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The Photoelectrochemical Reaction of the Chlorophyll-Irisquinone Electrode

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The role of irisquinone (IQ) in the chlorophyll-IQ electrode was studied by measuring the photoresponse under illumination and the photocurrent at the controlled potential. It was concluded that the hydrophobic property of IQ was necessary for the photoresponse to occur at the chlorophyll electrode, and that the photoexcited chlorophyll was likely to eject electrons to a counter electrode *via* an outer circuit and to pull electrons from the reduced IQ, which had been produced by the oxidation of a reducing compound in the electrolyte on the chlorophyll-IQ electrode.

Recently many photoelectrochemical studies of chlorophyll lined on the electrode have been reported.[1,2] We have already contributed to this field: We found that the potential shifts to a less noble value under illumination on the platinum electrode coated with a mixture of chlorophyll and quinone, such as 1,4-naphthoquinone or chloranil.[3] The conductive adhesive was used as the binder of quinone with an electrode to prevent the quinone spread on the chlorophyll layer from dissolving into the electrolyte. However, the existence of the conductive adhesive made it difficult to speculate on the role of quinone in producing a photocurrent from the electrode in the light. It was, therefore, thought to be necessary to investigate the photoelectrochemical reaction on the chlorophyll quinone electrode without the conductive adhesive.

Two of the present authors isolated a new quinone from the seed oil of *Iris pseudacorus* L.[4] The structure of the quinone has been identified as 2-(*cis*-10-heptadecenyl)-6-methoxy-*p*-benzoquinone,** which is insoluble in water, miscible with chlorophyll, and adhesive to the electrode. These properties were thought to be suitable for the study of the chlorophyll-quinone electrode.

This paper will present the results of photoelectrochemical studies of the chlorophyll-IQ electrode undertaken in order to clarify the role of quinone.

Experimental

Materials. The chlorophyll was purchased from Nihon Chlorophyll Kogyo Co., Ltd., and was purified to separate it from an oily material by elution through the talc column with 80% acetone. The chlorophyll used was a mixture of chlorophyll a and b. The chlorophyll was determined by the spectrophotometric method.[5] The IQ used was isolated by the method described in a previous paper.[4] All the other chemicals were of a reagent grade or were the best commercially available.

Electrodes and Electrolytes. A chlorophyll or IQ solution in hexane or acetone and a cholesteryl oleate solution in hexane were prepared. The requisite amounts of the chlorophyll solution or the mixture of these stock solutions were spread onto the platinum electrode (1 × 1 cm) and then dried to produce a homogeneous chlorophyll layer. The chlorophyll-coated electrode was then immersed in a M/40 phosphate-buffer (pH 6.9) or carbonate-buffer electrolyte adjusted at each pH; various redox compounds had been dissolved in the electrolytes. All the experiments were carried out at 35 °C by using 50-ml dual beaker containing the electrolyte, with nitrogen gas being passed through.

Equipment. The potential was measured by means of a Kikusui Denshi volt-ammeter model 116 connected to the recorder, with a calomel electrode as the reference electrode. A Hokuto Denko potentiostat HA101 and a linear scanner were used for the measurement of the photocurrent at each controlled potential. A platinum plate was used as a counter electrode. The potential-current curves were obtained by using a Yokogawa Denki Type 3036 X-Y recorder, with the scanning set at a rate of 100 mV/s. The projector lamp (100 V, 150 W) was used as the source of light. The light of wavelengths shorter than 460 nm was cut off by a color filter (V-Y46) to avoid the complication arising from the simultaneous photochemical reaction of IQ, which exhibited its λ_{max} at 363 nm.[4]

Results and Discussion

Photoresponse of the Chlorophyll-IQ Electrode. To investigate the effect of IQ on the electrode with respect to the photoresponse, the electrode was prepared by covering 0.01 μmol/cm^2 of a layer containing chlorophyll and IQ mixed in various molar ratios. Same typical results of the potential-time curve are shown in Fig. 1. In Fig. 2 the values of photovoltage (the potential under illumination subtracted that in the dark) of all the electrodes are plotted against the molar ratio of IQ to the total amount of chlorophyll and IQ. The photovoltage of the chlorophyll electrode was found to shift to a positive value under illumination. On the other hand, the photovoltage turned into a

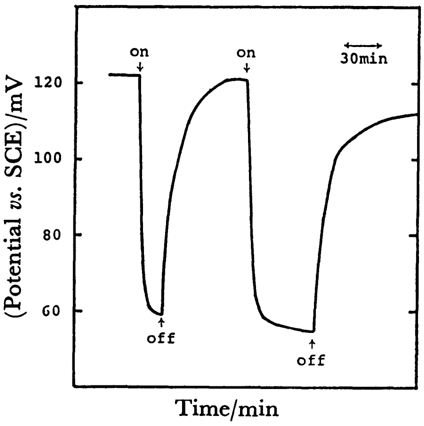

Fig. 1. Photoresponse of chlorophyll-IQ electrode.
pH 6.9, 35 °C, 6 × 10^4 lx, [Chl] + [IQ] = 0.01 μmol/cm^2, [Chl] : [IQ] = 1 : 3.

