Charge dynamics in conducting polyaniline–metal oxalate composites

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Abstract. Polyaniline (Pani) and its metal oxalate composites (~ 10 wt.%) of trivalent metal ions of Cr, Fe, Mn, Co and Al were synthesized by chemical oxidative polymerization technique with potassium perdisulphate oxidant in aqueous sulphuric acid medium. These materials were characterized by UV–VIS and EPR spectral techniques. Their d.c. electrical conductivities at room temperature and also as a function of temperature (307–453 K) were measured by four-probe technique. Presence of radical cation/polaron transition was indicated by UV–VIS absorption peak and EPR signals. Further, a close correlation existed between the conductivities and EPR parameters such as line width and peak ratio, which demonstrated that both mobile and fixed spins are involved in these composites. The dependence of conductivity on temperature, when analysed graphically by VRH, GB and TC mechanisms, pointed out that VRH is the predominant charge transport mechanism in these materials.

Keywords. Polyaniline; metal oxalate composites; charge transport; mobile and fixed spins; VRH conduction mechanism.

1. Introduction

Conducting polymers constitute an emerging new class of materials. Among the organic conducting polymers, polyaniline (Pani) is the only conducting polymer whose properties not only depend on the oxidation state but also on its protonation state/doping level and also on the nature of dopants. A remarkable property of Pani is, therefore, its insulator to metal transition as a function of protonation (Epstein *et al* 1987). When protonated with conventional protonic acid (Boara and Sparpaglione 1995), it exhibits relatively high conductivity and it can be processed in both the insulating emeraldine base form (MacDiarmid and Epstein 1991) as well as in the conducting emeraldine salt form (Andereatta *et al* 1988). Pani demonstrates a unique feature in the sense that it is not charge conjugation symmetric, i.e. the valence and conduction bands are asymmetric to a great extent. Consequently, the energy level positions of doping-induced (Epstein *et al* 1987) absorptions differ widely from those of the charge conjugation symmetric polymers (Epstein 1992). Studies on the above aspect and also on temperature dependence of conductivity and transport mechanism have generated a soaring interest. Elamin *et al* (1997) reported that Pani doped with H_3PO_4 or tartaric acid shows semiconductor behaviour and follows VRH mechanism. Abraham *et al* (1996) reported that the polymer blend of Pani and nylon

6 prepared from homogeneous solution in formic acid exhibits semiconducting behaviour in the range of temperatures between 300 K and 50 K and data fit to the VRH model. Holland *et al* (1996) found that Pani films prepared via the camphorsulphonic acid–*m*–cresol solution processing, with various doping levels exhibit heterogeneous model of fluctuation induced tunneling and metallic transport. Most of such studies are confined to the transport properties of the heavily protonated emeraldine salt materials with mineral/organic acids. In the present study, the focus is on conducting Pani–metal oxalate composites. The usage of metal complexes bearing negative charge as dopants in the place of conventional acids is a new approach. In our previous work (Murugesan and Subramanian 2002), we reported the impact of metal oxalate complexes of trivalent Cr, Fe, Mn, Co and Al as dopants on the structure and conductivity of Pani. Among the five metal oxalate complexes investigated, those of Al, Mn and Co on doping into Pani improve the polymerization yield, conductivity and thermal stability of polymer material, perhaps through their large molecular size, greater electron delocalization and support for crystallinity. Spectral and XRD studies provided evidences in favour of their dopant role and the work brought to light that anionic metal oxalate complexes could be regarded as better novel inorganic dopants for organic conductive polymers. The present work is an attempt to get further insight into the influence of metal oxalates on charge dynamics, i.e. the distribution of spin, charge transport and its mechanism in Pani.

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2. Experimental

2.1 *Materials*

All chemicals used were of analytical grade. Aniline (SD fine-chem, India) was purified by distillation over zinc dust. Water was used after two distillations. Other chemicals were used as such without any further purification. The following metal oxalate complexes were prepared and purified as per standard methodologies (Palmer 1965; Pass and Sutcliffe 1982): potassium trioxalatochromate(III) (TOCr), potassium trioxalatoferrate(III) (TOFe), potassium trioxalatomanganate(III) (TOMn), potassium trioxalatocobaltate(III) (TOCo) and potassium trioxalatoaluminate(III) (TOAl).

