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Proton-Ionizable Crown Compounds. 17. Transport Studies of Alkali Metal Ions in a H_2O–CH_2Cl_2–H_2O Liquid Membrane System by Macrocycles Containing Two Sulfonamide Groups Derived from *o*- and *m*-Phenylene Diamine

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Abstract. The transport of alkali metal cations by several macrocycles possessing two sulfonamide groups as a part of an 18-, 20-, or 21-membered macroring has been studied. Some of these compounds were found to be more effective transport agents than the proton-ionizable pyridone- and triazole-containing crown ethers reported previously. The factors affecting transport, such as ring size, source and receiving phase pH, and the nature of the groups attached to the sulfonamide nitrogen atoms were examined. Also, extraction experiments by some of the ligands were performed. The behavior of sulfonamide type crowns in single and competitive transport of the alkali metal cations is explained. The mechanism of transport appears to be complex. Transport of one or two cations per molecule of the disulfonamide carriers occurs. Complexation of these cations appears to occur both within and outside the macrocycle cavity. Our results also suggest that kinetic factors may play a significant role in transport rates and selectivities.

Key words. Proton-ionizable crown compounds, liquid membranes, alkali metal ion transport.

1. Introduction

There is an increasing interest in the separation of metal cations by selective transport across membranes [2]. Proton-ionizable ligands are of interest because they do not need an accompanying anion when the metal cation is extracted into the organic phase. This has been discussed more fully in previous papers [3–6]. Proton-ionizable crown compounds which have been studied include those with pendant arms containing carboxyl or phenolic groups [7–11], with phenolic groups wherein the hydroxy function is directed into the ring cavity [12, 13], and with the proton-ionizable group as part of the macroring cavity [3–6, 14, 15]. Members of the latter group include those which contain the 4-pyridone subcyclic unit (**1** and **2**,

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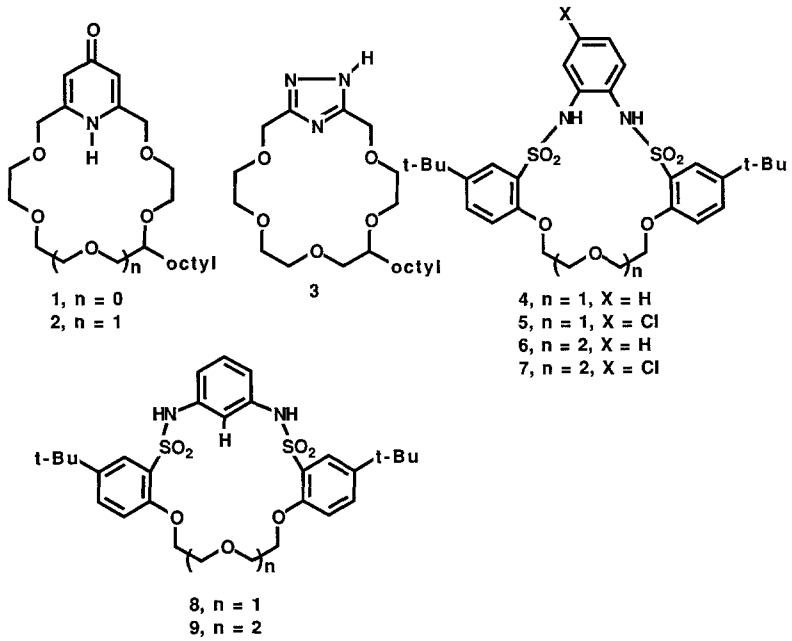

Fig. 1. Macrocyclic compounds.

Figure 1) which were selective for Li^+ and K^+ [4, 5], and those which contain the triazole unit (**3**) [16–18] which, although not highly selective, transported all of the alkali cations well.

