



# Electrical conduction of the Sensitized Polymer observed by a study of Steady-state dark conduction current

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## Abstract

Steady state dark conduction current has been studied for pure polyvinyl chloride (PVC) and Malachite Green sensitized PVC i.e. 6%, 7.5%, 10%, and 15% with field 30, 60, 90, and 120 kV/cm at temperatures i.e., 60, 75, 90, and 105<sup>o</sup>C. Furthermore, the magnitude of current in sensitized samples surpasses that of pure PVC. Based on these findings, it can be concluded that the study conducted, the steady-state dark conduction current is found to be dependent on voltage for both pure and sensitized samples at varying temperatures. The curves exhibit the typical ohmic behavior initially, up to 30 kV/cm, but transition to non-ohmic behavior at higher electric fields. In the lower field region, the slope value ranges from 0.52 to 0.94, while in the higher field region, the non-ohmic conduction is characterized by a slope between 1.47 to 1.97. The current increases throughout the studied range of temperature. The increase in electrical current could potentially be attributed to the formation of charge transfer complexes (CTC). The activation energy observed is less than 1 electron volt (eV). It may be caused by electronic conduction. The augmentation in conductivity and reduction in activation energy observed during sensitization indicates the occurrence of a plasticization effect.

**Keywords:** Richerdson plot, Arrhenius plots, Steady state dark conduction-current, electronic conduction, charge transfer complexes, and plasticizer effect.

## Introduction

It was not too long ago that the exploration of the electrical characteristics of polymers was predominantly focused on their capability as electrical insulators. However, this scenario has undergone a noteworthy transformation in recent years. The substitution of inorganic semiconductors and metals with organic macromolecules has recently been denoted as "Molecular Electronics". The considerable quantity of atoms present in each organic molecule allows for a wide range of potential modifications, thus enabling subtle alterations in electrical properties.

The conduction in polymers is an intricate process that occurs as a result of the generation of intrinsic charge carriers and the injection of charges from the electrode contact under high electric fields. Kao and Hwang have extensively conducted theoretical and experimental analyses on this matter<sup>1</sup>. Wintle, in his monograph thoroughly discusses the band theory, mobility theory, carrier production, and transport mechanisms<sup>2</sup>. Furthermore, Adamec and Calderwood provide a comprehensive review article on the topic of electrical conduction, addressing its various aspects<sup>3</sup>. Molitan has conducted recent research, presenting a theoretical model involving the SP<sup>2</sup> dangling band states, by performing conduction measurements on poly paraphenylen<sup>4</sup>. Chandra and Chandra have investigated the mixed anion effect in polyethylene oxide-based sodium-ion

conducting polymer electrolytes<sup>5</sup>. Ieda et al. have extensively discussed the high-field conduction and breakdown of low-density polyethylene, polystyrene, polyisobutylene, polyvinyl chloride, and polymethyl in their comprehensive review article<sup>6</sup>.

The electrical conductivity ( $\sigma$ ) of a solid is determined by the ratio of the current density (J) to the electric field (F). The magnitude of conductivity relies on the quantity of charge carriers and their ability to move. The mobility of these carriers represents the ease with which they can transition from one molecule to another. Considering the comparatively significant intermolecular spacing typically found in polymeric systems, the mobility values are several orders lower than those observed in conventional semiconductors<sup>7</sup>. The charge carriers can be inherently produced or derived from impurities, in which case they can exist as electrons, holes, or ions. Conversely, electrodes can introduce holes and electrons. Consequently, conduction can manifest in two forms - either as ionic carriers or electronic carriers, which are free ions or electrons. Polymers, in general, are considered insulating materials, exhibiting conductivities ranging from 10<sup>-10</sup> s/cm to 10<sup>-18</sup> s/cm for polyvinyl chloride and polytetrafluoro ethylene.

The first time the exponential relationship between conductivity and temperature in paraffin wax, as measured by Saegusa in 1926<sup>8</sup>.

