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Mark Spitler and Melvin Calvin

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Mark Spitler and Melvin Calvin

Laboratory of Chemical Biodynamics
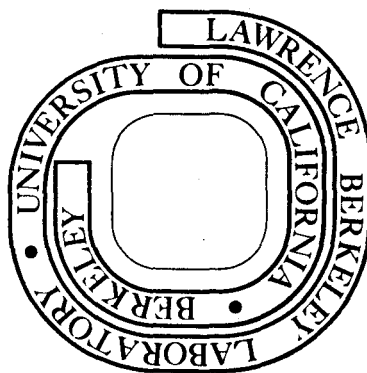
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ABSTRACT

The adsorption of rhodamine B on the (0001) face of ZnO single crystals from an aqueous solution was monitored through measurement of the absorbance of the adsorbed dye. Analysis of these spectra yielded a Langmuir type adsorption isotherm with a plateau surface concentration of 1.1×10^{-7} mmoles/cm^2. A comparison was made between the absorbance of the adsorbed dye and that of the dye in solution.

These data were correlated with electrochemical measurements of the photooxidation of this dye at ZnO crystals used as electrodes. The quantum efficiency of photooxidation was .027 which was approximately constant as a function of surface coverage. A kinetic model was formulated for the time decay of the photocurrent.

I.   Introduction

A simple and straightforward technique for investigation of dye sensitization of semiconductors involves employment of the solid as an electrode in an electrochemical cell.[1]   In the case of photooxidation of the adsorbed dyestuff, the semiconductor electrode can be positively polarized so that an electron injected by an excited dye molecule will be drawn off and measured as current.

A number of reports in the literature have been concerned with investigation of this phenomenon using this technique and most of these have utilized aqueous electrolytes and water soluble dyes.[2-4]   In these cases the dye must adsorb onto the electrode from solution before electron transfer can be observed.   Yet there have been few instances[5,6,] where the absorbance and adsorption characteristics of a dye adsorbed on single crystals have been established and compared with photocurrent data. This is not to say that this point has been overlooked; there have been several cases where data from the adsorption of these dyes onto powders has been applied to electrochemical results from single crystal studies.[3,7] It implies, rather, that the characterization of the absorbance and absorption of dyes on single crystals is a difficult task.

It is the purpose of this work to study the adsorption of rhodamine B on the (0001) face of ZnO single crystals and to compare the resultant data with electrochemical measurements of the photooxidation of this dye at electrodes constructed from these same crystals.   The absorbance of the adsorbed rhodamine B can be used to calculate the surface concentration of the dye and to determine the quantum efficiency of electron transfer.   A kinetic model formulated to explain the time decay of the photocurrent can also yield a value for the dye's surface concentration.

II. Experimental

Two different types of ZnO single crystals were used in these experiments. One was undoped and the other was Li doped.

The undoped crystals came in the form of cross sectional cuts from a large hexagonal prism with a diameter of 5 mm. A crystal cleaved perpendicular to the main or "c" axis of this prism, the orientation of the cut described here, will expose two different faces, one Zn (0001), and the other O (000$\bar{1}$). The crystals were cut with a string saw set at a thickness of 250 μ. After grinding with 9 μ SiC grit, both sides of the crystal were polished with 0.3 μ alumina until an optical surface was obtained. The final thickness was estimated to be 150 μ.

Real surfaces were created from these polished faces through the use of 85% H_3PO_4 as an etching agent. The crystals were mounted with beeswax on a glass slide so that only one face was exposed; the faces could then be separately etched. At one point the adsorption studies also utilized a Li doped single crystal of ZnO. This specimen was purchased from the Lambda-Airtron Corp. of Morris Plains, New Jersey, and had dimensions of 2 cm x 1 mm. The large exposed surfaces were the (0001) and (000$\bar{1}$) faces. Before use, the crystal was polished to a 1 μ finish, but it was not etched.

Absorbance measurements of the dye adsorbed at less than monolayer coverage of a single crystal surface were made by alignment of four of the undoped crystals (each with an adsorbed dye layer) in the light path of a Cary 118 spectrophotometer. Two special cells were constructed, each with four crystals, so that the use of one as a reference cell in the spectrophotometer resulted in the cancellation of the extrinsic, impurity, absorption of ZnO. Thus, the absorption spectrum of the rhodamine B adsorbed on the surface of the sample cell could be recorded easily.

Each crystal was mounted on a teflon circle over a hole 4 mm in diameter through which the spectrophotometer beam passed. They were oriented with the (0001) surface upwards. RTV silicone-rubber glue was used to secure the crystals around the edges.

The teflon circles were inserted in glass tubing cut so that the (0001) crystal faces were accessible (fig. 1). When the cell was placed on end with the Zn faces up, the dye solution could be deposited on the surfaces through the apertures in the surrounding glass.

About 1-2 ml of an aqueous dye solution were deposited on the Zn surfaces of the cell designated the sample cell. Rate studies showed that 20 min were required for the system to attain equilibrium after which the remaining solution was removed with a wash with nonane or octane. The cells were then placed in the spectrophotometer and spectra were recorded. Absorbance measurements of dye adsorbed on the Li doped crystal involved placing this crystal in the sample beam of the spectrophotometer.

The photoelectrochemical cell used for measurements of rhodamine B induced photocurrents has been described previously.[6] In this set-up the potential of the ZnO electrode was controlled potentiostatically; the light incident on the electrode surface was modulated at frequencies of 3 to 11 Hz using the ZnO electrode as the optical window. Only the undoped ZnO crystals were sufficiently conductive to be used as electrodes.

The rhodamine B was obtained commercially and purified through recrystallization in ethanol. An extinction coefficient of $1.1 \times 10^5 M^{-1} cm^{-1}$ monomer maximum in ethanol was used in this work.