We have also synthesized and have done preliminary testing on several proton-ionizable compounds containing two sulfonamide groups as part of the macroring [6, 19, 20]. These compounds have two proton-ionizable SO_2NH sites. Some of these new *bis*-sulfonamido-crown compounds were found to be more effective transporters than either the pyridono- or the triazolo-crown compounds that we have tested in the past in the bulk liquid membrane system. As with the pyridono- and the triazolo-crown compounds, these *bis*-sulfonamido-crown compounds transported best at high source phase pH values [6]. The aqueous pK_a value of the first proton of *bis*-sulfonamido-crowns is expected to be about 9 [21]. The pK_a of the second proton should be about 12. The second deprotonation of the *bis*-sulfonamido-crowns may allow for two rather than one univalent metal ion to accompany one ligand, thus enhancing transport. The pK_a values of the *bis*-sulfonamido-crowns are lower than those of the pyridone and triazole groups previously incorporated into macrocycles [3–6, 14, 15]. It was hoped that these lower pK_a values would be indicative of greater ease in exchanging alkali cations for protons in a membrane transport process.

This paper describes single and competitive alkali metal cation transport through a bulk liquid membrane by six of these *bis*-sulfonamido-crown ligands **4**–**9**. Macrocycle parameters studied include cavity diameter, presence or absence of chloro substituents, and the nature of the groups attached to the sulfonamido nitrogen atoms.

2. Experimental

2.1. MATERIALS

Compounds **4**–**9** were prepared as reported [6, 19, 20]. The following metal compounds were obtained in the highest purity available from the indicated suppliers and were used without further purification: hydroxides of Li^+ and K^+ (Spectrum), Rb^+ and Cs^+ (Aldrich), and Na^+ (Anachemia – carbonate free, Harleco – carbonate free), nitrates of Li^+ and Na^+ (Baker and Mallinckrodt), K^+ (Fisher, Baker, MCB), Rb^+ and Cs^+ (Fisher, Mallinckrodt, Aldrich). Reagent grade HNO_3 (Fisher, Mallinckrodt, Ashland) and spectroquality methylene chloride (CH_2Cl_2) (EM, B&J) were used. All aqueous solutions were prepared using distilled deionized water.

2.2. TRANSPORT PROCEDURE

The membrane transport experiments were carried out using bulk liquid membranes as described previously [4, 5, 22]. Each cell (Figure 2) consisted of a 3.0 mL membrane phase (CH_2Cl_2, 1.0 mM in carrier, stirred at 120 rpm by a magnetic stirrer) interfaced to both an 0.8 mL source phase (consisting of either 1.00M total cation or an equimolar cation mixture of known pH) and a 5.0 mL receiving phase (consisting of either distilled deionized water or an HNO_3 solution of pH 1.5). Source phases of different pH values were prepared using the appropriate amounts of MNO_3 and MOH. After 24 hours, the receiving phase was sampled and analyzed for cation concentration using a Perkin Elmer model 603 atomic absorption spectrophotometer. The pH values of the aqueous solutions were measured using a Sargent Welch miniature combination pH electrode. The initial source phase pH values were found to correspond closely to the calculated values. The pH values of the solutions listed in the Tables are the calculated values based upon the initial MOH concentration.

2.3. CALCULATIONS

Each experiment was repeated at least 3 times, and the results are reported as the average of the three determinations. The standard deviations from the mean among

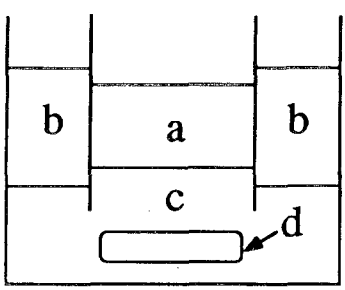

Fig. 2. Liquid membrane cell. (a) Source phase. $M^+(NO_3^-, OH^-)$ mixtures, H_2O; (b) Receiving phase. H_2O or HNO_3 (pH = 1.5); (c) Membrane. CH_2Cl_2, 1mM macrocycle; (d) Magnetic stirrer. 120 rpm/24 h.

the values in each experiment are less than ± 15% except where the flux was below 100 and in a few other cases indicated in the tables. High deviations when high transport occurred are probably a result of the inability to take samples in a reproducible manner when there is a high concentration gradient in the receiving phase (which is not stirred). Blank experiments with no carrier in the membrane showed cation fluxes to be less than 0.003×10^{-6} mol s^{-1} m^{-2}.

