

# INVESTIGATIONS OF CONDUCTION MECHANISM OF ORGANIC MOLECULES USED AS BUFFER HOLE INJECTING LAYER IN OLEDs

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## Abstract

*Thin film capacitors with Al-Polymer-Al sandwich structure were fabricated. The bottom and top aluminium (Al) electrodes were deposited by vacuum evaporation and copper phthalocyanine (CuPc), polyaniline-emeraldine base (Pani-EB) and cobalt phthalocyanine/polyaniline - emeraldine base (CoPc/Pani-EB) blend films (which can be used as buffer hole injection layer in OLEDs) were deposited by spin coating technique. X-ray diffractograms indicated amorphous nature of the polymer films whose thicknesses were measured by capacitance and Rutherford Backscattering Spectrometry (RBS) methods. AC conduction studies revealed that the conduction mechanism responsible in these films is variable range hopping of polarons. From D.C conduction studies, it is observed that, the nature of conduction is ohmic in the lower fields and at higher fields the dominating D.C conduction is of Poole-Frenkel type.*

## 1. Introduction

Light emitting diodes based on organic thin layers have been the subject of intense investigation because of their potential applications as emissive elements for flat panel color displays [1-3]. These organic molecule based LEDs use a multi-layer cell structure composed of emitted layers and carrier transport layers. Organic based LEDs are attractive because of low power consumption, low operating voltage, high fluorescence efficiencies (> 60%), emit at wavelengths that span the entire visible spectrum and long life. Although considerable research efforts have been carried out to enhance the performance suitable for practical use, however, a lot of problems to solve still remain, for example a well balanced injection of positive (hole) and negative (electron) charge carriers

into an emitting layer are considered a prerequisite for high luminous efficiency. Copper phthalocyanine, polyaniline-EB, & cobalt phthalocyanine/ polyaniline-emeraldine base blend can be used as hole injecting buffer layer in OLEDs [4-6]. The present work deals with the conduction mechanism of CuPc, Pani-EB and CoPc/Pani-EB films prepared by spin coating method.

## 2. Experimental

Pure aluminium was evaporated in a vacuum of  $10^{-5}$  Torr from a tungsten filament onto glass substrates to form the bottom electrode. The middle polymer layer such as CuPc, Pani-EB and CoPc/Pani-EB (30:70) film was formed over the bottom electrode by spin coating technique. Finally aluminium was evaporated over the polymer layer to complete Al-Polymer-Al sandwich structure. The glass substrates used were optically plane and cleaned by ultrasonic agitation and vapour degreasing. Thicknesses (d) of the polymer films were measured using a capacitance method and crosschecked by Rutherford Backscattering Spectrometry (RBS). Using an X-ray diffractometer (Seifert 3000p) the structure of the film was analyzed. A Hewlett Packard digital LCR meter (4275 A) was used to measure the capacitance and loss factor values of the Al-Polymer-Al structure. In DC conduction studies, the current as a function of applied voltage was measured using an electrometer amplifier (ECIL-EA 8155), with an accuracy of  $\pm 0.1\text{mV}$ , and a suitable micro ammeter.

## 3. Results and discussion

The molecular structure of Metallophthalocyanine (MPc where M= Cu or Co) and Polyaniline-emeraldine base used in the present investigation are shown in the figures 1 and 2.

