generally excellent and selective cation binders, while the monomers have low cation affinity.[16]

Experiments were carried out using calixarene **3** to measure the rate of Cs^+ transport under conditions of varying source phase pH to demonstrate the exchange of a proton for the cation at the source phase interface. Mixtures of $CsNO_3$ and CsOH were used as the source phase. The relative amounts of the two solutes were adjusted to maintain the total Cs^+ concentration at 1.00 M in each case. A plot of cation flux, J_M, vs. pH is shown in Figure 1. The values of J_M are small below a pH of 12, but rise rapidly beyond this point. This result confirms that a proton is removed from the ligand in the complexation process and that for appreciable transport to take place, the source phase must be quite basic.

All three of the calixarene ligands studied gave selective transport of Cs^+ over the other alkali metal cations with the order of selectivity being **3** < **2** < **1**. Ligand **1** is most selective for Cs^+, but the Cs^+ flux with this ligand is considerably less than that with either of the other ligands. Ligands **1**–**3** vary considerably in the size of their hydroxyl-end cavity, especially when one considers various possible conformations.[1b] Comparison of the relative magnitudes of the ligand cavity and cation diameters makes it apparent that the selectivities seen in Table II are determined by factors other than relative sizes. CPK models indicate that approximate hydroxyl-end cavity diameter ranges of the ligands are: **1**, 0.68–0.92 Å; **2**, 2.1–2.8 Å; **3**, 4.0–4.4 Å. The ionic diameters of K^+, Rb^+, and Cs^+ are 2.76, 2.98, and 3.40 Å, respectively.[17] It is likely that M^+ selectivity is related to the relative hydration energies of the cations studied, since partial or complete dehydration of the cation will occur in the complexation process. This hypothesis is supported by the fact that among the monovalent cations the cation of lowest hydration energy, Cs^+, is selected. Preliminary work with *p-tert*-pentylcalixarenes corresponding to **1** and **3** shows their alkali metal ion transport behavior and selectivities to be similar to those of **1** and **3**.

The lack of appreciable transport of either Ca^{2+}, Sr^{2+}, or Ba^{2+} by any of the calixarenes (Table II) is probably a result of the low water solubilities of their hydroxides. The observation that polyphenols may be responsible for the concentration of bivalent metal ions in brown algae[8] suggests that calixarenes may be effective as complexing agents for some bivalent cations.

The results described here indicate that calixarene compounds may be used as selective cation carriers in liquid membranes. Additional analogues of calixarenes may be envisioned with groups other than butyl in the *para* position of the phenol moiety which may serve to alter the acidity of the phenolic OH and thus the cation binding characteristics of the ligand. It is anticipated that further studies in our laboratory will elucidate the nature of cation binding by **1**–**3** and analogues of these macrocycles and the means by which such binding may be exploited in making chemical separations.

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Registry No. **1**, 60705-62-6; **2**, 78092-53-2; **3**, 68971-82-4; Li, 7439-93-2; Na, 7440-23-5; K, 7440-09-7; Rb, 7440-17-7; Cs, 7440-46-2; Ca, 7440-70-2; Sr, 7440-24-6; Ba, 7440-39-3.

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Cation Fluxes from Binary Ag^+–M^{n+} Mixtures in a H_2O-$CHCl_3$-H_2O Liquid Membrane System Containing a Series of Macrocyclic Ligand Carriers

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Abstract: Cation fluxes were determined for Ag^+–M^{n+} binary cation mixtures in a H_2O–$CHCl_3$–H_2O liquid membrane system, using macrocyclic ligands as carriers. Alkali metal, alkaline earth metal, Pb^{2+}, and Tl^+ cations served as M^{n+} in these experiments while macrocyclic polyether ligands having varying ring cavity radii, donor atom types, and substituents served as carriers. Correlations were found between relative cation transport rates and these ligand structural features as well as the equilibrium constant (*K*) for the formation of the various cation–macrocycle complexes. Selection of macrocycles having proper carrier cavity radii and appropriate combinations of oxygen with either nitrogen or sulfur donor atoms led to selective transport of Ag^+ in preference to any of the other cations studied. Transport was also enhanced by certain aliphatic substituents on the macrocycles. The most effective macrocycles in transporting large quantities of Ag^+ in the presence of M^{n+} were diketopyridino-18-crown-6 (DKP18C6), diketopyridino-21-crown-7 (DKP21C7), 4-octoxydiketopyridino-18-crown-6 (ODKP18C6), and dicyclohexano-18-crown-6 (DC18C6). Silver ion was transported selectively by these ligands over all M^{n+} cations studied except in the cases of Pb^{2+}, which was transported in preference to Ag^+ by DKP18C6, ODKP18C6, and DC18C6; Tl^+, which was transported preferentially by DKP21C7 and DC18C6; and Ba^{2+} and Sr^{2+}, which were transported selectively by DC18C6.

