron tunneling (OLPT) model [8] is given by

\[
\sigma_{ac}(\omega) = \frac{\pi^4}{12} e^2 (k_B T)^2 [N(E_F)]^2 \frac{\omega R^4}{2\alpha k_B T + W_{HO} r_p / R_w^2},
\]

(6.12)

where \( R_w \) is the tunnel distance at a frequency \( \omega \) determined by the quadratic equation

\[
(R_w)\left(\frac{1}{2} + [\beta W_{HO} + \ln(\omega \tau_p)] R_w - \beta W_{HO} r_p / R_w^2 = 0,
\]

(6.13)

where \( R_w = 2\alpha R_w \), \( r_p = 2\alpha r_p \), and \( \beta = 1/k_B T \).

The frequency exponent \( s \) of \( \sigma_{ac}(\omega) \) in this model can be evaluated as

\[
s = 1 - \frac{8\alpha R_w + 6\beta W_{HO} r_p / R_w}{(2\alpha R_w + \beta W_{HO} r_p / R_w)^2}.
\]

(6.14)

Thus the OLPT model predicts that \('s' \) should be both temperature and frequency dependent. It can also be seen from Eqn. (6.14) that \('s' \) decreases from unity with increasing temperature. For large values of normalized polaron radius (\( r_p \)), \('s' \) continues to decrease with increasing temperature, eventually tending to the value as predicted by the QMT model of non-polaron forming carriers. On the other hand, for small values of \( r_p \), \('s' \) exhibits a minimum at a certain temperature and subsequently increases with increasing temperature in a similar fashion to the case of small-polaron QMT.
6.2.3 Correlated barrier hopping (CBH) model

In the correlated barrier hopping (CBH) model for ac loss, first introduced by Pike [4] to account for loss in scandium oxide films and applied by Elliott [5] to ac loss measurements in chalcogenide films, the charge carrier is assumed to hop between site pairs over the potential barrier separating them. If we consider a single electron hopping between site pairs over the potential defect centers then the potential barrier will be reduced by the coulomb interaction (Fig. 6.1).

![Image of energy levels](image)

**Fig. 6.1 Parameters for a CBH hop between states 1 and 2.**

Pike has shown that the barrier height \( W \) is correlated with the separation \( R \) according to the relation

\[
W = W_m - \frac{ne^2}{\pi \varepsilon \varepsilon_0 R^2}
\]  

(6.15)

where, \( \varepsilon \varepsilon_0 \) is the background permittivity of the semiconductor, \( R \) the separation between the neighboring sites 1 and 2, and \( W \) the hopping barrier potential after lowering of the effective barrier \( (W_m) \) due to Coulomb wells overlap and \( n \) the number of charge carriers involved in hopping process. The frequency dependence of \( \sigma_{ac} \) in the form of Eqn. (6.1) can be deduced using the relation,

\[
s = \frac{d \ln \sigma_{ac}(\omega)}{d \ln \omega}
\]  

(6.16)
For single-electron coulomb reduced barrier (Eqn. 6.15), the equation for frequency exponent $s$ is of the form,

$$s = 1 - \frac{6kT}{W_m + kT \ln(\omega \tau_0)}$$  \hspace{1cm} (6.17)

Here, $s$ is predicted to decrease from unity with increasing temperature and the initial decrease will be linear with temperature. The relaxation time $\tau$ for the charge carrier to hop over the barrier of height $W$ is given by [27]

$$\tau = \tau_0 \exp \left( \frac{W}{k_B T} \right)$$  \hspace{1cm} (6.18)

where, $\tau_0$ is the inverse phonon frequency ($10^{-13}$ s) and $k_B$ is the Boltzmann constant.

Further, according to CBH model, the numerical value for the single polaron ac conductivity $\sigma_{ac}(\omega)$ can be calculated using the equation [27,28]

$$\sigma_{ac} = \frac{\pi^2 \varepsilon \varepsilon_0 N N_p \omega \omega_0^6}{6}$$  \hspace{1cm} (6.19)

Similarly, the ac conductivity due to bipolaron hopping can be calculated based on the relation

$$\sigma_{ac} = \frac{\pi^2 \varepsilon \varepsilon_0 N N_p \omega \omega_0^6}{6} \exp \left( \frac{e^2}{4\varepsilon \varepsilon_0 k_B T \tau R_w} \right)$$  \hspace{1cm} (6.20)

where $N$ is the total density of charged defect states, $N_p$ the number of pairs contributing to ac conduction, $T_g$ the glass transition temperature and $r_w$ and $R_w$ the optimum hopping range in single and bipolaron cases are defined as follows:

$$r_w = \left( \frac{e^2}{\pi \varepsilon \varepsilon_0 W_m} \right) \left[ 1 + \frac{k_B T}{W_m \ln(\omega \tau_0)} \right]^{-1}$$  \hspace{1cm} (6.21)

$$R_w = \left( \frac{2e^2}{\pi \varepsilon \varepsilon_0 W_m} \right) \left[ 1 + \frac{k_B T}{W_m \ln(\omega \tau_0)} \right]^{-1}$$  \hspace{1cm} (6.22)

Here, the effective barrier height in bipolaron ($W_m$) case corresponds to the value of the optical gap of the material, which was determined by optical absorption measurements (Chap. 3), whereas the effective barrier height in single polaron ($w_m$) case is treated as an adjustable parameter whose value can be less than or equal to half of the band gap value [27].
6.3 Experimental Techniques

