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Extraction of technetium(VII) by calix[4]arene tetraketones and tetraesters from acidic and basic media

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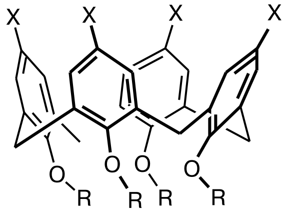
Tetrasubstituted on the lower rim calix[4]arenes, containing carbonyl and ester groups, and existing in a *cone* conformation are selective and efficient extracting agents for Tc^{VII} extraction from both acidic and basic solutions.

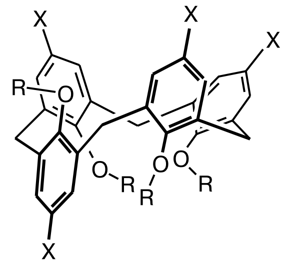
Key words: calix[4]arenes, extraction, technetium.

The intensive development of nuclear energetics and broadening the scope of exhausted nuclear fuel processing compel the treatment of the radiochemical industrial wastes. The highly active wastes contain both long-lived β/γ-emitters (^{99}Tc, ^{129}I, ^{135}Cs, ^{137}Cs, ^{90}Sr) and α-emitters (transuranium elements). The development of nuclear energetics in the Russian Federation assumes to perform the fractionation of the liquid radioactive wastes containing isotopes of Cs, Sr, Tc, and long-lived actinides for their subsequent separate solidification and disposal. One of the ways for their extraction from highly active acidic wastes with a complicated salt composition is extractional concentrating.[1] The data on the selective extraction of both transuranium elements[2—4] and artificial radionuclides Cs and Sr [4—6] by calixarenes are available from the literature. The most efficient extracting agents, *viz.*, dicarbollides, crown ethers, and functionalized calixarenes, were compared[7] to show that the latter are more preferential for cesium extraction from strongly acidic media.

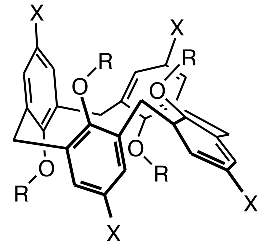
The calixarene molecules provide unique possibilities for the selective functionalization of the upper and lower rims of the macrocycle by heteroatomic groups to form a molecular system with several binding sites and for selective binding of various ions. The selectivity of ion binding by calix[4]arenes also depends on the macrocycle conformation: cone, partial cone, or 1,3- and 1,2-alternate.[8]



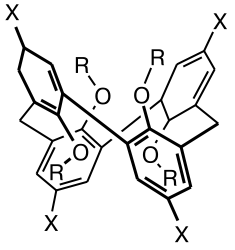
Cone



Partial cone



1,2-Alternate



1,3-Alternate

A series of complexation agents based on calix[4]arenes capable of binding the most diverse cations was synthesized.[2,3] The tetrasubstituted on the lower rim calixarenes containing donor groups, such as the carbonyl, ester, or amide group, were shown to manifest a high ionophoric activity toward alkaline metal cations,[2,9—12] and the binding selectivity can change dramatically.[11,12] For example, being in the *cone* conformation, these compounds efficiently extract Na$^+$ and very poorly extract Cs$^+$, whereas the 1,3-alternate conformation is characterized by the strictly opposite properties. The highest Cs$^+$/Na$^+$ selectivity (>30000) was demonstrated by calix[4]crown-6

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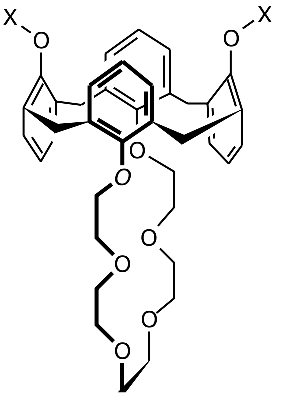
ethers **1—3**, which combine both the calixarene and crown ether structures in one molecule.[6,13,14] These macrocycles are presently used for the extraction of the ^{137}Cs isotope from radioactive wastes in which the Na^+ content exceeds that of the extracted Cs^+ ion by several orders of magnitude.



