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Electrical conductivity of ferric chloride-doped poly(acrylic acid-divinylbenzene)

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Polyacrylic acid divinylbenzene was doped with ferric chloride in non-aqueous medium and the effect of concentration of dopant salt on the electrical conductivity of polyacrylic acid divinylbenzene was investigated. The electrical conductivity of pure and doped polymer containing various percentages of iron was measured as a function of temperature (298–383 K) and applied voltage. A linear relationship of current for the entire range of applied voltage (50–500 V) at ambient temperatures suggest ohmic conduction of charge carriers. The electrical conductivity of 1.04, 1.46 and 2.85% ferric-polyacrylatedivinylbenzene at 333 K is 1.2×10^{-12}, 4.7×10^{-12} and 4.1×10^{-10} mho/cm, respectively. The increase in conductivity is facilitated by complex formation between carboxylic pendent groups of polymer matrix and ferric ions. Activation energies (-0.527 to -0.436 eV) are lower in the temperature range $298 \leq T \leq 353$ K but in the higher temperature region $353 \leq T \leq 383$ K the values tend to increase (0.842 to 1.585 eV).

Introduction

The polymers are traditionally accepted as electrical insulators. The discovery of conductive doped organic polymers has generated substantial research interest among chemists and physicists. The conductive polymers being inexpensive and light weight materials find wide applications in the field of solid state such as electrochemical displays [1, 2], batteries [3, 4], transistors [5, 6] and electrochemical sensors [7, 8].

A number of investigations have been reported to understand the conduction mechanisms in metallopolymers with respect to temperature, dopant concentration, time and irridiation [9, 10]. Many attempts have been made to produce and control conduction properties of polymers by introducing radicals or metal ions in polymer matrix [11, 12]. The properties of doped polymers are being investigated extensively, not only to study degradation [13–15], conductance, dielectric behaviour [16] and many other properties but also to understand the interaction of metal ions with polymeric materials [17]. The introduction of metal ions in the polymer matrix can make polymers stable, hard, insoluble in most of the solvents and influence the electrical properties.

In the recent years a number of metal doped conducting polymers were synthesised and found to possess good long term stability. Khwaja and co-workers analysed the conduction mechanism in transition metal polyacrylate and polymethacrylate by measuring their electrical conductivity as a function of temperature, concentration of dopant and the radiation dose. It has been established that in nickel-polymethacrylate, Ni^{2+} forms complex with carboxylic groups and exhibits semi-conductor behaviour [18]. Similarly metal polyacrylate complexes are also formed and are responsible for electrical conduction [19]. The presence of metal ions as impurity in the polymer matrix change the polymer properties.

In view of the growing interest to produce conducting polymers having high stability, polyacrylic acid divinylbenzene has been doped with ferric chloride. Iron polyacrylate samples containing 1.04, 1.46 and 2.85% iron (w/w) were prepared to study electrical conduction behaviour of iron polyacrylate.

Experimental

Synthesis of Iron(III) polyacrylatedivinylbenzene (Fe-PADVB)

Ferric chloride, anhydrous (E. Merck), methanol 99.5% (E. Merck) and polyacrylic acid divinyl benzene (Fluka) were used.

1.50 g of polyacrylic acid divinylbenzene (PADVB) was soaked in 50 ml of methanol for half an hour and 1.0 g of Iron(III) chloride dissolved in methanol was added to PADVB and stirred for 6 h at room temperature. The excess ferric chloride solution was removed by filteration and iron doped polymer was washed several times with methanol. The orange-brown iron doped PADVB was dried under vacuum. The amount of iron present in PADVB was estimated by atomic absorption and was 2.85%. Fe-PADVB samples containing 1.04 and 1.46% (w/w) iron were also prepared. A number

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of efforts were made to prepare Fe-PADVB containing more than 2.85% iron but did not succeed. It seems that PADVB retains only a limited amount of ferric chloride and the excess of it is eliminated by repeated washings with methanol. Doped PADVB samples were dried under vacuum and stored in a dessicator.

