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Doubly Crowned Calix[4]arenes in the 1,3-Alternate Conformation as Cesium-Selective Carriers in Supported Liquid Membranes

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Calix[4]biscrowns 9−15 in the 1,3-alternate conformation are prepared by a one-step procedure in $\sim$50-80% yields, which are sufficiently high enough to allow their use as selective cesium carriers in supported liquid membranes (SLMs). The application of the Danesi diffusional model allows the transport isotherms of trace level ^{137}Cs through SLMs (containing calix[4]biscrowns) to be determined as a function of the ionic concentration of the aqueous feed solutions. Compound 13 appeared to be much more efficient than mixtures of crown ethers and acidic exchangers, especially in very acidic media. Decontamination factors greater than 20 are obtained in the treatment of synthetic acidic radioactive wastes. Permeability coefficient measurements are conducted for repetitive transport experiments in order to qualify the SMLs' stability with time. Very good results (over 50 days of stability) and high decontamination yields are observed with 1,3-calix[4]biscrowns 13 and 14. The 1,3-calix[4]biscrowns are shown to be a new family of selective carriers for cesium removal from radioactive liquid wastes.

The chemistry of calixarenes is well documented. Several accounts[1] and three books[2] have appeared which give an overview of the development and chemistry of these compounds. *p-tert*-Butylcalix[4]arene, which is the cyclic tetramer of the series, has been shown to be the most important building block because (a) it can be produced selectively in large amounts from inexpensive starting materials,[3] (b) it can easily be chemically transformed at the phenolic oxygens (lower rim) and at the para positions (upper rim), and (c) the chemical modification associated with the conformational properties lead to a large variety of tailor-made receptors.[2]

Since Alfieri et al.[4] reported the synthesis of the first member of a new class of macropolycyclic crown compounds with two opposite OH groups in *p-tert*-butylcalix[4]arene bridged by a pentaethylene glycol chain, attention has been paid to the design, synthesis, and metal cation complexation properties of so-called "calixcrown" compounds. The 1,3-capping of calix[4]arenes at the lower rim has been achieved with poly(oxyethylene) chains leading to calixcrown ethers,[5] doubly crowned calixes,[5c,6] and a double calix crown.[7]

Due to the presence of a glycol chain in their framework, calixcrowns have been used as complexing agents of alkali and alkaline-earth metal cations.[2] The selectivities of complexation were shown to depend on the conformation (cone, partial cone, 1,2-alternate, 1,3-alternate) adopted by the rigidified calix[4]arene unit.[1d] For example the partial-cone isomer of 1,3-dimethoxy-*p-tert*-butylcalix[4]crown-5 exhibited the highest free energy for complexation of potassium cation[5b] and was used as selective carrier of this cation in supported liquid membranes (SLMs).[5c] The K$^+$ selectivities of three different conformers of 1,3-diethoxy-

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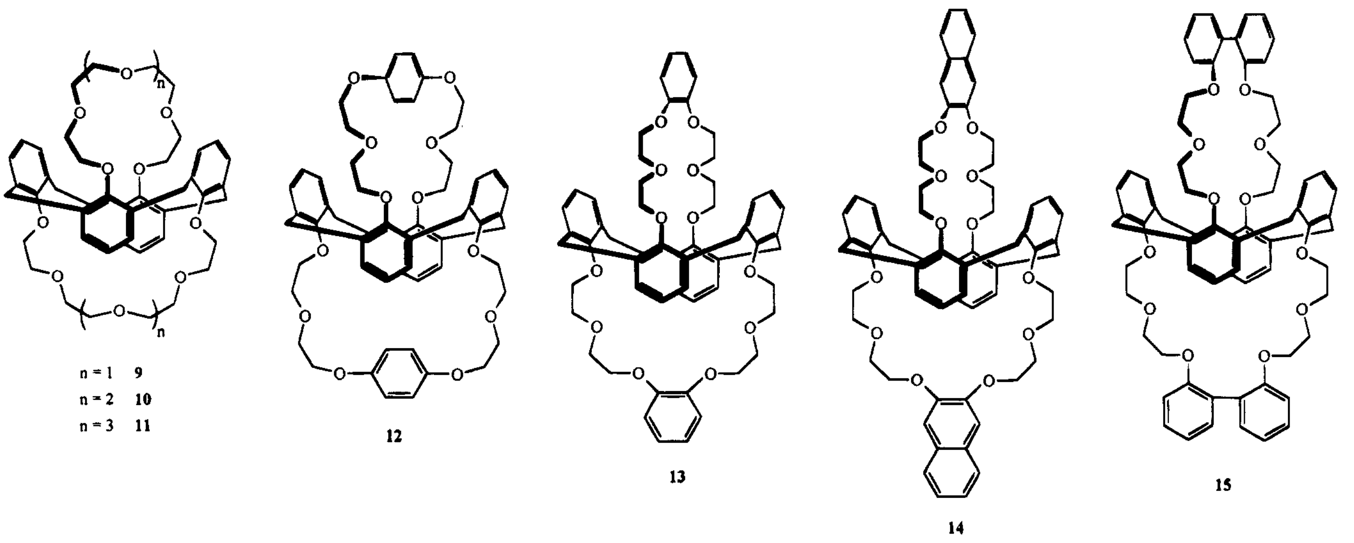
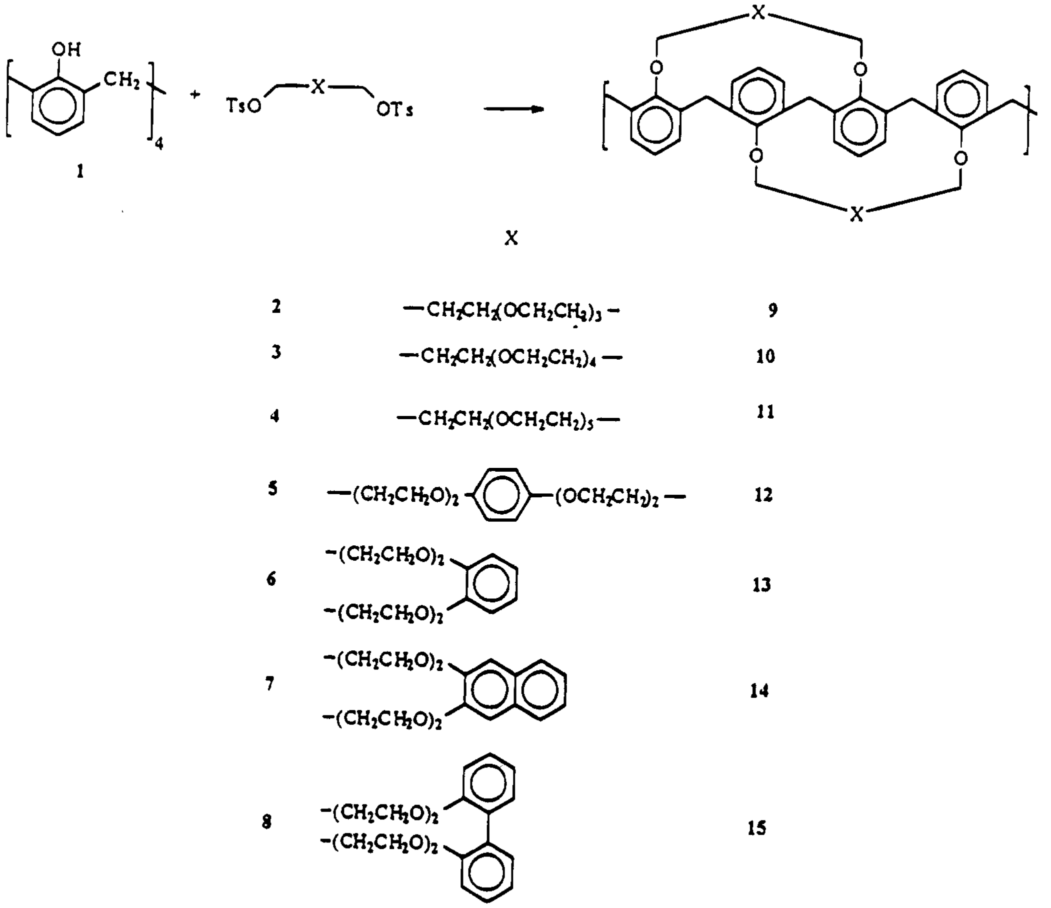
Chart 1. 1,3-Calix[4]biscrowns 9–15



