PHOTOELECTROCHEMICAL REACTIONS AT THE ANTHRACENE ELECTRODE

III. KINETICS IN A MEDIUM WITH A VARIABLE DIELECTRIC CONSTANT

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The present paper represents a study of injection of holes into optically excited anthracene electrode from solutions of iodine in a medium with a variable dielectric constant. Changes of the static dielectric constant $\varepsilon_{\mathrm{st}}$ were monitored by changing the ratio of components in the mixture water–acetic acid. In order to exclude the effects due to the changes of adsorptivity of iodine as a function of $\varepsilon_{\mathrm{st}}$, all measurements were carried out at the same surface coverage. The description of the experimental technique is given in [1].

Figure 1 shows plots of the photocurrent versus the static dielectric constant for various frequencies of optical excitation. It follows from Fig. 1 that the plots are nonlinear. At the energies of the exciting light quanta between 3.8 and 4.2 eV and the changes of $\varepsilon_{\mathrm{st}}$ in the 6-65 range, the photocurrent remains practically constant. However, in the 3.0-3.4-eV photon energy range a certain increase of the photocurrent is observed. A sharp increase of the photoconductivity is observed at $\varepsilon_{\mathrm{st}} > 65$ for all frequencies of optical excitation.

When the photon energies are larger than the threshold value which is determined by the width of the forbidden zone, the electrons from this zone participate in the electrochemical reduction of iodine [2]:

$$\mathrm{I}_{\mathrm{ads}} + e \rightarrow \mathrm{I}^-. \tag{I}$$

Assuming that the limiting step is the electron transfer through the interface boundary, we have attempted to quantitatively describe the obtained experimental results using the theory of oxidation–reduction reactions on semiconductors [3].

In a qualitative description of the magnitude of the effect, one has to realize that the photocurrent has an electronic ($i_{\mathrm{p}}^{\mathrm{e}}$) and a hole ($i_{\mathrm{p}}^{\mathrm{p}}$) component:

$$i_{\mathrm{p}} = i_{\mathrm{p}}^{p} + i_{\mathrm{p}}^{e}. \tag{1}$$

The expressions for the electronic component $i_{\mathrm{p}}^{\mathrm{e}}$ and the hole component $i_{\mathrm{p}}^{\mathrm{p}}$ have the following form:

$$i_{\mathrm{p}}^{e} \sim c_{\mathrm{I}} n_{\Phi}^{c} \rho_{\mathrm{c}} \exp[-E_a^c/kT], \tag{2}$$

$$i_{\mathrm{p}}^{p} \sim c_{\mathrm{I}} n_{\mathrm{p}}^{v} \rho_v \exp[-E_a^v/kT], \tag{3}$$

where c_{I} is the surface concentration of iodine, and $n_{\mathrm{p}}^{\mathrm{v,c}}$ and $\rho^{\mathrm{v,c}}$ are the concentration of electrons and the density of states in the hole zone and in the conductance zone, respectively. The activation energy has the form [3]

$$E_a^{v,c} = \frac{[|I^{\mathrm{i}}\ |^{v,c} - |I^{\mathrm{f}}\ | + E_r]^2}{4E_r}. \tag{4}$$

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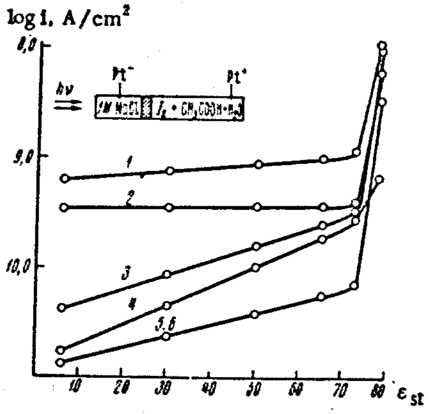

Fig. 1. Cathode photocurrent vs dielectric constant of the medium for the following exciting wavelengths: 1) 249; 2) 281.4; 3) 367; 4) 437; 5) 550; 6) 584 nm; $\theta = 0.1$, $E = 10^5$ V/cm; $h\nu$ (eV): 1) 5.0; 2) 4.45; 3) 3.4; 4) 2.86; 5) 2.28; 6) 2.14.