Additionally, Clark and Williams in 1933 conducted a comprehensive study on the conductivity of organic solids, conclusively confirming the exponential correlation between conductivity and temperature<sup>9</sup>. Fuoss<sup>10</sup> also conducted similar research on various polymers and substantiated the exponential relationship established by Clark and Williams Finally<sup>9</sup>. Akamatu et al.<sup>11</sup> confirmed the exponential relationship between conductivity and temperature in paraffin wax, as previously observed. In their groundbreaking research, Akamatu et al. were the first to observe the remarkably elevated conductivity exhibited by certain solid organic charge transfer complexes<sup>11</sup>. These conducting polymers have demonstrated a wide spectrum of properties, ranging from insulators to metals. Furthermore, the preparation of highly conducting polymers has been successfully achieved by leveraging the insights gained from the investigation of solid charge transfer complexes. Notably, Shirakawa et al.<sup>12</sup> demonstrated that the addition of minute amounts of certain substances can lead to the development of polymers with exceptional conductivity.

A wealth of information on the process of charge transport in polymeric film can be obtained from the measurement of electrical properties as a function of temperature, electric field, and frequency. There is ample evidence for ionic and electronic conduction in a variety of polymers. Various authors have reported that conduction in polymers is ionic in nature the conduction in polyvinyl chloride is reported to be ionic and attributed to H<sup>+</sup> and Cl<sup>-</sup> ion<sup>13-16</sup>. Few workers suggested protonic conduction in polyamides<sup>17-18</sup>. Electronic conduction in polymers have been extensively studied by Farmer F.T. and other<sup>19</sup>.

Some researchers have proposed protonic conduction as an alternative mechanism for charge transport in polymeric films, indicating a wealth of valuable insights that can be derived from the measurement of electrical properties under varying temperatures, electric fields, and frequency conditions. Additionally, there exists substantial evidence supporting both ionic and electronic conduction in a diverse range of polymer materials.

Notably, several authors have reported the predominantly ionic nature of conduction in polyvinyl chloride, specifically attributing it to the presence of H<sup>+</sup> and Cl<sup>-</sup> ions<sup>13-16</sup>. Protonic conduction in polyamides was proposed by only a limited number of workers<sup>17,18</sup>. The study of electronic conduction in polymers, particularly by Farmer F.T. and his colleagues, has been the subject of extensive research<sup>19</sup>. In the light of the above study, the work extended for sensitized PVC.

## Materials and Methods

Pure and various malachite-green sensitized Polyvinyl Chlorides were used for film formation and formed films by casting from the solution technique<sup>20</sup>.

The film so prepared was used for the dark conduction current study. In this method, the sample was sandwiched between aluminum foil electrodes in the thermostat and adjusted thermostat for the desired temperature i.e. 60, 75, 90 and 105°C respectively for the first half hour. After half an hour apply voltages 60, 90, 120 and 150 or Field 30, 60, 90, and 120kV/cm respectively through a high voltage unit for to next half hour. After a total of one hour measure the current when the current value is in a steady state position.

This procedure was used for pure and different malachite green sensitized samples i.e., 6%, 7.5%, 10%, and 15% and also for different fields and temperatures.

## Results and Discussions

Electrical conduction in pure and sensitized PVC has been studied by using different weight percentages of malachite green i.e. 06, 7.5, 10 and 15%. The dependence of steady-state dark conduction on voltage 60, 90, 120 and 150 volts, for pure and sensitized Polyvinyl Chloride (PVC) samples at different temperatures i.e. 60, 75, 90 and 105°C have been shown in Figure-1 to 4. The curves show usual ohmic behavior initially up to 30kV/cm which becomes non-ohmic at higher fields. The magnitude of the current is large in sensitized samples. The observed current increases throughout the studied range of temperature. The slope value in the lower field region lies between 0.52 to 0.94 and non-ohmic conduction with a slope between 1.47-1.97 in the higher field region is observed.

