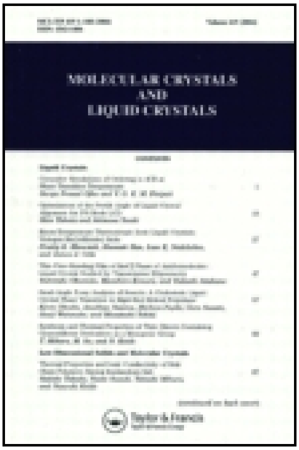

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Light Dependence of the Pigmented Liquid Crystal BLM Capacitance

Zdzislaw Salamon [a] [b] & H. Ti Tien [a]

[a] Biophysics Laboratory, (Giltner Hall), Physiology Department, Michigan State University, East Lansing, MI, 48824, USA

[b] Institute of Physics, Technical Univ. of Poznan, Poland

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Light Dependence of the Pigmented Liquid Crystal BLM Capacitance

ZDZISLAW SALAMON‡ and H. TI TIEN†

Biophysics Laboratory, (Giltner Hall) Physiology Department, Michigan State University, East Lansing, MI 48824 USA

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The light-induced capacitance changes and both photovoltage and photocurrent generated by pigmented liquid crystal bilayer (PBLM) with a fixed surface asymmetry were measured under continuous illumination. It is suggested that the origin of the photoresponses is due to electron injection across the two double layers resulting from the interaction of an excited photosensitizer located in the BLM with the acceptor ions in the solution. The photocurrent across the double layers affects their properties (potential across those layers, a dielectric constant and a concentration of acceptor ions around the double layers) which can be seen in the PBLM capacitance changes.

INTRODUCTION

A number of papers have appeared on the voltage dependence of the bilayer lipid membrane (BLM) capacitance.[1–6] They show that the capacitance of the bilayer can be changed by an external electric field (an applied potential across the membrane.) The experiments with solvent-containing bilayers exhibited a steady state transmembrane potential dependence of the form:

$$[C_{(v)} - C_{(o)}]/C_{(o)} = \gamma(V_o + V)^2 \qquad (1)$$

where C_o is the capacity at zero applied voltage, V is the applied voltage, V_o is the potential across the membrane due to surface charge asymmetry.[6] The coefficient γ depends on the percentage and type of organic solvent and is typically about 10 V^{-2}.[7–11]

[†] To whom all correspondence should be addressed.

[‡] *On leave from the Institute of Physics, Technical Univ. of Poznan (Poland).*

A similar equation describes the voltage dependence of the BLM capacitance for solventless bilayers but with the coefficient reduced by about two and one-half orders of magnitude to about 2×10^{-2} V^{-2}.[11,12]

Many experiments show that the electric field might cause both a compression of black lipid membranes (meaning decrease of thickness – t_m) and the increase of bilayer area (A).[13] Both parameters affected by the electric field are connected with the capacitance of the BLM. Therefore the voltage dependence of the membrane capacitance is generally understood as due to changes in the BLM thickness and area.

A number of laboratories have shown that BLM containing light sensitive pigments (the pigmented BLM – PBLM) exhibit interesting photoelectric effects, namely photovoltage and photocurrent [for reviews see 13–16]. According to the above mentioned experimental data the capacitance of such PBLM systems should also be sensitive on the photovoltage changes. Unfortunately, there is a surprising lack of experimental information on the possible capacitance changes due to the light. To explain observed photoresponses, several models have been proposed but they do not take into account the possibility of the PBLM capacitance changes.[17–19] Some suggestions have been made that the PBLM might change their capacitance upon the light. Mauzerall[15] has mentioned that the photoinjection of charges into an interfacial region of PBLM might cause the capacitance changes of that interfacial part of the membrane. Also Baker *et al.*[20] has indicated that the dyes located inside the membrane can reduce the effective thickness of the bilayer thereby changing its capacitance. One suggestion is that light might cause the changes in the double layers of PBLM which can be seen in the capacitance of the pigmented membrane.[18,21]

