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Photo-excitable Membranes. Ion-Selective Photoresponse of Poly(Vinyl Chloride)/Spirobenzopyran Membranes Doped with Nonactin and Valinomycin

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The magnitude of the photoinduced membrane potential across poly(vinyl chloride)/spirobenzopyran membranes doped with nonactin or valinomycin depended considerably upon the kind and the concentration of alkali-metal and NH_4^+ cations in the aqueous solution adjacent to the ultraviolet (UV)-irradiated surface of the membrane. The photoresponse was suppressed with increasing concentration of the cations. The ion-selectivity in the potentiometric photoresponse of the nonactin-entrapped membrane was in the order of $NH_4^+ > K^+ > Rb^+ > Cs^+ > Na^+ > Li^+$, whereas the order of selectivity of $Rb^+ > K^+ > Cs^+ > NH_4^+ > Na^+ > Li^+$ was observed for the valinomycin-doped membrane. The results can be explained in terms of the binding abilities of nonactin and valinomycin for alkali-metal and NH_4^+ cations.

Keywords ion-selectivity; photoinduced membrane potential; poly(vinyl chloride)/spirobenzopyran membrane; nonactin; valinomycin

Photochemical regulation of the membrane potential across polymer membranes doped with spirobenzopyran derivatives has been achieved by several groups.[1-6] We have succeeded in greatly improving the photoresponse of 1′-hexadecyl-3′,3′-dimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2′-indoline] (**1**)-containing membrane by the use of plasticized poly(vinyl chloride) (PVC) as a membrane matrix, and we showed that ultraviolet (UV)-irradiation induces membrane potential changes of more than 100 mV with a response time of 1—2 min.[7-10] Recently, we have found that the magnitude of the photoinduced membrane potential across PVC/**1** membranes doped with nonactin or valinomycin depends considerably upon the concentrations of NH_4^+ or K^+ ions when an aqueous solution containing these ions is in contact with the light-irradiated surface of the membrane.[11,12]

The present paper describes the ion-selectivity in the photoresponse of PVC/**1**/nonactin and PVC/**1**/valinomycin membranes and the application of these membranes as the sensitive layers of ion sensors.

Experimental

PVC (polymerization degree 1100; Wako Co., Ltd.) was used without further purification. Di-2-ethylhexyl phthalate (DEHP), tetrahydrofuran (THF), ammonium chloride (NH_4Cl), potassium chloride (KCl), rubidium chloride (RbCl), cesium chloride (CsCl), sodium chloride (NaCl), lithium chloride (LiCl), nonactin, and valinomycin were of extra pure reagent grade. The synthetic procedure and analytical data of **1** were reported elsewhere.[9]

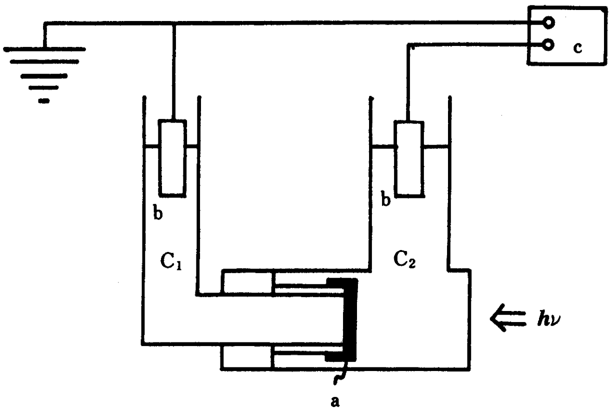


Fig. 1. Schematic Representation of the Cell for Measuring Membrane Potential

a, membrane; b, Ag/AgCl electrode; c, potentiometer.

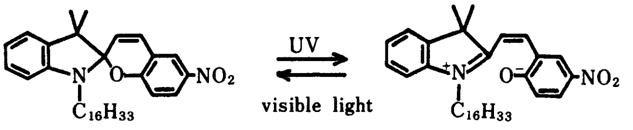
PVC/**1**/nonactin membrane was prepared by pouring the mixture of 250 mg of PVC, 0.5 ml of DEHP, 30 mg of **1**, 5 mg of nonactin and 20 ml of THF onto a flat Petri dish (8.5 cm diameter), and allowing the solvent to evaporate at room temperature. PVC/**1**/valinomycin membrane was prepared in the same manner using 5 mg of valinomycin in place of nonactin. The thickness of the membranes thus prepared was *ca.* 0.15 mm.

