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Extraction of *f* Elements by Binary Extractants Based
on 1,5-Bis[*o*-(dioxypophoryl)phenoxy]-3-Oxapentane
Derivatives and Trioctylamine

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Abstract—This is the first study of uranium(VI), thorium(IV), and lanthanum(III) extraction from nitric acid solutions in 1,2-dichloroethane (DCE) by binary extractants prepared from stoichiometric mixtures of diphosphonic acids, namely, 1,5-bis[*o*-(dioxypophoryl)phenoxy]-3-oxapentane or 1,5-bis[*o*-(dioxypophoryl)-*n*-ethylphenoxy]-3-oxapentane, and trioctylamine. The binary extractant comprised of 1,5-bis[*o*-(dioxypophoryl)-*n*-ethylphenoxy]-3-oxapentane and trioctylamine is found to selectively recover Th(IV) from solutions that contain both U(VI) and La(III), with separation factors exceeding 100. A method is developed for an efficient stripping of thorium(IV), uranium(VI), and lanthanum(III) from the saturated organic phase. Conditions are found for recovering the studied binary extractants after stripping to make them reusable.

Keywords: binary extractants, extraction, stripping, uranium(VI), thorium(IV), lanthanum(III), phosphoryl podands, diphosphonic acids, trioctylamine, organic salts, ionic liquids

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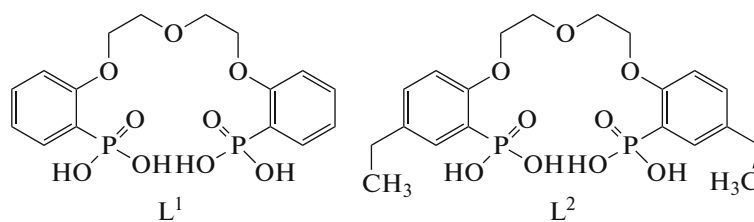
The looped nuclear fuel cycle concept suggests recycling of spent nuclear fuel based on the selective isolation of the *f* elements contained in the fuel, these elements being necessary for the industry and nuclear medicine [1–3]. Extraction methods using organic [4–9] and phosphororganic [10–13] extractants of neutral, anionic, or cationic type are widely used for this purpose.

Binary extractants are also known in the form of stoichiometric mixtures of cation- and anion-exchange extractants [14–16]. Binary extractants may also be classified as ionic liquids, which are melts of organic salts that are liquid at room temperature. The bulky organic cations and anions and the spatial charge separation hinder the crystal structure organization in these salts and are responsible for their ionic, rather than molecular, phase state. This explains the specificity of physical and chemical properties of ionic liquids, such as low melting temperatures, almost zero saturated vapor pressures, incombustibility, the ability to dissolve many compounds, and high polarity. Selecting the nature of constituent ions, one can tune the hydrophobicity and other properties of ionic liq-

uids, and this makes them very promising subjects of studies targeted at developing extraction and sorption technologies for the recovery of valuable components from multicomponent technogenic solutions [17–23].

Recent research showed that phosphoryl podands are acid sesquiesters of diphosphonic acids whose polyester chain contains two ethylene glycol units. In their *f*-element extraction characteristics, phosphoryl podands are far superior to di-2-ethylhexylphosphoric acid, the well-known extractant [24], and they are very promising compounds for use as selective extractants [25–27] and as components of the immobile phase of impregnated sorbents for the extraction-chromatographic recovery of ⁹⁹Mo [28] and ¹⁴⁷Pm [29].

Here, we report the first study of thorium(IV), uranium(VI), and lanthanum(III) extraction to 1,2-dichloroethane (DCE) by binary extractants that were prepared by mixing acid phosphoryl podands, namely, diphosphonic acid 1,5-bis[*o*-(dioxypophoryl)phenoxy]-3-oxapentane (L¹) or its lipophilic analogue 1,5-bis[*o*-(dioxypophoryl)-4-phenoxy]-3-oxapentane (L²), with trioctylamine (TOA) in the ratio 1 : 4.



There are no documents on the use of binary extractants based on acid-type phosphoryl podands; the only what is described is the synergistic effect and selective extraction-chromatographic separation of U(VI), Th(IV), Np(IV), and Pu(IV) by impregnated sorbents that comprise a mixture of acid sesquiester L^2 (1,5-bis[*o*-(oxyethoxyphosphoryl)-4-phenoxy]-3-oxapentane) and methyltrioctylammonium nitrate from solutions obtained upon recycling of spent nuclear fuel [30, 31].