Since their original synthesis by Pederson,[1] macrocyclic crown ethers have attracted much attention because of their ability to form stable complexes, particularly with alkali, alkaline earth, and post-transition-metal cations. The replacement of all or part of the inner solvation sphere of the cation by ligand donor atoms is thermodynamically favorable, providing a large driving force to favor complexation. In many cases, remarkable selectivity for certain cations over others is found in a given solvent. In addition, the solubility of the lipophilic crown ethers in many organic solvents has led to their widespread use as phase transfer catalysts to enhance the solubility of inorganic salts in these solvents.[2] An

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extension of this latter use has been the investigation of the selective transport by crown ethers of cations from a source aqueous phase across a liquid organic membrane and into a receiving aqueous phase.[3-17]

In earlier studies, we correlated the macrocycle-mediated transport of single cations across a H_2O–$CHCl_3$–H_2O liquid membrane with a variety of system parameters including ratio of ligand cavity radius to cation radius, cyclic vs. noncyclic ligands, ligand donor atom type, ligand ring substituents, relative ligand solubilities in H_2O and $CHCl_3$, cation charge, and cation type.[10] In addition, we have determined cation fluxes, J_M (mol/(s m^2)), in these membrane systems when two metal nitrate salts are initially present in one aqueous phase. The cation mixtures studied have included Na^+–M^{n+},[13] K^+–M^{n+},[14] Cs^+–M^{n+},[13] Tl^+–M^{n+},[14] Sr^{2+}–M^{n+},[13] and Pb^{2+}–M^{n+},[12] where M^{n+} includes other alkali, alkaline earth, and post-transtion-metal cations. A variety of crown ether and cryptand macrocycles were used as carriers in each case.

It has been found in studies of macrocycle-mediated transport of single cations in H_2O–$CHCl_3$–H_2O liquid membrane systems that J_M values are influenced significantly by the stabilities of the cation–carrier complexes.[7,9,11,18] The equilibrium constants, *K*, for the cation–macrocycle reactions which occur in $CHCl_3$ are those needed for an accurate evaluation of correlations between J_M and *K*. Log *K* data valid for complex formation in $CHCl_3$ are unavailable, but log *K* values for many cation–macrocycle interactions in water and in methanol have been determined. Log *K* values valid in water for the reactions of closely related (e.g., alkali metal) cations with a given macrocycle differ from those valid in methanol by a nearly constant amount, ~3,[7,11] and we assume that the values obtained in these two solvents reflect the trends valid in $CHCl_3$ for correlation with transport results in our membrane systems. Previous results show that the ligand donor atom type, the cation–ligand cavity size ratio, and ligand ring substituents can markedly affect the magnitude of log *K*.[19-23] As would be expected, these effects are reflected in the relative fluxes of the cations.[5,10,11]

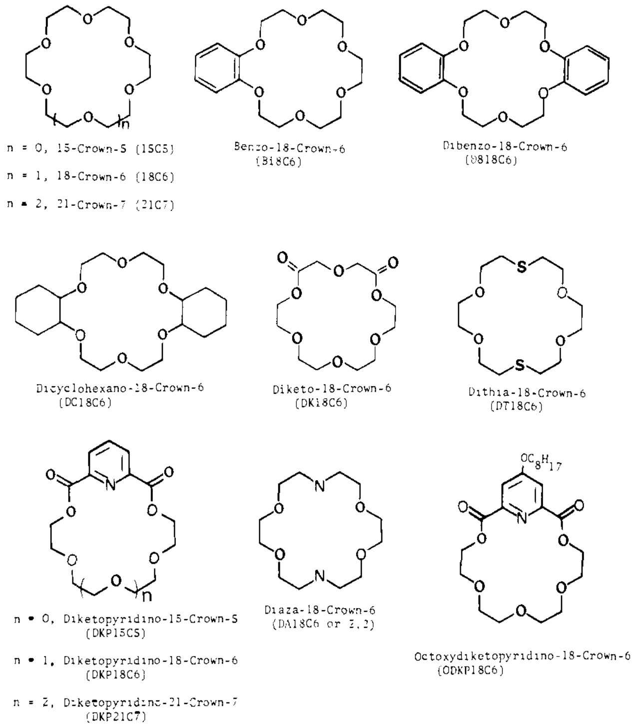

Figure 1. Structures and abbreviations for carrier molecules.

Maximum transport in liquid membrane systems of the type used here occurs when *K* values for M^{n+}–macrocycle complexation fall within a certain range.[7,18] If *K* is sufficiently low, cations are not extracted from the source phase into the membrane. On the other hand, if *K* is sufficiently large, cations are not released from the membrane into the receiving phase. These points have interesting implications in two-cation, competing systems. In general, the cation which forms the most stable complex with the carrier is favored in transport, effectively blocking migration of the other cation through the membrane. This effect is observed in the other binary transport systems we have studied,[12-14] and is also seen in our Ag^+–M^{n+} results. In addition, formation of a very stable complex by one of the cations results in extraction of that cation from the source phase but little, if any, release of it to the receiving phase, thus making the carrier unavailable for transport of the cation. In this way, the movement of both cations through the membrane may be blocked. Several examples of this effect are found in the present study.

