

## Extraction of Cesium and Americium with *p*-Alkylcalix[8]arenes from Alkaline Solutions

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**Abstract**—Previously unknown isononylcalix[8]arene was synthesized from commercially available isononylphenol. The properties of the product (solubility, extraction ability, tendency to aggregation) were compared with those of the known *tert*-butylcalix[8]arene. The extraction of <sup>137</sup>Cs, <sup>99m</sup>Tc, and <sup>241</sup>Am from alkaline carbonate solutions with solutions of *p*-alkylcalix[8]arenes (alkyl = *tert*-butyl, isononyl) in tetrachloroethylene was studied. The dependence of the distribution ratios on pH of the aqueous phase in the interval from 11 to 13.9 and on the nature of functional groups in the calixarene core was determined. The composition of extractable solvates of cesium and americium with calix[8]arenes was found. Calix[8]arenes extract cesium from alkaline solutions more efficiently than *p*-*tert*-butylphenol, their nonmacrocylic analog, does. *tert*-Butylcalix[8]arene exhibits the highest performance, which may be due to formation of aggregates 5.7 ± 0.8 nm in diameter in the organic phase at pH 13.5 of the aqueous phase. The isononyl derivative exists in the monomeric form (particle diameter 1.9 ± 0.5 nm).

**Keywords:** extraction, cesium-137, americium-241, alkaline solutions, calix[8]arenes, nanoaggregates

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Management of high-level liquid waste (HLW) from reprocessing of irradiated uranium is one of the most challenging problems of the radiochemical industry. Recovery of long-lived radionuclides, primarily of cesium and actinides, followed by their immobilization and disposal, considerably reduces the radioecological risks of HLW management. The integrated approach to HLW management, i.e., partitioning with recovery of several groups of radionuclides simultaneously in one cycle, shows much promise. The HLW partitioning prior to immobilization allows the cost of disposal of solidified HLW to be reduced via separating a small-volume fraction of long-lived radionuclides requiring disposal in deep geological formations. Also, the HLW partitioning allows the use of different methods and formulations for solidification of radionuclides differing in the chemical behavior, which, in turn, allows the firmness of the radionuclide fixation to be considera-

bly enhanced. Finally, the HLW partitioning will reduce the volume of HLW being solidified owing to removal of large amounts of nonradioactive metal (sodium, iron, chromium, nickel, etc.) salts.

The major fraction of HLW is constituted by nitric acid raffinate from the PUREX process for reprocessing irradiated uranium. Alkaline HLW is accumulated in a smaller amount than acidic HLW, but alkaline HLW partitioning is more difficult because of considerably higher content of nonradioactive element salts compared to nitric acid HLW.

In the course of implementation of the USSR Atomic Project, a system of storage tanks was constructed at the Mayak Production Association for collection and controllable storage of high-level waste. Today, about 18000 m<sup>3</sup> of alkaline HLW is stored in these tanks [1]. These wastes are multicomponent slurries containing aluminum, chromium, iron, and nickel

hydroxides, iron and nickel sulfides, and iron and nickel ferrocyanides against the background of high concentrations (hundreds of grams per liter) of sodium hydroxide, nitrate, and nitrite in the liquid phase. The main radioactivity is due to the presence of  $^{137}\text{Cs}$  (up to  $5 \times 10^{10} \text{ Bq L}^{-1}$ ) and transuranium elements. Technetium can also be present. Alkaline radioactive wastes of similar composition from defense programs are stored at the US National Laboratories in Hanford, Oak Ridge, and Savannah River [2]. Thus, the need for new efficient methods for alkaline HLW partitioning is obvious.

The CARBEX process for spent nuclear fuel reprocessing, which is being actively developed at the Mendeleev Russian University of Chemical Technology, is based on selective transfer of uranium and plutonium into a carbonate solution, followed by their decontamination from fission products by extraction with quaternary ammonium salts and solid-phase back-extraction of uranium and plutonium carbonates [3]. The alkaline high-level raffinate from the CARBEX process with high sodium carbonate content will require reprocessing, most probably by extraction partitioning.