The aim of this work was to form a pigmented bilayer lipid membrane (PBLM) with a fixed surface charge asymmetry, then under illumination, measure its photovoltage, photocurrent and capacitance and compare these with those measured in the absence of light. On the basis of these light-induced changes, we propose a model, using a recent theoretical treatment.[21]

MATERIALS AND METHODS

The PBLM forming solution consisted of 7,7,8,8-tetracyanoquinodimethane (TCNQ) which was saturated in a thermotropic liquid crystal, 4′-*n*-octyl-cyanobiphenyl (8CB), and then a solution of *n*-decane and butanol (1:1 v/v) was added to obtain a concentration of 8CB-solvent 1:4 (v/v).[22] BLMs were formed by ejecting a small amount of membrane forming solution with the help of a Hamilton microsyringe over the orifice (~1.5 mm) of a Teflon cup separating two aqueous solutions. The teflon cup was placed in a plexiglass chamber. Calomel electrodes with salt bridges were used for electrical contact. The thinning of the membranes to the black state was observed with a binocular microscope and also by measuring the time-course of membrane capacitance. The aperture of the membrane holder was, prior to the membrane formation, wetted with a lecithin solution.[22] 8CB (BDH Chemicals), and TCNQ (Aldrich) were used without further purification, and 0.1 M KCl was used as the bathing solution.

The electrical parameters (potential (V), current (i) across the membrane, and capacitance (C)) of PBLMs were measured as described previously with a high impedance electrometer (Keithley, Model 610BR), a 417 Keithley picoammeter and a low level capacitance meter (ICE/Electronics, Model I-G). The light intensity was 200 mW/cm^2 from a tungsten projector lamp. A heat filter was inserted between the light source and the sample. The TCNQ, 8CB-PBLM was chosen because we found that in this system we are able to create some potential across the membrane without adding compounds to the bathing solution.

To generate a potential across the membrane a small external potential (~2 mV), between the reference and working electrodes, was applied during the time of membrane formation. This external electric field causes a surface charge asymmetry after the PBLM formation. This asymmetry was usually in the range of 5–15 mV with a negative polarization of the working electrode.

RESULTS

The electrical properties of the TCNQ-BLM are shown in Table I. The addition of dye to pure liquid crystal BLM[22] alters all its parameters (Table I). The most pronounced changes occur in the membrane capacitance. Addition of TCNQ to the cyanobiphenyl liquid crystal membrane increases its high magnitude of capacitance, (which is 5 times higher than that of lecithin BLM—see Table I) about two times. Such a significant change of the high value of dark capacitance indicates that molecules of TCNQ can play an active role in a process of membrane formation. This suggestion has been confirmed by ad-

TABLE I

Electrical properties of the studied pigmented liquid crystal bilayers

Type of Sample	R_m [Ω cm^2]	C_m [μF/cm^2]	BDV [mV]
(8CB)BLM*	10^4	1.0	100
(TCNQ + 8CB)BLM	5×10^4	2.0	200
Lecithin BLM**	10^8	0.35	250

BDV-Breakdown voltage
*from Ref. 22.
**from Ref. 13.

ditional measurements prepared for publication.[23] It is also important to emphasize that those dark membrane properties are independent of the treatment of membrane holder prior to membrane formation.[22,23]

Figure 1 illustrates the typical photoresponses. The kinetics of all three measured parameters show the characteristic biphasic waveforms (an initial fast component followed by a slow one). Such an electrical relaxation of the membrane system was observed with different kinds of dyes and different chemical asymmetry of bathing solutions.[13-16] That biphasic photoresponse waveform was also observed with steady-state light illumination.[16] Both components of the photoresponse depend on light intensity as shown in Figures 2 and 3. The rise time of the fast component, however, cannot be estimated from our experiments.

