

is currently being investigated under more conventional catalytic conditions.

### Conclusions

Gas-phase methyl radicals may be produced in a catalytic manner from CH<sub>4</sub> over pure and lithium-doped MgO. The results suggest that surface O<sup>-</sup> ions are responsible for hydrogen atom abstraction, and in the lithium-doped samples the O<sup>-</sup> is present as a [Li<sup>+</sup>O<sup>-</sup>] center. This center is formed from the interaction of substitutional Li<sup>+</sup> ions with molecular oxygen at high tem-

peratures. Ethane probably occurs via the coupling of the gas-phase methyl radicals, but the conversion of methane is quite small.

**Acknowledgment.** We thank David L. Myers and Han-Fan Liu for their experimental assistance. We also acknowledge the conceptual contributions of Dr. John Kolts. The work was supported by the Division of Basic Energy Science, Department of Energy.

**Registry No.** MgO, 1309-48-4; methane, 74-82-8; methyl radical, 2229-07-4; lithium, 7439-93-2; hydrogen, 1333-74-0.

## Cation Transport from Multiple Alkali Cation Mixtures Using a Liquid Membrane System Containing a Series of Calixarene Carriers

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**Abstract:** Several new *p*-tert-pentylcalixarenes have been synthesized. These and other calixarenes have been used to study carrier-mediated alkali-metal cation fluxes at 25 °C in H<sub>2</sub>O-(organic solvent)-H<sub>2</sub>O liquid membranes. In addition to single cation systems, all possible equimolar, two-, three-, and four-cation mixtures of NaOH, KOH, RbOH, and CsOH were used in the study. In each case, alkali cation transport was coupled with the reverse flux of protons. Selective transport of Cs<sup>+</sup> over Rb<sup>+</sup>, K<sup>+</sup>, and Na<sup>+</sup> was seen in all mixtures studied. The greatest selectivity for Cs<sup>+</sup> was found for calix[4]arenes, but the largest flux of Cs<sup>+</sup> as well as the other alkali cations was seen with the calix[6]arenes and calix[8]arenes. The greater flux in these latter cases may be a result of each calixarene binding two cations. In experiments at low [Cs<sup>+</sup>]-to-[Rb<sup>+</sup>] ratios, *p*-tert-butylcalix[6]arene transports Rb<sup>+</sup> over Cs<sup>+</sup>. As these ratios increase, transport of Cs<sup>+</sup> becomes favored over that of Rb<sup>+</sup>, indicating that the cation flux depends, in part, on the relative concentrations of the cations in the source phase.

Calixarenes<sup>1</sup> are macrocyclic phenol-formaldehyde condensation products similar in structure to certain cyclic polyethers which are noted for their size-related selectivity in binding cations.<sup>2</sup> Calixarenes have been suggested as potential enzyme mimics because they possess a toruslike architecture similar to that of cyclodextrins.<sup>3</sup> The appealing features of cyclodextrins (which are naturally occurring macrocyclic glucose polymers containing a minimum of 6-D(+)-glucopyranose units, attached by α-(1,4) linkages) are their abilities to form host-guest complexes by trapping organic compounds, small ions, and gases in their toruslike cavities and to mimic enzyme functions.<sup>4</sup>

The calixarenes were first reported by Zinke and Ziegler in 1944.<sup>5</sup> More recently, Gutsche and his co-workers have demonstrated the condensation of *p*-tert-butylphenol and formaldehyde to yield *p*-tert-butylcalix[4]arene, -calix[6]arene, and -calix[8]arene<sup>1,3,6</sup> (Figure 1). Kämmerer and Happel have published methods for the multistep synthesis of several calixarenes, including a calix[5]arene and a calix[7]arene.<sup>7</sup>

Several unique features of calixarenes have been noted. First, their synthesis, in at least one case, is promoted by a template effect, e.g., the interaction between *p*-tert-butylcalix[6]arene and Rb<sup>+</sup>.<sup>6</sup> Second, they form molecular complexes with small molecules in the solid state.<sup>8</sup> Third, they are weak Brønsted-Lowry acids and act as anionic carriers in liquid membrane transport of alkali cations.<sup>9</sup> In a recent investigation,<sup>9</sup> we found that *p*-tert-butylcalix[4]arene, -calix[6]arene, and -calix[8]arene are effective in transporting individual alkali-metal cations from the aqueous solutions across haloform liquid membranes. Specifically,

these calixarenes transported Cs<sup>+</sup> at a much higher rate than they did other alkali cations when the source phase was a solution of the metal hydroxide. Selectivity for Cs<sup>+</sup> increased in the order [8] < [6] < [4] although the Cs<sup>+</sup> flux increased in the reverse order.