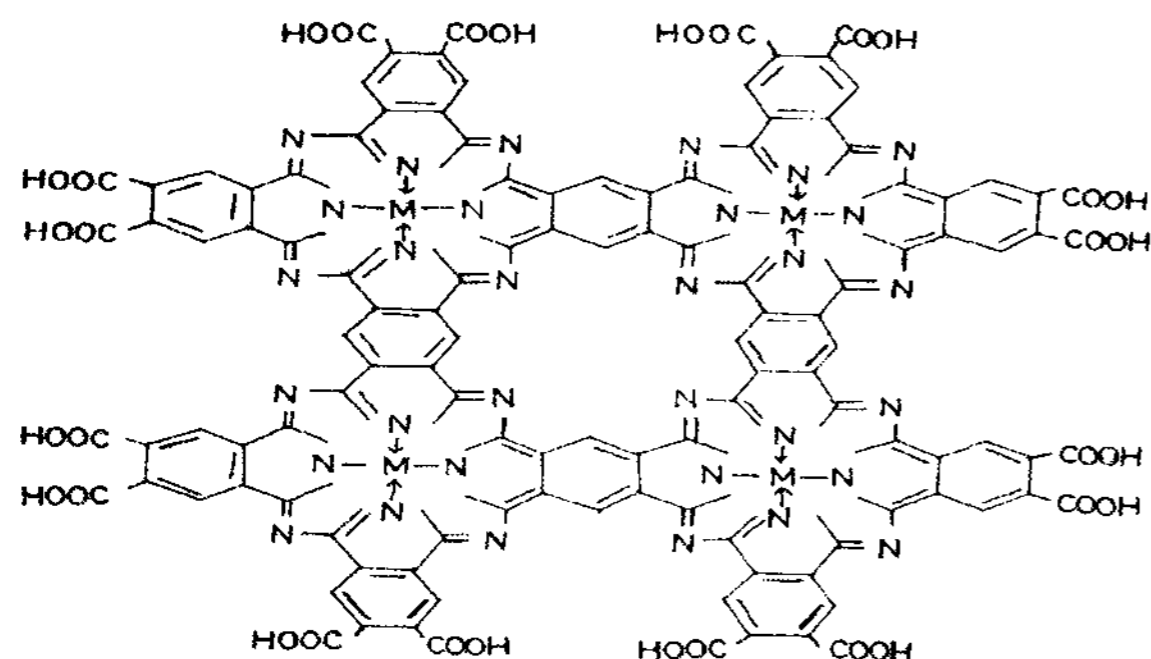


Figure 1 Structure of MPc (M= Cu or Co)

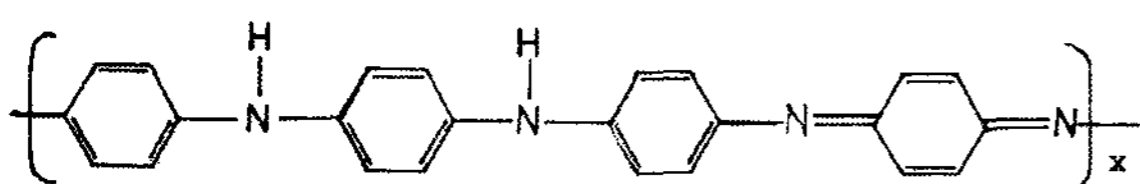


Figure 2 Structure of Pani-EB

The X-ray diffractogram of CuPc and CoPc/Pani-EB films of thickness 500nm are shown in the figures 3 and 4. The absence of any prominent peaks in the spectrum indicates the amorphous nature. However the small broad hump observed in the XRD spectrum of CuPc film indicates the presence of micro crystallites of very low dimensions.

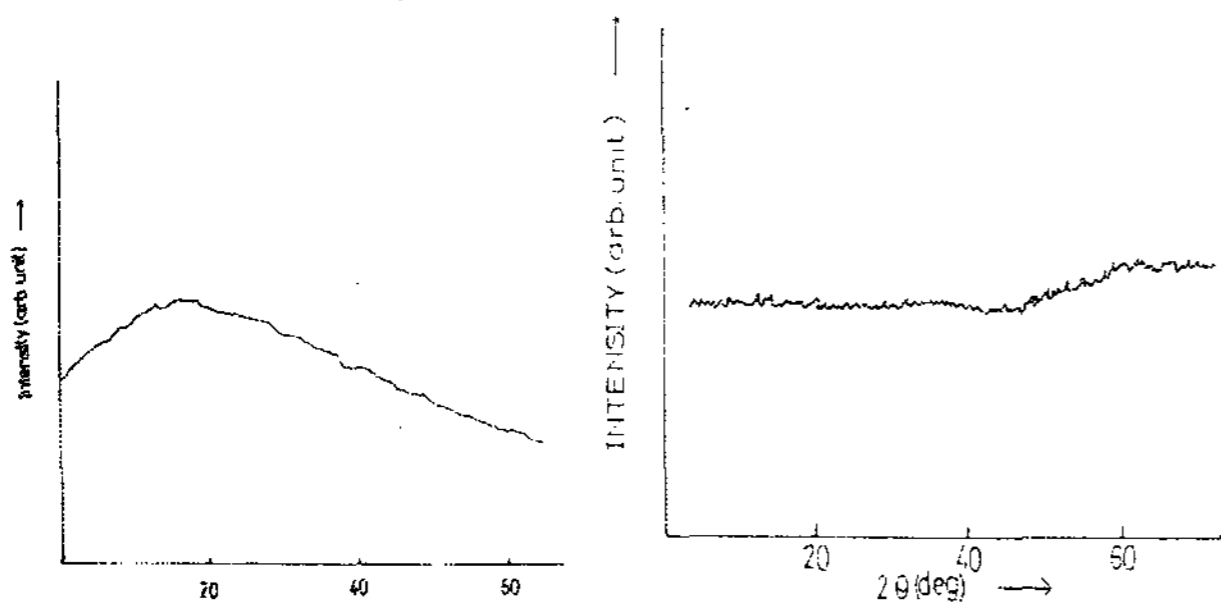


Figure 3 XRD of CuPc      Figure 4 XRD of CoPc/PaniEB

### 3.1 AC conductivity

The double logarithmic plots of the dependence of a.c conductivity on frequency (10 kHz-10 MHz) for different temperatures for CuPc film is shown in figure 5. The a.c conductivity varies according to the relation  $\sigma_{ac} \propto \omega^n$ , where the value of  $n$  depends on temperature and frequency. The value of  $n$  is found to be around 1 in the frequency range 10 kHz - 3 MHz. This value is in accordance with the theory of hopping conduction in amorphous materials where  $n = 0.81$  at low frequencies [7]. In CuPc, thermal treatment results in increase in the number of charge carriers and extended conjugated structures through decarboxylative polymerization reaction of the terminal COOH groups. The improvement in