Earlier studies[10] have shown that the influence of ligand substituents on cation fluxes is significant, and similar results are seen in the Ag^+–M^{n+} mixtures. In addition, since many macrocycles such as 18C6 (see Figure 1 for macrocycle names and abbreviations) are soluble in water, they partition extensively from the membrane into the aqueous source and receiving phases. To minimize this carrier loss, water-insoluble macrocycles having hydrocarbon side chains of various types have been used in previous studies.[10] One of these substituted macrocycles has been found to be a highly selective carrier for Ag^+.

We here report cation fluxes from several Ag^+–M^{n+} mixtures and show correlations between these J_M values and various macrocycle and cation parameters. Excellent selectivity for Ag^+

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Table I. Log *K* for the Reaction $M^{n+} + L \rightarrow (ML)^{n+}$ [a]

		ligands							
cation	solvent	15C5	18C6	21C7	DKP18C6	DT18C6	DA18C6	DB18C6	DC18C6[b]
Ag^+	H_2O	0.94^c	1.50^c			4.34	7.8	1.41	2.36
	CH_3OH	3.62^d	4.58^d	2.46^d	4.88^e				
Na^+	H_2O	0.70	0.8					1.16	1.21
	CH_3OH	3.48^d	4.36^d	1.73^d	4.29^e			4.5	4.08
K^+	H_2O	0.74	2.03					1.67	2.02
	CH_3OH	3.77^d	6.06^d	4.22^d	4.66^e	1.15	2.04	5.00	6.01
Rb^+	H_2O	0.62	1.56					1.08	1.52
	CH_3OH		5.32^d	4.86^d	4.24^e			3.76	
Cs^+	H_2O	0.8	0.99					0.83	0.96
	CH_3OH	2.18^d	4.79^d	5.01^d				3.55	4.61
Ca^{2+}	H_2O		<0.5						
	CH_3OH	2.18^d	3.86^d	$<1^f$					
Sr^{2+}	H_2O	1.95	2.72				2.56	1.0	3.24
	CH_3OH	2.63^d	5.8^g	1.77^d					
Ba^{2+}	H_2O	1.71	3.87				2.97	1.95	3.57
	CH_3OH		7.04^d	5.44^d				4.28	
Pb^{2+}	H_2O	1.85^c	4.27^c			3.13^c		1.89	4.95
Tl^+	H_2O	1.23^c	2.27^c			0.93^c		1.50	2.44

[a] Values from ref 22 unless otherwise noted. [b] Values given are for the cis-syn-cis isomer. Values for the cis-anti-cis isomer are ~0.5 log *K* unit lower in all cases. [c] Reference 21. [d] Reference 20a. [e] Reference 23. [f] Reference 11. [g] Reference 7.

is found in several cases. Although transport through the bulk liquid membranes employed here is too slow for use on an industrial scale, the cation separations achieved should be of interest for application in more practical systems, especially in view of the relatively low toxicities which have been reported[24] for several of the macrocyclic polyether ligands employed. Such systems might include the liquid emulsion membranes introduced by Li[25] and used by us[15–17] to effect rapid and quantitative cation separations, and the supported porous membranes employed by Babcock and co-workers.[26]

Experimental Section

Materials. The macrocycles used are shown in Figure 1. The following ligands were obtained in reagent grade quality from the sources indicated and used without further purification: 15C5, 18C6, 21C7, B18C6, DB18C6, DC18C6 (mixture of isomers), DT18C6 (Parish Chemical Co.); DA18C6 (MCB). The synthesis and purification procedures for the remaining diketo macrocycles except ODKP18C6[27] have been given.[28] The cation nitrates were obtained in reagent grade from the indicated suppliers and used without further purification: Ag^+ (Sargent Welch); Na^+ (Mallinckrodt); K^+, Ba^{2+} (Baker); Rb^+, Cs^+ (Alfa); Ca^{2+}, Pb^{2+} (Baker and Adamson); Sr^{2+} (Fisher); Tl^+ (ICN Pharmaceuticals). Reagent grade chloroform (Fisher) was used for all membrane solutions, and distilled deionized water was used to prepare all source and receiving phase solutions.

