ISSN 0036-0236, Russian Journal of Inorganic Chemistry, 2019, Vol. 64, No. 4, pp. 536–542. © Pleiades Publishing, Ltd., 2019.
Russian Text ©A.M. Safiulina, D.V. Ivanets, E.M. Kudryavtsev, D.V. Baulin, V.E. Baulin, A.Yu. Tsivadze, 2019, published in Zhurnal Neorganicheskoi Khimii, 2019, Vol. 64, No. 4, pp. 430–437.

PHYSICAL CHEMISTRY
OF SOLUTIONS

Liquid- and Solid-Phase Extraction of Uranium(VI), Thorium(IV), and Rare Earth Elements(III) from Nitric Acid Solutions Using Acid-Type Phosphoryl-Containing Podands

A. M. Safiulina[a, *], **D. V. Ivanets**[b], **E. M. Kudryavtsev**[c], **D. V. Baulin**[d],
V. E. Baulin[d, e], **and A. Yu. Tsivadze**[d]

[a] *Bochvar High-Technology Research Institute of Inorganic Materials, Moscow, 123098 Russia*
[b] *Rosatom State Corporation, Moscow, 119017 Russia*
[c] *National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Moscow, 115409 Russia*
[d] *Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Moscow, 119991 Russia*
[e] *Institute of Physiologically Active Substances, Russian Academy of Sciences, Chernogolovka, Moscow oblast, 142432 Russia*
**e-mail: AMSafiulina@bochvar.ru*

Received November 8, 2018; revised November 28, 2018; accepted December 10, 2018

Abstract—A possibility to use acid-type phosphoryl-containing podands with diethylene glycol polyether chain, which differ in substituent at the phosphoryl group, as extractants for the recovery of U(VI), Th(IV), and rare earth elements(III) from nitric acid solutions has been studied. Features of the effect of HNO_3 concentration on U(VI) and Th(IV) extraction with solutions of the phosphoryl-containing podands in dichloroethane has been revealed. Uranium(VI) is extracted as a normal intracomplex salt of dibasic acid UO_2L^3 with chelate coordination of both POO^- groups to one cation. Thorium(IV) produces a complex as a normal intracomplex salt of composition $Th(L^3)_2$ where two bivalent anions of ligand acid are coordinated via all four POO^- groups to Th(IV) cation. Sorption of U(VI), Th(IV), and REE(III) by impregnated sorbent based on LPS-500 polymer with 1,5-bis[2-(oxyethoxyphosphoryl-4-ethyl)phenoxy]-3-oxapentane from 0.052 and 3.52 mol/L HNO_3 has been studied. It has been established that the obtained sorbent shows high selectivity in the separation of U(VI), Th(IV), and REE(III). The separation factor for uranium(VI) and europium(III) ($\beta_{U/Eu}$) has been found to be 202 and ~55000 upon sorption from 3.52 and 0.052 mol/L HNO_3, respectively, at V/m = 500 mL/g. At thorium(IV) sorption from 3.52 and 0.052 mol/L HNO_3, $\beta_{Th/U}$ = 66 and ~5050, respectively.

Key words: extraction, sorption, nitric acid solutions, diphosphonic acids, acid-type phosphoryl-containing podands, impregnated-type sorbents, U(VI), Th(IV) and REE(III) preconcentration, U(VI), Th(IV) and REE(III) separation

DOI: 10.1134/S0036023619040181

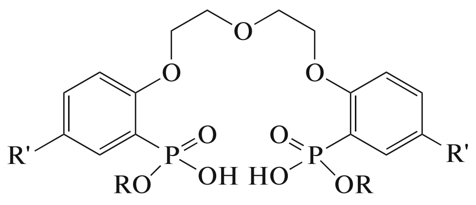
INTRODUCTION

Extraction is known to be one of efficient method for preconcentration and selective isolation of lanthanides and actinides [1, 2]. However, in recent time, there is stable trend to use preferably more industrially feasible sorption methods for the isolation of *f*-block elements. Efficient sorption materials are necessary for their implementation. Among known sorbents, synthetically available impregnated-type sorbents are of special interest, they are prepared by the non-covalent binding of organic extractants on the surface of macroporous carriers [3–5]. The sorption properties of impregnated-type sorbents are determined in a considerable extent by the extraction ability of used extractant toward recovered metal ions [6, 7]. Thus, the search for new efficient extractants and study of their properties is an urgent task for designing both extraction and sorption processes for the recovery and purification of a number of elements of industrial significance.

