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Photoinduced Potential Changes across Poly(vinyl chloride)/Crown Ether Membranes. Membrane Potential in the Presence of Alkaline Earth Metal Cations

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Synopsis. The potential change across poly(vinyl chloride)/crown ether membrane was induced by photoirradiation in the presence of alkaline earth metal cations. The photoresponse of the membrane potential depended markedly on the kind and concentration of the cation species, the magnitude of the potential shift lying in the order of $Mg^{2+}>Ca^{2+}\approx Sr^{2+}>Ba^{2+}$.

We[1–3] and Shinkai *et al.*[4–8] have reported independently that the cation binding and transporting properties of azobenzene-modified crown ethers are successfully regulated by photoirradiation. Recently, we have found that the potential across the poly(vinyl chloride) (PVC)/4,4′-bis[3,4-(1,4,7,10,13-pentaoxatridecane-1,13-diyl)benzyloxycarbonyl]azobenzene (**1**) membrane changes reversibly upon alternate UV and visible light irradiation in the presence of alkali metal chloride.[9–11] The photoresponse of the membrane potential has been explicated based on the surface potential changes originating from the enhanced uptake of the alkali metal cation onto the membrane surface by photogenerated *cis*-**1**. The purpose of this note is to describe a different aspect in the photoresponse of the potential across PVC/**1** membrane with alkaline earth metal chloride.

Experimental

Materials. PVC (molecular weight of *ca.* 70000) was purchased from Wako Pure Chemical Industry Ltd. and used without further purification. Dibutyl phthalate (DBP), tetrahydrofuran (THF), and alkaline earth metal chloride are of extra pure reagent grade. The synthetic procedure and analytical data of **1** were reported previously.[2,3]

Membrane Preparation. PVC/**1** membrane of *ca.* 0.1 mm thickness was prepared by pouring the mixture of 235 mg of PVC, 0.54 ml of DBP, 1.3 mg of **1**, and 20 ml of THF onto a flat Petri dish (9.2 cm diameter) and allowing the solvent to evaporate.

Membrane Potential Measurement. All measurements were conducted at 25 °C. The composition of the electrochemical cell for the membrane potential measurements was as follows; Hg, $Hg_2Cl_2(s)|KCl(sat.)|0.1\ mol\ dm^{-3}\ (CH_3)_4NCl|$ electrolyte solution $(c_1)|$PVC/**1** membrane| electrolyte solution $(c_2)|0.1\ mol\ dm^{-3}\ (CH_3)_4NCl|KCl(sat.)|Hg_2Cl_2(s)$, Hg. The electrode in the c_1 compartment was earthed. Photoirradiation was carried out with 500 W xenon lamp with cut-off filters Toshiba UV D-35 and Corning 3-74 to isolate UV ($320\ nm<\lambda<400\ nm$) and visible ($\lambda>410\ nm$) light, respectively.

Results and Discussion

In the previous papers[9–11] we have reported that the membrane potential across PVC/**1** membrane interposed between two alkali metal chloride solutions changes upon photoirradiation. The magnitude and sign of the photoinduced potential shift, $\Delta(\Delta\Phi)$, were dependent on the kind and concentration of the cations, **1** content in the membrane, and the direction from which the membrane was irradiated. The photoresponsive behavior of the membrane potential was explained based on the surface potential change of the membrane, which was caused by the charge density change of the membrane surface through the photoinduced variation in the binding ability of **1** for alkali metal cations. The photoresponse was presumed to arise from the formation of sandwich-type complexes in which *cis*-**1** trapps a cation by its two crown-ether moieties.

Figure 1 illustrates the photoresponse of the membrane potential in the presense of $MgCl_2$. After a steady state potential difference, $\Delta\Phi$, had been reached under dark conditions, a negative shift of the potential was induced upon UV irradiation from the c_2 compartment

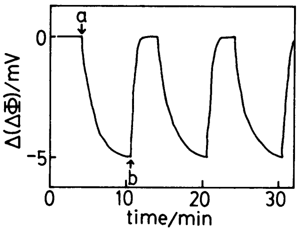


Fig. 1. Photoresponse of the membrane potential upon alternate UV (a) and visible (b) light irradiation. c_1; $[MgCl_2]=1\times10^{-3}$ mol dm^{-3}. c_2; $[MgCl_2]=5\times10^{-1}$ mol dm^{-3}.