electrical conductivity with increasing temperature

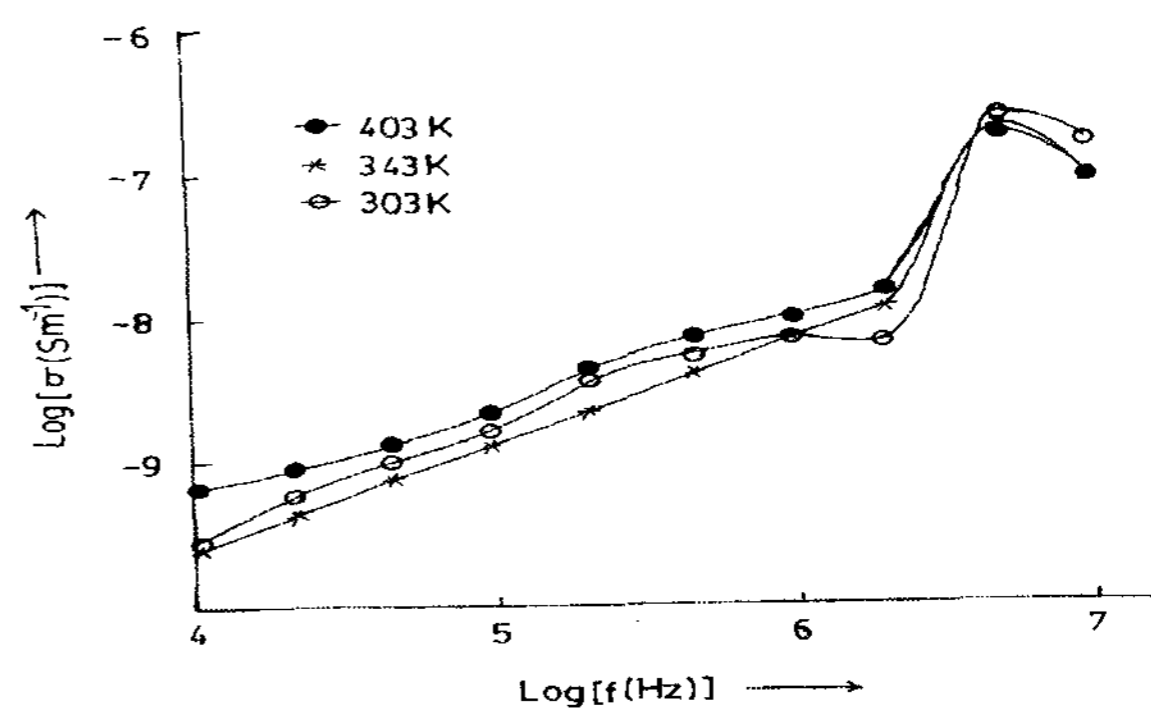


Figure 5 Log  $\sigma$  Vs log  $f$  of CuPc.

observed is due to the build up of ordered polycondensed rings, which allow charge transport. The charge carriers are generated through the formation of radical defects such as polaron and bipolaron during heat treatment. The variation of conductivity with temperature is due to the combined effect of change in conductivity with temperature and the nature of trap distribution in the sample [8]. This indicates that the conduction is taking place via hopping of charge carriers between randomly distributed trapping centers. When the charge carriers are 'localized' due to random electric field or a disordered arrangement of atoms, there is no free motion of charge carriers and the conduction proceeds via the phonon-assisted hopping of charge carriers between localized sites. The temperature dependence of conductivity at high temperature suggests the variable range hopping of charge carriers. From the slope of the plot between  $\log \sigma$  and  $1/T$  (Figures 6 and

