



# Application of Water Soluble Resorcinarenes in Nanofiltration-Complexation with Caesium and Strontium as Targets

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**Abstract.** Combined nanofiltration-complexation is applied to the separation of caesium and strontium from a solution containing a large concentration of sodium. Caesium and strontium complexation was studied using various water soluble resorcinarene-type ligands. Combined with nanofiltration these ligands improved the separation of caesium and strontium from sodium by the FILMTEC NF 70 membrane.

**Key words:** water soluble resorcinarenes, caesium and strontium binding, nanofiltration-complexation.

## 1. Introduction

Membrane separation processes are of major interest for water treatment due to the simplicity of their plant operating systems and their moderate energy consumption. They find important industrial applications for waste water purification, water reuse, and recovery of valuable materials [1].

Located between ultrafiltration and reverse osmosis, the “cut-off” of nanofiltration membranes is in the range of 300–1000 g.mol<sup>-1</sup> molecular weight. Nanofiltration is mainly used for mineral ions filtration [2]. To increase ion separation, nanofiltration can be combined with a selective complexation step. In this way, retention of the complexed element is improved because the ligand-metal complex does not pass through the membrane, whereas free ions pass through it (Figures 2, 3). During recent years, water soluble polymeric ligands like polyacrylic acid have been used to remove metal traces from industrial wastes by ultrafiltration [3]. Microfiltration or ultrafiltration complexation systems need polymeric ligands [4–5a], which cause viscosity. For nanofiltration-complexation systems, water soluble

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ligands with low molecular weights (about  $500 \text{ g}\cdot\text{mol}^{-1}$ ) can be used. Most of the long term radiotoxic nuclear wastes produced during spent nuclear fuel reprocessing are highly acidic ( $\text{HNO}_3$  1M). However reprocessing induced several washing steps including basic ones. Liquid nuclear wastes that are designated to be treated as part of this programme are highly salted (100–400 g/L of sodium), and their pH, typically between 7 and 13, will mainly depend on the further process development. Separation of strontium and caesium traces in a solution containing a high sodium concentration is of crucial interest for the nuclear industry. It is also a scientific challenge for which supramolecular chemistry could bring an efficient solution.

The aim of this article is to describe the synthesis of complexing agents for caesium and strontium and their use in a nanofiltration-complexation process in order to remove these cations from a sodium nitrate solution. Because our study is directed towards resorcinarenes applications in a membrane process, the conformations of these ligands and their possible changes upon complex formation were not studied. From the waste management point of view, the most attractive feature of this technique is its ability to separate radioactive effluents into two different solutions, a concentrated solution containing most of the radioactivity ( $^{90}\text{Sr} + ^{137}\text{Cs}$ ) and a relatively large volume of decontaminated effluent suitable for direct discharge. The achievement of higher volume reduction and decontamination factors are twin objectives, and efforts are underway in the development of new water soluble complexants which could fulfil these aims.

To concentrate caesium and strontium traces in a sodium nitrate medium, performances of the nanofiltration membrane were shown to be insufficient. According to the literature, phenolic resins possess high affinity for caesium [6] and strontium [7].

Resorcinarenes possessing phenolic groups are soluble in aqueous medium [8, 9]. Ligand **1** is caesium selective [10]. These cyclic polyphenols have been used as building blocks for cavitands and carcerands by Cram et al. [11]. They adopt a vase-like structure. Due to these properties [12], phenolic metacyclophanes can be used as ligands for nanofiltration-complexation systems (Figure 1). Each nanofiltration-complexation experiment requires the use of several liters of solution and thus a large quantity of the tested complexing agent. From a practical point of view, it is useful to evaluate the complexing properties by using a method which requires only a small amount of the tested ligand. In a solution containing sodium and caesium ions and a resorcinarene having selectivity for caesium ion, the chromophoric environment of the ligand was sufficiently modified to induce a significant change in the UV-Visible spectrum. Association constants were then evaluated and these values were compared with the efficiency of the nanofiltration-complexation system.

