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Photo-Excitable Membranes. Effects of pH of the Solution on the Photoresponse of Poly(vinyl chloride) Membrane Doped with a Spirobenzopyran Derivative

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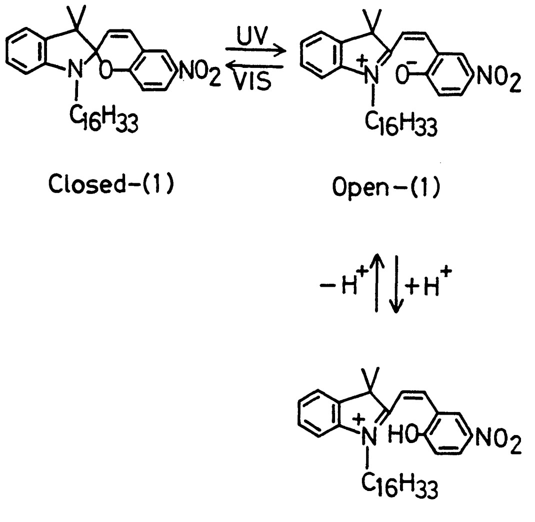
Synopsis. The magnitude of the photoinduced membrane potential across a poly(vinyl chloride)/spirobenzopyran membrane depends considerably on the pH of the solution adjacent to the membrane surface which is exposed to light. The photoresponse is enhanced in the acidic region, while is depressed in the alkaline region. The results are explained in terms of the formation of the asymmetric membrane and of the charge density on the membrane surface.

Several reports have appeared on the photoinduced membrane potential across the polymer membranes modified with spirobenzopyran derivatives.[1–6] To improve the photoresponse of the membranes, we have employed a plasticized poly(vinyl chloride) membrane doped with spirobenzopyran derivative **1** and found followings; (1) UV irradiation induces membrane potential changes of more than 100 mV with a response time of 1—2 min, (2) the photoinduced potential changes arise from the change in charge density on the membrane surface (i.e., surface potential change), which stems from the photo-generated open form of **1**, and (3) the content of open form of **1** is higher on the UV-irradiated surface than that on the nonirradiated surface (i.e., formation of asymmetric membrane).[7–11]

The effects of pH of the solution on the photoresponse were also checked in the range of pH 5.3—8.0.[9] In this pH range, the photoresponse of the PVC/**1** membrane slightly depended on the pH of the solution. The present paper reports the pH-dependent photoresponse of the PVC/**1** membrane over the wide pH range of 3—12 under the condition that the pH values of both aqueous solutions separated with the membrane are not equal with each other. To our knowledge, such systematic study of the pH effect on the photoresponse of the spiropyran-doped membrane has not appeared.



Experimental

Materials. PVC (molecular weight of ca. 70000) was purchased from Wako Co., Ltd. and used without further purification. Diisodecyl phthalate (DIDP) and tetrahydrofuran (THF) are of extra pure reagent grade. The synthetic procedure and analytical data of **1** were described previously.[9]

Membrane Preparation. PVC/**1** membrane of ca. 0.15 mm thickness was prepared by pouring the mixture of 250 mg of PVC, 0.5 ml of DIDP, 30 mg of **1**, and 20 ml of THF onto a flat Petri dish (8.5 cm diameter), and allowing the solution to evaporate at room temperature. The membrane was conditioned by soaking it in 5 mM (M=mol·dm^{-3}) Britton-Robinson buffer for ca. 15 h before use.

Membrane Potential Measurement. All measurements were conducted at 25 °C using a U-shaped glass cell (Fig. 1). The composition of the electrochemical cell for the membrane potential measurements was as follows; Ag/AgCl|0.1 M $(CH_3)_4NCl$|electrolyte solution (c_1)|PVC/**1** membrane| electrolyte solution (c_2)|0.1 M $(CH_3)_4NCl$|Ag/AgCl. The electrode in the c_1 compartment was earthed. The pH value of the solutions were regulated with 5 mM Britton-Robinson buffer. Photoirradiation was carried out from the c_2 side with a 500 W xenon lamp using cut-off filters to isolate UV (320 nm$<\lambda<$400 nm) and visible (490 nm$<\lambda$) light. Noise level in the potential was within 1 mV under the present experimental conditions.