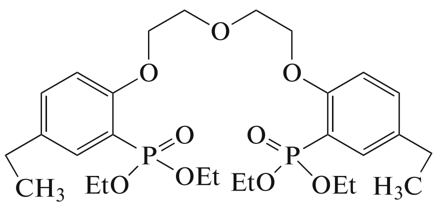
Diphosphonic acid derivatives are rather efficient extractants for lanthanides and actinides [8–14]. Increase in the length of the alkylene bridge between the phosphoryl groups of P,P'-di(2-ethylhexyl)methylenediphosphonic acid (D2EHMDPA) leads to decrease of extraction ability of reagent but increases extraction selectivity [15]. It should be noted that polymeric sorbents impregnated with D2EHMDPA provide efficient recovery of Th(IV), U(VI), Am(III), and REE(III) from nitric and hydrochloric acid solutions [16]. Synthetically available acid-type phosphoryl-containing podands also belong to the class of diphosphonic acids. These phosphoryl-containing podands include two fragments of 2-oxyphenylphosphonic acid (2-$C_6H_4P(O)(OR)(OH)_2$) connected by polyether chain of different length [17].

It was found that acid-type phosphoryl-containing podands under comparable conditions extract U(VI) and Th(IV) much more efficiently than known extractant, di-2-ethylhexyl phosphoric acid [18]. Comparison of uranium(VI), thorium(IV), and lanthanum(III) extraction from nitric acid solutions into 1,2-dichloroethane (DCE) with phosphoryl-containing podands with different length of polyether chain showed that diethylene glycol derivatives exhibit high extraction ability and are rather promising compounds for the recovery of *f*-block elements [19]. The use of these compounds as components of stationary phase of impregnated-type sorbent for extractive chromatographic separation of U(VI), Th(IV), Np(IV), Pu(IV) [20, 21], ^{99}Mo [22], and ^{147}Pm [23] from solutions obtained by reprocessing of spent nuclear fuel is known.

In this work, we study the possibility to use acid-type phosphoryl-containing podands H_2L^1–H_2L^6 with diethylene glycol polyether chain that differ in substituent at the phosphoryl group for the extraction and sorption separation of U(VI), Th(IV), and REE(III) from nitric acid solutions.



H_2L^1–H_2L^6



L^7

H_2L^1, R = Et, R' = H; H_2L^2, R = Bu, R' = H;
H_2L^3, R = Et, R' = Et; H_2L^4, R = Bu, R' = Et;
H_2L^5, R = Et, R' = Bu^t; H_2L^6, R = Bu, R' = Bu^t

EXPERIMENTAL

Acid-type phosphoryl-containing podands: 1,5-bis[2-(oxyethoxyphosphoryl)phenoxy]-3-oxapentane (H_2L^1), 1,5-bis[2-(oxybutoxyphosphoryl)phenoxy]-3-oxapentane (H_2L^2), 1,5-bis[2-(oxyethoxyphosphoryl-4-ethyl)phenoxy]-3-oxapentane (H_2L^3), 1,5-*bis*[2-(oxybutoxyphosphoryl-4-ethyl)phenoxy]-3-oxapentane (H_2L^4), 1,5-bis[2-(oxyethoxyphosphoryl-4-*tert*-butyl)phenoxy]-3-oxapentane (H_2L^5), and 1,5-bis[2-(butoxyoxyphosphoryl-4-*tert*-butyl)phenoxy]-3-oxapentane (H_2L^6) were obtained by the previously described procedure [24]. The synthesis of 1,5-bis[2-(diethoxyphosphoryl-4-ethyl)phenoxy]-3-oxapentane (L^7), a neutral analog of H_2L^3, was described previously [17].

Metal extraction study. Solutions were prepared using doubly distilled water, 1,2-dichloroethane (reagent grade), Arsenazo III (analytical grade), HNO_3 (high purity grade), uranium oxide (GSO 8363-2003, uranium content 84.784 ± 0.016%), $Th(NO_3)_4 \cdot 4H_2O$ (reagent grade), $La(NO_3)_3 \cdot 6H_2O$ (reagent grade), $Nd(NO_3)_3 \cdot 6H_2O$ (reagent grade), $Ho(NO_3)_3 \cdot 6H_2O$ (reagent grade), and $Yb(NO_3)_3 \cdot 6H_2O$ (reagent grade). Solutions were prepared by volumetric and weight methods. Solutions of metal nitrates under study were prepared by dissolution of weighed sample of the corresponding nitrate in 0.01 mol/L HNO_3 solution. The concentration of metal nitrate solutions (0.1 mmol/L) was refined by spectrophotometry by procedure [25] using a Thermo Scientific Gallery spectrophotometer. Concentration of HNO_3 solutions was determined by potentiometric titration with 0.1 mol/L NaOH using a Mettler Toledo S470 SevenExcellence™ conductivity meter with accuracy ± 0.01 pH units. Electrode pair was calibrated using standard buffer solutions with pH 1.68, 4.01, and 9.21 (Mettler Toledo) (at 20°C). Concentration of NaOH solution was refined by potentiometric titration with 0.1 mol/L HCl (standard solution).

