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***Dedicated to the memory of Prof. dr. Ioan Silaghi-Dumitrescu marking 60 years from his birth***

# STUDIES ON THE EUROPIUM AND PALLADIUM EXTRACTION WITH SOME CALIX[6]ARENE DERIVATIVES

**ALINA SAPONAR[a, *], ELISABETH-JEANNE POPOVICI[a],**
**IOANA PERHAIŢA[a], NICOLAE POPOVICI[a] AND**
**IOAN SILAGHI-DUMITRESCU[b]**

**ABSTRACT.** The capability of *p-tert*-butyl calix[6]arene functionalized at the lower rim with 2-butenyl, ethyl acetate and/or N,N-diethylacetamide groups to extract $Pd^{2+}$ and $Eu^{3+}$ ions from aqueous medium have been investigated. Good extraction yield was obtained for calix[6]arene derivatives functionalized with *tri-* and *hexa-* ethylacetate and *tri-* and *hexa-* N,N-diethylacetamide groups. It vas revealed that the half or total substituted *p-tert*-butyl calix[6]arene ester derivatives present interest as liquid-liquid extraction reagents for precious metal and rare earth ions.

***Keywords**: Calixarene, liquid-liquid extraction, metal ions.*

## INTRODUCTION

The development of efficient extraction agents to remove metal ions from both organic and aqueous effluents for either safe disposal or recycling has motivated research into the coordination properties of calixarene-based ligands.

Calixarenes are macrocycles made up of phenolic units linked by methylene bridges with host-guest properties. They are known as inexpensive, chemically stable molecular networks/systems utilizable as selective complexing agents for neutral molecules and ions [1-10]. Functionalised calix[n]arene (n = 4, 6, 8) have received much attention because of their increased molecular and ion binding capability revealed also by their ability to transport metal cations across organic membranes and to behave as metal carriers.

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[a] *Raluca Ripan Institute for Research in Chemistry, Babes Bolyai University, 400294, Cluj-Napoca, Romania,* salina@chem.ubbcluj.ro*

[b] *Faculty of Chemistry and Chemical Engineering, Babes-Bolyai University, 400084, Cluj-Napoca, Romania.*

Selective and efficient cation receptors can be prepared by functionalization of the parent calixarene with metal coordinating groups. Usually, this is performed at the "narrow rim", because of the easy synthesis of a great number of derivatives, which allows comparing the impact of some factors on the extraction behavior (i.e. cavity size, conformation, functional groups) and the flexibility to design a proper ligand to selectively recognize metal ions [11-23]. Liquid-liquid extraction experiments were carried out to recover metals from aqueous solution using as extractants calix[6]arene derivatives dissolved in organic solvents (i.e. chloroform, dichloromethane, toluene, acetonitrile), allowing the exploitation of the calixarene's cone-shape and the chelating ring of oxygen, nitrogen and phosphorus donor atoms that encircle the guests.

Herein we present our studies referring to the extraction of some rare earth and precious metals, using the parent calix[6]arene and some new calix[6]arene derivatives obtained by functionalization at the narrow rim with ester and/or amido and/or alkenyl donor groups.

In this respect, ten calixarene- based compounds were used as extracting agents i.e. *p-tert*-butyl calix[6]arene and *p-tert*-butyl calix[6]arene grafted with two, three and four E-2-butenyl groups, three and six ethylacetate groups, three and six N,N-diethylacetamide groups, three 2-butenyl and three ethylacetate groups and three 2-butenyl and three N,N-diethylacetamide groups, respectively. Their capability to act as extraction reagents for $Pd^{2+}$ and $Eu^{3+}$ ions was investigated.

## RESULTS AND DISCUSSION

A series of nine ester, amido and/or alkenyl calix[n]arene derivatives were tested as extracting reagent for precious metal and rare earth ions, in comparison with the parent calixarene (Figure 1).

