Synthesis and Properties of N,N-diethylacetamido Derivatives of *p-tert*-butyl calix[n]arene

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*New calix[n]arene derivatives i.e. 5,11,17,23,29,35-hexa-tert-butyl-bis[(N,N-diethylaminocarbonyl)metoxy]-tetrahydroxy-calix[6]arene (**3**), 5,11,17,23,29,35–hexa-tert-butyl-tetrakis-[(N,N-diethylaminocarbonyl) metoxy]- dihydroxy-calix[6] arene (**5**), 11,17,23,29,35,41,47-tert-butyl-tetrakis-[(N,N-diethylaminocarbonyl) methoxy]-tetra-hydroxy-calix[8]arene (**6**) and 5,11,17,23,29,35,41,47-tert-butyl-hexakis-[(N,N-diethylaminocarbonyl)methoxy]-dihydroxy-calix[8]arene (**7**) have been synthetised by reaction of the parent calix[n]arene (n=6,8) with α-Chloro-N,N-diethylacetamide and* K_2CO_3 *or NaH as base in organic solvents such as* CH_3CN*, THF, DMF or their mixture. The new calixarenes derivatives have been investigated by elemental analysis,* ^{1}*H-NMR, UV-Vis and FTIR spectroscopy and were tested for the extraction of precious metals from aqueous solutions.*

Keywords: calix[n]arenes, synthesis, functionalization, α-Chloro-N,N-diethylacetamide

Calixarenes, a family of [1n]metacyclophanes, are cyclic oligomers prepared from formaldehyde and *para*-substituted phenols, by condensation under alkaline conditions. It was suggested that the calixarenes could be regarded as the third generation of supramolecules, after crown ethers and cyclodextrins [1]. The cavity size of calixarenes is readily controlled by changing the number of the phenolic rings *per* one molecule as well as by introducing suitable functional groups at the "wide rim" or/and "narrow rim" of the calixarene skeleton.

Calixarenes can be functionalized both at the phenolic OH groups "narrow rim" e.g. esterification, etherification, and at the *para*-positions of the phenol rings "wide rim" e.g. sulfonation, nitration, alkylation. Modified calixarenes, having additional binding sites, both at the narrow rim and wide rim, enhance the binding ability of the parent calixarene [2]. Various methods for functionalizing calixarenes have been developed and numerous calixarene derivatives have been synthetized during the past two decades [3-13].

Calixarene derivatives incorporating ionophoric functional groups such as amine, amide and ester or acid linkages on the "narrow rim" exhibit excellent extraction/complexation properties [14-29].

In order to develop new ionophoric materials, calix[4,6,8]arene derivatives with variable number of identical or different alkenyl, ester and amido moieties graphted at the "narrow rim" were synthesized and tested for the extraction of rare earth and precious metals from aqueous solutions [3,5,30]. New extraction reagents for the metal extraction/sequestration from waste waters are targeted.

Herein we present our study referring to the synthesis and characterization of new derivatives of *p-tert*-butyl calix[6]arene and *p-tert*-butyl calix[8]arene with two, four, six and/or eight N,N-diethylamido groups (fig.1.). Due to the presence of the *p*-electrons from the amide groups, these compounds could be of practical interest for metal sequestration.

