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Selective Transport of Cesium and Strontium Ions Through Polymer Inclusion Membranes Containing Calixarenes as Carriers

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Cs^+ and Sr^{2+} are selectively removed over Na^+ from acidic aqueous solutions with high Na^+ concentrations by using membranes designed to selectively transport one of the two cations. To this end, calix[4]arene derivatives were used as carriers in polymer inclusion membranes (PIMs). The synthesis and characterization of new calix[4]arene derivatives (a bisamide (2) and three bisesters (3, 5 and 6)) used for the separation of Sr^{2+} are described. Another bisester (4) was employed for the same separation. In addition, a calix[4]arene-crown-6 (7) was incorporated into the membrane for Cs^+ extraction. The concentration of each membrane component (polymer, carrier and counter-ion) was optimized and the permeability coefficients (*P*, m sec^{-1}) of Cs^+, Sr^{2+} and Na^+ were determined. A synergistic effect between the calixarenes and dinonylnaphtalenesulfonic acid, used as counter-ion, (DNNS, 8) was observed. High selectivity of Cs^+ over Na^+ and of Sr^{2+} over Na^+ were obtained with compounds 7 and 3, respectively. The best *P* for Sr^{2+} was obtained with compound 4. A long-term experiment was carried out to demonstrate the durability of PIMs. PIMs are compared to classical supported liquid membranes.

Keywords: Transport, polymer inclusion membrane (PIM), nuclear waste, calix[4]arenes

INTRODUCTION

The problem concerning the removal of radioactive elements, namely ^{137}Cs and ^{90}Sr (β/γ emitters), from medium level waste [1] (MLW) has been dealt with by coupling separation, based on either chromatography or solvent extraction techniques [2], with precipitation methods [3]. Although these methods effectively reduce waste volumes, they do not entirely solve the problem since they do not remove the unwanted species selectively. As an alternative, selective and nearly complete removal may be achieved by using separation methods based on facilitated transport through liquid membranes [4].

Several membranes have been used for this purpose [5], among them, supported liquid membranes (SLM), the most successful type so far. SLM essentially consist of an organic solution, containing the carrier, that is adsorbed into the pores of a polymeric porous support.

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This polymeric sheet separates two aqueous phases, one of which (the source phase) reproduces the conditions of a waste solution, whereas the other (the receiving phase) is used to collect the transported metal ions. In one interesting configuration the organic solution containing the carrier is confined in the walls of a hollow fiber and is continuously pumped through the aqueous phases [6]. Although this latter method (HFSLM) especially has promise, at least on a bench scale level, SLM-based processes have not been exploited industrially owing to their poor durability [7].

In this context, the preparation of more stable systems, such as polymer inclusion membranes (PIM), represents a step forward towards the solution of the problem mentioned above. In fact, these membranes are stable over a long period of time; in addition, there is virtually no carrier loss to the environment, since the carrier is not simply adsorbed onto a porous matrix but is immobilized into the polymeric membrane, thus reducing carrier leakage to the aqueous phases [8].

Several macrocycles have been employed as carriers for the selective transport of a given cation across the membrane. Calixarenes have turned out to be good candidates for this application [9]. They are of particular interest in that (i) they are lipophilic, which minimizes their loss to the aqueous phases; and (ii) they can be designed to complex several metal ions, in their cavities [10].

Suitably functionalized calixarenes have been employed as carriers in the present study. The most promising ones for the complexation of Cs^+ and Sr^{2+}, as shown from picrate extraction experiments, have been incorporated into the membranes.

The groups used for the functionalization of calixarenes were those shown to be most promising through (i) picrate extraction experiments [11], (ii) chromatographic separations [12], (iii) potentiometric and/or calorimetric titrations [13]. For Sr^{2+}, amide and ester derivatives were chosen because these, together with carboxylates, extracted this ion best. A derivatized calix[4]arene crown-6, was employed for the selective extraction of Cs^+; this ligand was successfully used for the chromatographic separation of Cs^+ from Na^+ in a previous study [14].

RESULTS AND DISCUSSION

Carrier Synthesis and Characterization

The carriers used in the present investigation are shown in Scheme I.

All the syntheses yielded compounds having purities >95%, as indicated by ^{1}H NMR, FAB, TLC and elemental analysis. All new products (**2**, **3**, **5** and **6**) as well as compound **4** adopt a blocked *cone* conformation as shown by the chemical shift of the methylene bridge protons; [15] these give rise to an AX system with a J ranging from 12.9 to 13.6 Hz, which is clearly indicative of a *cone* conformation.