** Abbreviated to IQ, because we named it Irisquinone.

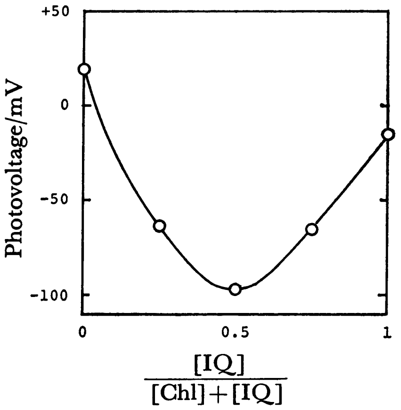

Fig. 2. Influence of the molar ratio to the photovoltage of chlorophyll-IQ electrode.
pH 6.9, 35 °C, 6×10^4 lx, [Chl]+[IQ]=0.01 μmol/cm².

negative value as the IQ content in the layer of the electrode increased. The maximum photoresponse was obtained at the molar ratio of IQ to chlorophyll of 1 : 1. The magnitude of the photovoltage became smaller at higher molar ratios of IQ, caused by the decrease in the amount of chlorophyll, which exhibited a photoconductive property. The values of the photovoltage were measured at various thicknesses of the chlorophyll-IQ layer (with the molar ratio of 1 : 1). The results are shown in Fig. 3a. The photovoltage was nearly constant at layer thicknesses thicker than 0.01 μmol/cm².

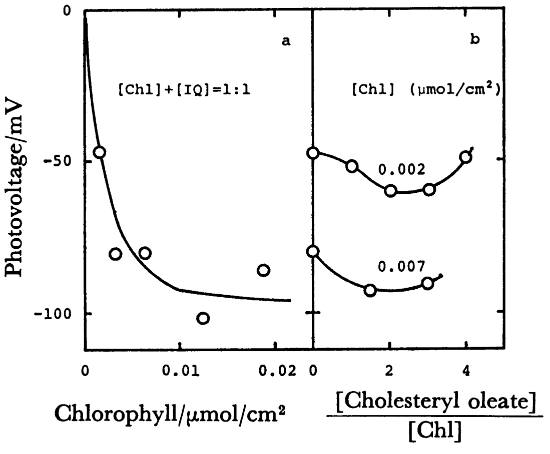

Fig. 3. Influence of the thickness of chlorophyll layer and the ratio of cholesteryl oleate to chlorophyll to the photovoltage.
pH 6.9, 35 °C, 6×10^4 lx.

It is very plausible that chlorophyll molecules are located in the hydrophobic region as a result of the existence of excess IQ, which is hydrophobic itself, and that, in turn, the chlorophyll-IQ electrode generates the photovoltage due to the photoexcitation of chlorophyll in the hydrophobic region. The chlorophyll-IQ-cholestery oleate electrode was prepared and illuminated in order to verify the influence of hydrophobicity on the photovoltage. Cholesteryl oleate is hydrophobic, miscible to chlorophyll and IQ, and exhibits the property of a liquid crystal. It is known that not only the molecules of a liquid crystal, but also guest molecules will be oriented in the electric field.[6] It was expected that the photovoltage might increase by the orientation of the photo-conductive chlorophyll molecules in the layer. The results of the photovoltage of the chlorophyll-IQ-cholesteryl oleate electrode are shown in Fig. 3b. The molar ratio of chlorophyll and IQ is 1 : 1, and the total amounts of chlorophyll and IQ in the layer were kept constant when the amount of cholesteryl, oleate was varied. The photovoltage was found to increase up to the molar ratio of chlorophyll, IQ, and cholesteryl oleate of 1 : 1 : 2, and then decrease as more cholesteryl oleate was added. It is said that the following reaction may occur in the hydrophobic region:[7]

$$\mathrm{Chl^* + Q \longrightarrow Chl^+ + Q^-}, \tag{1}$$

where Chl*, $\mathrm{Chl^+}$, and $\mathrm{Q^-}$ are a photoexcited chlorophyll, a cation of chlorophyll, and an anion of quinone, respectively. In a nonaqueous solvent, one-electron-reduced ubiquinone is known to be stable and to exhibit a remarkably negative (less noble) reduction potential.[8] Judging from the fact that the photoresponse of the chlorophyll-IQ electrode was observed in a negative direction, like an n-type semiconductor, an anion of IQ seems to exist inside the chlorophyll-IQ layer, apart from the interface of the electrode and the electrolyte.

