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Transport of alkali and alkaline earth cations by a crown ether-alkylphosphoric acid system

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Competitive transport of alkali and alkaline earth cations has been carried out by using a mixed carrier system composed of dibenzo-14-crown-4 and bis(2-ethylhexyl)phosphoric acid. In the absence of crown ether, bis(2-ethylhexyl)phosphoric acid transported alkaline earth cations with high selectivity. The combination of dibenzo-14-crown-4 and bis(2-ethylhexyl)phosphoric acid showed a synergistic enhancement in lithium transport, and the enhancement effect was not apparent in transport of other cations. On the other hand, the mixed carrier systems consisting of dibenzo-14-crown-4 and dodecylbenzenesulfonic acid, and of dibenzo-14-crown-4 and 1-bromohexadecanoic acid exhibited the enhancement effects both in lithium transport and in sodium transport. The formation of the synergistic complex was analyzed by using fast atom bombardment mass spectrometry.

INTRODUCTION

During the past two decades, considerable attention has been given to the transport of alkali and alkaline earth ions by macrocyclic polyethers through a liquid membrane. In an effort to control the selectivity of ions in transport, various types of macrocycles were synthesized and were examined as carriers in transport systems.[1] In addition, mixed carrier systems consisting of macrocycles and ionizable lipophilic compounds have been investigated for the alkali metal transport.[2] Recently, we have reported a mixed carrier system composed of dibenzo-14-crown-4 (DB14C4) and bis(2-ethylhexyl)phosphoric acid (B2EHPA), which performs lithium selective transport across a chloroform membrane.[3] In this work, we applied the mixed carrier system to the competitive transport of alkali and alkaline earth cations, and extended our transport studies to include crown ether-organosulfonic acid and crown ether-carboxylic acid systems. Further, fast atom bombardment mass spectrometry was used to assess the formation of the synergistic adducts in these transport systems.

RESULTS AND DISCUSSION

Competitive transport of alkali and alkaline earth cations across a bulk chloroform membrane by the dibenzo-14-crown-4/Bis(2-ethylhexyl)phosphoric acid system

We have previously reported the competitive transport of alkali metal cations by using the dibenzo-14-crown-4 (DB14C4)/bis(2-ethylhexyl)-phosphoric acid (B2EHPA) system.[3] To evaluate the ability of the mixed carrier system for alkaline earth ion transport, competitive transport experiments were carried out using the U-tube apparatus illustrated in Figure 1. The both aqueous phases (a source phase and a receiving phase) in the tube contained 0.2 mmol of alkaline earth chloride ($MgCl_2$ or $CaCl_2$) along with 0.2 mmol of NaCl and 0.2 mmol of LiCl. The source phase was adjusted initially to pH 9.2 by using Tris buffer solution to form an active transport system. The results of the transport experiments are summarized in Table 1.

In the absence of crown ether, bis(2-ethylhexyl)-phosphoric acid transported magnesium ion with high selectivity. On the other hand, sodium ion was not transported under these experimental conditions, and the initial transport rate of lithium was 0.7 μmol/h; value about one fifteenth that observed for magnesium. In the case of the mixed carrier system composed of DB14C4 and B2EHPA, the initial transport rate of lithium was 2.7 μmol/h, and the value is 3.9 times that of the B2EHPA system. As DB14C4 did not transport metal ions in the single carrier system,[3] these results suggest that DB14C4 and B2EHPA cooperate to enhance the lithium transport rate in the mixed system.

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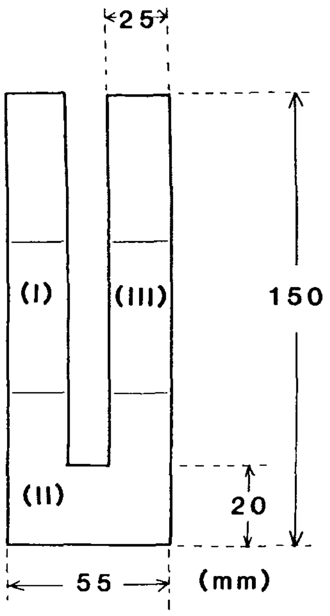

Figure 1 Liquid membrane transport cell with dimensions in mm, (I): source phase, (II): $CHCl_3$ membrane, (III): receiving phase.