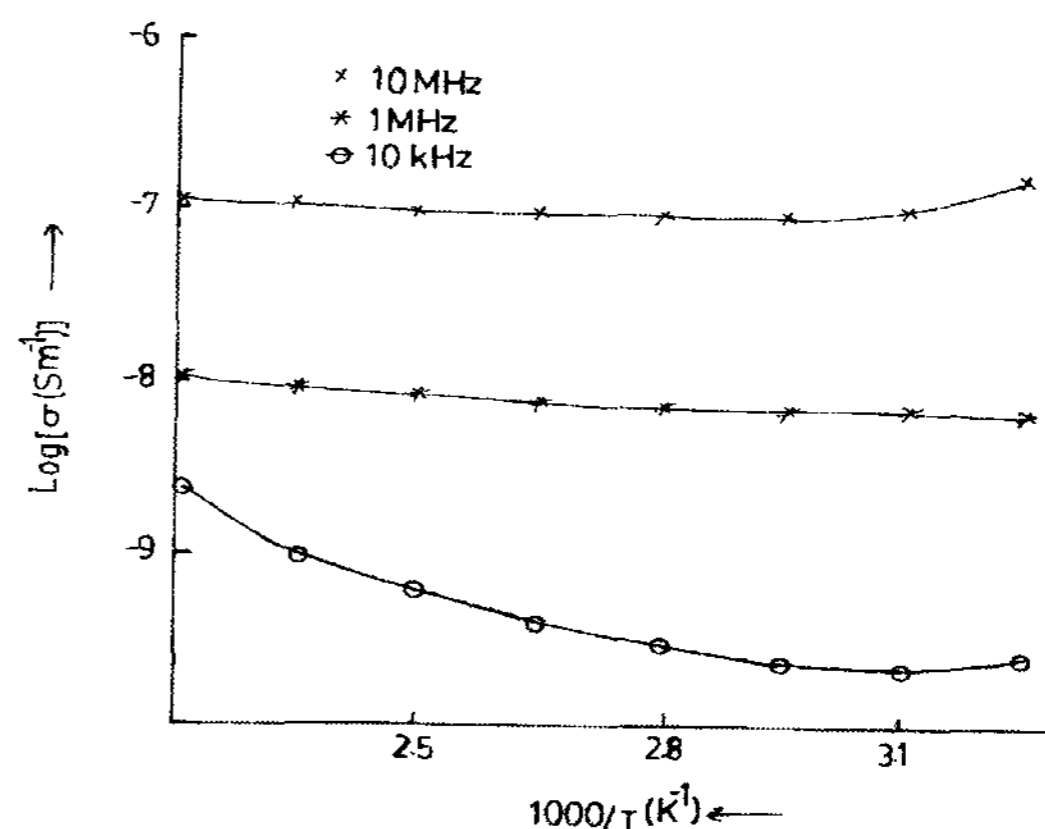


Figure 6 Variation of log  $\sigma$  Vs  $1000/T$  of CuPc film

7) activation energy (E) is calculated by using the relation

$$\sigma_{ac} = \sigma_0 \exp[-E/kT]. \quad (1)$$

where E is the activation energy, k is Boltzmann's

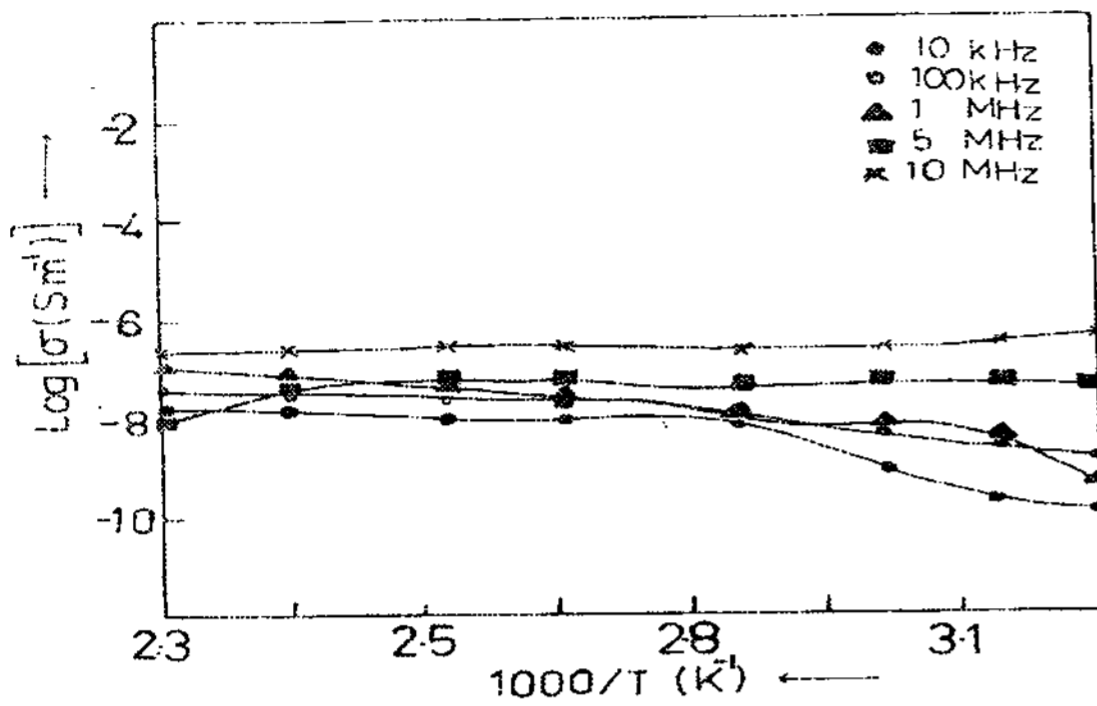


Figure 7 Log  $\sigma$  Vs  $1000/T$  of CoPc/PaniEB film

constant, T is the measured temperature and  $\sigma_0$  is the low field conductivity. The calculated activation energies are given in the table 1. The low values of activation energy indicate that the conduction may be due to the variable range hopping of charge carriers [9]. The process of interchain charge transport is controlled by the rate at which the charged excitation called polarons can hop between chains. In CuPc metallic strands or islands also take part in the conduction process.

