Photoelectrochemical Effects in the Electrolyte–Pigment–Metal System.

I. Metal-Free Phthalocyanine Film Description of Short-Circuit Photocurrents for Thin Films of Pigment

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Abstract

Using a semitransparent metallic electrode covered with a thin film of metal-free phthalocyanine, photoelectrochemical effects have been studied in the electrolyte-pigment-metal system. Measurement of the short-circuit photocurrent, produced by continuous illumination, allows description of a photodependent kinetic phase corresponding to the establishment of a stationary state in the charge separation region of the system after the creation of the current carriers.

Introduction

In 1949, accepting for the pigment structure of the primary photo-synthetic apparatus the model of a periodic two-dimensional arrangement, Katz [1] proposed two possibilities for the conversion of absorbed photons. One is to assume charge separation, and then the migration of charges, the other is to assume the formation of an exciton diffusing by transfer. Calvin and co-workers [2–6, 10], Arnold and co-workers [7–9], Tollin and co-workers [3, 10–12], and Bassham [13] have later formulated mechanisms, for the primary conversion, implying charge

separation. This conception has been criticized in its time, particularly by Rabinowitch [14] : Now it has been almost completely abandoned. The more general point of view is to assume exciton diffusion to a point on the photosynthetic unit where conversion into chemical energy takes place. The actual problem is about the nature of this trap together with his immediate partners, electron donors or acceptors; and the localization of this primary energy converter in a membraneous structure. In these conditions photoelectrochemical effects in the electrolyte-pigment–metal system offer possibilities for the study of interactions at the liquid–solid interface between excited molecules and oxydants or reductants present in the electrolyte. This type of work has already been undertaken by Evstigneev and co-workers [15–17], Putseiko and co-workers [27–29], and Kommissarov and co-workers [18–26]. We have done our studies [30–32] to obtain a good phenomenological description of the measured transients and a precise conclusion on the part played by the pigment-electrolyte interface with the production of the photoelectrochemical effects.

Methods

The semitransparent metallic electrode was formed by evaporation under vacuum of platinum on a microscope slide. The phthalocyanine (Theodordt Schuchard, Eastman Kodak) was purified in most cases by sublimation under reduced pressure: it has also been used after a recrystallization in α-chloronaphthalene or precipitation by water of a solution in sulfuric acid.

The film of pigment was deposited on the metallic electrode by sublimation under vacuum $(P < 10^{-5} \text{ mm Hg})$. If one considers the phthalocyanine film as a stack of monolayers of phthalocyanine molecules in an horizontal position, then the optical density of such a monolayer is 0.005 at the absorption maximum 620–625 nm. This is just a rough calculation, the absolute number of phthalocyanine molecules being determined by dissolving the film in α-chloronaphthalene and measuring the optical density of the solution.

The white light used in measurements has a maximal intensity in the plane of the electrode of 15×10^4 ergs cm^{-2} sec^{-1}. With monochromatic light the intensity varies between 6×10^3 and 15×10^3 ergs cm^{-2} sec^{-1}. For illumination by flashes we have used a "Strobotac" (General Radio) (Fig. 1).