The probability of thermal ionization leads to an elevation in the quasi-Fermi level, subsequently reducing the barrier for electron transport and resulting in ohmic electrical conduction. In the presence of low-energy fields, the injection of carriers from the electrodes is limited, thereby making the initial current predominantly influenced by the intrinsic free carriers within the materials. Conversely, under higher-energy fields, the alteration in thermal ionization probability occurs.

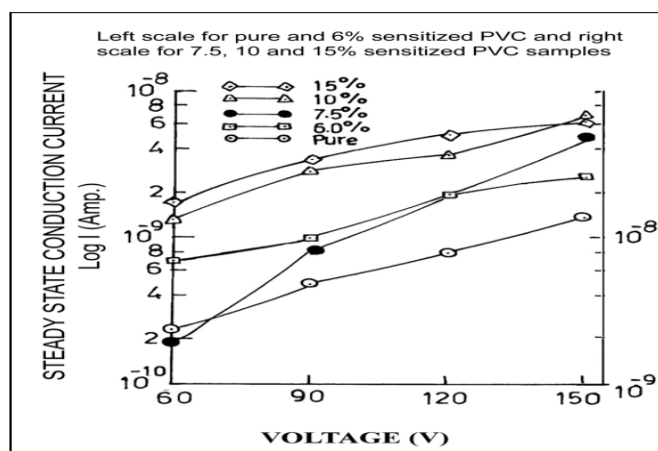
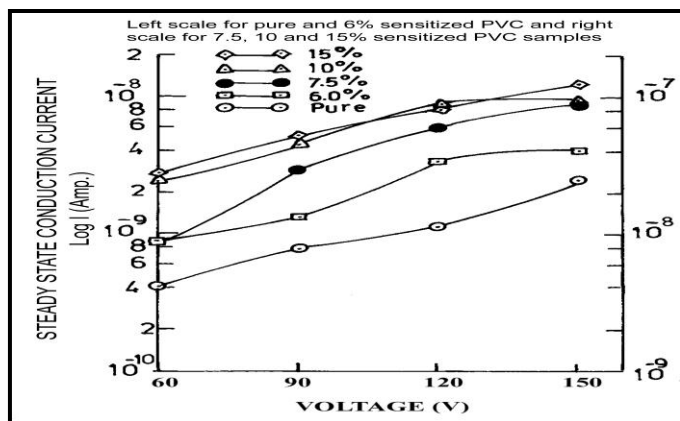
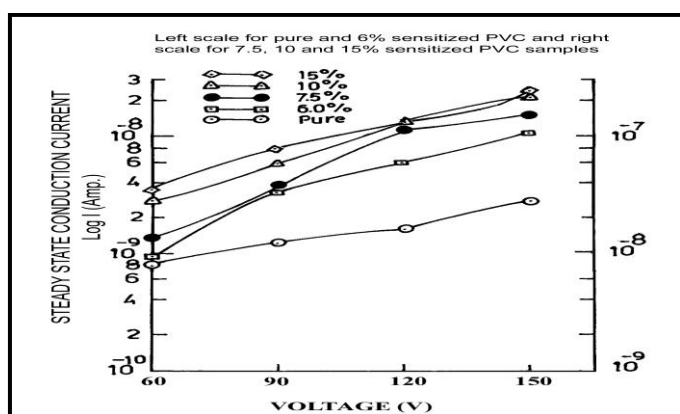


