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SYNTHESIS OF MONOAZACRYPTANDS AND THEIR EXCELLENT TRANSPORT ABILITY TOWARD ALKALI METAL CATIONS IN COMPARISON WITH MONOAZACROWN ETHERS

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Abstract. The effects of transport conditions and the structure of monoazacrown ethers on their transport ability for alkali metal cations through a bulk liquid membrane are summarized and discussed based on transport data obtained in our laboratories. To improve the transport ability, monoazacryptands have been prepared. A lipophilic derivative consisting of two 18-crown-6 rings and one 20-crown-6 ring can selectively transport K^+ from a mixture of Na^+, K^+, Mg^{2+}, and Ca^{2+} under pH control.

Key words: Monoazacryptand, monoazacrown ether, liquid membrane transport, alkali metal cation.

1. Introduction

Membrane transport is an important separation method for metal cations. A variety of macrocyclic polyethers and the related open-chain analogs have been successfully used as carriers especially for alkali metal cations [1,2]. The efficiency and selectivity in the transport process are dominated by molecular recognition of the cation size by a carrier. Improved design of ionophores should enhance their transport ability. For an active transport system, the carrier must change its complexing ability toward a specific cation between two interfaces. Proton-ionizable crown ethers are potentially useful for such a transport system [3]. On the other hand, we previously found that lipophilic monoazacrown ethers are also effective carriers for alkali metal cations by pH control [4-6]. Monoaza 12-crown-4, 15-crown-5, 18-crown-6 ethers showed selectivity toward Li^+, Na^+, and K^+, respectively. However, much higher selectivity is desirable for practical application, such as the separation of valued metals from sea water. In this paper, we briefly describe results obtained in transport using monoazacrown ethers and then report the synthesis and transport ability of monoazacryptands.

2. Experimental

^{1}H NMR spectra at 100 and 400 MHz were recorded with JEOL JNM-PS-100 and JNM-GSX-400 spectrometers using tetramethylsilane as an internal standard. IR spectra were obtained on a Hitachi 260-10 spectrophotometer. The mass spectra were measured with a JEOL JMS-DS 303 HF spectrometer.

2.1 PREPARATION OF POLYETHERS 7

Oligoethylene glycol bis(2-methylallyl)ethers **7** were prepared by the following sequence. Sodium metal (33.9 g, 1.47 mol) was dissolved in 400 mL of *t*-butyl alcohol containing ethylene glycol (45.7 g, 0.74 mol). To this stirred solution was dropwise added 2-methylallyl chloride (200 g, 2.21 mol) over a period of 5 h at 65 °C, and the resulting mixture was stirred for another 10 h. The insoluble matter was removed by filtration and the filtrate was evaporated *in vacuo*. Water (300 mL) was added to the residue and the solution was extracted with hexane (300 mL x 2). The organic layer was dried over $MgSO_4$ and evaporated *in vacuo* to give a brown viscous liquid. The crude product was distilled under reduced pressure (100-105 °C/20 Torr) to give 104.1 g (83%) of ethylene glycol bis(2-methylallyl) ether (**7a**) as a colorless oil. IR (neat): 3090, 2890, 1660, 1450, 1380, 1350, 1120, 910 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.68 (s, 6H), 3.36 3.44 (m, 4H), 3.82 (s, 4H), 4.76 4.92 (m, 4H). MS m/z (relative intensity): 170(M^+, 1), 155(2), 115(34), 73(61), 71(85), 55(100), 43(37). Calcd for $C_{10}H_{18}O_2$: C, 70.55%; H, 10.66%. Found: C, 70.15%; H, 10.82%.

By the same procedure but replacing ethylene glycol with diethylene glycol, diethylene glycol bis-2-(methylallyl)ether (**7b**) was obtained as a colorless oil in 81% yield. Bp 67-69 °C/0.05 Torr. IR (neat): 3090, 2860, 1660, 1450, 1380, 1350, 1110, 900 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.72 (s, 6H), 3.50-3.72 (m, 8H), 3.92 (s, 4H), 4.84-5.00 (m, 4H). MS m/z (relative intensity): 214(M^+, 0.3), 143(13), 117(10), 73(16), 55(100), 45(26), 43(12). Calcd for $C_{12}H_{22}O_3$: C, 67.25%; H, 10.35%. Found: C, 67.26%; H, 10.42%.