2.4. EXTRACTION

The crown ether solution in methylene chloride (4 mL) was vigorously stirred for 0.5 h at room temperature with 4 mL of 0.5 M aqueous NaOH, 0.5 M KOH or with a mixture of 2 mL each of both 1 M Na^+ and 1 M K^+ solutions. After the phases became completely clear, the organic phase was extracted with an equivalent volume of 0.1 M HNO_3. The amount of sodium and/or potassium in the extract was determined using atomic absorption spectroscopy. The pH of the source phase was adjusted using mixtures of 1 M KOH and 1 M MNO_3 solutions. Extraction results are shown in Table VII.

3. Results and Discussion

In those systems where appreciable cation transport occurred, the organic phase turned cloudy approximately one-half hour after stirring began. The cloudiness was much more intense for systems in which the receiving phase pH was 1.5 than for those consisting of pure water. This correlation between cloudiness and cation flux was not investigated further. The cloudiness may be a result of water being extracted with the cation into the membrane phase.

Ligands **4**–**9** were tested as carriers for the alkali metal cations. Flux values for the transport of metal ions in single M^+ experiments are given in Table I for **4**, **6**, **7**, and **9**. The data given in Tables I and II for alkali cation transport by ligand **4** were published previously [6], but they are included for a comparison with alkali cation fluxes by the other analogous crown ethers.

For all ligands studied, little or no transport of the alkali metal ions occurred at a source phase pH value below 13. This relationship between lack of transport and source phase pH is evidence that the transport occurs by a proton-ionizable mechanism. These results also demonstrate the potential danger of predicting complexation behavior in multi-solvent systems from single solvent data such as pK_a values. Data for carriers **5** and **8** are not included in the Tables. Ligand **5** did not transport alkali metal cations except for Cs^+ at fluxes of about 3.5×10^{-6} mol s^{-1} m^{-2} at a source phase pH of 13 to 14. Ligand **8** transports negligible amounts of alkali metal cations except for Rb^+ where transport equilibrium is reached and Cs^+ (over 68×10^{-6} mol s^{-1} m^{-2}) at pH = 14 in the source phase and pH = 7 in the receiving phase. Ligands **4**, **6**, **7**, **8**, and **9** were also tested for the competitive transport of two cations at a source phase pH value of 14 with both H_2O (pH = 7) and HNO_3 (pH = 1.5) receiving phases. Data for the competitive experiments are given in Tables II–VI.

In general, alkali metal cations were transported at a faster rate by the *bis*-sulfonamido-crowns than by previously reported proton-ionizable crowns. For

Table I. Single M^+ fluxes[a] in a bulk $H_2O-CH_2Cl_2-H_2O$ liquid membrane[b] system using **4**, **6**, **7** and **9** as carriers

M^+	Receiving Phase pH	Source Phase pH					
		13	13.5	14	13	13.5	14
		Ligand **4**[c]			Ligand **6**		
Li^+	7	1.1	4.2	35	2.1	5.1	13
	1.5	0.30	1.8	10	2.1	5.4	28
Na^+	7	0.34	19	21	2.6	7.5	9.6
	1.5	0.40	25	58	4.0	6.6	13
K^+	7	0.17	15	42	1.2	5.7	20
	1.5	0.28	11	54	1.4	12	24
Rb^+	7	0.25	10	3.7	0.81	7.5	29
	1.5	0.38	34	9.4	0.92	7.7	40
Cs^+	7	0.97	47	90	0.66	7.6	17
	1.5	0.98	68	41	0.90	12	21
		Ligand **7**			Ligand **9**		
Li^+	7	7.6	12	10	0.03	0.06	0.11
	1.5	12	14	8.4	0.03	0.06	0.17
Na^+	7	8.1	10	9.2	0.05	0.13	0.25
	1.5	13	12	16	0.07	0.20	0.26
K^+	7	22	80	26	0.06	0.31	30
	1.5	7.5	36	29	0.11	0.44	0.68
Rb^+	7	46	48	24	0.05	3.1	1.2
	1.5	121	91	33	0.10	1.8	9.1
Cs^+	7	3.0	19	19	0.21	–	–
	1.5	3.0	42	26	0.28	1.8	3.5

