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Photo-Excitable Membranes. Photoinduced Potential Changes across Poly(vinyl chloride)/Spirobenzopyran Membranes Doped with Valinomycin and Nonactin

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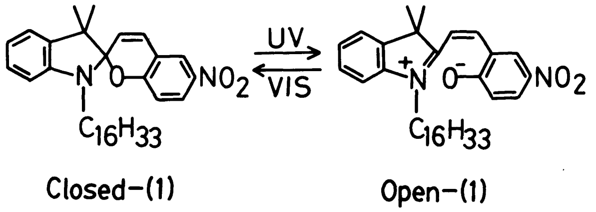
Poly(vinyl chloride)/spirobenzopyran membranes doped with valinomycin or nonactin were prepared to study the photoresponse of the membrane potential in the presence of K^+ or NH_4^+ ion. Ultraviolet (UV) light irradiation induced more than 100 mV of potential change across the membrane doped with valinomycin in the presence of 10^{-8}—10^{-6} M† KCl, whereas the potential change was extremely suppressed in the presence of higher KCl concentration ($>10^{-3}$ M). The photoresponse of the membrane potential depended upon the direction from which the membrane was irradiated. The nonactin-doped membranes showed a similar tendency in photoresponse in the presence of NH_4Cl to that observed for the valinomycin-doped membrane in the presence of KCl. The results were explained in terms of surface potential changes at the irradiated surface of the membrane, associated with the photochemical reaction of spirobenzopyran and the specific adsorption of cations to the surface of the membrane.

Several reports have described efforts to photochemically regulate the membrane potential across the polymer membranes doped with spiropyran derivatives. Suzuki et al. have reported that 20—30 mV of membrane potential can be induced by photoirradiating a cellulose/phosphatidylcholine composite membrane doped with 1′,3′,3′-trimethyl-6-nitrospiro-[2*H*-1-benzopyran-2,2′-indoline].[1,2] The results have been explained in terms of photochemically-induced changes in the fixed charge density in the membrane arising from the photochemical reaction of the spiropyran derivative. They have also prepared asymmetric membrane which contains spiropyran derivative at the surface of one side of the membrane.[3] Bellobono et al. have prepared cellulose membranes incorporating five kinds of spiropyran compounds to examine their photoresponse in membrane potential, with the intention of applying the membrane in constructing photoresponsive devices used in the field of optical data storage.[4,5] Synthetic polymers which contain spiropyran side chains have also been used to study photoresponse of the membrane. Irie et al. have prepared polymer membranes composed of poly(methacrylate) having spiropyran pendant groups and measured membrane potential under irradiation.[6] They have suggested the importance of the conformational changes of the polymer chains as well as the charge density in the membrane.

In all cases cited above, the magnitude of photoinduced potential was 20—30 mV and the response was somewhat slow. We have succeeded in highly improving the photoresponse in membrane potential across the spiropyran-contaning membrane, by the use of plasticized poly(vinyl chloride) (PVC) as a membrane matrix.[7—14] In the course of our study on the PVC/spiropyran membranes, the followings were found; (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, in turn, stems from the photo-generated open form of spiropyran, (3) the content of open form of spiropyran is higher on the UV-irradiated surface than that on the nonirradiated surface (i.e., formation of asymmetric membrane). The present paper describes the photoresponse in membrane potential across the PVC/1′-hexadecyl-3′,3′-dimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2′-indoline] (**1**) membranes doped with nonactin and valinomycin. These systems are useful for studying the effects of specific adsorption of ions on the membrane surface upon the photoresponse of the membrane, because valinomycin and nonactin are ionophores which bind K^+ and NH_4^+ ions, respectively.



Experimental

Materials. PVC (molecular weight of ca. 70000) was purchased from Wako Chemical Co. and used without further purification. Dibutyl phthalate (DBP), tetrahydrofuran (THF), ammonium chloride (NH_4Cl), potassium chloride (KCl), nonactin, and valinomycin are of extra pure reagent grade. The synthetic procedure and analytical data of **1** were reported elsewhere.[12]

Membrane Preparation. PVC/**1**/nonactin membrane was prepared by pouring the mixture of 250 mg of PVC, 0.5 ml of DBP, 30 mg of **1**, 5 mg of nonactin, and 20 ml of THF onto a flat Petri dish (8.5 cm diameter), and allowing the solvent to evaporate at room temperature. PVC/**1**/valinomycin membrane was prepared in the same manner

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† 1 M=1 mol dm^{-3}.

