

Electrical conduction mechanism in solution grown doped polyvinyl pyrrolidone films

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Abstract. A detailed study of electrical conduction mechanism in bimetalized ferrocene-doped polyvinyl pyrrolidone films was carried out. The measurements were carried out on films of about 20 μm thick, in the field range of $(2.0\text{--}8.0) \times 10^4$ V/cm at temperatures ranging from 363 to 423 K. An investigation of the effect of impurity such as ferrocene in the polymer matrix was undertaken. Lowering of activation energy and increase in current due to doping were observed. The results showed that the charge carriers were generated by field-assisted lowering of coulombic barriers at the traps and were conducted through the bulk of the material by a hopping process between the localized states by a Jonscher–Ansari modified Poole–Frenkel mechanism. The dependence of current and activation energy on the ferrocene concentration is explained on the basis of charge transfer type of interaction between dopant and polymeric material.

Keywords. Electrical conduction; polyvinyl pyrrolidone; ferrocene; Poole–Frenkel; hopping; charge transfer complex.

1. Introduction

Polymers with controlled conductivity and thermal sensitivity are very much desirable in various applications (Cassiers 1960; Dresner and Comizzoli 1972; Pillai *et al* 1980). Studies of the transport mechanisms in polymer films have gained importance in recent years owing to the potential applications of films in various device technologies (Seanor 1982). Based on current–voltage characteristics, the deduction of the responsible conduction mechanism amongst various possibilities is seldom simple. Different workers have given different interpretations of their results but it seems no ultimate view has yet been reached. The elucidation of the underlying charge injection and carrier migration process is vital to the future utility of these materials. It has been shown that charge storage property and carrier mobility can be greatly affected by impregnating the polymers with suitable dopant (Sinha and Srivastava 1979; Mizutani *et al* 1984; Narsimha Rao *et al* 1986; Mohana Raju *et al* 1990; Vinod Dubey *et al* 1990). Depending on their chemical structure and the way in which they react with the macromolecular matrix, doping decreases the resistivity of the polymer to different degrees. The structural

changes affect the conductivity by changing the number of charge carriers and/or their mobility.

Polyvinyl pyrrolidone (PVP) is known to have a growing pharmaceutical importance and possesses good electrical properties (Prescott 1965; Narsimha Rao and Kalpalatha 1987; Khare *et al* 1994a; Khare and Chandok 1995b), which are greatly modified by impregnating it with suitable dopant. The effect of impurity like ferrocene on electrical conduction, which can give a better understanding regarding the motion of molecules and the migration of charge carriers involved in the relaxation mechanism has not been studied before. Ferrocene, a nonpolar inorganic substance, was selected in the present case as a doping substance for two reasons: (i) it is a π -bonded cyclopentadiene complex and due to the active π -bond it allows nuclear substitutional reactions (Woodward 1952), which means the chances of its linking with polymer matrix are increased, and (ii) it is a monomer (Phadke *et al* 1978) i.e. a polymer making substance and hence its chances of changing the properties of polymer seem to be greater (Khare *et al* 1994b).

In this paper, the experimental results on electrical conduction of ferrocene-doped PVP with different combinations of vacuum coated electrodes are discussed to elucidate the mechanism of nature of electrical conduction which may prove to be interesting from both the scientific and technological points of view. The study is also

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aimed at finding the possibility of the existence and nature of distribution of traps and the role played by the carriers injected from the electrodes and volume-generated carriers.

2. Materials

Polyvinyl pyrrolidone (PVP) and ferrocene used in the present study were procured from M/s Glaxo Laboratory, Bombay. PVP is a polar polymer due to its carbonyl group of double bond in pyrrolidone ring (Tan and Challa 1976). The network structure of PVP has different lengths of π and σ bonds in between nitrogen, oxygen, carbon and hydrogen atoms (Kasha and Pullenan 1962; Palaska 1970; Standen and Scool 1970). The asymmetric distribution of electronic charges near different atoms (N, O, C and H) may be possible in PVP; hence it is a disordered material. Ferrocene is a π -bonded, orange, nonpolar crystalline solid. It is a cyclopentadiene complex having molecular formula $C_{10}H_{10}Fe$ in which an iron atom is sandwiched (Dunitz and Orgel 1953) between two cyclopentadiene anions. There are eighteen valence electrons (in addition to single C-H bonds and C-C bonds of the two rings), i.e. a pair for each of the nine orbitals of iron atoms. These nine pairs of electrons may be distributed on ten C-C and ten Fe-C bond positions using only stable orbitals of atoms. The Fe-C bonds have a small amount (12%) of ionic character.

3. Experimental

The isothermal immersion technique was utilized for preparing films of ferrocene-doped polyvinyl pyrrolidone (PVP). The solution was prepared in a glass beaker by first dissolving 2.4 g PVP in 30 ml of chemically pure chloroform at room temperature. The doping concentration was changed by varying the amount of ferrocene (i.e. 50, 100, 150 and 200 mg) added to the polymer matrix by weight quantities. A change of colour of doped films from white to yellow was noticed. A dopant concentration of 50 mg was used unless specified otherwise. The upper metal electrode was also vacuum deposited. The following electrode combinations were used—Al-Al, Al-Ag, Al-Cu and Al-Sn. The thickness of the samples was of the order of 20 μ m and estimated by measuring the capacitance of the fabricated sandwiches taking the value of dielectric constant, ϵ , of PVP as 2.5. Samples of different thicknesses were obtained by changing the concentration of polymer solution. The geometry of the sandwich configuration of the electrode and the variation of current in these structures as a function of the applied field, temperature and thickness was the same as reported previously (Khare and Srivastava 1992a, 1994; Khare et al 1993, 1994d). The current was recorded with a Keithley 610 C electrometer which was grounded and shielded to

avoid ground loops or extraneous electrical noise. The voltage was applied from a stabilized high voltage unit EC (HV 4800 D).

