

Transport and structural properties of polyaniline doped with monovalent and multivalent ions

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(Received 16 September 1996)

Sharp changes in the transport and structural properties were noticed when a pH-dependent study of polyaniline (PAN) with monovalent (Cl^-) and multivalent (PO_4^{3-}) ions was carried out. Scanning electron micrographs (SEM) of these samples reveal that the sharp changes induced by doping are more prominent at the pH where the transformation of the PAN lattice takes place. A channel formation has been observed at a pH of 3.0 in the case of HCl and 2.5 in the case of H_3PO_4 doping, with flattening of the structure. The d.c. conductivity of the samples in this pH range has been measured in the temperature range 77–300 K. The d.c. conductivity data have been analysed in the light of existing theoretical models. Mott's 3D variable range hopping (VRH) is the mechanism responsible for charge transport at low temperatures for HCl as well as H_3PO_4 doped samples, whereas a deviation is observed at higher temperatures for all the HCl doped samples. However, lightly doped H_3PO_4 samples give a $T^{-1/4}$ dependence. At a moderate doping level (pH 2.5), a deviation from 3D VRH is observed at higher temperatures, indicating thereby a temperature and composition dependent charge transport. A lesser conductivity is obtained in the case of H_3PO_4 doping in comparison to HCl for the same pH value, which may be due to cross-linking induced by the multivalent ion. © 1997 Elsevier Science Ltd.

(Keywords: polyaniline; protonation; variable range hopping (VRH))

INTRODUCTION

Polyaniline has started a new era due to its environmental stability and unique processibility, together with inexpensive monomer and high yield of polymerization. Its use in a variety of applications now seems to be a never ending process¹. On the one hand there is a challenge to increase its conductivity to match that of existing conventional materials, while on the other hand, there is a quest to understand the process of doping which brings about this remarkable change in conductivity. Recently, the mechanism of charge transport in PAN polymer has become of particular interest^{2–6}, partly because of the possibility of substitution of the aromatic rings⁵ and partly due to its doping with various acids⁶ which offer a renewed interest in this regard.

For the present investigations, HCl and H_3PO_4 have been selected as dopants. The literature is rich on HCl-doped polyaniline because it involves monovalent (Cl^-) ions, which makes the doping process simple. However, very few reports are available on PAN doped with multivalent ions⁷. Here we have undertaken pH-dependent studies on H_3PO_4 doped polyaniline. The data have been compared with doping of monovalent (Cl^-)

ions. It may be noted that our pH-dependent studies are confined to the pH range where sharp changes in the conductivity take place. This is accompanied by changes in the surface morphology of these samples. D.c. conductivity has been measured in the temperature range 77–300 K. The effect of doping on charge transport mechanism has been critically analysed in the light of existing theoretical models. Mott's 3D VRH has been found responsible for the mechanism of charge transport for HCl as well as H_3PO_4 doped samples at low temperatures. A deviation from this behaviour is observed at higher temperatures for all HCl doped and moderately H_3PO_4 doped (pH 2.5) samples. Lightly doped samples with H_3PO_4 (up to pH 3.0) exhibit 3D VRH for the whole temperature range studied.

EXPERIMENTAL

Emeraldine salt (ES) of PAN was prepared by chemical polymerization to which ammonium persulphate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) was added. After dedoping ES with ammonia solution for 24 h, a violet brown precipitate, emeraldine base (EB) was obtained. This EB was extracted with tetrahydrofuran (THF) in order to remove the oligomer. Fourier transform infra-red (FTi.r.) spectra (Figure 1) of

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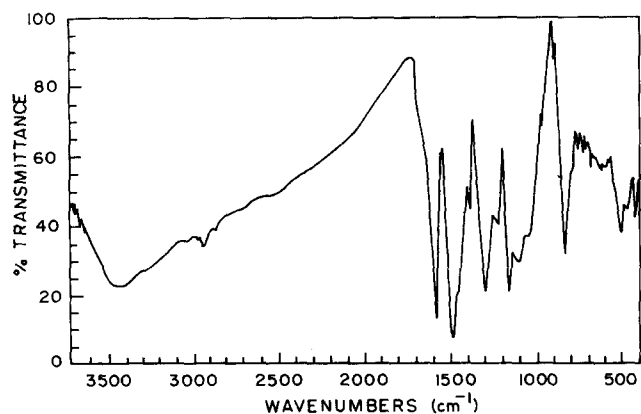