[a] $J_M = (\text{mol s}^{-1}\text{ m}^{-2}) \times 10^6$.

[b] Phase compositions: Source: 1.0 M in each metal cation using appropriate amounts of MNO_3 and MOH to achieve the initial source phase pH. Membrane: 0.001M **4**, **6**, **7**, and **9** in CH_2Cl_2. Receiving: initial pH of 7 (H_2O) or 1.5 (HNO_3), as indicated.

[c] Data for **4** were reported in Reference [6].

example, at source phase pH = 14, **2** transported K^+ with a flux of 16×10^{-6} mol s^{-1} m^{-2} into a receiving phase of pH 1.5 [2], while **4** transported K^+ at a flux of 54×10^{-6} mol s^{-1} m^{-2} under the same conditions [6]. Ligands **6** and **7** also gave high transport rates for the alkali metal ions (see Table I).

In comparing the transport by compounds **4** and **6** (Table I), all alkali metal ions except Rb^+ transported better using **4** at a source phase pH = 14 and a receiving phase pH = 7. Macrocycle **6** has a larger ring so that one would expect that it would transport the larger Rb^+ ions the best. In competitive systems for **4** (Table II) and **6** (Table III), **6**, in general, was found to be more selective, especially for Na^+. Indeed, macrocycle **4** exhibited little selectivity for any of the alkali metal ions. It was expected that **4** would be selective for Li^+ or Na^+, but this proved not to be the case.

Macrocycle **5**, which has the same structure as **4** but with a chloro substituent, was found to be a poor transport agent for the alkali metal ions [6]. A possible explanation for the substantially lower transport of metal ions by **5** is that the

Table II. Competitive M^+ fluxes[a] in a bulk H_2O–CH_2Cl_2–H_2O liquid membrane[b] system using **4** as carrier[c]

Metal Ions $\frac{M_1^+}{M_2^+}$	Aqueous Receiving Phase			
	pH = 7		pH = 1.5	
	Flux	*Ratio*	*Flux*	*Ratio*
$\frac{Li}{Na}$	$\frac{6.1}{11}$	0.55	$\frac{7.3}{21}$	0.35
$\frac{Li}{K}$	$\frac{10}{13}$	0.77	$\frac{10}{12}$	0.83
$\frac{Li}{Rb}$	$\frac{6.3}{9.5}$	0.66	$\frac{22}{30}$	0.73
$\frac{Li}{Cs}$	$\frac{7.8}{10}$	0.78	$\frac{27}{20}$	1.4
$\frac{Na}{K}$	$\frac{10}{9.0}$	1.1	$\frac{21}{17}$	1.2
$\frac{Na}{Rb}$	$\frac{13}{13}$	1.0	$\frac{25}{25}$	1.0
$\frac{Na}{Cs}$	$\frac{16}{13}$	1.2	$\frac{16}{15}$	1.1
$\frac{K}{Rb}$	$\frac{0.59}{1.0}$	0.59	$\frac{1.4}{2.2}$	0.64
$\frac{K}{Cs}$	$\frac{7.4}{14}$	0.53	$\frac{13}{26}$	0.50
$\frac{Rb}{Cs}$	$\frac{3.4}{4.0}$	0.85	$\frac{12}{13}$	0.92