Scheme 1. Synthesis of 9–15



p-tert-butylcalix[4]crown-5 have been measured for chemically modified field effect transistors (CHEMFETs)[5k] and membrane ion-selective electrodes (ISEs).[5d] The ionophores showed decreasing K^+/Na^+ selectivities in the order partial cone > 1,3-alternate > cone. The 1,3-Dialkoxycalix[4]crown-6 compounds in the 1,3-alternate conformation presented binding preference for cesium ion.[5e] The X-ray crystal structure of the 1:1 complex of 1,3-dimethoxycalix[4]crown-6 with the cesium picrate indicated the presence of cation/π-electron interactions.[5e]

In this paper we report the synthesis and complexing properties of macrotricyclic 1,3-calix[4]biscrowns **9–15** in the 1,3-alternate conformation (see Chart 1). Their use as selective cesium carriers in supported liquid membranes is described.

RESULTS AND DISCUSSION

Syntheses. 1,3-Calix[4]biscrowns **9–15** were prepared according to Scheme 1. Thus calix[4]arene **1** was reacted with 2–4 equivs of ditosylates **2–8** in refluxing acetonitrile in the presence of an excess of potassium carbonate for times that ranged from 6 to 14 days. The ditosylate and potassium carbonate were added in two portions (see Experimental Section). 1,3-Calix[4]biscrowns **9–15** were obtained pure as white precipitates of the crude

Table 1. Liquid–Liquid Extraction Experiments: Selectivity Determination[a]

no.	extracting agents used	D_{Na}	D_{Cs}	$\alpha_{(Cs/Na)}$
9	1,3-calix[4]biscrown-5	2×10^{-3}	0.4	
10	1,3-calix[4]biscrown-6	1.3×10^{-2}	19.5	1500
11	1,3-calix[4]biscrown-7	$<10^{-3}$	0.3	
12	1,3-calix[4]bis-*p*-benzo-crown-6	$<10^{-3}$	2×10^{-2}	
13	1,3-calix[4]bis-*o*-benzo-crown-6	1.7×10^{-3}	32.5	19000
14	1,3-calix[4]bisnaphthyl-crown-6	$<10^{-3}$	29.5	29000
15	1,3-calix[4]bisdiphenyl-crown-6	$<10^{-3}$	7×10^{-2}	
16	*n*-decylbenzo-21-crown-7	1.2×10^{-3}	0.3	250
17	*tert*-butylbenzo-21-crown-7	1.2×10^{-3}	0.3	250

[a] Aqueous feed solution, 5.0×10^{-4} M $M^+(NO_3^-)$ in 1 M HNO_3; organic solution, 10^{-2} M extracting agent in 1,2-nitrophenyl hexyl ether.

