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PHOTOELECTRIC EFFECTS IN BIMOLECULAR LIPID-DYE MEMBRANES

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SUMMARY

A cyanine dye is adsorbed to one side of a bimolecular lipid membrane. At a dye concentration of $5 \cdot 10^{-6}$ M there is one dye molecule per (200 Å)^2 of the membrane. Photoelectric effects are measured upon flashlight and continuous illumination. The various effects can be explained quantitatively by the following model: after excitation, within $2 \cdot 10^{-3}$ s every excited dye molecule (A*) accepts an electron from a donor (E) in the electrolyte solution of that side ($EA^* \rightarrow E^+A^-$). The recombination process $E^+A^- \rightarrow EA$ has a time constant of 10^{-1} s. The dipoles E^+A^-, by polarizing the electrolyte, produce a charging of the membrane capacity. At sufficiently long times of exposure the charge is compensated across the membrane resistance with the time constant $R_M C_M$.

In recent years several authors have studied photoeffects in monolayer assemblies[1,2] and bimolecular lipid membranes[3-11]. These investigations were stimulated by their possible relevance to the primary processes in photosynthesis of plants and vision of animals. Tien[3,4] has studied photoelectric effects at membranes made from a mixture of photosynthetic pigments, the signs being dependent on the direction of illumination. We have obtained asymmetric membranes by adsorbing dyes to one side of a bimolecular lipid membrane and found photovoltages at such membranes with the sign independent of the side from which the membrane is illuminated[6]. These investigations[6] have been extended by Tien and Verma[9] and Verma[10], who used an oxidized cholesterol membrane instead of a lecithin membrane and methylorange, rhodamine B and other dyes instead of an oxacyanine dye. Tien and Verma[9] studied photoelectric effects at membranes made from photosynthetic pigments and redox systems, and Trissl and Läuger[11] investigated membranes made from a mixture of chlorophyll *a* and dioleoyllecithin, which were made asymmetric by a redox system. It has been mentioned in ref. 6 that the photovoltages studied there may be interpreted quantitatively by a simple model, which will be further discussed below.

(1) *Experimental*

The experimental set up is shown schematically in Fig. 1. The apparatus consists of a glass cell, with a Teflon cell fixed inside. In the Teflon cell there is a hole of 1.7 mm diameter, in which the black lipid membrane is formed. Glass cell and Teflon cell are filled with an electrolyte (10^{-2} M solution of NaCl in bidistilled water).

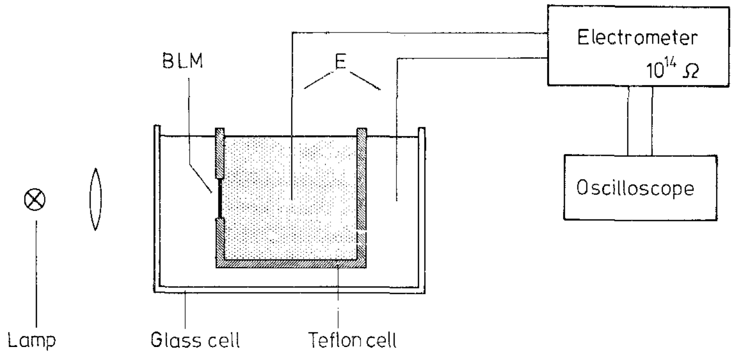
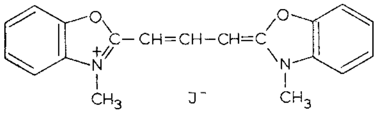


Fig. 1. Schematic representation of the experimental set up. The apparatus consists of a Teflon cell fixed in a glass cell. Both are filled with an aqueous solution of NaCl (10^{-2} M). The black lipid membrane (BLM) is in a small hole in the Teflon cell. To the electrolyte in the Teflon cell a small amount of a solution of Dye 1 is added. The saturated calomel electrodes E are connected *via* an amplifier (Keithley 610 c) to an oscilloscope. The black lipid membrane is illuminated with a 50-W halogen–tungsten lamp or a flashlight.

A saturated calomel electrode is immersed into the inner and the outer cell connected *via* an electrometer (Keithley 610 c, input resistance at voltage measurement $10^{14}\ \Omega$) to a recorder or an oscilloscope. The bimolecular lipid membranes are made from a saturated solution of egg lecithin (chromatographically pure from Koch–Light Laboratories) in *n*-octane by the method of Mueller and coworkers[12–14]. At one side of the bimolecular lipid membrane a solution of Dye 1 is added to the electrolyte so that it is for example 10^{-6} M with respect to the dye.

Dye 1



To illuminate the bimolecular lipid membrane light of a 50-W halogen–tungsten lamp is used and a flash of $0.4 \cdot 10^{-3}$ s half-width (flash arrangement, Braun "Hobby") and one of $3 \cdot 10^{-6}$ s half-width (own construction). The action spectrum is determined with light filtered by interference filters with a half-width of 20 nm. For all other measurements a colored glass filter (BG 18 from Schott and Gen.) is used.