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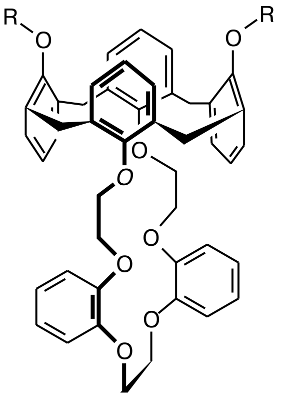

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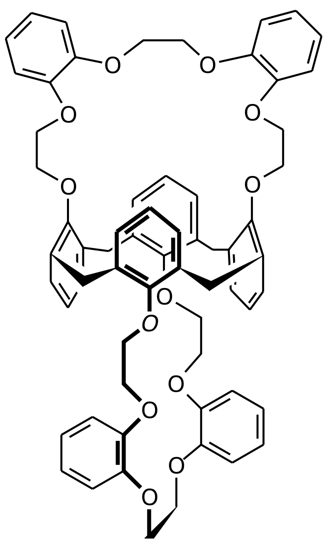


3

Alkaline-earth metal cations (Ca^{2+}, Sr^{2+}, Ba^{2+}) do not bind with calixarenes functionalized by ester and ketone groups,[2,3] although they efficiently interact with the corresponding tetramide.[2,5] However, the latter are simultaneously efficient extracting agents for sodium cations, which leads to a low Sr^{2+}/Na^+ selectivity. The latter increases sharply on going to calix[6]- and calix[8]areneamides[15,16] and, in several cases, exceeds 30000 (for comparison, the Sr^{2+}/Na^+ selectivity of dicyclohexyl-18-crown-6 is 47).

Published data on the extraction of technetium(VII) by calixarene derivatives are lacking. In this work, we studied the application of the calix[4]arenes tetrasubstituted on the lower rim for technetium(VII) extraction from acidic and basic media.

Experimental

^1H NMR spectra of functionalized calix[4]arenes in $CDCl_3$ were recorded on a Varian-XL-300 spectrometer, and chemical shifts were measured relatively to Me_4Si as the external standard. Molecular mass spectra were obtained on a MALDI-TOF Dynamo Finnigan mass spectrometer (1,8,9-trihydroxyanthracene was used as matrix). Solutions of ^{99}Tc and ^{241}Am in nitric acid, nitric acid (special purity grade), and sodium hydroxide and nitrate (reagent grade) were used. 1,2-Dichloroethane (DCE), the solvent for extraction, was purified using a known procedure.[17] Solutions of reagents in organic solvents were prepared using exact weighed samples.

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis[(ethoxycarbonyl)methoxy]-2,8,14,20-calix[4]arene (4). A mixture of *p-tert*-butylcalix[4]arene (5 g, 7.7 mmol), ethyl chloroacetate (9.8 g, 80 mmol), and anhydrous K_2CO_3 (8.28 g, 60 mmol) in anhydrous acetone (100 mL) was refluxed under argon for 60 h. The reaction course was monitored by TLC. Then the precipitate was filtered off and washed with chloroform (2×25 mL). The solvent and excess ethyl chloroacetate from the joint filtrates were removed under a reduced pressure. A mixture of dichloromethane (5 mL) and methanol (35 mL) was added to the residue. The mixture was left in a refrigerator until crystals formed (10—12 h). The precipitate was filtered off, washed with hexane (50 mL), and dried *in vacuo*. The product as a white crystalline substance was obtained in 81% yield (6.2 g).

Compound 4, cone conformation, m.p. 154—155 °C (Ref. 9: 154—155 °C). ^1H NMR ($CDCl_3$), δ: 1.07 (s, 36 H); 1.31 (t, 12 H, J = 7.6 Hz); 3.19 (d, 4 H, J = 13.3 Hz); 4.21 (q, 8 H, J = 7.6 Hz); 4.80 (s, 8 H); 4.85 (d, 4 H, J = 13.3 Hz); 6.77 (s, 8 H). MALDI TOF MS: 1016.3 $[M + Na]^+$. Found (%): C, 72.91; H, 8.11. $C_{60}H_{80}O_{12}$. Calculated (%): C, 72.58; H, 8.06.