Attempts of reprocessing of high-level alkaline waste were made since the 1950s, when a process for cesium recovery with extractants based on substituted phenols was developed in the United States. However, tests on real HLW failed because of low chemical stability of phenols [4]. In the subsequent 50 years, numerous procedures were suggested for alkaline HLW reprocessing, including selective sorption of radionuclides, extraction of sodium, precipitation of cesium tetraphenylborate, coprecipitation of actinides with a carrier, etc. Only several years ago a team of American radiochemists developed a commercial process for extraction recovery of cesium from alkaline HLW and put it into operation in Savannah River. The technology is based on using a calixarene crown ether as selective complexing agent for cesium, a fluorinated organic solubilizer, and an amine modifier in a paraffin diluent [5, 6]. However, this technology uses an extractant that is very difficult to synthesize and allows only cesium to be recovered from alkaline HLW, whereas actinides, strontium, and technetium, also present in such waste, are not recovered.

Calixarenes, macrocyclic polyphenol compounds prepared by precision cyclocondensation of *p*-substituted phenols with formaldehyde [7], show promise for cesium recovery from alkaline HLW. A procedure

for recovering cesium from alkaline solutions using cheap and available *tert*-butylcalix[4, 6, and 8]arenes was patented as early as 1984 [8]. We have shown that *tert*-butylcalix[6]arene in combination with 4-alkyl-2-di(2-hydroxyethyl)aminomethylphenol and trialkylphosphine oxide extracts Cs, Sr, Am, and Pu from alkaline solutions [9]. However, a distinctive feature of all *tert*-butylcalix[*n*]arenes is their extremely low solubility in organic solvents used in liquid extraction.

This study was aimed at preparing *p*-alkylcalix[8]arene that would be more soluble in organic solvents and at studying the extraction of Cs, Am, and Tc from alkaline solutions with this agent. The choice of the isononyl substituent for calix[8]arene is associated with the availability of *p*-isononylphenol produced in Russia at PAO Nizhnekamskneftekhim.

## EXPERIMENTAL

*p*-Isononylphenol was produced by PAO Nizhnekamskneftekhim. Its nonmacrocyclic analog *p*-*tert*-butylphenol (99%), paraform (96%), and solvents for HPLC and GPC were purchased from Acros Organics. All the chemicals and solvents were used without additional purification.

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded with a Bruker Avance 400 spectrometer. The MALDI mass spectra were taken with an UltraFlex III TOF/TOF mass spectrometer in the linear mode, with *p*-nitroaniline used as matrix. Positively charged ions were recorded. The IR spectra were recorded with a Bruker Alpha FT-IR spectrometer from KBr pellets in the range  $500\text{--}4000 \text{ cm}^{-1}$ . The melting points were determined with a Netzsch DSC 204 F1 Phoenix device. Elemental analysis was performed with a Perkin-Elmer 2400 Series II analyzer.

HPLC separation was performed using the Thermo Dionex UltiMate 3000 HPLC system. A Supelco Ascentis C18 column (particle size  $5 \mu\text{m}$ , length 250 mm, inside diameter 4.6 mm) was used in the experiments. The column temperature was  $35^\circ\text{C}$ , and the flow rate was  $1.0 \text{ mL min}^{-1}$ . The separation was performed in the gradient mode. The sample volume was 0.01 mL, and the substance concentration was  $0.1 \text{ mg mL}^{-1}$ .

The particle size (numerical distribution) of isononyl- and *p*-*tert*-butylcalix[8]arenes (concentration 0.005 M) in solution was determined by dynamic light scattering with a Malvern Nano ZS device in a PCS 1115 glass cell. The solvents were methylene chloride and tetrachloroethylene.

Separation by gel permeation chromatography (GPC) was performed with an Agilent 1260 Infinity system with RI detector using two PLgel MiniMix-C columns (particle size 5  $\mu\text{m}$ , length 250 mm, inside diameter 4.6 mm) and a PLgel MiniMix-C Guard protecting column. THF was used as a mobile phase for HPLC; the flow rate was 0.3 mL  $\text{min}^{-1}$ . The sample volume was 0.02 mL, and the substance concentration was 1.0 mg  $\text{mL}^{-1}$ . The GPC analysis of the products was made after seven-point calibration performed with polystyrene reference with narrow molecular-mass distribution in the molecular mass range from 500 to 7500.

