New Cesium-Selective Hydrophilic Ligands: UV Measures of Their Interactions toward Cs and Cs/Na Separation by Nanofiltration Complexation

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Separating traces of cesium from aqueous medium containing large sodium amounts is a difficult problem because cesium and sodium ions have a similar behavior in aqueous medium. We selected a highly cesium-selective ligand in aqueous medium, and we determined the best conditions for using this ligand in a nanofiltration−complexation process in order to achieve Cs^+/Na^+ separation. We also tried to find a relation between the ligand structure and its activity toward cesium complexation. Tetrahydroxylated bis-crown-6 calix[4]arene was found to be very cesium selective ($S = \beta(Cs^+)/\beta(Na^+) = 6600$). Combined with a nanofiltration process, this ligand helped reaching 90% cesium retention in a highly concentrated aqueous medium ($[NaNO_3] = 3$ mol/L).

Introduction

Among the different available separative methods (liquid−liquid and solid−liquid extractions, ion-exchange resins), nanofiltration (NF) is a new pressure-driven membrane process which produces very few additional wastes. Located between ultrafiltration and reverse osmosis, nanofiltration membranes " cutoffs " are in the range of 300−1000 g/mol molecular weight.[1−3] Moreover, to increase ionic separation, nanofiltration can be combined with a selective complexation step: retention of the target element is improved because the complex with the ligand, of larger size and mass than the target ion, prevents this ion from passing through the membrane.[4] For such a purpose, water-soluble ligands with molecular weight of about 500 g/mol can be used in the case of the nanofiltration−complexation association, whereas micro- or ultrafiltration−complexation systems need larger ligands and induce some specific problems of increasing viscosity and precipitation.[5]

Our laboratory has been developping the nanofiltration−complexation technique since 1993.[6−9] We showed that using EDTA with a Desal 5 DK or a Nanomax 50 membrane allowed a 100% retention (rejection) of Sr^{2+} and other polyvalent ions, and only a 10% retention of Na^+ and Cs^+ ions. Then, with the use of a cesium-selective ligand such as resorcinarene, Cs^+/Na^+ separation was also improved but not satisfactorily. In fact, to remove radioactive traces of cesium in highly salted aqueous medium, a minimum of 99% Cs^+ retention with a maximum of 10% Na^+ retention is required for industrial applications.

So the aim of the present study was to select a highly cesium-selective ligand in aqueous medium, and then to determine the best conditions for using this ligand in a nanofiltration−complexation process in order to achieve Cs^+/Na^+ separation. The first part of this article is the Experimental Section describing both the NF technique and the UV spectrophotometry for measuring Cs^+−ligand complex formation constants. The second part is an attempt to find a relation between the ligand structure and its activity toward cesium complexation. The final part shows the different aspects of the use of tetrahydroxylated bis-crown-6 calix[4]arene in a NF-complexation system for the Cs^+/Na^+ separation.

Experimental Section

UV−Vis Analysis. The aim of UV−vis analysis was to determine cesium−ligand complex formation constants. We used the Foster−Hammick−Wardley method[10] to calculate β_{CsL} stability constants from the absorption variations detected by UV spectrophotometry. Because these variations were generally small, results were not very accurate, and therefore a 10% of standard deviation for each β_{CsL} constant had to be taken into account. But even if the different β_{CsL} values were not accurate, they were supposed to give us at least a rough idea of what the ligand affinity toward cesium was.

Experimental Procedure. First, the different ligands were dissolved in an aqueous medium with a pH ranging from 11 to 13, because most of the chosen ligands were only soluble in basic aqueous medium, and their solubility was pH dependent. Then spectra of each ligand were recorded from 200 to 400 nm with a HP 8453 spectrophotometer using 1 cm path length quartz vessel.

The stability constants β of Cs−ligand complexes were determined by UV absorption spectrophotometry. β is the constant ratio $[CsL^+]/([Cs^+][L])$ corresponding to the equilibrium $Cs^+ + L \leftrightarrow CsL^+$ (L is the ligand). A progressive addition of a CsCl solution to a solution containing Cs-selective ligand

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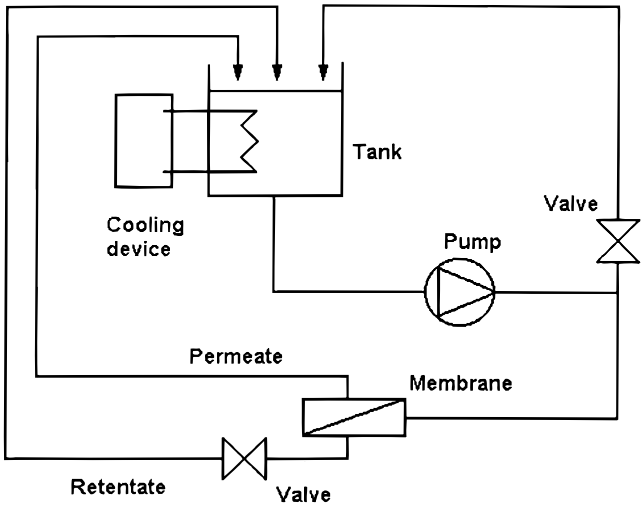


Figure 1. Scheme of the nanofiltration loop.

leads to a change in the ligand UV absorption spectrum. The resulting spectra usually cross in a single point, called isosbestic point, that indicates an equilibrium between two absorbing species in solution and the Cs−ligand complex formation. The spectral modifications allowed the calculation of β_{CsL} stability constants, according to the Foster−Hammick−Wardley method.[10]

Moreover, to obtain fully soluble ligands and to avoid interference with absorption caused by nitrate ions, we used a solution of NaOH, and cesium chloride as cesium source. Of course these conditions for determining β_{CsL} constants by UV spectrophotometry were quite different from what the conditions were in nanofiltration tests.

