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Extraction of Americium and Europium with Functionalized Thiacalix[4]arenes from Alkaline Solutions

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Abstract—The extraction of ^{241}Am and ^{152}Eu from alkaline carbonate solutions with solutions of functionalized thiacalix[4]arenes in *m*-nitrobenzotrifluoride was studied. The dependence of the radionuclide distribution ratios and separation factors on pH of the aqueous phase in the interval from 10 to 13.5, kind of the organic diluent, and position and electronic characteristics of functional groups in the thiacalixarene platform was examined. The composition of the extractable solvates of Am and Eu with functionalized thiacalix[4]arenes was determined by slope analysis. The hydrolytic stability of *tert*-butylthiacalix[4]arene in alkaline and acid solutions was evaluated. Thiacalix[4]arenes efficiently extract Am from alkaline solutions. The bromine-substituted thiacalix[4]arene exhibits the maximal selectivity, with the Am/Eu separation factor in extraction with this agent exceeding 30.

Keywords: extraction, americium, europium, alkaline solutions, functionalized thiacalix[4]arenes

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It is known that HLW partitioning prior to solidification allows reduction of the expenditures for the disposal of solidified HLW due to recovery of long-lived radionuclides requiring disposal in deep geological formations into a separate fraction of small volume. Also, it allows the use of different methods and host materials for solidification of radionuclides differing in the chemical behavior, which considerably enhances the firmness of the radionuclide fixation. Finally, it allows reduction of the solidified HLW volume due to separation of large amounts of salts of nonradioactive elements (Na, Fe, Cr, Ni, etc.).

Alkaline high-level wastes have been accumulated in Russia in considerably smaller amounts than acidic wastes, but their partitioning is a complex task because of very high content of nonradioactive salts. About 18000 m^3 of alkaline HLW formed in the course of implementation of the USSR Atomic Project is stored at the Mayak Production Association [1]. These wastes are multicomponent slurries containing precipitates of aluminum, chromium, iron, and nickel hydroxides and of iron and nickel ferrocyanides against the background of hundreds of grams of sodium hydroxide, nitrate, and nitrite per liter in the liquid phase. In the solid phase, ^{137}Cs and ^{90}Sr are present in large amounts (more than 10^{11} Bq L^{-1} each). The radioactivity of the liquid phase is caused by the presence of ^{137}Cs (up to 5×10^{10} Bq L^{-1}), actinides (4×10^6 Bq L^{-1}), and ^{90}Sr (2×10^8 Bq L^{-1}).

The CARBEX process based on selective transfer of U and Pu into a carbonate solution, followed by their separation from fission products by extraction with quaternary ammonium salts, is being actively developed for spent nuclear fuel reprocessing at the Mendeleev University of Chemical Technology of Russia [2]. The alkaline high-level raffinate of the CARBEX process with high sodium carbonate content will be subject to reprocessing, most probably, by partitioning.

Thus, the need for new efficient methods for alkaline HLW partitioning is obvious.

The development of extractants suitable for radionuclide partitioning in alkaline solutions is a challenging problem, because it is required to combine functional groups interacting with cesium, actinides, and strontium in one molecule. Calixarenes, macrocyclic polyphenol compounds, show promise as extractants for recovering various groups of radionuclides, because the calixarene platform allows different functional groups to be readily combined in one molecule [3].

We have shown previously that calixarenes can be used for alkaline HLW partitioning: hexahydroxy-*tert*-butylcalix[6]arene in combination with 4-alkyl-2-di(2-hydroxyethyl)aminomethylphenol extracts Cs, Sr, Am, and Pu from alkaline HLW [4]. Recently [5] we studied the extraction of Am and Eu with functionalized calixarenes in relation to pH of the aqueous phase (from 9.8 to 13.2) and to position and kind of functional groups (alkyl, pyridine, phosphoryl) in the calixarene platform. Phosphorylated dihydroxycalix[4]-arene showed the highest performance ($D_{\mathrm{Am}} = 2$ for 0.01 M solution in *m*-nitrobenzotrifluoride, NBTF), and tri-hydroxycalix[4]arene with the pyridine functional group showed the highest selectivity ($\beta_{\mathrm{Am/Eu}} > 3$). The possibility of joint extraction of Am and Cs from alkaline carbonate solutions with solutions of *tert*-butylcalix[8]arene in tetrachloroethylene was demonstrated in [6]. Unfortunately, the reached levels of extraction performance and selectivity are insufficient for alkaline HLW partitioning.

