

# TEMPERATURE DEPENDENCE OF SATURATION CURRENTS IN THE SYSTEM: ANTHRACENE — LIQUID REDOX ELECTRODE

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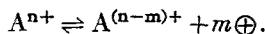
The saturation currents in the system: anthracene — redox electrode have been investigated. From the measurements of the temperature dependence of the currents the reorientation energy of the solvent molecules has been estimated.

## Introduction

The current, injected into an organic crystal from a liquid electrode tends to saturation value at sufficiently high voltage applied to the system [1–3]. Mehl [4] has shown that in the system: anthracene — solution of  $Ce^{4+}$  ions the saturation current density does not depend on the crystal thickness, being dependent on the solution properties only. The magnitude of saturation current is proportional to the concentration of an active component of the redox electrode (*i.e.* the oxidized form of the redox electrode in the case of hole injection and the reduced form, when electrons are injected) [4]. The concentration of the second form of the redox system is irrelevant to the saturation current [5].

## Outlines of theory

The hole injection into an organic crystal is due to the reaction occurring at the interface



Here  $A^{n+}$  and  $A^{(n-m)+}$  are oxidized and reduced forms of the redox system, respectively, and  $\oplus$  is the hole crossing the crystal — electrode interface.

At low voltages the current is limited not by the electrode — crystal interface properties, but by the space charge within the crystal [3, 4]. At high voltages, however, the electron transfer through the interface becomes the process limiting the current in the system;

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the current reaches the saturation value. After Hale and Mehl [6] the magnitude of the positive saturation current for the comparable concentrations of both forms of redox system is given by the equation:

$$i_p^0 = K c_{ox} \exp \left[ -\frac{\lambda}{4kT} \left( m + \frac{\Delta_s^p}{m\lambda} \right)^2 \right] \quad (1)$$

where  $K$  is a constant slightly dependent on temperature,  $c_{ox}$  is the concentration of the active component of the redox electrode,  $\lambda$  is the energy required to reorient the solvation layer of the active component until it becomes identical with that of inactive component of the redox system, and  $\Delta_s^p$  is the energy difference between the top of the hole band and the Fermi level at the crystal surface. The latter quantity can be expressed by the relationship:

$$\Delta_s^p = \Delta^p - e(V_s - V_{fb}) \quad (2)$$

where  $\Delta^p$  is the energy difference between the top of the hole band and the Fermi level in the bulk of the crystal,  $V_{fb}$  is the flat band electrode potential (equivalent to the steady — state Fermi level potential expressed in electrochemical scale), and  $V_s$  is the standard potential of the redox system.

The magnitude of the flat band potential can be determined from the following relationship (see also Fig. 1):

$$V_{fb} = \frac{1}{e} (I_c - W_h - \Delta^p). \quad (3)$$

Here  $I_c$  denotes the ionization potential of the molecule in the solid state and  $W_h$  is the work function of the standard hydrogen electrode. Assuming the values:  $W_h = 4.48$  eV [7],

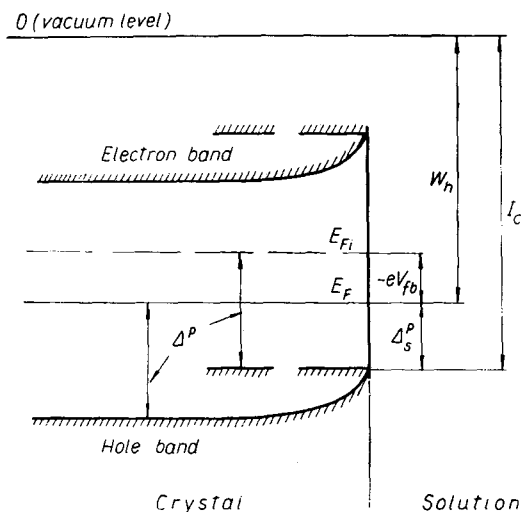


Fig. 1. The shape of the energy bands in the neighbourhood of the surface of an anthracene crystal contacted with the standard hydrogen electrode.  $E_F$  and  $E_{F_i}$  denote the "intrinsic" Fermi level and the Fermi level of anthracene contacted with the electrode in thermal equilibrium, respectively. For the other symbols — see text

$I_c = 5.65$  eV [8] and  $\Delta^p = 1.9$  eV [8, 9] we obtain for anthracene  $V_{fb} = -0.73$  eV, a result close to the value  $-0.7$  eV determined experimentally by Mehl [4].