Figure 1 FTIR spectra of the EB form of PAN

Table 1 The FTIR absorption peaks of the EB form of PAN

Band assignment	Present work (cm ⁻¹)	Ref. 8 (cm ⁻¹)	Ref. 9 (cm ⁻¹)
1. Secondary N-H	3391	3389	-
2. C=C quinoid ring	1591	1595	1591
3. C=C benzoid ring	1495	1501	1501
4. Vibration modes of C-N	1302	1308	1302
5. Oxidized repeat unit of PAN	1165	1167	1145
6. C-H vibration of para-coupled benzene ring	827	831	827

Table 2 Log σ_{dc} versus pH value for HCl and H₃PO₄ doped samples

Sample	pH value	σ_{dc} ($\Omega^{-1} \text{cm}^{-1}$)	Sample	pH value	σ_{dc} ($\Omega^{-1} \text{cm}^{-1}$)
A1	4.25	2.5×10^{-8}	B1	4.00	1.3×10^{-10}
A2	4.00	2.0×10^{-6}	B2	3.50	9.0×10^{-10}
A3	3.50	1.0×10^{-4}	B3	3.00	5.6×10^{-8}
A4	3.00	5.0×10^{-4}	B4	2.50	2.2×10^{-4}
A5	2.35	9.8×10^{-3}	B5	2.00	1.1×10^{-3}

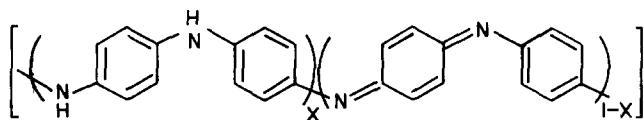


Figure 2 Structure of the EB form of PAN

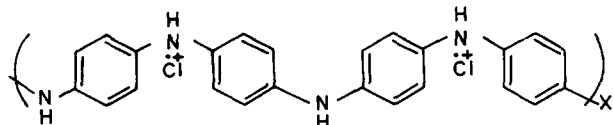


Figure 3 Structure of HCl doped PAN (PAN-ES)

this extracted EB were taken using a Nicolet Model 510P spectrometer. This confirmed the synthesis of the EB form of PAN. The band assignment of the major absorption peaks of the EB form of PAN is given in Table 1 along with earlier reported results^{8,9}. The violet

brown precipitate of EB was then treated with different known concentrations of HCl and H₃PO₄ acids to achieve the desired doping levels, which have been assigned as A1...A5 and B1...B5 respectively (Table 2). The resulting powders were dried in vacuum and then compacted under a pressure of 15 kpsi to form pill-shaped samples having a diameter of 10 mm and a height of 0.5–1 mm. Gold electrodes were vacuum deposited on both sides of these samples, making an Au-PAN-Au configuration. Before each measurement, samples were again dried in vacuum to eliminate the effect of absorbed water. The d.c. conductivity (σ_{dc}) of samples A2...A4 and B2...B4 was measured using a Keithley 617 electrometer in the temperature range 77–300 K as our interest lies in the pH range where sharp changes in the PAN lattice take place. Scanning electron micrographs of these samples have been taken using a JEOL JSM 840 and 35CF scanning electron microscopes.

RESULTS AND DISCUSSION

pH-dependent d.c. conductivity for HCl and H₃PO₄ doped samples

The results on the conduction mechanism of PAN with various doping levels of HCl and H₃PO₄ are given here. It is well known that PAN can be doped with various organic (HCOOH and p-toluene sulfonic acid (TSA) etc.) and inorganic acids (HCl, H₂SO₄, H₃PO₄, etc.) Doping with HCl is simple and well studied due to the monovalent nature of Cl⁻ counterions. The proposed

