Communications to the Editor

[Chem. Pharm. Bull. 33(12)5589–5592(1985)]

THE PHOTORESPONSE OF A PLATINUM ELECTRODE COATED WITH A POLY(VINYL CHLORIDE)/SPIROBENZOPYRAN MEMBRANE

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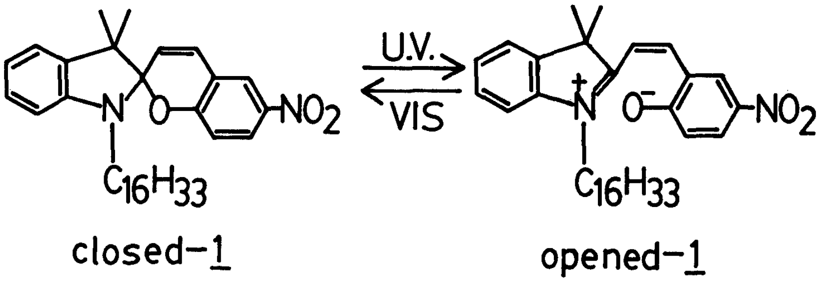
A platinum electrode was coated with an organic membrane composed of poly(vinyl chloride) and spirobenzopyran to regulate the electrode potential by photoirradiation. The electrode potential shifted rapidly toward the positive direction upon UV light irradiation. When the light was switched off, the potential decayed gradually. Visible light irradiation accelerated the decay of the electrode potential. The results are discussed in relation to the photochemical reaction of a spirobenzopyran derivative in the membrane and the ionic distribution at the metal/membrane and membrane/solution interfaces.

KEYWORDS——polymer-coated electrode; photoinduced potential; photoresponsive membrane; poly(vinyl chloride)/spirobenzopyran membrane; photo-electrode

The development of high performance polymer membranes is currently a focal subject in many diverse fields in science and technology.2-5) We have been engaged in developing photoresponsive membranes that change their potential when photoirradiated. Azobenzene derivatives6-12) and a spirobenzopyran derivative13,14) have been utilized as photoresponsive dye components in the membrane. Others have also reported the photoresponse of the spirobenzopyran-containing membranes.15-18) Heretofore, the photoresponse of these membranes has been studied by means of U-shaped glass cells in which the membrane separates two electrolyte solutions. The present paper describes preliminary results concerning the photoresponse of a poly(vinyl chloride) (PVC)/spirobenzopyran (1) membrane obtained by using a membrane-coated electrode, i.e., the PVC/1 membrane is coated on a platinum



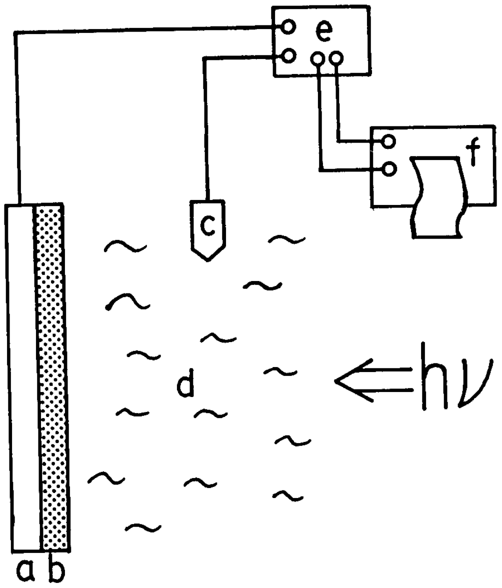


Fig.1. Schematic Representation of the Electrochemical Cell for Measuring the Electrode Potential under Irradiation

a) Platinum plate,
b) PVC/1 membrane,
c) reference electrode (S.C.E.),
d) NaCl solution,
e) potentiometer,
f) recorder.

electrode and dipped into an aqueous electrolyte solution. Such an application of the membrane is of considerable interest in connection with the development of photo-switchable electronic devices, e.g. photo-sensors and photo-transducers, based on organic materials.

Compound 1 was synthesized by the reaction of 5-nitrosalicylaldehyde with 1-hexadecyl-2,3,3-trimethylindolenium bromide according to the reported method.[19] A mixture of 250 mg of PVC, 0.50 ml of di-2-ethylhexyl phthalate, 20 mg of 1, and 20 ml of tetrahydrofuran was poured into a flat Petri-dish (9.2 cm diameter) in which a platinum (Pt) plate (40 mm x 30 mm x 0.2 mm) was placed. After evaporating the solvent, a PVC/1 membrane of ca. 80 μm thickness formed on the Pt plate. The spirobenzopyran derivative 1 in the membrane exhibited normal photochromism: a closed form (colorless) under visible light or in the dark and an opened form (purple) under UV light irradiation. The electrochemical cell for measuring the electrode potential is schematically sketched in Fig. 1. The composition of the cell was as follows: Pt|PVC/1 membrane|NaCl solution|S.C.E. The light source was 500 W Xe lamp and Toshiba UV-D35 and Y-45 glass filters were used for isolating UV (320 nm$<\lambda<$400 nm) and visible (450 nm $<\lambda$) light, respectively. Before use the membrane-coated electrode was conditioned for ca. 6 h by soaking it in a 0.1 M (M=mol/l) NaCl solution in the dark.