Procedure. The cells used for the transport experiments consisted of a 3-mL membrane phase (chloroform 1.0 mM in carrier, stirred at 120 rpm by magnetic stirrer) interfaced to both a 0.8-mL source phase (salt solution) and a 5.0-mL receiving phase (distilled, deionized water).[7,8,10] To prevent the light-induced reduction of Ag^+, the cells were covered by light-tight boxes during the experiments. Despite this precaution, dark brown films, which might be due to decomposition of the macrocycle, to aza macrocycle-catalyzed disproportionation of Ag^+[29] or to some other reaction, sometimes appeared on the sides of the cells when nitrogen-containing ligands such as DA18C6 or DKP18C6 were used. The temperature inside the boxes rose to 30 °C within 1 h of the start of the stirring motors and was maintained at 30 ± 2 °C thereafter. Previous experiments by us and other workers have shown that the increase in salt concentration in the receiving phase is linear with time.[3,5,8] Therefore, after the mixture was stirred for 24 h, 3-mL samples of the receiving phase were withdrawn and analyzed for transported cations with an atomic absorption spectrophotometer (Perkin-Elmer Model 603). The source phase was 0.5 M in $AgNO_3$ and 0.5 M in the nitrate salt of the second cation except in the cases of $Ba(NO_3)_2$ and $TlNO_3$, which were 0.15 M in the second cation (for solubility reasons) and in Ag^+. Since the anion forms an ion pair with the cation–macrocycle complex in the membrane, anion type has a large influence on the magnitudes of cation fluxes in these membranes.[8] Nitrate salts were used throughout to avoid transport differences due to different anions[6,8] and because nitrates have high water solubility and high fluxes, in general, compared with salts of other anions.[8]

Table II. Radii (Å) of Carrier Cavities[10,11] and Cations[31]

cation	radius, Å	cation	radius, Å	cation	radius, Å	crown ether	radius, Å
Na^+	1.02	Rb^+	1.49	Ca^{2+}	1.00	15C5	0.86–0.92
Ag^+	1.15	Tl^+	1.50	Sr^{2+}	1.16	18C6	1.34–1.43
K^+	1.38	Cs^+	1.70	Ba^{2+}	1.36	21C7	1.7
				Pb^{2+}	1.18		

Calculations. Transport experiments were repeated at least 3 times for each cation pair–macrocycle set. The results given are averages of at least three determinations. The standard deviation in each case is ~15% or less of the mean.

Results and Discussion

Macrocycle-mediated cation fluxes for Ag^+–M^{n+} binary systems can be explained in terms of the relative radii of the cations and the macrocycle cavities, the macrocycle donor atom type, and the macrocycle ring substituents. These factors are also related to the equilibrium constants for formation of the complexes (see Table I). Correlations between each of the above factors and cation fluxes are now discussed.

Size Effects. X-ray crystallographic data indicate that where macrocycle cavity and cation sizes are comparable, cations bind to crown ethers by occupying the ligand cavity.[30] Thus, the relative sizes of the cation and the ligand cavity (Table II) are important in determining the thermodynamic stability of the complex formed and consequently have a large influence on both the magnitude and the selectivity of carrier-facilitated transport. Fluxes for Ag^+ as well as for Ag^+–M^{n+} pairs using unsubstituted polyethers of different cavity radii (Table III) illustrate this effect.

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Table III. Cation Flux (J_{M}) (mol × 10^8/(s m^2)) from the Source Phase[a] for M^{n+}–Ag^+ Mixtures with Carriers of Varying Cavity Radii

	carriers		
cations[b]	15C5	18C6	21C7
Ag^+	170	507	322
Ag^+	184	460	256
Na^+	46	7	9
Ag^+	131	187	129
K^+	1	486	48
Ag^+	145	138	99
Rb^+	*c*	157	71
Ag^+	101	299	23
Cs^+	*c*	35	90
Ag^+	35	62	23
Tl^+	18	371	260
Ag^+	154	437	320
Ca^{2+}	1	5	2
Ag^+	163	76	320
Sr^{2+}	*c*	569	46
Ag^+	64	*c*	5
Ba^{2+}	*c*	5	5
Ag^+	71	2	92
Pb^{2+}	5	262	391

[a] Fluxes across the receiving phase–$CHCl_3$ phase boundary area are 0.286 times those given in the table. Cell dimensions are given in ref 10. Flux values have been multiplied by 10^8 to obtain the reported values. [b] Source solution 1.0 M in $AgNO_3$ for single-cation determinations and 0.5 M in each cation for the Ag^+–M^{n+} mixtures except in the cases of Ag^+–Ba^{2+} and Ag^+–Tl^+ which were 0.15 M in each cation. [c] Flux not significantly different from that of the blank, 0.7 × 10^{-8} mol/(s m^2), in which no carrier is present.

