Photoinduced Membrane Potential Changes. Poly(vinyl chloride) Membranes Entrapping a Photoresponsive Bis-(15-crown-5) Derivative

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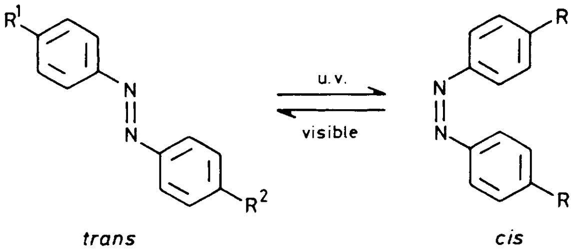
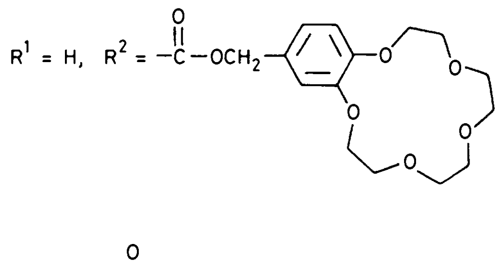
Plasticized poly(vinyl chloride) (PVC) membranes entrapping photoresponsive bis-(15-crown-5) with an azo-linkage (**2**) and its monomeric analogue (**1**) were prepared for the purpose of regulating their membrane potential by u.v. or visible light irradiation. The azobenzene moieties of (**1**) and (**2**) were found to undergo photochemical *trans–cis* isomerization reversibly in the membrane matrix. Alternating u.v. and visible light irradiation induced a significant reversibly potential change across the PVC–(**2**) membrane but did not for PVC–(**1**) membrane. Large potential shifts were induced by photoirradiation in the presence of KCl or RbCl, while the potential shifts, if observed, were small (−2.5 mV or less) in the presence of LiCl or NaCl. The photoinduced potential changes across the membranes were explained in terms of the change in binding ability of (**2**), resulting from *trans–cis* photoisomerization, for K^+ and Rb^+ at the membrane–solution interface. In other words the surface potentials at the two membrane–solution interfaces were considered to be perturbed by photoirradiation.

Azobenzene derivatives are well known to undergo *trans–cis* isomerization upon u.v. light irradiation and to return to the original *trans*-form thermally or photochemically under visible light. Recently photochemical isomerism of azobenzene derivatives has been extensively utilized for effecting photoregulation of various kinds of chemical and physical properties of such functional molecules as enzymes,[1,2] synthetic polymers,[3,4] polypeptides,[5–7] artificial lipids,[8,9] and cyclodextrins.[10–12] Azobenzene-modified crown ethers have also been subjected to photoirradiation by us[13–16] and Shinkai *et al.*[17–22] To date Shinkai *et al.* have intensively studied the photocontrol of cation-extracting and transporting properties of such crown ethers. We have studied the photocontrol of ion permeation through a plasticized poly(vinyl chloride) (PVC) membrane using an azobenzene-linked bis-(15-crown-5) (**2**) as a photoresponsive ion-carrier.[14,15] In the study it became apparent that the permeation rate of K^+ ion is accelerated by u.v. light irradiation. Further we have found that the membrane potential across the PVC membrane entrapping (**2**) is controlled by u.v. and visible light irradiation.[16] The purpose of this paper is to describe the photoinduced potential changes across PVC–(**1**) and PVC–(**2**) membranes in detail.



(**1**)


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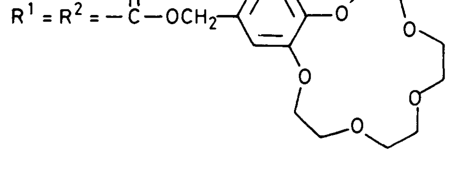

Experimental

Materials.—Poly(vinyl chloride) (PVC) (polymerization degree 1100) (Wako) was used without further purification. Di-n-butyl phthalate (DBP), tetrahydrofuran (THF), and alkali-metal chlorides (LiCl, NaCl, KCl, RbCl, and CsCl) were of extra pure reagent grade.