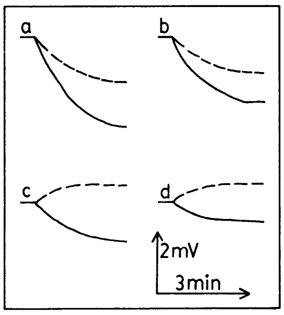
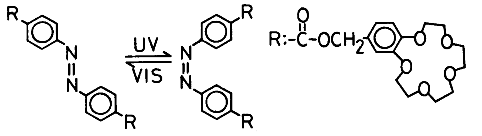


Fig. 2. Effect of the ionic concentration on the photoresponse in the presence of $MgCl_2$. Photoirradiation was conducted from c_1 (----) and c_2 (——) compartment sides. c_1; $[MgCl_2]=1\times10^{-2}$ (a), 1×10^{-1} (b), 5×10^{-1} (c), 1 (d) mol dm^{-3}. c_2; $[MgCl_2]=$ 1 mol dm^{-3}.

side. About 6 min sufficed to attain a steady state potential under UV light and the initial potential was recovered rapidly by switching the UV light to the visible one. The on-off cycle of the membrane potential was fairly reversible.

The effect of the ionic concentration on the photoresponse of the potential was examined by irradiating the membrane from the direction c_1 or c_2 compartment side. When the membrane was irradiated by UV light from the direction of c_2 compartment, the negative shift of the potential was always induced. The $\Delta(\Delta\Phi)$ values related closely to the ionic concentration in c_1 compartment. Larger $\Delta(\Delta\Phi)$ values were obtained in the case that the concentration gradient between the two solutions was increased. Even when the concentration gradient was zero ($c_1=c_2=1$ mol dm^{-3}), the potential shift was observed. On the other hand, the photoresponse was not simple when the membrane surface facing the compartment with a lower electrolyte concentration (c_1) was exposed to UV light. Under the conditions that the concentration gradient between the two electrolyte solutions was large, the membrane potential shifted to the negative direction (Figs. 2-a and 2-b). On the contrary, the positive shift of the potential was observed when the concentration gradient was small (Fig. 2-c). In the case of $c_1=c_2=1$ mol dm^{-3} (Fig. 2-d), the $\Delta(\Delta\Phi)$ value was equal in magnitude but opposite in sign to that obtained by irradiating from the c_2 side. This photoresponsive behavior was much the same as that observed for alkali metal cations.[9–11] We can explained the phenomena similarly to the case of alkali metal cations, that is, (i) the membrane potential changes are resulting from the fact that the charge density of the membrane surface (*i.e.*, surface potential) is perturbed by the photoinduced change in the binding ability of **1** for cations, (ii) the magnitude of the charge density changes of the membrane surface is determined by both factors of *trans*-**1**/*cis*-**1** ratio at the membrane surface and the ionic concentration in the solution, (iii) the *trans*-**1**/*cis*-**1** ratio at one surface of the membrane is different from that of the opposite surface under UV light. The third argument can be the reason why the membrane potential changed even when no concentration gradient existed between the two solutions.



trans-1 cis-1

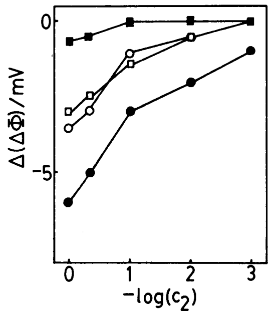


Fig. 3. Effect of the ionic concentration on the potential shift.

c_1; [Metal chloride]$=1\times10^{-3}$ mol dm^{-3}.

■; $BaCl_2$, □; $SrCl_2$, ○; $CaCl_2$, ●; $MgCl_2$.

Figure 3 shows the photoresponse for $MgCl_2$, $CaCl_2$, $SrCl_2$, and $BaCl_2$. In the high c_2/c_1 regions, the larger $\Delta(\Delta\Phi)$ values were obtained for all salts. The magnitude of the $\Delta(\Delta\Phi)$ values lies in the order of $MgCl_2>CaCl_2\approx SrCl_2>BaCl_2$. This dependence of $\Delta(\Delta\Phi)$ values on the kind of cation species does not coincide with the order expected from the fitness between each cation and *cis*-**1**; the diameters of Mg^{2+} and Ca^{2+} (1.22 Å and 1.98 Å, respectively) seem too small to form the sandwich-type complex, but the size of Ba^{2+} is appropriate (2.70 Å).[12] The data are incompatible with those obtained for alkali metal cations, where larger $\Delta(\Delta\Phi)$ values were observed for K^+ and Rb^+ which have suitable ionic sizes to form stable sandwich-type complexes with *cis*-**1**. Considering from these facts, any other factors, though not clear in the present stage, may participate in determining the binding ability of **1** for alkaline earth metal cations at the membrane/solution interface.

Thus, it became obvious that the potential across the PVC/**1** membrane interposed between two aqueous alkaline earth metal chloride changed upon photoirradiation in the different manner from that for alkali metal chloride although the factors governing the binding ability of **1** for alkaline earth metal cations at the membrane/solution interface remain equivocal.

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