J Incl Phenom Macrocycl Chem (2010) 67:117–126
DOI 10.1007/s10847-009-9685-8

ORIGINAL ARTICLE

Calixarenes functionalized with phosphine oxide and diamide functions as extractants and ionofores for rare-earth metals

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Received: 15 May 2009 / Accepted: 30 October 2009 / Published online: 21 October 2009

Abstract Calixarene-based ligands with phosphine oxide and diamide functions at wide and narrow rims are synthesized and studied as extracting agents for liquid extraction and ionophores for polymeric electrochemical ion sensors. Calixarene ligands are compared with corresponding phosphine oxide and diamide ligands which are not attached to the calixarene platform. Extraction and sensor properties of the ligands were studied in different metal ion solution with special attention paid to rare-earth metals. Attachment of phosphine oxide groups to the calixarene platform leads to the sharp increase of both extraction and sensing ability of the corresponding systems comparing to non-bonded phosphine oxide. In case of the diamide derivatives attached to the calixarene performance of corresponding ligands was similar to those of non-bonded diamides.

Keywords Calixarene-based ligands · Phosphine oxide functions · Diamide functions · TODGA · Lanthanides extraction · Electrochemical ion sensors

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Introduction

Calixarenes are widely known as very attractive molecular receptors for the variety of practical applications as they allow of fine tuning of wide range of sensor properties by chemical modification. Among a huge variety of different applications we will focus on radioactive waste management problem which is of great importance for all countries producing nuclear energy. Several different calixarene derivatives were suggested as ligands for liquid extraction systems in concentration and partitioning of constituents of spent nuclear fuel [1–3]. Great increase of extraction ability comparing to monodentate analogues (cooperative effect) was observed in some cases, for example, for CMPO-substituted calixarenes [4–7]. Popular explanation of this effect is so called pre-organization conception considering that the reaction centers of the ligand molecule are in suitable conformation for comlpex formation with metal ion; therefore the stability of such complexes is higher [8]. However this conception is not universal—the increase of extraction ability for more flexible calixarene molecules with not rigid conformations is sometimes higher [7].

It's known that different active compounds from the field of liquid extraction can be successfully used as membrane active compounds for producing potentiometric PVC-plasticized chemical sensors for determination of metals. Our previous research has shown that such compounds as carbamoylphosphine oxides, diphosphine dioxides, tetraoctyldiamide of diglycolic acid etc. [9, 10] typically used as extractants can be also employed for a preparation of the polymeric electrochemical membrane sensors. The resulted sensors have demonstrated rather high sensitivity towards triply charged lanthanide cations at pH 2 and different selectivity patterns depending on the

nature and structure of ionophores. The selectivity of the proposed sensors allows their implementation in multisensor arrays of "electronic tongue" type [11] for simultaneous determination of several metals. This result is of high interest as an alternative method for quantification of spent nuclear fuel constituents during reprocessing. The techniques currently used for this purpose are more expensive, complicated and time-consuming. However developing of "electronic tongue" technique for this application needs further novel sensors and sensor materials with various parameters of cross-sensitivity.

Different calixarenes were tested as ionophores for PVC-plasticized potentiometric sensors. The impressive range of various ions can be determined by calixarene-based sensor membranes [12–14]. Also sensors on the base of substituted calixarenes including calixarenes with P=O groups [14–16] or amido groups [17] were prepared and studied.

It is known that extraction ability of phosphine oxide-substituted calixarenes depends on the structure of the molecule. The highest cooperative effect was observed for the calixarenes with P=O groups at the wide rim [18, 19]. Calixarenes with phosphine oxide group at the narrow rim usually have very low cooperative effect or even none. However, this interesting effect has been never studied (to the best of our knowledge) in case of rare-earth metal electrochemical sensors.

In the present paper synthesis, liquid extraction properties and sensor performance of several calixarenes modified with phosphine oxide and diamide functions comparing with their monofunctional analogues are reported. The goal of this work was to compare the influence of a calixarene macrocycle on the extraction ability and electrochemical sensor characteristics of the corresponding systems.

Experimental

Chemicals

High molecular weight polyvinyl chloride (PVC) and o-nitrophenyloctyl ether (NPOE) were obtained from Fluka Chemical (Buchs, Switzerland) in Selectophore® grade and used as received. The cesium salt of chlorinated cobalt dicarbollide (CCD) was obtained from Katchem (Czech Republic). The CCD was converted to the acid (H^+) form prior to membrane preparation. The tetraoctyl-3-oxapentanediamide (TODGA) sample was kindly provided by Dr. B. Casensky (Katchem, Czech Republic). Trioctylphosphine oxide (TOPO) of puriss grade was purchased at Fluka Chemical (Buchs, Switzerland). The chemical structures of the substances used for sensor membrane preparation are presented in the Table 1.

Divalent metal nitrate salts of analytical grade were purchased at "Reaktiv" Company (St. Petersburg, Russia) and used as received. The rare-earth metals salts were provided by Khlopin Radium Institute as stock solutions of metal nitrates (0.5 M) in 0.1 M nitric acid. Doubly distilled water from GFL-2102 distiller was used throughout the experiments.

Synthesis of calix[4]arene compounds

5,11,17,23-tetrakis(dibutylphosphinylmethyl)-25,26,27,28-tetrapropoxycalix[4]arene (cone conformer) (calixarene **C1)** was synthesized according to [20].

5,11,17,23-tetra(diethylcarbamoylethoxymethyl-carboxamido)-25,26,27,28-tetrapropoxycalix[4]arene (calixarene C2) and 5,11,17,23-tetra-tert-butyl-25,26,27,28-tetrakis-[dibutylphosphinoylmethyloxy]-calix[4]arene (calixarene C3) were synthesized according to scheme in the Figs. 1 and 2.

5,11,17,23-tetra(chloroacetamido)-25,26,27,28-tetrapropoxycalix[4]arene

Tetraaminocalixarene [21](0.66 g, 1 mmol) solution in toluene (15 mL) was dropped to solution of chloroacetyl chloride (0.5 g, 4.4 mmol) in toluene (5 mL) with stirring. Obtained ruby-red suspension was boiled with stirring for 16 h in dry nitrogen atmosphere. After cooling precipitate formed was filtrated, dried on air, and kept in 5 mL of methanol for 3 h under ultrasound and then filtrated. Total yield (pale yellow solid) 0.73 g (80%).

