

# Photoelectrochemical Effects in the Electrolyte–Pigment–Metal System

## III. Chlorophyll Films

### Short-Circuit Photocurrent Transients Light Energy Conversion Efficiency

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*Received 26 July 1975*

#### *Abstract*

Short-circuit photocurrents produced by a semitransparent metallic electrode covered with multilayers of chlorophyll and immersed in an electrolyte have been studied. The action spectrum of maximum photocurrent is identical to the absorption spectrum of the film of pigment. The kinetics of rise of the photocurrent are photoindependent for thin multilayers but dependent on thickness. Comparison of efficiency of light energy conversion on the basis of short-circuit photocurrent seems to show that the stack of Chl *a* monolayers is the more efficient chlorophyll solid system. Introduction for the same number of Chl *a* molecules of vitamin K<sub>1</sub> and Phytol shows that vitamin K<sub>1</sub> acts probably like an excitation quencher as in monolayers at the water–air interface.

#### *Introduction*

The first step of energy conversion in the photosynthetic process is a redox reaction of a “special” excited chlorophyll molecule, exchanging an electron with an acceptor or a donor species closely bound with this “special” chlorophyll. The energy conversion unit is located in a

membrane called thylakoid, composed of proteins, lipids and pigments. In a "model system" approach of this energy conversion problem, two ways at least may be chosen: one is to build, taking into account in vivo structural data, a model structure system as close as possible to what is known, with the compounds extracted from the in vivo apparatus. Another one is to build an ordered well-defined system for the study of properties correlated with the imposed order. All the recent studies [1] on pigmented black lipid membranes belong to the first approach as black lipid membrane is now one of the best models for biological membranes. This work belongs to the second approach [2-6]: On the structural level, the analogy is based only on two aspects, a condensed quasi-solid structure for pigment and the existence in the system of two interfaces, liquid-pigment and pigment-metal; these two regions may be the site of specific charge separation processes as generally admitted for barrier or junction regions. Here we have studied the characteristics of short-circuit photocurrent transients in the electrolyte-chlorophyll-platinum system.

### *Methods*

Multimolecular chlorophyll films are built up by stacking chlorophyll monolayers formed at the water surface in a Langmuir trough (conventional procedure [7, 8]: distilled water, phosphate buffer pH 7.5-7.8  $10^{-3}M$ ). Solution of the pigment is made either in benzene-4% ethanol or in water saturated benzene (concentration  $2 \times 10^{-4}M$ , delivered volume 200  $\mu$ l). A main condition for getting a great number of monolayers stacked as generally admitted, is to use an hydrophobic surface. We have used a semitransparent platinum electrode obtained by evaporation of metal on a microscope slide. In some cases metallic electrodes have been first immersed in a "soluble silicon water solution" (Siliclad), then hot dried. In the ordinary situation for stacks of 3 and 6 monolayers, the red maximum in the absorption spectrum of the film is located between 675 and 677 nm. In the pretreatment case the red maximum appears at 670 nm. Gaines [2] has already noticed the special nature of the first stacked monolayers depending on the physicochemical nature of the solid substrate. We have not been successful in building up mixed monolayers stacks for chlorophyll-phytol and chlorophyll-vitamin  $k_1$ : in these cases we have used evaporated films from organic solutions of these mixtures. When evaporating organic solutions of chlorophyll, two kinds of films can be obtained using either low concentration solutions in pentane-ether, or more concentrated solutions in pentane. In the first case, the absorption spectrum in the visible range is typical of amorphous forms of pigment. In the second case one gets a mixed structure, two absorption bands

appearing at 450 and 740 nm: They are characteristic of strongly aggregated forms of chlorophyll, quasi-microcrystalline forms [3]. These different forms of "solid films" of chlorophyll have been used for a comparison of their efficiency in light energy conversion by means of the short-circuit photocurrent measurements.

## Results

### 1. Short-circuit Photocurrents of Chl a Multilayers

The measurement method has been described in previous papers [9-11] concerning the same kind of system using phthalocyanine instead of chlorophyll.