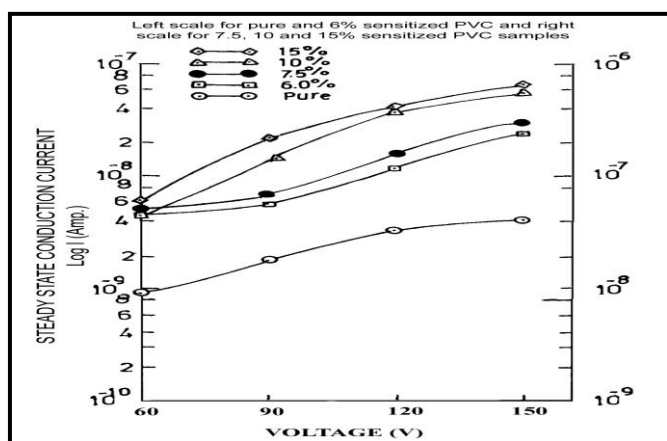
Figure-1: I-V Characteristics of pure and sensitized PVC at Temperature Tp= 60°C.



**Figure-2:** I-V Characteristics of pure and sensitized PVC at temperature  $T_p= 75^\circ\text{C}$ .



**Figure-3:** I-V Characteristics of pure and sensitized PVC at temperature  $T_p= 90^\circ\text{C}$ .



**Figure-4:** I-V Characteristics of pure and sensitized PVC at temperature  $T_p= 105^\circ\text{C}$ .

In the band gap, the continuous trap level distribution is typically supported by a slope coefficient of  $\geq 2$  of features. Defects and impurities have the ability to influence the conduction mechanism and serve as trapping centers that can be populated by injected charge carriers originating from the electrodes.

The slope value of the elevated field area suggests that the electrical conduction in this particular region is not governed by space charge limited current (SCLC). Nevertheless, because the entire current-voltage (I-V) characteristics exhibit nonlinearity, it suggests the existence of additional modes of electrical conduction. The nonlinearity observed might be attributed to the accumulation of space charge, leading to a non-uniform distribution of the electric field between the electrodes. Moreover, for higher energy fields, the deviation from Ohm's law arises from the disturbance of the active barrier, even without the influence of thermal and chemical factors.

The glass transition is a well-known process in which the relaxation time of an internal mechanism within a polymer aligns with the experimental time scale, resulting in enhanced movement and mobility of polymer segments. According to the research by Turnhout, polymer conductivity exhibits a notable surge in proximity to  $T_g$ <sup>21</sup>. The temperature-dependent current behavior demonstrates two distinct regions: one below  $T_g$  and another beyond  $T_g$ . Below  $T_g$ , thermal activation facilitates conduction by transporting carriers between different disordered states.

Current in the Schottky model is a result of the thermal activation of electrons across the barrier at the metal-insulator interface. This activation is further influenced by the applied field, which reduces the height of the barrier. When the temperature reaches glass transition temperature  $T_g$ , the motion of molecular chain segments significantly decreases the depth of the traps. As a result, trapped charges are released through thermal excitation. Above  $T_g$ , the temperature is high enough to induce segmental chain motion, which further mobilizes the traps. This sudden increase in conductivity occurs above  $T_g$ . Conversely, at low temperatures, the current remains low.

The small current observed is attributed to the trapping of injected charge carriers from electrodes at various levels<sup>22</sup>. Increasing the molecular movement of polymer chains is necessary to escape from these levels. When heat energy is applied to a polymer, its temperature rises, causing different transitions to occur within the polymer. The heightened molecular movement caused by the temperature increase leads to the thermal excitation of charge carriers, allowing them to be released from the traps, either directly or because the trap depth is reduced. The activation energy value was calculated from the slope of  $\log \sigma$  vs  $103/T$  (Arrhenius plot) Figure-5 to Figure-8. And shown that activation energy diminished with malachite green concentration. The activation electricity values for the numerous fields calculated from those plots have been proven in (Table-1 and Table-2). The low values of activation energy ( $<1\text{eV}$ ) indicate the predominance of electronic conduction within this case.

The boom in the conductivity and reduction within the activation energy advise that plasticization impact is taking region.