In the present study, the synthesis of several new calixarenes is reported. In addition, calixarene-mediated cation fluxes have been determined for Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, and Cs<sup>+</sup> (anion: OH<sup>-</sup>) both in single-cation systems and in all possible two-, three-, and four-cation mixtures of these cations using a H<sub>2</sub>O-CCl<sub>4</sub>-CH<sub>2</sub>-Cl<sub>2</sub>-H<sub>2</sub>O liquid membrane system. The purpose of the transport investigation was to learn whether the selectivity for Cs<sup>+</sup> observed earlier<sup>9</sup> is maintained in the mixtures and to determine the effect

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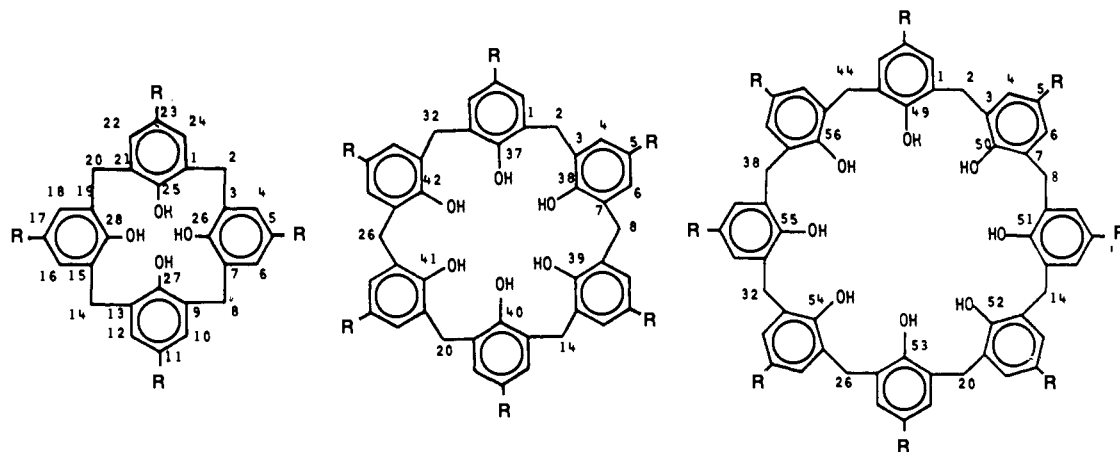


Figure 1. *p*-Alkylcalix[*n*]arene macrocycles: (*n* = 4, 6, or 8) (a) R = *tert*-butyl; (b) R = *tert*-pentyl.

on cation flux of modifying the calixarene structure. The structures of the calixarenes used in the study are presented in Figure 1.

### Experimental Section

**Materials.** Reagents for the liquid membrane experiments were obtained as follows. Metal hydroxide solutions were prepared from the highest grade materials available using distilled, deionized water. KOH (Spectrum) and NaOH (Fisher) were used as supplied. CsOH and RbOH (Cerac) were passed through a glass fiber microfilter (VWR Grade 13) before use. Reagent grade  $\text{CH}_2\text{Cl}_2$  and Spectrograde  $\text{CCl}_4$  (Fisher) were used as supplied.

The following chemicals were used in the synthetic portion of the study: *p*-*tert*-pentylphenol, melting range 92.5–93.5 (Pfaltz and Bauer); paraformaldehyde (Eastman Kodak white label); KOH (Mallinckrodt reagent grade); RbOH (Aldrich); tetralin (Matheson, Coleman and Bell practical grade); *p*-xylene (Eastman scintillation grade);  $\text{CHCl}_3$  (reagent grade); heptane (reagent grade); and  $\text{CH}_3\text{OH}$  (reagent grade).

