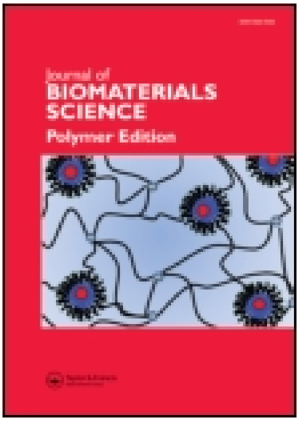

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Electrical conductivity of synthetic DOPA-melanin polymer for different hydration states and temperatures

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Electrical conductivity of synthetic DOPA–melanin polymer for different hydration states and temperatures

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Abstract—The dependence of the d.c. conductivity on the hydration and temperature (293–343 K) for synthetic DOPA–melanin polymer is presented. The hydration state of the melanin has been changed by varying the humidity conditions around the sample. It has been shown, that in the range of relative humidity values (0–100%), changes in the hydration state of melanin have predominant influence on electrical conductivity (10^{-13}–10^{-5}S cm^{-1}) in comparison to temperature. The influence of the two forms of water on the conductivity—the first form adsorbed mainly on the melanin surface and easily removed by drying, and the second one incorporated into the inner structure of the polymer, has been investigated. The temperature dependence of the conductivity in vacuum (0.8 and 0.04 mb) and thermal activation energy values (0.49–0.76 eV) for cooling and heating curves have been determined. The relationship between thermal activation energy and preexponential factor σ_0 (compensation effect) and possible charge transport mechanisms are discussed.

Key words: DOPA-melanin; hydration; electrical conductivity; organic semiconductor.

INTRODUCTION

Melanins are biopolymers, which occupy a unique position among the natural pigments because of their involvement in human pigmentation. Substantial amounts of melanin are present in the skin, hair, and eye. Smaller quantities have been found in the midbrain of primates and in the inner ear. It is generally accepted that the main biological function of epidermal melanin is the photoprotection of skin [1]. The presence of melanins in both illuminated and non-illuminated areas indicates that their biological role is complex and probably different in various organs.

Despite intensive investigations, the chemical structure of melanins is still far from being well understood. It is experimentally well documented, however, that eumelanin, the most abundant melanin in animals, is an indolequinone polymer deriving from enzymatic oxidation of tyrosine or DOPA (3,4-dihydroxyphenylalanine) [2, 3]. Polymerization occurs essentially in a random manner and some or all of the intermediates are likely to be incorporated into the final amorphous polymeric product. In this way an heteropolymer is formed. Some of the moieties that have been found to be present in eumelanin are shown in Fig. 1.

Naturally occuring melanins are very complex. They contain proteins, lipids, and metal ions. In this study, we have restricted the analysis to synthetic melanin obtained by

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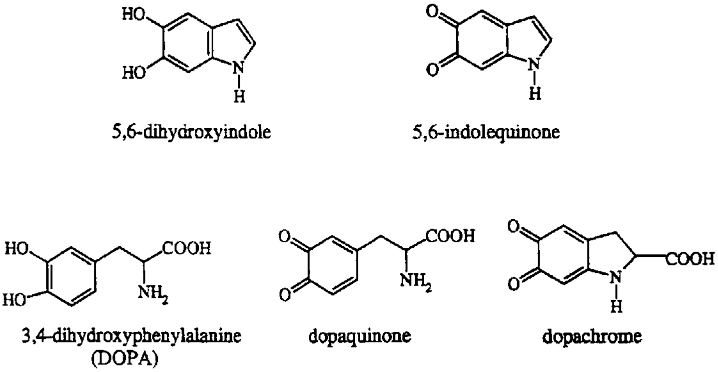

5,6-dihydroxyindole

5,6-indolequinone

3,4-dihydroxyphenylalanine (DOPA)

dopaquinone

dopachrome

Figure 1. The most common monomer units present in eumelanin [2, 3].

autoxidation of L-3,4-dihydroxyphenylalanine (L-DOPA). Previous studies on synthetic DOPA–melanin have shown that its main structural and physical properties are very close to those of natural eumelanins [2, 4].