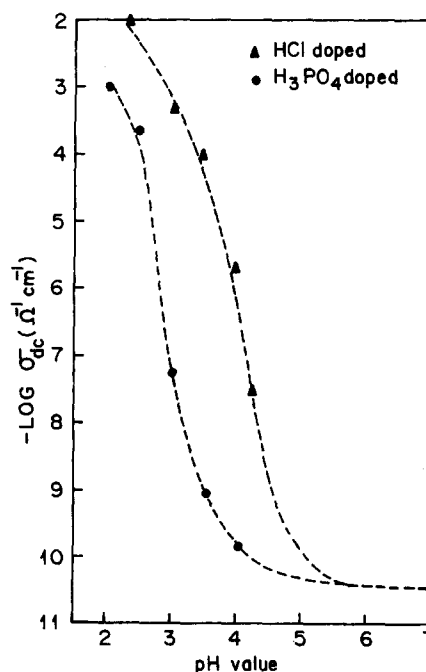


Figure 4 σ_{dc} plotted as a function of pH for HCl and H₃PO₄ doped samples

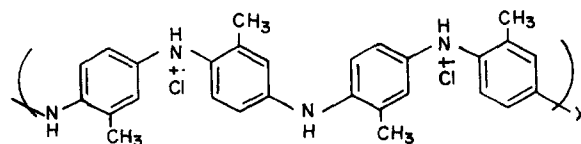


Figure 5 Structure of poly-o-toluidine doped with HCl (POT-ES)