Table 1 Initial transport rates of alkali and alkaline earth ions in Tris buffered transport systems[a]

		Initial transport rate (μmol/h)			
Run No.	*Carriers*	*Mg*	*Ca*	*Li*	*Na*
1	B2EHPA	10.3	—	0.7	0
2	B2EHPA/DB14C4	12.3	—	2.7	0
3	B2EHPA	—	14.0	1.1	0
4	B2EHPA/DB14C4	—	13.0	2.8	0

[a] Initial transport condition; source phase (20 mL), 0.2 mmol of $MgCl_2$ (or $CaCl_2$) and 0.2 mmol each of LiCl and NaCl in Tris buffer aq. soln.; organic phase (40 mL), 0.2 mmol of B2EHPA or 0.2 mmol each of B2EHPA and DB14C4 in $CHCl_3$; receiving phase (20 mL), 0.2 mmol of $MgCl_2$ (or $CaCl_2$) and 0.2 mmol each of LiCl and NaCl in 0.1 N HCl soln.

The magnesium transport rate was 12.3 μmol/h, a factor of only 1.2 for the mixed system, which suggests that this system offers little advantage for Mg^{2+} transport. Further, sodium was not transported in the mixed system (Run 2, see Figure 2).

In the transport experiments using an aqueous phase contaiining calcium iion (Runs 3 and 4), calcium ion was also transported effectively by the B2EHPA single carrier system. Addition of DB14C4 caused an increase in the lithium transport rate from 1.1 μmol/h to 2.8 μmol/h, but calcium flux was not significantly affected (see Table 1). In no case, was any significant transport of sodium observed. Therefore, the synergistic enhancement appears to occur only in the lithium transport case.

As shown in Table 2 and Figures 3, the transport rates for alkali and alkaline earth cations increased with increasing pH of the aqueous source phase. It should be noted that the source phase became turbid during these transport experiments. In addition, a synergistic enhancement was also observed in the case of lithium ion (factor 2.6) and was not apparent with any of other cations in the aqueous phase (factor for Mg:1.1, factor for Na:0.7).

From these results, it is concluded that the systems composed of B2EHPA transported alkaline earth cations selectively, and the enhancement effect by DB14C4 was observed only in the lithium transport.

Analysis of the synergistic adduct formation in the system

As fast atom bombardment mass spectrometry provides a rapid means to determine the complexation behavior of crown ether systems,[5] we applied the FAB/MS technique to the analysis of the synergistic complexation with DB14C4 and B2EHPA. The crown ether – metal ion complexes were prepared in a m-nitrobenzyl alcohol matrix on the probe of the mass spectrometer. In the case of the mixture of B2EHPA and lithium hydroxide, the spectrum shows a peak at m/z 651, which is assigned to $[Li+(X{\cdot}HX)+H]^+$ (X: $(RO)_2POO$), and a peak at m/z 329 which is assumed to be $[Li+(X{\cdot}HX)-X]^+$ or $[Li+X+H]^+$ (see Table 3). The results indicate that the lithium salt of B2EHPA in a 1:2 molar ratio formed in the mixture. When the mixture composed of DB14C4 and B2EHPA was treated with lithium hydroxide, an intense peak at m/z 307, $[C+Li]^+$ (C: crown ether), and a peak at m/z 935, $[2(C+Li)+X]^+$, were observed. This suggests the formation of the lithium synergistic complex with DB14C4 and B2EHPA in the system.[3] From the results, it seems that formation of the synergistic adduct of lithium is responsible for the enhanced lithium transport.