^{1}H NMR (δ, ppm, 300 MHz, (DMSO, TMS)): 0.96 (t, J = 7.4 Hz, 12H, O-CH_2-CH_2-CH_3), 1.90 (m, 8H, O-CH_2-CH_2-CH_3), 3.14 (d, J = 13.5 Hz, 4H, ArCH_{2eq}Ar), 3.79 (t, J = 7.4 Hz, 8H, O-CH_2-CH_2-CH_3), 4.13 (s, 8H, -CH_2Cl), 4.33 (d, J = 13.5 Hz, 4H, ArCH_{2ax}Ar), 6.94 (s, 8H, ArH), 9.88 (s, 4H, NH).

*5,11,17,23-tetra(diethylamidocarbamoylmethoxymethyl-carboxamido)-25,26,27,28-tetrapropoxy calix[4]arene (**C2**)*

NaH suspension (60%, in mineral oil, 0.137 g, 3.41 mmol) was washed by dry benzene (twice × 5 mL) in argon atmosphere and then dry DMF (1 mL) was added.

Solution of N,N-diethylamide of glycolic acid [22] (0.225 g, 1.72 mmole) in 5 mL DMF was dropped to obtained suspension and was stirred for 30 min. Then tetrachloroacetamidocalixarene solution (0.39 g, 0.43 mmol) in 5 mL DMF was added. After stirring for 48 h at room temperature, 0.1 mL of CH_3OH, 20 ml $CHCl_3$ and 20 mL

Table 1 Chemical structures of studied compounds

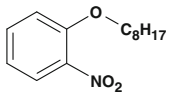
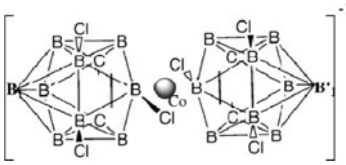
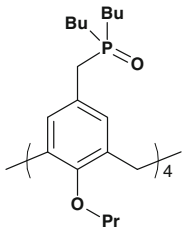
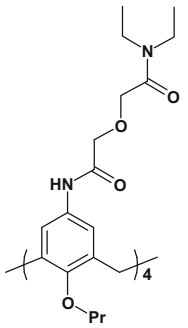
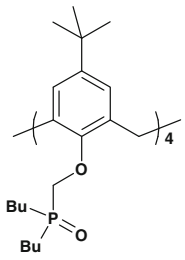
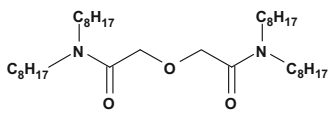
	o-nitrophenyloctyl ether (**NPOE**)
	Chlorinated cobalt dicarbollide (**CCD**)
	5,11,17,23-tetrakis-dibutylphosphinylmethyl- 25,26,27,28-tetrapropoxycalix[4]arene (cone conformer) (**C1**)
	5,11,17,23-tetra(diethylcarbamoylethoxymethyl-carboxamido)-25,26,27,28-tetrapropoxycalix[4]arene (**C2**)
	5,11,17,23-tetra-tert-butyl-25,26,27,28-tetrakis-[dibutylphosphinylmethyl-oxy]-calix[4]arene (cone conformer) (**C3**)
	tetraoctyl-3-oxapentanediamide (**TODGA**)

Table 1 continued

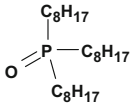
	Trioctylphosphine oxide (**TOPO**)

Fig. 1 The scheme of ligand **C2** synthesis

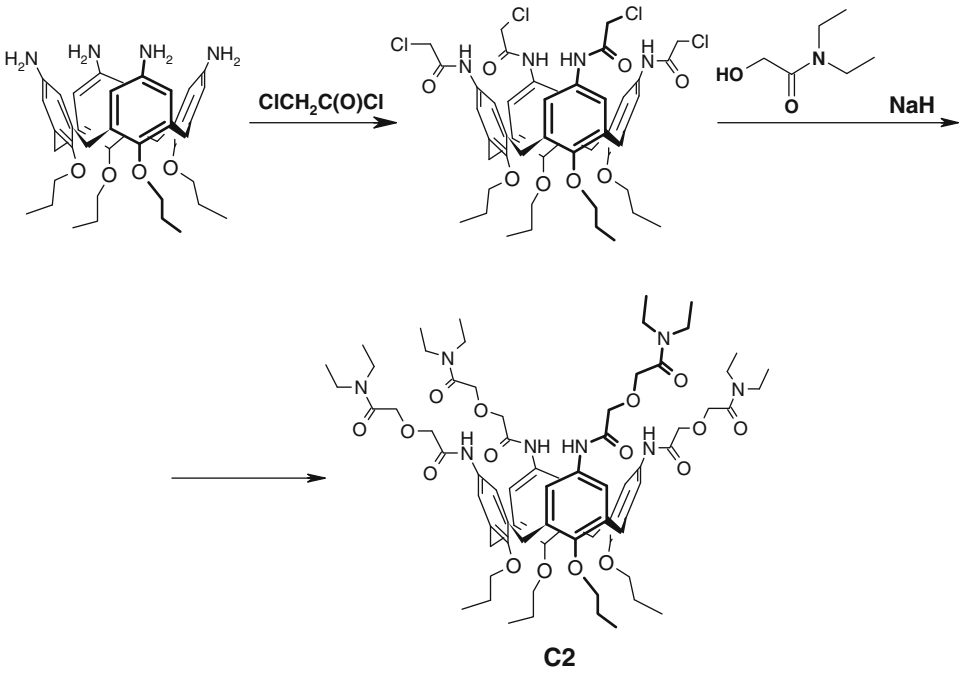
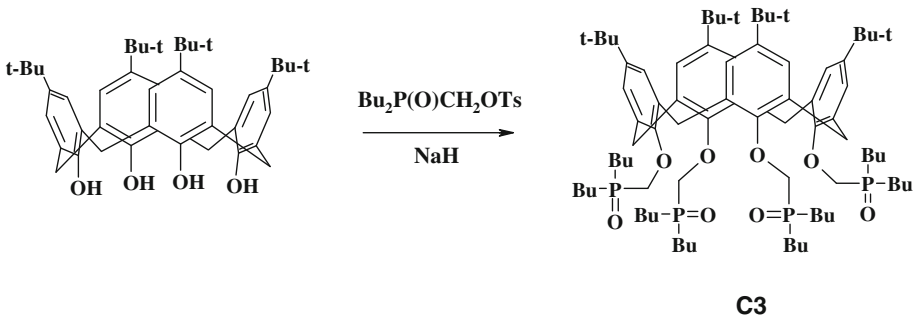


