STUDIA UBB CHEMIA, LVII, 2, 2012 (p. 157 - 167)

STUDIES ON THE PALLADIUM AND GOLD IONS EXTRACTION WITH SOME ESTER DERIVATIVES OF CALIX[N]ARENE

ALINA SAPONAR[a,*], ELISABETH-JEANNE POPOVICI[a],
IOANA PERHAITA[a], GABRIELA NEMES[b]

ABSTRACT. The capability of *p-tert*-butyl calix[n]arene [n = 4,6,8] functionalized at the lower rim with a variable number of ethyl acetate groups to extract palladium and gold ions from aqueous medium has been investigated. The influence of reagent molar ratio, acidity of the medium and time on the extraction efficiency was investigated by monitoring the concentration of the metallic ions from aqueous solution. In most of the cases, the half substituted calix[n]arene derivatives show a relative high extraction efficiency and are of interest as liquid-liquid extraction reagents for precious metal ions.

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

INTRODUCTION

The design of new compounds that can act as extractants for toxic or valuable metals from waters and soils represent a continuous need, both in environmental and economical point of view. The challenge is to find ligands that efficiently and selectively extract commercially useful metals from aqueous medium and allow them to be released in pure form [1]. Calixarene is a class of compounds that successfully fulfill these requirements [2, 3]. They can be used as receptors for a large variety of ions and small molecules, forming host-guest or supramolecular complexes [4-12].

Calixarenes are a family of cyclic oligomers prepared from formaldehyde and *para*-substituted phenols via cyclic condensation under alkalin conditions [2]. They are characterized by a wide upper rim formed from the *para* substituents of the phenolic rings, a narrow lower rim formed from the phenolic hydroxyl groups and a central annulus i.e. a hydrophobic cavity consisting of aromatic rings [3]. Calixarene derivatives, with their large diversity of functional groups grafted at the upper or lower rims as well as with their cavity-shaped architecture, have been used extensively as selective ligands for metal ions in liquid-liquid extraction, in selective transport, as ionophores in ion-selective electrodes or as chromophores in optical sensing [13-24].

---

[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, 40084, Cluj-Napoca, Romania

The ability of the calix[n]arene molecules functionalized with electron donor groups to coordinate metal ions has been investigated by liquid-liquid extraction methods. These methods are based on the transfer of the analyte from the aqueous sample to a water-immiscible solvent [25]. The calix[n]arene derivatives dissolved in organic solvents (i.e. chloroform, dichloromethane, toluene, acetonitrile) are used as extractants for the recovery of the metals from aqueous solutions. They allow the exploitation of both the calixarene's cone-shape and the chelating ring of oxygen and nitrogen donor atoms that encircle the guests [26, 27].

Herein we present our studies referring to the extraction of precious metals using some calix[n]arene derivatives obtained by functionalization at the narrow rim with ethyl acetate donor groups, as already reported in our previous work [28]. We describe some calixarene-based compounds that were used as extracting agents in chloroform i.e. *p-tert*-butyl calix[4]arene grafted with two and four ethyl acetate groups, *p-tert*-butyl calix[6]arene grafted with two, three, four and six ethyl acetate groups and *p-tert*-butyl calix[8]arene grafted with four, six and eight ethyl acetate groups, respectively. Their capability to act as extraction agents for Pd^{2+} and Au^{3+} ions was investigated.