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis(methylcarbonyl)methoxycalix[4]arene (5). A mixture of *p-tert*-butylcalix[4]arene (1 g, 1.54 mmol) and anhydrous K_2CO_3 (1.28 g, 9.25 mmol) in CH_3CN was refluxed with stirring for 1 h. Then α-bromoacetone (0.8 mL, 9.25 mmol) was added with vigorous stirring. The reaction mixture was stirred for 9.5 h at the boiling point of the solvent. The mixture was filtered through a 1.5-cm zeolite layer, and the precipitate was washed with chloroform (3×20 mL). The solvent was removed at a reduced pressure, 1 *M* HCl (20 mL) and $CHCl_3$ (30 mL) were added to the residue, and the resulting mixture was extracted for 30 min. The organic layer was separated and dried with $MgSO_4$, and the solvent was removed. The dry residue was recrystallized from a $CHCl_3$—EtOH mixture. The product as a white crystalline substance was obtained in 90% yield (1.21 g).

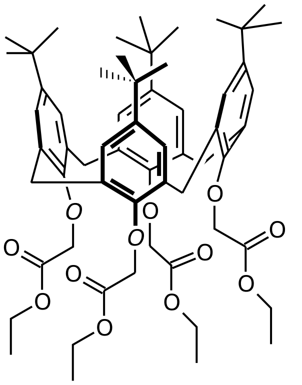
Compound 5, cone conformation, m.p. 216—217 °C (Ref. 9: 204—207 °C). ^1H NMR ($CDCl_3$), δ: 1.07 (s, 36 H); 2.21 (s, 12 H); 3.18 (d, 4 H, J = 13 Hz); 4.81 (d, 4 H, J = 13 Hz); 4.88, 6.80 (both s, 8 H each). MALDI TOF MS: 896.2 $[M + Na]^+$. Found (%): C, 77.30; H, 8.18. $C_{56}H_{72}O_8$. Calculated (%): C, 77.03; H, 8.31.

Procedure of extraction experiments. Solutions of Tc^{VII} and Am^{III} in nitric acid were placed in tubes with ground-glass stoppers. The concentrations of ^{99}Tc and ^{241}Am were

$1 \cdot 10^{-8}$—$1 \cdot 10^{-10}$ mol L^{-1}. Extraction was carried out by shaking of prepared aqueous solutions with an equal volume (as a rule, these were 1 cm^3 each) of an extracting agent solution in an organic solvent for 3 min (this time was sufficient for equilibration). After the phases were separated by centrifuging, aliquots were taken from each phase to measure the β-activity on a Protoka installation. These data were used for the calculation of the partition coefficients (*D*) of the elements under study. No formation of a third phase, violation of the activity balance, and scattering of results were observed in experiments on contact of solutions of calixarenes in organic solvents with nitric acid.

Results and Discussion

The purpose of this work was to study an application of calix[4]arenes tetrasubstituted on the lower rim for technetium(VII) extraction from acidic and basic media. For this purpose, two ligands containing four beforehand spatially organized groups on the calix[4]arene platform were synthesized: 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis[(ethoxycarbonyl)methoxy]-2,8,14,20-calix[4]arene (**4**) and 5,11,17,23-tetra-*tetra*-butyl-25,26,27,28-tetrakis[(acetyl)methoxy]-2,8,14,20-calix[4]arene (**5**).



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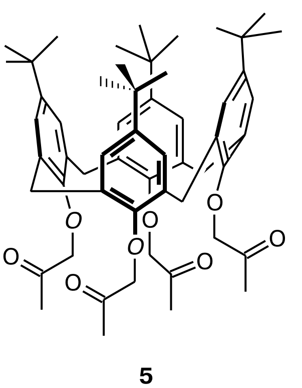

5

Of possible calix4]arene conformations (cone, partial cone, and 1,2- and 1,3-alternates), for extraction studies we chose the cone conformation in which all four functional groups are arranged on one side from the macrocycle plane formed by methylene bridges. In this case, the cooperative interaction of the four binding sites of the host and guest molecules can occur.