By means of adding a low molecular weight of dye to a polymer, the polymer chain could be loosely and the spine mobility may be multiplied without the difficulty related to the attached side group. In sensitized samples, intermolecular interplay will lead to a tremendous increase in the ionization of dipoles and the traps associated with these ionized species. Consequently, the effect of those traps within the rate carrier era and shipping is so effective that the pf mechanism is marked and the S.R. mechanism is predominated at higher temperatures. The effective metal potential barrier at a constant field was calculated from the slope of  $\log J/T^2$  vs  $1/kT$  plots (Richardson plot) Figure-9 to 13. The value of the effective metal potential barrier decreases with increasing the field and temperature.

The incorporation of sensitizers in sensitized polymer leads to an increase in current, demonstrating electrical conduction. The primary method for augmenting the current in organic material with concentration is through the creation of charge transfer complexes (CTCs)<sup>23,24</sup>. Malachite green possesses an amino group that retains an unshared pair of electrons<sup>25</sup>, potentially contributing to the formation of charge transfer complexes. These CTCS represent novel molecular complexes that arise from the interaction between electrons.

Such complexes show large electrical conductivity. Aromatic hydrocarbons and their substitution products are mainly electron donors and the adducts which they form are called complexes. The second major class of donors encompasses a large group of substances in which there are non-bonded (ion-pairs) electrons available for co-ordination, these are called n donors. It is reported that CTC formation included holes and electrons as its charge carriers<sup>26</sup>. Reports on CTC also indicate that due to sensitization the mobility of one type of carrier is enhanced, while that of the other is diminished<sup>27</sup>.

Electrical conduction in sensitized PVC samples shows that the current increases due to the incorporation of sensitizer. The conductivity of the system is enhanced due to either an augmentation in the concentration of carriers the improvement in carrier mobility, or a combination of both. The increase in current is achieved through the creation of charge transfer complexes (CTC).

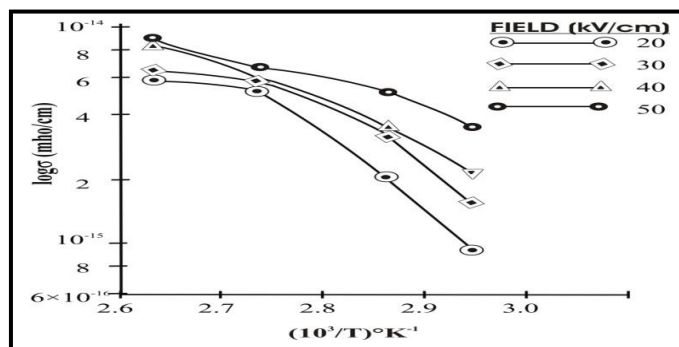


Figure-5:  $\log \sigma$  vs  $10^3/T$  plots for malachite green 6% sensitized PVC samples (Arrhenius plots).

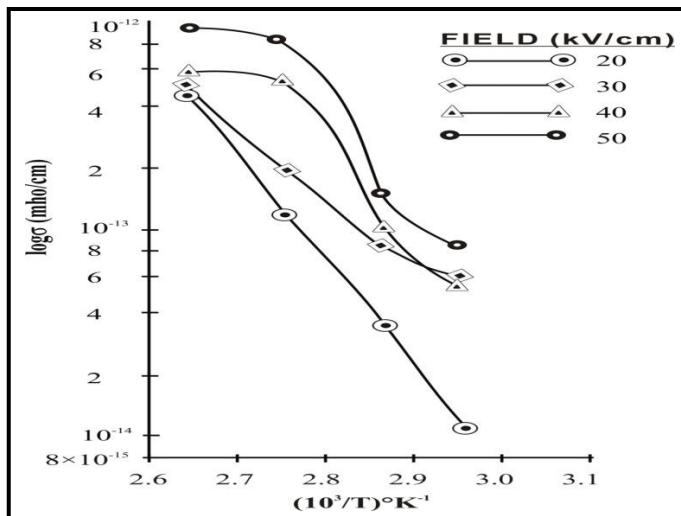


Figure-6:  $\log \sigma$  vs  $10^3/T$  plots for malachite green 7.5% sensitized PVC samples (Arrhenius plots).