The undoped and lightly doped (molar ratios of CSA to phenyl-nitrogen repeat units S/N = 0.1) polyaniline films of thickness 9.8 and 5 μm respectively were formed by solution-casting technique (Chap. 2). Gold films as a top and bottom electrodes were deposited at room temperature by vacuum (2.7×10⁻³ Pa) evaporation over and above the polymer film to form a parallel plate capacitor structure. A similar procedure was adopted for the fabrication of (PANI-CSA)ₓ - (PMMA)₁₋ₓ blend films. The typical thicknesses of the blend films for x = 0.25, 0.50, and 0.75 were 6, 6.6, and 6 μm respectively. The capacitance (C) and the dissipation factor (D) for these films were measured in the frequency range 10³ – 10⁶ Hz, utilizing an oscillating voltage with an amplitude of 10 mV (peak-to-peak), using a HP 4275A precision LCR meter. The capacitor area of each device was measured using a profile projector (Nikon-Japan) with 10 times magnification after fabrication to be approximately 5 × 10⁻⁶ m². The temperature of the device (150 – 380 K) could be lowered by the introduction of liquid nitrogen in the environmental chamber from a cryostat and raised by heating the sample fixture by means of a heater arrangement. A PT100 thermocouple connected with the temperature controller maintained the required temperature with a precision of 0.5 K. The capacitance and dissipation factor were transferred through a GPIB interface to PC (Chap. 2, Fig. 2.2) at each selected temperature and stored for further analysis. For all data presented here, the sample container was pumped for few hours before the data acquisition, to eliminate the effects of any absorbed moisture.

6.4 Results and Discussion

6.4.1 AC conductivity of undoped and lightly doped polyaniline films

Recently the polaronic behaviour of charge carriers in electron – phonon interaction systems [29, 30 ref. therein] has received considerable attention. Polarons in the limit of strong (weak) electron – phonon interactions are called small (large) polarons. The large polarons have an itinerant character due to their small effective
mass \((m^* \sim 2 - 4)\) [31], and the lattice distortion extended over wide spatial range. On the other hand, the small polarons could move only by tunnelling or thermally activated hopping between locally distorted lattice sites because of the large effective mass \((m^* \sim 10 - 100)\) [31] and the distortion of the lattice extended over a domain of one or a few atomic sites. The ac conductivity measurements performed in the frequency range of 10 kHz – 5 MHz for undoped and 10 kHz – 1 MHz for doped PANI samples utilizing an oscillating voltage with an amplitude of 10 mV peak-to-peak, show the prevalence of overlapping large polaron tunnelling (OLPT) and small polaron tunnelling mechanisms respectively.

Figs. 6.2 and 6.3 show the dependence of ac conductivity \(\sigma_{ac}\) on frequency for undoped polyaniline studied in the temperature ranges of 150 – 245 K and 260 – 380 K. Within these temperature regions and for a wide range of frequencies, \(\sigma_{ac}\) takes the form of a power law Eqn. (6.1). In the low frequency range \(\sigma_{ac}\) is strongly dependent on the absolute temperature while for high frequencies it becomes temperature independent (Fig 6.2). This behavior is attributed to the time constant of the high frequency ac stimulation, which is too short for charge carrier to relax, thus, giving rise to the temperature independent conductivity. However, an opposite behavior is observed in the temperature range of 260 – 380 K as shown in Fig. 6.3. The frequency dependence of \(\sigma_{ac}\) in the form of Eqn. (6.1) can be deduced using the relation (6.16). The value of the exponent 's' obtained from the slope of the solid lines in the plot of \(\log \sigma_{ac}\) versus \(\log \omega\) is found to decrease from 0.95 to 0.65 with increase of temperature in the range of 150 – 245 K and increases from 0.65 to 0.79 with increase of temperature in the range of 260 – 380 K.

To compare the various models (Sec. 6.2) with the experimental data, the detailed predictions of the temperature and frequency dependence of the ac conductivity need to be examined. According to the quantum mechanical tunnelling (QMT) model [22], the exponent 's' is almost equal to 0.8 and increases slightly with increasing temperature or temperature independent. Hence the QMT model may not be applicable to explain the obtained results of the present study. In the case of the correlated barrier-hopping (CBH) model [5], the exponent 's' decreases with increasing
temperature. Consequently, this model is also not applicable to explain the obtained results. The ac conductivity for the overlapping-large-polaron tunnelling (OLPT) model is given by the Eqn. (6.12) and the frequency exponent 's' can be evaluated using the Eqn. (6.14) and from this eqn. it is found that 's' decreases from unity with increase of temperature and exhibits a minimum at a certain temperature and subsequently increases with increasing temperature (Fig. 6.4 (inset)). Therefore the OLPT model might be a possible theory to explain the data of the present study.

![Fig. 6.2 Dependence of ac conductivity ($\sigma_{ac}$) as a function of frequency ($\omega$) in the temperature range 150-245 K for undoped PANI. The solid lines are the straight-line fits obtained by the least squares fitting procedure.](image-url)
Fig. 6.3 Dependence of ac conductivity ($\sigma_{ac}$) as a function of frequency ($\omega$) in the temperature range 260-380 K for undoped PANI. The solid lines are the straight-line fits obtained by the least squares fitting procedure.