Very interesting results were obtained in studying the radionuclide sorption onto an impregnate based on *tert*-butylthiacalix[4]arene and silica gel [7]. Very high values of K_{d} of Am (170 cm^3 g^{-1}) and Eu (2.5 cm^3 g^{-1}) at a record value of $\beta_{\mathrm{Am/Eu}} = 68$ were obtained in sorption from nitrate solutions with pH 4. The increase in the radionuclide distribution ratios with increasing pH from 1 to 6, noted in [7], suggests that thiacalixarenes will be capable of extracting Am from alkaline solutions also. The results of that study demonstrate high potential of thiacalixarenes as analytical reagents for selective recovery of Am.

This study deals with the extraction of Am and Eu from alkaline solutions with functionalized hydroxythiacalix[4]arenes of diverse structures (see below).

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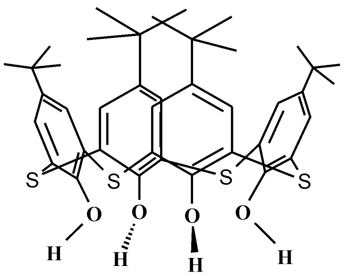

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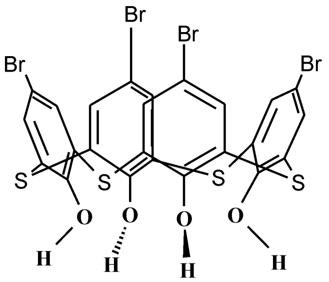

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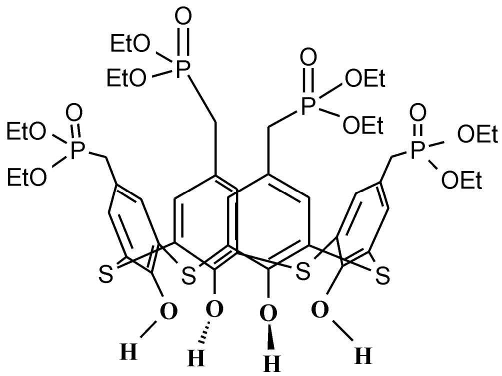

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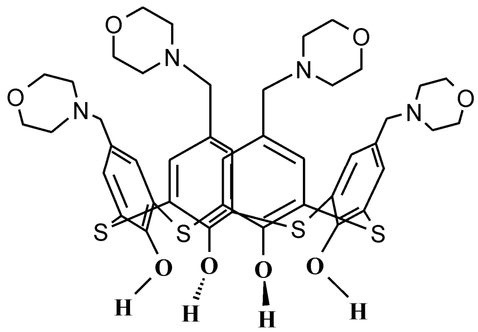

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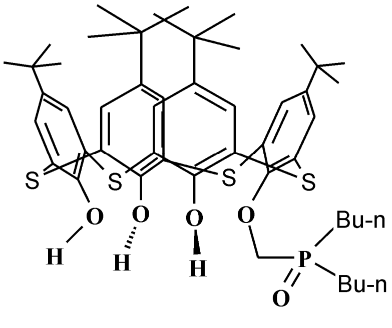

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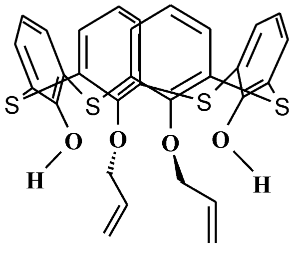

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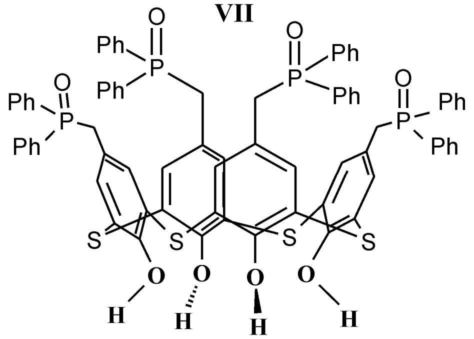

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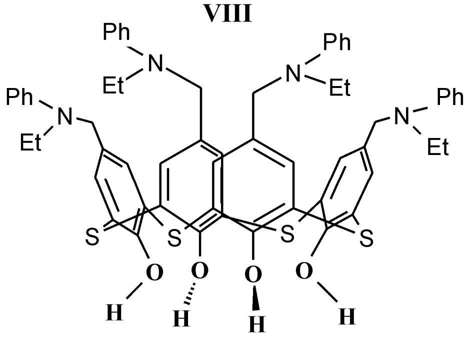