RESULTS AND DISCUSSION

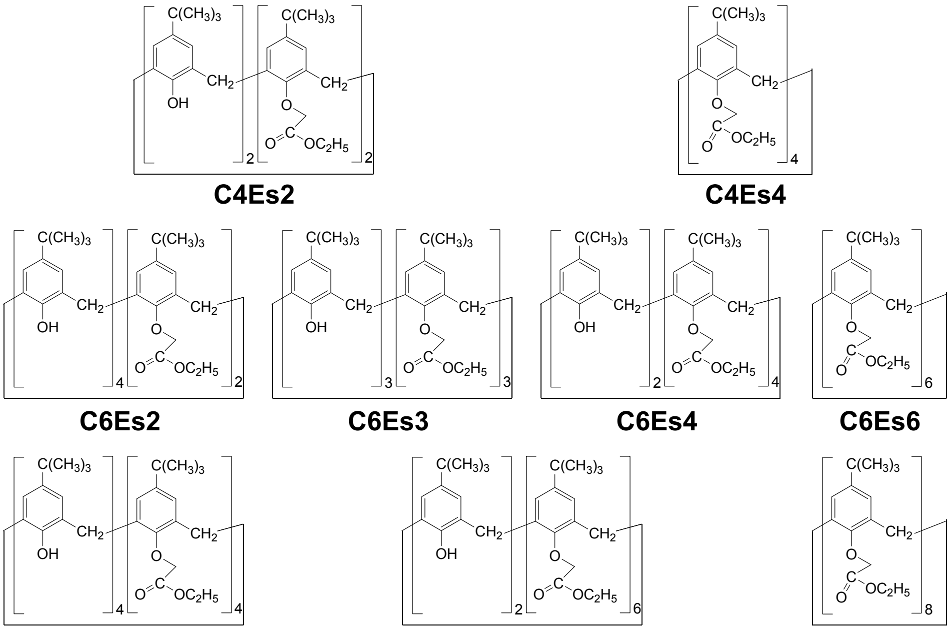
The calixarene-based compounds used as extracting reagents are schematically presented in Figure 1 as follows: *bis*-ethylacetate-calix[4]arene (**C4Es2**), *tetra*-ethylacetate-calix[4]arene (**C4Es4**), *bis*-ethylacetate-calix[6]arene (**C6Es2**), *tris*-ethylacetate-calix[6]arene (**C6Es3**), *tetra*-ethylacetate-calix[6]arene (**C6Es4**), *hexa*-ethylacetate-calix[6]arene (**C6Es6**), *tetra*-ethylacetate-calix[8]arene (**C8Es4**), *hexa*-ethylacetate-calix[8]arene (**C8Es6**) and *octa*-ethylacetate-calix[8]arene (**C8Es8**).

The liquid-liquid extraction experiments were performed using $1x10^{-3}$ M aqueous solutions of $PdCl_2$ or $HAuCl_4$ and a $1x10^{-3}$ M solution of calixarene (Cx) in chloroform. The influence of the reagent molar ratio, acidity of the aqueous medium and time on the extraction efficiency was investigated by monitoring the concentration of metallic ions from the aqueous solutions, using Inductively Coupled Plasma Optical Emission Spectrometry.

Extraction of Pd^{2+} ions

The capability of *p-tert*-butyl-calix[n]arene esteric derivatives to extract Pd^{2+} ions from aqueous solutions was determined in a medium with variable pH (1.9, 2.6 and 3.1) using different molar ratios of reagents ($Cx:Pd^{2+}$= 2:1, 1:1 and 1:2), and a variable time of extraction (t = 30 - 360 min).

In a first stage, the extraction experiments were carried out at pH=2.6, using variable volumes of metal ions and calixarenes to achieve the Cx:Pd^{2+} molar ratios of 2:1, 1:1 and 1:2, respectively.



C4Es2 **C4Es4**

C6Es2 **C6Es3** **C6Es4** **C6Es6**

C8Es4 **C8Es6** **C8Es8**

Figure 1. Calix[n]arene derivatives used as extracting agents

The dependence of the extraction yield (η) of the nine calixarene-based compounds on the ratios between the extractant and the extracted species is illustrated in Figure 2.

The yield for the extraction of Pd (II) ions from aqueous solution varies between 14.1% for **C6Es6** and 53.2% for **C6Es3**, in experiments with ratio Cx:Pd = 1:1, between 25.7% for **C8Es4** and 52.3% for **C4Es4** for Cx:Pd = 2:1 and between 18.2% for **C8Es6** and 40.9% for **C6Es3** for Cx:Pd = 1:2.

The highest extraction yield 53.2% was obtained for the **C6Es3** derivative, when calixarene:palladium ratio was 1:1.