In order to verify this prediction, the frequency exponent ‘$s$’ is plotted as a function of $k_B T/W_{HO}$ as shown in Fig 6.4. The solid line is a locus of experimental points guide to eye. It is found that at low temperature region ($k_B T/W_{HO} < 0.09$), the behaviour of ‘$s$’ is similar to the expected CBH model, where a strong internal correlation exists between the pair of sites and the value of ‘$s$’ drops linearly from unity. However, at high temperature region ($k_B T/W_{HO} > 0.09$) ‘$s$’ tends towards the pure tunnelling limit, where the strong internal correlation breaks and the relaxing species become independent of each other. If $r_p^{-1}$ is less than $-2/3\ln(\omega\tau_0)$, ‘$s$’ shows a minimum at 250 K (it is located at $-0.1 W_{HO}/k_B$) [8] and increases gradually at higher temperature tending to the small polaron-like behaviour when $\alpha \to 0$, which means that the internal correlation between the pair of sites breaks and the relaxing species become independent at 250 K. Bhattacharyya et al. [30] have made a similar observation on polypyrrole and poly (styrene-co-butyl acrylate) with the OLPT model.
Fig. 6.4 Frequency exponent ‘s’ as a function of $k_B T / W_{HO}$ for undoped PANI film.  

The solid line is a locus of experimental points guide to eye. Inset shows the temperature dependence of the frequency exponent ‘s’.

We want to emphasize that (to our knowledge) the OLPT model predicts a minimum in the temperature dependence of frequency exponent that strongly suggests polarons as charge carriers in PANI. Evidence of polarons in PANI has also been reported by Pinto et al. [32]. The barrier height for infinite site separation ($W_{HO}$) is estimated from the relation $T = 0.1 W_{HO} / k_B$ (corresponds to minimum value of s) as ≈ \(0.22\) eV. The values of static ($\varepsilon_s$) and infinite ($\varepsilon_{\infty}$) dielectric constants needed for the evaluation of effective dielectric constant ($\varepsilon_p = 8.4$) have been taken from the Cole - Cole plot (Fig. 6.5) drawn in the frequency range of 10 kHz - 5 MHz at 250 K. The polaron radius $r_p$ is calculated from Eqn. (6.11) as ≈ 25 Å. It is seen that the polaron radius $r_p$ is large compared to the reported interatomic distance ($R=20$ Å) [33] and therefore the polaron distortion clouds overlap. Therefore, from the above analysis, it is believed that overlapping large polaron tunnelling conduction mechanism is prevalent in the undoped polyaniline films.
The frequency and temperature dependence of tunnelling distance \( R_\omega \) on the PANI film is shown in Fig. 6.6. It is seen that the \( R_\omega \) increases linearly with temperature up to 250 K irrespective of the applied frequencies. However, beyond this temperature, it clearly deviates from linearity and tends to be constant at higher temperature satisfying the QMT limit in which \( R_\omega \) is independent of temperature. Regarding the frequency dependent of \( R_m \), it shows a high value at lower frequency side than in the higher frequency region. This may be attributed to the increase in polaron concentration / number of localized states participating in the charging / discharging processes with increase in frequency, which is responsible for high conductivity as shown in Table 6.1. The value of \( N(E_F) \), the density of states at Fermi level, is of the order of \( \approx 10^{20} \) states / eV-cm\(^3\), and is quite reasonable and is in good agreement with the values obtained for the other conducting polymers such as PPY [34] and several disordered materials [22]. It is also noted that the estimated \( N(E_F) \) value from the ac data is one order higher than dc data (Sec.5.4.1). Several authors [22,34] have pointed out that there is a difference in the values of \( N(E_F) \) calculated from the ac and dc data [35], which is in agreement with our observations.
Fig. 6.6 Frequency and temperature dependence on tunnelling distance \( (R_m) \).

The solid lines (guide to eye) indicate the deviation of tunnelling distance \( (R_m) \) from linearity at the specified temperature.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>( 10^4 ) Hz</th>
<th>( 10^5 ) Hz</th>
<th>( 10^6 ) Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \sigma_{ac} ) (S cm(^{-1} ))</td>
<td>( 7.05 \times 10^{-6} )</td>
<td>( 2.98 \times 10^{-5} )</td>
<td>( 1.94 \times 10^{-4} )</td>
</tr>
<tr>
<td>( N ) (states eV(^{-1} ) cm(^{-3} ))</td>
<td>( 2.8 \times 10^{20} )</td>
<td>( 2.5 \times 10^{20} )</td>
<td>( 2.3 \times 10^{20} )</td>
</tr>
</tbody>
</table>

Table 6.1. Frequency dependence of \( \sigma_{ac} \) and \( N \) \( (E_F) \) measured at 200 K
In the case of doped PANI samples, the dopant ions (CSA) reside adjacent to the polymer chain. The charge carriers along the chain are pinned or trapped, resulting in the formation of bound states. The charge carriers in the bound states can influence atoms or ions only at small distances (small polaron), whereas in the case of undoped samples the carriers affect the atoms or ions at large distances (large polaron). Figs. 6.7 and 6.8 show the dependence of ac conductivity ($\sigma_{ac}$) on frequency of lightly doped polyaniline studied in the temperature ranges of 153 – 273 K and 293 – 340 K. The ac conductivity measured in the temperature range of 153 – 273 K takes the form of a power law Eqn. (6.1) that can be deduced using the relation (6.21). The value of frequency exponent 's' obtained from the slope of the solid lines in the plot of $\log \sigma_{ac}$ versus $\log \omega$ (Fig. 6.7) is found to increase from 0.51 to 0.62 with increase of temperature in the range of 153 – 273 K. However, estimated value of $\sigma_{ac}$ in the temperature range 293– 340 K is independent of frequency at high temperature, which is the characteristic of small polaron of hopping type. Raghunathan et al. [36] have observed that the value of exponent 's' was found to be small (0.22 – 0.5) for all the aromatic acid doped PANI samples compared with the undoped PANI samples (0.97 for PANI-EB). This observation closely agrees with the estimated values of 's' for our undoped and CSA doped PANI films as shown in Table 6.2.