where $I^{i\ v,c}$ and I^f are the minimum energies of the system in the initial and the final states, expressed by the following equations:

$$\left.\begin{aligned} I^f &= -\varepsilon_e^{I^-} + \alpha_{\text{solv}}^{I^-} \\ I^{i\ c} &= E_c - e\varphi_k + \alpha_{\text{solv}}^{I} \\ I^{i\ v} &= E_v - e\varphi_k + \alpha_{\text{solv}}^{I} \end{aligned}\right\}, \tag{5}$$

where α_{solv}^{I} and $\alpha_{\text{solv}}^{I^-}$ are the solvation energies of the iodine atom and of the iodide ion, respectively; $\varepsilon_e^{I^-}$ is the electron affinity of the iodine atom; φ_k is the contact electrostatic potential; E_c is the energy of the bottom of the conductance zone; and E_v is the energy of the ceiling of the conductance zone. It is assumed that the difference in solvation energies $\alpha_{\text{solv}}^{I^-}$ and α_{solv}^{I} is equal to the electrostatic energy of solvation of the iodide ion:

$$\alpha_{\text{solv}}^{I^-} - \alpha_{\text{solv}}^{I} = \alpha_{\text{el}}^{I^-}.$$

The energy of the reorganization of the solvent E_r and the electrostatic portion of the solvation energy $\alpha_{\text{el}}^{I^-}$ can be calculated from the formulas

$$E_r = \frac{1}{8\pi}\left(\frac{1}{\varepsilon_{\text{opt}}} - \frac{1}{\varepsilon_{\text{st}}}\right)\int (\vec{D}_i - \vec{D}_f)^2 \cdot dV, \tag{6}$$

$$\alpha_{\text{el}}^{I^-} = \frac{1}{8\pi}\left(\frac{1}{\varepsilon_{\text{el}}} - 1\right)\int D_{I^-}^2 \cdot dV. \tag{7}$$

Because there is no charge on the iodine in the initial state, $\vec{D}_i = 0$. The induction $\vec{D}_f$ is the induction caused by the iodide ion. Considering the iodide ion as a metallic sphere with a charge e and a radius r_{I^-} and calculating the integrals in (6) and (7), one obtains

$$E_r = \frac{1}{2r_{I^-}}\left(\frac{1}{\varepsilon_{\text{opt}}} - \frac{1}{\varepsilon_{\text{st}}}\right); \quad \alpha_{\text{el}}^{I^-} = \frac{1}{2r_{I^-}}\left(\frac{1}{\varepsilon_{\text{st}}} - 1\right). \tag{8}$$

Using (1) and (8) and assuming that the expressions for the vacancy components of the photocurrent and the dark current are identical, one can determine the ratio between the photocurrent i_p and the dark current i_d:

$$\frac{i_p}{i_d} = \frac{i_p^v}{i_d} + \frac{i_p^e}{i_d} = 1 + \frac{i_p^e}{i_d}. \tag{9}$$

A quantitative evaluation of (9) gave a correct order of magnitude of the effect and enabled us to carry out a more detailed comparison of the theory and the experiment. Using Eqs. (2)-(8), the expression for the photocurrent can be given in the form

$$i = c_I n_c |L|^2 \frac{1}{\hbar\sqrt{E_r kT}} \exp\left\{-\frac{\left[\frac{e^2}{2r}\left(\frac{1}{\varepsilon_{\text{opt}}} - 1\right) + |E_c| - \varepsilon_e^{I^-} + e\varphi_k\right]^2}{(2e^2/r)(1/\varepsilon_{\text{opt}} - 1/\varepsilon_{\text{st}})kT}\right\}. \tag{10}$$

Changes in ε_{opt} are small when compared with ε_{st}. Because E_r is usually large, i.e., there is a reorganization of the particles in the volume of the solvent, ε_{st} can be considered as the dielectric constant in the solution volume. It follows from (10) that the photocurrent increases with increasing ε_{st}.

A more detailed comparison of the theoretical and experimental dependences was carried out under the assumption of small changes of the preexponential factor in (10). The radius of the iodide ion was taken as equal to its crystallographic value 2.1 Å [4]. In contrast to our previous paper [5], the contact electrostatic potential φ_k was chosen as a parameter whose value was determined from the experimental curve. Naturally, in this case both the theoretical and experimental dependences fully coincide. The value of the parameter obtained in this manner was found to be $\varphi_k = 0.8$, in agreement with [2].

Anthracene does not practically absorb in the 3.4–2.3-eV range; however, superposition of the photoconductance spectrum of anthracene and the optical absorption spectrum of iodine is observed. It is assumed that excited states of iodine participate in the electrochemical distribution of charge, these excited states being formed in the vicinity of the electrode. The excited molecules diffuse toward the surface; however, in contrast to [6], the slow step in the overall process is still the passage of the electron through the interface boundary:

$$I^* + A \rightarrow A^+ + I^- \rightarrow A + p + I^-. \tag{II}$$

Because electrons of the valency zone participate in the electrochemical reaction, the quantitative description of the results is analogous to that of the previously discussed case of the dark injection [5].