2.2 PREPARATION OF CROWN ETHERS 9

2,9-Bis(bromomethyl)-2,9-dimethyl-15-crown-5 (**9a**) was prepared by the following sequence [7]. To a stirred suspension of ethylene glycol (75.2 g, 1.2 mol) and N-bromosuccinimide (NBS; 43.2 g, 0.24 mol) was dropwise added ethylene glycol bis(2-methylallyl) ether (**7a**) (20.6 g, 0.12 mol) over a 1-h period at 45 °C. The mixture was stirred for 5 h at 50 °C. Aq. Na_2CO_3 solution (5%, 150 mL) was added and the mixture was extracted with dichloromethane (150 mL x 2). The organic layer was dried over $MgSO_4$ and evaporated *in vacuo* to give a brown viscous liquid. Ethylene glycol and other byproducts such as succinimide, were removed by distillation in a Kugelrohr apparatus (140 °C/0.01 Torr). The crude 4,11-bis(bromomethyl)-4,11-dimethyl-3,6,9,12-tetraoxatetradecan-1,14-

diol (**8a**) (43.0 g, 79%) was used for the next step without further purification. To a stirred suspension of powdered NaOH (96% purity, 14.39 g, 0.35 mol) in dioxane (250 mL) was added dropwise a mixture of the pentaethylene glycol derivative with two bromomethyl groups (**8a**) (31.24 g, 0.07 mol) and benzenesulfonyl chloride (12.2 g, 0.07 mol) dropwise over a 6-h period at 60 °C. The mixture was stirred for another 24 h at that temperature. The insoluble matter was removed by filtration and the filtrate was evaporated *in vacuo* to give a brown viscous liquid. Water (400 mL) was added and the mixture was extracted with dichloromethane (400 mL x 2). The dichloromethane layer was dried over $MgSO_4$ and evaporated *in vacuo* to provide the crude cyclization product, which was purified by silica gel column chromatography (acetone/hexane = 5/95, v/v) to give 9.80 g (overall yield of 21%, based on **7a**) of **9a** as a colorless oil. Calcd for $C_{14}H_{26}O_3Br_2$: C, 38.73%; H, 6.04%; Br, 36.81%. Found: C, 38.35%; H, 6.32%; Br, 36.43%.

This product was a mixture of the *cis* and *trans* isomers of 2,9-bis(bromomethyl)-2,9-dimethyl-15-crown-5 (**9a**). Two stereo isomers were separated by silica gel column chromatography (ethyl acetate/hexane = 1/4, v/v). The *trans* isomer was eluted before the *cis* isomer. Its structure was deduced based on the structure of the complex of its derivative (monoazacryptand) with KI, which was determined by X-ray crystallography [8]. *Trans* isomer: IR (neat): 2890, 1460, 1450, 1380, 1300, 1260, 1200, 1140, 970, 680 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.27 (s, 6H), 3.41-3.72(m, 20H). MS (CI, m/z%): 435(M^++3, 21), 355(98), 353(100). *Cis* isomer: ^1H NMR ($CDCl_3$) δ 1.28 (s, 6H), 3.40-3.73 (m, 20H). MS (CI, m/z%): 435(M^++3, 24), 355(98), 353(100).

2,12-Bis(bromomethyl)-2,12 dimethyl 18 crown 6 (**9b**) was obtained from **7b** by closely related procedure in an overall yield of 16% based on **7b**. Calcd for $C_{16}H_{30}O_6Br_2$: C, 40.18%; H, 6.32%; Br, 33.42%. Found: C, 40.11%; H, 6.58%; Br, 33.69%. Separation of *cis* and *trans* isomers was accomplished by the procedure given above for the isomers **9a**. *Trans* isomer: IR (neat): 2880, 1460, 1380, 1290, 1250, 1200, 1120, 1000, 670 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.29 (s, 6H), 3.45-3.70 (m, 24H). ^{13}C NMR ($CDCl_3$): δ 19.83, 37.33, 62.70, 70.69, 71.01, 71.17, 74.07, 77.36; MS (CI, m/z%): 479(M^++3, 24), 400(19), 399(100), 398(20), 397(99). *Cis* isomer: ^1H NMR ($CDCl_3$): δ 1.29 (s, 6H), 3.44-3.68 (m, 24H). ^{13}C NMR ($CDCl_3$): δ 19.89, 37.16, 62.67, 70.71, 70.93, 71.14, 74.12, 77.37. MS (CI, m/z%): 479(M^++3, 18), 400(20), 399(98), 398(20), 397(100).

