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NONCYCLIC POLYETHERS WITH TWO o-CARBOXYLPHENYL TERMINAL GROUPS EXHIBITING SELECTIVE TRANSPORT FOR ALKALINE EARTH METAL IONS THROUGH LIQUID MEMBRANES. EFFECT OF THE CONCENTRATION OF HYDROXIDE ION ON THE SELECTIVITY[1)]

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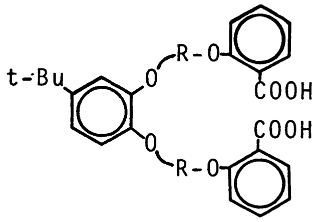
Three noncyclic polyethers containing o-carboxylphenyl groups as both end ones were synthesized. These synthetic carriers exhibit the selectivity for Ca^{++} or Ba^{++} in the competitive transport for Mg^{++}, Ca^{++}, and Ba^{++} in the source phase adjusted to initial pH 8.28 or 9.10 through liquid membranes. It was also found that the selective transport for alkaline earth metal ions can be changed by the concentration of hydroxide ion added.

It is well known that several natural occurring noncyclic ionophores, e.g., X537A and A23187, transport selectively one of alkaline earth metal ions through liquid membranes or biomembrane.[2)] There are, however, few reports about synthetic carrier exhibiting selective transport for them. Recently, Wierenga et al. reported a noncyclic polyether compound which can transport Ca^{++} effectively and of which the transport rate is comparable to that of A23187 in the single cation transport of Ca^{++} through liquid membranes.[3)] But it is ambiguous whether that synthetic ionophore exhibits the effective and selective transport of Ca^{++} in the competitive transport with other alkaline earth metal ions or not.

By the way, recently the attempts to change chemical and physical functions of cyclic polyether compounds reversibly by an extrinsic factor have increasingly received attention. For example, Shinkai et al. synthesized azobenzene-bridged crown ethers, aiming at photocontrolling the various functions of crown family compounds.[4)] However, there is no example that the selectivity of noncyclic polyether carrier for cations changes drastically by an extrinsic factor.

Our group and others have recently reported that even noncyclic polyether compounds can transport cations with high selectivity dependent on their chain structure and kinds of terminal groups.[5,6)] In this paper we wish to report three noncyclic polyether carriers containing o-carboxylphenyl groups as two end ones which exhibit the selective transport for alkaline earth metal ions dependent on their structures and the selectivity of only 1,2-bis{3'-(o-carboxylphenyloxy)-propyloxy}-4-t-butylbenzene (**1**) depends on the concentration of alkali hydroxide in the source phase and changes drastically from Ca^{++}- to Mg^{++}-selectivity when the large amount of alkali hydroxide adds into the source phase in the competitive transport of Mg^{++}, Ca^{++} and Ba^{++}. As carriers, **1** described above, 1,2-bis{2'-(o-carboxylphenyloxy)ethoxy}-4-t-butylbenzene (**2**), and 1,2-bis[2-{2-(o-carboxylphenyloxy)ethoxy}ethoxy]-4-t-butylbenzene (**3**) were synthesized.



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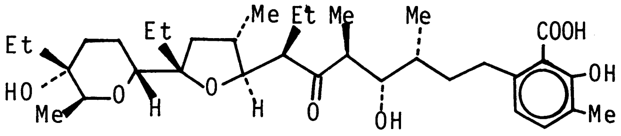
1 : $(CH_2)_3$
2 : $(CH_2)_2$
3 : $(CH_2)_2O-(CH_2)_2$



X537A

The competitive transport of alkaline earth metal ions (Mg^{++}, Ca^{++}, and Ba^{++}) by these polyether carriers through liquid membranes was carried out using a previously-reported U-type glass tube at 25 ± 0.2 °C.$^{5)}$ For comparison, the transport by a natural ionophore, X537A, was also investigated. The initial transport conditions of the transport experiment are shown in Table 1, and the amounts of cations transported were determined by atomic absorption analysis. In Table 1 are summarized the amounts of cations transported after 2 d by these carriers.