The following calixarene-based compounds were used as extracting reagents: *p-tert*-butyl-calix[6]arene (**C6**), *bis*-2-butenyl-calix[6]arene (**C6Cr2**), *tris*-2-butenyl-calix[6]arene (**C6Cr3**), *tetra*-2-butenyl-calix[6]arene (**C6Cr4**), *tris*-ethylacetate-calix[6]arene (**C6Es3**), *tris*-N,N-diethylacetamide- calix[6]arene (**C6Am3**), *hexa*-ethylacetate-calix[6]arene (**C6Es6**), *hexa*-N,N-diethylacetamide-calix[6]arene (**C6Am6**), *tris*-N,N-diethylacetamide-*tris*-2-butenyl-calix[6]arene (**C6Am3Cr3**) and *tris*-ethylacetate-*tris*-2-butenyl-calix[6]arene (**C6Es3Cr3**).

Extraction was performed using 5-10 $\times 10^{-4}$ M aqueous solution of $PdCl_2$ or $Eu(NO_3)_3$ and $1\times10^{-3}$ M solution of calixarene (Cx) in $CHCl_3$. Extraction yield was determined by monitoring the concentration of palladium or europium from the aqueous solutions, using Inductively Coupled Plasma Optical Emission Spectrometry.

### *Extraction of $Pd^{2+}$ ions*

The capability of *p-tert*-butyl calix[6]arene derivatives to extract $Pd^{2+}$ ions was determined by liquid-liquid extraction experiments that were performed using equal volumes and equal concentrations of metal ions and calixarenes ($Pd^{2+}$:Cx = 1 :1), and a variable pH of the aqueous medium (Figure 2).

The extraction capability of the different calixarene-based compounds, at pH=2.5, varies between ~54 % for **C6Am6** and ~73% for **C6Es6.** *p-tert*-butyl calix[6]arene **C6** shows an extraction yield of 65%.

