

those of K_1^{int} and K_2^{int} in Table I and are listed in Table II. As can be seen from this table, the values of k_1^{int} and k_{-1}^{int} are of the same order of magnitude as those of k_2^{int} and k_{-2}^{int} , respectively. This result indicates that there is no difference in the dynamic properties between mono- and divalent chromate ions, in contrast with the result for phosphate adsorption that the adsorption rate of HPO_4^{2-} is much faster than that of H_2PO_4^- .⁶ Comparing the values of the adsorption-desorption rate constants for chromate in Table II with those for phosphate reported previously,⁶ the values of the adsorption rate constants for HCrO_4^- and CrO_4^{2-} are 1 and 2 orders of magnitude smaller than those for H_2PO_4^- and HPO_4^{2-} , respectively, while the values of desorption rate constants for the former are 1 order of magnitude larger than those for the latter, respectively.

This fact also indicates that the interaction of chromate with AlOH_2^+ is weaker than that of phosphate with AlOH_2^+ .

The value of $C_1 = 180$ determined above, which is equal to that reported in the $\gamma\text{-Al}_2\text{O}_3$ -phosphate system,⁶ is slightly larger than that reported by Davis et al.⁷⁻⁹ This fact may result from an increase of dielectric constant of the electrical double layer caused by the large amount of chromate adsorbed.

Further systematic investigation will lead to a quantitative clarification of the dynamic behavior of anion adsorption-desorption on $\gamma\text{-Al}_2\text{O}_3$ surfaces.

Registry No. CrO_4^{2-} , 13907-45-4; HCrO_4^- , 15596-54-0; Al_2O_3 , 1344-28-1.

Dye Sensitization of a Zinc Oxide Electrode Studied by a Potential Modulation Technique

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A potential modulation technique has been developed and applied to the study of the dye sensitization phenomena. The lifetimes of oxidized sensitizing dyes, Rose Bengal and Rhodamine B, which are formed by electron transfer from the excited states to the conduction band of a ZnO electrode, are determined to be 60 ± 15 and 100 ± 25 ms, respectively. The rate constants for electron transfer from potassium iodide, L-tryptophan, and hydroquinone to oxidized Rose Bengal are also determined to be $1.2 (\pm 0.5) \times 10^4$, $4.0 (\pm 1.7) \times 10^5$, and $3.3 (\pm 1.4) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, respectively.

Introduction

The characterization of reaction intermediates formed on semiconductor electrodes is very important for establishing stable photoelectrochemical cells. For example, the photoanodic corrosion of an n-type semiconductor electrode can be suppressed if the electron supply from a reductant to the electrode is faster than the rate of photoanodic corrosion, which depends on the nature of the corrosion intermediates. The details of the mechanism and the kinetics of the reactions at semiconductor electrodes have been studied by use of spin trapping,¹ rotating ring-disk electrode (RRDE),² electroluminescence,³ etc.

For the dye sensitized semiconductor electrodes, the lifetime of an oxidized dye is a critical value for the stabilization of the photocurrent, since the dye-sensitized photocurrent decays by the irreversible reaction of the oxidized dye.⁴ The photocurrent can be stabilized when electrons are supplied to the oxidized dye from reductants in the solution. The fundamental properties of the dye-sensitized photocurrent, e.g., quantum efficiency,^{4,5} adsorptivity of the sensitizing dyes on the electrode,^{6,7} effects of reductants^{4,8} and surface states,⁹⁻¹² etc.,¹³ have been

clarified. However, the details of the kinetics are not known.

In this paper, we have determined the lifetimes of the oxidized dyes formed on a ZnO electrode by use of a potential modulation technique. The rate constants for electron transfer from the reductants to the oxidized dye will also be presented.

The lifetimes of oxidized dyes have been reported by use of the RRDE technique¹⁴ or flash photolysis.¹⁵ However, these methods give information about the dyes dissolved in solutions. In this paper we give results on the kinetics of the dye adsorbed on the semiconductor electrode, which is more important for the understanding of the dye sensitization phenomena at a semiconductor electrode.