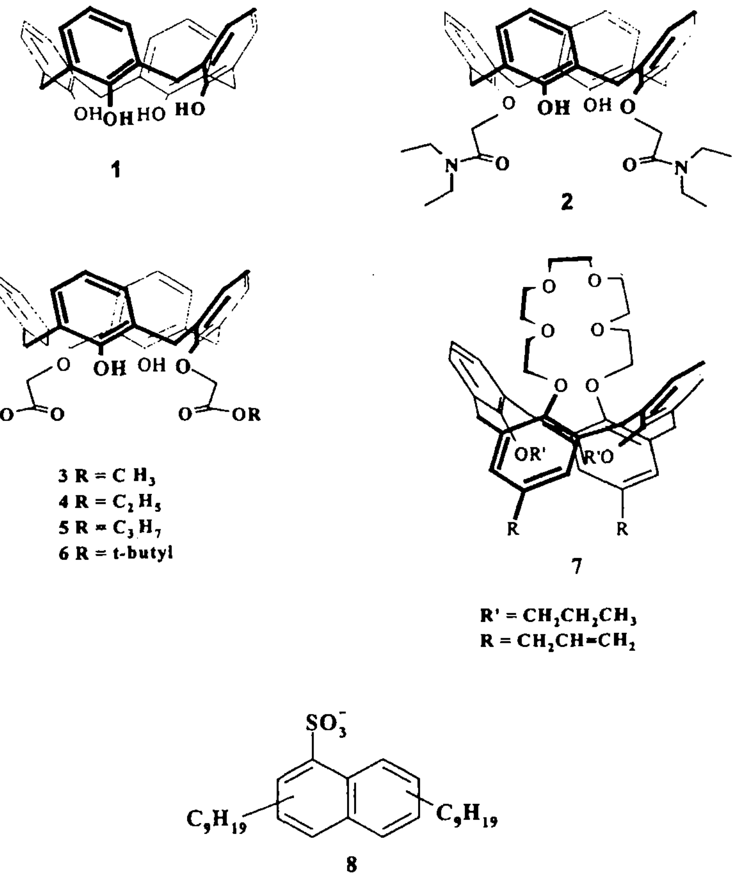
Compound **7** adopts a 1,3-alternate conformation [14].

Transport Kinetics

The kinetics of transport across the membrane may be described as a first order reaction with respect to the cation concentration in the source phase (Sr^{2+}, Cs^+ or Na^+) [16]. Permeability coefficients (P, ms^{-1}) were determined by plotting the logarithm of C_s/C_0 *vs.* time, according to Eq. (1)

$$\ln(C_s/C_0) = -(PS/V)t \qquad (1)$$

where C_s (mol dm^{-3}) is the metal ion concentration in the source phase as a function of time (t, s), C_0 (mol dm^{-3}) is the initial concentration of the cation in the source phase, S (m^2) is the effective membrane area, V (m^3) is the source phase volume. Typical plots are shown in Figure 1.



SCHEME I

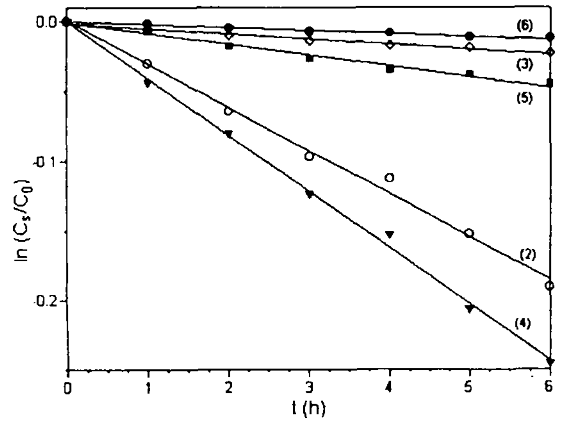


FIGURE 1 Kinetic plots of Sr^{2+} transport through PIMs containing different calixarenes. Numbers refer to the appropriate calixarenes shown in Scheme I.

Optimization of Membrane Components

This section describes the "optimum" conditions for all membrane components, such as supporting polymer, solvent, carrier and membrane counterion.

Supporting Polymer

Cellulose triacetate has been shown to be the polymer of choice for PIM preparation [8, 17]. The amount of CTA used yields membranes that are 40–50μm thick. This thickness is the best compromise between mechanical strength and cation flux. Thicker membranes (having a large

CTA content) have superior mechanical resistance but do not permit good cation flux; thinner membranes show the opposite behavior. In membranes having this optimum thickness, CTA amounts to 15% of the total membrane weight.

