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PROTON-IONIZABLE CROWN COMPOUNDS: TRANSPORT OF ALKALI AND ALKALINE EARTH CATIONS USING PROTON-IONIZABLE TRIAZOLO MACROCYCLES

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ABSTRACT

The macrocycle-mediated fluxes of the alkali and alkaline earth metal cations have been determined in a H_2O-CH_2Cl_2-H_2O bulk liquid membrane system. Water-insoluble proton-ionizable macrocycles of the triazolo type were used. The proton-ionizable feature allows the coupling of cation transport to reverse H^+ transport. This feature offers promise for the effective separation and/or concentration of alkali metal ions with the metal transport being driven by a pH gradient. A counter anion in the source phase is not co-transported. Transport of the alkali cations only occurred when the source phase pH was greater than the aqueous pK_a value for the carriers. Transport increased regularly with increasing source phase pH. Transport of alkaline earth cations from neutral pH source phases was minimal. The alkali cation selectivity order was $K^+ > Rb^+ > Cs^+ > Na^+ > Li^+$ for the 18-crown-6 sized macrocycles, while little selectivity was observed with the 15-crown-5 sized macrocycle.

INTRODUCTION

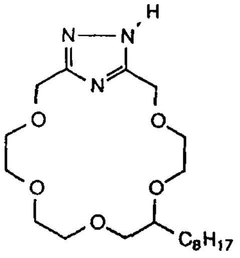
Earlier (1-3), we described the use of new water-insoluble proton-ionizable 18-crown-6 and 15-crown-5 pyridono macrocycles to selectively transport K^+ and Li^+, respectively, over the other alkali metal cations in a H_2O-CH_2Cl_2-H_2O bulk liquid membrane system. Previous work on cation transport using proton-ionizable macrocycles was referenced in these previous papers and in a recent communication by Kimura, et al. (4) on Cu^{2+} transport.

Our search for proton-ionizable macrocycles with particular selectivities has continued. Recently, we have synthesized a series of proton-ionizable macrocycles containing the triazole rather than the pyridone group. In this paper, the alkali and alkaline earth metal cation transporting properties of this new class of macrocycles are reported. We have also begun a study of selective transition metal cation transport using these ligands which will be reported in a separate article. In this paper, alkali metal cation transport will be shown to occur only when the pH of the source phase is greater than or equal to the aqueous pK_a value for the macrocycle. Alkali cation selectivity will be shown to be size dependent. However, the selectivities observed are not as great as those with the pyridone macrocycles (1-3). Finally, alkaline earth cation transport by these ligands will be shown to be minimal since concentrated solutions of these cations cannot be made at basic pH values and neutral mechanism transport (source phase anion co-transport) is minimal.

EXPERIMENTAL

Compounds 1-7 were prepared as reported previously (5). The following metal cation compounds were obtained in the highest grade 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 Ba^{2+} (Baker), Na^+, Mg^{2+} and Sr^{2+} (Mallinckrodt), K^+ (Fisher, Baker), Rb^+ and Cs^+ (Fisher, Mallinckrodt, Aldrich), and Ca^{2+} (B&A). Reagent grade HNO_3 (Fisher, Mallinckrodt, Ashland) and spectroquality methylene chloride (CH_2Cl_2) (EM) were used. All aqueous solutions were prepared using distilled deionized water.