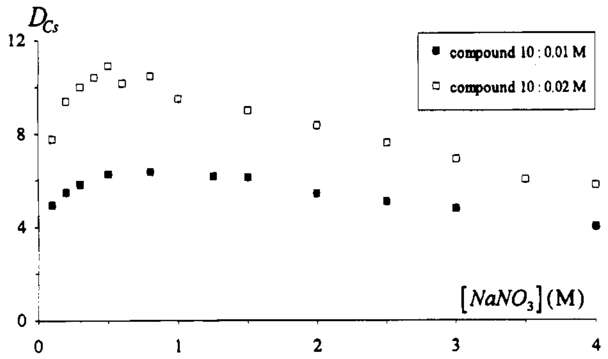


Figure 1. Extraction isotherms for ^{137}Cs in sodium nitrate solutions by 1,3-calix[4]biscrown-6 in 1,2-NPOE: aqueous solution, $NaNO_3$ at various concentrations (pH 2); organic solution, 1,3-calix[4]biscrown-6 in 1,2-nitrophenyl octyl ether.

products from appropriate solvents. The yields ranged from 48 to 79%. Doubly crowned calix[4]arenes **9–15** were fully characterized by ^1H NMR, FAB positive mass spectrometry, and elemental analysis. They were deduced to be in 1,3-alternate conformation from their ^1H NMR spectra, which showed singlets at 3.88, 3.87, 3.76, 3.68, and 3.76 ppm, respectively, for the $Ar-CH_2-Ar$ methylene protons in the macrorings of **9–15**. In this conformation, 1,3-calix[4]arene-biscrowns **9–15** present a special arrangement: one glycolic chain connects two opposite oxygen atoms while the second enforces the calix[4]arene to adopt the 1,3-alternate conformation by linking the two remaining oxygen atoms. This globular arrangement is verified in the X-ray structure of *p*-*tert*-butylcalix[4]biscrown-5.[6e]

Sodium–Cesium Extractions. The removal of cesium from medium-level radioactive wastes involves extraction of cesium from aqueous solutions that are 1 M in HNO_3 and 4 M in $NaNO_3$.[8] In a preliminary study, extraction experiments with ligands **9–15** were performed by mixing equal volumes (5–7 mL) of aqueous and organic solutions (calixarene, 10^{-2} M in 1,2-nitrophenyl hexyl ether) in sealed polypropylene tubes for 1 h at room temperature (25 ± 1 °C). The aqueous solutions contained either $NaNO_3$ or $CsNO_3$ (5.0×10^{-4} M) in HNO_3 (1 M) to assess the selectivity toward cesium in the hypothetical presence of sodium. A measure for the selectivity was assumed to be the ratio of the distribution coefficients obtained separately for both cations:

$$\alpha_{(Cs/Na)} = D_{Cs}/D_{Na} \quad \text{with } D_M = \sum[\bar{M}]/\sum[M]$$

where $\Sigma[\bar{M}]$ denotes the total concentration of the metal cation (complexed and uncomplexed) in the organic phase at equilibrium and $\Sigma[M]$ denotes its total concentration in the aqueous phase at equilibrium. $\Sigma[\bar{M}]$ and $\Sigma[M]$ were determined experimentally by analyzing aliquots (2 or 5 mL) of each phase by γ spectrometry after centrifugation.

From the data in Table 1, it is seen that ligands **10**, **13**, and **14** with six oxygen atoms in the glycol chain are much more selective toward cesium over sodium than **9** and **11**, with five or seven oxygen atoms in their rings, and **12** and **15**, in which the polyether chains are sterically constrained by the presence of phenyl units. We have previously noted that the glycolic chains containing five oxygens in *p*-*tert*-butylcalix[4]biscrown-5, related to **9**, are suitable for potassium and sodium cations but too small for large cesium.[6e] In comparison, **10**, **13**, and **14** show 100 times higher selectivities toward cesium than do crown ethers **16** and **17**, which are well-known for their abilities to complex and extract large alkali cations from acidic media.[8] One explanation is that the complexes with calixarene derivatives are best formed because they are stabilized by the π-bonding interactions with the phenyl rings present in the basket frame of 1,3-calix[4]biscrowns **10**, **13**, and **14**.[5e,9]

Although ligands **9–15** present two potential complexation sites, the complex stoichiometry was found to be 1:1 (calixarene: cesium cation).[10] This behavior may be explained by a negative allosteric effect, which has been found in complexing systems containing two conformationally related crown ether subunits.[11] These systems are only able to complex cations in one of their two subunits at a time because when one complex is formed, the other subunit has an unsuitable conformation to bind any species.[11]

As shown in Figures 1 and 2, which display cesium extraction isotherms for **10** as a function of aqueous salt concentrations ($0 < [NaNO_3] < 4$ M, $0 < [HNO_3] < 7$ M and cesium at trace level), back-extraction of cesium was usually allowed and favored in deionized water (where D_{Cs} is very small). This remarkable property allowed the use of **9–15** as cesium-selective carriers in supported liquid membranes. Since cesium extraction was strongly enhanced in concentrated acidic media for **9–15** as compared to mixtures of a crown ether such as *tert*-butylbenzo-21C7 (**17**)[12] and an acidic exchanger ligand, **9–15** might be used to treat medium-level radioactive wastes. The decrease of D_{Cs} for sodium nitrate concentrations greater than 0.5 M (see Figure 1) or for nitric acid concentrations greater than 2 M (see Figure 2) reveals both the competitive extraction of HNO_3 or $NaNO_3$ by the tested calixarenes and the decrease of the mean activity coefficient of trace-level cesium in a concentrated aqueous media.

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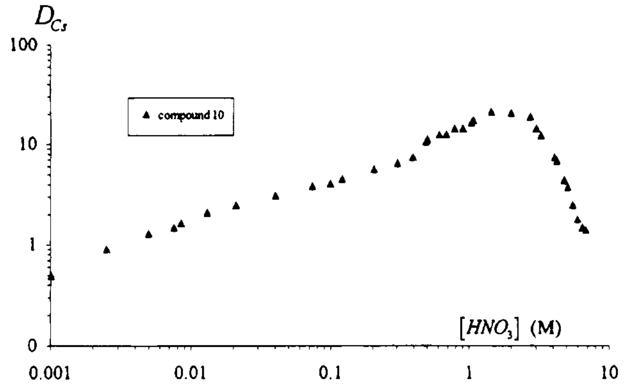

Figure 2. Extraction isotherm for ^{137}Cs in nitric acid solutions by 1,3-calix[4]biscrown-6 (10^{-2} M) in 1,2-NPOE: aqueous solution, HNO_3 at various concentrations; organic solution, 1,3-biscalix[4]-crown-6 (10-2 M) in 1,2-nitrophenyl octyl ether.

