

# Nuclear Waste Treatment by Means of Supported Liquid Membranes Containing Calixcrown Compounds<sup>\*</sup>

C. HILL, J.-F. DOZOL<sup>\*\*</sup>, V. LAMARE, H. ROUQUETTE, S. EYMARD and B. TOURNOIS

*S.E.P./S.E.T.E.D. Centre d'Etudes de Cadarache, Commissariat à l'Energie Atomique (C.E.A.), 13108 Saint-Paul-lez-Durance, France*

J. VICENS, Z. ASFARI and C. BRESSOT

*Ecole Européenne des Hautes Etudes des Industries Chimiques de Strasbourg, France*

and

R. UNGARO and A. CASNATI

*Dipartimento di Chimica Organica e Industriale, Università degli Studi di Parma, Italy*

(Received: 11 May 1994; in final form: 27 July 1994)

**Abstract.** Permeability variation with repeated caesium transport experiments has been chosen to measure the leaching of the supported liquid membrane by the contacting aqueous solutions. This allowed us to characterize the SLM stability. Whereas classical crown ethers such as the widely used 21C7 derivatives were revealed to be poorly efficient and poorly stable in SLMs, crown-6-calix[4]arene compounds in the so-called *1,3-alternate* configuration led to very stable (over 50 days), highly selective (concentration factor > 100) and efficient (decontamination factor = 20) SLMs, for the removal of caesium from high salinity and acidity media. These results were achieved by using proper organic diluents and introducing hydrophobic substituents in the frame of the calixarenes.

**Key words:** Caesium, calixcrown, transport, SLM stability.

## 1. Introduction

Nuclear fuel reprocessing operations produce both high and medium level activity liquid wastes (HLW/MLW). The major nuclides in these radioactive wastes are those with long half-lives, mainly  $\beta/\gamma$  emitters such as: Tc, I, Zr, Se, Cs, etc., or  $\alpha$  emitters such as transuranics: Np, Pu, Am, Cm, etc. [1]. That is why great efforts have been devoted throughout the world to propose harmless storage of these wastes.

The burial of vitrified reprocessed HLWs (containing fission products and  $\alpha$  emitters) has been considered as the safest method for their permanent disposal [2], whereas MLWs are treated by evaporation or other conventional techniques such as

<sup>\*</sup> This paper is dedicated to the commemorative issue on the 50th anniversary of calixarenes.

<sup>\*\*</sup> Author for correspondence.

chemical precipitation, ion exchange, etc., in order to concentrate their radioactivity into the smallest possible volume [3]. This treatment nevertheless leads to large volumes of concentrates composed of active and inactive salts (mainly:  $\text{NaNO}_3$ :  $4 \text{ mol L}^{-1}$  and  $\text{HNO}_3$ :  $1 \text{ mol L}^{-1}$  as the matrix). The greater part of these concentrates has to be disposed of in geological formations after embedding due to their activity in long-life radionuclides (actinides, strontium, caesium, etc.).

Therefore it would be desirable to remove these very long-life radionuclides from the contaminated liquid wastes before embedding, in both the above mentioned scenarios of treatment and storages. This would allow, on the one hand, the volume and the radiotoxicity of the wastes to be reduced, and, on the other hand, part of these decontaminated wastes to be directed to surface repositories. This goal could be achieved by separating the long-life radionuclides from the matrix and turning them into short-life radionuclides or at least into nonradioactive elements through transmutation.

One chemical separation process among others such as liquid–liquid extraction by specific extractants, or chemical precipitation to decontaminate HLWs and/or MLWs, could be *coupled transport* through supported liquid membranes (SLM) using specific carriers [4–5].

## 2. Process Description

A SLM consists of an organic liquid solution (mixture of an organic diluent and a carrier) absorbed by capillary forces onto a microporous support separating two aqueous solutions [6–8]: the first solution, referred to as the *feed solution* containing the permeating ions, is the solution of waste to be decontaminated, and the second solution, referred to as the *stripping solution*, initially free of ions (demineralized water) receives and concentrates the selectively transported radionuclides.

