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Extraction and Transport of Lithium Ion by a Crown Ether–Alkylphosphoric Acid System [1]

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Abstract. Mixed carrier systems composed of crown ethers and alkylphosphoric acids have been studied as lithium ionophores using a solvent extraction technique and in transport across liquid membranes. The combination of dibenzo-14-crown-4 and bis(2-ethylhexyl)phosphoric acid showed a synergistic enhancement on both lithium ion selectivity and transport rate. The synergistic effects depended strongly upon crown ether structure and the enhancement was observed only when the metal cation corresponded to the crown ether's cavity diameter. Complex formation in the organic phase was assessed by use of FAB-mass spectrometry.

Key words. Crown ether, alkylphosphoric acid, lithium transport.

1. Introduction

The use of macrocyclic polyethers as selective ionophores for alkali metal ions has been extensively investigated and increasing attention has been focused on lithium ionophores. Although simple crown ethers generally complex alkali metal cations, aqueous/organic phase distribution coefficients for inorganic salts of lithium and simple crown ethers are too low to be practical in such applications as the selective removal of lithium ion from natural and industrial water sources [2]. In an effort to control these distribution coefficients, several ionizable crown ether derivatives have been synthesized and examined [3]. An alternative solution to the problem would be the addition of ionizable lipophilic compounds to the organic phase together with the crown ethers. Although other synergistic mixtures have been investigated for alkali metal separation [4], no system has exhibited high extractability for lithium. We report here several complexing systems composed of dibenzo-14-crown-4 and dialkylphosphoric acids, which perform lithium selective transport across a chloroform membrane and extraction into an organic phase.

2. Experimental

Melting points were measured with an Ishii micro melting point apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JOEL FX90Q NMR spectrometer or a Varian XL-200 spectrometer as ca. 10% solutions in $CDCl_3$. The chemical shifts are reported in ppm(δ) downfield from internal Me_4Si.

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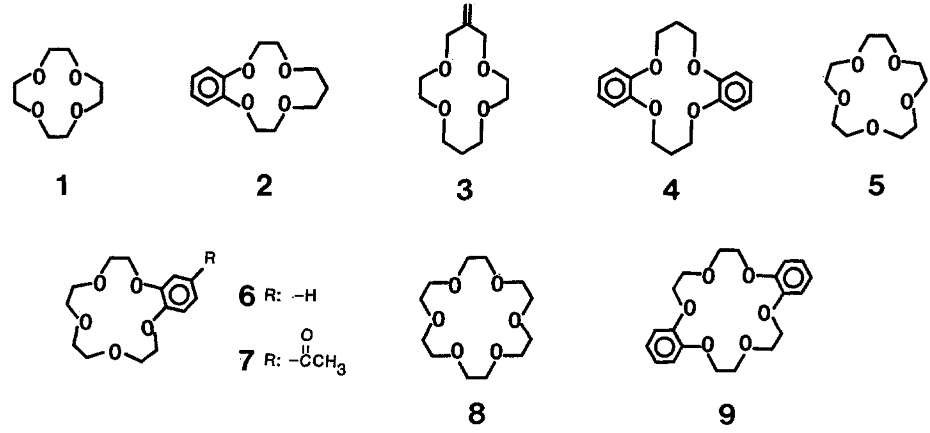


Chart 1

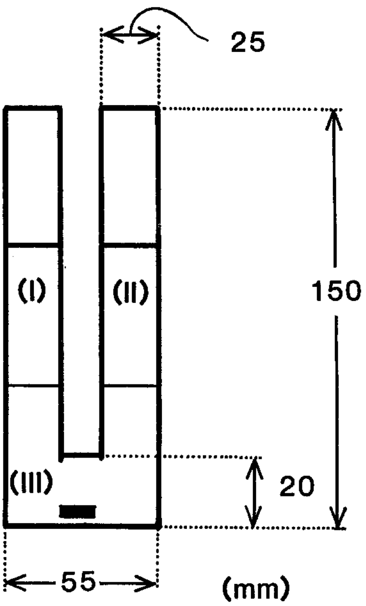
IR spectra were recorded on a JASCO A 202 infrared spectrometer either as neat samples or nujol mulls. Mass spectra were recorded on a JEOL JMS DX 303 mass spectrometer or a Hitachi RM 60 mass spectrometer. Concentrations of alkali metal cations were determined with a Hitachi 508 atomic absorption spectrometer.