Table IV. Cation Flux (J_{M}) (mol × 10^8/(s m^2)) from the Source Phase for Ag^+–M^{n+} Mixtures with S- and N-Substituted Carriers (Data for 18C6 Included for Comparison)

	carriers			
cations[b]	18C6	DT18C6	DA18C6	DKP18C6
Ag^+	507	51	84	718
Ag^+	460	67	78	414
Na^+	7	1	1	5
Ag^+	187	60	76	276
K^+	486	0.7	*c*	37
Ag^+	138	69	53	253
Rb^+	157	*c*	*c*	7
Ag^+	299	58	69	484
Cs^+	35	*c*	*c*	2
Ag^+	62	73	57	138
Tl^+	371	*c*	*c*	51
Ag^+	437	62	69	530
Ca^{2+}	5	*c*	0.7	2
Ag^+	76	64	53	345
Sr^{2+}	569	*c*	*c*	5
Ag^+	*c*	74	51	138
Ba^{2+}	5	1	0.9	1.6
Ag^+	2	67	74	166
Pb^{2+}	262	*c*	*c*	286

[a] See footnote *a*, Table III. [b] See footnote *b*, Table III. [c] See footnote *c*, Table III.

For example, Ag^+ by itself is bound better and transported more effectively by 18C6 than by 15C5, which is too small, or 21C7, which is much too large to accommodate this cation. Generally, this basic pattern is repeated in the binary Ag^+–M^{n+} pairs. The Ag^+–Cs^+ pair illustrates the effect on J_{M} when the diameter of one cation (Cs^+) matches the cavity diameter of one of the ligands (21C7). With 15C5, the smaller Ag^+ fits best and has the higher J_{M} value. Neither Cs^+ nor Ag^+ fits the 18C6 cavity well, but Ag^+ fits better and is transported more effectively. With 21C7, Cs^+ is favored in transport, a reversal from the selectivity of this ligand for Ag^+ over the other alkali metal cations studied. This observation is consistent with the data in Table II which indicate a close correspondence between the 21C7 cavity radius and the Cs^+ radius while the Ag^+ radius is much smaller.

The effect of the competing M^{n+} on the Ag^+ flux is apparent in the data for 18C6 and 21C7 with Ag^+–alkali metal cation pairs. For example, in the case of 21C7, Ag^+ flux values are highest for the Ag^+/Na^+ pair and decrease steadily as the alkali metal cations increase in size and more closely match the 21C7 cavity, until in the Ag^+/Cs^+ pair the Ag^+ transport value is the lowest in the series and the Cs^+ value is the highest of any alkali metal cation with this ligand.

Size considerations alone do not correctly predict the transport selectivities of the Ag^+–alkaline earth cation systems. This is not surprising since the 2+ charge of the alkaline earth cations makes comparisons with Ag^+ based solely on size less reasonable than size comparisons between monovalent alkali metal cations and Ag^+. However, with two exceptions, log K (methanol) data predict accurately the transport selectivities of 15C5, 18C6, and 21C7 in the Ag^+–alkaline earth pairs; i.e., the cation with the higher log K value is preferentially transported by a given ligand. The exceptions are found in the Ag^+–Ba^{2+} pair. Although a log K (methanol) value is unavailable for the interaction of Ba^{2+} with 15C5, corresponding values for Ba^{2+} interaction with both 18C6 and 21C7 are much larger than those for Ag^+ interaction with these macrocycles, but little transport of either cation is found with these two macrocycles. These results serve as reminders that log K data valid in methanol or water are only approximations of the log K values valid in $CHCl_3$ which are needed to predict transport selectivities.

The lack of log K (methanol) data for the post-transition cations Tl^+ and Pb^{2+} makes log K correlations difficult. Some log K (water) data are available, but are less useful for predicting transport selectivities than log K (methanol) because the latter log K values should more closely approximate the values expected in $CHCl_3$. However, J_{M} values for the Ag^+–Tl^+ binary system correlate well with the relative sizes of the cations and the carrier cavities. Ag^+ matches the 15C5 cavity best and transports best with this ligand, while Tl^+ matches the cavities of 18C6 and 21C7 better than Ag^+ and is transported preferentially by both of these macrocycles. The relative cation and carrier cavity sizes are also important in determining the transport selectivities of the Ag^+–Pb^{2+} mixtures. However, in this case the divalence of Pb^{2+} appears to be crucial since Pb^{2+} transport is highly favored with 18C6 and 21C7 even though the cavity sizes of these carriers accomodate Pb^{2+} only slightly better than Ag^+.

Donor Atom Effects. Transport data using sulfur-, amine nitrogen-, and pyridine nitrogen-substituted carriers are presented in Table IV. The substitution of these donor atoms for oxygen has a marked effect on complex stability and, consequently, on the transport selectivity of these carriers for Ag^+. Our results are supported by the findings of single-cation studies,[10] where the use of either DT18C6 or DA18C6 in place of 18C6 resulted in a near-total loss of transport of alkali metal cations, while the ability to transport Ag^+ was retained. Frensdorff[20b] noted that substitution of either sulfur or nitrogen for oxygen in 18C6 led to decreased stability for alkali metal cation complexes and greatly enhanced stability for Ag^+ complexes. Other workers have confirmed his findings.[11,20a,21] In view of the affinity of Ag^+ for either nitrogen or sulfur donors and the relatively low affinity of alkali cations for these donors, the transport results are not surprising. The enhanced stability of the Ag^+ complexes, as well as the lower stability of the M^{n+} complexes, led to the selective transport of Ag^+ in the alkali and alkaline earth binary systems.