The measurements were carried out with the polarizing fields ranging from $(2-8) \times 10^4$ V/cm at temperatures 363–423 K. The temperature and field range were limited, because, beyond these films showed breakdown.

4. Results and discussion

The current-voltage (I - V) characteristics of ferrocene-doped (50 mg) polyvinyl pyrrolidone (PVP) on a semilog scale are shown in figure 1, for various fixed temperatures (363, 373, 393, 403, 408, 413, 418 and 423 K). The effects of higher concentrations of ferrocene (i.e. 100, 150 and 200 mg) on I - V characteristics of polymer matrix (at a fixed temperature 373 K) have also been placed in the same figure. The I - V curves show two distinct regions corresponding to two different types of conduction. At lower fields (region I) the slope of the I - V curve lies between 0.92 and 1.13, suggesting ohmic behaviour in this region. At moderate fields (region II), the slope of the I - V curve ranges from 1.4–1.68, indicating

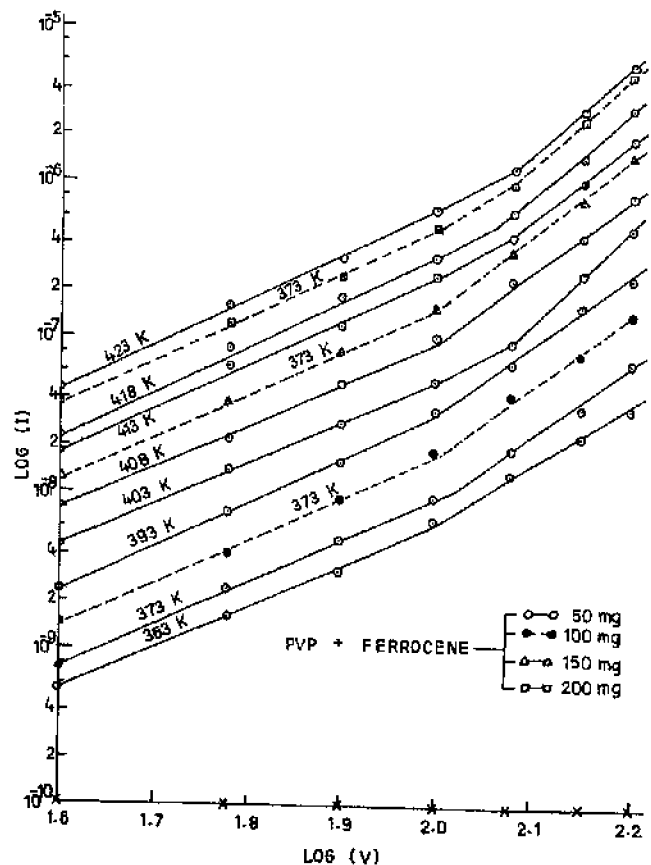


Figure 1. Log I vs log V plots of ferrocene-doped (50, 100, 150 and 200 mg by weight) PVP films.

non-ohmic behaviour. The transition voltage which separates the two regions was found to be independent of temperature. The above results indicate that with the increase of temperature the probability of thermal ionization of the trapping centres increases, thus causing a shift in the quasi-Fermi level, which gives rise to a lowering of the barrier across which electrons have to be transported and the conduction becomes more or less ohmic. The increase in current at high temperatures can be due to softening of the substance and because of this the injected charge carriers can drift more easily to the dielectric volume. This gives rise to a large current at high temperatures. At lower fields, the injection of carriers from the contact is less and the initial current is governed by the intrinsic free carriers in the materials. The current will be ohmic until the injected free carrier density becomes comparable with the thermal carrier density.

In materials having low conductivity such as polymers, electric currents induced by carriers injected from the electrodes are generally bulk limited. This bulk-limited current requires that a sufficient carrier reservoir, available for injection, is maintained at the contact. The steady state current in such a case varies as the square of the applied field. The current-voltage relationship, $I \propto E^2$, does not fit well with the experimental data. Hence the possibility of space charge limited current can be excluded.

In general, the polymers are homogeneous mixtures of polycrystalline and amorphous regions. Hence, there have been controversies over transport theories in the literature and no single mechanism was able to explain the entire conduction in these materials. However, the theories proposed for amorphous and polycrystalline inorganic solids are normally applied to describe the conduction behaviour of these materials with few limitations (Dasaradhudu and Narsimha Rao 1994). The other likely processes are tunneling (Emtage and Tantraporn 1962), ionic conduction (Mott and Gurney 1948), field-enhancement thermionic emission either over an interfacial barrier (Schottky emission) (Langyel 1966) or from localized coulombic traps in the dielectric material (Poole-Frenkel (P-F) mechanism) (Frenkel 1938).