The membrane transport experiments were carried out using bulk liquid membranes as described previously (6-8). Each cell (Figure 1) 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 a 0.8 ml source (consisting either of a 1.00 M total cation or an equalmolar 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 were prepared using the appropriate amounts of nitrate and hydroxide compounds. After 24 hours, the receiving phase was sampled and analyzed for cation concentration using a Perkin Elmer model 603 atomic absorption spectrophotometer and in some cases (large amounts of transport) nitrate ion concentration using a Dionex model 2000i ion chromatograph. 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 values predicted from molarity calculations. The pH values listed in the tables are



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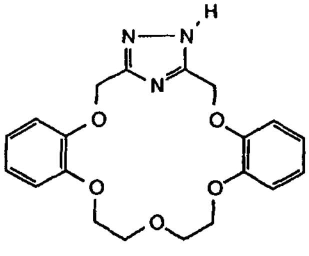

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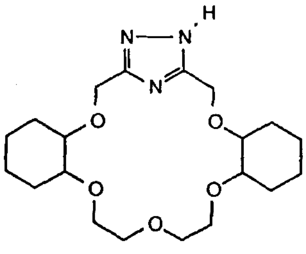

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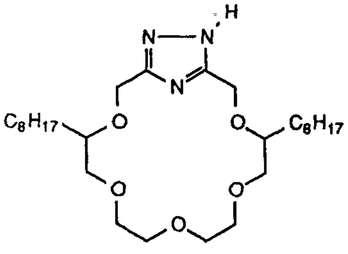

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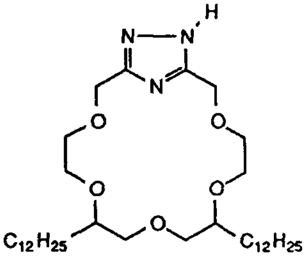

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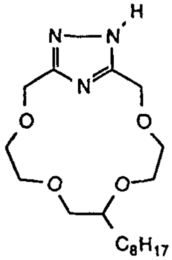

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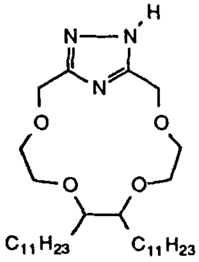

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COMPOUNDS

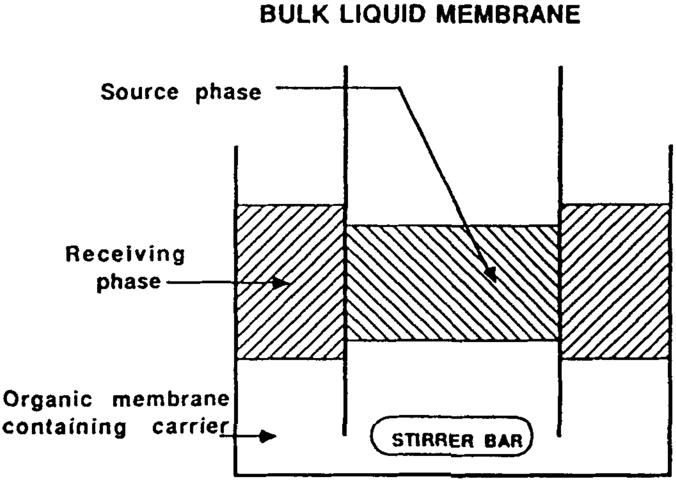

Figure 1. Bulk Liquid Membrane System

the calculated values since high pH value measurements are somewhat inaccurate.

Each experiment was repeated at least 3 times. The results are reported as the average of the determinations. The standard deviations from the mean among the values in each experiment are less than ±25%. Experiments performed in which no carrier was present in the membrane showed cation fluxes to be less than 0.3×10^{-8} moles $\cdot s^{-1} \cdot m^{-2}$.

RESULTS AND DISCUSSION

pH Effects

In Table I, flux values for the transport of alkali cations by 1 as a function of source and receiving phase pH are given. The transport trends with all five cations are similar. Transport is almost insignificant at pH 11, but shows an accelerated increase at pH values of 13, 13.5, and 14. Little difference in the flux values was observed in changing the initial receiving phase pH. Similar pH dependence trends were observed in the corresponding experiments with the other macrocycles studied. These data are available (9).