Figure 2 shows a typical photoresponse of the Pt electrode coated with PVC/1 membrane. After a steady-state potential of the electrode (E_{vis}=+250 mV) had been obtained under visible light irradiation, a positive shift of the electrode potential was induced by UV light irradiation ($E_{u.v.}$=+420 mV). About +170 mV of photoinduced potential developed in the response time of ca. 2 min. When the UV light was switched off, the electrode potential decayed. Visible light irradiation accelerated the decay of the electrode potential. With visible light irradiation, the potential shifted rapidly in the negative direction, then asymptotically approached the original value of the potential. Apparently the electrode potential

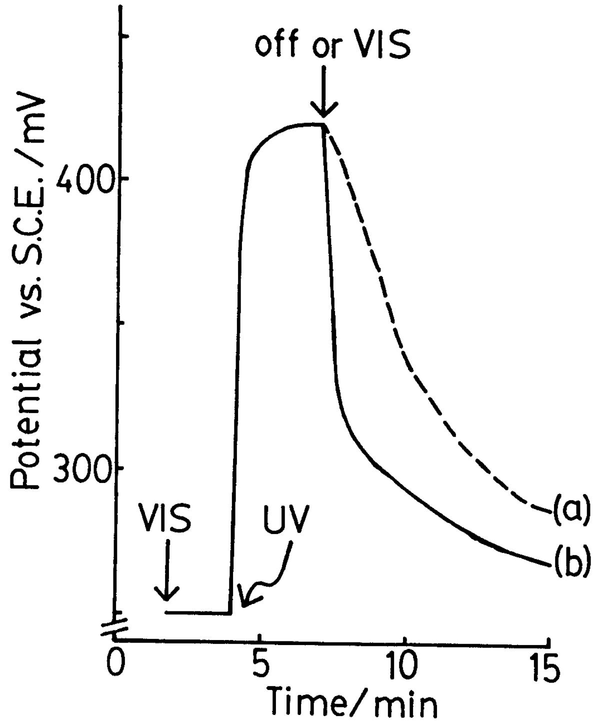


Fig. 2. Typical Photoresponse of the Pt Electrode Coated with PVC/1 membrane

NaCl concentration; 1 M.
Decay of the electrode potential was measured in the dark (a, ---) and under visible light (b, ——).

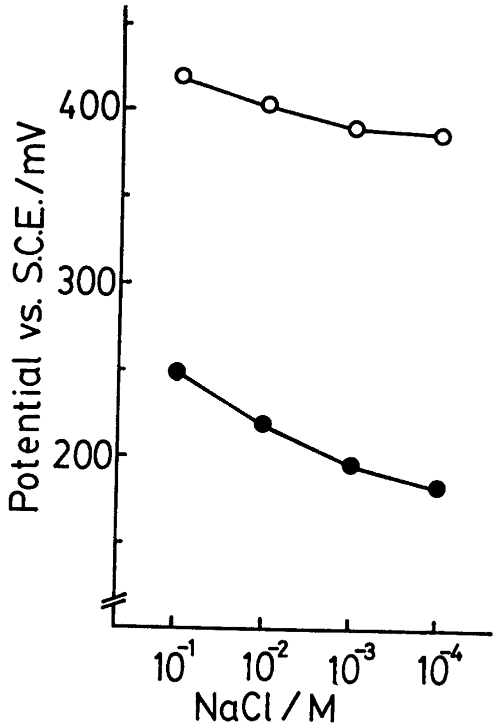


Fig. 3. Dependence of the Electrode Potential on the NaCl Concentration in the Aqueous Solution

—○— ; electrode potential under UV light irradiation.

—●— ; electrode potential under visible light irradiation.

was altered by changes in the fixed charge density of the membrane, which depended on the content of photochemically-generated opened-1 (charged-form of 1).

It should be noted here that the photoresponsive behavior of the PVC/1-coated electrode differs considerably from that of the membrane alone when it is interposed between two electrolyte solutions.[13,14] First, the magnitude of the photoinduced potential, $\Delta E=|E_{u.v.}-E_{vis}|$, was enhanced up to 170 mV or more in the present system. A more interesting aspect is that, under visible light, the decay curve of the potential was biphasic, with an initial faster phase followed by a slower second phase (Fig. 2-b). The first phase of the decay was completed within 30 s, during which the electrode potential shifted from +420 mV to +320 mV. The photochemical reaction of 1 from the opened form to the closed form in the membrane was also completed in this period, as confirmed by decoloring of the membrane. It follows, therefore, that the slower second phase of the decay under visible light irradiation does not involve a photochemical reaction in 1. These results imply that, in addition to the photochemical reaction of 1 in the membrane, some unknown factors are involved in the potential changes in the present system. The diffusion of ions such as Na^+ and Cl^- in the membrane may be an important factor in determining the electrode potential, because the potential differences at the

Pt/membrane and the membrane/solution interfaces should depend on the concentration and distribution of the ionic species at the interfaces. The present results provide valuable information in the mechanistic studies of the potentiometric response of the coated-wire type of ion selective electrodes.$^{20)}$

Figure 3 shows the effects of NaCl concentration on the electrode potential. Both the $E_{u.v.}$ and the E_{vis} values depended on the NaCl concentration in the solution. In the lower concentration region, the ΔE values were enhanced up to 200 mV or more.

Thus, we have shown that a Pt electrode can be endowed with photoresponse by coating it with an organic membrane composed of PVC and spirobenzopyran 1. Detailed examination of the mechanism of the photoinduced potential changes in the present system are now in progress.

ACKNOWLEDGEMENT The authors are grateful to the Ministry of Education, Science and Culture of Japan for support of this work through a Grant-in-Aid for Co-operative Research (NO. 59390012).

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(Received September 24, 1985)