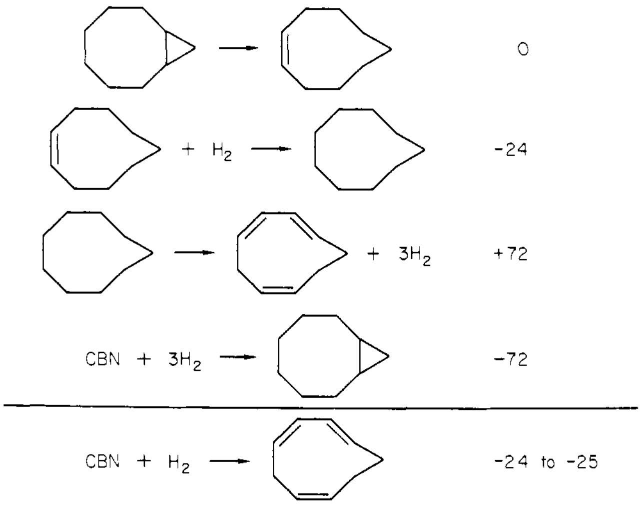
Scheme III[a]



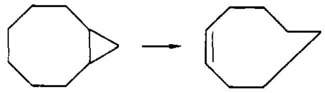
[a] $\Delta H°$ values are in kcal/mol.

CBN are plotted in Figure 4.

Acknowledgment. We with to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. We also thank the National Science Foundation (Grant CDP-8000535) for the purchase of the computer and data acquisition system. We are grateful to the Fulbright Foundation for their support of Dr. Concepcion, who is on leave from Universidad Catolica Madre y Maestra in the Dominican Republic.

Appendix

The heats of combustion of bicyclo[6.1.0]nonane and cyclononene are identical.[21-23] Thus, the tautomerization shown below has an enthalpy that is within 0.3 kcal/mol of being zero.



$\Delta H = 0 \pm 0.3$ (8)

The heat of hydrogenation of all nonplanar seven to nine member ring systems is between −24 and −25 kcal/mol per double bond.[22-24] This includes cyclononatetraene, cyclononene, cyclooctatetraene, and cycloheptatriene. Thus, the complete hydrogenation of CBN to bicyclo[6.1.0]nonane has an enthalpy of −72 to −75 kcal/mol. From Scheme III it is clear that the heat of hydrogenation of CBN to yield cyclononane is −25 kcal/mol.

Registry No. Anthracene, 120-12-7; *cis*-bicyclo[6.1.0]nona-2,4,6-triene, 26132-66-1; potassium, 7440-09-7; homo[8]annulene anion radical, 34526-28-8; homo[8]annulene dianion·2K, 36523-65-6; homo[8]-annulene, 7129-70-6.

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[21] Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: London, 1970.

[22] Nachod, F. C.; Zuckerman, J. J. "Determination of Organic Structures by Physical Methods"; Academic Press: New York, 1971, Vol. 3, pp 214–218.

[23] The heat of hydrogenation of cyclononene to yield cyclononane is −24 kcal/mol. See ref 22.

[24] Schock, L. E.; Stevenson, G. R., unpublished results.

Selective M^+–H^+ Coupled Transport of Cations through a Liquid Membrane by Macrocyclic Calixarene Ligands

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Contribution from the Departments of Chemistry and Chemical Engineering and Contribution No. 252 from the Thermochemical Institute, Brigham Young University, Provo, Utah 84602.
Received July 27, 1981

Abstract: Macrocyclic *p-tert*-butylcalix[4]arene, -calix[6]arene, and -calix[8]arene have been studied as cation carriers in H_2O–(organic solvent)–H_2O liquid membranes. When the source water phase is a solution of the metal nitrate salt, no cation transport through the membrane ($CHCl_3$) is observed with these ligands in contrast to measurable transport when the macrocyclic carrier, 18-crown-6, is present. However, if the source phase is a solution of the metal hydroxide, transport of cations is observed with calixarenes but not with 18-crown-6 in the membrane (25% v/v CH_2Cl_2–CCl_4). Transport by the calixarenes is selective for Cs^+ over other alkali metal cations with the selectivity increasing in the order [8] < [6] < [4]. Preliminary work with *p-tert*-pentylcalix[4]arene and -calix[8]arene shows transport behavior to be similar to that of the corresponding *p-tert*-butylcalixarenes. These calixarene ligands offer several features desirable to membrane carriers: (1) low water solubility, (2) formation of neutral complexes with cations through loss of a proton, and (3) the potential for coupling cation transport to the reverse flux of protons.

