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ACTIVE TRANSPORT OF URANYL ION BY MACROCYCLIC POLYCARBOXYLATE-HYDROPHOBIC AMMONIUM CARRIERS

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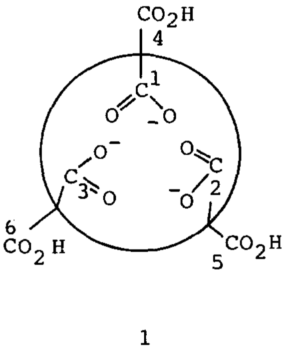
The active transport of uranyl ion through a liquid membrane was facilitated synergetically by macrocyclic polycarboxylate anion and hydrophobic ammonium cation.

Recovery of uranium from sea water has been a challenging possibility to get a huge energy source and investigated primarily by the adsorption method[1]. This project is restricted by the extremely low uranyl concentration, 3.3 ppb. Membrane transport may give an interesting alternative to the adsorption. Uranyl ion is transferred from bulk aqueous into the membrane phase by the complexation and penetrated and dissociated into receiving aqueous phase. The appropriate coupling with chemical potentials may drive the transport against the concentration gradient to produce active transport, enabling automatic accumulation of uranyl ion. We have synthesized several "Uranophiles" which possess extraordinary large stability constants by hexadentate polyanions [2]. The same line of idea was followed recently by Lagrange et al.[3] and Shinkai et al.[4] These compounds seem to be an interesting candidate for the carrier of active membrane transport of uranyl ion. In this communication, we have tried a regiospecific functionalization of macrocyclic hexacarboxylate to produce appropriate carrier molecules for the uranyl transport.

Compound 1 possesses six carboxylate groupings for coordinating to uranyl by using three in-ring carboxylate anions 1 ~ 3. Other three carboxylates 4 ~ 5 can be subjected to a further functionalization. Therefore, t-butyl ethyl malonate was employed partially instead of diethyl malonate in the construction of macrocyclic skeleton via malonate synthesis[2c] shown in the following Scheme.



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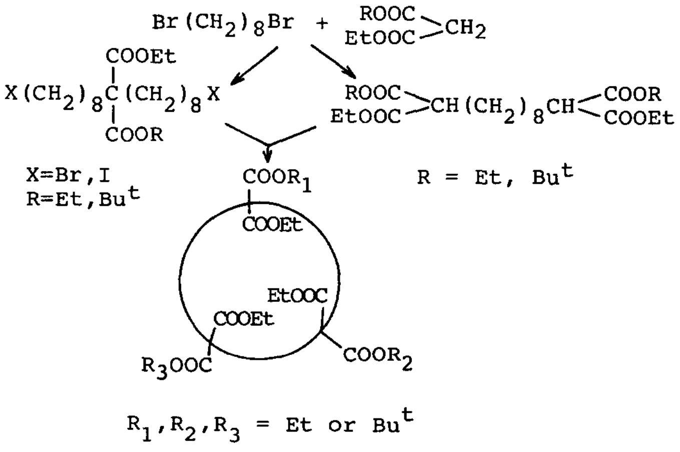
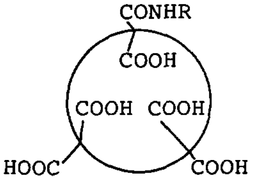
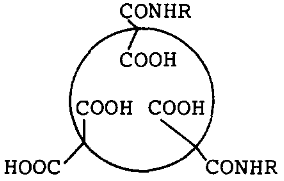


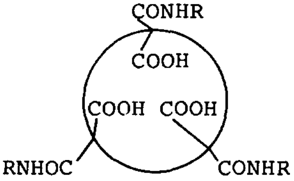
t-Butyl moiety was then selectively converted to carboxylic acid by the introduction of HCl gas into CH_2Cl_2 solution of macrocyclic hexaester. Mono-, di-, and tricarboxylic acids obtained were then converted via acid chlorides to the respective stearylamides to introduce hydrophobic long alkyl chain. The remaining ethyl ester moiety was then hydrolized by aqueous alcoholic KOH to give monoamide-pentacarboxylic-(2), diamide-tetracarboxylic(3) and triamide-tricarboxylic acids (4)5). All of these compounds satisfy hexacoordination by three in-ring carboxylate groupings.



2 $R=C_{18}H_{37}$
mp. 55-57°



3 $R=C_{18}H_{37}$
waxy mass



4 $R=C_{18}H_{37}$
waxy mass

Transport experiments were conducted by using U-tube (ϕ = 16 mm). The source aq. phase I containing uranyl acetate (3.3×10^{-5} M, 8 mL) was brought in contact with a solution of 3 (1.0×10^{-4} M, 8 mL) in $CHCl_3$, which was again in contact with another receiving aq. phase II containing sodium bicarbonate (1.0 M, 8 mL). The transport was too slow and trioctylmethylammonium chloride (5) (1.0×10^{-4} M) was added to the $CHCl_3$ phase. Then the uranyl appeared in aq. II with much higher rate showing a sigmoidal curve with a corresponding monotonous decrease from aq. I. This behavior reflects the initial accumulation of uranyl in $CHCl_3$ layer by complexation followed by dissociation into carbonate solution. Even after 3 hours, the transport continuously proceeded against the concentration gradient of uranyl between two aqueous phases giving rise to the active transport. At the final, more than 98 % uranyl ion originally present in aq. I was transported into the receiving phase II. The ammonium salt itself did not transport uranyl at all.