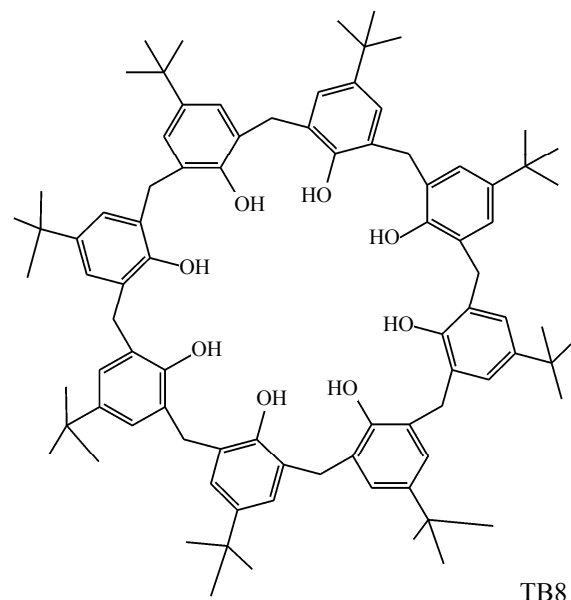
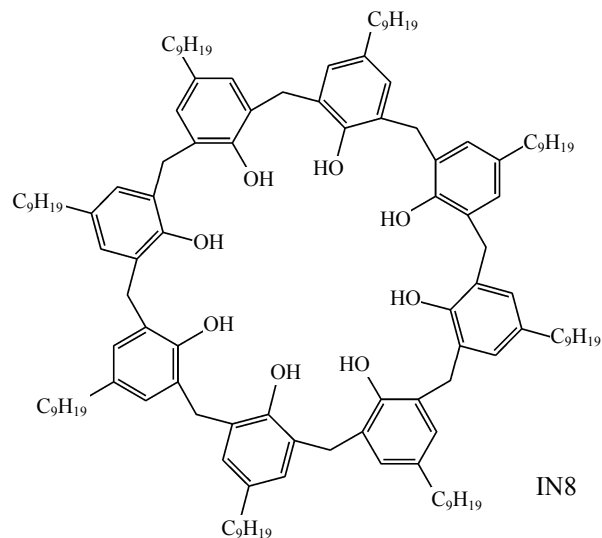
Pure grade tetrachloroethylene (Vekton, St. Petersburg, Russia) washed with a sodium carbonate solution and with water was used as solvent for liquid-liquid extraction. Solutions of the extractants in tetrachloroethylene were prepared from accurately weighed portions of the substances. Inorganic chemicals of no less than analytically pure grade (Vekton, St. Petersburg, Russia) were used without additional purification.

$^{241}\text{Am}$ ,  $^{137}\text{Cs}$ , and  $^{99\text{m}}\text{Tc}$  (in the form of sodium pertechnetate), all containing no less than 99.9% target radionuclide, were produced at the Khlopin Radium Institute.

*p*-*tert*-Butylcalix[8]arene (TB8) (see below) was synthesized by the known procedure [10].

**Synthesis of isononylcalix[8]arene (IN8).** A 100-mL two-necked flask equipped with a Dean-Stark trap and a magnetic stirrer was charged with 22 g (0.1 mol) of isononylphenol, 3.91 g (0.125 mol) of paraform, and 25 mL of *p*-xylene. The mixture was heated to 50°C, after which 0.3 g of a 20% aqueous NaOH solution was added. The mixture was heated with stirring to 80°C, kept at this temperature for 30 min, then heated to reflux, and refluxed for 4 h. After that, the light brown reaction mixture was cooled to 90°C, placed in a 500-mL flask, and dried in a vacuum (residual pressure down to 1 mbar) to obtain a friable yellow-brown powder. Then, the powder was dissolved in 250 mL of hot acetone and cooled to room temperature. The precipitate was filtered off, washed with 20 mL of 1 M HCl, 100 mL of distilled water, and 10 mL of acetone, and dried at 120°C in a vacuum (1 mbar) for 4 h. Yield 30% (white powder); mp 290–299°C (DSC); GPC:  $M_w = 1867$ ,  $M_n = 1864$ , polydispersity index PD = 1.00.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$ , ppm: 0.52–1.64 m (152H,



$\text{C}_9\text{H}_{19}$ ), 3.49 br.s (8H,  $\text{CH}_2$ ), 4.41 br.s (8H,  $\text{CH}_2$ ), 7.0–7.2 m (16H, ArH), 9.49 br.s (8H, OH). IR,  $\nu$ ,  $\text{cm}^{-1}$ : 3178 (OH). MALDI-MS:  $m/z$  1881.4 [ $\text{M} + \text{Na}$ ], 1897.4 [ $\text{M} + \text{K}$ ].