2.2 *Synthesis of Pani and its composites with metal oxalate*

Pani and its composites with metal oxalate complexes were prepared with 0.1 M aniline at room temperature by *in situ* chemical oxidative polymerization technique using 0.1 M potassium perdisulphate (PDS) as oxidant adopting the literature-described procedure (Trivedi 1997) in sulphuric acid and in a mixture of metal oxalate complex (100 mg/100 ml) and sulphuric acid, respectively. The polymer formed was filtered, washed with distilled water and then with methanol and acetone until the filtrate became colourless and dried in an air oven at 80°C for about 4 h.

2.3 *Spectral characterization*

The UV–VIS spectra of the polymer samples in 8 M H_2SO_4 were recorded in matched 1 cm quartz cuvettes with Perkin-Elmer spectrophotometer, model Lambda 3B. EPR measurements at room temperature were carried out in a Varian E-112 ESR spectrometer operating in the X-band under the following instrumental conditions: scan range, 50 gauss; time constant, 0.5 s; modulation amplitude, 3.2 gauss; field set, 3200 gauss; microwave power, 20 mW; modulation frequency, 100 kHz and microwave frequency, 9.46 GHz; using 1,1′-diphenyl-2-picrylhydrazyl (DPPH) as the standard. This characterization was performed at RSIC, Indian Institute of Technology, Chennai.

2.4 *Measurement of conductivity*

D.c. electrical conductivity of the polymer materials was measured at room temperature on pressed pellets. Three pellets of different dimensions were prepared from the same material with the help of a hydraulic press (KIMAYA Engineers, India, model WT-324) by applying 3 metric ton pressure. These pellets were then subjected to conductivity measurements in four-probe technique (Scienti-

fic Equipment Services, India, model DEP-02). Current–voltage measurements (*I–V* values) in triplicate of each pellet were made which yielded more or less the same value within the experimental error. The mean *I–V* values were plotted according to Ohm's law and the resistances were obtained from the slope of the plot. Conductivities were then computed from the values of resistance and pellet dimension.

Conductivities as a function of temperature from 307 to 453 K were measured in a similar way in a temperature controlled chamber for each material, after ensuring the reproducibility of the room temperature conductivity value each time.

3. Results and discussion

The polymer samples were subjected to intensive characterization in our preceding work (Murugesan and Subramanian 2002) both by chemical methods for sulphate and oxalate contents and by instrumental methods involving XRD, spectral (UV–VIS and IR) and TGA techniques. The chemical analyses established that the metal oxalates were incorporated into Pani materials to the extent of around 10 wt.% and the instrumental characterization revealed their dopant role influencing the structure, conductivity and thermal stability of the materials. Consequent to this detailed study on synthesis and characterization of Pani–metal oxalate composites, the present work is directed to the investigation of influence of metal oxalate dopants on charge dynamics with EPR and other techniques.

3.1 *UV–VIS spectra*

Figure 1 shows the absorption spectra of Pani materials in 8 M H_2SO_4. Two intense broad bands appear, one around 780 nm and another around 450 nm. These bands arise as explained in many studies (Sindhimeshram and Gupta 1995; Koul *et al* 1997; Rao *et al* 2000), out of electronic transitions of emeraldine salt and radical cation, respectively. Normally a conducting Pani salt should show bands at 420 nm and 830 nm (Rao *et al* 2000). The observation of peak at 780 nm in the present work, as witnessed previously by Patil *et al* (2000), might be due to intermediate species, possibly a mixture containing major amount of conducting emeraldine salt and a little amount of its base. Anyhow the observation of 450 nm peak confirms the presence of radical cation or polaron transition (Rao *et al* 2000).

3.2 *EPR studies*

The EPR spectra of the polymer materials are illustrated in figures 2a and b. For the sake of clarity, the spectra of only three materials are shown in each figure. Generally

the spectra are single, smooth and sharp signals without hyperfine splitting except that for Pani-SO$_4^{2-}$/TOFe sample where the signal is modestly broadened. The appearance of such spectra itself validates the fact that the Pani materials consist of movable free electrons responsible for conductivity. The spectral data comprising the *g*-value, peak ratio (*A/B* ratio), line width (Δ*Hpp*) and the difference in field strengths experienced by sample (*Hs*) and reference (*Hr*) i.e. DPPH, are given in table 1 along with room temperature conductivity value for the purpose of correlation.