The capability of calixarene-based compounds to “fix” palladium ions from aqueous medium can be estimated by the molar ratio **r** between the amount of extracted metal ion and the amount of extracting calixarene, a ratio that illustrates the number of mols of metal ion extracted by 1 mol of calixarene.

In our extraction conditions, the maximum extraction capability **r** was shown by the half- and totally substituted calix[6]arene, namely the compounds **C6Es3** (**r** = 0.82) and **C6Es6** (**r** = 0.93), when the ratio Cx:Pd^{2+} was 1:2.

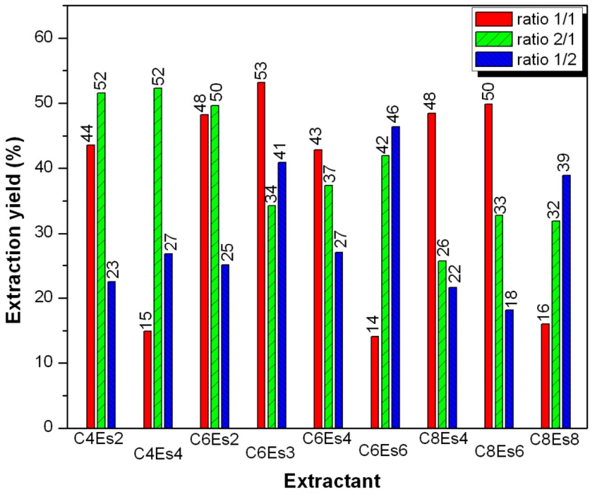


Figure 2. Extraction yield of Pd^{2+} with different calixarene-based compounds, using different Cx:Pd^{2+} ratios (pH=2.6, t=30 min)

The capability of *p-tert*-butyl calix[n]arene derivatives to extract palladium ions was also determined by liquid-liquid extraction experiments that were performed in an aqueous medium with variable pH, using equal volumes and equal concentrations of metal ions and calixarenes (Cx:Pd = 1:1). The results are summarized in Table 1.

Table 1. Extraction data for palladium ions, using different calixarene-based compounds at different pH (Cx:Pd^{2+} = 1:1; t=30 min)

Calixarene-based compounds	pH=1.9		pH=2.6		pH=3.1	
	η (%)	**r**	η (%)	**r**	η (%)	**r**
C4Es2	42.9	0.47	43.6	0.44	22.5	0.26
C4Es4	27.7	0.32	14.9	0.18	22.9	0.26
C6Es2	39.5	0.43	48.2	0.48	31.4	0.34
C6Es3	42.3	0.46	53.2	0.53	18.5	0.22
C6Es4	24.0	0.29	42.9	0.43	16.2	0.19
C6Es6	29.1	0.33	14.1	0.17	24.5	0.28
C8Es4	19.9	0.25	48.5	0.48	32.6	0.36
C8Es6	13.4	0.19	49.9	0.49	26.0	0.29
C8Es8	17.3	0.22	16.0	0.16	16.9	0.21

The extraction yield varies between 13.4% for **C8Es6** and 42.9% for **C4Es2** at pH 1.9, between 14.1% for **C6Es6** and 53.2% for **C6Es3** at pH=2.6 and between 16.2% for **C6Es4** and 31.4% for **C6Es2** at pH=3.1. It is obvious that the extraction yield of the Pd^{2+} ions with calixarene-based compounds depends on the acidity of the aqueous medium. Excepting the fully functionalized calix[n]arenes, all the calixarenele-based compounds show the maximum extraction efficiency at pH=2.6. For the calixarenes compounds **C4Es4**, **C6Es6** and **C8Es8,** the extraction efficiency is maximum at pH=1.9.

The highest extraction yield 53.2% was obtained for the **C6Es3** derivative, at pH=2.6. This compound shows the best extraction capability illustrated by the highest **r** value, namely 0.53. Good results were also obtained for **C4Es2** (η =42.9%, **r** = 0.47) at pH=1.9 and **C8Es4** (η =48.5%, **r** = 0.48) at pH=2.6.

It seems that the half-substituted compounds are more efficient as extracting reagents than the total functionalized compounds, whatever the pH. This could be due to a steric effect that is favourable for metal ion coordination.