2.1. CHEMICALS

12-Crown-4 (**1**), 15-crown-5 (**5**), benzo-15-crown-5, (**6**), 18-crown-6 (**8**) and dibenzo-18-crown-6 (**9**) were purchased from Aldrich Chemical Co. Benzo-13-crown-4 (**2**), 2-methylene-14-crown-4 (**3**), dibenzo-14-crown-4 (**4**), and 4′-acetyl-benzo-15-crown-5 (**7**) were prepared according to literature methods [8–11]. All spectral and analytical data were in agreement with the published data. Bis(2-ethylhexyl)phosphate (**13**), dibutylphosphate (**10**), tributylphosphate (**11**), and trioctylphosphine oxide (**15**) were obtained from Kanto Chemical Co., Inc. 2-Ethylhexylphosphonic acid 2-ethylhexyl ester (**16**) was purchased from Daihachi Chemical Co. 2-Ethylhexylphosphate (**12**) and tris(2-ethylhexyl)phosphate (**14**) were synthesized as previously described [12]. Other reagents were the best grade commercially available and were distilled or used without further purification, as appropriate or as specified.

2.2. EXTRACTION EXPERIMENTS

Chloroform and water were pre-equilibrated with each other, in order to minimize volume changes during extraction. The chloroform solution (2 mL) of extractants and the same volume of 15 mM aqueous lithium hydroxide solution were shaken for 1 h in a 10 mL centrifuge tube at 25°C. After equilibrium was reached, the mixture was centrifuged for 20 min. at 2000–2500 rpm and allowed to stand at 25°C. The lithium concentration of the aqueous phase was measured with an atomic absorption spectrometer.



Initial transport conditions (25 °C)

Source Phase (I)	$CHCl_3$ membrane (III)	Receiving Phase (II)
LiOH: 10mM	B2EHPA: 0.2mmol	LiCl: 10mM
NaOH: 10mM	Crown Ether: 0.2mmol	NaCl: 10mM
(H_2O, 20ml)	($CHCl_3$, 40ml)	(1N-HCl, 20ml)

Fig. 1. Liquid membrane transport cell and conditions of transport.

2.3. TRANSPORT EXPERIMENTS

The liquid membrane transport experiments were conducted for 24 h at 25°C with the cell illustrated in Figure 1. The organic phase (40 mL) was 0.2 mmol in the crown ether and 0.2 mmol of **13** in chloroform. The aqueous source phase (20 mL) was 10 mM solution of LiOH and NaOH, and the receiving phase was 20 mL of 0.1 N HCl containing 0.2 mmol of LiCl and 0.2 mmol of NaCl.

2.4. CALCULATION OF INITIAL TRANSPORT RATES

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

2.5. ANALYSIS OF SYNERGISTIC COMPLEXES

Analysis by FAB mass spectrometry was performed on a JEOL JMS DX 303 mass spectrometer. The spectra were obtained in the positive mode. The atom gun was operated at 6 kV and xenon was employed as the bombarding gas. For the analysis of the complex, *m*-nitrobenzyl alcohol was used for the matrix. The procedure for formation of the complex and FAB-MS measurement are as follows:

m-Nitrobenzyl alcohol (1 μL) was loaded onto the probe and 0.5 μL of a 100 mM solution of **4** in $CHCl_3$, 0.5 μL of a 100 mM solution of **13** in $CHCl_3$ and 1 μL of a 50 mM aqueous solution of lithium 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. Spectra were recorded immediately after insertion of the sample.