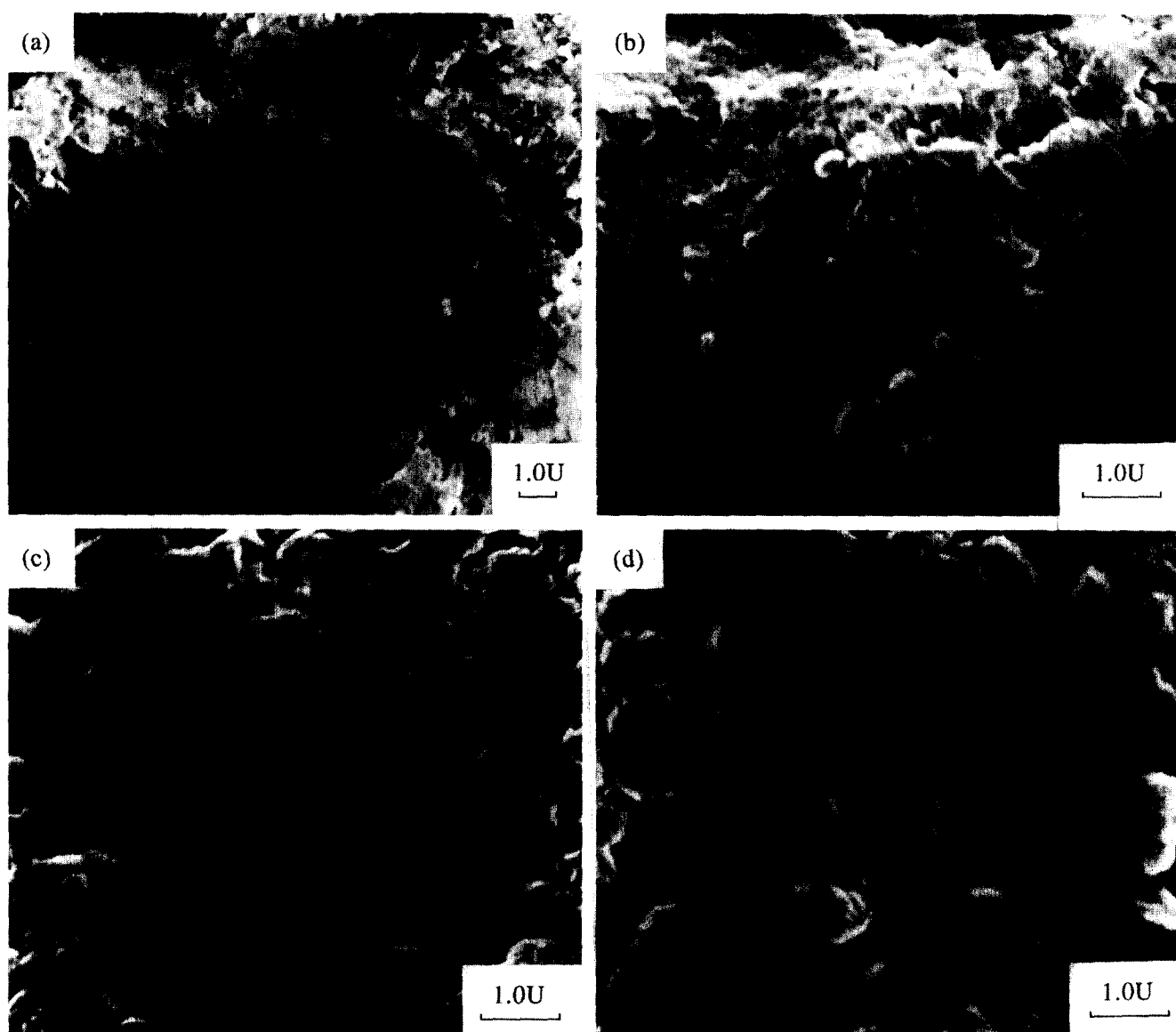


Figure 6 Scanning electron micrographs of HCl doped and EB forms of PAN: (a) EB; (b) pH 3.5; (c) pH 3.0; (d) pH 0.0

structure of the base form of PAN, confirmed by Hagiwara *et al.*¹⁰ by the analysis of C-n.m.r. spectra, is shown in Figure 2.

The process of doping with monovalent ions (Cl^-) has been under excessive discussion till today. Huang *et al.*¹¹ suggested the formation of bipolaron on the imine sites, which is inconsistent with band structure calculations by Stafstrom *et al.*¹² and magnetic studies¹³ in which electron spin resonance is a useful technique to distinguish between polarons and bipolarons by the presence of an e.s.r. signal. Later on, Epstein¹⁴ and Wnek¹⁵ suggested that the bipolaron is unstable and can be dissociated into polarons. MacDiarmid *et al.*¹⁶ suggested that polaron is of semi-quinone form. Later, Jozefowicze *et al.*¹⁷ proposed that the polaron is resident on the crystalline region and bipolaron on the amorphous region. Ray *et al.*¹⁸ suggested that protonation can take place on amine segments of the ES chain to form an $-\text{NH}_2^+$ group before protonation on the imine segments of the polyemeraldine chain. Recently, Wan and Yang¹⁹ have shown that doping is through imine sites for monovalent ions (Cl^-).

Doping is a chemical as well as a diffusion process. Protons (H^+) and counterions (Cl^-) diffuse into the polymer chain and polarons are created on imine sites as

a result of doping, which is consistent with e.s.r. results. The structure on the basis of the above-mentioned studies is given in Figure 3, and is responsible for bringing a remarkable change in conductivity. Still, there are very few reports on the crucial pH range when a drastic change in conductivity occurs. Huang and MacDiarmid²⁰ have shown, using spectroscopic techniques, that sharp changes in the spectra take place in the pH range 3–4. Here we have observed from our d.c. conductivity (σ_{dc}) measurements that σ_{dc} varies sharply in the pH range 3.5–4.25 for HCl doped samples (Figure 4). This figure also includes the measured d.c. conductivity data for H_3PO_4 doped samples. It indicates that, for the same pH value, the d.c. conductivity of H_3PO_4 doped samples is lower in magnitude than that of HCl doped samples. In the case of HCl doping, the proposed structure of polaron formation on imine sites, consistent with the magnetic studies, is found to be responsible for the mechanism of charge transport. However, there are very few reports on the proposed structure of PAN doped with multivalent ions. It is quite probable that in the case of PO_4^{3-} , due to the trivalent nature of phosphate ions, there is a possibility of crosslinking between the chains or intrachain sharing of the same dopant species, which

