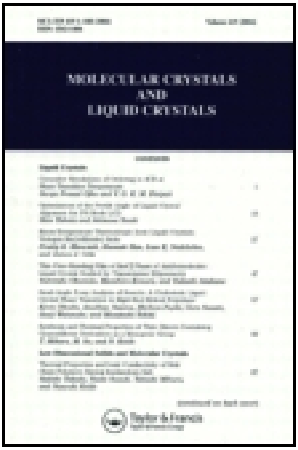

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Study on Electrical Properties of Some New N-(p-aminobenzoyl)-L-Asparagine Derivatives in Thin Films

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Study on Electrical Properties of Some New *N*-(*p*-aminobenzoyl)-*L*-Asparagine Derivatives in Thin Films

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The synthesis of some *N*-(*p*-aminobenzoyl)-*L*-asparagine derivatives and temperature dependence of the electrical conductivity and Seebeck coefficient for these compounds are studied. The measurements have been performed using the thin-film samples deposited from dimethylformamide solutions of the compounds. All investigated compounds show typical semiconducting characteristics. Some correlation between these characteristics and molecular structure are established. The values of some parameters (activation energy, concentration and mobility of charge carriers, ratio of carrier mobility etc.) of the studied samples have been determined. The nature of the mechanism of electrical conduction is also discussed.

Keywords: *N*-(*p*-aminobenzoyl)-*L*-asparagine derivatives; organic semiconductors; electrical conductivity; Seebeck coefficient; organic thin films

I. INTRODUCTION

In recent years organic semiconducting compounds have been one of theoretical and experimental areas of the solid-state science and technology [1–5].

The interest for this interdisciplinary topic is strongly stimulated by the important role of these organic compounds in our everyday life. We consider that in present the impact of investigations in this field is not yet fully appreciated but it will be of a considerable help in the near future for solving some of the crucial problems (energy conversion, genetic engineering technology, catalyst manufacture etc.).

Particularly, the organic semiconducting films are promising materials for the development of various modern and future technologies of solid-state devices [3,4,6].

Generally, by studying the electrical and thermoelectric properties of semiconductor materials very useful information can be obtained about the mechanism of electrical conduction, predominant scattering mechanism of charge carriers, concentrations and mobility of charge carriers etc [7–11].

For many years a considerable attention has been paid to the experimental study of electrical conductivity of a large number of organic semiconducting compounds of quite different classes (monomers, polymers, charge transfer complexes etc.) and some correlation between their chemical structure and semiconducting properties have been established.

The experimental data concerning the Seebeck coefficient of organic semiconductors are rather poor [1,2,12]. The information on the Seebeck coefficient of organic compounds containing metallic ions in their molecules are rather few [9–12].

In previous papers [8–11,13,14] we studied the temperature dependence of the electrical conductivity and the Seebeck coefficient of a great number of organic compounds which showed typical semiconducting characteristics. The values of some fundamental parameters (activation energy, ratio of carrier mobilities etc.) of the studied compounds have been determined.

In the present paper we extended these investigations on some *N*-(*p*-aminobenzoyl)-*L*-aspargine derivatives containing silver ions in their molecules in order to find some correlations between the semiconducting properties and the chemical structure.

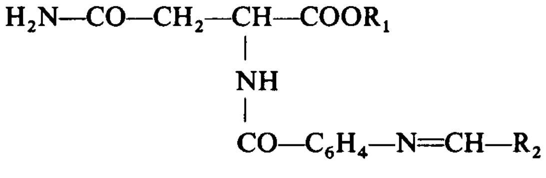
The nature of the mechanism of electrical conduction in the investigated samples is also discussed.

II. EXPERIMENTAL

2.1. Synthesis of Compounds

The compounds under study have been synthesized by the condensation of *N*-(*p*-aminobenzoyl)-*L*-aspargine with *o*-, *m*- and *p*-nitrobenzaldehyde when *N*-[*p*′-(*o*-, *m*-, *p*-nitrobenzyliden)-aminobenzoyl]-*L*-aspargyne resulted (compounds I-III). By their dissolution in a sodium bicarbonate solution followed by the addition of a silver nitrate solution the silver salts of the *β*-amido-*N*-[*p*'-(*o*-, *m*-, *p*-nitrobenzyliden)-aminobenzoyl]-*L*-asparagic acids resulted as precipitates (compounds IV-VI).