Table V. Cation Flux (J_M) (mol × 10^8/(s m^2)) from the Source Phase^a for M^{n+}-Ag^+ Mixtures with Diketopyridino Carriers of Varying Cavity Radii

	carriers		
cations^b	DKP15C5	DKP18C6	DKP21C7
Ag^+	150	718	507
Ag^+	138	414	368
Na^+	2	5	2
Ag^+	122	276	391
K^+	*c*	37	7
Ag^+	64	253	207
Rb^+	*c*	7	14
Ag^+	127	484	391
Cs^+	*c*	2	18
Ag^+	9	138	62
Tl^+	*c*	51	253
Ag^+	111	530	345
Ca^{2+}	*c*	2	*c*
Ag^+	122	345	461
Sr^{2+}	*c*	5	*c*
Ag^+	12	138	99
Ba^{2+}	5	1.6	1.5
Ag^+	78	166	437
Pb^{2+}	*c*	286	37

^{a} See footnote *a*, Table III. ^{b} See footnote *b*, Table III. ^{c} See footnote *c*, Table III.

Table VI. Cation Flux (J_M) (mol × 10^8/(s m^2)) from the Source Phase^a for Ag^+-M^{n+} Mixtures with 18C6 Carriers with Varying Substituents

	carriers					
cations^b	18C6	B18C6	DB18C6	DC18C6	DK18C6	ODKP18C6
Ag^+	507	437	81	1036	*c*	829
Ag^+	460	297	62	783	0.7	829
Na^+	7	9	7	14	3	2
Ag^+	187	145	39	622	*c*	553
K^+	486	214	150	368	7	35
Ag^+	138	136	35	599	*c*	622
Rb^+	157	23	3	115	*c*	7
Ag^+	299	136	64	760	*c*	783
Cs^+	35	32	1.4	21	1	0.9
Ag^+	62	37	2	161	*c*	299
Tl^+	371	276	23	622	*c*	55
Ag^+	437	207	55	921	*c*	645
Ca^{2+}	5	2	0.7	30	0.9	1
Ag^+	76	177	55	265	*c*	898
Sr^{2+}	569	58	*c*	967	*c*	12
Ag^+	*c*	67	2	161	*c*	414
Ba^{2+}	5	*c*	*c*	668	5	1
Ag^+	2	28	131	5	*c*	368
Pb^{2+}	262	711	242	507	*c*	691

^{a} See footnote *a*, Table III. ^{b} See footnote *b*, Table III. ^{c} See footnote *c*, Table III.

Even though the selectivities of DT18C6 and DA18C6 for Ag^+ were high, the Ag^+ fluxes were low in comparison to those obtained with unsubstituted 18C6 as carrier. This high selectivity–low transport situation is expected when one of the cation–carrier complexes is very stable.[7] DT18C6 and DA18C6 bind Ag^+ too strongly to serve as effective carriers; as a result they extract Ag^+ into the membrane but little Ag^+ is released to the receiving phase. Therefore, Ag^+ transport was less than optimal, while the transport of all other cations was virtually blocked. In single-cation studies, DA18C6 transported Ca^{2+}, Sr^{2+}, and Ba^{2+} better than Ag^+,[10] but from mixtures of Ag^+ with each of these cations, Ag^+ was favored. Again, this result agrees with stability data: log *K* values in water indicate that the Ag^+ complex is more stable than that of either Sr^{2+} or Ba^{2+}. As with DT18C6, Ag^+ was transported while the second cation was blocked and the Ag^+–DA18C6 complex was too stable for optimal release into the receiving phase, resulting instead in extraction of Ag^+ into the membrane.

In contrast to DT18C6 and DA18C6, DKP18C6, which contains one pyridine nitrogen donor, showed Ag^+ fluxes in the Ag^+–M^{n+} mixtures which were either comparable to or larger than those with 18C6. These larger J_M values suggest that the Ag^+–DKP18C6 complex is less stable than the Ag^+–DA18C6 and Ag^+–DT18C6 complexes. Thus, both DA18C6 and DT18C6 promote extraction but show little release of Ag^+ into the receiving phase, while the Ag^+–DKP18C6 complex must have a lower stability which is nearly optimal for transport. In addition, DA18C6 selectively transports Ag^+ over Pb^{2+} while DKP18C6 is selective for Pb^{2+} over Ag^+. DKP18C6, unlike DA18C6, does not form a Ag^+ complex stable enough to block Pb^{2+} transport. The observed differences between DA18C6 and DKP18C6 are consistent with the fact that the pyridine nitrogen is less basic than the amine nitrogen, so that the electrons of the pyridine nitrogen participate in coordinate bonding less readily than those of the amine nitrogen.