3,4-(1,4,7,10,13-*Pentaoxatridecane*-1,13-*diyl*)*benzyl* p-(*Phenylazo*)*benzoate* (**1**).—Compound (**1**) was prepared by condensation of 4-(chlorocarbonyl)azobenzene (0.54 g) with 4-(hydroxymethyl)benzo-15-crown-5 (0.66 g) in chloroform in the presence of pyridine, yield 57%, m.p. 120 °C (Found: C, 65.8; H, 6.0; N, 5.9. Calc. for $C_{28}H_{30}N_2O_7$: C, 66.4; H, 5.9; N, 5.5%); $\delta(CDCl_3)$ 3.6—4.3 (16 H, m, CH_2 of crown ether), 5.3 (2 H, s, benzyl), 6.8—6.9 (3 H, m, benzocrown H), 7.2—8.2 (9 H, m, azobenzene H); ν 1 720 cm^{-1} (ester).

4,4′-*Bis*-[3,4-(1,4,7,10,13-*pentaoxatridecane*-1,13-*diyl*)*benzyloxycarbonyl*]*azobenzene* (**2**).—This compound was synthesized by refluxing 4,4′-bis(chlorocarbonyl)azobenzene (1.0 g) and 4-(hydroxymethyl)benzo-15-crown-5 (2.0 g) in chloroform in the presence of pyridine for 12 h, yield 73%, m.p. 169—170 °C (Found: C, 63.5; H, 5.9; N, 3.1. Calc. for $C_{44}H_{50}N_2O_{14}$: C, 63.6; H, 6.1; N, 3.4%); $\delta(CDCl_3)$ 3.6—4.3 (32 H, m, CH_2 of crown ether), 5.3 (4 H, s, benzyl), 6.9—7.1 (6 H, m, benzocrown H), and 7.8—8.4 (8 H, m, azobenzene H); ν 1 715 cm^{-1} (ester).

Preparation of Membranes.—PVC membrane containing (**1**) or (**2**) (0.1 mm thickness) was prepared by pouring the mixture of PVC (235 mg), DBP (0.54 ml), appropriate amounts of (**1**) or (**2**) and of THF (120 ml) onto a flat Petri dish (9.2 cm diameter) and allowing the solvent to evaporate. Thicker membranes (0.2 and 0.4 mm thickness) were prepared in a similar manner. Membranes thus obtained possessed satisfactory mechanical strength for spectroscopic and electrochemical measurements.

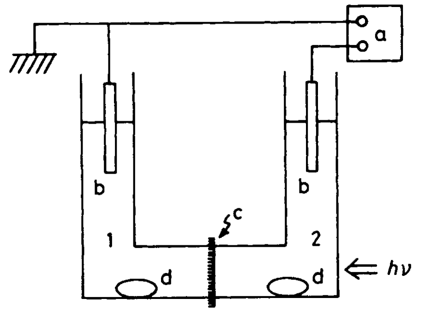

Figure 1. Schematic representation of the cell for the membrane-potential measurements: a; potentiometer, b; saturated calomel electrode, c; membrane, d; stirring bars

Table 1. Effect of alkali-cations on the *trans*-(**2**):*cis*-(**2**) ratio and the half-life of *cis*-(**2**) in the membrane[a]

	None	LiCl	NaCl	KCl	RbCl	CsCl
cis-(**2**) (%)	29	29	28	30	30	31
Half-life (h)	45	51	39	42	44	45

[a] Membranes were immersed in 1 M-alkali-metal chloride solution for *ca.* 18 h before irradiation. The content of (**2**) in the membrane is 2.0×10^{-5} g cm^{-2}.

