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Electrical Conductivity of Phenoxazine–Iodine (2 : 3) and Phenothiazine–Iodine (2 : 3) Crystals

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Single crystals of phenoxazine–iodine (2 : 3) and phenothiazine–iodine (2 : 3) salts are found to be highly conducting ($\sigma_{R.T.} = 5$–20 ohm^{-1} cm^{-1}). The observed deviation from the exponential temperature dependence of the conductivities is ascribed to the degenerate semiconducting phases or alternatively to the metallic phases with impurities. However, phenoxazine–iodine and phenothiazine–iodine are perfect semiconductors below 220 °K with activation energies of 0.12 eV and 0.14 eV, respectively. The absorption features related with (phenoxazine)$_2^+$ and (phenothiazine)$_2^+$ cations are observed in the infrared spectra of the salts.

1. INTRODUCTION

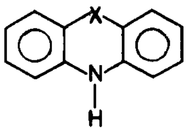
Many charge transfer complexes and radical-ion salts composed of organic donors and iodine are found to exhibit metallic or semiconducting properties.[1-3] In most of the complexes the stacks of organic donors conduct. Because of charge transfer the density of carriers in the conduction band increases by a large amount.[4] The iodine chain complexes without charge transfer are found to be wide band gap semiconductors.[5-8]

There are some charge transfer salts in which the major electronic conduction is most probably along the iodine chains. These are the iodine complexes of oligoanilines and aromatic diamines.[4] The negative thermoelectric powers of the iodine complexes of phenoxazine, phenothiazine and *N*-methyl-phenothiazine at low temperatures indicate that the major electrical conduction should be along the iodine chains.[9-10] Several materials of this class exhibit semiconducting nature in the form of compressed powder or fused samples.[9-13] Polycrystalline samples are found to exhibit breaks in $\log \rho$ vs $1/T$ (ρ is resistivity and T is temperature) plots corresponding to a reduction in the activation energies at low temperatures and changes in the slope or sign of thermoelectric powers. Such complex salts are expected to be metallic in the form of single crystals.[14] *N*-Methyl–phenothiazine–iodine (*N*-MePT-iodine) (2 : 3) crystals are found to have metallic conductivity ($\sigma = 95$ ohm^{-1} cm^{-1}) at room temperature.[15] Single crystals of phenoxazine–iodine (2 : 3) and phenothiazine–iodine (2 : 3) are studied in the present work. The molecular structures of the donors are shown in Fig. 1.

2. EXPERIMENTAL DETAILS AND RESULTS

The complex salts of phenoxazine–iodine (2 : 3) and phenothiazine–iodine (2 : 3) were crystallized from the mixed solutions of the donors and iodine in hot benzene by slow cooling.[6] The iodine content was found to be 64–68% by weight loss determination after removing iodine by heating. Phenoxazine–iodine (2 : 3) crystals were blue-black needles of the dimensions of $1.5 \times 1.2 \times 0.5$ mm^3 and phenothiazine–iodine (2 : 3) crystals were also blue-black needles of the dimensions of $1.5 \times 1.2 \times 0.5$ mm^3. The crystals were stiff without rope-like behaviour indicating the presence of appreciable interchain interactions like the crystals of other quasi-one-dimensional semiconductors.

The electrical resistances along the needle direction were measured with conventional two-probe and four-probe techniques using col-



1.Phenoxazine , X = O
2.Phenothiazine , X = S

FIGURE 1 Molecular structures phenoxazine and Phenothiazine.

loidal graphite paste and stainless steel leads as electrodes for the electrical contacts. The contacts with small crystals were made under a 10 × 10 magnification microscope. Constant currents of 500 nA-1.00 μA were passed through the samples from a Keithley 222 model constant current sources and the voltage drops were measured using a Keithley *d.c.* null detector. Current-voltage characteristics were found to be linear for appreciably large currents. Phenoxazine–iodine (2 : 3)