Cesium Transport through Supported Liquid Membranes (SLMs). Selective alkali cation permeation through liquid membranes has been intensively studied to mimic natural antibiotics, to transduce chemical information into electronic signals, or to treat radioactive wastes.[13] For instance, taking advantage of the phenolic ionization of parent calixarenes (*p-tert*-butyl- and *p-tert*-pentylcalix[*n*]arenes) under basic conditions, Izatt et al. achieved quantitative cesium transport through bulk liquid membranes (25% v/v CH_2Cl_2–CCl_4) from aqueous feed solutions of CsOH (pH > 12) to water.[14] However, no cesium permeation was observed in the case of neutral metal nitrate salts in the feed solutions during similar experiments.[14] Polyether-bridged calix[4]arenes were first applied to SLMs in order to study potassium/sodium permeation selectivities as compared to those of valinomycin.[13a] We therefore decided to determine the selective ionophoric properties of calix[4]biscrowns **9–15** by measuring under similar experimental conditions (stirring rates, concentration gradients) the permeability coefficients of cesium as described in the Danesi model of trace-level cation permeation through SLMs.[15] Although the Danesi model was applied to ion-pair extraction in apolar solvents, constant permeability coefficients have also been observed on long-term transport experiments (over 10 h) using a more polar organic solvent such as nitrophenyl octyl ether.[16]

The use of **9–15** as carriers in SLMs led to coupled cotransport of cesium and nitrate ions from aqueous feed solutions of 4 M in $NaNO_3$ and 1 M in HNO_3—simulating concentrated medium-level radioactive wastes—to deionized water (the receiving solution) because of the NO_3^- concentration gradient. The decrease of ^{137}Cs radioactivity in the feed solutions was followed by regular measurements with γ spectrometry analysis (1500 $kBq\cdot L^{-1} <$ ^{137}Cs initial aqueous activity $< 2500\ kBq\cdot L^{-1}$).

Table 2. ^{137}Cs Transport Experiments through Flat Sheet-Supported Liquid Membranes: Permeability Determination after 6 h of Permeation[a]

no.	carriers used	P_{Cs} ($cm\cdot h^{-1}$)
9	1,3-calix[4]biscrown-5	9×10^{-2}
10	1,3-calix[4]biscrown-6	1.3
11	1,3-calix[4]biscrown-7	4×10^{-2}
12	1,3-calix[4]bis-*p*-benzo-crown-6	3×10^{-3}
13	1,3-calix[4]bis-*o*-benzo-crown-6	2.8
14	1,3-calix[4]bisnaphthyl-crown-6	2.7
15	1,3-calix[4]bisdiphenyl-crown-6	0.1
16	n-decylbenzo-21-crown-7	9×10^{-2}

[a] Aqueous feed solution, $NaNO_3$ (4 M) and HNO_3 (1 M); aqueous strip solution, deionized water; organic solution, 10^{-2} M carrier in 1,2-nitrophenyl octyl ether.

Table 3. Transport Yields (after 24 h) of Sr, Rb, Y, Zr, Ru, Rh, Cs, Ba, La, Ce, and Eu Permeation from Simulated High-Active Wastes to Deionized Water by 1,3-Calix[4]biscrown-6, by 1,3-Calix[4]bis-*o*-benzo-crown-6, and by 1,3-Calix[4]bisnaphthyl-crown-6 (10^{-2} M) in 1,2-NPOE[a]

element	init concn in feed soln ($mg\cdot L^{-1}$)	M concn in receiving soln after 24 h ($mg\cdot L^{-1}$)		
		10	**13**	**14**
Sr	87.6	$<5 \times 10^{-2}$	$<5 \times 10^{-2}$	$<5 \times 10^{-2}$
Rb	85.5	34	63	47
Y	88.9	$<5 \times 10^{-3}$	$<5 \times 10^{-3}$	$<5 \times 10^{-3}$
Zr	91.2	$<5 \times 10^{-2}$	$<5 \times 10^{-2}$	$<5 \times 10^{-2}$
Ru	101.0	$<5 \times 10^{-3}$	$<5 \times 10^{-3}$	$<5 \times 10^{-3}$
Rh	102.9	$<5 \times 10^{-3}$	$<5 \times 10^{-3}$	$<5 \times 10^{-3}$
Cs	132.9	92	125	105
Ba	137.3	$<5 \times 10^{-2}$	$<5 \times 10^{-2}$	$<5 \times 10^{-2}$
La	138.5	$<5 \times 10^{-3}$	$<5 \times 10^{-3}$	$<5 \times 10^{-3}$
Ce	140.1	$<5 \times 10^{-3}$	$<5 \times 10^{-3}$	$<5 \times 10^{-3}$
Eu	151.9	$<5 \times 10^{-3}$	$<5 \times 10^{-3}$	$<5 \times 10^{-3}$

[a] Aqueous feed solution, 3 M HNO_3 and 10^{-3} M element; aqueous stripping solution, deionized water; SLM, **10**, **13**, or **14** (10^{-2} M) in 1,2-nitrophenyl octyl ether.

Permeability coefficients P_M ($cm\cdot h^{-1}$) for cesium permeation through the SLMs were graphically determined by plotting the logarithm of the ratio $C/C°$ vs time:[15]

$$\ln (C/C°) = (\theta S/V)P_M t \qquad (1)$$

where C is the concentration of the cation in the feed solution at time t (M); C° is the initial concentration of the cation in the feed solution (M); θ is the volumic porosity of the SLM (%); S is the membrane surface area (cm^2) depending on the device; V is the volume of feed and stripping solutions (cm^3) depending on the device; and t = time (h).

The data summarized in Table 2 confirm the results obtained previously in sodium–cesium extraction studies (see Table 1) although the organic solvent used in these experiments (1,2-nitrophenyl octyl ether) is a slightly more polar and more viscous diluent than 1,2-nitrophenyl hexyl ether. Carriers **10**, **13**, and **14** with six oxygen atoms in the glycol chain are much more efficient to transport cesium through SLMs than **9** and **11**, with five or seven oxygen atoms in their rings, and **12** and **15**, in which the polyether chains are sterically constrained.