For all the materials the *g*-values are comparable to the free electron's value of 2·0023 and this indicates that all Pani samples exist primarily as polysemiquinone radical cations (Roy *et al* 2001), supplementing the UV–VIS spectral observation of 450 nm peak. The peak ratio is considerably higher for Pani-SO$_4^{2-}$ salt (1·44), which demonstrates unsymmetry nature in its spectrum. However, this ratio declines and becomes close to unity on metal oxalate doping, revealing symmetry nature in the spectra. Gupta *et al* (1993) noticed such an observation and have attributed the higher ratio to the domination of mobile spins and that the diffuse motion of spin during delocalization leads to interchain coupling causing unsymmetry in the signal shape.
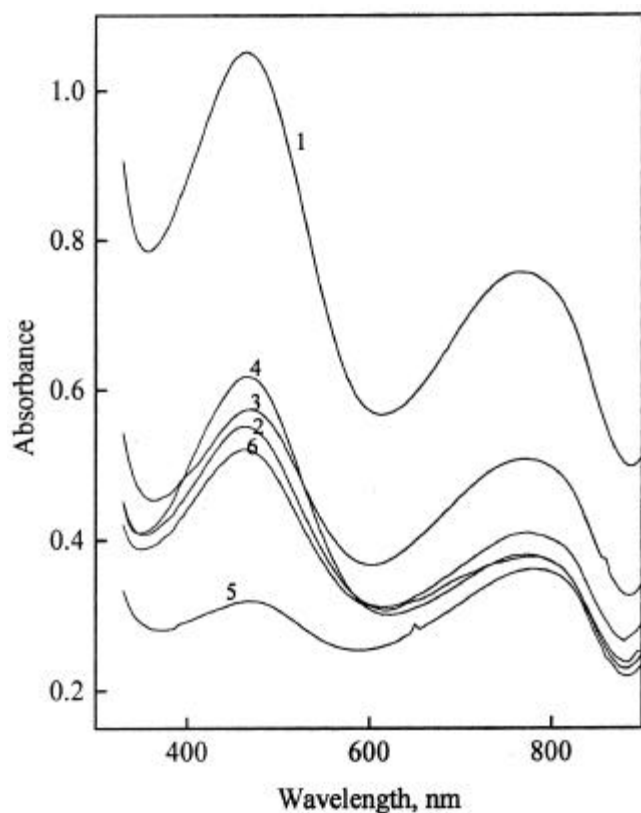