In order to find out whether the observed capacitance changes are due to photovoltage changes, the voltage dependence of capacitance was also measured (see Figure 4). As can be seen from the curve shown in Figure 4 the obtained capacitance-voltage relationship of our type of PBLM is different in comparison with the usually reported pure BLM systems. Comparing the results from Figures 1C and 4 one can also see that capacitance changes due to light can not be simply correlated with the photovoltage changes. It is because the external voltage applied across the membrane always causes a decrease of the initial capacitance (Figure 4) whereas in photocapacitance changes we have observed an initial increase of the dark capacity of the PBLM (Figures 1C and 3).

DISCUSSION

There are two ways of treating PBLM: (i) it is assumed that a pigmented bilayer behaves as an organic semiconductor,[16,19] and (ii)

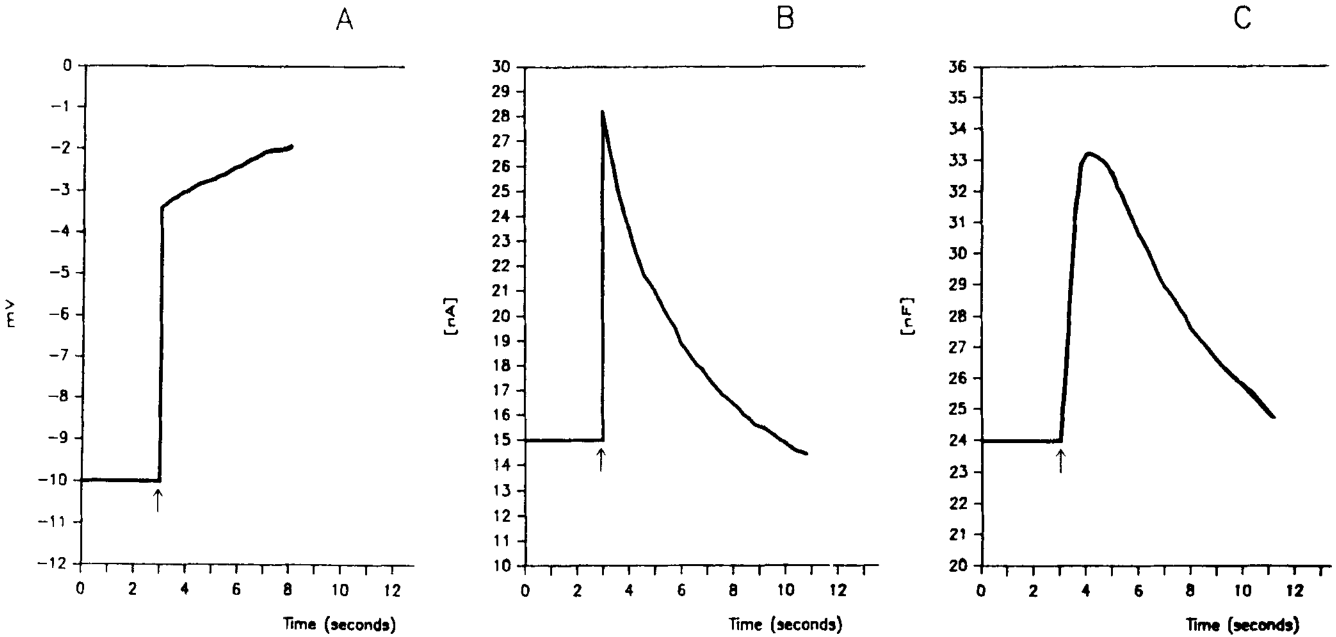

FIGURE 1 Time course of the photovoltage (A), photocurrent at the external voltage U_{ext} = 50 mV (B) and photocapacitance (C) under continuous illumination with white light (200 mW/cm^2) for 8CB-BLM containing TCNQ. Arrows indicate light on.