Nanofiltration Tests. The aim of the nanofiltration−complexation tests was to measure the ligands ability to help improving the separation of cesium from sodium by the nanofiltration process.

Apparatus. Figure 1 shows a schematic of the nanofiltration loop used in our experiments. By totally recycling the permeate and the retentate, the feed remains at constant composition during the experiments. NF was carried out with either a Nanomax 50 plane membrane (Millipore) or a Desal 5 DK plane membrane (Desalination), with a surface area of 0.015 m^2, designed for tangential filtration. Both membranes have the same following specifications: a high retention of multivalent ions and neutral organic molecules with a molecular weight above 400 g/mol, and a low retention of monovalent ions and neutral organic molecules with a molecular weight under 100 g/mol. They both showed the same behavior when used for Cs$^+$/Na$^+$ separation tests.

Retention rate (%) of a substance i was calculated as follows: $R_{\mathrm{i}} = 100(1 - C_{\mathrm{ip}}/C_{\mathrm{ir}})$, where C_{ip} is the concentration of i in the permeate and C_{ir} is the concentration of i in the retentate.

NF Test Procedure for the Ligands Screening. For each ligand to be tested, an aqueous solution containing 15 mg/L of cesium ($CsNO_3$) and 8.5 g/L (0.1 mol/L) of sodium nitrate was filtrated on a NF membrane. Different known amounts of ligand were then progressively added to the solution, and samples of permeate and retentate were taken a half-hour after each ligand addition. This first experiment was designed to check the ligand ability to improve cesium retention by the membrane in an aqueous medium containing low levels of sodium nitrate.

The second experiment was designed only for ligands having shown some cesium selectivity during the first experiment. To a solution containing 15 mg/L of cesium and a fixed ratio [ligand]/[cesium], known amounts of sodium nitrate were progressively added, and the resulting solution was filtrated on a NF membrane. Samples were taken as described above. This second experiment was designed to measure the Cs$^+$/Na$^+$ selectivity of the ligand.

For all the following NF results, sodium retention remained under 10%, because both Nanomax 50 and Desal 5 DK membranes were chosen to be very permeable to monovalent ions. NF tests were carried out using a transmembrane pressure of 0.6 MPa and a temperature of 293 K.

Chemicals and Reagents. $NaNO_3$ (99%, Aldrich), $CsNO_3$ (99,99%, Aldrich), CsCl (99,99%, Aldrich) were used as sodium and cesium sources. Ligands were synthesized as described in refs 11−14.

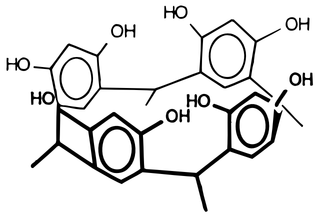
Analytical. Cesium concentration was determined by atomic absorption spectroscopy in an air-acetylene flame (apparatus: PU 9100X PHILIPS atomic absorption spectrometer). Each result must be considered with a 5% standard deviation.

Results and Discussion

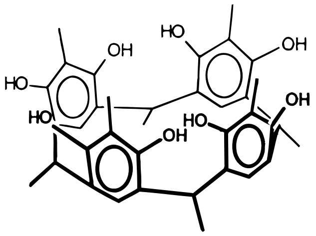
In a previous study,[8] we looked at the metal-complexing ability of resorcinarene **1** through a nanofiltration−complexation system. It was shown that cesium retention increased with resorcinarene **1** concentration while no significant consequence on sodium retention was noticed. In this way, Cs$^+$/Na$^+$ separation was improved. However, the ligand excess did not allow a complete cesium complexation. Moreover, with an increase of sodium concentration, cesium retention rapidly decreased.

The following section is an attempt to first evaluate the β_{CsL} formation constant of different ligands by a UV spectrophotometry method, and second to assess this β_{CsL} constant by another method, the nanofiltration−complexation tests.

Resorcinarenes. *1. Determination of Cs−Ligand Complex Formation Constant by UV Spectrophotometry.* Resorcinarenes had very high β_{CsL} formation constants (see Table 1), but it must be kept in mind that this kind of β_{CsL} constants determined by UV spectroscopy were measured at pH and at metal/ligand concentration conditions that were quite different from NF-complexation conditions. In fact, these constants showed the resorcinarenes ability to complex cesium in an aqueous medium containing low levels of sodium salts, but they did not measure the Cs$^+$/Na$^+$ selectivity of the ligands.