Solvent

2-nitrophenyl octyl ether (NPOE) was the solvent employed for membrane preparation. This water-insoluble and non-volatile solvent was previously employed for supported liquid membrane preparation [18]. It acts as (i) polymer plasticizer and (ii) organic solvent for the chemical species to be transported. Membranes which were 60% NPOE showed good mechanical resistance while permitting good cation flux.

Carrier and Counterion

Four different sets of tests were performed to optimize carrier and counterion concentration. These involved the preparation of membranes having (i) varying amounts of carrier (calixarene **2**–**7**) only; (ii) varying amounts of counterion but lacking the carrier; (iii) fixed carrier and varying counterion amounts; and (iv) fixed counterion and varying carrier concentrations. The carrier concentration is expressed in terms of the volume of NPOE employed. For example, Table I shows the results obtained for Sr^{2+} when using **2** as carrier. Step (i) aimed at determining the carrier concentration that produced the best values of permeability coefficients (*P*) of Sr^{2+} or Cs^+ and Na^+. Table I-(i) shows that the permeability coefficients increase with increasing carrier concentration and reach a maximum at 0.185 mol dm^{-3}. *P* decrease when concentrations are greater than 0.2 mol dm^{-3} and this is very likely related to an increase of membrane viscosity.

The tests carried out with DNNS only were prompted by earlier findings that addition of DNNS dramatically increased cation permeability [18].

TABLE I Logarithm of permeability coefficients of Sr^{2+} and Na^+ using (i) different concentrations of carrier **2**; (ii) different concentrations of DNNS; (iii) constant concentrations of carrier **2** and different concentrations of DNNS and (iv) *viceversa**

	C (mol dm^{-3}) carrier **2**	C (mol dm^{-3}) DNNS	log *P* Sr^{2+}	log *P* Na^+
	0.062	0	−8.2	−9.5
	0.123	0	−7.8	−9.3
(i)	**0.185**	**0**	**−7.6**	**−9.1**
	0.246	0	−7.9	−9.5
	0.310	0	−8.3	−9.7
	0	0.434	−9.1	−9.0
(ii)	**0**	**0.868**	**−8.8**	**−8.6**
	0	1.302	−9.2	−8.9
	0	1.736	−9.3	−9.1
	0.185	0	−7.6	−9.1
	0.185	0.434	−7.1	−8.5
(iii)	**0.185**	**0.868**	**−6.4**	**−7.8**
	0.185	1.302	−7.5	−8.8
	0.185	1.736	−7.8	−9.0
	0.062	0.868	−6.9	−8.5
	0.123	0.868	−6.6	−8.0
(iv)	**0.185**	**0.868**	**−6.4**	**−7.8**
	0.246	0.868	−6.7	−8.1
	0.310	0.868	−7.0	−8.5

*All the concentrations are expressed in mol dm^{-3} in NPOE. The standard deviation is 5%.

Table I-**(ii)** shows that (i) cation transport is maximized at DNNS concentrations of *ca* 0.9 mol dm^{-3} (*ca* 25%); and (ii) replacement of the carrier with DNNS produces a virtually unselective (−8.8 *vs.* −8.6) membrane. The same applies to experiments performed with Cs^+ and Na^+. The results obtained when using various calixarene-DNNS combinations (Tab. I-**(iii)** and **(iv)**) show that (i) the carrier and DNNS concentrations which gave the best *P* values in steps (i) and (ii) and also give the best permeability coefficient values when combined; (ii) Sr^{2+} and Na^+ permeability coefficients are 1.2 log units greater than those obtained with the carrier alone; (iii) selectivity of Sr^{2+} over Na^+ achieved in experiments with the carrier alone, is still maintained. Within experimental error, the same results are obtained with calixarenes **3**–**6** for Sr^{2+}–Na^+ and with calixcrown **7** for Cs^+–Na^+ transport experiments.

The dramatic improvement of membrane performance obtained when using the calixarene in conjunction with DNNS is better explained by the graphs reported in Figure 2.

The plots clearly indicate that when only the carrier is present in the membrane, a mere 5% of Sr^{2+} is transported, whereas this jumps to 53% when DNNS is also incorporated in the membrane. This synergistic effect will be discussed in the Transport Mechanism section.

Membrane Stability

Several tests were performed with all the calixarenes described in the present work. These tests have shown that our membranes were stable over a long time period; the average permeability was still 98% after three months. This shows that the calixarenes are effectively "trapped" in the membrane and do not diffuse either into the source or the receiving phase.

All the results obtained using the "optimum" conditions described above are summarized in Table II.