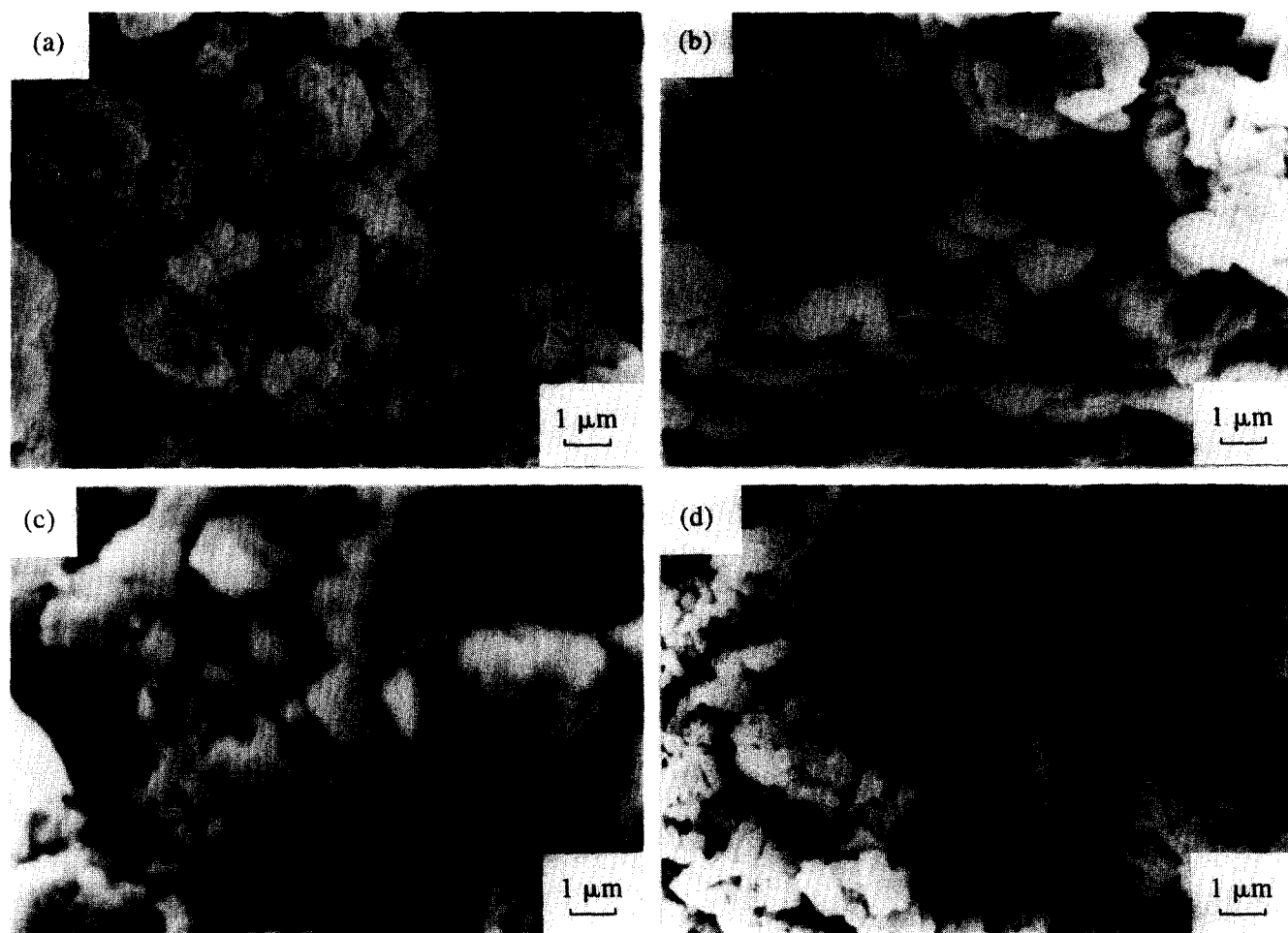


Figure 7 Scanning electron micrographs of H_3PO_4 doped and EB forms of PAN: (a) EB; (b) pH 3.0; (c) pH 2.5; (d) pH 0.5

results in a hindrance in electron transport. This may be the cause of the decreased conductivity and subsequent increase in the activation energy. The 'g' value of the salt form⁷ of H_3PO_4 is ~ 2.0034 – 2.0041 and is in good agreement with the g value of the free electron (~ 2.0023), which indicates that the radical is localized on or in the vicinity of the nitrogen atom. But no information is available on the structure, and further studies are needed in this regard.