(2) *Flash induced photovoltage*

1 or 2 min after addition of the dye solution voltage pulses appear upon flashlight illumination*. They gradually become higher until they reach a constant value after about 1 min. This indicates that the dye is slowly inserted into the bimolecular lipid membrane. The final constant value of the pulses suggests that the dye remains at one side of the bimolecular lipid membrane, *i.e.* no noticeable diffusion across the membrane takes place. In the following all voltages refer to the electrode immersed in the solution without dye. In Fig. 2 the voltage change ΔU at flashlight illumination is plotted against time t. Rise and drop of the voltage change can be expressed by:

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*The development of a dark potential when adding the dye solution to the solution in the cell, as described in ref. 6, is not observed, when both solutions have the same ionic strength.

$$\Delta U = \text{const.}\cdot(1 - e^{-t/\tau_1})\cdot e^{-t/\tau_2},$$

where the time constants are $\tau_1 = 2$ ms and $\tau_2 = 100$ ms. With light of various wavelengths the maximum photovoltage $\Delta U_{\max}$ and the energy at each flash falling onto the bimolecular lipid membrane, E, is measured. When $\Delta U_{\max}/E$ is plotted against wavelength λ of incident light an action spectrum (Fig. 3, circles) is obtained, which is in good agreement with the absorption spectrum of the dye in aqueous solution (with 10^{-2} M NaCl) (Fig. 3, full curve). From this it can be concluded that the generation of photovoltage is due to the excitation of the dye.

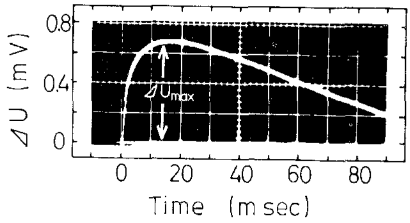


Fig. 2. Time dependence of change of voltage ΔU upon flashlight illumination of the membrane (half-width of flashlight 0.4 msec). $\Delta U_{\max}$ (maximum voltage change) in 15 ms.

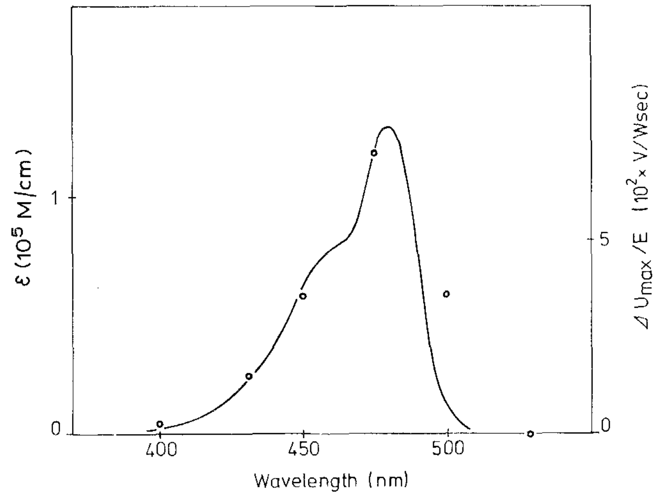


Fig. 3. Absorption spectrum of Dye 1 in 10^{-2} M aqueous solution of NaCl (full curve; absorption coefficient ε *vs* wavelength λ) and action spectrum (circles; $\Delta U_{\max}/E$ *vs* λ, $\Delta U_{\max}$ is the maximum voltage change after flash illumination, E the energy falling at each flash onto the bimolecular lipid membrane).

(3) *Photovoltages at continuous illumination*

In Fig. 4 the time dependence of the voltage U is shown at exposures of 1/125 s up to 4 s. When the light is turned on the voltage rises sharply, reaching its maximum value after 0.3 s, and returning slowly to zero. At exposures of more than 0.3 s the maximum voltage change $\Delta U_{\max}$ is constant (value S). At exposures shorter than 0.3 s, $\Delta U_{\max}$ is proportional to the time of exposure initially and then approaches the final value S. When the light is turned off a deflection $\Delta U_{\min}$ to the opposite

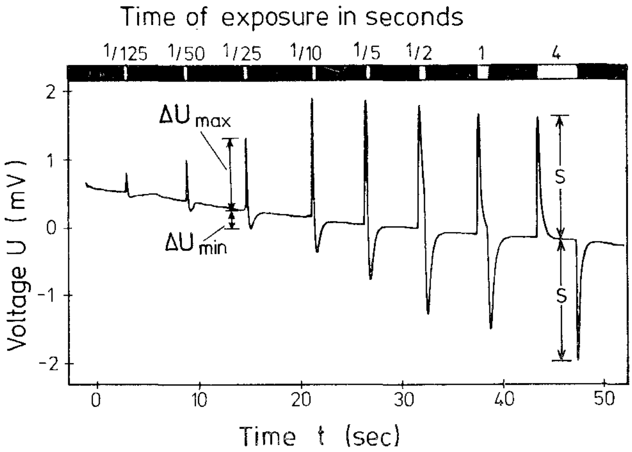


Fig. 4. Time dependence of voltage U at exposures of 1/125 s up to 4 s. S = Maximum value of ΔU_{max} at long duration of exposure.

side is obtained. First $-\Delta U_{min}$ is proportional to the time of exposure and then goes towards the final value $-\Delta U_{min} = S$, the same as the final value of ΔU_{max}.