The electrical measurements were carried out with a current amplifier having a very low entry impedance so that we can measure the short-circuit current between the pigmented electrode and a silver–silver chloride reference electrode. In a stirred aqueous medium the lifetime of our pigmented electrodes is too short to allow for a correct description
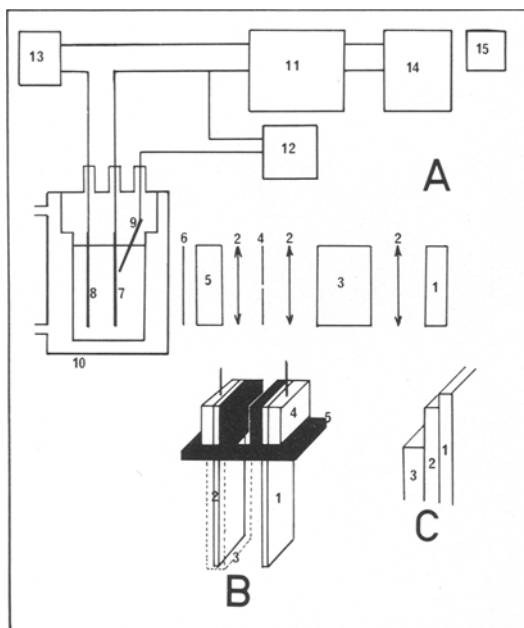
Figure 1. (A) Schematic representation of apparatus. Illumination apparatus: (1) Xe Lamp (450 W); (2) lens; (3) monochromator; (4) shutter; (5) water cuvet; (6) calflex filter. Electrochemical cell: (7) Pigmented electrode; (8) Ag–AgCl electrode (distance between the two electrodes 0.5 cm); (9) calomel electrode; (10) electrochemical cell with a thermostating jacket. Measurements apparatus: (11) Short-circuit current amplifier (low entry impedance); (12) voltage measurer (high entry impedance); (13) polarizing circuit; (14) oscilloscope; (15) photographic recorder. (B) Schematic representation of electrodes holder. (1) Pigmented electrode; (2) Ag–AgCl electrode; (3) dashed line stands for a shelter (black tissue) preventing silver electrode from illumination; (4) copper contact; (5) leucite holder for electrodes and contacts. (C) Schematic description of pigmented electrode. (1) Glass microscope slide; (2) platinum evaporated film; (3) pigment evaporated film.

of the photocurrent transients. In spite of the high viscosity, we have employed a 96% glycerol medium (4% KC1 saturated : so[KC1] = 0.18 M); the functioning of the system is stable for several hours or more, under these conditions.

Results

1. *Current–voltage characteristics.* To describe the dark current-voltage characteristics the potential jumps (100 mV) are carried out at regular time intervals ($t = 15$–20 sec). Current is measured 5 or 10 sec
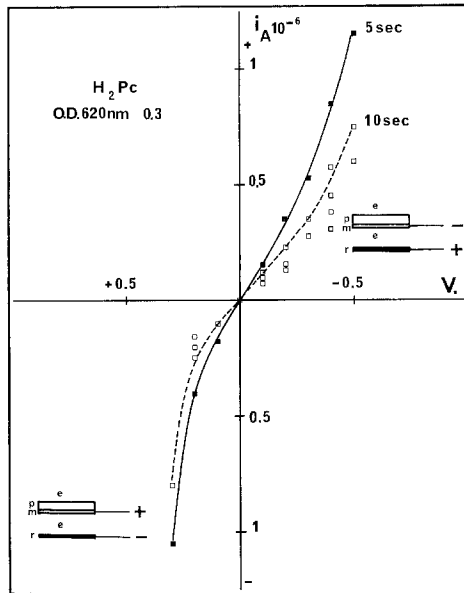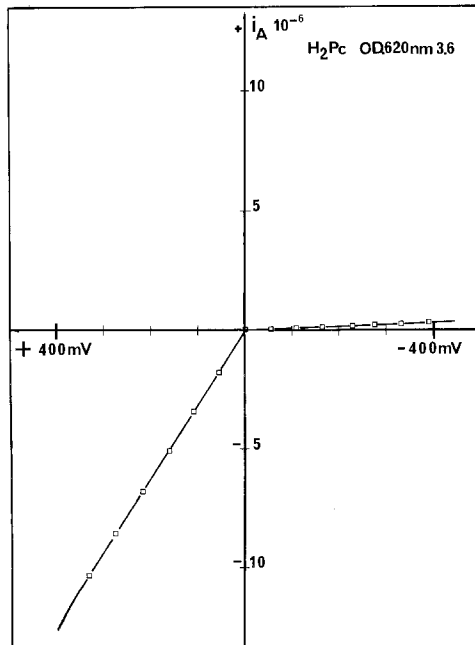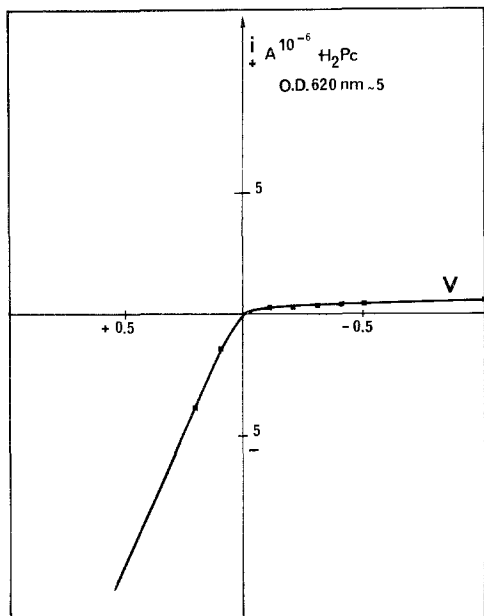
Fig. 2(a).