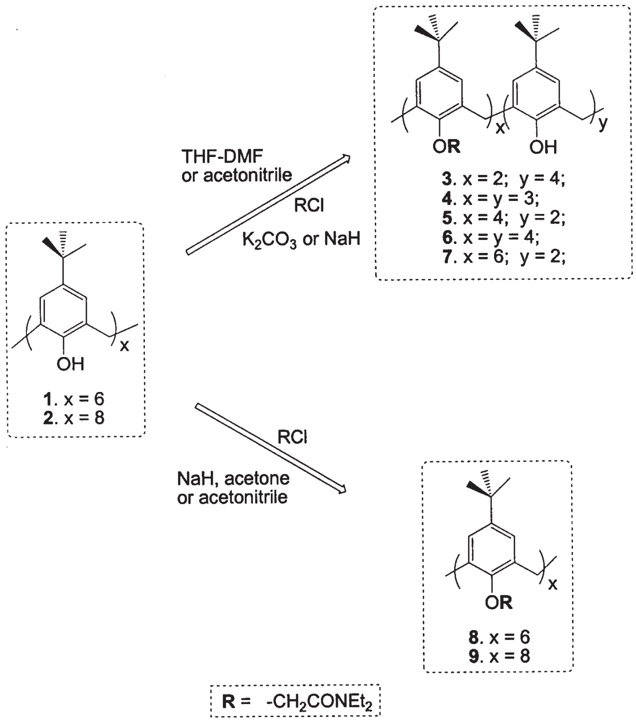

Fig. 1. The synthesis scheme of calix[n]arene derivatives (n = 6, 8)

Experimental part

All reactions were performed under nitrogen atmosphere using oven-dried glassware. Reagents were obtained from commercial suppliers and were used without further purification. All solvents were dried over standard drying agents and distilled prior use. Reactions time was monitored by TLC on Kiselgell 60 F_{254} plates with detection by UV or iodine. Melting points (M.P.) were determined with POINT METER KSP II apparatus in a sealed capillary and are uncorrected values. ^{1}H-NMR spectra were recorded on VARIAN GEMINI 300S (300 MHz) spectrometer. Deuterated chloroform ($CDCl_3$) was used as solvent and tetramethylsilane (TMS) as reference. Infrared absorption

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spectra were recorded on Thermo Scientific Nicolet 6700 FT-IR spectrometer, using KBr pellets technique. UV-Vis spectra were recorded on UNICAM UV 4 spectrometer, from $CHCl_3$ solution ($1x10^{-4}$ mol/L). Elemental analysis (E.A.) was performed with a Vario EL analyser.

The ability of the calixarene derivatives to extract precious metals from aqueous solution was determined by liquid-liquid extraction from $1x10^{-3}$ mol/L $PdCl_2$, using $1x10^{-3}$ mol/L solution of calixarene in $CHCl_3$. The metal concentration was determined in the aqueous medium, before and after extraction, using a Perkin Elmer ICP-OES spectrometer (OPTIMA 2100 DV).

Different calixarenes derivatives with a variable number of N,N-diethylamido groups were synthesized following the scheme depicted in figure 1. The starting calixarene 5,11,17,23,29,35-hexa-*tert*-butyl-calix[6]arene-37,38,39, 40,41,42-hexol (compound **1**) and 5,11,17,23,29, 35,41,47-octa-*tert*-butyl-calix[8]arene-49,50,51, 52, 53,54,55,56-octol (**2**) as well as 5,11,17,23,29,35-hexa-*tert*-butyl-37,38,39,40,41,42-hexakis [(N,N- diethylaminocarbonyl) methoxy]-calix[6]arene (**8**) and 5,11,17,23,29, 35,41,47-octa-*tert*-butyl-49,50,51,52,53,54,55,56,-octakis-[(N,N-diethylaminocarbonyl) methoxy]-calix[8]arene (**9**) were prepared according to the procedures described in literature [31-34]. Synthesis of 5,11,17,23,29,35-hexa-*tert*-butyl-37,38,39-tris[(N,N-diethylaminocarbonyl)methoxy]-40,41, 42-trihydroxy-calix[6]arene (**4**) was reported by us earlier [30]. The synthesis of the new N,N-diethylamido derivatives of *p-tert*-butyl calix[6,8]arene and their characteristics are presented bellow.