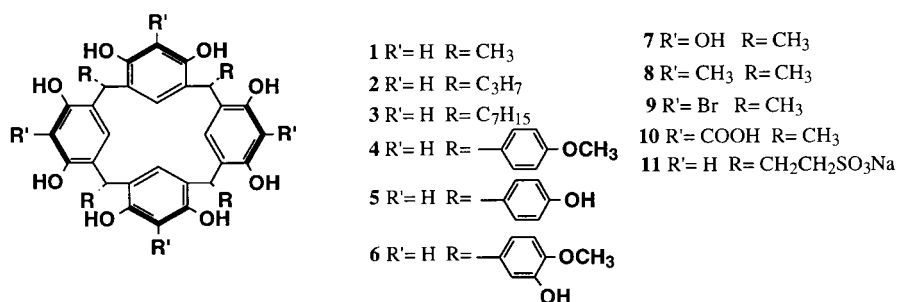


Figure 1. Resorcinarenes substituted in position 2 (R') or on the ethylidene bridge (R).

## 2. Experimental

### 2.1. MEMBRANE SYSTEM

Figure 2 shows a scheme of the nanofiltration loop. Nanofiltration was carried out with the FILMTEC NF 70 (2514) spiral wound membrane. The membrane surface area is 0.5 m<sup>2</sup> and the water permeability is about 5 L.h<sup>-1</sup>.m<sup>-2</sup>.bar<sup>-1</sup>. The permeate is totally recycled thus the feed remains at constant composition during the experiment. Although the synthetic model solutions are not radioactive, they simulate a nuclear effluent ( $T = 298\text{--}313\text{ K}$ ). They contain caesium and strontium traces (1 mmol.L<sup>-1</sup>) in 6 liters of a sodium nitrate medium (0.47 mol.L<sup>-1</sup>). The simulated aqueous wastes are prepared by dissolution in bidistilled water. The experimental pH is 10–11 and the pH is adjusted with nitric acid and sodium hydroxide. Figure 3 shows the scheme of the ionic separation by the membrane. Complexes M<sup>+</sup>-Ligand are retained by the membrane, sodium ions pass through. The retention (Ri) is calculated as follows:

$$Ri = ((C_{ir} - C_{ip}) / C_{ir}) \cdot 100$$

with C<sub>ir</sub> being the *i* solute concentration in the retentate and C<sub>ip</sub> being the *i* solute concentration in the permeate

### 2.2. ANALYTICAL PROCEDURES

Solvents and all compounds were commercial reagents and used without further purification. <sup>1</sup>H-NMR spectra were recorded at 200 MHz on a Bruker AC 200 spectrometer. <sup>13</sup>C-NMR spectra were recorded at 50 MHz on a Bruker AC 200 spectrometer. FTIR spectra were recorded on a 1720-X Perkin Elmer spectrometer. Microanalyses, high and low resolution mass spectra were performed by the "CNRS, Service Central d'Analyse, Vernaison, France". UV-Visible spectra were recorded on a HP 8453 spectrophotometer. Caesium and strontium concentrations were determined by atomic emission in an acetylene-air flame (Perkin Elmer 3110 or Philips PU 9100X).

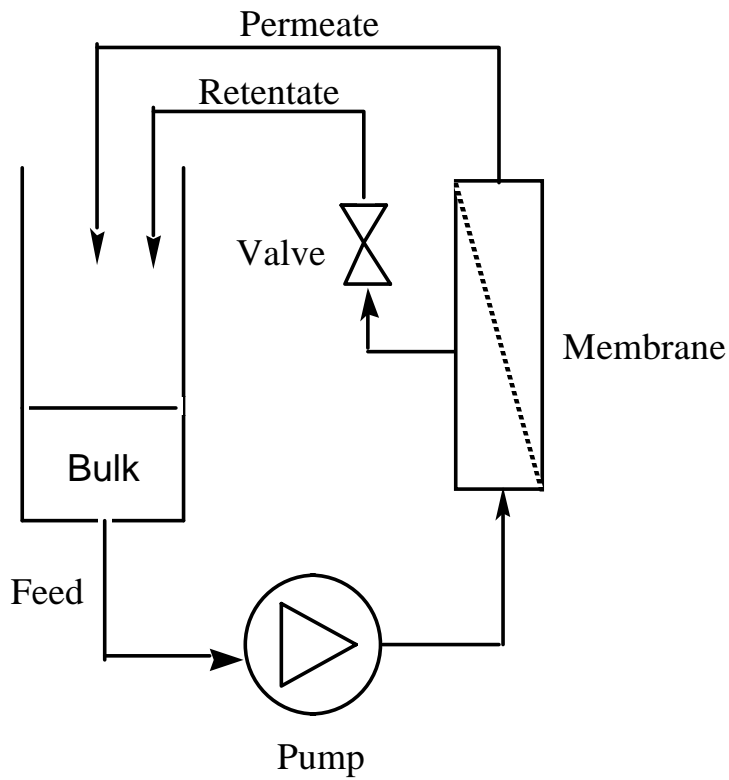


Figure 2. Scheme of the nanofiltration loop.