The polaron hopping energy ($W_h$) may be assumed approximately equal to high-temperature activation energy for dc conduction [37] (0.041 eV) (Chap.5, Sec. 5.13). Theoretical values of 's' calculated using Eqn (6.8) show the same increasing trend as the experimental values. It indicates a deviation of 5% from the theoretical value up to 200 K and the deviation reduces to 2% above 200 K as shown in Fig. 6.9. The observed experimental data compared with the various models (Sec. 6.20), similar to undoped sample, showed that the exponent 's' decreases with decrease of temperature (Fig. 6.9) according to the relation (6.8) indicating the presence of small polaron tunnelling in low temperature regime. In this temperature limit, the ac conductivity of small polaron depends upon frequency according to the expression (6.9) and the double logarithmic plots of ac conductivity with square of frequency should be a straight line. Fig. 6.10 shows the linear behaviour of ac conductivity with square of frequency ($\log (\sigma_{ac})$ versus $\log \omega^2$) revealing the existence of small polaron tunneling in the lightly doped PANI films.
Fig. 6.7 Dependence of ac conductivity ($\sigma_{ac}$) as a function of frequency ($\omega$) in the temperature range 153 - 273 K for doped PANI. The solid lines are the straight-line fits obtained by the least squares fitting procedure.

Fig. 6.8 Dependence of ac conductivity ($\sigma_{ac}$) as a function of frequency ($\omega$) in the temperature range 293 - 340 K for doped PANI. The solid lines are guide to eye.
Table 6.2 AC conduction parameters for undoped and doped PANI films

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ac conduction mechanism</th>
<th>Frequency exponent (s) (150 – 273 K)</th>
<th>Tunnelling Range ($R_{\infty}$) (m) at 1 MHz (273 K)</th>
<th>Density of States $N (E_F)$ (eV$^{-1}$cm$^{-3}$) at 1 MHz (273 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped PANI</td>
<td>Large polaron tunnelling</td>
<td>0.95 – 0.65</td>
<td>$3.4 \times 10^9$</td>
<td>$2.4 \times 10^{20}$</td>
</tr>
<tr>
<td>Doped PANI</td>
<td>Small polaron tunnelling</td>
<td>0.51 – 0.62</td>
<td>$2.35 \times 10^8$</td>
<td>$2.1 \times 10^{18}$</td>
</tr>
</tbody>
</table>

Fig. 6.9 Frequency exponent 's' as a function of temperature ($T$) of doped PANI film
Fig 6.10 Linear behaviour of ac conductivity ($\sigma_{ac}$) with square of frequency ($\omega^2$) for doped PANI film. The solid lines are the straight-line fits.

6.4.2 AC conductivity of (PANI-CSA)$_x$ – (PMMA)$_{1-x}$ blend films

The electronic properties of conducting polymer blends exhibit curious behaviour [38-40]. The frequency dependent studies are very useful to obtain better understanding of the charge transport mechanism present on these materials [38-40]. From the ac conductivity and dielectric measurement, Kohlman et al. [41] have shown that insulator-metal transition in PANI doped with CSA arises from the percolation in the presence of inhomogeneous disorder and quasi one-dimensional localization. The positive dielectric constant observed by Joo et al. [42] in PANI doped with HCl suggests an inhomogeneous disorder model in which three-dimensional crystalline metallic regions connected through the amorphous insulating regions induced by one-dimensional localization. Dutta et al. [43] have studied the frequency dependent conductivity of PANI – PVA blend films and shown that the conduction is due to the correlated barrier hopping (CBH). The ac conductivity and its numerical calculations on (PANI-CSA)$_x$ – (PMMA)$_{1-x}$ blend films have not yet been studied in detail.
In the present work, experimental ac conductivity \( (\sigma_{ac} = \omega C_p \tan \delta d / A) \) of (PANI-CSA)\( \times \) - (PMMA)\( \times \) blend films with various weight fractions of PANI-CSA \( (x = 0.25, 0.50, 0.75) \) in PMMA matrix are calculated from the measured capacitance \( (C_p) \) and dissipation factor \( (\tan \delta) \). The thickness of the film and the active area of the capacitor were \( d \approx 6 \mu m \) and \( A \approx 5 \mu m^2 \), respectively. The experimental ac conductivity measurements performed on (PANI-CSA)\( \times \) - (PMMA)\( \times \) blend sandwich devices (Au / polyblend / Au), in the frequency range of 10 kHz - 10 MHz for \( x = 0.25 \) and 10 kHz - 1 MHz for \( x = 0.50 \) and 0.75, utilizing an oscillating voltage with an amplitude of 10 mV peak-to-peak, show the prevalence of correlated barrier hopping (CBH) mechanism.