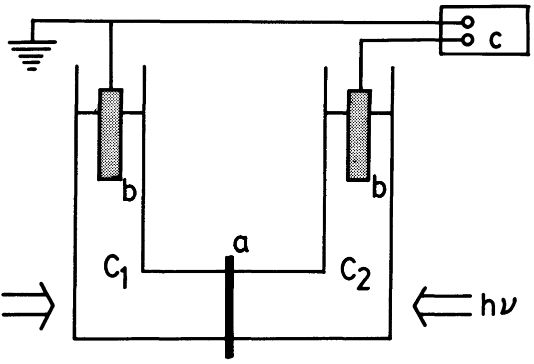

Fig. 1. Schematic representation of the cell for measuring membrane potential.
a; Membrane, b; Ag/AgCl electrode, c; potentiometer.

using 5 mg of valinomycin in place of nonactin. The thickness of the membranes thus prepared was ca. 0.15 mm.

Measurements. Membrane potential measurements were conducted at 25 °C using a U-shaped glass cell illustrated in 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/nonactin or PVC/1/valinomycin membrane|electrolyte solution (c_2) |0.1 M $(CH_3)_4NCl$|Ag/AgCl. The electrode in the c_1 compartment was earthed. Photoirradiation was carried out from the c_1 or c_2 side with a 500 W xenon lamp using cut-off filters Toshiba UVD-35S and O-55 to isolate UV (320 nm$<\lambda<$400 nm) and visible ($\lambda>$490 nm) light, respectively. Noise level in the potential was within 1 mV under the present experimental conditions. Absorption spectra of the membrane were recorded on a Shimadzu UV-visible spectrophotometer (Type UV-250).

Results and Discussion

We have already reported that the membrane potential across the PVC/1 membrane changes upon photoirradiation, associated with the photochemical interconversion of **1** between closed form and open form.[7-14] The photoinduced membrane potential was ascribed to changes in charge density at the UV-irradiated surface of the membrane, arising from the photochemically-generated open form of **1**.

Figure 2 depicts a typical photoresponse of the membrane potential across the PVC/1/valinomycin membrane. When the membrane was exposed to UV light from c_2 side, the membrane potential shifted in the negative direction and, subsequently, the membrane potential was restored to the original value upon visible light irradiation. The photoresponsive behavior of the PVC/1/valinomycin membrane was essentially comparable to those previously observed for valinomycin-free PVC/1 membrane.[12] This was also the case for photoresponse of the PVC/1/nonactin membrane. These results suggest that valinomycin and nonactin have scarcely any influence on the photochemical reaction of **1** in the membrane.

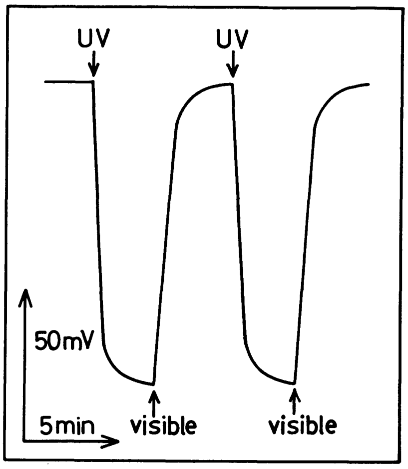

Fig. 2. Typical photoresponse of the membrane potential across the PVC/1/valinomycin membrane. c_1 side; pure water, c_2 side; 10^{-4} M KCl.

PVC/1/Valinomycin Membrane. In general, the potential difference across a charged membrane (membrane potential, $\Delta\phi$) is given as an algebraic sum of the diffusion potential in the membrane and the surface potential difference at membrane-solution interfaces.[15-18] In the case of plasticized PVC membranes, the contribution from the diffusion potential is considered small due to the depressed ionic permeability in the highly hydrophobic membrane interior, as was discussed for PVC/crown ether membranes in the previous paper.[19] For the PVC/1/valinomycin membrane, it is reasonable to assume that the surface potentials at the membrane-solution interfaces depend on the density of the ions which are adsorbed to the membrane surface by forming complexes with valinomycin, as well as on the content of open-**1**.

