CHEMISTRY LETTERS, pp. 1443-1446, 1985.

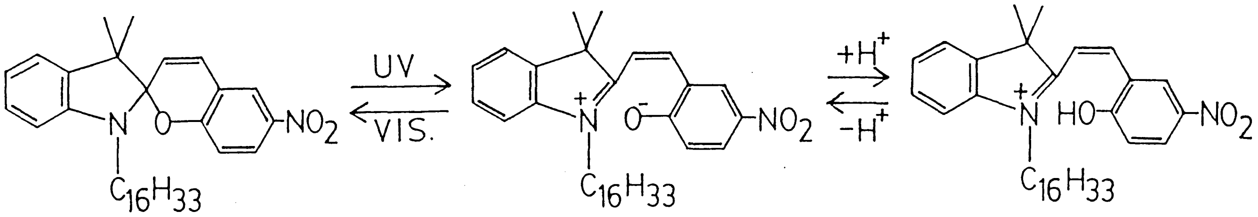
PHOTOCHEMICALLY-INDUCED ASYMMETRIC MEMBRANE POTENTIAL ACROSS POLY(VINYL CHLORIDE)/SPIROBENZOPYRAN MEMBRANES

Jun-ichi ANZAI, Hiroshi SASAKI, Akihiko UENO, and Tetsuo OSA*
Pharmaceutical Institute, Tohoku University,
Aobayama, Sendai 980

The membrane potential across poly(vinyl chloride)/spirobenzopyran (1) membrane changed reversibly by UV and visible light irradiation even when no concentration gradient of electrolyte existed between two external solutions separated by the membrane. The photoresponse of the membrane potential strongly depended on the 1 content of the membranes. The results are explained in terms of formation of asymmetric membrane, namely the opened-1:closed-1 ratios of the two surfaces of the membrane were different from each other under UV light.

We have been interested in the reversible control of membrane characteristics such as ion permeability and membrane potential using polymer membranes. We have already reported that the ion permeability and the membrane potential across the poly(vinyl chloride) (PVC) membranes containing azobenzene-modified crown ethers change reversibly upon photoirradiation.[1)] Photochemical transformation of spirobenzopyran derivatives between closed-form and opened-form has been utilized in order to regulate the membrane potential by Kato et al.,[2)] Irie et al.,[3)] and us.[4)] We have found that the photoresponse of the spirobenzopyran membrane is highly improved by the use of plasticized PVC as a membrane matrix.[4)] The present paper will focus on the photoinduced potential changes across the PVC/spirobenzopyran (1) membranes observed under the conditions that no concentration gradient of electrolyte existed between the two aqueous solutions, i.e., an asymmetric membrane potential.

Closed-1 was obtained by the reaction of 5-nitrosalicylaldehyde with 1-hexa-



Closed-1 Opened-1

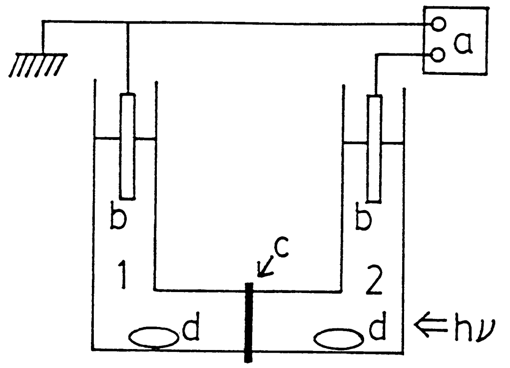


Fig. 1.
Schematic representation of the cell for membrane potential measurements.

a) Potentiometer,
b) saturated calomel electrodes,
c) PVC/1 membrane,
d) stirring bars.

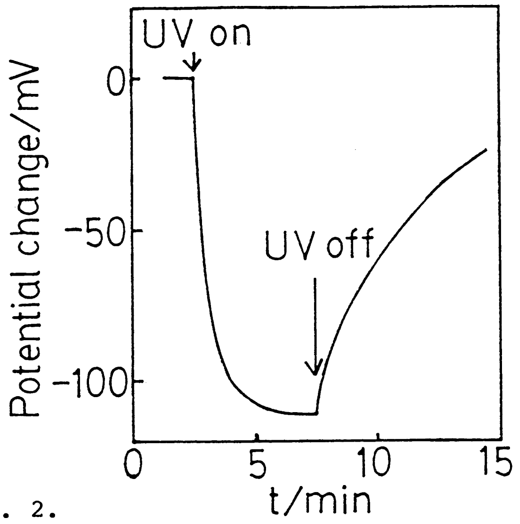


Fig. 2.
Asymmetric membrane potential upon UV light irradiation from c_2 side.

