Selective Extraction and Transport of UO_2^{2+} with Calixarene-based Uranophiles

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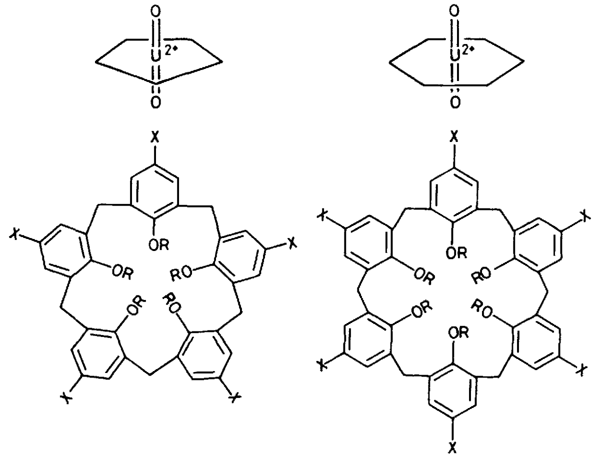
Hexacarboxylate derivatives of *p*-t-butylcalix[6]arene (**2b**) and *p*-hexylcalix[6]arene (**3b**) extract uranyl ion (UO_2^{2+}) efficiently and selectively from water into organic media. This high selectivity can be attributed to the nature of calix[6]arene; this is suitably structured for the binding of UO_2^{2+}, which requires a pseudo-planar hexaco-ordination. When trioctylmethylammonium cation (TMA^+) is added to the organic phase, the stoicheiometry of the extraction species [UO_2^{2+}/(**2b**)] changes from 1:3 to 1:1–2. This implies that an additional 1–2 mol of UO_2^{2+} are adsorbed to (**2b**) to form 'neutral' extraction species and can be displaced by added TMA^+. UO_2^{2+} is transported by (**2b**) across a liquid membrane from a neutral IN (source) aqueous phase (pH 8.5) to an acidic OUT (receiving) aqueous phase (0.1 mol dm^{-3} HCl) in an active transport manner. The rate-determining step is the release of UO_2^{2+} from the membrane to the OUT aqueous phase. On the basis of these basic data, we have prepared polymer/liquid-crystal (*N*-4′-ethoxybenzylidene-4-butylaniline, EBBA/TMA^+Cl^-) composite membranes immobilising (**2b**) and have found that the rate of UO_2^{2+} transport is efficiently controlled by the changes in pH and temperature. These are novel examples for the selective transport of UO_2^{2+}.

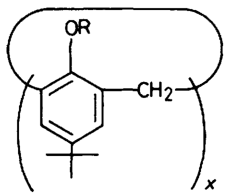
The selective extraction of uranium from sea water has attracted extensive attention from chemists because of its importance in relation to energy problems. In order to design such a ligand that can selectively extract uranyl ion (UO_2^{2+}), one faces a difficult problem, namely, the ligand must strictly discriminate between UO_2^{2+} and other metal ions which are present in great excess in sea water. A possible unique solution for this problem is to use a cyclic ligand suitably structured to perform the UO_2^{2+}-binding: as UO_2^{2+} complexes adopt either a pseudoplanar pentaco-ordinate or hexaco-ordinate structure,[1] a macrocyclic host molecule with a nearly coplanar arrangement of either five or six donating groups would serve as a specific ligand for UO_2^{2+} (*i.e.*, as a uranophile).[2–4] We recently found that calix[5]arene-*p*-pentasulphonate derivatives (**1**; $x = 5$) and calix[6]arene-*p*-hexasulphonate derivatives (**1**; $x = 6$) have remarkably large stability constants ($K_{uranyl} = 10^{18.7-19.2}$ mol dm^{-3}) and selectivity factors ($K_{uranyl}/K_{M^{n+}} = 10^{10-17}$) in water.[5,6] The remarkably high selectivity is attributed to the rigid skeleton of calix[5]arene and calix[6]arene which can provide the pre-organised penta- or hexaco-ordination geometry for the binding of UO_2^{2+} but cannot accommodate a square-planar or tetrahedral co-ordination geometry appropriate for other metal cations in an 'induced-fit' manner.

In this paper, we report the synthesis and application of lipophilic calix[6]arene derivatives (**2**) and (**3**) as carriers for the selective solvent extraction and membrane transport of UO_2^{2+}. We have found that these lipophilic calix[6]arene derivatives can selectively extract UO_2^{2+} and carry it in an active transport manner across a liquid and a polymer/liquid-crystal composite membrane.