### Experimental Procedures

**pH measurements.** The pH values of the working solutions were determined 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 the small test tubes used for extraction experiments. The pH meter was calibrated using the built-in semiautomatic calibration procedure with standard buffer solutions with pH 7.01 and 10.01.

**Extraction of radionuclides.** The distribution ratios of radionuclides were determined as follows. A 1.5-mL polypropylene centrifuge test tube was charged with 0.6 mL of an aqueous phase of preset composition. Aqueous phases with the preset pH values were prepared by mixing 1 M NaHCO<sub>3</sub> and NaOH solutions, which ensured the constancy of the solution ionic strength. The equilibrium pH value was determined directly in the test tube. Then, the tracer was added, and the mixture was stirred and allowed to stand for 15 min. After that, 0.6 mL of the organic phase (solution of the compound studied in tetrachloroethylene with preset concentration) was added, and the mixture was stirred at 21–23°C for 15 min. Preliminary experiments showed that this time was sufficient for the equilibrium in the system to be attained. The phases were separated by centrifugation at 3000 rpm for 10 min. 0.4-mL portions of the organic and aqueous phases were taken for the measurement. The amounts of the radionuclides in both phases were determined radiometrically from the  $\gamma$ -radiation of the corresponding isotope. The extraction relationships were studied with tracer amounts of <sup>241</sup>Am and <sup>99m</sup>Tc. In the case of <sup>137</sup>Cs,  $\sim 10^{-5}$  M stable cesium was added into the aqueous phase. Radiometric measurements were performed with a DeskTop InSpector scintillation  $\gamma$ -ray spectrometer (Canberra) based on a 51 × 51 mm well-type NaI detector. The sample measurement time was chosen so that the uncertainty of radiometric measurements be within 10%. The distribution ratios were calculated by the formula  $D = A_{\text{org}}/A_{\text{aq}}$ , where  $A$  is the specific activity of the radionuclide in the organic or aqueous phase.

**Determination of the solubility of *tert*-butylcalix[8]arene and isononylcalix[8]arene.** A set of 10-mL vials was charged with 0.1 g of the substance each, and 5 mL of appropriate solvent was added. The substance to solvent ratio was chosen so that the dissolution be incomplete. The vials were placed in an ultrasonic bath and kept there at 40°C for 1 h. After that, the vials were transferred into a dry air thermostat and kept for 72 h at 20.0°C to reach the equilibrium. The contents of the vials were filtered through a syringe filter with a pore diameter of 0.2  $\mu\text{m}$  at 20°C, 1 mL of the filtrate was placed in a 10 cm<sup>3</sup> volumetric flask, and the solution was brought to the mark with tetrahydrofuran. The amount of the dissolved substance was determined by HPLC using calibration dependences. The correlation coefficients of the calibration dependences are 0.9991 for *tert*-butylcalix[8]arene and 0.9989 for isononyl-

**Table 1.** Solubility of calix[8]arenes in organic solvents at 20°C (mg dm<sup>-3</sup>)

Solvent	TB8	IN8
Hexane	0.7	10 800
Formal {bis[(2,2,3,3,4,4,5,5-octafluoropentyl)oxy]methane}	1.3	49
Acetonitrile	67	10
Ethyl acetate	130	4900
Xylene	340	24 600
Acetone	444	1420
Tetrachloromethane	660	177 000
Tetrahydrofuran	2100	24 000
Methylene chloride	2900	33 000
Toluene	8600	55 000
Tetrachloroethylene	4700	197 000

calix[8]arene. At substance concentrations above the upper limit of the calibration plot, the solutions were diluted to the required extent.