The mentioned substances correspond to the following general formula:



$$\begin{array}{l} H_2N{-}CO{-}CH_2{-}\underset{\displaystyle \begin{array}{l} | \\ NH \\ | \\ CO{-}C_6H_4{-}N{=}CH{-}R_2 \end{array}}{CH}{-}COOR_1 \end{array}$$

The substituents R_1 and R_2 as well as the corresponding melting points are given in Table I:

The preparation methods and some properties of these compounds are discussed in detail in [15]. They were obtained as polycrystalline powders and showed chemical stability under normal ambient atmosphere.

2.2. Preparation of Samples. Study on Temperature Dependence of Both Electrical Conductivity and Seebeck Coefficient

For the study of the temperature dependence of the electrical conductivity and Seebeck coefficient the thin films were deposited onto glass substrates from dimethylformamide solutions of the compounds.

The experimental conditions (solution concentrations, solvent evaporation rate) have so established as to obtain samples of compact structure and uniform thickness over sufficiently large areas of the substrate. The sub-strate temperature during the film growth was of 320–340 K. Under these conditions the solvent evaporated very slowly and films adherent at the substrate have been obtained.

TABLE I The substituients R_1 and R_2 and melting points T_m for investigated compounds

Compound	R_1	R_2	$T_m(K)$
I	–H	$-C_6H_4-NO_2-$ortho	466
II	–H	$-C_6H_4-NO_2-$meta	425
III	–H	$-C_6H_4-NO_2-$para	433
IV	–Ag	$-C_6H_4-NO_2-$ortho	580
V	–Ag	$-C_6H_4-NO_2-$meta	570
VI	–Ag	$-C_6H_4-NO_2-$para	585

The dependence of the electrical conductivity, σ, on the temperature was studied with surface-type cells [9, 10]. Thin silver films were used as electrodes. Silver films were deposited by thermal evaporation under vacuum before the deposition of the organic compounds.

The measurements were performed by applying electric fields of low intensities ($\varepsilon < 10^2$ V/cm). Under these conditions nonohmic effects were not noticed.

The thickness, d, of organic films ranged between 0.20 and 2.75 μm and were measured by an interferometric method.

The experiments showed that the samples with thickness $d > 4$ μm are characterized by a less compact structure.

The surface structure of the films was investigated by means of a metallographic microscope. The films of the organic compounds were found experimentally to have generally a granular structure.

The experimental arrangements used for the study of temperature dependence of the electrical conductivity and Seebeck coefficient were similar to those described in [8–10]. The Seebeck coefficient was measured by using sonde electrodes [16]. The temperature difference between electrodes was of 10–15 K.

The Seebeck voltage was determinate by a standard DC-potentiometric method.

III. RESULTS AND DISCUSSION

The electrical conductivity of the films depends on their thickness. For all samples electrical conductivity increases with increasing thickness, in a manner similar to that described in [17–19].

In order to obtain samples with stable structure and reproducible electrical and thermoelectric properties all films were submitted to a heat treatment. This consisted of a several heatings and coolings within a certain temperature range, ΔT, characteristic for each compound (Tab. II).

The thermal stability of the respective compounds within these temperature ranges was verified.

The study of temperature dependence of the electrical conductivity of several samples with different thickness provided valuable information on the processes taking place during this treatment.

For a great number of organic compounds of similar chemical structure [9, 10, 13, 14] we found that the temperature dependence of the electrical conductivity, σ, obeys the well-known exponential law [7, 20, 21].

TABLE II Values of characteristic parameters for some investigated samples. d = film thickness, ΔT = temperature range in which the heat treatment of the sample was performed; σ_c = electrical conductivity at room temperature before the heat treatment; σ_T = electrical conductivity at room temperature after the heat treatment; σ_s = electrical conductivity at upper limit of range ΔT; T_c = characteristic temperature for respective sample

