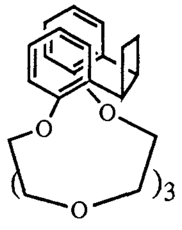
CHEMISTRY LETTERS, pp. 1751-1754, 1991.

Li^+ Ion Selective Transport by Crownophanes[1]

Seiichi INOKUMA, Reiko KATOH, Takamasa YAMAMOTO, and Jun NISHIMURA*
Department of Chemistry, Gunma University, Tenjincho, Kiryu 376

Crownophanes, which were easily prepared by photocycloaddition, exhibited high Li^+ ion selectivity on the competitive passive transport in the presence of dodecanoic acid as a co-carrier.

The transport of alkali and alkaline earth metal ions has been carried out by using crown ethers, acyclic polyethers, and their derivatives. Much effort has been paid to increase their selectivity as well as their efficiency. Especially making highly Li^+ ion selective ionophores is always a primary concern of this area, because a large quantity of the metal will have to be extracted from sea water for the use in nuclear fusion generators. Although a variety of Li^+ ion selective ionophores[2,3] and even a spherand with perfect Li^+ ion selectivity[3] have been designed and synthesized, simple and easily available ones are limited. Among the lithiophilic crown compounds, some 13-crown-4[4] and 14-crown-4[5] derivatives prepared by Okahara and co-workers showed a good affinity toward Li^+ ion over other alkali metal cations in spite of their relatively simple structures. Recently, we have synthesized a new kind of crown compounds fused with cyclophane skeletons in excellent yields, and have named them "crownophanes".[6] Since efficient and selective transport systems for Na^+, K^+, Cs^+, and Ba^{2+} ions have been developed by use of cooperative carriers composed of a simple and conventional crown ether[7] or an acyclic polyether[8] with an alkanoic acid, we were prompted to investigate the selectivity of the alkali metal ion transport by the cooperative carriers composed of a crownophane and an alkanoic acid. In this paper, we would like to report the Li^+ ion transport ability and the structural effect of the carriers on this respect.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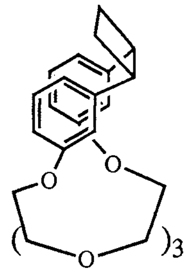
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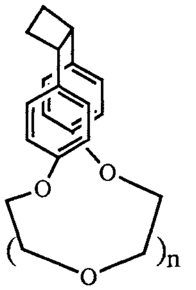

3a n=1
3b n=2
3c n=3
3d n=4

Crownophanes **1**-**3** were prepared by our methods.[3] Analytical data of new materials prepared are given.[9] Most plausible conformers for crownophanes **1** and **2** at this moment are deduced from the data and given above. Reagent grade 12-crown-4 **4** and dodecanoic acid were used without further purification. Dibenzo-14-crown-4 **5** was prepared by the reported method.10)

Phase I	Liquid membrane	Phase II
LiOH 0.1 M NaOH 0.1 M KOH 0.1 M HCl 0.2 M (H_2O, 15 ml)	Crownophane: 1.5×10^{-4} mol Dodecanoic acid: 1.5×10^{-4} mol ($CHCl_3$, 30 ml)	HCl 0.1 M (H_2O, 15 ml)

Fig. 1. Initial conditions of the transport experiments.

Table 1. Transport of Alkali Metal Cations by Crownophane-Dodecanoic Acid Cooperative Carriers

Crownophane	Transport rate (x 10^{-6} mol/h)[a]			Selectivity	
	Li^+	Na^+	K^+	Li^+/Na^+	Li^+/K^+
1	1.88	0.41	0.46	4.6	4.1
2	2.01	0.23	0.27	8.6	7.6
3b	0.69	0.37	0.21	1.9	3.2
3c	1.86	0.26	0.41	7.2	4.5
3d	1.32	1.33	0.79	1.0	1.7
4	1.65	0.30	0.62	5.5	2.7
5	2.33	0.66	0.62	3.5	3.8

a) Reproducibility, ±10%.

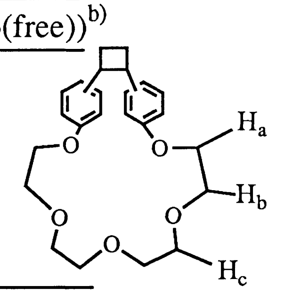
Passive transport of alkali metal cations was accomplished by using the same U-tube apparatus as that described previously,7) at 30 °C under the initial conditions shown in Fig. 1. The transport rates were calculated from the initial rates of the appearance of metal cations into the receiving phase II, which were determined by atomic absorption and/or flame analyses.

Results are summarized in Table 1. Typical crownophane **3c** without dodecanoic acid hardly mediated competitive passive transport of alkali metal nitrates driven by concentration gradient of the salts. Most of crownophanes, however, showed reasonable efficiency and moreover higher selectivities than conventional lithiophilic crown ethers **4** and **5** for Li^+ ion transport in this system. Interestingly the highest selectivity toward Li^+ ion is attained by **3c** with five ether oxygen atoms in the series of *p*-crownophanes, whose structures differ from those of so-called lithiophilic crown compounds with four ethereal oxygen atoms such as **4** and **5** (vide infra). Among the isomers possessing five ether oxygen atoms, crownophane **2** shows the highest Li^+ ion selectivity. These results clearly suggest that the combination of number of oxyethylene units and the shape of the ether cavity leads to the suitable ionophore for Li^+ ion selective transport.