(4) *Model*

To explain the experimental results discussed in Sections 2 and 3 the following model is proposed. To one side of the bimolecular lipid membrane Dye 1 is adsorbed. When a dye molecule is excited ($A \rightarrow A^*$) it can accept an electron from a Donor E in the electrolyte: $EA^* \rightarrow E^+A^-$ (Fig. 5: transition a → b; Fig. 6: transition a′ → b′). The dipole E^+A^- immediately (*i.e.* in about 10^{-6} s) attracts charges from the electrolyte on both sides of the bimolecular lipid membrane (Fig. 5: transition b → c;

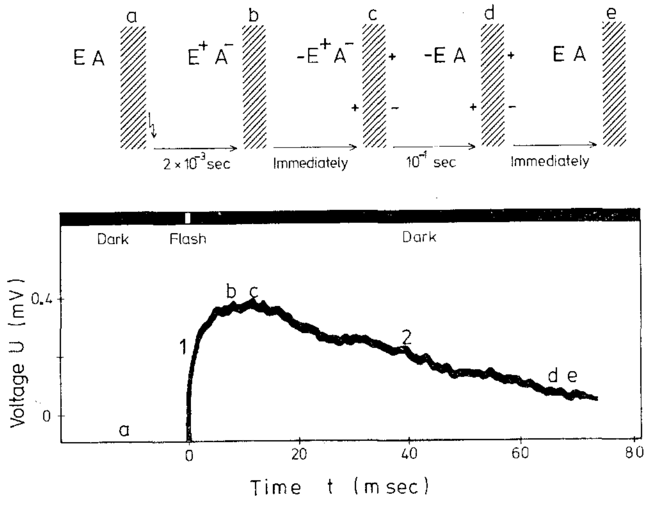


Fig. 5. Model for generation of photovoltage ΔU by flashlight illumination (E = donor, A = dye). a→b: dipole generation ($EA \rightarrow E^+A^-$); $\tau_1 = 2 \cdot 10^{-3}$ s; b→c: polarisation of the electrolyte; c→d: dipoles recombination ($E^+A^- \rightarrow EA$); $\tau_2 = 10^{-1}$ s; d→e: depolarisation of the electrolyte.

Fig. 6: transition b′ → c′). Free positive and negative charges remain and load the capacity formed by the membrane (Fig. 5: voltage rise 1; Fig. 6: voltage rise 1′).

At flashlight illumination the charge returns from Dye A to Donor E in about 10^{-1} s: $E^+A^- \rightarrow EA$ (Fig. 5: transition c → d, voltage decay 2) and the polarisation of the electrolyte disappears immediately (Fig. 5: transition d → e).

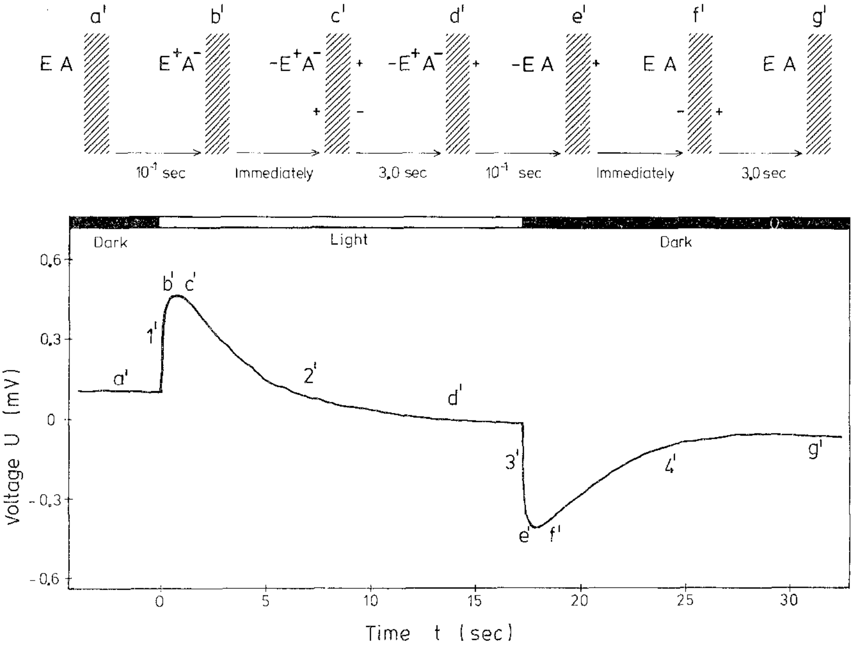


Fig. 6. Model for generation of the photovoltage ΔU by continuous illumination. a′→b′: dipole generation ($EA \rightarrow E^+A^-$, $\tau_1' = 10^{-1}$ s); b′→c′: polarisation of the electrolyte; c′→d′: charge compensation across the bimolecular lipid membrane ($\tau_2' = R_M C_M$); d′→e′: dipole recombination ($E^+A^- \rightarrow EA$; $\tau_3' = 10^{-1}$ s); e′→f′: depolarisation of the electrolyte; f′→g′: charge compensation across the bimolecular lipid membrane ($\tau_4' = R_M C_M$).

