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Extraction of americium(III), plutonium(IV, V) and neptunium(V) with calixarenes

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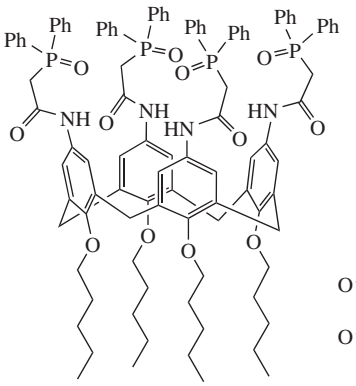
The distribution coefficients of Am^{III}, Pu^{V}, Pu^{IV} and Np^{V} on extraction from aqueous media with solutions of calix[4]arenes in 1,2-dichloroethane and their dependence on the structure of the macrocycles have been determined.

Due to the macrocyclic structure of calixarenes, their functionalization with various, particularly, organophosphorus substituents makes it possible to obtain derivatives with the preorganization favourable for the enhancement of extraction efficiency. Calixarenes contain reaction centers that allow one to modify easily their structure. At present, carbamoylmethylphosphine oxides (CMPO) are most actively used in the extraction and separation of transuranic elements from strongly acidic and salt solutions.[1,2] The introduction of four CMPO functions into the upper or lower rim of calix[4]arenes afforded ligands much more (at least 100-fold) efficient than the monomeric CMPO ligand.[3]

This study was devoted to the extractive power of calixarenes with respect to Pu^{5+}, Pu^{4+}, Np^{5+} and Am^{3+}.† The search for extraction conditions (concentration of the counter ion and its nature, the choice of solvent, the transfer of plutonium in different oxidation states to separate the studied radionuclides from a mixture of them) was conducted. 1,2-Dichloroethane was chosen as a solvent to ensure greater selectivity of the separation of radionuclides.[4]

In acidic and weakly acidic solutions, the studied elements can exist as Am^{3+}, NpO_2^+ and PuO_2^+ (within a short period of time) cations. The extraction of EO_2^+ cations requires only one counter ion in contrast to the extraction of ions in other oxidation states. This factor enhances the extraction of these ions because, in extraction of ionic associates, it is the absolute ion charge, which is important: extraction is usually impaired with an increase in the ion charge. On the other hand, the tendency to complexation decreases in the order $E^{4+} > E_2^{2+} > E^{3+} > EO_2^+$.[5] Bearing in mind this fact, one can conclude that plutonium and neptunium ions in an oxidation state of 5+ should be extracted less actively than the ions in other oxidation states because extraction is favoured by the high stability of extracted components (the high stability constant).



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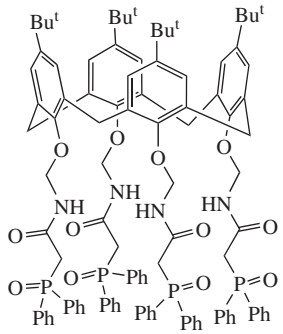

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Macrocycle **1**, calix[4]arene modified in the upper rim by four CMPO functions, is the most thoroughly studied and exhibits sufficiently high efficiency in the extraction of cations of transuranic elements.[12] The phenol groups in the lower rim are protected by pentyl radicals, which prevent the intramolecular inversion of the macrocycle.

For americium, the extraction efficiency substantially increased with an increase in acidity (Table 1). For plutonoyl and neptunoyl ions, this dependence was less pronounced. The efficiencies of

† The total concentration of americium in the aqueous phase was 5×10^{-7} mol dm^{-3}.