Extraction studies were performed by the following procedure. A test tube with ground stopper was filled with 1.5 mL of 5.15 mol/L nitric acid solution, 0.5 mL of 0.1 mmol/L metal nitrate solution, and 2 ml of 0.001 mol/L ligand solution in DCE. Phases were stirred for 20 min in a BioSan Multi RS-60 multi rotator (80 rpm). Extraction equilibration time was verified by increasing phase contact time up to 120 min, distribution ratios in this case remain constant. Phases were separated by centrifugation. After phase separation, metal cation concentration in aqueous phase was determined by spectrophotometry [25]. At least three independent experiments were conducted for each concentration. Relative value of confidence limit of total error was $\delta = 0.33$ for $n = 3$ and confidence coefficient $P = 0.95$. Confidence interval of metal concentration determined by spectrophotometry is 3.3×10^{-6} mol/L [26].

All experiments were conducted at 20 ± 1°C. Distribution ratios ($D = [M]_{org}/[M]_{aq}$) were determined at constant extractant concentration in DCE of 1 mmol/L and initial metal concentration in aqueous phase of 0.025 mmol/L.

The presence of aggregated particles in organic phase was determined using a Nano-ZS Malvern Zetasizer Nano particle size analyzer.

Metal sorption study. The content of H_2L^3 in the studied sorbents was 33 wt %. Carrier used was a LPS-500 styrene–divinylbenzene copolymer manufactured by Tekhnosorbent Ltd. (Moscow), which according to manufacturer's certificate had the following characteristics: fraction size 40–70 μm, surface area 700–800 m^2 per 1 g of carrier, pore volume 2.0 mL per 1 g of carrier, pore diameter 5–50 nm.

Procedure of styrene–divinylbenzene copolymer impregnation with phosphoryl-containing podands H_2L^1–H_2L^6. A solution of 3.3 g of phosphoryl-containing podand in 100 cm^3 of chloroform (analytical grade) was placed in a 250-cm^3 beaker, 6.7 g of granulated LPS-500 polymer was added. The resultant mixture was carefully stirred for 2 h on a magnetic stirrer and the solvent was removed on a rotary evaporator. The residue was dried at ambient temperature in a fume hood until dry state (8–10 h). Sorbent yield 10.0 g (100%). Ligand H_2L^3 distribution in sorbent pores was not studied.

Sorption of the elements was studied in a static mode from solutions containing 0.1 mmol/L of uranium(VI), thorium(IV), and rare earth elements(III) nitrates in 0.052 and 3.52 mol/L HNO_3. Sorbent weight was 200 mg, solution volume was 100 mL (V/m = 500 mL/g). The phases were stirred using a WAB Glen Mills Turbula T2F Mixer shaker, 50 rpm. Concentration of U(VI), Th(IV), and REE(III) in initial and equilibrium aqueous solutions was determined by inductively coupled plasma mass spectrometry (ICP-MS) using a VG Elemental PlasmaQuad mass spectrometer (GB).

Distribution ratios were determined on the basis of analyses by the formula [27]:

$$D = \frac{V}{m}\frac{[C_{\text{init}}] - [C_{\text{equil}}]}{[C_{\text{equil}}]},$$

where C_{init} and C_{equil} are ion concentrations in initial solution and filtrate, respectively, mol/L; V is liquid phase volume, mL; m is sorbent weight, g. In all experiments, sorbent weight was 200 mg, solution volume was 100 mL.

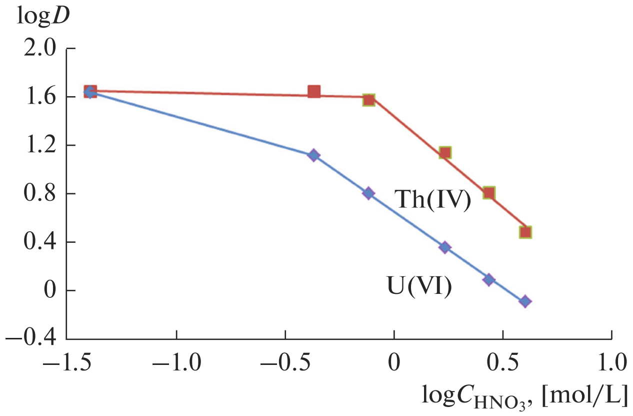


Fig. 1. Logarithmic dependence of distribution ratios for U(VI) and Th(IV) on HNO_3 concentration in aqueous phase upon extraction with 0.001 mol/L H_2L_3 solutions in DCE.