The *p*-*tert*-butylcalix[4]arene, -calix[6]arene, and -calix[8]arene macrocycles were synthesized by minor modifications of the procedures of Gutsche and his co-workers,<sup>6,10</sup> as have been described,<sup>9</sup> wherein different experimental procedures favor formation of octamer, hexamer, or tetramer. *p*-*tert*-Pentylcalix[4]arene, -calix[6]arene, and -calix[8]arene were prepared similarly to the *p*-*tert*-butyl homologues. *p*-*tert*-Pentylcalix[4]arene was separated as a coproduct from reaction mixtures which provided the corresponding *p*-*tert*-calix[8]arene; solubility characteristics of the octamer and tetramer differed sufficiently to allow separation. However, *p*-*tert*-pentylcalix[6]arene was obtained from mixtures made under reaction conditions known to favor formation of the hexamer.<sup>6</sup>

The melting behavior of calixarenes is sometimes not reproducible.<sup>11</sup> Some of the calixarenes used in this study were poorly characterized by their melting points; however, spectral and thin-layer chromatography (TLC) data showed when homogeneous samples were at hand. Melting points were determined in evacuated, sealed capillaries with several kinds of calibrated apparatus (Thomas-Hoover "Unimelt", Laboratory Devices "MelTemp", and Gallenkamp block). Melting points are uncorrected. Infrared spectra were taken on Beckman Acculab-2 and Perkin-Elmer PE-457 spectrophotometers. TLC separations were performed on E. Merck plastic-supported silica gel strips. Molecular weights were determined osmotically in chloroform solutions with a Hitachi Perkin-Elmer 115 instrument. Combustion analyses were performed by M-H-W Laboratories, Phoenix, AZ.

***p*-*tert*-Pentylcalix[4]arene.** The tetramer was isolated from the octamer crude reaction mixtures. The filtrate from the crude *p*-*tert*-pentylcalix[8]arene was concentrated to about a 60% volume, whereupon shiny white plates could be removed by filtration. Further crops could be obtained, but such were of lesser purity. The tetramer of good purity was obtained in 6–7% crude yields. Recrystallization from  $\text{CHCl}_3$ , followed by vacuum drying, afforded shiny white plates, an analytical sample with no discernible impurities. IR (KBr) 3190 br, 428, 398  $\text{cm}^{-1}$  inter alia, with nothing corresponding to these last two bands in infrared spectra of the octamer or hexamer. TLC (2:1  $\text{CHCl}_3$ /heptane) single spot  $R_f$  0.66. The analytical sample showed mp 301–303 °C.<sup>12</sup>

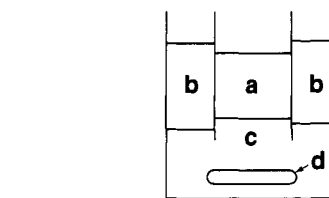


Figure 2. Liquid membrane cell: (a) source phase; (b) receiving phase; (c) membrane phase; and (d) magnetic stirring bar.

Anal. Calcd for  $\text{C}_{48}\text{H}_{64}\text{O}_4$ : C, 81.77; H, 9.15;  $M_w$  705. Found: C, 81.55; H, 9.01;  $M_w$  715.

***p*-*tert*-Pentylcalix[6]arene.** A slurry of 10.01 g (60.9 mmol) of *p*-*tert*-pentylphenol, 4.01 g (133 mmol) of paraformaldehyde, 3.08 g of 99% RbOH (29.7 mmol), and 5.5 mL of water in 100 mL of *p*-xylene was heated and stirred under nitrogen according to the procedure of Gutsche for the hexamer.<sup>6</sup> The *p*-*tert*-pentyl hexamer of good purity was recovered by filtration of the cooled reaction mixture in 30% crude yield. As with the octamer, further crops were available; however, they proved to be mixtures of the hexamer and other oligomers. Recrystallization from chloroform–methanol, followed by warming under high vacuum to remove residual solvents, afforded white microcrystals, an analytical sample with no discernible impurities. IR (KBr) 3170 br, 875, 799, 781, nothing around 400  $\text{cm}^{-1}$  inter alia. TLC (2:1  $\text{CHCl}_3$ /heptane) single spot  $R_f$  0.72. The analytical sample showed poorly defined melting behavior, melting around 320–328 °C with decomposition.

Anal. Calcd for  $\text{C}_{72}\text{H}_{96}\text{O}_6$ : C, 81.77; H, 9.15;  $M_w$  1058. Found: C, 81.62; H, 8.91;  $M_w$  1138.