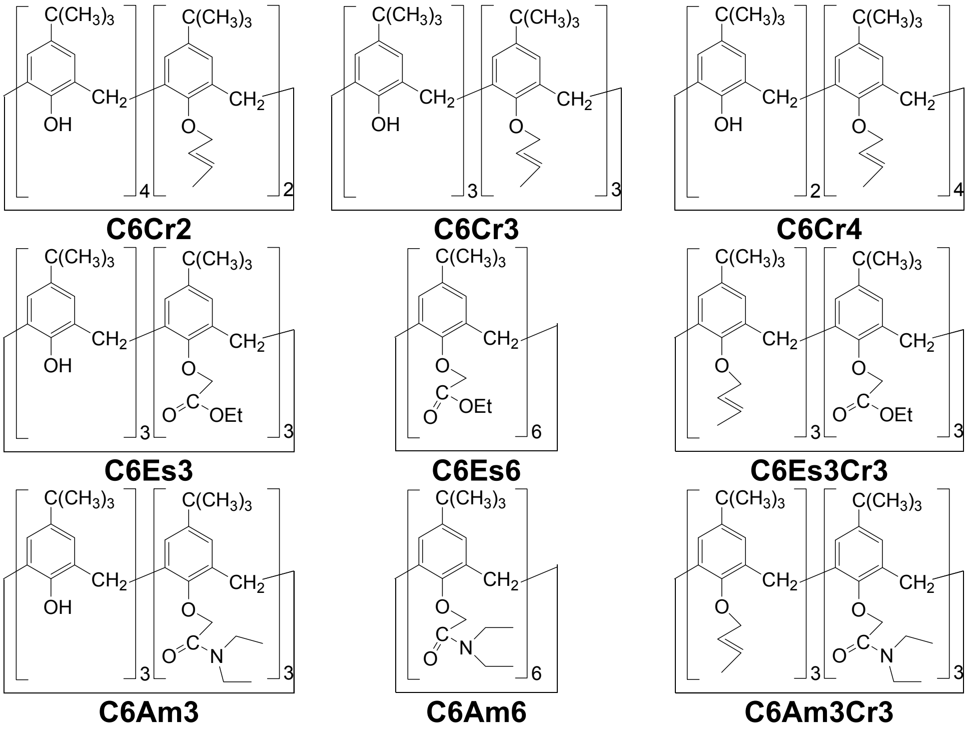

**Figure 1.** The calixarene derivatives used as extracting agents

The grafting of two or three alkenyl- as well as four or six amido-groups decreases the yield as compared with the parent calixarene. Favourable effect is shown by the functionalisation with ester groups. The highest extraction yield i.e. over 70 % is shown by calixarene-derivatives with the highest level of functionalisation i.e. compounds **C6Am3Cr3**, **C6Cr4** and **C6Es6**.

The extraction yield of the $Pd^{2+}$ ions with calixarene-based compounds depends on the acidity of the aqueous medium. Excepting the *hexa*-ester calix[6]arene derivative, extraction yield from aqueous solutions with pH=4.1 is relatively low (under 60%). The highest extraction yield was obtained for **C6Es6** derivatives, namely 72.6% at pH=2.5 and 75.8% at pH = 4.1, respectively.

By comparing the total functionalized calixarene with the half substituted compounds, it can be concluded that, at pH=2.5, the *hexa* functionalized ester derivative (**C6Es6**) is more efficient as extractant than the *tri* functionalized one (**C6Es3**).

The capability of calixarene-based compounds to extract palladium ions in well defined extraction conditions can be estimated by the ratio ***r*** representing the ratio between the mol number of metal ion and calixarene.

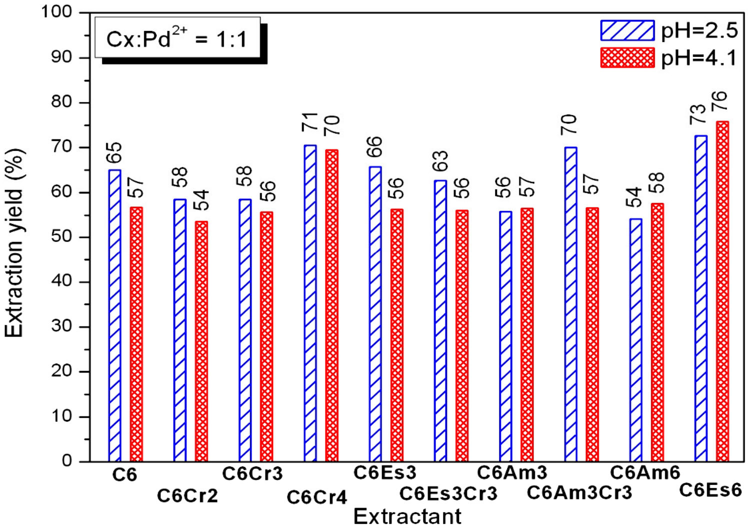

**Figure 2.** Variation of the extraction yield of $Pd^{2+}$ from solutions with variable pH, using different calixarene-based compounds ($c_{Cx}$=1x $10^{-3}$mol/l; $c_{PdCl2}$= 1x$10^{-3}$ mol/l)

In our extraction conditions, for the ester calix[6]arene derivatives, the maximum r value was obtained at pH =2.5 for **C6Es3** (0.657) and at pH=4.1 for **C6Es6** (0.758) whereas for amido calix[6]arene derivatives, at pH =4.1 for both **C6Am3** (0.565) and **C6Am6** (0.575) compounds.

### *Extraction of* $Eu^{3+}$ *ions*

The capability of *p-tert*-butyl calix[6]arene derivatives to extract $Eu^{3+}$ ions was determined by liquid-liquid extraction experiments that were performed using variable volumes with equal concentrations of metal ions and calixarenes so that Cx :Eu ratio be varied between 2:1 and 1:2, and variable pH of the aqueous medium.

The extraction yield (η) and the ratio (***r***) representing the mol number of $Eu^{3+}$ extracted by 1 mol of calixarene-based compounds, at pH=2.8 are shown in Table 1. Extraction experiments were performed for 1:1, 2:1 and 1:2 ratio between the extractant (Cx) and the extracted species (Eu).