The results based on the isothermal I - V characteristic indicate thermally activated conduction over the entire temperature range (figure 1). Hence, the possibility of a tunneling mechanism being operative in the present case can be ruled out. The Richardson-Schottky (R-S) plots between $\log I$ and \sqrt{E} at different temperatures are shown in figure 2. The nature of these plots indicates that the conduction process is governed by a mechanism in which the charge carriers are released by thermal activation over a coulombic potential barrier that is decreased by the applied electric field. The nature of such a barrier can be understood in two ways. The

charge carriers (electrons) can cross over the barrier between cathode and dielectric, as is the case with Schottky emission, taking the image force into consideration. Alternatively, carriers can be released due to ionization of impurity centres in the dielectrics (Poole-Frenkel effect). In both the above processes there is the current-field relationship of the form

$$I \propto \exp \beta E^{1/2}.$$

The restoring force in R-S and P-F effects is the Coulomb interaction between the escaping electron and positive charge. They differ in that the positive image charge is fixed for P-F barriers but mobile for Schottky emission. This results in a barrier lowering twice as much for the P-F effect.

To determine the actual conduction mechanism, the value of the β -factor at different temperatures calculated from the slope of $\log I$ vs \sqrt{E} are compared with the

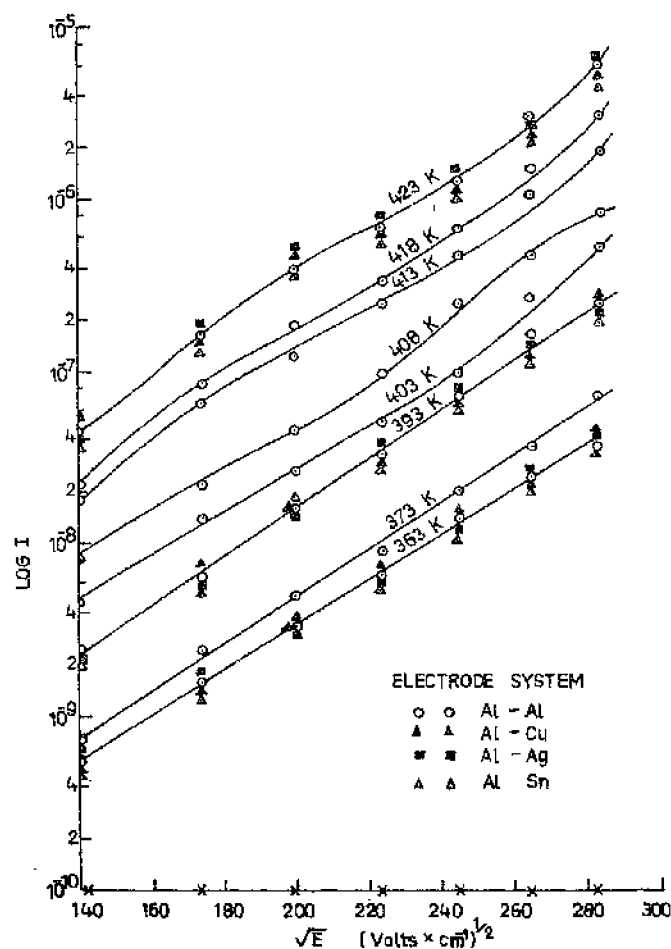


Figure 2. $\log I$ vs \sqrt{E} plots (Schottky plots—similar (Al-Al) and dissimilar (Al-Cu, Ag-Ag and Al-Sn) electrode combinations) for ferrocene-doped PVP films.

theoretically calculated value of β assuming a particular mechanism to be operative. The theoretical values of β_{PF} may be obtained from the relationship

$$\beta_{PF} = 2\beta_{RS} = 2 \left[\frac{e^3}{4\pi \epsilon \epsilon_0} \right]^{1/2}, \quad (1)$$

where ϵ_0 is the permittivity of free space, ϵ the high frequency dielectric constant and e the electronic charge.

The experimental and theoretical values of β for Richardson–Schottky and Poole–Frenkel mechanisms are shown in table 1. The experimental values of β are in close agreement with the theoretically calculated values of β_{PF} . Hence, the P–F mechanism seems to be the governing mechanism in the present case.

The variation of current with thickness of ferrocene-doped PVP films was also studied to predict the conduction mechanism (figure 3). With the decrease in the thickness of the films the value of currents increases. The charge release is determined by the thickness of the charge layer relative to that of the sample. Thin samples will release more charges than thick ones because the charge carriers responsible for electret effect do not penetrate to a depth of more than few microns. The shallow traps are filled first and the charges move to the deeper traps afterwards. If the sample is thin, all the charges trapped in shallower traps is released immediately, however, the charge carriers that have moved to the deeper traps are not released immediately, consequently, charge released in case of thin samples is greater than the thicker ones. The nature of the plot is such that the space charge conduction (SCLC) mechanism in these films can be ruled out because SCLC predict a linear variation of current with thickness.

However, mere compatibility between β_{exp} and β_{theor} values cannot be taken as evidence for deciding the actual conduction mechanism (Simmons 1967), since β values depend on a number of experimental conditions. Further, there are a number of shortcomings in Schottky emission theory as it suffers from large deviations in its constants, which may not correlate with theoretical and experimental results (Lamb 1967). Similarly, the

Poole–Frenkel mechanism maintains Richardson–Schottky formalism, taking into consideration the barriers due to traps. Several workers have tried to distinguish between the two mechanisms by a comparison of β values but point out that values of β may vary with condition of traps in the bulk of the polymer (Mark and Hartman 1967; Yeagan and Taylor 1968; Rehnbaker 1969). The P–F mechanism assumes that once the carriers are thermally activated from their trapping sites with the assistance of the field, they are free to move unobstructed within the conduction band of the insulator. However, the concept of unobstructed motion of charge carriers is incompatible owing to the low mobility of the charge carriers observed in polymers ($\mu < 10^{-7} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) (Cresswell et al 1972). According to Jonscher and Ansari (1971), conduction in polymeric dielectrics with low mobility charge carriers should be interpreted as conduction by localized charge carriers performing hopping.