For the mixture of B2EHPA with magnesium hydroxide, a peak at m/z 1311, $[Mg+2(X{\cdot}HX)+H]^+$, and a peak at m/z 989, $[Mg+2(X{\cdot}HX)-X]^+$, or $[Mg+(X{\cdot}HX)+X+H]^+$, were observed in the spectrum. The peaks indicate that the magnesium salt of B2EHPA in a 1:4 molar ratio formed in the solution. Schematic structures of the complexes described above are shown in Figure 4.

In the magnesium cation case, addition of DB14C4 did not cause a significant change in the FAB mass spectrum and peaks of the synergistic complex with crown ether were not observed (see Table 3). These results suggest that formation of the stable highly coordinated magnesium complex is responsible for the selective transport of magnesium ion in the B2EHPA single carrier system and the formation of crown ether complex of magnesium did not occur in the mixed carrier system.

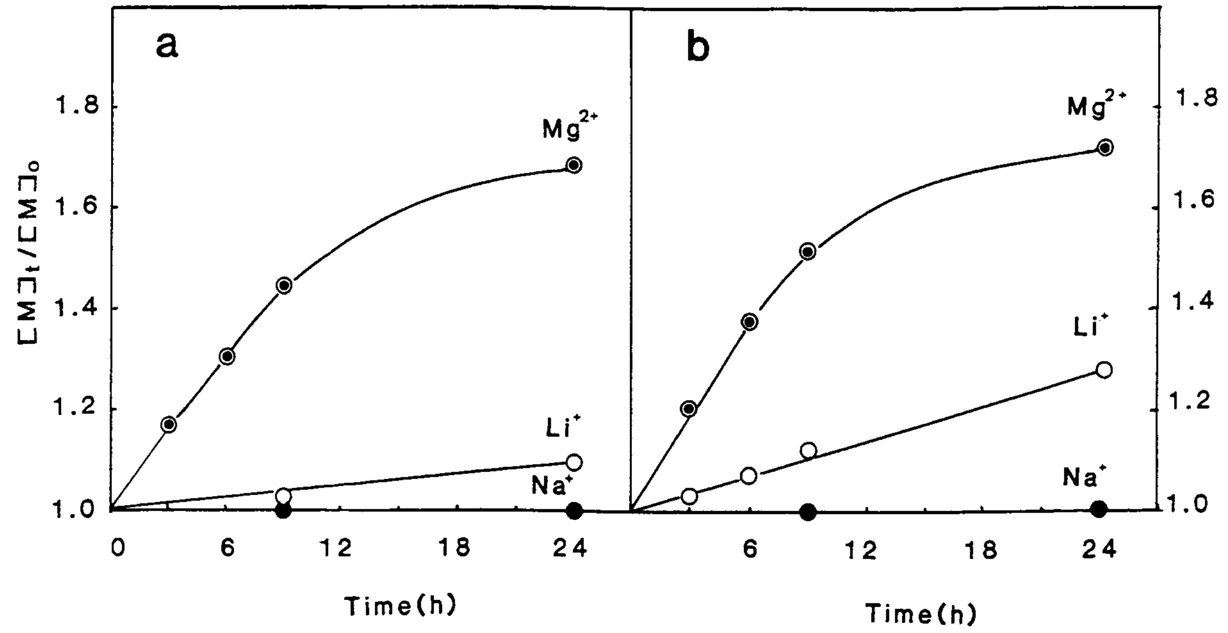

Figure 2 Competitive transport of alkali and alkaline earth ions by B2EHPA (a), and DB14C4/B2EHPA (b) in the Tris buffer systems. $[M]_t$ and $[M]_0$ refer to metal ion concentrations at time t and 0, respectively.

Table 2 Initial transport rates of alkali and alkaline earth ions in the transport systems with metal hydroxides[a]

		Initial transport rate (μmol/h)			
Run No.	*Carriers*	*Mg*	*Ca*	*Li*	*Na*
5	B2EHPA	18.6	—	2.7	2.3
6	B2EHPA/DP14C4	21.0	—	7.0	1.6

[a] Initial transport condition; source phase (20 mL), 0.2 mmol of $Mg(OH)_2$ and 0.2 mmol each of LiOH and NaOH in water; organic phase (40 mL), 0.2 mmol of B2EHPA or 0.2 mmol each of B2EHPA and DB14C4 in $CHCl_3$; receiving phase (20 mL), 0.2 mmol of $MgCl_2$ and 0.2 mmol each of LiCl and NaCl in 0.1 N HCl soln.