The equation (1), after simple transformations, becomes identical with that obtained earlier by Dogonadze and Chizmadzhev [10, 11].

### Experimental

Thin crystals of anthracene were grown from the material previously submitted to sublimation and extensive zone melting by slow sublimation in nitrogen atmosphere. The measuring cell, made from quartz of teflon, and mounted in the thermostatic shield, as well as the electrical circuit were described elsewhere [12, 13].

### Results

In the present paper the results of the temperature dependence of the saturation current measurements in the system: anthracene — redox electrode are given.

As the injecting (positive) electrode the redox system:  $\text{Ce}^{4+}/\text{Ce}^{3+}$  in 1 M and 3 M  $\text{H}_2\text{SO}_4$ ,  $\text{Fe}^{3+}/\text{Fe}^{2+}$  in 3 M  $\text{H}_2\text{SO}_4$  and  $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$  in 3 M  $\text{H}_2\text{SO}_4$  were used. The 0.1 M  $\text{Na}_2\text{SO}_4$  aqueous solution was used each time as the negative (neutral) electrode. The temperature dependence of the saturation currents for the solutions in 3 M  $\text{H}_2\text{SO}_4$  follows the relationship:

$$i_p^0 = A \exp\left(-\frac{B}{T}\right) \quad (4)$$

where  $A$  and  $B$  are constants. The value of  $B$  is practically independent on the concentration of the oxydized component.

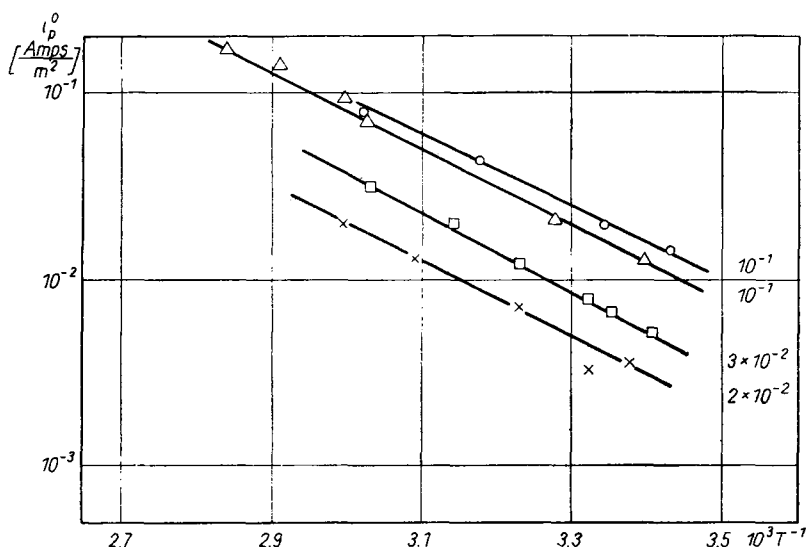


Fig. 2. Saturation currents for several anthracene crystals contacted with  $\text{Ce}^{4+}/\text{Ce}^{3+}$  electrode in 3 M  $\text{H}_2\text{SO}_4$ . The molar concentrations of  $\text{Ce}^{4+}$  ions are given on the figure

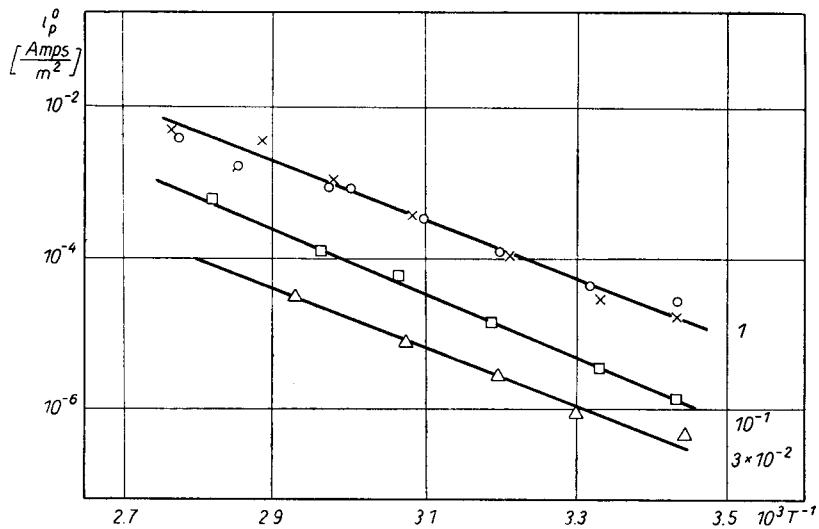


Fig. 3. Saturation currents for anthracene contacted with  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox electrode