Certain assumptions of the Danesi model[15] (transport being only controlled and limited by diffusion) allow the permeability coefficients P_M to be evaluated by

$$P_M \approx D_M/\Delta_o \qquad (2)$$

where D_M is the distribution coefficient of the permeating cation

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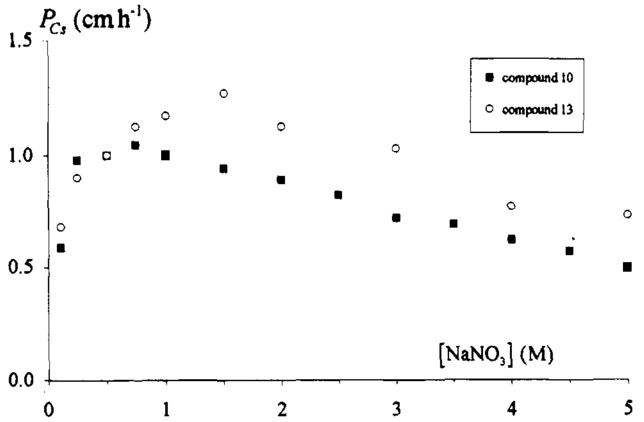

Figure 3. Transport isotherms for ^{137}Cs from sodium nitrate solutions to deionized water by 1,3-calix[4]biscrown-6 and by 1,3-calix[4]bis-*o*-benzocrown-6 (10^{-2} M) in 1,2-NPOE: aqueous feed solution, $NaNO_3$ in various concentrations (pH$_i$ 1.4); aqueous stripping solution, deionized water; SLM, **10** or **13** (10^{-2} M) in 1,2-nitrophenyl octyl ether.

and Δ_o, the ratio of the organic path length (thickness of the membrane × tortuosity) to the organic diffusion coefficient, $^o\tau)/D_o$.

Equation 2 shows that P_M is proportional to D_M, which directly depends on the organic carrier concentration in the SLM. That is why the cesium transport isotherms shown in Figures 3 and 4 for **10** reproduced the same trends as those found previously in extraction isotherms (Figures 1 and 2): (1) an increase of cesium permeability coefficient for $[NaNO_3] < 1$ M in the feed solution (Figure 3) and for $[HNO_3] < 2$ M in the feed solution (Figure 4) as D_{Cs} previously increased with salt concentration in the feed solution (Figures 1 and 2); (2) a maximum of transport kinetics due to the maximum of D_{Cs}; (3) a decrease of P_{Cs} for $[NaNO_3] >$ 1 M or $[HNO_3] >$ 2M, revealing three different phenomena, namely, (a) a decrease of D_{Cs} due to sodium nitrate or nitric acid competitive extraction and transport of sodium nitrate or nitric acid; (b) a decrease of trace-level cesium mean activity coefficient with the increase of salt concentration in the aqueous feed solutions; and (c) leaching of the SLMs by the feed and the receiving solutions favored by the partitioning of the carrier, especially in the case of **10**, which shows very poor lipophilicity.

The higher selectivity and efficiency of **13** compared to **10** can easily be noticed by comparing both transport isotherms shown in Figures 3 and 4.

Time stability of the most efficiently prepared SLMs was estimated by repeating transport experiments in which both aqueous feed and stripping solutions were renewed every day while the SLMs remained the same. Consequently, daily partitioning of the carrier from the membrane phase to the renewed aqueous solutions caused a decrease of the carrier concentration in the SLMs, thus a decrease of D_M and, proportionally, of P_M. The evolution of the permeability coefficients vs the number of runs was therefore a way to describe the leaching of the membrane by the aqueous solutions and characterized the SLMs' stability with time.

As shown in Figure 5, repeated cesium transport experiments showed that **10** rapidly leached out of the SLMs ($P_{Cs} < 0.1$ cm·h^{-1} after 15 runs), because of its low partition constants between 1,2-nitrophenyl octyl ether and the aqueous solutions. Very good stability and efficiency were observed with the more lipophilic compounds **13** and **14**, for which the cesium permeability coefficients were 5 times higher than those of the crown ether **16** even when the concentration of the crown ether was 50 times higher in 1,2-nitrophenyl octyl ether.

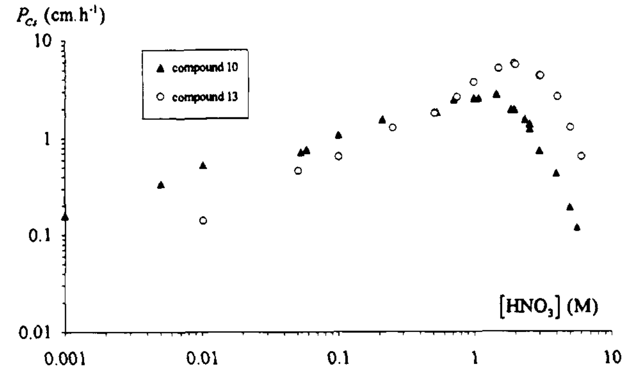

Figure 4. Transport isotherms of ^{137}Cs from nitric acid solutions to deionized water for 1,3-calix[4]biscrown-6 and for 1,3-calix[4]bis-*o*-benzo-crown-6 (10^{-2} M) in 1,2-NPOE: aqueous feed solution, HNO_3 in various concentrations; aqueous stripping solution, deionized water; SLM, **10** or **13** (10^{-2} M) in 1,2-nitrophenyl octyl ether.