As for transients produced by thin films of phthalocyanine (see paper I [II]) the short-circuit photocurrent transient on continuous illumination may be described as

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

where  $i_t$  stands for photocurrent at time  $t$  and  $i_M$  is the maximum photocurrent reached on illumination. For this first rise step the approximation  $i_t = i_M [1 - \exp(-kt)]$  is valid. The second slower decrease step may be written also as a sum of two exponential terms.

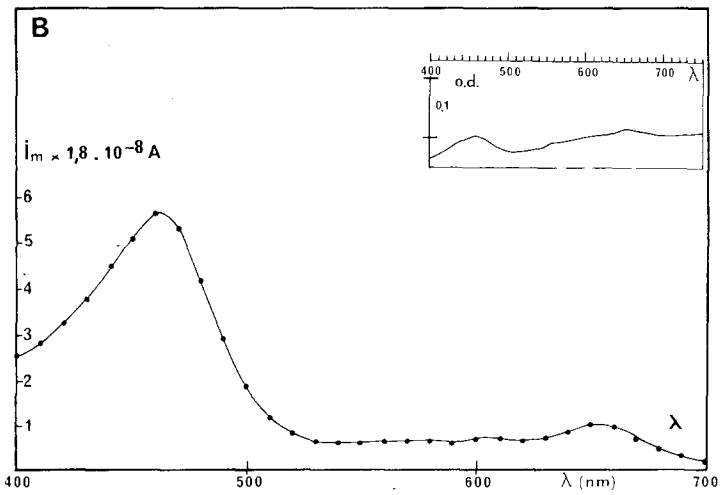
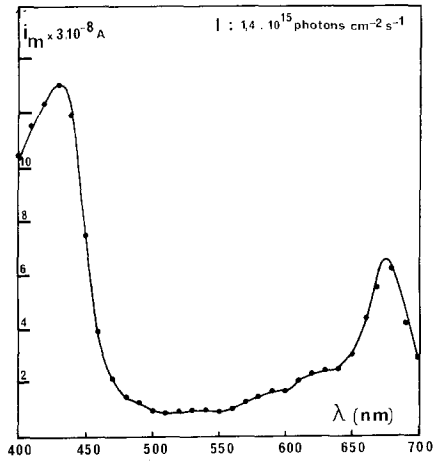
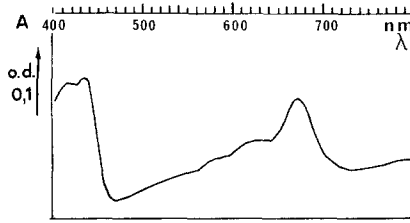
In the thickness range studied here, the maximum short-circuit photocurrent is proportional to light intensity  $i_M = \alpha I$ , and the kinetic constant  $k$  is independent of light intensity. This kinetic constant increases with the thickness of the film (Table I).

In darkness one gets a symmetrical description for the transient. In the thickness range studied here, the maximum photocurrent  $i_M$  is proportional to the optical density of the film at 675 nm.

The action spectrum drawn for the maximum photocurrent is identical here with the absorption spectrum in the visible range.

TABLE I. Variation of the rise time constant of the maximum photocurrent with the optical density of the chlorophyll film (thickness) and incident light intensity  $I$ .

$I$	$6 \times 10^4 \text{ erg cm}^{-2} \text{ sec}^{-1}$	$0.56 \times 6 \times 10^4 \text{ erg cm}^{-2} \text{ sec}^{-1}$
Optical density at 675 nm		
0.120	$k \approx 295 \text{ sec}^{-1}$	
0.120	$k \approx 230 \text{ sec}^{-1}$	225 $\text{sec}^{-1}$
0.03	$k \approx 30 \text{ sec}^{-1}$	