Ligand **4** was synthesized according to a described procedure[9] using cheaper ethyl chloroacetate instead of ethyl bromoacetate. This replacement did not virtually change the yield of the product (88 and 81%, respectively). Compound **5** was synthesized in a considerably higher yield (90%) than that described in the literature[9] (51%). This was achieved by the introduction of substantial changes in the procedure of synthesis. Instead of unstable iodoacetone formed *in situ* in acetone from a mixture of chloroacetone and NaI, we used a less active bromo derivative but the higher-boiling solvent (acetonitrile instead of acetone). In addition, to prevent bromoacetone decomposition in a basic medium, a mixture of calix[4]arene with the K_2CO_3 base was preliminarily stored at the boiling point, and only then bromoacetone was added. The conformational structures of macrocycles **4** and **5** were proved by ^1H NMR spectroscopy. The presence of two doublets of the methylene bridging protons indicates unambiguously that compounds **4** (δ 3.19 and 4.85) and **5** (δ 3.18 and 4.81) exist in the cone conformations.[8]

The extraction ability of the synthesized macrocycles toward the Tc^{VII} ion, which exists as the TcO_4^- pertechnetate anion in aqueous solutions, was studied by the two-phase extraction in a water—1,2-dichloroethane (DCE) system. Earlier, technetium was isolated from the liquid waste of uranium fission products by the extraction of TcO_4^- by dipolar aprotic solvents (ethyl methyl ketone,[18] pyridine[19]). Therefore, a high extraction ability could be expected for ligands **4** and **5** bearing four carbonyl groups on the lower rim of the macrocycle. Logarithms of the partition constants of Tc^{VII} ($\log D_{Tc}$) between water or the organic phase, which is a 0.0025 *M* solution of ligands **4** and **5** in DCE, at different concentrations of acid and base in the extracted solution are presented in Table 1.

Both synthesized ligands demonstrated a high extraction ability toward the pertechnetate ion. The data obtained (Fig. 1) show that in weakly acidic media the extraction ability of ligand **5** containing carbonyl groups on the lower rim is much higher than that of ligand **4**. The partition constants differ more than 50-fold. Thus, the replacement of the ethoxy group by methyl enhances the efficiency of Tc^{VII} extraction by the calixarene derivatives.

For understanding of this effect, one has to consider the donor ability of carbonyl and ester groups. To estimate quantitatively this ability, we used the Lewis basicities of acetone and ethyl acetate, which can simulate the donor properties of the functional groups present in the macrocycles under study. For their estimation, the Kamlet—Taft solvatochromic basicity parameter (β)[20] along with the Gutman (DN or $\Delta H^0_{SbCl_5}$ (donor num-

Table 1. Logarithms of the partition constants of Tc^{VII} ($\log D_{Tc}$) in the system of water and a 0.025 *M* solution of ligands **4** and **5** in DCE at different concentrations of acid and base

$[HNO_3]$	[NaOH]	$\log D_{Tc}$	
mol L^{-1}		**4**	**5**
0.001	—	0.51	—
0.01	—	0.26	1.22
0.1	—	0.02	—
0.5	—	0.004	0.928
1	—	−0.07	0.658
3	—	−0.32	−0.11
5	—	−0.72	−0.7
—	0.001	0.39	0.67
—	0.028	0.4	1.29
—	0.01	0.97	2.31
—	1	2.56	>4

ber))[21] and Maria—Gal[22] ($\Delta H^0{}_{BF_3}$) calorimetric scales were used. The latter characterize the energy of donor-acceptor interactions and are determined as a change in the enthalpy upon the formation of the 1 : 1 adduct between the Lewis acid ($SbCl_5$ or BF_3) and an electron pair of the donor compound. The Lewis basicities of acetone and ethyl acetate determined relatively to the soft acid $SbCl_5$ ($\Delta H^0{}_{SbCl_5}$) are virtually the same (−71.3 and −71.5 kJ mol^{-1}, respectively).[21] The published data[20,22] show that the ethoxycarbonyl group interacts with the Lewis acid much more weakly than the methylcarbonyl group does. Both the β (0.48 and 0.45) and $\Delta H^0{}_{BF_3}$ (−76.03 and −75.55 kJ mol^{-1}, respectively) parameters for acetone are somewhat higher than those for ethyl acetate. Thus, the increase in the extraction ability of compound **5** over that of compound **4** can be attributed to an increase in the donor ability of the ligand groups arranged on the lower rim of calix[4]arene.