[a] $J_M = (\text{mol s}^{-1}\,\text{m}^{-2}) \times 10^6$.
[b] Phase compositions. Source: initial pH of 14, 0.5M in each metal hydroxide. Membrane: 0.001M **4** in CH_2Cl_2. Receiving: initial pH of 7 (H_2O) or 1.5 (HNO_3), as indicated.
[c] Data taken from Reference [6].

chlorine atom may sterically interfere to block the metals from the ring cavity. Evidence supporting this argument is found in the crystal structure of **4** in which the molecule is in the form of a shallow cup and the benzene ring is part of the lip of that cup [19]. A relatively large chlorine substituent on the benzene ring could at least partially block the cavity so that normal complexation does not take place. Compound **7**, which is the chloro-substituted analog of **6**, on the other hand, transported the alkali metal ions about as well as **6** in single M^+ systems at a source phase pH = 14 (Table I). Macrocycle **7** was a better transport agent than **6** at source phase pH values of 13.5 and 13, especially for Rb^+. In competitive experiments for **6** (Table III) versus **7** (Table IV), **6** had excellent selectivity, $Na^+ > Li^+ > K^+ > Rb^+ > Cs^+$, while **7** was less selective. Although the chloro

Table III. Competitive M^+ fluxes[a] in a bulk H_2O–CH_2Cl–H_2O liquid membrane[b] system using **6** as carrier

Metal Ions $\frac{M_1^+}{M_2^+}$	Aqueous Receiving Phase			
	pH = 7		pH = 1.5	
	Flux	*Ratio*	*Flux*	*Ratio*
Li/Na	1.7/4.1	0.41	2.0/4.2	0.48
Li/K	9.4/3.3	2.9	8.7/3.0	2.9
Li/Rb	10/2.9	3.4	9.6/2.4	4.0
Li/Cs	12.3/2.3	5.4	8.2/1.2	6.8
Na/K	24/7.2	3.3	33/5.2	6.4
Na/Rb	37/7.7	4.8	37/5.1	7.3
Na/Cs	33/4.0	8.3	28/3.2	8.8
K/Rb	23/24	0.96	17/17	1.0
K/Cs	25/25	1.0	13/21	0.62
Rb/Cs	42/37	1.1	15/20	0.75

[a] $J_M = (\text{mol s}^{-1}\,\text{m}^{-2}) \times 10^6$.
[b] Phase compositions. Source: initial pH of 14, 0.5M in each metal hydroxide. Membrane: 0.001M **6** in CH_2Cl_2. Receiving: initial pH of 7 (H_2O) or 1.5 (HNO_3), as indicated.

substituent may not interfere directly with the transport in the larger and more flexible ligand **7**, as it does with the smaller compound **5**, it does appear to affect selectivity.

Both **8** and **9** gave substantially lower single cation transport rates of alkali metal ions than their counterparts **4** and **6**. Ligand **9** (Table I) was observed to transport only the larger cations with low fluxes at a source phase pH value of 13.5 and 14. The lower transport rate by **9** when compared to **4** and **6** (Table I) is probably caused by the intraannular hydrogen atom (on the benzene carbon between the two nitrogens) in **9**. This hydrogen atom would be directed into the cavity causing steric hindrance.

In competitive experiments, **8** (Table V) showed little or no transport of any

Table IV. Competitive M^+ fluxes[a] in a bulk H_2O–CH_2Cl_2–H_2O membrane[b] system using **7** as carrier