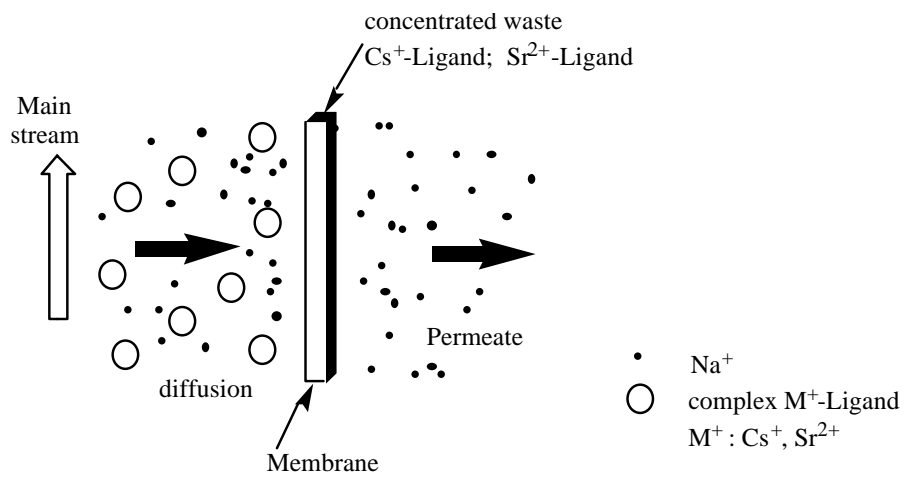


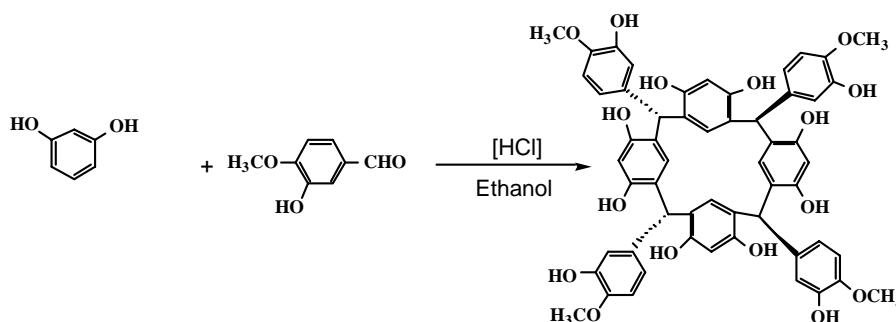
Figure 3. Ionic separation by the membrane.

## 2.3. CHEMICALS AND REAGENTS

Resorcinarenes were prepared via a simple one step acid-catalysed condensation. In this procedure, resorcinol (or one of its derivatives) was heated with an aldehyde at reflux in a mixture of ethanol or ethanol/H<sub>2</sub>O and concentrated HCl for several hours. For each aldehyde, the reaction conditions were optimized. Compounds **1,2-4<sup>a</sup>**, **5<sup>b</sup>**, **7<sup>c</sup>**, **8-9<sup>e</sup>**, **10<sup>d</sup>** and **11<sup>f</sup>** were synthesized using previously established procedures [14, 13a,b,c,d,e,f].

The yield of macrocycle **10** was too low (10%) and could therefore not be tested by nanofiltration-complexation since one test requires the use of 20–30 g of ligand. The purification of resorcinarene **11** was delicate, since three dialyses were necessary (yield: 50%). For this reason it was difficult to obtain a sufficient amount of this product for one test. Nevertheless the complexing properties of these ligands were studied by UV-Visible spectroscopy.

2.4. SYNTHESIS OF 2,8,14,20-TETRAKIS(3-HYDROXY-4-METHOXYPHENYL)PENTACYCLO[19.3.1.1<sup>3,7</sup>.1<sup>9,13</sup>.1<sup>15,19</sup>]OCTACOSA-1(25),3,5,7(28),9,11,13(27), 15, 17, 19(26), 21, 23-DODECAENE-4, 6, 10, 12, 16, 18, 22, 24-OCTOL (**6**)



Scheme 1. Synthesis of resorcinarene **6** (isomer rctt).