2.3 PREPARATION OF CRYPTANDS **10**

1,11-Dimethyl-3,9,12,15,18,20,23-heptaoxa-6-azabicyclo[9.7.6]tetracosane (**10a**, a N-unsubstituted monoazacryptand [18,17,15]) was prepared by the following sequence [8]. A solution of diethanolamine (4.84 g, 46 mmol) and *cis*-2,9-bis(bromomethyl)-2,9-dimethyl-15-crown-5 (**9a**) (4.00 g, 9.2 mmol) in diglyme (150 mL) was dropwise added to a suspension of diglyme (150 mL) containing NaH (2.01 g, 55% in mineral oil, 46 mmol, which was washed with hexane before use) over a 5-h period at 120 °C. The mixture was stirred at that

temperature for another 24 h. The insoluble matter was removed by filtration and the diglyme was evaporated *in vacuo*. The residue was purified by alumina column chromatography (methanol/dichloromethane = 1/49, v/v). The product was distilled under reduced pressure in a Kugelrohr apparatus (150-170 °C/0.09 Torr) to give a slightly yellow viscous oil (1.01 g, 29%). IR (neat): 3600-3100, 3000-2500, 1620, 1460, 1360, 1290, 1180-1040, 950, 720 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.11 (s, 6H), 2.70 (s, 1H), 2.75-2.91 (m, 4H), 3.49-3.86 (m, 24H); MS (CI, m/z%): 378(M^++1, 100). Calcd for $C_{18}H_{35}O_7N$: C, 57.27%; H, 9.35%; N, 3.71%. Found: C, 57.10%; H, 9.38%; N, 3.44%.

1,11-Dimethyl-3,6,9,13,19,21,24,27-octaoxa-16-azabicyclo[9.9.7]heptacosane (**10b**, a N-unsubstituted monoazacryptand [20,18,18]) was obtained similarly from *cis*-2,12-bis(bromomethyl)-2,12-dimethyl-18-crown-6 (**9b**) in 27% yield. IR (neat): 3600-3100, 3000-2700, 1620, 1460, 1360, 1290, 1170-1040 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.11 (s, 6H), 2.83 (s, 1H), 2.83 (t, 4H), 3.44-3.86 (m, 28H). MS (CI, m/z%): 422(M^++1, 100). Calcd for $C_{20}H_{39}O_8N \cdot H_2O$: C, 54.65%; H, 9.40%; N, 3.19%. Found: C, 54.53%; H, 9.33%; N, 3.19%.

2.4 PREPARATION OF CRYPTAND 1

6-Dodecyl-1,11-dimethyl-3,9,12,15,18,20,23-heptaoxa-6-azabicyclo[9.7.6]tetracosane (**1**, a N-dodecyl monoazacryptand [18,17,15]) was prepared by the following sequence. A solution of *n*-dodecyl bromide (1.78 g, 7.2 mmol), Na_2CO_3 (0.76 g, 7.2 mmol), and N-unsubstituted monoazacryptand [18,17,15] (**10a**) (0.54 g, 1.4 mmol) in dioxane (10 mL) was refluxed for 20 h. The solvent was evaporated *in vacuo* and the residue was distilled under reduced pressure in a Kugelrohr apparatus (155 °C/0.08 Torr) to give a slightly yellow viscous oil (0.66 g, 85%). IR (neat): 3600-3100, 3000-2500, 1620, 1450, 1360, 1290, 1160-980, 960, 800 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.88 (t, 3H), 1.11 (s, 6H), 1.26 (m, 18H), 1.42 (m, 2H), 2.44 (t, 2H), 2.78 (m, 4H), 3.46-3.88 (m, 24H); MS (CI, m/z%): 546(M^++1, 100). Calcd for $C_{30}H_{59}O_7N \cdot H_2O$: C, 63.90%; H, 10.91%; N, 2.48%. Found: C, 63.50%; H, 10.99%; N, 2.48%.