The Redox Compounds in the Electrolyte. The electrolyte should contain an equi-molar concentration of the oxidized and reduced forms of the redox compound in order to keep the composition of the electrolyte constant during the photoelectrochemical reaction, so that the oxidized form of the redox compound might be reduced at the cathode and the reduced form might be oxidized at the anode. Therefore, the redox compounds were surveyed for a photocell producing as

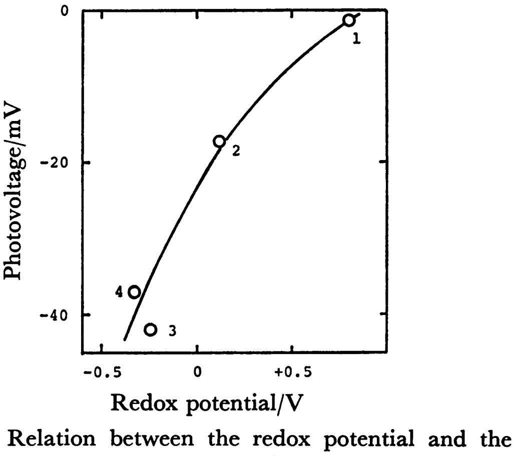

Fig. 4. Relation between the redox potential and the photovoltage. Total concentration of redox compound 2 mM. Molar ratio of oxidized and reduced form = 1 : 1.
1: Quinone hydroquinone (+0.80V), 2: $\mathrm{Fe^{3+}}$EDTA/$\mathrm{Fe^{2+}}$EDTA (+0.12 V), 3: 1/2 GSSG/GSH (−0.24 V), 4: $\mathrm{NAD^+}$/NADH (−0.32 V), pH 6.9, 35 °C, 5×10^4 lx, chlorophyll-IQ electrode: [Chl] : [IQ] = 1 : 5, thickness of chlorophyll: 0.02 μmol/cm².

high a photovoltage and photocurrent as possible. The photovoltage was measured on the system of a chlorophyll-IQ (the molar ratio: 1 : 5) electrode immersed into an electrolyte containing a different redox compound. The concentrations of the oxidized and reduced forms of the redox compound were 1 mM each. The results are shown in Fig. 4. The photovoltage was found to shift to a more negative value as the oxidation-reduction potential of the redox compound became less noble. The highest photovoltage was obtained when the mixture of glutathione-oxidized (GSSG) and -reduced (GSH) was used. The photovoltage in the system of the chlorophyll-IQ electrode connected with GSSG or GSH alone in the electrolyte was −58 or −45 mV, while that in the system of the chlorophyll electrode connected with GSSG or GSH alone was +53 or +39 mV respectively.

The Photocurrent at the Controlled Potential. In order to clarify the role of IQ on the chlorophyll-IQ electrode, the photocurrent was measured at the controlled potential on the various electrodes immersed into the electrolyte. The molar ratio of chlorophyll to IQ or that of chlorophyll to reduced IQ (IQH_2) in the layer of the electrode was 1 : 5. A typical anodic photocurrent-time curve is shown in Fig. 5, while the curves of the photocurrent at various controlled potentials are shown in Fig. 6. The maximum photocurrent was obtained around +0.2 V *vs.* SCE in every case. The same reaction may occur by the photoexcitation of chlorophyll in all cases. It is known that the half-wave oxidation potential of the chlorophyll a appears at +0.52 V (SCE) in acetonitril.[9] This is not a photoelectrochemical reaction. Judging from these facts, the photocurrent may be produced by the following reaction:

$$\mathrm{Chl} + h\nu \longrightarrow \mathrm{Chl}^* \longrightarrow \mathrm{Chl}^+ + \mathrm{e}. \qquad (2)$$

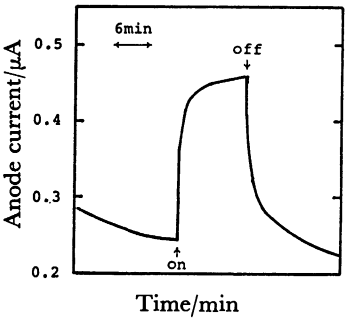

Fig. 5. Photocurrent at controlled potential.
pH 6.9, 35 °C, 5×10⁴ lx, chlorophyll-IQ electrode: [Chl] : [IQ] = 1 : 5, thickness of chlorophyll: 0.02 μmol/cm², electrolyte : 1 mM GSH, controlled potential at +0.22 V *vs.* SCE.