RESULTS AND DISCUSSION

All extractants of H_2L^1–H_2L^6 series are rather strong dibasic diphosphonic acids. The ability of complexation to metal and therefore extraction ability of organic acids is known to be dependent on the value of dissociation constant. The logarithm of stepwise dissociation constants for phosphoryl-containing podand H_2L^3 in 5% aqueous dimethylformamide are $pK_1 = 2.77$, $pK_2 = 4.21$, which is higher than the similar values for the known acid-type extractants [28]. The presence of dissociated POO$^-$ functional groups provides a possibility of metal cation extraction via cation-exchange mechanism [28]. Consequently, uranium(VI) and thorium(IV) extraction with H_2L^1–H_2L^6 solutions can proceed preferably via cation-exchange mechanism [28]. Fig. 1 shows the dependence of distribution ratios for uranium(VI) and thorium(IV) upon extraction with H_2L^3 solution in DCE on nitric acid concentration in aqueous phase.

The dependence of distribution ratios for U(VI) and Th(IV) on HNO_3 concentration displays that metal recovery proceeds preferably by cation-exchange mechanism. Starting from 0.04 mol/L, there is a monotonic decrease of distribution ratios (D) when acid concentration rises. Increase in nitric acid concentration suppresses H_2L^3 dissociation, chelating effect of –POO$^-$ groups is blocked, and therefore extraction ability of the compounds toward thorium and uranium decreases [28]. Upon further increase in HNO_3 content, uranium and thorium recovery into organic phase proceeds only due to neutral PO groups whose coordination ability is considerably decreased owing to solvation in acid medium. The values of D_{Th} decrease when HNO_3 content in aqueous phase is enhanced in the range 0.75–3.86 mol/L. At HNO_3 concentration of 0.04–0.75 mol/L, the values of D_{Th} do not change (Fig. 1) because of high aggregation of

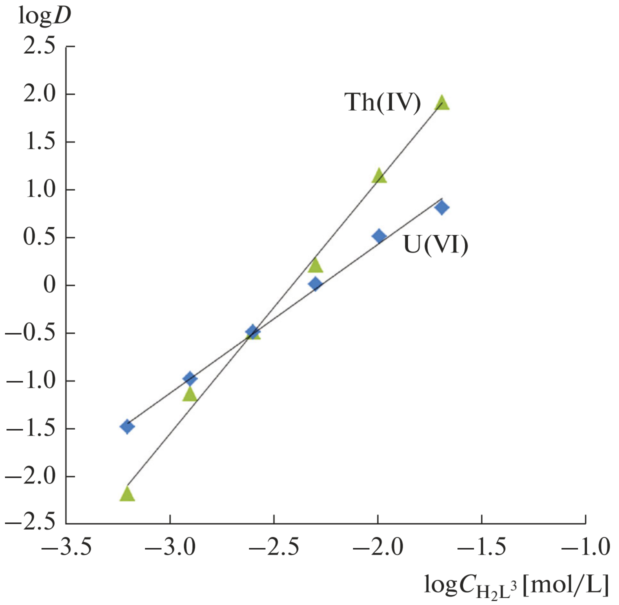


Fig. 2. Logarithmic dependence of distribution ratios for uranium(VI) and thorium(IV) on ligand H_2L^3 concentration.

lipophilic H_2L^3 anions to form macromolecular associates, which were observed upon laser light scattering in organic phase [24]. The composition of associates $[Th(L^3)_2(H_2L^3)_n]^0$, $[Th(HL^3)_2(L^3)(H_2L^3)_n]^0$, and $[Th(HL^3)_4(H_2L^3)_n]^0$ was suggested on the basis of molar weight determination by measuring diffusion coefficients [29].