Membrane potential measurements were conducted at 25 °C using a U-shaped glass cell as illustrated in Fig. 1. The composition of the electrochemical cell for the membrane potential measurements was as follows: Ag/AgCl | 0.1 M $(CH_3)_4$ NCl | electrolyte solution (C_1) | PVC/**1**/nonactin or PVC/**1**/valinomycin membrane | electrolyte solution (C_2) | 0.1 M $(CH_3)_4$-NCl | Ag/AgCl. The electrode in the C_1 compartment was earthed. The pH of the solution was regulated at 6.0 with HCl. Photoirradiation was carried out from the C_2 side. The light source was a 500 W xenon lamp (Ushio Electric Inc.) and cut-off filters (Toshiba UV-D35 and O-55) were employed for isolating UV ($320\,\text{nm} < \lambda < 400\,\text{nm}$) and visible ($\lambda > 550\,\text{nm}$) light, respectively. Noise level was *ca.* ±1 mV under the present experimental conditions.

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 and open forms.[7-10] 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**. Thus, under UV-irradiation, the content of the open form of **1** is higher on the irradiated surface than that on the unirradiated surface of the membrane (*i.e.*, the membrane becomes asymmetric with respect to the charge density).

Figure 2 illustrates a typical photoresponse of the membrane potential, $\Delta\phi = \phi_{c1} - \phi_{c2}$, induced by alternate UV and visible light irradiation of the PVC/**1**/nonactin mem-



1 (closed) **1** (open)

Chart 1

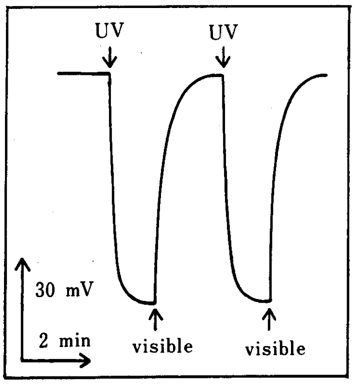


Fig. 2. Typical Photoresponse of the Membrane Potential across the PVC/**1**/Nonactin Membrane

C_1 side: the concentration of NH_4Cl was zero. C_2 side: 10^{-5} M NH_4Cl.

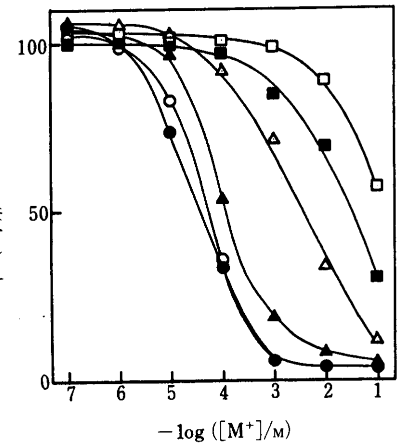


Fig. 3. The Photoinduced Membrane Potential across the PVC/**1**/Nonactin Membrane in the Presence of Alkali-Metal and NH_4^+ Ions

C_1 side: the concentration of alkali-metal and NH_4^+ ions was zero. C_2 side: NH_4^+ (—●—), K^+ (—○—), Rb^+ (—▲—), Cs^+ (—△—), Na^+ (—■—), Li^+ (—□—). The pH of the solutions was adjusted to 6.0.

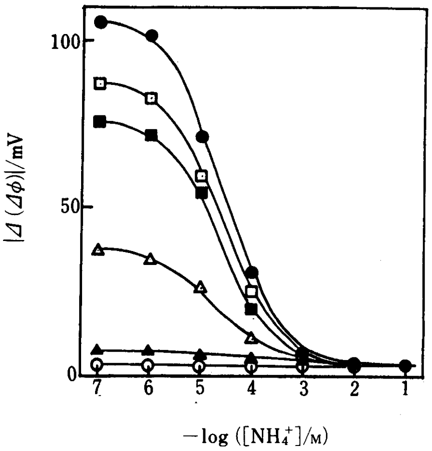


Fig. 4. The Photoinduced Membrane Potential across the PVC/**1**/Nonactin Membrane in the Solution Containing both NH_4^+ and Interfering Ions

Interfering ion of C_2 side (10^{-2} M): none (—●—), K^+ (—○—), Rb^+ (—▲—), Cs^+ (—△—), Na^+ (—■—), Li^+ (—□—). C_1 side: the concentration of alkali-metal and NH_4^+ ions was zero.