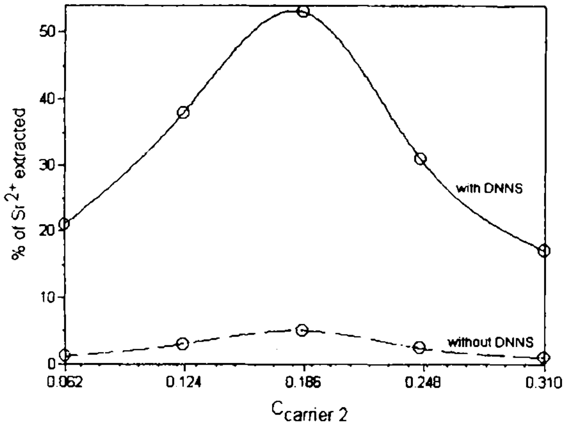


FIGURE 2 Percentages of Sr^{2+} extracted as a function of the carrier concentration (**2**) with (solid line) and without (broken line) DNNS. The percentages of Sr^{2+} extracted were determined at t=24 h.

TABLE II Logarithm of permeability coefficients of Sr^{2+}, Na^+, and Cs^+ using the best optimal concentrations of carrier (0.185 mol dm^{-3} in NPOE) and DNNS (0.868 mol dm^{-3} in NPOE).*

Carrier	log P Sr^{2+}	log P Na^+	log P Cs^+
2	−6.4	−7.8	
3	−7.3	−8.8	
4	−6.3	−7.5	
5	−7.0	−7.3	
6	−7.6	−6.9	
7		−8.5	−5.6

*All the concentrations are expressed in mol dm^{-3} in NPOE. The standard deviation is 5%.

Sr^{2+}/Na^+ Separation

Neither carrier **5** nor carrier **6** can be exploited for transport purposes; in fact, **5** shows little Sr^{2+}/Na^+ selectivity (0.3 log units), whereas **6** shows a slight preference for Na^+ over Sr^{2+}. Carriers **2**, **3** and **4**, provide rather interesting results. The methylic bis-ester (**3**) shows a selectivity for Sr^{2+} over Na^+ (expressed by the difference between the log P values) greater than that shown by the ethylic bis-ester (**4**) (1.5 *vs.* 1.2 logarithmic units). However, this latter carrier gives a Sr^{2+} permeability coefficient larger than that obtained with **3** (−6.3 *vs.* −7.3). The bisethylamide derivative **2** is intermediate in that it transports Sr^{2+} over Na^+ with a selectivity close to that of **3** (the most selective carrier of the series) and has a log P that is 0.1 lower than that of **4** (the carrier yielding greatest permeability); thus, **2** turns out to be the best compromise for Sr^{2+} separation. Compared to **3**, the greater permeability observed with **4** can be ascribed to the larger stability of its Sr^{2+} complex, as indicated by picrate extraction experiments.

Cs^+/Na^+ Separation

Good permeability values for Cesium were obtained only with **7** (Tab. II). The incorporation of **7** into the membrane produces permeability coefficients for Cesium comparable to those obtained using similar calixarenes in SLM [19, 20]. However, the addition of DNNS causes an increase of P, and as much as 45% of the Cesium is transported to the receiving phase after three hours only, compared to 18% transported in the absence of DNNS. Cs^+/Na^+ selectivity is very good (−5.6 *vs.* 8.5). Such selectivity results from the almost ideal fit of Cs^+ into the ligand cavity. In addition, the presence of two allyl groups and two propyl chains at the upper and lower rim, respectively, increases the lipophylicity of the calixcrown, which, in turn, renders the membrane very stable even after exposure to the two aqueous phases for a long period of time.

Transport Mechanism

The mechanism of transport across supported liquid membranes has been reviewed recently by Reinhoudt [21]. The model proposed implies that (i) the carrier is actually immobilized in the membrane and does not diffuse into the aqueous phases; (ii) the salt (complexed cation + counter ion) is totally dissociated in the membrane; (iii) the transport mechanism is diffusion controlled. The same transport mechanism may be used for the PIM. In the first step, the cations (Sr^{2+}, Na^+ or Cs^+) diffuse through the boundary layer together with their counter ions (NO_3^-). This diffusion is accelerated in the presence of DNNS for reasons that will be discussed below. In the second step, the cation forms a membrane-bound complex with the calixarene carrier; membrane neutrality is maintained by NO_3^-. The calixarene complex (together with NO_3^- ions) diffuse across the membrane. In the final step, both the cation and the anion are released into the receiving phase and the uncomplexed host is ready to complex another cation again. When the cation salt to be transported is the only species present in the source phase, this process ends when an equilibrium condition is reached between the two phases, *i.e.*, when 50% of the cation has been moved from the source to the receiving phase. However, when, as in our case, a salt of the cation not to be transported (*e.g.*, $NaNO_3$) is also present in large excess in the source phase, the anion gradient rather than the cation gradient provides the driving force [22]; this can result in the virtually total extraction of the desired species from the source phase. Under favorable conditions, as much as 98.5% of Cs^+ and 60% of Sr^{2+} are removed within the first 24 hours by carrier 7 and carrier 4, respectively (Fig. 3).