3. Results and Discussion

3.1. SOLVENT EXTRACTION OF LITHIUM HYDROXIDE FROM WATER INTO CHLOROFORM BY CROWN ETHER–ORGANOPHOSPHORUS COMPOUNDS SYSTEMS

To evaluate the ability of crown ethers as lithium extractants, the extraction experiments were carried out by using the crown ethers listed in Chart 1. The percent extractabilities, defined as percent of lithium ion, refers to the total amount of lithium and are shown in Table I. These crown ethers exhibited very low lithium extractability under the experimental conditions.

It is known that organophosphorus compounds form lipophilic salts or adducts with metal ions to enhance extractabilities of many extraction systems [5]. We thus examined the extraction ability of mixed systems composed of dibenzo-14-crown-4 (**4**, DB14C4) and organophosphorus compounds. The organophosphorus compounds used in the experiments are listed in Chart 2. As shown in Table II, the dibenzo-14-crown-4 (**4**)–bis(2-ethylhexyl)phosphoric acid (**13**,B2EHPA) system showed the highest Li^+ extractability (37%) among the mixture systems examined. Bis-(2-ethylhexyl)phosphoric acid (**13**) extracted less lithium (15%) than did the DB14C4–B2EHPA system. It was therefore concluded that enhanced Li^+ extraction resulted from synergy between dibenzo-14-crown-4 (**4**) and bis(2-ethylhexyl)phosphoric acid (**13**).

Table I. Extraction of lithium hydroxide by crown ethers[a]

Crown ether	Lithium extracted(%)	Crown ether	Lithium extracted(%)
1	<0.1	**6**	1.6
2	1.0	**7**	1.8
3	3.3	**8**	0.5
4	2.7	**9**	1.8
5	0.3		

[a] Initial extraction conditions: 25°C; organic phase, 15 mM crown ether in $CHCl_3$; aqueous phase, 15 mM LiOH.

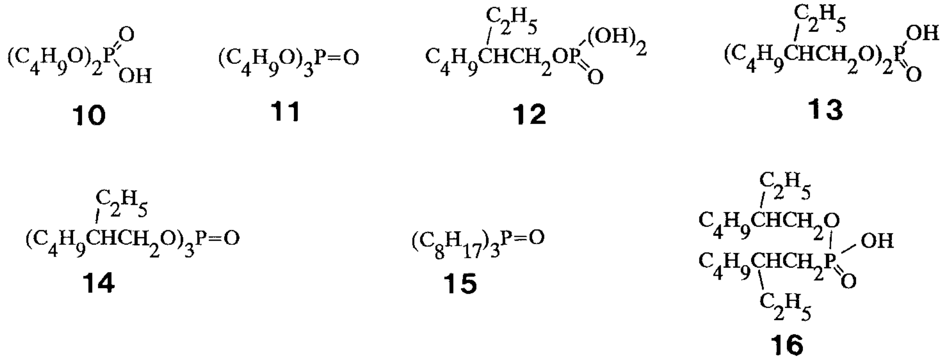


Chart 2

In order to assess the effect of crown ether structure on the synergistic enhancement, extraction experiments were performed by using mixed systems with B2EHPA and the crown ethers shown in Chart 1. The extraction results are recorded in Table III. The synergistic enhancement was observed in the case of methylene-14-crown-4 and was not apparent with any other of the crown ethers tested.

Table II. Extraction of LiOH by phosphorus compounds-DB14C4 systems.[a]

Phosphorus compound	Lithium extracted(%)	Phosphorus compound	Lithium extracted(%)
10	1.0	**14**	3.0
11	1.6	**15**	1.3
12	<0.1	**16**	10.0
13	37.0		
	13	15^b	

[a] Initial extraction conditions: organic phase, 15 mM DB14C4(**4**) and 15 mM phosphorus compound in $CHCl_3$; aqueous phase, 15 mM LiOH.

[b] Organic phase, 15 mM B2EHPA(**13**) in $CHCl_3$ with no DB14C4(**4**)

Table III. Extraction of LiOH by B2EHPA–crown ether systems.[a]

Crown ether	Lithium	Crown ether extracted(%)	Lithium extracted(%)
1	$15(0)^b$	**6**	17(2)
2	15(0)	**7**	20(5)
3	32(17)	**8**	16(1)
4	37(22)	**9**	15(0)
5	18(3)		

[a] Organic Phase, 15 mM crown ether and 15 mM B2EHPA; Aqueous Phase, 15 mM LiOH.