Fig. 2(b).

Fig. 2(c).

Figure 2. Current–tension characteristics for semitransparent platinum electrodes covered with a film of metal-free phthalocyanine. (electrolyte: 96% glycerol, 4% saturated KCl aqueous solution, pH 7.8; reference electrode: Ag/AgCl; active surface of electrodes 6.25 cm^2). Abcissa; external applied potential. Ordinate: dark short-circuit current. 2(a). Optical density at the maximum of absorption 620 nm: 0.3 (thickness of the film $\simeq$ 0.06 μ). Values of current have been measured 5 sec and 10 sec after the potential jump; without external applied potential dark current is 3.10^{-9} A/cm^2. 2(b). Optical density at the maximum of absorption 620 nm: 3.6 (thickness of the film $\simeq$ 0.7 μ). 2(c) Optical density at the maximum of absorption 620 nm $\simeq$ 5 (thickness of the film $\simeq$ 1 μ). Schematic picture of electrodes configuration. L: light; p: pigment; m: metal; r: Ag/AgCl electrode; e: electrolyte.

after the peak following the potential jump. For a thin film of metal-free phthalocyanine (optical density 0.3 at 620 nm), without an external applied potential, the dark current is 3.10^{-9} A cm^{-2} (active surface of electrode 6.25 cm^2). In this thickness range (0.06 μ) one is obliged to limit the applied voltage to +0.5 V, −0.5 V as irreversible degradation effects appear for higher voltages. One can see that the $\Delta i/\Delta v$ ratio is slightly higher in the positive applied potentials region than in the negative one (Fig. 2a).

The current–voltage characteristic becomes more and more assymetric on each side of the zero applied potential point when the thickness of the film increases, i.e., when the distance between the two interfaces,

pigment–electrolyte and pigment–metal, increases (Figs. 2b, 2c). For a
thickness 1μ this characteristic is analogous to a rectifying system like a
junction; the "reverse direction" corresponding to the motion of
electrons in the direction metal–pigment–electrolyte, the "direct direc-
tion" to the motion of electrons in the direction electrolyte–pigment–
metal. Using this analogy one expects a photocurrent contribution on
illumination in the potential region corresponding to the "reverse
direction" in darkness.

2. *Short-circuit photocurrent (metal-free phthalocyanine film: optical
density 0.3 at 620 nm—Fig.* 3). In continuous white light the photo-
current transient shows two stages: the first is a fast rise to a maximum
value i_M, the second is a slower decrease to a quasistationary value i_s. A
semilogarithmic analysis of the first step allows us to describe it as an
exponential process and to write

$$i_t = i_M [1 - \exp(-kt)]$$

where i_t stands for the photocurrent at time t and k kinetic constant (of
photochemical nature, see latter in text). The second slower step, in the
same way, can be described in a first approximation as the sum of two
exponential processes that may be written

$$i_t = i_s + (i_M - i_s)[(1 - \alpha) \exp(-k_1 t) + \alpha \exp(-k_2 t)]$$

where α, $1 - \alpha$ stands for the contribution of each exponential term,
kinetic constants of which are k_1 and k_2. Introducing $\beta = i_s / i_M$ one gets

$$i_t = i_M [\beta + (1 - \beta)(1 - \alpha) \exp(-k_1 t) + \alpha(1 - \beta) \exp(-k_2 t)]$$