2.5 PREPARATION OF CRYPTAND 2

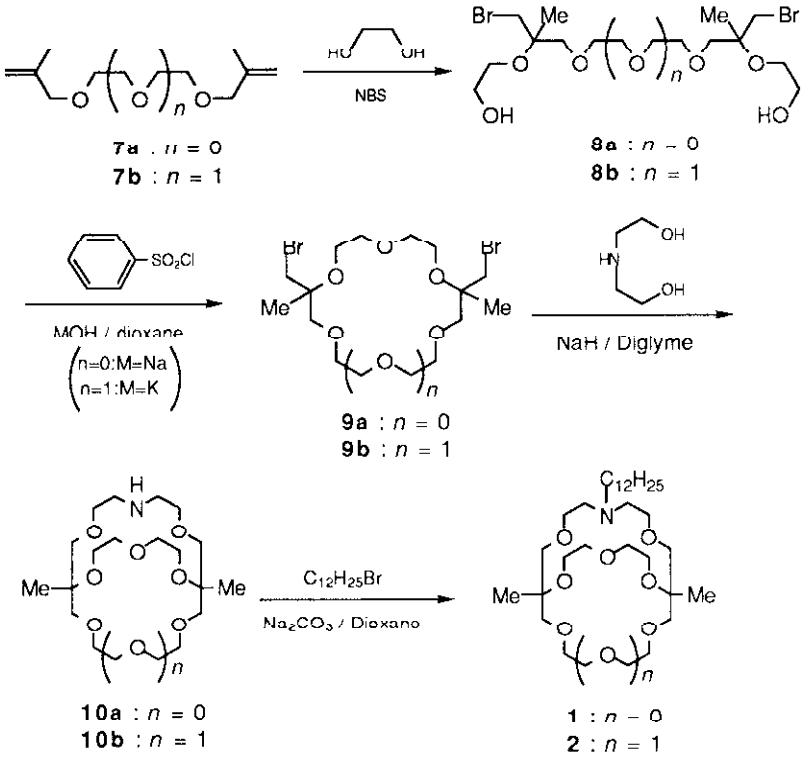
16-Dodecyl-1,11-dimethyl-3,6,9,13,19,21,24,27-octaoxa-16-azabicyclo[9.9.7]heptacosane (**2**, a N-dodecyl monoazacryptand [20,18,18]) was obtained in 38% yield by a closely related procedure. ^1H NMR ($CDCl_3$): δ 0.88 (t, 3H), 1.08 (s, 6H), 1.27 (m, 18H), 1.37 (m, 2H), 2.54 (t, 2H), 2.66 (m, 4H), 3.42-3.84 (m, 28H). MS (CI, m/z%): 590(M^++1, 100). Calcd for $C_{32}H_{63}O_8N \cdot 0.5H_2O$: C, 64.18%; H, 10.77%; N, 2.34%. Found: C, 64.39%; H, 10.73%; N, 2.38%.

2.6 BULK LIQUID MEMBRANE TRANSPORT

Transport experiments were carried out in a U-tube cell at 25 °C as described in an earlier paper [9]. For each transport experiment four cells

were used. A dichloromethane solution (20 mL) containing the synthetic ionophore was placed in the bottom of the cell and two aqueous solutions (10 mL) were carefully added on the top of it. Both surface areas were 2.0 cm^2. The organic phase was magnetically stirred at 500 rpm. Details of the transport conditions are summarized in the footnotes of Tables I-IV. Each receiving phase sampled after 6, 12, 18, and 24 h and the cation concentration was determined with a Nippon Jarrel-Ash AAA-8500 atomic absorption spectrometer. The values reported in the Tables are averages for the quadruplicate runs and the standard deviations were less than 10%.

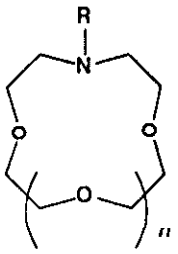
3. Results and Discussion



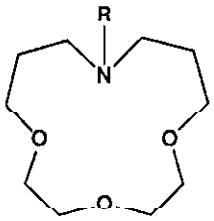
Scheme 1.