*5,11,17,23,29,35-hexa-tert-butyl-bis[(N,N-diethylaminocarbonyl)metoxy]-tetra hydroxy-calix[6]arene (compound **3**)*

To a mixture of 5.1 mmol calix[6]arene (**1**) in THF-DMF mixture (400 mL), 20.4 mmol of K_2CO_3 was added. The mixture was stirred 30 min at 40°C. After cooling at room temperature, 20.4 mmol of α-Chloro-N,N-diethylacetamide in THF-DMF (20mL) was added dropwise and the mixture was refluxed 20h. Then the mixture was poured on ice, concentrated HCl was added and extracted with dichloromethane. The dichloromethane extract was successively washed with water and brine and dried over anhydrous $MgSO_4$. After filtration, the dichloromethane solution was concentrated and methanol was added. The suspension was allowed to cool in refrigerator (24h) and the solid material was filtered and was recrystallized from dichloromethane-ethanol mixture yielding 3.08g (~50 %) of compound **3** as white crystals**.**

M.P. = 332.5°C.

M.W. calculated for $C_{78}H_{106}N_2O_8$ = 1200.

E.A. Calcd. (%): C = 78.09; H = 8.91; N = 2.34; Found (%): C = 77.87; H = 8.44;

N = 2.43.

UV-Vis [$CHCl_3$; λ_{max} (nm) / ε ($M^{-1}cm^{-1}$)] = 281/15660; 287/15890.

FTIR (KBr, $\nu_{max.}$, cm^{-1}) $\nu_{C=O}$ = 1647; ν_{OH} =3409.

*5,11,17,23,29,35-hexa-tert-butyl-bis[(N,N-diethylaminocarbonyl)metoxy]-tetra hydroxy-calix[6]arene (compound **4**)*

To a mixture of 5.1 mmol calix[6]arene (**1**) in acetonitrile (200 mL), 30.6 mmol of NaH was added. The mixture was stirred 30 min at 40°C. After cooling at room temperature 30 mmol of α-Chloro-N,N-diethylacetamide in acetonitrile (20mL) was added dropwise and the mixture was refluxed 20h. Then the mixture was poured on ice, concentrated HCl was added and extracted with dichloromethane. The dichloromethane extract was successively washed with water and brine and dried over anhydrous $MgSO_4$. After filtration, the dichloromethane solution was concentrated and methanol was added. The suspension was allowed to cool in refrigerator (24h) and the solid material was filtered and recrystallized from dichloromethane-methanol mixture yielding 2.8g (~41 %) of compound **4** as white crystals.

M.P. = 272.5°C.

M.W. calculated for $C_{84}H_{117}N_3O_9$ = 1313.

E.A. Calcd. (%): C = 76.85; H = 8.98; N = 3.20; Found (%):C =75.57;H = 8.44; N = 3.03;

UV-Vis [$CHCl_3$; λ_{max} (nm) / ε($M^{-1}cm^{-1}$)] = 281/12040; 288/11170.

FTIR (KBr, $\nu_{max.}$, cm^{-1}) $\nu_{C=O}$ = 1644; ν_{OH} =3248.

*5,11,17,23,29,35–hexa-tert-butyl-tetrakis-[(N,N-diethylaminocarbonyl)metoxy]- dihydroxy-calix[6] arene (compound **5**)*

To a mixture of 5.1 mmol calix[6]arene (**1**) in THF-DMF mixture (400 mL), 81.6 mmol of 50% paraffin oil - dispersed NaH was added. The mixture was stirred 30 min at 40°C. After cooling at room temperature 40.8 mmol of α-Chloro-N,N-diethylacetamide in THF-DMF (20mL) was added dropwise and the mixture was refluxed 20h. The subsequent operations are similar to that described for compound **3**. The solid material was recrystallized from dichloromethane-ethanol mixture yielding 3.29g (~ 45 %) of compound **5** as white crystals**.**

M.P. = 302.8°C.

M.W. calculated for $C_{90}H_{128}N_4O_{10}$ = 1426.

E.A. Calcd. (%): C =75.80; H = 9.05; N=3.93; Found (%): C =75.57; H = 8.76; N = 4.08.