The study of the influence of the nitric acid content in the aqueous phase on technetium(VII) extraction by solutions of calix[4]arenes **4** and **5** showed that in the region from 10^{-3} *M* to 5 *M* the partition coefficients D_{Tc} decrease and become the same at the 5 *M* acid concentration (Fig. 2). This behavior can be explained in the framework of the following scheme of interaction. Extraction proceeds *via* the protonation of one of the carbonyl groups of macrocycles **4** and **5**, and the other donor sites are likely also involved in the coordination of the pertechnetate anion. This conclusion seems valid, because aliphatic ketones in this concentration (0.025 mol L^{-1}) do not extract Tc^{VII} to the organic phase. In other words, the ion-pair mechanism of extraction can take place in which the protonated form of the extracting agent acts as a cation capable of additional binding the anion due to the interaction with the beforehand organized donor sites.

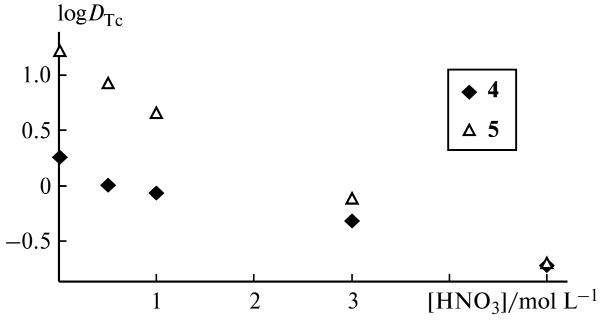

Fig. 1. Partition coefficients of Tc (D_{Tc}) for extraction by 0.025 *M* solutions of calix[4]arenes **4** and **5** in dichloroethane as functions of the HNO_3 concentration in the aqueous phase.

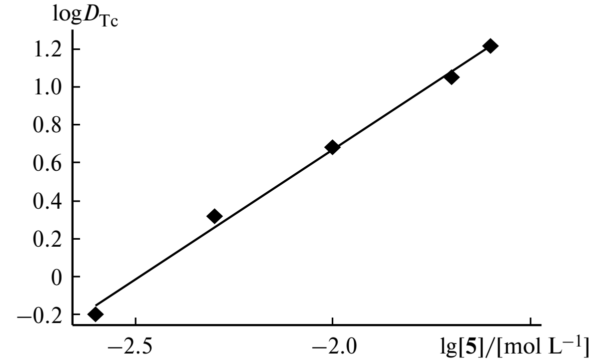

Fig. 2. Extraction of Tc^{VII} from 0.01 *M* solutions of HNO_3 by solutions of calix[4]arene **5** in dichloroethane as a function of the ligand concentration.

The influence of acidity can be related to two factors. First, the pertechnetate ion concentration decreases because of the transition to the $HTcO_4$ molecule with an increase in the medium acidity. Second, the protonation of the donor sites of the ligands begins with an increase in the acid concentration, and their ability to bind Tc^{VII} decreases gradually. The more donor methyl ketone group is protonated more efficiently and, as a result, the difference in the D_{Tc} constants decreases and becomes zero at a concentration of 5 mol L^{-1}. In this case, all donor sites of the macrocycles under study are completely protonated, and their complexation ability becomes equally low.

To reveal the composition of complexes formed in the organic phase, we determined the dependence of the D_{Tc} values on the concentration of ligand **5** at $[HNO_3]$ = 0.01 mol L^{-1}. In the interval of ligand concentrations from 0.0025 to 0.025 mol L^{-1}, the D_{Tc} values change from 0.63 to 16.6. In the $\log D_{Tc}$—log[L] coordinates, this dependence is described by a straight line with the slope close to 1, which indicates that the 1 : 1 complex between macrocycle **5** and Tc^{VII} is formed in the organic phase. This result is quite expected, because the cone conformation is mostly characterized by 1 : 1 complexes with ions.