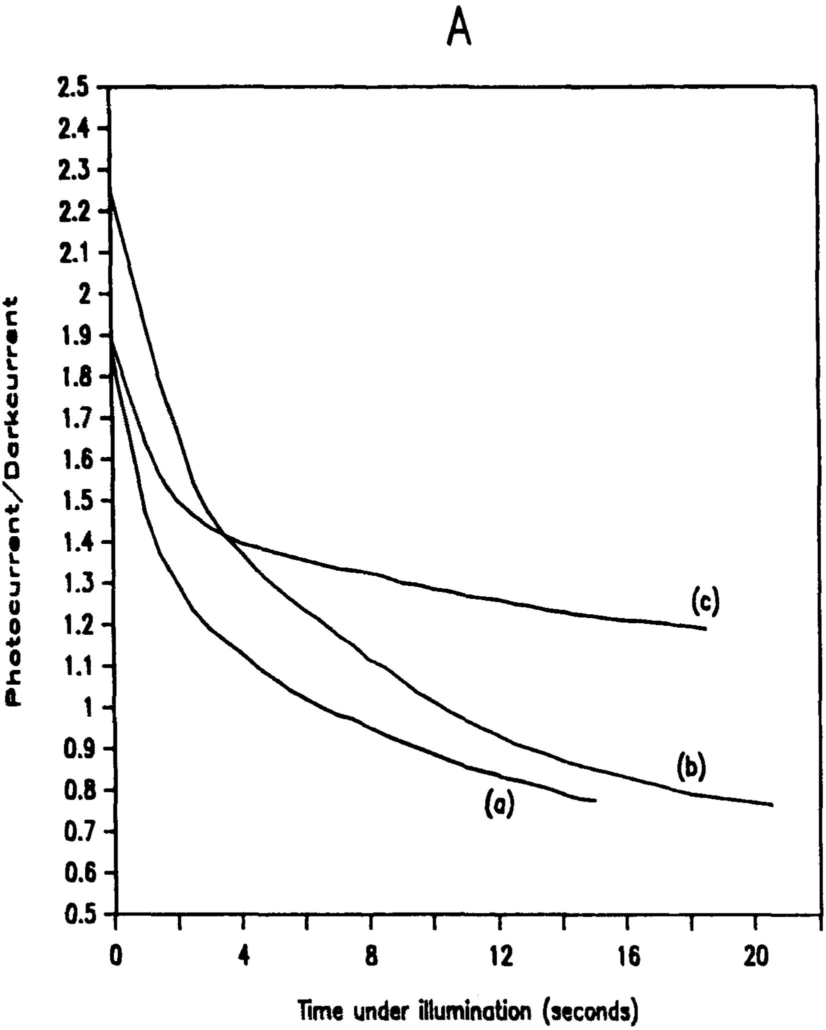

FIGURE 2 A. The light intensity dependence of the photocurrent at U_{ext} = 50 mV of TCNQ-BLM. Intensity of light: (a) 200 mW/cm^2 (b) 170 mW/cm^2 (c) 80 mW/cm^2. B. The light intensity dependence of the initial photocurrent transient ($i_{(t=0)}$).

there is a number of experimental results indicating that the PBLM can be described by two double layers connected by an ionic current.[14] If the first case is granted, the observed photoelectric effects of PBLM are easily explained in terms of the band theory of semiconductors,[6,24] with particular reference to the charge functions betwen metals (in experiments as ionic solutions) and semiconductors (PBLM). The