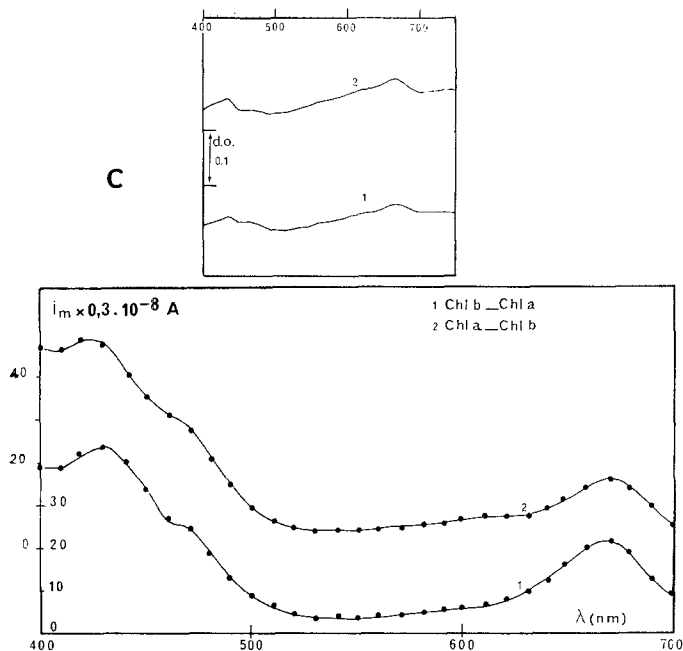


Figure 1. Action spectrum of the maximum short-circuit photocurrent produced by a semitransparent platinum electrode covered with a film of chlorophyll (electrolyte 96% glycerol 4% saturated KCl aqueous solution; reference electrode Ag-AgCl; active surface of electrodes  $6.25 \text{ cm}^2$ ). (A) film = stack of chlorophyll *a* monolayers; absorption spectrum and action spectrum. (B) film = stack of chlorophyll *b* monolayers; absorption spectrum and action spectrum. (C) film = 1: stack of 6 chlorophyll *b* monolayers, 6 chlorophyll *a* monolayers. 2: stack of 6 chlorophyll *a* monolayers, 6 chlorophyll *b* monolayers. Ordinate: maximum photocurrent. Abcissa: wavelength nm;  $I = 1.4 \times 10^{15} \text{ photons cm}^{-2} \text{ sec}^{-1}$ .

These spectra are presented in Fig. 1 for films of Chl *a*, Chl *b* and Chl *a*-Chl *b*. So one can write the maximum photocurrent as  $i_M = a \epsilon(\lambda) I l$ , where  $I$  stands for light intensity,  $\epsilon(\lambda)$  stands for an extinction coefficient,  $a$  is a yield coefficient, and  $l$  corresponds to the thickness of the layer in the range studied here. The phase of appearance of  $I_M$  then is

$$i_t = a \epsilon(\lambda) I l [1 - \exp(-kt)]$$

It is impossible to exclude completely the presence of defects through the film, so we cannot easily choose between an "ionic mechanism" of photocurrent production or an "electronic mechanism". The first one would schematically correspond to reaction of excited chlorophyll molecules with a redox species in solution, the product being later

oxidized or reduced at the platinum electrode where it is not covered by the film. Photocurrent rise is related to kinetics of formation of the electroactive species or to diffusion processes of this species to the metallic electrode.

The second one is more likely charge separation in a barrier region at the electrolyte-pigment interface or at the pigment-metal interface, as other authors [12, 13] have concluded for thicker films.

Some experiments made with lipid-chlorophyll-metal or chlorophyll-lipid-metal show a strong reduction of transients amplitude correlated with faster kinetics: If one assumes the same presence of defects in lipid layers as in chlorophyll layers, the important reduction factor observed for amplitude implies that in the production of photocurrent the two contacts are necessary, i.e., pigment-electrolyte and pigment-metal.

## 2. Conversion Efficiency

As indicated before, different kinds of solid films have been compared on the basis of maximum photocurrent magnitude and action spectra.

For the first case of evaporated films, the action spectrum of maximum photocurrent is identical to the absorption spectrum. The