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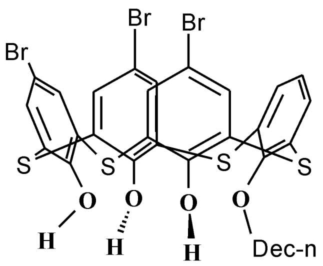

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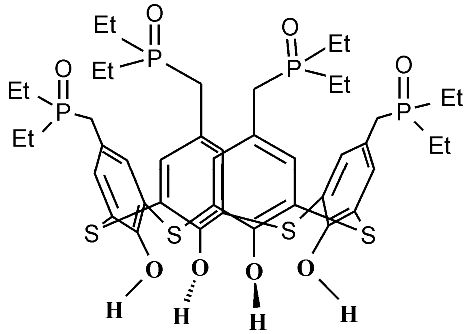

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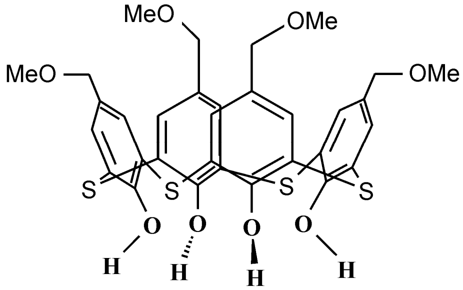

EXPERIMENTAL

Thiacalixarenes were synthesized at the Institute of Organic Chemistry, National Academy of Sciences of Ukraine (Kyiv) by the procedures described in [8–12].

m-Nitrobenzotrifluoride (NBTF) produced by Rhodia (France) and used in our previous studies on extraction of Am and Eu with substituted calixarenes from nitric acid and alkaline solutions [5, 11–16, 17] was chosen as diluent. The ^{152}Eu and ^{241}Am isotopes of >99.9% purity were purchased from Izotop (St. Petersburg, Russia). Inorganic chemicals were of analytically pure grade, were purchased from Vekton (St. Petersburg, Russia), and were used without additional purification. Solutions of the extractants in NBTF were prepared from accurately weighed portions.

Experimental Procedures

pH of solutions was measured with an HI-8314 digital pH meter (Hanna Instruments) equipped with an I-1330B microelectrode. This electrode allows the measurements to be performed directly in micro test tubes used for the extraction. The calibration showed that the device readings differed from the nominal values by no more than ±0.03 pH unit. This accuracy level was sufficient for our study.

Radionuclide extraction. The raduionuclide distribution ratios were determined as follows. A 1.5-mL centrifugal polypropylene micro test tube was charged with 0.6-mL portions of the organic and aqueous phases of the required composition. The radioactive tracer was added, and the phases were stirred at 20–22°C for 10 min and then were separated by centrifugation. Preliminary experiments showed that this time was sufficient to attain the equilibrium in the system. Aqueous phases with the required pH value were prepared by mixing 1 M $NaHCO_3$ and NaOH solutions, which ensured constant ionic strength of the solutions. The equilibrium pH value of the aqueous phase was determined directly in the micro test tube, after which 0.4-mL portions of each phase were taken for the analysis. The radionuclide amounts in both phases were determined radiometrically from the γ-radiation of the corresponding isotope. The extraction relationships were studied using ^{241}Am and ^{152}Eu radioisotopes introduced jointly in the presence of $\sim 10^{-6}$ M stable Eu. Radiometric measurements were performed with a DeskTop InSpector scintillation γ-ray spectrometer based on a 51 × 51 mm well-type NaI detector (Canberra). The sample measurement time was chosen so as to ensure no more than 10% uncertainty of the radiometric measurements. The distribution ratios

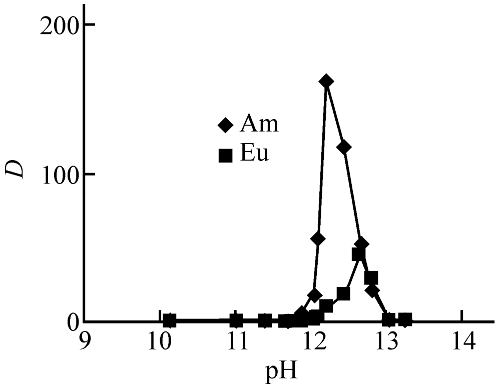

Fig. 1. Distribution ratio of Am(III) and Eu(III) in extraction from alkaline carbonate solutions with a 2 × 10^{-4} M solution of **I** in NBTF as a function of pH of the aqueous phase.