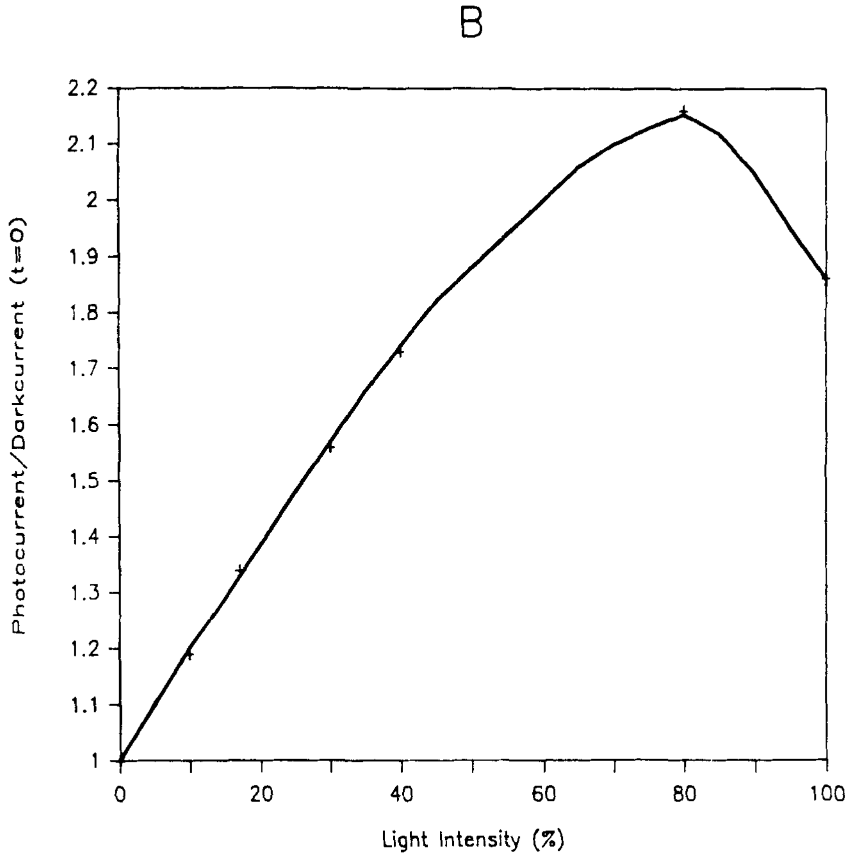

FIGURE 2 (*continued*)

second scheme is based on a macroscopic molecular model and the Gouy-Chapman double layer theory. In such a model the PBLM system involves two interfacial photoreactions coupled by transmembrane diffusion of pigment molecules (ionic current).[17]

In this report we propose to combine these two descriptions into one model. Such a model is based on an analytical expression for the photocurrent as a function of the physical properties of a semiconductor and the neighboring electrolyte solution.[16,21] We assume that PBLM represents a kind of semiconductor with two semiconductor-solution interfaces.[16,24] This assumption in our particular PBLM system is based on the following facts: (1) TCNQ is well known as an organic metal material (for review see Ref. 25), and (2) in TCNQ-BLM system, as has been already shown,[26] transmembrane move-

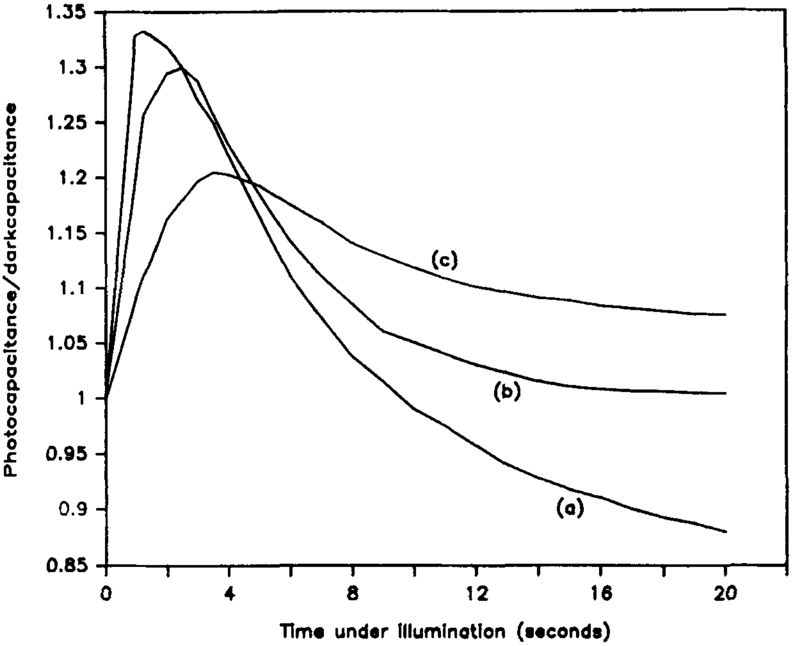

FIGURE 3 The light intensity dependence of the time course of the TCNQ-BLM photo-capacitance. Intensity of light: (a) 200 mW/cm^2, (b) 40 mW/cm^2 (c) 17 mW/cm^2.