Compound	*Sample*	d (μm)	ΔT (K)	σ_c ($\Omega^{-1}cm^{-1}$)	σ_T ($\Omega^{-1}cm^{-1}$)	σ_s ($\Omega^{-1}cm^{-1}$)	T_c (K)	ΔE (eV)
I	02.H.08	0.83	300–440	5.85×10^{-7}	5.05×10^{-8}	1.00×10^{-4}	320	1.75
I	06.H1.12	1.30	300–435	9.30×10^{-7}	1.15×10^{-7}	8.25×10^{-5}	325	1.70
II	11.H2.06	0.65	300–415	1.80×10^{-7}	1.85×10^{-8}	3.70×10^{-5}	325	1.90
II	14.H2.16	1.65	300–410	5.05×10^{-7}	4.15×10^{-8}	7.85×10^{-5}	330	1.95
III	03.H3.04	0.42	300–415	3.05×10^{-8}	3.25×10^{-9}	1.65×10^{-6}	350	1.60
III	08.H3.12	1.24	300–410	5.50×10^{-8}	7.55×10^{-9}	9.15×10^{-6}	350	1.65
IV	02.A1.03	0.35	300–490	1.05×10^{-6}	1.50×10^{-7}	2.05×10^{-4}	345	1.50
IV	05.A1.10	1.06	300–500	5.05×10^{-6}	1.85×10^{-7}	4.30×10^{-4}	350	1.50
V	01.A2.05	0.50	300–485	8.30×10^{-7}	5.60×10^{-8}	1.15×10^{-4}	350	1.60
V	03.A2.15	1.47	300–490	1.35×10^{-6}	8.75×10^{-8}	3.70×10^{-4}	345	1.60
VI	01.A3.08	0.80	300–480	1.00×10^{-6}	9.20×10^{-8}	1.25×10^{-4}	355	1.35
VI	02.A3.15	1.50	300–485	3.75×10^{-6}	3.20×10^{-8}	2.10×10^{-5}	350	1.40

$$\sigma = \sigma_0 \exp(-\Delta E/2kT) \quad (1)$$

where ΔE denotes the thermal activation energy of electrical conduction, k is Boltzmann's constant and σ_0 is a parameter depending on the semiconductor nature.

According to this, we have examined the shape of the ln $\sigma = f(10^3/T)$ curves during the heat treatment and found them to depend on the compound nature, preparation conditions of the films and film thickness. However, some behaviour similarities were noticed for all samples. The experimental results for two of them are presented in Figures 1 and 2.

In these figures the respective samples were submitted to two successive heatings and coolings. During the first heating the electrical conductivity decreased with increasing temperature within the lower temperature range ($T > 350$ K). This behaviour could be explain by the elimination of the adsorbed and absorbed gases, solvent molecules and other impurities from the samples [9, 10, 12, 13]. Besides, some changes in the film structure also occur [13–15].

These factors are well-known to influence strongly the electrical properties of the organic semiconductors in thin films [2, 12].

For higher temperature domains ($T > 360$ K) an exponential increase of the electrical conductivity with temperature was noticed for all samples.

For the first cooling the ln $\sigma = f(10^3/T)$ curves are typical for semiconducting substances. They show two distinct parts: a part of a smaller slope where the extrinsic conduction probably prevails and a part of larger slope corresponding to an intrinsic conduction. The intrinsic conduction domain begins at certain temperature, T_c, characteristic of every sample.

The T_c values were found to depend on the compound nature and film thickness.

The experiments showed that after 2–4 series of successive heatings and coolings the temperature dependence of the electrical conductivity becomes reversible. This fact indicated the stabilization of the sample structure within the respective temperature range.

For a number of organic compounds showing semiconducting characteristics a detailed analysis of the ln $\sigma = f(10^3/T)$ curves during the heat treatment is given in [9–11, 13–15].

In Figure 3 the dependence of the electrical conductivity on the temperature is illustrated for six heat-treated samples.

The values of thermal energy of electrical condition, ΔE, calculated from these dependences within the intrinsic conduction domain are listed in Table II:

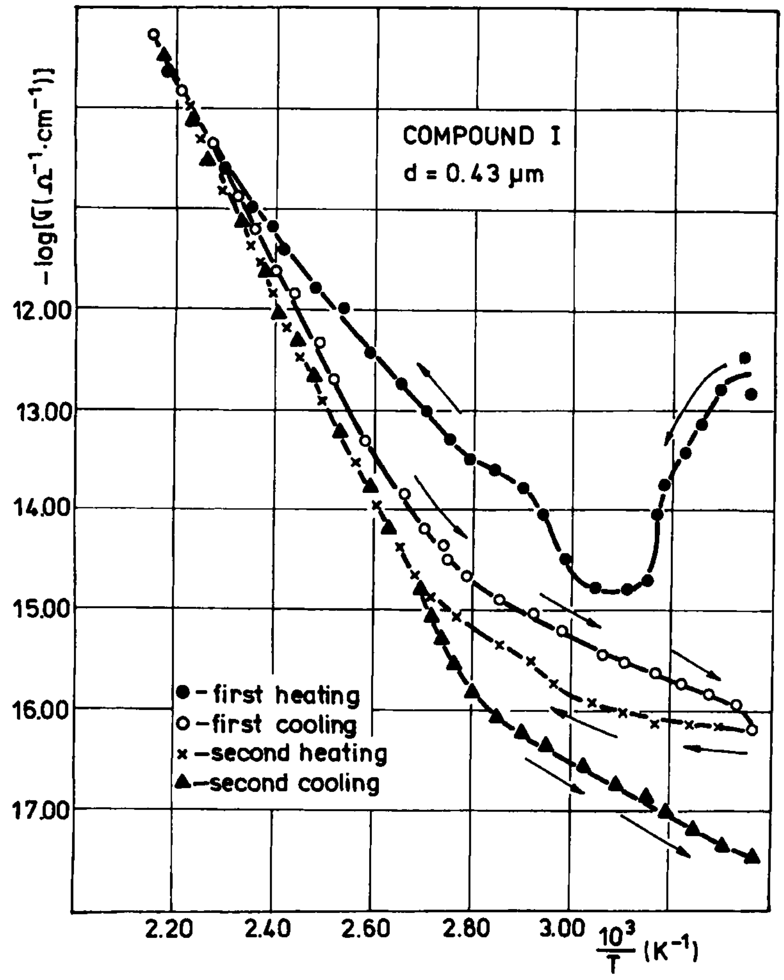


FIGURE 1 Temperature dependence of the electrical conductivity during heat treatment.

The calculations were made by taking into account the relationship (1).

In Table II the some characteristic parameters of the studied samples are also given.

The semiconducting properties of the investigated compounds are determined by their chemical structure which affords extended conjugation of the electrons.

The nature and position of the substituents R_1 and R_2 (Tab. I) significantly influence the values of the activation energy, ΔE. These values are smaller for extended conjugation systems.