Electrical conductivity measurements

Circular shaped pallets of Fe-PADVB having mass 0.17–0.21 g, diameter 1.3 cm and thickness 0.14–0.16 cm were prepared by Beckman dye RIIC model KB-0112 (1.3 cm diameter). The pressure used to prepare pallets was 45 KN. All samples were dried under vacuum for 24 h. before recording current data. Auto ranging picometer model 485 (Kiethley) was used for current measurements. The circuit diagram, the technique to measure current (Ampere) in samples and the calculations of conductivity are already cited in literature [18].

Results and discussion

PADVB has been doped with ferric chloride to investigate conducting behaviour of Fe-PADVB. A comparison of the conductivity of pure and doped PADVB has been made. The current-voltage relationship, concentration and temperature dependence of conductivity, activation energies and possible mechanism of conduction are discussed.

Current-voltage characteristics

Variation of electric current with applied voltage (50–500 V) in the temperature range 298–383 K for 2.85% Fe-PADVB is shown in Fig. 1. The figure shows that there is a linear relationship between current and voltage. A similar behaviour is also observed for 1.04 and 1.46% Fe-PADVB samples, however, maximum current flow is recorded for 2.85% Fe-PADVB (Fig. 1). The maximum current flow is 8.03×10^{-7} Amp at 333 K but further increase in temperature lowers the flow. A linear relationship of current for the entire range of applied voltage at ambient temperatures suggests ohmic conduction mechanism [20]. The possibility of Pool Frenkel type conduction mechanism can safely be excluded as the current-voltage dependence does not follow $I \propto \exp(\beta V^{1/2})$ expression. Similarly the tunneling mechanism can also be ruled out because samples used were thick and field was relatively low. Another evidence in favour of ohmic conduction mechanism is obtained from $\ln(I)$ vs $\ln(V)$ data (Fig. 2).

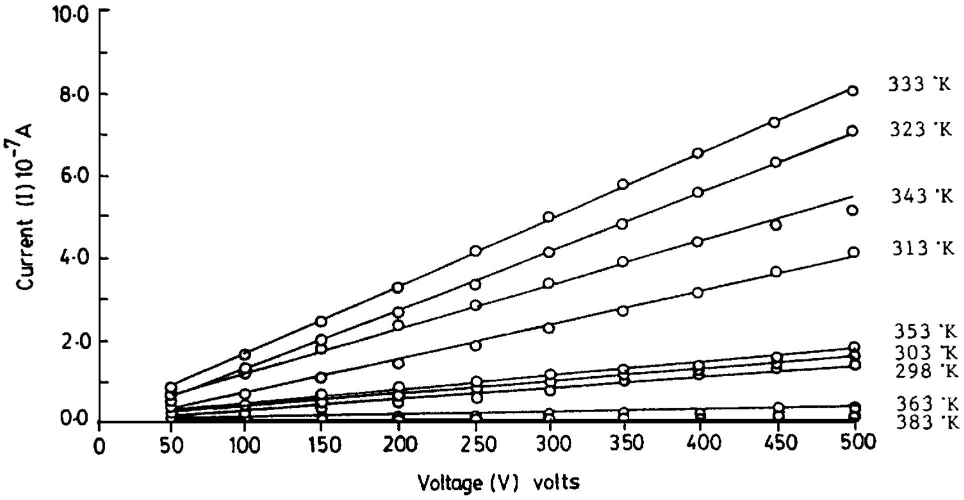

Figure 1 Current-voltage relationship of 2.85% Fe-PADVB.