In order to decide the type of conduction mechanism operating in the polymer films, the effect of the nature of the electrodes of different work functions on the I – V characteristic was studied, since electrodes of different work functions induce different amounts of charge carriers into the bulk of the dielectric in the case of R–S mechanism, whereas the current flowing through the bulk of the film will be independent of the electrode materials in the case of the P–F mechanism. Therefore, if one takes an asymmetric metal–insulator–metal structure with two electrodes of different work functions, the current in the case of the Schottky effect will be asymmetrical when polarities are reversed (Khare et al 1994a) but will remain practically unchanged in the case of the Poole–Frenkel effect, since it does not depend on potential barriers of the interfaces. This is the proper way of distinguishing between the Poole–Frenkel and Schottky mechanisms as suggested by Jonscher and Ansari (1971) and Carchano and Vanentin (1975). Figure 2 shows Richardson–Schottky plots with aluminium electrodes along with corresponding curves for silver, copper and tin electrodes. It may be observed from these curves that the effect of different electrode materials on the

Table 1. Theoretical and experimental values of β and activation energies for ferrocene (50 mg)-doped polyvinyl pyrrolidone films.

Temperature (K)	Dielectric constant (ϵ)	β_{RS} ($\dots \times 10^{-2}$)	β_{PF} ($\dots \times 10^{-2}$)	β_{exp} ($\dots \times 10^{-2}$)	Field ($\dots \times 10^4$) (V/cm)	Activation energy (eV)
363	2.70	2.897	5.694	4.982	2.0	0.97
373	2.64	2.613	5.226	4.766	3.0	0.91
393	2.62	2.591	5.182	4.529	4.0	0.84
403	2.63	2.522	5.044	4.769	5.0	0.772
408	2.60	2.397	4.794	4.139	6.0	0.720
413	2.57	2.422	4.844	3.989	7.0	0.66
418	2.54	2.264	4.528	3.491	8.0	0.62
423	2.55	2.187	4.374	3.586		

I - V characteristics is negligible within the experimental error. Hence conduction is not electrode limited, and therefore the P-F conduction mechanism seems to be a more appropriate mechanism.

The electrical conduction, in general, may be attributed to ions, impurity incorporations and electrons which migrate along the polymer chains and also to the charges released by electrolytic dissociation under thermal activation. The distinction between electronic and ionic conduction is difficult but it is suggested that ionic conduction is characterized by low mobilities and high activation energies, while electronic conduction is associated with relatively higher mobilities and lower activation energies. It is not possible to give definite limits for activation energy, but Jonscher and Ansari (1971) suggest that values less than 0.8 eV would normally be considered as the electronic conduction mechanism, while values around and excess of 0.8 eV would normally be attributed to ionic support. The modified P-F model (Jonscher and Ansari 1971) assumes that the electrons produced as a

result of the field-assisted thermal ionization of donor-like centres perform thermally activated hopping between localized states. The effect of an external field is to lower the potential barrier between the hopping states from the initial value W_0 to a value $W_0 - \nu E^{1/2}$ where $\nu = (e^3/\pi\epsilon\epsilon_0)^{1/2}$ and has the same value as in the classical P-F mechanism. The modified P-F mechanism predicts an activation energy which is decreasing with the square root of the applied field.

The conductivity was evaluated from the measured values of current from the plots of figure 1 at different temperatures, the characteristics of which are shown in figure 4. Two distinct regions are seen and these indicate different slopes at lower and higher temperature regions. Two cases are readily distinguishable experimentally simply by comparing the activation energies at lower and higher temperatures in different regions. In case of many polymers, glass transition temperature T_g can be measured from the change in slope of σ vs $10^3/T$ plots. A change in slope in σ vs $10^3/T$ plot of figure 4 is also observed in the present case and indicates a transition temperature of doped PVP ~ 393 K. The T_g of pure PVP (Pałaska 1970; Standen and Scool 1970) is 413–433 K, but in the present case, it is found to be 393 K, indicating that dopant reduces T_g of the polymer matrix. The dependence of conductivity on temperature for doped samples shows two distinct regions (figure 4) i.e. one below T_g and the other beyond T_g .