The *p-tert*-butyl calix[6]arene **C6** shows an extraction yield of only 23.9%, when working with calixarene: metal ratio equal to 1:1. The grafting of two alkenyl-groups slowly increases the yield as compared with the parent calixarene whereas the attaching of three or four alkenyl-groups decreases it. Opposite results were obtained in the case of experiments with calixarene: metal ratio equal to 2:1. The grafting of three or six ester groups increase the yield as compared with the parent calixarene or the other calixarene derivatives. Favorable effect is shown by the functionalization with ester groups, whatever the calixarene: metal ratio.

**Table 1**. The extraction data for europium ions, using different calixarene-based compounds (pH=2.8;$c_{Cx}$=1x$10^{-3}$mol/l; $c_{Eu(NO3)3}$= 1x$10^{-3}$ mol/l)

| Calixarene-based compounds | Ratio Cx:Eu=1:1 | | Ratio Cx:Eu = 2:1 | | Ratio Cx:Eu = 1:2 | |
|---|---|---|---|---|---|---|
| | η (%) | ***r*** | η (%) | ***r*** | η (%) | ***r*** |
| **C6** | 23.9 | 0.238 | 26.1 | 0.130 | 13.2 | 0.263 |
| **C6Cr2** | 31.9 | 0.319 | 21.3 | 0.106 | 20.4 | 0.408 |
| **C6Cr3** | 18.7 | 0.187 | 42.6 | 0.213 | 23.8 | 0.475 |
| **C6Cr4** | 12.5 | 0.124 | 38.6 | 0.193 | 29.6 | 0.592 |
| **C6Es3** | 57.1 | 0.570 | 58.3 | 0.291 | 44.6 | 0.891 |
| **C6Es3Cr3** | 34.2 | 0.342 | 55.2 | 0.276 | 61.1 | 1.222 |
| **C6Am3** | 38. 7 | 0.386 | 13.4 | 0.067 | 25.0 | 0.500 |
| **C6Am3Cr3** | 29. 9 | 0.298 | 16.8 | 0.083 | 20.3 | 0.405 |
| **C6Am6** | 50.1 | 0.500 | 18.3 | 0.091 | 27.9 | 0.557 |
| **C6Es6** | 51.9 | 0.519 | 48.5 | 0.242 | 26.2 | 0.523 |

The extraction yield of Eu(III) ions from aqueous solution (pH=2.8) varies between 12.5% for **C6Cr4** and 57.1% for **C6Es3**, in experiments with calixarene: metal ratio Cx:Eu= 1:1, between 13.4% for **C6Am3** and 58.3% for **C6Es3** for Cx:Eu= 2:1 and 13.2% for **C6** and 61.1% for **C6Es3Cr3** for Cx:Eu= 1:2.

Unexpectedly, the highest extraction yield for europium ions (61.1%) was obtained for **C6Es3Cr3** derivatives, when calixarene: metal ratio was 1:2. The grafting of alkenyl-groups alone or together with ester ones improve the calixarene capability to extract Eu(III) ions.

The extraction yield of the $Eu^{3+}$ ions with calixarene-based compounds depends on the calixarene: metal ratio (Figure 3). In this case, the total functionalised ester calix[6]arene derivative is less efficient than the half substituted compound, contrary to the palladium situation. The maximum efficiency appears at **C6Es3** derivatives, for Cx:Eu= 2:1.

The capability of calixarene-based compounds to extract europium ions in well defined extraction conditions was estimated by the ratio ***r*** representing the mol number of metal ion extracted by 1 mol of calixarene. In our extraction conditions, for the ester substituted calix[6]arene, the maximum ***r*** value was obtained for Cx:Eu = 1:2, namely 0.891 for **C6Es3** and 0.523 for **C6Es6**. The additional grafting of three butenyl-groups to the **C6Es3** compound increases the ***r*** value to 1.222 thus suggesting that for **C6Es3Cr3** compound, a more complicated $Eu^{3+}$ sequestration process is involved.