As demonstrated in various experiments [5, 6], melanins are always hydrated and water is so strongly bound that it is very difficult to remove it completely. The hydration degree influences many physical properties of the melanin. Investigations of the threshold switching phenomenon have shown that the increase of the hydration of the melanin lowers the threshold temperature and electric field required for producing a low resistance state [7, 8]. Measurements were performed with samples kept in air or using helium gas. A vacuum environment ruined the switching behaviour of melanin [8]. Significant differences in photoacoustic signals have been observed for synthetic DOPA–melanin samples prepared first as a dense aqueous suspension and then as a dried powder or pellet [9]. Electron paramagnetic resonance measurements are mostly performed on hydrated melanin suspension because of the strong influence of drying on the free radical content in melanins [2].

X-ray [5], IR [10], and thermally stimulated depolarization current [6] studies performed on dried melanin powder clearly show the presence of water particles incorporated into the melanin structure. Heating treatment can remove part of the water, whereas some water is retained in the inner structure of the polymer. It was demonstrated by thermogravimetry and differential scanning calorimetry measurements that changes in the hydration state of melanin can be accompanied by a phase transition phenomenon [11].

The hydration state of melanin thus seems to be a very important factor in electrical conductivity investigations. According to the experimental results of many authors, melanin polymers can act as amorphous semiconductors [12–14]. On the basis of optical absorption, d.c. dark- and photoconductivity measurements [12, 15] as well as on theoretical calculations [16], band structures of melanins were proposed. Taking into account only synthetic DOPA–melanin polymers, one can notice significant discrepancies in the room temperature conductivity (10^{-5}–10^{-9}S cm^{-1}) and bandgap (0.8–1.4 eV) values reported by various authors. According to the assumption of Sarna [17], the discrepancies may reflect not only the possible different melanin preparation used but also different hydration states of the samples tested. Unfortunately until now, little attention has been paid to investigation of this effect in detail.

In this paper we study the effect of hydration and temperature on the d.c. conductivity of synthetic DOPA–melanin polymer.

EXPERIMENTAL

Preparation of synthetic DOPA–melanin

Synthetic DOPA–melanin was obtained by oxidative polymerization of L-DOPA (Reanal, Hungary). The solution of L-DOPA in Tris-HCl buffer (0.005 mol l^{-1}, pH = 7.4) was aerated at 22°C for 72 h. After acidification with concentrated hydrochloric acid to a final pH of 2.0, the precipitated melanin was separated by centrifugation (1500 *g* for 20 min). The melanin sediments obtained were washed carefully with distilled water until they yielded a negative chloride reaction and then dried over phosphorous pentoxide.

d.c. conductivity measurements

Powdered and dried melanin was pressed under a pressure of 500 MPa into pellets 1 mm thick and 5 mm in diameter. Another kind of melanin sample was prepared from the hard melanin disc which was obtained from a melanin suspension after drying at 313 K in air for 2 days. Small pieces 1 mm thick and 1.5 mm in diameter were cut from the pellet and the disc and used as samples. Hereafter, these two kinds of samples will be called melanin-pellet and melanin-disc samples, respectively. The purpose of using these two kinds of melanin samples was to test if there is some influence of sample preparation, i.e. powdered and pressed form or only dried form, on the electrical conductivity at various hydration states modified by humidity changes around the sample. The melanin sample was placed into a closed glass vessel where the relative humidity (0–100%) and temperature (293–343 K) conditions were maintained and monitored.