***p*-*tert*-Pentylcalix[8]arene.** A slurry of 29.57 g (0.180 mol) of *p*-*tert*-pentylphenol, 9.02 g (0.300 mol) of paraformaldehyde, 0.260 g (3.95 mmol) of 85% KOH, and 0.10 g of water in 150 mL of tetralin was heated and stirred under nitrogen according to the pattern described earlier for the synthesis of the *p*-*tert*-butyl octamer.<sup>6</sup> The *p*-*tert*-pentyl octamer of good purity was recovered by filtration of cooled reaction mixtures in 37–41% crude yields. Additional crops, although of lesser purity and apparently consisting of increasing amounts of other oligomers, could also be obtained. Recrystallization from  $\text{CHCl}_3$ , followed by warming under high vacuum to remove residual solvent, afforded tiny white crystals, an analytical sample with no discernible impurities. IR (KBr) 3240 br, 873, 786, nothing around 400  $\text{cm}^{-1}$  inter alia. TLC (2:1  $\text{CHCl}_3$ /heptane) single spot  $R_f$  0.87. The analytical sample showed poorly defined melting behavior, melting around 375–385 °C with decomposition.

Anal. Calcd for  $\text{C}_{96}\text{H}_{128}\text{O}_8$ : C, 81.77; H, 9.15;  $M_w$ , 1410. Found: C, 81.83; H, 9.02;  $M_w$  1383.

**Procedures for Measuring Cation Transport Rates.** Membrane transport experiments were conducted as reported earlier<sup>9,13</sup> by using a bulk liquid membrane apparatus (Figure 2) based on the concept of the Schulman bridge.<sup>14</sup> The membrane (3 mL of a 1.0 mM solution of the macrocycle in a 25/75 v/v  $\text{CH}_2\text{Cl}_2$ / $\text{CCl}_4$  solvent) was stirred at 25 °C for 24 h by a 13-mm Teflon-coated magnetic stirrer driven by a Hurst

(12) The melting point for this *p*-*tert*-pentyl tetramer is said to be 356 °C in ref 8. Thus, the identity of Zinke's "tetramer" appears uncertain.

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(11) For example, see ref 6, Table I, Footnote 30, and attendant comments therein.

**Table I.** Single-Cation Flux from Basic Solution by Various Calixarenes

source-phase cation <sup>a</sup>	flux ( $\times 10^{-8}$ mol/s·m <sup>2</sup> )				
	calixarene				
	<i>p</i> -tert-butyl-calix[4]-arene <sup>b,c</sup>	<i>p</i> -tert-pentyl-calix[4]-arene <sup>b</sup>	<i>p</i> -tert-butyl-calix[6]-arene <sup>b,c</sup>	<i>p</i> -tert-butyl-calix[8]-arene <sup>b,c</sup>	<i>p</i> -tert-pentyl-calix[8]-arene <sup>b</sup>
Cs <sup>+</sup>	260	414	810	996	925
Rb <sup>+</sup>	6	12	71	340	111
K <sup>+</sup>	d	1	13	10	23
Na <sup>+</sup>	2	3	22	9	10

<sup>a</sup> 1.0 M aqueous metal hydroxide solutions. <sup>b</sup> Membrane = 0.001 M carrier in 25% v/v CH<sub>2</sub>Cl<sub>2</sub> in CCl<sub>4</sub> solution. Blank determinations were  $< 0.7 \times 10^{-8}$  mol/s·m<sup>2</sup> in all cases. <sup>c</sup> Values are from ref 9. Determination of these values was repeated in this study, and the results agreed with the earlier values within 20%. <sup>d</sup> Less than 0.7.

synchronous motor. The membrane was at the bottom of a 3-dram vial (i.d. = 18 mm). An 0.8-mL quantity of an aqueous cation solution (source phase) and 5.0 mL of distilled, deionized water (receiving phase) were placed on top of this organic phase. The two water phases were separated by a glass tube (i.d. = 8 mm). The single-cation hydroxide concentrations in the source phase were 1.0 M, except in the case of CsOH with *p*-tert-butylcalix[6]arene where the CsOH concentration was varied from 0.001 to 1.0 M. For cation mixtures, the total source-phase concentration equaled 1.0 M (e.g. a mixture of three hydroxide salts contained each at 0.33 M). The experimental units were maintained at 25 °C. The receiving phase was sampled and analyzed for cation content by atomic absorption spectrophotometry (Perkin-Elmer Model 603) at the end of the 24-h stirring period.