The influence of aqueous phase pH on transport can best be understood by considering the driving force for transport to occur. The transport steps are (i) the exchange of an alkali cation for a macrocycle proton by the ligand at the source phase-membrane inter-

TABLE 1

Single Alkali Cation Fluxes in a Bulk Liquid Membrane System[a] Containing 1 as Carrier with Varying Source and Receiving Phase pH Values

Cation	Receiving Phase pH	Flux[b]				
		Source Phase pH				
		11	12	13	13.5	14
Li^+	7	<1	<1	472	1202	2438
	1.5	0	0	409	1057	2490
Na^+	7	11	33	347	2378	1953
	1.5	10	57	648	1727	2478
K^+	7	11	30	548	1459	2835
	1.5	4	13	640	1539	3841
Rb^+	7	5	33	569	2432	2523
	1.5	2	15	614	2147	2708
Cs^+	7	9	47	426	669	1137
	1.5	2	40	501	1102	1342

[a] A 1.0 M cation (appropriate combination of hydroxide and nitrate)/ 0.001 M 1 in CH_2Cl_2/H_2O or HNO_3(pH = 1.5) bulk liquid membrane.
[b] $Moles{\cdot}s^{-1}{\cdot}m^{-2}{\cdot}10^8$.

face; (ii) diffusion of the complex across the membrane; (iii) release of the cation to the receiving phase and reprotonation of the ligand; and (iv) the return of the ligand to the source phase-membrane interface to begin the cycle anew. Thus, the driving force for transport (9,10) is given by Eq. (1) where $[M^+]$ and $[H^+]$ are the alkali metal cation and proton concentrations, respectively, and the

$$\text{Driving force} = [M^+]^s/[H^+]^s - [M^+]^r/[H^+]^r \qquad (1)$$

superscripts s and r indicate the source and receiving phases respectively. The equilibrium constants and/or kinetics of the interfacial reactions along with the membrane phase diffusion coefficients of the transporting species also affect the rate of transport. However, the effects of these steps in the transport cycle for a particular cation only involve equilibrium constants and the species concentrations of Eq. (1). Hence, the pH effects on the relative amounts of transport of a particular cation by a specific ligand should be readily predicted from the equation (10,11). The total amount of ligand present in the membrane is also a constant in these experiments.

In the experiments of Table 1, the initial $[M^+]^s$ value is always 1 M. Furthermore, since a very small fraction of the cation leaves the source phase during the course of the experiment, $[M^+]^s$ is virtually constant at 1 M. For similar reasons, it can be assumed that the source phase hydroxide concentrations and, hence, the $[H^+]$ values are constant. The $[M^+]^r/[H^+]^r$ term of Eq. 1 is negligible in comparison to the source phase term throughout the experiments of Table I due to the small amounts of transport. The validity of these assumptions is exemplified by the transport of K^+ at initial source and receiving phase pH values of 14 and 7, respectively. The flux value in this experiment is the equivalent of 0.024 M K^+ in the receiving phase after 24 hours. This amount of transport is also equivalent to a final receiving phase pH of 12.4 since water hydrolysis is necessary to reprotonate the macrocycle. Similar H^+-cation mass balances have been demonstrated (3). Negligible amounts of NO_3^- were detected in the H_2O phases which also indicates that cation transport occurs exclusively via a counter-H^+ transport mechanism. The initial and final values of the transport driving force for this experiment as calculated by Eq. (1) are 1×10^{14} and 7.2×10^{13}, respectively. The percent change in the transport driving forces over the course of the experiments are even less for the other fluxes of Table 1. Hence, the regular increase in flux with increasing source phase pH is a result of the regular change in the transport driving force. The small effects of receiving phase pH on transport are due to the small amounts of cation transport and proton counter-transport involved in the experiments.

The source phase pH value necessary for alkali cation transport to occur coincides with the aqueous pK_a value, 11.0, for the triazole type macrocycles (5). A similar effect was observed with the pyridone macrocycles (1-3). The affinity of the alkali cations for these nitrogen-containing ligands is such that the macrocycle must already be negatively charged in order for complexation to occur. A lack of affinity of alkali cations for neutral macrocycles containing nitrogen donor atoms has been observed (12).

