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Fig. 1. Electrolytic capacitor

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Abstract

Full Text

PHYSICAL CHEMISTRY

E. K. PUTSEIKO

SPECTRAL DISTRIBUTION OF THE PHOTOPOTENTIAL IN LAYERS OF PHTHALOCYANINES AND CHLOROPHYLL IN CONTACT WITH AN ELECTROLYTE

(Presented by Academician A. N. Terenin, January 28, 1963)

The photosemiconductor properties of chlorophyll and of its closest analogue —phthalocyanine—have in recent years been the subject of numerous studies ([1–11]). Of particular interest is the question of the semiconductor properties of these pigments under heterogeneous conditions. There are grounds to suppose that the photochemical reactions of chlorophyll in the granules of chloroplasts proceed especially intensively at phase boundaries. In 1951, V. B. Evstigneev and A. N. Terenin ([1]) established the appearance of a considerable photopotential, reaching tens and hundreds of millivolts, upon illumination of solid films of chlorophylls and phthalocyanines on a platinum electrode in aqueous electrolyte solutions. The photosensitizing action of chlorophyll and phthalocyanines under heterogeneous conditions has recently been investigated by Evstigneev ([12]). Information on the action spectrum in the appearance of photopotentials in these pigments at contact with liquid electrolytes is absent from the literature.

Fig. 1. Electrolytic capacitor

The present work is devoted to the study of the spectral sensitivity and sign of the photopotential in layers of metal-free phthalocyanine and magnesium phthalocyanine immersed in an aqueous medium and in electrolytes with reducing and oxidizing molecules.

Method of investigation

Measurement of the spectral distribution of the photopotential in layers of phthalocyanines in air and under vacuum conditions was carried out with the aid of the electrolytic capacitor A, shown in Fig. 1. Layers of phthalocyanines were deposited by sublimation in vacuum onto the glass finger of a vacuum vessel,

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Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

bearing on its surface a sputtered platinum electrode 1 with an area of 5 cm^2. To increase the resistance of electrode 1 to the action of water and various solvents, the platinum layer on the finger was first fixed by heat treatment at 500°. The second electrode was a piece of pure platinum foil of about 3 cm^2, 0.2 mm thick, which was placed in the vessel below the front electrode. Electrode 2 always remained in the dark and served as the reference electrode. As electrolyte, pure distilled water and its solutions with oxidizing agents and reducing agents were used. Degassing of the electrolyte and of the pigment layers under study was carried out by pumping out the air to 10^{-5} mm Hg. For this purpose the electrolyte was first poured into vessel B, where it was degassed by repeated (4-5 times) thawing and freezing with liquid air.

Measurement of the spectral distribution of the potential difference between

the pigment layer and the darkened reference electrode was carried out with intermittent monochromatic illumination at a frequency of 150 Hz. The alternating photopotential arising between the illuminated pigment layer and electrode 2 was fed to the high-resistance input of an AC amplifier with an amplification factor of $(1 \div 3) \cdot 10^5$. The voltage sensitivity of the setup was 0.1 μV. A synchronous detector connected to the amplifier output was preliminarily calibrated against a standard voltage source and made it possible to determine the sign of the photopotential relative to the darkened reference electrode.

Fig. 2. Spectral distribution of the photopotential in metal-free phthalocyanine layers in contact with an electrolyte in air, as a function of their thickness: **1** —thin layer $\sim 0.005\,\mu$; **2** —thick layer $\sim 1\,\mu$; **3** —layer **1** with adsorbed chloranil molecules.

Fig. 3. Spectral distribution of the photopotential in a metal-free phthalocyanine layer in contact with an electrolyte: **1** —in air; **2** —in a degassed electrolyte down to 10^{-4} mm Hg; **3** —same as **2**, after prolonged (3–5 days) residence in the degassed electrolyte.

The spectral distribution of the photopotential was determined on an ISP-17 glass monochromator in the wavelength interval from 400 to 1500 mμ, with a spectral-band width of 1-5 mμ/mm. The energy illumination beyond the output slit of the monochromator from a 70 W incandescent lamp in the visible part of the spectrum was measured with a thermoelement and varied within the range from 10^{-7} to 10^{-4} W/cm^2/s.

The spectral curves shown below in Figs. 2-4 are referred to the same incident

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monochromatic energy.

Results of the measurements and their discussion

1. The spectral distribution of the photopotential was determined for sublimed layers of metal-free phthalocyanine of different thicknesses, in the amorphous and crystalline states, for which, according to our measurements ([2],[5],[6]), the photocurrent carriers were positive charges. Under monochromatic illumination, the magnitude of the photopotential reached values from 10^{-7} to 10^{-3} V and, within these limits, varied linearly with illumination. Experiments showed that the potential of this pigment in contact with distilled water in air, and also in vacuum upon switching on