ment of electrons via the TCNQ molecules takes place and the whole system has the properties of a typical semiconductor. Therefore, assuming a p-type of semiconductor and a surface charge asymmetry, the following schematic picture of the semiconductor-solution interfaces can be seen in Figure 5. Photoelectrochemical transfer of charges at the semiconductor-solution interface involves transition through the interfacial barrier to acceptor ions in solution. This model consists of the main physical properties of the PBLM membrane with two interfaces and can be visualized by the two following equivalent circuits (see Figure 6): The first describes the electrical parameters of the pure BLM system which contains a capacitor C_m connected parallel with a resistor R_m. The second equivalent circuit describes the changes which are introduced by the pigment molecules. Generally, this second one can also contain a capacitor (C_{p1}, C_{p2}) connected parallel with resistor (R_p) but also a difference of potential (V) which is the result of the surface charge asymmetry. A physical understanding of those parameters is as follows: C_m is composed from three capacitors (two double layer capacitors and a geometrical capacitor

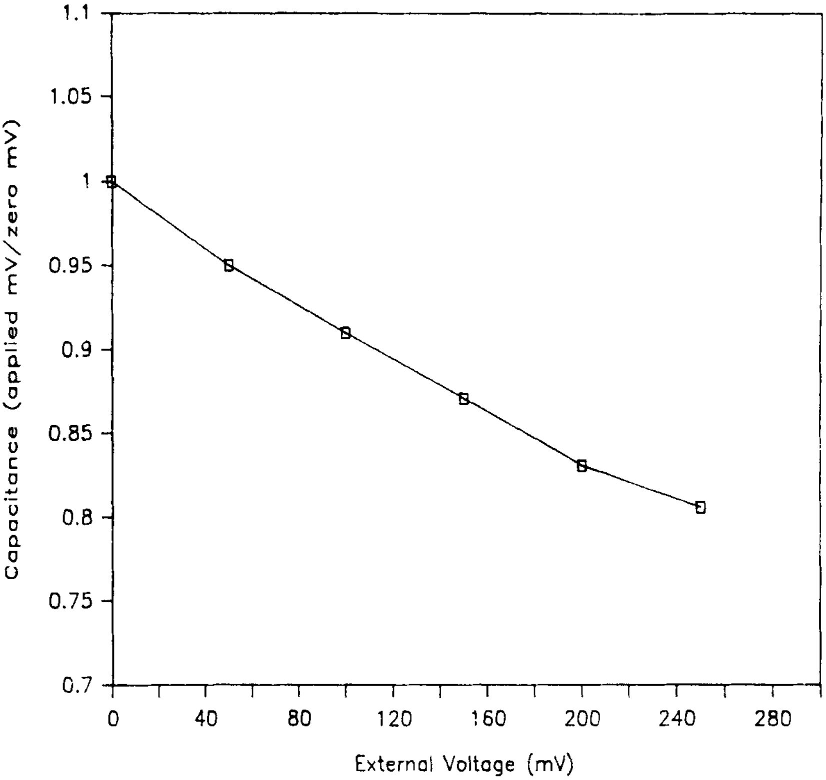

FIGURE 4 The voltage dependence of TCNQ-BLM capacitance.

of the membrane) connected in series. R_m describes a dark membrane conductivity (usually understood as an ionic conductivity). C_{p1} and C_{p2} describe the changes of C_m by introducing the pigment molecules. Pigment can change the membrane capacitance mainly by changing the parameters of two double layers.