Calix[4]resorcinarene **1**



Tetramethylcalix[4]resorcinarene **2**

TABLE 1: Determination of Cs−Ligand Complex Formation Constants by UV Spectrophotometry for Ligands 1 and 2

ligand	**1**	**2**
M (g/mol)	544	600
[ligand] (mol/L)	2×10^{-5}	4×10^{-5}
$[Na^+]$ (mol/L)	0.1	0.1
pH	13	13
$\lambda_{calculation}$	303 nm	299 nm
β_{CsL} (without unit)	1 400 000	1 300 000

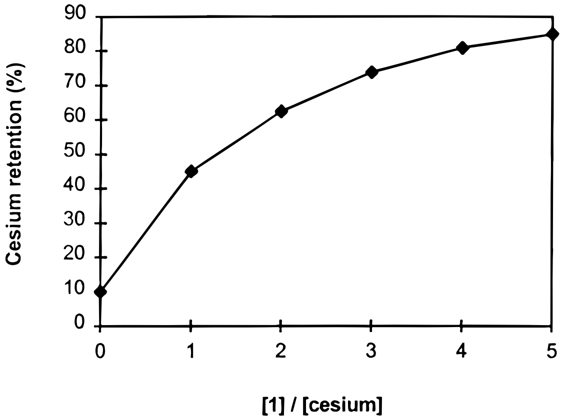


Figure 2. Cesium retention as a function of [resorcinarene **1**]/[cesium] ratio ([cesium] = 15 mg/L, $[NaNO_3]$ = 0.1 mol/L, pH = 11, T = 293 K).

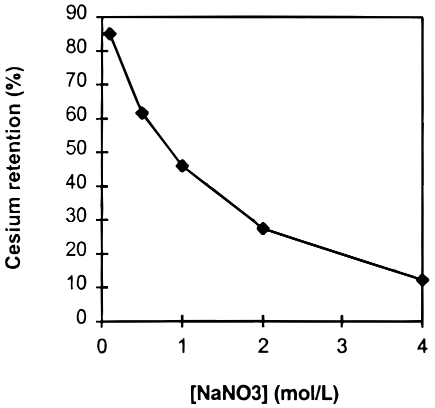


Figure 3. Cesium retention as a function of $[NaNO_3]$ ([cesium] = 15 mg/L, [**1**]/[cesium] = 5, pH = 11, T = 293 K).

Figure 6 shows the changes in UV absorption spectrum of ligand **11** with CsCl addition. Variations of absorption resulted in a single isosbestic point, which proved that ligand **11** formed a 1:1 complex with Cs^+ in aqueous medium.

2. Determination of Cs−Ligand Complex Formation Constant by NF-Complexation Tests. Used in a nanofiltration−complexation system, resorcinarene **1** helped to increase considerably cesium retention when added to a basic aqueous medium containing 0.1 mol/L of sodium nitrate (Figure 2). However, the Cs^+/Na^+ selectivity was not high enough to allow at least a 90% cesium retention in a 3 mol/L $NaNO_3$ aqueous medium (Figure 3). This target might be obtained by increasing the [resorcinarene]/[cesium] ratio, but calculation showed that a minimum of 8 g/L of ligand would have been required, which was a too high concentration for applications.

Both nanofiltration−complexation tests described in Figures 2 and 3 allowed the calculation of distinct cesium−ligand- and sodium−ligand-complexation constants.

By considering that cesium retention curves (from NF) are homothetic to cesium complexation curves (by ligand), cesium complexation rates could be deduced from cesium retention rates. Because the resulting five equations included seven variables, computer in-house-written programs were necessary to solve the problem. The following complexation constants were found to be the more realistic, that is to say that cesium theoretical retention calculated from these K_{CsL} and K_{NaL} was in good agreement with cesium experimental retention rates (Table 2).

TABLE 2: Cesium−Ligand and Sodium−Ligand Complexation Constants of Ligand 1

ligand	K_{CsL} (L/mol)	K_{NaL} (L/mol)
1	45 000	35

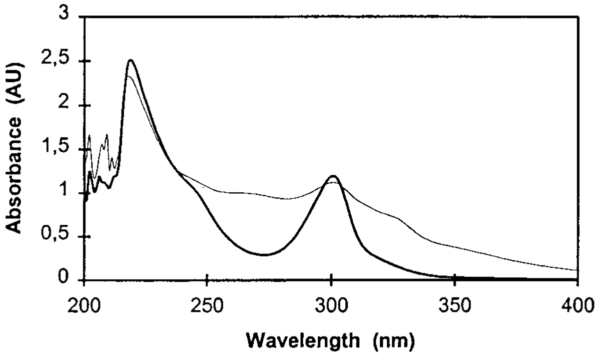


Figure 4. UV absorption spectrum of ligand **1** in aqueous medium (bold line) and a 4-day period later (thin line) ([**1**] = 2×10^{-5} mol/L, pH = 13).

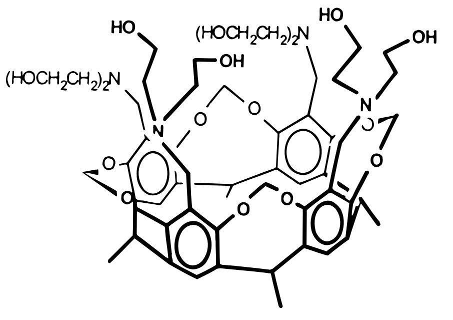
It appeared that the K_{CsL}/K_{NaL} ratio was equal to 1300 for resorcinarene **1** which therefore measured the Cs^+/Na^+ selectivity of this ligand.