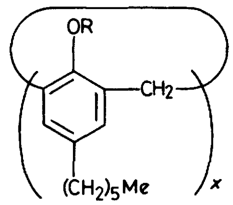


$x = 5$ $x = 6$

(**1**) calix[x]arenes
a; R = H
b; R = CH_2CO_2H
X = SO_3Na



(**2**; x = 6)

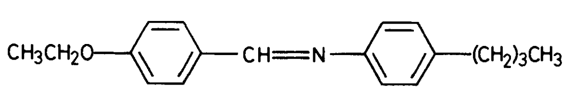


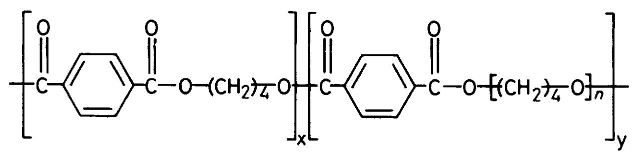
(**3**; x = 6)

a; R = H
b; R = CH_2CO_2H

Experimental

Materials.—The preparation of *p*-t-butylcalix[6]arene (**2a**) has been described previously.[6] 37,38,39,40,41,42-Hexakis(*O*-carboxymethyl)-*p*-t-butylcalix[6]arene (**2b**) was synthesised from (**2a**) according to the method of Chang and Cho,[7,8] *i.e.* (**2a**) was treated with ethyl monobromoacetate in the presence of NaH followed by hydrolysis of the ester with Me_4NOH (60%), m.p. 251–253 °C (lit.,[8] 252–255 °C). The product gave





Pelprene

Table 1. Solvent extraction of UO_2^{2+} at 30 °C.

Extraction agent	ex%[a] pH 8.0[b]	ex%[a] pH 10.0[b]
(**2a**)	4.6	0
(**2b**)	100	93.3
(**3a**)	22.5	0
(**3b**)	100	90.0
Dicyclohexyl-18-crown-6	1.36	0

[a] Organic phase (*o*-dichlorobenzene 10 cm^3): [extraction agent] = 2.10 mmol dm^{-3} aqueous phase (25 cm^3): [$UO_2(CH_3CO_2)_2$] = 0.037 mmol dm^{-3}. [b] Buffered with 4.0 mmol dm^{-3} borate. This is the pH of sea water.

a satisfactory elemental analysis and spectral (n.m.r., i.r.) properties consistent with the assigned structure.*

p-Hexylcalix[6]arene (**3a**) was synthesised from formaldehyde and *p*-hexylphenyl according to the method of Nakamoto *et al.*[9] (51%), m.p. (decomp.) 305–306 °C; $\nu_{max.}$(KBr) 3 150 (OH) cm^{-1}; δ(CDCl$_3$) 0.88 (18 H, t, Me), 1.28 [48 H, br s, $(CH_2)_4$], 2.46 (12 H, t, ArCH$_2$), 3.80 (12 H, br s, ArCH$_2$Ar), 6.85 (12 H, s, ArCH$_2$), and 10.32 (6 H, s, OH); *m*/*z* M^+ 1 140 (Found: C, 81.9; H, 9.4. Calc. for $(C_{13}H_{18}O)_6$: C, 82.1; H, 9.5%).

Compound (**3a**) was converted into 37,38,39,40,42-hexakis-(*O*-carboxymethyl)-*p*-hexylcalix[6]arene (**3b**) in a manner similar to that described above. 37,38,39,40,41,42-Hexakis-(ethoxycarbonylmethyl)-*p*-hexylcalix[6]arene (51%), m.p. 101–103 °C; $\nu_{max.}$(KBr) 1 750 cm^{-1} (C=O); δ(CDCl$_3$) 0.84 (18 H, t, Me in hexyl), 0.95–2.12 [66 H, m, $(CH_2)_4$ and Me in ethyl], 2.33 (12 H, t, ArCH$_2$), 3.97 and 4.25 (12 H, dd, ArCH$_2$Ar), 4.11 (12 H, q, CO$_2$CH$_2$), 4.50 (12 H, s, OCH$_2$), and 6.63 (12 H, s, ArH) [Found: C, 74.0; H, 8.9. Calc. for $(C_{17}H_{24}O_3)_6$: C, 73.9; H, 8.8%]. 37,38,39,41,41,42-Hexakis(carboxylmethoxy)-*p*-hexylcalix[6]arene (**3b**) (78%), m.p. 205–208 °C; $\nu_{max.}$(KBr) 3 600–2 750 (OH), 1 740 cm^{-1} (C=O); δ(CDCl$_3$) 0.84 (18 H, t, Me), 1.24 [48 H, br s, $(CH_2)_4$], 2.36 (12 H, t, ArCH$_2$), 4.07 (12 H, br s, ArCH$_2$Ar), 5.34 (12 H, s, OCH$_2$), and 6.71 (12 H, s, ArH) [Found: C, 71.5; H, 8.3. Calc. for $(C_{15}H_{20}O_3)_6 \cdot H_2O$: C, 71.7; H, 8.2%].

