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Conference Paper

Photoelectrochemical Reactions at an Anthracene Cathode*

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Investigation of the peculiarities of the photoconductivity of an anthracene cathode in the redox system iodine-iodide has supplied information on the kinetics of photoelectrochemical reactions injecting holes into anthracene. The effect of the surface coverage of anthracene with adsorbed iodine, the dielectric constant of the solvent, and of the energy of exciting photons on the photoconductivity of an anthracene cathode has been studied. It is shown that at photon energies from 3.8 to 5.0 eV, greater than the forbidden zone width, the conduction band electrons participate in the iodine reduction reaction. In the spectral region of singlet absorption of anthracene, excitons participate in the electrochemical charge separation reaction. In the case of contact with a polar solvent, excitons break up at the surface levels formed by adsorbed iodine. In the case of contact with a weakly-polar solvent, excitation is transferred to adsorbed iodine. In the spectral region of weak optical absorption of anthracene, iodine particles excited directly by the light that had passed through the crystal participate in the reaction.

This paper is concerned with some peculiarities of the photoconductivity of anthracene single crystals with electrolytic contacts. An important characteristic of electrolytic contacts is the fact that the charge transfer through the anthracene/electrolyte interface is accompanied by an electrochemical reaction. For this reason, investigation of photoelectrical phenomena in anthracene crystals with electrolytic contacts can supply certain information on the kinetics of electrochemical reactions.

EXPERIMENTAL

A redox system I^-/I^0 was used as an electrochemical system injecting holes into anthracene. A 1 *M* NaCl solution was used in all cases as the second electrolytic contact through which the anthracene membrane was illuminated. The polarity of the applied voltage was such as to cause a cathodic process of iodine reduction to occur on the back surface of the anthracene crystal. The current-voltage curves obtained had a limiting current section. In all subsequent figures only the limiting current values were used. The technique of measurement has been described in more detail elsewhere.[1,2]

RESULTS

As the investigation of the dark injection has shown, the specificity of the redox system I^-/I^0 is that iodine is adsorbed on the anthracene surface. Iodine adsorption isotherms were obtained under different conditions, which

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allowed to relate the surface concentration of iodine particles with the level of hole injection into anthracene[3,4]. Being adsorbed on anthracene surface, iodine changes the zone bending near the surface at the contact, which with other parameters being constant, determines the rate of cathodic iodine reduction and thus the level of hole injection into anthracene.

The change in the zone bending near the surface during iodine adsorption was measured by the space charge-limited current method[5]. The dependence of the injection efficiency on the static dielectric constant of the solvent ε_{st} was also studied[6]. The injection efficiency is understood to be the ratio of the number of charges, passing through unit surface in unit time, to iodine surface concentration. The injection efficiency gives an idea of the fraction of reactive particles relative to all particles present on the surface, and is a quantity characterizing the kinetics of an electrochemical reaction.

A change of ε_{st} was achieved by mixing acetic acid and water in varying proportion. The surface coverage of anthracene with adsorbed iodine remained unchanged. For this purpose iodine adsorption isotherms on anthracene were obtained in solvents with different ε_{st}. The dependence of the injection efficiency on ε_{st} is shown in Fig. 1. The figure shows that with increasing ε_{st} the injection efficiency increases by two orders of magnitude.

The data on the photoconductivity were correlated with the results of the investigation of dark injection. Fig. 2 shows the dependence of the photoinjection current on the dielectric constant of the solvent at different energies of the exciting light quanta. Just as for dark injection, the injection efficiency values were obtained from the corresponding limiting current values. It is clear from analysis of Fig. 2 that the photoinjection efficiency increases with rising ε_{st}. This is valid for all the energies of the exciting light photons studied. Another parameter characterizing the electrolytic phase of contact is the surface coverage of anthracene with adsorbed iodine. Fig. 3 shows the photoinjection efficiencies *versus* surface coverage in aqueous