3. Stability of Cs Complex Ligand ***1.*** Both of the following spectra of resorcinarene **1** were recorded within a 4-day period (Figure 4). The shape of the second spectrum was different enough from the first one so that it could be assumed that resorcinarene structure was not stable in basic aqueous medium. Moreover, other NF experiments showed that cesium retention decreased with time because of the resorcinarene structure modification during the NF experiments. This was in agreement with UV results, i.e., that resorcinarene structure was not stable in basic aqueous medium.

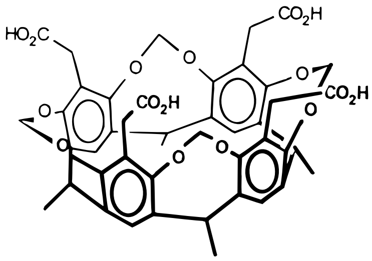
Meanwhile resorcinarene **1** was kept as a reference in matter of cesium selectivity in aqueous medium. It was compared to all the others ligands in the following nanofiltration experiments.

We could suggest three main reasons for having resorcinarene a so good cesium-selective ligand:[15] the size of its cavity that correctly matched with cesium ion, the number (eight) of phenolic hydroxyl groups, and the deprotonation in basic aqueous medium of these hydroxyl groups that made an ideal geometric disposition of the O−H−O arrangement. The following experiments involved new hydrosoluble ligands that were supposed to be cesium selective, i.e., possessing some of these three structure characteristics.

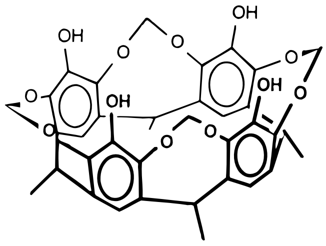
Cavitands. Because resorcinarene **1** had proved to be a good cesium-selective ligand, its structure was kept and its stability in basic aqueous medium improved. In fact, the three following cavitands[12] had methylene bridges that were supposed to mimic the O−H−O arrangement geometry of resorcinarenes in basic conditions. Their solubility in aqueous medium was due to different hydrophilic groups: basic groups (**3**), acidic groups (**4**), and phenolic groups (**5**). These hydrophilic groups were supposed to ensure their fitness as good cesium-selective ligands.



Cavitand **3**



Cavitand **4**



Cavitand **5**

1. Determination of Cs−Ligand Complex Formation Constant by UV Spectrophotometry. Cavitands gave low β_{CsL} constants regarding their structure similar to these of resorcinarenes (Table 3). Cavitand **5** with phenolic groups was the only one to have a Cs−ligand constant high enough to be correctly assessed. However, the three cavitands were selected for a nanofiltration−complexation test, to prove that low β_{CsL} UV constants corresponded to a low cesium retention in a nanofiltration−complexation process.

2. Determination of Cs−Ligand Complex Formation Constant by NF-Complexation Tests. Through a NF-complexation system, cavitands **3**−5 proved to be low cesium-selective ligands (Figure 5). Therefore, cavitands were not selected for having their Cs^+/Na^+ selectivity to be tested through NF experiments. It can be noticed that, among the three cavitands, cavitand **5** with phenolic functions gave the highest cesium retention. This result must be compared with UV results: cavitand **5** was the only one to have a Cs−ligand formation constant high enough to be correctly assessed.

Nevertheless no β_{CsL} formation constant could be calculated from NF-complexation experiments because of their too low Cs-complexation effect.

Bis-crown-6 Calix[4]arenes. Ungaro[16] and Vicens[17] showed that bis-crown-6 calix[4]arene (called BC6) had a preference for Cs^+ in extraction and in complexation, resulting in a remarkable Cs^+/Na^+ selectivity ($S = \beta(Cs^+)/\beta(Na^+) = 2 \times 10^3$ in methanol for BC6). This selectivity was mainly due to the excellent size match between the cation and the ether loop of the ligand, and to the impossibility for the crown part, attached to the calixarene, to wrap around the smaller Na^+ cation.

TABLE 3: Determination of Cs−Ligand Complex Formation Constants by UV Spectrophotometry for Ligands 3, 4, and 5

ligand	3	4	5
M (g/mol)	1060	824	656
[ligand] (mol/L)	10^{-4}	5×10^{-5}	5×10^{-5}
[Na^+] (mol/L)	10^{-3}	10^{-2}	10^{-2}
pH	11	12	12
$\lambda_{calculation}$			293 nm
β_{CsL} (without unit)	low	low	35 000

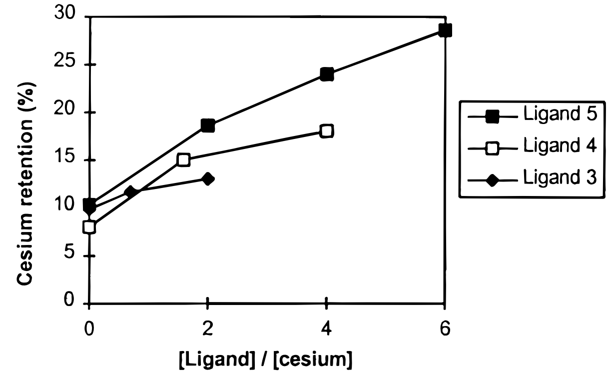


Figure 5. Cesium retention as a function of [ligand]/[cesium] ratio ([cesium] = 15 mg/L, [$NaNO_3$] = 0.1 mol/L, pH = 11, T = 293 K).