To obtain different relative humidity (RH) values at room temperature (293 K), saturated aqueous solutions of different chemical compounds were used, according to [18] (Table 1). The RH values of 50, 3.2, and 0% were obtained using ambient air humidity, a continuous stream of argon gas (~ 1.5 l min^{-1}), and vacuum pump (0.04 and 0.8 mb), respectively. Humidity measurements were performed using the relative humidity and temperature probe HMP 36/090 connected to the indicator unit HMI 31 (Vaisala Sensor System, Finland). As can be seen from Table 1, RH values measured in the closed glass vessel are not always exactly the same, especially for lower humidities [18]. The observed discrepancies do not influence our results because measurements with humidity probe allowed us to determine the actual RH value with an accuracy of ± 1%.

After putting the sample into the closed vessel over the saturated solution no less than 1 hour was spent to obtain a hydration equilibrium state between the sample and the surroundings. As an indication that the equilibrium state has been reached, no changes in

Table 1.
Relative humidity within a closed space over a saturated aqueous solution of the given solid phase at 293 K: (a) measured and (b) according to [18].

Chemical compound	Relative humidity (RH%)	
	a	b
$CaCl_2 \cdot 6H_2O$	35	32.3
$NaHSO_4 \cdot H_2O$	67	52
$Na_2S_2O_3 \cdot 5H_2O$	80.5	78
$(NH_4)_2SO_4$	82	81
$ZnSO_4 \cdot 7H_2O$	90	90

conductivity of the sample on time are observed. In this way, we can assume, that the relative humidity value measured inside the vessel during the experiment is proportional to the hydration state of the melanin sample.

Temperatures were measured by means of a silicon diode sensor (DT-470-SD-13) in vacuum or using the Pt-temperature sensor, with which the humidity probe was equipped.

d.c. conductivity measurements were performed using a Keithley 617 electrometer with the ± 100 V internal voltage source. Electrodes to the melanin sample were made with graphite paste. The electric field was equal to about 400 V cm^{-1}. The whole apparatus was fitted with an electrostatic screen. Current-voltage (I-V) characteristics were measured for all examined melanin samples. A linear dependence between the current and voltage was obtained in the whole voltage range investigated. No changes in I-V characteristics were observed when the electrode polarity was changed. These results show that the electric contacts were ohmic.

We can classify the d.c. conductivity measurements which are presented in this paper into three parts according to the range of relative humidity used. The first part contains d.c. conductivity measurements in a wide range of humidity values from about 30 to 100% using saturated solutions of different chemical compounds. The second part are the d.c. conductivity measurements performed at low humidity values, i.e. below 10% using a continuous Ar stream. The last part contains measurements in vacuum (0.8 and 0.04 mb).

RESULTS AND DISCUSSION

The dependence of the d.c. conductivity of the melanin-pellet sample on relative humidity, at room temperature, is shown in Fig. 2. According to the experimental conditions used, the hydration state of the melanin is proportional to the relative humidity of the atmosphere around the sample. This statement is supported by the considerable adsorption capacities of the melanin polymer. Melanin is known as a material with a high specific surface area, which facilitates the penetration of various vapours and gases into the interior of melanin. The specific surface area of synthetic DOPA–melanin calculated from the adsorption-desorption and BET isoterms of water reaches the high value of about 250 m^2g^{-1} [19].

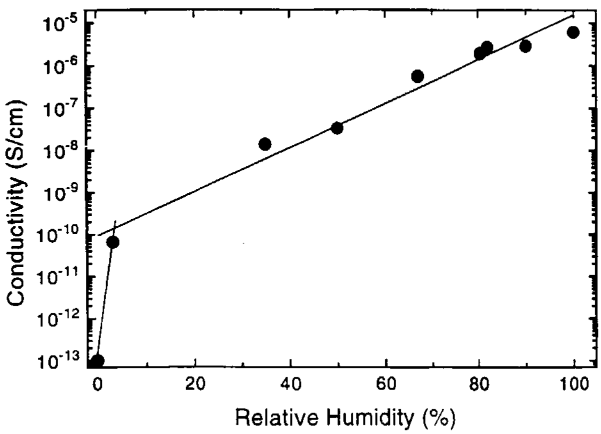

Figure 2. Conductivity vs. relative humidity for melanin-pellet sample, at room temperature.