^1H NMR titration of **2** and **3c** with Li^+ or Na^+ ion clearly suggested that the complexes are composed of 1:1 molar ratio of the two components. This experiments also gave an important information on the metal ion binding sites of crownophanes. In Table 2 are summarized chemical shift differences of oxyethylene units between those recorded in the presence or absence of metal salts. The largest shifts ($\Delta\delta_{EO}$) were observed for H_b in both experiments with **2** and **3c**, especially when lithium salt was added. Consequently, the metal in these complexes is located at the one corner of oxyethylene ring units farthest from the aromatic nuclei. The structure of these complexes is also supported by the framework examination which clearly shows the crownophanes taking the shape of a spoon with the aromatic part as a bail.

Table 2. ^1H NMR Shift Data for Alkali Metal-Crownophane Complexes[a)]

Metal ion	Chem. shift difference ($\Delta\delta_{EO}$= δ(complex)- δ(free))[b)] Crownophane **2** H_a			Crownophane **3c** H_a		
	Crownophane **2**			Crownophane **3c**		
	H_a	H_b	H_c	H_a	H_b	H_c
Li^+	0.02	0.09	0.06	0.02	0.03	0.02
Na^+	0.05	0.06	0.06	0.02	0.02	0.00
K^+	0.02	0.02	0.02	0.00	0.01	-0.02
Cs^+	0.01	0.01	0.01	0.00	0.00	0.00



a) Recorded on a Varian Gemini-200 FT NMR spectrometer. Experimental conditions: [MBF_4 or AcOCs] / [**2** or **3c**]=5; in CD_3CN. Resolution, 0.01 Hz. Reproducibility, ±10%. b) In ppm.

Table 3. Competitive Extraction of Alkali Metal Ions by Crownophane-Dodecanoic Acid System[a)]

Crownophane	Decrease of ions in aqueous solution (%)						Selectivity (Li^+ / M^+)			
	Li^+	Na^+	K^+	Rb^+	Cs^+	Total	Na^+	K^+	Rb^+	Cs^+
1	25.2	1.3	4.1	5.1	6.1	41.8	19.4	6.1	4.9	4.1
2	29.4	1.2	4.3	6.0	7.9	48.8	24.5	6.8	4.9	3.7
3a (n=1)	19.1	1.6	2.3	3.8	4.6	31.4	11.9	8.3	5.0	4.2
3b (n=2)	27.9	1.1	4.4	4.6	4.8	42.8	25.4	6.3	6.1	5.8
3c (n=3)	28.3	1.9	4.6	5.3	5.5	45.6	14.9	6.2	5.3	5.1
3d (n=4)	27.9	1.2	4.6	4.8	6.5	45.0	23.3	6.1	5.8	4.3

a) Experimental conditions: composition of cations in 1.0 ml of initial aqueous layer; [LiOH] = [NaOH] = [KOH] = 0.1 mol dm^{-3}, [RbCl] = [CsCl] = 0.1 mol dm^{-3}, [HCl] = 0.2 mol dm^{-3}. Composition of organic layer; 0.05 mmol of crownophane-dodecanoic acid 1:1 mixture in 2.0 ml of chloroform. Reproducibility, ±10%.

Rates of the transport should be controlled by the extraction and/or release processes. Generally the extraction process is responsible for the rate. In the present case we could decide which process controls the transport, determining the competitive extraction of alkali metal ions by the crownophane-dodecanoic acid system; i.e., the competitive extraction experiments show the high Li$^+$ ion selectivity, so that the extraction step really controls the transport. Data in Table 3 show that the Li$^+$ ion selectivity to Na$^+$ ion in the extraction was higher than 10 for every system.

Consequently, the cooperation of the crownophane with the alkanoic acid leads the selective metal ion complexation and the high lipophilicity, making the ternary complex, in which Li$^+$ ion is favorably surrounded by the oxyethylene chain and alkanoate anion acts as a secondary ligand.

This work was supported in part by grants from the Ministry of Education, Science, and Culture, Japan, and from Toray Science Foundation. We are indebted to them.

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9) **1**: oil. HRMS Found: m/z 398.2069. Calcd for $C_{24}H_{30}O_5$: M, 398.2094. **2**: mp 65.3-66.5 °C. Found: C, 72.23; H, 7.60%. Calcd for $C_{24}H_{30}O_5$: C, 72.34; H, 7.59%. **3a**: mp 102.0-103 °C. Found: C, 76.94; H, 7.16%. Calcd for $C_{20}H_{22}O_3$: C, 77.39; H, 7.14%. **3b**: mp 35.0-36.0 °C. Found: C, 74.58; H, 7.30%. Calcd for $C_{22}H_{26}O_4$: C, 74.55; H, 7.39%.
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(Received July 15, 1991)