The distribution ratios of uranium(VI) upon extraction with H_2L^3 solution in DCE decrease in all studied range of HNO_3 concentration because of suppression of H_2L^3 dissociation. The logarithmic plot of D_U on nitric acid concentration shows a break at 0.42 mol/L HNO_3. Like thorium, uranium(VI) is extracted in H_2L^3 solution in dichloroethane as salts $[UO_2(HL)_2(H_2L)_n]^0$ and $[UO_2(L)(H_2L)_n]^0$ in the region of low HNO_3 concentrations when H_2L^3 shows maximum aggregate formation. When nitric acid concentration rises, general trend to decrease distribution ratios for thorium and uranium is observed; it is explained by the degradation of associates and suppression of H_2L^3 diphosphonic acid dissociation. The corresponding logarithmic plots of D_{Th} and D_U vs HNO_3 concentration show two regions (Fig. 1). Different positions of breaks on diagram for thorium and uranium can result from the formation of complexes of different composition. After extraction experiment at 0.04 mol/L HNO_3, we found associates in organic phase by laser light scattering, their size is dependent on metal nature. In thorium(IV) extraction, larger associates formed (the main size is 60 nm, more than 60%) as compared with associates produced upon uranium(VI) recovery (the main size is 30 nm, > 60%).

It should be noted that neutral phosphoryl-containing podand L^7, isodentate analog of H_2L^3, does not extract U(VI) and Th(IV) under these conditions ($\log D < -2$). We also revealed that neutral phosphoryl-containing podands in organic phase produce no associates in organic phase. The extraction ability of these compounds toward uranium and thorium is caused only by PO group coordination.

We studied the dependence of distribution ratio on ligand H_2L^3 concentration (Fig. 2) by equilibrium shift method at low extractant concentrations. Solvation number determined by equilibrium shift method at low H_2L^3 concentration in dichloroethane was found to be close to 1 for uranium and 2 for thorium. Consequently, under these conditions, uranium is extracted as monosolvates, while thorium as disolvates.

$$UO^{2+}_{2(aq)} + H_2L^3_{(org)} \rightarrow UO_2L^3_{(org)} + 2H^+_{(aq)}, \qquad (1)$$

$$Th^{4+}_{(aq)} + 2H_2L^3_{(org)} \rightarrow Th(L^3)_{2(org)} + 4H^+_{(aq)}. \qquad (2)$$

It should be noted that stable complex UO_2L^3, whose composition and structure agree well with data of elemental analysis and IR spectroscopy, was isolated from extract obtained under similar conditions [24].

Thus one can suppose that extracted uranyl compound is a normal intracomplex salt of dibasic acid UO_2L^3 with chelate coordination of both POO^- groups to one cation. One can suppose that, by the analogy to uranyl, extracted thorium complex is also a normal intracomplex salt of composition $Th(L^3)_2$ where two divalent anions of ligand acid are coordinated via all four POO^- groups to Th(IV) cation.

Compounds containing lipophilic alkyl substituents completely recover uranium(VI) and thorium(IV) from nitric acid solutions up to 1 mol/L [24]. Trivalent REE under these conditions are not extracted, the extraction ability of compounds H_2L^1–H_2L^6 toward REE(III) increases with nitric acid concentration [24].

The data for U(VI), Th(IV), La(III), Nd(III), Ho(III), and Yb(III) extraction with 1 mol/L solutions of compounds H_2L^1–H_2L^6 from 3.86 mol/L HNO_3 are presented in Table 1.

Extraction of U(VI) and Th(IV) with compounds H_2L^1–H_2L^6 from 3.86 mol/L HNO_3 is slightly lower than from 1 mol/L HNO_3 [24]. However, it should be noted that 1 mol/L solutions of ligands H_2L^1–H_2L^6 extract more than 90% of Th(IV) from 3.86 mol/L HNO_3 in one stage. Distribution ratios for Th(IV) (D_{Th}) vary from 2.5 to 3.3 (Table 1). Extraction efficiency for U(VI) from 3.86 mol/L HNO_3 is lower than for thorium, distribution ratios for U(VI) are 0.7 for H_2L^1, 0.8–0.85 for H_2L^3, H_2L^4 and H_2L^5, while D_U =

Table 1. Distribution ratios of elements upon extraction with 1 mmol/L solutions of compounds H_2L^1–H_2L^6 in 1,2-dichloroethane from 3.86 mol/L HNO_3

Compound	*D*					
	La(III)	Nd(III)	Ho(III)	Yb(III)	Th(IV)	U(VI)
H_2L^1	0.1	0.68	0.75	0.68	2.5	0.7
H_2L^2	0.05	0.42	0.61	0.63	2.5	0.9
H_2L^3	0.05	0.42	0.85	0.79	3.0	0.8
H_2L^4	0.05	0.34	0.51	0.53	1.93	0.83
H_2L^5	0.10	0.64	0.63	0.68	3.3	0.8
H_2L^6	0.025	0.6	0.71	0.83	0.02	0.28

0.9 for H_2L^2, i.e., 45% of U(VI) on average is extracted in one stage.