## RESULTS AND DISCUSSION

As noted above, one of the problems of using *tert*-butylcalix[ $n$ ]arenes in extraction processes is their low solubility in organic solvents used in liquid–liquid extraction. Therefore, making these macrocyclic compounds more soluble is a topical problem. The most obvious way to accomplish this goal is to make the molecule more lipophilic by introducing large alkyl substituents into the calixarene structure. Because hydroxy groups ensure complexation of metal ions in alkaline solutions, the possible synthetic route to making these macrocycles more lipophilic is modification of the *p*-position of the aromatic rings. Examples of one-step synthesis of calixarenes from phenols containing large alkyl substituents have been described in the literature [11]. In this study, we prepared a lipophilic calix[8]arene using the raw material produced in Russia by PAO Nizhnekamskneftekhim.

Replacement of the *tert*-butyl substituent by the isononyl substituent considerably increased the solubility of the macrocyclic compound in nonpolar and low-polarity solvents. Data on the solubility of *tert*-butylcalix[8]arene (TB8) and isononylcalix[8]arene (IN8) are given in Table 1.

The most pronounced increase in the solubility was observed in nonpolar hexane: it increased by a factor of more than 10<sup>4</sup>. In low-polarity solvents such as chlorinated compounds, aromatic hydrocarbons, and ethers, the solubility increased by a factor of 10–100.

High solubility in polyhalogenated derivatives, which can be used as diluents in the extraction of radionuclides, should be particularly noted. It is quite natural that the more lipophilic calixarene is less soluble in highly polar solvents.

The nonmacrocylic analog of calixarenes, *p-tert*-butylphenol, extracted the radionuclides under consideration poorly. The distribution ratio of technetium did not exceed  $10^{-4}$ , and that of cesium was 0.002 at pH 13.5. Americium was extracted with the maximal distribution ratio of 0.3 at pH 13.3–13.6. All the experiments were performed with a 0.08 M *p-tert*-butylphenol solution, which was 8 times more concentrated than calix[8]arene solutions, to ensure equal concentrations of the complexing hydroxy groups.

It should be noted that technetium was not extracted by the calixarenes under consideration (the technetium distribution coefficients were lower than 0.001 throughout the examined pH interval).

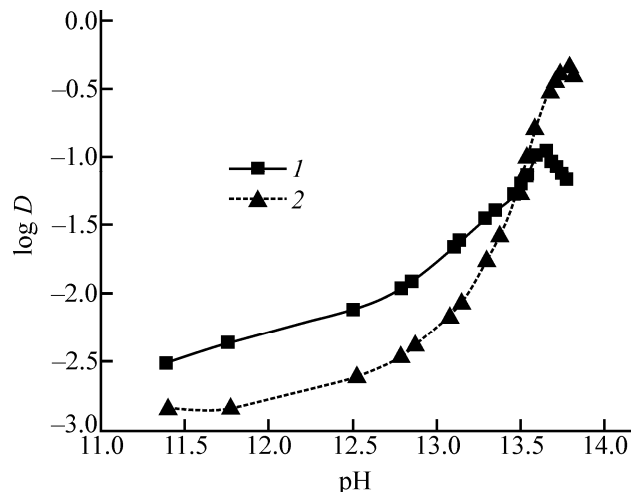
Data on extraction of cesium with *tert*-butylcalix[8]arene (TB8) and isononylcalix[8]arene (IN8) are shown in Fig. 1.

First, it should be noted that the dependences of the cesium distribution ratios on pH of the aqueous phase are typical of phenols with a maximum at pH 13.6–13.9. The initial growth of the cesium distribution ratios, associated with an increase in the dissociation of phenol groups with increasing pH, is followed by a decrease caused by competing extraction of sodium. As compared to the nonmacrocylic analog of calixarenes, *p-tert*-butylphenol, the cesium distribution ratios increased by a factor of 175 for TB8 and by a factor of 50 for IN8. This fact suggests polydentate binding of the cesium cation by hydroxy groups of calixarenes. The replacement of *tert*-butyl groups in calix[8]arene by isononyl groups leads to a considerable decrease in the extraction ability.

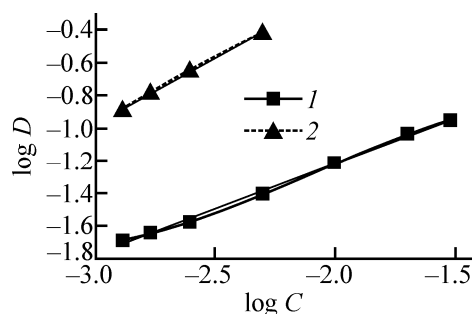
The composition of solvates formed by calixarenes with the cesium cation in the organic phase was estimated by slope analysis. The results are shown in Fig. 2.