Two-phase Solvent Extraction.—An organic solution (*o*-dichlorobenzene) containing calixarene-based uranophiles was mixed with an aqueous solution [pH 8–10 with 4.0 mol dm^{-3} borate and pH 5.9 with 10 mol dm^{-3} 'Bis-Tris,' $(HOCH_2)_3CN(CH_2CH_2OH)_2$] containing $UO_2(CH_3CO_2)_2$ and competing metal cations. 'Bis-Tris' was used to avoid the precipitation of the competing metal cations at pH 5.9. The mixture was sitrred at 30 °C for 15 h (the extraction equilibria were usually attained within 5 h). The aqueous phase was subjected to the analysis with Arsenazo III[10,†] to determine the decrease in the UO_2^{2+} concentration. The decrease in other metal cations was determined by atomic absorption spectroscopy.

UO_2^{2+} Transport in a Liquid Membrane System.—UO_2^{2+} transport across an *o*-dichlorobenzene liquid membrane was examined within a U-tube immersed in a thermostatted water-bath (40 °C). The concentration of UO_2^{2+} transported to the OUT aqueous phase was determined by analysis with Arsenazo III.[10] Further details are described in the caption to Figure 2.

UO_2^{2+} Transport in a Polymer/Liquid-crystal Composite Membrane System.—The composite membrane was prepared by casting 5 cm^3 of a chloroform solution containing the following compounds on a glass plate: Pelprene 40H (a copolymer of terephthalic acid and tetramethylene glycol, supplied from Toyobo Co. Ltd.) (0.12 g), *N*-4′-ethoxybenzylidene-4-butylaniline (EBBA) (0.17 g), (**2b**) (0.082 g), and trioctylmethylammonium chloride (TMA^+Cl^-) (0.050 g). Thus, the ratio of Pelprene 40H:EBBA is 40:60 (w/w) and the molar ratio of EBBA:(**2b**):TMA^+Cl^- is 10:1:2. After 1 day, the membrane was dried at 0.1 mmHg for 4 h and then kept under reduced pressure for 3 days. The thickness of the membrane was 80 µm. We thus obtained a homogeneous, transparent film suitable for UO_2^{2+} transport. When other polymers [*e.g.* poly(vinyl chloride), polycarbonate, *etc*] were used as a binder of EBBA containing (**2b**), they did not give homogeneous films. Pelprene 40H, which is *a priori* flexible and shows excellent compatibility with EBBA, is most suited to the present purpose. In the UO_2^{2+} transport experiments, membrane surface contact with the glass plate was directed toward the IN (source) aqueous phase.

UO_2^{2+} permeation across the composite membrane was estimated by means of a U-tube which sandwiched the membrane at its bottom centre. The membrane area was 3.46 cm^2 and IN and OUT aqueous phase (30 cm^3 each) were stirred at a constant speed (*ca.* 400 rpm). Further details of the UO_2^{2+} transport experiments are recorded in the caption to Figure 4.

Results and Discussion

Two-phase Solvent Extraction.—The results of solvent extraction are summarised in Table 1. It was confirmed on the basis of the spectroscopic method that calixarene-based uranophiles (**2**) and (**3**) do not leak out into the aqueous phase. Examination of Table 1 reveals that (**2b**) and (**3b**) exhibit excellent extractability (ex%) as expected from the large stability constant of (**1b**; $x = 6$).[5,6] The slight decrease in ex% at higher pH is attributed to the hydrolysis of $UO_2(CH_3CO_2)_2$. On the other hand, (**2a**) and (**3a**) showed moderate ex% at pH 8.0 but almost no extraction ability at pH 10.0. We have found that (**1a**; $x = 5$) and (**1b**; $x = 6$) show stability constants comparable to (**1b**; $x = 5$) and (**1b**; $x = 6$). The low ex% for (**2a**) and (**3a**) is thus attributed to the pK_a of the OH groups which is sensitive to the nature of the *para* substituents: the pK_a values in (**1a**; $x = 5$) and (**1a**; $x = 6$) are lowered by the electron-withdrawing sulphonate groups, so that the ligands can associate well with UO_2^{2+} at neutral to slightly-basic pH.[6] In contrast, the pK_a values in (**2a**) and (**3a**) are too high to use as uranophiles in this pH region. Also in contrast, as the pK_a