The solutions of plutonium(V) were prepared by the oxidation of its stock solution ($c = 2.2 \times 10^{-6}$ in 1 M HNO_3) with a 0.1 M solution of potassium bromate up to the oxidation state 6+ during the day (completeness of oxidation monitored spectrophotometrically), which was followed by its dilution, neutralization with 2.5 M NaOH and reduction with a 30% solution of hydrogen peroxide for 1 h at room temperature.[6,7]

To purify plutonium(V), we used liquid extraction to separate Pu^{IV} and Pu^{VI} trace impurities with a 0.01 M solution of di-2-ethylhexylphosphoric acid in heptane from nitric acid solutions and then neutralized the solution with NaOH up to pH 4–5.[9]

Solutions of Pu^{IV} were prepared by the addition of $NaNO_2$ to a nitric acid solution containing a mixture of Pu^{IV} and Pu^{VI}.[6,7] Yield of Pu^{IV} was controlled by extraction with a 0.5 M solution of 2-thenoyltrifluoroacetone (TTA) in cyclohexane.[9] In the extraction experiments, the Pu^{IV}–P^{V} concentration was 2.2×10^{-8} mol dm^{-3}.

To purify Np from daughter ^{233}Pa and other contaminations, liquid extraction with a 0.5 M TTA solution in cyclohexane was used.[10] The solution purity was controlled by liquid-scintillation spectrometry. The concentration of neptunium in the aqueous phase was 2×10^{-5} mol dm^{-3}. Calixarenes used in this study were prepared according to a published procedure.[1] 2-Adamantyl-2-sulfanylethanoic acid was prepared as described elsewhere.[11]

In the test tube for extraction poured 2.0 ml of the aqueous phase, 0.02 ml of actinide and 2.0 ml of organic phase (a solution of calixarene in 1,2-dichloroethane) were shaken for 15 min. Samples of 1.0 ml of each phase were taken after the complete phase separation (15–20 min) and placed in special tubes for radioactivity measurements.

The radioactivity of americium was measured using a CEM-10-P4 semiconductor coaxial detector with a well and that of plutonium and neptunium, on a Tri-Carb 2700TR liquid-scintillation spectrometer.

The molar distribution coefficient was calculated using the formula $D = I_{org}/I_{aq}$, where I_{org} and I_{aq} are the count rates of organic and aqueous phases, respectively. To determine the distribution coefficients, three parallel experiments were performed.

Table 1 Extraction of actinides with calix[4]arene **1** ($c = 10^{-3}$ mol dm^{-3} in 1,2-dichloroethane) from nitric acid solutions.

Aqueous phase	$D(Am^{3+})$	$D(NpO_2^+)$	$D(PuO_2^+)$	$D(Pu^{4+})$
3 M HNO_3	22.5±3.4	2.4±1.2	3.6±0.6	381±56
1 M HNO_3	13.8±2.5	1.1±0.5	1.3±0.6	55±13
0.5 M HNO_3	12.5±2.5	0,6±0,4	0.4±0.2	35±12
0.1 M HNO_3	2.9±1.7	0.2±0.2	0.3±0.3	8.8±4.5
1.5 M H_2SO_4	0.004±0.002	0.1±0.1	0.3±0.2	—
5×10^{-3} M AdCH(COOH)SO_3H	8.3±1.9	0.4±0.3	1.2±0.5	18.2±6.8

extraction of plutonium(V) and neptunium(V) ions were close to one another and one order of magnitude lower than that of americium. The distribution coefficients of Pu^{IV} substantially exceeded those of the other ions and did not coincide with the published data for similar conditions ($D_{Pu} = 5.2$, $c_L = 10^{-3}$ mol dm^{-3} in 1,2-dichloroethane, 3 M HNO_3).[13,14] Thus, in this case, the tendency of ions to complexation did not prevail over the effect of the absolute charge of ions.

In this process, the extractive power of the calixarene under study was higher, as compared with its mono analogue taken in the corresponding concentration,[1,15] and the dependence of the efficiency of extraction of phosphorylated calix[4]arenes on the HNO_3 concentration in the aqueous phase was similar to the pH dependence of conventional phosphine oxides.

For extraction from sulfuric acid solutions, the low extraction of all actinides was observed. If in place of sulfuric acid, 2-adamantyl-2-sulfanylethanoic acid was taken in the concentration comparable with the calixarene concentration (Table 1), then the extraction factor increased by several orders of magnitude (Figure 1). In the process, the selectivity with respect to americium and plutonoyl ions and, especially, neptunoyl ion is observed. The 2-adamantyl-2-sulfanylacetate ion is probably more lipophilic than the hydrosulfate ion; hence, the corresponding compound can be used as the counter ion for the efficient and selective extraction.