Membrane-potential Measurements.—All measurements were carried out at 25 °C with a **U**-shaped glass cell illustrated in Figure 1. Double-junction-type saturated calomel electrodes were employed. Both solutions were stirred vigorously. The effective membrane area of the cell is 2.54 cm^2. The composition of the electrochemical cell for the membrane potential measurements was as follows; Hg_2Cl_2(s), Hg|KCl (sat.)|0.1M-$N(CH_3)_4$ Cl|electrolyte solution (c_1)|membrane|electrolyte solution (c_2)|0.1M-$N(CH_3)_4$Cl|KCl(sat.)|Hg_2Cl_2(s), Hg. The electrode in the lower-concentration compartment was earthed. Photoirradiation was performed with a 500 W xenon lamp (Ushio Electric Inc.) using cut-off filters Toshiba UV D-35 and Corning 3-74 for isolating u.v. and visible light, respectively. Noise level was *ca.* ±0.2 mV in the present experimental conditions.

Absorption Spectra.—*trans–cis* Isomerization of (**1**) and (**2**) in the membrane and in solution was monitored by measuring the absorption spectra. The *cis* percentage of the samples was calculated from the decrease in absorption intensity at the π–π^* absorption maximum, assuming that the absorbance of the *cis*-isomer at this wavelength is negligibly small compared with that of the *trans*-isomer. Only one surface of the membrane, unless otherwise noted, was exposed to u.v. light.

Results and Discussion

Photoisomerization of (**1**) *and* (**2**).—Photochemical and thermal isomerization of (**1**) and (**2**) in the PVC membrane and in dichloromethane solution was studied. In dichloromethane solution, *trans*-(**1**) showed absorption bands at 324 (ε 33,600) and 452 nm (ε 960) associated with π–π^* and n–π^* transitions of the azobenzene chromophore, respectively. The absorption intensity at 324 nm decreased markedly on u.v. light irradiation through a Toshiba UV D-35 cut-off filter, confirming the *trans–cis* isomerization of (**1**).[23] A similar spectral change was observed for (**2**), the absorption maxima of which in the *trans*-form being 331 (ε 32,500) and 459 nm (ε 900). The *cis*-proportion in irradiated samples of (**1**) and (**2**) in the photostationary state was 66 and 33%, respectively. The half-lives of the *cis*-isomers under dark condition were *ca.* 50 h for (**1**) and 67 h for (**2**).

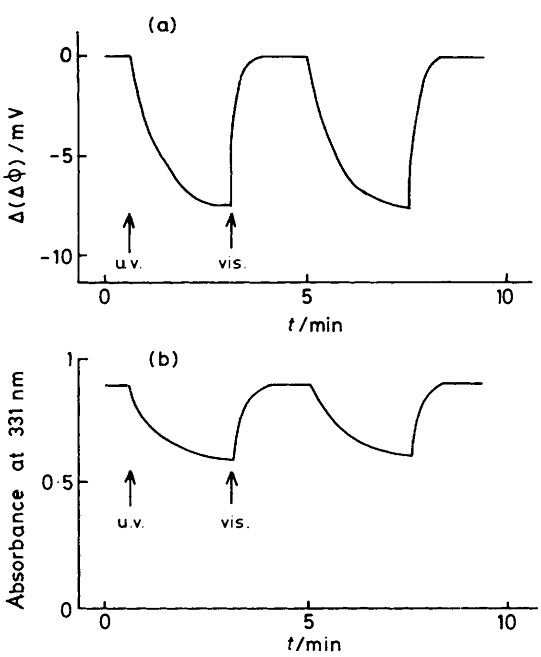

Figure 2. (a) Photoresponse of the membrane potential; alternate u.v. and visible irradiation. c_1 = 10mM- and c_2 = 500mM-KCl. (**2**) Content in the membrane is 2.0×10^{-5} g cm^{-2}. Membrane thickness, 0.1 mm. (b) Change in absorbance of the membrane at 331 nm