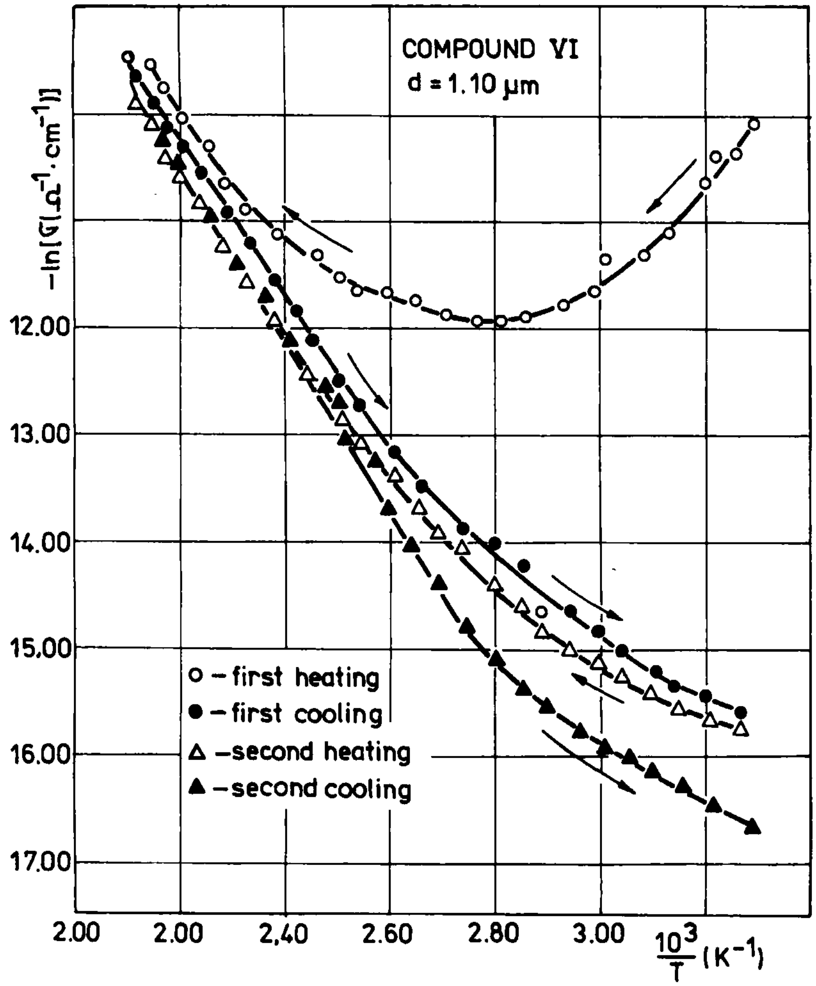


FIGURE 2 Temperature dependence of the electrical conductivity during heat treatment.

The values of electrical conductivity of the compounds under study are rather higher in comparison with other organic semiconductors.

This fact could be explained by the presence of the extended conjugation system involving the two aromatic rings and the nitro group.

The Ag^+-containing compounds are characterized by higher electrical conductivity and lower activation energies. This fact is probably caused by the formation of charge-transfer complexes between the carboxylic group anion and the Ag^+ metallic cation.

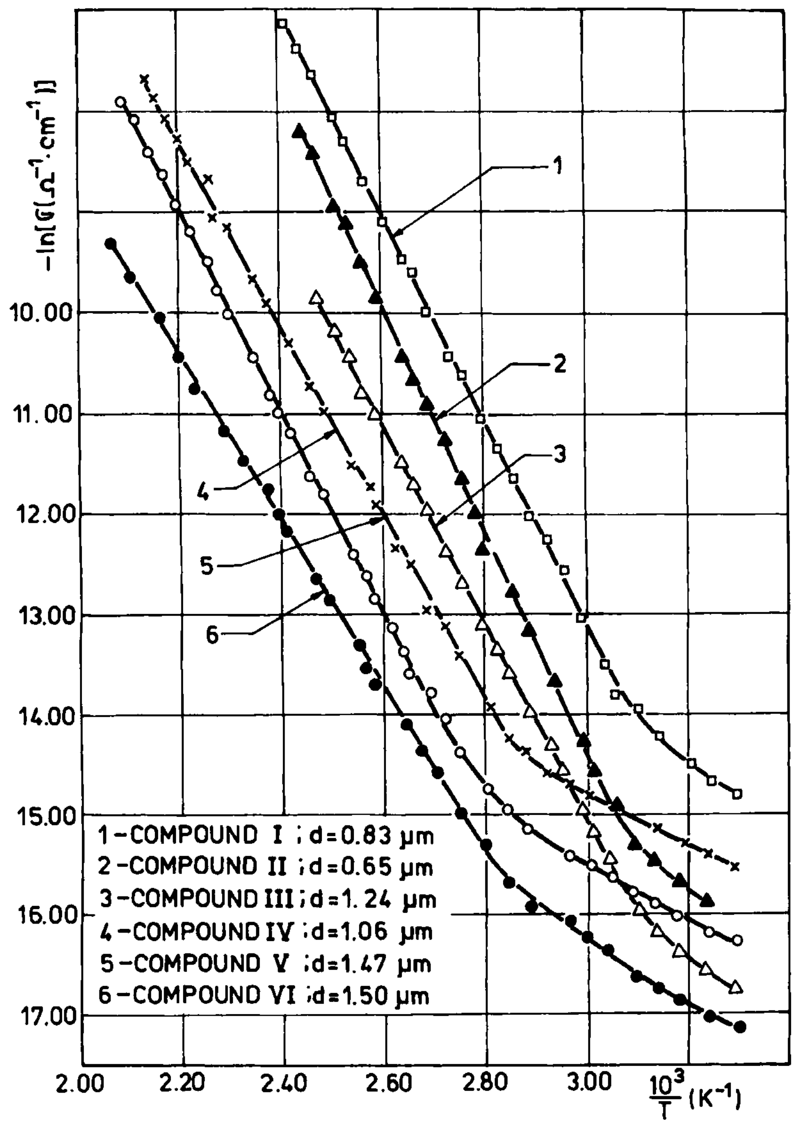


FIGURE 3 Temperature dependence of the electrical conductivity for heat-treated samples.