In Table 1, **1** exhibits fairly good Ca^{++}-selectivity, and both **2** and **3** transport Ba^{++} selectively, when the solution of the source phase was adjusted initially to pH 8.28 or 9.10 by the Tris buffered solution. The Ba^{++}-selectivity of **2** is superior to that of **3**. It is noteworthy that **2** exhibits high Ba^{++}-selectivity and amount of Ba^{++} transported comparable to natural ionophore X537A$^{7)}$ under the same conditions. The amounts of cations transported depends on the initial pH in the source phase, but the selectivity for cations is almost unchanged.$^{8)}$

Table 1. Cation Transport through Liquid Membranes

Run No.	Polyether	Conditions$^{a)}$	Cation transported after 2 d (mmol) Mg	 Ca	 Ba	 Li
1	**1**	Tris(pH 8.28)	≈0	0.10	≈0.01	-
2	**1**	Tris(pH 9.10)	≈0.01	0.18	0.03	-
3	**1**	0.1 M LiOH	0.53	0.12	≈0	≈0
4	**1**	0.2 M LiOH	1.13	0.22	0.03	0.03
5	**1**	0.3 M LiOH	(0.62	0.06	0	0.06)$^{b)}$
6	**2**	Tris(pH 9.10)	≈0	0.06	0.26	-
7	**2**	0.1 M LiOH	≈0	0.05	0.26	≈0
8	**3**	Tris(pH 8.28)	0	0.06	0.10	-
9	**3**	Tris(pH 9.10)	0	0.12	0.18	-
10	X537A	Tris(pH 9.10)	0	≈0	0.30	-
11	X537A	0.1 M LiOH	0	≈0	0.27	≈0

a) Other conditions are described below.
b) These values are amounts of cation after 12 h.

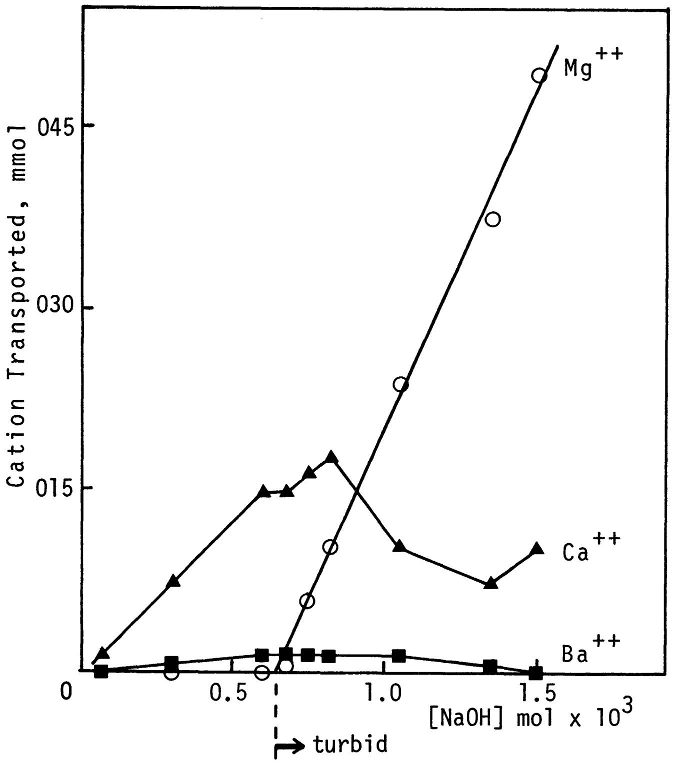
Initial transport conditions (25 °C):

(Source phase)	(Chloroform membrane)	(Receiving phase)
0.1 M $MgCl_2$ 0.1 M $CaCl_2$ 0.1 M $BaCl_2$ + (a) 15 ml	Polyether 1.5 x 10^{-4} mol $CHCl_3$ 30 ml	0.1 M H_3PO_4 15 ml

Surprisingly, when 0.1 M LiOH was added into the source phase (Run 3), **1** transported preferentially Mg^{++} instead of Ca^{++} and moreover the amounts of cation transported increased about three fold more than in the case of Run 2. In this case, the solution in the source phase became whitely turbid as soon as LiOH added into it.

This white turbidity resulted all from the formation of $Mg(OH)_2$.[9)] It is a very interesting phenomenon that the amount of Mg^{++} transported increased preferentially in spite of the formation of hardly soluble $Mg(OH)_2$ in the source phase, and the more the amount of LiOH added the more the transport rate and amount of Mg^{++} transported, i.e., when 0.3 M LiOH was added into the source phase, the amount of Mg^{++} transported reached 0.62 mol after only 12 h (Run 5). In the case of Runs 3~5, the white turbidity became thinner with time to disappear finally, while the solution in the source phase kept turbid even after 2 d in other cases, Runs 7 and 11. Additionally, any effect of the addition of LiOH on the selectivity and amounts of cation transported was not observed when **2** and X537A were used as carrier.