Single Alkali Cation Transport

Although the effect of aqueous phase pH on the transport of a specific cation by a particular triazole macrocycle is regular, the actual amount of transport for a particular cation-ligand combination varies with the macrocycle used. This is to be expected since the interfacial reaction equilibrium and/or kinetics can vary greatly from case to case. Variations for the transport of a single alkali cation by the triazole ligands in systems initially containing pH 14 and 7 source and receiving phases, respectively, are illustrated in Table 2.

TABLE 2

Single Alkali Cation Fluxes in a Bulk Liquid Membrane System[a] Containing Various Triazolo Macrocycles as Carriers

Cation	Flux[b]						
	Macrocycle						
	1	2	3	4	5	6	7
Li^+	2438	125	87	631	---	2216	712
Na^+	1953	875	326	455	---	431	772
K^+	2835	91	366	614	1434	663	901
Rb^+	2523	1339	382	849	1455	2365	---
Cs^+	1137	1617	958	849	1053	2531	---

[a] A pH 14, 1.0 M metal hydroxide/0.001 M ligand in CH_2Cl_2/H_2O bulk liquid membrane. [b] $Moles \cdot s^{-1} \cdot m^{-2} \cdot 10^8$.

In these single cation systems, overall transport is greater with the macrocycles containing a single alkyl arm (1 and 6) as a hydrophobic substituent group. The reduced transport with 2 is due to the reduced macrocycle-cation interactions observed when electron withdrawing groups such as benzo are added to the macrocycle (7,8, 12,13). The reduced transport observed with ligands 3, 4, 5, and 7 appears to be due to the increased surface activity of these ligands. The increased hydrophobic exterior relative to 1 and 6 of these latter ligands provides for the greater surface activity when the proton is removed. The majority of the surface active molecules are assumed to be unavailable to act as carriers. All of the ligands are expected to be nearly quantitatively partitioned to the membrane phase since the aqueous to organic volume ratio is only ≈2:1 and the ligands are quite hydrophobic (1,2,14).

Competitive Alkali Cation Transport

Only small differences in the single cation transport rates were observed. However, some selectivity in the competitive experiments was noted. Similar fluxes in the single systems occur since the extraction interactions are small and not highly selective so that transport of each cation occurs only because extremely large aqueous concentration gradients exist (see discussion of Eq. (1)). In the competitive experiments, on the other hand, selectivity is determined solely by the interfacial reactions since the aqueous concentration gradient is the same for both cations. Competitive transport data for two alkali cations under the same system condi-

TABLE 3

Competitive Alkali Cation Fluxes in a Bulk Liquid Membrane System[a] Containing Various Triazolo Macrocycles as Carriers

	Fluxes[b]				
	Macrocycle				
Cation 1 Cation 2	1	2	3	4	6
Li^+ Na^+	313 874	31 810	30 223	249 209	1236 1127
Li^+ K^+	254 1012	2 132	32 282	146 295	1168 1226
Li^+ Rb^+	179 1215	11 804	34 223	236 725	1470 1601
Li^+ Cs^+	187 3417	8 1272	33 72	162 398	1321 1601
Na^+ K^+	787 1278	19 149	131 241	160 440	1119 1403
Na^+ Rb^+	544 1088	221 921	241 227	234 895	1283 1685
Na^+ Cs^+	1097 4941	106 1231	166 535	231 454	1217 5527
K^+ Rb^+	1089 1113	241 104	250 173	244 298	1594 1840
K^+ Cs^+	1404 560	187 25	206 85	383 159	1171 433
Rb^+ Cs^+	1071 963	434 170	186 106	425 170	1474 452

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[a] pH 14, 0.5 M in each metal hydroxide/0.001 M ligand in CH_2Cl_2/H_2O bulk liquid membrane. [b] $Moles \cdot s^{-1} \cdot m^{-2} \cdot 10^8$.

tions are given in Table 3. The 18-crown-6 sized ligands 1, 3, and 4 show small, but similar selectivities with the order being $K^+ \approx Rb^+ > Cs^+ > Na^+ > Li^+$. The Rb^+ vs. Na^+ result with 3 appears to be anomalous.