Results and Discussion

Figure 2 shows the magnitude of photoinduced membrane potential, $\Delta(\Delta\phi)$, as a function of pH of the c_2 side solution. The pH value of the c_1 side solution was maintained constant at 3 or 12, and the membrane surface facing the c_2 solution was exposed to light. In the range of pH 3—7, the $\Delta(\Delta\phi)$ value scarcely depended on the pH of the c_2 solution, while, above pH 8, the $\Delta(\Delta\phi)$ value decreased almost linearly with increasing the pH. Such tendency was observed for both cases when the pH of the c_1 solution was maintained at 3 and 12.

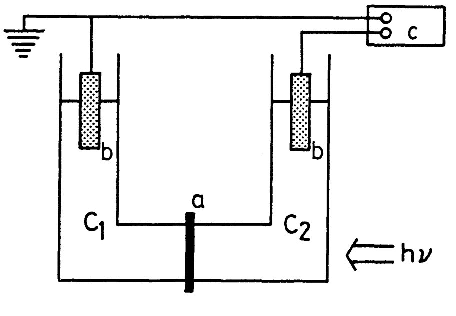


Fig. 1. Schematic representation of the cell for measuring membrane potential. a; Membrane, b; Ag/AgCl electrode, c; potentiometer.

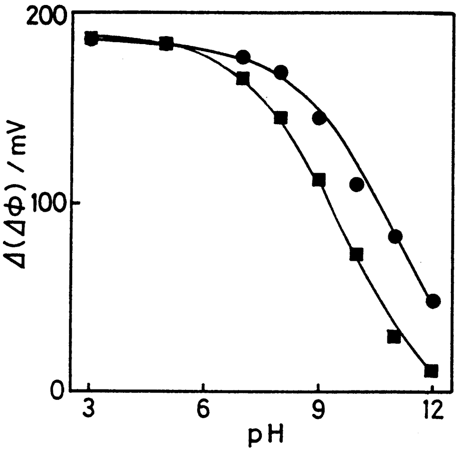


Fig. 2. Effects of pH of the c_2 solution on the photoresponse of the PVC/1 membrane. The pH value of the c_1 solution was constant at 3 (—■—) or 12 (—●—). The membrane surface facing the c_2 solution was exposed to light.

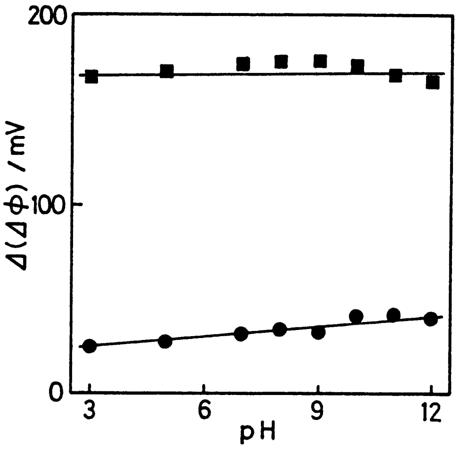


Fig. 3. Effects of pH of the c_1 solution on the photoresponse of the PVC/1 membrane. The pH value of the c_2 solution was constant at 3 (—■—) or 12 (—●—). The membrane surface facing the c_2 solution was exposed to light.

These results are compatible with our idea[7–11] that the photoinduced membrane potential stems from the change in charge density on the UV-irradiated surface of the membrane. In the case of the PVC/**1** membrane, the charge density of the membrane surface is considered to depend on the amount of the protonated form of **1** which has an electrically positive net charge. It is envisaged that the pH of the c_2 side solution considerably affects the equilibrium of protonation to the open **1** on the irradiated surface.

Figure 3 shows the results obtained when the pH of the c_1 side solution was varied from 3 to 12 with keeping the pH of the opposite side solution constant at 3 or 12. The membrane surface facing c_2 solution was exposed to light. Contrary to the data shown in Fig. 2, the effects of pH of the c_1 solution was small. When the c_2 solution was maintained at pH 3, the photoinduced potential of 160—180 mV was observed irrespective of pH value of c_1 solution. This result consists with the fact that the photochemical reaction from the closed-**1** to the open form is severely depressed on the nonirradiated surface of the membrane (i.e., asymmetric membrane), as was previously shown spectrophotometrically.[11] On the other hand, the $\Delta(\Delta\phi)$ value decreased to 20—40 mV when the pH of the c_2 solution was 12. These observations also show that the photoresponse of the PVC/**1** membrane depends on the change in charge density of the irradiated surface, not of the opposite surface, of the membrane. These findings should be important in relation to the mechanistic study on the pH-dependent photoresponse of the enzyme-modified PVC/**1** membrane,[10] which can be used as a sensitive layer of a novel class of potentiometric enzyme sensors.[12]

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