The extraction of americium(III) as a representative of a transuranium element was studied for the estimation of

Table 2. Extraction of Tc^{VII} as a concentration of ligand **5** in DCE

[**5**] /mol L^{-1}	log[**5**]	logD_{Tc}
0.0025	−2.6	−0.2
0.005	−2.3	0.32
0.01	−2.0	0.68
0.02	−1.7	1.05
0.025	−1.6	1.22

the selectivity of extraction of radioactive waste by ligands **4** and **5**. It turned out that Am^{III} is not extracted at all under these conditions. Taking into account the available published data on the extraction of cesium and strontium,[5,6,13—16] one can assert that the calix[4]arene derivatives under study are selective and efficient extracting agents for Tc^{VII} extraction from radioactive solutions with the acid content below 1 *M*.

Our experiments showed that in a basic medium both reagents under study are characterized by the extremely high extraction ability toward pertechnetate ions. For example, for compound **4** containing the ester group an increase in the NaOH concentration from 0.001 to 1 *M* during Tc extraction increases D_{Tc} from 2.4 to 360, whereas for compound **5** bearing the methyl ketone group D_{Tc} increases from 4.6 to 100% ($D_{Tc} > 4$) of extraction under the same conditions (Fig. 3).

The increase in the D_{Tc} partition coefficients with an increase in the alkali concentration in the aqueous phase can indicate the ion-pair mechanism of pertechnetate anion extraction by the ligands studied. These macrocycles in the cone conformation are known to efficiently bind the sodium cation[9] due to the inclusion of the sodium cation suitable in size into the pseudo-cavity formed by eight oxygen atoms on the lower rim of the macrocycle. Therefore, calixarenes **4** and **5** bind Na^+, and the pertechnetate anion moves to the organic phase as a counterion formed due to the complexation of the lipophylic cation. Our data on the influence of the salt background on Tc^{VII} extraction confirm the proposed extraction mechanism. The introduction of the competitive nitrate anion into the aqueous phase decreases the partition coefficients. For example, for the extraction of technetium(VII) by solutions of ligand **4** from (1 *M* NaOH + + 1 *M* $NaNO_3$) solutions $D_{Tc} = 142$, while for the extraction from (1 *M* NaOH + 2 *M* $NaNO_3$) solutions $D_{Tc} = 102$. For ligand **5**, D_{Tc} are 118 and 108, respectively, under the same conditions. As can be seen, the influence of nitrate anion on D_{Tc} is not too significant. Even with a manifold excess of nitrate anions (>8—10 orders of magnitude), the partition coefficients remain high (>100). In both basic and acidic media, Am^{III} is not extracted by compounds **4** and **5** ($D_{Am} < 0.02$).

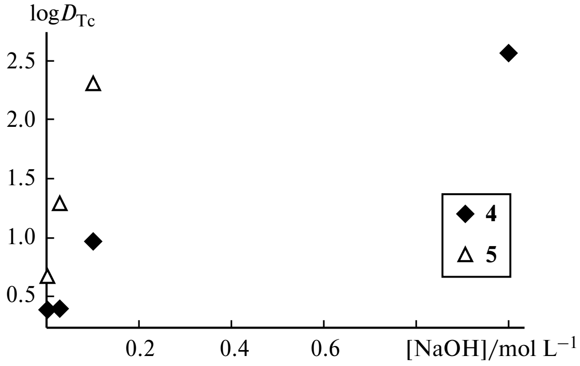

Fig. 3. Extraction of Tc^{VII} by 0.025 *M* solutions of calix[4]arenes **4** and **5** in dichloroethane as a function of the NaOH concentration.

Thus, the present studies showed that the calix[4]arenes tetrasubstituted on the lower rim and containing carbonyl and ester groups are selective and efficient extracting agents for Tc^{VII} extraction from both acidic and basic radioactive solutions.

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