Resorcinol (16.5 g; 0.15 mol) was dissolved in 250 mL of 96% ethanol. To this solution was added 3-hydroxy-4-methoxybenzaldehyde (22.8 g; 0.15 mol). After dissolution, 30 mL of 37% HCl was added dropwise. The solution was stirred and a precipitate formed rapidly. Stirring was continued at 60 °C for 4 h. Cooling in an ice bath, and filtration, yielded a red solid which was washed with ethanol and water and air-dried; 33.9 g (90%), m.p. >300 °C. <sup>1</sup>H-NMR (200 MHz; [D<sub>6</sub>]D<sub>2</sub>O—NaOD, δ 6.56–6.37 (m, 12H, CH), 6.15 (s, 2H, CH), 5.73 (d, 4H, CH), 5.28 (s, 2H, CH), 3.65 (s, 4H, ArCH), 3.56 (s, 12H, OCH<sub>3</sub>). <sup>13</sup>C NMR: δ 152.5, 145.0, 144.6 (Ar—OH), 138.3, 137.2, 121.3, 120.8, 119.9, 101.6 (Ar), 116.7 (Ar—OCH<sub>3</sub>), 55.5 (OCH<sub>3</sub>), 20.2 (HC—Ar). FTIR (KBr) 3405 cm<sup>-1</sup> (OH); 1610 cm<sup>-1</sup> and 1509 cm<sup>-1</sup> (aromatic C=C). Mass spectrum (Fab<sup>+</sup>): m/z 977.29 (Calc. 977.30). Anal. Calcd for C<sub>56</sub>H<sub>48</sub>O<sub>16</sub>·4HCl·1H<sub>2</sub>O: C, 58.96; H, 4.77. Found: C, 58.64; H, 4.05.

## 2.5. COMPLEXATION STUDIES BY UV ABSORPTION

For similarity with nanofiltration-complexation conditions, UV-Visible studies were carried out in an aqueous medium containing 0.1M NaOH. Stability constants of 1 : 1 complexes  $\beta_{MLn} = [M_nL]/[L][M]^n$  were evaluated according to the Foster–Hammick–Wardley procedure [15], i.e., the stepwise addition of CsCl solution to a resorcinarene solution changes the absorbance spectrum of the ligand. The spectra were recorded between 200 and 400 nm.

With this method only caesium complexation was studied, previous results having shown that poly(acrylic acid) combined with a nanofiltration membrane was a selective strontium ligand [5b]. Strontium complexation by resorcinarenes was also studied in this paper in order to investigate their properties towards this divalent ion.

## 3. Results and Discussion

Resorcinarenes can lead to the formation of host-guest complexes in solution [9, 10]. The easy syntheses and functionalisations of the bowl-shaped octols could provide potential sources of molecular “vessels” for the preparation of polyfunctional host systems. The solubility of the cavitands should be increased by the introduction, at positions remote from the cavity, of a number of hydrophilic groups [16, 17]. Schneider et al. showed that in NaOD solutions, the boat isomer of **1** is exclusively present as the tetraphenolate [8, 17]. Hydrogen bonding and delocalisation of the negative charges contribute towards the high stability of this tetra-anion. The tetraphenolate part of resorcinarene may serve as the anionic host for caesium. The selective complexation of caesium may occur because of its dimensional matching to the cavity of resorcinarene [18], cooperative caesium-arene interactions [18, 19], and the selectivity of phenolic groups for caesium [6]. So the Cs<sup>+</sup> may be included in the calixarene cup by interaction with negative charge delocalised over the aromatic rings. The cation metal was involved in direct coordinate bonding to the phenol/phenolate oxygen atoms.

### 3.1. UV VISIBLE STUDY

The resorcinarene derivatives were tested by UV-Visible spectroscopy in order to evaluate the complexation of these ligands with caesium to select them and to test them by nanofiltration-complexation.