Table 1. Activation energy (E) of CuPc, Pani-EB & CoPc/Pani-EB films

Frequency (kHz)	E (eV)		
	CuPc	Pani-EB	CoPc/PaniEB
10	0.28	0.75	0.65
100	0.13	0.51	0.41
1000	0.04	0.26	0.24

### 3.2. DC conduction

Figure.8 and 9 shows the log current (I) versus log voltage (V) characteristic of Pani-EB and CoPc/PaniEB blend thin films for various temperatures ranging from 303-443 K. The current exhibits a voltage dependence of the form  $I \propto V^n$ , where n depends on the field region and temperature. As the temperature increases the value of current increases, which may be due to the build up of ordered poly condensed rings allowing charge transport through

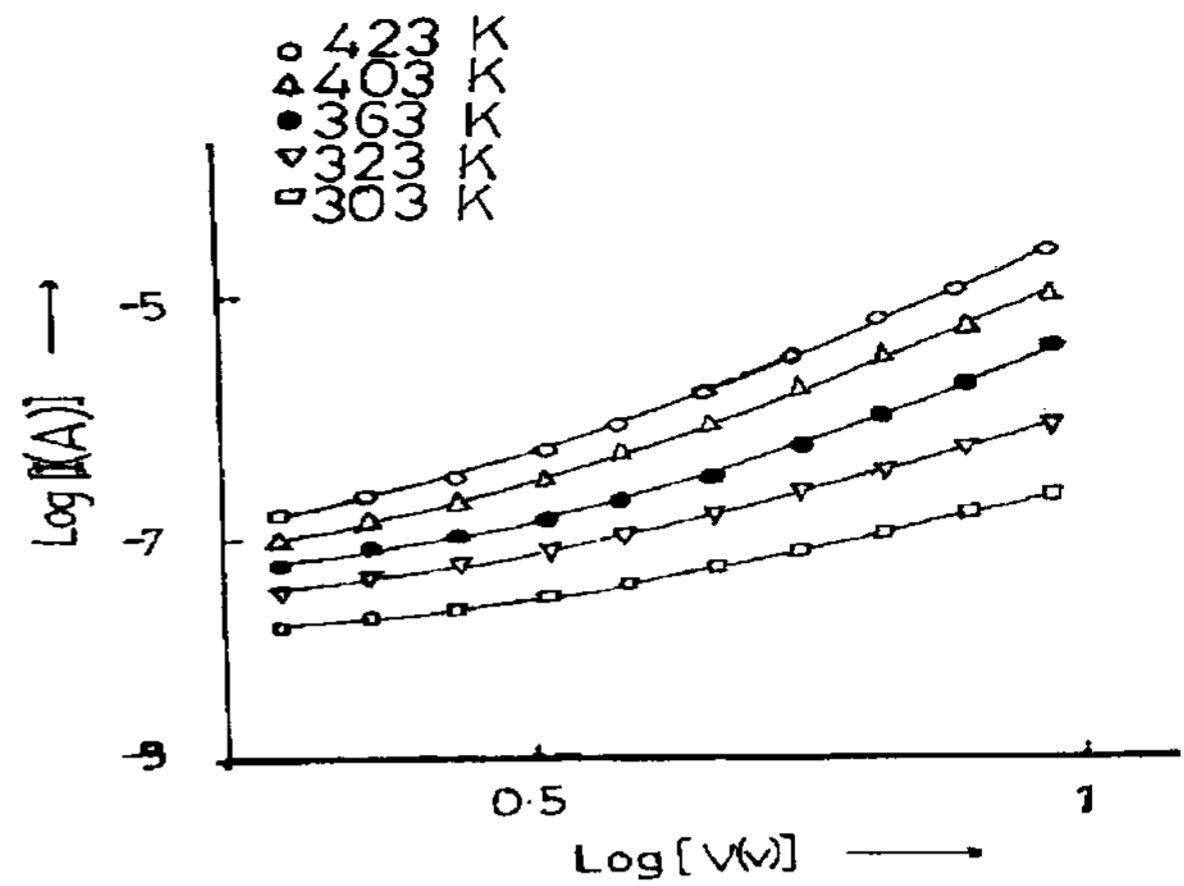


Figure 8 Log I Vs Log V of Pani-EB film

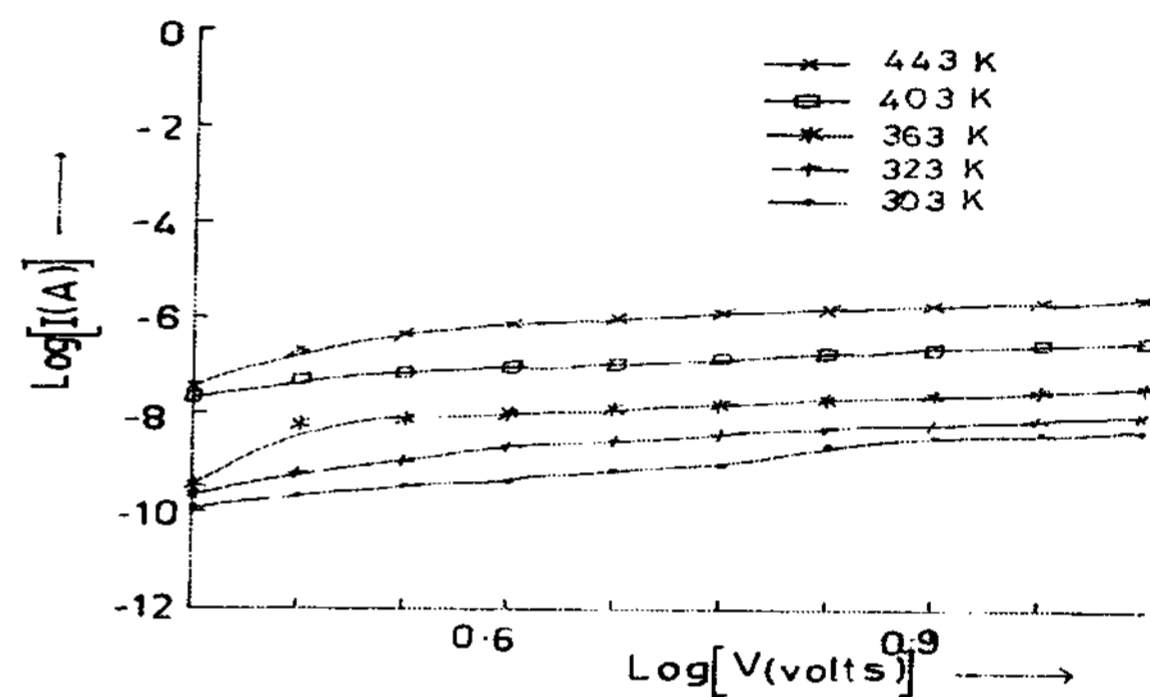


Figure 9 Log I Vs Log V of CoPc/PaniEB film