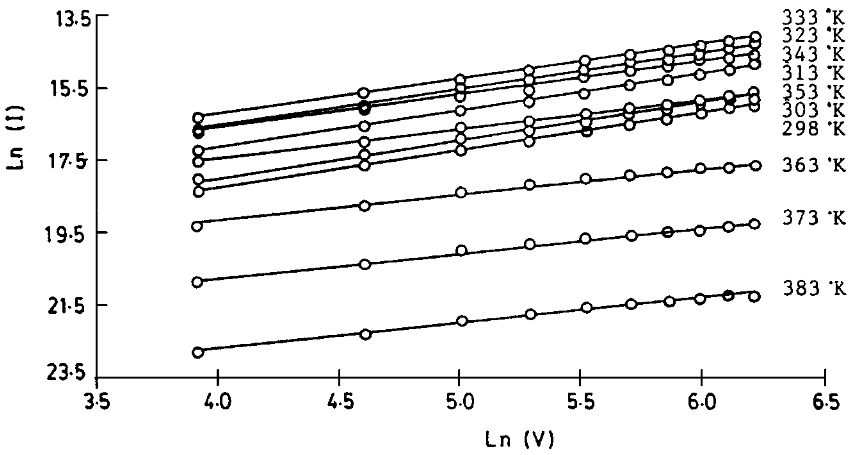

Figure 2 $\ln(I)$ and $\ln(V)$ relationship of 2.85% Fe-PADVB.

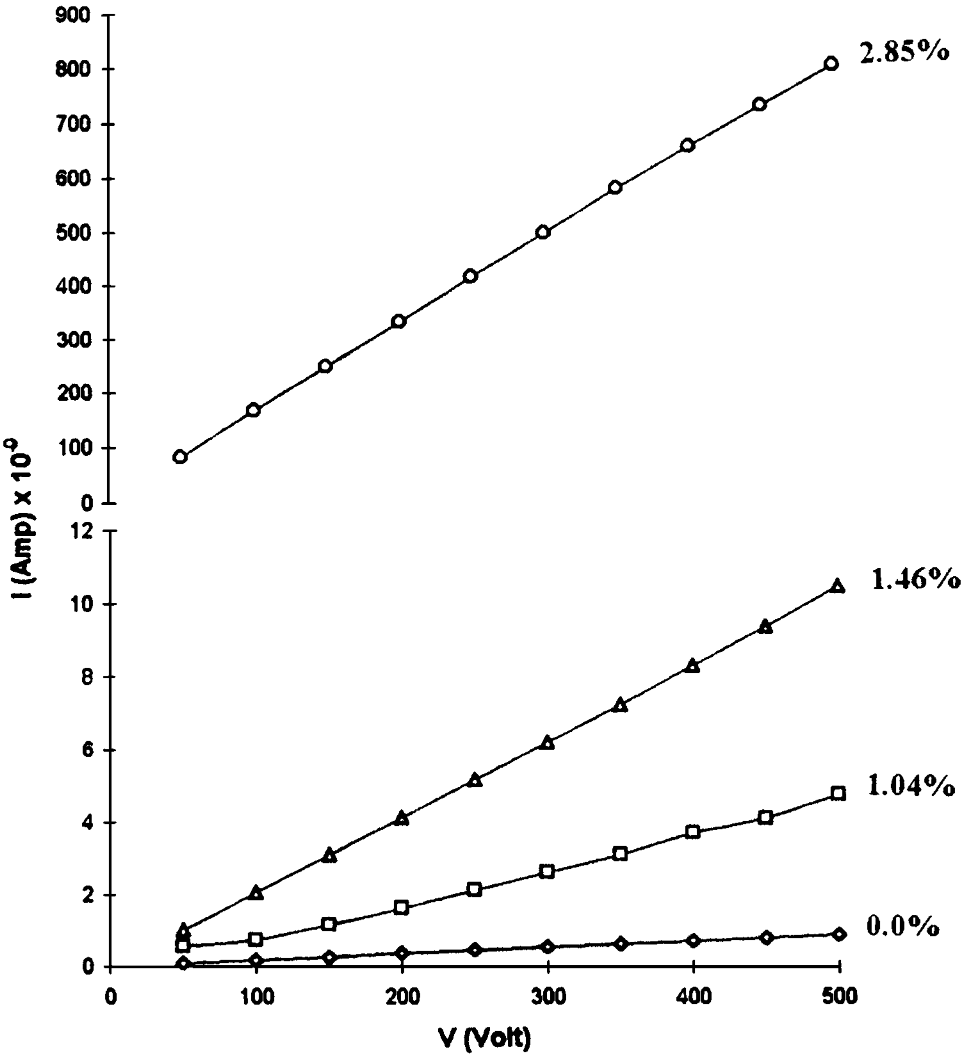

Figure 3 Current-voltage characteristics of 0.0, 1.04, 1.46 and 2.85% Fe-PADVB at 333 K.