Fig. 2 The scheme of calixarene C3 synthesis



of 1% hydrochloric acid were added. The organic layer was separated, washed by water and NaCl solution (10 mL each). After solvent removal, residue (yellow oil) was purified by column chromatography (eluent $CHCl_3/CH_3OH$ v/v, 14:1). Total yield (pale yellow solid) 0.19 g (35%).

^{1}H NMR (δ, ppm, 300 MHz, ($CDCl_3$, TMS)): 0.94 (t, J = 7.4 Hz, 12H, O-CH2-CH2-CH3), 1.13 (m, 24H, N-CH_2-$\underline{CH_3}$), 1.85 (m, 8H, O-CH_2-$\underline{CH_2}$-CH_3), 3.16 (d, J = 13.5 Hz, 4H, Ar$\underline{CH_{2eq}}$Ar), 3.20 (m, 8H, N-$\underline{CH_2}$-CH_3), 3.37 (m, 8H, N-$\underline{CH_2}$-CH_3), 3.78 (t, J = 7.4 Hz, 8H, O-CH2-CH2-CH3), 4.10 (s, 8H, C(O)-CH2-O), 4.29

(s, 8H, O-$\underline{CH_2}$-C(O)N(C_2H_5)$_2$), 4.37 (d, J = 13.5 Гц, 4H, Ar$\underline{CH_{2ax}}$Ar), 6.81 (s, 8H, Ar$\underline{H}$), 9.25 (s, 4H, N$\underline{H}$). Anal. calc. for $C_{72}H_{104}N_8O_{16}$: C 64.65%, H 7.84%, N 8.38%. Found: C 64.06%, H 7.47%, N 8.20%.

*5,11,17,23-tetra-tert-butyl-25,26,27,28-tetrakis-[dibutylphosphinoylmethyloxy]-calix[4]arene (**C3**)*

The sodium hydride (10 mmol) was added to solution tetrahydroxycalixarene 1 mmol in 50 ml of dry DMF. The resulted mixture was stirred at 80–85 °C for 5 h. Then the dibutyl-phosphinoylmethyltosylat (5 mmol) was added and reaction mixture was stirred at 85-90 °C for 48 h. Excess of the sodium hydride was neutralized by methanol. Solvent was evaporated under reduced pressure, residue was dissolved in chloroform and washed with 5% HCl solution and distilled water. Then organic layer was dried upon Na_2SO_4. Solvent was evaporated under reduced pressure and residue was crystallized from hexane. Total yield (colorless crystal) 70%.

^{1}H NMR (δ, ppm, 300 MHz, ($CDCl_3$, TMS)): 0.87 (t, 24H, O-CH2-CH2-CH3), 1.1 (s, 36H, t-Bu), 1.25–1.70 (m, 48H, P-C$\underline{H_2}$-C$\underline{H_2}$-C$\underline{H_2}$-CH_3), 3.28 (d, J = 13.5 Hz, 4H, Ar$\underline{CH_{2eq}}$Ar), 4.61 (s, 8H, O-C$\underline{H_2}$-P), 4.98 (d, J = 13.5 Гц, 4H, Ar$\underline{CH_{2ax}}$Ar) 6.76 (c, 8H, ArH). 31P NMR (δ, ppm 80.95 MHz, CDCl3): 43.40. Anal. calc. for C80H 132O8P4: C 71.40%, H 9.89%, P 9.21%. Found: C 71.48%, H 9.78%, P 9.28%.

Extraction experiments

^{152}Eu extraction experiments were carried out using 5 ml plastic vials. 1 ml of organic phase and 1 ml of aqueous phase were placed in vials. The organic phase was the ligand solution in *meta*-nitrobenzotrifluoride (F-3). The aqueous phase contained nitric acid of desired concentration and 1 × 10^{-5} mol/L of europium nitrate spiked with tracer amount of ^{152}Eu. Samples were vigorously agitated for 3 min at room temperature (21 ± 1 °C). Phases were separated after a short centrifugation for 5–10 min, and aliquots (0.4 mL) were taken for analysis. The distribution ratios were determined radiometrically by using a DeskTop InSpector-1270 scintillation γ-spectrometer designed on the base of a well-type NaI-detector 51 × 51 mm "Canberra" Co. Distribution ratios (D) were calculated as $D = C_{org}/C_{aq}$ where C_{org} is metal concentration in equilibrium organic phase and C_{aq} is metal concentration in equilibrium aqueous phase. Metal concentration in equilibrium organic phase was calculated as difference between initial concentration in aqueous phase and concentration in equilibrium aqueous phase.

The extraction of rare-earth and some other metals was studied. For this purpose the *multielement standard solution* contained 22 elements (1 × 10^{-2} mol/l of each metal in 1 mol/l nitric acid) was used. The initial aqueous phase solutions were prepared by dilution of this standard with required amounts of nitric acid and deionized water and contained 22 metals, namely, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Fe, Cu, Zn, Cd, Pb, Pd, Zr and Mo (5 × 10^{-6} mol/l of each metal) and nitric acid of desired concentration. Metal concentrations in initial and equilibrium aqueous phases were determined by ICP MS method with ELAN® DRC-e ICP-MS (Perkin Elmer, USA).