Each experiment was repeated at least 3 times, and the results are reported as the mean of these determinations; the sample standard deviation from this mean was typically less than  $\pm 20\%$ . A statistical *Q*-test (90% confidence level) was performed to eliminate any divergent values in cases where more than three experimental determinations were made. Experiments performed in which no carrier was present in the membrane showed cation fluxes to be less than  $0.7 \times 10^{-8}$  mol/s·m<sup>2</sup>.

## Results and Discussion

**Single-Cation Transport.** Table I lists the single-cation fluxes of Cs<sup>+</sup>, Rb<sup>+</sup>, K<sup>+</sup>, and Na<sup>+</sup> from basic solutions by various *p*-tert-butyl- and *p*-tert-pentylcalixarenes. Metal hydroxides were used because the source phase must be strongly basic (pH > 12.5) in order for significant flux to occur.<sup>9</sup> The transport of Cs<sup>+</sup> was much greater than that of any of the other cations with each of the five calixarene ligands. The larger ionic diameter of Cs<sup>+</sup> compared to those of Rb<sup>+</sup>, K<sup>+</sup>, and Na<sup>+</sup> suggests that Cs<sup>+</sup> should not be transported selectively if close correspondence between the relative magnitudes of the cation and ligand cavity diameters is the most important factor in determining cation-calixarene interaction and subsequent cation transport. The ionic diameters of the cations are Cs, 3.40 Å, Rb<sup>+</sup>, 2.98 Å, K<sup>+</sup>, 2.76 Å, and Na<sup>+</sup>, 2.04 Å.<sup>15</sup> CPK models indicate that approximate hydroxyl end cavity diameter ranges of the ligands are *p*-tert-butyl(pentyl)calix[4]arene, 0.68–0.92 Å, *p*-tert-butyl(pentyl)calix[6]arene, 2.1–2.8 Å, and *p*-tert-butyl(pentyl)calix[8]arene, 4.0–4.4 Å. We found earlier<sup>9</sup> that the *p*-tert-butylcalixarenes transported Cs<sup>+</sup> selectively and suggested that factors other than cation diameter and ligand cavity size may be responsible for that selectivity (e.g., relative hydration energies of the cations, Cs<sup>+</sup> having the lowest).

In this study, the *p*-tert-pentylcalixarenes behaved like the *p*-tert-butylcalixarenes in that they transported Cs<sup>+</sup> selectively over either Rb<sup>+</sup>, K<sup>+</sup>, or Na<sup>+</sup>. In addition, they transported each of the four cations (except Rb<sup>+</sup> with *p*-tert-pentylcalix[8]arene) at a rate equal to or higher than that of the corresponding *p*-tert-butylcalixarenes. In the absence of structural and thermodynamic data for these M<sup>+</sup>-calixarene systems, explanations for these observations must remain speculative.

An interesting possibility for the approximately twofold increase in Cs<sup>+</sup> flux (even more in the case of Rb<sup>+</sup>) from the calix[4]arene

**Table II.** Cation Flux from Basic Solution Source Phase for Two-Cation Mixtures by Various Calixarenes

source-phase cation <sup>a</sup>	flux ( $\times 10^{-8}$ mol/s·m <sup>2</sup> )				
	calixarene				
	<i>p</i> -tert-butyl-calix[4]-arene <sup>b</sup>	<i>p</i> -tert-pentyl-calix[4]-arene <sup>b</sup>	<i>p</i> -tert-butyl-calix[6]-arene <sup>b</sup>	<i>p</i> -tert-butyl-calix[8]-arene <sup>b</sup>	<i>p</i> -tert-pentyl-calix[8]-arene <sup>b</sup>
Cs <sup>+</sup>	285	289	660	583	666
Rb <sup>+</sup>	6	8	37	176	208
Cs <sup>+</sup>	299	332	757	865	579
K <sup>+</sup>	1	c	10	92	77
Cs <sup>+</sup>	197	281	774	858	670
Na <sup>+</sup>	2	2	4	88	61
Rb <sup>+</sup>	3	5	21	152	157
K <sup>+</sup>	c	c	7	65	65
Rb <sup>+</sup>	5	8	68	68	4
Na <sup>+</sup>	1	2	4	16	2
K <sup>+</sup>	0.9	c	29	8	1
Na <sup>+</sup>	1	2	3	5	2

<sup>a</sup> Aqueous solutions 0.50 M in each metal hydroxide. <sup>b</sup> Membrane = 0.001 M carrier in 25% v/v CH<sub>2</sub>Cl<sub>2</sub> in CCl<sub>4</sub> solution. Blank determinations were  $< 0.7 \times 10^{-8}$  mol/s·m<sup>2</sup> in all cases. <sup>c</sup> Less than 0.7.