So, in order to investigate the relationship between the behavior of cation transport by **1** and the amount of alkali hydroxide added into the source phase, the transport experiments were carried out changing the amount of alkali hydroxide. In these experiments, NaOH was used instead of LiOH. The amounts of cations transported after 1 d to the amount of NaOH added inotially are shown in Fig. 1. As indicated in Fig. 1, the starting point of turbidity in the source phase accords with the beginning point of Mg^{++} transport. Apparently, the Mg^{++} transport increases linearly with the increase of the concentration of NaOH in the source phase. The maximum amount of Ca^{++} transported was obtained with the concentration of about 0.65×10^{-3} mol (0.043 M) NaOH. Carrier **1** can hardly transport alkaline metal ions, i.e., Li^+ and Na^+, under these experimental conditions and also can hardly transport Ba^{++} in the all range of the concentration of NaOH investigated. Apparently, carrier **1** can exhibit the highly selective transport of Ca^{++} in the range of the concentration of



Initial transport conditions(25 °C):

(Source phase)	($CHCl_3$ membrane)	(Receiving phase)
0.1 M $MgCl_2$ 0.1 M $CaCl_2$ 0.1 M $BaCl_2$ Sørensen's buffered solution$^{a)}$ 15 ml	Carrier **1** 1.5×10^{-4} mol $CHCl_3$ 30 ml	0.1 M H_3PO_4 15 ml

a) Sørensen's buffered solutions were adjusted by the mixture of 0.1 M NaCl, 0.1 M glycine, and 0.1 M NaOH solutions. Amount of Na^+ transported was about zero in the all range.

Fig. 1. Relationship between the amounts of cation transported after 1 d and the concentration of NaOH added into the source phase.$^{a)}$

NaOH lower than 0.043 M, while **1** can transport Mg^{++} more than Ca^{++} in the range of that of NaOH higher than 0.6 M. It is noted that the selective transport for alkaline earth metal ions by **1** can control by the change of the amount of alkali hydroxide added into the source phase. Such phenomena were not observed in the other carriers, **2**, **3**, and X537A, at all. Thus, it was found that the selectivity of **1** for them can reversed by the concentration of hydroxide ion added into the source phase;

$$\mathbf{1} : Ca^{++}\text{-selectivity} \underset{\text{low concn of OH}^-}{\overset{\text{high concn of OH}^-}{\rightleftarrows}} Mg^{++}\text{-selectivity}$$

Next, the extractability of **1** for alkaline earth metal ions from aqueous layer to organic layer was examined. The results in Table 2 are consisted with those of the transport through liquid membranes. Magnesium ion is extracted selectively by the addition of LiOH, while it can not be extracted at all in the absence of LiOH.

Table 2. Extraction of Cations with **1**

Conditions[a]	Extractability, % (25 °C)			
	Mg	Ca	Ba	Li
I	0	6	1	-
II	41	3	0	0
III	48	-	-	0
IV	0	-	-	-

a) In every case chloroform phase (5 ml) contains 1.5×10^{-4} mol of **1**.

(I): Aqueous phase, 0.1 M $MgCl_2$ + 0.1 M $CaCl_2$ + 0.1 M $BaCl_2$, Tris(pH 9.10) 15 ml.

(II): Aqueous phase, 0.1 M $MgCl_2$ + 0.1 M $CaCl_2$ + 0.1 M $BaCl_2$ + 0.1 M LiOH 15 ml.

(III): Aqueous phase, 0.1 M $MgCl_2$ + 0.1 M LiOH 15 ml.

(IV): Aqueous phase, 0.1 M $MgCl_2$, Tris(pH 9.10) 15 ml.

The structural cause of **1** concerning to the specific behavior is now under investigation.

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7) It is known that ionophore X537A can transport alkaline earth metal ions in the order as follows: $Ba^{++} \gg Sr^{++} > Ca^{++} > Mg^{++}$.[2]
8) The source phase is clear in the both cases adjusted to initial pH 8.28 and 9.10 by the Tris buffered solution.
9) This was confirmed by atomic absorption analysis. In the controll experiment (without carrier), Mg^{++} in the turbid solution can not remove from the source phase to the receiving phase at all.

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