At continuous illumination the free charges at the membrane compensate across the membrane (Fig. 6: transition c′ → d′, voltage decay 2′). Turning off the continuous light the dye molecule and the donor recombine and are not excited again (Fig. 6: transition d′ → e′). The charge bound to the dipole is freed immediately (Fig. 6: transition e′ → f′, voltage decay 3′) and compensate across the membrane (Fig. 6: transition f′ → g′, voltage rise 4′).

At continuous illumination (Fig. 6) the time constant of the voltage decay 2′ (τ_2') and of the voltage rise 4′ (τ_4') are determined by the time the charge needs to compensate across the membrane. Independent from the resistance of the respective membrane τ_2' is equal to τ_4'. They are also equal to $\tau_M = R_M \cdot C_M$, where R_M is the membrane resistance and C_M is the membrane capacity. In the example of Fig. 6 the experimental values are $R_M = 6.2 \cdot 10^8\ \Omega$, $C_M = 6.0 \cdot 10^{-9}$ F (membrane area $F_M = 2.0 \cdot 10^{-2}$ cm^2); hence $\tau_2' = \tau_4' = R_M C_M = 3.7$ s. In good agreement with this value in Fig. 6 there is $\tau_2' = \tau_4' = 3.0$ s.

The voltage drop 2 after flashlight illumination (Fig. 5) and the voltage drop

3′ after continuous illumination (Fig. 6) are determined by the time constant τ_r of the recombination ($E^+A^- \rightarrow EA$). τ_r also determines the voltage increase 1′ at continuous illumination: When the continuous illumination is turned on, the number n of the dipoles E^+A^- is given by:

$$\frac{dn}{dt} = B(n_0 - n)I - \frac{1}{\tau_r} \cdot n \tag{2}$$

where B is a constant, I is the intensity of the light falling onto the membrane, n_0 is the total number of dye molecules adsorbed to the membrane. Therefore $n_0 - n$ is the number of dye molecules at the time t in the ground state (the number of the excited dye molecules A^* is neglected as compared to the number of molecules A and A^-). At sufficiently low intensities ($n \ll n_0$):

$$n = n_{\max} \cdot (1 - e^{-t/\tau_r}) \tag{3}$$

with

$$n_{\max} = I \cdot B \cdot \tau_r \cdot n_0.$$

As expected the measured time constants τ_2, τ_3' and τ_1' of Figs 5 and 6 agree with each other. They are 10^{-1} s and thus τ_r is 10^{-1} s.

The voltage rise at flashlight illumination (time constant τ_1) is determined by the rate of charge transfer from a donor to a dye molecule ($EA^* \rightarrow E^+A^-$) and by the rate of deactivation of the dye molecules ($A^* \rightarrow A$), *i.e.*

$$1/\tau_1 = 1/\tau_{A^* \rightarrow A} + 1/\tau_{EA^* \rightarrow E^+A^-}$$

The obtained relations between the time constants are summarized in Table I.

TABLE I

VALUES OF THE TIME CONSTANT OF RECOMBINATION (τ_r) AND OF CHARGE COMPENSATION ACROSS THE MEMBRANE (τ_M) OBTAINED FROM EXPERIMENT BY USING THE RELATION GIVEN IN BRACKETS

Time constant $\tau_r \times 10$ (s)	*Time constant τ_M (s) (for the example of Fig. 6)*
0.9 ± 0.3 ($\tau_r = \tau_2$)	3.0 ($\tau_M = \tau_2'$)
1.0 ± 0.3 ($\tau_r = \tau_1'$)	3.0 ($\tau_M = \tau_4'$)
1.0 ± 0.4 ($\tau_r = \tau_3'$)	3.7 ($\tau_M = R_M \cdot C_M$)
0.6 ± 0.1 (Eqn 4)	
0.7 ± 0.1 (Eqn 8)	

In state f′ the charge on the membrane capacity is the same as in state c′, but has opposite sign, and it is evident that $-\Delta U_{\min}$ has to be equal to $+\Delta U_{\max}$ and to S. The model is confirmed by the experimental result (Fig. 4). The same voltage change must occur if the illuminating light is turned off at a time t, when the charge is not yet fully compensated across the membrane (*i.e.* in the interval between c′ and d′ (voltage ΔU_t)). Thus $\Delta U_{\min} = \Delta U_t - S$. This too is confirmed by the experiment (Fig. 4).

