Photo-induced Potential Changes across Poly(vinyl chloride)–Crown Ether Membranes

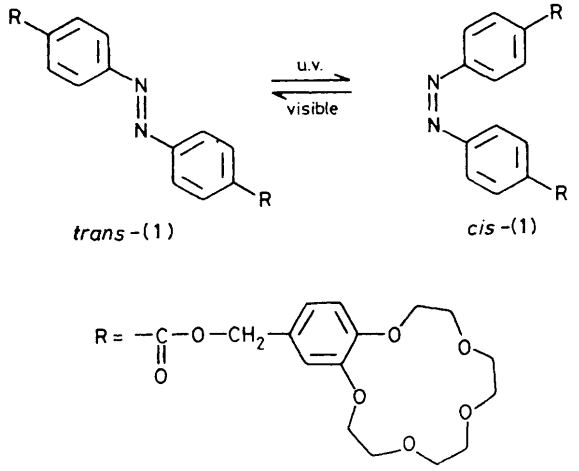
Jun-ichi Anzai, Hiroshi Sasaki, Akihiko Ueno, and Tetsuo Osa*

Pharmaceutical Institute, Tohoku University, Aobayama, Sendai 980, Japan

The potential across a plasticized poly(vinyl chloride) membrane entrapping a crown ether was reversibly controlled by photoirradiation in the presence of potassium ions.

In the process of vision, potential changes in the photoreceptor cell membrane resulting from ion-permeability changes play an important role in the conversion of light signals into neural impulses.[1] In this connection, pigmented lipid membranes have been studied as model systems by many researchers,[2,3] but no report has appeared on synthetic polymer membrane systems. We report here some preliminary results on photo-induced membrane potential changes obtained using a plasticized poly(vinyl chloride) (PVC) membrane containing a photo-responsive crown ether (**1**) as the ionophore.

The membrane of *ca.* 0.1 mm thickness was prepared by pouring a solution, which contained 235 mg of PVC, 0.54 ml of di-n-butyl phthalate, 5.4 mg of *trans*-(**1**), and 20 ml of tetrahydrofuran, onto a rimmed glass plate (9.2 cm diameter) and allowing the solvent to evaporate. With this membrane, acceleration of the permeation rate on u.v. irradiation was observed with K^+ but not with Na^+.[4] The phenomenon may



be explained in terms of the enhancement of the K^+ flux in the membrane associated with the binding ability of (**1**) for the cation at the membrane–solution interface by forming a sandwich type (**1**)–K^+ complex. The composition of the electrochemical cell for the membrane potential measurements was as follows; Hg_2Cl_2(s),Hg|KCl(sat.)|0.1 M NH_4NO_3| electrolyte solution(c_1)|membrane|electrolyte solution(c_2)| 0.1 M NH_4NO_3|KCl (sat.)|Hg_2Cl_2(s), Hg. The electrode in the lower concentration compartment was earthed.

Repeated reversible *trans–cis* isomerization was achieved by using u.v. and visible light alternately, the *cis* content being about 55% after u.v. irradiation, Figure 1(b). The membrane potential changes induced by irradiation in the presence of NaCl or KCl are also illustrated, Figure 1(a). After a steady state potential difference $\Delta\phi$ had been obtained in the dark, a negative shift of the membrane potential was induced by irradiation ($320 < \lambda < 380$ nm). About 15 min was required to attain a steady state potential under u.v. irradiation and the initial potential was recovered rapidly by visible irradiation ($\lambda > 410$ nm). With regard to the photo-responsive behaviour of the membrane, two important aspects should be noted. First, the photo-induced membrane potential changes were entirely synchronized with the absorption change at 331 nm of the membrane, *i.e.*, *trans–cis* isomerization of (**1**) in the membrane. Secondly, a marked dependence of the potential changes on the cation species was observed. U.v. irradiation resulted in a membrane potential shift of -7 mV in the presence of KCl, whereas no significant change [$\Delta(\Delta\phi) < -1$ mV] was induced in the presence of NaCl. The exact mechanism by which the permselectivity and potential of neutral carrier-based PVC membranes are determined is still not clear in spite of the intensive investigation of such membranes, especially for cation selective electrodes.[5,6] However, the present result suggests that the enhanced K^+ flux in the membrane, which stems from the increase in K^+ uptake at the

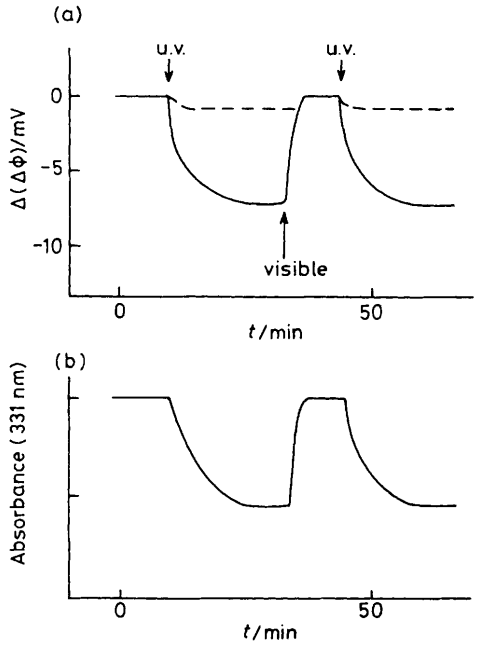


Figure 1. (a) Photo-response of the membrane potential; alternate u.v. and visible light irradiation [c_1 = 1 mM, c_2 = 500 mM NaCl (– – –) or KCl (——)]. (b) Change in absorbance at 331 nm of the membrane.

membrane–solution interface by the irradiated *cis*-form of (**1**), is the origin of the photo-induced potential changes.

The photo-induced potential change depends on the concentration ratio of KCl in c_1 and c_2 ($\gamma = c_2/c_1$; c_1 was always fixed at 1 mM), being significant in the higher γ value region; a change of 8 mV was attained at $\gamma = 1000$ whereas the potential change was only 2 mV at $\gamma = 10$. This result also suggests that the enhancement of K^+ flux in the membrane by irradiation exerts a significant influence on the potential.

Thus, we have shown that the changes of membrane potential are induced by photo-irradiation by use of a neutral carrier-based PVC membrane.

Received, 4th July 1983; Com. 891

References

1 D. A. Baylor and M. G. Fuorters, *J. Physiol. (London)*, 1970, **207**, 77.
2 J. S. Huebner, *Biochim. Biophys. Acta*, 1975, **406**, 178.
3 D. F. O'Brien, *Photochem. Photobiol.*, 1978, **29**, 679.
4 J. Anzai, A. Ueno, H. Sasaki, K. Shimokawa, and T. Osa, *Makromol. Chem., Rapid Commun.*, submitted for publication.
5 A. P. Thoma, A. V. Nauer, S. Arvanitis, W. E. Morf, and W. Simon, *Anal. Chem.*, 1977, **49**, 1567.
6 R. P. Buck, *Anal. Chem.*, 1978, **50**, 17R.