We therefore measured the membrane potential across the PVC/1/valinomycin membrane under visible and UV light in the presence of 10^{-8}—10^{-1} M KCl in the c_2 side solution (Fig. 3). In the dark or under visible light, where **1** assumes wholly closed form (noncharged form), the $\Delta\phi$ values increased linearly with increasing concentration of K^+ ion over the range of 10^{-5}—10^{-1} M. This should be caused by adsorption of K^+ ions on the membrane surface as a result of complexation between K^+ ions and valinomycin. This means that the charge density on the membrane surface reflects the concentration of K^+ ion in the aqueous solution adjacent to the membrane surface. The $\Delta\phi$ values measured under UV light irradiation from c_1 or c_2 side were also affected by the concentration of K^+ ion. UV irradiation from the c_1 side induced positive shift of the membrane potential, while the potential shifted in the negative direction upon UV irradiation from c_2 side. The polarity of the potential shift was reasonably explained based on the asymmetric membrane formation under UV light irradiation.[12]

Figure 4 shows the $\Delta(\Delta\phi)$ values, the difference between the $\Delta\phi$ value under UV light irradiation and that in the dark or under visible light, observed upon UV irradiation from c_1 or c_2 side. When the membrane was irradiated from c_2 side, an approximately linear relationship existed between the $\Delta(\Delta\phi)$ values and the concentration of K^+ ion over the range of 10^{-6}—10^{-3} M. The magnitude of $\Delta(\Delta\phi)$ value was enhanced in the lower concentration region of K^+ ion, whereas, over 10^{-2} M KCl, the photoresponse was suppressed, being 5 mV or less. On the contrary, the $\Delta(\Delta\phi)$ values were always about 100 mV when the membrane surface facing the c_1 solution, where K^+ ion was absent, was exposed to UV light. These observations imply that the higher charge density on the irradiated surface of the membrane is not favorable for the enhanced photoresponse.

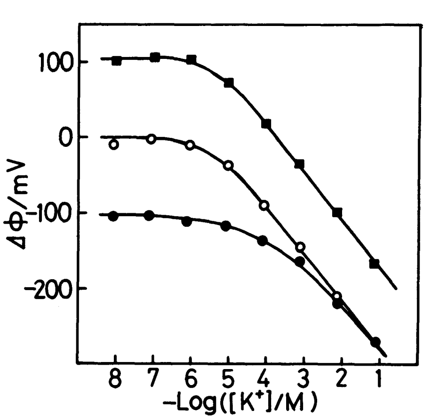

Fig. 3. The membrane potential across the PVC/1/valinomycin membrane under UV light irradiation from c_1 side (—■—) and c_2 side (—●—) and visible light (—○—) from c_2 side as a function of KCl in the c_2 solution. The concentration of KCl in the c_1 side solution was zero.

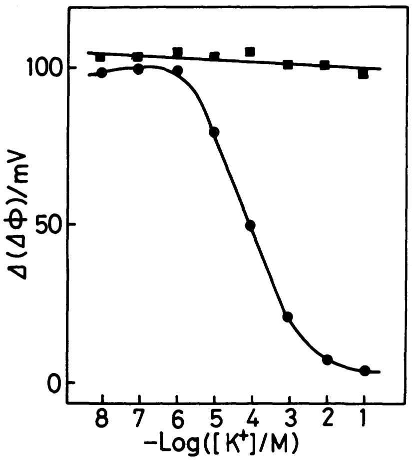

Fig. 4. The effects of KCl concentration on the $\Delta(\Delta\phi)$ value. The membrane was irradiated from c_1 side (—■—) and c_2 side (—●—). The concentration of KCl in the c_1 side solution was zero.

Figure 5 shows the $\Delta\phi$ values across the membrane under the conditions that KCl concentrations in both sides are equal with each other. The membrane potential was always near to zero under visible light or in the dark. UV light irradiation from c_1 or c_2 side induced shifts in membrane potential in the positive or negative direction, respectively, in spite of the conditions of $c_1=c_2$. This can be ascribed to asymmetric membrane formation under UV light irradiation,[20—22] i.e., the photochemical reaction of **1** from closed form to open form proceeds more efficiently on the irradiated surface of the membrane than on the opposite surface. Therefore, the content of open-**1** on the irradiated surface is higher than that on the nonirradiated surface. This is the reason why photoinduced potential changes were observed even for $c_1=c_2$. The $\Delta(\Delta\phi)$ values were dependent on the KCl concentration, in both cases when irradiated from c_1 and c_2 sides. These results can be also explained based on the idea that the higher charge density on the irradiated surface of the membrane suppresses the photoresponse in membrane potential.

We also checked the photoresponse of PVC/**1** membrane without valinomycin in the presence of KCl, and found that the $\Delta(\Delta\phi)$ values were always about 100 mV irrespective of KCl concentration. This means that valinomycin is essentially required for binding K^+ ions to regulate the charge density on the membrane surface.