[b] (Extracted lithium by mixed system) – (Extracted lithium by B2EHPA)

3.2. COMPETITIVE TRANSPORT OF ALKALI METAL CATIONS ACROSS A BULK CHLOROFORM MEMBRANE BY THE CROWN ETHER-B2EHPA MIXED CARRIERS

The efficacy of B2EHPA-crown ether systems as carriers for alkali ion transport were evaluated in proton-driven competitive transport experiments using the U-tube apparatus illustrated in Figure 1.

When dibenzo-14-crown-4 (**4**) was tested in the absence of a phosphorus compound, no cation was transported across the chloroform membrane under the specified experimental conditions. In the absence of crown, bis(2-ethylhexyl)phosphoric acid (**13**) transported lithium and sodium ions with low selectivity. The initial transport rate of lithium in the B2EHPA system was 4.6 μmol/h and that of sodium was 3.2 μmol/h [selectivity ratio Li/Na = 1.3 (see Figure 2)].

The dibenzo-14-crown-4 (**4**)/bis(2-ethylhexyl)phosphoric acid (**13**) mixed carrier system exhibited an initial sodium transport rate the same as for the B2EHPA system. In contrast, the lithium transport rate was 11.2 μmol/h. The factor of 2.4 observed for the mixed system (see Figure 3) suggests that dibenzo-14-crown-4 (**4**) and bis(2-ethylhexyl)-phosphoric acid (**13**) cooperate to enhance both the selectivity and the lithium ion transport rate.

On the other hand, the mixed carrier system composed of benzo-15-crown-5 (**6**) and bis(2-ethylhexyl)phosphoric acid (**13**) was more efficient than the B2EHPA system in sodium ion transport. The sodium transport rate was 10.0 μmol/hr using this mixture: 3.1 times greater than for B2EHPA. The lithium transport rate was the same as that of the B2EHPA system. The results are shown in Figure 4.

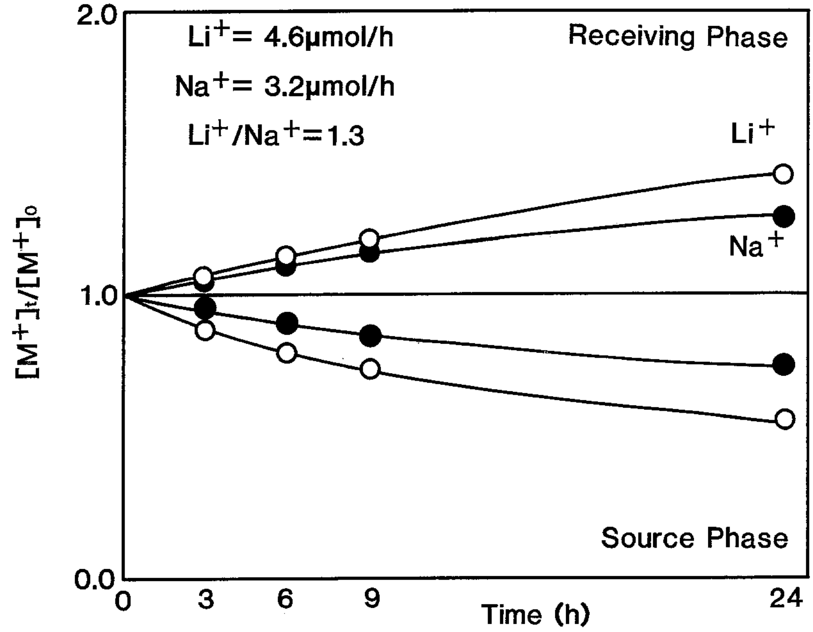


Fig. 2. Competitive transport of alkali metal cations by B2EHPA(**13**). $[M^+]_t$ and $[M^+]_0$ refer to metal ion concentrations at time = t and 0, respectively.