Compounds (**1**) and (**2**) also isomerized from *trans* to *cis* and *vice versa* in the PVC membrane. About 5 min was required for giving a photostationary state mixture of *trans* and *cis* isomers under u.v. light irradiation. The *cis* proportion in the irradiated PVC–(**1**) and PVC–(**2**) membranes of 0.1 mm thick were 61 and 29%, respectively. The original spectrum was recovered rapidly (< 30 s) by irradiating the membrane with visible light (λ >410 nm). Thus, it was found that the alternate u.v. and visible light irradiation induces a reversible *trans–cis* photoisomerization of (**1**) and (**2**) in the PVC membrane. The absorption spectra of (**1**) and (**2**) in the membrane and in solution were previously illustrated elsewhere.[15,*]

The effect of alkali-metal cations on the percentage of *cis*-(**2**) in the photostationary state and the half-life of the resulting *cis* isomer in the membrane was examined (Table 1). Alkali-metal cations had scarcely any influence on the *trans*:*cis* ratio in PVC–(**2**) membrane in the photostationary state. The effect of the cation on the thermal isomerization rate from *cis* to *trans* in the membrane was rather small. Shinkai *et al.* reported similar observations on the two kinds of azobenzene-modified bis-(crown ether)s in *o*-dichlorobenzene–Bu^{n}OH solution.[20] It should be noted here that the influence originating from the thermal *cis–trans* isomerization is negligible during the measurements of the membrane potential because the thermal isomerization rates of (**1**) and (**2**) in the membrane were

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[*] The *cis* percentage at the photostationary state was dependent on the optical property of the cut-off filter used for isolating u.v. light. The *cis* percentage of the *trans–cis* mixture irradiated through a Corning 7-37 filter (320 nm < λ < 380 nm), which was used in ref. 15, was higher than the value obtained when irradiated through a Toshiba UV D-35 filter. We used the Toshiba UV D-35 throughout this study because of its high transparency for u.v. light, which permitted the rapid response of the photoinduced potential change.

Table 2. Photoinduced potential changes, Δ(ΔΦ)/mV, across PVC–(2) membrane[a]

Electrolyte	(2) content in membrane (g cm^{-2})	c_2 concentration (mM) 1	10	100	500	1 000
LiCl	2.0 × 10^{-5}	−0.5	−0.5	−1.5	−2.0	−2.5
NaCl	2.0 × 10^{-5}	~0	~0	~0	~0	~0
KCl	1.0 × 10^{-5}	−2.0	−5.5	−10	−13	−14
KCl	2.0 × 10^{-5}	−2.0	−6.5	−10	−12	−13
RbCl	1.0 × 10^{-5}	−1.0	−5.5	−10	−13	−15
RbCl	2.0 × 10^{-5}	−2.5	−6.5	−11	−13	−14
CsCl	1.0 × 10^{-5}	−0.5	−2.5	−4.0	−4.5	−5.0
CsCl	2.0 × 10^{-5}	−1.5	−4.5	−6.5	−8.0	−8.5

[a] c_1 concentration was 1mM. The membrane surface facing c_2 compartment was exposed to u.v. light. The average values of three independent measurements were listed.

negligibly small compared with the response time of the photoinduced potential change.

Photoinduced Potential Change.—Figure 2a illustrates the time-response of the potential change of the membrane induced by alternating u.v. and visible light irradiation. After a potential difference at a steady state had been obtained in the dark, a negative shift of the membrane potential was induced by u.v. irradiation. About 3 min sufficed to attain a steady-state potential under u.v. light and the initial potential was recovered rapidly by visible light irradiation. The membrane potential change must come from the *trans–cis* photoisomerization of (2) in the membrane in view of the fact that the potential change is entirely synchronized with the absorption change at 331 nm of the membrane, *i.e.*, *trans–cis* isomerization of (2) in the membrane (Figure 2b).