However, they were lipophilic ligands, and the only way to use them in an aqueous medium for NF-complexation systems was to modify their structure by adding hydrophilic groups,[13,14] hopefully keeping them cesium selective. The resulting molecules had basic (**6**) or neutral (**7**), carboxylic (**8** and **9**), or phenolic (**10** and **11**) hydrophilic substituants.

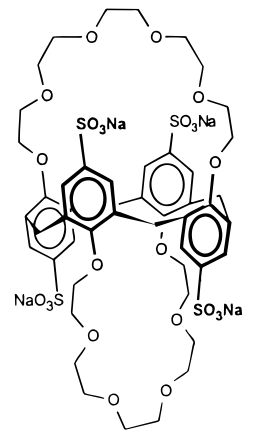
1. Determination of Cs−Ligand Complex Formation Constant by UV Spectrophotometry. Ligands **6** and **7** with sulfonated groups were soluble in basic or neutral aqueous medium, but they gave low β_{CsL} constants. Sulfonated groups probably hindered the selective complexation of Cs^+ by the BC6 structure (Table 4).

Ligands **8** and **9** with carboxylic groups gave respectively 75 000 and 60 000 as β_{CsL} constants in the same experimental conditions. It seemed that having two carboxylic groups was more favorable to Cs^+ complexation than having four carboxylic groups. However, ligands **8** and **9** showed approximately the same affinity toward Cs^+.

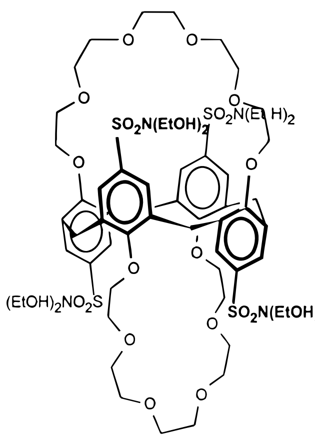
Ligands **10** and **11** with hydroxyl groups gave respectively 245 000 and 425 000 as β_{CsL} constants. They did not behave as ligands **8** and **9**, that is to say, that ligand **11** with four hydrophilic groups had a twice higher β_{CsL} constant than that of ligand **10** with two hydroxyl groups. The main limitation concerning the use of ligand **10** and **11** was their solubility in basic aqueous medium. At high ligand concentrations (more than 1 g/L), a minimum of pH = 12 was required to have them completely water soluble.

2. Determination of Cs−Ligand Complex Formation Constant by NF-Complexation Tests. The three calix[4]arenes BC6 **6**−**8** were the first ones to be tested through NF experiments. Although cesium retention did not increase as much with these BC6 as with resorcinarene (Figure 7), BC6 Cs^+/Na^+ selectivity seemed to be higher than the resorcinarene one. In fact cesium retention decreased more slowly with BC6 than with resorcinarene under $NaNO_3$ addition as shown on Figure 8.

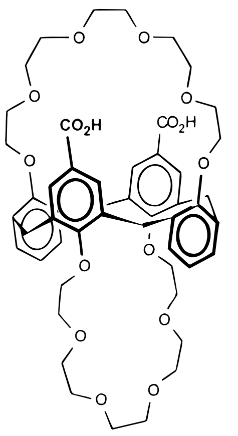
For ligands **6**−**8**, no K_{CsL} or K_{NaL} formation constants could be calculated from NF-complexation results because of their too low cesium complexation effect. Both hydroxylated BC6 **10** and **11** were then tested through NF experiments.



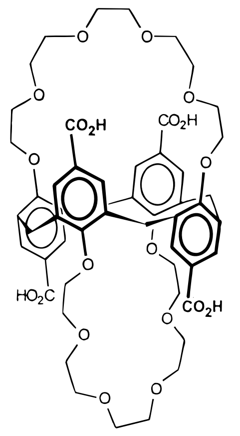
6. tetrasulfonated BC6



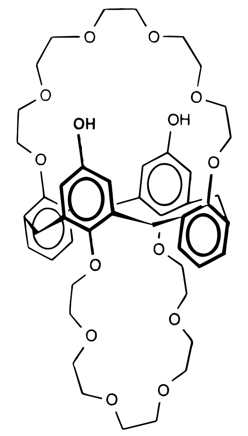
7. N,N-diethanolsulfonamide BC6



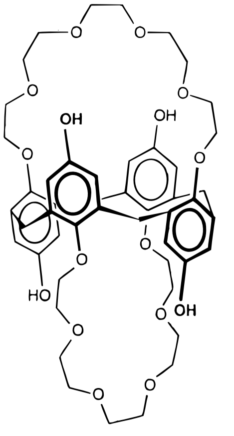
8. dicarboxylated BC6



9. tetracarboxylated BC6



10. dihydroxylated BC6



11. tetrahydroxylated BC6

First, dihydroxylated BC6 **10** showed a good affinity toward cesium, not as high as that of the resorcinarene one, but much higher than the affinities of the first three BC6 complexes. What was remarkable was the ligand **10** Cs^+/Na^+ selectivity: under $NaNO_3$ addition, cesium retention by dihydroxylated **10** did not decrease as much as that with resorcinarene **1** (Figures 9 and 10).

