Steady state conduction current of polyvinylidene fluoride film electrets

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Abstract : The steady state conduction current in solution grown polyvinylidene fluoride (PVDF) films (about 20 μm thick) was investigated with different poling fields (10–100 kV cm^{-1}) as a function of temperature in the range 40–80°C. The steady state current showed a strong dependence on temperature. To identify the possible mechanism of conduction, current *versus* square root of field characteristics were drawn with aluminium and silver electrodes. The current-electric field characteristics show two regions of conduction with a slope of curve 1.2–1.5 at lower and with a slope 1.97–2.00 at higher fields. The current-electric field characteristics are analyzed and quantitative information about the transport parameters is derived. The result of current-electric field measurements on PVDF film electrets have been interpreted to show that the Richardson mechanism alongwith space-charge limited conduction is the controlling mechanism. The other mechanism for the non linear behaviour *e.g.* field assisted injection or Poole-Frenkel (PF) mechanism is excluded.

Keywords : Polyvinylidene fluoride, Poole-Frenkel and Richardson-Schottky effect, space charge limited conduction.

PACS Nos. : 77.84.Jd, 77.22.Jp, 77.22.Gm

1. Introduction

The study of electrical conduction is of considerable significance from two major points of view-firstly, for its own sake, because charge transfer characteristics are of fundamental interest and secondly for the information such studies can provide on the nature of electrical contacts which may have a great influence on the measured electrical properties [1]. Steady state conduction in polymers has been extensively studied in the last decade [2–8] since it provides an understanding of charge carrier,

molecular motion, mobility of sub molecules and chemical and physical structure of polymers. It arises due to both electrons and positive ions (mainly protons).The glass transition temperature (T_g) is usually the dividing line between protonic (above T_g) and electronic (blow T_g) conductivities.

Study of electrical conductivity in polymers becomes important due to their utility as insulators since dielectric loss is associated with dc conductivity [9]. In polymers, the dielectric movement of charge carriers has received much attention because of its importance in science and technology which includes leakage current in electrical insulation [10], charge injection from electrodes which may lead to premature breakdown [11], various forms of photoconduction and of transient pulse drift and induced conductivity [12]. The study of steady state conduction provides an understanding of charge carrier transport, molecular motion, mobility of submolecules and chemical and physical structure of polymers. It arises due to both electrons and positive ions (mainly protons). The glass transition temperature (T_g) is usually the dividing line between protonic (above T_g) and electronic (below T_g) conductivities. Study of dc conductivity in polymers becomes important due to their utility as insulators, since dielectric loss is associated with dc conductivity [13].

Polyvinylidene fluoride (PVDF) is semicrystalline polymer with exceptional mechanical and electrical properties. For technical application this polymer is popular mainly for its strongly piezo and pyro electricity [14,15]. Although the basic repeat unit is chemically simple ($-CH_2-CF_2-$), the physical properties are in a great extent variable. Besides the nanocrystalline (amorphous) phase there are known three crystal forms designated as I, II and III, which are all stable at room temperature [16]. The present paper, describes the electrical transport in polyvinylidene fluoride samples. The aim is to find out the possibility of the existence and nature of distribution of traps and to know the role played by the carriers injected from the electrodes and volume generated the steady state conduction studies have been undertaken using unconventional electrode geometry.

2. Experimental details

Commercial polyvinylidene fluoride (PVDF) used in the present investigation has been procured from Glaxo Laboratory, Bombay. The isothermal immersion technique was utilized for preparing the films of polyvinylidene fluoride. The method of preparation of films, the geometry of configuration of the electrodes the measurement of thickness and steady state currents has been the same as reported earlier [17,18]. The sample polarization and steady state current measurements have been carried out in a cell using an assembly which is dry, rigid and well established. The cell and assembly have the following properties : (i) high insulating resistance, (ii) freedom from picking up of spurious potentials and induced charges due to physical motion of the system and (iii) negligible leakage current and less microphonic. To achieve the required degree of precision every consideration of perturbing parameters was taken into account while taking the measurement. All the efforts have been made to minimize the

any type of experimental errors. The steady state conduction current was recorded by a 600C Keithley electrometer which was carefully shielded and grounded to avoid ground loops or extraneous electrical noise. The electrometer is specially designed to measure very small direct current, low DC potentials from high impedence source, small charges and high resistance. The field was applied from a high voltage unit EC 4800D. The temperature of the sample was recorded with a calibrated thermocouple attached in close neighbourhood of the sample. The sample thickness was of the order of 20 µm.