Table 2 describes the effects of the kinds of cation species and the ionic concentration in the solutions on the photoinduced potential change, Δ(ΔΦ), across the PVC–(2) membrane. A marked dependence of Δ(ΔΦ) values on the cation species was observed. U.v. irradiation resulted in large Δ(ΔΦ) values in the presence of KCl and RbCl, while they were only −2.5 mV or less in the presence of LiCl and NaCl. These observations strongly suggest that the potential changes stem from the enhanced binding ability of (2) for the larger cations (K^+ and Rb^+) at the membrane–solution interface. We reported previously that the binding ability of (2) for K^+ and Rb^+ cations was improved by u.v. light irradiation due to 2:1 sandwich-type complex formation between *cis*-(2) and the cations.[14,15]

In general, the potential difference across a charged membrane (membrane potential, ΔΦ) is given as an algebraic sum of the surface potential differences at membrane–solution interfaces and the diffusion potential in the membrane.[24,25] In the case of the plasticized PVC membrane, the contribution from the diffusion potential on the ΔΦ value is considered to be always small irrespective of the electrolyte concentration on the basis of the following two reasons. First, the PVC–(2) membrane has low permeability for alkali-metal chlorides compared with the diffusion of the salts in the aqueous phase, though electrically conductive. Secondly, an ion-pair complex between the crown ether and alkali-metal chloride, which is electrically neutral, is the predominant species in the hydrophobic interior of the membrane (dielectric constant of DBP is 6.42 at 25 °C).[26] Thus it may be said that one can scarcely find any charged species in the hydrophobic interior of the membrane and, therefore, that the potential gradient in the membrane phase is approximately zero.

In the PVC–(2) membrane system, it is reasonable to assume that the distribution equilibrium holds with regard to the alkali-metal cation at the membrane–solution interface and that the main factor governing the equilibrium constant is the binding ability of (2) for the cations. Since there is apparently no fixed charge in the PVC membrane, the charge density at the membrane surfaces is inevitably determined by the amount of alkali-metal cation bound to (2) at the membrane surface. As is obvious from the above discussion, *trans–cis* isomerization of (2), by which the binding ability of (2) for K^+, Rb^+, and Cs^+ is enhanced, increases the charge density, that is, surface potential. This mechanism of the potential change reasonably agrees with the results that high Δ(ΔΦ) values were observed in the high salt concentration regions. Another important aspect is that, even for $c_1 : c_2 = 1$ (1mM), potential shifts were observed. 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.[27,28] Indeed, in our case, the membrane potential was almost zero at $c_1 = c_2$ under dark and visible light, where (2) assumed wholly the *trans*-form. This discrepancy may be explained in terms of an asymmetric membrane formation under u.v. light irradiation.[29] In other words, the *cis*-(2):*trans*-(2) ratios of the two surfaces of the membrane are different from each other under u.v. light. It seems that the *trans–cis* photoisomerization reaction of (2) proceeds more efficiently on the irradiated surface of the membrane than that on the opposite surface and, therefore, that the *cis*-(2) content of the irradiated surface is higher than that of

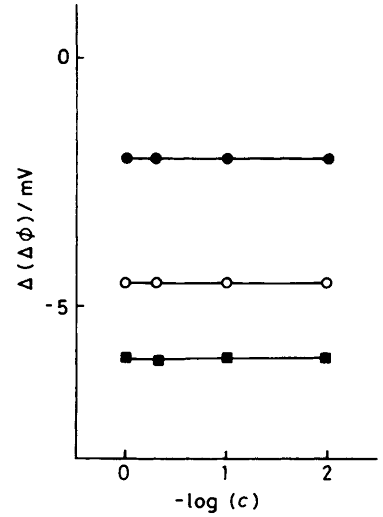

Figure 3. Effects of membrane thickness and KCl concentration on the asymmetric membrane potential. The KCl concentration in both solutions is equal ($c_1 = c_2$). Membrane thickness: 0.1 mm (●), 0.2 mm (○), and 0.4 mm (■)

Table 3. Photoinduced potential change, $\Delta(\Delta\Phi)$/mV, across PVC–(**1**) membrane[a]

Electrolyte	c_2 concentration (mM) 1	10	100	500	1 000
LiCl	0	0	0	0.5	0.5
NaCl	0	0	0	0	0
KCl	0	0	0.5	0.5	0.5
RbCl	0	0	0.5	0.5	1.0
CsCl	0	0	0	0	0.5

[a] (**1**) Content in membrane is 2.4 × 10^{-5} g cm^{-2}. c_1 Concentration is 1mM. The membrane surface facing c_2 compartment was exposed to u.v. light.

