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# THE DIRECT CURRENT ELECTRICAL CONDUCTIVITY OF THE CHARGE TRANSFER COMPLEXES OF SOME THIAZOLES AND BENZOTHIAZOLES WITH CERTAIN DI- AND TRINITROBENZENE DERIVATIVES [a]

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## ABSTRACT

The DC electrical conductivity of 2-aminothiazole (**I**), 2-aminobenzothiazole (**II**), 2-amino-4-methylbenzothiazole (**III**) and 2-amino-6-nitrobenzothiazole (**IV**) and their charge transfer (CT) complexes with the acceptors, 1,3-dinitrobenzene (*1*), 3,4-dinitrobenzoic acid (*2*) and picric acid (*3*) were investigated. The positive temperature coefficients of the electrical conductivity of these thiazoles suggested their semiconducting characteristics. The CT complexes were classified into two main groups. The first group included the complexes $\mathbf{I}_1$, $\mathbf{I}_2$ and $\mathbf{IV}_{1,2,3}$. All these complexes had negative temperature coefficients of resistance and revealed conventional semiconducting behaviour. Two different activation energies for the complexes $\mathbf{I}_2$, $\mathbf{IV}_2$ and $\mathbf{IV}_3$ indicated the presence of more than one conduction mechanism. The second group contained the complexes $\mathbf{I}_3$, $\mathbf{II}_{1,2,3}$ and $\mathbf{III}_{1,2,3}$. The thermal conductivity plots exhibited curves with two inflections and three regions. The slope of the line of a region and also its temperature range were found to depend upon the nature and structure of the complex. No correlation was found between the activation energies of the CT complexes and either the electron affinities of acceptors or the ionization potentials of donors. This was explained by assuming that the geometrical, and not the electronic, structure of the complexes was the determining factor.

## INTRODUCTION

In the last two decades, a vast number of organic compounds has been discovered to exhibit pertinent electrical characteristics [1–4]. Charge trans-

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fer complexes are the most important organic species studied because of their special type of interaction, which is accompanied by transfer of an electron from the donor to the acceptor. The temperature dependence of the direct current electrical conductivity of these complexes is usually correlated with the ionization potential of the donor and the electron affinity of the acceptor [4]. In a preceding paper, we have reported the synthesis and spectroscopic studies of the CT complexes of some thiazoles and benzothiazoles with certain di- and trinitrobenzene derivatives [5]. The existence of these complexes in the solid state, as well as their relatively high thermal stability, have prompted us to investigate their electrical conductivity.

## EXPERIMENTAL

All the reagents used in this investigation were of highly pure grade, and most were used without further purification. They were purchased from either Aldrich Chemical Company or British Drug Houses (BDH). The donor compounds were: 2-aminothiazole (**I**), 2-aminobenzothiazole (**II**), 2-amino-4-methylbenzothiazole (**III**) and 2-amino-6-nitrobenzothiazole (**IV**). The acceptors were: 1,3-dinitrobenzene (*1*), 3,4-dinitrobenzoic acid (*2*) and picric acid (*3*). The charge transfer complexes were prepared as described in our previous paper [5].

Measurements of DC electrical conductivity were carried out by using a Super Megohmmeter Model RM 170 (AVO Ltd., Dover, England). For the measurements, the test sample was compressed under a pressure of ca. 600 kg $cm^{-2}$ to form a cylindrical disc of diameter $\approx 0.6$ cm and thickness $\approx 0.12$ cm. The measurements were taken at 15 min intervals for each temperature equilibration. Duplicate experiments were carried out and reproducible data were obtained.

The linearity of the current–voltage ($I-V$) ohmic relationship was checked before measuring the conductivity of the solid state charge transfer complexes. This was done to ensure that there was no failure of contact, which might cause erroneous results. Linear $I-V$ characteristics were obtained for the various CT complexes. It should be noted that this linear dependence was expected up to a given voltage, depending on the particular substance.

## RESULTS AND DISCUSSION

The variations of the DC electrical conductivity ($\log \sigma$) as functions of the reciprocal of the absolute temperature ($1000/T$) for 2-aminothiazole, 2-aminobenzothiazole, 2-amino-4-methylbenzothiazole and 2-amino-6-nitrobenzothiazole are represented in Fig. 1. Within the investigated temperature ranges, the plots for 2-aminothiazole and 2-aminobenzothiazole dis-

