Photo-excitable Membranes. Photoinduced Membrane Potential Changes across Poly(vinyl chloride) Membranes Doped with Azobenzene-modified Crown Ethers

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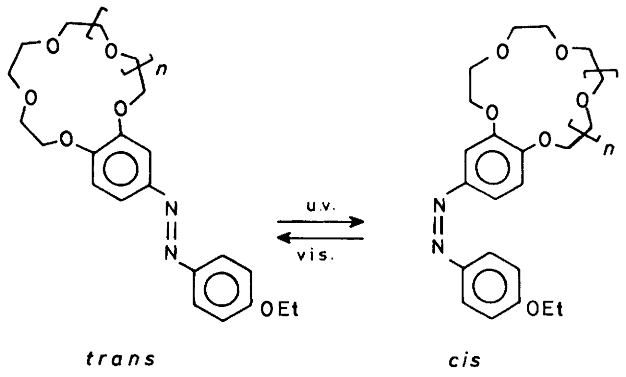
The membrane potentials across a plasticized poly(vinyl chloride) (PVC) membrane entrapping azobenzene-modified 15-crown-5 (**1**) or 18-crown-6 (**2**) were measured under conditions of u.v. and visible light irradiation. Irradiation induced significant potential changes across the membranes, of a magnitude depending on the cation species, on the ionic concentration in the solution, and on the crown ether content in the membrane. The sign of the potential shift was dependent upon the direction from which the membrane was irradiated. The results are explained in terms of surface potential changes at both surfaces of the membrane, associated with the release of cations from the membrane phase into the solution upon irradiation.

Recently the development of polymer membranes possessing characteristics such as ion permeability and membrane potential which can be switched on or off by photochemical and/or electrochemical techniques has received increasing attention. Burgmayer and Murray have reported that the impedance and ionic permeability of poly(pyrrole) membrane deposited on a gold minigrid electrode can be regulated by changing the electrode potential.[1,2] They employed the electrochemical redox reaction of the pyrrole moiety to control the hydrophobicity of the membrane. Electrochemical control of the ionic permeability of collagen membrane has been studied by Eisenberg and Grodzinsky.[3] They have reported that the electric field can serve as a switch to control the swelling state and the resulting pore size of the membrane by changing the pH or ionic concentration inside the membrane. The permeability of bilayer membranes has also been regulated electrochemically by Okahata *et al.*[4] We[5,6] and Kumano *et al.*[7] have independently prepared poly(vinyl chloride) (PVC) membranes containing azobenzene-modified crown ethers which change their binding abilities for cations upon photoirradiation. These studies have shown that ion transport through the membranes can be facilitated by irradiation with u.v. light.

The membrane potential across polymer membranes has also been made subject to photoregulation. Kato *et al.*,[8–10] and recently we[11–13] and Irie *et al.*[14] have studied the photoresponse of the membrane potential across polymer membranes pigmented with spirobenzopyran derivatives as photoresponsive dyes. In these systems the photochemical transformation of the spirobenzopyran derivatives between neutral and charged forms has been utilized successfully to regulate the fixed charge density in the membrane. Large potential shifts (200 mV or more), in some cases, were induced by photoirradiation using the hydrophobic membrane materials.[13] Another example of photoinduced potential changes across a polymer membrane has been demonstrated by Takizawa *et al.* using azobenzene-modified polypeptide membranes.[15] They explain their results in terms of the hydrophobicity change induced by photochemical *trans–cis* isomerization of azobenzene residues in the side chain of the polymers.

In previous papers we have reported that the membrane potential across the PVC membrane doped with an azobenzene-linked bis-(15-crown-5) derivative can be regulated by u.v. and visible light irradiation.[16–22] In these studies it became obvious that the potential-generating mechanism involves perturbation of the surface potentials by charge-density changes at the membrane surfaces, originating from the change in the distribution equilibrium of alkali-metal cations between the membrane phase and the solution phase. In other words, photoinduced uptake of cations by the crown ether from the solution phase into the membrane contributes to the shifts of potential.



(**1**) $n = 1$
(**2**) $n = 2$

This paper describes the detailed results obtained by the use of azobenzene-substituted 15-crown-5 (**1**) and its 18-crown-6 analogue (**2**) as photoresponsive membrane components. The photoresponse of the membrane potential across the PVC-(**1**) and the PVC-(**2**) membranes will be discussed in relation to the u.v.-induced release of cations from the membrane phase into the solution, which results from the reduction in binding abilities of (**1**) and (**2**) upon u.v. light irradiation.