As with resorcinarene **1**, both nanofiltration−complexation tests carried out with ligand **10** allowed the calculation of distinct cesium−ligand and sodium−ligand complexation constants. Cesium theoretical retention rates calculated from the following K_{CsL} and K_{NaL} were in good agreement with cesium experimental retention rates (Table 5).

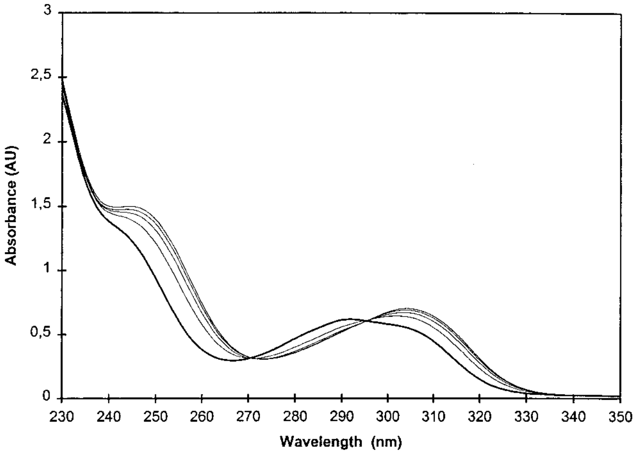


Figure 6. Changes in UV absorption spectrum of **11** (bold line) with CsCl addition in water ([**11**] = 10^{-4} mol/L, pH = 12).

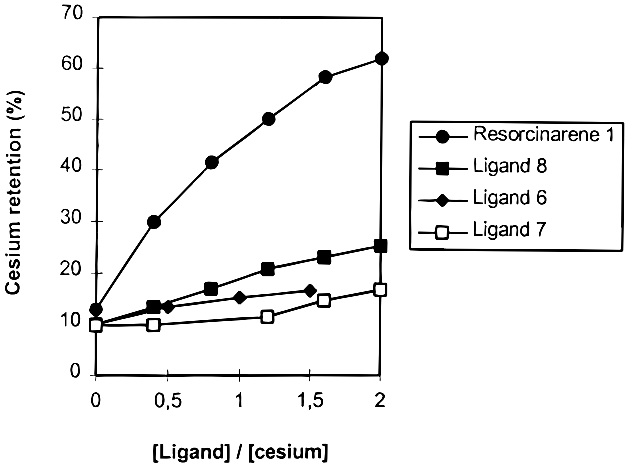


Figure 7. Cesium retention as a function of [ligand]/[cesium] ratio ([cesium] = 15 mg/L, $[NaNO_3]$ = 0.1 mol/L, pH = 11, T = 293 K).

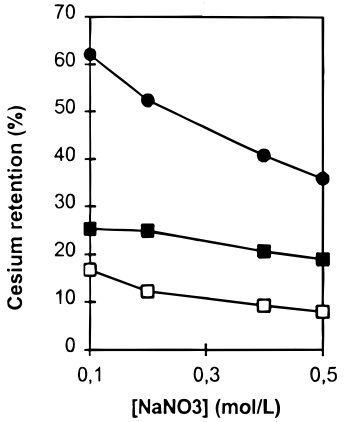


Figure 8. Cesium retention as a function of $[NaNO_3]$ ([cesium] = 15 mg/L, T = 293 K, pH = 11, [ligand]/[cesium] = 2).

It appeared that K_{CsL} for **1** was 10 times that for **10**, which explained why **1** was more cesium-selective than **10** (Figure 9). However, the ratio K_{CsL}/K_{NaL} was equal to 1290 for **1** and to 1950 for **10**, and therefore Cs^+/Na^+ selectivity for **10** was greater than that for **1** (Figure 10).

Finally, tetrahydroxylated BC6 **11** showed both a good affinity toward cesium, quite the same as that of the resorcinarene one, and an outstanding Cs^+/Na^+ selectivity that overtook by far that of resorcinarene **1**. In fact, in a 4 mol/L $NaNO_3$ basic aqueous medium, cesium retention by a NF

TABLE 4: Determination of Cs−Ligand Complex Formation Constants by UV Spectrophotometry for Ligands 6−11

ligand	**6**	**7**	**8**	**9**	**10**	**11**
M (g/mol)	1 236	1 496	916	1 004	860	892
[ligand] (mol/L)	4×10^{-5}	10^{-4}	5×10^{-5}	2×10^{-5}	10^{-4}	10^{-4}
$[Na^+]$ (mol/L)	10^{-3}	10^{-7}	10^{-2}	10^{-2}	10^{-3}	10^{-2}
pH	11	7	12	12	11	12
$\lambda_{\text{calculation}}$	/	/	245 nm	245 nm	303 nm	304 nm
β_{CsL} (without unit)	low	low	75 000	60 000	245 000	425 000

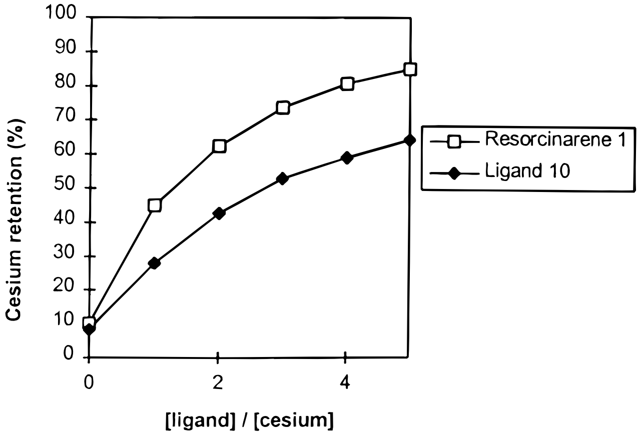


Figure 9. Cesium retention as a function of [ligand]/[cesium] ratio ([cesium] = 15 mg/L, $[NaNO_3]$ = 0.1 mol/L, pH = 11, T = 293 K).