With $\beta \ll 1$, in the case studied here, in a first approximation, it is
possible to write

$$i_t = i_M [\beta + (1 - \beta - \alpha) \exp(-k_1 t) + \alpha \exp(-k_2 t)]$$

Since $k \gg k_1$ and $k \gg k_2$ a general equation of the over-all kinetics of
the photocurrent transient may be given as

$$i_t = i_M [\beta + (1 - \beta - \alpha) \exp(-k_1 t) + \alpha \exp(-k_2 t) - \exp(-kt)]$$

In darkening the current transient starting from the quasistationary value
$i_s = i_M \beta$ has a symmetrical form: First a rapid decrease down to a
negative maximum value $i_{M'}$ followed with a slower increase to the
stationary dark value. In a way similar to that described for the light
transient, these two steps may be written

$$i_t = i_M \beta - i_{M'} [1 - \exp(-k't)]$$

and

$$i_t = i_M \beta - i_{M'} [\gamma + (1 - \gamma - \delta) \exp(-k_1 t) + \delta \exp(-k_2 t)]$$
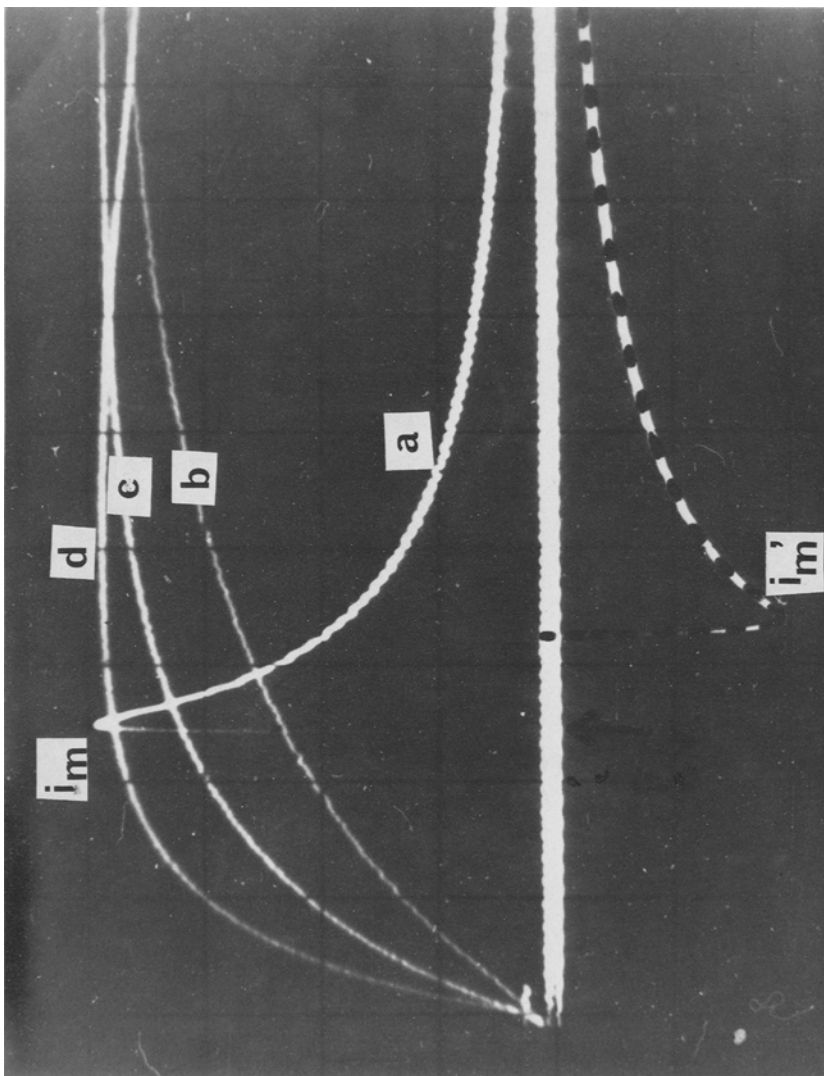
Figure 3. Short-circuit photocurrent transient produced by a semitransparent platinum electrode covered with a thin film of metal-free phthalocyanine (optical density at the maximum of absorption 620 nm: 0.3 thickness of the film ≈ 0.06 μm)— 96% glycerol 4% saturated KCl aqueous solution, pH 7.8); white light intensity 30,000 ergs cm^{-2}sec^{-1}. Full line: transient on continuous illumination time scale: (a) 100 msec div.; (b) 0.5 msec/div.; (c) 1 msec/div. (d) 2 msec/div. Ordinate: i_M maximum photocurrent 1.6 10^{-6} A/div. Dashed line: transient on darkness: time scale 100 msec/div. i_M' maximum dark current transient.