Experimental

Materials.—Poly(vinyl chloride) (PVC) (polymerization degree 1 100; Wako Ltd.) was used without further purification. Di-2-ethylhexyl phthalate (DEHP), tetrahydrofuran (THF), and alkali-metal chlorides (LiCl, NaCl, KCl, and RbCl) were of extra pure reagent grade.

4′-(p-*Ethoxyphenylazo*)*benzo*-15-*crown*-5† (**1**).—This compound was prepared by ethylation of 4′-(*p*-hydroxyphenyl-

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† 15-(*p*-Ethoxyphenylazo)-2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecine.

azo)benzo-15-crown-5, synthesized according to the reported procedure,[23] with ethyl bromide. A mixture of 4'-(*p*-hydroxyphenylazo)benzo-15-crown-5 (1 g), ethyl bromide (0.4 g), potassium hydrogen carbonate (0.33 g), and acetone (25 ml) was refluxed for about 6 h. After cooling, the precipitate was filtered off and the filtrate was evaporated to dryness. The resulting crude *product* was purified by column chromatography (silica gel; $CHCl_3$–EtOH 1:1); yield 0.6 g (49%), m.p. 142—143 °C (Found: C, 62.95; H, 6.7; N, 6.5. $C_{22}H_{28}N_2O_6$ requires C, 63.45; H, 6.8; N, 6.7%); δ($CHCl_3$) 1.3—1.5 (3 H, t, CH_3CH_2), 3.6—4.3 (18 H, m, CH_3CH_2 and CH_2 of crown ether), and 6.8—7.9 (7 H, m, aromatic).

4'-(p-*Ethoxyphenylazo)benzo*-18-*crown*-6* (**2**).—Compound (**2**) was prepared by a similar procedure from 4'-(*p*-hydroxyphenylazo)benzo-18-crown-6 (1 g).[23] The crude *product* was recrystallized from ethanol; yield 0.5 g (45%), m.p. 124—125 °C (Found: C, 62.2; H, 6.9; N, 5.9. $C_{24}H_{32}N_2O_7$ requires C, 62.6; H, 7.0; N, 6.1%); δ($CDCl_3$) 1.3—1.6 (3 H, t, CH_3CH_2), 3.6—4.3 (22 H, m, CH_3CH_2 and CH_2 of crown ether), and 6.8—7.9 (7 H, m, aromatic).

Absorption Spectra.—Photoisomerization of (**1**) and (**2**) in the membrane and in solution was monitored by measuring the absorption spectra. The *cis* percentage of the samples was estimated from the decrease in absorption intensity at the absorption maximum, assuming that the absorbance of the *cis* isomer at the wavelength used is negligibly smaller compared with that of the *trans* isomer.

Liquid–Liquid Extractions.—Liquid–liquid extractions were carried out according to the method developed by Pedersen.[24] An aqueous solution (5 ml) of picric acid that contained metal hydroxide (500mM) was vigorously shaken in a separating funnel with an equal volume of CH_2Cl_2 that contained the crown ether derivative (**1**) or (**2**). After sufficient agitation at 25 °C the concentration of picric acid in water was measured by u.v. spectroscopy at 354 nm. The amount of crown ether transported to the water layer was negligibly small.

Preparation of Membranes.—A PVC membrane entrapping (**1**) or (**2**) was prepared by pouring the mixture of PVC (250 mg), DEHP (0.5 ml), an appropriate amount of (**1**) or (**2**), and THF (20 ml) onto a flat Petri dish (9.2 cm diam.) and allowing the solution to evaporate. The thickness of the membrane thus obtained was *ca.* 0.15 mm. Before use the membrane was conditioned for *ca.* 3 h by soaking in alkali-metal chloride solution (1mM) in the dark.

Membrane Potential Measurements.—A U-shaped glass cell (Figure 1) was used for all measurements at 25 °C (effective membrane area 2.54 cm²). Both solutions were stirred vigorously and an Ag/AgCl electrode was used. The electrode in the lower-concentration compartment (c_1 side), unless otherwise noted, was earthed. The composition of the electrochemical cell for the membrane potential measurements was as follows; Ag/AgCl|electrolyte solution (c_1)|PVC-(**1**) or PVC-(**2**) membrane|electrolyte solution (c_2)|Ag/AgCl. The light source was a 500 W xenon lamp (Ushio Electric Inc.) and cut-off filters Toshiba UV-D35 and Y-49 were used for isolating u.v. (320 nm $< \lambda <$ 400 nm) and visible (450 nm $< \lambda$) light, respectively. Noise level was *ca.* +1 mV in the present experimental conditions.