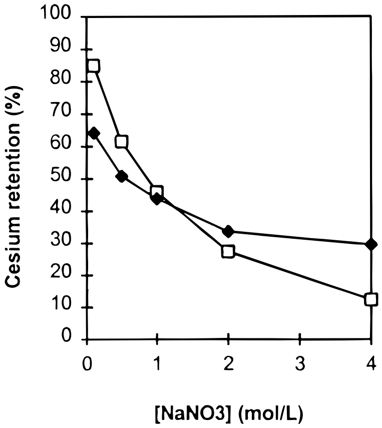


Figure 10. Cesium retention as a function of $[NaNO_3]$ ([cesium] = 15 mg/L, T = 293 K, pH = 11, [ligand]/[cesium] = 5).

TABLE 5: Cesium−Ligand and Sodium−Ligand Complexation Constants of Ligand 10

ligand	K_{CsL} (L/mol)	K_{NaL} (L/mol)
10	3 900	2

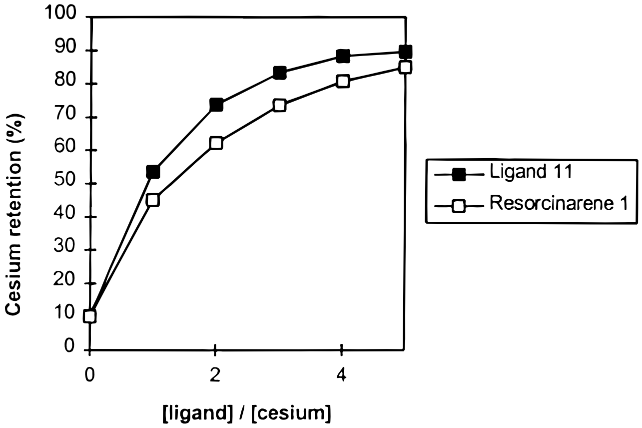


Figure 11. Cesium retention as a function of [ligand]/[cesium] ratio ([cesium] = 15 mg/L, $[NaNO_3]$ = 0.1 mol/L, pH = 11, T = 293 K).

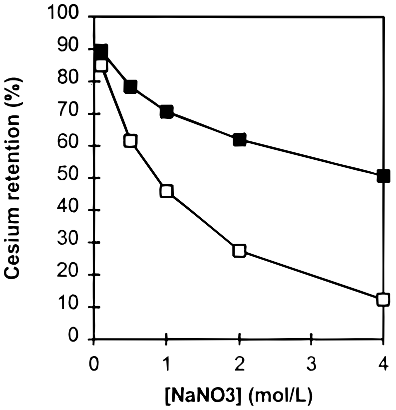


Figure 12. Cesium retention as a function of $[NaNO_3]$ ([cesium] = 15 mg/L, T = 293 K, pH = 11, [ligand]/[cesium] = 5).

TABLE 6: Cesium−Ligand and Sodium−Ligand Complexation Constants of Ligand 11

ligand	K_{CsL} (L/mol)	K_{NaL} (L/mol)
11	23 000	3.5

membrane was still as high as 50% with a [ligand]/[cesium] ratio equal to 5 (Figures 11 and 12).

As for ligands **1** and **10**, both nanofiltration−complexation tests carried out with ligand **11** allowed the calculation of cesium−ligand and sodium-−ligand complexation constants (Table 6).

It appeared that K_{CsL} for **1** was only twice that for **11**, which explained why retention curves were quite similar for both ligands (Figure 11). However, the ratio K_{CsL}/K_{NaL} was equal to 1290 for **1** and to 6570 for **11**, so Cs^+/Na^+ selectivity for **11** was 5 times that for **1** (Figure 12).

3. Stability of Cs Complex with Ligand ***11.*** Ligand **11** was much more stable in basic aqueous medium than resorcinarene **1**. For instance, both following spectra of tetrahydroxylated BC6 **11** were recorded within a 7-day period (Figure 13). The shape of the second spectrum was similar to the first one. Therefore, it could be assumed that this ligand remained stable in basic aqueous medium.

Use of Tetrahydroxylated Bis-crown-6 Calix[4]arene for the Separation of Cs^+ in Highly Salted Aqueous Medium

Separating cesium traces in highly concentrated sodium salt medium is a challenging research subject.

First, it is a scientific challenge because the Cs^+/Na^+ separation is far from easy whatever the method is. Moreover, separating Cs^+ traces (some microgrammes per liter) in medium containing very high amounts of sodium salts is a far more difficult project.