with $i_s = i_{M'}\beta = i_{M'}\delta$. k_1 and k_2 have the same values for the slow decreasing phase under illumination but the relative contributions of these two exponential terms, $(1 - \gamma - \delta)$ and δ, are reversed—that is, $(1 - \beta - \alpha)/\alpha \sim \delta/1 - \gamma - \delta$. So in darkness the current transient may be globally described in the same way under the form

$$i_t = i_M\beta - i_{M'}[\gamma + (1 - \gamma - \delta)\exp(-k_1 t) + \delta\exp(-k_2 t) - \exp(-k't)]$$

Speaking in terms of electrical equivalence this transient is analogous to the response of a circuit, including resistive and capacitive terms, submitted to the entry functions $E_1 = E_0 [1 - \exp - (kt)]$ and $E_2 = E_0 \exp - (k't)$. The rapid phases to maximum values i_M and $i_{M'}$ have the significance of rise of E_1 in light and decrease of E_2 in darkness. The following slow phases correspond to the kinetics of charge and discharge of parts of the circuit including capacitive terms. Several kinds of equivalent electrical schemes have been proposed for photovoltaic cells, junctions, electrochemical systems, or membrane model systems. In our case the equivalent electrical scheme must be able to account for the different forms of the transients, according to whether the exit impedance of the circuit is high or low. We are still working on an electrical equivalent circuit describing precisely all the features of the recorded transients. It then appears that the photopotential kinetics previously described by Evstigneev and Savkina [17] have the same kinetic significance as the slow phases in the short-circuit photocurrent transient.

3. Varying the illumination intensity I gives the following relations for the first rapid phase to the maximum photocurrent i_M: $i_t = i_M [1 - \exp(-kt)]$, $k = c + dI$, $1/i_M = a1/I + b$ (Fig. 4) with $c/d = a/b$. That allows us to write for i_t

$$i_t = \frac{Id}{b(c + dI)}[\{1 - \exp[-(c + dI)t]\}]$$

In darkness, the kinetic constant k' is not strictly light independent in the range of low intensities.

In this thickness scale the ratio of the light and darkness maximum currents is constant. The parameters k_1, k_2, α, β, γ, δ for the description of the slow phases are invariant. In a first approximation this means that in the terms of an electrical equivalence one may admit that the impedance terms of the equivalent circuit are photoindependent; and that only the kinetic parameters of the "photoelectrical" function at the entry of the circuit are photodependent.

The formal description used for the function $i_M = f(I)$ is based on the linearity of the function $1/i_M = g(1/I)$ in the light intensity and thickness range used here.