Figure 1. UV–VIS spectra of Pani materials in 8·0 M H$_2$SO$_4$: (1) Pani-SO$_4^{2-}$, (2) Pani-SO$_4^{2-}$/TOCr, (3) Pani-SO$_4^{2-}$/TOFe, (4) Pani-SO$_4^{2-}$/TOMn, (5) Pani-SO$_4^{2-}$/TOCo and (6) Pani-SO$_4^{2-}$/TOAl.
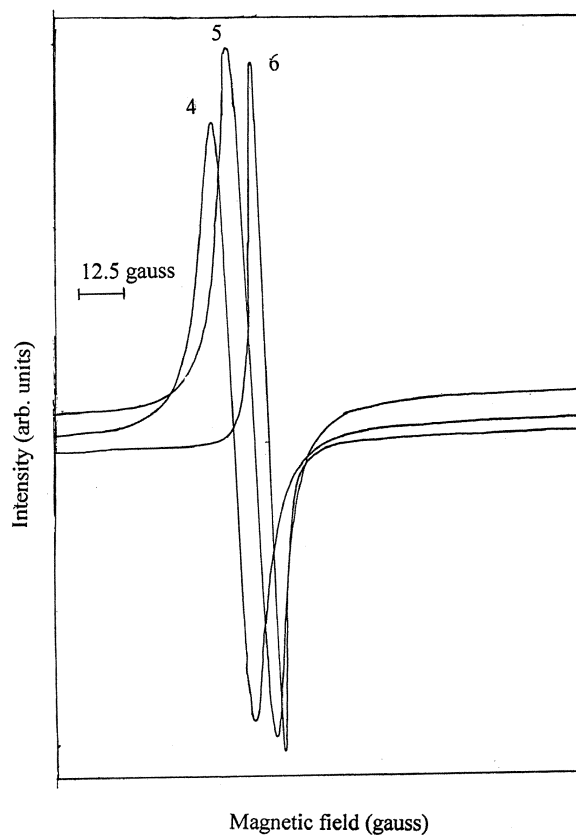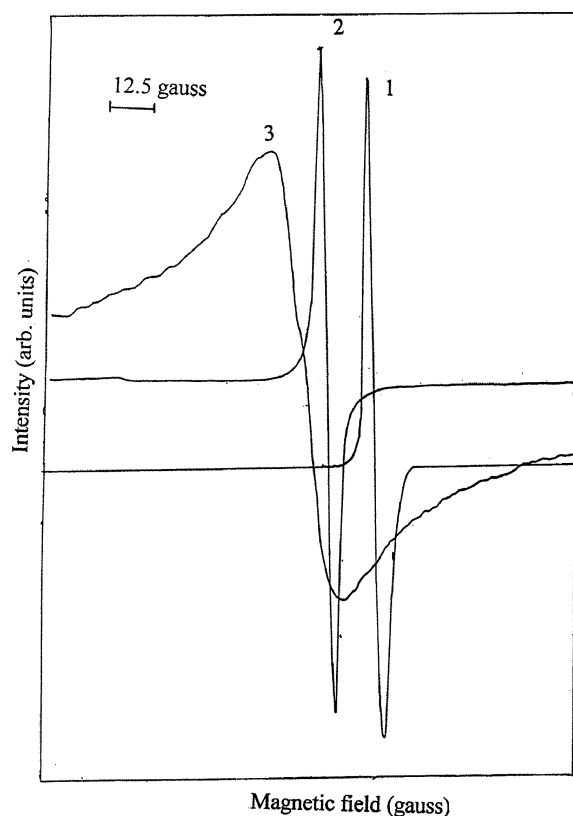
Figure 2. EPR spectra of Pani materials: (1) Pani-SO$_4^{2-}$, (2) Pani-SO$_4^{2-}$/TOCr, (3) Pani-SO$_4^{2-}$/TOFe, (4) Pani-SO$_4^{2-}$/TOMn, (5) Pani-SO$_4^{2-}$/TOCo and (6) Pani-SO$_4^{2-}$/TOAl.

Table 1. Conductivity and EPR data of Pani materials.

Sample	s (S/cm)	g-value	A/B	ΔHpp (Gauss)	Difference in Hs and Hr (Gauss)
Pani-SO_4^{2-}	1·24	1·9917	1·44	5·0	6·0
Pani-SO_4^{2-}/TOCr	1·02	2·0021	1·06	5·0	4·5
Pani-SO_4^{2-}/TOFe	0·60	2·0066	1·12	25·0	4·0
Pani-SO_4^{2-}/TOMn	4·12	2·0011	1·06	9·7	0·3
Pani-SO_4^{2-}/TOCo	2·35	2·0066	1·07	9·4	0·5
Pani-SO_4^{2-}/TOAl	6·50	2·0034	1·28	5·6	0·3

Hs and Hr are fields of sample and reference.