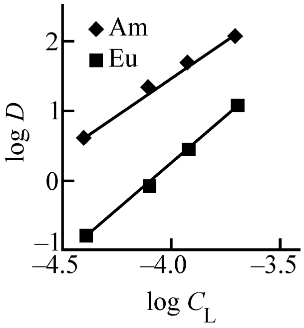

Fig. 2. Distribution ratio of Am(III) and Eu(III) in extraction from alkaline carbonate solutions (pH 12.1) with solutions of **I** (L) in NBTF as a function of the extractant concentration.

were calculated by the formula $D = A_{org}/A_{aq}$, where A is the activity concentration of a radionuclide in the corresponding (organic or aqueous) phase.

RESULTS AND DISCUSSION

One of the factors hindering the use of calixarenes in extraction processes is their low solubility in organic diluents used in solvent extraction. For example, the solubility of *tert*-butylthiacalix[4]arene **I** in NBTF, according to our data, only slightly exceeds 10^{-4} M. An obvious way to make the molecule more lipophilic is replacement of *tert*-butyl substituents in the upper rim or partial alkylation of phenol groups (hydroxyls ensure complexation of radionuclides in alkaline solutions) in the lower rim of a thiacalixarene. Some of thiacalixarenes functionalized in this way appeared to be appreciably more soluble in NBTF (the solubility of **III**, **VI**, **VII**, and **VIII** exceeds 0.03 M), whereas the solubility of other compounds (**IX**, **X**, **XI**) remained on the level of 10^{-4} M. Two readily soluble thiacalixarenes, **VII** и **VIII**, formed an abundant precipitate on contact with alkaline solutions, which made extraction experiments with them impossible. Thus, for studying the extraction properties we chose thiacalix[4]arenes **I–VI**.

*Tetrahydroxythiacalix[4]arenes **I–IV***

Published data allowed us to hope that the extraction ability would increase in going to macrocyclic platforms based on thiacalix[4]arenes in which the benzene rings are linked via sulfur atoms behaving as pronounced electron donors. To check this assumption, we studied the extraction of Am(III) and Eu(III) with *tert*-butylthiacalix[4]arene **I**. The results of studying the influence of pH and extractant concentration on the extraction of Am and Eu are shown in Figs. 1 and 2.

The solubility of **I** in NBTF only slightly exceeds 2 × 10^{-4} M, but even these dilute thiacalix[4]arene solutions are capable to efficiently extract radionuclides, with the Am distribution ratios exceeding 100. As seen from Fig. 1, the pH intervals of maximal extraction are different for Am and Eu (12.13–12.56 for Am and 12.51–12.85 for Eu). Owing to this feature, there are pH intervals in which the separation factors are high [β_{max}(Am/Eu) = 18].

The $\log D_M = f(\log C_L)$ plots are linear (Fig. 2). The slopes of the straight lines suggest formation of di- and trisolvates of **I** with Am and Eu in the organic phase.

Our data unambiguously demonstrate good prospects for using thiacalix[4]arenes for recovering and separating Am and Eu by extraction from alkaline carbonate solutions. It should be noted that the phosphorylated dihydroxycalix[3]arene that we studied previously [5] extracted Am worse by a factor of several hundreds at concentrations higher by a factor of several tens (D_{Am} = 2 for 0.01 M solution in NBTF).

The next extractant that we studied, **II**, is the closest structural analog of **I** with Br atoms in the upper rim. Figure 3 shows the influence of pH on the extraction of Am and Eu with calixarene **II**. As can be seen, replacement of *tert*-butyl radicals by the Br atoms in the thiacalix[4]arene molecule led to a significant decrease in the extraction ability, but enhanced the selectivity of the Am extraction [β_{max}(Am/Eu) = 30]. The pH interval of the maximal extraction of Am has not noticeably changed in going from **I** to **II**.