The influence of the extraction time on the process efficiency was investigated for the totally functionalized calixarene derivatives, namely compounds **C4Es4**, **C6Es6** and **C8Es8**. The study was carried out in an aqueous medium with pH=2.6, using equal volumes and equal concentrations of metal ions and calixarenes (Cx:Pd = 1:1). The time of extraction was varied between 30 and 360 min (Figure 3).

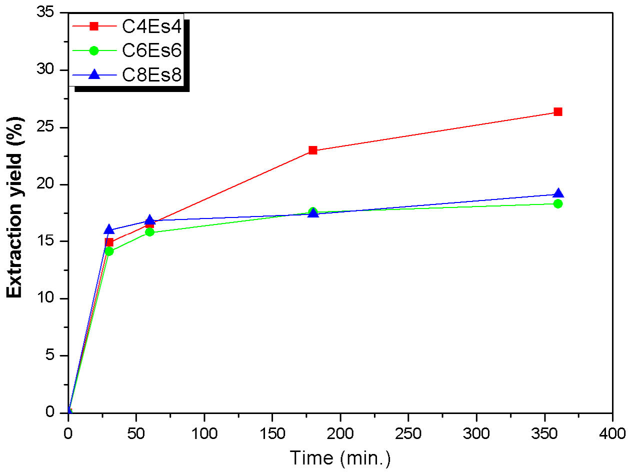


Figure 3. Variation of the extraction yield of Pd^{2+} with time, for some calixarene-based compounds (pH=2.6, Cx:Pd^{2+} =1:1)

For the tetraester calix[4]arene **C4Es4,** the extraction yield increases from 14.9% (30 min) to 16.6% (60 min) and 22.9% (180 min) and reaches the maximum value at 26.3% (360 min). Similar results are obtained for hexaester calix[6]arene and octaester calix[8]arene, when the efficiency varies between

14.1% (30 min) and 18.3% (360 min) for **C6Es6**, and 16.0% (30 min) and 19.2% (360 min) for the **C8Es8** compound.

In all cases, the extraction yield increases with time and tends toward saturation. The highest effect is observed for **C4Es4** compound which, in 6 hrs, extracts 0.29 mol Pd^{2+} ions/mol calixarene and attains the maximum **r** value.

Extraction of Au^{3+} ions

The capability of *p-tert*-butyl calix[n]arene ester derivatives to extract Au^{3+} ions from aqueous solutions was determined in a medium with variable pH (2.2, 3.2 and 4.1), using a variable time of extraction (t = 30 -1440 min).

First, the extraction of Au^{3+} ions was performed at a fix pH of 3.2, using equal volumes with equal concentrations of solutions of metal ions and calixarenes to achieve the ratio Cx:Au^{3+} = 1:1; the extraction time was 30 min (Figure 4).

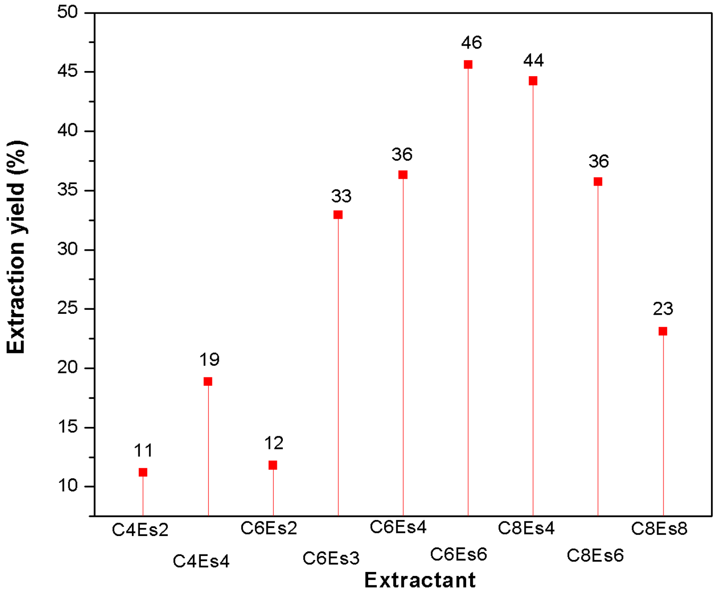


Figure 4. Extraction yield of Au^{3+} using different calixarene-based compounds (pH=3.2, Cx:Au^{3+} = 1:1, t = 30 min)