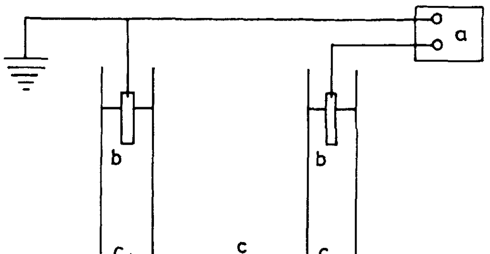

Figure 1. Schematic representation of the cell for the membrane-potential measurements: a, potentiometer; b, Ag/AgCl electrode; c, PVC membrane; d, stirring bar

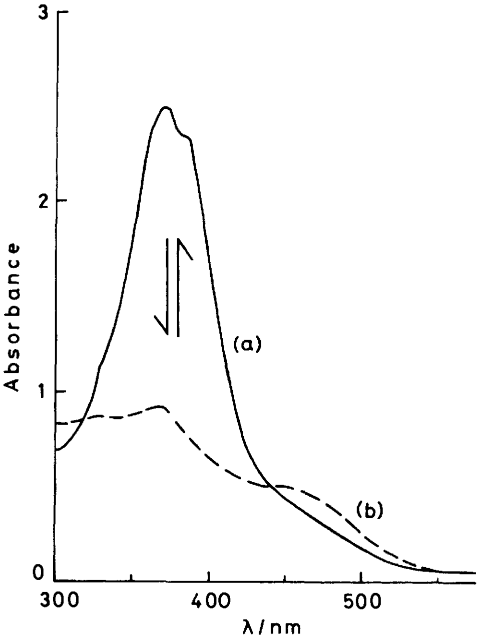

Figure 2. U.v. spectra of PVC-(**1**) membrane: (a) under visible light or in the dark, and (b) under u.v. light

Results and Discussion

Photoisomerization of the Crown Ether Derivatives (**1**) *and* (**2**).—Photochemical and thermal isomerization of (**1**) and (**2**) between the *trans*- and the *cis*-form was studied. When *trans*-(**1**) was dissolved in dichloromethane, a strong absorption band associated with the π→π* transition of the azobenzene chromophore was found at 367 nm (ε 29 000). Upon u.v. irradiation through a Toshiba UV-D35 filter the absorption intensity at 367 nm decreased markedly, showing the formation of a *trans–cis* mixture.[25] The *cis* proportion was *ca.* 78%. After the photostationary state was attained, the original u.v. spectrum was recovered rapidly upon irradiation with visible light. A similar spectral change was observed for (**2**). The absorption maximum of *trans*-(**2**) was at 368 nm (ε 25 500), and the *cis* proportion at the photostationary state was *ca.* 77%.

Absorption spectra of the PVC-(**1**) membrane are illustrated in Figure 2. The spectral change of (**1**) was almost the same as that in dichloromethane solution. The band at 368 nm decreased upon irradiation with u.v. light, and *ca.* 3 min sufficed to give a photostationary-state mixture of *trans*- and *cis*-(**1**) in

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* 18-(*p*-Ethoxyphenylazo)-2,3,5,6,8,9,11,12,14,15-decahydro-1,4,7,10,13,16-benzohexaoxacyclo-octadecine.

Table 1. Liquid–liquid extraction of alkali-metal picrates with (**1**) and (**2**)[a]

Crown ether	Extracted picrate (%)			
	Li	Na	K	Rb
trans-(**1**)	2.8	25	34	18
Irradiated (**1**)[b]	1.4	22	20	10
trans-(**2**)	2.0	23	91	78
Irradiated (**2**)[c]	1.5	19	88	74

[a] Organic phase (dichloromethane): [crown ether] = 0.5mM; aqueous phase: [picric acid] = 0.1mM; [metal hydroxide] = 500mM. [b] *cis*-Form 65%. [c] *cis*-Form 72%.