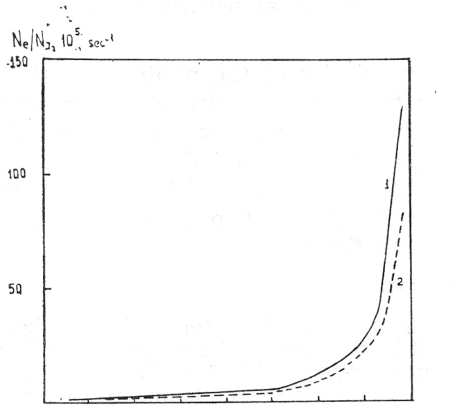


Fig. 1. Dependence of the dark injection efficiency on the dielectric constant of an acetic acid-water mixture at constant surface coverage of adsorbed iodine on anthracene $\theta = 0.03$; $E = 10^5$ v/cm. *1:* Experimental curve; *2:* Theoretical curve.

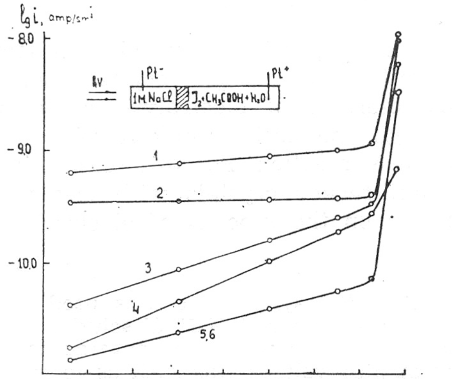
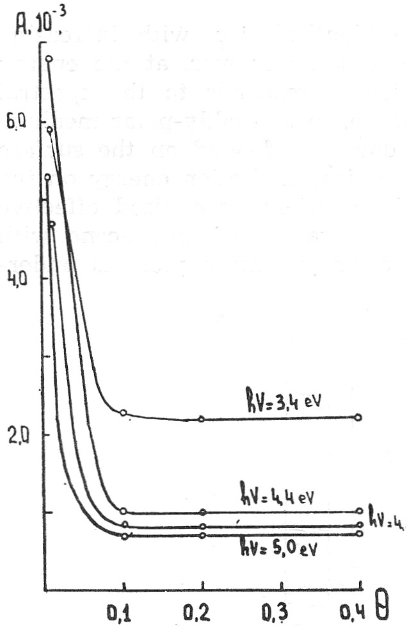


Fig. 2. Dependence of the photoinjection current on the dielectric constant of an acetic acid-water mixture at constant surface coverage of adsorbed iodine on anthracene $\theta = 0.05$; $E = 10^5$ v. cm. *1:* $h\nu = 4.45$ eV; *2:* $h\nu = 3.4$ eV; *3:* $h\nu = 3.04$ eV; *4:* $h\nu = 2.8$ eV; *5:* $h\nu = 2.28$ eV; *6:* $h\nu = 2.1$ eV.



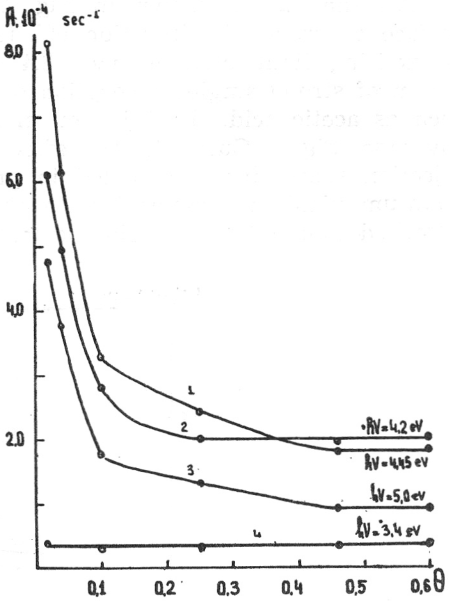


Fig. 3. Dependence of the hole photoinjection efficiency into anthracene on the surface coverage from aqueous iodine-iodide solutions; E = 10^5 v/cm.
1: hv = 3.4 eV; *2:* hv = 4.4 eV; *3:* hv = 4.2 eV; *4:* hv = 5.0 eV.