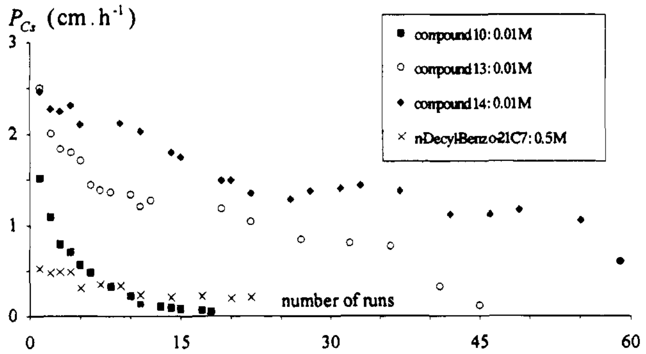

Figure 5. Repetitive transport experiments of ^{137}Cs from simulated medium-active liquid wastes for 1,3-calix[4]biscrown-6, for 1,3-calix[4]bis-*o*-benzocrown-6 and for 1,3-calix[4]bis-1,2-naphthylcrown-6 (10^{-2} M) in 1,2-NPOE: aqueous feed solution, $NaNO_3$ (4 M) and HNO_3 (1 M); aqueous stripping solution, deionized water; SLM, **10**, **13** or **14** (10^{-2} M) in 1,2-nitrophenyl octyl ether.

1,3-Calix[4]biscrowns **13** and **14** allowed selective removal of ^{137}Cs from sodium-containing solutions. Less than 100 mg of the ~100 g of sodium (initially present in the feed solution) was transported in 24 h by **14**, whereas more than 95% of trace level ^{137}Cs was concentrated in the stripping solution. Nitric acid transport, due to the basicity of both the organic diluent and the calixarene, could not be limited to less than 5% (0.05 M) in 24 h leading to concentration factors (ratio of initial waste concentration to final waste concentration) greater than 100 for a single-step process.

To summarize, 1,3-calix[4]biscrowns containing six oxygen atoms appeared to be a promising family of carriers for the selective removal of cesium from high-salinity media, such as medium-level radioactive liquid wastes, with SLMs. By choosing a highly hydrophobic organic diluent, 1,2-nitrophenyl octyl ether, and a very lipophilic calix[4]biscrown in the 1,3-alternate conformation suitable for cesium complexation over that of sodium, very selective and stable SLM can be obtained (over a period of 50 days).

Transport of Cesium from Simulated Fission Product Solutions. Application of calix[4]biscrowns **10**, **13**, and **14** to decontaminate medium- or high-level radioactive wastes, such as fission product solutions, was also investigated. Figure 6 shows

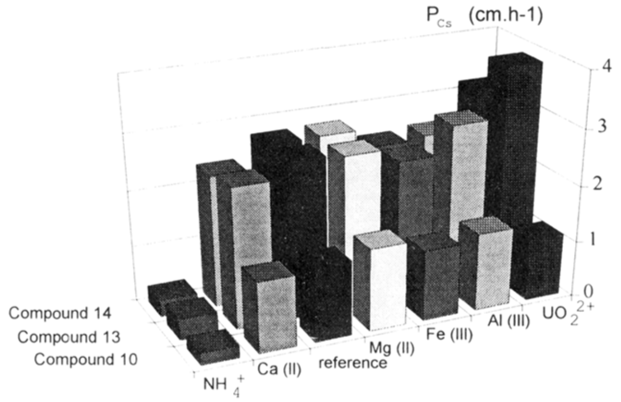

Figure 6. Influence of the presence of nitrate salts on the permeation of ^{137}Cs from simulated medium-active liquid wastes to deionized water by 1,3-calix[4]biscrown-6, by 1,3-calix[4]bis-*o*-benzocrown-6 and by 1,3-calix[4]bisnaphthylcrown-6 (10^{-2} M) in 1,2-NPOE: aqueous feed solution $NaNO_3$ (4 M), HNO_3 (1 M), and nitrate species (NH_4^+, Ca^{2+}, Mg^{2+}, Fe^{3+}, Al^{3+}, or UO_2^{2+}at 0.1 M); aqueous stripping solution deionized water; SLM, **10**, **13**, or **14** (10^{-2} M) in 1,2-nitrophenyl octyl ether.

the effect of the presence of six different nitrate salts (NH_4^+, Ca^{2+}, Mg^{2+}, Fe^{3+}, Al^{3+}, UO_2^{2+}) on cesium permeation from aqueous feed solutions simulating medium-active concentrates (4 M in $NaNO_3$ and 1 M in HNO_3) to receiving solutions of deionized water. Except for ammonium nitrate salts, which usually behave like alkali cations and drastically hinder cesium separation in classical industrial decontamination processes (coprecipitation, ion exchange, etc.), none of the other five added species (Ca^{2+}, Mg^{2+}, Fe^{3+}, Al^{3+}, UO_2^{2+}) potentially present in medium-active wastes disfavored trace level cesium permeation through the SLMs.

Table 2 records the transport yields of 11 main elements (out of 34 present in very high-level radioactive liquid wastes, such as fission products solutions) from nitric acid feed solutions (3 M in HNO_3 and 10^{-3} M in element) to deionized water. Metal cation concentrations were determined by atomic absorption spectrometry of aliquots sampled in the receiving solutions after 24 h of permeation. Except for rubidium, whose chemical behavior is similar to that of cesium among other alkali cations, the high selectivity of the tested 1,3-calix[4]biscrowns toward cesium is maintained in the presence of the other nine elements.

CONCLUSION

The preparation of calix[4]biscrowns **9−15** in the 1,3-alternate conformation by one-step procedures has been achieved in yields sufficiently high for their use as Cs carriers in supported liquid membranes. Application of the Danesi diffusional model allowed the transport isotherms of trace-level ^{137}Cs through SLMs (containing calix[4]biscrowns) to be determined as a function of the ionic concentration of the aqueous feed solutions. Compound **13** appeared to be much more efficient than a combination of crown ether and an acidic exchanger, especially in very acidic media. This allowed a one-step treatment of synthetic acidic radioactive wastes with decontamination factors greater than 100. Permeability coefficient measurements were also conducted in repetitive transport experiments in order to characterize SML stability with time. Very good results (over 50 days of stability) and high decontamination yields were observed with 1,3-calix[4]biscrowns **13** and **14**. The 1,3-calix[4]biscrowns are shown to be a new family of selective carriers for cesium removal from radioactive liquid wastes leading to 1:1 stoichiometry complexes (1,3- calix[4]biscrown−Cs).