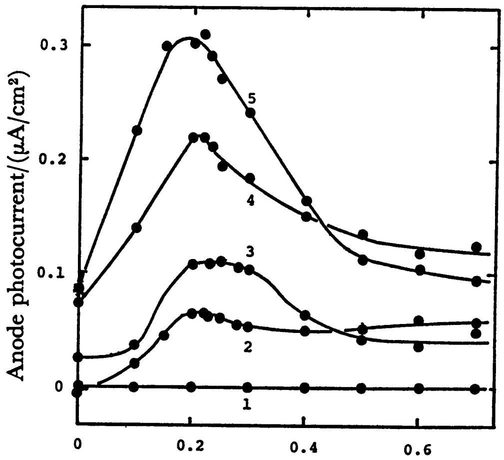

Fig. 6. Anode photocurrent at controlled potential.
pH 6.9, 35 °C, 5×10⁴ lx, 0.02 μmol/cm² chlorophyll, molar ration of Chl : IQ = 1 : 5, 1: E(none)/buffer, 2: E(Chl)/buffer, 3: E(Chl, IQ)/buffer, 4: E(Chl, IQ)/ 1 mM GSH, 5: E(Chl, IQH_2)/buffer.

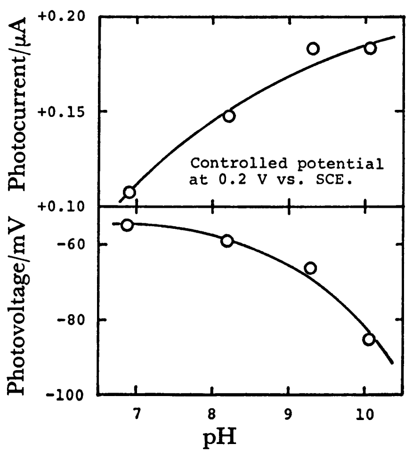

Fig. 7. Influence of pH to photovoltage and photocurrent. 35 °C, 5×10⁴ lx, 0.02 μmol/cm² chlorophyll, molar ratio of Chl : IQ = 1 : 5.

The anodic photocurrent at +0.2 V on the chlorophyll-IQ electrode was found to increase at higher pH values, in other words, at higher concentrations of OH^-, as is shown in Fig. 7. OH^- is as the only anode-active substance in the electrolyte. It may, therefore, be assumed that the IQ on the electrode is reduced in the process of the anodic reaction of OH^- and, in turn, that reduced IQ reacts with Chl^+ to reproduce IQ and chlorophyll. The assumptions can be expressed as follows:

$$\mathrm{IQ} \xrightarrow{\mathrm{OH}^-} \mathrm{IQH_2} \qquad (3)$$

$$2\,\mathrm{Chl}^+ + \mathrm{IQH_2} \longrightarrow 2\,\mathrm{Chl} + \mathrm{IQ} + 2\,\mathrm{H}^+. \qquad (4)$$

This is plausible, because the photocurrent in the case of the chlorophyll-IQ electrode is larger than that in the case of the chlorophyll electrode, and because the photocurrent produced by the chlorophyll-IQH_2 electrode is 2.8 times as large as that of the chlorophyll-IQ electrode, as is shown in Fig. 6.

The photocurrent and the dark current of the system of the GSH-containing electrolyte were twice and 1.4 times as large as these of the system omitting GSH. It is very possible that the IQ on the electrode is reduced to form IQH_2 in the dark as follows:

$$\mathrm{IQ} + 2\mathrm{GSH} \longrightarrow \mathrm{IQH_2} + \mathrm{GSSG}. \qquad (5)$$

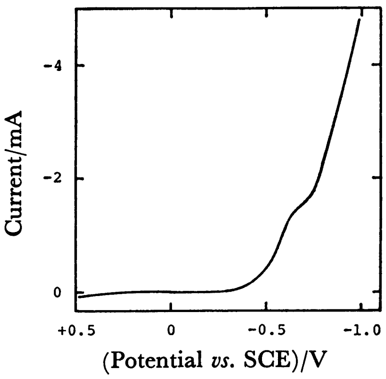

Fig. 8. Potential-current curve of IQ on Pt electrode. pH 6.9, 35 °C, 0.05 μmol of IQ on Pt (1 × 1 cm^2), The potential was scanned at a rate of 100 mV/s.

Then, the photocurrent can be obtained in the same way as with the chlorophyll-IQH$_2$ electrode.

The IQ layer was spread onto the platinum electrode to determine the reduction potential, because the redox potential of IQ was not yet known. The reduction wave of IQ appeared around −0.5 V (SCE), as is shown in Fig. 8. This fact suggests that IQ$^-$ tends to release electrons. The electrons could transfer from IQ$^-$ to platinum at +0.2 V. Then, the chlorophyll-IQ electrode produced the anodic photocurrent by means of Eqs. 1 and 2 at +0.2 V. No matter ho w Eq. 1 might participate, the maximum photocurrent was produced at the same potential in every system in Fig. 6. Therefore, the reaction of Eq. 2 appears to occur predominantly rather than the reaction of Eq. 1. It is concluded that the IQ on the electrode plays a role in the accelaration of the anodic reaction.

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