A similar electrical circuit model for the PBLM has been proposed by Hong and Mauzerall[14,15] on the basis of short laser pulse measurements. They introduced the capacitor, C_p, as a chemical capacitor. On the basis of the PBLM model sketched in Figure 5 one can estimate the photovoltage and photocurrent changes. In such an asymmetric model the potential across the membrane (V) is as follows:

$$V_{(t)} = [(V_{2H} + V_{2S}) - (V_{1H} + V_{1S})]_t \qquad (2)$$

where t is time of the sample illumination. The light which is absorbed by the pigment molecules of the PBLM membrane causes its discharge

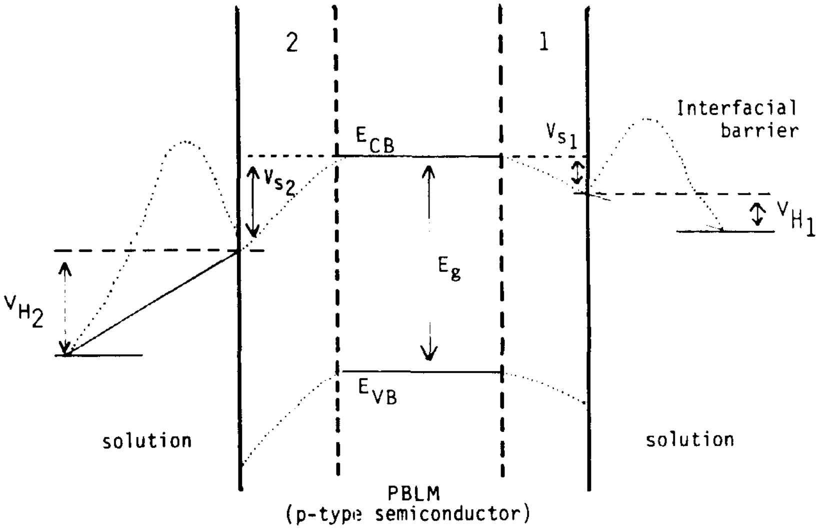

FIGURE 5 Schematic representation of the PBLM model with two solution interfaces. In the semiconductor side E_{VB}, E_{CB}, E_g represent the energy at the top of the valence band, the energy at the bottom of the conduction band, and the band gap energy, respectively. V_s represents the potential drop inside the semiconductor. In the solution side of the interface V_H represents potential drop in the Helmholtz layer.

($V_{(t)}$ drops to zero: $V_{(t=\infty)} = 0$), it means a new equilibrium state is reached in which: $(V'_{2H} + V'_{2S}) = (V'_{1H} + V'_{1S})$. A time course of the across membrane voltage ($V_{(t)}$) depends on the rate of membrane discharge. The rate of this discharge is measured by the photocurrent:

$$i_{ph(t)} = (dQ/dt)_t \tag{3}$$

where Q means a charge asymmetry of two surfaces of PBLM, and

$$i_{ph(t)} = [i_{1ph(t)} - i_{2ph(t)}] + i_{p\ ph(t)} \tag{4}$$

where: $i_{1ph(t)}$ and $i_{2ph(t)}$ represent the movement of electrons across the two double layers, and $i_{p\ ph(t)}$ is an ionic current due to movement of pigment ions across the membrane. The electronic photocurrent through the double layers can be expressed in terms of electronic charge (e_o), charge-transfer rate constant (k_{CT}), and the density of photoexcited electrons at the surface of the semiconductor (n) and can be expressed as follows:

$$i_{1ph(t)} = e_o n_{1(t)}{}^{k_{1CT}};\ i_{2ph} = e_o n_{2(t)}{}^{k_{2CT}} \tag{5}$$