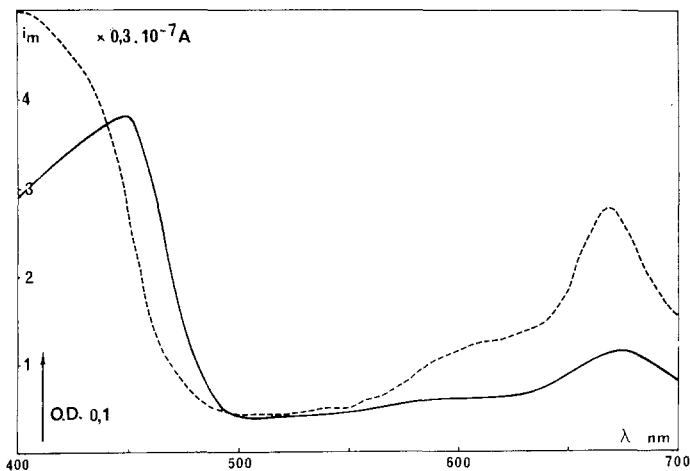


Figure 2. Action spectrum of the maximum short-circuit photocurrent produced by a semitransparent platinum electrode covered with a film of chlorophyll *a* obtained by evaporation of a solution in pentane (electrolyte 96% glycerol 4% saturated aqueous solution; reference electrode Ag-AgCl; active surface of electrodes 6.25 cm<sup>2</sup>). Dashed line: action spectrum; full line: absorption spectrum of the film of pigment. Abcissa: wavelength nm:  $I = 1.4 \times 10^{15}$  photons cm<sup>-2</sup> sec<sup>-1</sup>. Ordinate: optical density and maximum photocurrent  $\times 0.3 \cdot 10^{-7}$  A.

second kind of evaporated film, partly quasicrystalline, shows an action spectrum somewhat different: The blue maximum is located at 430 nm as for amorphous films and not at 450 nm, which is the maximum of absorption for quasicrystalline forms in this region of spectrum (Fig. 2).

So this is an argument in favor of a lower efficiency of crystalline forms of Chl *a* in this kind of system for the energy conversion process giving rise to the short-circuit photocurrent.

Nevertheless, in our conditions of measurement, the more efficient structure is the film of stacked Chl *a* monolayers (Fig. 3). This structure

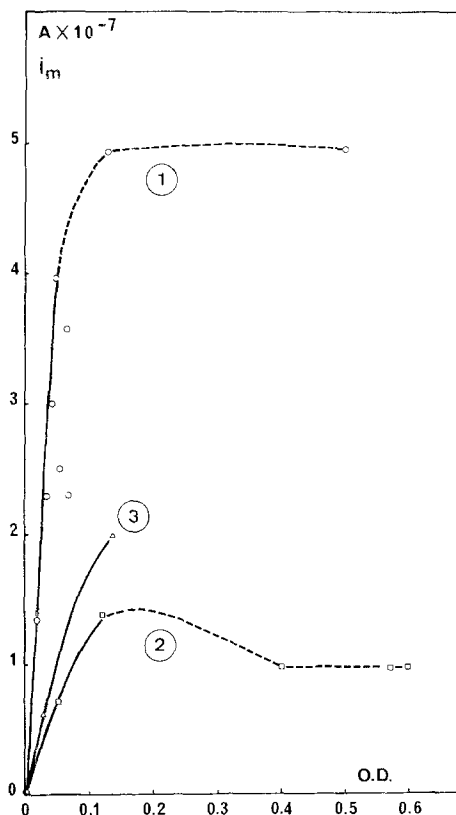


Figure 3. Variation of magnitude of the maximum short-circuit photocurrent produced by a semitransparent platinum electrode covered with a chlorophyll film (under continuous illumination), with increasing film thickness (electrolyte 96% glycerol 4% saturated KCl aqueous solution; reference electrode Ag-AgCl; active surface of electrodes  $6.25 \text{ cm}^2$ ). Wavelength of illumination 440 nm;  $I = 2 \times 10^{15} \text{ photons cm}^{-2} \text{ sec}^{-1}$ . Ordinate: maximum photocurrent:  $\times 10^{-7} \text{ A}$ . Abcissa: optical density at 440 nm. (1) stack of chlorophyll *a* monolayers; (2) evaporated film of chlorophyll *a* from a solution in an organic solvent; (3) stack of chlorophyll *b* monolayers (dashed line indicates variations of measured values).

is at first the "most ordered" one, but different from the crystalline solid state. If a certain order is maintained on the solid substrate, it is essentially an order normal to the plane of the film. In fact, further studies are necessary for deciding if the larger efficiency of stacked monolayers is due either to the absence of aggregates, at least a short time after stacking, like crystalline parts, or to the presence of some aspects of order normal to the plane of the film due to dissymetry of the chlorophyll molecule.