The net charge on the dye will depend on the pK of the carboxyl function; the molecule will be either cationic or neutral. To determine the region of charge neutrality for this dye, isoelectric focusing was

used.[8] An LKB Uniphor Column Electrophoresis system was employed for this determination.

The dye was spread evenly over the entire pH range of the ampholyte. After 48 hours in this set-up, all the dye at low pH had moved to a higher pH. There was a distinct break between colorless and colored portions of the column at a pH of 4.85. Higher than this pH there appeared to be no movement of the dye indicating that above pH 4.85 the dye is electro-neutral. To confirm this result, a 6 x 10^{-3} M solution of the dye was titrated yielding a pK of 3.5 for the dye which is consistent with the observation that the isoelectric point of a molecule is about 2 pH units higher than its pK.

III. Results

A. Absorbance Spectra

Using the optical cells, absorbance measurements were recorded for rhodamine B adsorbed on the (0001) face of undoped ZnO at dye concentrations of up to 4 x 10^{-4} M. The rhodamine B solutions were prepared using doubly distilled water with the pH adjusted to 6.5.

An example of the baseline of the sample cell without adsorbed dye can be seen in fig. 2a. In the spectral region from 450 nm to 700 nm, the baseline was flat to within an absorbance of .003. The absorption spectra of the adsorbed dye can also be seen in fig. 2a for a range of solution concentrations of the dye . The flat baseline allows observation of a shift of the monomer maximum form 557 to 562 nm as the dye concentration of the solution from which it is adsorbed ranges from 1 x 10^{-5} M to 4 x 10^{-4} M. In fig. 2b is a plot of the optical density of the monomer peak versus the concentration of the dye in solution with which the surface is in equilibrium.

B.   Photocurrent ActionSpectra

At an applied bias of sufficient magnitude to draw off all injected
charge, the current will vary with the wavelength of the light incident
on the dye-semiconductor interface. An example of such an action spectrum
for rhodamine B at a ZnO electrode is given in fig. 3. The absorbance
of the dye on the crystal surface is also included in this figure; it
is taken from the data of fig. 2a. For this measurement, the crystal was
maintained at a bias of + 1.0 V (SCE) and exposed to light modulated at
11.6 Hz through backside illumination. The bandwidth of incident light
for both spectra was 0.5 nm.

C.   Photocurrent vs Solution Concentration

As has already been established, the adsorption of rhodamine B on
ZnO will vary with solution concentration. Consequently, the photocurrent
in an electrochemical arrangement can also be expected to change with
the solution concentration of the dye. It should be informative to compare
the data from the absorbance spectra of fig. 2b with data from similar
photocurrent measurements to obtain a measure of the quantum efficiency
of charge transfer as a function of solution concentration.

However, the photocurrent measurement requires the presence of an
electrolyte in solution and this may affect the adsorption of the dye.
At pH 6.5, though, rhodamine B is a neutral species so that coulombic
forces can be expected to have little influence on adsorption. This
was demonstrated through the measurement of the absorbance of the rhodamine
B that was adsorbed onto the Li doped ZnO crystal from a 3.0×10^{-5} M
solution of the dye in the presence of 0.25 M solutions of KNO_3 and KCl.
Compared with the optical density of the dye adsorbed from water (.0045)

there is little difference in the amount of dye adsorbed from the two electrolytes (KNO_3-.0044, KCl-.0047). This confirms literature reports that the adsorption of rhodamine B onto ZnO is independent of KCl concentration.[3]

The magnitude of the photocurrent at the dye's absorbance maximum was determined for solutions up to 3.0×10^{-4} M in rhodamine B for .25 M KNO_3 and KCl solutions. The results can be seen in fig. 4 along with the optical density measurements from fig. 2b. The three curves are very similar. Each point is the average of six to ten measurements of the photocurrent at its initial value before any time decay. The bias was + 0.50 (SCE). After each measurement the crystal was washed with successive baths of doubly distilled water, methanol, and distilled water. A twenty minute equilibration time was allowed after immersion of the electrode before illumination and measurement.

The photon flux was 2.1×10^{15} photons/cm^2-sec at 560 nm with a bandwidth of 8 nm at half of the maximum intensity. The calculated efficiency, Φ, of electron transfer for each surface concentration is listed in Table 1 for both KCl and KNO_3 as electrolytes. For a KCl electrolyte the average value of Φ was .037; for KNO_3 the result was .027. This is in agreement with reports that Cl^- functions as a reducing agent for the adsorbed dye while KNO_3 proves to be inert.[3,9] This feature of the Cl^- electrolyte has been examined and will be discussed in detail elsewhere.[10]

D. Time Decay of Photocurrent

As can be seen in fig. 6 the photocurrent by rhodamine B at a ZnO surface diminishes with time. After 10 minutes the rate of photoinjection has dropped to 40% of the initial value as the dye on the surface is oxidized.

It is evident that aprolonged exposure of the interface to illumina-tion results in a decrease in the number of photoactive dye molecules at the surface. Gradually the surface must become covered with inactive, oxidized rhodamine B which is only slowly replaced with new dye from solution. This picture of the time decay implies that the magnitude of the photocurrent after initial exposure will depend on the relative rates of photooxidation of the dye and replacement of the oxidized molecule.

These procedures have been depicted in fig. 7. At the beginning of illumination there is an equilibrium between the dye on the surface, D_{ad}, and the dye in solution, D_{sol}. The exposure of the electrode to a photon flux results in oxidation of D_{ad} and creation of the adsorbed oxidized species D_{ad}^+. Continued illumination of the surface converts D_{ad} to D_{ad}^+, and the photocurrent produced at the interface decreases.