3. Results and discussion

The steady state conduction current-field (I-E) characteristics of polyvinylidene fluoride films (20 µm thick) at temperature (ranging 40–80°C) for Al-Al and Ag-Ag electrode combinations are show in Figures 1 and 2. The increment in the current was approximately similar throughout the studied range of temperature. Figures 3 and 4 exhibit the conduction current-temperature plots with different poling fields (*i.e.* 10, 25, 50, 75 and 100 kV/cm) for Al-Al and Ag-Ag electrode systems. The magnitude of current was found to be higher in Ag-Ag electrode system. The I-E curves shows two regions of conduction *i.e.* ohmic conduction for electric fields below 30 kV/cm and a non ohmic conduction at higher fields. There is a departure from straight line and knees appear in all the curves. The slop value (*m*) in the lower field region lies between 1.2–1.5 and 1.97–2.00 at higher field strength. 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. At lower fields, the injection of carriers from 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 thermally created carrier density, however at sufficiently higher fields, the carriers are mainly due to injected space charges [12–19].

Various mechanisms such as Schottky emission [20], Poole-Frenkal effect [21], space charge limited conduction [22], tunneling [23] and hopping conduction [24] have been proposed to explain the electrical transport in thin insulating films. In most cases either Schottky emission or the Poole-Frenkel effect is the controlling process. The observed relation between the current and voltage points to a conduction mechanism in which the charge carriers are released by thermal activation over a coulombic potential barrier that decreases with the applied electric field. The physical nature of such a potential barrier can be interpreted in two basic ways : (i) barrier between the electrodes and dielectric taking the classic image force into consideration (Schottky emission) and (ii) barriers due to trapping centres in the dielectric Poole-Frenkel (P-F) effect.