A series of experiments in which the ionic strength of solutions was virtually constant and the solution acidity differed was also carried out (Table 2). In this case, the distribution coefficient of americium is virtually independent of the solution acidity. For plutonoyl and neptonoyl ions with the constant concentration of nitrate ions, as the solution acidity increased, only an insignificant rise in the efficiency of radionuclide extraction was observed. In an acidic medium, the protonation of carbamoyldiphenylphosphine oxide groups and their mutual electrostatic repulsion occur. As the result, the calixarene cup opens and the randomly oscillating CMPO functions no longer prevent the penetration of a cation into the calixarene cavity.

Comparing this with the data in Table 1, one can conclude that the efficiency of extraction of metal cations by this calixarene substantially grows with the concentration of the nitrate counter ion in the aqueous solution. The higher the counter-ion concentration, the more advantageous is its transition from the aqueous phase to the organic phase. The permanent increase in actinide extraction factors from nitric acid solutions is hence mainly associated with the increase in the nitrate ion concentration rather than with the acidity of the medium.

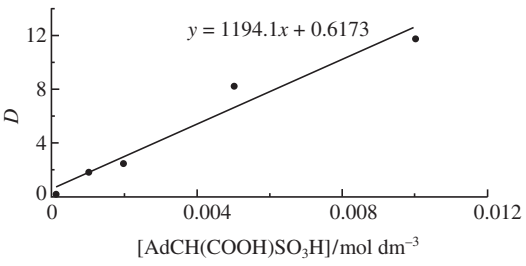

Figure 1 The dependence of the distribution coefficient of americium on the extraction with calixarene **1** ($c = 10^{-3}$ mol dm^{-3} in 1,2-dichloroethane) on the concentration of 2-adamantyl-2-sulfanylethanoic acid.

Table 2 Extraction of actinides with calix[4]arene **1** ($c = 10^{-3}$ mol dm^{-3} in 1,2-dichloroethane) from mixed nitric acid and potassium nitrate solutions.

Aqueous phase	$D(Am^{3+})$	$D(NpO_2^+)$	$D(PuO_2^+)$
2.5 M HNO_3 + 0.5 M KNO_3	17.7±0.2	0.7±0.2	2.9±0.6
2 M HNO_3 + 1 M KNO_3	17.2±0.8	0.4±0.2	2.2±0.5
1.5 M HNO_3 + 1.5 M KNO_3	17.0±0.8	0.5±0.3	2.4±0.3
1 M HNO_3 + 2 M KNO_3	17.1±2.5	0.3±0.1	2.1±0.6
0.5 M HNO_3 + 2.5 M KNO_3	16.3±1.8	0.3±0.2	0.8±0.3
0.1 M HNO_3 + 2.9 M KNO_3	15.0±2.0	0.2±0.1	0.5±0.2

The presence of europium nitrate in the nitric acid solution of the aqueous phase reduces the efficiency of extraction (Table 3). Europium(III) acts as a competitive ion and, for its concentration equal to the ligand concentration (10^{-3} mol dm^{-3}), the efficiency of extraction of americium decreases approximately by a factor of 3.

For neptunoyl and plutonoyl ions, their coextraction was observed and the extraction efficiency on the contrary increased. Thus, for $c(Eu^{3+}) = 5\times10^{-5}$ mol dm^{-3}, the distribution coefficients rose by a factor of 4.3 for Pu^{+5} and by a factor of 3.8 for Np^{+5}.

The use of lithium picrate solutions (pH 6.4) as the aqueous phase appears promising due to the relative lipophilicity of the picrate ion, which is considered as the optimal counter ion for calixarene complexes with metal ions (Table 4). This effect was observed for the extraction of several metals by another class of macrocyclic compounds, crown ethers.[16] The high degree of americium extraction from picrate solutions [c(LiPic) = 5×10^{-3} mol dm^{-3}] was reached for the lithium picrate concentration comparable with the calixarene concentration.