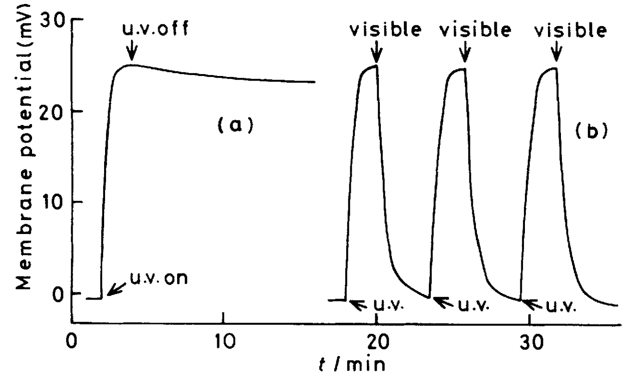

Figure 3. Typical photoresponse of the membrane potential across the PVC-(**2**) membrane; $c_1 = c_2 =$ 1mM-KCl; (**2**) content in the membrane 7.6 × 10^{-5} g cm^{-2}

the membrane. The *cis*-(**1**) proportion in the irradiated PVC-(**1**) membrane was *ca.* 65%. The original spectrum was obtained by irradiating the membrane with visible light. This photochemical interconversion between *trans*- and *cis*-(**1**) was fairly reversible and reproducible. The spectral changes of the PVC-(**2**) membrane upon photoirradiation were similar. The *cis*-(**2**) content in the irradiated PVC-(**2**) membrane was *ca.* 64%. The thermal isomerization of *cis*-(**1**) and *cis*-(**2**) to the *trans*-form in the membrane was also studied. The first-order rate constants of *cis–trans* thermal isomerization of (**1**) and (**2**) were 3.9 × 10^{-3} ($t_{\frac{1}{2}}$ 178) and 4.2 × 10^{-3} min^{-1} ($t_{\frac{1}{2}}$ 165 min), respectively. Thus, it was clear that alternate u.v. and visible light irradiation induces a reversible *trans–cis* isomerization of (**1**) and (**2**) in the plasticized PVC membrane.

Liquid–Liquid Extractions.—In order to estimate the cation-binding properties of (**1**) and (**2**), liquid–liquid extractions were carried out with water–dichloromethane. Alkali-metal picrates dissolved in water were extracted with (**1**) and (**2**) dissolved in the organic phase. Table 1 lists the results for (**1**) and (**2**). *trans*-(**1**) Extracted K$^+$ cation more efficiently than the other cations examined, though the extraction selectivity was not so high. These characteristics of (**1**) in cation extraction are in accord with those of other benzo-15-crown-5 derivatives.[26–28] The extraction percentages were reduced for all cations upon u.v. light irradiation. This shows that the binding ability of *cis*-(**1**) is weaker than that of *trans*-(**1**). U.v. light irradiation also weakened the cation-binding ability of (**2**). Although the exact mechanism of the photoinduced changes in the binding abilities of (**1**) and (**2**) is not obvious, steric hindrance by the ethyl group in the *cis*-form may be a factor. In connection with the membrane potential changes (discussed in detail later), it is important that the cation-binding abilities of (**1**) and (**2**) decrease upon u.v. light irradiation.

Table 2. Photoinduced potential changes [Δ(Δφ)/mV] across PVC-(**1**) and PVC-(**2**) membranes[a]

Membrane	Electrolyte	c_2/mM			
		1	10	100	1 000
PVC-(**1**)	LiCl	19	14	11	9
PVC-(**1**)	NaCl	18	12	10	10
PVC-(**1**)	KCl	21	20	21	23
PVC-(**1**)	RbCl	15	15	13	15
PVC-(**2**)	LiCl	20	18	16	14
PVC-(**2**)	NaCl	20	22	23	31
PVC-(**2**)	KCl	25	25	30	40
PVC-(**2**)	RbCl	20	20	22	21

[a] c_1 1mM; the membrane surface facing the c_2 compartment was exposed to u.v. light; average values of two independent measurements listed.