The capability of *p-tert*-butyl calix[6]arene derivatives to extract $Eu^{3+}$ ions was also determined at pH=4.6, using europium nitrate solutions with different concentrations.

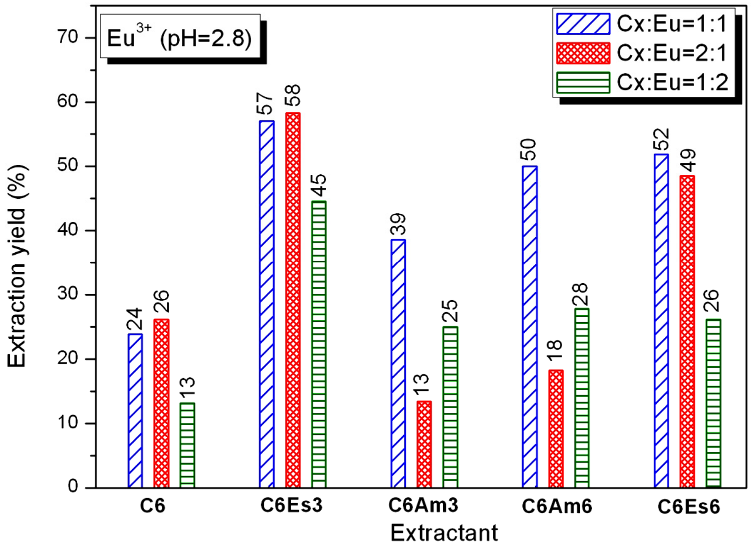

**Figure 3.** Variation of the extraction yield of $Eu^{3+}$ using variable calixarene-to-europium ratios and different calixarene-based compounds ($c_{Cx}=1x10^{-3}$mol/l; $c_{Eu(NO3)3}= 1x10^{-3}$ mol/l)

The extraction yield (η) and the ratio (***r***) representing the mol number of $Eu^{3+}$ extracted by 1 mol of calixarene for different calixarene-based compounds, at pH=4.6 are shown in Table 2. Extraction experiments were performed for 1:1 ratio between the extractant (Cx) and the extracted species (Eu).

**Table 2**. The extraction data for europium ions, using different calixarene-based compounds and $Eu^{3+}$ solutions with variable concentration (pH=4.6; Cx:Eu=1:1; $c_{Cx}=1x10^{-3}$mol/l)

| Calixarene-based compounds | $1x10^{-3}$ mol $Eu^{3+}$ /L | | $5x10^{-4}$ mol $Eu^{3+}$ /L | |
|---|---|---|---|---|
| | η (%) | ***r*** | η (%) | ***r*** |
| **C6** | 32.4 | 0.324 | 23.2 | 0.231 |
| **C6Cr2** | 26.8 | 0.268 | 26.0 | 0.260 |
| **C6Cr3** | 30.3 | 0.303 | 25.3 | 0.253 |
| **C6Cr4** | 30.2 | 0.301 | 22.1 | 0.220 |
| **C6Es3** | 32.2 | 0.321 | 20.8 | 0.208 |
| **C6Es3Cr3** | 29.0 | 0.290 | 21.1 | 0.210 |
| **C6Am3** | 30.5 | 0.304 | 24.8 | 0.247 |
| **C6Am3Cr3** | 25.0 | 0.250 | 25.9 | 0.258 |
| **C6Am6** | 34.8 | 0.347 | 19.9 | 0.198 |
| **C6Es6** | 37.4 | 0.374 | 41.9 | 0.419 |

The extraction capability of the different calixarene-based compounds to extract $Eu^{3+}$ ions in solutions with pH=4.6 is low. *p-tert*-butyl calix[6]arene **C6** shows an extraction yield of only 32.4% and 23.2% when working with $1x10^{-3}$ mol $Eu^{3+}$ /L and $5x10^{-4}$ mol $Eu^{3+}$ /L, respectively. In the first case, almost all calixarene-derivatives show a lower extraction capability than the parent calixarene. The only exceptions are the total substituted calix[6]arene with ester- and amido- groups (**C6Es6**; **C6Am6**).