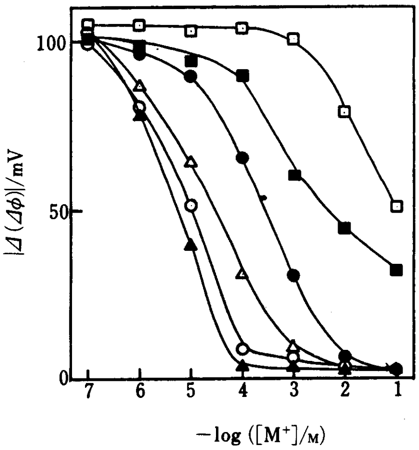


Fig. 5. The Photoinduced Membrane Potential across the PVC/**1**/Valinomycin Membrane in the Presence of Alkali-Metal and NH_4^+ Ions

C_1 side: the concentration of alkali-metal and NH_4^+ ions was zero. C_2 side: NH_4^+ (—●—), K^+ (—○—), Rb^+ (—▲—), Cs^+ (—△—), Na^+ (—■—), Li^+ (—□—).

brane in the presence of NH_4^+ ion in the C_2 side solution.[11] When the membrane was exposed to UV light, the membrane potential shifted in the negative direction, and reached a maximum value within 1—2 min. The original potential was recovered within 2 min by subsequent visible light irradiation. A similar photoresponsive behavior was observed for the PVC/**1**/valinomycin membrane in the presence of K^+ ion.[12]

Figure 3 plots the magnitude of the photoinduced potential change, $\Delta(\Delta\phi)$ = membrane potential under visible light − membrane potential under UV light, across the nonactin doped-PVC/**1** membrane in the presence of alkali-metal and NH_4^+ cations in the C_2 side solution. Photoinduced potentials of about 100 mV, for all cases, were induced in the lower concentration region of the cations, whereas the $\Delta(\Delta\phi)$ value was suppressed with increasing concentration of the cations. An approximately linear relationship existed between the $\Delta(\Delta\phi)$ value and the ionic concentration over the range of 10^{-6}—10^{-3} M NH_4^+ ion, but above 10^{-3} M, the photoresponse was suppressed, with the values smaller than 5 mV. The suppression of the photoresponse of the membrane potential is attributable to the enhanced ion density on the irradiated surface of the membrane, arising from the complex formation between NH_4^+ ion and nonactin at the membrane surface.[11,12] Similar dependency was observed in the cases of K^+ and Rb^+ ions. The calibration curves obtained for Cs^+, Na^+ and Li^+ ions showed the dynamic ranges to be in the higher concentration regions of the cations. The different calibration curves should reflect the binding abilities of the ions to nonactin. The specific adsorption of cations on the membrane surface exposed to UV light affected the magnitude of $\Delta(\Delta\phi)$ value. Namely, because of the increase of the charge density on the irradiated surface of the membrane, the addition of H^+ to the photo-generated open form of **1** may be suppressed. Another possible explanation is that the contribution of surface potential changes associated with the photochemical reaction of **1** is partially cancelled out by the enhanced charge density resulting from the specific adsorption of cations at the surface of the membrane.

The potentiometric ion-selectivity coefficients of the NH_4^+ ion-selective membrane, $K^{pot}_{NH_4^+,M^+}$, were estimated using Eq. 1,

$$K^{pot}_{NH_4^+,M^+} = a_{NH_4^+}/a_{M^+} \tag{1}$$

Table I. Selectivity Coefficients of PVC/**1**/Nonactin Membrane

Selectivity coefficient	Interfering cations					
	Li^+	Na^+	K^+	Rb^+	Cs^+	NH_4^+
$K^{pot}_{NH_4^+,M^+}$	2.5×10^{-4}	1.7×10^{-3}	5.4×10^{-1}	1.1×10^{-1}	1.6×10^{-2}	1.0

The $a_{NH_4^+}$ and a_{M^+} values which afford $\Delta(\Delta\phi) = 70\,mV$ were used to calculate the $K^{pot}_{NH_4^+,M^+}$ values.

Table II. Selectivity Coefficients of PVC/**1**/Valinomycin Membrane

Selectivity coefficient	Interfering cations					
	Li^+	Na^+	K^+	Rb^+	Cs^+	NH_4^+
$K^{pot}_{K^+,M^+}$	1.2×10^{-4}	4.6×10^{-3}	1.0	1.6	4.6×10^{-1}	3.7×10^{-2}

The a_{K^+} and a_{M^+} values which afford $\Delta(\Delta\phi) = 70\,mV$ were used to calculate the $K^{pot}_{K_4^+,M^+}$ values.