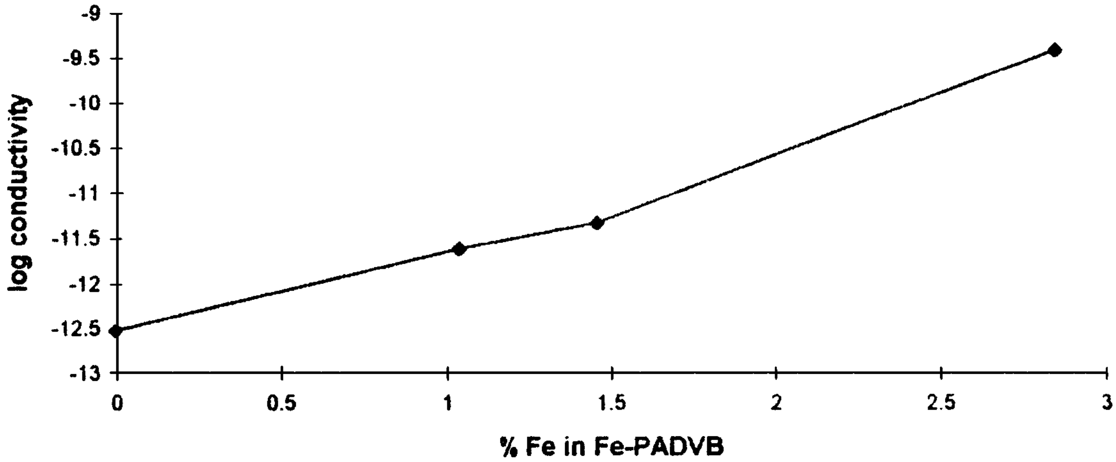

Figure 4 Effect of dopant concentration on log electrical conductivity of PADVB.

Concentration dependence of conductivity

The effect of iron concentration on electrical conductivity was investigated by measuring current flow in Fe-PADVB samples containing 1.04, 1.46 and 2.85% iron. It has been observed that electrical conduction in doped polymer is strongly dependent on concentration of iron.

The current-voltage relationship of PADVB, doped with varying amounts of iron indicates that this relationship is linear for all concentrations of iron and the current flow is influenced by the iron percentage in the polymer matrix (Fig. 3). Fig. 4 shows concentration dependence of conductivity at 333 K. Initially there is a small increase in conductivity when concentration of iron is changed from 1.04 to 1.46% but when the concentration is raised to 2.85%, a sharp increase in conductivity is observed. The electrical

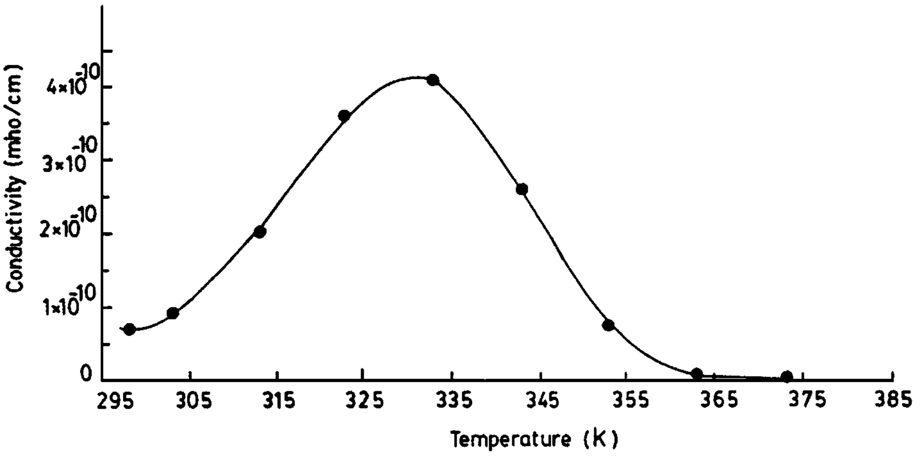

Figure 5 Electrical conductivity (σ) vs temperature for 2.85% Fe-PADVB.