Other formulations for measurements of the same kind on dry systems [10] have been proposed, particularly as $i = \alpha I^n$, n being fractional and
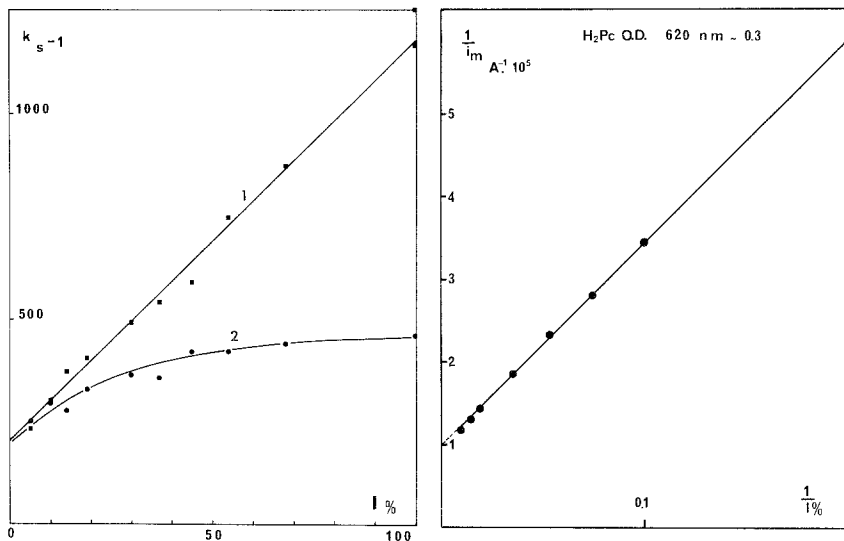
Figure 4. White-light intensity dependence of the kinetic parameters of the phase of appearance of the maximum photocurrent i_M in the short-circuit transient produced by a semitransparent platinum electrode covered with a thin film of metal-free phthalocyanine (thickness $\simeq 0.06\ \mu m$). (left) Variation with light intensity of kinetic constants k (1) and k' (2) corresponding to $i_t = i_M [1 - \exp - (kt)]$ and $i_t = i_M\beta - i_M'[1 - \exp - (k't)]$ (right) Variation of the inverse of the magnitude of the maximum photocurrent i_M with the inverse of light intensity. Maximum light intensity 15×10^4 ergs cm^{-2} sec^{-1}.

dependent on the light intensity scale. In our case the nonlinearity of the function $i_M = f(I)$ is not due to a "reduction" effect on i_M, as a consequence of the kinetic composition of increasing and decreasing exponential terms. The two expressions $I/a + bI$ and αI^n are numerically equivalent. Depending on the values of the terms a, b, I, the expression $I/a + bI$ is identical, for low values of I, to Ia^{-1}, that is αI^n for $n = 1$. For high values of I, $I/a + bI$ has b^{-1} as a limit, that is αI^n for $n = 0$. For intermediate values of I, the equivalence exists in the same way with n fractional varying between 1 and 0.

4. We have studied the response of the system either in its dark or light stationary state with a flash superimposed. In both cases the kinetic constant of the return transient in the corresponding stationary state is identical to the kinetic constant of the first rapid phase corresponding to the establishment of light or darkness. I_e, the intensity of the flash, being much larger than I, the intensity of the continuous illumination, one verifies that the ratio of the flash-transients amplitudes has the same
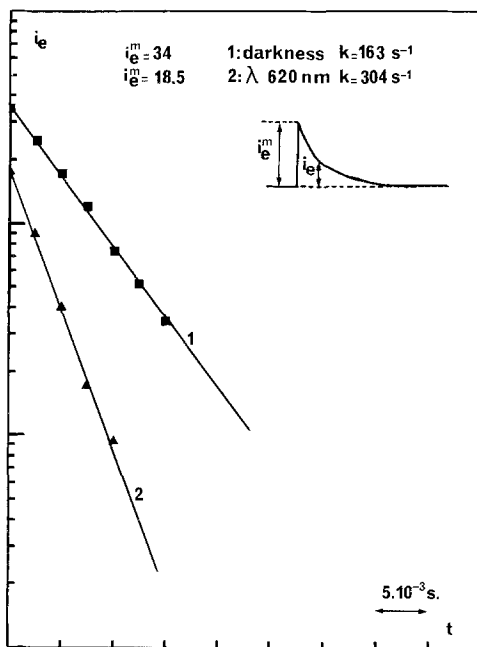
Figure 5. Semilogarithmic plot of the decreasing phase of the short-circuit photo-current transient produced by a semitransparent platinum electrode covered with a thin film of metal-free phthalocyanine submitted to a flash illumination: (1) In darkness; (2) Superimposed on a continuous illumination with $\lambda = 620$ nm. Ratio of magnitude of transients $(34/18.5) = 1.8$. Ratio of kinetic constants $(304/163) = 1.8$.

value as the ratio $c + dI/c$, which is a first approximation of the theoretical value

$$\frac{[c + d(I + I_e)]\,[c + dI]}{[c + dI_e]\,c}$$

(Fig. 5). These data are in accord with the analogous description proposed, in which one distinguishes between fast and slow phases in the short-circuit photocurrent transient; the fast phase corresponding to the establishment of a "photoelectrical" function which is in its stationary state during the following slow phases of short-circuit photocurrent.