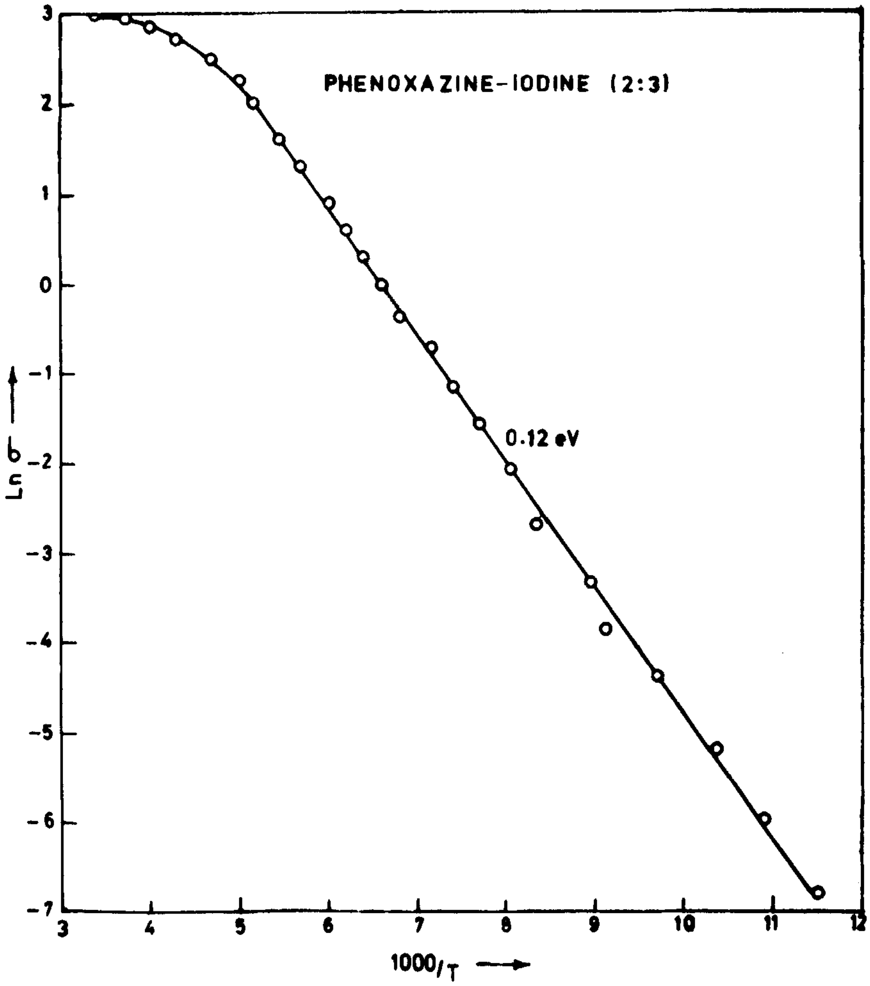


FIGURE 2 Temperature dependence of conductivity of phenoxazine–iodine (2 : 3) crystal along the chain direction.

crystals were found to have a room temperature *d.c.* electrical conductivity ($\sigma_{R.T.}$) of 15–20 ohm^{-1} cm^{-1} along the needle direction. The *d.c.* conductivities of phenothiazine–iodine (2 : 3) crystals were found to be 6–12 ohm^{-1} cm^{-1}. Several single crystals of both the salts showed an anisotropy of conductivity of ($\sigma_{11}/\sigma_{\perp}$) of more than 50. This shows quasi-one-dimensional nature of these complexes.

The temperature dependence of the parallel-to-chain conductivities (σ_{11}) was studied down to 77 °K using a continuous flow crystat discussed elsewhere.[6,16] These measurements reveal that above 200 °K the electrical conduction in these materials is not simply due to