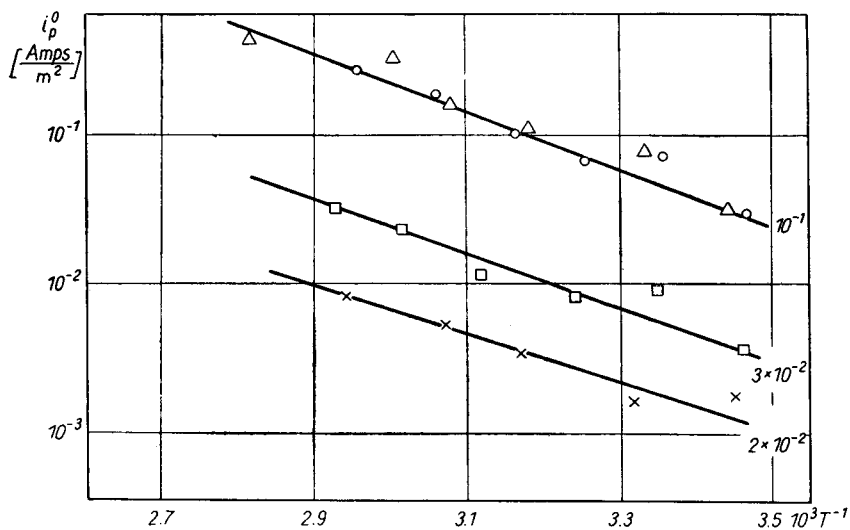


Fig. 4. Temperature dependence of the saturation currents in the system: anthracene —  $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$  electrode in 3 M  $\text{H}_2\text{SO}_4$

The measurements made with the solutions in 1 M  $\text{H}_2\text{SO}_4$  were restricted to the narrow temperature range because of secondary effects presumably connected with the formation of solid oxidation products on the crystal surface. The results obtained in low temperature range were, however, close to those obtained with the solutions in 3 M  $\text{H}_2\text{SO}_4$ .

The crystals, obtained by sublimation, were not polished prior to measurements thus differing considerably one from another in their surface areas. This explains rather poor reproducibility of the values of  $i_p^0$ . The effect is, however, irrelevant to the value of  $di_p^0/dT^{-1}$ . The mean values are given in Table I.

TABLE I

Redox system	Standard potential of the system	$\frac{d \log i_p^0}{d(1/T)}$
Ce <sup>4+</sup> /Ce <sup>3+</sup>	+1.44 V	2.0 × 10 <sup>3</sup>
Fe <sup>3+</sup> /Fe <sup>2+</sup>	+0.77 V	4.0 × 10 <sup>3</sup>
Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> /Cr <sup>3+</sup>	+1.33 V	1.8 × 10 <sup>3</sup>

### Discussion

The rate of the electron transfer reaction at the redox electrode — crystal interface depends chiefly on two quantities: the energy difference between the Fermi level and the hole band edge at the interface, and the reorientation energy of the solvation layer.

#### a) Ce<sup>4+</sup>/Ce<sup>3+</sup> system

For Ce<sup>4+</sup>/Ce<sup>3+</sup> system the former of the parameters mentioned is unimportant. Inserting into Eq. (2) the numerical values one obtains  $\Delta_f^p = -0.27$  eV, *i.e.* the Fermi level crosses the top of the hole band at the interface. The reorientation energy of the solvation atmosphere evaluated from Eq. (1) amounts to 1.52 eV.

#### b) Fe<sup>3+</sup>/Fe<sup>2+</sup> system

The energy difference between the Fermi level and the top of the hole band at the surface evaluated from Eq. (2) amounts to 0.40 eV. The electron transfer through the interface is limited by both mentioned parameters of the system. Insertion of the numerical values into Eq. (1) gives for the reorientation energy the value 2.39 eV.

#### c) Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>/Cr<sup>3+</sup> system

One obtains from Eq. (2) the value of  $\Delta_f^p$  equal to  $-0.16$  eV. The interpretation of the results similar to those obtained with the two above redox systems is, however, impossible. The electrochemical reaction at the interface is complicated and the slowest process is unknown. The values of  $i_p^0$  and  $di_p^0/dT^{-1}$  close to those of Ce<sup>4+</sup>/Ce<sup>3+</sup> electrode suggest that in the system the change of the configuration of water molecules around the redox ions limits the rate of the electron transfer reaction.

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