In previous papers,[7—14] we have explained the photoresponse of **1**-doped PVC membranes in terms of the formation of asymmetric membrane under UV irradiation. To obtain a further evidence for this, we

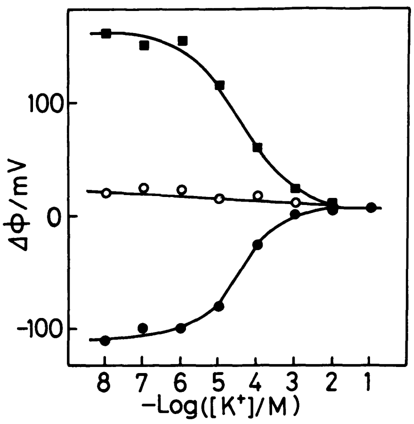

Fig. 5. The asymmetric membrane potential across the PVC/1/valinomycin membrane in the presence of KCl under UV light irradiation from c_1 side (—■—) and c_2 side (—●—) and under visible light from c_2 side (—○—). The concentration of KCl in both solutions was equal with each other.

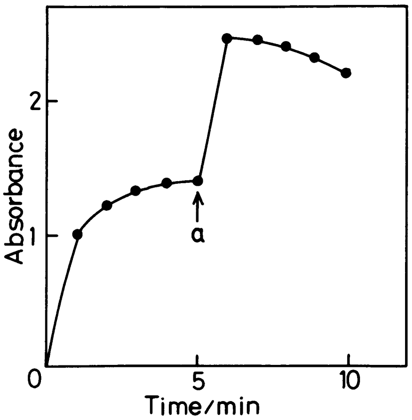

Fig. 6. Change of absorbance of the membrane at 565 nm under UV light irradiation. After 5 min-irradiation from one side of the membrane, the opposite surface of the membrane was exposed to UV light at (a).

measured absorption spectra of the membrane. As depicted in Fig. 6, the absorbance of the membrane at 565 nm, which is absorption maximum of open-**1**, increased rapidly at the initial stage of UV irradiation and declined to reach a steady-state value after about 5 min. The absorbance no longer increased even after prolonged irradiation from the same direction. When the membrane, after the steady-state value of absorbance had been attained by UV irradiation from one side of the membrane, was exposed to UV light, in turn, from the opposite direction, a further increase of the absorbance was observed. This is a clear evidence for the formation of asymmetric membrane under UV light irradiation.

PVC/1/Nonactin Membrane. Photoresponse of PVC/**1**/nonactin membrane was also examined in the presence of NH_4^+ ions. We have already reported some results concerning photoresponse of the PVC/**1**/nonactin membrane.[14] Figure 7 shows the dependence of $\Delta\phi$ values on the NH_4Cl concentration in the aqueous solution. The basic profiles of the membrane potentials under visible and UV light were essentially the same as those observed for PVC/**1**/valinomycin membrane in the presence of KCl.

The $\Delta(\Delta\phi)$ values were shown in Fig. 8. When the membrane surface facing c_1 solution was exposed to UV light, the $\Delta(\Delta\phi)$ values measured 180—190 mV irrespective of the concentration of NH_4Cl in c_2 solution. The $\Delta(\Delta\phi)$ values, in contrast, depended remarkably on the NH_4Cl concentration when irradiated from c_2 side. This behavior can be explained based on the same idea which explicated the photoresponse of PVC/**1**/valinomycin membrane in the presence of KCl. Namely, the specific adsorption of NH_4^+ ions on the membrane surface facing c_2 solution affected the magnitude of the $\Delta(\Delta\phi)$ values.

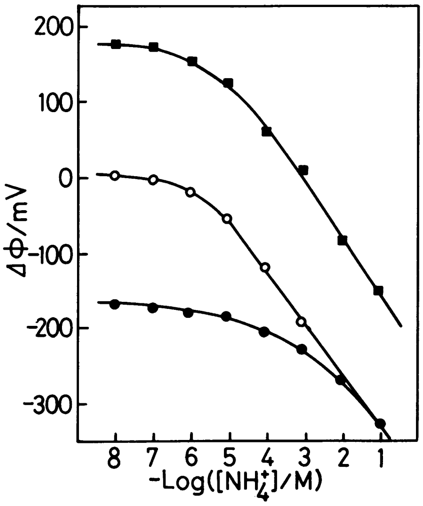

Fig. 7. The membrane potential across the PVC/**1**/nonactin membrane in the presence of NH_4Cl under UV light irradiation from c_1 side (—■—) and c_2 side (—●—) and under visible light from c_2 side (—○—). The concentration of NH_4Cl in the c_1 side solution was zero.