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* In the synthesis of 37,38,39,40,41,42-hexakis-(*O*-ethoxycarbonylmethyl)-*p*-t-butylcalix[6]arene, one must use EtOH to decompose the NaH remaining in the reaction mixture. If MeOH is used, the base-catalysed ester exchange takes place to yield the methyl ester derivative of (**2b**). For example, Chang and Cho[8] reported m.p. 208–210 °C for the ethyl ester derivative of 25,26,27,28-tetrakis(*O*-ethoxycarbonylmethyl)-*p*-t-butylcalix[4]arene, but we found that this compound is the methyl ester derivative. When we used MeOH to decompose excess NaH, we obtained this compound (m.p. 210–211 °C). In contrast, when we used EtOH, we obtained the ethyl ester derivative (m.p. 125–127 °C). We have carefully characterised these products by i.r., n.m.r., and mass spectroscopy to confirm this conclusion.

† 2,2′-(1,8-dihydroxy-3,6-disulphonaphthylene-2,7-bisazo)bisbenzenearsonic acid.

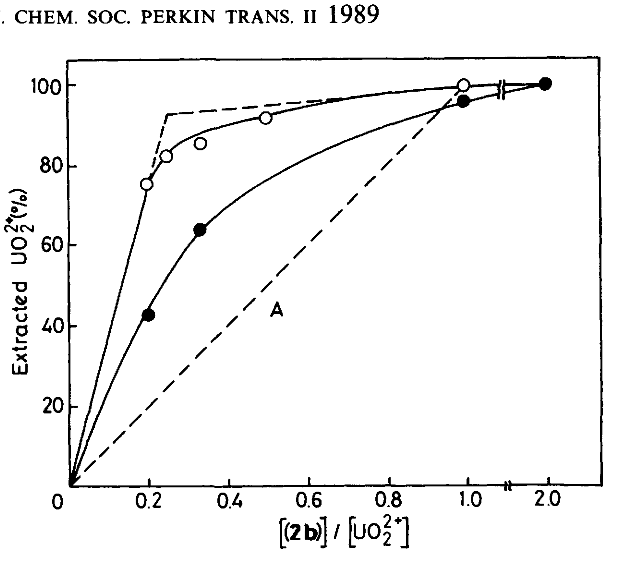

Figure 1. Extraction of UO_2^{2+} (added as acetate salt) from water (pH 5.9 with 10 mmol dm^{-3} 'Bis-Tris') to *o*-dichlorobenzene. [(**2b**)] = 0.10 mmol dm^{-3}, [TMA^+Cl^-] = 1.00 mmol dm^{-3} for ●. The concentration of (**2b**) was maintained constant while that of $UO_2(CH_3CO_2)_2$ was varied.

Table 2. Solvent extraction of UO_2^{2+} in the presence of competing metal cations at 30 °C.

Metal (conc./mmol dm^{-3})	ex%[a] (**2b**)	ex%[a] (**2b**) TMA^+Cl^- [b]
None	100	100
Mg^{2+} (100)	72	100
Ni^{2+} (0.25)	93	100
(1.00)	77	100
Zn^{2+} (0.73)	63	90
(1.20)	51	84

[a] Organic phase (*o*-dichlorobenzene, 5 cm^3): [(**2b**)] = 0.10 mmol dm^{-3}, aqueous phase (25 cm^3, pH 5.9 with 10 mmol dm^{-3} 'Bis-Tris'): [$UO_2(CH_3CO_2)_2$] = 0.020 mmol dm^{-3}. Competing metal cations were precipitated above this pH, whereas (**2b**) lost its extraction ability below this pH. [b] [TMA^+Cl^-] = 1.0 mmol dm^{-3}.

values in (**2b**) and (**3b**) are scarcely affected by the nature of the *para* substituents, they can behave as excellent uranophiles at pH 8–10. We thus used (**2b**) for the following extraction and transport experiments.