Introduction

Macrocyclic phenol–formaldehyde condensation products, which have been designated as calixarenes,[1] are similar in structure to certain cyclic polyethers and other macrocyclic ligands which are noted for their size-related selectivity in binding cations[2]. The calixarenes, first reported by Zinke and Ziegler,[3] have received careful synthetic study by Gutsche and his co-workers, who have published methods for the "one-flask" synthesis of *p-tert*-butyl-

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[1] (a) Gutsche, C. D. Muthukrishnan, R. *J. Org. Chem.* **1978**, *43*, 4905–4906. (b) Gutsche, C. D.; Levine, J. A. *J. Am. Chem. Soc.* **1982** *104*, 2652–2653. (c) Ninagawa, A.; Matsuda, H. *Makromol. Chem. Rapid Commun.* **1982**, *3*, 65–67.

[2] (a) Lamb, J. D.; Izatt, R. M.; Christensen, J. J.; Eatough, D. J. In "Coordination Chemistry of Macrocyclic Compounds"; Melson, G. A., Ed.; Plenum Press: New York, 1979; pp 145–217. (b) Lamb, J. D.; Izatt, R. M.; Swain, C. S.; Christensen, J. J. *J. Am. Chem. Soc.* **1980**, *102*, 475–479.

[3] Zinke, A.; Ziegler, E. *Chem. Ber.* **1944**, *77*, 264–272.

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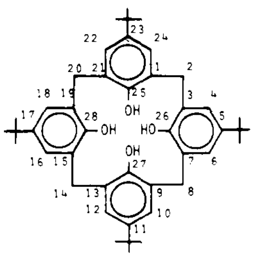
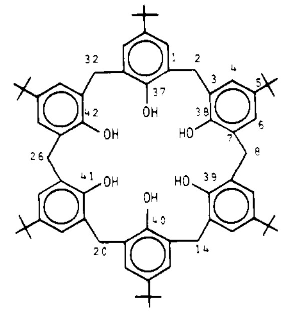
calix[4]arene (**1**), -calix[6]arene (**2**), and -calix[8]arene (**3**) in good yields,[1,4] and by Kämmerer and Happel, who have published methods for the multistep synthesis of several calixarenes, including a calix[5]arene and calix[7]arene.[5] Since the calixarenes are Bronsted–Lowry acids, they offer the potential of serving as anionic macrocyclic ligands in binding to cations of the alkali, alkaline earth, and other types.



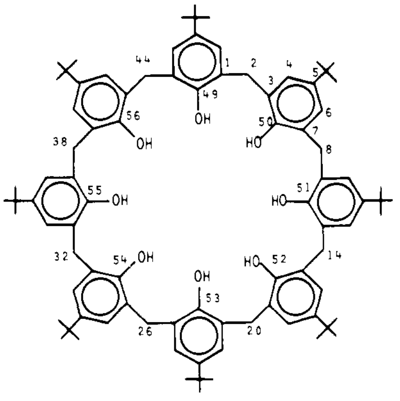
p-tert-butylcalix[4]arene

(1)



p-tert-butylcalix[6]arene

(2)



p-tert-butylcalix[8]arene

(3)

Gutsche and his co-workers[4] noted that RbOH is the most effective base in the preparation of *p-tert*-butylcalix[6]arene, and they attributed this result to a template effect due to interaction between the ligand and Rb^+. However, to the best of our knowledge,the present investigation is the first detailed study of cation complexation by these compounds. Specifically, the calixarenes are found in the present study to be effective membrane carriers of cations because: (i) they demonstrate a high degree of transport selectivity for Cs^+ over other alkali and alkaline earth cations, (ii) they exhibit very low solubility in water, preventing loss from the membrane to the adjacent water phases, (iii) they can form neutral cation complexes through loss of a proton so that the anion need not accompany the cation through the membrane, and (iv) because of feature (iii), it may be possible to couple the transport of cations to the reverse flux of protons through the membrane. This latter feature may conceivably be exploited in coupling the transport of cations through hydrophobic liquid membranes to the reverse flux of protons, a procedure successfully used by Cussler and his co-workers[6] to drive the flux of Na^+ against the concentration gradient of Na^+ using the macrocyclic ligand monensin.

Table I. Transport of Cation Nitrate Salts through Chloroform Liquid Membranes Containing Either **3** or 18-Crown-6

source phase[a]	flux (mol × 10^8/s m^2)[b] **3**	flux (mol × 10^8/s m^2)[b] 18-crown-6[c]
$NaNO_3$	*d*	25
KNO_3	*d*	645
$RbNO_3$	*d*	484
$CsNO_3$	*d*	161
$Ca(NO_3)_2$	*d*	60
$Sr(NO_3)_2$	*d*	728
$Ba(NO_3)_2$	1.8	41

[a] 1.0 M aqueous solutions except $Ba(NO_3)_2$ which was 0.3 M. [b] Membrane = 0.001 M carrier in chloroform. Flux values have been multiplied by 10^8 to obtain reported values. [c] Reference 11. [d] Less than 0.7 mol × 10^{-8}/s m^2.