SLMs containing selective carriers (ionophores) give higher fluxes and selectivities than conventional semipermeable porous polymeric membranes, because diffusion is faster in liquids than in solids. The carrier dissolved in the liquid membrane favours the distribution of one species out of a mixture by specific complexation and extraction, if properly chosen [9].

Although they have not yet been industrially applied, SLMs are of great interest both for potential technological applications (in hollow fibers), and for basic research (in flat sheet SLMs) to determine the transport mechanisms. Because they require only small amounts of organic solutions, SLMs allow the study of very sophisticated tailor-made compounds. Unfortunately, one of their major drawbacks is their great instability. This instability is caused by the disfavoured volume ratio between the aqueous solutions and the organic membrane, which leads to substantial partitioning of the diluent and/or the carrier in the aqueous solutions [10].

That is why very lipophilic carriers and very hydrophobic diluents have to be used to avoid their partitioning. Membrane stability can be improved by choosing the proper diluent of high interfacial tension with water and low water solubility,

TABLE I. Physico-chemical characteristics of organic diluents.

Alkyl group	Mol. weight (g mol <sup>-1</sup> )	Density (g cm <sup>-1</sup> )	Dielectric Cst. (Debye)	Viscosity (centipoise)	Surface tension (dynes cm <sup>-1</sup> )
Hexyl	223.3	1.066	25.7	8.9	34.3
Octyl	251.3	1.036	31.8	12.4	34.3

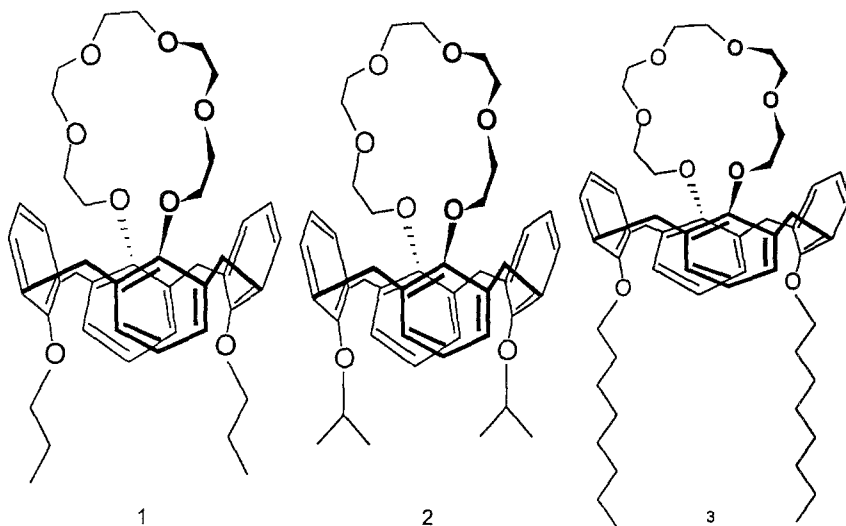


Fig. 1. 1,3-Dialkoxy-2,4-crown-6-calix[4]arenes (compounds 1, 2, 3) in the 1,3-alternate conformation.

lower surface tension than the solid microporous support (e.g.: 35 dynes cm<sup>-1</sup> for polypropylene), high boiling-point, etc., such as Nitrophenylalkylethers (number of carbon atoms > 5) and modified carriers with hydrophobic alkyl or aryl groups [10–12].

### 3. Experimental

#### 3.1. REAGENTS

The organic diluents: 1,2-nitrophenylhexyl/octylether (*o*-NPH/OE), were synthesized at the CHIMIE PLUS laboratory and used without further purification. Their physico-chemical characteristics are summarized in Table I. The tested mono-crown-6-calix[4]arene compounds 1, 2 and 3 (Figure 1) were synthesized by Professor R. Ungaro of the University of Parma, in the framework of a European Community program collaboration with the French Atomic Energy Commission (CEA). The bis-crown-6-calix[4]arene compounds 4, 5, 6, 7 and 8 (Figure 2) were synthesized by Drs. J. Vicens and Z. Asfari of the University of Strasbourg (E.H.I.C.S.) [13].