Fig. 4. Dependence of the hole photoinjection efficiency into anthracene on the surface coverage from iodine solutions in acetic acid. E= 10^5 v/cm.
1: hv = 4.2 eV; *2:* hv = 4.45 eV; *3:* hv = 5.0 eV; *4:* hv = 3.4 eV.

iodine-iodide solution at different energies of the exciting light quanta. In Fig. 4 are shown the same relations obtained for the injection from iodine solutions in acetic acid. Finally, Fig. 5 gives the curves for the case of dark injection.

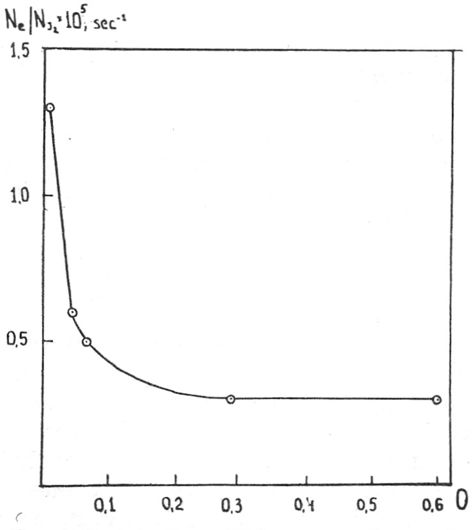


Fig. 5. Dependence of the dark injection efficiency on the surface coverage from iodine solutions in acetic acid. E = 10^5 v/cm.

All the curves shown in Fig. 3—5 are identical, *i. e.* with increasing surface coverage, the injection efficiency decreases. However, at the energy of exciting light photons $h\nu = 3.4$ eV, which corresponds to the spectral region of strong singlet absorption of anthracene, in a weakly-polar medium, such as acetic acid, the injection efficiency does not depend on the surface coverage (Fig. 4, Curve 4). The effect of the optical excitation energy on the injection specificity is revealed in greater detail when normalized effective quantum yield is correlated with the surface coverage of anthracene with adsorbed iodine (Fig. 6). The normalized effective quantum yield is understood to be the number of electrons participating in the electrochemical reaction per one photon. Normalization consisted in that each value of the effective quantum yield β at a definite optical excitation wave length was referred to its value at $\Theta = 0$.

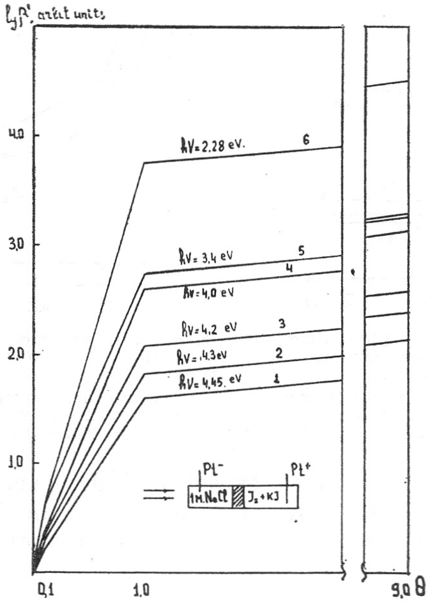


Fig. 6. Dependence of the effective normalized quantum yield on the surface coverage in aqueous iodine-iodide solution. $E = 10^5$ v/cm.
1: hν = 4.45 eV; *2:* hν = 4.3 eV; *3:* hν = 4.2 eV; *4:* hν = 4.0 eV; *5:* hν = 3.4 eV; *6:* hν = 2.28 eV.

$$\beta'(\lambda, \Theta) = \frac{\beta(\lambda, \Theta)}{\beta(\lambda, \Theta = 0)} = \frac{n_e(\lambda, \Theta)}{n_e(\lambda, \Theta = 0)}$$

where η_e is the number of charges passing per unit time through unit surface. In a more explicit form the effect of the photons energy on the charge separation process shows up in the dependence of the normalized effective quantum yield on the photon energy at a fixed surface coverage plotted from the data of Fig. 6 and given in Fig. 7. It can be concluded from the figure that there are three spectral regions where the values of β' are essentially different. At photon energies $h\nu$ from 5.2 to 4.2 eV, greater than the forbidden zone width of anthracene, the value of β' increases as their energy decreases.