Figure 1 shows plots of ex% *versus* [(**2b**)]/[UO_2^{2+}]. If the extraction species is the 1:1 (**2b**)/UO_2^{2+} complex and the extraction equilibrium constant is large enough, the plot should give a straight line connecting the origin and ex% = 100 at [(**2b**)]/UO_2^{2+}] = 1.0 (dotted line A in Figure 1). However, the experimental plots appeared above the straight line, suggesting the formation of a 1:3 (**2b**)/UO_2^{2+} complex. It has been established that in an aqueous system, (**1b**; x = 6) forms a 1:1 complex with UO_2^{2+}.[6] The most important difference between the homogeneous aqueous system and the two phase solvent extraction system is that the species extracted into the organic phase must be 'neutral.' The above finding suggests, therefore, that (**2b**)$^{6-}$ forms a 1:1 complex with UO_2^{2+} and the resultant complex [(**2b**)·UO_2]$^{4-}$ is neutralised by two UO_2^{2+} ions adsorbed as counter-cations. This results in the 'neutral' extraction species (**2b**)·$(UO_2)_3$. If this is the case, two UO_2^{2+} ions bound to the complex would be easily displaced by cations added to the organic phase. We thus repeated the extraction experiments in the presence of a lipophilic organic cation, trioctylmethylammonium chloride (TMA^+Cl^-) (Figure 1)[11,12] and found that the plots become closer to the theoretical line expected for the 1:1 complex with increasing TMA^+ concentration. This supports the view that the unusual stoicheiometry is due to the 'neutralisation' of the primary extraction species.

We carried out solvent extraction of UO_2^{2+} in the presence of competing metal cations. 'Bis-Tris' buffer was used to obviate the precipitation of the competing metal cations. Previously, the UO_2^{2+} selectivity of (**1b**; x = 6) was evaluated by competitive binding with other metal cations in an aqueous system. It was found that the absorption spectrum of the (**1b**; x = 6)·UO_2^{2+} complex is not affected at all by the addition of an excess quantity of competing metal cations.[5,6] This indicates that K_{uranyl} is much greater than the stability constants for other metal cations ($K_M{}^{n+}$). We thus expected that in solvent extraction ex% for UO_2^{2+} would be scarcely affected by the addition of these metal cations. Contrary to our expectation, the ex% values for UO_2^{2+} were significantly reduced (Table 2), indicating that these metal cations can apparently compete with UO_2^{2+} for a binding site in (**2b**). The disagreement would be again rationalised in terms of the special requirement for the two-phase solvent-extraction system: that is, even though (**2b**) forms the UO_2^{2+} complex selectively, [(**2b**)·UO_2]$^{4-}$ further adsorbs other metal cations as counter-cations non-selectively. To resolve this dilemma, we carried out solvent extraction in the presence of excess TMA^+, expecting that the adsorption of other metal cations would be competitively suppressed by added TMA^+. As shown in Table 2, the selectivity in the presence of TMA^+ was significantly improved and the UO_2^{2+} ion was extracted in 100% selectively even in the presence of excess Mg^{2+} and Ni^{2+}. These findings indicate that the excellent selectivity of (**1**) as 'super-uranophiles' can be reproduced in the solvent extraction system by taking the special requirement for the solvent extraction into account.

UO_2^{2+} *Transport in a Liquid-membrane System.*—Although ion extraction with calixarene esters and related compounds has been reported by several groups,[7,8,13–18] the study of ion transport across a membrane has been very limited. Izatt *et al.*[19,20] studied the cation transport system with unmodified *p*-t-butylcalix[*x*]arene (x = 4, 6, 8) in H_2O–organic solvent–H_2O liquid-membranes. They found that transport by the calixarenes is selective for Cs^+ over other alkali metal cations with the selectivity increasing in the order [8] > [6] > [4]. Alfieri *et al.*[16] used a crowned *p*-t-butylcalix[4]arene as an ion carrier in the model liquid-membrane system and found that the transport ability is greatly improved owing to the intramolecularly combined ionophilic crown and ionisable OH groups.

Here, we tested the UO_2^{2+} transport ability of (**2b**) in a similar liquid-membrane system. As described above, UO_2^{2+} is extracted more efficiently at neutral pH than at basic pH. According to our previous work,[5,6] the binding ability of (**1b**; x = 6) is almost constant above pH 7.5. We thus adjusted the pH of the IN aqueous phase at pH 8.5. The OUT aqueous phase was kept acidic with 0.1 mol dm^{-3} HCl to enforce the decomplexation. In order to test if all UO_2^{2+} ions are carried from IN to OUT according to the active transport mechanism, the quantity of (**2b**) used is greater than that of transported UO_2^{2+}. As illustrated in Figure 2, UO_2^{2+} transport occurred in an active transport manner (○ and □): a rapid UO_2^{2+} decrease in the IN aqueous phase is followed by a relatively slow UO_2^{2+} increase in the OUT aqueous phase. The membrane phase was stirred efficiently by a magnetic bar (*ca.* 400 rpm), so that if the UO_2^{2+} uptake from the IN aqueous phase to the membrane phase is the rate-determining step, the UO_2^{2+} increase in the OUT aqueous phase should be equal to the UO_2^{2+} decrease in the IN aqueous phase. The disagreement between those two rates suggests that the rate-determining step is UO_2^{2+} release to the OUT aqueous phase.