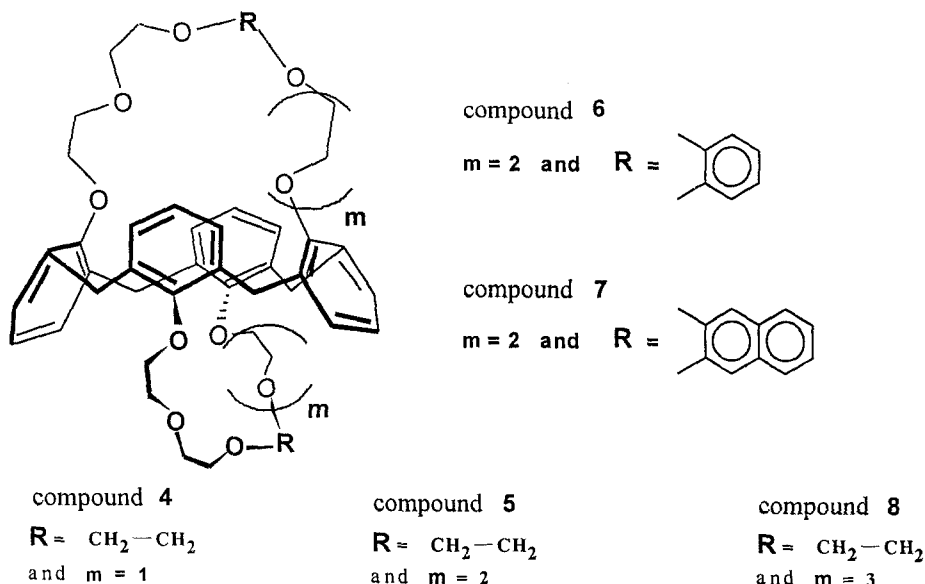


Fig. 2. Bis-crown-calix[4]arenes (compounds 4, 5, 6, 7 and 8).

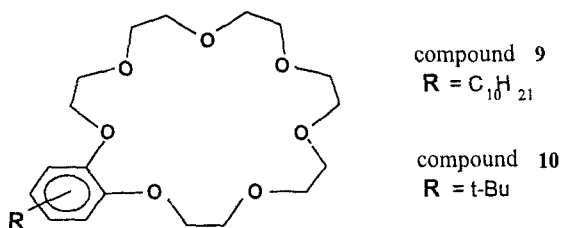


Fig. 3. Compound 9: *n*-decyl-benzo-21-crown-7. Compound 10: *t*-butyl-benzo-21-crown-7.

The inorganic salts used to prepare the synthetic feed solutions ( $\text{NaNO}_3$ ,  $\text{HNO}_3$ ) were analytical-grade products from Prolabo and Aldrich. Radioactive  $^{137}\text{Caesium}$  was provided by the Amersham company.

### 3.2. CAESIUM EXTRACTION

In the search for specific extractants able to achieve sufficiently high separation rates of the major radionuclides of interest (*vide supra*), substituted calixarenes are new macrocycles in addition to crown ethers or cryptands which promise selective complexation and high extraction yields.

For the removal of caesium from HLW to MLW, for instance, crown ethers (compounds 9 and 10, Figure 3) are well known for their ability to complex and extract alkali cations from acidic media. The stability of the complexes is linked to the relative size of the cavity of the crown ether as compared to the complexed

cation: the most strongly bound cation is the one which best fits into the crown cation, according to the *complementarity principle* [15–18].

Unfortunately, caesium (0.338 nm) which corresponds to the cavity of 21-crown-7 derivatives (0.34–0.43 nm), is not efficiently and selectively extracted from ML concentrates which contain large amounts of sodium salts and nitric acid as the inactive matrix [4].

On the other hand, crown-6-calix[4]arene compounds which consist of a calixarene frame (i.e., phenolic units *meta*-linked by methylene groups) in the so-called *1,3-alternate* conformation (where two opposite phenolic units are flipped upward and bridged with a polyethylene glycol chain of various length, Figure 1, compounds **1**, **2**, **3**), simultaneously offer the selectivity of crown compounds through the polyether-chain ring size, and the preorganization of calixarenes fixed in a more or less rigid conformation [19–21].