Transport of alkali metal ions by mixed carrier systems composed of DB14C4 and ionizable lipophilic compounds other than B2EHPA

As B2EHPA exhibited a selective synergistic effect with DB14C4 in the mixed carrier system, we examined other lipophilic compounds as carriers as well. The compounds examined were 2-bromo-hexadecanoic acid (BHDA) and dodecylbenzenesulfonic acid (DBSA). These results of the transport experiments are summarized in Table 4.

As shown in Table 4, 2-bromohexadecanoic acid (BHDA) did not transport alkali metal ions in the single carrier system. In contrast, the mixed carrier system with DB14C4 and BHDA transported both lithium and sodium ions. The transport rates for lithium and sodium cations were measured to be 4.9 μmol/h and 2.0 μmol/h, respectively. In the absence of the ionizable lipophilic compound, DB14C4 did not transport either of these metal ions.[3] Therefore, the synergistic enhancement on both lithium transport and sodium transport was observed but the enhancement was not so selective as that in the DB14C4/B2EHPA system. In the case of dodecylbenzenesulfonic acid (DBSA), similar results were obtained in both single and mixed carrier systems (see Table 4). From these results, it became clear that only bis(2-ethylhexyl)phosphoric acid exhibits the interesting selectivity and synergistic enhancement of lithium transport. At present, we cannot account for this unique property of B2EHPA in the transport system although work to clarify this particular issue is in progress.

CONCLUSIONS

In the competitive transport of alkali and alkaline earth cations, bis(2-ethylhexyl)phosphoric acid transported alkaline earth cations with high selectivity. The combination of dibenzo-14-crown-4 and bis(2-ethylhexyl)phosphoric acid showed a synergistic enhancement in lithium transport by forming a synergistic adduct, and the enhancement effect was not apparent in transport of other cations. In the dibenzo-14-crown-4/dodecylbenzenesulfonic acid system and the dibenzo-14-crown-4/1-bromohexadodecanoic acid system, the enhancement effects were observed both in lithium transport and in sodium transport.

EXPERIMENTAL SECTION

Melting points were measured with an Ishii micro melting point apparatus and were uncorrected. ^1H