The synthetic procedure for formation of the monoazacryptands is shown in Scheme 1. N-unsubstituted monoazacryptands **10** were prepared by the reaction of *cis*-2,9-bis(bromomethyl)-2,9-dimethyl-15-crown-5 (**9a**) and *cis*-2,12-bis(bromomethyl)-2,12-dimethyl-18-crown-6 (**9b**) ethers with diethanolamine under basic conditions. N-Dodecyl monoazacryptands **1** and **2** were prepared by N alkylation of **10** using *n*-dodecyl bromide in the presence of Na_2CO_3 in dioxane. All structures were ascertained by ^1H NMR and IR spectroscopy, mass spectrometry and elemental analyses. The

X-ray crystal data of complexes of N-methyl substituted monoazacryptands derived from **10a** with NaI and KI also supported the structures [8]. The starting material, bis(bromomethyl)-dimethyl-crown ethers (**9**) were obtained from the bromoalkoxylation of oligoethylene glycol bis(2-methylallyl) ethers (**7**) with ethylene glycol followed by an intramolecular Okahara one-pot cyclization procedure using benzenesulfonyl chloride under basic conditions [10]. The mixture of *cis* and *trans* isomers was separated by silica gel column chromatography.



3a : $n = 1$, C_8H_{17}-
3b : $n = 1$, $C_8H_{17}OCH_2CH_2$-
4a : $n = 2$, C_8H_{17}-
4b : $n = 2$, $C_8H_{17}OCH_2CH_2$-
5a : $n = 3$, C_8H_{17}-
5b : $n = 3$, $C_8H_{17}OCH_2CH_2$-
5c : $n = 3$, $C_{12}H_{25}$-



6a : C_8H_{17}-
6b : $C_8H_{17}OCH_2CH_2$-

TABLE I. Competitive active transport of Na^+ and K^+ by monoazacrown ethers

Ionophore	Transported Cations (%)[a] thiocyanate [c]		picrate [d]		Stability Constants[b]	
	Na^+	K^+	Na^+	K^+	Na^+	K^+
4 a	4	6	65	7	3.08	2.82
4 b	12	8	54	16	3.83	3.58
5 a	5	26	8	75	3.49	4.87
5 b	12	57	8	50	4.21	5.73

[a] After 48 h. [b] In MeOH, at 25 °C, ref. 14 [c] Ref. 4. Transport conditions: basic phase (water, 10 mL), [KSCN] = [NaSCN] = [Me_4NOH] = 0.1 M; liquid membrane (dichloromethane, 20 mL), [ionophore] = 2.5 mM; acidic phase (water, 10 mL), [KSCN] = [NaSCN] = [HCl] = 0.1 M. [d] Ref. 5b. Transport conditions: basic phase (water, 10 mL), [KCl] = [NaCl] = [LiCl] = [Me_4NOH] = 0.1 M; liquid membrane (dichloromethane, 20 mL), [ionophore] = [picric acid] = 2.5 mM; acidic phase (water, 10 mL), [KCl] = [NaCl] = [LiCl] = [HCl] = 0.1 M.

Transport experiments were carried out at 25 °C in a U-type cell as reported in the literature [9]. Dichloromethane was the liquid membrane. The two aqueous phases were adjusted to be basic and acidic using tetramethylammonium hydroxide and hydrochloric acid, respectively. For the active transport system, equimolar amounts of alkali metal ions were added to each phase.