where $a_{NH_4^+}$ and a_{M^+} denote the concentrations of NH_4^+ and interfering M^+ ions, respectively, which afford an identical $\Delta(\Delta\phi)$ value. The potentiometric ion-selectivity of the conventional type of ion sensors can be estimated based on similar expression.[13)] Table I shows the selectivity coefficients of the PVC/**1**/nonactin membrane. The magnitude of selectivity ratio of NH_4^+ for alkali-metal cations, which corresponds to the cation-binding abilities of nonactin, was in the order of $K^+ > Rb^+ > Cs^+ > Na^+ > Li^+$. This tendency was in line with that observed for an NH_4^+ ion-selective electrode in which nonactin entrapped PVC membrane was used as the sensitive phase.[14)]

Figure 4 shows the calibration curves measured with the solutions containing both NH_4^+ and interfering cations, keeping the background concentration of interfering cations at 10^{-2} M. In the lower concentration region of NH_4^+ (10^{-7}—10^{-3} M), the photoresponse was drastically affected by the kind of interfering cations. When the interfering cations were K^+ and Rb^+, the $\Delta(\Delta\phi)$ values were depressed below 10 mV irrespective of the concentration of NH_4^+. On the other hand, the useful calibration curves were obtained in the presence of background Li^+, Na^+ and Cs^+ ions. These results suggest that this system is applicable to photo-assisted potentiometric sensing for NH_4^+ ion even in the presence of interfering Li^+ and Na^+ ions.

The ion-selectivity in photoresponse of the PVC/**1**/valinomycin membrane was elucidated in a similar manner (Fig. 5). The photoinduced potential decreased almost linearly with the concentration of K^+ and Rb^+ ions over the concentration range of 10^{-7}—10^{-4} M. On the other hand, the $\Delta(\Delta\phi)$ values were 90—100 mV in the presence of 10^{-7}—10^{-4} M Na^+ and Li^+ ions. This can be explained similarly to the photoresponse of PVC/**1**/nonactin membrane. Namely, the cation-binding ability of valinomycin for the cations was solely responsible for the $\Delta(\Delta\phi)$ value.

The selectivity coefficients of the PVC/**1**/valinomycin membrane are listed in Table II. Selectivity was in the order of $Rb^+ > K^+ > Cs^+ > NH_4^+ > Na^+ > Li^+$, which is similar to that reported for K^+ ion-selective electrodes based on valinomycin-doped PVC membrane.[15—18)]

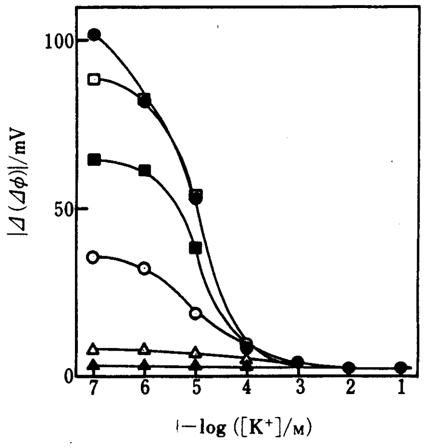


Fig. 6. The Photoinduced Membrane Potential across the PVC/**1**/Valinomycin Membrane in the Solution Containing both K^+ and Interfering Ions

Interfering ion of C_2 side (10^{-3} M): none (—●—), NH_4^+ (—○—), Rb^+ (—▲—), Cs^+ (—△—), Na^+ (—■—), Li^+ (—□—). C_1 side: the concentration of alkali-metal and NH_4^+ ions was zero.

Figure 6 shows the photoresponse across the PVC/**1**/valinomycin membrane in the presence of 10^{-7}—10^{-1} M KCl in the C_2 side solution, with and without 10^{-3} M interfering cations. The $\Delta(\Delta\phi)$ values in the range of 10^{-7}—10^{-5} KCl depended markedly on the species of the interfering cations, whereas over 10^{-3} M KCl, the photoresponse was negligibly affected by the cations, being suppressed by less than 10 mV in all cases. These results suggest that the PVC/**1**/valinomycin membrane can be used for the determination of K^+ ion in the presence of interfering Li^+ and Na^+ ions.

In conclusion, these membranes are applicable to a novel class of ion sensors which exhibit a change of the $\Delta(\Delta\phi)$ value in response to the concentration of ions such as NH_4^+ and K^+ in aqueous solution. It is interesting that higher output signals, $\Delta(\Delta\phi)$, could be obtained for sample solutions of lower ionic concentration. This indicates the applicability of the sensor for the determination of rather low concentration samples. Another important characteristic of the present system is that the sensor can be switched on and off by means of a light signal. This property enables us to use the membranes in constructing a new type of signal transducing system which responds to both chemical (ion) and physical (light) signals.

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