While the expression for the current density in Schottky emission is

$$J_{SR} = A^*T^2 \exp(-\phi/kT)\exp[e/kT(eE/4\pi\varepsilon)^{1/2}]$$ (1)
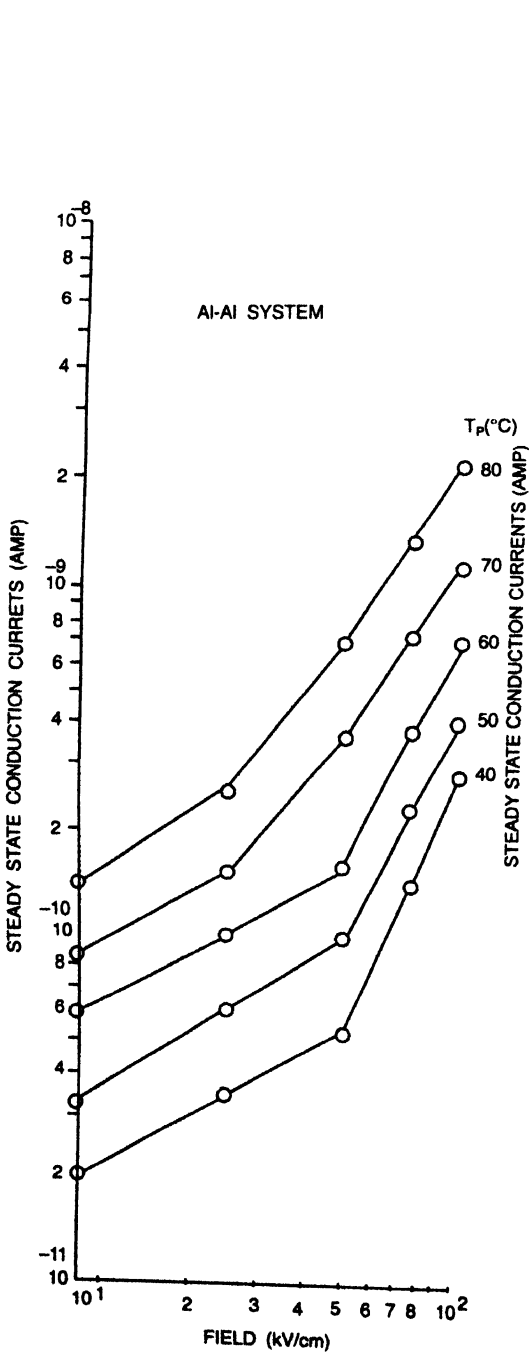
Figure 1. log *I versus* field curves for polyvinylidene fluoride samples at different temperatures (*i.e.* 40, 50, 60, 70 and 80°C) for Al-Al system.
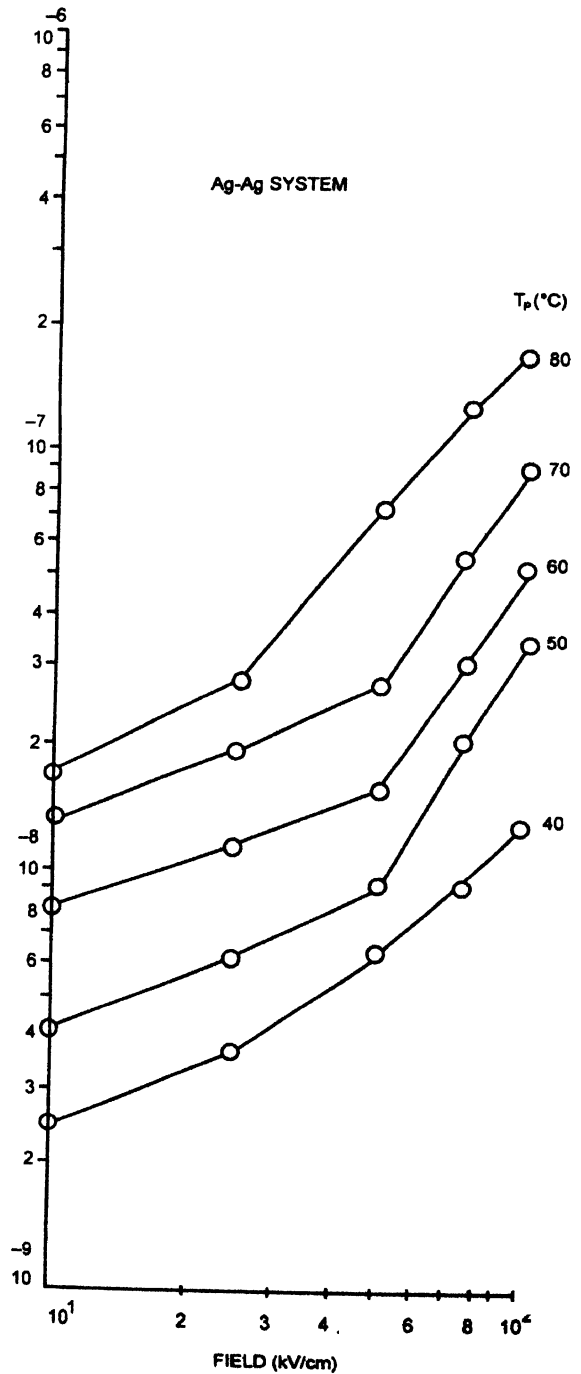
Figure 2. log *I versus* field curves for polyvinylidene fluoride samples at different temperatures (*i.e.* 40, 50, 60, 70 and 80°C) for Ag-Ag system.