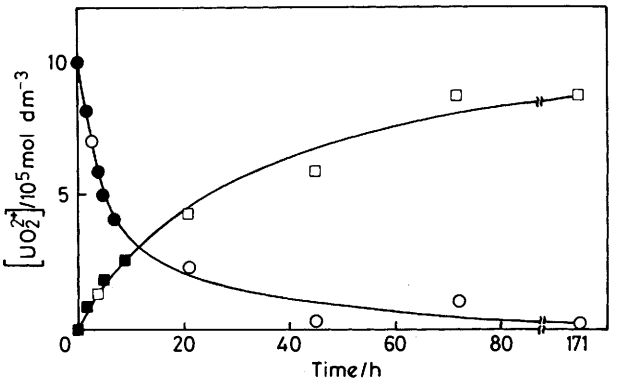

Figure 2. UO_2^{2+} transport across membrane. IN aqueous phase (10 cm^3): $[UO_2(CH_3CO_2)_2]$ = 0.10 mmol dm^{-3}, pH 8.5 with 4.0 mmol dm^{-3} borate buffer. Membrane phase (40 cm^3 *o*-dichlorobenzene): [(**2b**)] = 0.10 mmol dm^{-3}. OUT aqueous phase (10 cm^3): [HCl] = 0.10 mol dm^{-3}. Open plots indicate the UO_2^{2+} transport system consisting of IN $\longrightarrow$ membrane $\longrightarrow$ OUT. Filled plots indicate the changes in the UO_2^{2+} concentration determined separately for IN $\longrightarrow$ membrane and membrane $\longrightarrow$ OUT.

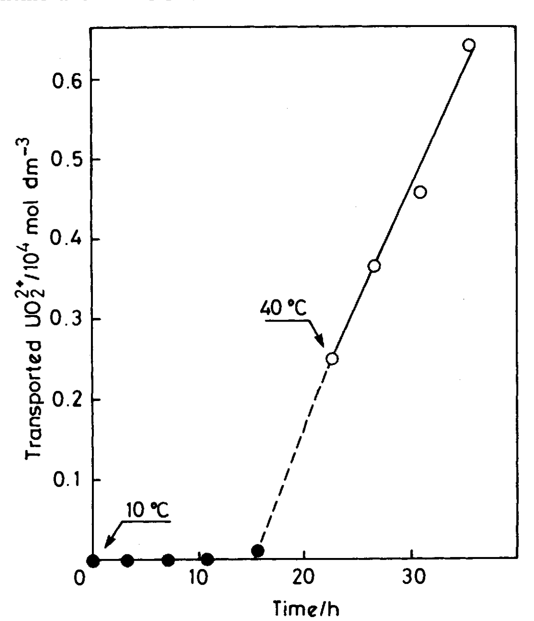

Figure 3. Temperature control of the UO_2^{2+} release from the polymer/EBBA/(**2b**)/TMA$^+$Cl$^-$ composite membrane to the OUT aqueous solution. IN aqueous phase (30 cm^3): $[UO_2(CH_3CO_2)_2]$ = 1.0 mmol dm^{-3}, pH 8.5 with 0.10 mol dm^{-3} 'Bis-Tris'. OUT aqueous phase (30 cm^3): [HCl] = 0.10 mol dm^{-3}.

In order to identify the rate-determining step, we evaluated the rates of UO_2^{2+} uptake and UO_2^{2+} release independently using the same transport apparatus. When UO_2^{2+} uptake from the IN aqueous phase to the membrane phase was monitored, the OUT aqueous phase was replaced with air. After completion of the UO_2^{2+} extraction, the organic phase was separated and placed in a new U-tube with the OUT aqueous phase. The rate of UO_2^{2+} release was evaluated by following the UO_2^{2+} increase in the OUT aqueous phase. The result is illustrated in Figure 2 (● and ■). Examination of Figure 2 reveals that the rates determined independently for IN $\longrightarrow$ membrane and membrane $\longrightarrow$ OUT are in good agreement with those determined for the IN $\longrightarrow$ membrane $\longrightarrow$ OUT transport system. If the UO_2^{2+} extraction from the IN aqueous phase is the rate-determining step, the rate for membrane $\longrightarrow$ OUT should be faster than that for the transport system. The good agreement between the independently determined rates and the transport rates therefore supports the view that the rate-determining step in UO_2^{2+} transport is the UO_2^{2+} release to the OUT aqueous phase. The finding suggests the possibility that the transport rate would be further accelerated by the enhancement of the acid concentration in the OUT aqueous phase.