The only way that D_{ad} can be replenished is through desorption of D_{ad}^+ at a rate $k_3[D_{ad}^+]$ followed by adsorption of D_{sol} molecules on the vacated sites. It should be expected that at some point during the time decay of the photocurrent, desorption of D_{ad}^+ should be rate limiting and the rate of consumption of D_{ad} should equal the rate of desorption of D_{ad}^+ and adsorption of D_{sol}.

An attempt will be made to correlate this intuitive picture of the time decay with the observed decline in the photocurrent using a kinetic model. Two sets of data are available for examination. One is the time behavior of the photocurrent for rhodamine B in an inert electrolyte, 0.25 M KNO_3, and the other is the corresponding decay for the dye in 1.0 M KCl.

The two electrolytes used in this investigation of the time behavior of the photocurrent were 1.5 x 10^{-4} M in rhodamine B, a concentration which corresponds to the plateau region of the adsorption isotherm of

of fig. 2b. Qualitatively, the results were similar although the magnitude

of the photocurrent from the KCl experiments was larger than the KNO_3

results. The photocurrent always represents that obtained at a saturation

bias; monochromatic illumination through the crystal as an optical window

at the dye's absorbance maximum was used. The solutions were deoxygenated

and stirred with ultrapure N_2.

As shown in fig. 6, the photocurrent decays smoothly with time.

This logarithmic analysis does reveal, though, two limiting regions denoted

by "F" and "S". They correspond to an initial, fast decay succeeded by

a slower, long term decrease in the photocurrent.

At this point it is appropriate to mention that accompanying this

photocurrent decay is a dc dark current that results from the potentiostatic

control of the electrode bias potential. As a polarizable semiconductor

electrode ZnO is nearly ideal with dark currents of about 5 nanoamps

in these experiments at pH 6.5. This current is thought to be partially

ionic in character and has been attributed to two sources:[11] the anodic

dissolution of the ZnO lattice into Zn^{++} ions and O_2 gas, and the ionic

migration of interstitial Zn^+ to the surface where it is oxidized and

solvated. The dark current decays with time.

Several experiments serve to clarify the role of this potentiostatic

dark current in the long term decay of the dye sensitized photocurrent;

two of these experiments are shown in fig. 8. In this figure the photo-

current was measured as a function of time, but with significant periods

during which the crystal was in the dark. It can be seen that the long

term decay is dependent on the dark current; if the experiment is run

with an interruption of the light and the potentiostatic control then

this decay in the dark is halted (fig. 8b). These results indicate that

the long term decay originates in processes closely tied to the dark current. In fig. 9 can be seen an extension of the experiments depicted in fig. 8. Here the dependence of the long term decay on the dark current is easily seen.

The time decay of the photocurrent was not quantitatively reproducible. The photooxidation of the dye is expected to be very sensitive to the condition of the electrode surface, and this will change with long periods of anodic polarization. A 5 nanoamp dark current should lead to dissolution of 50% of the surface after 2000 seconds of polarization. Furthermore, the dye's adsorption and desorption rates are dependent on the stirring of the electrolyte. With the apparatus used in these experiments, it was not possible to reproduce this stirring rate from experiment to experiment.

It was also recognized that the modulation technique used for measurement of the photocurrent can influence the rate of photo-induced decay. In the light chopping cycle each exposure of the surface to light is followed by a dark period during which the system can recover to some extent. Consequently, the observed decay is not as fast as it would be under a condition of continuous illumination. In order to permit a quantitative analysis of the decay, the photocurrent behavior under constant illumination was measured, an example of which is shown in fig. 6 for a KNO_3 electrolyte.

IV. Discussion

A. Absorbance of Adsorbed Rhodamine B

A comparison of the absorbance of rhodamine B adsorbed on ZnO with the solution absorbance (fig. 5) reveals that there is but little difference between the two. The relative concentrations of the monomer and dimer species may change in going from solution to surface, but no new transitions

appear upon absorption to change the envelope of the absorption spectrum. The most significant difference is a red shift of the absorption maxima from their corresponding energies in solution.

This is a commonly observed phenomenon for adsorbed sensitizing dyes[12] and is a consequence of a slight stabilization of the excited state of the dye relative to the ground state. Adsorption of the dye from solution places the molecule next to a solid which has a higher optical dielectric constant, $E = n^2$, and with which the dye has a greater dispersion interaction. In solvents where only dispersion forces are present, an increase in the n of the environment will result in a shift of the electronic spectrum of a solvated species.[19]

Therefore, if electrostatic forces or hydrogen bonding are not involved in the adsorption process, this red shift in the absorbance spectra should be a measure of the optical dielectric constant at the surface.[14] Although this may be true for adsorption of a dye like rose bengal,[6,14] it is probably not the case for rhodamine B since hydrophobic interactions do appear to play a significant role in aggregation[15] and in adsorption on organic solids.[1]

With only these small changes in the excitation spectra, it can be concluded that no major modification of the electronic structure of the chromophore is involved in the adsorption of this dye. Although this is not always the case with sensitizing dyes,[5] the interaction between the chromophoric function of rhodamine B and the underlying substrate must be only a slight perturbation from that between the dye and the solvent from which it was adsorbed.

It can be seen from fig. 2a that rhodamine B adsorbs from solution as a monomer. Evidently, adsorption must occur in an orientation that interferes with dimer formation. A model[16] for dimer formation of rhodamine

B pairs the molecules through apposition of the chromophoric planes with the attached phenyl groups oriented about 180¼ apart. An inhibition of this aggregation would ensue if the molecule were adsorbed with the chromophoric amino groups next to the surface as has been proposed for adsorption of this dye on organic single crystals.[1]

No experimental measurement of the amount of dye adsorbed on the semi-conductor surface was made because of the small surface area of the crystals. However, a theoretical analysis of these absorbance spectra can yield the surface concentration, C_s, of the dye if it is assumed that the transition moment for the excitation is conserved after the dye enters the adsorbed state. From this theoretical calculation, adsorption isotherms can be constructed and a heat of adsorption can be determined.