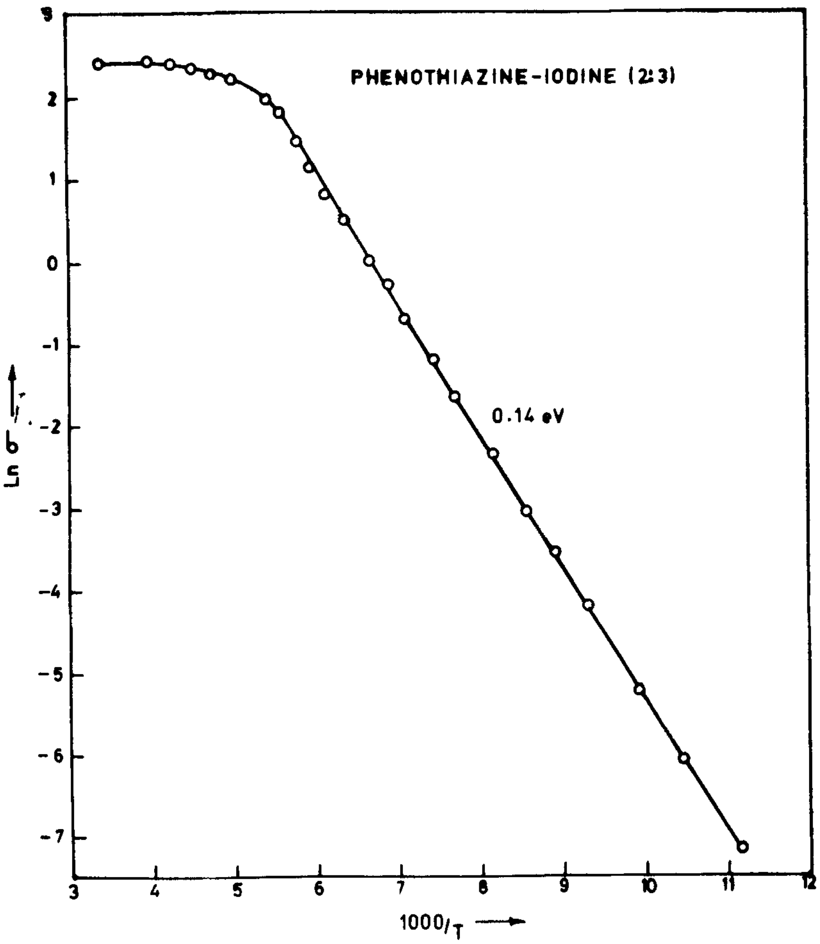


FIGURE 3 Temperature dependence of conductivity of phenothiazine–iodine (2 : 3) crystals along the chain direction.

thermal activation of the charge carriers across a band gap (Figures 2 and 3). There is departure from linearity in $\ln \sigma$ vs $1000/T$ plots. In phenothiazine–iodine salt, there is change to a completely semiconducting state having an activation energy (E_a) of 0.12 eV below 220 °K (Figure 2). Phenothiazine–iodine crystals are found to be semiconducting with $E_a = 0.14$ eV below 240 °K (Figure 3). No increase in the conductivities was observed while lowering the temperature for both the salts. The conductivities are suppressed in comparison with the activated values. This shows that the salts are not perfectly metallic but are either semimetallic or disordered semiconducting in nature in the high temperature range.

The thermoelectric powers of the polycrystalline compactions at room temperature were measured. Phenoxazine–iodine salt was found to have a Seeback coefficient of $+5\ \mu$V/ °K and phenothiazine–iodine salt had a coefficient of $+150\ \mu$V/ °K as observed earlier.[10] These values give $\mu_e = 2.11\ \mu_h$ for the phenoxazine salt and $\mu_e = 0.7\ \mu_h$ for the phenothiazine salt.

3. DISCUSSION

There are two possibilities regarding the conducting nature of these salts.

(a) Since a negative temperature coefficient of conductivity is not found, the salt may be degenerate semiconductors above 200 °K and do not seem to be perfectly metallic. Either the small band gap of 0.12 eV or 0.14 eV is filled with the impurity levels as in the case of degenerate semiconductor or the random potential arising from defects, disorder and impurities suppressed the gap at high temperatures.

If $\Delta/K_B T_{\max} = 2$ to 5 is assumed as found in various similar systems[17] where Δ is the single particle gap and $T_{\max}$ is the temperature for the conductivity-maximum then $\Delta \leq 0.15$ eV for these salts for $T_{\max} = 300$ °K. This is consistent with the activation energies of 0.12 eV and 0.14 eV for these salts below 220 °K. If the random potential W is larger than Δ, i.e., $W > 0.15$ eV, the band gap can be suppressed at high temperatures. This estimate of the random potential is not unreasonable for slightly displaced (thermally disordered) iodine atoms or tri-iodide ions[18] or for random orientations of the symmetric donor molecules.[19] The salts become perfect semiconductors below 220 °K because the effects of disorders might be limited to determine the temperature dependence of σ_0 in $\sigma = \sigma_0 \exp(-E_a/K_B T)$ which is effective only in the high temperature range and is not sufficient to suppress the semiconducting state with a large band gap at low temperatures. Only a weak disorder is expected because the salts are found to be stoichiometric.

Both the salts studied in the present work are similar, at least in the temperature dependence of conductivities, to TEtA$(TCNQ)_2$, 4,4'-BIP$(TCNQ)_2$ and TTN-TCNQ (TEtA = triethyl ammonium, 4,4'-BIP = 4,4'-bipyridinium, TTN = tetrathionaphthalene and TCNQ = 7,7,8,8-tetracyano-*p*-quinodimethane) which are coupled chain semiconductors with well-defined forbidden energy gaps at low temperatures.[20-22] In the case of these salts and quinolinium $(TCNQ)_2$ the deviation from $\ln \sigma \sim 1/T$ arises in the high temperature region and the power laws of metallic conduction are also not appropriate. Similar situation is found in the present study (Figure 4). Thus the flattening off of the conductivities above 220°-240°K in these salts can be assigned alternatively to the temperature dependence of σ_0 as suggested for 4,4'-bipyridinium $(TCNQ)_2$.[21] This has been explained more specifically with the diffusive conduction mechanism as explained in the case of quinolinium $(TCNQ)_2$.[23] The diffusion coefficient rather than mobility may be temperature dependent and the diffusion coefficients and conductivities have the same anisotropy ratios in such a disorder model. However, the study of relaxation time with nuclear magnetic resonance is required for confirming this.