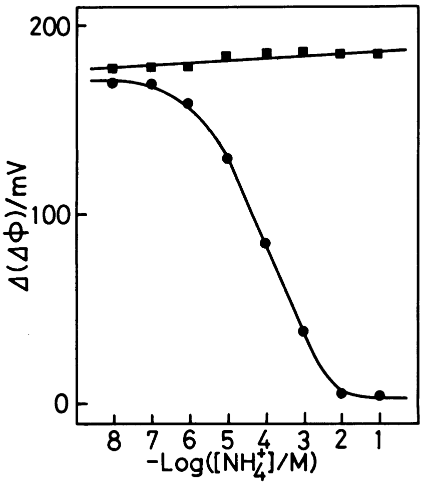

Fig. 8. The effects of NH_4Cl concentration on the $\Delta(\Delta\phi)$ value. The membrane was irradiated from c_1 side (—■—) and c_2 side (—●—). The concentration of NH_4Cl in the c_1 side solution was zero.

Figure 9 shows the $\Delta\phi$ values across the PVC/**1**/nonactin membrane under the conditions that the concentrations of NH_4Cl in c_1 and c_2 solutions are equal with each other. The membrane potentials under visible light or in the dark were always near to zero. UV irradiation from c_1 or c_2 side induced positive or negative shift of the membrane potential, respectively. The $\Delta\phi$ values observed under UV light irradiation drastically depended on the NH_4Cl concentration in the aqueous phase.

We elucidated the effects of nonactin concentration in the membrane on the magnitude of $\Delta(\Delta\phi)$ values in the presence of 10^{-4} M NH_4Cl (Fig. 10). When the nonactin-free membrane was irradiated, more than

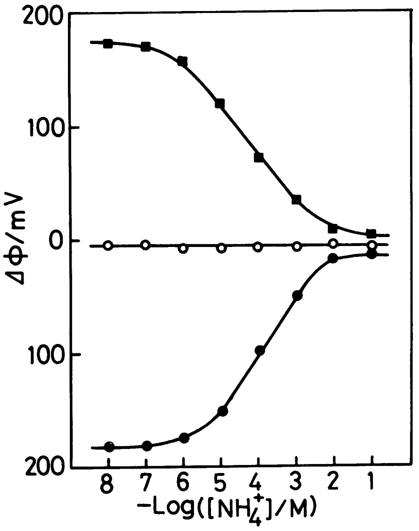

Fig. 9. The asymmetric membrane potential across the PVC/1/nonactin membrane in the presence of NH_4Cl under UV light irradiation from c_1 side (—■—) and c_2 side (—●—) and under visible light (—○—). The concentration of NH_4Cl in both side solutions was equal with each other.

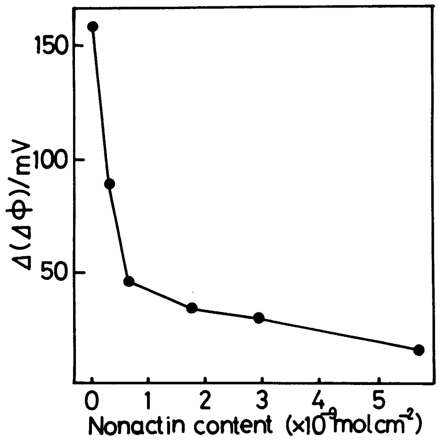

Fig. 10. Effects of nonactin content in the membrane on the photoresponse of the PVC/1/nonactin membrane. The concentration of NH_4Cl in both side solutions was 10^{-4} M.

150 mV of photoinduced potential was observed. On the other hand, the $\Delta(\Delta\phi)$ values lowered to 50 mV or less in the presence of 1×10^{-9}—5×10^{-9} mol cm^{-2} of nonactin in the membrane. This clearly indicates that the formation of nonactin/NH_4^+ ion complexes on the membrane surface has a serious influence on the $\Delta(\Delta\phi)$ values.

In conclusion, the photoresponse in membrane potential across the PVC/1 membranes doped with valinomycin and nonactin drastically depended on the concentration of K^+ and NH_4^+ ions, respectively, in the aqueous solution adjacent to the UV-irradiated surface of the membrane. These membranes may be applicable to the sensitive layer of a novel class of ion sensors which change the $\Delta(\Delta\phi)$ value in response to the concentration of ions such as K^+ and NH_4^+ in the solution.

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