Such a theoretical analysis was carried out using the spectra of figs. 2 and 5 after the manner of Pandolfe and Bird.[17] There are errors in these calculations which originate in the treatment of the rhodamine B spectrum as one transition when it is, in fact, two. However, they were small and have been neglected.

A calculation for C_s was performed for each spectrum of fig 2a and an adsorption isotherm was established as seen in fig. 2b. The envelope of the absorbance spectra changed so little from the lowest to highest surface concentration that the calculated value for C_s was found to be proportional to the optical density of the absorbance maximum of each spectrum. Thus, the absorbance data of fig. 2b reflect an adsorption isotherm which can be described by the ordinate on the right side of this figure.

At the plateau of the isotherm, the surface coverage of 1.1×10^{-7} mmoles/cm^2 yields an area of 150 Å^2 per molecule. An examination of a model of rhodamine B indicates that 100 Å^2 would be a reasonable approximation of

the area occupied by the adsorbed dye molecule. Thus, this plateau appears to represent a monolayer coverage of the surface.

This isotherm of fig. 2b conforms to Langmuir type adsorption. Analysis of these data with a Langmuir expression for adsorption[18] allows an estimation of 6.2 kcals/mole for the heat of adsorption of rhodamine B on ZnO. This value for ΔH is in the same range as heats of adsorption reported for sensitizing dyes on powder substrates[19] and indicates an adsorption governed by dispersion forces and, to some small extent, coulomb forces.[12,20]

Overall, these results for adsorption of rhodamine B onto ZnO single crystals do not differ to a great extent from the behavior observed for adsorption of similar dyes onto powders.[12,20] This has also been found to be true for adsorption of rose bengal on TiO_2 single crystals[6] and several other dye/semiconductor single crystal combinations.[24] The conclusions to these single crystal studies must perforce be similar to those drawn from work performed with powders. However, it will be seen how the single crystal absorbance data can be used to effect further conclusions when correlated with photocurrent measurements at the same crystallographic face.

B. Comparison of Absorbance and Photocurrent Measurements

The photocurrent action spectrum of rhodamine B on ZnO reflects the absorbance spectrum of the adsorbed dye. Aside from minor differences, the envelopes of two sample spectra (fig. 3) are the same, showing that the efficiency of electron transfer is constant over the spectral range of the dye. Therefore, as expected, the higher energy excitation of the adsorbed shoulder must then decay quickly ($10^{-11} - 10^{-12}$ sec) to a lower energy excited state from which oxidation occurs.

The absorbance spectrum of fig. 3 is red shifted from the action spectrum by several nanometers. There is also a slightly higher shoulder in the action spectrum where the dimer absorbance of the dye is found. Both of these

differences are probably due to the presence of the salt in solution. The electrolyte could salt out the dye to form dimers on the surface to some small extent; the Helmholtz layers formed by these ions produce an electrostatic environment greatly different from the solid/gas interface at which the absorbance spectra were taken. With only these minor differences, though, the action spectrum can be seen as a measure of the absorbance of the adsorbed dye layer.

The probability that an excited, adsorbed dye will transfer energy to a neighboring dye molecule has been discussed in previous investigations.[6,21] It was concluded, for example, that a weak, long range energy transfer does occur between rose bengal molecules adsorbed on a TiO_2 electrode.[6] An energy exchange by A Förster mechanism is also possible for rhodamine B on ZnO, but only via a weak, long range mechanism since the absorbance spectra of fig. 2a do not exhibit the spectral characteristics of a stronger inter-action.

This phenomenon would be dependent on the surface concentration of the dye. With the data of fig. 7, it can be determined if the efficiency of electron transfer is a function of the dye concentration on the electrode. The results of such a calculation are listed in table 1 for each surface concentration at which photocurrent measurements were taken. Complete surface coverage, $\Theta = 1.0$, is defined as 1.1×10^{-7} mmoles/cm^2.

The quantum efficiency of electron transfer appears to be constant with surface coverage although the KNO_3 data are not too convincing. The effect of the salt on adsorption may account for the discrepancies as the curve described by the KNO_3 photocurrent data of fig. 4 is different from the curves of the optical density and KCl data. However, the relatively small range of the Θ data does require consideration of the probability that the efficiency of the charge injection does not depend on the surface concentration of the
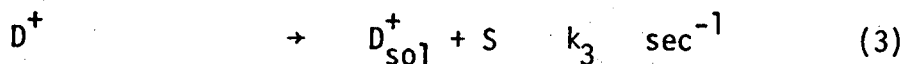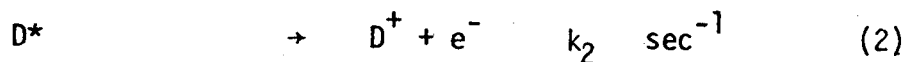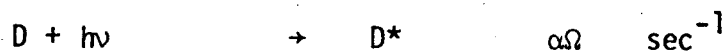
dye over this range of Θ. Two conclusions are possible. Either excitation does not occur or its effect on the charge transfer efficiency has saturated before the surface coverage of 4.0×10^{-8} mmoles/cm^2 ($\Theta = 0.4$) has been reached.

The rate of this type of energy transfer will drop off sharply once the intermolecular separation exceeds 50 A. This limit would correspond to a surface coverage of $\Theta = .01$ which is much lower than the surface concentrations of Table I. Therefore, the data of fig. 4 are inconclusive concerning the question of the existence of energy transfer in this system.