conductivity of 1.04, 1.46 and 2.85% Fe-PADVB at 333 K is 1.2×10^{-12}, 4.7×10^{-12} and 4.1×10^{-10} mho/cm, respectively. The increase in iron content increases the effective free volume in the polymer matrix and facilitates the mobility of ions or molecules. The phenomena of conductivity in doped polymer may be explained due to complex formation between carboxylic groups of polymer and metal ions [21]. When concentration of metal is about 1% it involves lesser number of carboxylic groups in bonding and the gap between metal complex centers is more. This gap decreases with increase in concentration of iron as more and more carboxylic pendent groups become coordinated to the metal. The chain of coordinated complexes in polymer matrix thus facilitates electrical conduction.

Temperature dependence of conductivity

The electrical conductivity of Fe-PADVB is influenced by increase in temperature. The conductivity as a function of temperature for 2.85% Fe-PADVB (Fig. 5) shows that conductivity initially increases in the temperature range 298–333 K with a positive slope. Maximum conductivity is observed at 333 K and beyond this there is a decrease in conduction.

This behaviour indicates development of discrete phases and their conducting or insulating character in polymer texture. The initial increase in conductivity with increase in temperature may be due to the formation of local ordered regions in the otherwise disordered amorphous matrix of polymer [22]. These local ordered regions degrade on further heating and hence conductivity is decreased.

A comparison of temperature dependence of conductivity of Fe-PADVB samples having different iron concentrations is shown in Table I. It is notable that 1.04% Fe-PADVB shows maximum conductivity at 353 K while 1.46 and 2.85% Fe-PADVB at 333 K. This phenomena is explained on the basis of lesser complex formation in 1.04% Fe-PADVB because there is not sufficient concentration of iron avaible, to involve most of the carboxylic groups of the polymer in complex formation. Thus the number of ligand metal complex centers are less, scattered and the gap between them is more and as a result higher temperature is required to activate charge carriers.

TABLE I Concentration and temperature dependence of Conductivity (mho/cm) for Fe-PADVB

Temp (K)	1.04% Fe	1.46% Fe	2.85% Fe
313	5.9×10^{-13}	1.5×10^{-12}	2.0×10^{-10}
323	1.2×10^{-12}	4.3×10^{-12}	3.6×10^{-10}
333	2.5×10^{-12}	4.7×10^{-12}	4.1×10^{-10}
343	4.4×10^{-12}	2.7×10^{-12}	2.6×10^{-10}
353	5.6×10^{-12}	1.6×10^{-12}	7.6×10^{-11}
363	4.0×10^{-12}	2.0×10^{-13}	1.2×10^{-11}
373	2.1×10^{-12}	9.8×10^{-14}	2.3×10^{-12}
383	8.9×10^{-13}	5.5×10^{-14}	3.2×10^{-13}

Time relaxation phenomena in doped polymer was also studied. When the doped polymer is kept at a constant temperature, the electric current passing through the sample decreases with increase of heating time. Initially there is a linear but sharp decrease in current flow but with increase of heating time, a gradual decrease is observed (Fig. 6).

Activation energies for Fe-PADVB were calculated from the plots of $\ln \sigma$ vs $1/kT$. The observed linear dependence of $\ln \sigma$ upon the $1/kT$ can be expressed by the Arrhenius equation.

$$\sigma = \sigma_0 \exp(-E_a/kT)$$

where σ is conductivity, σ_0 is a constant, E_a is activation energy, k is Boatsman's constant and T is the absolute temperature. The Arrhenius equation is obeyed with a constant activation energy in the low temperature range $298\,\text{K} \leq T \leq 353\,\text{K}$ for 1.04% Fe-PADVB (Fig. 7) but at higher temperature range Arrhenius equation is not obeyed. Activation energies for Fe-PADVB are given in Table II.

A deviation from Arrhenius behaviour and temperature dependence of conductivity above a critical temperature (T_c) may be explained on the basis, that increase in thermal energy may lead to (i) breaking of bonds between metal and pendent groups of polymer matrix (ii) structural changes by weakening of bonds between the atoms (iii) increase in lattice vibrations.