The line width values excluding that for Pani-SO_4^{2-}/TOFe, lie in the range 5–10 G which are in agreement with the literature values observed for Pani emeraldine salt (Rao *et al* 2000). The exceptionally broad signal of Pani-SO_4^{2-}/TOFe material with lower conductivity value could be ascribed to the presence of both Fe^{2+} and Fe^{3+} ions in the matrix formed due to the well-known photosensitive nature of TOFe and hence to the exchange/delocalization of Pani spins with the two ions. In other cases the considerable increase in line width brought about by metal oxalate doping roughly correlates with the conductivity value and could be explained by the improvement in delocalization of spins caused by electron spin–spin dipolar coupling. Besides this, the difference between Hs and Hr also has a correlation, with inverse relationship with conductivity. As Hs becomes closer to Hr and since the g values are also closer, it may be construed that the free electrons in both the sample and reference become comparable on energy and chemical terms. This in turn means, on taking line width values also into consideration, that metal oxalate doping especially in the case of TOMn, TOCo and TOAl, improves electron delocalization through mobile spins. The IR spectra reported in our preceding publication (Murugesan and Subramanian 2002) also suggest from the charge delocalization peak the same inference. A similar observation on greater line width and improved electron delocalization has been made by us on the effect of organic dopants on Pani (Murugesan and Subramanian 2003). Genoud *et al* (2000) demonstrated that motionally narrowed polaron EPR line of Pani salt could be broadened by interaction of its mobile spins with fixed paramagnetic species present in the polymer matrix. This behaviour is observed in our case and is very explicit in Pani-SO_4^{2-}/TOFe material. Nevertheless, the observation of symmetrical EPR spectral peaks for composites relative to Pani-SO_4^{2-}, as deduced from A/B ratio, implies the prevalence of localized/fixed spins. This might have resulted from emeraldine base whose presence is indicated by the 780 nm band in the UV–VIS spectrum. On the whole it appears that the composite materials have mobile and fixed spins, the former being, of course, facilitated.
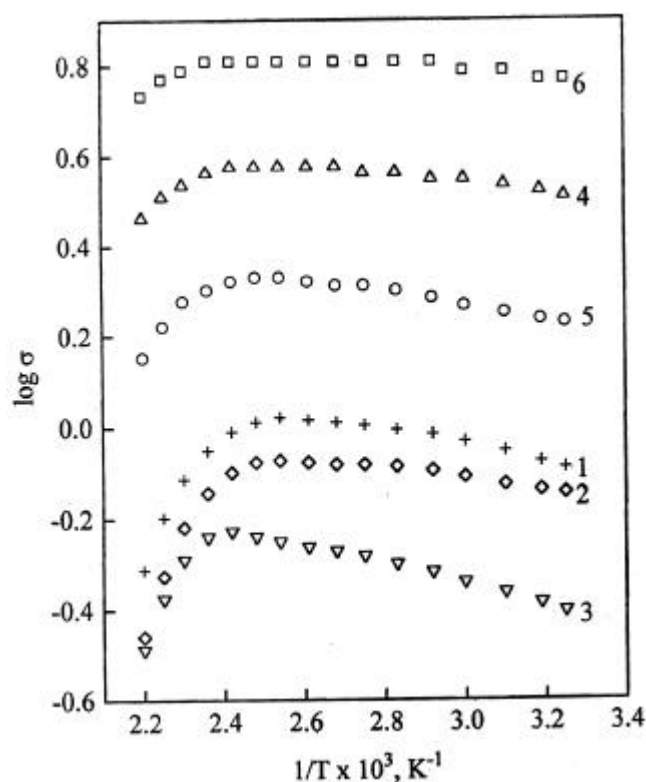

Figure 3. Conductivity of Pani materials as a function of temperature: (1) Pani-SO_4^{2-}, (2) Pani-SO_4^{2-}/TOCr, (3) Pani-SO_4^{2-}/TOFe, (4) Pani-SO_4^{2-}/TOMn, (5) Pani-SO_4^{2-}/TOCo and (6) Pani-SO_4^{2-}/TOAl.

3.3 Conductivity characteristics

The temperature dependence of conductivity of all the samples is depicted in figure 3. Initially there is an increase in conductivity followed by a decrease. This dip in electrical conductivity may be due to the loss of moisture by the sample, since the conductivity depends on the moisture content and the environmental humidity (Travers and Nechtschein 1987; Javedi *et al* 1988). Conductivity increases steadily up to 120°C for sulphate and TOCr doped Pani, 130°C for TOFe and TOCo doped Pani, 140°C for TOMn doped Pani and 150°C for TOAl doped

Pani showing semiconductor behaviour, afterwards it decreases gradually. A similar trend has been reported for poly(N-ethylaniline) (Borkar and Gupta 1990). The linear portion of the graph is fit to Arrhenius type equation (1) and log s vs $1/T$ plots were made for all materials. Figure 4A is a representative of such plots.

$$s\,(T) = s_0\,\exp\,(-\,Eg/2kT). \tag{1}$$

The activation energy of conductivity, Eg calculated from the slope is given in table 2 and it varies from 0·046 to 0·086 eV for different polymer materials. These values are comparable to those for poly(N-ethylaniline) (0·078 eV) (Borkar and Gupta 1990) and polyaniline–tetrafluoro-borate (0·082 eV) (Choi *et al* 1989). The follow up of Arrhenius behaviour is regarded as a good approximation to band theory.