When the light is shut off before the maximum of the voltage change is reached, the charge on the capacitance C_M is smaller by the ratio $n/n_{\max}$. (The voltage decay by discharging C_M over R_M can be neglected because $\tau_M \gg \tau_r$.) Thus $\Delta U_{max} = n/n_{max} \cdot S$. Using Eqn 3 we find for sufficiently short times of exposure ($t_e \ll \tau_r$)

$$\Delta U_{max} = \frac{t_e}{\tau_r} \cdot S \tag{4}$$

In this case ΔU_{max} is proportional to the time of exposure t_e in agreement with the experimental finding (Fig. 4), and the value $\tau_r = 0.6 \cdot 10^{-1}$ s is obtained from Fig. 4 and Eqn 4. This value agrees with the value estimated above:

$$\tau_r = \tau_2 = \tau_3' = \tau_1' = 10^{-1}\,\mathrm{s}$$

At times of exposure shorter than τ_r the minimum voltage change ΔU_{min} is determined by the discharge of the membrane capacity during exposure, and after exposure as long as $\Delta U > 0$. We consider the process at short times of exposure ($t_e \ll \tau_r$). The charge flowing across R_M during the exposure is in this case small as compared to the charge flowing across R_M after exposure. At the end of exposure the whole charge $q_{max} = C_M \cdot \Delta U_{max} = C_M \cdot S \cdot t_e/\tau_r$ is assumed to be at the membrane capacity. It decreases partly by the disappearance of the dipoles E^+A^- with the time constant τ_r, partly by the current $J = \Delta U/R_M$ flowing across the membrane resistance. Without the second component we would have

$$Q = Q_{max} \cdot e^{-t/\tau_r} \text{ or } \frac{dQ}{dt} = -Q_{max} \cdot \frac{1}{\tau_r} e^{-t/\tau_r}$$

where t is the time after turning off the light. With the second part we obtain:

$$\frac{dQ}{dt} = C_M \cdot \frac{d\Delta U}{dt} = -\frac{Q_{max}}{\tau_r} e^{-t/\tau_r} - \frac{\Delta U}{R_M} \tag{5}$$

and therefore:

$$\Delta U = \frac{S \cdot t_e}{1 - \tau_r/\tau_M} \left[\frac{1}{\tau_r} e^{-t/\tau_r} - \frac{1}{\tau_M} e^{-t/\tau_M} \right]. \tag{6}$$

ΔU_{min} is reached at:

$$t_{min} = \frac{2 \ln (\tau_M/\tau_r)}{(1/\tau_r) - (1/\tau_M)}. \tag{7}$$

With the above value $\tau_r = 0.6 \cdot 10^{-1}$ s and the $\tau_M = 0.5$ s taken from Fig. 4 the value $t_{min} = 0.35$ s is obtained and by introducing in Eqn 6 follows:

$$\frac{\Delta U_{min}}{S} = -1.1 \cdot t_e \cdot s^{-1}.$$

$\Delta U_{min}/S$ is indeed proportional to the time of exposure, t_e for the case $t_e \ll \tau_r$ (Fig. 4). The measurements show a broad scatter in the values of the proportionality constant and are found between 0.5 and 5 s^{-1}, and for t_{min} values between 0.3 and 0.6 s are measured in fair agreement with the theoretical result. All details of the behaviour at continuous illumination can be simulated by a system with equivalent circuit (Fig. 7).

(5) *Lifetime of the dipoles* E^+A^- *from the intensity dependence of* $\Delta U_{\max}$

In Fig. 8 the dependence of the maximum voltage change $\Delta U_{\max}$ at continuous illumination is shown as a function of the intensity I falling onto the bimolecular lipid membranes. $\Delta U_{\max}$ increases proportional to the intensity and then changes into saturation. According to the described model the maximum voltage change at C_M

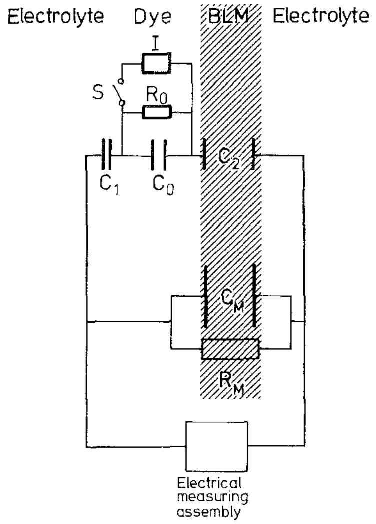
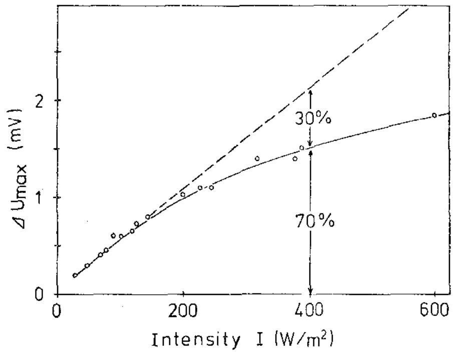


Fig. 7. Circuit reproducing the properties of voltage change at continuous illumination of bimolecular lipid membranes (BLM). Dipole generation is substituted by opening switch S at the current source I and loading the capacitance C_0. Resistance R_0 and capacitance C_0 are given by the relation $\tau_r = C_0R_0$. The electrolyte is regarded as a conductor. The polarisation of the electrolyte by the dipoles is substituted by loading the capacitors C_1 (electrolyte on the left side) and C_2 (electrolyte on the right side). C_1 is large as compared to C_2 and can be neglected. The membrane is substituted by capacity C_M and the resistance R_M which are connected to the electrical measuring assembly.