Sensor membrane preparation and experiments

The polymeric membranes were produced according to the following standard procedure. The weighted amounts of membrane components were dissolved in freshly distilled tetrahydrofuran (THF) and stirred for about 20 min on a magnetic stirrer. Once the components were dissolved in the THF, the membrane cocktail was poured into a flat bottom teflon beaker and allowed to stand overnight at room temperature to evaporate the solvent. Disks (8 mm in diameter and 0.5 mm thick) were cut from the parent membranes and glued with PVC-cyclohexanone mixture to the end of PVC tubes (10 mm in diameter) used as electrode bodies. At least three replicate sensors of each respective composition were prepared. The electrodes were filled with 0.01 M NaCl solution and then immersed and stored in the same solution for 48 h prior to measurements.

The compositions of the prepared sensor membranes (in grams) are presented in the Table 2.

The neutral ligand:CCD molar ratio was chosen 5:1 to provide the excess of neutral carrier over cation-exchanger CCD. It is well known that polar solvents promote higher sensitivity towards multi charged ions, therefore in these membranes o-nitrophenyloctyl ether (NPOE) as a polar plasticizer was used.[9] F-3 and NPOE are very close in influence on extraction. Preliminary extraction data were done with F-3 as a diluent. So we suppose that it's reasonable to compare extraction and sensor properties in these two diluents.

Electrochemical measurements were carried out in the following galvanic cell:

$$\mathrm{Cu|Ag\,|\underline{AgCl},\ KCl_{sat}\big|sample\ solution\,|membrane|}$$
$$\mathrm{NaCl, 0.01\ M|\,AgCl|\,Ag|\,Cu.}$$

The electromotive force (sensor potential) values were measured with 0.1 mV precision against the standard Ag/AgCl reference electrode (EVL-1M3.1, ZIP, Gomel, Belorussia) using a homemade multi-channel digital high impedance voltmeter connected to a PC for data

Table 2 The compositions of sensor membranes

Sensor	Components	Mass (g)	Molality (mol/kg)
TOPO	PVC	0.1073	
	NPOE	0.2146	
	TOPO	0.0064	0.050
	CCD	0.0018	0.010
TODGA	PVC	0.1062	
	NPOE	0.2124	
	TODGA	0.0096	0.050
	CCD	0.0018	0.010
C1	PVC	0.1020	
	NPOE	0.2040	
	C1	0.0210	0.050
	CCD	0.0018	0.010
C2	PVC	0.1020	
	NPOE	0.2040	
	C2	0.0220	0.050
	CCD	0.0018	0.010
C3	PVC	0.1020	
	NPOE	0.2040	
	C3	0.0220	0.050
	CCD	0.0018	0.010

Molality for membrane active compounds is presented as mol/kg of membrane

acquisition. A glass pH electrode (ESL-43.07, ZIP, Gomel, Belorussia) for sample solutions acidity monitoring was used.

The sensors sensitivity was studied by sensors calibration performed in the solutions with metal ion concentration range between 10^{-7} and 10^{-2} M. In the case of trivalent metal cations the acidity of the sample solutions was always fixed at pH 2 using nitric acid to control metal hydrolysis. No special acidity fixation was needed for the solutions of divalent metals. The slopes of the linear parts of the calibration curves (sensor sensitivities) were calculated for the concentration range between 10^{-4} and 10^{-3} M. As we were dealing only with diluted solutions of RE (10^{-3} M was the highest RE concentration) we neglect the activity coefficients and use concentration values instead of the activity for all calculations with Nikolsky equation.

Selectivity of the sensors was determined with bi-ionic potential method (BIP) in the RE solutions of 10^{-3} M concentration. BIP method (also known as separate solution method (SSM)) is based on the measurement of sensor potential in two separate solutions of primary and interfering ions of the same concentration. These potentials are employed for the calculation of the selectivity coefficient according to the following equation:

$$\log k_{IJ}^{pot} = \left(\frac{z(I)F \times (E(J) - E(I))}{2.302 \times R \times T} + \log \left(\frac{a(I)}{a(J)^{z(I)/z(J)}} \right) \right)$$

In the present study we have used 10^{-3} M solutions of RE metals for selectivity estimation.

All the data presented below were averaged over at least five replicate measurements.

Results and discussions

It is well known that modification of calixarene platform by different functional groups can lead to significant changes in extraction behavior of calixarene. To clarify if this cooperative effect can also be of some use in sensor preparation we have chosen the following substances: calixarenes phosphorylated in the upper rim (**C1**) and lower rim (**C3**), and trioctylphosphine oxide (TOPO) as monofunctional analogue, and also calixarene with diamide functions in the upper rim (**C2**) and tetraoctyl-3-oxa-pentanediamide (TODGA). Both extraction and sensor properties of these compounds were thoroughly studied and reported below.

The extraction of europium and americium with **TODGA** and **C2** from nitric acid solutions was studied. The obtained results are presented in the Table 3. Every **C**2 molecule contains four "TODGA-like" reaction centers, therefore it's reasonable to study europium extraction with 0.01 M **C2** to compare with 0.04 M TODGA. It is shown that extraction ability of both ligands is almost the same for corresponding concentration level, i.e. no significant cooperative effect was observed in this case. The data on Am and Eu extraction from nitric acid with C1, C3 and TOPO are also presented in Table 3.

In the Fig. 3 data on the extraction of rare-earth elements (RE) with 0.01 M TODGA solution in F-3 from nitric acid solutions are presented. There is an obvious growth of extraction ability from lanthanum to lutetium for all the nitric acid concentrations studied (1, 3 and 5 M). These data are in good accordance with previous data on lanthanide extraction with TODGA solutions in hydrocarbon diluent. [24]

For all studied concentration of nitric acid the lanthanides distribution ratios increase with increasing of atomic number. The ionic radii of lanthanides decrease with increasing of atomic number, i.e. from La to Lu. At the same time the stability constant of Ln(III)-hard donor complexes increase across the lanthanide series as the ionic radii decrease, which corresponds to an increase in the positive charge density of the lanthanide ion [25]. That is why the heavier lanthanides are extracted better than lighter one.