Our results also show that there is a synergistic effect between the carrier and DNNS. In fact, (i) the presence of DNNS increases the permeability coefficient of all the ions investigated, and (ii) the selectivity of all carriers remains unchanged in the presence of DNNS. These results show that DNNS influences the rate of transport only while leaving selectivity unchanged. DNNS, a surfactant, when immobilized in the membrane polymer will expose its polar groups (SO_3^-) to the aqueous phase while leaving the apolar tail directed towards the interior of the membrane. As shown by an elegant molecular dynamics study presented by Wipff recently for water–chloroform interfaces containing calixarenes [23] or podands [24] as carriers, the disposition of negative charges at the boundary layer drives the cations thus facilitating the complexation by the membrane immobilized carrier. This is possible since at the pH of the source phase a large fraction of DNNS is still in its unprotonated form. The transport rate increases since the number of cation particles in

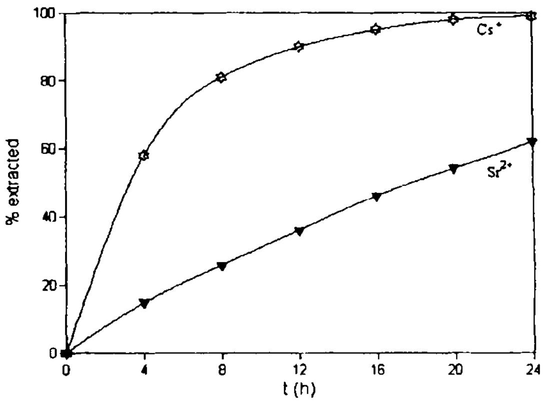


FIGURE 3 Percentages of Cs^+ and Sr^{2+} extracted by carriers 7 and 4, respectively, as a function of time.

the boundary layer increases. The results shown in Table II are in line with this interpretation; in fact DNNS increases *P* only while it has practically no effect on the selectivity. To support this explanation we have run a few tests, increasing the acid concentration of the source phase from 0.1 to 1.0 mol dm^{-3}. As shown in Figure 4, log *P* decreases as the acid concentration increases. This shows that as the fraction of DNNS which is protonated increases, the capability of DNNS to "concentrate" the cations at the boundary layer decreases, owing to the decreased negative charge density.

CONCLUSIONS

The calixarene carriers investigated in the present work are able to separate Cs^+ and Sr^{2+} from Na^+ with relatively high permeability coefficient values. Calixarenes are amenable to a variety of substitutions that can modulate their cavity sizes, the upper and lower rim substituents as well as their lipophylicity. Compared to SLM, PIMs (i) require a lesser amount of carrier (*ca* 4%) be immobilized and (ii) are stable over long time intervals. Risk of carrier loss to the aqueous phases is almost *nil* as demonstrated by the stability of the polymeric membrane over time intervals as long as 3 months.

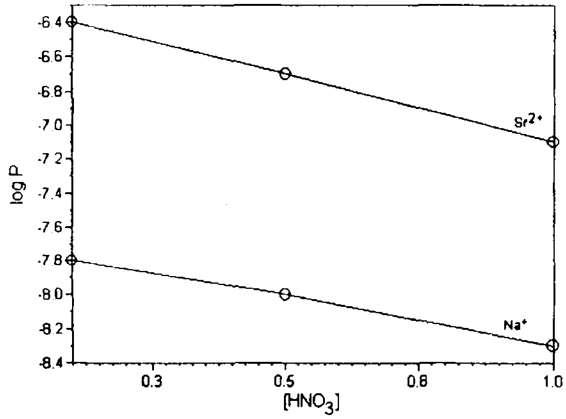


FIGURE 4 Logarithm of permeabilities of Sr^{2+} and Na^+ determined with carrier **2** as function of the concentration of HNO_3.