hopping between aromatized rings. The value of n is around 1 at lower fields indicates the ohmic type of conduction. At higher fields n varies from 1.7–3.04 indicating the existence of Richardson-Schottky (R-S) or Poole-Frenkel (P-F) or Space charge limited (SCLC) type of conduction.

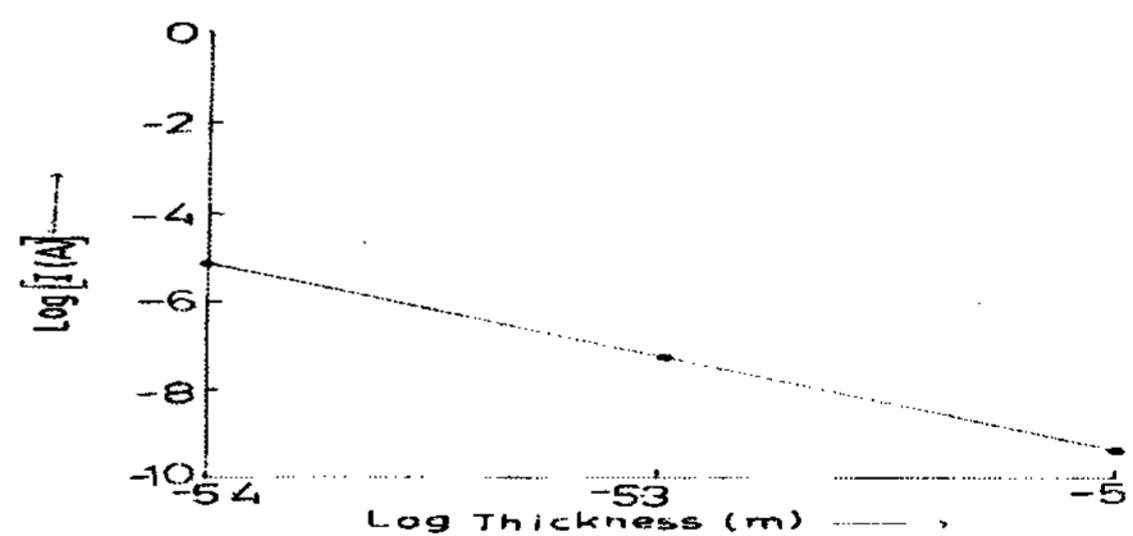


Figure 10 Log I Vs Thickness. of CoPc/Pani-EB

In SCLC theory, the current requires a thickness dependence of the form  $I \propto d^{-n}$ , where n is a parameter that depends on the trap distribution ( $n \geq 3$ ). The value of n is found to be  $< 3$  for CuPc, Pani-EB and CoPc/Pani-EB films (Figure 10) eliminates the presence of SCLC. Linear behavior observed in the high field region of the plot between log I and  $F^{1/2}$

(Figure 11 and 12) indicates the presence of either RS or PF type of conduction mechanism.