Table 3 Europium and americium extraction with different neutral ligands solutions in *meta*-nitrobenzotrifluoride (F-3) from nitric acid[a]

C_{HNO3}	0.01 M **C1**[19]		0.01 M **C2**		0.04 M **TODGA**		0.01 M **C3** [23]		0.04 M **TOPO** [23]	
	D_{Am}	D_{Eu}	D_{Am}	D_{Eu}	D_{Am}	D_{Eu}	D_{Am}	D_{Eu}	D_{Am}	D_{Eu}
0.1	1.5	4.0	0.3	0.1	1.2	8.3	0.04	0.13	0.04	0.04
0.3	1.3	3.5	0.9	0.7	6.7	74	0.05	0.05	0.04	0.05
1.0	0.27	0.68	3.8	2.5	39	430	0.03	0.03	0.01	0.006
3.0	0.01	0.03	8.6	12	72	800	<0.01	<0.01	<0.01	<0.01
6.0	<0.01	<0.01	22	35	7.6	52	<0.01	<0.01	<0.01	<0.01

[a] For europium extraction ^{152}Eu-isotope was used

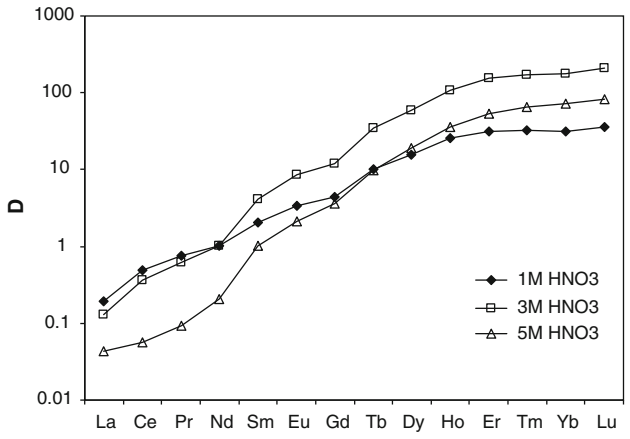


Fig. 3 Extraction of RE metals with 0.01 M **TODGA** in F-3 from simulated solution with different nitric acid concentration

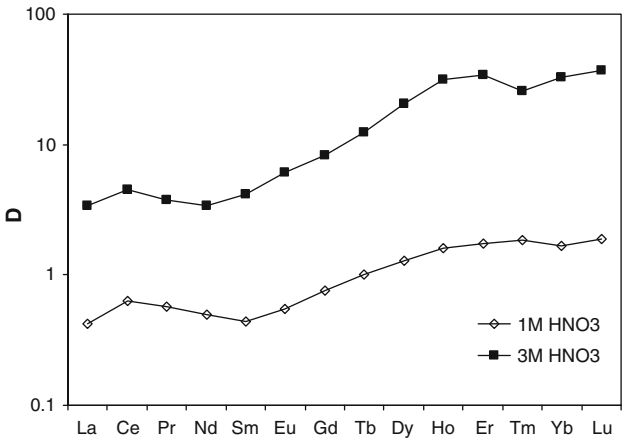


Fig. 4 Extraction of RE metals with 0.01 M **C2** in F-3 from 1 and 3 M HNO_3

With increasing of nitric acid concentration the metal distribution ratios increase. It can be explained by different solvation degree of lanthanides ions in water solutions at different nitric acidity. An increasing of nitric acid concentration (from 1 to 3 M HNO_3 in the Fig. 4) corresponds to a reduction in water activity; therefore, the energy requirement to dehydrate a lanthanide is decreased and the formation of ligand–metal complex which is highly hydrophobic becomes easier. At the same time the lanthanide patterns change slightly.

On the other hand it should be noted that even all neutral ligands and also some diluents extract nitric acid. The extraction of nitric acid and extraction of metal ion are competing reaction. At higher nitric acid concentration the extraction of nitric acid with F-3 and ligand is very significant (strong); metal distribution ratios values decrease with increasing of acidity (from 3 to 5 M HNO_3 in the Fig. 4) and the lanthanides pattern doesn't change the view.

The dependence of lanthanides pattern on aqueous phase acidity, ligand type and concentration were perfectly examined and analyzed in paper [26]. The present data on lanthanide extraction by new calixarenes fully confirm the conclusions drawn there.

The similar extraction data for **C2** are shown on the Fig. 4. Comparing Figs. 3 and 4 one can conclude that the difference in D values for light and heavy RE is significantly lower in case of **C2** (3 orders of magnitude for **TODGA** versus 1 order for **C2**). Also it can be concluded that no any growth of extraction ability associated with cooperative effect was observed, and behavior of both mono-analogue (**TODGA**) and polyfunctional modified calixarene (**C2**) is rather similar. One of the possible reasons for that is the steric factor which prevents the numerous reaction centers in **C2** molecule from solvation of RE cations, i.e. **TODGA** molecule acts as a tridentate ligand and TODGA-like groups in **C2** molecule could not bind the metal ions, as they are too far from the ion. However, to prove this suggestion further experimental data on complex structure are needed.

The extraction ability of **C2** and TODGA toward some transition metals was studied. The distribution ratios for iron, palladium, zirconium and molybdenum at different HNO_3 concentrations are shown in the Fig. 5.

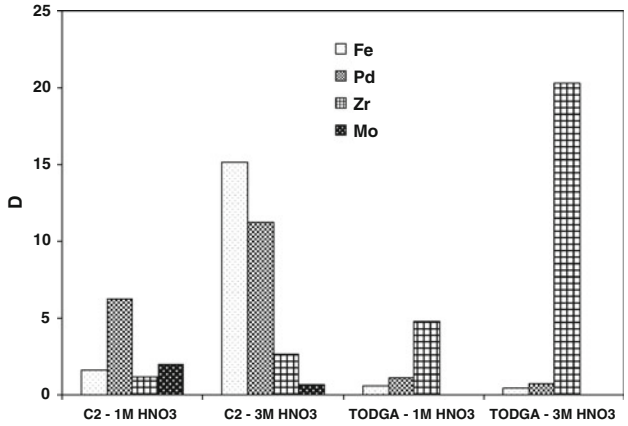


Fig. 5 Extraction of several transition metals with 0.01 M **C2** and **TODGA** in F-3 from 1 and 3 M HNO_3

The attachment of diamide moiety to the calixarene macrocycle leads to the growth of iron, palladium and molybdenum extraction, while zirconium distribution ratios decrease significantly (almost 10 times for 3 M HNO_3). Molybdenum distribution ratios in the case of **TODGA** extraction are less than 0.01. According to the data published in paper [27] four **TODGA** molecules take part in Zr-complexation (Zr·4TODGA). So one calix[4]arene molecule should complex Zr but diamide groups attached to the calixarene platform are spatially oriented and it could be hardly imaged that all four bulky TODGA-like groups would complex one zirconium ion. The formation of Zr complex with two or more **C2** molecules is also very unlikely. Therefore we can see the decreasing of extraction ability when we change **TODGA** on **C2**.