UV-Vis [$CHCl_3$; λ_{max} (nm) / ε($M^{-1}cm^{-1}$)] = 280/8920; 287/8000.

FTIR (KBr, $\nu_{max.}$, cm^{-1}) $\nu_{C=O}$ = 1662; ν_{OH} = 3450.

*11,17,23,29,35,41,47-tert-butyl-tetrakis-[(N,Ndiethylaminocarbonyl)methoxy]-tetra-hydroxy-calix[8]arene (compound **6**)*

To a mixture of compound **2** (3.85 mmol) in THF-DMF (400 mL), 61.6 mmol of 50% paraffin oil - dispersed NaH was added. The mixture was stirred 30 min at 40°C. After cooling at room temperature, 30.8 mmol of α-Chloro-N,N-diethylacetamide in THF-DMF (20mL) was added dropwise and the mixture was refluxed 20h. The subsequent operations were similar to those described for compound **3**. The solid material was recrystallized from chloroform-methanol mixture yielding 3.70g (~55%) of compound **6** as white crystals.

M.P. = 360.9 °C.

M.W. calculated for $C_{112}H_{156}N_4O_{12}$ = 1750.

E.A. Calcd.(%):C= 76.85; H = 8.98; N = 3.20; Found (%): C = 77.07; H = 9.14; N = 3.03.

UV-Vis [$CHCl_3$; λ_{max} (nm) / ε($M^{-1}cm^{-1}$)] = 282/13200; 291/14850.

FTIR (KBr, $\nu_{max.}$, cm^{-1}) $\nu_{C=O}$ = 1649; ν_{OH} = 3412.

*5,11,17,23,29,35,41,47-tert-butyl-hexakis-[(N,N-diethylaminocarbonyl)methoxy]-dihydroxy-calix[8]arene (compound **7**)*

To a mixture of compound **2** (3.85 mmol) in THF-DMF (400 mL), 92.4 mmol of 50% paraffin oil - dispersed NaH was added. The mixture was stirred 30 min at 40°C. After cooling at room temperature, 46.2 mmol of α-Chloro-N,N-diethylacetamide in THF-DMF (20mL) was added dropwise and the mixture was refluxed 20h. The subsequent operation were similar to that described for compound **3**.

The solid material was recrystallized from chloroform-methanol mixture yielding 3.95g (~52%) of compound **7** as white crystals**.**

M.P. = 385.5°C.

M.W. calculated for $C_{124}H_{178}N_6O_{14}$ = 1977.

E.A. Calcd. (%): C = 75.34; H = 9.08; N = 4.25; Found (%): C = 75.97; H = 9.54;
N = 4.15.

UV-Vis [$CHCl_3$; λ_{max} (nm) / $\varepsilon(M^{-1}cm^{-1})$] = 281/11700; 291/12820.

FTIR ($\nu_{max.}$, KBr, cm^{-1}) $\nu_{C=O}$ = 1650; ν_{OH} = 3424.

Results and discussions

The synthesis route for calix[6] and calix[8]arene derivatives, which contain N,N-diethylacetamido functionality at the "narrow rim" is depicted in figure 1. Reaction of *p-tert*-butyl-calix[6]arene (**1**) and *p-tert*-butyl-calix[8]arene (**2**) with the appropriate amount of α-Chloro-N,N-diethylacetamide in the presence of K_2CO_3 or NaH as a base, in organic solvents, yielded calix[6,8]arene derivatives which contain bi **(3)**, tri **(4)**, tetra **(5,6)**, hexa **(6,7)** and octa **(9)** N,N-diethylacetamido groups, respectively.

Elemental analysis, UV-Vis, FTIR and ^{1}H-NMR investigations confirmed the formation of the desired calix[n]arene derivatives.