C.   Kinetic Model of Photocurrent Decay

A kinetic model for the time decay of the photocurrent was formulated with the consideration that the rhodamine B is adsorbed at a variety of sites on the surface. These sites do not influence the quantum efficiency of dye photooxidation, but some of them are disabled for photoactive purposes through the dark current processes revealed in fig. 9. Analysis of the data with this assumption yields information concerning desorption rates of the oxidized dye and the total surface concentration of the dye.

An analysis of the kinetics of this time decay without consideration of the dark current blockage of surface sites requires consideration of these events at the electrode surface:

$$D_{sol} + S \rightleftharpoons D \qquad K \quad M^{-1} \qquad (1)$$

$$D + h\nu \rightarrow D^* \qquad \alpha\Omega \quad sec^{-1}$$

$$D^* \rightarrow D^+ + e^- \qquad k_2 \quad sec^{-1} \qquad (2)$$

$$D^+ \rightarrow D^+_{sol} + S \qquad k_3 \quad sec^{-1} \qquad (3)$$

$$D^* \rightarrow D \qquad k_4 \quad sec^{-1} \qquad (4)$$

The photocurrent measured at an interface reflects the oxidation of the excited dye:

$$J = k_2 [D*] \qquad (5)$$

Here $[D*]$ is in units of molecules cm^{-2} and J in electrons cm^{-2}. In the steady state during illumination

$$[D*] = \frac{\alpha\Omega}{k_2 + k_4} [D] \qquad (6)$$

so that $\qquad J = \alpha\Omega\phi [D] = Q[D]$

where $\phi = k_2(k_2 + k_4)$ is the quantum yield for photoinjection.

The time dependence of $[D]$, and therefore J, may be described by considering reactions (1) and (3) above. At the solution concentrations of rhodamine B used in these experiments it can be assumed that the equilibrium (1) always lies far to the right so that the surface concentration of vacant sites, $[S]$ is small. Thus, new D appears on the surface at a rate limited by the desorption of D^+ (reaction (3)), while it disappears when electron injection occurs. The time dependence of $[D]$ is therefore given by

$$\frac{d[D]}{dt} = k_3 [D^+] - Q[D] \qquad (7)$$

The total surface occupancy can be written

$$[D_0] = [D] + [D^+] \qquad (8)$$

since $[D*]$ is negligibly small. This gives for the solution of equation (7)

$$[D] = \frac{[D_0]}{k_3 + Q} \left[k_3 + Qe^{-(k_3 + Q)t} \right] \qquad (9)$$

and for the photocurrent

$$J = \frac{Q[D_0]}{k_3 + Q} \left[k_3 + Qe^{-(k_3 + Q)t} \right] \qquad (10)$$

However, it was observed (fig. 9) that continuous potentiostatic control of the crystal results in long term time decay in region "S" that occurs even in the dark. This can be explained qualitatively as a decrease in the number of surface sites available for occupation by photoactive molecules. Thus, in the mass balance expression (8), the number of sites available for occupation, D_0, should not be constant but will decay as a monotonically decreasing function of time.

Such a blockage of the surface may proceed through several pathways. The dark current production of oxygen at the crystal surface may result in adsorption of molecular oxygen and subsequent abstraction of an electron to form O_2^- at the electrode. The oxygen could also react with the adsorbed dyestuff to form non-desorbable oxidation products. Both of these reactions would result in a physical occupation of the surface by photo-inactive species other than the oxidized dye molecule.

In order to interpret the time decay of fig. 6 according to eqn. (10), the long term decay of $[D_0]$ in region "S" must be extrapolated to t = 0. This intersection of the curve and the ordinate can be determined through light intensity measurements. If the photon flux is doubled while the photocurrent is in the "S" region of decay, eqn. (10) predicts this relationship:

$$J (2 \, \Omega)/J(\Omega) = 2(k_3 + Q)/(k_3 + 2Q)$$

This permits evaluation of the ratio (k_3/Q). In this manner the long term decay curve can be extended to t = 0 with the aid of a power curve fit of the intervening points as shown by the dashed line in fig. 6.

The difference between the measured photocurrent and the extrapolated photocurrent in the "F" region can be plotted logarithmically to extract a value for $(Q + k_3)$, but a good linear fit was not always obtained owing

to the approximations involved in the extrapolation procedure. This evalua-
tion of the fast decay constant permits calculation of Q and k_3 since the
ratio (k_3/Q) is already known. Using eqn. (10) at $t = 0$, this knowledge
of the values for Q, k_3, and D_0 are listed in table 2. The light intensity
was doubled during the time decay to evaluate $J(2\Omega)/J(\Omega)$, Its value was
determined to be 1.65 independent of the time in the "S" region at which
it was measured.

Through this model the dye concentration on the surface was found to
be $3.3 \times 10^{14}/cm^2$ which is four times that calculated from the absorbance
date. This overestimate originates in the value of Q from which D_0 was
derived. Another example supporting possible error in Q can be found in the
evaluation of α from the expression $Q = \alpha\Omega\Phi$. Given that $\Phi = 1.7 \times 10^{15}$
photons/cm^2-sec and $\Phi = .026$, α was evaluated to be $9 \times 10^{-17} cm^2$ which
is about three times smaller than a measured value of $3 \times 10^{-16} cm^2$.[1]

This interpretation of the photocurrent time decay has been based on
the empirically derived assumption that the adsorption sites are gradually
occupied by non-photoactive species. The occupation of sites appears to occur
at a variety of rates and is a consequence of the bias applied to the crystal.
Inspection of the time decay of fig. 6 shows that this undefined dark
current process is responsible for the greater part of the decline in photo-
current over the time range of the experiment.