Figure 2 shows that the conductivity increases about five orders of magnitude when the humidity rises from 3 to 100% and this relationship has a linear form, when log σ is plotted against RH. Extrapolation of the plot of log σ vs RH to 0% gives a conductivity of 8×10^{-11}S cm^{-1}, whereas from the measurements in vacuum (0.04 mb) the value 10^{-13}S cm^{-1} has been obtained. The significant difference between these two results may indicate that not only adsorbed but also more strongly bound water exists in the melanin structure. The first part of water, corresponding to the linear part of the curve, can be easily removed from the polymer structure e.g., by drying in air following different humidity conditions. This adsorbed water has a strong influence on the electrical conductivity of melanin (five orders of magnitude changes in σ). The second part of water, corresponding to the vacuum measurement, is hard to remove from the melanin polymer by simply drying in air. However, a vacuum (0.04 mb) can partially remove this water reducing considerably the electrical conductivity of the polymer.

The presence of the two parts of water in the so-called dry melanin samples, kept over P_2O_5 or under a stream of dry nitrogen, has also been observed in thermally stimulated depolarization current (TDSC) studies [6] and in thermogravimetry and differential scanning calorimetry experiments [11]. It is postulated, according to the spatial model of the melanin structure described by Tchathachari [20, 21] and more recent analyses performed by Albanese *et al.* [5], that water molecules can be present between the layers composed of the planar indole-quinone monomer units with an interlayer spacing of about 3.4 Å. Hydrogen bonds or water bridges between individual water molecules and carboxy, hydroxy, and amino groups can be formed. In the course of melanin heating or dynamic vacuum treatment the weakening and partial breaking of hydrogen bonds between planar layers may occur and influence the electrical conductivity of melanin.

The above conductivity measurements of melanin-pellet sample at different hydration states have been performed at room temperature. Figure 3 shows temperature and relative humidity dependence of the resistance for a melanin-pellet sample (curves a, b, and c) and for a melanin-disc sample (curve d). The initial RH value was obtained by use of the proper saturated aqueous solution (see Table 1). The heating process raised this value to 100%.

In all measurements presented in Fig. 3, the resistance of melanin decreases when the temperature rises from 293 to 320 K and at the same time the humidity, from about 20 to 100%. According to the strong humidity dependence of the conductivity (see Fig. 2), the decrease of the resistance observed in Fig. 3 seems to be mostly due to the increase of humidity, rather than the temperature and may be ascribed to the water adsorbed by melanin. However, we can see from Fig. 3, that the resistance is continuously decreasing with temperature even after the humidity reaches a constant value of 100%. In conclusion, in the wide range of relative humidity values, i.e. from about 30 to 100%, changes in the hydration state of melanin induced by various humidity conditions, have a predominant influence on the electrical conductivity of melanin in comparison to temperature. This behaviour corresponds to the adsorbed water being easily removed from the melanin polymer. We also notice that there are no significant differences in temperature and humidity dependence of the resistance for the melanin-pellet sample and melanin-disc sample. Despite differences in the packing of melanin granules and probably different surface properties for water adsorption in these two samples, they react to the temperature and humidity changes in a very similar manner.

Using a continuous stream of Ar, it was possible to obtain the temperature and humidity dependence of the resistance for low humidities, i.e. below 10%. A presentation of this dependence is shown in Fig. 4. An increase of temperature involves a decrease of resistance, but takes place only up to a temperature of about 305 K. For higher temperatures, the resistance starts to rise. At the same time the humidity continuously decreases down to about 0%. The initial decrease of resistance is mostly generated by the increase of temperature. To explain the increase of the resistance observed above 305 K we have to look once more at Fig. 2. When humidity becomes lower than about 3%, a sharp drop of conductivity takes place. This phenomenon is predominant in such low humidity values and can explain the increase of resistance above 305 K.