Relationship between Size Effects and Donor Atom Effects. The combined effects of macrocycle cavity size and donor atom type were studied by using a series of diketopyridino carriers of increasing size (see Table V). When M^{n+} was either an alkali or alkaline earth cation, the affinity of Ag^+ for the pyridine nitrogen of the carrier overrode size considerations in determining transport selectivities. However, the effects of the size relationship are still evident in several ways. The generally better transport of Ag^+ by 18C6 relative to that by either 15C5 or 21C7 (Table III) is likely due to the fact that Ag^+ fits the 18C6 cavity better than it fits the cavities of either 15C5 or 21C7. The same pattern is seen in the data for Ag^+ transport by the diketopyridino analogues of these three ligands. The flux of Ag^+, by itself and in combination with all but three of the other cations studied, was higher with the carrier DKP18C6 than with either DKP15C5 or DKP21C7. The three exceptions are the Ag^+–K^+, Ag^+–Sr^{2+}, and Ag^+–Pb^{2+} pairs.

In the Ag^+–K^+ pair, Ag^+ transport increased with increasing ligand size, while K^+ transport peaked with DKP18C6. Although Ag^+ transport is favored by this series of ligands, K^+ competes for DKP18C6 effectively enough that Ag^+ transport is slightly inhibited and does not reach its peak value until DKP21C7 is used and K^+ no longer competes significantly. In the cases of the Ag^+–Sr^{2+} and Ag^+–Pb^{2+} pairs, the three cations have nearly identical radii. In both cases Ag^+ is transported preferentially by DKP15C5 and DKP21C7 as was also the case with 15C5 and 21C7 (Table III). However, the preference of Ag^+ for N is evidenced by the fact that in the case of 18C6 Sr^{2+} transport is favored over Ag^+ transport while with DKP18C6 Ag^+ transport is favored. Pb^{2+} also has affinity for N donors and the transport selectivity of 18C6 for Pb^{2+} over Ag^+ is retained by DKP18C6. The affinity of Ag^+ for N is seen in the higher Ag^+ flux in the presence of Pb^{2+} with DKP18C6 than with 18C6.

The Ag^+–Tl^+ pair provides an interesting example of the direct correlation of transport selectivities with size. Both cations have affinity for the nitrogen donor atom so its presence does not in itself favor the transport of either. Transport of Ag^+ is greatest with DKP18C6, while Tl^+ transport is greatest with the ligand which fits it best, DKP21C7.

Substituent Effects. The effects of various substituents on cation fluxes, shown in Table VI, were studied by using substituent-bearing analogues of 18C6. Addition of substituents to the carrier can have at least three effects. First, increased hydrophobic bulk decreases the carrier's solubility in water while enhancing its affinity for the organic membrane. For example, ~5 M solutions of 18C6 in water can be prepared, while the water solubility of DB18C6 is 9×10^{-5} M.[1b] Low water solubility is especially desirable in industrial applications where it is desired to minimize loss of carrier to the aqueous phases. In addition, increased hydrophobic bulk should lead to increased transport by restricting the ligand to the membrane where it can function as a carrier. This has been observed in single-cation transport studies.[10] Second, the substituents may have steric effects, either blocking the approach of the metal to the donor atoms or limiting the conformational flexibility of the carrier. In either case, steric effects should lead to decreased transport. Third, there may be electronic effects as the substituents withdraw or donate electrons to the donor atoms. Electronic effects could either enhance or detract from the effectiveness of the ligand as a carrier. All three types of effects were observed.

In the series 18C6, B18C6, and DB18C6, the J_M values generally decreased for both cations with increased benzo substitution except when Ag^+ was paired with Sr^{2+}, Ba^{2+}, or Pb^{2+}. Previous single-cation transport studies also generally showed decreased fluxes for benzo- and dibenzo-substituted 18C6 carriers compared to 18C6 itself.[10] With these benzo-substituted ligands, steric and electronic effects tending to decrease transport override the expected tendency toward higher transport due to decreased water solubility. For example, chloroform solutions of DB18C6 equilibrated with water showed no detectable loss of macrocycle to the aqueous phase,[32] yet in most cases studied DB18C6 was a less effective carrier than 18C6 which has a chloroform/water partition coefficient of 6.3. Except with the Ag^+–Sr^{2+} and Ag^+–Ba^{2+} pairs, the transport selectivity of 18C6 was preserved with B18C6 and DB18C6. Both Sr^{2+} and Ba^{2+} were favored in transport over Ag^+ when 18C6 was the carrier. With B18C6, transport of Sr^{2+} and Ba^{2+} was sharply diminished while the Ag^+ flux continued to be appreciable. Log K (water) values indicate that the drop in Sr^{2+} and Ba^{2+} transport is due to a drop in complex stability when the benzo substituents are added to the carrier (see Table I). The Ag^+–Pb^{2+} binary mixture was of interest in that both cations transported better with B18C6 than with 18C6. Ag^+ transport increased further with DB18C6, but Pb^{2+} transport decreased. Unitary Pb^{2+} transport shows the same pattern: enhancement with the benzo ligand and a decrease with the dibenzo ligand.[10] The reasons for this anomalous behavior are unclear. The ability of Pb^{2+} to block the transport of a second cation has been noted[11,12,15,16] and was also apparent in our data, but the new results show that the ability to block Ag^+ decreased as benzo substituents were added to the carrier.