Figs. 6.11 - 6.13 show the dependence of experimental ac conductivity \( (\sigma_{ac}) \) of (PANI-CSA)\( \times \) - (PMMA)\( \times \) blend films on frequency in the temperature ranges of 152 - 380 K for \( x = 0.25 \), 141 - 362 K for \( x = 0.50 \) and 144 - 350 K for \( x = 0.75 \). The experimental ac conductivity measured in the specified temperature range takes the form of a power law Eqn. (6.1) can be deduced using the relation (6.16). Generally, decrease of conductivity with increasing frequency is associated with a band type conduction process, and increase of conductivity with increasing frequency is of hopping-type conduction mechanism [44]. In addition to the gradual increase of conductivity as a function of frequency, the values of frequency exponent 's' (slopes of the straight lines) have also been found to decrease with increasing temperature, which can be attributed to the temperature dependent carrier movement (carrier movement between and within the defect wells). In particular, for low frequency and low temperature regime the exponent 's' increases linearly with decreasing temperature as shown in Figs. 6.14 - 6.16. This behaviour is consistent with the correlated barrier-hopping (CBH) model for carriers (single polaron or bipolaron) over the potential barrier separating two centers (Fig. 6.1) in a random distribution [5]. A similar behaviour is observed for PANI - PVA blend films by Dutta et al. [43].
Fig. 6.11 Dependence of ac conductivity ($\sigma_{ac}$) as a function of frequency ($\omega$) in the temperature range 152-380 K for (PANI-CSA)$_{0.25}$ (PMMA)$_{0.75}$. The solid lines are the straight-line fits obtained by the least squares fitting procedure.

Fig. 6.12 Dependence of ac conductivity ($\sigma_{ac}$) as a function of frequency ($\omega$) in the temperature range 141-362 K for (PANI-CSA)$_{0.5}$ (PMMA)$_{0.5}$. The solid lines are the straight-line fits obtained by the least squares fitting procedure.
Fig. 6.13 Dependence of ac conductivity ($\sigma_{ac}$) as a function of frequency ($\omega$) in the temperature range 144-350 K for (PANI-CSA)$_{0.75}$ - (PMMA)$_{0.25}$. The solid lines are the straight-line fits obtained by the least squares fitting procedure.

Fig. 6.14 Temperature dependence of exponent ‘s’ of (PANI-CSA)$_{0.25}$ - (PMMA)$_{0.75}$ blend film. The error bars show 1% deviation of the experimental value with numerical one.
Fig. 6.15 Temperature dependence of exponent ‘s’ of (PANI-CSA)$_{0.5}$–(PMMA)$_{0.5}$ blend film. The error bars show 1% deviation of the experimental value with numerical one.

Fig. 6.16 Temperature dependence of exponent ‘s’ in (PANI-CSA)$_{0.75}$–(PMMA)$_{0.25}$ blend film. The error bars show 1% deviation of the experimental value with numerical value.
In addition to the temperature dependence of \( s \), its magnitude at any temperature is governed by the binding energy \( (W_m) \) of the charge carriers. \( W_m \) is the energy difference between the ground state of the potential well and ionized state (i.e., the charge carrier localized state). The value of \( W_m \) in bipolaron case corresponds to the value of the optical band gap [45], which was determined by optical absorption measurements (Chap. 4). In single polaron case, \( W_m \) is treated as an adjustable parameter \( (w_m) \) whose value can be less than or equal to half of the band gap value [45]. The numerical values of the frequency exponent \( s \) calculated for all compositions \( (x = 0.25, 0.50, 0.75) \) of \((PANI-CSA)_{x-(PMMA)_{1-x}}\) blend films measured in the specified temperature range using the Eqn. (6.17) are well fit with the experimental results (Figs. 6.14 – 6.16), and supports the prevalence of single polaron hopping.

6.4.2.1 Numerical calculations on ac conductivity

To fit the numerical single polaron ac conductivity (Eqn. 6.19) with experimental data, the value of \( NNP \) is adjusted by taking the value \( w_m \) for single polaron as being equal to half of the band gap. The best fit gives the values of \( NNP \) in the range of \( 10^{43} - 10^{48} \) cm\(^{-6}\). Table 6.3 lists the fitting parameters for single polaron case. The values of the dielectric constants are obtained from the dielectric measurements (Chap. 6). Figs. 6.17 – 6.19 show the numerical single polaron ac conductivity for the \((PANI-CSA)_{x-(PMMA)_{1-x}}\) blend films \( (x = 0.25, 0.50, 0.75) \) calculated at two frequencies (100 kHz and 1 MHz) along with the experimental ac conductivity at those corresponding frequencies. It is clearly observed from these figures that the numerical single polaron ac conductivity is almost coinciding with the experimental ac conductivity plots (Figs. 6.17 – 6.19). Similarly, the numerical bipolaron conductivity is calculated using eqn (6.20) by taking the reported values of glass transition temperature [46] and optical band gap obtained from optical studies (Chap. 4), showed a significant deviation from the experimental data points. From the above observations, it is found that the ac conductivity of \((PANI-CSA)_{x-(PMMA)_{1-x}}\) blend film \( (x = 0.25,0.50,0.75) \) samples is due to single polaron hopping. Inspection of Table 6.3 indicates that there is an increasing trend of \( NNP \) values, suggesting that a higher PANI content produces more defect states in the polyblend matrix.
Fig. 6.17 Experimental and calculated numerical $\sigma_{ac}$ as a function of $1000/T$ in (PANI-CSA)$_{0.25}$- (PMMA)$_{0.75}$ blend film at (a) 100 kHz and (b) 1 MHz. The error bars show 5% deviation of the experimental value with theoretical value.
Fig. 6.18 Experimental and calculated numerical $\sigma_{ac}$ as a function of $1000/T$ in 
(PANI-CSA)$_{0.5}$ - (PMMA)$_{0.5}$ blend film at (a) 100 kHz and (b) 1 MHz. 
The error bars show 5% deviation of the experimental value with 
theoretical value.
Fig. 6.19 Experimental and calculated numerical $\sigma_{ac}$ as a function of $1000/T$ in (PANI-CSA)$_{0.75}$–(PMMA)$_{0.25}$ blend film at (a) 100 kHz and (b) 1 MHz. The error bars show 3% deviation of the experimental value with theoretical value.
Table 6.3 Numerical single polaron conductivity fitting parameters for (PANI-CSA)$_x$-(PMMA)$_{1-x}$ blend films