The nitro group position also influences the semiconducting properties of the compounds. Lower ΔE values were obtained with the compounds containing para-NO_2 groups.

In previous papers [9–11, 13–15] similar correlation between the chemical structure and the parameters characterizing the semiconducting properties were found for a great number of organic compounds of different classes.

These results are also in a good agreement with those reported by other authors who studied the structure – semiconducting properties correlation of organic semiconductors.

In order to obtain other information on the mechanism of electrical conduction, in the studied compounds the temperature dependence of the Seebeck coefficient was studied with several samples.

In the 340–450 K the Seebeck coefficient, α, was found to be positive for all samples under study and to decrease with increasing temperature within the intrinsic conduction domain.

The dependence $\alpha = f(10^3/T)$ is presented in Figure 4 for six samples of different compounds.

The Seebeck coefficient values and the shape of its temperature dependence also depend on the chemical structure of the compound. The compounds containing Ag^+ were noticed to show higher values of the Seebeck coefficient.

The σ and α values for the organic semiconductors containing metallic ions in their molecules are generally higher than those reported for the free metal organic compounds [10, 11, 13]. This behaviour is probably caused by the increase in the carrier mobility.

The aspect of the $\ln \sigma = f(10^3/T)$ and $\alpha = f(10^3/T)$ dependences shows that the models advanced for inorganic semiconductors could be used as "macroscopic" models for explaining the charge carrier transfer mechanism in the compounds under study.

In this connection some values of the characteristic parameters of the compounds could be estimated based on these dependences. The methods of determining the respective parameters are described in detail in references [9–11]. Within intrinsic conduction domain the dependence of the carrier concentration (electrons and holes) on the temperature is given by [7, 20].

$$n_i = 2(2\pi kT)^{3/2} h^{-3} (m_e \cdot m_h)^{3/4} \cdot \exp(\Delta E / 2kT), \tag{2}$$

where m_e and m_h are the effective masses of the electrons and of the holes, respectively, h is Planck's constant and k is Boltzmann's constant.

The temperature dependence of the Seebeck coefficient within the intrinsic domain can be written in the following form [7, 9, 11, 21].

$$\alpha_i = -\frac{k}{|e|} \cdot \frac{b-1}{b+1} \left(2 + \frac{\Delta E}{2kT} \right), \tag{3}$$

where b is ratio of the carrier mobility ($b=\mu_e/\mu_h$, where μ_e denotes the electron mobility and μ_h is the hole mobility) and e is the electron charge.

The relations (2) and (3) were deduced for nedegenerate semiconductors when the classical Boltzmann distribution may be used instead of the Fermi-Dirac distribution.

The equation (3) is written by assuming that the carrier scattering on the lattice vibrations is predominant for the investigated samples [7, 12].

The rates of carrier mobility can be estimated by means of the relationship [21].