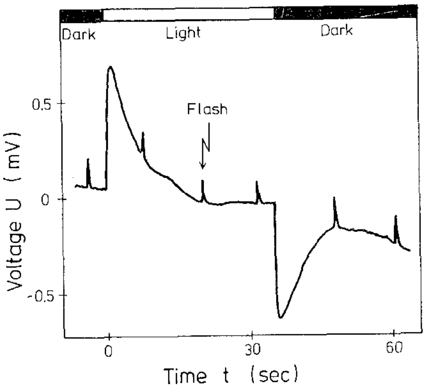


Fig. 8. Continuous illumination. Maximum voltage change $\Delta U_{\max}$ *vs* intensity I of bimolecular lipid membrane illumination (full curve). The experimental value at $I = 400$ W/m^2 is 30% below the broken line: 30% of the dye molecules are in the form E^+A^-.

Fig. 9. Flashlight illumination superimposed on continuous illumination (intensity $I = 400$ W/m^2; *i.e.* 1 quantum in 0.24 s is absorbed by a dye molecule). The maximum voltage change $\Delta U_{\max}$ generated by a flash is only 77% during continuous illumination. 23% of all dye molecules are in the form E^+A^-. The average lifetime of the excited form is $0.24\ \text{s} \cdot 0.23/(1-0.23) = 0.7 \cdot 10^{-1}$ s.

is proportional to the number of dipoles E^+A^-, which is proportional to the intensity at low intensities. At high intensities all the dye molecules are in the form E^+A^-. As shown in Fig. 8 the experimental values are 30 % below the broken line at an intensity of 400 W/m^2 (with colored glass filter BG 18). Thus we find that 30 % of all the adsorbed dye molecules at the membrane are in the excited form.

Another method to determine the number of dipoles E^+A^- is to superimpose flashlight on continuous illumination. As can be seen from Fig. 9, the voltage pulses upon flash become smaller, when the continuous light is turned on, they have a constant height during the illumination and grow to their old height after turning off the constant light source. *E.g.* at continuous illumination with 400 W/m^2 (with colored glass filter BG 18) $\Delta U_{\max}$ decreases by 23 ± 2 % as compared to the value obtained without continuous illumination (Fig. 9). The continuous illumination causes 23 % of the dye molecules to be in the excited form, and they are not available to flash excitation. This value is in good agreement with the 30 % obtained from the intensity dependence of ΔU. From this the lifetime of the excited form can be calculated. At an intensity I_0 each dye molecule absorbs the power $W_{\text{molecule}} = I_0 \cdot \varepsilon / N_L$, where ε is the absorption coefficient of the dye and N_L is Avogadro's constant. The average absorption coefficient of Dye 1 in the range of the colored glass filter (BG 18) is $\varepsilon = 0.25 \cdot 10^5$ M^{-1} cm^{-1}. With the given intensity of continuous illumination (I = 400 W/m^2) $W_{\text{molecule}} = 1.7 \cdot 10^{-18}$ W, *i.e.* each non-excited dye molecule absorbs a quantum of light after an average time of $t_a = 0.24$ s. Since we know from the above that 77 % of the dye molecules are in the non-excited form, we may conclude that the average lifetime of the excited form is $\tau_a = 7 \cdot 10^{-2}$ s: In the photo-stationary state the relation between the number of dye molecules n_g and n_a in the ground state and in the excited form, respectively, is $n_g(1/t_a) = n_a \cdot (1/\tau_a)$ and thus:

$$\tau_a = t_a \cdot \frac{\varphi}{1 - \varphi}, \tag{8}$$

where $\varphi = n_a/(n_g + n_a)$ is 0.23, hence $\tau_a = 7 \cdot 10^{-2}$ s. At other intensities of illumination this consideration leads to the same result. The value of τ_a agrees with the value τ_r for the lifetime of the excited form E^+A^-. This result confirms the assumption that the excited form is represented by E^+A^- and that nearly every molecule changes into this form after having captured a light quantum. To demonstrate this let us assume that only every tenth dye molecule, after excitation, is transferred to the excited form discussed above. Then the observed diminution in the number of unchanged dye molecules at continuous illumination can only be interpreted by assuming a 10-fold increase of the lifetime of the excited form. τ_a being ten times larger then τ_r (lifetime of the form E^+A^-), the form E^+A^- can only constitute a negligible part of the excited form. In this interpretation the above agreement of τ_r and τ_a appears purely accidental.