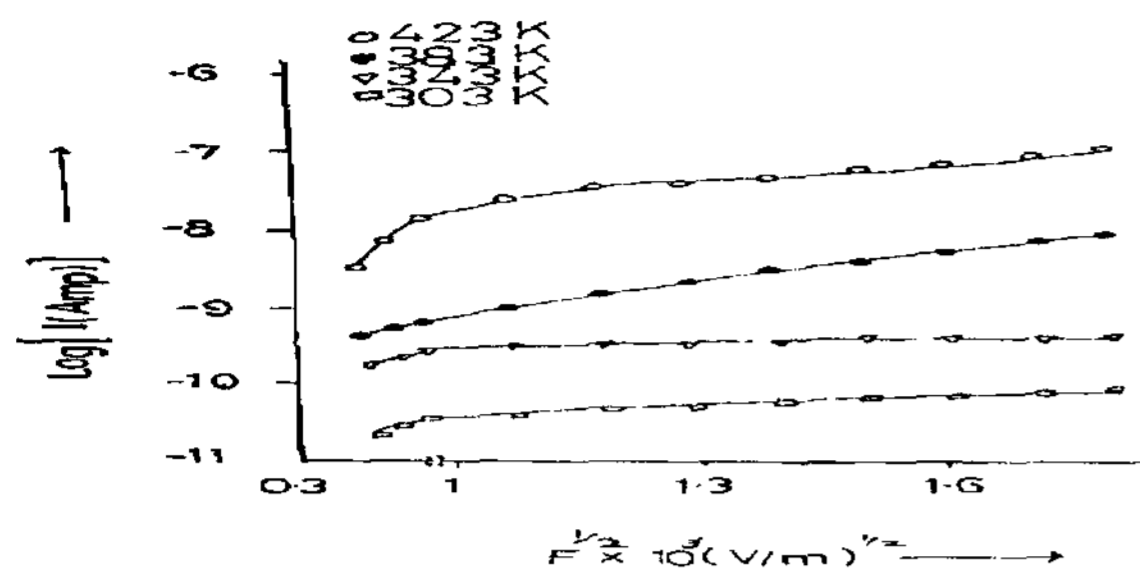


Figure 11 Log I Vs  $F^{1/2}$  of Pani-EB film

In order to confirm RS or PF type of conduction, the experimental value of  $\beta$  (in  $10^{-23}V^{-1/2}cm^{1/2}$ ) is calculated from the plot log I versus  $F^{1/2}$  and is compared with theoretical value of  $\beta$  calculated from the relation.

$$\beta_{PF} = [e^3/\pi\epsilon'\epsilon_0]^{1/2} = 2. \beta_{RS}$$

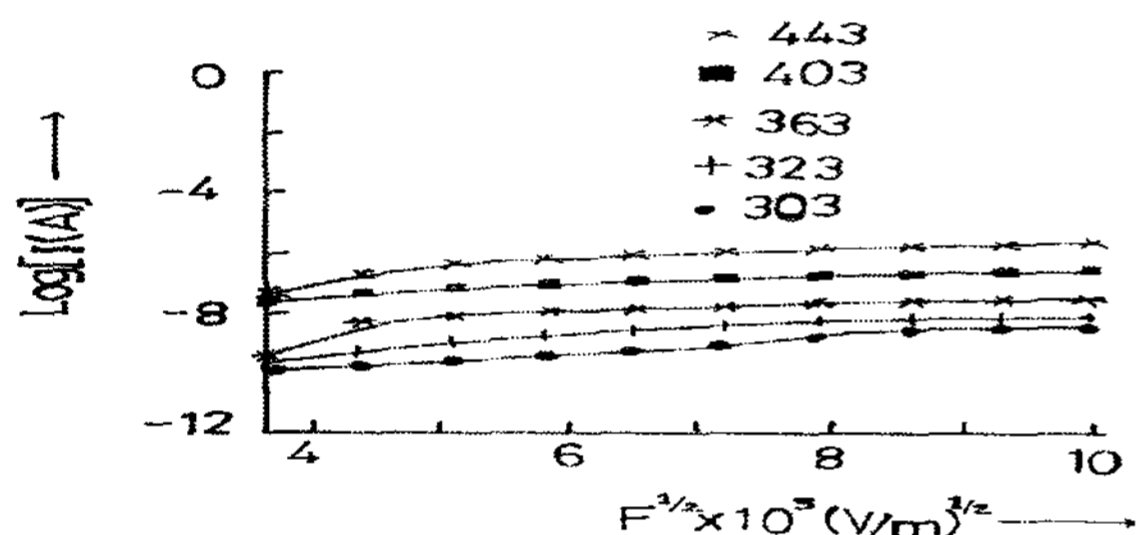


Figure 12 Log I Vs  $F^{1/2}$  of CoPc/Pani-EB.

