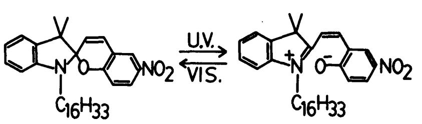
Photo-Excitable Membranes. Effects of Nonactin as a Membrane Additive on the Photoresponse of Poly(vinyl chloride)/ Spirobenzopyran Membrane

Jun-ichi ANZAI, Yasushi HASEBE, Akihiko UENO, and Tetsuo OSA*
Pharmaceutical Institute, Tohoku University, Aobayama, Sendai 980
(Received September 11, 1986)

Synopsis. The magnitude of the photoinduced membrane potential across the poly(vinyl chloride)/spirobenzopyran/nonactin composite membrane depends considerably on the concentration of ammonium ion in the aqueous solution. The results are explained in terms of the charge density on the membrane surface.

Several groups have reported that the membrane potential across the polymer membranes doped with spirobenzopyran derivatives changes reversibly upon photoirradiation.[1-7] We have found that the photoinduced potential changes of more than 100 mV can be attained with rapid response time by the use of plasticized poly(vinyl chloride) (PVC) as a membrane matrix.[5-7] The low density of the fixed charge in the membrane and/or on the membrane surface may be favorable for the enhanced photoresponse. To verify the effects of the charge density on the photoresponse, a macrocyclic ionophore, nonactin, is immobilized in the membrane together with spirobenzopyran derivative (**1**). Since nonactin is an ionophore selective for NH_4^+ ion, it is possible to regulate the charge density on the membrane surface by varying the NH_4Cl concentration in the solution. This paper describes the effects of nonactin as a membrane additive on the photoresponse of the PVC/**1** membrane.



Closed-(1) Open-(1)

Experimental

Materials. PVC (molecular weight of ca. 70000) was obtained from Wako Co. Ltd. and used without further purification. Dibutyl phthalate (DBP), tetrahydrofuran (THF), and ammonium chloride (NH_4Cl) are of extra pure reagent grade. Nonactin was purchased from Fluka Co. The synthetic procedure and analytical data of **1** were reported previously.[7]

Membrane preparation. PVC/**1**/nonactin membrane of ca. 0.15 mm thickness was prepared by pouring the mixture of 250 mg of PVC, 0.5 ml of DBP, 20 mg (0.038 mmol) of **1**, 5 mg (0.007 mmol) 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. The membrane was conditioned by soaking it in 0.1 mM (M=mol dm^{-3}) NH_4Cl solution before use.

Membrane Potential Measurement. All measurements were conducted at 25 °C using a U-shaped glass cell. The composition of the electrochemical cell for the membrane potential measurements was as follows; Ag/AgCl| 0.1 M $(CH_3)_4NCl$| buffer solution (C_1)| PVC/**1**/nonactin membrane| NH_4Cl solution (C_2)| 0.1 M $(CH_3)_4NCl$| Ag/AgCl. The electrode in the C_1 compartment was earthed. All solutions were prepared using 5 mM Britton-Robinson buffer (pH 5.1). 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<$400 nm) and visible ($\lambda>$490 nm) light. Noise level in the potential was within 1 mV under the present experimental conditions.

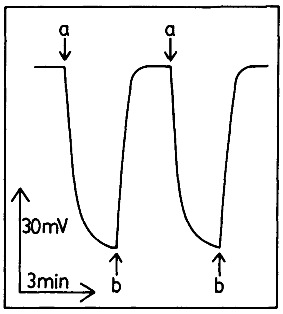


Fig. 1. Photoresponse of the membrane potential across the PVC/**1**/nonactin membrane. The C_2 side solution contained 10^{-5} M NH_4Cl. (a); UV light irradiation and (b); visible light irradiation.