To eliminate the humidity parameter, which strongly influences the electrical conductivity of melanin, vacuum measurements of the temperature dependence of conductivity have been performed. Figure 5 shows log σ vs $1/T$ plots for 0.8 and 0.04 mb vacuum. Conductivity is increasing with temperature according to the equation characteristic for a semiconductor material:

$$\sigma = \sigma_0 \exp(-\Delta E_a/kT) \tag{1}$$

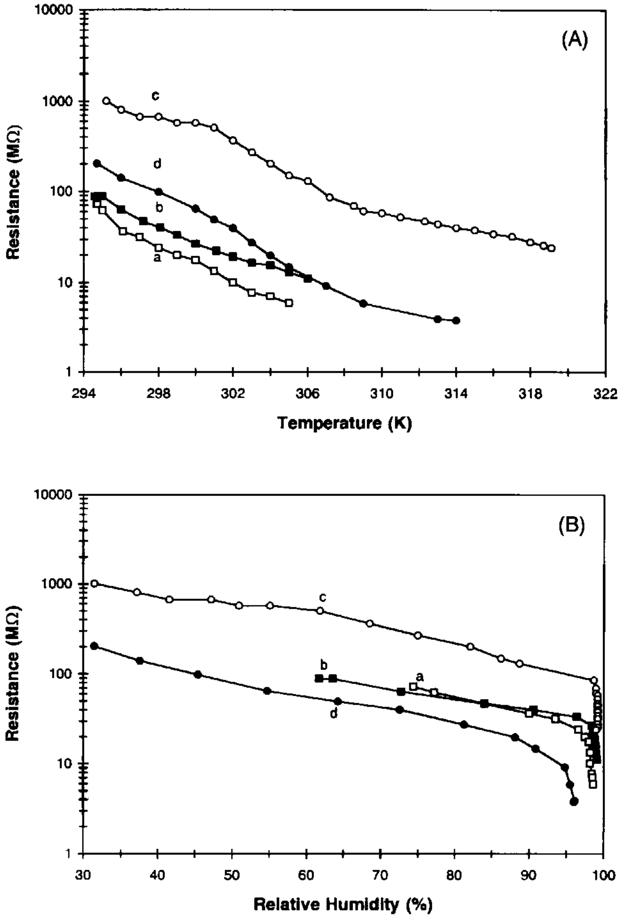

Figure 3. Temperature and humidity dependence of resistance for: (a) melanin-pellet sample (□), saturated solution of $Na_2S_2O_3 \cdot 5H_2O$; (b) melanin-pellet sample (■), saturated solution of $NaHSO_4 \cdot H_2O$; (c) melanin-pellet sample (○), saturated solution of $CaCl_2 \cdot 6H_2O$; and (d) melanin-disc sample (●), saturated solution of $CaCl_2 \cdot 6H_2O$ (see Table 1, high RH).

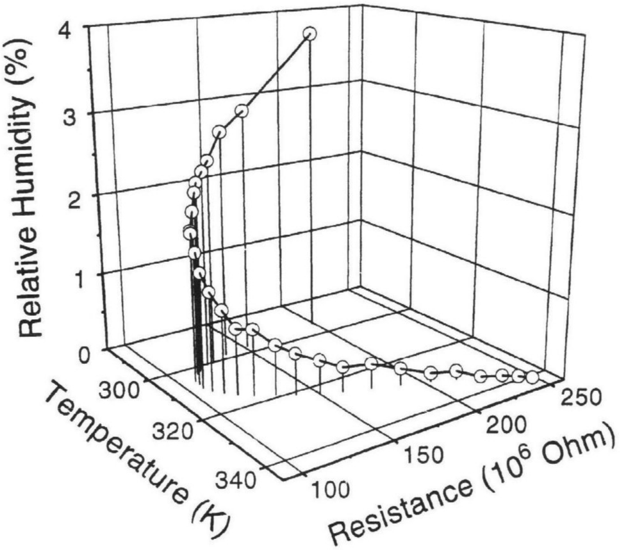

Figure 4. Three dimensional presentation of temperature and humidity dependence of resistance for melanin-pellet sample (intermediate RH (<10%)).