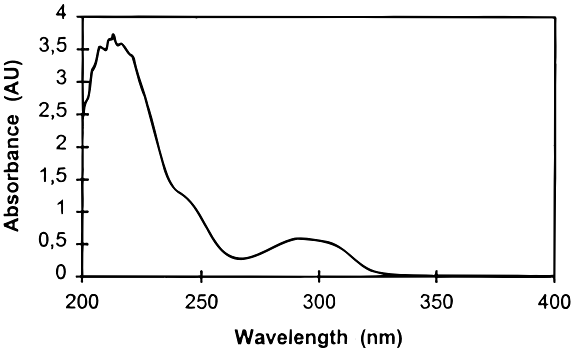


Figure 13. UV absorption spectrum of **11** in aqueous medium (pH = 12, [**11**] = 10^{-4} mol/L).

TABLE 7: Cesium Retention as a Function of Cesium Concentration ($[NaNO_3] = 0.1$ mol/L, [Ligand 11] = 0.5 g/L, pH = 12)

[cesium] (mg/L)	cesium retention (%)
1.5	90
3	87
7.5	87
15	86

TABLE 8: Cesium Retention as a Function of Sodium Nitrate Concentration ([Cesium] = 12.5 mg/L, [11]/[Cesium] = 40, pH = 12)

$[NaNO_3]$ (mol/L)	cesium retention (%)
0.1	98.5
1	96.1
2	93.6
3	90.6

Second, it is an economic challenge, because there is an important demand for an efficient, reliable, and clean process for such a separation. For instance, the removal of cesium radioactive traces in nuclear effluents containing highly concentrated sodium salts requires a process that could remove 99% of cesium and less than 5% of sodium salts in one stream (for a long-term storage), and less than 1% of cesium and much of the sodium salts in the other stream (for an eventual discharge).

Nanofiltration−complexation could meet these requirements only at the condition of having a highly cesium-selective ligand. So tetrahydroxylated BC6 **11** was involved in the following experiments as our selected ligand for Cs^+/Na^+ separation by nanofiltration−complexation, with some experimental conditions that were supposed to simulate industrial conditions.

1. It seemed that the [ligand]/[cesium] ratio was not the key factor for cesium retention by nanofiltration−complexation. In Table 7, cesium concentration was increased during a NF test involving **11** and a 0.1 mol/L sodium nitrate solution. It appeared that cesium retention did not change much under cesium addition. Calculation confirmed that the real key factor was the ligand total concentration itself.

2. Another experiment pointed out the fact that reaching a 90% cesium retention by NF in a 3 mol/L sodium nitrate aqueous medium was possible with ligand **11**. With a basic aqueous solution containing 12.5 mg/L of Cs, a 3.4 g/L of ligand **11** was required to reach 90% of cesium retention (Table 8).

3. After use in NF tests, **11** was regenerated by acidification of the solution ($5 < pH < 6$) with HCl with a 60% yield. It was shown that results with newly synthesized **11** and results with regenerated **11** were quite similar, proving again that this ligand does not deteriorate in basic aqueous medium.

TABLE 9: Cesium Retention as a Function of Reaction Time after Addition of Ligand 11 ($[NaNO_3] = 3$ mol/L, pH = 12, [Cesium] = 15 mg/L, [Ligand] = 3.4 g/L)

reaction time (mn)	cesium retention (%)
0	5.4
5	80.0
20	89.1
40	89.9
80	90.6
170	91.3
270	91.2

TABLE 10: Cesium Retention as a Function of Temperature ($[NaNO_3] = 3$ mol/L, [Ligand] = 3.4 g/L, [Cesium] = 15 mg/L, pH = 12)

temperature (K)	cesium retention (%)
293	91.2
298	90.4
303	88.4
313	85.0

4. A kinetic study of the cesium complexation by **11** was carried out to ensure that all our previous NF experiments had been achieved at the chemical equilibrium.

It appeared that a minimum of 20 min after the ligand addition was required to allow the NF-complexation system to reach an equilibrium at 90% of cesium retention (Table 9).

5. All the previous NF experiments were carried out at the temperature of 293 K. Here, temperature was increased to measure the temperature influence on cesium retention.

At constant ligand concentration, cesium retention decreased while temperature increased (Table 10). This phenomenon was proved to be reversible.

All these experiments proved that tetrahydroxylated bis-crown-6 calix[4]arene **11** was a high-performing ligand for an eventual Cs^+/Na^+ separation by nanofiltration−complexation in aqueous medium. It allowed us to reach 90% of cesium retention in a 3 mol/L $NaNO_3$ aqueous medium. By combining two stages of such a process, it would now be possible to remove 99% of cesium traces and not more than 10% of initial sodium salts.

Conclusion

UV spectroscopy seemed to be a reliable method for determining cesium−ligand complex formation constants, especially with very cesium-selective ligands in order to select new hydrophilic ligands for the Cs^+/Na^+ separation. At least they allowed us to compare, in the first approach, the cesium selectivity of different ligands.

Tetrahydroxylated bis-crown-6 calix[4]arene **11** showed a high Cs^+/Na^+ selectivity. Through a nanofiltration−complexation process, it allowed us to separate traces of cesium in a highly salted aqueous medium. Such efficient separation had never been performed before with other filtration methods. Compared to liquid−liquid extraction, nanofiltration does not require solvent addition, which is a great advantage in matter of environment preservation. Nanofiltration applications in chemical industrial processes are currently traces removal, valuable metal recovery, and products/catalysts separation in homogeneous catalytic processes. Thanks to its wide industrial applications, NF should be predicted a promising development.

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