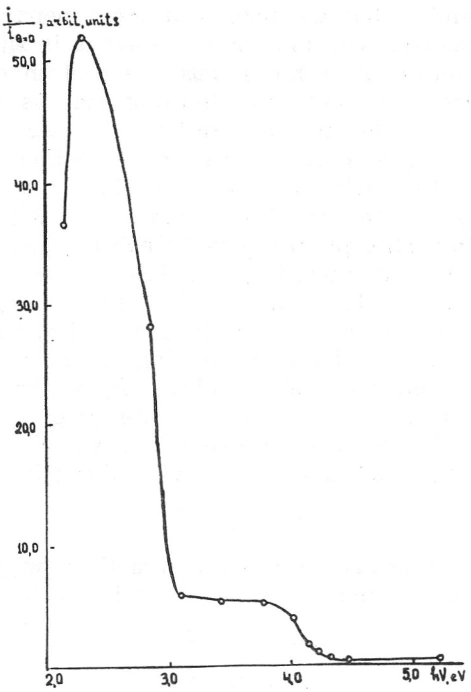


Fig. 7. Dependence of the normalized effective quantum yield on the exciting light photon energy at constant surface coverage $\theta = 1.0$ in aqueous iodine-iodide solution. $E = 10^5$ v/cm.

The second region in Fig. 7 corresponds to the photons energies from 3.8 to 3.1 eV, which coincides with the region of strong singlet absorption of anthracene. In this spectral region the value of β' does not depend on the energy of the exciting light quanta. At the energies $h\nu$ from 3.0 to 2.3 eV the photoconductivity spectrum of anthracene overlaps the iodine absorption spectrum and the value of β' increases with decreasing photons energy.

DISCUSSION

The comparison of the experimental dependence of the injection efficiency on ε_{st} with the theory of redox processes at semiconductors developed by Dogonadze-Levich-Kuznetsov[7] has given a satisfactory agreement of theory and experiment (Fig. 1). The calculation was carried out with the use of the iodine-ion radius and the value of the zone bending near the surface as parameters[6]. In the theory of Dogonadze-Levich-Kuznetsov the assumption that the transfer of the electron through the interface is the limiting step is of principal importance. Therefore satisfactory agreement between theory and experiment is an important argument in favor of the concept that it is the electron transfer which determines the rate of the electrochemical reaction injecting holes into anthracene.

The presence of a saturation section on the current-voltage curve proves that the electrochemical reaction rate determines the level of injection into anthracene[1]. According to Mehl[8,9], the saturation current value is determined by the exchange current of the electrochemical reaction. It follows from analysis of Figs. 1 and 2 that the nature of the dependence of the injection efficiency on the dielectric constant of the solvent is similar for dark- and photoinjections. Therefore, it is not impossible that in optical excitation of an anthracene electrode as well, the limiting step is the charge transfer through the interface. Under this assumption, the decrease in the injection efficiency with the surface coverage can be explained by increase of the adsorption potential drop with increasing surface coverage with adsorbed iodine (Figs 3—5). As it follows from Curve 4 in Fig. 4, in the spectral region of strong singlet absorption ($h\nu = 3.4$ eV) the photoinjection efficiency does not depend on Θ and, accordingly, neither on the change in the work function determined by it. Therefore, in this spectral region the transfer of the electron proper step is not the limiting one, *i. e.* the specificity of the electrochemical reaction can change depending on the energy of the exciting light photons. This conclusion also follows from the dependence of the normalized effective quantum yield on the energy of quantum optical excitation presented in Fig. 7. The normalization was carried out under the assumption that at the interface, along with the adsorbed iodine reaction

$$e + I_{ads} \rightarrow I^- \qquad \text{(I)}$$

there can occur simultaneously competing reactions with some acceptor. In principle, two types of reactions with acceptors in aqueous phase are possible.