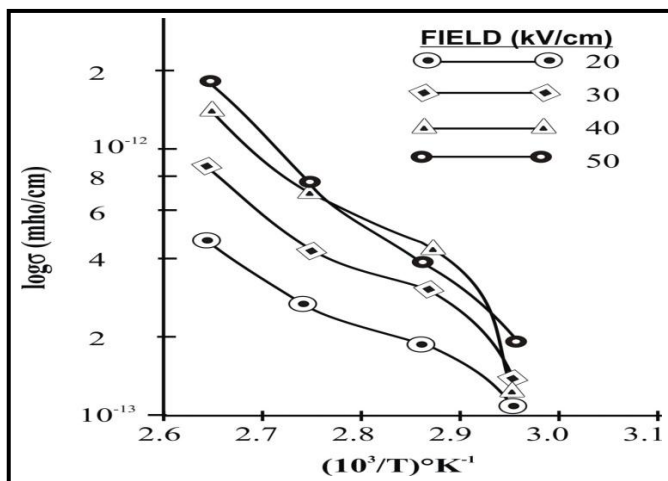


Figure-7:  $\log \sigma$  vs  $10^3/T$  plots for malachite green 10% sensitized PVC samples (Arrhenius plots).

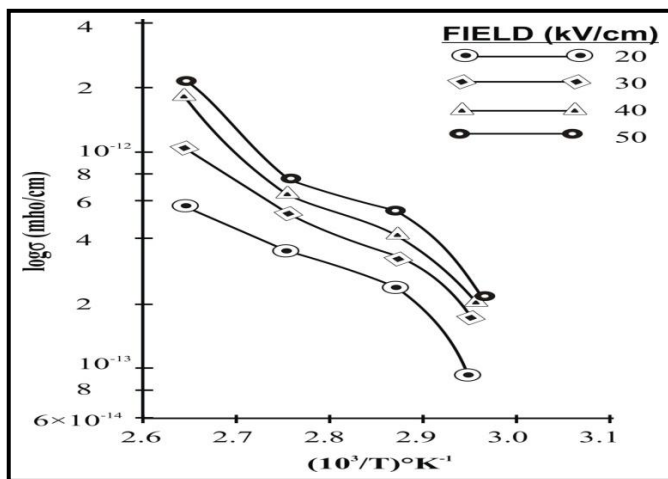


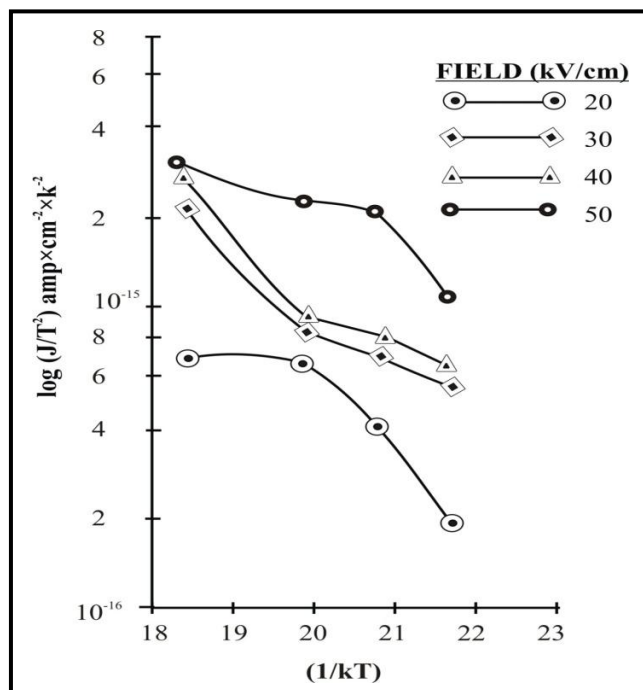
Figure-8:  $\log \sigma$  vs  $10^3/T$  plots for malachite green 15% sensitized PVC samples (Arrhenius plots).