where J is the current density the electronic charge and E the field applied at T and A^* and ϕ are the Richardson constant and potential barrier, respectively at the metal-insulator interface in the absence of a field, the current-fields relationship in Poole-Frenkel
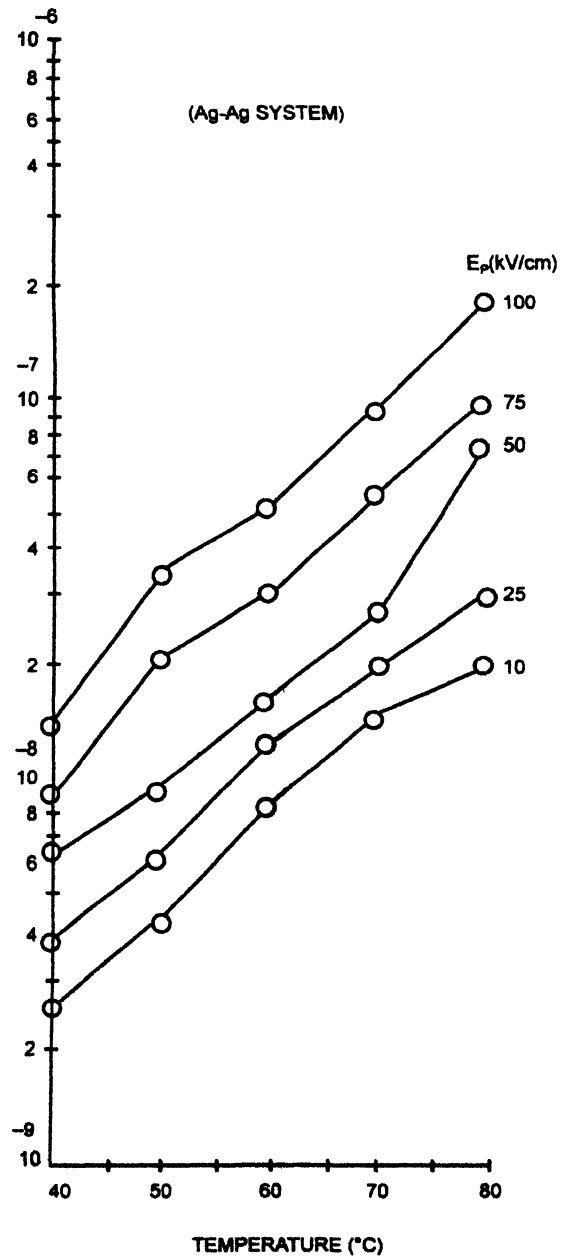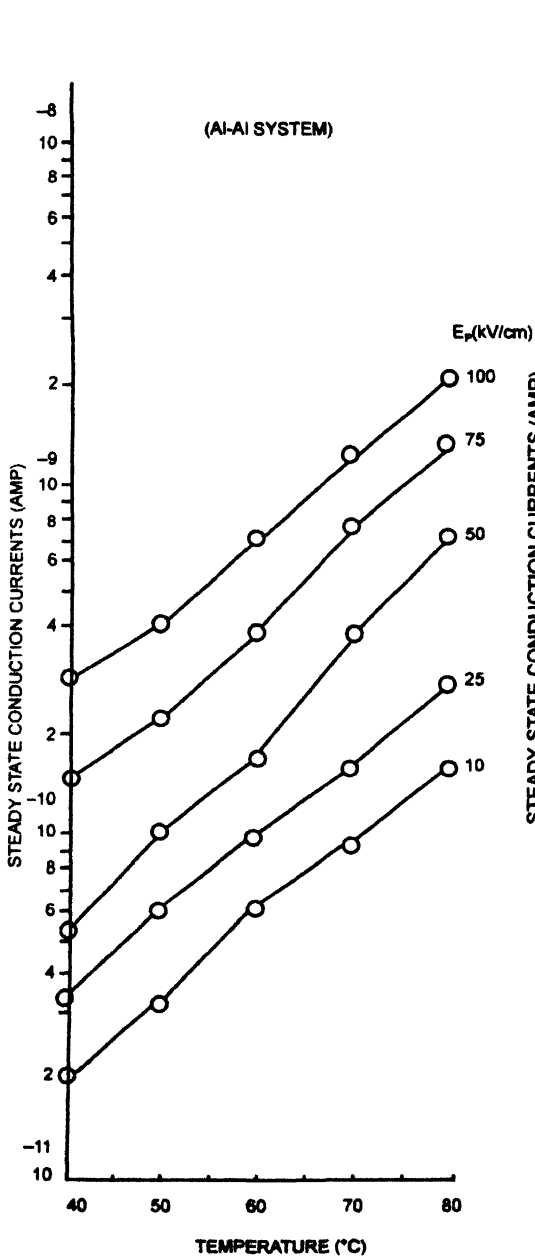