Table 1. Coefficients of the equations describing the dependences of the radionuclide distribution ratios D on the extractant concentration C_L, $\log D = a \log C_L + b$, and possible composition of the solvates

L	pH	Radionuclide	a	b	R^2	Solvate
I	12.1	Am	2.11	9.92	0.99	ML_2, ML_3
		Eu	2.72	11.1	0.99	
II	11.9	Am	3.18	10.1	0.99	ML_3
		Eu	2.71	7.5	0.99	
III	11.4	Am	1.28	3.55	0.99	ML
		Eu	1.47	3.65	0.99	
IV	12.7	Am	1.72	3.20	0.99	ML_2
		Eu	1.99	3.75	0.99	
V	12.5	Am	0.87	1.80	0.99	ML
		Eu	0.60	0.48	0.99	
VI	12.7	Am	0.69	1.55	0.98	ML
		Eu	0.47	0.24	0.99	

As in the case of **I**, the composition of the extractable Am and Eu solvates was determined by analyzing the slope of the $\log D_M = f(\log C_L)$ dependence. Data in Table 1 indicate that the predominant extractable species are trisolvates of **II** with Am and Eu.

In thiacalix[4]arene **III**, *tert*-butyl substituents were replaced by methylenediphosphonate groups, which considerably increased the solubility in NBTF. The results of studying the influence of pH and extractant concentration on the extraction of Am(III) and Eu(III) with solutions of **III** are given in Fig. 4 and Table 1.

Thiacalix[4]arene **III** shows fairly high performance in extraction of the elements from alkaline carbonate solutions, though not so high as compounds **I** and **II** do. The pH interval of the maximal extraction is noticeably shifted toward acidic medium compared to **I** and **II**: 10.63–11.58 for Am and 11.93–12.86 for Eu. The differences in the position of the extraction maximum for Am and Eu ensure high selectivity of **III** with the separation factor β_{max}(Am/Eu) = 20.

The linearity of the $\log D_M = f(\log C_L)$ dependence with the slope slightly higher than 1 suggests predominant formation of monosolvates of **III** with Am and Eu in the organic phase (Table 1).

Thiacalix[4]arene **IV** with morpholine substituents in the upper rim, compared to **III**, exhibits similar extraction ability but considerably lower selectivity. The results of studying the influence of pH and extractant concentration on the extraction of Am(III) and Eu(III) with solutions of **IV** are given in Fig. 5 and Table 1.

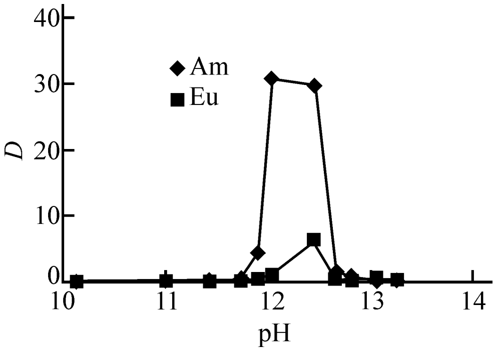

Fig. 3. Distribution ratio of Am(III) and Eu(III) in extraction from alkaline carbonate solutions with a 0.001 M solution of **II** in NBTF as a function of pH of the aqueous phase.

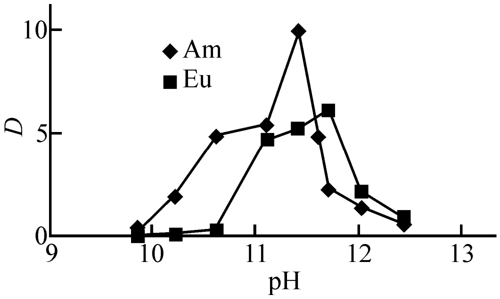

Fig. 4. Distribution ratio of Am(III) and Eu(III) in extraction from alkaline carbonate solutions with a 0.01 M solution of **III** in NBTF as a function of pH of the aqueous phase.

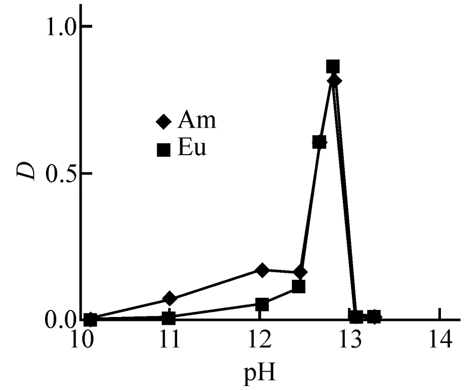

Fig. 5. Distribution ratio of Am(III) and Eu(III) in extraction from alkaline carbonate solutions with a 0.001 M solution of **IV** in NBTF as a function of pH of the aqueous phase.