Theory

The energy models of an n-type semiconductor electrode, polarized anodically and at the flat-band potential, and an excited dye molecule are shown in Figure 1. The electrons injected from the excited dye to the electrode surface move into the bulk when a depletion layer is

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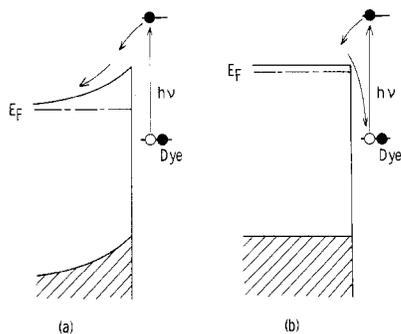


Figure 1. Energy level diagrams of an excited dye adsorbed on an n-type semiconductor electrode with a depletion layer (anodic polarization) (a) and without a depletion layer (flat-band potential) (b).

formed at the electrode surface (Figure 1a). On the other hand, the injected electrons recombine with the oxidized dye (D^+), causing no photocurrent, when the electrode has no depletion layer (Figure 1b). The reactions occurring at the electrode surface are as follows:



In solutions without any reductant, the oxidized dye (D^+) formed at the anodically polarized electrode undergoes irreversible reactions (reaction 3). On the other hand, at potentials close to or more cathodic than the flat-band potential, electron back transfer from the conduction band to the oxidized dye (reaction 4) occurs much faster than reaction 3 as will be shown later. Therefore, under this condition, reaction 4 occurs at the same rate as reaction 2 at the stationary state. Under the potential modulated at a certain frequency between anodic and cathodic polarizations, the oxidized dye is formed at an anodic polarization, and electron transfer from the conduction band to the oxidized dye occurs at a cathodic polarization. However, if the modulation frequency is too low, most of the oxidized dyes undergo irreversible reactions. The potential modulation technique can thus determine the rate of reaction of the oxidized dye.

The details of the potential modulation technique are as follows. The potential of a semiconductor electrode is modulated rectangularly with a period of T_{mod} between an anodic potential (U_a) and a flat-band potential (U_{fb}), as shown in Figure 2. The electrode is illuminated for the period T_{il} , while the potential is modulated. Therefore, the total period of illumination under anodic polarization is $T_{il}/2$. The concentrations of the adsorbed dye on the electrode before and after the illumination, C_b and C_a , respectively, are given by

$$C_a/C_b = \left\{ 1 - (1/C_b) \int_0^{T_{\text{mod}}/2} v dt + (1/C_b) \int_0^{T_{\text{mod}}/2} v \exp(-t/\tau) dt \right\}^{T_{il}/T_{\text{mod}}} \quad (6)$$

where τ is the lifetime of the oxidized dye and v is the rate of D^+ production. The exchange rate between the dye in the solution and the products formed by reaction 3 is neglected in the derivation of eq 6, since the initial decay of the photocurrent is not affected by the exchange.⁴

When the change of v during illumination is not so serious, eq 6 can be roughly approximated with a truncation

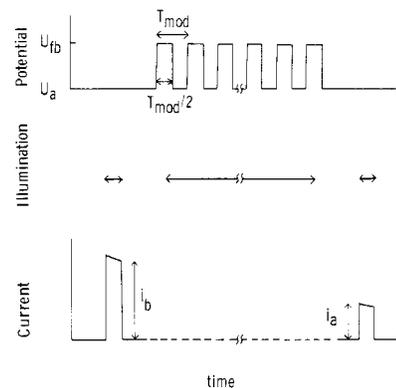


Figure 2. Procedure for the potential modulation experiment.

after the first-order terms of the expansion on the right side of the equation as follows:

$$C_a/C_b = (1 - vT_{il}/2C_b) + (T_{il}\tau v/T_{\text{mod}}C_b)\{1 - \exp(-T_{\text{mod}}/2\tau)\} \quad (7)$$