As seen from Fig. 2, the experimental points in the log–log coordinates are well approximated by straight lines. The slopes of the straight lines are numerically equal to the solvate numbers: 0.8 for TB8 and 0.6 for IN8. This fact suggests that the predominant extractable cesium species are monosolvates.

The results of similar experiments on the extraction



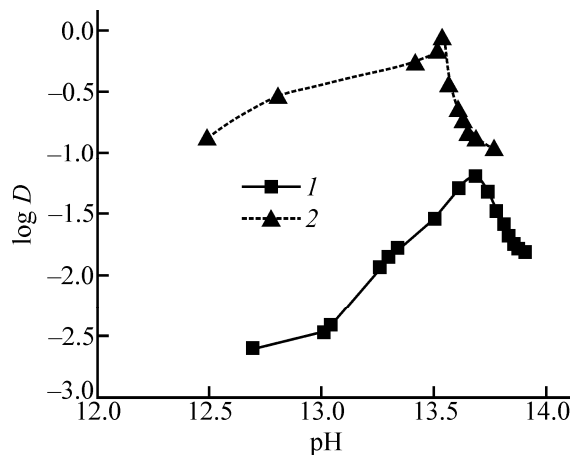
**Fig. 1.** Extraction of  $^{137}\text{Cs}$  from alkaline carbonate solutions with 0.01 M solutions of (1) isononylcalix[8]arene and (2) *tert*-butylcalix[8]arene in tetrachloroethylene as a function of pH of the aqueous solution.



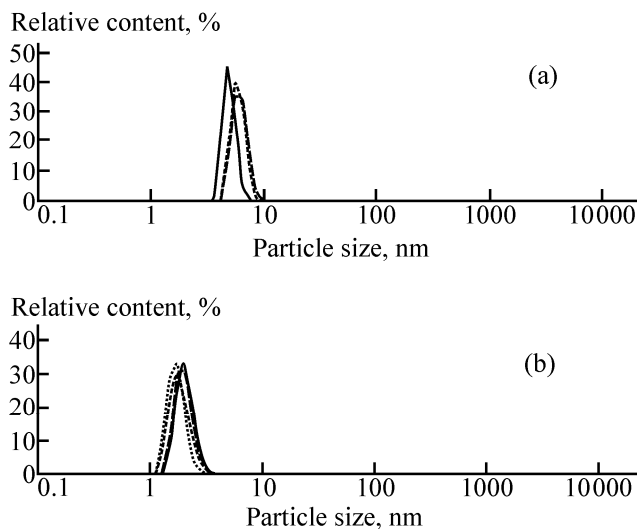
**Fig. 2.** Extraction of  $^{137}\text{Cs}$  from alkaline carbonate solutions (pH 13.55) with solutions of (1) isononylcalix[8]arene and (2) *tert*-butylcalix[8]arene in tetrachloroethylene as a function of the extractant concentration. Regression equations: (1)  $\log D = 0.5574 \log C - 0.1096$  ( $R^2 = 0.9963$ ) and (2)  $\log D = 0.8016 \log C + 1.4331$  ( $R^2 = 0.9985$ ).

of americium with *p*-alkylcalix[8]arenes are shown in Fig. 3.

As in the case of the cesium extraction, the dependences of the americium distribution ratio on pH of the aqueous phase are typical of phenols with a maximum at pH 13.4–13.9. In contrast to the extraction of cesium, only *tert*-butylcalix[8]arene (TB8) demonstrated an appreciable cooperative effect, an increase in the americium distribution ratios by a factor of 3 compared to the nonmacrocylic analog, *p-tert*-butylphenol. The predominant formation of americium monosolvates with TB8 and IN8 was proved by slope analysis. The equations of the approximating straight lines for the extraction of  $^{241}\text{Am}$  are as follows:



**Fig. 3.** Extraction of  $^{241}\text{Am}$  from alkaline carbonate solutions with 0.01 M solutions of (1) isononylcalix[8]arene and (2) *tert*-butylcalix[8]arene in tetrachloroethylene as a function of pH of the aqueous solution.