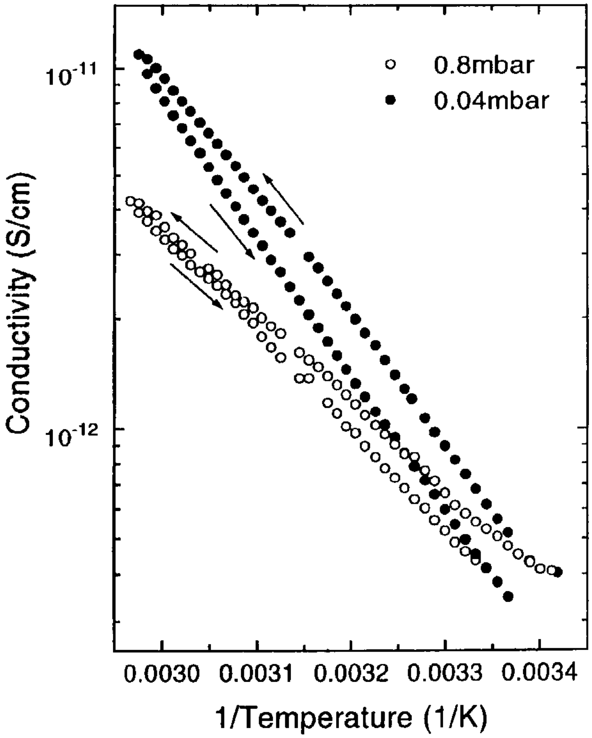

Figure 5. Temperature dependence of conductivity for melanin-pellet sample. Measurements in vacuum: 0.04 and 0.8 mb. In 0.04 mb vacuum thermal activation energies are equal to 0.69 eV for heating and 0.76 eV for cooling. In 0.8 mb vacuum 0.49 eV for heating and 0.56 eV for cooling.

where ΔE_a is the thermal activation energy and σ_0 is the preexponential factor. We can see that the conductivity does not follow the same route when the temperature is going up and down. This behaviour affects the values of the thermal activation energy, which are: 0.49 eV (heating) and 0.56 eV (cooling) for 0.8 mb vacuum and 0.69 eV (heating) and 0.76 eV (cooling) for 0.04 mb vacuum. The values of ΔE_a obtained from cooling curves are higher than those obtained from heating curves. Moreover, activation energies for 0.04 mb vacuum are higher in comparison to the results obtained for 0.8 mb vacuum. It may indicate, that a higher thermal activation energy corresponds to a lower hydration state of melanin caused by the temperature cycle or lower vacuum pressure. Similar behaviour has been found for oxidized cholesterol, where the change of hydration state from dry to fully hydrated has caused a decrease of the ΔE_a value from about 2 to 1.4 eV [22]. There is experimental evidence that for melanin this phenomenon can be more complex. It was shown, that for DOPA–melanin a phase transition occurs at 336 K [11, 23]. According to the model for the spatial structure of melanin, breaking of interplanar couplings and displacement of stacked layers may occur in the course of melanin heating or dynamic vacuum treatment. Further studies are needed to explain in detail transport properties of synthetic DOPA–melanin polymer with respect to this phase transition phenomenon.

One can notice that ΔE_a values presented here in the range 0.5–0.8 eV differ significantly from energies calculated on the basis of thermopower measurements (~ 0.2 eV at 293 K and p-type conductivity, ~ 0.3 eV at 325 K and n-type conductivity) [24]. The observed differences can be due to the existence of potential barriers between grain boundaries in the sample. Whereas the barriers limit the d.c. conductivity they do not necessarily have an influence on the thermopower [25]. In addition, melanin samples investigated in thermopower measurements were more hydrated. Conductivity was about five orders of magnitude higher than in our measurements. On the other hand, if conduction is by small polarons the activation energy difference could correspond to the polaron hopping energy [26].