The approximation used in the derivation of eq 7 is found to be reasonable under our experimental conditions as will be shown later. The lifetime, therefore, can be determined by measuring C_a against T_{mod} , since C_b , τ , and T_{il} are constants under our experimental conditions. In the following experiments, we will measure the photocurrent densities observed before and after the modulation, i_b and i_a , respectively, instead of C_b and C_a (see Figure 2), because the photocurrent density sensitized by xanthene dyes is proportional to the concentration of the adsorbed dyes.⁶ Thus the following expression can hold:

$$i_a/i_b = C_a/C_b \quad (8)$$

Experimental Section

A disk of ZnO sintered by us was used as a semiconductor electrode. The procedure for the preparation of the sintered disk has been reported earlier.⁴ The photoelectrochemical measurements were made by using a platinum electrode as a counterelectrode, a saturated calomel electrode as a reference electrode, a potentiostat (Hokutodenko, HA-201), and a function generator (Hokutodenko, HB-107A). An aqueous solution of 0.1 M NaNO_3 (pH 6.0) was used as the electrolyte, and it was bubbled with high-purity nitrogen gas before the measurements. The time constant of the total circuit was less than 0.1 ms, fast enough for the potential modulation experiment. Before the measurement, the ZnO electrode was polished, etched in 2 M HCl, washed with water, dried, and immersed in the electrolyte solution for 60 s. A 500-W xenon lamp (Ushio Electric Inc.) equipped with a monochromator (Japan Jarrell-Ash) was used as a light source. The light intensity was set at $1 \times 10^{-4} \text{ W cm}^{-2}$ unless otherwise noted. The illumination was made at the wavelengths of 562 and 556 nm for Rose Bengal and Rhodamine B, respectively.

In the potential modulation experiments (see Figure 2), the electrode was illuminated for 10 s ($= T_{il}$) during the potential modulation, and for 0.5 s for the measurements of i_b and i_a . The U_a and U_{fb} values in Figure 2 were set at 0.3 and -0.4 V vs. SCE , respectively, the latter being a little more cathodic than the actual flat-band potential.

Rose Bengal and Rhodamine B were purified by passing through alumina columns. Other chemicals were of reagent grade and were used without further purification.

Results and Discussion

The ratio of the photocurrents observed after and before the illumination, i_a/i_b , in $6 \times 10^{-6} \text{ M}$ Rose Bengal plotted

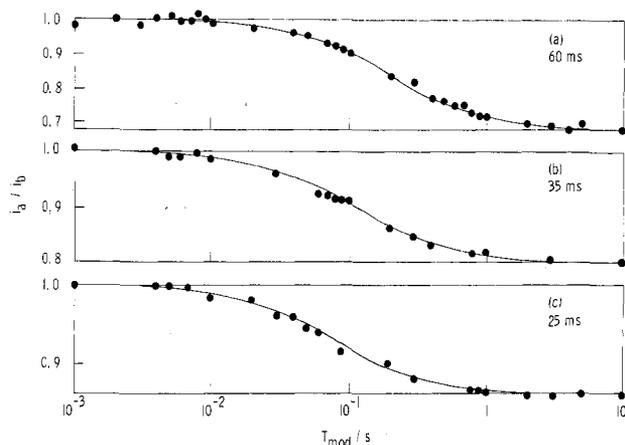


Figure 3. The i_a/i_b vs. T_{mod} observed in a 6×10^{-6} M Rose Bengal solution (pH 6.0) without any reductant (a), with 1.0×10^{-3} M potassium iodide (b), and with 2.0×10^{-3} M potassium iodide (c). The solid lines show the theoretical curves calculated according to eq 7 and 8 for an oxidized dye with the lifetimes shown in the figure.

against the period of the modulation, T_{mod} , is shown in Figure 3a. The i_a/i_b value is close to 1.0 when T_{mod} is shorter than 10^{-2} s. This means that almost all the oxidized dyes formed at 0.3 V vs. SCE (U_a) are regenerated while the potential is at -0.4 V vs. SCE (U_b). The ratio begins to decrease with an increase of T_{mod} , due to the irreversible reactions of the oxidized dyes (reaction 3). Then, i_a/i_b levels out at $T_{\text{mod}} = \text{ca. } 2$ s, presumably because most of the oxidized dyes cannot obtain electrons from the conduction band before they undergo irreversible reactions. The saturation value of i_a/i_b is expected to correspond to $1 - vT_{\text{il}}/2C_b$, since the last term of the right side of eq 7 can be neglected at high T_{mod} .

The i_a/i_b value was ca. 1.0 when the potential was modulated at any period (T_{mod}) in the dark or when the electrode was kept at -0.2 V vs. SCE or more cathodic potentials during the illumination. These results suggest that the irreversible reactions of the oxidized dye do not occur without illumination, and that almost all the injected electrons recombine with the oxidized dye unless a depletion layer is formed at the semiconductor surface.