**Fig. 4.** Size distribution of particles formed in the organic phase of the  $\text{C}_2\text{Cl}_4$ -water two-phase system at pH 13.5 of the aqueous phase. (a) TB8 and (b) IN8. Different curves refer to different experiments; the same for Fig. 5.

$$\log D_{\text{Am}} = 0.95 \log C_L + 1.71, R^2 = 0.94 \text{ for TB8};$$

$$\log D_{\text{Am}} = 0.75 \log C_L + 0.53, R^2 = 0.96 \text{ for IN8}.$$

*tert*-Butylcalix[8]arene extracts both Cs and Am approximately 10 times more efficiently than isononylcalix[8]arene does. Presumably, this effect is connected with the association of extractant molecules in the organic phase, rather than determined by electronic factors.

To check this assumption, we examined the self-organization of the calixarenes studied by dynamic

light scattering (DLS) in the solvent used in the extraction experiments, tetrachloroethylene. As we found, nanoparticles with the hydrodynamic diameter of  $5.7 \pm 0.8$  (for TB8) and  $1.9 \pm 0.5$  nm (for IN8) are formed in the organic phase (at pH 13.5 of the aqueous phase (Fig. 4). The hydrodynamic diameter of 1.9 nm corresponds to the volume of the spherical particle (approximation of the DLS method) equal to  $3.6 \text{ nm}^3$ , which is consistent with the molecular volume of *tert*-butylcalix[8]arene, calculated from the X-ray diffraction data [12].

Whereas nanoparticles formed by the isononyl derivative IN8 can be considered as monomeric, the *tert*-butyl analog apparently forms relatively large aggregates of inverse micelle type.

To determine whether this is a common trend, we examined the aggregation of TB8 and IN8 in dichloromethane, a solvent with weaker ability to solvate these calixarenes. The conclusion that the ability of dichloromethane to solvate TB8 and IN8 is lower than that of tetrachloroethylene is based on the solubility data for these macrocycles. As seen from Table 1, the solubility of TB8 and IN8 in going from tetrachloroethylene to dichloromethane decreases by a factor of 1.6 and 6, respectively; hence, the solvation energy decreases.

This fact seems to be rather unexpected, because dichloromethane is a more polar solvent. It should be noted, however, that the dielectric constant of the solvent, which is frequently considered as a characteristic of the solvent polarity, is not the only parameter determining the energy of solvation of the solute and, correspondingly, the degree of the solute aggregation. In lipophilic compounds, dispersion interactions are no less important. As we found, both calixarenes are better solvated in the less polar but more polarizable tetrachloroethylene. For the more lipophilic isononyl derivative, the difference in the solubility and hence in the solvation is considerably larger.

Naturally, with an increase in the solvation energy the aggregation processes, which decrease the energy of the system owing to interaction of molecules with each other, are enhanced. From this viewpoint, in going to a less solvating solvent (dichloromethane in our case) the difference in the aggregation behavior of TB8 and IN8 should become more pronounced, which is indeed the case.

Calixarene IN8 in dichloromethane, according to DLS data, forms particles  $1.3 \pm 0.5$  nm in diameter

**Table 2.** Extraction of  $^{137}\text{Cs}$  and  $^{241}\text{Am}$  from alkaline carbonate solutions with solutions of *tert*-butylphenol and functionalized calix[8]arenes in tetrachloroethylene

Radionuclide	pH of maximal extraction	Radionuclide distribution ratio $D$	Cooperative effect ( $D_{\text{calixarene}}/D_{\text{phenol}}$ )
<i>p</i> - <i>tert</i> -Butylphenol (0.08 M)			
$^{137}\text{Cs}$	13.0–13.5	0.002	–
$^{241}\text{Am}$	13.3–13.6	0.3	–
<i>tert</i> -Butylcalix[8]arene (0.01 M). Solubility in $\text{C}_2\text{Cl}_4$ 0.0051 M			
$^{137}\text{Cs}$	13.6–13.8	0.5	175
$^{241}\text{Am}$	13.4–13.6	0.9	3
Isononylcalix[8]arene (0.01 M). Solubility in $\text{C}_2\text{Cl}_4$ 0.11 M			
$^{137}\text{Cs}$	13.6–13.7	0.07	50
$^{241}\text{Am}$	13.6–13.7	0.08	0.3

(Fig. 5). This size, taking into account the measurement uncertainty, is close to that of the monomeric particles formed in tetrachloroethylene ( $1.9 \pm 0.5$  nm). In the case of TB8, the aggregation processes in the solution are dramatically enhanced, and coarse aggregates are formed. Their size significantly depends on pH of the aqueous medium:  $137 \pm 1$  nm at pH 11.4 and  $287 \pm 3$  nm at pH 13.5.