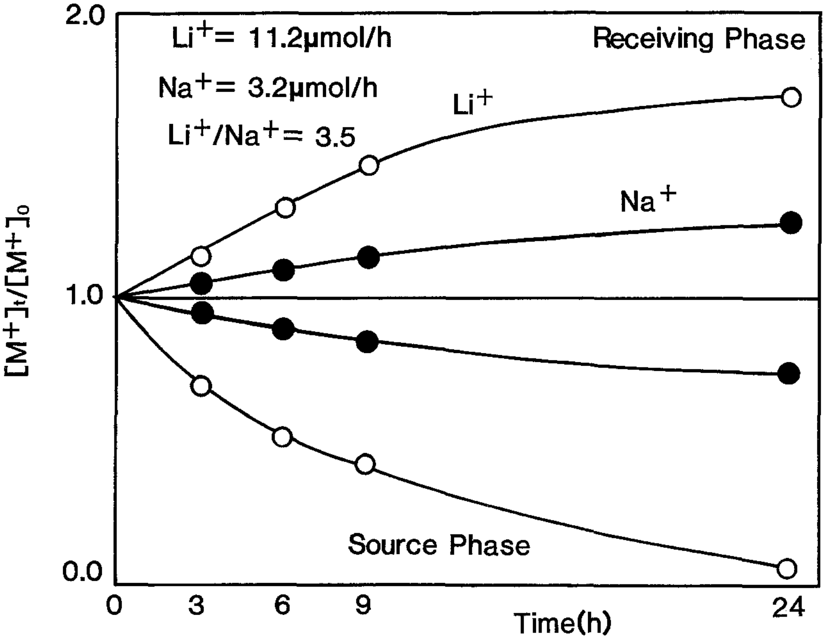


Fig. 3. Competitive transport of alkali metal cations by B2EHPA(**13**)–DB14C4(**4**) system.

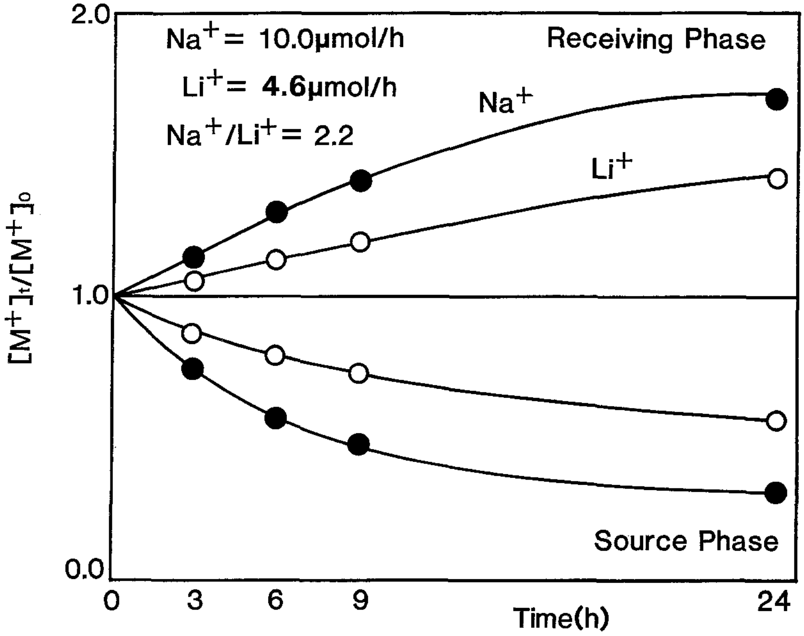


Fig. 4. Competitive transport of alkali metal cations by B2EHPA(**13**)–B15C5(**6**) system.

The foregoing results imply that synergistic transport enhancements are observed only when the crown ether and cation diameters correspond. It is well known that mixed adducts are formed in an organic phase in the process of synergistic extraction [6], and it seems reasonable to assume that synergistic adducts were formed in our crown ether–B2EHPA systems.