Future work is directed in two directions: (i) determination of the stoichiometry and stability constants of the complexes of ligands **9−15** with alkali cations by spectrophotometric studies and NMR experiments and (ii) determination of the X-ray crystal structure of these complexes.

EXPERIMENTAL SECTION

Starting Materials for Syntheses. The solvents and all compounds were commercial reagents and were used without further purification.

Analytical Procedures. The melting points (mp) were taken on a Büchi 500 apparatus in capillaries sealed under nitrogen. Silica gel columns were prepared with Kiesielgel Merck (No.11567). Elemental analyses were performed at the Service de Microanalyse of the Institut de Chimie de Strasbourg. The ^{1}H NMR spectra were recorded at 200 MHz on a Bruker SY200 spectrometer. The FAB mass spectra were obtained on a VG-Analytical ZAB HF apparatus.

Syntheses. Preparation of 9. According to a procedure described by us,[17] a 1-L round-bottomed flask was equipped with a condenser and charged with acetonitrile (700 mL), calix[4]arene **1** (6.00 g, 14.2 mmol), and potassium carbonate (19.62 g, 142 mmol). The reaction mixture was stirred at room temperature for 30 min. Tetraethylene glycol ditosylate **2** (7.14 g, 14.2 mmol) was added, and the mixture was refluxed for 7 days. The same quantities of potassium carbonate and tetraethylene glycol ditosylate **2** were added, and the reflux was continued for 7 additional days. After cooling to room temperature, the solvents were removed in vacuo (45 °C bath). Dichloromethane (600 mL) was added and the suspension was neutralized by 1 N HCl. The organic layer was dried over sodium sulfate. The filtered solution was concentrated and precipitated with methanol−diethyl ether to yield pure **9** as a white solid: mp 117−118 °C; yield 53%; ^{1}H NMR ($CDCl_3$) γ 7.09 (d, 8H, J_{H-H} = 7.5 Hz, meta Ar*H*), 6.89 (t, 4H, J_{H-H} = 7.5 Hz, para Ar*H*), 3.88 (s, 8H, ArCH_2Ar), 3.59−3.06 (m, 32H, OCH_2CH_2O); FAB positive, 740.3. Elemental analysis calcd for $C_{44}H_{52}O_{10}.CH_3OH$: C, 70.02; H, 7.18. Found: C, 70.23; H, 6.92.

Preparation of 10. Same as for **9**; calix[4]arene **1** (0.85 g, 2 mmol), potassium carbonate (5.52 g, 40 mmol), pentaethylene glycol ditosylate **3** (2.28 g, 4 mmol), and acetonitrile (100 mL); 14 days; yield 48%; white solid from methanol−diethyl ether: mp 145−146 °C; ^{1}H NMR ($CDCl_3$) δ 7.10 (d, 8H, J_{H-H} = 8.0 Hz, meta Ar*H*), 6.87 (t, 4H, J_{H-H} = 8.0 Hz, para Ar*H*), 3.87 (s, 8H, ArCH_2-Ar), 3.70−3.28 (m, 40H, OCH_2CH_2O). FAB positive, 828.4. Elemental analysis calcd for $C_{48}H_{60}O_{12}.CH_3OH$: C, 70.02; H, 7.18. Found: C, 70.23; H, 6.92%.

Preparation of 11. Same as for **9**; calix[4]arene **1** (1.70 g, 4 mmol), potassium carbonate (5.52 g, 40 mmol), hexaethylene glycol ditosylate **4** (2.36 g, 4 mmol); acetonitrile (200 mL). The same quantities of potassium carbonate and hexaethylene glycol ditosylate were added after 10 days: total reflux time 14 days; white solid from methanol−diethyl ether; mp 120−121° C; yield 62%; ^{1}H NMR ($CDCl_3$) δ 7.14 (d, 8H, J_{H-H} = 7.5 Hz, meta Ar*H*), 6.80 (t, 4H, J_{H-H} = 7.5 Hz, para Ar*H*), 3.79−3.42 (m, 48H, OCH_2CH_2O), 3.57 (s, 8H, ArCH_2Ar). FAB positive, 916.4. El-

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[17] Wenger, S. Asfari, Z. Vicens, J. *Tetrahedron Lett.* **1994**, *35*, 8369.

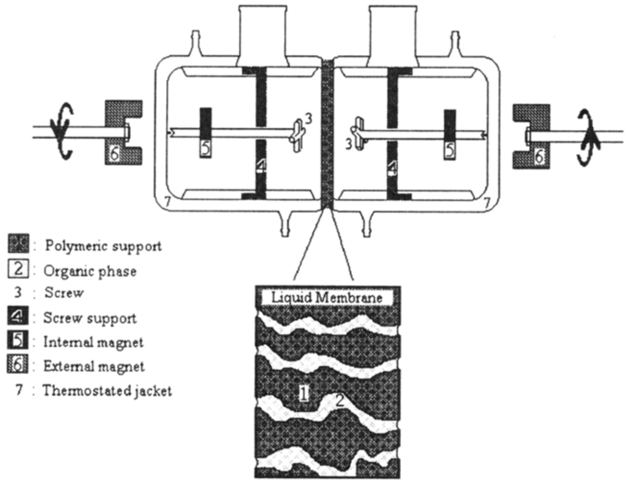

Figure 7. Flat-sheet supported liquid membrane device for transport experiments.

emental analysis calcd for $C_{56}H_{76}O_{16}$: C, 68.10, H 7.47. Found: C, 68.30, H, 7.27.