The model provides a reasonable explanation of the photocurrent decay
in that the initial, sharp decline of electron injection can be seen
as a depletion of the dye on the surface until a steady state is reached be-
tween oxidation of excited dye molecules and adsorption of new dye from
solution. This value of the photocurrent decreases because of obstruction of
sites by some unknown species. At this quasi steady state limit the photocur-
rent is not linearly proportional to Ω, but is a function of the rates for

creation, $\alpha \Omega \Phi$, and desorption, k_3, of the oxidized dye.

An analysis of the time decay when the electrolyte contains a reducing agent would be more complex than the simple model presented here. The complexity results from the competition between the two energetically plausible reactions of a reducing agent, R:

$$R + D^* \rightarrow D^- + R^+ \tag{14}$$

$$R + D + \rightarrow D^- + R^+ \tag{15}$$

If one reaction could be excluded, a relatively simple analysis could be formulated for the other. However, until some measure of the relative values of k_{14} and k_{15} has been made, such an analysis would be speculative and has not been attempted here.

Furthermore, a much more rigorous control of experimental conditions would be required in an examination of this decay. Specifically, a rotating disc electrode would be necessary for accurate and complete control of the diffusion processes at the surface.

SUMMARY

Rhodamine B adsorbs weakly to the (0001) face of ZnO with a ΔH of 6.2 kcal/mole. However, this heat is of sufficient magnitude to result in a complete surface coverage of 1.1×10^{-7} mmoles/cm^2 corresponding to an area of 150 Å/molecule.

The adsorption orientation of the dye must preclude aggregation on the surface since the absorbance of the adsorbed molecule differs very little from the solution spectrum of the monomer. The absorbance of the adsorbed rhodamine B was closely reflected in the photocurrent action spectrum observed in an electrochemical system.

As the surface coverage of the electrode by the dye climbed from

$\Theta = 0.4$ to $\Theta = 1.0$, the quantum efficiency of electron transfer from the excited dye to the conduction band remained constant. This increase in the surface concentration of the dye does not result in a significant quenching of the excited state of the rhodamine B.

The time decay of the photocurrent can be described by a kinetic model which ascribes the rate limiting step to the desorption of the oxidized dye.

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Table 1   The quantum efficiency of electron transfer as a function of surface coverage Θ.

	Solution Concentration $(10^{-5}M)$	KNO_2	KCL	
1.0	30	.025	.037	
1.0	15	.026	.035	
.95	9	.026	.035	
.70	3	.033	.036	
.60	1.5	.031	.043	
.45	0.75	.020	.038	
		.027	.037	$\bar{\Phi}$
		17%	7%	σ

Table 2   Data derived from analysis of the time decay of fig. 6

Q	4.3×10^3	sec^{-1}
k_3	1.57×10^{-2}	sec^{-1}
$[D_o]$	3.3×10^{14}	cm^{-2}
α_o	9×10^{-17}	cm^2

FIGURE CAPTIONS

Figure 1: A glass cell was constructed for absorbance measurements in which the crystals were held perpendicular to the light path.

Figure 2: (a) The absorbance of four layers of the adsorbed dye is shown at various surface concentrations. The OD at the monomer maximum is plotted as a function of the solution concentration of the dye in (b). The ordinate on the right of (b) calibrates the absorbance in terms of surface coverage.

Figure 3: This is a comparison of the absorbance and action spectra of rhodamine B adsorbed on a ZnO single crystal from a 5×10^{-5} M solution of the dye. The bias potential was 1.0 V and the bandwidth of the light was 0.5 nm.

Figure 4: Photocurrent measurements are shown as a function of the dye's solution concentration for a KNO_3 electrolyte $\square\square\square$ and a KCl electrolyte $\triangle\triangle\triangle$. The absorbance of the adsorbed dye 000 is taken from fig. 2b; the surface area of the electrode was .126 cm^2.

Figure 5: The absorbance of a 6.3×10^{-7} M aqueous solution of rhodamine B in H_2O (1 cm path length) and of the dye adsorbed on ZnO from a 4×10^{-4} M solution are compared.

Figure 6: The time decay of the photocurrent exhibits an initial fast decline, "F", which is followed by a slower one, "S". The slow decay curve can be extrapolated to the t = 0 axis as shown by the dashed line. A KNO_3 electrolyte was used with the crystal biased at + 0.5 V. The photon flux was 1.7×10^{15} $cm^{-2}sec^{-1}$; the light was not modulated.