The two remaining phenolic units are either derived with long alkyl chains to enhance carrier lipophilicity or bridged with a second polyethylene glycol chain to rigidify the calixarene frame leading to bis-crown-calix[4]arene (Figure 2: compounds **4**, **5**, **6**, **7** and **8**).

Although these latter compounds present two potential complexing sites, complex stoichiometry studies have proved that it was of the 1 : 1 type (calixarene : caesium cation). Moreover, introducing aryl substituents such as phenyl or naphthyl into the polyether ring(s) (**6**, **7**) greatly enhances the *carrier lipophilicity* which favours SLM stability.

These two properties (complementarity and preorganization) lead to great efficiency and selectivity by favouring the distribution of caesium cations over that of sodium cations. Table II summarizes some extraction results obtained with calixcrown compounds and classical crown ethers on simulating synthetic MLW solutions. Extraction experiments were performed by mixing equal volumes (5 to 7 mL) of aqueous and organic solutions in sealed tubes for an hour. Aliquots of each phase were analyzed by  $\gamma$  spectrometry after centrifugation. The selectivity of the tested compounds towards caesium, in the presence of sodium, is expressed as the ratio of the distribution coefficients obtained separately for both cations:

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

where  $\sum[\bar{M}]$  denotes the metal species total concentration in the organic phase and  $\sum[M]$  the metal species total concentration in the aqueous phase.

As shown in Table II, calixcrown compounds containing six oxygen atoms in the ring(s) are much more selective than classical crown ethers. The complexes best formed with the least hydrated alkali cations (caesium) are probably stabilized by the  $\pi$ -bonding interactions arising from the phenyl rings of the *1,3-alternate* phenolic units of the calixcrown compounds [22].

TABLE II. Liquid-liquid extraction experiments: selectivity  $\alpha_{(Cs/Na)}$  determination. Aqueous feed solution:  $M^+(\text{NO}_3^-)$ :  $5 \times 10^{-4} \text{ mol L}^{-1}$  in  $\text{HNO}_3$ :  $1 \text{ mol L}^{-1}$ . Organic solution: extracting agent:  $0.01 \text{ mol}^{-1}$  in *o*-NPHE.

No.	Extracting agent used	$D_{\text{Na}}$	$D_{\text{Cs}}$	$\alpha_{\text{Cs/Na}}$
1	1,3-dipropoxy-2,4-crown-6-calix[4]arene	$1.8 \times 10^{-3}$	<b>19.2</b>	<b>10 500</b>
2	1,3-diisopropoxy-2,4-crown-6-calix[4]arene	$< 10^{-3}$	<b>28.5</b>	<b>&gt; 28 500</b>
3	1,3-di( <i>n</i> -octyloxy)-2,4-crown-6-calix[4]arene	$< 10^{-3}$	<b>33</b>	<b>&gt; 33 000</b>
4	bis-crown-5-calix[4]arene	$2.3 \times 10^{-3}$	0.5	220
5	bis-crown-6-calix[4]arene	$1.3 \times 10^{-2}$	<b>19.5</b>	<b>1500</b>
6	bis-(1,2-benzo-crown-6)-calix[4]arene	$1.7 \times 10^{-3}$	<b>32.5</b>	<b>19 000</b>
7	bis-(1,2-naphtho-crown-6)-calix[4]arene	$< 10^{-3}$	<b>29.5</b>	<b>&gt; 49 000</b>
8	bis-crown-7-calix[4]arene	$< 10^{-3}$	0.3	> 300
9	<i>n</i> -decyl-benzo-21-crown-7	$1.3 \times 10^{-3}$	0.3	250
10	<i>t</i> -butyl-benzo-21-crown-7	$1.3 \times 10^{-3}$	0.3	250

### 3.3. TRANSPORT EXPERIMENTS

The transport of ions through the SLM occurs because a chemical gradient is established between the *feed solution* and the *stripping solution*. The use of neutral carriers such as calixcrown compounds leads to the coupled cotransport of cations and anions through the SLM [20]. When concentrates or fission product solutions are used as the *feed solution* and demineralized water as the *stripping solution*, the concentration gradient of the nitrate anions will force the transport of caesium cations against their own concentration gradient, thus leading to a concentration of radioactive caesium in the stripping solution. Nevertheless, the basicity as well as the polarity of the organic diluent that we have chosen to use in order to improve caesium extraction – by a better solvation of the complex paired anion in the membrane (nitrates are hydrated anions not easily extracted in major conventional organic solvents) – lead to substantial transport of nitric acid from the feed to the stripping solution. This reduces caesium permeation through the SLM by decreasing the nitrate concentration gradient.