The ability of nonmacrocyclic polyphenols to complex metal ions has been observed by others. Bukin and his co-workers[7] found the order of extraction into kerosine of alkali metal ions by polymerized alkyl-substituted phenol to be $Cs^+ > K^+ > Rb^+ > Na^+ > Li^+$ and it has been reported[8] that brown algae exude polyphenols which may be responsible for their ability to concentrate bivalent metal ions.

Experimental Section

The metal solutions were prepared using distilled, deionized water from the highest grade materials available from the indicated suppliers. Metal hydroxides were Li^+ (Matheson, Coleman, and Bell), Na^+ and Ca^{2+} (Fisher), K^+ (Spectrum), Rb^+ (Aldrich), Cs^+ (Alfa), Sr^{2+} (City Chemical), Ba^{2+} (Mallinckrodt). Metal nitrates were Na^+ and Sr^{2+} (Mallinckrodt), K^+ and Ca^{2+} (Baker), Rb^+ and Cs^+ (Alfa), Ba^{2+} (J. T. Baker). The following reagents were obtained from the indicated sources and used as supplied: $CHCl_3$, CH_2Cl_2, and CCl_4 (Fisher reagent); 18C6 (Parish); phenol (Mallinckrodt); *p-tert*-butylphenol (Matheson, Coleman and Bell).

The macrocyclic *p-tert*-butylcalixarenes **1**, **2**, and **3** were synthesized by minor modifications of the procedure of Gutsche and his co-workers.[4,9] For preparation of the cyclic octamer, **3**, we found it advantageous to use tetralin as solvent, rather than *p*-xylene, and slightly longer reaction times. Our yields of **3** exceeded 60% without attempts to optimize reaction conditions; this compound was readily isolated from reaction mixtures and recrystallized. Infrared spectral data (indentical peak-for-peak with a spectrum for authentic octamer obtained from Professor Gutsche), melting behavior, and molecular weight measurements by both osmometric and mass spectral techniques all verified that we had the cyclic octamer at hand. The only discernible impurity proved to be the solvent used for recrystallization, $CHCl_3$ (<1%). Similarly, cyclic tetramer, **1**, and hexamer, **2**, were prepared in somewhat lesser yields and recrystallized to satisfactory purity. Again, consonant melting behavior and infrared spectra (identical peak-for-peak with spectra from authentic tetramer and hexamer) were observed, establishing the identity of the samples. *p-tert*-Pentylcalixarenes corresponding to **1** and **3** have also been prepared.

Membrane transport experiments were carried out using bulk liquid membranes described previously.[10] The membrane (3 mL of a 1.0 mM solution of the macrocycle in a hydrophobic organic solvent) was stirred by magnetic stirrer at 120 rpm at the bottom of a 3-dram vial (i.d. = 18 mm). Atop the organic layer was placed 0.8 mL of the aqueous cation solution (source phase) and 5.0 mL of distilled, deionized water (receiving phase), the two water phases being separated by a glass tube (i.d. = 8 mm). The cation nitrate and cation hydroxide concentrations in the source phase were 1.0 M, except in the cases of $Ba(NO_3)_2$ which was 0.3 M and $Ca(OH)_2$, $Sr(OH)_2$, and $Ba(OH)_2$ which were used as saturated solutions (0.02, 0.03, and 0.2 M, respectively). After 24 h, the receiving

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(4) Gutsche, C. D.; Dhawan, B.; No, K. H.; Muthukrishnan, R. *J. Am. Chem. Soc.* **1981**, *103*, 3782–3792.

(5) Kammerer, H.; Happel, G. *Makromol. Chem.* **1980**, *181*, 2049–2062.

(6) Choy, E. M.; Evans, D. F.; Cussler, E. L. *J. Am. Chem. Soc.* **1974**, *96*, 7085–7090.

(7) Bukin, V. I.; Plyushchev, V. E.; Reznik, A. M. *Russ. J. Inorg. Chem.* **1973**, *18*, 1011–1013.

(8) Ragan, M. A.; Smidsrod, O.; Larsen, B. *Marine Chem.* **1979**, *7*, 265–271.

(9) Gutsche, C. D.; Muthukrishnan, R.; No, H. K. *Tetrahedron Lett.* **1979**, 2213–2216.