REE(III) are extracted from 3.86 mol/L HNO_3 much better (Table 1) than from 1 mol/L HNO_3 [24]. The change in the lipophilicity of phosphoryl-containing podands has no effect on their extraction ability toward REE(III) (Table 1). When nitric acid concentration rises, the share of anionic triple complexes of lanthanides with organic ligand increases (equation (3)) and distribution ratio is smoothly enhanced [28], which is observed in experiment.

$$\begin{gathered}\mathrm{Nd}^{3+}_{(\mathrm{aq})} + 3\mathrm{NO}^{-}_{3(\mathrm{aq})} + \mathrm{H}_2\mathrm{L}^3_{(\mathrm{org})} \\ \rightarrow \mathrm{Nd}(\mathrm{L}^3)\mathrm{NO}_{3(\mathrm{org})} + 2\mathrm{H}^{+}_{(\mathrm{aq})} + 2\mathrm{NO}^{-}_{3(\mathrm{aq})}.\end{gathered} \tag{3}$$

The composition and structure of complex $Nd(L^3)NO_3$ were confirmed by IR spectroscopy and elemental analysis [24]. A general trend is observed: La(III) is not extracted into organic phase. The values of D_{Nd} vary in the range from 0.4 to 0.7. Ho(III) is better extracted than Nd(III) with distribution ratios 0.65–0.85, while distribution ratios for Yb(III) are comparable with D_{U}.

Thus, synthetically available phosphoryl-containing podands H_2L^1–H_2L^6 are promising extractants for the recovery and separation of U(VI), Th(IV), and REE(III). Differences in *D* values for the studied elements can be explained by change in the lipophilic properties of these extractants and different association degree of compounds H_2L^1–H_2L^6 in organic phase [29].

Impregnated sorbent with 33 wt % of phosphoryl-containing podand H_2L^3 was obtained for the further study of acid-type phosphoryl-containing podands, matrix used was LPS-500 styrene–divinylbenzene copolymer. The use of H_2L^3 as extractant is caused by its synthetic availability and revealed extraction properties.

The sorption characteristics of the obtained sorbent were studied in static mode from both solutions of individual U(VI), Th(IV), and Nd(III) salts and from solutions of mixtures of U(VI), Th(IV), and REE(III) salts in nitric acid at concentration 0.052 and 3.52 mol/L.

The study of time dependence of distribution ratio for Th(IV), U(VI), and Nd(III) between phases upon sorption showed that 30 min contact is sufficient for system equilibration (Fig. 3). According to the data of Fig. 3, we calculated static exchange capacity (SEC, mg/g) of the sorbents and recovery extent (*E*, %) for thorium(IV), uranium(VI), and neodymium sorption. The calculation of SEC for sorbents and recovery extent was carried out by standard procedure [30].

$$\mathrm{SEC} = \frac{(C_{\mathrm{init}} - C_{\mathrm{equil}})V}{g}, \tag{4}$$

$$E = \frac{C_{\mathrm{init}} - C_{\mathrm{equil}}}{C_{\mathrm{init}}} \times 100, \tag{5}$$

where *g* is the weight of dry sorbent, g; *V* is solution volume, L; C_{init} is metal concentration in initial solution, mg/L; C_{equil} is equilibrium metal concentration in solution, mg/L. The static exchange capacity of sor-

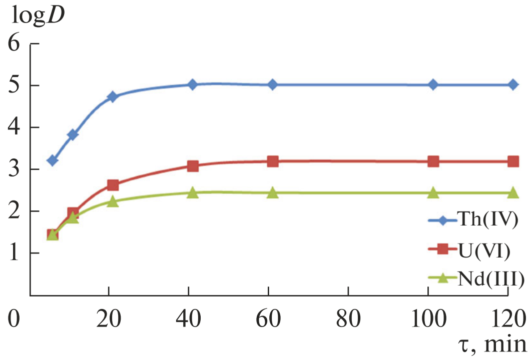


Fig. 3. Dependence of distribution ratios for uranium(VI), thorium(IV), and neodymium(III) on stirring time upon sorption from 3.52 mol/L HNO_3. Sorbent weight is 200 mg, initial solution volume is 100 mL, sample volume for assay is 0.5 mL.