Metal Ions $\frac{M_1^+}{M_2^+}$	Aqueous Receiving Phase			
	pH = 7		pH = 1.5	
	Flux	*Ratio*	*Flux*	*Ratio*
$\frac{Li}{Na}$	$\frac{7.5}{11}$	0.68	$\frac{2.9}{5.9}$	0.49
$\frac{Li}{K}$	$\frac{8.7}{11}$	0.79	$\frac{7.2}{10}$	0.72
$\frac{Li}{Rb}$	$\frac{8}{9}$	0.9	$\frac{15}{15}$	1.0
$\frac{Li}{Cs}$	$\frac{16^c}{21^c}$	0.8	$\frac{18}{26}$	0.69
$\frac{Na}{K}$	$\frac{7.6}{5.7}$	1.3	$\frac{11}{4}$	2.8
$\frac{Na}{Rb}$	$\frac{12}{8.0}$	1.5	$\frac{15}{8.3}$	1.8
$\frac{Na}{Cs}$	$\frac{11}{9}$	1.2	$\frac{13}{9}$	1.4
$\frac{K}{Rb}$	$\frac{16^c}{16^c}$	1.0	$\frac{13}{13}$	1.0
$\frac{K}{Cs}$	$\frac{12}{5}$	2.4	$\frac{14}{5.4}$	2.6
$\frac{Rb}{Cs}$	$\frac{15}{6}$	2.5	$\frac{12}{4.9}$	2.4

[a] $J_M = (\text{mol s}^{-1}\,\text{m}^{-2}) \times 10^6$.
[b] Phase compositions. Source: initial pH of 14, 0.5M in each metal hydroxide. Membrane: 0.001M **7** in CH_2Cl_2. Receiving: initial pH of 7 (H_2O) or 1.5 (HNO_3), as indicated.
[c] Deviation > ±25%.

alkali cation when Li^+ or Na^+ were the cocations, but **8** transported K^+, Rb^+ or Cs^+ in the competitive M^+ experiments. The selectivity of **8** was not substantial: $K^+ > Rb^+ > Cs^+$ into an H_2O receiving phase and $Rb^+ > K^+ > Cs^+$ into the HNO_3 receiving phase (see Table V). Competitive fluxes for **9** (Table VI) showed low transport of all alkali metal ions, which is to be expected, since flux values were low in the single cation experiments. The best selectivity of **9** was Cs^+ over both Li^+ and Na^+ (Table VI). There is a reversal in selectivity between **6** (Table III) where $Na^+ > Cs^+$ and **9** (Table VI), where $Cs^+ > Na^+$.

The high fluxes observed for the *bis*-sulfonamides may be a result of high extractabilities (Table VII), formation of a 1:2 (ligand to metal cation) complex

Table V. Competitive M^+ fluxes[a] in a bulk $H_2O-CH_2Cl_2-H_2O$ liquid membrane[b] system using **8** as carrier

Metal Ions $\frac{M_1^+}{M_2^+}$	Aqueous Receiving Phase			
	pH = 7		pH = 1.5	
	Flux	*Ratio*	*Flux*	*Ratio*
Li/Na	0/0.1		0/0.06	
Li/K	0/0.02		0/0.02	
Li/Rb	0/0.03		0/0.02	
Li/Cs	0.02/<0.01		0/0.10	
Na/K	0.03/0.03		0.02/0.01	
Na/Rb	0.04/0.03		0.03/0.04	
Na/Cs	0.10/0.45	0.22	3.7/4.0	0.93
K/Rb	6.0/2.9	2.1	18/24	0.75
K/Cs	27/11	2.5	40/17	2.4
Rb/Cs	83/36	2.3	82/31	2.6

[a] $J_M = (\text{mol s}^{-1}\ \text{m}^{-2}) \times 10^6$.
[b] Phase compositions. Source: initial pH of 14, 0.5M in each metal hydroxide. Membrane: 0.001M **8** in CH_2Cl_2. Receiving: initial pH of 7 (H_2O) or 1.5 (HNO_3), as indicated.