**Table-1:** Effective metal potential barrier and activation energy with different fields at constant temperature 60°C.

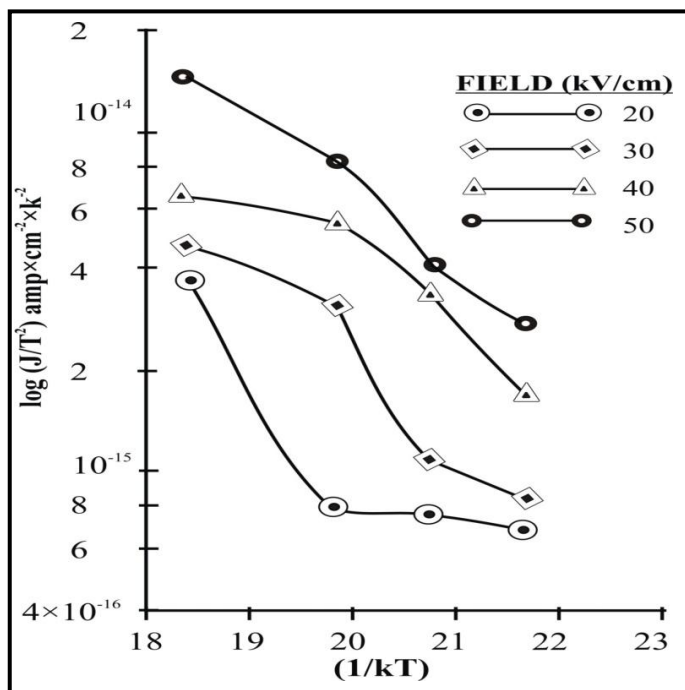
Field (kV/cm)	Effective Metal Potential Barrier	Activation energy (eV)				
		Pure PVC	Sensitized samples			
			6%	7.5%	10%	15%
20	0.648	0.657	0.639	0.615	0.610	0.597
30	0.630	0.638	0.625	0.610	0.607	0.587
40	0.609	0.617	0.611	0.598	0.587	0.574
50	0.598	0.608	0.598	0.581	0.563	0.553

**Table-2:** Effective metal potential barrier and activation energy with different fields at constant temperature 105°C.

Field (kV/cm)	Effective Metal Potential Barrier	Activation energy (ev)				
		Pure PVC	Sensitized samples			
			6%	7.5%	10%	15%
20	0.645	0.649	0.628	0.608	0.591	0.518
30	0.625	0.638	0.615	0.590	0.586	0.575
40	0.618	0.629	0.601	0.588	0.582	0.563
50	0.610	0.618	0.586	0.568	0.553	0.532



**Figure-9:**  $\log J/T^2$  vs  $1/kT$  plots for pure PVC sample (Richardson plots).



**Figure-10:**  $\log J/T^2$  vs  $1/kT$  plots for malachite green 6% sensitized PVC samples (Richardson plots).

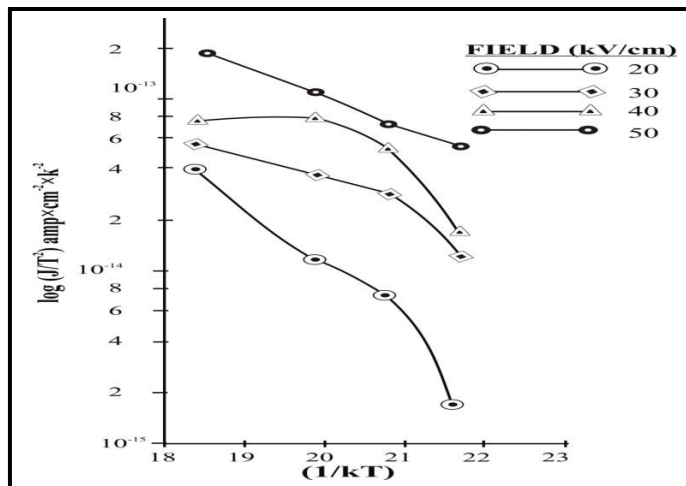


Figure-11:  $\log J/T^2$  vs  $1/kT$  plots for malachite green 7.5% sensitized PVC samples (Richardson plots).