Table 2. Logarithms of metal distribution ratios upon sorption from 0.052 and 3.52 mol/L HNO_3 solutions in static mode. Sorbent weight is 200 mg solution volume is 100 mL

M	log *D*	
	3.25 mol/L	0.052 mol/L
U	3.18	5.0
Th	5.0	8.7
La	0.91	0
Ce	0.58	–0.12
Pr	2.25	1.01
Nd	2.43	1.68
Sm	2.8	1.66
Eu	0.87	0.26
Gd	0.96	0.35
Tb	2.48	1.56
Dy	2.66	1.67
Ho	2.12	1.18
Er	1.55	0.93
Tm	1.84	1.2
Yb	1.78	1.14
Lu	1.13	0.52

bent with H_2L^3 based on LPS-500 polymer is 11.36 mg/g for thorium(IV), 8.75 mg/g for uranium(VI), and 2.48 mg/g for neodymium(III). Under experimental conditions (sorbent weight 200 mg, initial solution volume 100 mL), recovery extent was 99.5% for thorium(IV) sorption, 75% for uranium(VI), and 35% for neodymium(III). A possibility of selective recovery of U(VI), Th(IV), and REE(III) in static mode from solutions containing a mixture of these elements at HNO_3 concentration of 0.052 and 3.52 mol/L was studied (Table 2).

Decrease of distribution ratios for Th(IV) and U(VI) upon sorption when nitric acid concentration in aqueous solution rises has a general character with liquid extraction (Table 2). Distribution ratios for uranium(VI) and thorium(IV) sorption decrease when acid concentration in initial solution rises. Thus, $\log D_U = 5$ and $\log D_{Th} = 8.7$ for sorption from 0.052 mol/L HNO_3, while $\log D_U = 3.18$ and $\log D_{Th} = 5$ for sorption from 3.52 mol/L HNO_3. It should be noted that, upon increase in HNO_3 concentration, trivalent REE recovers into sorbent phase better, like in the case of extraction process. This fact can be used for the selective isolation of rare earth elements upon sorption from solutions with HNO_3 concentration higher 4 mol/L and for selective desorption of uranium(VI) and thorium(IV).

The studied sorbent shows high selectivity in separation of U(VI), Th(IV), and REE(III). For sorption from 3.52 mol/L HNO_3, separation factor for uranium(VI) and europium(III) ($\beta_{U/Eu}$) reaches 202, while $\beta_{U/Eu} \approx 55000$ at $V/m = 500$ mL/g for 0.052 mol/L HNO_3. Separation factor for uranium(VI) and thorium(IV) ($\beta_{Th/U}$) is 66 for sorption from 3.52 mol/L HNO_3 while $\beta_{Th/U} \approx 5050$ for 0.052 mol/L HNO_3. It should be noted that selectivity decreases when nitric acid concentration in initial solution increases.

We used 0.05 mol/L $(NH_4)_2C_2O_4$ (ammonium oxalate) solution in 0.05 mol/L HNO_3 as a reagent for uranium(VI), thorium(IV), and REE(III) desorption. The use of ammonium oxalate is caused by the high values of stability constants of actinide and lanthanide oxalate complexes and their stability in acid media. The desorption of uranium(VI), thorium(IV), and REE(III) with 0.05 mol/L ammonium oxalate solution in 0.05 mol/L HNO_3 is quantitative.

CONCLUSIONS

The obtained data show that the acid-type phosphoryl-containing podands comprising diethylene glycol chain and two fragments of 2-oxyphenylphosphonic acid display high extraction ability toward U(VI) and Th(IV). Sorbents non-covalently modified with these reagents can be used for selective recovery and preconcentration of U(VI), Th(IV), and REE(III) from nitric acid solutions.

ACKNOWLEDGMENTS

This work was performed under the State Assignment (theme no. 0090-2017-0024) and supported in part by the Presidium of the RAS (Fundamental Research Program no. 34 “Actual problems of surface physical chemistry and design of novel composites”) as well as by the Russian Foundation for Basic Research (project no. 18-29-24069).

REFERENCES

1. M. Y. Alyapyshev, V. A. Babain, and Y. A. Ustynyuk, Russ. Chem. Rev. **85**, 943 (2016). doi 10.1070/rcr4589
2. K. L. Nash, R. E. Barrans, R. Chiarizia, et al., Solvent Extr. Ion Exch. **18**, 605 (2000). doi 10.1080/07366290008934700
3. O. B. Mokhodoeva, G. V. Myasoedova, and E. A. Zakharchenko, Radiochemistry **53**, 35 (2011). doi 10.1134/S106636221101005X
4. G. V. Myasoedova, Ross. Khim. Zh. **49**, 72 (2005).
5. G. V. Myasoedova, E. A. Zakharchenko, N. P. Molochnikova, et al., Radiochemistry **50**, 482 (2008). doi 10.1134/S1066362208050093
6. A. N. Turanov, V. K. Karandashev, A. N. Yarkevich, et al., Radiochemistry **44**, 559 (2002). doi 10.1023/A:1022376225458
7. E. P. Horwitz, D. R. McAlister, and M. L. Dietz, Sep. Sci. Technol. **41**, 2163 (2006). doi 10.1080/01496390600742849