Figure 3. log I *versus* temperature curves for polyvinylidene fluoride samples at different poling field (*i.e.* 10, 25, 50, 75 and 100 kV/cm) for Al-Al system.

Figure 4. log I *versus* temperature curves for polyvinylidene fluoride samples at different poling field (*i.e.* 10, 25, 50, 75 and 100 kV/cm) for Ag-Ag system.

(P-F) mechanism is given by

$$J_{PF} = CE\exp(-\phi/2kT)\exp[e/kT(-eE/\pi\epsilon)^{1/2}] \tag{2}$$

where C is the constant independent of field and temperature and ϕ is the barrier height.

To determine the actual conduction mechanism, the value of β-factor calculated from the slope of the plots log I *versus* $\sqrt{E}$ (Figures 5 and 6), were compared with

Figure 5. log I *versus* $\sqrt{\text{field}}$ curves for polyvinylidene fluoride samples at different temperatures (*i.e.* 40, 50, 60, 70 and 80°C) for Al-Al system.
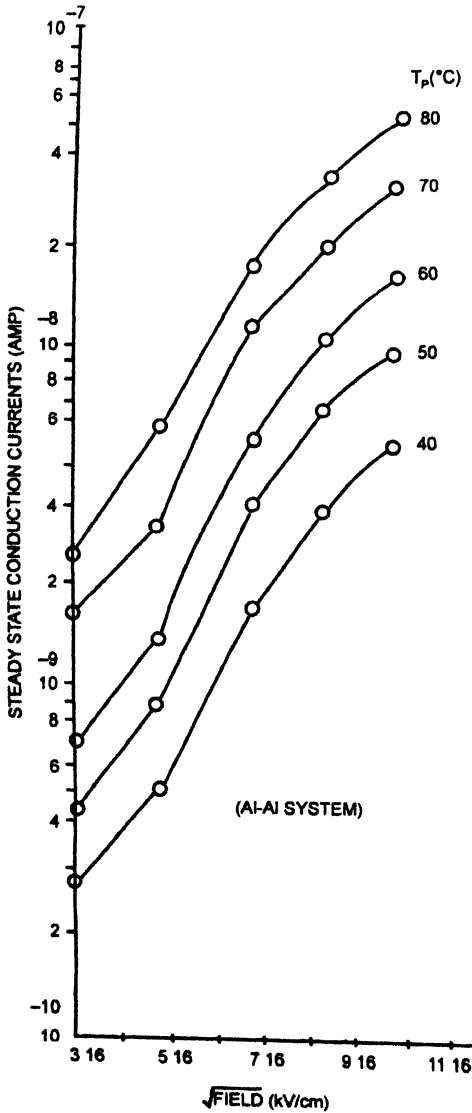
Figure 6. log I *versus* $\sqrt{\text{field}}$ curves for polyvinylidene fluoride samples at different temperatures (*i.e.* 40, 50, 60, 70 and 80°C) for Ag-Ag system.
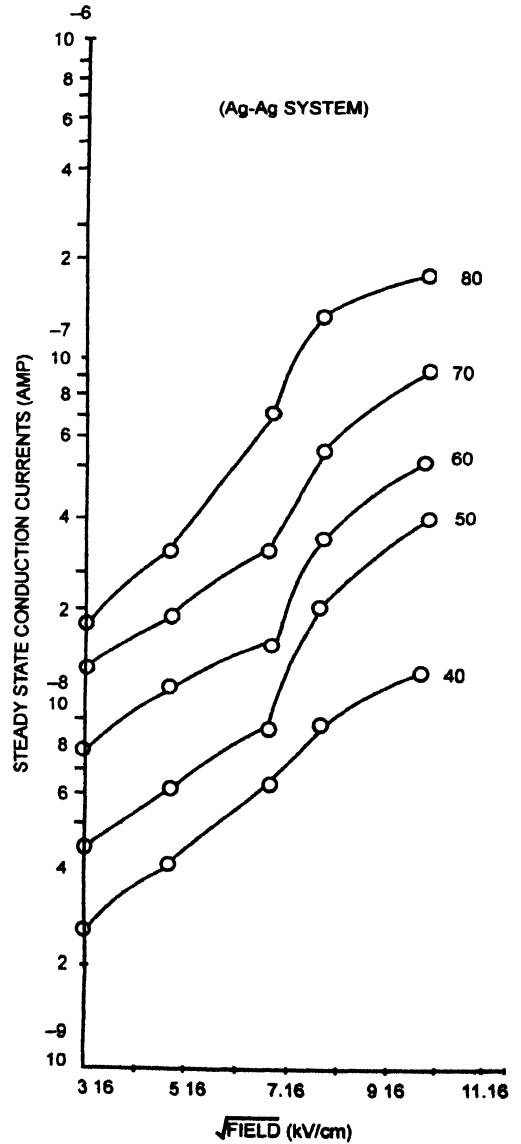
the theoretically calculated value of β, based on premise that one of the mechanisms was operating. The experimental values of β (Table 2), in the present case were close