#### 3.3.1. Permeability Determination

The transport of caesium from synthetic aqueous solutions of  $\text{NaNO}_3$ :  $4 \text{ mol L}^{-1}/\text{HNO}_3$ :  $1 \text{ mol L}^{-1}$ , spiked with  $^{137}\text{Cs}$  ( $\# 2000 \text{ kBq L}^{-1}$ ) was followed by regular measurement of the decrease of radioactivity in the feed solution by  $\gamma$  spectrometry analysis, using a detection chain from Intertechnique, equipped with germanium detectors. The counting was always sufficiently long to insure a relative error in the activity measurements of less than 5%. This allowed graphical determination of the constant permeabilities  $P_M$  ( $\text{cm h}^{-1}$ ) of caesium cation per-

meation through the SLM for 6–7 h by plotting the logarithm of the ratio  $C/C^0$  versus time, as described in the model of mass transfer proposed by P. Danesi [5]:

$$\ln \left( \frac{C}{C^0} \right) = -\frac{\varepsilon S}{V} P_M t, \quad (1)$$

where  $C$  = concentration of the cation in the feed solution at time  $t$  ( $\text{mol L}^{-1}$ );  $C^0$  = initial concentration of the cation in the feed solution ( $\text{mol L}^{-1}$ );  $\varepsilon$  = volumic porosity of the SLM (%);  $S$  = membrane surface area ( $\text{cm}^2$ );  $V$  = volume of feed and stripping solution (mL); and  $t$  = time (h).

If experiments are performed under the same conditions (stirring rates, concentration gradients) determination of the permeabilities  $P_M$  allows the selectivity and efficiency of different tested carriers to be characterized and quantified.

With certain assumptions (limited diffusion and controlled process), the permeabilities  $P_M$  can be evaluated by the formula:

$$P_M = \frac{D_M}{D_M \Delta_a + \Delta_o}, \quad (2)$$

where  $D_M$  is the distribution coefficient of the permeating cation;  $\Delta_a$  is the ratio of the thickness of the aqueous diffusion boundary layer to the aqueous diffusion coefficient;  $\Delta_o$  is the ratio of the thickness of the membrane to the organic diffusion coefficient.

Expression (2) shows that under certain conditions where  $\Delta_a$  is constant throughout the experiments and  $D_M \Delta_a$  negligible in front of  $\Delta_o$ ,  $P_M$  is proportional to  $D_M$  (and  $D_M$  directly depends on the actual organic carrier concentration in the SLM).

When repeated transport experiments are performed, in which both the aqueous feed and receiving solutions are renewed every day while the membrane remains the same as in the first run, daily partitioning of the carrier from the SLM to the renewed aqueous solutions causes a decrease of the carrier concentration in the membrane and thus a decrease of  $D_M$  and proportionally of  $P_M$ . The evolution of the permeability measurements versus the number of runs is a way to describe SLM leaching by the aqueous solutions and characterizes SLM stability in time.

### 3.3.2. Materials and Device

We used a thin flat sheet SLM device described by T. Stolwijk [23] and shown in Figure 4. The volume of both aqueous solutions was 50 mL. The membrane was a Celgard<sup>Å</sup> 2500 (of 25  $\mu\text{m}$  thickness and 45% volume porosity) polypropylene microporous support soaked with a solution  $10^{-2} \text{ mol L}^{-1}$  of the tested calixarenes in 1,2-nitrophenyloctylether (*O*-NPOE). The surface area of the membrane was about 15–16  $\text{cm}^2$ , depending on the device.