(6) *Density of the dipoles E^+A^-*

The maximum number of charge carriers on the membrane can be calculated from the capacity C_M and the maximum voltage change at illumination $\Delta U_{\max}$. When illuminating with 400 W/m^2 the charge Q_M on the membrane capacity C_M at condition c′ (see Fig. 6) is given by $Q_M = C_M \Delta U_{\max} = 6.0 \cdot 10^{-9}\,\text{F} \times 2.0 \cdot 10^{-3}\,\text{V} = 1.2 \cdot 10^{-11}$ C (membrane area $F_M = 2.0 \cdot 10^{-2}$ cm^2). This corresponds to the charge of one electron in an area of $2.7 \cdot 10^6$ Å^2. The following consideration suggests an area of $27 \cdot 10^4$ Å^2 per dipole or an area of $6 \cdot 10^4$ Å^2 per dye molecule (that is the area of a square of edge-length 200 Å).

Each pair of molecules EA is substituted by a capacity c_0, with the charge $q = e$ on it: $c_0 = f \cdot D_0/4\pi d_0$ (f = area of the dye molecule, d_0 = distance dye–donor, D_0 = dielectric constant of the medium between dye and donor). This capacitance is connected *via* the capacitance $c_2 = f \cdot D/4\pi d$ (f = area of the dye molecule, D = dielectric constant of the membrane, d = membrane thickness) to the capacitor c_M, which is depicted by the area of the membrane with one dipole E^+A^- on it (Fig. 7). The charge on c_M is

$$q_M = \frac{q}{c_0\left(\frac{1}{c_2} + \frac{1}{c_M}\right) + 1}$$

The charge on the membrane capacity C_M is $Q_M = q_M n$ where n is the number of dipoles E^+A^-.
Thus

$$Q_M = \frac{e \cdot n}{C_0\left(\frac{1}{C_2} + \frac{1}{C_M}\right) + 1}$$

The membrane area with the charge of one electron on it ($2.7 \cdot 10^6$ Å^2) is large compared to the area of one dye molecule (100 Å^2). Therefore $C_M \gg C_2$ and

$$Q_M = \frac{en}{(C_0/C_2) + 1} = \frac{en}{(d/d_0)(D_0/D) + 1}$$

If one assumes that the dye molecule and the donor are at a molecular distance, then $d_0 \approx 5$ Å and the dielectric constant of the medium between dye and donor is $D_0 \approx D$. The membrane thickness is about $d = 50$ Å. With $Q_M = 1.2 \cdot 10^{-11}$ C one obtains $n = 7.5 \cdot 10^8$. Then the membrane area for each dipole has the value given above $F_M/n = 27 \cdot 10^4$ Å^2. Since 23 %, of the dye molecules are in the form E^+A^- the area per dye molecule is given by the above value of $6 \cdot 10^4$ Å^2.

(7) *Examination of the model with further experiments*

(a) When increasing the light intensity from I_1 to I_2 the number of excited dye molecules increases according to the described model. A charge flows onto capacitor C_M which is determined by the number of generated dipoles, and this charge then compensates across R_M. From the equivalent circuit one expects the same time dependence for the rise and drop of the voltage as for turning on the light. $\Delta U_{\max,1}$ and $\Delta U_{\max,2}$ being the photovoltages obtained by illuminating the membrane with intensities I_1 and I_2, it is expected that the maximum voltage change $\Delta U_{\max,\Delta I}$ at an intensity change of $\Delta I = I_1 - I_2$ is given by:

$$\Delta U_{\max,\Delta I} = \Delta U_{\max,2} - \Delta U_{\max,1} \tag{9}$$

The expected time dependence of U and the Relation 9 is verified experimentally (Fig. 10). The same agreement with the model is obtained upon decrease of the intensity. At high intensities of continuous illumination one expects the time constants τ_1 and τ_3 to be no longer equal. Independent of the intensity, $\tau_3' = \tau_r$. However, from Eqn 2 Eqn 10 is obtained in this more general case. It is reduced to Eqn. 3 for small values of light intensity I.