EXPERIMENTAL

For the purpose of extracting Th(IV), U(VI), and La(III), we studied 0.001 mol/L solutions of organic salts in DCE; these organic salts were prepared by mixing exact weights of phosphoryl podand L^1 or L^2 and 97% trioctylamine (Acros Organics) in the ratio 1 : 4 mol/mol. The synthesis of L^1 and L^2 was performed as described previously [25]. Working solutions were prepared using bidistilled water, 1,2-dichloroethane (chemically pure grade), Arsenazo III (pure for analysis grade), HNO₃ (specialty grade), UO₂(NO₃)₂ · 6H₂O (chemically pure grade), Th(NO₃)₄ · 4H₂O (chemically pure grade), and La(NO₃)₃ · 6H₂O (chemically pure grade). The solutions were prepared by a volumetric–gravimetric method. Actinide and lanthanum solutions were prepared by dissolving the relevant nitrate weight in 0.01 mol/L HNO₃. The exact concentrations of metal nitrate solutions (0.1 mmol/L) were determined spectrophotometrically as described in [32] on a Cary50 Scan (Varian) spectrophotometer. HNO₃ concentration was determined by potentiometric titration with 0.1 mol/L NaOH using a Radelkis-125 (model OP-300) pH/ion analyzer accurate to ±0.01 pH units. The electrode pair was calibrated against standard buffer solutions with pH of 1.68, 4.01, and 9.22 (at 20°C). Exact NaOH concentration was determined by potentiometric titration with 0.1 mol/L HCl (standard solution).

The extraction of metal cations was studied as follows. To a ground-stoppered reaction tube, added were a 1.5-mL portion of aqueous nitric acid (the acid concentration was varied from 0.054 to 5.15 mol/L), 0.5 mL of a 0.1 mmol/L metal nitrate solution, and 2 mL of a 1 mmol/L ligand solution in DCE. Phases were stirred for 20 min in a rotator (a Multi RS-60 multi-rotator, BioSan, 80 rpm). The extraction equilibrium attainment was verified by increasing the

phase contact time to 120 min; the distribution ratios did not change in response to this. Phase separation was provided by centrifugation. The lanthanum(III) concentration in the aqueous phase was determined spectrophotometrically [32]. For improving the quality of analysis, the contents of actinides in organic and aqueous phases were monitored radiometrically using a Beckman LS 6500 Liquid Scintillation Counter (WS-BECKLS65, Beckman Instruments). For this purpose, indicator amounts of ²³³U(VI) and ²³⁹Pu(IV) were added to uranyl and thorium solutions in extraction experiments. At least three replica runs were carried out for every concentration. All experiments were performed at 20 ± 1°C.

Distribution ratios ($D = [M]_{\text{org}}/[M]_{\text{aq}}$) were determined at constant concentrations of the extractant (1 mmol/L in DCE) and the metal (0.025 mmol/L in the aqueous phase).

A Malvern Zetasizer Nano (Nano-ZS) particle size analyzer was used to detect nanosized aggregates in the organic phase. Extracts were studied after a solution of L^2 + TOA (1 mmol/L of the podand in DCE) was brought in contact with a 0.025 mmol/L thorium nitrate solution in 0.04 mol/L HNO₃.

RESULTS AND DISCUSSION

Our studies of Th(IV), U(VI), and La(III) extraction by L^1 solutions in DCE showed that L^1 has a very limited solubility in DCE (at most 0.003 mol/L). An analysis of the Th(IV), U(VI), and La(III) distribution ratios as a function of nitric acid concentration upon extraction by 0.001 mol/L L^1 in DCE implies that the efficacy of Th(IV), U(VI), and La(III) recovery to DCE is insignificant (Figs. 1–3).

The ethyl substituent in the position 4 of the aromatic ring (compound L^2) increases the solubility in DCE and the recovery of Th(IV) and U(VI) (Figs. 1, 2), but has almost no effect on La(III) recovery (Fig. 3).

The distribution ratio versus nitric acid concentration plots are descending, characterizing the typical acid nature of extractants L^1 and L^2 . At low nitric acid concentrations, the acid extractant is dissociated, and the metal cation is bound by the cation exchange mechanism. The dissociation is inhibited by increasing nitric acid concentrations, so the thorium and uranium extraction capacity of the compounds decays.