The lifetime of oxidized Rose Bengal is estimated to be 60 ± 15 ms by the curve-fitting method based on eq 7 and 8 as shown in Figure 3a, where the observed value of i_a/i_b at 10 s of T_{mod} was substituted for $1 - vT_{\text{il}}/2C_b$. When the intensity of the illumination was lowered to 1/4, the τ value did not change though i_a/i_b shifted upward. This result suggests that the approximation used for the derivation of eq 7 is valid under our experimental conditions. Similarly, the lifetime of oxidized Rhodamine B is determined to be 100 ± 25 ms according to eq 7 and 8. No effect of dissolved oxygen was found for the lifetimes.

When potassium iodide was added to the solution of Rose Bengal the saturation value of i_a/i_b increased and the curve shifted toward a shorter modulation period, as shown in Figure 3, b and c. This means that the lifetime of the oxidized dye decreases in the presence of the iodide ion due to an electron donation reaction (reaction 5). The lifetime of the oxidized dye in the solution with a reductant is given by

$$1/\tau = (1/\tau_0) + k_5[\text{R}] \quad (9)$$

where τ_0 is the lifetime in the absence of the reductant, [R] the concentration of the reductant, and k_5 the rate constant of reaction 5.

The reciprocal value of the lifetime of oxidized Rose Bengal increases linearly with the concentration of po-

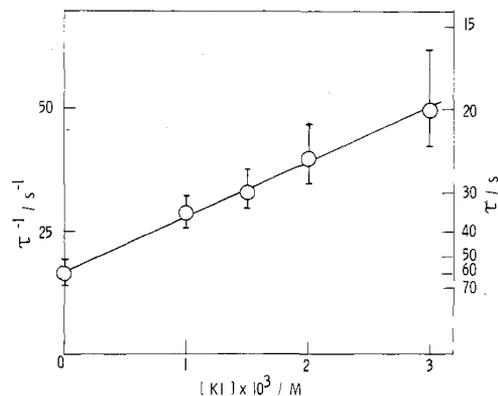


Figure 4. The reciprocal value of the lifetime of oxidized Rose Bengal vs. the concentration of potassium iodide in the solution.

TABLE I: Rate Constants for Electron Transfer from Various Reductants to Oxidized Rose Bengal^a

reductants	$k_s/\text{M}^{-1} \text{s}^{-1}$	
	a	b
KI	$1.2 (\pm 0.5) \times 10^4$	$0.6 (\pm 0.2) \times 10^4$
L-tryptophan	$4.0 (\pm 1.7) \times 10^5$	$1.7 (\pm 0.5) \times 10^5$
hydroquinone	$3.3 (\pm 1.4) \times 10^6$	$3.9 (\pm 1.2) \times 10^6$

^a Determined by the potential modulation technique (column a) and by analysis of the decay of the photocurrent (column b).

tassium iodide as shown in Figure 4. By substituting the gradient into eq 9, we determined the rate constant for electron transfer from an iodide ion to the oxidized dye to be $1.2 (\pm 0.5) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. Similarly, the rate constants for electron transfer from L-tryptophan and hydroquinone are determined as shown in column a of Table I.

We studied the lifetime of oxidized Rose Bengal dissolved in an aqueous solution by the flash photolysis method. A solution containing 4×10^{-7} M Rose Bengal and 1×10^{-4} M potassium hexacyanoferrate (III) was irradiated after bubbling with high-purity nitrogen gas. A transient increase of photoabsorption was observed at the wavelengths around 450 nm, which is attributable to the absorption band of oxidized Rose Bengal by analogy with that of oxidized Eosine Y.¹⁶ The lifetime of oxidized Rose Bengal is determined to be ca. 2 ms from the analysis of the decay of the photoabsorption at 450 nm. A much longer lifetime was obtained by the potential modulation method. This may be explained by assuming that the reactive site of the oxidized dye is covered by the electrode surface.