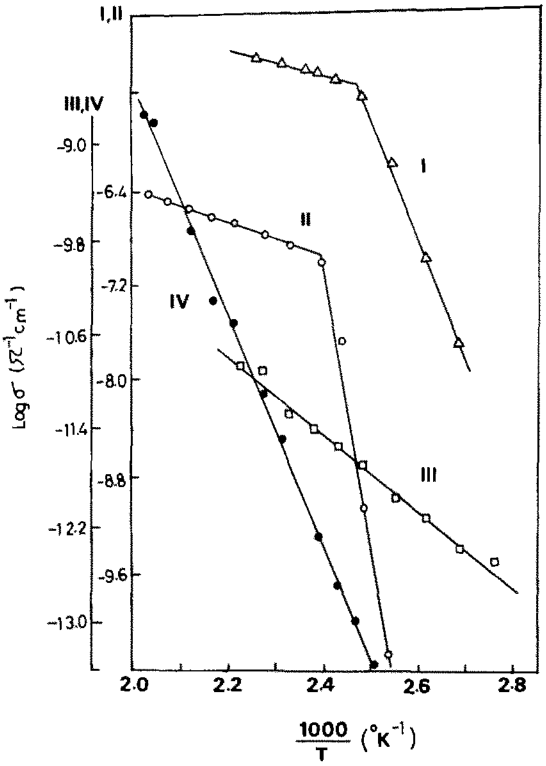

Fig. 1. Variation of DC electrical conductivity as a function of the reciprocal of absolute temperature of the investigated donors.

played two activation energy values for each donor. On the other hand, only one activation energy value was observed for either 2-amino-4-methylbenzothiazole or 2-amino-6-nitrobenzothiazole. Table 1 lists the values of the electrical conductivity at 35 °C, the activation energy $\Delta E$, and the energy gap $E_g$ for the investigated donors. As can be seen from Fig. 1, there are positive temperature coefficients of the electrical conductivity ($d\sigma/dT$), which suggest that the donors have semiconducting characteristics. The activation energy values for 2-aminothiazole and 2-aminobenzothiazole (Ta-

TABLE 1

Values of electrical conductivity ($\sigma$) at 35 °C, activation energy ($\Delta E$) and energy gap ($E_g$) for the investigated donors

| Donor | $\sigma$ ($\Omega^{-1}$ cm$^{-1}$) | $\Delta E \times 10^{22}$ (kJ) | $E_g \times 10^{22}$ (kJ) |
|---|---|---|---|
| I | $2.500 \times 10^{-11}$ | 3.489, 0.357 | 6.979 |
| II | $2.512 \times 10^{-14}$ | 7.610, 0.476 | 15.221 |
| III | $6.310 \times 10^{-14}$ | 0.952 | 1.903 |
| IV | $1.580 \times 10^{-16}$ | 3.092 | 6.184 |

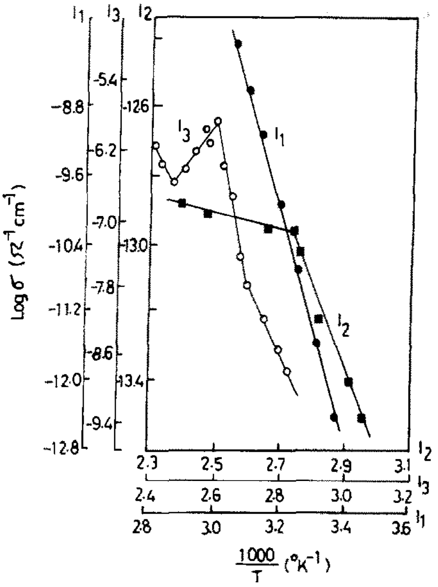

Fig. 2. Variation of DC electrical conductivity as a function of the reciprocal of absolute temperature of 2-aminothiazole complexes.

ble 1) imply that there is more than one conduction mechanism. It is reasonable to assume that the first step in the conduction process is intrinsic. The small activation energy values for the second step in the conduction process of these donors probably corresponds to an extrinsic mechanism. Therefore, the activation energy in this case can be interpreted by a band model containing a partially occupied set of trap states near the centre of the energy gap between the valence and conduction bands. 2-Amino-4-methylbenzothiazole and 2-amino-6-nitrobenzothiazole each exhibit only one activation energy due to an intermolecular extrinsic conduction mechanism.

The variations of the DC electrical conductivity as a function of temperature for the various charge transfer complexes are represented in Figs. 2–5. The values of electrical conductivity of these CT complexes at 35 °C, the activation energy values and the energy gap values are given in Table 2. According to the data obtained, the investigated CT complexes can be classified into two main groups.