CsCl addition to resorcinarene **1** is not accompanied by the appearance of a new absorption band (Benesi–Hildebrand band) in contrast to electron donor-acceptor complexes [20]. However it induced a significant hyperchromic and bathochromic effect of the main absorption band intensity, at the studied wavelength of 303 nm (Figure 4). This shift is characteristic of a  $\pi - \pi^*$  transition. The polar cavity has to be sufficiently rigid to maximise selectivity and the ion-dipole interaction strong enough to ensure that the process represented by equilibrium (1) below favoured the right-hand side to the degree defined in equation (2):

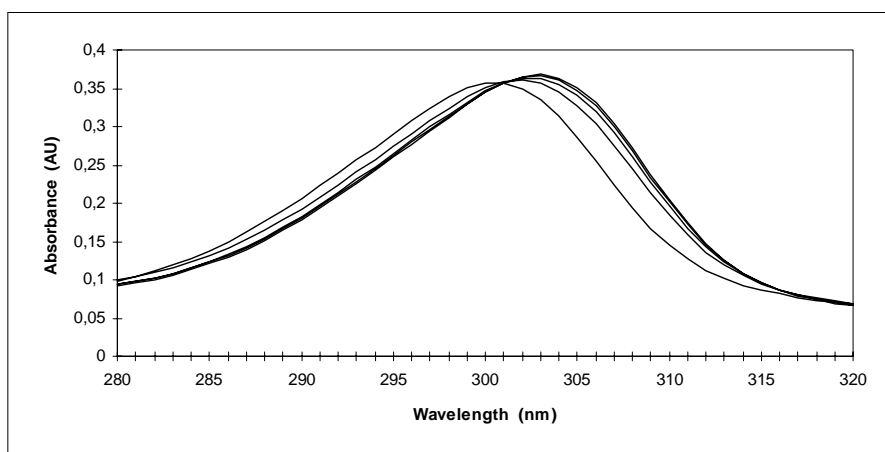


Figure 4. Changes in the UV/visible absorption spectrum of resorcinarene **1** upon addition of CsCl in NaOH 0.1 M concentration of  $[1] = 2 \times 10^{-5} \text{ mol.L}^{-1}$ .



with  $M$ , being the alkali cation

$$\beta = \frac{[M_nL]}{[M]^n[L]} \quad (2)$$

with  $L$  being the ligand and  $\beta$  the association constant.

Previously, the Foster–Hammick–Wardley procedure was used assuming 1 : 1 complexation in solution. The plot of  $\Delta \text{Abs}/[\text{CsCl}]$  versus  $\Delta \text{Abs}$  is linear (Figure 5). According to this procedure, it is characteristic of a 1 : 1 complex.

From the slope, the association constant  $\beta = ([\text{CsL}]/[\text{L}][\text{Cs}]) \text{ (L.mol}^{-1}\text{)}$  can be calculated. The association constant without units is  $\beta' = ([\text{CsL}][\text{H}_2\text{O}]/[\text{L}][\text{Cs}]) = \beta[\text{H}_2\text{O}] = 1.288 \times 10^6$  with  $[\text{H}_2\text{O}] = \rho_{\text{H}_2\text{O}}/M_{\text{H}_2\text{O}}$ . The standard free energy is given by  $\Delta G^\circ = -R.T. \ln \beta' = -34.9 \text{ kJ.mol}^{-1}$ .

The spectral modifications allow calculation of the association constant  $\beta'$  with this method. Resorcinarenes **7**, **8**, **10** and **11** were also evaluated and the results are given in Table I.

Resorcinarenes **1** and **8** showed the same selectivity with caesium in alkali medium; the standard free energies were similar ( $\Delta G^\circ$  **1** and **8** = - 34.9 kJ.mol<sup>-1</sup>). By using the nanofiltration-complexation process, the Cs-**1** association constant was also determined and found to be similar [10]. Resorcinarene constants of **4**, **5** and **6** were not evaluated by this spectroscopic method. By comparison, tetrasulfonate **11** bound caesium less efficiently. Pyrogallene **7** and tetracarboxylate **10** did not display affinity with caesium. Spectral modifications were not observed upon CsCl addition and association constants could therefore not be calculated. The UV spectroscopic method cannot be used in the case of very weak interactions.