In the strong singlet absorption region $h\nu = 3.4$ eV, excitons participate in the electrochemical distribution of the charge. In principle, there are two different possibilities how this process can occur. The first possibility is the decay of excitons on surface levels formed by adsorbed iodine. The second possibility is the escape of the excitons into the electrolyte phase and the subsequent reaction leading to the formation of the iodide ion. The expression for the current due to the decay of excitons into free carriers at surface levels can be represented in the form

$$i = ec_{\mathrm{I}} \left| L_{\mathrm{exc}}^{\mathrm{I}^-} \right|^2 \left(\frac{\pi}{\hbar^2 E_r kT} \right)^{1/2} n_{\mathrm{exc}} \exp\left\{ - \frac{[E_r + |I^{\mathrm{i}}| - |I^{\mathrm{f}}|]^2}{4E_r kT} \right\}. \tag{11}$$

The expressions for the minimum energies for the initial and final states I^{i} and I^{f}, respectively, have the form

$$I^{\mathrm{i}} = E_{\mathrm{exc}} + E_{\mathrm{I}}^{\mathrm{ads}}, \quad I^{\mathrm{f}} = -\varepsilon_e^{\mathrm{I}^-} + \alpha_{\mathrm{solv}}^{\mathrm{I}^-}, \tag{12}$$

where E_{exc} and $E_{\mathrm{I}}^{\mathrm{ads}}$ are the energy of the exciton level in anthracene and the adsorption energy of iodine molecules, respectively.

When considering the possibility of the transition of the exciton into the electrolyte phase, it is necessary to pose the question about the limiting step in the process of the charge distribution. The independence of the effectiveness of the photoinjection of the surface coverage which was discussed in [7] enables us to reach a conclusion that the limiting step of the overall process is the transfer of an uncharged particle, viz., the exciton:

$$A^* + I_{\mathrm{ads}} \rightarrow A + I_{\mathrm{ads}}^* \rightarrow A^+ + I^- \rightarrow A + p + I^-.$$

If the situation were contrary to the above assumption, one would observe an interphase potential jump due to the specific adsorption of iodine, which also occurs in acetic acid.

The transition of the exciton into the electrolyte phase leads to the excitation of iodine molecules at the surface. In this case the expression for the photocurrent can also be obtained within the framework of the theory of oxidation–reduction processes on semiconductors [3]:

$$i = e \cdot n_{\mathrm{I}_{\mathrm{ads}}^*} \left| L_{\mathrm{exc}}^{\mathrm{I}^-} \right|^2 \left(\frac{\pi}{\hbar^2 E_r kT} \right)^{1/2} \exp\left\{ - \frac{[E_r^* + E_{\mathrm{I}^-} - E_{\mathrm{I}_{\mathrm{ads}}^*}]^2}{4E_r^* kT} \right\}. \tag{13}$$

All designations in (13) are the same as in (10) and (11). The quantity $n_{\mathrm{I}_{\mathrm{ads}}^*}$ is the number of excited iodine particles at the surface and is equal to the product of the concentration of excitons in the anthracene phase, the concentration of iodine particles at the surface c_{I}, and the term $\vec{W}/(\overleftarrow{W} + W_q)$, where $\vec{W}$ is the probability of transition of excitons into the electrolyte phase, $\overleftarrow{W}$ is the probability of the reverse transition (into the anthracene phase), and W_q is the probability of exciton quenching:

$$n_{\mathrm{I}^*} = c_{\mathrm{I}} n_{\mathrm{exc}} \vec{W} / (\overleftarrow{W} + W_q). \tag{14}$$

Neglecting $\overleftarrow{W}$ in (14) and solving for $\vec{W}$, we obtain

$$n_{\mathrm{I}^*} = c_{\mathrm{I}_{\mathrm{ads}}} n_{\mathrm{exc}} \frac{1}{W_q} \left| L_{\mathrm{exc}}^{\mathrm{exc}} \right|^2 \times \left(\frac{\pi}{\hbar^2 kT E_r} \right)^{1/2} \times \exp\left\{ - \frac{[E_r^{\mathrm{exc}} + E_{\mathrm{I}^*} - E_{\mathrm{exc}}]^2}{4E_r \cdot kT} \right\}. \tag{15}$$

The analysis of (13) shows that, if n_{I^*} = const, this expression represents a stronger dependence on ε_{st} than (11) and is similar to that in (10). The expression (15) gives an overall stronger dependence of the current on ε_{st} than, e.g., for the spectral region of interzonal transitions (10). This might explain why the curves 1-4 in Fig. 1 are different. When the electrochemical reaction occurs with the participation of excitons, two processes take place simultaneously. The first process includes the decay of excitons on surface levels formed by adsorbed iodine, and the particle crossing the interface boundary is then an electron, i.e., a charged particle. The second process is the transition of excitons into the electrolyte phase. It is difficult to estimate the relative contributions of both processes; however, it follows from the above qualitative conclusions that the latter process is more likely at small ε_{st}, whereas the former process is more likely at large ε_{st}.

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