^{1}H-NMR spectra

Table 1 collects the relevant ^{1}H-NMR data of compounds 3-9 in comparison with the parent calixarenes 1 and 2. The "narrow rim" functionalization of the parent calixarene is well illustrated by ^{1}H-NMR spectrometric data which are in agreement with the expected structure of the synthesized derivatives. The ^{1}H-NMR spectra show the differences in the chemical shifts of the phenolic OH groups of calixarene derivatives in comparison with the parent calixarenes. The chemical shift of the phenolic OH groups (Ar-O$\underline{H}$) appears at 10.55 ppm for 1 and at 9.86 ppm for 2 while for the calixarene derivatives 3-9 , the chemical shift appears beetwen 7.09 and 7.36 ppm. Moreover, the signals associated with the N,N-diethylacetamido groups (O-$\underline{CH_2}$-CO) appear at about 4.33 ppm for calix[6]arene derivatives and at 4.47 – 4.93 ppm for the calix[8]arene derivatives.

FTIR spectra

The graphting of a variable number of N,N-diethylamido groups on the *p-tert*-butyl calix[6,8]arenes can be monitored by infrared spectroscopy (fig.2 and fig.3). The parent calixarenes i.e. *p-tert*-butyl calix[6]arenes (**1**) and *p-tert*-butyl calix[8]arenes (**2**) show the characteristic absorption band assigned to the OH stretching vibration at 3149 and 3244 cm^{-1}, respectively, whereas the intermediates **3-7** show it at 3409 (**3**), 3248 (**4**), 3450 (**5**), 3412 (**6**) and 3424 cm^{-1} (**7**), due to the destroying of the circular strong hydrogen bonds by functionalization. For the totally substituted calixarenes, the OH absorption band at about 3446 (**8**) and 3436 (**9**) cm^{-1}, respectively, could be due to the solvent capture (i.e. methanol).

FTIR spectra of the N,N-diethylamido derivatives of the *p-tert*-butyl calix[6,8]arenes (3-9) exhibit the strong absorption peak assigned to the carbonyl stretching vibration at 1647 (**3**), 1644 (**4**), 1662 (**5**), 1649 (**6**) 1650 (**7**), 1661 (**8**) and 1648 (**9**) cm^{-1}, respectively. The absorption intensity of the characteristic C=O vibration band proportionally increases with the number of the N,N-diethylamido groups graphted on the parent calix[6]arene (fig.2) and calix[8]arene (fig.3), relative to the absorption bands from the calixarene fingerprint domain (1500-1000 cm^{-1}).

Table 1
^{1}H-NMR DATA OF N,N-DIETHYLACETAMIDO CALIXARENES DERIVATIVES

Compound	$C(C\underline{H_3})_3$	$N\text{-}CH_2\text{-}\underline{CH_3}$	$N\text{-}\underline{CH_2}\text{-}CH_3$	$ArC\underline{H_2}Ar$	$O\text{-}\underline{CH_2}\text{-}CO$	$Ar\underline{H}$	$ArO\underline{H}$
C6A (1)	1.27, s	-	-	3.78, brs	-	7.16, s	10.55, s
C6Am2 (3)	0.96 - 1.24, m		3.28 - 3.76, m		4.33, s	6.70, s 7.02, s	7.20, s
C6Am3 (4)	1.09, s 1.26, s	0.92 - 0.97, t	3.11- 3.18, q	3.62, s	4.33, s	6.72, s 7.03, s	7.09, s
C6Am4 (5)	0.89 - 1.32, m		3.22 - 4.94, m			6.88, s 7.08, s	7.28, s
C6Am6 (8)	0.82 - 1.41, m		3.27 - 4.52, m			7.24, s	-
C8A (2)	1.26, s	-	-	3.53, d 4.39, d	-	7.17, s	9.86, s
C8Am4 (6)	0.85 - 1.28, m		3.20 - 4.85, m		4.90, s	6.95, s 7.10, s	7.35, s
C8Am6 (7)	0.94 - 1.33, m		3.40 - 4.80, m		4.93, s	6.84, s 6.99, s	7.36, s
C8Am8 (9)	0.89 - 1.21, m		3.20 - 4.21, m		4.47, s	6.82, s	-