It seems worthwhile to mention here that substitution on polyanilines with various groups (methyl, ethyl, propyl, etc.) also results in decreased conductivity. Wang *et al.*⁵ have observed a decrease in conductivity in the case of HCl doped poly-*o*-toluidine (POT) salt in comparison to HCl doped PAN. This has been attributed to increased localization arising due to the substitution of CH_3 on the benzene ring (Figure 5). This causes a reduction in interchain coherence and increased interchain separation.

It can be seen from Figure 4 that there is not much change in conductivity of the doped samples up to a pH of 3.5 in the case of H_3PO_4 doping. However, in the case of HCl doping there is a sharp change in the conductivity at this pH. This may be due to the nature of the dopant ions which are contributing towards the changeover of the conductivity. Cl^- ions, which are smaller in size and monovalent in nature, are able to diffuse easily onto the polymer chain so that even a very small concentration is able to bring about a change in conductivity. In the case of PO_4^{3-} ions, due to their heavier and multivalent nature, these are not able to diffuse easily into the

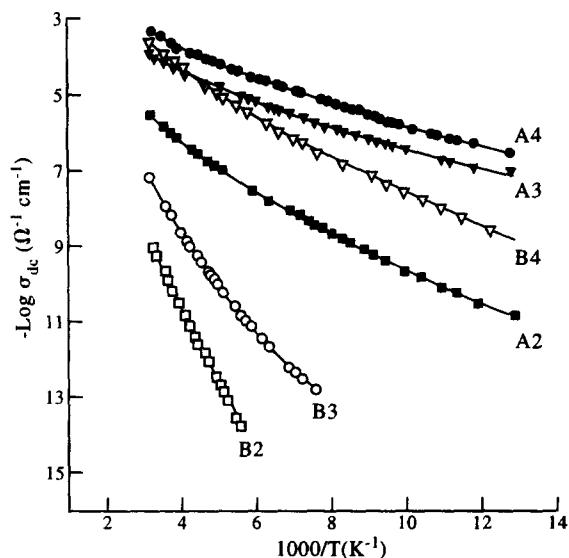
polymer backbone up to a pH of 3.5. Therefore, there is a minimum threshold at which marked changes in the conductivity spectra are observed (Figure 4), which is accompanied by structural changes at that pH value.

Doping-induced structural changes

Scanning electron micrographs (SEM) taken on pressed pellets in the case of HCl (Figure 6) and on powder form in the case of H_3PO_4 (Figure 7) indicate that changes are prominent at a pH value where sharp changes in the conductivity are observed. It is evident from Figure 6 that, due to pressing, lumps of the material are compressed in the case of HCl doped PAN. SEM taken on the powdered samples of the H_3PO_4 doped PAN (Figure 7) show individual three-dimensional lumps. A channel formation with flattening of the surface can be seen at a pH of 3.0 in the case of HCl doping, shifting to pH 2.5 in the case of H_3PO_4 doping. Finally, for the salt (pH \sim 0.5), a finer structure is obtained with the density of the smaller particles having an average particle size of *ca.* $0.25\ \mu\text{m}$. It is evident from these figures that, at the pH value before the channel formation, only lumps of the material with no finer structure can be seen, which finally integrate to form a channel at a particular pH value. For the salt form, the particle size and shape change drastically.

Temperature variation of d.c. conductivity

The d.c. conductivity has been measured in the temperature range 77–300 K for samples in the pH range