Membrane thickness is ca. 0.1 mm. NaCl concentrations are 1000 mM for both solutions. The content of 1 in the membrane is 0.30 mg/cm^2.

decyl-2,3,3-trimethylindolenium bromide according to the reported procedure.$^{5)}$ The typical procedure for preparing the membrane of ca. 0.1 mm thickness was that the solution, which contained 233 mg of PVC, 0.53 ml of di-n-butyl phthalate, 20 ml of tetrahydrofuran, and an appropriate amount of closed-1, was poured onto a flat Petri-dish (9.2 cm diameter) and the solvent was allowed to evaporate. The compound 1 exhibited normal photochromism in the membrane: a closed-form (colorless) under visible light and an opened-form (purple) under UV light irradiation. The absorption maximum of opened-1 in the membrane was found at 578 nm. The composition of the electrochemical cell for the membrane potential measurements was as follows: $Hg_2Cl_2(s)|Hg|KCl$ (sat.)$|$0.1 M $(CH_3)_4NCl$, NaCl solution $(c_1)|$PVC/1 membrane$|$NaCl solution (c_2), 0.1 M $(CH_3)_4NCl|KCl$ (sat.) $Hg_2Cl_2|Hg$ (M=mol·dm^{-3}). The electrode in the c_1 solution was earthed (Fig. 1). NaCl concentration in the solution c_1 was equal to that of c_2 in this study. 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.

Figure 2 illustrates the potential changes across the PVC/1 membrane induced by UV irradiation. After a potential difference at a steady state, $\Delta\psi_{VIS}$, had been obtained under visible light illumination, a negative shift of the potential was induced by UV light irradiation from the c_2 side. About 3 min sufficed to reach a steady state potential under UV light, $\Delta\psi_{UV}$, and, when the light was switched off, the membrane potential decayed with a half life of ca. 3.5 min. It is clear that the potential shifts arise from the change in the fixed charge density of the membrane.$^{2)}$

The membrane potential changes induced by alternate UV and visible light irradiation are shown in Fig. 3. When the membrane surface facing the c_2 compartment was exposed to UV light, the membrane potential shifted negatively and then the initial potential was recovered rapidly by visible light irradiation. On

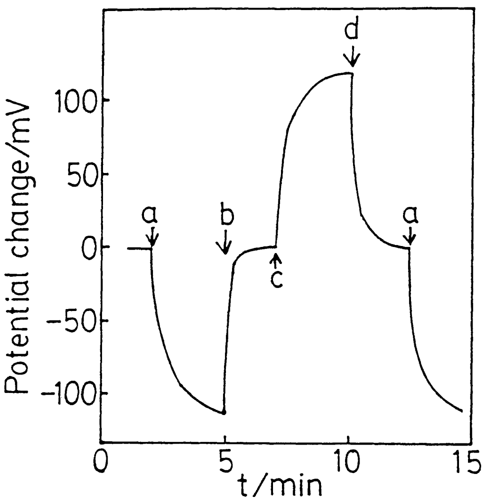


Fig. 3.
Photoresponse of the membrane potential upon UV and visible light irradiation.

The thickness and 1 content of the membrane are the same as that used in Fig. 2. NaCl concentrations are 1000 mM for both solutions.
a) UV light irradiation from c_2 side,
b) visible light irradiation from c_2 side,
c) UV light irradiation from c_1 side,
d) visible light irradiation from c_1 side.

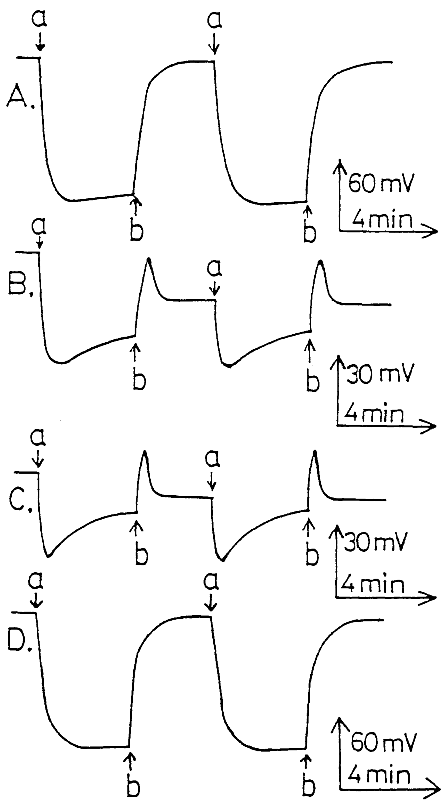


Fig. 4.
Biphasic behavior of the photoresponse.

Membrane thickness, 0.1 mm (A, B, and C) and 0.2 mm (D). The contents of 1 in the membranes are 0.30 mg/cm^2 (A), 0.15 mg/cm^2 (B), and 0.11 mg/cm^2 (C). The composition of the membrane D is the same as that of the memrane B. Irradiation was performed from c_2 side with UV(a) and visible(b) light.

the other hand, the polarity of the photoresponse was reversed when irradiated from c_1 side.