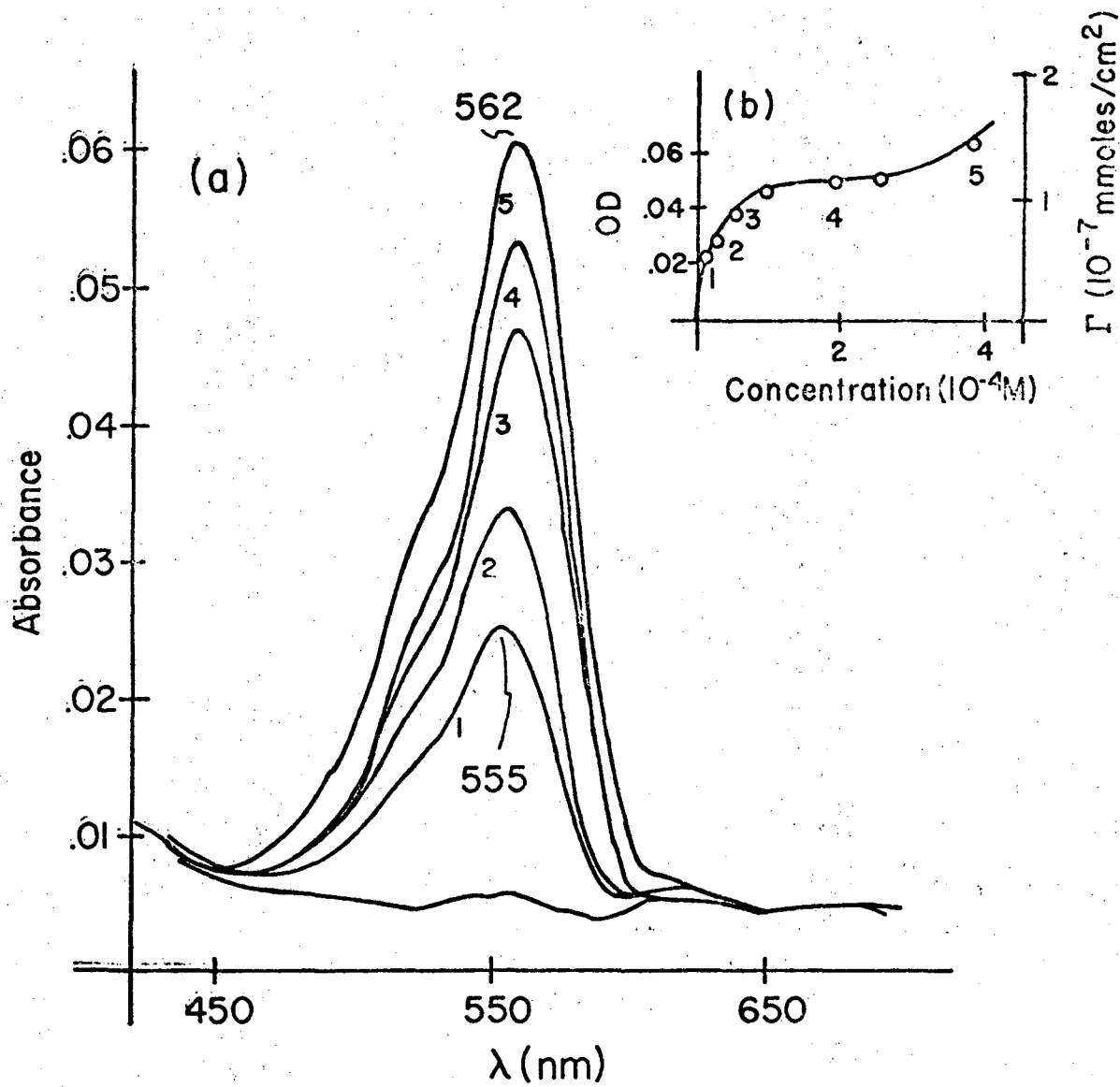Figure 7: A schematic presentation is given of the processes occuring at a sensitized semiconductor electorde. Adsorption of a dye molecule from solution, D_{sol}, to create D_{ad} results in either desorption, k_{-1}, or oxidation, k_2, following excitation by the proton flux Ω. The oxidized dye, D_{ad}, can be desorbed, k_3.

Figure 8: (a) Potentiostatic control of the crystal results in a long term decay of the photocurrent even when the interface is not exposed to light. (b) Removal of potentiostatic control allows a recovery of the photocurrent and halts the long term decay. A KCl electrolyte was used with a +1.0 V bias on the electrode.