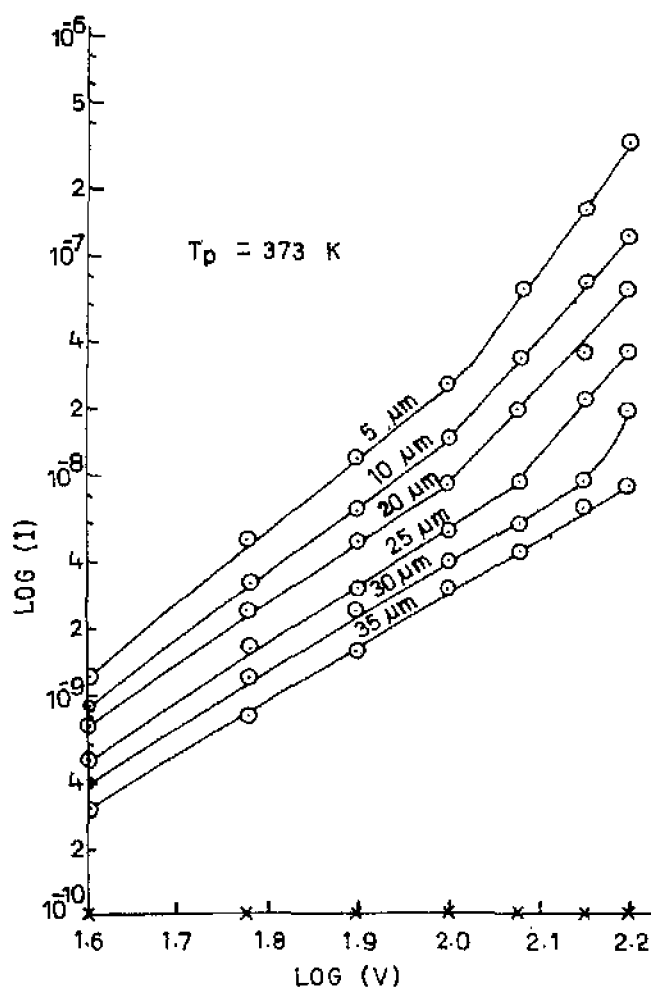


Figure 3. $\log I$ vs $\log V$ plots for different thicknesses (5, 10, 20, 25, 30 and 35 μm) of ferrocene-doped PVP films.

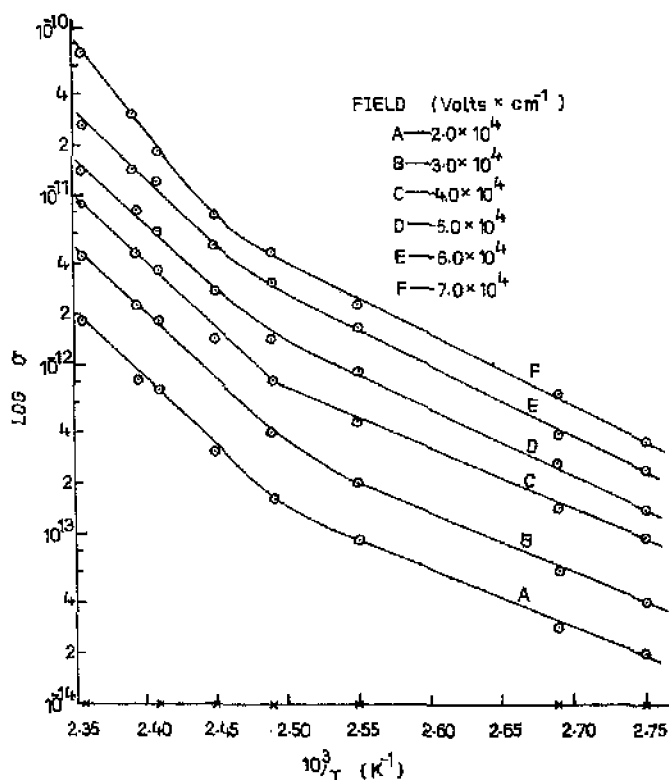


Figure 4. $\log I$ vs $10^3/T$ plots at different fields for ferrocene-doped PVP films.

The low-temperature slope is an arbitrary one and depicts the complex temperature dependence of distributed relaxation processes (Vanderschuren and Linkens 1978). The high-temperature slope ($T > T_g$) is generally related to an ionic conduction process. According to Van Turnhout (1975), conductivity in polymers shows a sharp increase near T_g . At T_g , molecular motion of the chain segments lowers the trap depth considerably and trapped charges are released by thermal excitation. Above T_g , life time of carriers in the conduction band is more which increases the conductivity rapidly. At low temperatures, conductivity is low. The small conductivity is due to trapping of injected charge carriers from electrode at different levels (Perlman 1972). Detrapping from these levels requires increased molecular motion of polymer chains. When thermal energy is supplied to a polymer its temperature increases which induces various transition in them. Increased molecular motion due to increase of temperature causes thermal excitation of charge carrier from the traps, either directly or due to lowering of trap depth. Molecular motions also result in release of trapped carriers due to loss of trapping sites.

The electrical conductivity for samples doped at lower concentration remains low even beyond T_g . It seems that chain motion is not effective in mobilizing the traps formed by dopant molecules and charge carriers released from mobilized traps, are again trapped in traps provided by dopant molecular sites. Thin polymer films are known to be a mixture of amorphous and crystalline regions

(Chopra *et al* 1971). The conductivity behaviour of such films may be dominated by the properties of the amorphous regions (Kosaki *et al* 1971). The presence of amorphous regions gives rise to localized states. Since there are many localized states, the release or excitation of the carriers in these states dominates the conduction process. Consequently, doping should not affect the conductivity too much (Marikhin *et al* 1965), unless the dopant is present in sufficient quantities to markedly affect the position of the Fermi level. Dopant molecules enter either the amorphous regions of the polymer or the defect regions like chain folds. If they are present in low concentrations, they will give rise to additional molecular sites for trapping of charge carriers (Jonscher 1967). Such localized sites can be defined in molecular terms using the difference in ionization potential as an indication of trap depth. As the dopant concentration is increased, the molecules start bridging the gap separating the two localized states and lowering the potential barrier between them thereby facilitating the transfer of charge carriers (Sinha and Srivastava 1979; Kulshrestha and Srivastava 1980).

The activation energies were calculated from the slopes of figure 4 and were plotted against the square root of the applied voltages. A straight line (figure 5) is obtained. The intercept of this straight line at zero field gives a value of $W_0 = 1.568 \times 10^{-19} \text{ J}$ (0.98 eV). Its slope gives the value of $\nu = 5.976 \times 10^{-24} \text{ J m}^{1/2} \text{ V}^{-1/2}$, which is in agreement with its theoretical value of $6.214 \times 10^{-24} \text{ J m}^{1/2} \text{ V}^{-1/2}$. Hence, our data fits fairly well in the modified P-F equation.