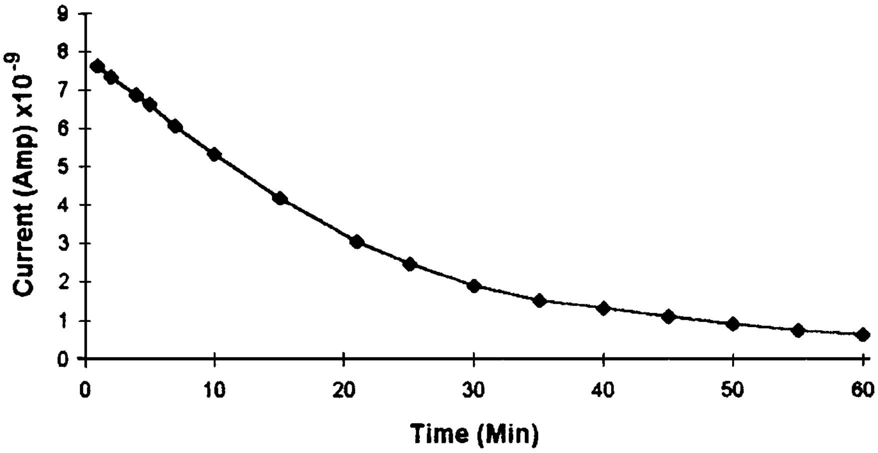

Figure 6 Current-time relationship of 1.04% Fe-PADVB at 333 K and at electrical potential of 230 V.

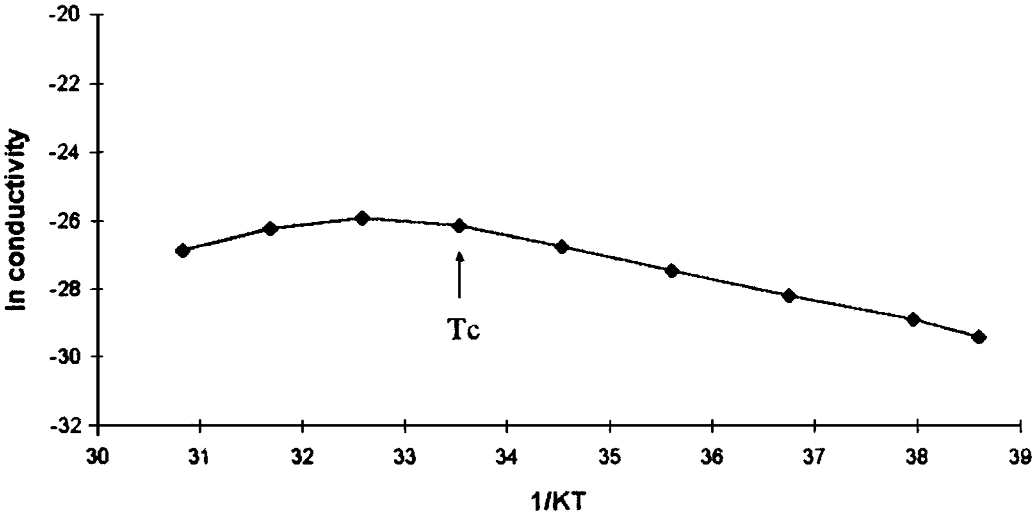

Figure 7 Relationship between ln(σ) and $1/kT$ for 1.04% Fe-PADVB.

TABLE II Activation energies (E_a) of Fe-PADVB at low and high temperatures

% Iron in Fe-PADVB	E_{a_1} (eV) in low temp range	E_{a_2} (eV) in high temp range
1.04	−0.527 (298–353 K)	0.842 (353–383 K)
1.46	−0.462 (298–353 K)	1.321 (353–383 K)
2.85	−0.436 (298–333 K)	1.585 (333–383 K)

The higher activation energies in high temperature regions support the above findings.

Conclusions

1. Ferric chloride doped PADVB is many folds more conductor than pure PADVB. This may be due to donor acceptor type complex formation.

2. Fe-PADVB exhibits ohmic conduction.

3. The electrical conductivity has strong concentration and temperature dependence.

4. The conductivity varies non-monotonically with rise in temperature.

5. Activation energies are lower in the temperature range 298–353 K but beyond 353 K the values are high.

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