In many respects, both the salts have similar nature of conduction. However, there are certain differences between the properties of these two salts. Although the temperature dependence of the conductivities of both the salts are almost identical, their thermoelectric powers change remarkably in different manners with temperature variation.[10-12]

The Seeback coefficient (S) of phenoxazine–iodine was small, positive and changed sign to negative at lower temperature and deviates significantly from $S \sim 1/T$ dependence because $S \sim \ln K_B T$ terms of extrinsic semiconduction seems to mainly determine the temperature dependence of electronic conduction. In the case of phenothiazine–iodine, the thermoelectric power is large, remains positive down to 77°K with only a change of slope and the rectangular hyperbolic term ($S \sim 1/T$) in S vs $1/T$ plots of intrinsic semiconduction dominates.

(b) Alternatively, it is possible that the materials are metallic near room temperature and undergo a broad, smeared-out metal-to-semiconductor transition at low temperatures. The semiconducting states below 220°-240°K are fitted with $\sigma = 10{,}000$ ohm^{-1} cm^{-1} and

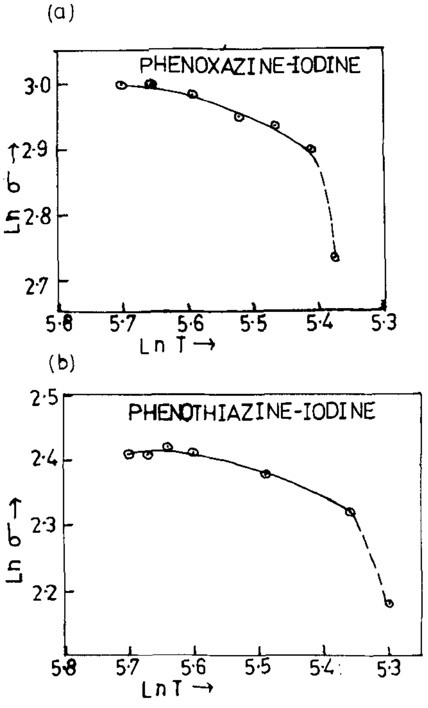


FIGURE 4 ln σ vs ln T plot in the high temperature range for (a) phenoxazine–iodine and (b) phenothiazine–iodine.

$E_a = 0.12$ eV for the phenoxazine salt and with $\sigma_0 = 50{,}000$ ohm^{-1} cm^{-1} and $E_a = 0.14$ eV for the phenothiazine salt. The values of σ_0 are much higher than the maximum conductivities ($\sigma_{\max} = 20$ ohm^{-1} cm^{-1} for phenoxazine–iodine and $\sigma_0 = 12$ ohm^{-1} cm^{-1} for phenothiazine–iodine). This indicates metallic delocalization (extended states) of the charge carriers above 220°–240°K as found for 4,4′-bipyridinium $(TCNQ)_2$.[21] The mean free paths calculated from the relation $\lambda = (\pi\hbar/2ea)\,\mu_e$ where a is lattice constant and μ_e is electron mobility using the thermoelectric powers measured at room temperature are found to be $\lambda = 30a$ and $\lambda = 10a$ for phenoxazine–iodine and phenothiazine–iodine, respectively. These values support the metallic nature of the salts at high temperatures. The small thermoelectric power of $+5$ μV/°K of the phenoxazine salt itself suggests a metallic phase near room temperature.

A depression of conductivity and a small positive temperature coefficient of conductivity can arise in a metallic phase from impurities. Since the salts are found to be stoichiometric in compositions, a change in the conducitivities as caused by impurities or defect concentration is not neglected. Conducitivities slowly decrease at low temperatures in a metal due to impurities. The impurity levels are enough to decrease the conductivity in the metallic phase but are not sufficient enough to fill up the forbidden energy gap when a broad metal-to-semiconductor transition occurs below 220 °K. The impurities will not severely reduce mean free paths and the mean free paths of 10–30 lattice constants are not unreasonable even for impure metals. These values may be even higher for the pure metallic states. A large effective mass, of the order of $m^* = 10m_e$ would result in a reduction by a factor of three on λ. Then λ values will be only $10a$ for phenoxazine–iodine and $3a$ for phenothiazine–iodine. However, the varification of this needs further studies.