<table>
<thead>
<tr>
<th>(PANI-CSA)$<em>x$-(PMMA)$</em>{1-x}$</th>
<th>$\varepsilon'$</th>
<th>$w_m$ (eV)</th>
<th>NN$_p$ (cm$^{-6}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x = 0.25$</td>
<td>28</td>
<td>1.10</td>
<td>$1.24 \times 10^{43}$</td>
</tr>
<tr>
<td>$x = 0.5$</td>
<td>34</td>
<td>1.00</td>
<td>$4.12 \times 10^{44}$</td>
</tr>
<tr>
<td>$x = 0.75$</td>
<td>110</td>
<td>0.90</td>
<td>$6.19 \times 10^{48}$</td>
</tr>
</tbody>
</table>

6.5 Dielectric Studies

6.5.1 Coulomb's law and dielectric constant

According to Coulomb, the force of attraction or repulsion between two charge carriers kept at a distance $d$ in a medium of permittivity $\varepsilon$ is

$$F = \frac{q_1 q_2}{4\pi \varepsilon_0 \varepsilon d^2}$$  \hspace{1cm} (6.23)

where $q_1$ and $q_2$ are charges of the two carriers and $\varepsilon = \varepsilon_0 \varepsilon_r$ is the absolute dielectric constant. Here, $\varepsilon_0$ is the permittivity of free space ($8.854 \times 10^{-12}$ F/m) and $\varepsilon_r$ is the relative permittivity. Let a potential $V$ be applied to a parallel plate capacitor of area $A$, separated by a distance $d$ in a medium and the capacitor carries a charge $Q$, then the permittivity of the medium $\varepsilon$ is given by

$$\varepsilon = (Q/A)/(V/d)$$  \hspace{1cm} (6.24)

since $Q/V$ is capacitance $C$, we can write the above equation as

$$\varepsilon = C \frac{d}{A}$$  \hspace{1cm} (6.25)
Since the absolute dielectric constant is written as $\varepsilon = \varepsilon_r \varepsilon_0$, then relative permittivity of the parallel plate capacitor, neglecting edge effects is given by

$$\varepsilon_r = \frac{C d}{\varepsilon_0 A}$$

(6.26)

where $C$ is the capacity of a capacitor.

**6.5.2 Dielectric loss**

If a capacitor is charged by and applied ac voltage, the electric filed ($E$) will be time varying and the polarization of the capacitor will take place under the time varying electric filed with frequency $\omega = 2\pi f$. However, due to the presence of damping and frictional forces in a solid during interaction of charges with an electrical filed the polarization will lag behind the field $E$ by a phase angle $\delta$. Then the electric field ($E$) and the flux displacement ($D$) is expressed as

$$E = E_0 \cos \omega t$$

(6.27)

and

$$D = D_0 \cos (\omega t - \delta) = D_1 \cos \omega t + D_2 \sin \omega t$$

(6.28)

where $\delta$ is the phase angle and $D_1 = D_o \cos \delta$, $D_2 = D_o \sin \delta$. Generally $D_o$ is proportional to $E_o$, but the ratio $D_o / E_o$ is dependent both on frequency and the phase shift. To describe this situation, frequency dependent dielectric constants $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ are introduced which are given by

$$\varepsilon'(\omega) = D_1 / E_o = (D_o / E_o) \cos \delta$$

(6.29)

and

$$\varepsilon''(\omega) = D_2 / E_o = (D_o / E_o) \sin \delta$$

(6.30)

and hence from the above two expressions we have

$$\tan \delta = \varepsilon''(\omega) / \varepsilon'(\omega)$$

(6.31)
which is often called as loss factor, but more correctly as loss tangent or dissipation factor. This parameter is of great significance in determining the suitability of a capacitor in a circuit.

6.5.3 Frequency dependent dielectric constant and dielectric loss

The dielectric constant $\varepsilon'$ and loss factor $\tan \delta$ are not absolute constants for an actual dielectric. Both these constants depend on many factors, namely temperature, frequency, magnitude of the alternating voltage, humidity of air etc. The frequency dependence of $\tan \delta$ in thin films is a very important factor. Usually the dielectric constant decreases with increasing frequency. At very low frequencies, the dipoles are oriented with the electric field without time lag. In this case the orientation of the dipoles is not accompanied by any loss of energy and hence $\tan \delta$ is very low. At very high frequencies the dipoles are unable to follow the variations of the field, whereas the normal agitation is still present. The loss factor of thin film dielectric shows a general behavior of increasing loss at very high frequencies with a wide maximum in the intermediate range, as a result of superposition of various loss mechanisms.