**Table III.** Cation Flux from Basic Solution Source Phase for Three-Cation and Four-Cation Mixtures by Various Calixarenes

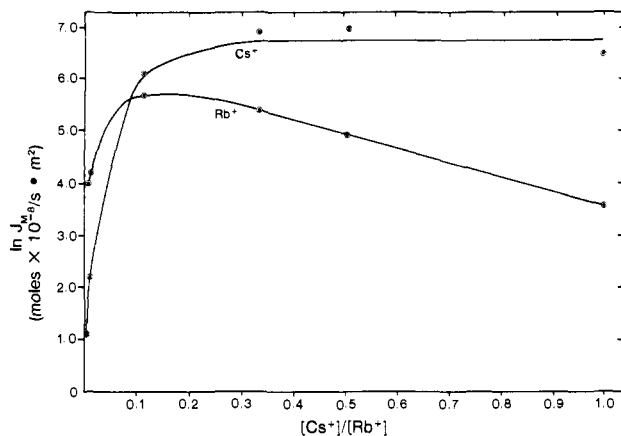
source-phase cation <sup>a</sup>	flux ( $\times 10^{-8}$ mol/s·m <sup>2</sup> )				
	calixarene				
	<i>p</i> -tert-butyl-calix[4]-arene <sup>b</sup>	<i>p</i> -tert-pentyl-calix[4]-arene <sup>b</sup>	<i>p</i> -tert-butyl-calix[6]-arene <sup>b</sup>	<i>p</i> -tert-butyl-calix[8]-arene <sup>b</sup>	<i>p</i> -tert-pentyl-calix[8]-arene <sup>b</sup>
Cs <sup>+</sup>	250	212	831	416	649
Rb <sup>+</sup>	6	8	72	127	140
K <sup>+</sup>	2	2	24	61	72
Cs <sup>+</sup>	171	180	727	339	434
Rb <sup>+</sup>	3	5	74	146	116
Na <sup>+</sup>	4	0.9	7	56	36
Cs <sup>+</sup>	202	201	391	666	297
K <sup>+</sup>	5	3	12	81	54
Na <sup>+</sup>	5	1	3	77	44
Rb <sup>+</sup>	3	8	31	74	5
K <sup>+</sup>	4	c	8	30	2
Na <sup>+</sup>	3	4	3	18	2
Cs <sup>+</sup>	154	151	845	412	345
Rb <sup>+</sup>	5	6	79	127	101
K <sup>+</sup>	3	2	34	58	44
Na <sup>+</sup>	9	3	8	51	32

<sup>a</sup> Aqueous solutions 0.33 M in each metal hydroxide for three-cation mixtures and 0.25 M in each metal hydroxide for four-cation mixtures. <sup>b</sup> Membrane = 0.001 M carrier in 25% v/v CH<sub>2</sub>Cl<sub>2</sub> in CCl<sub>4</sub> solution. Blank determinations were  $< 0.7 \times 10^{-8}$  mol/s·m<sup>2</sup> in all cases. <sup>c</sup> Less than 0.7.

to calix[6]arene and calix[8]arene is that these latter calixarenes can "pinch" transannularly to form two circularly hydrogen bonded arrays containing three and four OH groups, respectively. Thus, two cations could be bound and transported by a single calixarene species. Such "pinched" conformations for these macrocycles in solvents of low dielectric constants have been proposed by Gutsche<sup>3</sup> based on temperature-dependent NMR data which showed coalescence temperatures for the *t*-butyl tetramer and *t*-butyl octamer to be 43 and 44 °C, respectively. The close correspondence of the coalescence temperatures indicates that conformational effects are similar in the tetramer and the octamer. In similar NMR studies in our laboratory,<sup>16</sup> coalescence temperatures of 62 and  $< 30$  °C were found for the *t*-pentyl octamer and the *t*-pentyl