### 3. Mixed films

To get new information on the mechanism of the production of short-circuit photocurrent, we have used two kinds of mixed evaporated films; vitamin K<sub>1</sub> and phytol have been introduced in organic solutions of chlorophyll *a* of constant concentrations. For a valuable comparison,

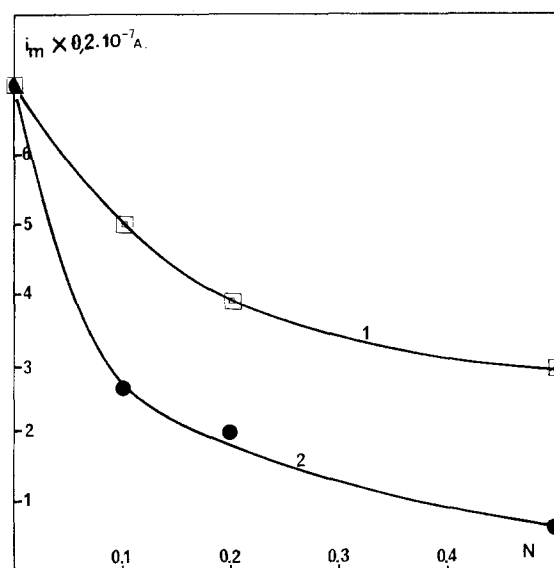


Figure 4. Variation of the maximum short-circuit photocurrent produced by a semitransparent platinum electrode covered with a mixed film of (1) chlorophyll *a*-phytol, (2) chlorophyll *a*-vitamin K<sub>1</sub>; with increasing phytol or vitamin K<sub>1</sub> concentration (electrolyte 96% glycerol 4% saturated KCl aqueous solution; reference electrode Ag-AgCl; active surface of electrodes 6.25 cm<sup>2</sup>). Ordinate: maximum photocurrent. Abscissa: ratio of the number of phytol or vitamin K<sub>1</sub> molecules to the number of chlorophyll *a* molecules for a constant number of chlorophyll *a* molecules. Wavelength of illumination 440 nm;  $I = 2 \cdot 10^{15}$  photons cm<sup>-2</sup>. Film of chlorophyll *a* without phytol or vitamin K<sub>1</sub>; optical density at 440 nm: 0.6.



we have used two criteria: (1) an absorption spectrum characteristic of "amorphous" forms of chlorophyll to control the absence of strongly aggregated forms leading, as seen before, to a reduction of the photocurrent magnitude, and (2) a low value of dark short-circuit current, corresponding to a good covering of the metallic electrode. In that way one excludes a reduction effect by direct contact between electrolyte and metallic electrode.

We conclude that at the same concentration the amplitude of the maximum photocurrent is reduced more efficiently by vitamin K<sub>1</sub> than by phytol (Fig. 4). Studies on monolayers in situ [14-17] at the water-air interface have shown that vitamin K<sub>1</sub> is a quencher of chlorophyll excitation, the presence of phytol imposing only an average distance between chlorophyll molecules. So it appears that vitamin K<sub>1</sub> probably reduces the photocurrent amplitude by quenching of chlorophyll excitations. If the effect of phytol is the same as for monolayers in situ, the reduction effect could be correlated with a reduction of excitation transfer efficiency between chlorophyll molecules, the transfer taking a part in the production of photocurrent.

### *Conclusion*

We have shown that the study of the photoelectrochemical transients of such stacked chlorophyll monolayers can provide useful information for elucidating some mechanisms of light energy conversion by solid structures of such pigment. However, it is necessary to get more information in the case of the "quasicrystalline" layers, which appear less efficient: Authors generally seem to consider that strong interactions between chlorophyll molecules, as in a crystalline state, is in favor of a better yield for light energy conversion [18].

As a model system for conversion in the primary photosynthetic apparatus, evidently we are far from the in vivo structure; but we think that this system has to be considered as a complement for other model studies using, for instance, black lipid membranes.

### *Acknowledgments*

I wish to thank Prof. Dr. J. Lavorel for helpful discussions and Miss B. Peteri for her help in the correction of the manuscript

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