From the experimental and theoretical values of  $\beta$  (table 2) it is identified that the dominating DC conduction mechanism is of Poole-Frenkel type in Pani-EB, CuPc and CoPc/Pani-EB films. DC activation energy calculated from the plot log I Vs  $1/T$

Table 2. Experimental and theoretical values of  $\beta$

Temp (K)	CuPc		Pani-EB		CoPc/Pani	
	$\beta_{expt}$	$\beta_{theo}$	$\beta_{expt}$	$\beta_{theo}$	$\beta_{expt}$	$\beta_{theo}$
303	2.12	$\beta_{PF}=4$	0.22	$\beta_{PF}=0.15$	0.349	$\beta_{PF}=0.47$
343	3.09	$\beta_{RS}=2$	0.31	$\beta_{RS}=0.07$	-	$\beta_{RS}=0.24$
403	3.21		0.52		0.363	

Table 3. DC activation energy.

Volts	CuPc(E in eV)	Pani (E in eV)	CoPc/Pani(E in eV)
3	0.36	0.55	0.54
5	0.34	0.51	0.49
9	0.31	0.48	0.38

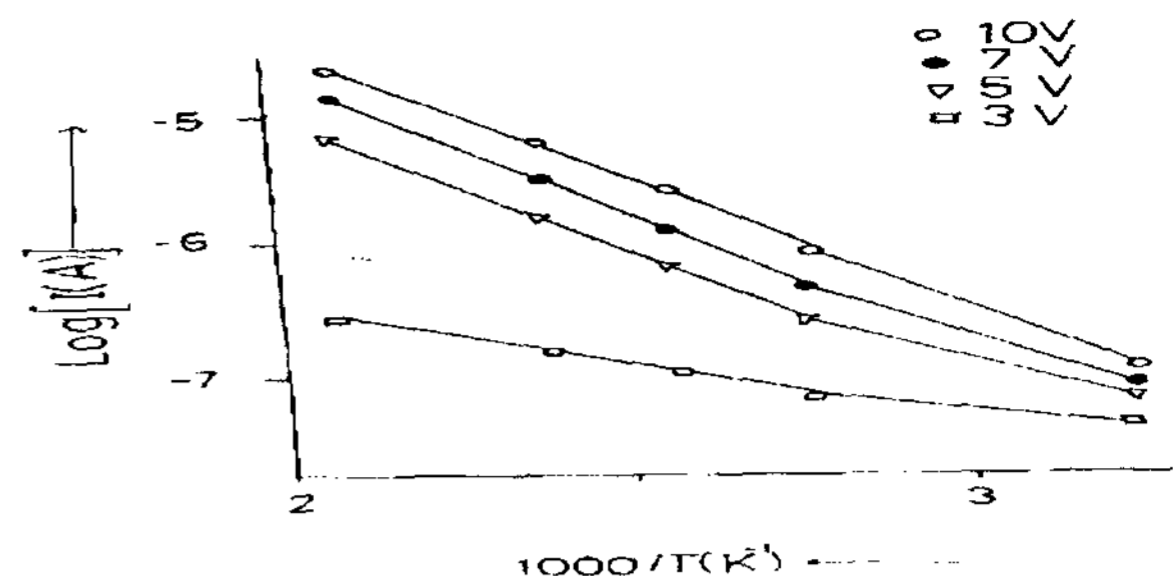


Figure 13 Log I Vs  $1000/T$  of Pani-EB film.

(figure 13) is given in the table 3. The decrease of activation energy with increasing electric field indicates that the potential barrier for conduction lowers with the application of external electric field.

#### 4. Conclusion

XRD studies indicate the amorphous nature of the films studied. The AC conduction studies suggest the variable range hopping of charge carriers like polarons are responsible for conduction. From D.C conduction studies, it is observed that, the nature of conduction is ohmic in the lower fields and at higher fields the dominating D.C conduction is of Poole-Frenkel type.

#### 5. References:

- [1]. Shaheen, S.E., Jabbour, G.E., Morrel, M.M., Kawabe, Y., Kippelen, B., Peyghambarian, N., Nabor, M.F., Schlaf, R., Mash, E.A. and Armstrong, N.R., J.Appl. Phys. 84, 2324 (1998).
- [2]. Lee, J.H., Woo, H.S., Kim, T.W. and Park, J.W., Optical Materials, 21, 225 (2002).
- [3]. Kim, S.K., Chung, T.G., Chung, D.H., Lee, H.S., Song, M.J., Park, J.W., Lee, J.U. and Kim, T.W., Optical Materials, 21, 159 (2002).
- [4]. Van Slyke, S.A., Chen, C. H. and Tang, C.W., Appl. Phys. Lett., 69, 2160 (1996).
- [5]. Parthasarathy, G., Burrows, P.E., Khalfin, V., Kozlov, V.G. and Forrest, S.R., Appl. Phys. Lett., 72, 2138 (1998).
- [6]. Cersosimo, D., Pinto, N.J. and MacDiarmid, A.G., Proceeding of The National Conference On Undergraduate Research (NCUR), (2002)
- [7]. Pollak, M and Geballe, T.H., Phys. Rev., 122, 1742 (1961).
- [8]. Lampert, M.A., Phys. Rev., 103, 1648 (1956).
- [9]. Misra, S.C.K. and Chandra, S, Ind. J. Chem., 33A, 583 (1994).