With the exception of **C6Es3** and **C6Am3Cr3** derivatives, the best extraction results were obtained when working with $1x10^{-3}$M solutions.

In order to investigate whether the concentration of europium solutions influences also the extraction yield in more acidic medium, liquid-liquid extraction experiments were performed for some of the *hexa* substituted calix[6]arene, using diluted europium solutions ($5x10^{-4}$ mol $Eu^{3+}$/L) and variable Cx:Eu ratio (Figure 4)

The extraction of europium from diluted solution with pH=2.7 take place with a yield that varies between ~41% (**C6Am6**) and ~77 (**C6Es6**) for Cx:Eu=2:1 and ~26% (**C6Am3Cr3**) and 31% (**C6Am6**) for Cx:Eu=2:1. Although the extraction yield obtained with *hexa* ester calix[6]arene derivative is high (77%), in our experimental conditions, the ratio *r* representing the mol number of $Eu^{3+}$ extracted by 1 mol of calixarene is only 0.191.

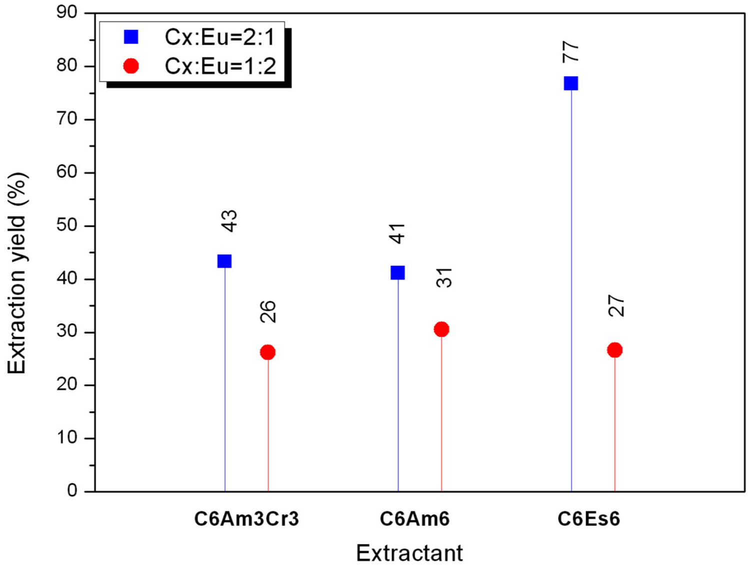

**Figure 4.** Variation of the extraction yield of $Eu^{3+}$ using different calixarene-to-europium ratios and different calixarene-based compounds (pH=2.7; $c_{Cx}=1x10^{-3}$mol/L; $c_{Eu(NO3)3}= 5x10^{-4}$)

## CONCLUSIONS

The capability of *p-tert*-butyl calix[6]arene functionalised at the lower rim with 2-butenyl, ethyl acetate and/or N,N-diethylacetamide groups to extract precious or rare earth metallic ions have been investigated by liquid-liquid extraction experiments. Partial or total substituted calix[6]arenes with alkenyl and/or ester and/or amido donor groups were used to extract $Pd^{2+}$ and $Eu^{3+}$ ions from aqueous medium, in different experimental conditions i.e. pH, cation concentration, calixarene/metal ratio.

The best extraction capability was shown by calix[6]arene derivatives functionalized with *tri*- and *hexa*- ethylacetate groups. For palladium ions, the total functionalized calixarene derivative is more efficient as extractant than the half substituted compound; opposite results were obtained for europium extraction. The highest extraction yield is achieved at pH=2...3 for europium and 4...5 for palladium. In general, the capability of *p-tert*-butyl calix[6]arene derivatives to extract $Eu^{3+}$ ions is smaller than for $Pd^{2+}$, whatever the pH value.