The data on lanthanides extraction with 0.01 M solution of **C1** in F-3 are presented in the Fig. 6. The metal distribution ratios increase with the increasing of the atomic

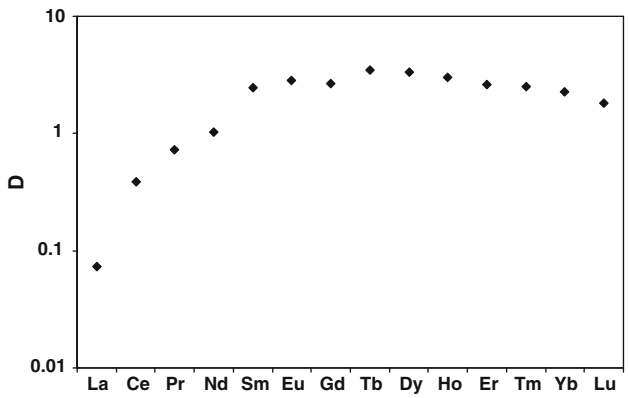


Fig. 6 Extraction of lanthanides with solution of 0.01 M **C1** in F-3 from 0.3 M HNO_3

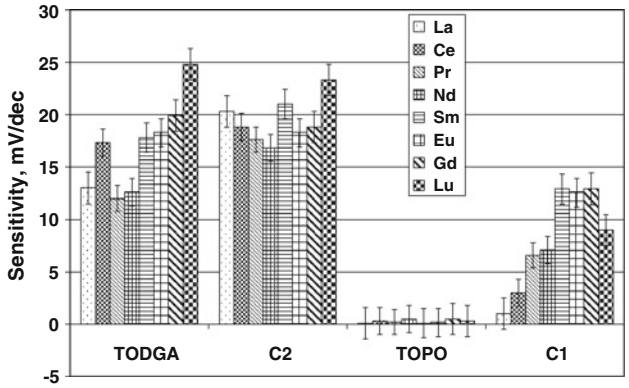


Fig. 7 Sensitivities of the polymeric sensors on the base of studied ligands in RE metal solutions with pH 2

number and this is in a good agreement with the data on lanthanides extraction with phosphine oxide [28].

The influence of the calixarene platform on sensor sensitivities was studied. The sensor sensitivities values (slopes of the linear parts of the calibration curves) in the Fig. 7 allows to conclude that in case of diamide the attachment of ionophores to the calixarene cycle leads to the smoothing of sensor sensitivities toward lanthanides (compare e.g. sensitivities to La, Pr and Nd for **TODGA** and **C2** sensors). This fact is in a good agreement with liquid extraction data for similar systems described above: the difference in D values for light and heavy RE is significantly lower when using **C2** comparing to **TODGA**.

The attachment of phosphine oxide groups to the upper rim of the calixarene macrocycle (**C1**) leads to the development of electrode function for RE metals at pH 2, while **TOPO** sensors were not sensitive to these metal ions under experimental conditions obviously due to the high protonation of P = O group in **TOPO** at low pH preventing it from interaction with RE cations. This trend is similar to the extraction data where one can see the increase of extraction ability of **C1** ligand in comparison with **TOPO**.

The sensors made on the base of **C3** have not shown any significant response to the RE metals in the acidic media, response curves of the corresponding sensors was almost parallel to the log(a_i) axis of the calibration plot with only 3–5 mV/dec growth in the highest RE concentration. Such a trend is also in a good agreement with extraction data—**C3** shows practically negligible cooperative effect to compare with **TOPO**.

The selectivity of the sensors was determined with bi-ionic potential method (BIP) in the RE solutions of 10^{-3} M concentration and $\log K^{pot}_{La,RE}$ values were calculated. Results of the selectivity determination are presented in the Fig. 6. No values for **TOPO** and **C3** sensors are shown as they did not possessed any response to RE under the experimental conditions (pH 2).

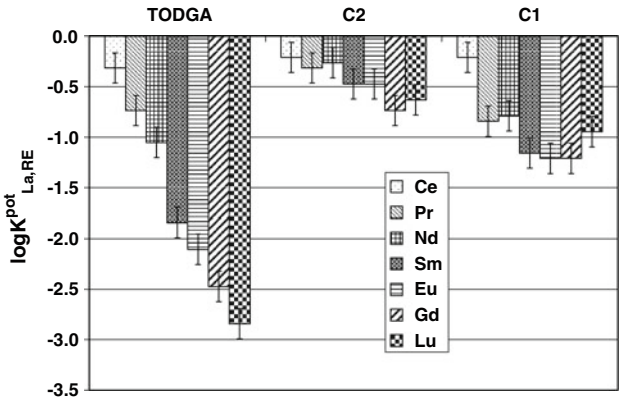


Fig. 8 Selectivity of the developed sensors to RE metals determined by BIP method