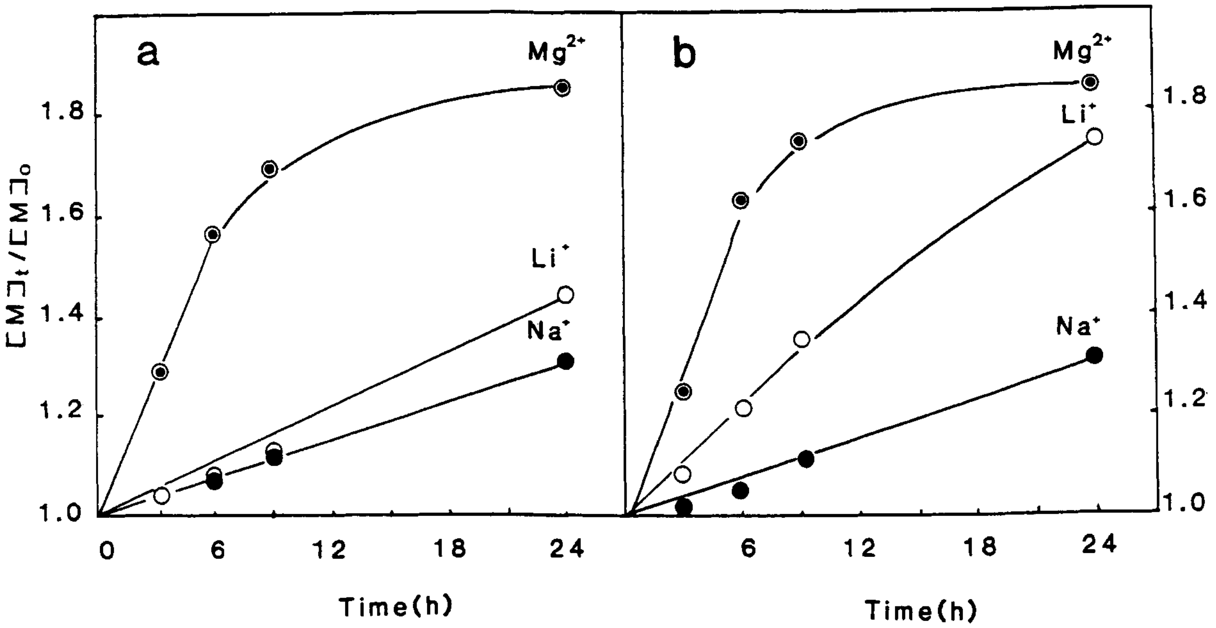

Figure 3 Competitive transport of alkali and alkaline earth ions by B2EHPA (a), and DB14C4/B2EHPA (b) in metal hydroxide systems.

Table 3 Fragment peaks of FAB mass spectra

Metal	*Ligand*	*M/Z*	*Stoichiometry*	*Assignment*[a]
Mg	B2EHPA	989	$MH_2X_3^+$	$[M+2(X{\cdot}HX)-X]^+$ or $[M+(X{\cdot}HX)+X+H]^+$
		1311	$MH_3X_4^+$	$[M+2(X{\cdot}HX)+H]^+$
	B2EHPA/DB14C4	989	$MH_2X_3^+$	$[M+2(X{\cdot}HX)-X]^+$ or $[M+(X{\cdot}HX)+X+H]^+$
		1311	$MH_3X_4^+$	$[M+2(X{\cdot}HX)+H]^+$
Li	B2EHPA	329	MHX^+	$[M+(X{\cdot}HX)-X]^+$ or $[M+X+H]^+$
		651	$MH_2X_2^+$	$[M+(X{\cdot}HX)+H]^+$
	B2EHPA/DB14C4	307	MC^+	$[C+M]^+$
		935	$M_2C_2X^+$	$[2(C+M)+X]^+$

[a] M: metal ion, X: phosphate ion, C: crown ether, H: proton

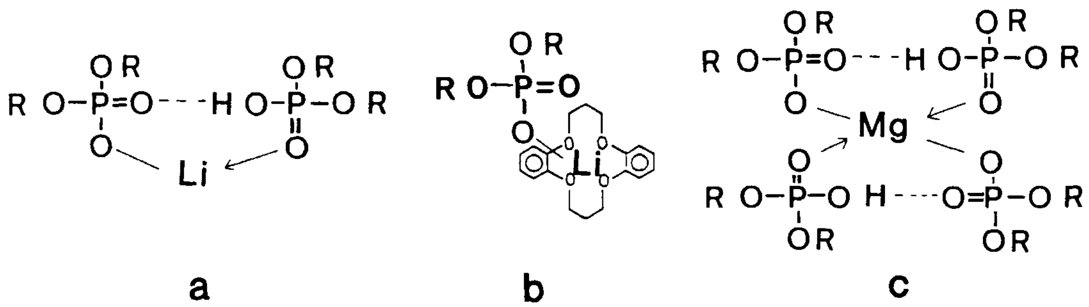

Figure 4 Schematic structures of the metal complexes. (a) Lithium salt, (b) synergistic complex of lithium, (c) magnesium salt.

NMR and ^{13}C NMR were recorded on a JEOL FX 90Q nmr spectrometer or a JEOL GSX-400 spectrometer as ca. 10% solutions in $CDCl_3$. The chemical shifts are reported in ppm (δ) down field from internal Me_4Si. Infrared spectra were recorded on a A202 infrared spectrometer either as neat samples or nujol mulls. Mass spectra were acquired on a JEOL JMS DX303 mass spectrometer by using a 6–8 KeV xenon primary beam and a m-nitrobenzyl alcohol matrix. Concentrations of alkali and alkaline earth cations were determined with a Hitachi 508 atomic adsorption spectrometer.