As compared to phosphorylated thiacalix[4]arene **III**, the Am/Eu separation factor for **IV** decreased to 2,

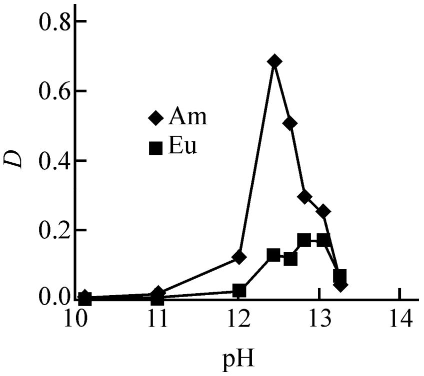

Fig. 6. Distribution ratio of Am(III) and Eu(III) in extraction from alkaline carbonate solutions with a 0.005 M solution of **V** in NBTF as a function of pH of the aqueous phase.

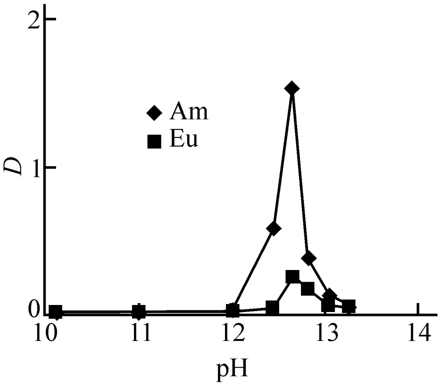

Fig. 7. Distribution ratio of Am(III) and Eu(III) in extraction from alkaline carbonate solutions with a 0.01 M solution of **VI** in NBTF as a function of pH of the aqueous phase.

i.e., by an order of magnitude. The linearity of the $\log D_\mathrm{M} = f(\log C_\mathrm{L})$ with the slope close to 2 (Table 1) suggests predominant formation of disolvates of **IV** with Am and Eu in the organic phase.

To conclude the analysis of the extraction properties of functionalized tetrahydroxythiacalix[4]arenes, it should be noted that replacement of *tert*-butyl substituents in the upper rim by any other substituents appreciably enhances the solubility of thiacalix[4]arenes in NBTF, but significantly reduces their extraction ability.

*Tri- and Dihydroxythiacalix[4]arenes **V** and **VI***

In the last two thiacalix[4]arenes that we studied, **V** and **VI**, the phenol groups in the lower rim were partially alkylated to increase the solubility. The results of studying the influence of pH and reagent concentration on the extraction of Am and Eu with solutions of **V** and **VI** in NBTF are given in Figs. 6 and 7 and in Table 1.

First, low extraction ability of thiacalix[4]arenes **V** and **VI** should be noted. They extract Am to approximately the same extent as compounds **III** and **IV** functionalized at the upper rim do. Thiacalix[4]arenes with one (**V**) and two (**VI**) substituents in the lower rim do not differ significantly in the extraction ability, but the solubility of **VI** in NBTF is several times higher than that of its monosubstituted analog **V**. Both thiacalixarenes exhibit similar selectivity with the separation factor $\beta_\mathrm{max}(\mathrm{Am/Eu}) = 5–6$. The composition of the extractable solvates of Am and Eu was determined by analyzing the slope of the $\log D_\mathrm{M} = f(\log C_\mathrm{L})$ dependence. The data given in Table 1 suggest predominant formation of monosolvates of **V** and **VI** with Am and Eu in the organic phase.

Thus, both approaches to making the thiacalix[4]arene molecule more lipophilic, replacement of *tert*-butyl substituents in the upper rim and partial alkylation of phenol groups in the lower rim, do make the extractants more soluble in NBTF. However, in all the cases this is accompanied by a considerable decrease in the efficiency, and sometimes also in the selectivity, of the Am extraction.

*tert-Butylthiacalix[4]arene **I***

Because *tert*-butylthiacalix[4]arene showed the highest performance among the compounds tested, we studied in more detail its properties: influence of organic diluents on the extraction efficiency and selectivity and resistance to hydrolysis.

Data on the extraction of Am and Eu with solutions of **I** in various diluents are given in Table 2.