To evaluate the transport ability of monoazacryptands, it is desirable to compare their transport behavior with that of monoazacrown ethers, which have been reported by our group to be effective synthetic ionophores for alkali metal cations [4-6]. Competitive active transport data from a basic phase to an acidic phase using monoazacrown ethers are shown in Table I. Thiocyanate ion was used as the counter anion in our early transport experiments, and only monoaza-18-crown-6 with an electron-donating sidearm (**5b**) effectively transported alkali metal cations among the monoaza-15-crown-5 and 18-crown-6 ethers examined [4]. In this case, the transport rate using monoaza 15-crown-5 compounds **4a**, **4b** was rather slow compared to the corresponding monoaza 18-crown-6 derivatives **5a**, **5b**. Stability constants (log K in MeOH at 25 °C) of these monoazacrown ethers were in the range of 3-6 and the carrier with the highest stability constant (**5b**) showed the highest transport velocity in the transport system using thiocyanate ion. In other words, the transport velocity was found to be highly dependent on the stability constant of the ionophore with the metal cation, which may be explained by considering that the stability constant affects the extent of the transfer of the complex from aqueous phase to organic phase, *ie* extractability. Lamb *et al.* reported that the transport velocity is remarkably affected by the lipophilicity of the counter anion [11]. On the basis of their findings, the counter anion was changed from thiocyanate ion to more lipophilic picrate ion. In the transport using picrate anion, it should be stressed that the amount of the picrate ion used is equimolar to the ionophore as shown in the footnote of Table I. The transport efficiency using a monoaza 15-crown-5 with a lower complexing ability (log K (Na^+) = 3.08) (**4a**) was remarkably increased by this change of counter anion. This result shows that the use of the picrate anion succeeds in enlarging the scope of the effective carriers since there are many host compounds having such stability constants (log K >3).

Competitive passive transport data for monoazacrown ethers using picrate anions as the counter ions are summarized in Table II. Although the stability constants of monoaza-12-crown-4 and 14-crown-4 ethers are estimated to be even lower than those of monoaza 15-crown-5 ethers, as judged from their extractabilities for alkali metal cations [6, 12], the use of picrate anion enabled the effective and selective transport of lithium ion.

A possible transport mechanism is considered as follows. At the basic interface, the ionophore selectively complexes with the alkali metal cation based on the ring size. The ionophore transports the cation with a counter anion across the liquid membrane to the acidic phase. At the acidic interface, the nitrogen atom of the ionophore is protonated to release the cation. The ammonium picrate of the monoazacrown ether is easily soluble in the liquid membrane and moves to the basic phase across the membrane. In the basic phase, the ammonium salt is deprotonated to

give free monoaza crown ether. According to this cycle, alkali metal cations are concentrated in the acidic phase. In this transport, the leak of the picrate ion into the acidic phase could hardly be detected (<0.1%) as long as the release phase was maintained to be acidic [5a]. This finding shows that the exchange of the proton and the metal cation occurs at the interface between the organic layer and the acidic phase. Consequently the ammonium picrates of the monoazacrown ethers are regarded as the equivalents with proton-ionizable crown ethers.

Table II also shows the selectivity toward alkali metal cations observed for the monoazacrown ether derivatives. For example, the K^+/Na^+ transport selectivity using monoaza 18-crown-6 compounds **5a**, **5c** is about 20. Since the concentration ratio of K^+ to Na^+ in sea water is about one to forty or fifty, much higher selectivity is desirable. Therefore, we prepared monoazacryptands as mentioned above and examined their transport ability.

TABLE II. Competitive passive transport of Li^+, Na^+, and K^+ by monoazacrown ethers using picrate ion as the counter anion[a]

Ionophore	Transported Velocity[b]				Selectivity			Reference
	Li^+	Na^+	K^+	ΣM^+	Li^+/Na^+	Na^+/K^+	K^+/Na^+	
3a	5.78	0.71	0.18	6.7	8.3	-	-	6
3b	5.44	6.71	1.78	13.9	0.8	-	-	6
4a	0.13	11.5	1.0	12.6		12		5b
4b	0.82	9.8	2.4	13.0	-	4.1	-	5b
5a	0.04	0.71	16.9	17.7	-	-	24	5b
5b	<0.01	1.18	14.9	16.1			13	5b
5c	0.02	0.68	12.8	13.5	-	-	19	5b
6a	1.35	0.21	0.03	1.6	6.3	-	-	6
6b	7.18	0.30	0.07	7.6	24	-	-	6

[a] Transport conditions: basic phase (water, 10 mL), [KCl] = [NaCl] = [LiCl] = [Me_4NOH] = 0.1 M; liquid membrane (dichloromethane, 20 mL), [ionophore] = [picric acid] = 2.5 mM; acidic phase (water, 10 mL), [HCl] = 0.1 M.