MATERIALS AND METHODS

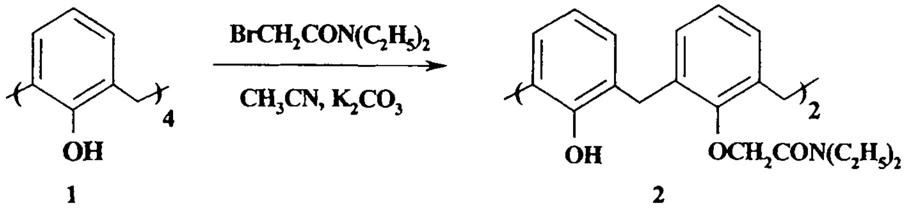
Ligand Synthesis and Characterization

Melting points were determined on a Büchi 500 apparatus in capillaries sealed under nitrogen. 1H NMR and ^{13}C NMR spectra were recorded with a Varian Gemini 300 spectrometer with Me_4Si as internal standard. Mass spectra were performed using the JEOL JMS-SX 102A spectrometer (FAB using 3-nitrobenzyl alcohol as a matrix). In the NMR spectra, the ⟨⟨Ar⟩⟩ notation indicates the aromatic nuclei of the calixarene backbone, considering the phenol oxygen as the main substituent to which the *ipso*, *ortho*, *meta*, and *para* position refer. Elemental analyses were obtained with a Elemental analyzer EA6059 (Carlo Erba Instruments). Analytical TLC were performed on precoated silica gel plates (SiO_2, Merck, 60 F_{254}).

Methanol, hexane, bromoalkylacetates (alkyl=methyl, propyl, *t*-butyl), potassium carbonate and magnesium sulfate were commercial reagents by Aldrich and were used without further purification. Acetonitrile (Carlo Erba-RPE) was dried over molecular sieves (3Å). Dichloromethane by LabScan was dried over calcium chloride before use. 2-bromo-*N*,*N*-diethylacetamide was prepared according to the procedure described in the reference [25]. Compound **1**, 25,27-bis(ethoxycarbonylmethoxy) calix[4]arene (**4**) and 5,17-bis-(1-allyl)-25,27-bis-(1-propyloxy) calix[4]arene-crown-6 1,3 alternate (**7**) were prepared as described in Refs. [26, 27, 14] respectively.

25,27-bis(*N*, *N*-diethylaminocarbonylmethoxy) calix[4]arene (**2**) was synthesized according to Scheme II.

Potassium carbonate (0.53 g; 3.88 mmol) was added to a suspension of calix[4]arene **1** (1.5 g; 3.53 mmol) in acetonitrile (150 mL). The mixture



SCHEME II

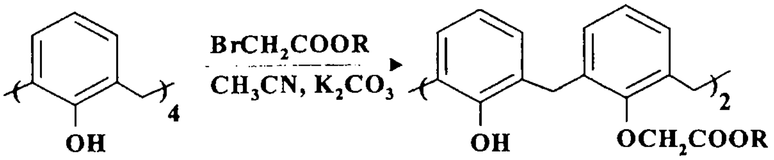
was stirred at room temperature for half an hour. 2-bromo-*N,N*-diethylacetamide (1.37 g; 7.06 mmol) was then added and the reaction was kept under stirring and refluxed for 15 h. The course of the reaction was monitored by TLC using hexane: ethylacetate (7:3) as developing solvents. Then, the solvent was removed under reduced pressure and the residue was quenched with 50 mL of 10%HCl and 50 mL of dichloromethane. The organic phase was separated and washed with a saturated solution of NH_4Cl (50 mL) and then with distilled water (50 mL). Dichloromethane solution was dried over anhydrous $MgSO_4$ and distilled off to yield a white solid which was crystallized from a mixture of dichloromethane and methanol (1:6) to give a pure compound. Yield 85%. m.p. 198–200 °C. ^1H NMR ($CDCl_3$) δ 8.14 (s, 2H, OH), 6.99 and 6.92 (d, J=7.5 Hz, 4H each, ArH meta), 6.75 and 6.59 (t, J=7.3, 4H each, ArH para), 4.78 (s, 4 H, OCH_2C), 4.50 (d, J=13.2 Hz, 4H $ArCH_2$-Ar), 3.48 (2q, 8H, NCH_2), 3.36 (d, J=13.2 Hz, 4H $ArCH_2Ar$), 1.27 and 1.20 (2t, 12H, NCH_2CH_3). 13C NMR ($CDCl_3$) δ 167.04 (C=O), 153.48 and 152.55 (Ar ipso), 133.71 and 129.01 (Ar ortho), 128.30 and 128.08 (Ar meta), 125.29 and 118.81 (Ar para) 73.76 (OCH_2C), 41.11 and 40.09 (NCH_2CH_3), 31.6 ($ArCH_2Ar$), 14.26 and 12.91 (NCH_2CH_3). MS (FAB, positive), 650.2. (M^+ calcd 650.8). Anal. Calcd for $C_{40}H_{46}N_2O_4$: C, 73.82; H, 7.12; N, 4.30. Found C, 73.85; H, 7.08; N, 4.38.