As seen from Table 2, the diluent effect on the extraction efficiency and selectivity is extremely strong. Under equal other conditions, the Am distribution ratios vary from 104 to 0.07, and the Am/Eu separation factors, from 43 to 6.5. The most probable causes of such a strong sensitivity of the extraction system to the kind of the diluent are host–guest interactions of the thiacalixarene with the diluent and/or changes in the degree of aggregation of *tert*-butylthiacalix[4]arene in different diluents. Of course, additional studies will be required to elucidate the causes of this interesting phenomenon, but the possibility of controlling the extraction efficiency and selectivity by choosing appropriate diluent is an indubitable advantage of the extraction system based on *tert*-butylthiacalix[4]arene.

Acceptable hydrolytic stability of an extractant is a necessary condition of its use in practice. The hydrolytic stability of *tert*-butylthiacalix[4]arene (**I**) was evaluated as follows. A solution of **I** (2×10^{-4} M in NBTF) was placed in a test tube and mixed with an equal volume of 3 M acid (nitric or perchloric) or 1 M Na_2CO_3 (pH 12.2), after which the test tube was tightly stoppered and heated on a boiling water bath for the preset time (1–20 h). After the heating completion, the test tube was removed and cooled to room temperature, and the phases were separated. The organic phase was used for the Am extraction. The extraction in all the cases was performed from alkaline carbonate solutions with pH 12.2. The resistance of the reagent to hydrolysis was evaluated from a decrease in the extraction ability with increasing heating time.

As we found, the distribution ratios decrease by a factor of 2 after 11-h treatment in the carbonate solution, whereas on contact with acids the reagent virtually fully loses the extraction ability within less than 1 h. This fact proves that compound **I** can be used for radionuclide extraction from alkaline solutions only. Additional experiments on acid hydrolysis of *tert*-butylthiacalix[4]arene, performed at room temperature, showed that a twofold decrease in the Am distribution ratios occurred after 3–3.5-h contact with a 3 M HNO_3 or $HClO_4$ solution. The similarity of the results obtained in nitric and perchloric acid solutions confirms the occurrence specifically of acid hydrolysis of *tert*-butylthiacalix[4]arene, rather than of its oxidative degradation.

The extraction performances of the compounds studied are compared in Fig. 8, where the data are presented for equal extractant concentrations (0.001 M) and the same diluent.

To conclude, it should be primarily noted that, among the thiacalix[4]arenes studied, we found compounds efficiently extracting Am from alkaline solution at the extractant concentration as low as 0.001 M. The interval of the maximal extraction of Am with the majority of the thiacalix[4]arenes studied is at pH 12–13.5, i.e., these compounds are suitable for extracting radionuclides from alkaline HLW. The prevalent extractable species formed by the thiacalix[4]arenes studied with Am are di- and trisolvates.

Replacement of the *tert*-butyl substituent in the thiacalix[4]arene molecule enhances the solubility in tetrachloroethylene, but reduces the efficiency and selectivity of the Am extraction. Similar changes occur upon partial alkylation of hydroxy groups in the lower rim of thiacalix[4]arene.

Table 2. Extraction of Am(III) and Eu(III) from alkaline carbonate solutions (pH 12.15) with a 2×10^{-4} M solution of thiacalixarene **I** in various organic diluents

Diluent	D_{Am}	D_{Eu}	β(Am/Eu)
1,2-Dichloroethane	104.0	2.4	43.3
CCl_4	30.1	0.88	34.2
NBTF	55.2	3.0	18.4
1,2-Dichlorobenzene	2.9	0.18	16.1
Phenyl trifluoromethyl sulfone	7.0	0.47	14.8
p-Xylene	31.7	2.2	14.1
n-Dodecane	25.0	1.9	13.1
Toluene	75.6	8.2	9.2
Chlorobenzene	0.072	0.011	6.5

The organic diluent exerts very strong influence on the extraction efficiency and selectivity. The Am distribution ratios vary in the interval covering 3–4 orders of magnitude, and the Am/Eu separation factors, in the interval covering almost an order of magnitude. Such a strong sensitivity of the extraction system to the kind of the diluent may be due to host–guest interactions of the thiacalix[4]arene with the diluent and/or to changes in the degree of aggregation of *tert*-butylthiacalix[4]arene in different diluents.