[23], and to some extent, to the compact shape of ligand molecules containing small, highly lipophilic, *t*-butyl groups. As the small crown ethers (**4**, **5**, **8**) may carry only one cation in the cavity, it seems reasonable to assume that the second cation is outside the cavity, and plays the role of a co-cation [23]. This model explains some of the transport properties of the *bis*-sulfonamides, i.e., the high fluxes for large cations (Cs^+ for **4**; Rb^+ for **7** and **8**; Table I) which have lower hydration energies [24]. Non-selective co-transport of a second cation also may explain the decrease of Rb^+ fluxes for **8** in comparing competitive conditions to single cation source phases, because the co-cation would be less selectively extracted so that the rate of Rb^+ transport decreases with simultaneous increase of fluxes of other cations. On the other hand, dramatic changes in selectivity in competitive experiments as

Table VI. Competitive M^+ fluxes[a] in a bulk H_2O–CH_2Cl_2–H_2O liquid membrane[b] system using **9** as carrier

Metal Ions $\frac{M_1^+}{M_2^+}$	Aqueous Receiving Phase			
	pH = 7		pH = 1.5	
	Flux	*Ratio*	*Flux*	*Ratio*
$\frac{Li}{Na}$	$\frac{0.07}{0.13}$	0.54	$\frac{0.06}{0.18}$	0.33
$\frac{Li}{K}$	$\frac{0.27}{0.40}$	0.68	$\frac{0.21}{0.38}$	0.55
$\frac{Li}{Rb}$	$\frac{0.43}{0.77}$	0.56	$\frac{0.13}{0.50}$	0.26
$\frac{Li}{Cs}$	$\frac{0.48}{5.2}$	0.09	$\frac{1.1}{4.3}$	0.26
$\frac{Na}{K}$	$\frac{0.16}{0.25}$	0.64	$\frac{0.26}{0.38}$	0.68
$\frac{Na}{Rb}$	$\frac{0.22}{0.55}$	0.40	$\frac{0.39}{0.65}$	0.60
$\frac{Na}{Cs}$	$\frac{0.17}{5.0}$	0.03	$\frac{0.36}{2.6}$	0.14
$\frac{K}{Rb}$	$\frac{4.0}{5.0}$	0.80	$\frac{4.2}{4.9}$	0.86
$\frac{K}{Cs}$	$\frac{4.4}{2.1}$	2.1	$\frac{4.5}{2.3}$	2.0
$\frac{Rb}{Cs}$	$\frac{12}{9.6}$	1.3	$\frac{5.5}{2.3}$	2.4

[a] $J_M = (\text{mol s}^{-1}\,\text{m}^{-2}) \times 10^6$.
[b] Phase compositions. Source: initial pH of 14, 0.5M in each metal hydroxide. Membrane: 0.01M **9** in CH_2Cl_2. Receiving: initial pH of 7 (H_2O) or 1.5 (HNO_3), as indicated.

compared to single cation transport may be understood assuming the strict geometrical requirements for the cation which fits into the cavity, whereas the nature of the co-cation should be of lesser importance. Extraction experiments with open chain *bis*-sulfonamides [23] showed that the less solvated tetramethylammonium cation was a better co-cation than either Na^+ or K^+.

In general, it is assumed that transport across bulk liquid membranes is controlled thermodynamically [25]. Thus, cation fluxes increase in the order of increasing stability of their respective complexes. In these cases, selectivity of one cation over another as determined in a competitive transport experiment should be similar to that based on single cation transport fluxes.

The *bis*-sulfonamide enhanced transport is probably not thermodynamically

controlled. First, single and competitive transport selectivities are very different. For example, the competitive cation selectivities of **4** for Li^+ over Rb^+ and Na^+ over Rb^+ (receiving phase pH = 7) were 0.66 and 1.0, respectively (Table II), while the calculated selectivity using flux data for single cation transport studies (Table I, receiving phase pH = 7, source phase pH = 14) are 9.5 and 5.7, respectively. In the case of ligand **6**, the competitive selectivities (Table III, receiving phase pH = 7) of Na^+ over K^+ and Na^+ over Cs^+ were 3.33 and 8.25, respectively, while the corresponding calculated selectivities (Table I) are 0.48 and 0.56, respectively. Second, the fluxes do not always increase with an increased pH value in the source phase. For example, fluxes of Rb^+ decreased at a source phase pH = 14 using **4** and **7** as carriers (Table I). Third, the fluxes of many cations changed markedly when the pH of the receiving phase was changed (see Table I). Since even a neutral receiving phase is acidic enough to protonate the sulfonamide anion, there should be little difference in fluxes into either a neutral or acidic receiving phase in a thermodynamically controlled transport system.