(10) Lamb, J. D.; Christensen, J. J.; Oscarson, J. L.; Nielsen, B. L.; Asay, B. W.; Izatt, R. M. *J. Am. Chem. Soc.* **1980**, *102*, 6820–6824.

Table II. Cation Transport from Basic Solution by Calixarenes (**1**, **2**, and **3**), 18-Crown-6, Phenol, and *p-tert*-Butylphenol

	flux, mol × 10^8/s m^2					
source phase[a]	**1**[b]	**2**[b]	**3**[b]	18-crown-6[b]	phenol[c]	*p-tert*-butylphenol[c]
LiOH	*d*	10 ± 1	2.0 ± 0.2	*d*	*d*	*d*
NaOH	1.5 ± 0.4	13 ± 2	9 ± 2	*d*	*d*	*d*
KOH	*d*	22 ± 3	10 ± 4	*d*	*d*	*d*
RbOH	5.6 ± 0.7	71 ± 8	340 ± 20	*d*	*d*	*d*
CsOH	260 ± 90	810 ± 80	996 ± 280	*d*	*d*	*d*
$Ca(OH)_2$	*d*	*d*	*d*		*d*	*d*
$Sr(OH)_2$	*d*	*d*	*d*		*d*	*d*
$Ba(OH)_2$	1.6 ± 0.7	3.2 ± 1.6	*d*		*d*	

[a] 1.0 M aqueous solutions except $Ca(OH)_2$, $Sr(OH)_2$, and $Ba(OH)_2$, which were 0.02, 0.03, and 0.2 M, respectively. [b] Membrane = 0.001 M carrier in 25% v/v CH_2Cl_2 in CCl_4 solution. Flux values have been multiplied by 10^8 to obtain reported values. [c] Membrane = 0.001 M carrier in CCl_4 solution. [d] Less than 0.9 mol × 10^{-8}/s m^2.

phase was sampled and analyzed for cation concentration using a Perkin-Elmer Model 603 atomic absorption spectrophotometer. Each experiment was repeated at least three times, and the results are reported as the average of the three determinations, with the standard deviation among the values in each experiment less than ±15%. Experiments performed in which no carrier was present in the membrane showed cation fluxes to be less than 0.7 × 10^{-8} mol/(s m^2).

Results and Discussion

Fluxes of cation nitrate salts through a chloroform membrane of the type described above are given in Table I for the neutral macrocyclic carrier 18-crown-6[11] and **3** under conditions of neutral pH in the source phase. The ligand 18-crown-6, which binds cations essentially independent of pH, showed appreciable cation fluxes under these neutral source phase conditons and was selective in transporting K^+ over the other alkali metal cations studied. This transport selectivity for K^+ has been related through a diffusion transport model[10] to the value of the equilibrium constant for the formation of the 1:1 complex. The value of the equilibrium constant is highest for K^+ among alkali metal ions because of the correct fit of K^+ in the cavity at the center of the cyclic ligand. In contrast to 18-crown-6, **3** provided little or no measurable transport through the membrane of any of the cations under neutral pH conditions, except for a very small flux of Na^+.

Membrane experiments similar to those using nitrate salts were performed with the carriers 18-crown-6 and **1**–**3** using cation hydroxides in the source phase and the results are reported in Table II together with transport data measured under the same conditions for two noncyclic analogues of the calixarenes (phenol and *p-tert*-butylphenol). The data in Table II were obtained using 25% v/v CH_2Cl_2–CCl_4 mixtures as the membrane solvent because the hydroxide solutions (source phase) reacted with chloroform. The methylene chloride was added to the carbon tetrachloride to solubilize the carrier ligands to 1.0 mM.

The data in Table II demonstrate that when the source phase is basic the calixarene ligands are effective carriers for the heavier monovalent alkali metal cations, while 18-crown-6 is a poor carrier for these cations. With respect to the carriers, this behavior is opposite to that observed when the source phase is neutral (Table I). Transport results with 18-crown-6 obtained under neutral (Table I) and basic (Table II) source phase conditions have been understood according to the following reasoning.[10,12] When neutral macrocyclic ligands such as 18-crown-6 bind to cations, positively charged complex species result. When such ligands serve as cation carriers in hydrophobic liquid membranes, anions must accompany the cation complexes through the membrane to maintain electrical neutrality. Consequently, the anion has a large effect on cation fluxes when neutral carriers are used, due to the hydration energy of the anion.[12] Specifically, NO_3^- anions allow cation fluxes several orders of magnitude higher than OH^- anions. Hence, 18-crown-6 demonstrates measurable transport from NO_3^- solutions, but not from OH^- solutions. One additional factor is responsible for the differences in results between experiments using NO_3^- solutions and OH^- solutions. In a separate study it has been shown that cation fluxes by neutral macrocycles using NO_3^- as the anion are approximately an order of magnitude smaller in carbon tetrachloride than in chloroform.[13] These observations make the Cs^+ transport results, particularly with calixarenes **2** and **3**, even more impressive.