These significant differences in the aggregation behavior of the two calixarenes differing in the lipophilicity of alkyl substituents at the upper rim of the macroring are reflected in their extraction properties. It is well known that the aggregation of functionalized calix[4]arene derivatives enhances their extraction ability [13, 14]. In the case of formation of inverse micelles, the hydrophilic area inside the nanoparticle favors more efficient binding of radionuclide cations and

their transfer into the organic phase. Therefore, monomeric calixarenes interact with target cations less efficiently than supramolecular aggregates do. Similar effect was revealed when comparing the efficiency of liquid–liquid and micellar extraction of americium with water-soluble phosphorylated calixarenes [15].

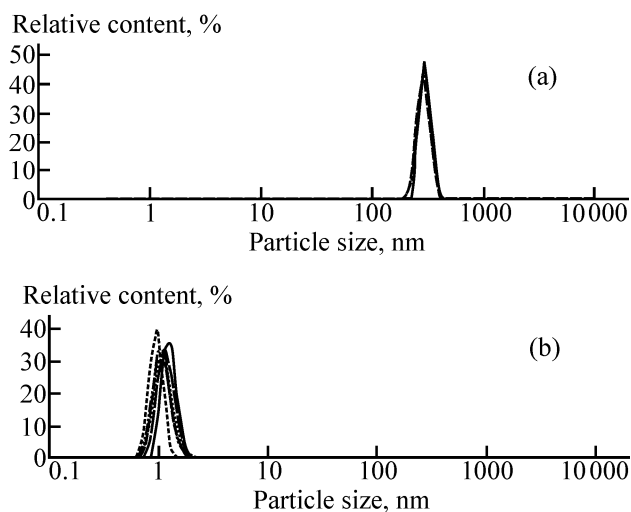
Thus, the possible cause of differences in the extraction ability of the *p*-alkylcalix[8]arenes studied is the difference in the self-aggregation of their particles in the solution. The higher is the degree of aggregation, the more efficient is the extraction of radionuclides from water into the organic phase.

The main results of experiments on the extraction of Am and Cs with functionalized calix[8]arenes from alkaline solutions are summarized in Table 2.

First, it should be noted that the replacement of the *tert*-butyl radical in the calix[8]arene molecule by the isononyl radical appreciably increases the solubility in nonpolar and low-polarity organic solvents. Unfortunately, this is accompanied by a decrease in the extraction ability of calix[8]arene, caused by the presence of only monomeric species in the organic phase, which extract radionuclides from the aqueous phase less efficiently than nanoaggregates of the *tert*-butyl derivative do.

As seen from Table 2, the maximal extraction of cesium and americium with both calixarenes studied is at pH in the interval 13–14, which allows these extractants to be used for radionuclide recovery from strongly alkaline HLW.

In going from nonmacrocylic *p*-*tert*-butylphenol to macrocylic calix[8]arene, the distribution ratio of Cs increases by a factor of several hundreds, whereas that of Am changes only slightly. The calixarenes studied appreciably extract Cs and Am from alkaline solutions



**Fig. 5.** Size distribution of particles formed in the organic phase of the  $\text{CH}_2\text{Cl}_2$ –water two-phase system at pH 13.5 of the aqueous phase. (a) TB8 and (b) IN8.

at the extractant concentration as low as 0.01 M. At a concentration of 0.1 M, isononylcalix[8]arene will efficiently extract Cs and Am from alkaline HLW. Technetium is not efficiently extracted by any of the examined compounds.

Thus, the calix[8]arenes studied are accessible and promising extractants for recovering Am and Cs from alkaline solutions, but new approaches should be developed for increasing their solubility in organic diluents without loss in the extraction ability.

#### ACKNOWLEDGMENTS

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