In relation to the photoresponse of the PVC/1 membrane illustrated in Figs. 2 and 3, we emphasize that the photoinduced potential changes were observed under the conditions that no concentration gradient of NaCl existed between the two aqueous solutions. It is well established that the membrane potential should be zero when the charged membrane is placed between two 1:1 electrolyte solutions having the same activity.$^{6)}$ In our case, the membrane potential, in fact, showed the value near to zero at c_1=c_2=1000 mM under visible light, where 1 assumed wholly the closed-form. The membrane potential induced by UV irradiation in spite of c_1=c_2 may originate from the unequal distribution of the fixed charge in the direction of membrane thickness, i.e. an asymmetric membrane.$^{7)}$ In other words, the opened-1:closed-1 ratios of the two surfaces of the membrane are different from each other under UV light. The photochemical reaction of 1 from closed-form to opened-form seems to proceed more efficiently on the irradiated surface of the membrane than that on the opposite surface. This inevitably establishes the situation that the surface potential at the membrane/solution interface facing the light source is different from that of the opposite side due to the difference in charge density, which depends on the content of charged species (opened-1), between the two membrane surfaces. Thus the potential changes illustrated in Figs. 2 and 3 can be ascribable to the asymmetric membrane formation with respect to the opened-1 content under UV light.

We can find a further evidence for the formation of asymmetric membranes in Fig. 4, which depicts the remarkable dependence of the photoresponsive behavior on the content of 1 in the membrane. When the membrane with a higher content of 1 was irradiated by UV light (Fig. 4-A), the membrane potential shifted nearly exponentially to reach a steady state value after ca. 3 min, and then the further potential shift was small even under the prolonged irradiation. The time response of the membrane potential upon visible light irradiation is also quasi exponential. In contrast, when the membranes with lower contents of 1 were exposed to UV light (Figs. 4-B and 4-C), the time response of the potential was not exponential but biphasic. The membrane potential showed the rapid negative shift followed by the gradual recovery. The biphasic behavior of the potential change was also observed upon visible light irradiation presumably due to the uneven decoloring of the membrane. The thicker membrane did not exhibit the biphasic behavior because of the lower transparency (Fig. 4-D). These observations strongly suggest that the photoresponse of the membrane potential was composed of two surface potential changes occurring independently at the both sides of the membrane, i.e., the irradiated and the opposite membrane/solution interfaces. The value of $\Delta\psi_{UV}-\Delta\psi_{VIS}$ became small under the prolonged irradiation in the case of Fig. 4-C, suggesting that the opened-1 content of the irradiated surface of the membrane is close to that of the opposite surface presumably due to the improved transparency for UV light of the membrane. Thus, we have shown that the asymmetric membrane potential is induced across the PVC/1 membranes under UV light. Further studies on the exact mechanism of the photoresponse are currently in progress in this laboratory.

This work was supported in part by a Grant-in-Aid for Co-operative Research (No.59390012) from the Ministry of Education, Science and Culture of Japan.

References

1) J.Anzai, A.Ueno, H.Sasaki, K.Shimokawa, and T.Osa, Makromol.Chem., Rapid Commun., 4, 731(1983); J.Anzai, H.Sasaki, A.Ueno, and T.Osa, J.Chem.Soc., Chem.Commun., 1983, 1045; J.Anzai, H.Sasaki, A.Ueno, and T.Osa, Chem.Lett., 1984, 1205; and references cited therein.
2) S.Kato, M.Aizawa, and S.Suzuki, J.Membr.Sci., 1, 289(1976); S.Kato, M.Aizawa, and S.Suzuki, ibid., 2, 39(1977); S.Kato, M.Aizawa, and S.Suzuki, Kobunshi Ronbunshu, 34, 793(1977).
3) M.Irie, A.Menju, and K.Hayashi, Nippon Kagaku Kaishi, 1984, 227.
4) J.Anzai, A.Ueno, and T.Osa, J.Chem.Soc., Chem.Commun., 1984, 688.
5) T.Shimizu and M.Yoshikawa, J.Membr.Sci., 13, 1(1983).
6) G.Scatchard, J.Am.Chem.Soc., 75, 2883(1953); J.W.Lorimer, E.I.Boterenbrood, and J.J.Hermans, Discuss. Faraday Soc., 21, 141(1956); Y.Kobatake, Y.Toyoshima, and N.Takeguchi, J.Phys.Chem., 70, 1187(1966).
7) A.M.Liquoli and C.J.Botre, J.Phys.Chem., 71, 3765(1967); S.Ohki, J.Colloid Interface Sci., 37, 318(1971); N.Kamo and Y.Kobatake, ibid., 46, 85(1974); M.Nakagaki and R.Takagi, Chem.Pharm.Bull., 32, 3812(1984).

(Received May 16, 1985)