Both solubility and steric effects are apparent when transport data with 18C6 are compared with those with DC18C6. In general, transport using DC18C6 was greater than that using unsubstituted 18C6. It has been suggested[10] that this is a result of the lower water solubility of DC18C6 (chloroform/water partition coefficients: 18C6, 6.3; DC18C6, 454).[33] Thus, less DC18C6 is extracted into the aqueous layers and more remains available in the $CHCl_3$ layer for cation transport. Models of carrier-facilitated transport have assumed that complexation takes place within the membrane[7] and enhanced transport with hydrophobic carriers such as DC18C6 supports this hypothesis. In general, the transport selectivity of 18C6 was preserved by DC18C6, but the one exception (Ag^+–K^+) provides an interesting example of steric effects. Subsitution of two cyclohexano groups on 18C6 to form DC18C6 results in a more rigid ligand which forms a complex in water with K^+ of either the same or lower stability (compared to 18C6), depending upon which DC18C6 isomer is considered (Table I). On the other hand, the stability of the Ag^+–DC18C6 complex (either isomer) in water is larger than that of the Ag^+–18C6 complex. These effects must be large enough in $CHCl_3$ to explain the observed reversal in K^+–Ag^+ transport by 18C6 and DC18C6.

The ligand ODKP18C6 always gave equal or higher Ag^+ transport rates in the binary systems than were obtained with DKP18C6 (Table V). The greater organic bulk of ODKP18C6 makes it less soluble in water so it remains in the membrane as a functioning carrier to a greater extent than does DKP18C6. Also, since the 4-alkoxy substituent can increase the electron density on the pyridine nitrogen by donating electrons into the aromatic ring,[34] electronic effects may be significant. The electronic effects should be largest for Ag^+ and Pb^{2+}, which have affinity for nitrogen donor atoms. This was observed in that Ag^+ transport was enhanced by ODKP18C6 over that by DKP18C6 in all of the systems studied and the Ag^+–Pb^{2+} binary system was the only Ag^+–M^{n+} system where M^{n+} transport was significantly enhanced by this substitutent.

Conclusions

Macrocyclic ligand sizes, donor atom types, and substituents all have important, interrelated effects on fluxes for Ag^+–M^{n+} binary cation systems. Complex stability constants in water and in methanol also provide insight into cation fluxes and selectivities. The following generalizations can be made concerning the Ag^+–M^{n+} systems: (1) A good fit of a cation in the carrier cavity leads to effective transport from binary cation pairs with carriers the size of 21C7 and smaller. However, size considerations alone do not allow the prediction of all of the observed selectivities. (2) Sulfur, amine nitrogen, and pyridine nitrogen donor atoms enhance transport selectivity for Ag^+. (3) Substituents can influence cation flux through solubility, steric, and electronic effects. Appropriate substituents decrease the water solubility of the carrier without impairing its selectivity for Ag^+.

In view of these findings, use of macrocyclic carriers to separate Ag^+ from other cations appears promising. Such uses include recovery of Ag^+ from waste solutions and refining of silver ores in hydrometallurgical operations. In addition, certain of these ligands have promise for use in Ag^+ detection devices, as phase transfer catalysts for silver(I) salts, and as reagents to investigate the coordination chemistry of higher oxidation states of silver.

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Registry No. Ag, 7440-22-4; Pb, 7439-92-1; Tl, 7440-28-0; Na, 7440-23-5; K, 7440-09-7; Rb, 7440-17-7; Cs, 7440-46-2; Ca, 7440-70-2; Sr, 7440-24-6; Ba, 7440-39-3; 15C5, 33100-27-5; 18C6, 17455-13-9; 21C7, 33089-36-0; B18C6, 14098-24-9; DB18C6, 14187-32-7; DC18C6, 16069-36-6; DK18C6, 62796-84-3; DT18C6, 296-39-9; DKP15C5, 68436-49-7; DKP18C6, 64379-58-4; DKP21C7, 68436-52-2; DA18C6, 23978-55-4; ODKP18C6, 84731-50-0.

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