$$e + O_2 \rightarrow O_2^- \qquad \text{(II)}$$

$$e + H_2O \rightarrow H_2O^- \qquad \text{(III)}$$

However, using the data on the constants of the reactions (II)—(III), it is possible to find the particle life-time before capture, defined as

$$(\tau)^{-1} = K \cdot [C_x] \qquad (1)$$

Since $k_{O_2} = 1.5 \times 10^{10}$ l/mole · sec[10], $k_{H_2O} = 16$ l/mole · sec[11] and $C_{O_2} \approx 10^{-2}$ *M*/l and $C_{H_2O} \approx 56$ *M*/l, the most likely competing reaction is the reaction with oxygen. The efficiency of both processes is determined by the surface coverage with adsorbed iodine, as well as by photon energy. Accordingly, the value of the quantum yield measured will consist of the sum of the quantum yields of the first — β_1 and the second — β_2 reactions.

$$\beta(\lambda, \Theta) = f(\lambda) [\beta_1(\lambda, \Theta) \cdot \Theta + \beta_2(\lambda)(1 - \Theta)] \qquad (2)$$

where $f(\lambda)$ is the efficiency of the energy supply to the back interface.

It follows from expression (2) that at fixed photon energy, the efficiency of electrochemical charge separation in the function of Θ is determined by the quantum yield of the reactions (I) and (II). The sense of carrying out normalization lies in that the process of optical excitation supply to the back interface is excluded from consideration, provided the mechanism of supply for each wave length is assumed to be independent of the state of the back surface

$$\beta' = \frac{\beta(\lambda, \Theta)}{\beta(\lambda, \Theta = 0)} = \frac{f(\lambda) [\beta_1(\lambda, \Theta) \cdot \Theta + \beta_2(\lambda)(1 - \Theta)]}{f(\lambda) \cdot \beta_2(\lambda)} = \frac{\beta_1(\lambda, \Theta)}{\beta_2(\lambda)} + (1 - \Theta) \qquad (3)$$

It can be concluded from the consideration of the dependence of the normalized effective quantum yield on the exciting light photons energy that there are three regions with different nature of the electrochemical charge separation process.

In the region of strong singlet absorption, $h\nu$ from 3.1 to 3.8 eV, excitons participate in the electrochemical reaction. The reaction mechanism, however, is to a considerable extent determined by the dielectric constant of the electrolytic contact. In a polar solvent (aqueous iodine-iodide solution) the injection efficiency depends on the coverage (Fig. 3, Curves 1—4). This suggests that a charged particle, electron, passes through the interface, *i. e.* that excitons break up at the surface levels formed by adsorbed iodine particles. Therefore the increase of the quantum yield with the coverage in this spectral region (Fig. 6) is explained by increased concentration of surface states and the effects of the field on the surface charge which controls the degree of filling of the surface levels. The monoenergetics of the exciton state accounts for the independence of the normalized effective quantum yield of the exciting light photons energy (Fig. 7). In a weakly-polar medium (iodine solution in acetic acid) the injection efficiency in the spectral range of strong singlet absorption does not depend on the coverage (Fig. 4, Curve 4). This leads to the conclusion that it is the neutral state transfer step, rather than the charge transfer step, which is the limiting step of the overall process:

$$A^* + I_{ads} \rightarrow A + I^*_{ads} \rightarrow A^+ + I^- \rightarrow A + p + I^- \qquad \text{(IV)}$$

Otherwise, we would inevitably have to deal with the interfacial potential drop due to specific iodine adsorption, which occurs in acetic acid as well. Equation IV describes the excitation transfer from anthracene to adsorbed iodine molecules. The expression for the photocurrent can be obtained also in terms of the theory of redox processes at semiconductors[7].