Table 1. Slope (m) value.

Temp. (°C)	At lower fields		At higher fields	
	Al-Al	Ag-Ag	Al-Al	Ag-Ag
40	1.1	1.3	2.00	1.98
50	1.2	1.2	1.97	1.97
60	1.4	1.5	1.99	1.95
70	1.5	1.1	1.96	2.00
80	1.3	1.4	1.98	1.96

Table 2. Theoretical and experimental value of β_{RS} and β_{PF}.

Temp. (°C)	β_{RS} (Theo.) $\times 10^{-4}$	β_{RS} (Expt.) $\times 10^{-4}$	β_{PF} (Theo.) $\times 10^{-4}$	β_{PF} (Expt.) $\times 10^{-5}$
40	8.46	9.87	16.92	8.79
50	8.17	9.67	16.34	7.66
60	7.85	8.95	15.70	6.82
70	7.68	8.93	15.36	5.99
80	7.32	8.11	14.64	5.24

to the theoretically arrived values of β_{RS} based on the premise that RS mechanism was the particular mechanism that was operating. Jonscher and Ansari [25] pointed out that instead of basing the distinction between the two mechanisms, on the magnitude of β, it should be based on the studies taking an asymmetric M-I-M structure with two electrodes of different work functions. The current in the case of Schottky effect will be symmetrical when the polarities are reversed. On the otherhand it will remain particularly unchanged in the case of PF effect, since it does not depend on potential barrier at the interface. However, mere compatibility between β_{exp} and β_{theo}. Values can not be taken as evidence for deciding the actual conduction mechanism, since β values depends on a number of experimental conditions. It localized states (traps) are distributed throught in an insulator then the band edges are in general severely distorted at the electrode insulator interface. A peculiar effect called the barrier layer effect is found at the contact between the metal and insulator. These layers at the junction with metal electrodes or with other insulators when their contact potentials are different. The differences in contact potentials indicate that the binding energies for electrons are different. The electrons pass through such contacts from the sides, where the energy is high, to the side where it is low curtil. That side has acquired charges sufficient to balance out the difference in contact potential. The conduction current is differ in Al-Al and Ag-Ag electrode systems. This shows the effect of the material of the electrodes on the conduction current of the sample sandwiched between them. The values of conduction current seem to be controlled by the effective work function for metal-insulator-metal interfaces. These observation are consistent with the proposed RS

mechanism and suggest that in the higher field region, the conduction is governed by RS effect, in which carriers are injected over the field-dependent polymer electrode interfacial barrier.