Photoinduced Membrane Potential.—Figure 3 shows the photoresponse of the membrane potential across the PVC-(**2**) membrane. The electrode in the c_1 side solution was earthed, and the membrane surface facing the c_2 side solution was exposed to u.v. or visible light. The membrane potential was near to zero in the dark, which was quite reasonable because of the identical ionic concentrations of the c_1 and c_2 solutions (1mM-KCl). Upon u.v. light irradiation the membrane potential showed a positive shift and declined, to reach a steady-state value after *ca.* 2 min. About 25 mV of photoinduced potential developed, *i.e.* $\Delta(\Delta\varphi) = \varphi_{\text{u.v.}} - \Delta\varphi_{\text{vis.}} = 25$ mV. When u.v. light was switched off, the membrane potential decayed gradually [Figure 3(a)]. The membrane potential changes induced by alternate u.v. and visible light irradiation are shown in Figure 3(b). After a steady-state potential had been obtained under u.v. light irradiation, a rapid negative shift of the potential was induced by visible light irradiation. About 3 min sufficed to reach a steady-state value of the membrane potential under visible light irradiation. The value of the membrane potential under visible light was identical with that recorded in the dark. This on–off switching of the membrane potential was fairly reversible and reproducible within our experimental period (3—4 h). The long-term stability of the membrane, however, was not adequate, owing to the gradual oozing of the crown ether from the membrane phase into the solution.

Table 2 lists the values of photoinduced potential changes, Δ(Δφ), across the PVC-(**1**) and PVC-(**2**) membranes in the presence of alkali-metal chlorides over the range 1—1 000mM. The most remarkable feature is that the potential shifted positively in all cases when irradiated from the c_2 compartment side. We reported the reverse tendency in our studies of PVC membranes doped with an azobenzene-linked (15-crown-5) derivative.[16–22] The membrane potential shifted negatively when the PVC membrane containing the bis-(15-crown-5) derivative was irradiated with u.v. light from the c_2 side.[16,21] This negative shift was explained in terms of an increase in binding ability of the bis-(15-crown-5) derivative for cations at the membrane–solution interface. In other words the photoinduced uptake of cations from the solution onto the membrane surface was the origin of the negative shift of the potential across the PVC membrane doped with the bis-(15-crown-5) derivative. On the other hand, the present positive shifts of the potential across the PVC-(**1**) and PVC-(**2**) membranes can be explained reasonably on the basis of photoinduced cation release from the membrane surface into the solution, in view of the fact that the cation-binding abilities of (**1**) and (**2**) decrease upon u.v. light

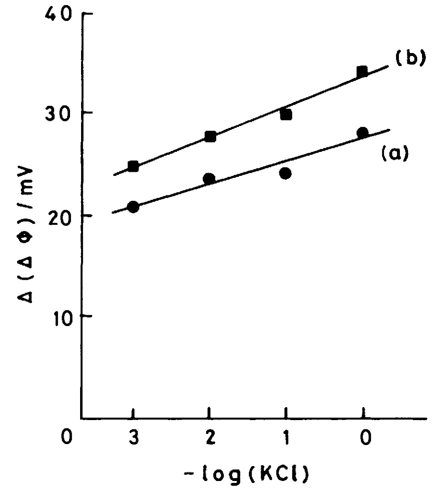

Figure 4. Effects of ionic concentration on the asymmetric membrane potential under u.v. light irradiation. The KCl concentration of the c_1 side solution is always equal to that of the c_2 side solution. Content of (**2**) in the membrane is 7.6×10^{-5} g cm^{-2}. (a) Membrane potential across the PVC-(**1**) membrane; (b) membrane potential across the PVC-(**2**) membrane

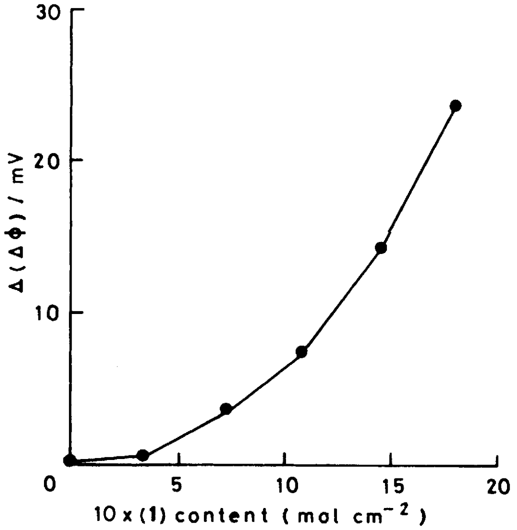

Figure 5. Effects of (**1**) content in the membrane on the photoinduced membrane potential; c_1 = 1mM, c_2 = 1 000mM (KCl)