The typical procedure followed for the synthesis of 25,27-dialkylestercalix[4]arene (**3**, **5** and **6**) is illustrated in Scheme III.

1 (2.04 g, 4.80 mmol), and potassium carbonate (0.72 g, 5.20 mmol) were dissolved in acetonitrile (150 mL) and placed in a 250 mL round-bottomed flask, equipped with a condenser. The reaction mixture was stirred at room temperature for 30 min. Bromoalkylacetate (9.90 mmol) was added, and the mixture was refluxed for 8 h. The course of the reaction was monitored by TLC using hexane:ethylacetate (8:2) as developing solvents. The solvents were removed *in vacuo* after cooling down to room temperature. The residue was dissolved in dichloromethane (70 mL) and extracted with 1 N HCl. The organic layer was dried over anhydrous $MgSO_4$. The filtered solution was concentrated and precipitated with dichloromethane:methanol (1:4) to yield pure products **3**, **5** and **6** as white solids.

25,27-bis(methoxycarbonylmethoxy) calix[4]arene (3)

Yield 78%; m.p. 168–170 °C. ^1H NMR ($CDCl_3$) δ 7.54 (s, 2H, OH), 7.04 and 6.90 (d, J=7.5 Hz, 4H each, ArH meta), 6.74 and 6.65 (t, J=7.2, 4H each, ArH para), 4.74 (s, 4H, OCH_2C), 4.46 (d, J=12.9 Hz, 4H $ArCH_2Ar$), 3.86 (s, 6H, OCH_3), 3.38 (d, J=12.9 Hz, 4H, $ArCH_2Ar$). ^{13}C NMR ($CDCl_3$) δ 169.28 (C=O), 152.90 and 152.25 (Ar ipso), 133.13 and 129.14 (Ar ortho), 128.49 and 128.17 (Ar meta), 125.60 and 119.18 (Ar para), 72.53 (OCH_2C), 52.20 ($COOCH_3$), 31.43 ($ArCH_2$-Ar). MS (FAB, positive), 568.1. (M^+ calcd 568.6). Anal. Calcd for $C_{34}H_{32}O_8$: C, 71.82; H, 5.67. Found C, 71.85; H, 5.58.



1

3 R = CH_3,
5 R = C_3H_7,
6 R = t-butyl.

3, 5 and 6

SCHEME III

25,27-bis(propoxycarbonylmethoxy) calix[4]arene (5)

Yield 82%; m.p. 183–184 °C. ^{1}H NMR ($CDCl_3$) δ 7.59 (s, 2H, OH), 7.04 and 6.90 (d, J=7.5 Hz, 4H each, ArH meta), 6.76 and 6.47 (t, J=7.2 Hz, 4H each, ArH para), 4.73 (s, 4H, OCH_2C), 4.48 (d, J=13.2 Hz, 4H $ArCH_2Ar$), 4.23 (t, 4H, OCH_2C), 3.39 (d, J=13.2 Hz, 4H, $ArCH_2Ar$), 1.74 (m, 4H, $OCH_2CH_2CH_3$), 0.99 (t, 6H, $OCH_2CH_2CH_3$). ^{13}C NMR ($CDCl_3$) δ 168.97 (C=O), 152.98 and 152.41 (Ar ipso), 133.12 and 129.11 (Ar ortho), 128.45 and 128.11 (Ar meta), 125.54 and 119.06 (Ar para), 72.43 (OCH_2C), 66.99 ($OCH_2CH_2CH_3$), 31.43 ($ArCH_2Ar$), 21.91 ($OCH_2CH_2CH_3$), 10.35 ($OCH_2CH_2CH_3$). MS (FAB, positive), 624.2. (M^+ calcd 624.7). Anal. Calcd for $C_{38}H_{40}O_8$: C, 73.06; H, 6.45. Found C, 73.18; H, 6.38.