The same selectivity order is observed with 2, but the selectivities are much greater than with the other 18-crown-6 sized macrocycles. This may be due to the rigidity of the macrocycle ring size when benzo substituent groups are present. Similar arguments for benzo additions to other macrocycles have been made (15). The cation selectivity order of these ligands is primarily a function of the fit of the cations in the macrocycle ring. Hence, a reduced ability of the macrocycle to conform to the size of the cation should increase size related selectivity. The $K^+ > Rb^+$ selectivity observed with 2 is particularly illustrative of this point.

The greatly reduced transport of K^+ by 2 in the single systems is also interesting. Potassium selectivity with 2 in the competitive experiments occurs, but single K^+ transport is small (Table 2). Hence, it appears that K^+ is readily extracted into the membrane phase but is not released to the receiving phase. Similar behavior in other systems where cation release is not favorable due to reaction kinetics or equilibria has been observed (11, 16-18).

Selectivity with the 15-crown-5 sized macrocycle, 6, is quite different than that observed with ligands 1 - 4. The transport of Li^+ with 6 is comparable to the other cations, although slight $Cs^+ > Li^+$ selectivity was observed. Similarly, only Cs^+ was selectively transported over Na^+ to any particular degree. These Cs^+ selectivities are unusual since K^+ and Rb^+ are selectively transported over Cs^+. This latter selectivity would be expected when considering the size of the macrocycle cavity compared to the cation sizes. Perhaps a different type of concerted complexation is possible with the larger alkali cations and either Li^+ or Na^+ systems. Certainly the smaller sized ring allows for Li^+ and Na^+ to compete effectively with the larger alkali cations for complexation with the macrocycle.

Transport of Alkaline Earth Cations

Transport of the alkaline earth cations was only studied at neutral pH values since 1 M solutions of the nitrate salts were not completely soluble at basic pH values. Neutral and pH 1.5 (HNO_3) receiving phases, however, were studied. Flux values for any of the alkaline earth cations by any of the ligands was never greater than 4×10^{-8} moles·s^{-1}·m^{-2}. In fact, the only cation for which transport could be safely assumed to be greater than in the blank experiments was with Sr^{2+} and the 18-crown-6 sized ligands.

This lack of transport with neutral source phases is to be expected. Alkaline earth cations do not have strong affinity for neutral macrocycles containing nitrogen donor atoms (12). The macrocycle will not be deprotonated at these source phase pH values unless the cation has more affinity for the macrocycle than do protons. Counter-proton transport also requires two negative carrier molecules per alkaline earth cation for these monoprotic ligands. The slight transport of Sr^{2+} seems consistent with its better fit into the macrocycle cavity.

CONCLUSIONS

Alkali metal cations are transported by a proton-coupled mechanism in bulk liquid membranes when the source phase pH is greater than the aqueous pK_a value of the triazolo macrocycle. Beyond this point, transport increases regularly with increasing source phase pH. Alkaline earth cation transport by these macrocycles is minimal since only neutral and acidic pH source phases solubilize 1 M cation solutions. The alkali cation selectivities of these macrocycles are small, especially with the 15-crown-5 sized ligand. The selectivity order of the 18-crown-6 sized macrocycles is $K^+ > Rb^+ > Cs^+ > Na^+ > Li^+$. The greatest K^+ selectivity is obtained with the dibenzo ligand since the macrocycle cavity is more rigid. The selectivities observed are cation *vs.* macrocycle size related.

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