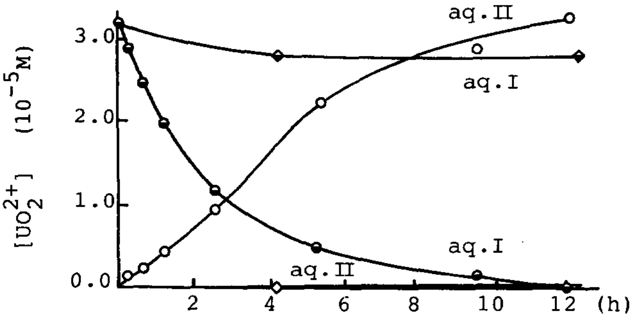


Fig. 1 Time Course of UO_2 Concentration in Aq. Phases in the Transport by Using 3

With addition of 5
Without addition of 5

The effect of the addition of ammonium salt was so dramatic. Fig. 2 shows the concentration dependence of the ammonium salt on the transport rate at the constant concentration of 3. The transport rate increased almost linearly with the ratio up to 1:1 composition of 3 and 5. After this specific point, the rate was not influenced by the further addition of the ammonium salt.

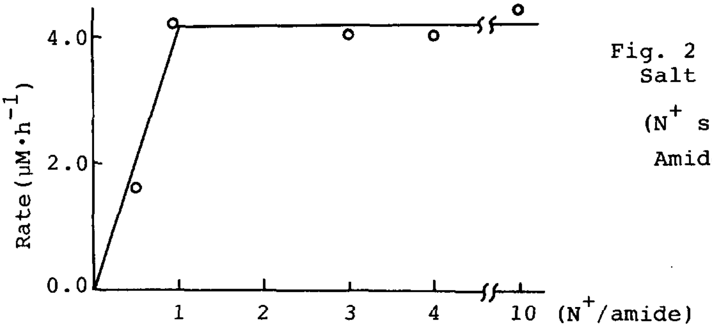
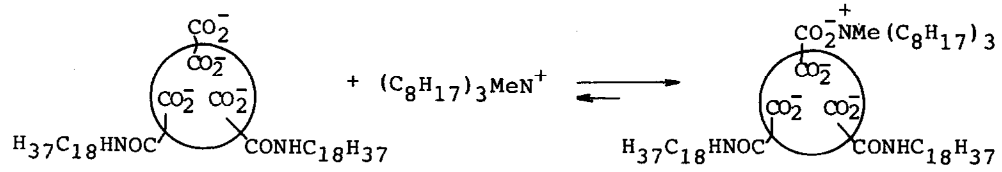


Fig. 2 Effect of Ammonium Salt on Transport Rate

(N^+ salt : 5
Amide : 3)

This behavior clearly shows that a 1:1 complex is formed between ammonium and tetracarboxylate and that the complex is the real carrier in the uranyl transport. The linear increase of the rate with the composition indicates that the equilibrium is shifted far to the right in the solution. It may be reasonable to assume that one of the carboxylates (out-ring) is complexed with



trioctylmethylammonium cation to give a hydrophobic complex not to be eluted from the organic to the aqueous phase. Since three remaining carboxylates are employed for the complexation with uranyl ion, a further addition of ammonium does not influence the transport rate.

Table 1 shows the structural effect of polycarboxylate 2, 3, 4 with a combination of tetraalkylammonium salts which include trioctylmethyl-, cetyltrimethyl-, lauryltrimethyl-, benzyltrimethyl- and tetraethylammonium chloride in a 1:1 molar ratio. The transport rate was evaluated from the linear slope after the initial induction period.

The structural effect of tetraalkylammonium chloride is understood by the relative hydrophobicity of the ammonium cation which must be the counter cation of polycarboxylates. The transport rate decreased in the order. trioctylmethyl-, cetyltrimethyl-, lauryltrimethyl-, benzyltrimethyl- and tetraethylammonium chloride. This order corresponds exactly to the decreasing carbon/nitrogen ratio, being 25, 17, 15, 10 and 8, therefore the decreasing order of hydrophobicity. The hydrophobic ammonium cation could protect the polycarboxylate to be eluted into the aqueous solution. On the other hand, the effect of polycarboxylate does not follow a simple dependence of hydrophobicity. The order may suggest the requirement of the appropriate balance

Table 1. Transport Rate of Uranyl by 1:1 Composition of Polycarboxylic Acid and Tetraalkylammonium Chloride a)

Polycarboxylic Acid	Tetraalkylammonium Chloride $R_1R_2R_3R_4$	Transport Rate $\mu M \cdot h^{-1} \cdot cm^{-2}$
monoamide-pentacarboxylic acid **2**	trioctylmethyl **5**	1.19
diamide-tetracarboxylic acid **3**	〃 **5**	1.94
triamide-tricarboxylic acid **4**	〃 **5**	0.62
diamide-tetracarboxylic acid **3**	cetyltrimethyl	1.76
〃	lauryltrimethyl	1.45
〃	benzyltrimethyl	0.26
〃	tetraethyl	——— b)

a) aq.1: $[UO_2] = 3.3 \times 10^{-5}$ M pH 4.8 ~ 5.1; aq.2: $[NaHCO_3] = 1.0$ M pH 8.2 ~ 9.0; $CHCl_3$ phase: [Polycarboxylate] $= 1.0 \times 10^{-4}$ M, [Tetraalkylammonium chloride] $= 3.3 \times 10^{-5}$; 8 mL each. b) No significant transport was observed.

of hydrophobicity to accept, transport and release the uranyl ion across the interphases of the liquid membrane. It is interesting to note that the observed transport rates lie in the order of fast transport rates observed for alkali metal cations through the liquid membrane6).

References

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