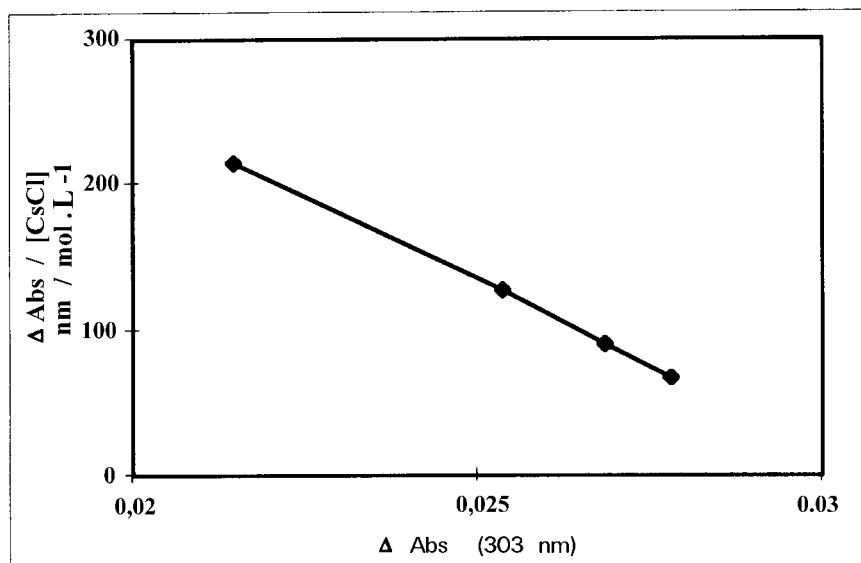


Figure 5. Plot of  $\Delta \text{Abs} / [\text{CsCl}] = f(\Delta \text{Abs})$  with different concentration of CsCl with **1** in NaOH 0.1 M at room temperature.

Table I. Association constants of Cs-resorcinarenes calculated by UV-Visible analysis

Resorcinarenes	[Resorcinarenes] (mol.L <sup>-1</sup> )	$\lambda$ (nm)	$\beta'$	$\Delta G^\circ$ (kJ.mol <sup>-1</sup> )
<b>1</b>	$2 \times 10^{-5}$	303	$1.288 \times 10^6$	-34.9
<b>7</b>	$4 \times 10^{-5}$	311	-	-
<b>8</b>	$4 \times 10^{-5}$	299	$1.312 \times 10^6$	-34.9
<b>10</b>	$2 \times 10^{-5}$	321	-	-
<b>11</b>	$3.5 \times 10^{-5}$	305	$4.52 \times 10^5$	-32.3

### 3.2. LIGANDS EVALUATION BY NANOFILTRATION-COMPLEXATION

After this spectroscopic study, these resorcinarenes were subsequently used as specific ligands for caesium and strontium in a nanofiltration-complexation process; the obtained results are shown in Figure 6.

At the studied concentrations, the structure of the ligands showed no influence on sodium retention. Only 10% of sodium was retained by the FILMTEC membrane. However competitive complexations between caesium and strontium but also caesium, strontium and sodium could take place. The sodium molar concentration was 6000 times higher than the caesium and/or strontium molar concentrations.



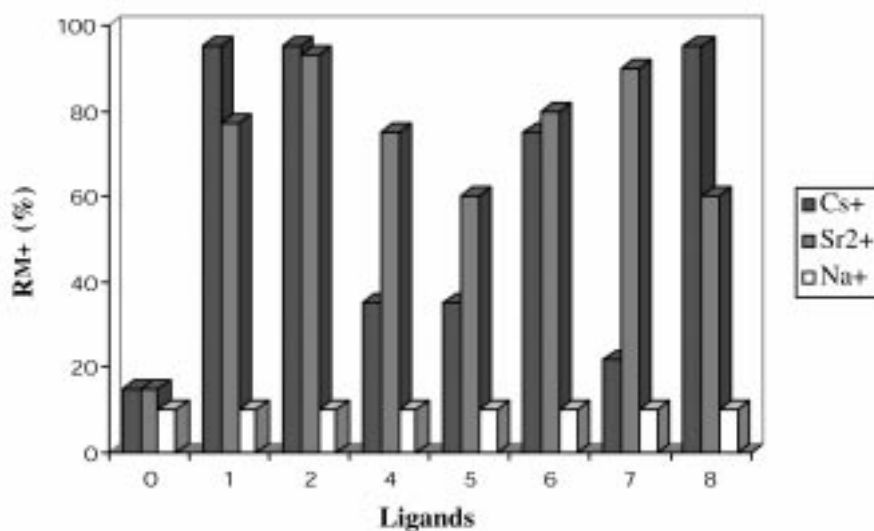


Figure 6. Ligand effect on caesium and strontium retention. Conditions:  $[\text{NaNO}_3] = 40 \text{ g L}^{-1}$ ;  $[\text{Cs}^+] = [\text{Sr}^{2+}] = 0.075 \text{ mmol.L}^{-1}$  [resorcinarene]/ $[\text{Cs}^+]$  or  $[\text{Sr}^{2+}] = 50$ .  $\Delta P = 1.5 \text{ MPa}$ ;  $T = 293 \text{ K}$ .  $\circ$  = without ligand.