5. If we vary the external applied potential, then the photocurrent maximum i_M increases in the negative potential region and decreases in the positive potential region until a value near zero is reached (Fig. 6). Data on the dependence of the different parameters of the first rapid phase of the photocurrent can be summarized as follows:

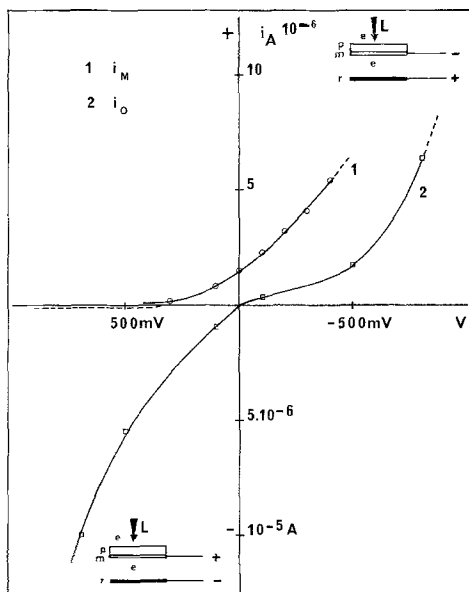$$i_t = \frac{dI}{f(V)\,[g(V) + dI]}\,\{1 - \exp\,-[g(V) + dI]\,t\}$$

Figure 6. Current–tension characteristic for a semitransparent platinum electrode covered with a thin film of metal-free phthalocyanine [electrolyte 96% glycerol 4% saturated KCl aqueous solution (active surface of electrode 6.25 cm^2), pH 7.8]. Abcissa: external applied potential; ordinate: short-circuit currents: (1) Maximum short-circuit photocurrents: white light illumination i_M; (2) dark short-circuit current: i_0. Schematic picture of electrodes configuration. L: light; p: pigment; m: metal; r: Ag AgCl electrode; e: electrolyte.

where V is the potential, and where $f(V)$ and $g(V)$ are functions of the applied voltage V. The slow phases become slower in the negative potentials region, which means that the corresponding impedance terms in the electrical equivalent circuit are dependent on the potential.

In the same way varying the temperature (10°C, 20°C, 30°C) gives

$$i_t = \frac{dI}{l(T)[h(T)+dI]} \{1 - \exp - [h(T) + dI]t\}$$

where T is temperature, and where $l(T)$ and $h(T)$ are functions of the temperature T. Thus it is possible to give for the first rapid phase the description

$$i_t = \frac{dI}{f(V,T)[g(V,T)+dI]} \{1 - \exp - [g(V,T) + dI)t\}$$

where $f(V,T)$ and $g(V,T)$ are functions of applied voltage V and temperature T. The consideration of the signs of variation with potential and temperature leads to the high possibility that the functions $f(V,T)$ and $g(V,T)$ are of the classical form for rate constants in electrochemical processes:

$$k_0 \exp(-E(RT) \, \exp[f(V)/RT]$$

Here we simply distinguish in the expression of the photocurrent

$$i_t = \frac{dI}{b(c+dI)} \, [1 - \exp - (c+dI)t]$$

the term d which is purely photochemical, and the terms b and c which depend on temperature and applied potential.

6. With monochromatic light, the global description of the transient remains the same for all wavelengths between 400 and 700 nm. The kinetic constants and amplitudes of the exponential terms for the slow phases are identical for all wavelengths. For the first rapid phase one gets

$$i_t = \frac{f(\lambda)I}{b[c+f(\lambda)I]} \, \{1 - \exp - [c+f(\lambda)I]t\}$$

where λ stands for wavelengths.

The function $f(\lambda)$ is identical to the absorption spectrum of the film between 400 and 700 nm, that is $f(\lambda) = \alpha\epsilon(\lambda)l$ where $\epsilon(\lambda)$ has the sense of an extinction coefficient, α of a yield and l stands for the increase of thickness in the range studied. The action spectrum can be drawn using the inverse of the slope in the function $1/i_M = a1/I + b$, this term $1/a$ corresponds well to the expression of (di_M/dI) for $I = 0$ that is d/bc or $f(\lambda)/bc$ (Fig. 7a, 7b).