To distinguish between thermodynamic and kinetic control, extraction of Na^+ and K^+ under single and competitive conditions was performed using ligands **4** and **6** dissolved in methylene chloride. Results are shown in Table VII. These data show that the stoichiometry of the complexes was predominantly, if not solely, 1:2 (ligand to metal ions) (for example, 1.21 moles of Na^+ and 0.62 moles of K^+ were extracted in the competitive experiments by 1 mole of ligand **6**).

The fact that the ligand to metal ion ratio is not exactly two indicates that either extraction is not quantitative or some 1:1 metal:ligand extraction occurs. Moreover, the ratio of sodium to potassium ions in the organic phase under thermodynamically controlled equilibrium conditions favors sodium (again 1.21 to 0.62). These results differ substantially from selectivities determined by single and competitive transport experiments as mentioned above. The obvious difference between the thermodynamic extraction experiment and the transport data indicates that there is a significant influence of kinetic factors on cation transport by these ligands. Notice,

Table VII. Extraction of Na^+ and K^+ from aqueous solutions into CH_2Cl_2 containing crowns **4** and **6** in single and competitive systems

Ligand (conc.)	M^+ (conc.)	*Single cation extractions* Moles of M^+ extracted per mole of ligand	*Competitive extractions* moles of M^+ extracted per mole of ligand
4 (5×10^{-3}M)	0.5M NaOH	1.89 moles Na^+	
	0.5M KOH	0.10 mole K^+	
	1:1 Mixture of 1M NaOH and 1M KNO_3		0.76 mole Na^+ and 0.50 mole K^+
6 (1×10^{-3}M)	0.5M NaOH	1.1 moles Na^+	
	0.5M KOH	0.87 mole K^+	
	1:1 Mixture of 1M NaOH and 1M KOH		1.21 mole Na^+ and 0.62 mole K^+

that extractabilities of Na^+ and/or K^+ differ in single and competitive extraction. Since Na^+ is extracted to a greater degree than K^+ (see Table VII), we assume that Na^+ forms a stronger complex with both ligands, and that, in this case, Na^+ is a better co-cation than K^+. A conclusion that Na^+ is the better co-cation is unusual because of its high hydration energy. But in the case of the 1:2 (ligand:metal ion) species, four different complexes are possible: two with Na^+ in the cavity (one with Na^+ as a co-cation and one with K^+ as co-cation) and two with K^+ in the cavity (again one with Na^+ as co-cation and one with K^+ as co-cation). According to the extraction data, evidently the complex with two sodium ions is the most stable structure. Perhaps this greater complex stability overcomes the difference in hydration energy between K^+ and Na^+.

4. Conclusions

The results show that alkali metal ion transport in a bulk $H_2O-CH_2Cl_2-H_2O$ liquid membrane system can be enhanced by the second deprotonation of the *bis*-sulfonamide carrier when source phase pH values are high enough and by altering the receiving phase pH. Other factors affecting transport may include ring size, substituents and the nature of the groups attached to the sulfonamide nitrogen atoms. Greatest over all selectivity was observed with **6**, which was selective for sodium over all the other alkali cations.

Many unusual properties of alkali cation transport mediated by macrocyclic *bis*-sulfonamides may be attributed to the formation of 1:2 (ligand:cation) complexes in which both cations possess different properties and to the (at least partial) control of the transport by kinetic factors.

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