Results and Discussion

A typical photoresponse of the membrane potential across the PVC/**1**/nonactin membrane is depicted in Fig. 1. When the membrane was exposed to UV light, the membrane potential shifted in the negative direction rapidly and, then, the original value of the potential was recovered by the subsequent visible light irradiation. The photoresponse of the membrane potential stems from the photochemical reaction of **1** accompanied with the generation of the fixed charge in the membrane, as was discussed for the PVC/**1** membrane previously.[5-7]

Figure 2 illustrates the membrane potential ($\Delta\phi$) across the PVC/**1**/nonactin membrane in the presence 1×10^{-7}—1×10^{-2} M of NH_4Cl in the C_2 side solution. In the dark, the $\Delta\phi$ values depend linearly on the concentration of NH_4^+ ion in the solution over the range of 1×10^{-5}—1×10^{-2}M, showing that NH_4^+ ions are adsorbed on the membrane surface by forming complexes with nonactin. In other words, the charge density on the membrane surface is determined by the concentration of NH_4^+ ion in the aqueous solution adjacent to the membrane surface. The $\Delta\phi$ values measured under UV light irradiation are also affected by the concentration of NH_4^+ ion in the range of 1×10^{-4}—1×10^{-2} M.

The photoinduced membrane potential ($\Delta(\Delta\phi)$), the difference between the $\Delta\phi$ value under UV light irra-

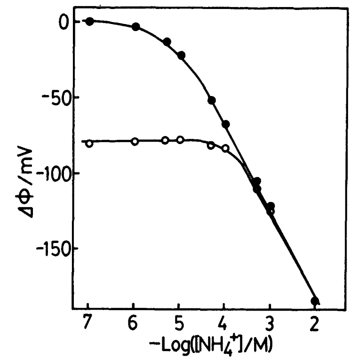


Fig. 2. The membrane potential across the PVC/**1**/nonactin membrane in the presence of NH_4Cl under UV light irradaition (—O—) and in the dark (—●—). The concentration of NH_4Cl in the C_I side solution is zero.

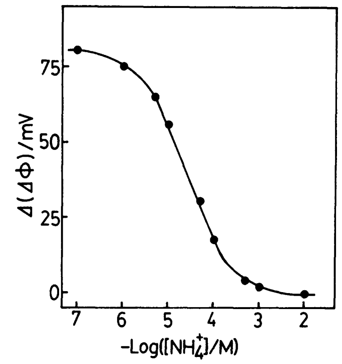


Fig. 3. The effects of the NH_4Cl concentration on the $\Delta(\Delta\phi)$ value.

diation and the one in the dark, is shown in Fig. 3. An approximately linear relationship exists between the $\Delta(\Delta\phi)$ values and the concentration of NH_4^+ ion over the range of 5×10^{-6}—1×10^{-4} M. It is clear that the photoresponse is enhanced in the lower concentration region of NH_4^+ ion. In the case of NH_4^+ ion concentration over 5×10^{-4} M, the photoresponse of the membrane potential is severely suppressed, being only 5 mV or less. This implys that the higher charge density on the membrane surface is not favorable for the enhanced photoresponse.

It is worth noting that these membranes can be applied to the sensitive layer of a novel class of ion sensors which change the $\Delta(\Delta\phi)$ value in response to the concentration of NH_4^+ ion. Furthermore, the membrane may be used for constructing the biosensors by coupling it with microorganisms and enzyme reactions that consume or produce NH_4^+ ion. The development of such biosensors is now in progress in this laboratory.

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 Special Project Research (No.61127003).

References.

1) S. Kato, M. Aizawa, and S. Suzuki, *J. Membr. Sci.*, **1**, 289 (1976).

2) S. Kato, M. Aizawa, and S. Suzuki, *J. Membr. Sci.*, **2**, 39 (1977).

3) I. R. Bellobono, B. Marcandalli, E. Selli, and S. Calgari, *Photogr. Sci. Eng.*, **28**, 162 (1984).

4) M. Irie, A. Menju, and K. Hayashi, *Nippon Kagaku Kaishi*, **1984**, 227.

5) J. Anzai, A. Ueno, and T. Osa, *J. Chem. Soc., Chem. Commun.*, **1984**, 688.

6) J. Anzai, H. Sasaki, A. Ueno, and T. Osa, *Chem. Lett.*, **1985**, 1443.

7) J. Anzai, Y. Hasebe, A. Ueno, and T. Osa, *Kobunshi Ronbunshu*, **43**, 683 (1986).