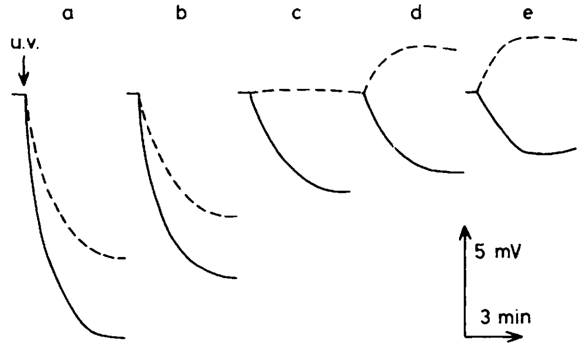

Figure 4. Photoinduced potential changes across PVC–(**2**) membrane; irradiated from c_1 side (– – –) and c_2 side (——). c_1 = 1mM(a), 10mM(b), 100mM(c), 500mM(d), 1 000mM(e), and c_2 = 1 000mM-KCl. (**2**) Content in the membrane is 2.0 × 10^{-5} g cm^{-2}. Membrane thickness, 0.1 mm. Electrode in c_1 compartment is earthed

the non-irradiated surface. On this point, further discussion will be given later.

Figure 3 shows the photoinduced potentials observed under the conditions $c_1 = c_2$ = 10, 100, 500, and 1 000mM-KCl using the membranes 0.1, 0.2, and 0.4 mm thickness. The magnitude of $\Delta(\Delta\Phi)$ values is independent of the ionic concentration over the range of 10—1 000mM. On the other hand, the $\Delta(\Delta\Phi)$ values depend remarkably on the membrane thickness, the thicker membrane resulting in higher values. This dependence of $\Delta(\Delta\Phi)$ values on the membrane thickness is compatible with the interpretation that an asymmetric membrane is formed under u.v. light. It is reasonable to assume that the *cis*-(**2**) content of the non-irradiated side of the thicker membrane is suppressed at a lower level than that of the thinner membrane.

Table 3 lists the photoinduced potential changes across PVC–(**1**) membrane. The potential change was zero or, if observed, very small for all cations. The difference between the photoresponse of PVC–(**1**) and PVC–(**2**) membranes arises from the fact that 15-crown-5 is a poor ionophore for larger cations (K^+, Rb^+, and Cs^+) when acting alone. The binding ability of (**2**) for the cations can be improved upon u.v. irradiation by the forming *cis*-isomer, where two 15-crown-5 moieties of (**2**) are located in the favourable position for sandwich-type 2:1 complex formation with the cations. U.v. irradiation, however, does not improve the binding ability of (**1**) because the 15-crown-5 moiety of (**1**) always interacts alone with the cations. The cation binding ability of (**1**) may be slightly reduced by u.v. light irradiation considering the fact that the membrane potential was shifted in the opposite direction, *i.e.* positive shift, of that observed for PVC–(**2**) membrane.