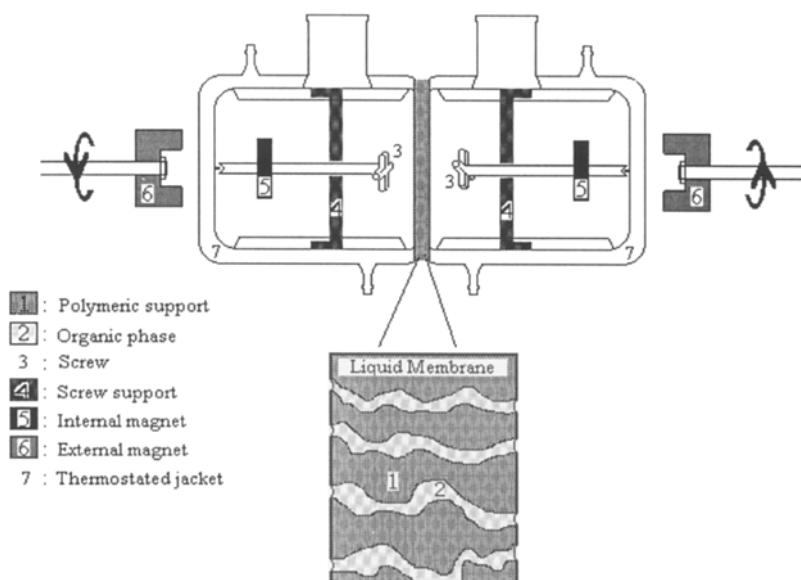


Fig. 4. Flat sheet supported liquid membrane device for transport experiments.

### 3.3.3. Results and Discussion

As summarized in the following diagram (Figure 5), repeated caesium transport experiments show that 1,3-di(*n*-octyloxy)-2,4-crown-6-calix[4]arene (compound **3**), is more efficient and above all more stable in an SLM than the classical crown ether 21-C-7 (which is 50 times more concentrated in *o*-NPOE). The pendant alkyl chains attached to the remaining phenolic units furthermore enhance the calixarene solubility in *o*-NPOE.

Whereas bis-crown-6-calix[4]arene (compound **5**) rapidly leaks out of the SLM ( $P_{Cs} < 0.1 \text{ cm h}^{-1}$  after 15 runs) because of its low partition constants between the organic diluent and the aqueous solutions, very good stability and efficiency have been observed with the more lipophilic benzo (compound **6**) and naphtho (compound **7**) derivatives.

Both families of calixcrown compounds allowed selective removal of  $^{137}\text{Cs}$  from sodium containing solutions: less than 100 mg of sodium is transported within 24 h for compound **7**, whereas more than 95% of trace level  $^{137}\text{Cs}$  is 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% ( $0.05 \text{ mol L}^{-1}$ ) within 24 h, thus leading to concentration factors (ratio of initial waste concentration to final waste concentration) greater than 100 for a single step process.



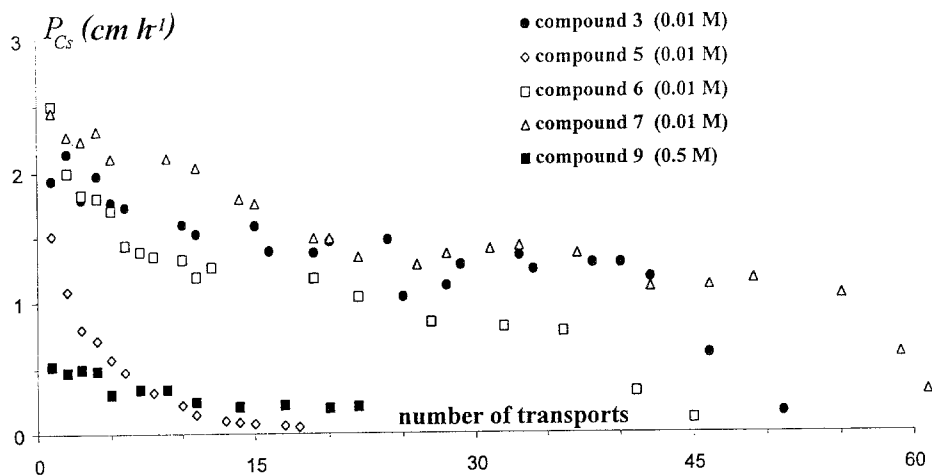


Fig. 5. Caesium permeability measurements for repeated transport experiments.