The activation energy values observed in the present case are fairly high. Therefore, the possibility of charge carrier species inside the polymer bulk ionic in nature cannot be completely ruled out. Ionic conduction in polymeric materials is a controversial subject. Adamc and Calderwood (1978) have reported the existence of free charge carriers in polymers. Lilly and McDowell (1968) have also reported ionic space charge conduction under high field conduction.

A comparison of currents of pure PVP and ferrocene-doped PVP reveals that an increase in current is observed with doping. Ferrocene is markedly aromatic in character and has three trap levels (Sauthgate 1976). The presence of trap levels may be due to morphological changes in structure. Addition of impurities like ferrocene, introduces charge carriers and trapping levels in PVP-ferrocene matrices (Khare *et al* 1997). The increase in current and decrease in activation energy in ferrocene-doped PVP films can be explained in terms of charge transfer complex formation as evidenced by the optical absorption spectra of pure ferrocene and ferrocene-doped PVP films.

The formation of charge-transfer complexes is characterized by the appearance of a new absorption band or shifting of the absorption band in addition to the broad-

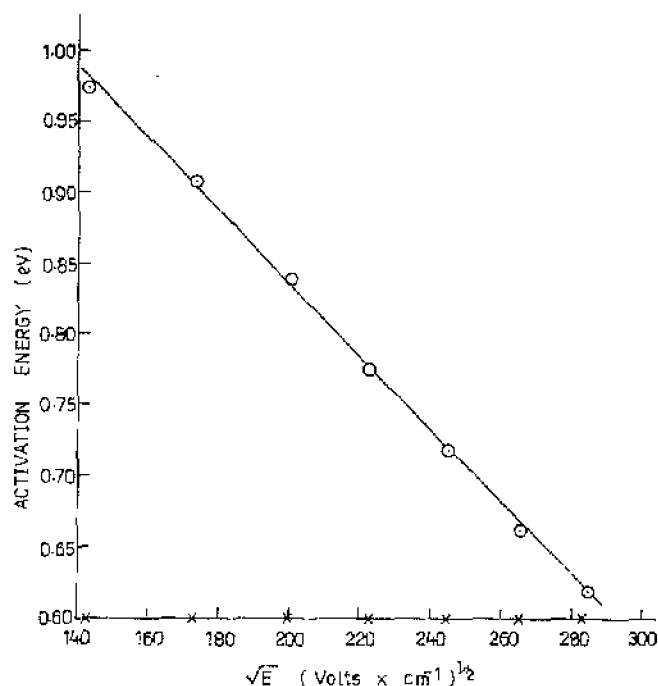


Figure 5. Activation energy vs square root of field for ferrocene-doped PVP films.

ening in the absorption band in the UV-visible region of the spectrum (Rao 1967). The UV spectrum of ferrocene, undoped and ferrocene (50 mg)-doped PVP are shown in figures 6 and 7, respectively. A well-defined sharp band at 246 nm for PVP was observed. The UV spectrum for ferrocene consists of one ill-defined band, along with a sharp and a wide band at 252, 284 and 440 ± 20 nm, respectively. However, in the case of ferrocene (50 mg)-doped PVP, UV spectrum exhibits all the three bands (as in the case of pure ferrocene) at 252.5, 294 and 440 nm, respectively. The width and intensity of the bands have been found to increase with dopant incorporation.

The effect of dopant incorporation may also be interpreted on the basis of the microscopic structure of the polymer in thin film form. The polymer film, in general, consists of crystalline regions in which the molecular chains of the polymer are regularly folded or entangled. These crystalline regions are connected to amorphous regions in which the molecular chains of the polymer

are irregularly folded. The motion of carriers is impeded at these crystalline-amorphous interfaces. Dopants, which may be present either as molecules or as molecular aggregates, generally tend to diffuse preferentially into the amorphous regions of the polymer (Khare and Singh 1994). The presence of dopants in these regions causes a reduction of the crystalline-amorphous interface, which provides conductive pathways through the amorphous regions.

Table 2. Activation energy for ferrocene-doped polyvinyl pyrrolidone films at 373 K.

Field ($\times 10^4$ V/cm)	Activation energy (eV \pm 1.5%)			
	Ferrocene content in polymer matrix			
	50 mg	100 mg	150 mg	200 mg
2.0	0.97	0.952	0.948	0.939
5.0	0.772	0.769	0.751	0.749
8.0	0.62	0.619	0.608	0.597