Preparation of 12. Same as for **9**; calix[4]arene **1** (0.64 g, 1.5 mmol), potassium carbonate (0.83 g, 40 mmol), ditosylate **5** (0.89 g, 1.5 mmol), and acetonitrile (60 mL). The same quantities of potassium carbonate and ditosylate were added after 4 days. Total reflux time, 8 days: white solid from methanol–diethyl ether: mp 81–82 °C; yield 54%; ^1H NMR ($CDCl_3$) δ 7.07 (d, 8H, J_{H-H} = 7.5 Hz, meta Ar*H*), 7.03 (s, 8H, Ar′*H*), 6.83 (t, 4H, J_{H-H} = 7.5 Hz, para Ar*H*), 3.82–3.67 (m, 32H, OCH_2CH_2O), 3.76 (s, 8H, $ArCH_2Ar$). FAB positive, 924.4. Elemental analysis calcd for $C_{56}H_{60}O_{12}$: C, 72.70; H, 6.54. Found: C, 72.48; H, 6.44.

Preparation of 13. Same as for **9**; calix[4]arene **1** (1.14 g, 2.69 mmol), potassium carbonate (3.72 g, 26.9 mmol), ditosylate **6** (1.60 g, 2.69 mmol), and acetonitrile (130 mL). The same quantities of potassium carbonate and ditosylate were added after 7 days: total reflux time 14 days; yield 54%; white solid from methanol–diethyl ether; mp 188–189 °C. ^1H NMR ($CDCl_3$) δ 7.07 (d, 8H, J_{H-H} = 7.5 Hz, meta Ar*H*), 6.99 (s, 8H, Ar′*H*), 6.80 (t, 4H, J_{H-H} = 7.5 Hz, para Ar*H*), 3.72–3.64 (m, 32H, OCH_2CH_2O), 3.68 (s, 8H, $ArCH_2$-Ar); FAB positive, 925.6. Elemental analysis calcd for $C_{56}H_{60}O_{12}$: C, 72.70, H, 6.54. Found: C, 72.42; H, 6.41.

Preparation of 14. Same as for **9**; calix[4]arene **1** (2.13 g, 5 mmol), potassium carbonate (6.91 g, 50 mmol), ditosylate **7** (3.15 g, 5 mmol), and acetonitrile (250 mL). The same quantities of potassium carbonate and ditosylate were added after 3 days: total reflux time 6 days; yield 78%; white solid from acetone : mp 108–109 °C; ^1H NMR ($CDCl_3$) δ 7.75–7.24 (m, 12H, naphthyl *H*), 7.09 (d, 8H, J_{H-H} = 8.0 Hz, meta Ar*H*), 6.67 (t, 4H, J_{H-H} = 8.0 Hz, para Ar*H*), 4.28 (t, 8H, J_{H-H} = 5.0 Hz, OCH_2CH_2OAr), 3.86 (t, 8H, J_{H-H} = 5.0 Hz, OCH_2CH_2OAr), 3.76 (s, 8H, $ArCH_2Ar$), 3.65 (t, 16H, J_{H-H} = 5.0 Hz, naphthyl-OCH_2CH_2O), 3.45–3.29 (m, 8H, naphthyl-OCH_2CH_2O); FAB positive 1025.2. Elemental analysis calcd for $C_{64}H_{64}O_{12}$: C, 74.97, H, 6.30. Found: C, 74.90; H, 6.35.

Preparation of 15. Same as for **9**; calix[4]arene **1** (2.13 g, 5 mmol), potassium carbonate (6.91 g, 50 mmol), ditosylate **8** (3.36 g, 5 mmol), and acetonitrile (250 mL). The same quantities of potassium carbonate and ditosylate were added after 4 days: total reflux time 8 days; yield 79%; white solid from acetone; mp 82–83 °C. ^1H NMR ($CDCl_3$) δ 7.41–7.04 (m, 16H, diph-*H*), 7.21 (d, 8H, J_{H-H} = 8.0 Hz, meta Ar*H*), 6.78 (t, 4H, J_{H-H} = 8.0 Hz, para Ar*H*), 4.03 (t, 8H, J_{H-H} = 5.0 Hz, OCH_2CH_2OAr), 3.86 (t, 8H, J_{H-H} = 5.0 Hz, OCH_2CH_2OAr), 3.72 (s, 8H, $ArCH_2Ar$), 3.62–3.50 (m, 8H, diphenyl-OCH_2CH_2O), 3.45–3.29 (m, 8H, diphenyl-OCH_2CH_2O); FAB positive, 1077.03. Elemental analysis calcd for $C_{68}H_{68}O_{12}$: C, 75.82%; H, 6.36. Found: C, 75.80; H, 6.44.

Starting Materials for Extraction and SLMs Transports. The inorganic salts used to prepare the synthetic aqueous feed solutions for extraction and transport experiments ($NaNO_3$, $CsNO_3$, etc.) were analytical grade products from Prolabo and Aldrich. Radioactive ^{22}Na and ^{137}Cs used to spike the aqueous solutions (1500 $kBq{\cdot}L^{-1}$ < initial aqueous activity < 2500 $kBq{\cdot}L^{-1}$) were provided by the Amersham Co. The ^{22}Na and ^{137}Cs γ spectra were obtained on a detection chain from Interchnique, an EGSP-2000-20R γ spectrometer equipped with germanium detectors. The counting was always sufficiently long to ensure a relative error in activity measurement of less than 5%. The organic diluents, 1,2-nitrophenyl hexyl ether (1,2-NPHE) and 1,2-nitrophenyl octyl ether (1,2-NPOE) used to dissolve **9–15** were synthesized by Chimie Plus and used without further purification.

Transport Measurements. The same flat-sheet supported liquid membrane device described by Stolwijk et al.[18] and shown in Figure 7 was used for the transport experiments. The volume of both aqueous solutions (feed and stripping) was ranging from 45 to 55 mL, depending on the glass devices manufactured by Prodilab and Verre & Science Co. The aereas of circular membranes were about 15–16 cm^2 made of polypropylene Celgard 2500 microporous support (of 25 μm thickness and 45% internal volumic porosity) soaked with a 10^{-2} M solution of **9–15** in 1,2-nitrophenyl octyl ether. The measurements were performed at a constant temperature of 25 °C.

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