As described above, the UO_2^{2+} selectivity of (**2b**) was significantly improved by the addition of TMA$^+$Cl$^-$ to the organic phase. Then, how is the rate of UO_2^{2+} transport affected by the addition of TMA$^+$Cl$^-$? We determined the rates for IN $\longrightarrow$ membrane and membrane $\longrightarrow$ OUT separately in the presence of TMA$^+$Cl$^-$ (1.0 mmol dm^{-3}). The initial rate for IN $\longrightarrow$ membrane (1.0×10^{-7} mol h^{-1}, estimated from Figure 2) was enhanced to 1.3×10^{-7} mol h^{-1} in the presence of TMA$^+$Cl$^-$. Similarly, the initial rate for membrane $\longrightarrow$ OUT (4.5×10^{-8} mol h^{-1}, estimated from Figure 2) was enhanced to 1.2×10^{-7} mol h^{-1} in the presence of TMA$^+$Cl$^-$. The results indicate that TMA$^+$Cl$^-$ increases not only the UO_2^{2+} extraction from the IN aqueous phase to the membrane phase but the UO_2^{2+} release from the membrane phase to the OUT aqueous phase. However, the observed rate augmentation was relatively small. The addition of TMA$^+$Cl$^-$ would potentially accelerate the rate of UO_2^{2+} extraction due to the formation of hydrophobic ion pairs but the number of UO_2^{2+} ions extracted with one (**2b**) molecule would decrease from 3 to 1–2. Presumably, these two opposing effects offset the change in the speed of extraction and lead to a small rate increase. On the other hand, it is not clear yet why the rate of the UO_2^{2+} release is also increased by the addition of TMA$^+$Cl$^-$. Anyhow, the rate-determining step is still the UO_2^{2+} release, even in the presence of TMA$^+$Cl$^-$.

UO_2^{2+} *Transport in a Polymer/Liquid-crystal Composite Membrane System.*—A liquid-membrane as described above is very convenient and can provide a large transport flux but the system is not necessarily useful for practical applications. On the other hand, a polymeric membrane is more useful for practical applications but is often hampered by a low transport flux. The polymer/liquid-crystal composite membrane, in which the fluid liquid crystalline material is embedded in a polymer matrix,[21–23] can compensate for these disadvantages. It is apparently a polymeric solid membrane but can provide a relatively large transport flux above the crystal-liquid crystal phase-transition temperature. This is due to the high fluidity of the liquid crystalline material which forms the continuous phase in the polymer matrix.[21–23] Therefore, the polymer/liquid-crystal composite membrane could be called an 'immobilised liquid membrane'.

We prepared a composite membrane composed of polymer (Pelprene 40H)/liquid-crystal (EBBA)/(**2b**)/TMA$^+$Cl$^-$. After a detailed examination of the preparation conditions, we finally found out the method with which to prepare the homogeneous composite membrane (see Experimental). Figure 3 shows UO_2^{2+} transport across the composite membrane from the IN aqueous phase (pH 8.5) to the OUT aqueous phase (pH 0.1 mol dm^{-3} HCl). The EBBA phase in the composite membrane has T_{KN} (crystal-nematic liquid crystal phase-transition temperature) at 32 °C.[21–23] It is seen from Figure 3 that UO_2^{2+} is not transported at all at 10 °C ($< T_{KN}$) while it is rapidly transported across this membrane at 40 °C ($> T_{KN}$). The thermal molecular motion of EBBA is frozen $< T_{KN}$. Thus, the diffusion of the (**2b**)·UO_2 complex immobilised in the crystal lattice would be almost disregarded. Above T_{KN}, on the other hand, the EBBA phase is so fluid that (**2b**) can easily carry UO_2^{2+} ion across this membrane.