Figure 9: An extension of the experiment depicted in fig. 8a shows a smooth time decay dependent on the dark current.
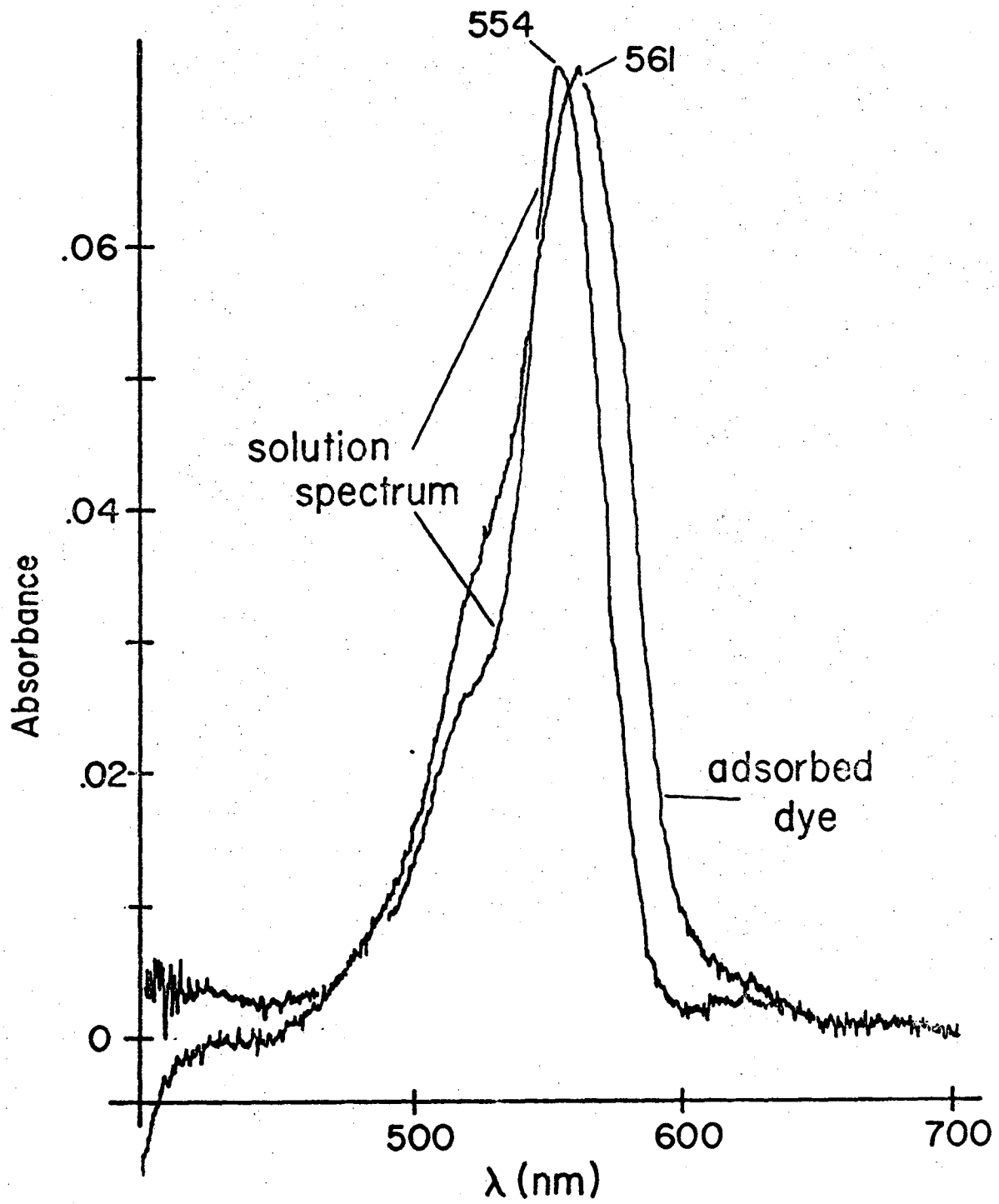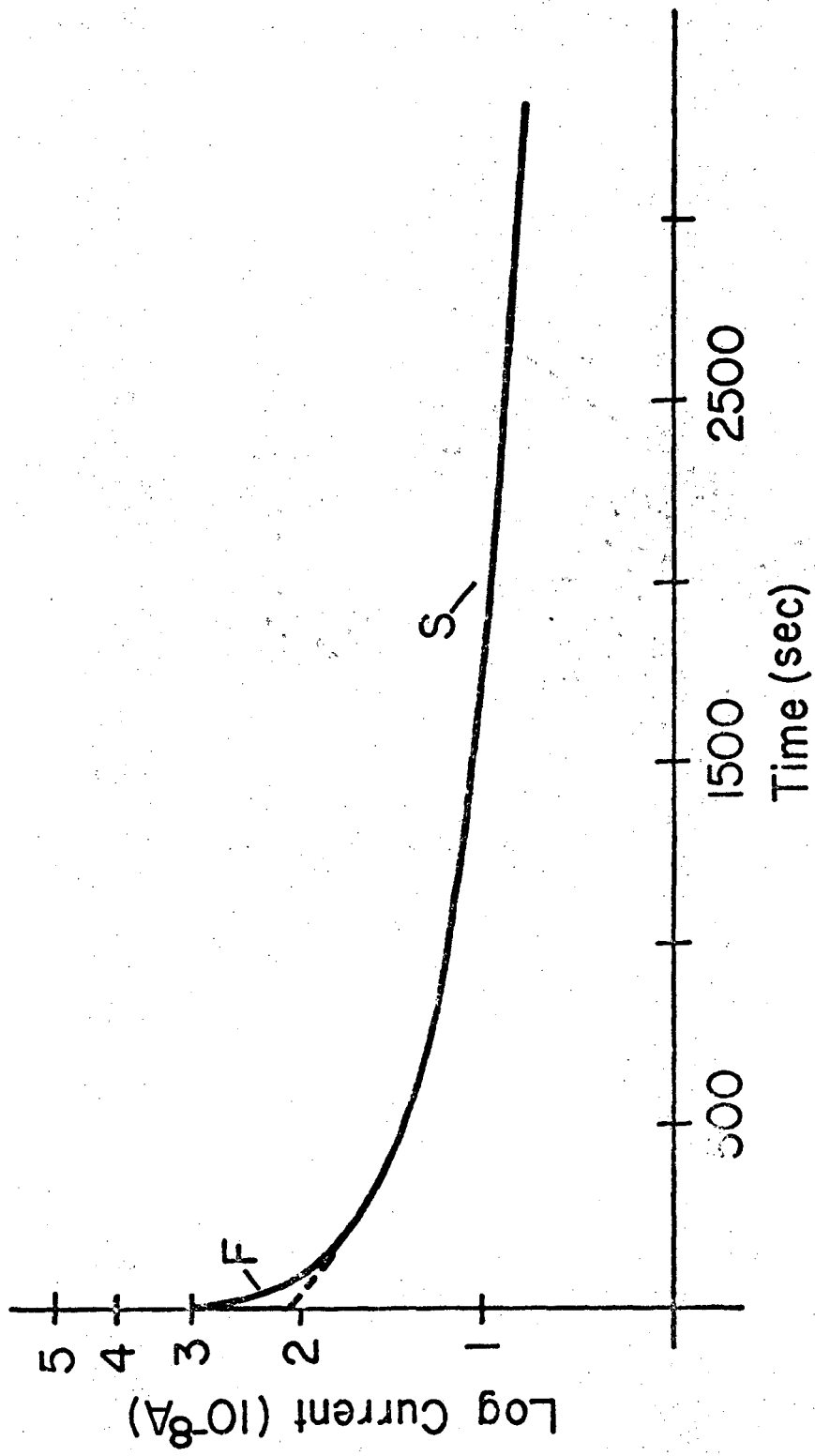
TEFLON DISKS

CRYSTALS (OOOI) FACE

GLASS TUBING

LIGHT PATH

XBL773-4249

Spitler & Calvin
Fig. 1

XBL 773-4253

Spitler & Calvin
Fig. 2

XBL773-4254

Spitler & Calvin
Fig. 3

XBL 773-4248

Spitler & Calvin
Fig. 4

XBL 773-4252

Fig. 6

XBL773-4250

XBL 773 - 4255

XBL 7734246

Spitler & Calvin
Fig. 8

Fig. 9

XBL773-4247