25,27-bis(1,1dimethylethoxycarbonylmethoxy) calix[4]arene (6)

Yield 90%; m.p. 195–196 °C. ^{1}H NMR ($CDCl_3$) δ 7.68 (s, 2H, OH), 7.06 and 6.89 (d, J=7.5 Hz, 4H each, ArH meta), 6.73 and 6.54 (t, J=7.2 Hz, 4H each, ArH para), 4.59 (s, 4H, OCH_2C), 4.48 and 3.39 (d, J=13.6 Hz, 4H each, $ArCH_2Ar$), 1.57 (s, 18H, $OC(CH_3)_3$). ^{13}C NMR ($CDCl_3$) δ 168.24 (C=O), 153.14 and 152.54 (Ar ipso), 133.04 and 129.04 (Ar ortho), 128.42 and 128.00 (Ar meta), 125.41 and 118.85 (Ar para), 82.44 ($COOC(CH_3)_3$), 73.18 (OCH_2C), 31.48 ($ArCH_2Ar$), 28.12 (COOC $(CH_3)_3$). MS (FAB, positive), 652.2. (M^+ calcd 652.8). Anal. Calcd for $C_{40}H_{44}O_8$: C, 73.60; H, 6.79. Found C, 73.85; H, 6.58.

Membrane Preparation and Transport Experiments

Sodium nitrate, strontium nitrate, cesium nitrate, cellulose triacetate (CTA), 2-nitrophenyl octyl ether (NPOE), lithium acetate, lithium hydroxide and H_4EDTA were commercial reagents (Aldrich) and were used without further purification. Nitric acid was purchased from Mallinkrodt; its solutions were standardized by titration with standard NaOH solutions (Fisher). Commercial dinonylnaphtalenesulfonic acid (DNNS, 8) was obtained from Alpha as a 50% (w/v) solution and could not be used as such owing to the presence of heptane.

For this reason, the solvent was completely removed by reduced pressure using a rotary evaporator before DNNS could be used for membrane preparation. The solid compound was dissolved in dichloromethane and the solution was titrated against alcoholic NaOH. The concentration value was used to make up stock solutions of DNNS in dichloromethane (the solvent employed for membrane preparation).

Typically source phases, prepared to mimic nuclear wastes, were 1 mol dm^{-3} in $NaNO_3$, 0.1 mol dm^{-3} in HNO_3 and 0.1mmol dm^{-3} in either $CsNO_3$ or $Sr(NO_3)_2$. Li_4EDTA (in combination with lithium acetate) was used in the receiving phase to improve the transport rate of

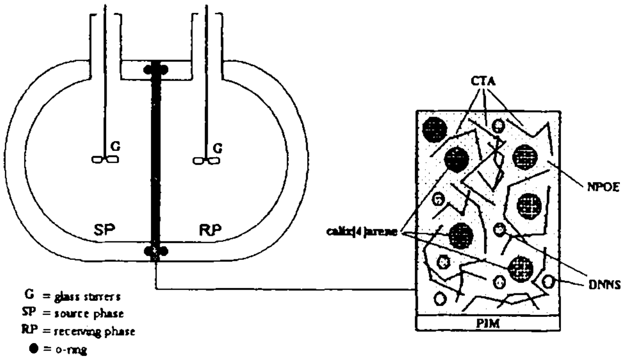


FIGURE 5 Experimental apparatus. In the PIM enlargement, calix[4]arene represents the appropriate calixarene used for the experiment.

Sr^{2+} without changing the percentage of Sr^{2+} transported. For comparison purposes, Li_4EDTA was also used in the experiments involving Cs^+ even though the EDTA salt did not have any influence on this process.

Membranes were made by combining (i) a solution made by dissolving 1.25 g of CTA in 727 mL of dichloromethane, (ii) 0.30 mL of NPOE and (iii) appropriate amounts of calixarene solution in dichloromethane and DNNS (10% w/v in dichloromethane) in a 9 cm Petri glass dish. The dish was covered and allowed to stand for approximately 15–16 hours until complete evaporation of the dichloromethane was achieved, and the CTA membrane was set.

The polymeric membrane obtained was carefully placed between two 727 mL cylindrical glass cells and sealed with a rubber O-ring, as shown in Figure 5.

The area of the membrane exposed to the two aqueous solutions was *ca* 21.8 cm^2. Both source and receiving phases were stirred with glass propellers at 600 rpm. Periodically, 1 mL samples were taken from the source phase to monitor the transport process and replaced with 1 ml of distilled, deionized water.

Experiments were performed at 25°C at least three times. The standard deviation in these measurements is at most 5%.

The concentration of transported ion was monitored by a Perkin-Elmer inductively coupled plasma II emission spectrometer (Na^+ and Sr^{2+}) or by a Perkin-Elmer (2380) Atomic Emission Spectrophotometer with an air-acetylene flame (Cs^+). In both cases a standard calibration curve covering the entire concentration range explored was determined in separate experiments.

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