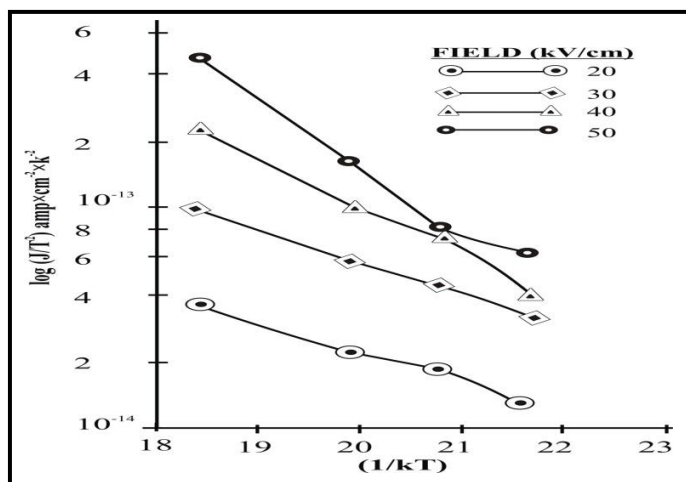


Figure-12:  $\log J/T^2$  vs  $1/kT$  plots for malachite green 10%-sensitized PVC samples (Richardson plots).

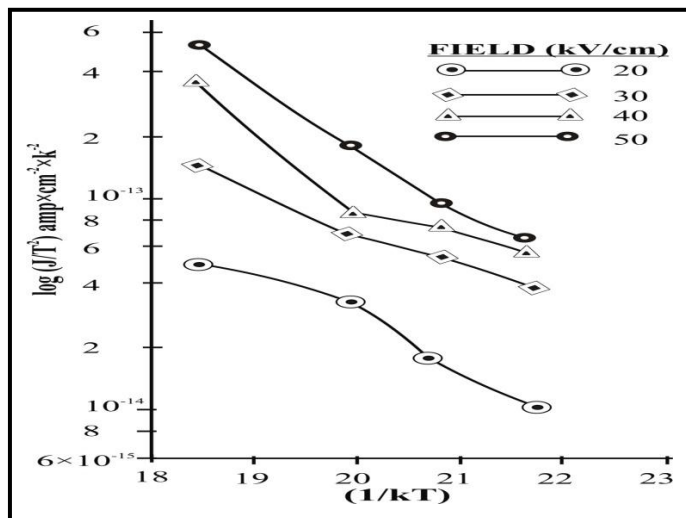


Figure-13:  $\log J/T^2$  vs  $1/kT$  plots for malachite green 15%-sensitized PVC samples (Richardson plots).

## Conclusion

According to our findings, it can be inferred that as the temperature rises, there is an augmented likelihood of thermal ionization occurring within the trapping centers, consequently leading to a displacement in the quasi-Fermi level. As a consequence of this displacement, the barrier through which electrons are conveyed is diminished, resulting in ohmic electrical conduction.

Electrical conduction in sensitized PVC samples shows that the current increases due to the incorporation of sensitizer. The enhancement in current also may be the formation of charge transfer complexes (CTC). The increase in the conductivity and decreases in the effective metal potential barrier and activation energy with malachite green sensitization also may be due to the cause of change in the inter and intramolecular attraction<sup>28,29</sup>. Hence plasticization effect is taking place. The plasticization behaviour is reported earlier<sup>30</sup>.

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