At pH=3.2, the highest extraction yield 45.6% was obtained for the hexaester calix[6]arene derivative. In our conditions, the extraction capability of the **C6Es6** compound is of 0.36 mol Au^{3+}/ mol calixarene. Relative good results were also obtained for compounds **C8Es4** (η =44.3%, **r** = 0.35), **C6Es4** (η =36.3%, **r** = 0.26) and **C8Es6** (η =35.8%, **r** = 0.25).

It seems that for Au^{3+} ions, the half substituted calixarenes exhibit the highest extraction capability only for the large-cavity compound **C8Es4**. The calixarene derivatives with four and six interconnected aromatic rings exhibit the maximum extraction efficiency when they are totally substituted. One can suppose that the highest extraction capability of the **C6Es6** compound is due to an optimum match between the trivalent charge of the gold ions and number of ligands i.e. six ester-groups grafted on the six interconnected aromatic rings.

The influence of the extraction time on the yield was investigated for the calixarene derivatives that show the maximum efficiency, namely compounds **C6Es6**, **C8Es4** and **C8Es8.** Experiments were carried out at pH=3.2, using equal volumes with equal concentrations of solutions of metal ions and calixarenes to achieve the ratio Cx:Au^{3+} = 1:1. The time of extraction was varied between 30 and 1440 min (Figure 5).

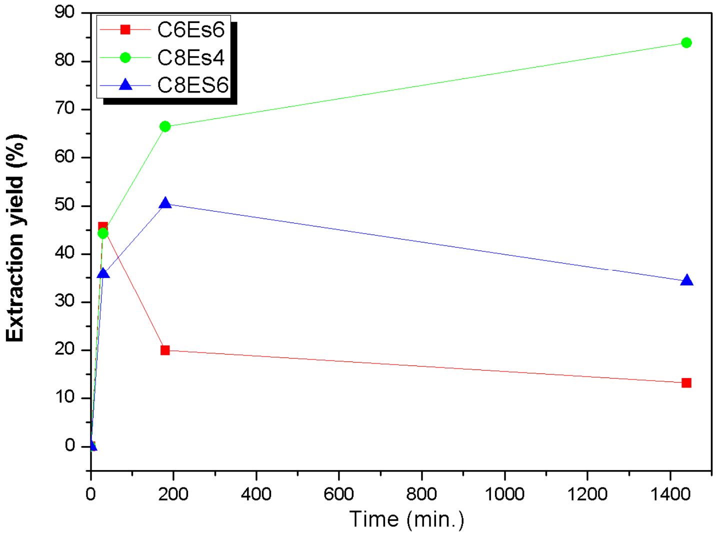


Figure 5. Dependence of the extraction yield of Au^{3+} on the time of extraction for some calixarene-based compounds (pH=3.2; Cx:Au^{3+} =1:1)

For the ester derivatives tested, the extraction yield shows an irregular dependence with time. For **C8Es4**, the yield increases from 44.3% (30 min) to 66.5% (180 min) and reaches the maximum values 83.9%, in 24 hrs.. For **C8Es6**, the yield increases from 35.8% (30 min) to 50.4% (180 min) and then decreases at 34.3% (1440 min). For **C6Es6**, the extraction efficiency decreases from 45.6% (30 min) to 19.9% (180 min) and reaches the minimum value, 13.2 % in 1440 min.

In our conditions, only the **C8Es4** compound shows a tendency toward saturation with time. This compound has the highest extraction capability (maximum **r** value), whatever the extraction time. Moreover, the **C8Es4** compound extracts in 24 hrs, 0.82 mol $Au^{3+/}$ mol calixarene.

It is obvious that for **C6Es6** and **C8Es8** compounds, the increase of the extraction time is unfavourable for the extraction process. It seems that, in our experimental conditions, a reverse process appears when the extraction lasts too much and part of the gold ions hosted by the calixarene is released in the medium.