In order to determine the conductivity parameters, the temperature dependence of conductivity (linear portion) is fit to the following equations (Wang *et al* 1991)

$$s\,(T) = s_0\,\exp - (T_0/T)^{1/2}, \tag{2}$$
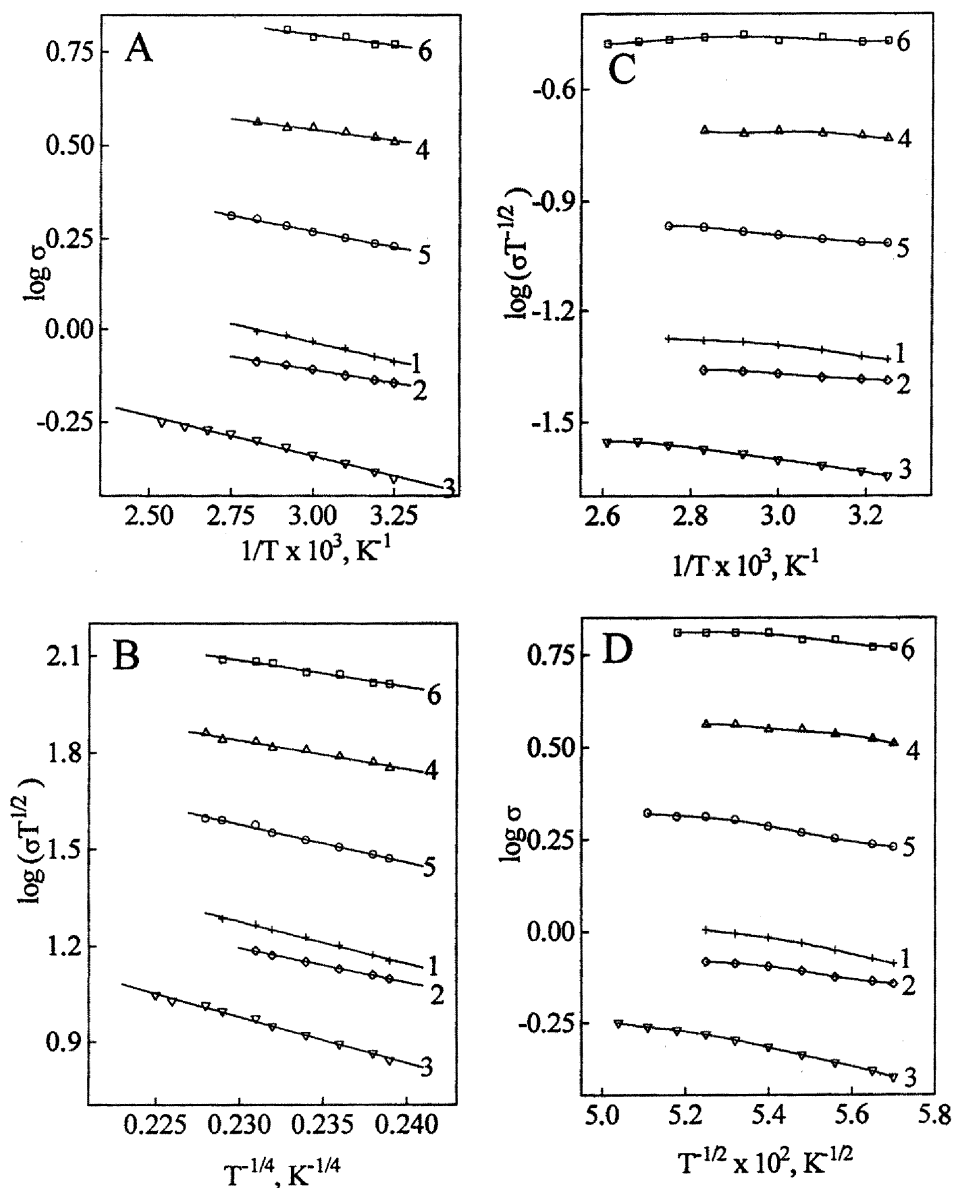
$$T_0 = 8a/D\,(E_F)Zk, \tag{3}$$

Figure 4. **A.** Arrhenius plot and (**B**, **C** and **D**) plots of VRH, GB and TC mechanisms of (1) Pani-SO$_4^{2-}$, (2) Pani-SO$_4^{2-}$/TOCr, (3) Pani-SO$_4^{2-}$/TOFe, (4) Pani-SO$_4^{2-}$/TOMn, (5) Pani-SO$_4^{2-}$/ TOCo and (6) Pani-SO$_4^{2-}$/TOAl. (Plots were drawn using Origin 4.0 software. A and B – linear-fit plots; C and D polynomial plots with order 4 or 5).