3.3. ANALYSIS OF THE SYNERGISTIC LITHIUM COMPLEX WITH DIBENZO-14-CROWN-4 AND BIS(2-ETHYLHEXYL)PHOSPHORIC ACID BY FAB-MASS SPECTROMETRY

As previously reported [7], FAB-mass spectrometry can be used to investigate complex formation between metal cations and crown ethers. The formation of synergistic complexes was therefore assessed by the FAB-MS method. The spectrum, obtained as described in the Experimental section, is shown in Figure 5. Ions were observed at *m*/*z* values corresponding to $[\mathrm{Cr} + \mathrm{Li} + \mathrm{X} + \mathrm{H}]^+$, (Cr; crown ether, Li; lithium ion, X; phosphate anion,), and $[\mathrm{Cr} + \mathrm{Li}]^+$, which arose from the loss of X^- from $[\mathrm{Cr} + \mathrm{Li} + \mathrm{X}]$. These observations led us to conclude that dibenzo-14-crown-4 (**4**) and the lithium salt of bis(2-ethylhexyl)phosphate form a synergistic complex of the type $[\mathrm{Cr} + \mathrm{Li} + \mathrm{X}]$.

3.4. POSTULATED TRANSPORT MECHANISM FOR THE MIXED CARRIER SYSTEM

A possible mechanism for lithium transport by the benzo-14-crown-4 (**4**)–bis(2-ethylhexyl)phosphoric acid (**13**) system is illustrated in Figure 6.

Since sodium ion seems to be transported by Path B with B2EHPA, it was thought that the lithium selectivity would increase with decreasing Na flux (Path B). Competitive transport experiments were done by using 0.2 mmol of DB14C4 and 0.1 mmol of B2EHPA in 40 mL of chloroform in order to obtain a higher lithium selectivity. Under these conditions, a higher selectivity (Li/Na = 14.7) was obtained and the results indicate that the lithium selectivity can be controlled by changing the DB14C4:B2EHPA ratio in the membrane (see Figure 7).

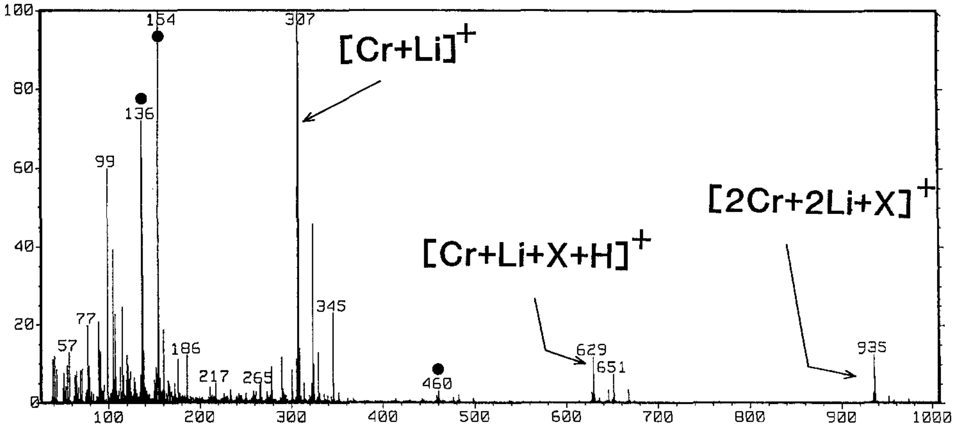


Fig. 5. FAB spectrum of the synergistic complex. Cr; crown ether, X; phosphate ion, H; proton, ●; peaks originating from the matrix system.