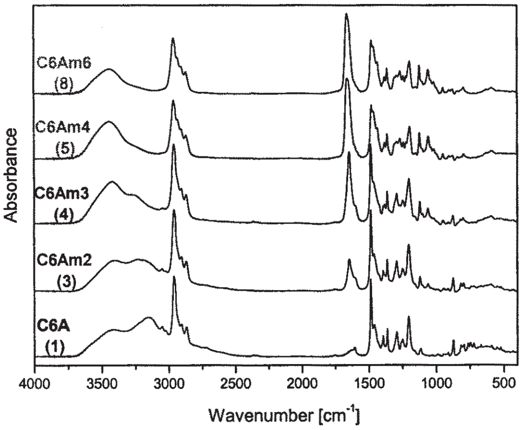

Fig. 2. FTIR spectra of compounds **1** (parent calix[6]arene), **3** (diamido derivative), **4** (triamido derivative), **5** (tetraamido derivative)and **8** (hexaamido derivative)

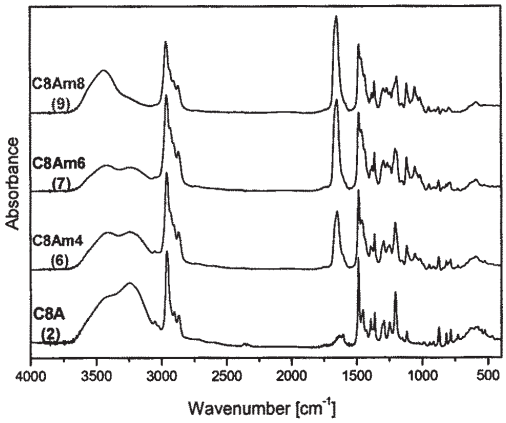

Fig. 3. FTIR spectra of compounds **2** (parent calix[8]arene), **6** (tetraamido derivative) **7** (hexaamido derivative) and **9** (octaamido derivative)

Table 2
UV-VIS DATA OF N,N-DIETHYLACETAMIDO CALIXARENES DERIVATIVES

Compound	Peak # 1		Peak # 2	
	λ_{max} (nm)	ε (l x mol^{-1} x cm^{-1})	λ_{max} (nm)	ε (l x mol^{-1} x cm^{-1})
C6A (1)	280	13730	288	14400
C6Am2 (3)	281	15660	287	15890
C6Am3 (4)	281	12040	288	11170
C6Am4 (5)	280	8920	287	8000
C6Am6 (8)	273	4760	279	4710
C8A (2)	283	19480	291	24690
C8Am4 (6)	282	13200	291	14850
C8Am6 (7)	281	11700	291	12820
C8Am8 (9)	272	6960	279	7280

UV-VIS spectra

The UV-vis absorption spectra of the N,N-diethylacetamido calix[6,8]arene derivatives **3-9** illustrate the functionalisation of the parent p-tert-butyl calix[6,8]arenes [5, 30]. Table 2 presents the characteristic UV-vis absorption data i.e. peak position (λ_{max}) and molar absorbtion coefficient (ε) of the of calixarene derivatives.

The absorption spectra of the *p-tert*-butyl-calix[6,8]arene consist in two strong specific UV-Vis absorption bands centered at 280 - 285 (peak #1) and 287 - 292 nm (peak #2). The spectral characteristics of these specific charge-transfer bands are influenced by the N,N-diethylacetamido functionalisation.