Table 2. Charge transport properties of Pani materials.

Sample	Eg (eV)	$T_0 \times 10^{-3}$ (K)	a^{-1} (Å)	R (Å)	w (eV)
Pani-SO$_4^{2-}$	0·076	2·18	108·4	73·04	0·049
Pani-SO$_4^{2-}$/TOCr	0·057	1·35	174·7	92·65	0·030
Pani-SO$_4^{2-}$/TOFe	0·086	2·79	84·5	64·42	0·063
Pani-SO$_4^{2-}$/TOMn	0·047	0·70	335·9	128·27	0·016
Pani-SO$_4^{2-}$/TOCo	0·069	1·27	186·6	95·89	0·028
Pani-SO$_4^{2-}$/TOAl	0·046	0·50	472·8	152·60	0·011

$$R = a^{-1}(T_0/16T)^{1/2}, \tag{4}$$

$$w = ZkT_0/16, \tag{5}$$

where T_0 is related to the charge localization length (a^{-1}), k the Boltzmann constant, $D(E_F)$ the density of states at Fermi level (E_F) which is 1·6 state per eV (2 rings) of Pani (Wang *et al* 1991), Z the number of nearest neighbouring chains (~ 4), R the average hopping distance and w the charge hopping energy. The values of T_0 obtained from the linear plots were used to calculate a^{-1}, R and w. All these parameters are presented in table 2. It is observed that T_0 for Pani and its composites is lower when compared to Pani with chloride ion ($3·98 \times 10^3$) and trichloroacetate ion ($2·52 \times 10^4$) (Gupta *et al* 1997). a^{-1} and R values increase with increase in conductivity of Pani and its composites but w has a reverse trend. All these trends are quite understandable for enhancement in conductivities of polymer composites and are in agreement with the EPR spectral observations. Also they closely resemble with the behaviour observed in studies (Gupta *et al* 1997) on substituted derivatives of Pani and on Pani with different dopants.

3.4 *Charge transport mechanism*

The linear portion of the plots in figure 3 is further subjected to graphical analysis according to (6)–(8) (Zeller 1972; Mott 1980; Matare 1984) in order to identify the conduction mechanism of the samples.

$$s\,T^{1/2} = \exp(-B/T^{1/4}), \tag{6}$$

$$s = AT^{1/2}\exp(-Ea/kT), \tag{7}$$

$$s = s_0\exp(-A/T^{1/2}). \tag{8}$$

These equations represent variable range hopping (VRH), grain boundary barrier (GB) and tunneling conduction (TC) mechanisms, respectively. Plots of log ($s\,T^{1/2}$) vs $T^{-1/4}$ are linear while those of log ($s\,T^{-1/2}$) vs $1/T$ and log s vs $T^{-1/2}$ are curved for all polymer samples specifying obeyance of (6) among the three. This is shown in figures 4B, C, and D for all Pani materials. This implies that the conduction in Pani and its composites is predominantly performed by variable range hopping process of elec-

trons. Elamin *et al* (1997) reported that Pani doped with H_3PO_4 or tartaric acid shows semiconductor behaviour and follows VRH mechanism.

4. Conclusions

UV–VIS and EPR spectral studies indicate that all the Pani samples exist primarily as polysemiquinone radical cations. The observation of symmetrical EPR signals with increased line width for composites relative to Pani-SO$_4^{2-}$ imply the prevalence of both fixed and mobile spins, with the domination of latter. Further, the temperature dependence of conductivity, the follow up of Arrhenius behaviour and Mott equation (6) indicate that the conduction in Pani and its composites is predominantly performed by variable range hopping process. Thus, the polorans act as charge carriers hopping from state to state in all of our polymer samples.

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