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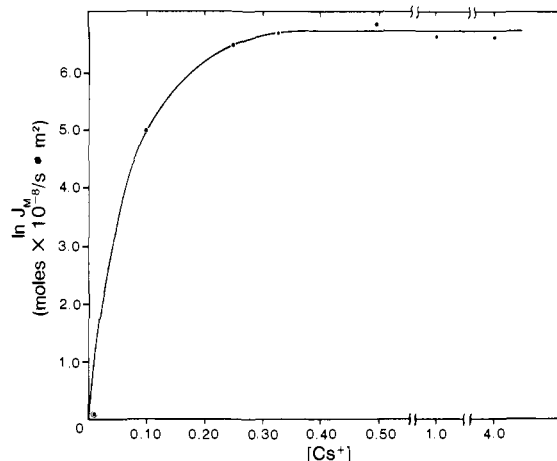
**Figure 3.** Plot of  $\text{Cs}^+$  flux and  $\text{Rb}^+$  flux ( $J_M$ ) as a function of the ratio of the concentrations of  $\text{Cs}^+$  to  $\text{Rb}^+$  in 1.0 M metal hydroxide solution: membrane, 0.001 M *p*-tert-butylcalix[6]arene in 25% v/v  $\text{CH}_2\text{Cl}_2$  in  $\text{CCl}_4$  solution. In the absence of  $\text{RbOH}$ ,  $\ln J_M$  of 1.0 M  $\text{CsOH} = 6.7$ . In the absence of  $\text{CsOH}$ ,  $\ln J_M$  of 1.0 M  $\text{RbOH} = 4.3$ .

tetramer, respectively. The greater constraint of the octamer, as indicated by these results, is unexpected and is not predicted from molecular models.

**Cation Transport from Mixtures.**  $\text{Cs}^+$  is transported selectively by each ligand when present in either two-, three-, or four-cation mixtures with  $\text{Rb}^+$ ,  $\text{Na}^+$ , or  $\text{K}^+$  (Tables II and III). Cation-calixarene binding and the calixarene-mediated flux of cations depend on physical parameters (i.e., stirring rate and relative cation concentrations) and chemical effects. These factors are now discussed.

**1. Variation of Flux with Physical Parameters.** *p*-tert-Butylcalix[6]arene transports  $\text{Rb}^+$  selectively over  $\text{Cs}^+$  at low  $[\text{Cs}^+]$ -to- $[\text{Rb}^+]$  ratios (Figure 3). As  $[\text{Cs}^+]$ -to- $[\text{Rb}^+]$  ratios increase, the flux of  $\text{Cs}^+$  becomes favored over that of  $\text{Rb}^+$ . The dependence of selectivity on cation concentration indicates that the cation flux is partially a function of the relative concentrations of cations in the source phase. The flux of  $\text{Cs}^+$  when present alone first increases rapidly and then levels off as the  $\text{Cs}^+$  concentration increases (Figure 4). We found the same relationship between salt concentration and flux for the iodide, thiocyanate, and nitrate salts of potassium.<sup>17</sup> The data presented in Figures 3 and 4 suggest that cation flux by calixarenes is diffusion-controlled. Indeed, as stirring speed was increased from 20 to 200 rpm, there was a four-fold increase in  $\text{Cs}^+$  flux (from  $352 \times 10^{-8}$  to  $1407 \times 10^{-8}$  mol/s·m<sup>2</sup>), mediated by *p*-tert butylcalix[6]arene ( $\text{CsOH}$  concentration was held constant at 1.0 M).

**2. Chemical Effects.** Comparison of the flux data in Table I with those in Tables II and III shows that  $\text{Cs}^+$  transport is maintained at a level comparable to the single-cation flux when  $\text{Cs}^+$  is in two-, three-, and four-cation mixtures even though the  $[\text{Cs}^+]$  is lowered two, three, and fourfold, respectively, in these systems. Apparently, the constant  $\text{OH}^-$  concentration provides a sufficient common ion effect to maintain a nearly constant  $\text{Cs}^+$  flux in these systems. Similar effects have been found in other studies involving mixtures.<sup>18,19</sup> The data in Figure 2 show a similar effect although the anion concentration is not held constant but decreases with  $[\text{Cs}^+]$ . The selectivity of the calixarenes for  $\text{Cs}^+$  over the other cations decreases with increasing ligand size. Both the calix[6]arene and calix[8]arene ligands mediate the flux of all cations in either a two- or a three-cation mixture at a level comparable to or above that of the single-cation flux. With these larger ligands, there appears to be a synergistic effect among the cations. Furthermore,  $\text{Cs}^+$  plays an important role in this effect.