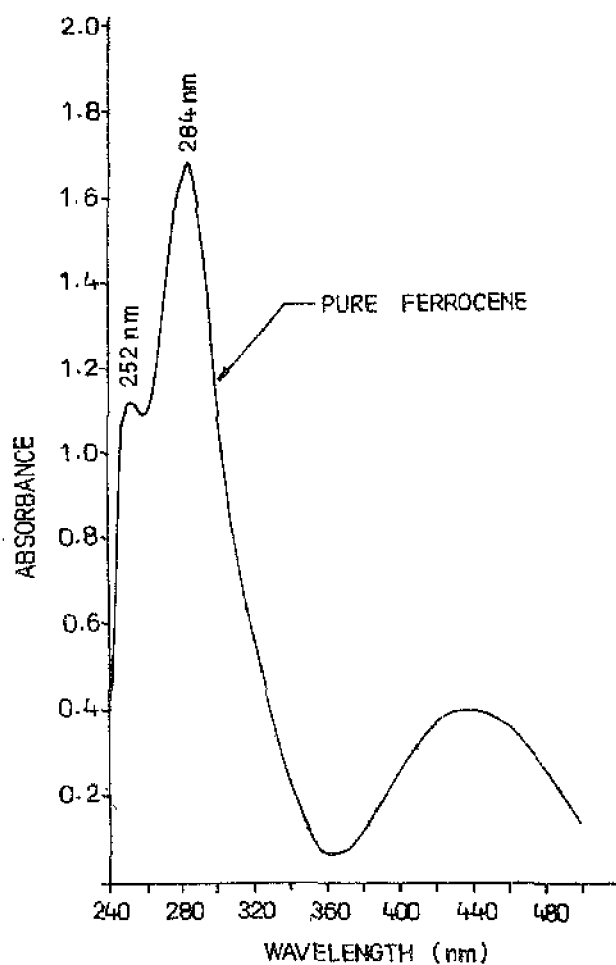


Figure 6. UV spectrum of pure ferrocene.

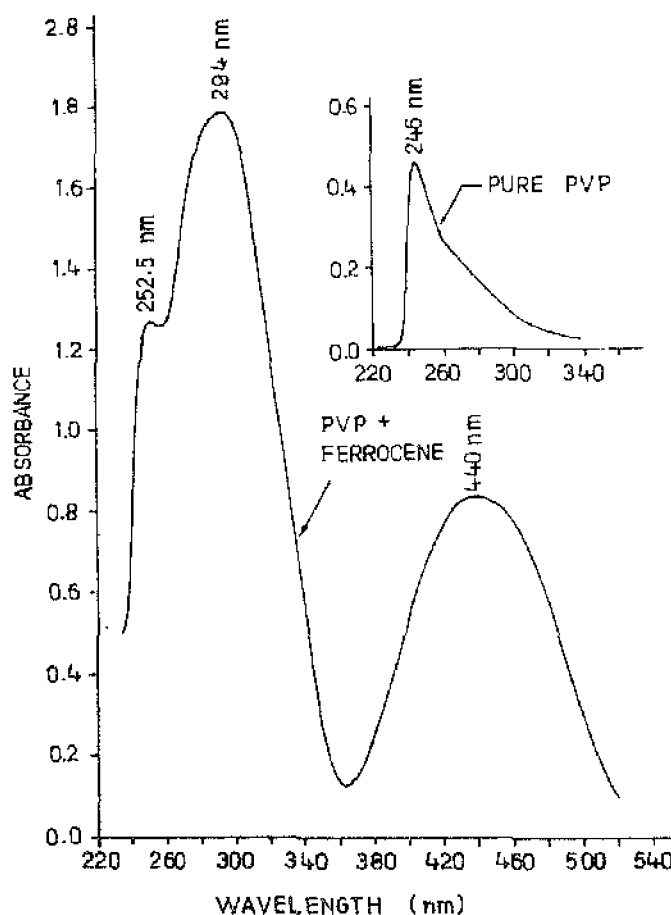


Figure 7. UV spectrum of pure and ferrocene-doped PVP

In polymers, surface states, chain folding, molecular disorders, crystalline–amorphous boundaries and chain ends may act as trapping sites. In addition polymer contains polar groups, where each dipole can act as an electron or hole trap (Seanor 1982). Polar groups may act as trapping sites and the chain folding also acts as traps. The charge carriers trapped at these trapping sites may be excited and contribute to the total conduction. PVP is a polar polymer. The polar side group moiety, pyrrolidone ring in PVP has carbonyl group of double bond. This group is attached to the main chain with an amide bond. The active groups of PVP are carbonyl groups and tertiary nitrogen atoms attached to the amide bond, which are in a reactive position at certain temperatures. The higher electronegativity of different atoms such as oxygen or nitrogen of PVP suggests the formation of CTC with ferrocene (Khare and Jain 1997). The side group of PVP (π electrons) may form CTC by donating the electrons to ferrocene or nitrogen atom may also be involved in CTC formation at certain higher temperatures after the side group rotation of PVP. Ferrocene is π -bonded nonpolar crystalline solid. Increase in ferrocene concentration in PVP increases the anisotropy (Khare and Chandok 1995a), which may be responsible for the creation of new trapping sites. Due to active π -bond it allows nuclear substitutional reaction which may result in the formation of charge transfer complexes. This agrees with the earlier findings (Khare and Srivastava 1992b; Khare et al 1993).

5. Conclusion

The current–voltage characteristics of ferrocene-doped PVP films show two regions corresponding to two different types of conduction. The conduction in low-field region is nearly ohmic while in moderate field region it is controlled by a Jonscher–Ansari modified P–F mechanism. The dependence of current and activation energy on the ferrocene concentration is attributed to charge transfer type of interaction.