The modified P-F mechanism predicts an activation energy which decreases with
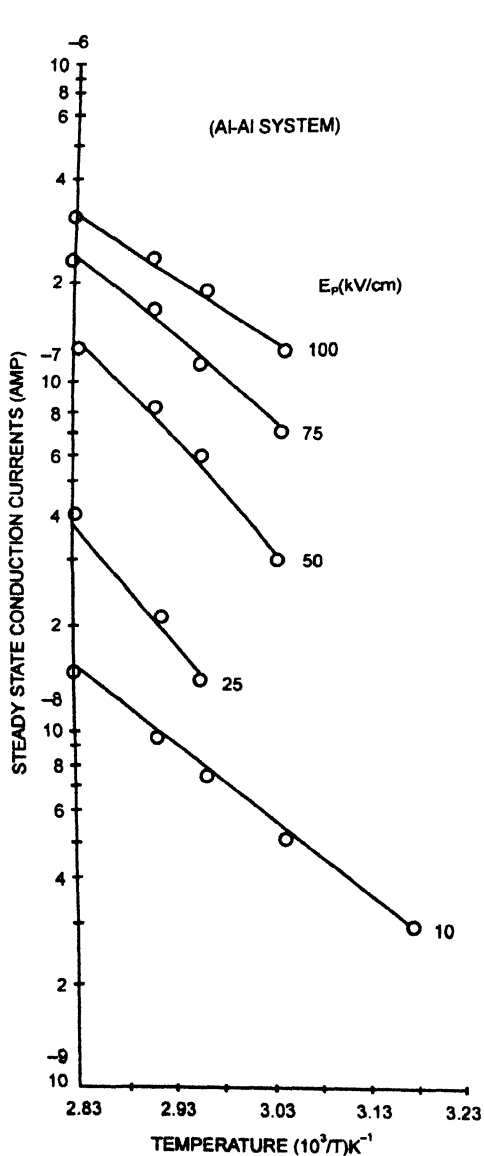

Figure 7. log *I versus* temperature (1000/*T*) K^{-1} curves for polyvinylidene fluoride samples at different poling fields (*i.e.* 10, 25, 50, 75, and 100 kV/cm) for Al-Al system (initial rise curve).