6.6 Experimental Techniques

The dielectric studies on undoped, lightly doped (molar ratio of CSA to phenyl-nitrogen repeat units $S/N = 0.1$) polyaniline and (PANI-CSA)$_x$ - (PMMA)$_{1-x}$ blend films are carried out by forming metal-polymer-metal (MPM) structures. Polymer is deposited over gold electrodes coated on glass substrate. This acts as bottom electrode of the capacitor and gold coated on the surface of polymer acts as top electrode, hence forming a capacitor. The capacitance ($C$) and the dissipation factor ($D$) for these films were measured in the frequency range $10^3$ - $10^6$ Hz, utilizing an oscillating voltage with an amplitude of 10 mV (peak-to-peak), using a HP 4275A precision LCR meter with a basic accuracy of 0.1%. The typical thickness of the undoped, doped polyaniline and blend polyaniline films were 9.8, 5 and $\sim 6$ μm respectively. The active conduction area of each device was measured using a profile projector (Nikon-Japan) with 10 times magnification after fabrication to be approximately $5 \times 10^{-6}$ m$^2$. All the measurements were carried out under a rotary vacuum condition. A pre-calibrated PT100
thermocouple was used to measure the temperature in the required range with a precision of 0.5 K.

6.7 Results and Discussion

6.7.1 Frequency and temperature dependent dielectric permittivity

Dielectric parameters such as dielectric constant and dielectric loss reveal significant information about the physical and chemical state of polymers. These properties are drastically affected by the presence of another polymer or a dopant in the polymer [47]. The study of dielectric relaxation provides valuable information about the intermolecular interaction. The frequency and temperature dependence of the complex dielectric function, \( \varepsilon^*(f, T) = \varepsilon'(\omega) - i \varepsilon''(\omega) \), is important for determining the charge transport mechanism [48].

The variation of real permittivity \( \varepsilon' \), with frequency and temperature on undoped and doped polyaniline analyzed in the frequency range of 10 kHz – 5 MHz and 10 kHz – 1 MHz respectively in the temperature range of 150 – 300 K are shown in the Figs. 6.20 and 6.21. Figs. 6.22 and 6.23 show the frequency spectra of the real permittivity \( \varepsilon' \) of (PANI-CSA)\(_x\) – (PMMA)\(_{1-x}\) blend films (\( x = 0.25 \) and 0.75) in the frequency range of 10 kHz – 1 MHz and 10 kHz – 5 MHz respectively in the temperature range 150 – 300 K. A general trend of decrease in dielectric permittivity with increase of frequency is observed in figs. (6.20-6.23). This decrease is rapid at lower frequencies and slower at high frequencies, indicating the existence of a dielectric relaxation. The high value of dielectric permittivity \( \varepsilon' \) at low frequencies and at high temperatures does not correspond to the bulk dielectric permittivity of the polymers. It may be attributed to free charge building up at the interfaces within the bulk of the samples (interfacial or Maxwell-Wagner-Sillars (MWS) polarization) and at the interface between the sample and the electrodes (space-charge polarization) [49,50].
Fig. 6.20 Dielectric permittivity ($\varepsilon'$) as a function of frequency at different temperature for undoped PANI film of typical thickness 9.8 µm.

Fig. 6.21 Dielectric permittivity ($\varepsilon'$) as a function of frequency at different temperature for doped PANI film of typical thickness 5 µm.
Fig. 6.22 Dielectric permittivity ($\varepsilon'$) as a function of frequency at different temperature (PANI-CSA) $0.25$ – (PMMA) $0.75$ film of typical thickness $6 \mu m$

Fig. 6.23 Dielectric permittivity ($\varepsilon'$) as a function of frequency at different temperature for (PANI-CSA) $0.75$ – (PMMA) $0.25$ film of typical thickness $6 \mu m$
The contribution of interfacial polarization may be due to the inhomogeneous nature of the samples (impurities in the undoped PANI film and conducting, non-conducting phases in the doped PANI film) or due to the accumulation of charge carriers at the interface between hard and soft segment phases [51] (PANI-CSA and PMMA phases in the polyblend samples), thus causing buildup of macroscopic charge separation or space charge with a relatively long relaxation time [52]. Moreover, the electrode polarization, in general, is attributed to the blocking charge carriers at the electrodes justifying the abnormal increase of the real permittivity at low frequencies and high temperatures [53].

At low frequencies, there is sufficient time for the charge carriers to move over macroscopic distance and build up at the interfaces between the sample and the electrodes within half cycle of the applied ac field, resulting in very high values of the dielectric permittivity [49]. Whereas, at higher frequencies there is practically no time for building up of the charges at the sample-electrode interfaces, however, the transport of charges take place over microscopic dimensions and charges build up at the boundaries of conducting species in the materials (MWS polarization). In the high frequency range, the charges cannot follow the changes in the electric field and only bulk polarization mechanisms of the molecular structure contribute to the electric polarization and thus to permittivity [54]. Hence doped and blended samples are characterized by very high dielectric constant value could be attributed to the presence of semiconducting grains dispersed in insulating grain boundaries (insulating polymer matrix). This gives rise to barriers at grain-grain boundary interfaces, which impart a very high value of dielectric constant to the resulting polymeric blends.