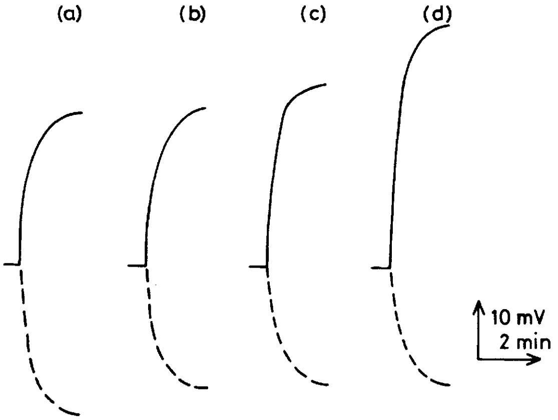

Figure 6. Photoinduced potential changes across the PVC-(**2**) membrane; irradiated from the c_1 side (- - - -) and from the c_2 side (——); c_1 = 1mM-KCl, c_2 = 1mM- (a), 10mM- (b), 100mM- (c), or 1 000mM-KCl (d); Content of (**2**) in the membrane 7.6×10^{-5} g cm^{-2}; Electrode in c_1 compartment is earthed.

irradiation. In general, the potential difference across a charged membrane (membrane potential, $\Delta\varphi$) is given as an algebraic sum of the diffusion potential in the membrane and the surface potential differences at membrane–solution interfaces.[29–32] In the case of the plasticized PVC membrane, the contribution from the diffusion potential is considered small, as was discussed in the previous paper.[20] In the PVC-(**1**) and PVC-(**2**) membranes, it is reasonable to assume that the distribution equilibrium holds with regard to the alkali-metal cations at the membrane–solution interface and that the main factor governing the equilibrium is the binding ability of the crown ether (**1**) or (**2**) for the cations. This means that the binding abilities of (**1**) and (**2**) for cations directly affect the magnitude of charge density at the membrane surfaces, since there is apparently no fixed charge in the PVC membrane. Accordingly, *trans–cis* isomerization of the crown ethers, reducing their binding abilities, alters the charge densities, that is the surface potentials. Another interesting aspect is that, even for $c_1 = c_2$ (1mM), potential shifts were observed. This can be ascribed to asymmetric membrane formation under u.v. light irradiation,[33–35] *i.e.* the *trans–cis* photoisomerization of (**1**) and (**2**) proceeds more efficiently on the irradiated surface of the membrane than on the opposite surface; therefore, the content of *cis*-isomer on the irradiated surface is higher than that on the non-irradiated surface. Consequently, the surface potentials at the two surfaces of the membrane also have different values. This is the reason why a photoinduced potential change was observed even for $c_1 = c_2$. On this point we have already reported some experimental results and discussed them in our previous papers.[17,20,22]

Cation selectivity in the photoinduced potential change is rather small because the photoresponse of (**1**) and (**2**) does not involve a mechanism with cation-size dependence such as the 'bis-crown effect', which operated in the case of the PVC-azobenzene-linked bis-(15-crown-5) membrane.[21] The dependence of the magnitude of $\Delta(\Delta\varphi)$ on the ionic concentration is somewhat complicated. The photoresponse of the PVC-(**1**) membrane in the presence of KCl and RbCl and that of the PVC-(**2**) membrane in the presence of RbCl did not depend on the ionic concentration in the solution. The $\Delta(\Delta\varphi)$ values obtained for the PVC-(**1**) membrane in the presence of LiCl and NaCl and for the PVC-(**2**) membrane in the presence of LiCl reduced with increase in the ionic concentration. The reverse was observed for the PVC-(**2**) membrane in the presence of NaCl and KCl. Figure 4 shows the dependence of asymmetric membrane potentials on the ionic concentration. The $\Delta(\Delta\varphi)$ values depend slightly on the concentration of KCl.

Figure 5 shows the dependence of the $\Delta(\Delta\varphi)$ values on the content of (**1**) in the membrane. A photoinduced membrane potential was not observed for the membrane without (**1**), and the $\Delta(\Delta\varphi)$ values were enhanced with increasing content of (**1**) in the membrane. This is clear evidence for the importance of the distribution equilibrium of cations at the membrane surface governed by the crown ether. There is an upper limit of about 18×10^{-8} mol cm^{-2} to the content of (**1**), due to its solubility in the membrane.