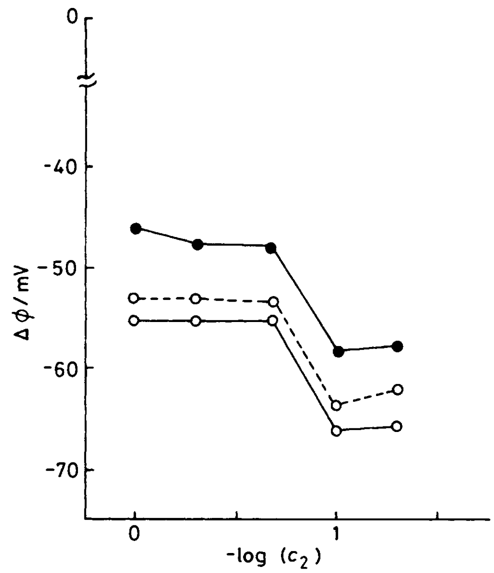

Figure 5. Membrane potential across PVC–(**2**) membrane under dark (●) and under u.v. light irradiation from c_1 (- - ○ - -) and c_2 side (—○—) c_2/c_1 is fixed at 50. Electrode in c_1 compartment is earthed. Membrane thickness, 0.1 mm

The photoresponse of the membrane potential was closely related to the direction from which the irradiation was performed. All data in Figures 2 and 3 and Tables 2 and 3 were always obtained by exposing the membrane surface facing the high concentration compartment to the light. Figure 4 shows the potential changes induced by u.v. light irradiation onto the membrane surface facing the higher or lower concentration compartment. When the membrane surface facing the higher concentration compartment was exposed to u.v. light, negative shifts of the potential were always obtained. Larger $\Delta(\Delta\Phi)$ values were obtained when the concentration gradient between the two solutions was increased. On the other hand, the photoresponse when irradiated from the opposite side of the membrane was somewhat complicated. The negative shift of the potential was observed for c_1. 1 and 10mM whereas the sign of $\Delta(\Delta\Phi)$ values was positive in the higher c_1 concentration region. These photoresponsive behaviours of the membrane potential when irradiated from the direction of the lower concentration compartment may be reasonably explicated based on the difference of *cis*-(**2**):*trans*-(**2**) ratios between two surfaces of the membrane under u.v. light irradiation. The *cis*-(**2**):*trans*-(**2**) ratio of the irradiated surface of the membrane seems to be much higher than that of the other surface. For c_1 1 or 10mM, the negative shift of the potential resulted from the fact that K^+ uptake by *cis*-(**2**) at the non-irradiated surface surpassed that at the irradiated surface in spite of the low *cis*-(**2**) content because of the high c_2 concentration. However, in low c_2/c_1 regions, the difference of the amount of K^+ uptake by *cis*-(**2**) at two membrane surfaces depended on the *cis*-(**2**) content rather than the K^+ concentration in two solutions. For c_2/c_1 = 1(1M), the potential shift read 2.0 mV, the same absolute value as that obtained by irradiating from the side of the higher concentration compartment (−2.0 mV). To ascertain that the *cis*-(**2**) content of the irradiated surface of the membrane is not equal to that of the opposite surface, we irradiated the membrane of 0.1 mm thickness, after the photostationary state was attained by u.v. light irradiation for 10 min from one side of the membrane [*cis*-(**2**) content was 29%], from the opposite side. Thereupon, a further increase in the *cis* content (*ca.* 5%) was reached. By similar treatment of the PVC–(**1**) membrane, *cis*-(**1**) content was enhanced from 61 to 67%. These results also strongly suggest the asymmetric membrane formation under u.v. light irradiation.

Figure 5 illustrates the effect of the c_2 concentration on the membrane potential at $c_2:c_1 = 50:1$. The dependence of $\Delta(\Delta\Phi)$ values on the ionic concentration was small.

Conclusions.—We have shown that the membrane potential across the PVC–bis-(15-crown-5) membrane can be controlled by u.v. and visible light irradiation. The photoresponsive behaviour of the membrane potential is significantly dependent on the cation species and the ionic concentration. Photoinduced potential changes were also affected by which surface of the membrane was exposed to u.v. light. Though further study is required for clarifying the exact mechanism quantitatively by which the membrane potential is generated, the fundamental concept described in this paper will be useful not only for the investigation of biological photoresponsive systems but also for the development of artificial sensor membranes which transduce a light signal into electric output.

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