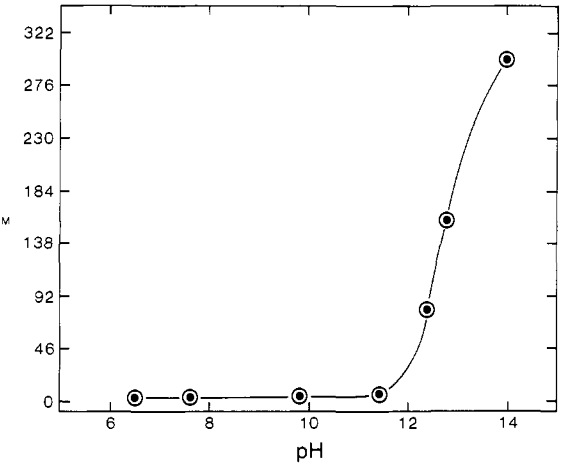

Figure 1. Plot of Cs^+ flux (J_M, mol × 10^8/s m^2) as a function of source phase pH. Membrane: 0.001 M *p-tert*-butylcalix[8]arene in 16% v/v CH_2Cl_2/CCl_4 solution. [Cs^+] = 1 M. Anion = NO_3^-/OH^-. T = 25 °C.

The lack of cation transport with **3** under neutral source phase conditions (Table I) and the contrasting excellent transport and selectivity observed for it and the other calixarenes when a basic source phase was used may be explained in that **1**, **2**, and **3** are acidic. The deprotonated calixarene anion can form neutral cation complexes, which may pass through the membrane without any accompanying anion. While the neutral phenol ligand may show a relative lack of affinity for alkali metal cations (ion–dipole interactions) the phenolate anion demonstrates a measurable affinity for these cations (ion–ion interactions). In this way, simple, unsubstituted (monomeric) phenol and its *p*-substituted homologues have been used in the solvent extraction of alkali metal ions, a process which involves exchanging a proton for the cation.[14,15] However, when either monomeric phenol or *p-tert*-butylphenol was used as membrane carrier rather than a calixarene, no cation transport was observed (Table II). These results imply that the much higher cation affinity seen for the calixarenes is a result of the cooperative effect of the oxygen donor atoms in binding the large alkali metal ions. These findings are reminiscent of those involving cyclic polyethers in which the macrocycles are

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(11) Lamb, J. D.; Izatt, R. M.; Garrick, D. G.; Bradshaw, J. S.; Christensen, J. J. *J. Membr. Sci.* **1981**, *9*, 83–107.

(12) Lamb, J. D.; Christensen, J. J.; Izatt, S. R.; Bedke, K.; Astin, M. S.; Izatt, R. M. *J. Am. Chem. Soc.* **1980**, *102*, 3399–3403.

(13) Izatt, R. M.; Brown, P. R.; Christensen, J. J.; Lamb, J. D., unpublished results.

(14) Egan, B. Z.; Zingaro, R. A.; Benjamin, B. M. *Inorg. Chem.* **1965**, *4*, 1055–1061.

(15) Sekine, T.; Hasegawa, Y. "Solvent Extraction Chemistry"; Marcel Dekker: New York, 1977.

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.

Acknowledgment. The liquid membrane experiments were funded by the U. S. Department of Energy, Contract No. DE-AS02-78ER05016. We express our appreciation to Professor C. D. Gutsche for disclosing detailed synthesis procedures for cyclic oligomers derived from *p-tert*-butylphenol, and also for copies of infrared spectra for pure samples.

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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[16] Haymore, B. L.; Lamb, J. D.; Izatt, R. M.; Christensen, J. J. *Inorg. Chem.* **1982**, *21*, 1598–1602.

[17] Shannon, R. D.; Prewitt, C. T. *Acta* Crystallog. **1969**, *B25*, 925–946.

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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Contribution from the Departments of Chemistry and Chemical Engineering and Contribution No. 283 from the Thermochemical Institute, Brigham Young University, Provo, Utah 84602.

Received August 19, 1982

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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[1] (a) Pedersen, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 2495–2496. (b) Pedersen, C. J. *Ibid.* **1967**, *89*, 7017–7036.

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