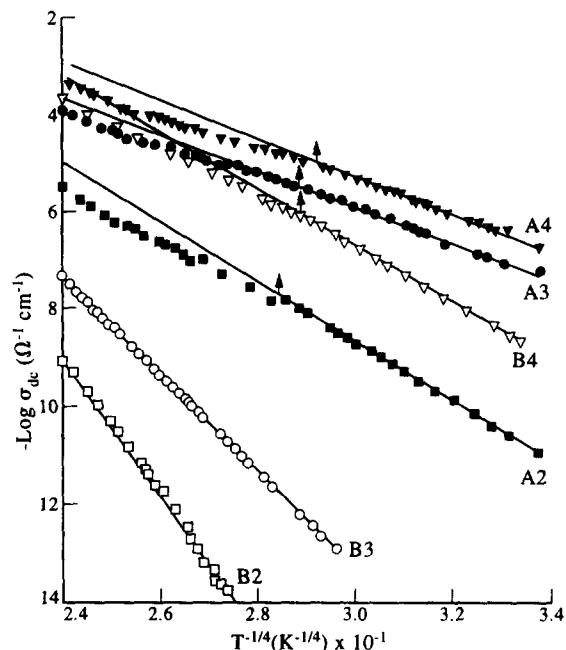
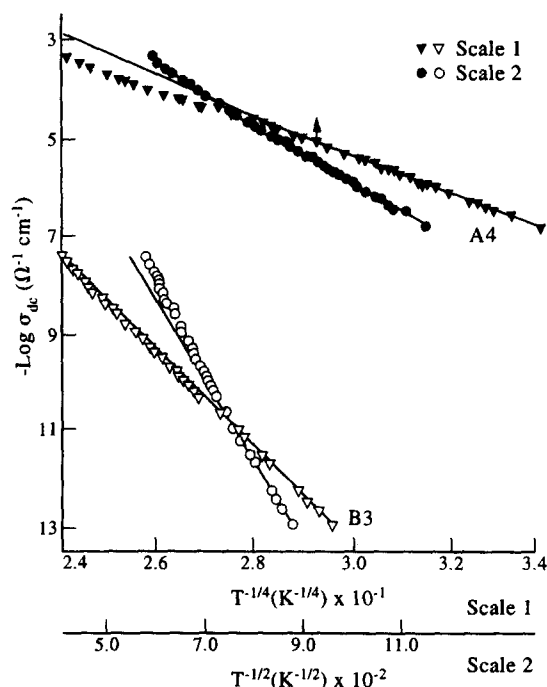

Figure 8 $\text{Log } \sigma_{\text{dc}}$ vs $1000/T$
Table 3 Evaluation of various parameters

Sample	$E_A(300\text{K})$ ($\text{eV} \times 10^{-1}$)	T_0 ($T^{-1/4}$) (K)	Temperature up to which $T^{-1/4}$ is valid (K)
A2	2.30	3.64×10^8	154
A3	1.85	6.43×10^7	148
A4	1.60	3.67×10^7	145
B2	4.34	1.24×10^{10}	300
B3	3.70	2.81×10^9	300
B4	2.20	2.99×10^8	144

where sharp changes are observed (A2...A4, B2...B4). The activation energies for these samples have been calculated from $\log \sigma_{\text{dc}}$ vs $1000/T$ plot (Figure 8) and are given in Table 3. The activation energy decreases with increase in the doping level in the case of both HCl and H_3PO_4 doped samples. The activation energy for H_3PO_4 doped PAN is higher than with HCl for the same pH value. The samples having a higher doping level give higher conductivity, due to semi-quinone radical cations formed by H-bonding between neighbouring polymers. Here the new states are formed between the valence and conduction bands by the doping and are responsible for conduction, thereby decreasing the activation energy in the case of HCl doping²¹.

Figure 8 shows the variation of d.c. conductivity as a function of reciprocal temperature for these samples. The non-linearity of the curves cannot be accounted for within the framework of a band conduction model²². In the field of conducting polymers, Mott's 3D variable range hopping has extensively been applied, with varying degree of success, to doped acetylene^{23,24}, undoped poly(3-hexathiophene)²⁵, polypyrrole²⁶ and the emeraldine form² of PAN. Recently, Reghu *et al.*⁶ have shown the applicability of Mott's VRH model to polyaniline. Sheng and Klafter²⁷ have used the critical path method²⁸ to demonstrate that the conductivity $\sigma = \sigma_0 \exp(-T_0/T)^m$ with $m = 1/4$ for $T \rightarrow 0$ and $m > 1/2$ (but < 1) for $T \rightarrow \infty$.