The influence of the acidity of the aqueous medium on the extraction yield of Au^{3+} ions was also investigated. The liquid-liquid extraction experiments were performed for the triester and hexaester calix[6]arene derivatives, two compounds with a rather good extraction capability. Experiments were carried out for 30 min, using equal volumes with equal concentrations of solutions of metal ions and calixarenes to achieve the molar ratio $Cx:Au^{3+}$ = 1:1. The dependence of the extraction yield on the pH of the medium is illustrated in Figure 6.

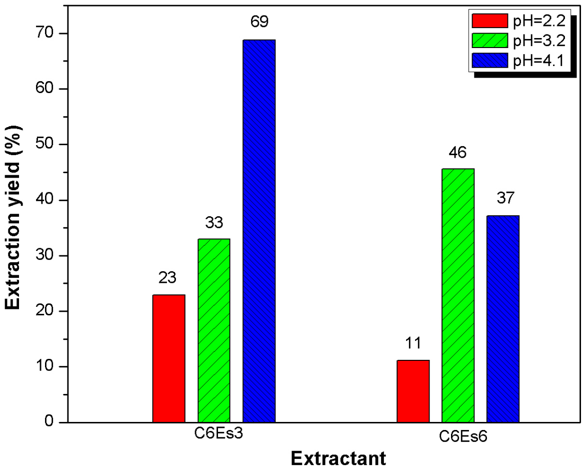


Figure 6. Variation of the extraction yield of Au^{3+} from solutions with variable pH, using different calixarene-based compounds ($Cx:Au^{3+}$ =1:1; t=30 min)

Compound **C6Es3** extracts between 22.9% (pH=2.2) and 68.8% (pH=4.1) of the amount of Au^{3+} ions from solution, while compound **C6Es6** pull out only from 11.2% (pH=2.2) to 37.2% (pH=4.1). For both calixarene compounds, the extraction efficiency increases with the pH of the medium (the only exception is **C6Es6**, which shows a relative lower value at pH=4.1).

In our extraction conditions, compound **C6Es3** exhibits the maximum extraction capability and efficiency at pH=4.1(**r** = 0.64; η = 68.8%) whereas compound **C6Es6** shows it at pH=3.2 (**r** = 0.36; η = 45.6%).

CONCLUSIONS

The capability of *p-tert*-butyl calix[n]arene functionalized at the lower rim with ethyl acetate groups to extract precious metallic ions has been investigated by liquid-liquid extraction experiments. Partial or total substituted calix[n]arenes with ester donor groups were used to extract Pd^{2+} and Au^{3+} ions from aqueous media, in different experimental conditions i.e. calixarene/ metal ratio, pH of the medium and time of extraction.

The highest extraction yield for palladium ions (53.2%) was obtained for **C6Es3** derivatives, when the calixarene:metal ratio was 1:1. Almost all calixarene-based compounds shows the maximum extraction efficiency at pH = 2.6. The highest extraction yield for gold ions was obtained for the **C6Es6** derivatives, namely 45.6% at pH=3.2.

The extraction yield can be considerably improved by modifying the extraction conditions: the time of extraction, pH of aqueous solution, etc. For example, for the extraction of palladium ions with the **C4Es4** derivative, when the time of extraction is modified, the extraction yield increase from 14.9% (30 min) to 26.3% (360 min). Also, for the extraction of gold ions with **C6Es3** derivative, at different pH of the aqueous medium, the extraction yield increase from 22.9% (at pH = 2.2) to 68.8% (at pH = 4.1).

In most of the cases, the half substituted calix[n]arene derivatives functionalized with ethyl acetate groups show a relative high extraction efficiency and are of interest as liquid-liquid extraction reagents for precious metal ions.