According to UV-vis spectra, the specific absorption bands appear at 280, 288 (**1**) and 283, 291 (**2**) nm for the parent calix[n]arene and at 281, 287 (**3**), 281, 288 (**4**), 280, 287 (**5**), 282, 291 (**6**) 281, 291 (**7**), 273, 279 (**8**) and 272, 279 nm (**9**), for the N,N-diethylacetamido calix[n] arene derivatives, respectively. The UV absorption of p-tert-butyl-calix[8]arene is characterised by absorption maxima situated in the UV domain of lower energy and a larger molar absorptivity, as compared with *p-tert*-butyl-calix[6]arene that contains a smaller number of interconnected phenolic rings. On the other hand, functionalization brings about the shift of the characteristic bands toward higher energy and the decrease of the molar absorptivity, in parallel with the increase of the number of N,N-diethylacetamido groups graphted on the calix[6,8]arenes skeleton.

Ability to extract palladium ions from aqueous solution

The capability of *p-tert*-butyl calix[6]arene functionalised at the lower rim with N,N-diethylacetamide groups to extract precious metallic ions have been investigated by liquid-liquid extraction. The experiments were performed at *p*H=2.1, using equal volumes of 1x10^{-3} mol/L aqueous solution of $PdCl_2$ and 1x10^{-3} mol/L $CHCl_3$ solution of calixarene and the extraction was monitored by ICP-OES spectroscopy.

In our experimental conditions, almost all the N,N-diethylacetamide calix[6,8]arene derivatives show a quite good capability to extract the divalent palladium ions from aqueous medium. The extraction yields for the di-, tetra- and hexaamido calix[6]arene derivatives (**3, 5, 8**) and tetra-, hexa- and octaamido calix[8]arene derivatives (**6, 7, 9**) vary between 61-68 % and 45 -64 %, respectivley (fig. 4). The relative low extraction yield (34%) of the triamido calix[6]arene derivative (**4**) could be related with the un-match between the electric charge (+2) of the metallic ion and the odd number of functional groups /mol calixarene derivative.

The higest ability to extract palladium ions was found for the tetra subtitued calix[6]arene or calix[8]arene, as illustrated by their corresponding extraction yield i.e. 68% for compound **5** and 64% for compound **6.**

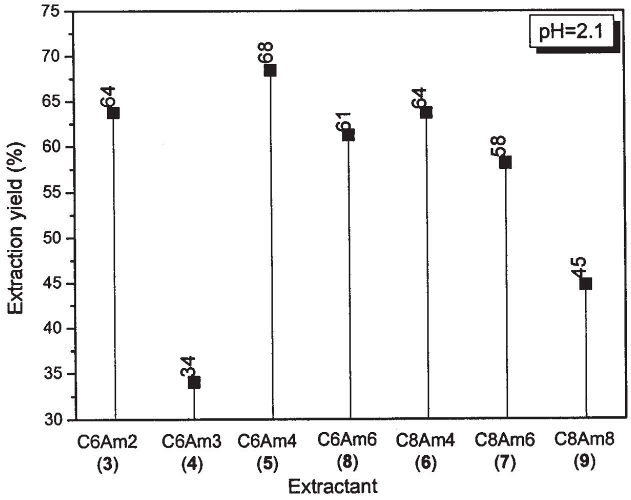

Fig.4. Extraction yield of Pd^{2+} (aq) for some N,N-diethylacetamido calix[6,8]arene derivatives

Conclusions

The UV-Vis, FTIR and ^{1}H-NMR spectroscopic investigations confirmed the formation of *p-tert*-butyl calix[6]arene and *p-tert*-butyl calix[8]arene functionalized at the “narrow rim” with a variable number of N,N-diethylacetamide groups i.e two (**3**), three (**4**), four (**5, 6**), six (**7, 8**) and eight (**9**), respectively. The capability of the N,N-diethylacetamide derivative of *p-tert*-butyl calix[6,8]arene to extract precious metallic ions (palladium) from aqueous medium was also put in evidence.

The best extraction capability was shown by calix[6,8]arene derivatives functionalized with four N,N-diethylacetamide groups (**5,6**). Additional experiments are to be performed in order to evaluate and prove the possibility to use these *p-tert*-butyl calix[6,8]arene derivatives for the sequestration/extraction of precious and rare earth metals from waste waters.

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