6.7.2 Temperature and frequency dependents of loss tangent

For an ideal parallel plate capacitor no energy losses should occur and the current should lead the applied voltage by exactly 90°. In reality the total current transversing such a capacitor is inclined by a power factor angle $\theta < 90^\circ$ against the applied voltage $V$. The main reason causing this type of behavior is the existence of internal capacitor resistance $(R)$ (for an ideal capacitive element $R = 0 \, \Omega$) that leads to
dissipation of power. Under these circumstances, the phase angle between current and voltage will be less than 90° and the loss factor \((\tan \delta)\) can be defined by

\[
\tan \delta = \frac{1}{\omega RC} = \frac{G}{\omega C}
\]

where \(C\) is the measured capacitance and \(G\) the conductance of the device.

Temperature dependence of loss tangent \((\tan \delta)\) at different frequencies for undoped and doped polyaniline films are shown in Figs. 6.24 and 6.25 respectively. For undoped PANI film, \(\tan \delta\) has been found to increase with temperature (Fig. 6.24) at different frequencies, pass through a maximum value \((\tan \delta)_{\text{max}}\) and thereafter decreases. As the temperature is increased, the frequency at which occurred \((\tan \delta)_{\text{max}}\) shifted to higher temperatures. The above loss peaks and their shifts with temperature suggest a dielectric relaxation process. In doped PANI film, the loss peaks occur at 260 K for all frequencies. It is found that as frequency increases loss tangent increases but there is no shift towards high temperature region (Fig. 6.25). The doped PANI shows a higher \(\tan \delta\) value than that of the undoped PANI may be due to some power loss, because of the work done to overcome the fractional damping forces encountered by the dipoles (polarons and bipolarons) during there rotation at higher frequencies coincides with the reported result [55].

![Fig. 6.24 Tangent dielectric loss (\(\tan \delta\)) as a function of temperature at different frequencies for undoped PANI film](image-url)
Fig. 6.25 Tangent dielectric loss (tan δ) as a function of temperature at different frequencies for doped PANI film.

Fig. 6.26 Tangent dielectric loss (tan δ) as a function of temperature at different frequencies for (PANI-CSA) 0.25 - (PMMA) 0.75 blend film.
Fig. 6.26 and 6.27 illustrate the temperature dependence of loss tangent (tan δ) at different frequencies for (PANI-CSA)_{x} - (PMMA)_{1-x} blend (x = 0.25 and 0.75) films respectively. Fig. 6.26 illustrates the variation of tan δ as a function of temperature for (PANI-CSA)_{0.25} - (PMMA)_{0.75} blend film at various frequencies. It is apparent from figure, that tan δ decreases with increasing frequency while tan δ increases with increasing temperature. The observations on tan δ with frequency and temperature of (PANI-CSA)_{0.75} - (PMMA)_{0.25} blend films show many relaxation peaks whose tan δ has been found to increase with temperature (Fig. 6.27) at different frequencies, pass through a maximum values (tanδ)_{max}, and thereafter decreases. As the temperature is increased, the frequency at which (tanδ)_{max} occurred shifted to higher temperatures. The above loss peaks (corresponds to regions of PANI-CSA and PMMA phases) and their shifts with temperature suggest the multiple relaxation process in the measured temperature range.
6.8 Conclusions

1. The ac conduction and dielectric properties of undoped, doped and (PANI-CSA) \( x \) – (PMMA) \( 1-x \) blend films (9.8, 5 and \( \sim \) 6 µm respectively) are studied as a function of selective frequencies and temperatures in the sandwich structure devices employing symmetric gold ohmic contacts.

2. The ac conductivity of undoped PANI obeys power law \( \omega^s \) (0.95 \( \geq \) s \( \geq \) 0.65 at \( T = 150 - 250 \) K and 0.65 \( \leq \) s \( \leq \) 0.79 at \( T = 260 - 380 \) K) confirms the applicability of the OLPT model to the investigated system. Our experimental data substantiate the presence of polarons with a dimension of 25 Å.

3. The value of the frequency exponent \( s \) (0.51 \( \leq \) s \( \leq \) 0.62) and its temperature dependence (153 \( \leq \) T \( \leq \) 273 K) confirmed the applicability of the small polaron tunnelling model to the investigated doped PANI film.

4. Numerical values of the frequency exponent \( s \) calculated for all compositions \( (x = 0.25, 0.50, 0.75) \) of (PANI-CSA) \( x \) – (PMMA) \( 1-x \) blend films measured in the selective temperature range fit well with the experimental results and support the prevalence of correlated barrier hopping (CBH) of single polaron.

5. Comparison of experimental ac conductivity with numerical ac conductivity of (PANI-CSA) \( x \) – (PMMA) \( 1-x \) blend films showed that the single polaron conductivity matches with the experimental behaviour.

6. The frequency and temperature dependence of dielectric permittivity and loss were studied for undoped, doped and polyaniline blend samples in the temperature range 150 – 300 K at selective frequencies. It was observed that the interfacial and space charge polarizations were responsible for large increase of permittivity at low frequencies and relatively high temperatures for all investigated samples.

7. The observations on tan \( \delta \) with frequency and temperature for undoped, doped and (PANI-CSA) \( x \) – (PMMA) \( 1-x \) \( (x = 0.25 \) and 0.75) blend films show relaxation peaks whose tan \( \delta \) has been found to increase with temperature.
References