#### 4. Conclusion

Calixcrown compounds appear to be a new promising family of carriers for the selective removal of caesium from high salinity and acidity media such as MLW through an SLM. By choosing a highly hydrophobic organic diluent, *o*-NPOE, and a lipophilic crown-6-calix[4]arene derivative in the *1,3-alternate* conformation suitable for caesium complexation over that of sodium, very selective and stable SLMs can be obtained (over a period of 50 days).

#### References

1. J. Lefevre: *Techniques de l'Ingénieurs – Mécanique et Chaleur* **B8 II**, B 36600-1 à B 3361-10 (1990).
2. *Revue Générale Nucléaire*, No. 5 September–October (1992).
3. P. Chauvet and T. Dippel: *Radioactive Waste Management*, Vol. 1, Harwood, London (1979).
4. J. F. Dozol, S. Eymard, R. Gambade, G. La Rosa, and J. Casas i Garcia: *Rapport EUR 13887 FR*.
5. P. R. Danesi: *Sep. Sci. Technol.* **19** (11 & 12), 857 (1984–1985).
6. J. D. Lamb, R. L. Bruening, R. M. Izatt, Y. Hirashima, P.-K. Tse, and J. J. Christensen: *J. Memb. Sci.* **37**, 13 (1988).
7. J. D. Way, R. D. Noble, and B. R. Bateman: *Advances in Chemistry Series*, No. 269 (1985).
8. D. Y. Takigawa: *Sep. Sci. Technol.* **27**(3), 325 (1992).
9. W. F. Van Straaten-Nijenhuis, F. De Jong, and D. Reinhoudt: *Recl. Trav. Chim. Pays-Bas* **112**, 317 (1993).
10. T. B. Stolwijk, E. J. R. Sudhölter, and D. N. Reinhoudt: *J. Am. Chem. Soc.* **111**, 6321 (1989).
11. J. F. Dozol, J. Casas, and A. Sastre: *J. Memb. Sci.* **82**, 237 (1993).
12. J. F. Dozol, H. Rouquette, and B. Tournois: *1993 Intern. Conf. Nuclear Waste Manag. Environ. Remediat.*, Prague, Czech Republic, March (1993).
13. Z. Asfari, S. Pappalardo, and J. Vicens: *J. Incl. Phenom.* **14**(2), 189 (1992).
14. P. R. Brown, J. L. Hallman, L. W. Whaley, D. H. Desai, M. J. Pugia, and R. A. Bartsch: *J. Memb. Sci.* **56**, 195 (1991).
15. I. H. Gerow and M. W. Davis, Jr.: *Sep. Sci. Technol.* **14**(5), 395 (1979).

16. I. H. Gerow, J. E. Smith, Jr., and M. W. Davis, Jr.: *Sep. Sci. Technol.* **16**(5), 519 (1981).
17. W. J. McDowell and G. N. Case: *Anal. Chem.* **64**, 3013 (1992).
18. E. Blasius and K. H. Nilles: *Radiochim. Acta*, Part I, **35**, 173 (1984).
19. E. Ghidini, F. Ugozzoli, R. Ungaro, S. Harkema, A. El-Fadl, and D. N. Reinhoudt: *J. Am. Chem. Soc.* **112**, 6979 (1990).
20. W. Nijenhuis, E. Buitenhuis, F. De Jong, E. Sudhölter, and D. N. Reinhoudt: *J. Am. Chem. Soc.* **113**, 7963 (1991).
21. P. J. Dijkstra, J. Brunink, K. Bugge, D. N. Reinhoudt, S. Harkema, R. Ungaro, F. Ugozzoli, and E. Ghidini: *J. Am. Chem. Soc.* **111**, 7567 (1989).
22. R. Ungaro, A. Casnati, F. Ugozzoli, A. Pochini, J. F. Dozol, and H. Rouquette: *Angew. Chem.* (in press, 1994).
23. T. B. Stolwijk, E. J. R. Sudhölter, and D. N. Reinhoudt: *J. Am. Chem. Soc.* **109**, 7042 (1987).