References

- Adamec V and Calderwood J M 1978 *J. Phys. D, Appl. Phys.* **11** 781
- Carchano H and Vanentin M 1975 *Thin Solid Films* **30** 335
- Cassiers P M 1960 *Photogr. Sci. Engg.* **4** 199
- Chopra K L, Rastogi A C and Malhotra G L 1971 *Thin Solid Films* **24** 125
- Cresswell R A, Perlman M M and Kabayama M A 1972 *Dielectric properties of polymers* (ed.) F E Karasz (New York: Plenum Press)
- Dunitz J D and Orgel L E 1953 *Nature* **171** 121
- Dresner J and Comizzoli R B 1972 *Photogr. Sci. Engg.* **16** 43
- Dasaradhudu Y and Narsimha Rao V V R 1994 *Polymer Int.* **35** 329
- Emtage P R and Tantraporn W 1962 *Phys. Rev. Letts* **8** 267
- Frenkel J G 1938 *Phys. Rev.* **54** 647
- Jonscher A K 1967 *Thin Solid Films* **1** 213
- Jonscher A K and Ansari A A 1971 *Philos. Mag.* **23** 205
- Kasha M and Pullenan B P 1962 *Horizon in biochemistry* (Albert Szent Gyooryi Dedicatory Vol.) (New York: Academic) p. 364
- Khare P K and Srivastava A P 1992a *Indian J. Pure & Appl. Phys.* **30** 131
- Khare P K and Srivastava A P 1992b *Indian J. Pure & Appl. Phys.* **30** 326
- Khare P K and Ranjeet Singh 1994 *Polym. Int.* **34** 403
- Khare P K and Srivastava A P 1994 *Indian J. Pure & Appl. Phys.* **32** 14
- Khare P K and Chandok R S 1995a *J. Polym. Mater.* **12** 23
- Khare P K and Chandok R S 1995b *Indian J. Phys.* **A69** 545
- Khare P K and Jain S K 1997 *Indian J. Pure & Appl. Phys.* (to be published)
- Khare P K, Gaur M S, Alka Bajpai, Pandey R K and Srivastava A P 1993 *Indian J. Pure & Appl. Phys.* **31** 326
- Khare P K, Alka Bajpai and Srivastava A P 1993 *Indian J. Pure & Appl. Phys.* **31** 405
- Khare P K, Sandeep Shrivastava and Srivastava A P 1994a *Indian J. Phys.* **A68** 129
- Khare P K, Keller J M, Gaur M S, Ranjeet Singh and Datt S C 1994b *Polym. Int.* **35** 337
- Khare P K, Vishwakarma H L and Srivastava A P 1994c *Indian J. Phys.* **A68** 571
- Khare P K, Chandok R S, Neeraj Dubey and Srivastava A P 1994d *Polym. Int.* **35** 153
- Khare P K, Jain S K and Paliwal S K 1997 *Bull. Mater. Sci.* **20** 1001
- Kosaki M, Yoda M and Ieda M 1971 *J. Phys. Soc. Jpn* **31** 1598
- Kulshreshtha Y K and Srivastava A P 1980 *Thin Solid Films* **69** 269
- Lamb D R 1967 *Electrical conduction mechanisms in thin insulating films* (London: Methuen and Co. Ltd)
- Langyel G 1966 *J. Appl. Phys.* **37** 807
- Lilly A C and McDowell J R 1968 *J. Appl. Phys.* **39** 141
- Marikhin V A, Shitsker A I and Yastrebinskii A A 1965 *Sov. Phys. Solid State* **7** 352
- Mark P and Hartmann T E 1967 *J. Appl. Phys.* **39** 2163
- Mizutani T, Mitani K and Ieda M 1984 *J. Phys. D: Appl. Phys.* **17** 1477
- Mohana Raju K, Reddi P M and Murthy N M 1990 *Indian J. Pure & Appl. Phys.* **28** 47
- Mott N F and Gurney R W 1948 *Electronic processes in ionic crystals* (London: Oxford University Press) 2nd edn
- Narsimha Rao V V R, Subba Rao T and Narsing Das N 1986 *J. Phys. Chem. Solids* **47** 35
- Narsimha Rao V V R and Kalpalatha A 1987 *Polymer* **28** 648
- Palaska E J (ed.) 1970 *Encyclopedia of chemical technology* (New York: John Wiley) Vol. 21, p. 427
- Prescott F J 1965 *Drug & Cosmetic Indus.* **97** 621
- Perlman M M 1972 *J. Electrochem. Soc.* **119** 892
- Phadke Shireesh D, Sathianadan K and Karekar R N 1978 *Thin Solid Films* **27** L-11
- Pillai P K C, Gupta A K and Goel M 1980 *Macromol. Chem* **181** 951

- Rao C N R 1967 *Ultraviolet and visible spectroscopy* (London: Butterworth) p. 147
- Rehnbaker W B 1969 *IBM J. Res. Dev.* **13** 686
- Simmons J G 1967 *Phys. Rev.* **155** 657
- Sauthgate P D 1976 *Appl. Phys. Letts* **28** 200
- Seanor D A (ed.) 1982 *Electrical properties of polymer* (New York: Academic Press)
- Sinha H C and Srivastava A P 1979 *Indian J. Pure & Appl. Phys.* **17** 726
- Standen A and Scool A (eds) 1970 *Plasma extenders in kirk othmer*, in *Encyclopedia of chemical technology* (New York: Interscience) 1st ed., Vol. 10, p. 421
- Tan Y Y and Challa G 1976 *Polymer* **17** 739
- Van Turnhout J 1975 *Thermally stimulated discharge of polymer Electrets* (Amsterdam: Elsevier)
- Vanderschuren J and Linkens A 1978 *J. Appl. Phys.* **49** 786
- Vinod Dubey, Pavan Khare and Saraf K K 1990 *Indian J. Pure & Appl. Phys.* **28** 579
- Woodward R B 1952 *J. Am. Chem. Soc.* **74** 3458
- Yeargan Y and Taylor H L 1968 *J. Appl. Phys.* **39** 5600