The above example implies that (**2b**)-mediated UO_2^{2+} permeation can be controlled by the temperature switch. As the binding constant of (**1b**; $x = 6$) for UO_2^{2+} is pH-dependent,[5,6] similar permeation control may be attained by the pH change. We have found that in a liquid membrane system the rate-

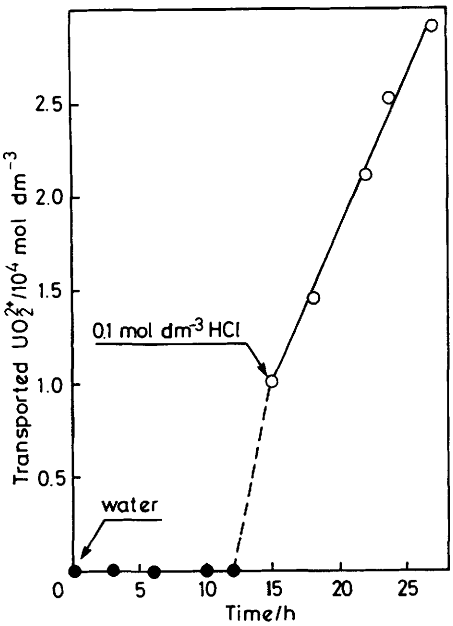

Figure 4. pH control of the UO_2^{2+} release from the polymer/ EBBA/ (**2b**)/TMA^+Cl^- composite membrane to the OUT aqueous solution at 40 °C. The transport conditions are similar to Figure 3 except the pH change in the OUT aqueous solution.

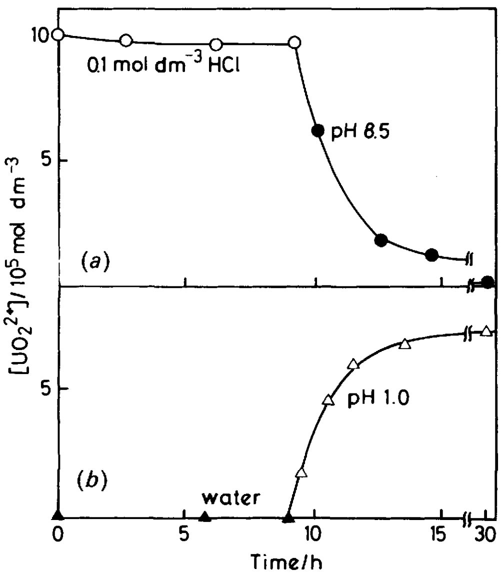

Figure 5. pH-controlled catch-and-release of UO_2^{2+} ion at 40 °C: (*a*) UO_2^{2+} catch by the membrane, (*b*) UO_2^{2+} release from the membrane.

determining step is the release of UO_2^{2+} to the OUT aqueous phase. We thus tried to control the rate of UO_2 transport by a change of pH in the OUT aqueous phase. As shown in Figure 4, UO_2^{2+} was scarcely released to the neutral OUT aqueous phase (pH 6.5, not buffered). When the OUT aqueous phase was acidified with conc. HCl, a rapid release of UO_2^{2+} took place. This indicates that the (**2b**)·UO_2^{2+} exists in the membrane as a stable complex at neutral pH region but is decomposed by contact with the acidic aqueous solution. Thus, the UO_2^{2+} permeation rate can be efficiently controlled by the pH change in the OUT aqueous phase.

The pH-controlled UO_2^{2+} uptake to and release from the composite membrane can be demonstrated more clearly by the so-called 'catch-and-release'.[22] Several pieces of the composite membrane [0.067 g containing 1.25 × 10^{-5} mol of (**2b**)] were added to a 0.1 mol dm^{-3} HCl solution (25 cm^3) containing 2.5 × 10^{-6} mol of $UO_2(CH_3CO_2)_2$. As shown in Figure 5(*a*), the concentration of UO_2^{2+} ion in the solution scarcely decreased in 0.1 mol dm^{-3} HCl. When the solution pH was enhanced to pH 8.5, rapid adsorption of UO_2^{2+} ion occurred. This indicates that (**2b**) in the membrane catches UO_2^{2+} at this pH. After 40 h the membrane pieces were recovered by filtration, washed with cold water and then put into a new aqueous solution (pH 6.5, not buffered). As shown in Figure 5(*b*), UO_2^{2+} release was scarcely observed. When the solution pH was lowered to pH 1.0, rapid UO_2^{2+} release took place. These sensitive responses to medium pH would be useful for practical UO_2^{2+} recovery and the regeneration of the membrane.

Conclusions.—The present study has demonstrated that novel UO_2^{2+} transport systems can be set up using calixarene-based uranophiles which exhibit remarkably high stability and selectively. We learned through this study, however, that in order to design an efficient UO_2^{2+} transport system one must pay more attention to the special requirement that the extraction species be formally neutral. This requirement was partly satisfied by the addition of lipophilic organic cations. As a future idea, one may expect that calixarenes which have a intramolecular cationic cap would act as better UO_2^{2+} carriers.

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Received 20*th September* 1988; *Paper* 8/03635G