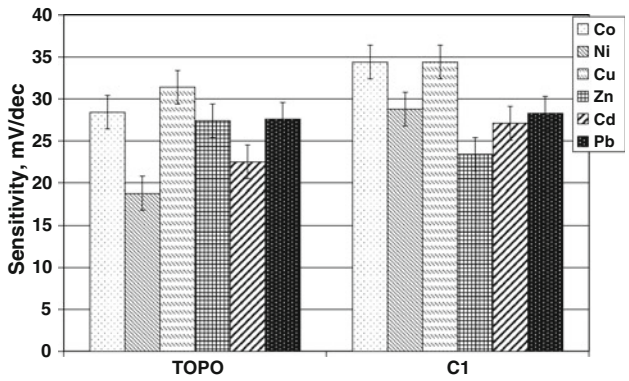


Fig. 9 Sensitivity of the polymeric sensors prepared with TOPO and **C1** in transition metal solutions

TODGA sensors exhibit growing selectivity with the growth of the lanthanide atomic number and the most preferable ion is Lu^{3+}. It is noteworthy that in spite of rather similar chemical properties of the lanthanides the $\log K^{pot}_{La,RE}$ values differs quite strong—almost three orders of magnitude between La and Lu. The attachment of the diamide groups to the calixarene cycle leads to the sharp smoothing of selectivity and **C2** sensors do not discriminate between different RE ions. Probably the sensors with this type of selectivity pattern may be practically applicable for the determination of the sum of the lanthanides in the sample solution. As for sensors based on calixarene with phosphine oxide functions **(C1)**, selectivity pattern is also rather smooth, but taking into account their low (<15 mV/dec) sensitivities these electrodes could hardly be applied for any practical task.

The response time for all of the studied sensors does not depend on the membrane composition and t_{95} was 10–15 s in RE solutions at pH 2 (Fig. 8).

As **TOPO**-based sensors have not shown a response to the RE metals a separate study with a number of transition metals was performed for **TOPO** and **C1** sensors to estimate the impact of calixarene on the sensor properties. In the Fig. 9 **TOPO-** and **C1**-based sensors sensitivity towards cobalt, nickel, copper, zinc, cadmium and lead in water solutions of the individual ions is presented.

Both **TOPO** and **C1** have shown high sensitivity to the transition metals. Such result is not surprising as both of these types of substances were previously used for sensor preparation and different transition metals determination [29, 30]. **C1**-based sensors show 2–5 mV/dec higher sensitivities comparing to the sensors based on their monodentate analogue—**TOPO**; in case of **C1** sensor response for copper and zinc turns to slightly super-Nernstian values.

Conclusion

Extraction and sensor properties of the calixarenes modified with diamide and phosphine oxide functions were studied and compared with the properties of mono-analogues. Both extraction and electrochemical sensing properties are influenced in a similar way when comparing calixarene and mono-analogues. The attachment of phosphine oxide groups to the calixarene upper rim leads to sharp increase of both extraction and sensing ability of the corresponding systems comparing to non-bonded phosphine oxide. In case of diamide functions performance of corresponding calixarene-based ligands was similar to those of non-bonded diamides. Although both liquid extraction and sensor performance of the ligands are associated with complex formation equilibrium and data on liquid extraction provide a good basis for selection of ionophores to be used in polymeric electrochemical sensors. No direct projection of these properties can be done due to the obvious differences in extraction and sensor systems (solvent media, polarity, viscosity, etc.)

Acknowledgements Partial financial support of this research from ISTC project 3364 "Development of an Analytical Methodology for Quantification of Stable Elements in Radioactive Solutions Using Electronic Tongue Multisensor Systems" and STCU Grant No. 3863 "Phosphorylated calixarenes for selective extraction of actinides from radioactve waste" is gratefully acknowledged. Authors are grateful to Prof. Vitaly I. Kalchenko for wholesome consultations and fruitful discussions.

References

1. Arnaud-Neu, F., Schwing-Weill, M.-J., Dozol, J.F.: Calixarenes for nuclear waste treatment. In: Asfari, Z., Böhmer, V., Harrowfield, J., Vicens, J. (eds.) Calixarenes 2001. Kluwer Academic Publishers, The Netherlands (2001)
2. Gutsche, C.D.: Calixarenes: an introduction, 2nd edn. RSC-Publishing, Cambridge (2008)