$$i = e \cdot n_{I^*} \cdot |L^{I^-}_{ex}|^2 \cdot \left(\frac{\pi}{\hbar^2 \cdot kT \cdot E^*_r}\right)^{1/2} \exp\left\{-\frac{[E^*_r + E_{I^-} - E_{I^*_{ads}}]^2}{4E^*_r \cdot kT}\right\} \qquad (4)$$

where e is the electron charge, $L^{I^-}_{ex}$ — the exchange integral, E^*_r — the solvent reorganization energy, $E_{I^*_{ads}}$— the initial state energy E_{I^-} — the final state energy, $\hbar$ the Dirac constant, k — the Boltzmann constant. $n_{I^*_{ads}}$ — the number of excited iodine particles on the surface is equal to the product of the excitons concentration of the anthracene phase, the iodine particles concentration on the surface $c_{I_{ads}}$ and the term $\dfrac{\overrightarrow{W}}{\overleftarrow{W} + W_{quench}}$ in which $\overrightarrow{W}$ is the probability of excitation transfer to adsorbed iodine, $\overleftarrow{W}$ — the probability of back transfer of excitons (to the anthracene phase), W_{quench} — the probability of excitons quenching

$$n_{I^*_{ads}} = c_{I_{ads}} \cdot n_{ex} \cdot \frac{\overrightarrow{W}}{\overleftarrow{W} + W_{quench}} \qquad (5)$$

Ignoring in (5) $\overleftarrow{W}$ and writing out $\overrightarrow{W}$, we can obtain

$$n\,I^{*}_{\mathrm{ads}} = c_{I_{\mathrm{ads}}} \cdot n_{\mathrm{ex}} \cdot \frac{1}{W_{\mathrm{quench}}} \left| L^{\mathrm{ex\text{-}ex}} \right|^{2} \cdot \left(\frac{\pi}{\hbar \cdot kT \cdot E_{r}} \right)^{1/2} \cdot$$

$$\cdot \exp \left\{ - \frac{\left[E_{r}^{\mathrm{ex\text{-}ex}} + E\,I^{*}_{\mathrm{ads}} - E_{\mathrm{ex}} \right]^{2}}{4\,E_{r} \cdot kT} \right\} \tag{6}$$

Two processes occur simultaneously during an electrochemical reaction with participation of excitons: excitons break up at surface levels formed by adsorbed iodine and a charged particle, electron, passes through the interface. The second process is of excitation transfer to adsorbed iodine. It is very difficult to estimate the relative contribution of each process. However, it follows from the above considerations that at small ε_{st} the second process is the more likely one, and at large ε_{st} the first.

Since the reaction occurs at the crystal side not illuminated directly, we can assume that it proceeds with participation of triplet excitons formed by intercombination inversion from singlet excitons and reaching the reaction zone due to diffusion. Owing to reabsorption of the luminescence light, the singlet excitons formed at the back surface must also make a certain contribution to the photocurrent being measured.

The change in the quantum yield with the surface coverage (Fig. 6) in the spectral region $h\nu$ from 5.2 to 3.8 eV (interband transfers) can be explained in terms of the theory of redox processes at semiconductors if the electron proper transfer through the anthracene/electrolyte interface is assumed to be the limiting step of the electrochemical reaction (1). The expression for the quantum yield can be written as[6]:

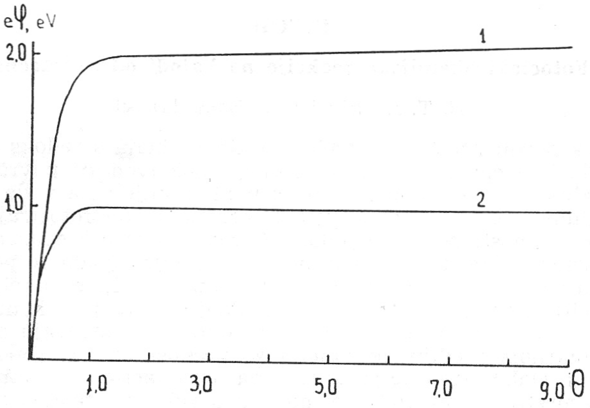
$$\beta = c_{s} \cdot n_{c} \cdot |\tilde{L}|^{2} \frac{1}{\hbar \sqrt{E_{r} \cdot kT}} \exp \left[\frac{\left[\frac{e^{2}}{2\,r} \left(\frac{1}{\varepsilon_{\mathrm{opt}}} - 1 \right) + |E_{c}| + \varepsilon_{I}^{e} + e\,\varphi_{k} \right]^{2}}{\frac{2\,e^{2}}{r} \left(\frac{1}{\varepsilon_{\mathrm{opt}}} - \frac{1}{\varepsilon_{\mathrm{st}}} \right)} \right] \tag{7}$$