The conductivity data have been plotted as a function of $T^{-1/4}$ in Figure 9, which signifies that 3D VRH is the mechanism responsible for charge transport for HCl as well as H_3PO_4 doped samples at low temperatures. A


Figure 9 $\text{Log } \sigma_{\text{dc}}$ vs $T^{-1/4}$

Figure 10 $\text{Log } \sigma_{\text{dc}}$ vs $T^{-1/2}$ and $T^{-1/4}$

deviation from this behaviour is observed at higher temperature for all HCl doped samples as well as for moderately H_3PO_4 doped samples (pH 2.5). A composition-dependent T_0 is obtained (Table 3) which decreases with increase in the doping level for both monovalent and multivalent ions. However, for lightly doped H_3PO_4 samples (pH values 3.5 and 3.0), 3D VRH is valid for the whole temperature range studied. It may be pointed out that for very low doping levels ($\sigma_{300\text{K}} < 10^{-8} \Omega^{-1} \text{cm}^{-1}$), Mott's 3D VRH characteristic of three-dimensional hopping is valid and, as the doping level is increased (in the case of H_3PO_4) or temperature is increased, a deviation from this behaviour is observed.

As a representative result, the measured d.c. conductivity (for pH 3.0 of HCl as well as H_3PO_4 doped samples)

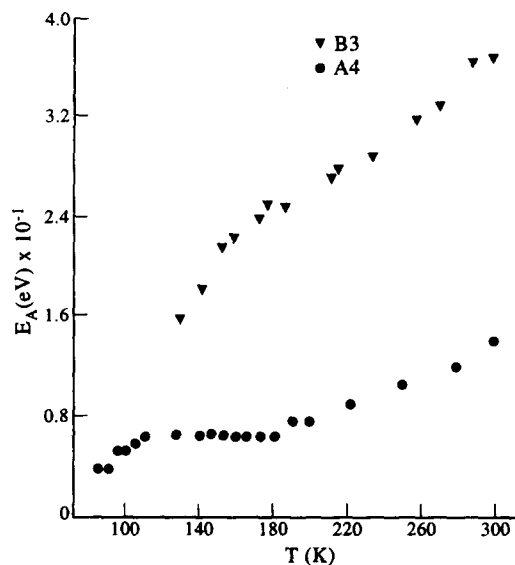


Figure 11 Activation energy (E_A) plotted as a function of temperature

as a function of $T^{-1/2}$ and $T^{-1/4}$ is shown in Figure 10. A 3D-VRH is valid for the H_3PO_4 doped sample and quasi 1D-VRH for the HCl doped sample of the same pH value for the whole temperature range studied. It may be pointed out that a number of functions can be fitted into a limited temperature range, but we have carried out the d.c. conductivity measurements on these samples in identical conditions and a qualitative comparison supports the above-mentioned results.

The variation of activation energy as a function of temperature is shown in Figure 11 for HCl and H_3PO_4 doped PAN having a pH value of ~ 3.0 . A temperature-dependent activation energy²⁹ has been observed for both HCl and H_3PO_4 doped PAN; however, in the case of HCl doped PAN some independent region is also noticed in the vicinity of the temperature where the deviation from 3D-VRH takes place. For a better understanding of the mechanism of charge transport in these systems, further investigations regarding structure-conductivity correlations are in progress.

CONCLUSIONS

A decrease in conductivity has been observed in case of multivalent ion doping. Sharp changes in conductivity take place in a particular pH range for both monovalent and multivalent ions, and are accompanied by structural changes. A temperature and composition dependent charge transport is observed.

ACKNOWLEDGEMENTS

The authors are thankful to Professor E. S. R. Gopal, Director, National Physical Laboratory, New Delhi, for his keen interest and permission to publish this work. One of us (V. A.) is thankful to the Council of Scientific

and Industrial Research (CSIR), New Delhi, for the award of a Senior Research Fellowship (SRF). Financial assistance from the Department of Biotechnology, Government of India, is gratefully acknowledged. Thanks are due also to Dr N. C. Mehra (D. U.) and Mr K. B. Ravat (N. P. L.) for extensive help in taking scanning electron micrographs. The authors are also thankful to Mr S. S. Pandey and Mr S. U. M. Rao of N. P. L. for many useful discussions.

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