EXPERIMENTAL SECTION

Chemical reagents for extraction

The calixarene-based compounds were synthesized according to the methods described in our previous paper [28]. The following calixarene ester derivatives were used for the present study: 5,11,17,23 -tetra-*tert*-butyl-25, 27- bis[(ethoxycarbonyl) methoxy)]-26, 28 - dihydroxy-calix[4]arene (**C4Es2**); 5,11,17,23-tetra-tert-butyl-25,26,27,28-tetrakis[(ethoxycarbonyl)methoxy)]-calix[4]arene (**C4Es4**); 5,11,17,23,29,35 -hexa-*tert*-butyl-bis[(ethoxycarbonyl) methoxy)]-tetra hydroxy-calix[6]arene (**C6Es2**); 5,11,17,23,29,35-hexa-*tert*-butyl-37,38,39-tris[(ethoxycarbonyl)methoxy)]-40,41,42-trihydroxy-calix[6]arene

(**C6Es3**); 5,11,17,23,29,35-hexa-*tert*-butyl-tetrakis[(ethoxycarbonyl) methoxy)]-dihydroxy-calix[6]arene (**C6Es4**); 5,11,17,23,29,35-hexa-*tert*-butyl-37,38,39, 40,41,42-hexakis[(ethoxycarbonyl)methoxy]- calix[6]arene (**C6Es6**); 5,11,17,23, 29,35,41,47-*tert*-butyl-tetrakis-[(ethoxycarbonyl)methoxy)]-tetra-hydroxy-calix[8]arene (**C8Es4**); 5,11,17,23,29,35,41,47-*tert*-butyl-hexakis-[(ethoxycarbonyl) methoxy)]-dihydroxy-calix[8]arene (**C8Es6**) and 5,11,17,23,29,35,41,47-octa-*tert*-butyl-49,50,51,52,53,54,55,56-octakis[(ethoxycarbonyl)methoxy]-calix[8]arene (**C8Es8**).

$PdCl_2$ (p.a. Fluka) and $HAuCl_4x4H_2O$ (p.a. Merck) were used as supplier of Pd^{2+} and Au^{3+} metal ions ionic. Analytical-grade chloroform and deionized water were employed as solvents in the liquid-liquid extraction experiments.

Instrumentation and analysis

The metal concentration in aqueous medium was determined before and after extraction using Inductively Coupled Plasma Optical Emission Spectrometry. The analysis was performed with a Perkin Elmer ICP-OES spectrometer (OPTIMA 2100 DV), working with λ = 340.458 nm (D.L.= 0,003 mg/l) for palladium and λ = 267.595 nm (D.L.= 0,004 mg/l for gold.

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 solution of metallic ions was prepared by dissolving the required amount of $PdCl_2$ or $HAuCl_4x4H_2O$ in acidulated water to obtain $1x10^{-3}$ mol/L solutions. The acidity of the aqueous medium was monitored with a pH-instrument. The pH was adjusted with HCl for Pd^{2+} or HNO_3 for Au^{3+} solution.

Liquid-liquid extraction experiments were carried out using different calixarene:metal $Cx:M^{z+}$ ratios. For the ratio $Cx:M^{z+}$ =1:1, the extraction was performed by introducing 15 mL of the organic solution and 15 mL of the aqueous solution into extraction funnels and vigorously shaking them, 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 (η%) was calculated from the equation [29]:

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

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

ACKNOWLEDGEMENTS

This work was possible with the financial support of the Sectoral Operational Programme for Human Resources Development 2007-2013, co-financed by the European Social Fund, under the project number POSDRU 89/1.5/S/60189 with the title “**Postdoctoral Programs for Sustainable Development in a Knowledge Based Society”.**