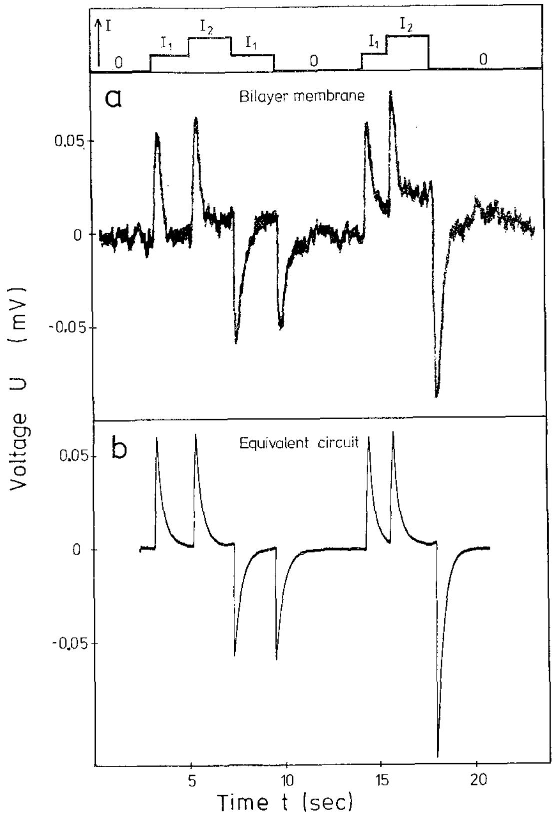


Fig. 10. Voltage at illumination of bimolecular lipid membranes with light of intensity $I_1 = 360$ W/m² and $I_2 = 720$ W/m² (curve a). The intensity variation of $\Delta I = I_2 - I_1$, generates a voltage change: $\Delta U_{\max,\Delta I} = \Delta U_{\max,\, I_2} - \Delta U_{\max,\, I_1}$. Voltage simulated by equivalent circuit Fig. 7 (Curve b).

$$n = n_{\max}(1 - e^{-t(1/\tau_r + B \cdot I)}) \tag{10}$$

where

$$n_{\max} = n_0 \frac{1}{\dfrac{1}{B \cdot I \cdot \tau_r} + 1}$$

Therefore one gets:

$$\frac{1}{\tau_1'} = \frac{1}{\tau_r} + B \cdot I \tag{11}$$

As shown in Section 4 at an intensity of $I = 400$ W/m² 23 % of the dye molecules are in the form E^+A^-, therefore $n/n_0 = 0.23$. From Eqn 10 one obtains with $\tau_r = 10^{-1}$ s

(Section 4) $B = 7.5\cdot 10^{-3}$ $m^2\cdot W^{-1}\cdot s^{-1}$. At this intensity it follows from Eqn 11 $\tau_1' = 0.8\ \tau_r$. The deviation between τ_1' and τ_3' is within the experimental error. The photovoltage ΔU at $t \ll \tau_r$ is proportional to the number n of generated dipoles $\Delta U = K\cdot n$, where K is a proportionality constant. With Eqn 10 one obtains:

$$\Delta U = K\cdot n_{\max}(1 - e^{-t(1/\tau_r)+B\cdot I)})$$

If $t \ll 1/\tau_r + B\cdot I$ one gets

$$\Delta U = K\cdot n_0\cdot B\cdot I\cdot t$$

Therefore at sufficiently low intensities ΔU is proportional to the incident energy $I\cdot t$. This property of the photovoltage is verified experimentally.

(b) At various dye concentrations one expects different values of photovoltages $\Delta U_{\max}$.

As can be deduced from the model the height of the photovoltage $\Delta U_{\max}$ is proportional to the number of molecules adsorbed to the membrane. One expects that at higher concentrations of the dye in the electrolyte more dye molecules are adsorbed to the membrane. By flash experiments according to Sections 1 and 2 using different amounts of Dye 1, a proportional rise of the photovoltage $\Delta U_{\max}$ with the concentration and at a concentration of 10^{-5} M a change into a saturation was observed.

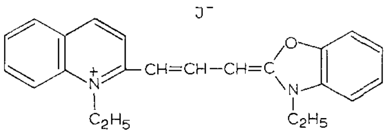
(c) It is deduced from the model that the time constants τ_1, τ_2, τ_1', τ_2', τ_3' and τ_4' are independent of incident intensity and energy of illumination (limitation see Section 7a). This result is verified by the experiment.

(8) *Additions to the electrolyte*

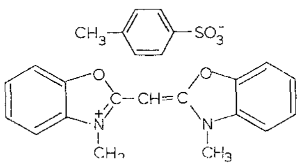
The electrolyte is an aqueous solution of NaCl (10^{-2} M). By varying the electrolyte concentration and replacing NaCl by KCl, the described properties of the photovoltage are unchanged within experimental accuracy and reproducibility.

When using Dye 2 instead of Dye 1 very similar effects are observed. Again the time constants τ_1' and τ_3' are 10^{-1} s and τ_2' and τ_4' are for example 2 sec. Eqn 4 gives $\tau_r = 0.7\cdot 10^{-1}$ s. In the case of Dye 3 the effects are smaller by a factor of 10

Dye 2



Dye 3



The increase of the pH to 13 and the decrease to 2 does not lead to a variation of the photovoltage. From this it can be deduced that the processes taking place are independent of the pH.

Exchanging the NaCl solution (in which the bimolecular lipid membrane is generated) by a NaI solution of the same concentration, the membrane resistance is lowered by about three orders of magnitude[15]. Taking a solution of I_2 + NaI of the same concentration, this effect is intensified. Solutions of the same molar fractions I^- and I_2 are added in various concentrations. Taking a concentration which reduces the membrane resistance by half, according to the model (Section 3) the decay times τ_2' and τ_4' have to decrease by half, the time constants τ_1, τ_2, τ_1' and τ_3' remain unchanged and the pulse height at flashlight and continuous illumination are nearly constant. This only holds, when the system is unchanged except for the resistance. Nevertheless, it is found that after such an addition of NaI + I_2 the photoeffects disappear. From this it must be deduced that the resistance change cannot be the only change of the system.

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