Figure 8. log *I versus* temperature (1000/*T*) K^{-1} curves for polyvinylidene fluoride samples at different poling fields (*i.e.* 10, 25, 50, 75, and 100 kV/cm) for Ag-Ag system (initial rise curve).
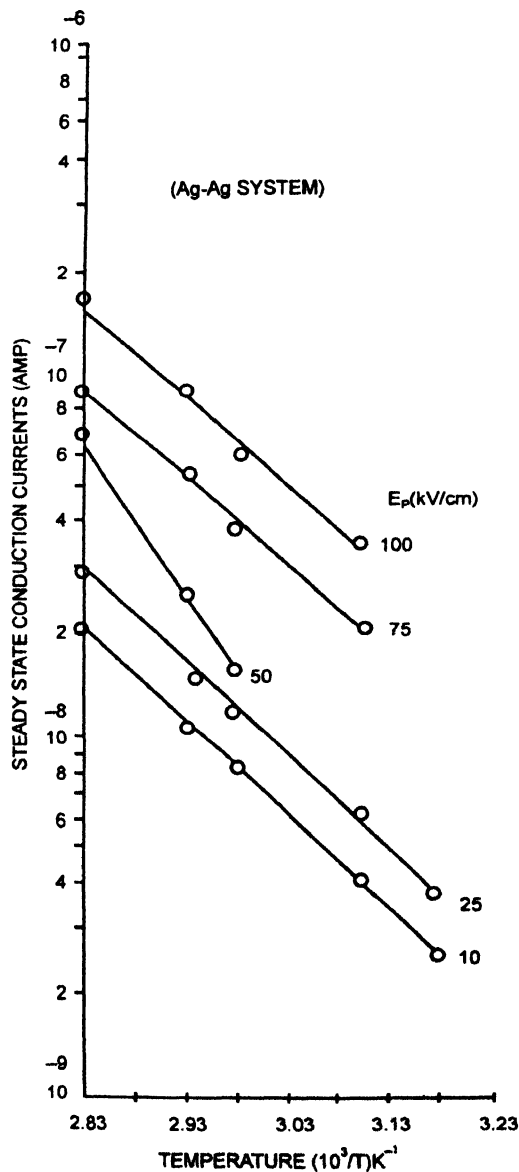
the square root of the applied field. The activation energy found to be independent of the applied field suggesting that the potential barriers are higher due to applied field and supports RS mechanism. This suggests that the applied field interacts with the field of the ionozable center so that the energy required for an electron to escape in a direction opposite to the field direction (*i.e.* in the field assisted or forward direction) is reduced by an amount. As the activation energy values obtained in the present case is high, therefore, the possibility of charge carrier species inside the polymer bulk ionic in nature can not be ruled out. The injection of charge carriers into the bulk of the material is found to give rise to a current flow, which is limited by space charge effects. In the higher field conduction region *i.e.* region II, the I-E characteristics have a slope of about 2 and it is also suggested that the region may be governed by space charge limited currents. In the present case film thickness was high, the conduction mechanism by tunneling is ruled out.

The non-linearity may be due to space charge build up giving rise to non-uniformity of the field distribution between the electrodes. The value of slope coefficients (~2) of I-E characteristics are the typical proofs for the continuous trap level distribution in the band gap of semi insulating material. The defects and impurities can govern the conduction mechanism and also act as trapping centers and get populated by injected charge carriers from the electrodes. Charge carriers from these localized levels are thermally excited to their respective transport bands causing thermally activated ohmic conduction. Depending upon the population of these levels and their respective transport bands, the conduction may charge from ohmic to Schottky emission. Surface states are one of the factors which affect injection phenomena. Donor like surface states located between the conduction band and Fermi level, after contact, tend to bend the band edge towards the Fermi level, making electron injection from the metal much easier. On the ortherhand, accepter like surface states located between the valence band and Fermi level act as a stepping stone for electrons injected from the valence band of the insulator to the metal, thus enhancing hole injection from the metal. The amount of charge injected depends on the barrier height at the metal-polymer interface [26]. The order of current is different for different electrode system. In addition the activation energy, of the charge carriers calculated from the slope of log I *versus* $10^3/T$ plots are found to be independent of the field which further supports the suggested RS mechanism of conduction.

Table 3. Activation energy for Al-Al and Ag-Ag system with different field values.

Field (kV/cm)	Activation energy (eV)	
	Al-Al system	Ag-Ag system
10	0.61	0.62
25	0.63	0.64
50	0.64	0.65
75	0.65	0.67
100	0.66	0.68

The introduction of deep trapping centers in the solid can result in a higher power dependence of current on electric field than the square law relation. It is evident that as more and more electrons are injected into a solid, the traps will gradually get filled up and eventually no more injected electrons are trapped. Lampert [27] considered a model containing a set of defect states at a single discrete energy level. The main regions of the log current-log electric field curve that he predicted may be readily understood by studying the variation in position of the Fermi level with applied electric field. The lowest region of the curve corresponds to the situation where the injection of excess carriers is negligible. Accordingly there is no significant departure of the Fermi level from its value and provided there are free electrons in the solid at thermal equilibrium, ohmic law is observed at low voltages. The first threshold electric field is that where the ohmic current crosses over to being limited by space charge. The second electric field threshold is that which corresponds to the Fermi level approaching the discrete level of trapping states. That is, once the trap filled voltage is reached all the injected space charge enters the transport band, thus causing a steep rise in current-electric field characteristic.

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