8. I. Boulenouar, M. KaiD, O. Abbers, et al., Solvent Extr. Res. Develop., Japan **23**, 51 (2016). doi 10.15261/serdj.23.51
9. M. Jensen, R. Chiarizia, J. S. Ulicki, et al., Solvent Extr. Ion Exch. **33**, 329 (2015). doi 10.1080/07366299.2015.1046292
10. R. Chiarizia, Jr. R. E. Barrans, J. R. Ferraro, et al., Sep. Sci. Technol. **36**, 687 (2001). doi 10.1081/SS-100103615
11. R. Chiarizia, D. R. Mcalister, and A. W. Herlinger, Sep. Sci. Technol. **40**, 69 (2005). doi 10.1081/SS-200041762
12. J. Wang, G. Chen, S. Xu, and L. Li, Hydrometallurgy **154**, 129 (2015). http://dx.doi.org/10.1016/j.hydromet.2015.04.001.
13. A. N. Turanov, V. K. Karandashev, A. N. Yarkevich, et al., Radiochemistry **45**, 568 (2003). doi 10.1023/B:RACH.0000015753.31087.ef
14. G. J. Lumetta, S. I. Sinkov, J. A. Krause, et al., Inorg. Chem. **55**, 1633 (2016). doi 10.1021/acs.inorgchem.5b02524
15. E. P. Horwitz, R. Chiarizia, and M. L. Dietz, React. Funct. Polym. **33**, 25 (1997).
16. R. Chiarizia, A. W. Herlinger, Y. D. Cheng, et al., Solvent Extr. Ion Exch. **16**, 505 (1998). doi 10.1080/07366299808934537
17. V. E. Baulin, V. Kh. Syundyukova, and E. N. Tsvetkov, Russ. J. Gen. Chem., **59**, 62 (1989).
18. A. N. Turanov, V. K. Karandashev, V. E. Baulin, et al., Radiochemistry **56**, 22 (2014). doi 10.1134/S1066362214010056
19. A. M. Safiulina, A. G. Matveeva, and D. V. Ivanets, et al., Russ. Chem. Bull. **64**, 161 (2015). doi 10.1007/s11172-015-0837-2
20. E. V. Chukhlantseva, A. N. Usolkin, O. V. Kovalenko, et al., Analitika I Kontrol' **17**, 219 (2013). doi 10.15826/analitika.2013.17.2
21. E. V. Chukhlantseva, A. N. Usolkin, V. E. Baulin, et al., Analitika i Kontrol' **17**, 314 (2013). doi 10.15826/analitika.2013.17.3.007
22. V. E. Baulin, O. V. Kovalenko, A. Yu. Tsivadze, et al., Radiochemistry **57**, 61 (2015). doi 10.1134/S1066362215010099
23. V. E. Baulin, I. P. Kalashnikova, and O. V. Kovalenko, et al., Prot. Met. Phys. Chem. Surf. **52**, 996 (2016). doi 10.7868/S0044185616060085
24. A. M. Safiulina, A. G. Matveeva, and D. V. Ivanets, et al., Russ. Chem. Bull. **64**, 169 (2015). doi 10.1007/s11172-015-0838-1
25. S. B. Savvin, *Organic Reagents of Arsenazo III Group* (Atomizdat, Moscow, 1971) [in Russian].
26. *OST 95 10353-2008. Branch Standard. Branch System for the Unity of Measurements. Algorithms for Assessment of Metrological Characteristics on Measurement Procedures Attestation. Accepted and Put into Action by the Federal Atomic Energy Agency on 2008* [in Russian].
27. Yu. V. Egorov, N. D. Betenekov, and V. D. Puzako, *Methods for Preconcentration and Separation of Radionuclides: A Tutorial* (Ural Univ., Yekaterinburg, 2016) [in Russian].
28. A. M. Rozen and B. V. Krupnov, Russ. Chem. Rev. **65**, 973 (1996). doi 10.1070/RC1996v065n11ABEH000241
29. G. I. Timofeeva, A. G. Matveeva, and A. M. Safiulina, et al., Russ. Chem. Bull. **64**, 224 (2015). doi 10.1007/s11172-015-0847-0
30. *STO RosGeo 08-002-98. Technological Methods for the Investigation of Mineral Raw Materials. Text* (RosGeo, Moscow, 1998), p. 33 [in Russian].

Translated by I. Kudryavtsev