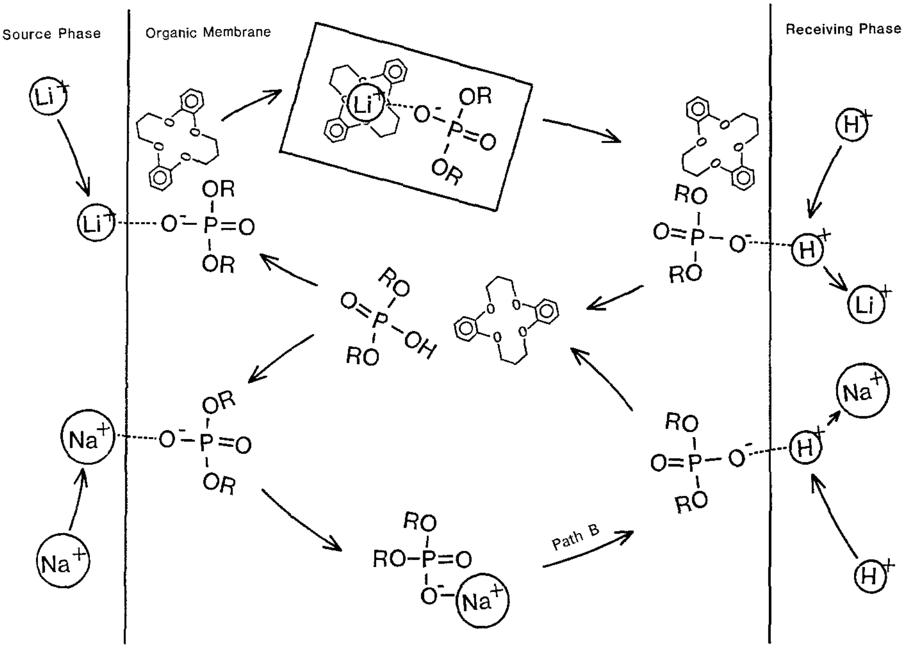


Fig. 6. Postulated mechanism of active transport using B2EHPA(**13**)–DB14C4(**4**) system.

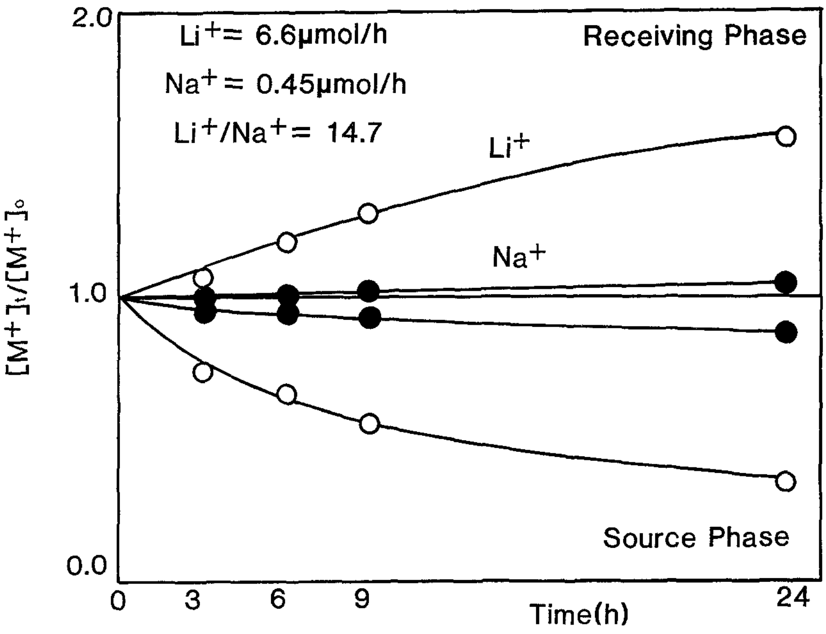


Fig. 7. Competitive transport of alkali metal cations by DB14C4(**4**)–(1/2)B2EHPA(**13**) system, DB14C4 0.2 mmol, B2EHPA 0.1 mmol.

4. Conclusions

Mixed complexing agent systems composed of 14-crown-4 derivatives and dialkylphosphoric acids have been studied as lithium ionophores in both solvent extraction and transport across liquid membranes. The dibenzo-14-crown-4/bis(2-ethylhexyl)phosphoric acid system showed enhanced lithium selectivity, apparently by forming synergistic adducts in the organic phase. A high lithium selectivity of Li/Na = 14.7 was observed in the transport experiment. The formation of the adduct was confirmed by using FAB-mass spectrometry.

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References and Notes

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