The Nujol mull absorption spectra in the infrared range were taken at ambient temperature for the donors and the iodine salts complexes in the present study for further characterization. The infrared spectrophotometer with IR detectors and appropriate filters was used placing the samples between the two IR-transmitting KBr plates.

The infrared absorption spectra of the donors and the complex iodine salts are shown in Figure 5 (a–d). Several bands corresponding to the vibrational levels of the donor molecules are quite common between the spectra of phenoxazine and phenothiazine because of their similar structures (Figure 5a, c). The absorption spectra of the iodine salts are quite different from the spectra of donors (Figure 5b, d). These spectra of the complex salts of iodine involves the bands of complex radical cations $(\text{phenoxazine})_2^+$ and $(\text{phenothiazine})_2^+$ as observed earlier.[13] A low energy electronic absorption at 1.92 μ in the near-infrared spectrum was ascribed to the electronic intermolecular interaction when a unit positive charge is shared by two neighbouring donor molecules; i.e. to the delocalization of a positive charge.[13] The vibrational levels of the complex (dimeric) monocation are completely different from the vibrational levels of the neutral molecules.

Since molecular iodine and the polyiodide anions are infrared inactive, a comparison of the spectra of the iodine salts (Figure 5b, d) provides useful information. The bands corresponding to C—C stretching vibration near 9.7 μ of the armatic rings of the donor molecules are shifted to about 9.3 μ in the spectra of the iodine salts. The bands shift to higher frequency in the spectra of iodine salts because the C—C band achieves double band character as a result of charge transfer from the whole ring. The doublets corresponding to the C—O stretching vibrations in the phenoxazine spectrum at 8.5 μ

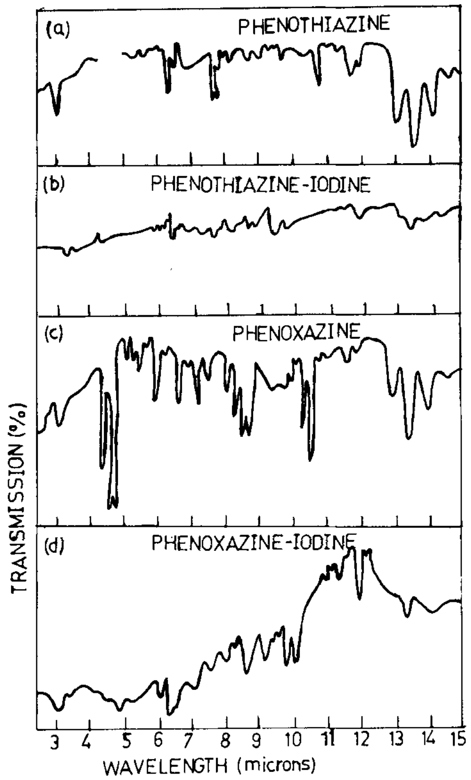


FIGURE 5 Infrared absorption spectra of phenoxazine phenothiazine and their iodine salts in 2.5 μ–15 μ range.

and C—S stretching vibrations at 8.8 μ are found to broaden and become asymmetric.

The C—O and C—S bonds will also achieve partial double bond character due to rehybridization due to charge transfer. Similarly, the charge transfer enhances the double bond nature of the C—N stretching and deformation vibrations are affected.[24] The C—N bands also show a shift to shorter wavelength in the spectra of iodine complexes. The bands around 6.6 μ in both the spectra of the donors are the typical imine bands. These bands are diminished in the spectra of the iodine salts but are not absent which indicates that the hydrogen atom is not removed from the donors.

The band around 10.8 μ in the spectra of the donors corresponding to N—H wagging mode is found to disappear in the spectra of the complex salts. This is a remarkable effect of dimerization. The reduction in donor-donor distance giving rise to pairing of donor molecules with a shared charge sterically and electronically hinders the N—H wagging motion. The inhibition of N—H wagging can also be a consequence of N—H—I hydrogen bonding contacts in the complexes.

A new band is found at 9.2 μ in the spectra of the iodine salts which has no correspondance with any vibration of the donor molecules. A new band at 23.9 μ was observed at the expense of neighbouring absorptions which was ascribed to the C–N deformation vibration indicative of the electronic and vibronic alterations of the phenothiazine ring by charge transfer.[24]

In summary, phenoxazine–iodine (2 : 3) and phenothiazine–iodine (2 : 3) are most probably coupled-chain semiconductors at low temperatures but are either degenerate semiconductors or impure metals around room temperature. The determination of the conduction mechanism requires the detailed studies of structural, optical and other physical properties. The resonance and steric effects of methyl substitution on electrical conduction in this class of complexes are studied.[25,26]

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