[b] mol/h x 10^6

The transport results are shown in Tables III and IV. When picrate anion was used as the counter anion in this transport system, a disappointing result was obtained. In this case, N-dodecylmonoaza-18-crown-6 **5c** was found to exhibit a higher selectivity for K^+ than the monoazacryptand [20,18,18] (**2**). This is ascribed to the high complexing ability of monoazacryptands since these cryptands easily transfer the complexes into the organic phase as shown by extraction experiments [8]. The counter anion was then changed from picrate anion to more hydrophilic thiocyanate and chloride anions. This change resulted in

attaining a remarkably high K^+ selectivity in the case of **2**, which consists of two 18-crown-6 rings and one 20-crown-6 ring, when chloride ion was used. It should be noted that its transport velocity is remarkably higher (> 200 times) in comparison with the monoaza-18-crown-6 **5c**.

TABLE III. The effect of counter anions on competitive passive transport of Li^+, Na^+, and K^+ by monoaza cryptands and crown ethers

Ionophore	Counter Anion	Transport Velocity[a]				Selectivity	
		Li^+	Na^+	K^+	ΣM^+	Na^+/K^+	K^+/Na^+
1	picrate[b]	0.05	7.5	5.0	12.5	1.5	-
2	picrate[b]	<0.002	1.5	14.3	15.8	-	10
1	thiocyanate[c]	0.016	7.8	3.3	10.6	2.4	-
2	thiocyanate[c]	<0.002	1.1	12.7	13.8	-	12
1	chloride[d]	<0.002	7.0	1.0	8.0	7.0	-
2	chloride[d]	nd[e]	0.019	7.8	7.8	-	410
5c	chloride[d]	nd[e]	0.006	0.029	0.035	-	4.8

[a] mol/h x 10^6 [b] Transport conditions are given in Table II. [c] Transport conditions: basic phase (water, 10 mL), [KSCN] = [NaSCN] = [LiCl] = [Me_4NOH] = 0.1 M; liquid membrane (dichloromethane, 20 mL), [ionophore] = 2.5 mM; acidic phase (water, 10 mL), [HCl] = 0.1 M. [d] Transport conditions: basic phase (water, 10 mL), [KCl] = [NaCl] = [LiCl] = [Me_4NOH] = 0.1 M; liquid membrane (dichloromethane, 20 mL), [ionophore] = 2.5 mM; acidic phase (water, 10 mL), [HCl] = 0.1 M. [e] not detected.

TABLE IV. Competitive passive transport data using ionophore **2** for artificial sea water

Transported Cations (%)[a]				Selectivity
Na^+	K^+	Mg^{2+}	Ca^{2+}	K^+/Na^+
0.0242	10.8	<0.01	0.0326	445

Transport conditions: source phase (water, 10 mL), [NaCl] = 466 mM, [KCl] = 9.9 mM, [$CaCl_2$] = 10.5 mM, [$MgCl_2$] = 54.2 mM; liquid membrane (dichloromethane, 20 mL), [ionophore] = 2.5 mM; receiving phase (water, 10 mL), [HCl] = 0.1 M.

[a] After 12 h. The data reported were normalized based on the amount of potassium ion.

Since cryptand **2** can selectively transport K^+ using chloride ion as the counter ion, we examined the possibility of the selective separation of the K^+ from a mixture of Na^+, K^+, Mg^{2+}, and Ca^{2+} (Table IV). The

concentrations of these salts in the source phase were arranged to be almost the same concentrations of sea water. Potassium ion was selectively transported from the source phase into the receiving phase, even though alkaline earth metal cations were present. Since a carboxylic-type ionophore is known to prefer alkaline earth metal cations to alkali metal cations [13], it is noteworthy that the selectivity toward K^+ was attained even in the presence of alkaline earth metal cations.

4. Conclusion

The transport ability of lipophilic monoazacrown ethers were briefly summarized. To improve their transport ability, monoazacryptands were prepared and their complexation properties toward alkali metal cations were examined by liquid membrane transport. A lipophilic derivative consisting of two 18-crown-6 rings and one 20-crown-6 ring was found to be a highly selective K^+ carrier through a bulk liquid membrane under pH control in the absence of lipophilic anions.

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