The extraction yield can be considerably improved by modifying the extraction conditions: ratio between calixarene derivatives and metallic ions, solutions concentration, the number of the extraction cycles, etc. The extraction yield of europium could be increased with 20-30% when the calixarene: metal ratio is modified from 1:1 to 2:1.

The *p-tert*-butyl calix[6]arene derivatives functionalized with *tri-* and *hexa-* ethyl acetate groups present great interest as liquid-liquid extraction reagents for precious metal and rare earth ions.

## EXPERIMENTAL SECTION

### *Chemical reagents*

All the calixarene-base compounds were synthesized according to the described methods [25-27]: *hexa-t*-butylcalix[6]arene (abbreviated **C6**), *hexa*–tbutyl–bis[(but-2-enyloxy]- *tetra*hydroxy calix[6]arene (**C6Cr2**), *hexa*-tbutyl-*tris*[(but-2-enyloxy]-*tri*hydroxy-calix[6] arene (**C6Cr3**), *hexa*–tbutyl–*tetra*kis-[(but-2-enyloxy]- dihydroxy calix[6] arene (**C6Cr4**),*hexa*-tbutyl-*tris*-[(ethoxycarbonyl)metoxy]-*tri*hydroxy-calix[6]arene(**C6Es3**), *hexa*-tbutyl-*tris* [(N,N-diethylamino carbonyl) methoxy]- *tri*hydroxy-calix[6] arene (**C6Am3**), *hexa-t*-butyl-*hexakis*-[(ethoxycarbonyl)metoxy]-calix[6]arene(**C6Es6**), *hexa*-tbutyl-*hexakis* [(N,N-diethylamino-carbonyl)methoxy] calix[6]arene (**C6Am6**), *hexa*-tbutyl-*tris*[(N,N-diethylamino-carbonyl)methoxy]- *tris*-(but-2-enyloxy)-calix[6]arene (**C6Am3Cr3**) and *hexa*- tbutyl-*tris* [(ethoxycarbonyl)methoxy]-*tris*-(but-2-enyloxy)-calix[6]arene (**C6Es3Cr3**).

Analytical-grade chloroform and deionized water were employed as solvents in the liquid-liquid extraction experiments. All others inorganic and organic reagents were standard grade and used without further purification.

### *Instrumentation and analysis*

The metal concentration in aqueous medium was determined before and after extraction with ICP-OES - Spectroflame D Spectrophotometer ($\lambda$=340,458 nm and detection limit=0,01919 mg/l for palladium; $\lambda$=381,966 nm and detection limit=0,0081 mg/l for europium).

### *Liquid-liquid extraction of metal ions*

The organic solutions were prepared by dissolving the required amount of calixarene derivative, in chloroform, to obtain a solution with $1x10^{-3}$ M concentration.

The aqueous solutions of metals were prepared by dissolving the required amount of $PdCl_2$ or $Eu(NO_3)_3.5H_2O$ in acidulated water to obtain $5...10x10^{-4}$ mol/L solutions. The acidity of the aqueous medium was monitored with a pH-instrument. The pH was adjusted to pH 2.5 and 4.1 with HCl, for $Pd^{2+}$ solution and to pH 2.7-2.8 or 4.6 with $HNO_3$, for $Eu^{3+}$ solutions.

Liquid-liquid extraction experiments were carried out by introducing the organic and aqueous solutions (1:1, 2:1 and 1:2 volumetric ratios) into extraction funnels and vigorously shaking them, for 30 minutes, using a mechanical shaker. The aqueous phase was left to settle, washed with $CHCl_3$, separated and analysed.

The measurements were carried out with an ICP-OES instrument, using standard conditions calibration. The extraction yield ($\eta$%) was calculated from the equation [28]:

$$\eta = ( A_0 - A ) / A_0 \times 100\ \%$$

where $A_0$ and A are the initial and the final concentration (mg/L) of the metal salt before and after extraction, respectively.

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