The photoresponse of the membrane potential was closely related to the direction from which the irradiation was performed. Figure 6 shows the potential changes induced by u.v. light irradiation on the membrane surface facing the higher or lower concentration compartment. When the membrane

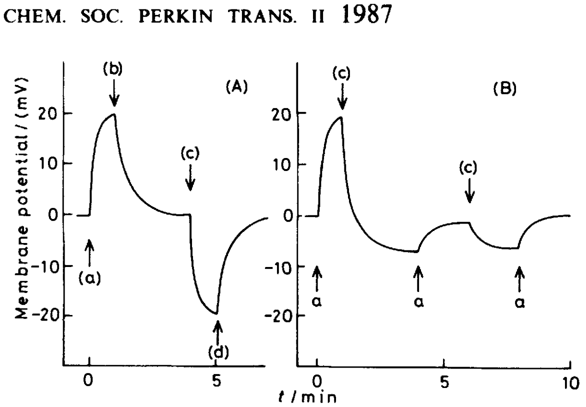

Figure 7. Photoresponse of the membrane potential across the PVC-(2) membrane: alternate u.v. and visible light irradiation from c_1 side and c_2 side (A), and repeated u.v. light irradiation from both sides (B); $c_1 = c_2 =$ 100mM (RbCl); electrode in the c_1 compartment earthed; (a) u.v. light irradiation from c_2 side, (b) visible light irradiation from c_2 side; (c) u.v. light irradiation from c_1 side; (d) visible light irradiation from c_1 side

surface facing the higher concentration compartment was exposed to u.v. light, the membrane potential always shifted positively. Larger $\Delta(\Delta\varphi)$ values were obtained when the concentration gradient between the two solutions was increased. In contrast, negative shifts of the potential were observed on irradiation from the opposite side of the membrane. These results suggest that cation release from the membrane surface into the solution at the irradiated interface always surpassed that at the non-irradiated interface, irrespective of the ionic concentration.

Figure 7(A) depicts the photoresponse of the PVC-(**2**) membrane when irradiated with u.v. and visible light from both sides alternately. About +20 mV of photoinduced membrane potential developed when the membrane surface facing the c_2 solution was exposed to u.v. light, and the original value of the potential was recovered upon visible light irradiation. U.v. light irradiation from the c_1 side induced a negative shift of the potential of the same magnitude as observed upon irradiation from the c_2 side. Figure 7(B) shows the photoresponse when both sides of the membrane were exposed to u.v. light alternately. After a steady-state value of the membrane potential had been obtained under u.v. light irradiation from the c_2 side, the potential shifted negatively, through 0 mV, to reach *ca.* −6 mV upon u.v. light irradiation from the c_1 side. This negative shift of the potential induced by u.v. light irradiation has a different mechanism from that observed on irradiation with visible light. The potential shift from +20 mV to 0 mV illustrated in Figure 7(A) can be ascribed to the photoisomerization of (**2**) from *cis-* to *trans*-form under visible light irradiation, which means that (**2**) was wholly in the *trans*-form when the potential read 0 mV. In the case of the negative shift of potential under u.v. light irradiation, (**2**) does not isomerize from *cis* to *trans* photochemically. It is considered that u.v. light irradiation from the c_1 side induces a further isomerization of (**2**) from *trans* to *cis* at the membrane surface facing the c_1 compartment and, consequently, that the difference in *cis*-(**2**) content between the two surfaces of the membrane is reduced. When the membrane potential read 0 mV, the *cis*-(**2**) content of the irradiated surface was equal to that of the opposite surface of the membrane, *i.e.* the membrane was symmetric. Then, with prolonged irradiation, the membrane potential became negative in sign, suggesting the formation of an asymmetric membrane with reversed polarity. This is presumably due to the gradual progress of thermal decay of *cis*-(**2**) to the *trans*-form at the non-irradiated surface as well as to photochemical *cis*-(**2**) formation at the irradiated surface. The magnitude of the potential shift decreased to 5—6 mV upon repeated irradiation with u.v. light; this is ascribable to the reduced difference in *trans*-(**2**):*cis*-(**2**) ratios between the two surfaces of the membrane.

Conclusions.—We have shown that the membrane potential across the PVC membranes containing azobenzene-modified crown ethers can be regulated by photoirradiation. The polarity of the potential shift is directly determined by whether cations adsorb on or desorb from the membrane surface upon irradiation. The photoresponsive behaviour of the membrane potential was significantly dependent upon which surface of the membrane was exposed to u.v. light, confirming the formation of an asymmetric membrane as the origin of the photoinduced potential.

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