Preliminary experiments demonstrated fairly high hydrolytic stability of thiacalix[4]arene. On heating a solution of *tert*-butylthiacalix[4]arene in NBTF with a 1 M Na_2CO_3 solution on a boiling water bath, the Am distribution coefficients decrease by a factor of 2 only in 11 h.

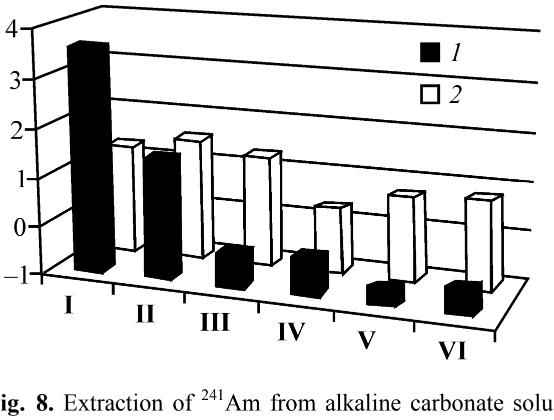

Fig. 8. Extraction of ^{241}Am from alkaline carbonate solutions with a 0.001 M solution of thiacalix[4]arenes in NBTF. (*1*) $\log D_{max}$(Am) and (*2*) log β(Am/Eu).

Thus, substituted thiacalix[4]arenes are of interest as high-performance selective extactants for the recovery of Am and Eu from alkaline carbonate solutions and their separation.

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REFERENCES

1. Kozlov, P.V., Remizov, M.B., Logunov, M.V., and Koltyshev, V.K., *Vopr. Radiats. Bezopasn.*, 2013, no. 2, p. 34.
2. Stepanov, S.I., Boyarintsev, A.V., Vazhenkov, M.V., et al., *Ross. Khim. Zh.*, 2010, vol. 54, no. 3, pp. 25–34.
3. Mokhtari, B., Pourabdollah, K., and Dallali, N., *J. Radioanal. Nucl. Chem.*, 2011, vol. 287, pp. 921–934.
4. Smirnov, I.V., Shadrin, A.Yu., Babain, V.A., and Logunov, M.V., *ACS Symp. Ser.*, 2009, vol. 757, ch. 8, pp. 107–111.
5. Smirnov, I.V., Stepanova, E.S., Drapailo, A.B., and Kal'chenko, V.I., *Radiochemistry*, 2016, vol. 58, no. 1, pp. 42–51.
6. Smirnov, I.V., Stepanova, E.S., Tyupina, M.Yu., et al., *Radiochemistry*, 2016, vol. 58, no. 4, pp. 381–388.
7. Kikuchi, T., Goto, I., and Suzuki, K., *Prog. Nucl. Energy*, 2005, vol. 47, nos. 1–4, pp. 397–405.
8. Kumagai, H., Hasegawa, M., Miyanari, S., et al., *Tetrahedron Lett.*, 1997, vol. 38, pp. 3971–3972.
9. Kasyan, O., Swierczynski, D., Drapailo, A., et al., *Tetrahedron Lett.*, 2003, vol. 44, pp. 7167–7170.
10. Kas'yan, O.V., Functional derivatives of thiacalix[4]-arene, *Cand. Sci. (Chem.) Dissertation*, Kyiv, 2007.
11. Kharchenko, S., Drapailo, A., Shishkina, S., et al., *Supramol. Chem.*, 2014, vol. 26, pp. 864–872.
12. Kasyan, O., Healey, E.R., Drapailo, A., et al., *J. Inclus. Phenom. Macrocycl. Chem.*, 2007, vol. 58, pp. 127–132.
13. Smirnov, I., Babain, V., Efremova, T., and Kalchenko, V., *J. Nucl. Sci. Technol.*, 2002, vol. 3, pp. 321–324.
14. Klimchuk, O., Atamas, L., Miroshnichenko, S., et al., *J. Inclus. Phenom. Macrocycl. Chem.*, 2004, vol. 49, pp. 47–56.
15. Smirnov, I., Karavan, M., Babain, V., et al., *Radiochim. Acta*, 2007, vol. 95, pp. 97–102.
16. Arnaud-Neu, F., Karavan, M., Hubscher-Bruder, V., et al., *J. Inclus. Phenom. Macrocycl. Chem.*, 2010, vol. 66, pp. 113–123.
17. Smirnov, I.V., Karavan, M.D., Efremova, T.I., et al., *Radiochemistry*, 2007, vol. 49, no. 5, pp. 482–492.

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