7. To summarize: The fast rapid induction phase of the maximum photocurrent can be characterized by a kinetic constant $k = g(V,T) + \alpha\epsilon(\lambda)lI$ and the amplitude of the maximum photocurrent

$$i_M = [f(V,T)]^{-1} \, \frac{\alpha\epsilon(\lambda)lI}{g(V,T) + \alpha\epsilon(\lambda)lI}$$

Conclusion

Study of the short-circuit photocurrent allows the description in the evolution of the electrolyte–pigment–metal system under continuous illumination of a kinetic phase directly photodependent with its kinetic constant and magnitude: Under the same conditions this was not possible with photopotential measurements. The induction kinetics of the maximum photocurrent correspond to the establishment of a stationary state in the region of the system where charge separation and
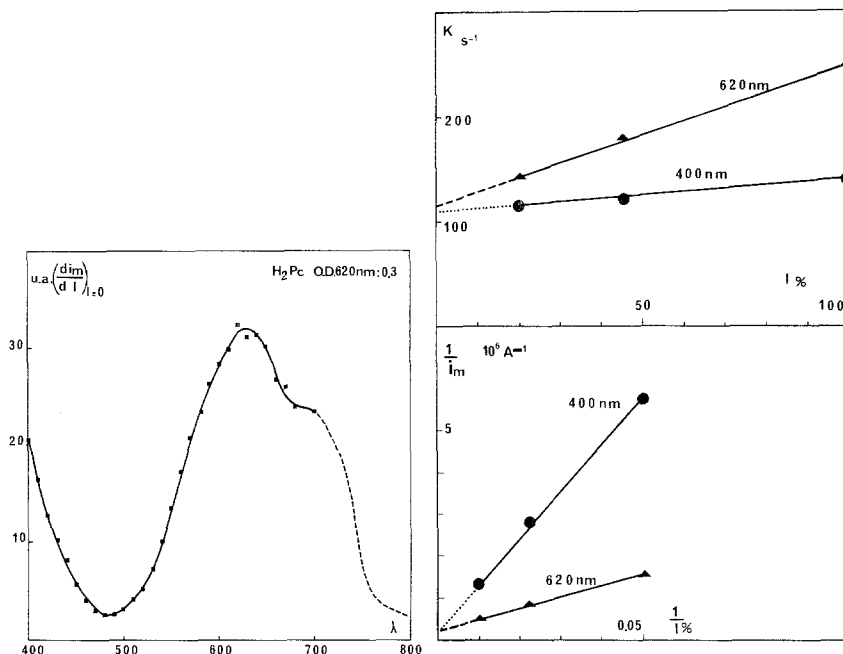
Figure 7. (Left) Action spectrum of the maximum photocurrent produced by a semitransparent platinum electrode covered with a thin film of metal-free phthalocyanine (thickness $\simeq 0.06\mu$m) (electrolyte = 96% glycerol, 4% saturated KCl aqueous solution). Abcissa: wavelength of illumination, ordinate: values of $(di_M/dI)_{I=0}$ arbitrary units. (Right) Light intensity dependence of the kinetics parameters of the phase of appearance of maximum photocurrent: $i_t = i_M[1 - \exp - (kt)]$ for two wavelengths 620 nm and 400 nm. (Right, top) Kinetic constant k; (right, bottom) inverse of the magnitude of the maximum photocurrent versus inverse of light intensity: in (percent)$^{-1}$; light maximum 2×10^{14} photons cm^{-2} sec^{-1}.

stabilization take place; the following slow phases correspond to the establishment of an electrical stationary state in the whole system, as could be seen with an electrical equivalent circuit. Kinetic analysis of the fast phase has to be pursued particularly using flashes and convenient electronic measurements devices for getting nearer to the real primary events of light energy conversion: It will be useful to use different kinds of redox system in the electrolyte, to describe more clearly the events at the pigment–electrolyte interface for thin films of pigment; here we can only retain the analogy with a junction for the whole system.

It is for this purpose that we have in the following paper characterized the evolution of the short-circuit photocurrent with increasing film thickness.

Aknowledgments

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