**Figure 4.** Plot of  $\text{Cs}^+$  flux ( $J_M$ ) as a function of  $\text{Cs}^+$  concentration in basic solution: membrane, 0.001 M *p*-tert-butylcalix[6]arene in 25% v/v  $\text{CH}_2\text{Cl}_2$  in  $\text{CCl}_4$  solution.

When  $\text{Cs}^+$  is present either in a two- or three-cation mixture with  $\text{Na}^+$  (Tables II and III),  $\text{Na}^+$  flux is increased significantly over that when  $\text{Na}^+$  is present alone (Table I). Mixtures of  $\text{Rb}^+$  and/or  $\text{K}^+$  with  $\text{Na}^+$  do not produce the same effect.

In two-, three-, and four-cation mixtures, *p*-tert-butylcalix[8]arene generally mediates greater cation flux than *p*-tert-pentylcalix[8]arene. This difference is most apparent in mixtures of  $\text{Rb}^+/\text{Na}^+$  (Table II) and  $\text{Rb}^+/\text{Na}^+/\text{K}^+$  (Table III). Interestingly, when  $\text{Cs}^+$  is added to these mixtures (i.e.  $\text{Cs}^+/\text{Rb}^+/\text{Na}^+$  and  $\text{Cs}^+/\text{Rb}^+/\text{Na}^+/\text{K}^+$ ) the difference is not nearly as dramatic. Neither the effect of  $\text{Cs}^+$  nor the role of a pentyl (vs. a butyl) substituent on the ligand-cation binding and flux properties is clear. There is no significant difference between the cation fluxes mediated by *p*-tert-butylcalix[4]arene and *p*-tert-pentylcalix[4]arene. Thus, the effects of  $\text{Cs}^+$  and the pentyl substituent only manifest themselves in the larger calix[8]arenes. Perhaps these effects are related to the ability of the calix[8]arenes to restructure the architecture of their toruslike cavities. This restructuring could allow more than one cation to be transported simultaneously as mentioned earlier.

The data presented herein show that (1) the calixarene ligands are selective for  $\text{Cs}^+$  over  $\text{Rb}^+$ ,  $\text{K}^+$ ,  $\text{Na}^+$ , (2) the pentyl derivative of calix[4]arene greatly increases single-cation flux, (3) cation flux is diffusion-controlled to a significant extent, (4)  $\text{Cs}^+$  plays a central role in allowing the calix[8]arenes to mediate the flux of  $\text{Na}^+$ , and (5) in the calix[8]arenes, substitution of pentyl groups for butyl groups affects cation flux from mixtures in a significant way, especially in the cases where  $\text{Rb}^+$  and  $\text{Na}^+$  are in the same mixture. However, several questions remain unanswered and must be investigated before this complex chemical-physical system is fully understood. Specifically, the structure of the calixarenes (by X-ray crystallography) and the manner of cation binding (i.e., is the binding site inside the cavity or on the exterior) must be determined. Cation-ligand binding constants and ligand pK values are necessary to understand why  $\text{Cs}^+$  has such a dramatic effect on transport and why  $\text{Na}^+/\text{Rb}^+$  mixtures greatly inhibit cation flux with *p*-tert-pentylcalix[8]arene.

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**Registry No.** *p*-tert-Pentylcalix[4]arene, 77769-14-3; *p*-tert-pentylcalix[6]arene, 93503-76-5; *p*-tert-pentylcalix[8]arene, 93503-77-6; *p*-tert-butylcalix[4]arene, 60705-62-6; *p*-tert-butylcalix[6]arene, 78092-53-2; *p*-tert-butylcalix[8]arene, 68971-82-4; *p*-tert-pentylphenol, 80-46-6; paraformaldehyde, 30525-89-4; KOH, 1310-58-3;  $\text{Cs}^+$ , 18459-37-5;  $\text{Rb}^+$ , 22537-38-8;  $\text{K}^+$ , 24203-36-9;  $\text{Na}^+$ , 17341-25-2.

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