### 3.2.1. Effect on Cation Retention of Alkyl Substituents on the Methylene Bridge

Without ligand, the performances of the FILMTEC NF 70 membrane were not sufficient, whereas nanofiltration combined with caesium complexation by resorcinarene **1** or **2** showed a caesium retention of 95%. Ligand **2** exhibited a higher strontium retention than **1**. The solubility of the cyclotetramers decreased with the length of the alkyl chain. Ligand **2** was surface active. In alkali solution, it foamed in the bulk. Cyclotetramer **3** was only partially soluble in the aqueous phase at pH = 11 and it could not be tested with the nanofiltration loop.

### 3.2.2. Effect on Cation Retention of Benzyl Substituents on the Methylene Bridge

In order to improve the selectivity of caesium and strontium from sodium, resorcinarenes with hydroxy and/or methoxy substituents on the aryl groups of the methylene bridge were prepared and tested. Compounds **4** and **5** displayed higher levels of complexation with strontium than with caesium, strontium retention was 75% for **4** and 60% for **5**, and caesium retention was 35% for both. The cyclotetramer **6** showed the same retention for caesium and strontium ( $R_6 \text{ Cs}^+, \text{Sr}^{2+} = 80\%$ ). Macrocycle **4** without a hydroxyl functionality on the phenyl group of the bridge was less soluble than **5** and **6**, but showed approximately the same caesium and strontium retentions as **5**. The presence of a functional aryl group did not improve caesium retention but these ligands displayed a good retention with strontium cation.

### 3.2.3. *Effect on Cation Retention of Substituents in the 2 Position of Resorcinol*

The structure of resorcinarene was modified at position 2 of resorcinol. Cyclotetramer **7** having twelve hydroxyl groups did not bind with caesium, which is in agreement with UV-Visible spectroscopy but it complexed selectively with strontium, probably due to the presence of the “5-membered chelate ring” [7].

Tetramethyl cavitand **8** displayed good selectivity for caesium ( $R_8 \text{ Cs}^+ = 95\%$ ). The methyl group at position 2 of the resorcinol did not decrease the solubility of the corresponding resorcinarene. It complexed caesium in contrast with the results using ligand **7**. This result confirmed those obtained by the UV-Visible study.

The methyl group in the 2 position of resorcinol did not hinder cation complexation. Electronic effects were partly responsible for this behaviour towards complexation, the two hydroxy groups being mainly responsible for the selectivity toward caesium. In contrast, the hydroxy group in the 2 position inhibits the complexation of caesium cations. Macrocycle **7** is a selective strontium ligand. Resorcinarene **9** was not soluble in alkali solution but it could be used like a chemical intermediate to synthesize hydrosoluble cavitands. It could not be evaluated in nanofiltration-complexation.

## 4. Conclusion

This study showed binding properties of resorcinarenes in a basic medium with alkaline cations. In combination with nanofiltration these ligands improved the separation of caesium and strontium from a solution containing a large concentration of sodium by the FILMTEC NF 70 membrane ( $[\text{Na}^+]/[\text{M}^+] = 6300$ ). Depending on the functionality of the resorcinarene, retention of strontium and/or caesium was observed.

Association constants of resorcinarene were evaluated by UV-Visible absorption and this of **1-Cs** was compared with the value obtained by nanofiltration-complexation. UV-Visible analysis allowed selection of ligands and to test them when they showed interaction with the caesium cation. Results with nanofiltration-complexation and UV-Visible spectroscopy absorption were similar. Finally a qualitative correlation between both methods has been established.

At present new hydrosoluble macrocycles like cavitands are being synthesized in order to increase the stability and selectivity toward caesium of these macrocycles in alkali solution. Within the context of the combination of nanofiltration and complexation, resorcinarenes will be further investigated because these ligands can easily be extracted from the effluent in acidic medium: resorcinarenes precipitate and can subsequently be reused after filtration.

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