where C_{s} is the concentration of the »active« component on the surface, n_{c} — the electron concentration in the conduction band, L — the exchange integral, E_{r} — the solvent reorganization energy, r — the iodine-ion radius, E_{c} — the energy of the conduction band bottom, $\varepsilon^{e}_{I^{-}}$ — the electron affinity of iodine, φ_{k} — the electrostatic potential at the contact, $\varepsilon_{\mathrm{opt}}$ and $\varepsilon_{\mathrm{st}}$ — the optical and statical dielectric constants of the solvent. From the experimental curves and expression (7), assuming the change in the pre-exponential in (7) to be small, we determined the relative change in the value of zone bending near the surface at the contact — $\Delta\varphi$ as a function of the surface coverage

$$\Delta\varphi = \varphi_{k} - \varphi_{o}$$

φ_{o} — is the potential of flat zones.

The dependence thus obtained is given in Fig. 8 (Curve 2). For comparison, a similar dependence is shown in this figure, which was obtained directly from experiment in the absence of optical excitation[5]. (Curve 1). A complete coincidence of the results was hardly to be expected because the experimental conditions were different, but the shape of the curves is the same. This leads to the conclusion that the theory gives a satisfactory



7Fig. 8. Dependence of the parameter $e\varphi_K$ on the surface coverage in the case of injection from aqueous iodine-iodide solutions curve 1. Curve 2: taken from ref. 5.

qualitative description of the experimental results obtained. In the spectral region of weak anthracene absorption (hν from 3.0 to 2.3 eV) the photoconductivity spectrum of anthracene overlaps the spectrum of the optical iodine absorption. The iodine particles excited by the light that has passed through the anthracene crystal, and adsorbed on anthracene participate in the charge separation process at the interface.

$$A + I^* \rightarrow A^+ + I^- \rightarrow A + p + I^- \qquad (V)$$

Unlike presented recently[12], we consider the transfer of the electron proper to be the slow stage rather than diffusion of excited states to the interface, since there occurs iodine adsorption on the anthracene surface. The increase of the normalized effective quantum yield with decreasing photon energy is due to increased quantum yield of reaction (V), as the absorption maximum of molecular iodine is approached. The experimental results obtained in this spectral region also could be described in terms of the theory of redox processes at semiconductors.

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IZVOD

Fotoelektrokemijske reakcije na katodi od antracena

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Opisani su eksperimenti fotoelektrokemijskih reakcija s redoks parom na antracenovoj elektrodi. Proučavan je utjecaj stupnja pokrivenosti površine jodom, utjecaj promjene dielektrične konstante tekućeg medija smjesama vode i octene kiseline te energije upadnih fotona na fotostruju. Pokazano je da fotostruja opada s porastom stupnja pokrivenosti površine jodom. Porast fotostruje opažen je i za otopine dielektrične konstante iznad 60. Kvantno iskorištenje opada s porastom energije fotona, s time da za energije između 3,8 i 5,0 eV u reakciji redukcije joda sudjeluju i elektroni iz vodljivog pojasa. Mehanizam reakcije je dvojak: kontaktu s polarnom otopinom ekscitoni se gube na površinskim nivoima koje stvaraju adsorbirani atomi joda; u slabo polarnom mediju ekscitacija se prenosi na adsorbirani jod. U spektralnom području slabe apsorpcije antracena ekscitacija se prenosi direktno na atome joda. Interpretacija rezultata je moguća u skladu s teorijom o redoks procesima na poluvodičkim elektrodama koju su ranije objavili Dogonadze, Levič i Kuznetsov.

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