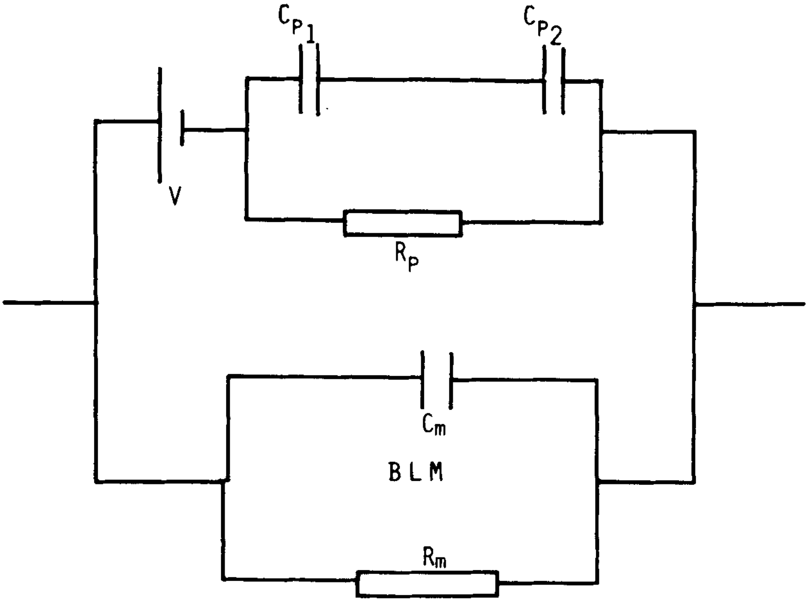

FIGURE 6 Proposed model of equivalent circuit. V is the membrane potential. R_m and C_m are the ordinary membrane resistance and capacitance, respectively. R_p and C_{p1}, C_{p2} are the resistance and capacitances introduced by a dye incorporated into the membrane.

The ionic current can be expressed as:

$$i_{p\ ph(t)} = e_o[n_{1p(t)} - n_{2p(t)}]\mu_p F \tag{6}$$

where: $n_{1p(t)}$, $n_{2p(t)}$ describe the pigment ionic density at two surfaces of the PBLM, μ_p is the diffusion coefficient constant of pigment ions, and F is the intensity of the electric field across the membrane. To obtain a final analytical expression for the photocurrent one should have an explicit function of $n_{(t)}$. This function can be evaluated by solving the basic transport equations in semiconductors (for details see the recent treatment done by Khan and Bockris).[21] From such treatment it can be seen that $n_{(t)}$ depends on time and linearly on the light intensity. In our case, at the beginning of light processes, for $t = 0$, the electronic current $(i_{1ph} - i_{2ph})$ has its maximum value. Figure 2B shows the linear dependence of the initial value of photocurrent on the intensity of light under low light intensities. For the higher light intensities dropping of $(n_{1(t)}k_{1CT(t)} - n_{2(t)}k_{2CT(t)})$ value is fast enough (in comparison to time resolution of our experimental setup) and we are not able to register the true initial value of the

$i_{ph}(t = 0)$. In such cases the initial value of photocurrent can be even smaller than that of the low light one. This is clearly seen in Figure 2.

The photocurrent flow through both double layers changes all physical properties of those membrane regions. On the other hand it is known from interfacial electrochemistry[27] that the capacity of a double layer depends on many factors, between them, on: (a) potential across that layer, (b) a dielectric constant, and (c) a concentration of solvent ions around the double layer. We believe that all three parameters can be changed by light causing the changes of the double layer capacitance of the PBLM (C_{p1}, C_{p2} in Figure 5). Such indication supports the suggestion made by Mauzerall.[15] He has mentioned that photoinjection of charge into the interfacial regions might cause the capacitance changes of those interfacial parts of the membrane.

In conclusion, it has been shown, for the first time, that there is a BLM system which reacts to the light changing its main electrical parameters (i, V, C). It should also be pointed out that this particular system described in this report might be especially useful not only in future scientific experimental study of photoelectronic processes and factors that control overall quantum yield of all kinds of photoelectrochanges, but also such a system might greatly help an experimental approach towards the application of the BLM systems in the area of biomolecular electronic devices.

Acknowledgments

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