3. Calixarenes for separations. In: Lumetta, G.J., Rogers, R.D., Gopalan, A.S. (eds.) ACS symposium series, vol. 757 (2000)
4. Arnaud-Neu, F., Böhmer, V., Dozol, J.-F., Grüttner, C., Jakobi, R.A., Kraft, D., Mauprivez, O., Rouquette, H., Schwing-Weill, M.-J., Simon, N., Vogt, W.: Calixarenes with diphenylphosphoryl acetamide functions at the upper rim. A new class of highly efficient extractants for lanthanides and actinides. J. Chem. Soc., Perkin Trans. 2 **6**, 1175–1182 (1996)
5. Barboso, S., Carrera, A.G., Matthews, S.E., Arnaud-Neu, F., Böhmer, V., Dozol, J.-F., Rouquette, H., Schwing-Weill, M.-J.: Calix[4]arenes with CMPO functions at the narrow rim. Synthesis and extraction properties. J. Chem. Soc., Perkin Trans. 2 **4**, 719–723 (1999)
6. Sansone, F., Fontanella, M., Casnati, A., Ungaro, R., Böhmer, V., Saadioui, M., Liger, K., Dozol, J.-F.: CMPO-substituted calix[6]- and calix[8]arene extractants for the separation of An^{3+}/Ln^{3+} from radioactive waste. Tetrahedron **62**(29), 6749–6753 (2006)
7. Motornaya, A., Vatsouro, I., Shokova, E., Hubscher-Bruder, V., Alyapyshev, M., Babain, V., Karavan, M., Arnaud-Neu, F., Böhmer, V., Kovalev, V.: Adamantylcalixarenes with CMPO groups at the wide rim: synthesis and extraction of lanthanides and actinides. Tetrahedron **63**(22), 4748–4755 (2007)
8. V. Böhmer. CMPO-substituted calixarenes. In: Lumetta, G.J., Rogers, R.D., Gopalan, A.S. (eds.) Calixarenes for separations. ACS symposium series, vol. 757, pp. 135–149 (2000)
9. Legin, A., Babain, V., Kirsanov, D., Borovoy, A.V., Herbst, R.S.: Cross-sensitive rare-earth metal sensors based on bidentate neutral organophosphorus compounds and chlorinated cobalt dicarbollide. Anal. Chim. Acta **572**, 243–247 (2006)
10. Legin, A.V., Babain, V.A., Kirsanov, D.O., Mednova, O.V.: Cross-sensitive rare earth metal ion sensors based on extraction systems. Sens. Actuators B Chem. **131**, 29–36 (2008)
11. Vlasov, Yu.G., Legin, A.V., Rudnitskaya, A.M.: Electronic tongue: chemical sensor systems for analysis of aquatic media. Russ. J. Gen. Chem **78**(12), 2532–2544 (2008)
12. Bühlmann, P., Pretsch, E., Bakker, E.: Carrier-based ion-selective electrodes and bulk optodes. 2. Ionophores for potentiometric and optical sensors. Chem. Rev. **98**(4), 1593–1688 (1998)
13. Ludwig, R., Dzung, N.T.: Calixarene-based molecules for cation recognition. Sensors **2**(10), 397–416 (2002)
14. Kalchenko, V.I.: Calixarene receptors of environmentally hazardous and biorelevant molecules and ions. Pure Appl. Chem. **80**(7), 1449–1458 (2008)
15. Bocheńska, M., Zielińska, A., Pomećko, R., Hubscher-Bruder, V., Arnaud-Neu, F.: Lower rim substituted tert-butyl calix[4]arene (part VII): ionophoric properties of calix[4]arene-crown-6 derivatives in plasticized PVC-membrane electrodes and in solution. J. Incl. Phenom. Macro. Chem. **52**(1), 129–134 (2005)
16. Bocheńska, M., Hoffmann, M., Lesińska, U., Luks, E., Radecka-Paryzek, W.: Lower rim substituted tert-butylcalix[4]arenes. Part 8: calix[4]arenes with dialkoxyphosphoryl functions. Synthesis and complexing properties. Tetrahedron **61**(52), 12307–12313 (2005)
17. Shokova, E.A., Motornaya, A.E., Shestakova, A.K., Kovalev, V.V.: p-(3-Carboxy- and 3-carboxymethyl-1-adamantyl)calix[4]arenes: synthesis and arming with amino acid units. Tetrahedron Lett. **45**(34), 6465–6469 (2004)
18. Smirnov, I., Babain, V., Efremova, T., Kal'chenko, V.: Extraction of americium and europium by phosphorylated calix-arenes. J. Nucl. Sci. Technol. **39**(Suppl. 3), 321–324 (2002)
19. Smirnov, I.V., Karavan, M.D., Efremova, T.I., Babain, V.A., Miroshnichenko, S.I., Cherenok, S.A., Kal'chenko, V.I.: Extraction of Am, Eu, Tc, and Pd from nitric acid solutions with phosphorylated calixarenes. Radiochemistry **49**(5), 482–492 (2007)
20. Klimchuk, O., Atamas, L., Miroshnichenko, S., Kalchenko, V., Smirnov, I., Babain, V., Varnek, A., Wipff, G.: New wide rim phosphomethylated calix[4]arenes in extraction of americium and europium. J. Incl. Phenom. Macro. Chem. **49**(1–2), 47–56 (2004)
21. Van Wageningen, A.M.A., Snip, E., Verboom, W., Reinhoudt, D.N., Boerrigter, H.: Synthesis and application of iso(thio)cyanate-functionalised calix[4]arenas. Liebigs Ann **1997**(11), 2235–2245 (1997)
22. Boyko, V.I., Rodik, R.V., Severenchuk, I.N., Voitenko, Z.V., Kalchenko, V.I.: A novel method for the synthesis of 2, 2-dimethyl-1, 3-dioxolan-4-one, and its reactions with secondary amines. Synthesis **2007**(14), 2095–2096 (2007)
23. Pokhitonov, Yu., Smirnov, I., Shadrin, A., Karavan, M.: Palladium extraction recovery from the high level liquid wastes by phosphorylated calixarenes solutions. Proceedings of the 15th Pacific Basin Nuclear Conference, Sydney 2006; (http://www.pacificnuclear.org/pnc/2006-Proceedings/pdf/0610015final00087.pdf)
24. Zhu, Z.-X., Sasaki, Y., Suzuki, H., Suzuki, S., Kimura, T.: Cumulative study on solvent extraction of elements by N, N, N′, N′-tetraoctyl-3-oxapentanediamide (TODGA) from nitric acid into n-dodecane. Anal. Chim. Acta **527**(2), 163–168 (2004)
25. Nash, K.L., Jensen, M.P.: Analytical separations of the lanthanides: basic chemistry and methods. In: Gschnedner, K.A., Jr., Eyring, L. (eds.) Handbook on the Physics and Chemistry of Rare Earths, vol. 28, 311–371. Elsevier Science B.V. (2000)
26. Narita, H., Yaita, T., Tachimori, S.: Extraction of lanthanides with N, N′-Dimethyl-N, N′-diphenyl-malonamide and -3, 6-dioxaoctanediamide. Solv. Extr. Ion Exch. **22**(2), 135–145 (2004)
27. Sasaki, Y., Zhu, Z.-X., Sugo, Y., Suzuki, H., Suzuki, H., Kimura, T.: Extraction capacity of diglycolamide derivatives for Ca(II), Nd(III) and Zr(IV) from nitric acid to n-dodecane containing a solvent modifier. Anal. Sci. **21**(10), 1171–1175 (2005)
28. Li, W., Wang, X., Zhang, H., Meng, S., Li, D.: Solvent extraction of lanthanides and yttrium from nitrate medium with CYANEX 925 in heptane. J. Chem. Technol. Biotechnol. **82**(4), 376–381 (2007)
29. Xu, D., Katsu, T.: Application of tri-n-octylphosphine oxide as an ionophore for a vanadyl ion-selective membrane electrode. Electroanalysis **13**(10), 868–871 (2001)
30. Cadogan, F., Kane, P., McKervey, M.A., Diamond, D.: Lead-selective electrodes based on calixarene phosphine oxide derivatives. Anal. Chem. **71**(24), 5544–5550 (1999)