Table 4 Initial transport rates of alkali metal ions in the transport systems composed of the ionizable lipophilic compounds[a]

		Initial transport rate (μmol/h)		
Run No.	*Carriers*	*Li*	*Na*	*Li/Na*
7	BHDA	0	0	–
8	BHDA/DB14C4	4.9	2.0	2.5
9	DSBA	0	0	–
10	DSBA/DB14C4	8.6	5.3	1.6

[a] Initial transport condition; source phase (20 mL), 0.2 mmol each of LiCl and NaCl; organic phase (40 mL), 0.2 mmol of BHDA (or DSBA) or 0.2 mmol each of BHDA and DB14C4 (or DSBA and DB14C4) in $CHCl_3$; receiving phase; 0.2 mmol each of LiCl and NaCl in 0.1 N HCl soln.

Reagents

Dibenzo-14-crown-4 was prepared according to the literature method.[4] Bis(2-ethylhexyl)phosphoric acid and sodium dodecylbenzenesulfonate were obtained from Wako Pure Chemical Ind., LTD. Sodium dodecylbenzenesulfonate was treated with HCl to get the acid prior to use. 2-Bromohexadodecanoic acid was obtained from Eastman Kodak Company. Other reagents were of the best grade commercially available and were distilled or used without further purification.

Transport experiment of alkaline earth and alkali cations

The liquid membrane transport experiments were conducted for 24 h and 25 °C with the cell illustrated in Figure 1. The organic phase (40 mL) was 0.2 mmol of dibenzo-14-crown-4 and 0.2 mmol of bis(2-ethylhexyl)phosphoric acid in chloroform. The aqueous source phase (20 mL) was prepared by dissolving 0.2 mmol $MgCl_2$ (or $CaCl_2$) along with 0.2 mmol each of LiCl and NaCl, and was adjusted initially to pH 9.2 by addition of Tris buffer solution. The receiving phase was 20 mL of 0.1 N HCl containing 0.2 mmol of $MgCl_2$ (or $CaCl_2$), 0.2 mmol each of LiCl and NaCl. For the transport studies at higher pH, the aqueous source phase (20 mL) was 10 mM solution of $Mg(OH)_2$ (or $Ca(OH)_2$), LiOH and NaOH.

Transport of alkali cations by dibenzo-14-crown-4 and an ionizable lipophilic compound other than B2EHPA

The transport experiments were carried out under conditions similar to those of the alkali metal transport by DB14C4/B2EHPA system.[3] Instead of B2EHPA, 0.2 mmol of the ionizable lipophilic compound (2-bromohexadecanoic acid or dodecylbenzene-sulfonic acid) was used as the carrier in this system.

Calculation of initial transport rates

For each transport experiment, the initial transport rate was calculated from the increase of metal cation concentration in the receiving phase after a period of 6 h or 9 h.

Analysis of the complexes

The procedures for the formation of the complexes and FAB-MS measurement are as follows. In the case of the metal salt of the ionizable lipophilic compound, m-nitrobenzylalcohol (1 μL) was loaded onto the probe and 1 μL of a 50 mM solution ($CHCl_3$) of the lipophilic compound and 1 μL of a 50 mM aqueous solution of metal hydroxide were carefully added. The mixture was allowed to stand for 20 min. The mixture was then carefully stirred and placed in the ion source. The spectra were recorded immediately after the insertion of the sample. For the synergistic adduct, 0.5 μL of a 100 mM solution of the lipophilic compound and 0.5 μL of a 100 mM solution of DB14C4 (in $CHCl_3$), and 1 μL of a 50 mM aqueous solution of metal hydroxide were added to 1 μL of a m-nitrobenzylalcohol.

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