The dye-sensitized photocurrent decays with steady illumination when the electrode is biased anodically. The decay rate becomes slow when a reductant is added to the solution. The rate constant for electron transfer from the reductant to the oxidized dye can also be obtained by analysis of the decay curves of the photocurrent together with the lifetime of the oxidized dye in the absence of the reductant. The details of the analysis of the decay curve have been reported earlier.⁴ The time constant for the decay of the photocurrent in the solution containing a reductant, t_w , is determined by the rates of reactions 3 and 5, and is given by

$$t_w/t_{w0} = 1 + \tau_0 k_5 [\text{R}] \quad (10)$$

where t_{w0} is the decay time constant in the solution having no reductant. The k_5 values obtained from t_w/t_{w0} vs. [R]

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plots are shown in column b of Table I, which coincide fairly well with the values obtained from the potential modulation method.

It has been well-known that the dye-sensitized photocurrent can be stabilized by addition of hydroquinone to the dye solution.^{17,18} This is attributable to the high rate

constant for electron transfer to the oxidized dye as determined above.

Acknowledgment. The authors are indebted to Dr. A. Yoshimura (Faculty of General Education, Osaka University) for the flash photolysis experiments and for useful discussions.

Registry No. KI, 7681-11-0; ZnO, 1314-13-2; Rose Bengal, 11121-48-5; Rhodamine B, 81-88-9; L-tryptophan, 73-22-3; hydroquinone, 123-31-9.

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Molecular Aspects of the System Water/Monomolecular Surface Film and the Occurrence of a New Anomalous Dispersion Regime at 1.43 GHz

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(Received: December 14, 1982; In Final Form: May 2, 1983)

The physicochemical implications of airborne microwave radiometer measurements at 1.43 GHz and at 2.65 GHz over a sea surface covered with a monomolecular 9-octadecen-1-ol, *Z* isomer (oleyl alcohol), surface film are discussed. These measurements indicate that "icelike" clathrate structures with average O...O distances of about 5.8×10^{-10} m and a free activation enthalpy $\Delta G = 5.53$ kJ/mol are induced by the monolayer in a water layer of $d \leq 190$ μ m thickness. This "penetration depth" is further substantiated by evaluating about 30 experiments published elsewhere, from which comparable penetration depths can be deduced. In light of the molecular interactions between the surface film and the adjacent water layer, and in the framework of the Debye relaxation theory, the occurrence of a new additional dispersion regime at a frequency $f_s = 1.43$ GHz (relaxation time $\tau_s = 1.11 \times 10^{-10}$ s) and the anomalously high dielectric constant $\epsilon^* \geq 5.2 \times 10^4$ at this frequency can be explained. It is suggested that anomalies of the upper water layer may occur, when a water-structuring influence by a surface-active compound (or a solid) and microscopic local disturbances of the surface film order are present. The ordering effects within the system surface film/water and the relaxation processes of disturbances of this order are investigated by laboratory measurements in an automatic Langmuir trough. The thus determined relaxation time for disturbances of the surface film order $\tau_{\text{comp}} = 16$ min is about 10^{13} times larger than the relaxation time τ_s of the water molecules.

Introduction

In the years 1909-1936 several scientists attempted to determine the anomalous dispersion regime of water in the frequency range between 0.1 and 20 GHz.¹ But the first results reported between 1909 and 1921 were very inconsistent and showed various anomalous dispersion regimes ranging from 252 MHz (wavelength $\lambda = 1.188$ m) to 1.43 GHz ($\lambda = 0.21$ m).¹ However, some years later (1927-1936) other authors¹ could not confirm these anomalous dispersion regimes when performing experiments in the frequency range 83 MHz ($\lambda = 3.6$ m) to 2.22 GHz ($\lambda = 0.135$ m) using improved instruments. Today it is well established² that anomalous dispersion of pure water occurs at about 14.5 GHz ($\lambda = 0.021$ m) for a water temperature of 287 K.

Some investigators conjectured that the occasionally observed higher dielectric constants were caused by

boundary layer forces and they tried to verify this hypothesis by performing high-precision dielectric constant measurements of thin water layers. But no values significantly different from those for bulk water were obtained,³ with the exception of data for very thin water layers of thickness $d \leq 10^{-8}$ m, which approach the value for ice,⁴ being only slightly higher than those for bulk water.

In our view, the occasionally measured anomalous dispersion regimes of water at frequencies below 14.5 GHz are probably due to interfacial phenomena. Either contamination of the free-water surface with surface-active molecules or long-range ordering effects at the solid boundaries of the measuring instrument presumably affected the measurements.

In a recent airborne remote sensing experiment performed over the North Sea, Alpers et al.⁵ demonstrated

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