Changes of the hydration state of the organic substances are often used when one wants to investigate the compensation effect, which is expressed by the formula [27]:

$$\ln \sigma_0 = a\Delta E_a + b \tag{2}$$

where a and b are constants. Thus, the conductivity can be written in the form:

$$\sigma = \sigma'_0 \exp(\Delta E_a/kT_0) \exp(-\Delta E_a/kT) \tag{3}$$

where $\sigma'_0 = \exp(b)$ and $T_0 = 1/ka$. T_0 is called the 'characteristic temperature' of the material. Figure 6 shows the dependence of $\ln \sigma_0$ on ΔE_a obtained from vacuum measurements for synthetic DOPA–melanin. The linear dependence indicates that the compensation law is valid here. The characteristic temperature T_0 calculated from the slope of the curve is equal to about 300 K, which is of the same order of magnitude as the experimental values 272, 490, and 338 K obtained by Rosenberg *et al.* [22] for retinal, oxidized cholesterol, and nucleic acids, respectively. For synthetic melanin they, however, obtained $T_0 = \infty$ (a horizontal $\ln \sigma_0$ vs ΔE_a plot), which differs significantly from our result.

Kemeny and Rosenberg [28, 29] have proposed the tunnelling of small polarons in thermally activated energy levels of molecules as a conduction mechanism for the explanation of the compensation effect in some organic and biological semiconductors. According to this model, the characteristic temperature is related to the Debye temperature. The strong electron–phonon coupling [30], the ability to retain the polarized state [6, 24], and the very small mobility of the carriers (about 10^{-6} cm^{2}V^{-1}s^{-1}) calculated from thermopower

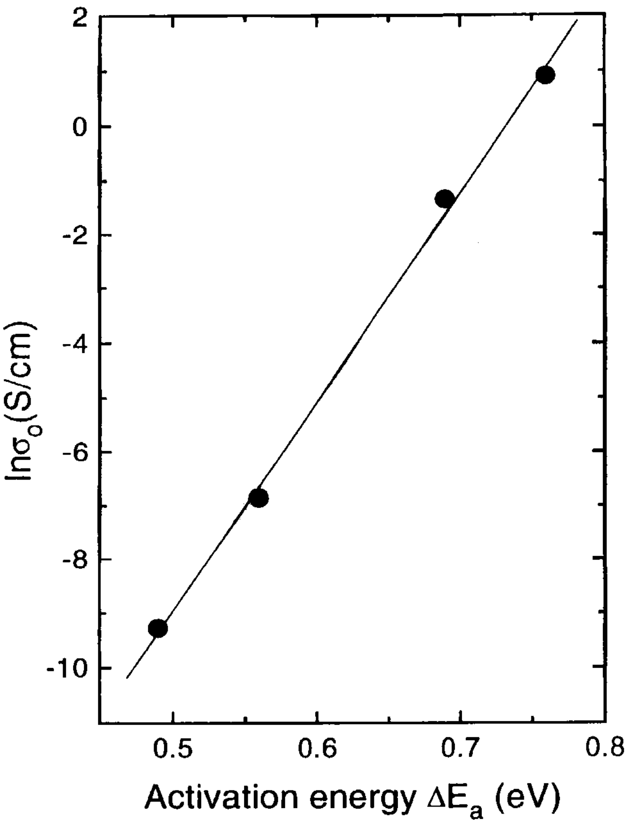

Figure 6. Dependence of $\ln\sigma_0$ on ΔE_a for melanin-pellet sample. Measurements in 0.04 and 0.8 mb vacuum. The solid line is the best linear fit to the points.

measurements [24], can support polaron formation and the proposed model. Although the small polaron tunnelling model is in qualitative agreement also with our experiments, further studies are needed to explain in detail the origin and motion of the charge carriers in synthetic DOPA–melanin biopolymer.

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