(a) The first group includes the charge transfer complexes having negative temperature coefficients of resistance ($\mathrm{d}R/\mathrm{d}T$). These complexes are $I_1$, $I_2$ (Fig. 2) and $IV_{1,2,3}$ (Fig. 3). All the complexes classified into this group reveal conventional semiconducting behaviour, since the conductivity increases on increasing the temperature. The temperature dependence conductivity curves for the complexes $I_2$, $IV_2$ and $IV_3$ show two regions, indicating the presence of more than one conduction mechanism. The two regions are characterized by different values of the activation energy. The activation energy values of

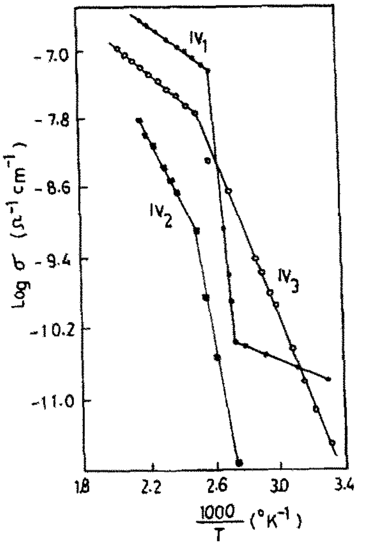

Fig. 3. Variation of DC electrical conductivity as a function of reciprocal of absolute temperature of 2-amino-6-nitrobenzothiazole complexes.

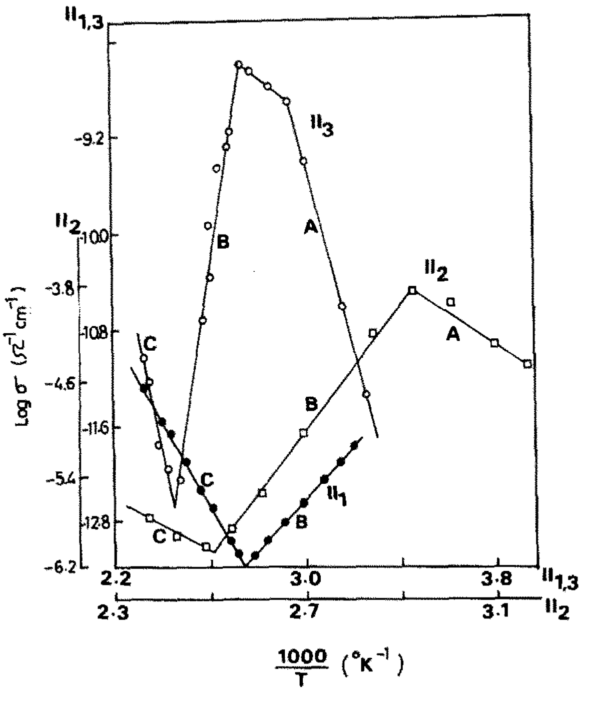

Fig. 4. Variation of DC electrical conductivity as a function of the reciprocal of absolute temperature of 2-aminobenzothiazole complexes.

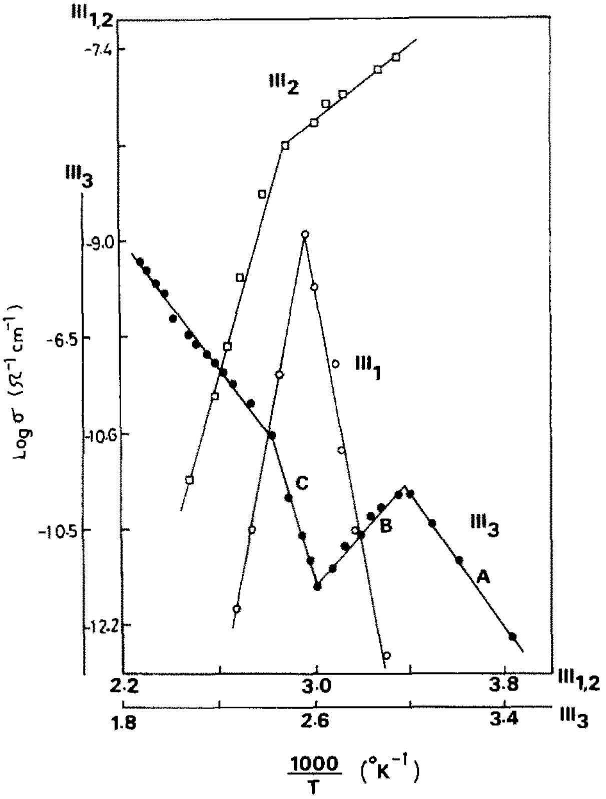

Fig. 5. Variation of DC electrical conductivity as a function of the reciprocal of absolute temperature of 2-amino-4-methylbenzothiazole complexes.

the first region of the low temperature range are larger than those of the second region (Table 2). In these cases, it is assumed that the higher values are related to the transition of an electron between valence bands or localized levels and the conduction band. On the other hand, the smaller activation energies can be due to electron hopping, which is a thermally activated process. The electrical conductivity curve of the complex $\mathbf{IV}_1$ displays three regions with two inflection points within a very narrow temperature range. The first region, at lower temperature range, reveals an activation energy value which is almost half the value of that of the third region (Table 2). Thus, this CT complex presumably passes from an extrinsic to an intrinsic conduction mechanism.