Calixarene **2** was synthesized by modifying calix[4]arene with CMPO functions at the lower rim and introducing *tert*-butyl substituents in the upper rim. Table 5 shows the extraction factors of americium with this calixarene from aqueous solutions of different composition. The general trend in their variation is similar to that observed for calixarene **1**; however, the factors are smaller by approximately a half. Thus, for the extraction from nitric acid solutions, a considerable increase in the extraction efficiency with the acid concentration growth was observed, and the extraction from the lithium picrate solution was the most efficient [c(LiPic) = = 10^{-3} mol dm^{-3}].

According to published data, the diameter of an americium ion (2.14 Å) exceeds the cavity diameter at the lower rim of calix[4]arene (1.0 Å[17]); hence, the americium cation is too large

Table 3 Extraction of actinides with calix[4]arene **1** ($c = 10^{-3}$ mol dm^{-3} in 1,2-dichloroethane) from acidic solutions of europium(III) nitrates.

Aqueous phase	$D(Am^{3+})$	$D(NpO_2^+)$	$D(PuO_2^+)$
1×10^{-3} M $Eu(NO_3)_3$ in 3 M HNO_3	7.6±0.5	1.5±0.7	6.3±2.9
5×10^{-4} M $Eu(NO_3)_3$ in 3 M HNO_3	8.5±0.3	2.1±1.2	8.2±1.5
1×10^{-4} M $Eu(NO_3)_3$ in 3 M HNO_3	15.0±2.6	2.9±0.8	7.8±1.1
5×10^{-5} M $Eu(NO_3)_3$ in 3 M HNO_3	12.8±3.0	9.1±1.9	15.4±3.4

Table 4 Extraction of actinides with calix[4]arene **1** ($c = 10^{-3}$ mol dm^{-3} in 1,2-dichloroethane) from lithium picrate solutions.

Aqueous phase	$D(Am^{3+})$	$D(NpO_2^+)$	$D(PuO_2^+)$
5×10^{-3} M LiPic	46.8±4.1	9.1±3.2	6.7±3.5
1×10^{-3} M LiPic	8.1±0.9	1.5±1.0	3.9±2.0
1×10^{-4} M LiPic	0.8±0.1	0.2±0.2	0.4±0.3
1×10^{-5} M LiPic	0.3±0.1	0.2±0.2	0.5±0.3

Table 5 Extraction of americium with calix[4]arene **2** ($c = 10^{-3}$ mol dm^{-3} in 1,2-dichloroethane) from aqueous solutions.

Aqueous phase	$D(Am^{3+})$	Aqueous phase	$D(Am^{3+})$
3 M HNO_3	14.1±2,1	10^{-3} M LiPic	11±2.3
1 M HNO_3	10.9±1.3	10^{-4} M LiPic	1.8±0.3
0.5 M HNO_3	8.9±0.9	10^{-3} M $Eu(NO_3)_3$ in 3 M HNO_3	2.1±0.7
0.1 M HNO_3	0.6±0.2	10^{-4} M $Eu(NO_3)_3$ in 3 M HNO_3	10.5±1.7
5×10^{-3} M LiPic	45.5±9.9	2.9 M KNO_3 in 0.1 M HNO_3	2.0±0.5

to be bound inside a square formed by four oxygen atoms of calix[4]arene; however, this cation fits the cavity of calixarene **1** due to stabilization by strong cation-ϖ-interactions. For calixarene **2**, the cation fixed by four CMPO functions lacks such stabilization due to its size; hence, the efficiency of extraction by this calixarene is lower, as compared with macrocycle **1**.

Thus, we can postulate that the efficiency of extraction of Am^{3+} is determined by the calixarene structure; dialkylphosphine oxide calixarenes containing substituents in the upper rim demonstrated the higher distribution coefficients for Am^{3+} as compared with their analogues containing substituents in the lower rim or the corresponding mono analogue.

The data obtained can be used in the preparative radiochemistry and analytical chemistry. In the future, we intend to study resistance to ionizing radiation of both the macrocycles and ion-exchange resins with grafted macrocycle with an estimate of their possible using in the separation of radionuclides from high-level solutions. The use of calixarenes for allocating ^{137}Cs from high-level waste has been recently reported.[18]

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