REFERENCES

1. C. Fontas, E. Antico, F. Vocanson, R. Lamatine, P. Seta, *Separation and Purification Technology*, **2007**, *54*, 322.
2. C.D. Gutsche, In *Calixarene revisited*, J.F. Stoddart, Ed., Royal Society of Chemistry: Cambridge, **1998**.
3. Z. Asfari, V. Bohmer, M.McB. Harrowfield, J. Vincens, *Calixarenes 2001*, Kluwer, Dordrecht, **2001**.
4. Y. Yang, G. Arora, F.A. Fernandez, J.D. Crawford, K. Surowiec, E.K. Lee, R.A. Bartsch, *Tetrahedron*, **2011**, *67*, 1389.
5. O.H. Altshuler, N.V. Malyshenko, G.J. Shkurenko, H.N. Altshuler, *Theoretical Foundations of Chemical Engineering*, **2009**, *43(1)*, 43.
6. S. Erdemir, M. Bahadir, M. Yilmaz, *Journal of Hazardous Materials*, **2009**, *168*, 1170.
7. M. Bayrakci, S. Ertul, M. Yilmaz, *Tetrahedron*, **2009**, *65*, 7963.
8. M. Atanassova, V. Lachkova, N. Vassilev, S. Varbanov, I. Dukov, *Polyhedron*, **2010**, *29*, 655.
9. L Elsellami, V. Chartron, F. Vocanson, P. Conchon, C. Felix, C. Guillard, L. Retailleau, A. Houas, *Journal of Hazardous Materials*, **2009**, *166*, 1195.
10. K. Ohto, H. Ishibashi, H. Kawakita, K. Inoue, T. Oshima, *Journal of Inclusion Phenomena and Macrocyclic Chemistry*, **2009**, *65*, 111.
11. A. Hamdi, R. Souane, L. Kim, R. Abidi, L. Mutihac, J. Vicens, *Journal of Inclusion Phenomena and Macrocyclic Chemistry*, **2009**, *64*, 95.
12. G. Daneshvar, A. Jabbari, Y. Yamini, D. Paki, *Journal of Analytical Chemistry*, **2009**, *64(6)*, 602.
13. N. Singh, D. Jang, *Supramolecular Chemistry*, **2009**, *21(5)*, 351.
14. A.V. Tenkovtsev, M.M. Dudkina, L.I. Scherbinskaya, V. Aseyev, H. Tenhu, *Polymer*, **2010**, *51*, 3108.
15. S. Sayin, F. Ozcan, M. Yilmaz, *Journal of Hazardous Materials*, **2010**, *178*, 312.
16. J. Kulesza, M. Guzinski, V. Hubscher-Bruder, F. Arnaud-Neu, M. Bochenska, *Polyhedron*, **2011**, *30*, 98.

17. V.I. Isaeva, A.L. Tarasov, O.P. Tkachenko, G.I. Kapustin, I.V. Mishin, S.E. Solov'eva, L.M. Kustov, *Kinetics and Catalysis*, **2011**, *52(1)*, 94.
18. P. Dinake, P.E. Prokhorova, V.S. Talanov, R.J. Butcher, G.G. Talanova, *Tetrahedron Letters*, **2010**, *51*, 5016.
19. M. Atanassova, N. Vassilev, I. Dukov, *Separation and Purification Technology*, **2011**, *78*, 214.
20. M. Atanassova, V. Lachkova, N. Vassilev, S. Varbanov, I. Dukov, *Polyhedron*, **2010**, *29*, 655.
21. B.B. Adhikari, K. Ohto, M. Gurung, H. Kawakita, *Tetrahedron Letters*, **2010**, *51*, 3481.
22. M. Atanassova, V. Lachkova, N. Vassilev, S. Varbanov, I. Dukov, *Polyhedron*, **2010**, *29*, 655.
23. M.C. Semedo, A. Karmali, P.D. Barata, J.V. Prata, *Journal of Molecular Catalysis B: Enzymatic*, **2010**, *62*, 97.
24. O. Karakus, H. Deligoz, *Analytical Letters*, **2010**, *43(5)*, 768.
25. F. Pena-Pereira, I. Lavilla, C. Bendicho, *Spectrochimica Acta Part B,* **2009**, *64*, 1.
26. X. Liu, K. Surowiec, R.A. Bartsch, *Tetrahedron*, **2009**, *65*, 5893.
27. M. Surowiec, R. Custelcean, K. Surowiec, R.A. Bartsch, *Tetrahedron*, **2009**, *65*, 7777.
28. A. Saponar, E.-J. Popovici, R.Grecu, I. Silaghi-Dumitrescu, N. Popovici, *Studia UBB Chemia,* **2009**, *LIV (4),* 203.
29. S. Sayin, M. Yilmaz, M. Tavasli, *Tetrahedron*, **2011**, *67*, 3743.