(b) The second group includes the complexes $\mathbf{I}_3$, $\mathbf{II}_{1,2,3}$ and $\mathbf{III}_{1,2,3}$. The temperature dependence of the conductivity plots exhibits curves with two inflections and three regions A, B and C (Figs. 2, 4 and 5). In some cases, region A or C is missing within the investigated temperature range. The regions A and C have positive temperature coefficients of electrical conductivity, while region B has a negative coefficient value. Consequently, we have

TABLE 2

Values of electrical conductivity ($\sigma$) at 35 °C, activation energy ($\Delta E$) and energy gap ($E_g$) for the different CT complexes

| CT complex | $\sigma$ ($\Omega^{-1}$ cm$^{-1}$) | $\Delta E \times 10^{22}$ (kJ) | $E_g \times 10^{22}$ (kJ) |
|---|---|---|---|
| **I**$_1$ | $1.380 \times 10^{-11}$ | 1.875 | 3.749 |
| **I**$_2$ | $1.122 \times 10^{-14}$ | 0.729, 0.095 | 1.458, 0.189 |
| **I**$_3$ | $7.943 \times 10^{-10}$ | 1.322, 3.172, −0.849, 2.531 | 2.644, 6.345, 5.063 |
| **II**$_1$ | $1.737 \times 10^{-13}$ | 1.110, −0.673 | 2.220 |
| **II**$_2$ | $1.585 \times 10^{-5}$ | 0.846, −1.645, 0.721 | 1.692, 1.452 |
| **II**$_3$ | $6.310 \times 10^{-13}$ | 2.221, −4.441, 2.820 | 4.438, 5.640 |
| **III**$_1$ | $9.772 \times 10^{-13}$ | 3.174, −5.175 | 6.345 |
| **III**$_2$ | $1.995 \times 10^{-8}$ | −1.968, −0.476 | |
| **III**$_3$ | $5.620 \times 10^{-13}$ | 2.597, −1.340, 4.759, 2.852 | 5.191, 9.517, 5.705 |
| **IV**$_1$ | $1.819 \times 10^{-11}$ | 0.285, 2.451, 0.490 | 0.570, 4.904, 0.981 |
| **IV**$_2$ | $1.580 \times 10^{-16}$ | 3.732, 1.184 | 7.463, 2.368 |
| **IV**$_3$ | $1.738 \times 10^{-13}$ | 1.586, 0.540 | 3.172, 1.080 |

positive activation energy values for regions A and C and negative activation energies for region B. In region A, a relatively low activation energy is obtained, accompanied by an increase in the conductivity as the temperature increases. This increase could be due to the activation of electrons from the donor level to the conduction band, i.e., extrinsic behaviour. Region B is characterized by a decrease of conductivity as the temperature is increased. This is presumably due to the scattering of carriers by phonons as a result of lattice vibrations within the temperature range of this region. It is interesting to note that the slope of the line of a region, as well as its range of temperature, varies widely depending upon the nature and structure of the complex. Region C is found to have a positive temperature coefficient with an activation energy value higher than that of region A. Therefore, this part represents the intrinsic region of conductivity.

The activation energy values of the investigated CT complexes show no correlation with either the electron affinities of the acceptors or the ionization potentials of the donors [5]. This unexpected behaviour indicates that the electronic structure is not the dominating factor in the activation process. Rather, the most probable determining factor is the geometrical structure of the complexes. In other words, configurational interactions play a considerable role in the electronic activation process of these species. This is presumably due to the presence of more than one nitro group in the acceptor molecules, in addition to possible orientations of the interacting acceptors and donors in stack arrangements. The configurational interaction, in its simplest form, is electron–phonon interaction. Accordingly, it stimulates some forbidden electronic transition, which may lead to ease of electron migration. In other words, it facilitates the conduction mechanism and hence decreases the activation energies.

The activation energies of the CT complexes are lower than the corresponding values for the donors. The complexation facilitates the mobility of the electrons and, thus, increases the conductivity of the complexes. That means in the CT complexes the energy gap between the valence band (the highest occupied molecular orbital, or HOMO, of the donor moiety) and the conduction band (the lowest unoccupied molecular orbital, or LUMO, of the acceptor part) is narrower than that of the HOMO in the valence band and the LUMO in the conduction band of the donor itself. Also, the activation energies of the CT complexes formed by $\pi$–$\pi^*$ transitions and resonance stabilization of proton transfer (complexes derived from acidic acceptors) are generally lower than those of the CT complexes derived from 1,3-dinitrobenzene ($\pi$–$\pi^*$ transition). The resonance stabilization of the proton transfer causes high stability of the CT complexes, and hence the interaction between the molecular orbitals of donor and acceptor increases. This makes both the valence and the conduction bands wider and consequently the energy gap will be small.

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