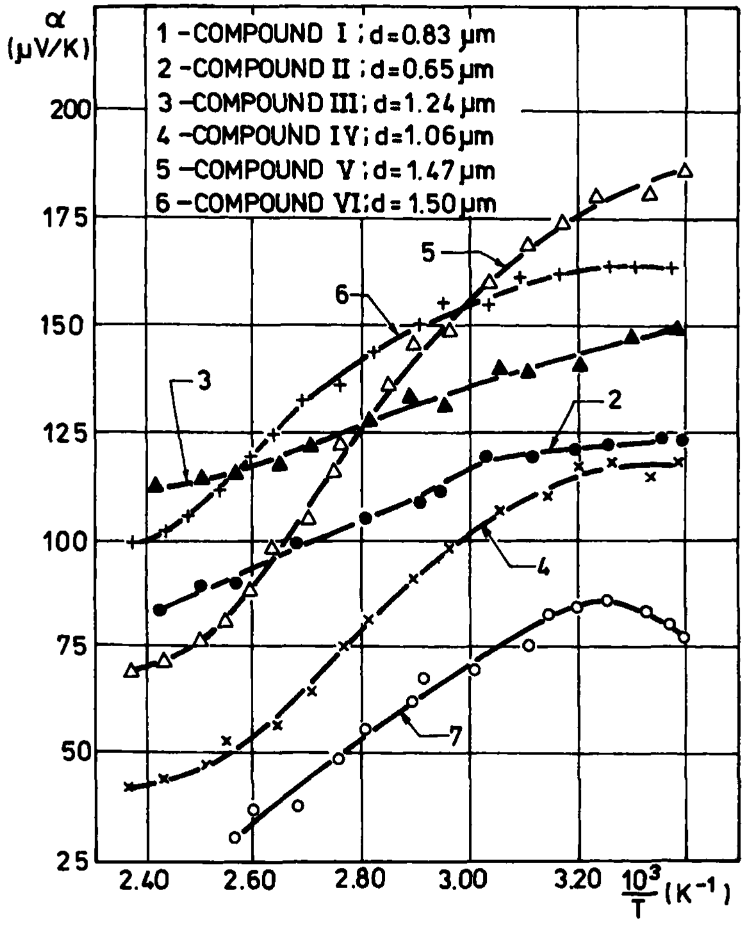


FIGURE 4 Temperature dependence of the Seebeck coefficient for heat-treated samples.

$$b=\frac{\Delta E/2\cdot\Delta(1/T)-|e|\cdot\Delta\alpha}{\Delta E/2\cdot\Delta(1/T)+|e|\cdot\Delta\alpha} \tag{4}$$

where $\Delta\alpha$ is the variation of the Seebeck coefficient corresponding to a determined variation $\Delta(1/T)$ of the temperature.

The hole mobility within the intrinsic domain is given by [9–11].

$$\mu_h=\frac{\sigma_i}{n_i\cdot e\cdot(b+1)} \tag{5}$$

where σ_i is the electrical conductivity.

By means of the relation (4) the ratio of the carrier mobility, b, has been calculated. The amounts $\Delta\alpha$ and $\Delta(1/T)$ have been estimated from the curves $\alpha=f\,(10^3/T)$ presented in Figure 4. The obtained values are to be found in Table III.

In Table III the following characteristic parameters of the investigated samples are also given: σ_i-electrical conductivity at $T=400$ K; n_i-carrier concentration at the same temperature, calculated by means of the relation (2); μ_h- the hole mobility at $T=400$ K calculated by means of the relation (5).

It is known, that the effective mass of charge carries in organic semiconducting films can be determined from the static current-voltage (J-U) characteristic of thin-film sandwich structures of the metal organic/semiconductor/metal type. The method is based on the analysis of these characteristics in the intermediate region between thermionic and thermionic-field emission [8,27]. For the investigated samples the values of effective mass of charge carries calculated from I-U characteristics are approximately 0.8 m_0 to 0.9 m_0 (m_0 is free electron mass).

For a great number of organic semiconductors the effective masses of charge carries can be considered to be approximately equal to the free electron mass [2,8–12].

TABLE III Values of characteristic parameters for some studied samples. d is film thickness; σ_i and n_i electrical conductivity and concentration of charge carries at temperature $T=400$ K; μ_h-hole mobility at some temperature, b-ratio of carrier mobilities

Compound	*Sample*	d *(μm)*	σ_i $(\Omega^{-1}\times cm^{-1})$	n_i (cm^{-3})	μ_h $(cm^2\times V^{-1}\times s^{-1})$	b
I	02.H1.08	0.83	3.38×10^{-4}	2.3×10^{12}	510	0.8
II	11.H2.06	0.65	1.23×10^{-4}	5.9×10^{11}	685	0.9
III	08.H3.12	1.24	4.54×10^{-5}	5.8×10^{12}	25.5	0.9
IV	05.A1.10	1.06	1.67×10^{-5}	2.4×10^{13}	2.5	0.7
V	03.A2.15	1.47	6.14×10^{-6}	9.1×10^{12}	2.3	0.8
VI	02.A3.15	1.50	2.50×10^{-6}	5.6×10^{13}	0.2	0.7

The results obtained by studying the transport phenomena in the investigated compounds can be lead to conclusion that the band conduction model could explain the dependence of electrical conductivity and Seebeck coefficient on the temperature. But is a "macroscopic" model, since the real mechanism of electron transfer in organic semiconducting compounds having a complex molecular structure is at present unknown [1, 2, 12, 23–25].

The investigated films have a granular structure. In these conditions, the grain size and shape as well as the characteristics of the contact between them strongly influence the kinetic phenomena. Therfore it is possible to use the models elaborated for explaining the mechanism of electrical conduction in thin films with discrete structure [5, 8, 9, 17, 18, 26].

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