under intermittent illumination almost inertially reaches an equilibrium value and, relative to the darkened platinum reference electrode, exhibits a positive sign. These experiments show that the sign of the photopotential of the pigment layer in contact with the electrolyte is directly connected with the hole mechanism of photoconductivity of the dye. The positive value of the photopotential was preserved for layers of different thicknesses, but the magnitude and the course of the spectral distribution of the potential depended on the thickness of the pigment layer and on the surrounding liquid medium. Figure 2 gives the spectral distribution of the photopotential at a platinum electrode bearing on its surface a layer of metal-free phthalocyanine of various thicknesses. In the case of a thin pigment layer in contact with water, the spectral curve of the photopotential (curve 1) reproduces the absorption spectrum of the pigment film*, whereas for a thicker layer a sharp decrease of the photopotential is observed in the region of strong absorption by the pigment, and two narrow "fictitious" maxima appear on the descending branch of the optical-absorption curve, as shown by curve 2 of the same Fig. 2. It is not difficult to see that the change in the spectrum of the photopotential as a function of pigment thickness in an electrolyte is in principle no different from the form of the photoconductivity spectra for dry layers of this pigment of various thicknesses ([4,7]). Obviously, the spectral distribution of the photopotential of metal-free phthalocyanine in contact with an electrolyte, like its photoconductivity spectra, depends on the character of the recombination processes of the photogenerated carriers at the surface and in the bulk of this semiconductor. Sharp changes in the photopotential spectrum were also observed for a thin layer of this pigment as air was removed from the electrolyte by evacuation, as shown by curves 1, 2, and 3 (Fig. 3). It is possible that removal of the electron acceptor—oxygen—in the electrolyte changes the aggregation state and the rate of charge recombination at the pigment surface, and therefore the photopotential spectrum changes. The phenomenon is reversible, and after admitting air, in 1-2 hours the spectral-sensitivity curve of the pigment photopotential is restored again.

Fig. 4. Spectral distribution of the photopotential in layers of phthalocyanine on mica in contact with an electrolyte: 1 —in vacuum in the amorphous state; 2, 3 —in air in the crystalline β-form of the pigment.

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Fig. 4. Spectral distribution of the photopotential in layers of phthalocyanine on mica in contact with an electrolyte: 1 —in vacuum in the amorphous state; 2, 3 —in air in the crystalline β-form of the pigment

Figure 4: Fig. 4. Spectral distribution of the photopotential in layers of phthalocyanine on mica in contact with an electrolyte: 1 —in vacuum in the amorphous state; 2, 3 —in air in the crystalline β-form of the pigment

We found that if electron-acceptor molecules of chloranil were adsorbed from dilute ethanol solutions onto a layer of metal-free phthalocyanine with hole conductivity, the positive magnitude of the photopotential increased considerably, while the form of the photopotential spectrum did not change (see curve 3 of Fig. 2). Similar results were obtained with layers of this pigment when electronegative molecules of quinone and other oxidizers were added to the electrolyte solutions (in air and in vacuum). These experiments indicate an increased photoconductivity in the surface layers of this pigment in the presence of electron-acceptor molecules; therefore, the spectra of the photopotentials in electrolytes containing oxidizer molecules are not disturbed.

In contrast to oxidizers, the introduction into the electrolyte of reducing molecules (ascorbic acid, hydroquinone, sulfites, etc.) in the case of hole-

* And also the spectral distribution for photoconductivity and photo-e.m.f. ([7]).

of the phthalocyanine layer causes a considerable decrease in the photopotential, reaching twentyfold and more. At the same time the inertia of the process increases sharply, but the form of the photopotential spectrum is not disturbed. The reverse regularities were observed for metal-free phthalocyanine after its conversion into the crystalline β-form of the pigment, in which the carriers of the photocurrent were negative charges ([6]).

2. Magnesium phthalocyanine amorphous layers sublimed in vacuum, in an aqueous electrolyte in air, upon switching on the light, show a small positive potential, which gradually decreases with time. In contrast to experiments in air, layers of amorphous magnesium phthalocyanine under vacuum conditions at the contact with a deoxygenated aqueous electrolyte solution, upon switching on the light, show a stable positive potential (curve 1, Fig. 4).

The absolute value of the photopotential for amorphous layers of this pigment at the spectral maximum reaches several tenths of a microvolt per microwatt. In subsequent experiments, the same layers of amorphous magnesium phthalocyanine, deposited on platinum electrodes by introducing foreign molecules (water, acetone, ethanol, quinone, etc.), were converted into another, more stable and more sensitive crystalline β-form of the pigment ([5,13]). The spectral distribution of the photopotential of a thin magnesium phthalocyanine layer after its conversion into the crystalline β-form of the pigment is shown by curves 2, 3 in Fig. 4. It is not difficult to see that the sensitivity of the layer under these con-

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ditions increased, and the spectral course of the photopotential reproduces well the spectrum of photoconductivity and absorption, with the principal maximum at 840 mμ, established by us earlier for the crystalline β-form of the pigment ([5,13]). The introduction of quinone molecules into the electrolyte increases the positive value of the photopotential in magnesium phthalocyanine layers, but the distribution of the photopotential over the spectrum does not change.

The presence in the electrolyte of molecules of reducing agents, which readily give electrons to the semiconductor, sharply decreases the magnitude of the pigment photopotential and noticeably increases the inertia of the process.

The observed increase of the photopotential in phthalocyanine layers with hole conductivity in electrolytes under the action of electronegative oxidizer molecules, reaching tenfold and more, can be explained by the fact that on the pigment surface under these conditions a potential barrier arises, the field of which increases the diffusion of electrons to the external electrode and hinders the diffusion of holes to the electrolyte surface. This leads to a decrease in the rate of surface recombination of electrons and to an increase in the diffusion length of the majority current carriers. The potential barrier arising at the contact of the hole pigment with the electrolyte under the influence of electron donors hinders the diffusion of holes to the platinum electrode, which reduces the magnitude of the photopotential.

In conclusion, I consider it my pleasant duty to express gratitude to Acad. A. N. Terenin for his constant interest in the work and valuable advice.

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