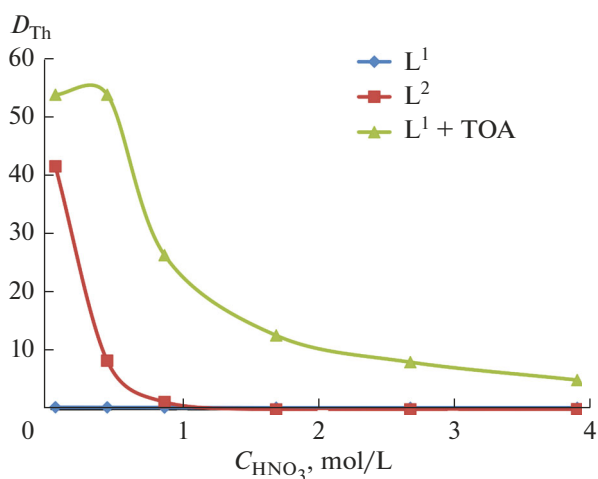
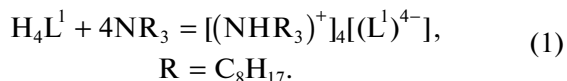


Fig. 1. Th(IV) distribution ratio versus nitric acid concentration in extraction by L^1 , L^2 , and $L^1 + \text{TOA}$ (0.001 mol/L ligand) solutions in DCE.

Phosphoryl podands L^1 and L^2 are rather strong acids (the logarithmic stepwise dissociation constants for phosphoryl podand L^1 in water added with 3.5% ethanol are $pK_1 \leq 1$, $pK_2 = 2.97 \pm 0.03$, $pK_3 = 7.39 \pm 0.02$, and $pK_4 = 8.31 \pm 0.03$); they are poorly soluble in 1,2-dichloroethane, but when 4 equiv trioctylamine is added, L^1 completely passes to dichloroethane to form a salt according to the equation



The thorium and uranium extraction efficacy of binary extractant $L^1 + \text{TOA}$ is far higher compared to the efficacy of extractant L^1 in the same concentration (Figs. 1 and 2). In uranium(VI) extraction, L^2 provides high distribution ratios compared to those for $L^1 + \text{TOA}$, likely due to the lower lipophilicity of L^1 . The curves for U(VI) and Th(IV) have similar trends. Tervalent lanthanum has higher distribution ratios when $L^1 + \text{TOA}$ are used than with L^1 alone. The highest uranium and thorium distribution ratios are observed for low nitric acid concentrations (below 1 mol/L). The extraction capacity drops dramatically as the aqueous nitric acid concentration rises, indicating the degradation of binary extractant $L^1 + \text{TOA}$ to free L^1 and TOA. A further increase in nitric acid concentration has no considerable effect on the recovery efficacy, indicating that uranium and thorium are extracted only by TOA.

The Th(IV), U(VI), and La(III) extraction capacity of binary extractant $L^2 + \text{TOA}$ in DCE was studied in a similar manner (Figs. 1–3).

Noteworthy is the quantitative Th(IV) recovery over the entire range of nitric acid concentrations, which is important for spent nuclear fuel recycling

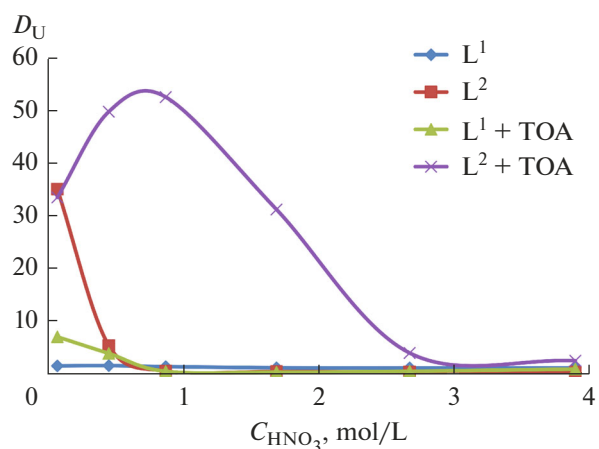


Fig. 2. U(VI) distribution ratio versus nitric acid concentration in extraction by L^1 , L^2 , $L^1 + \text{TOA}$, and $L^2 + \text{TOA}$ (0.001 mol/L ligand) solutions in DCE.

[33, 34] and signifies the potential usefulness of this extractant for selective separation of Th(IV) from solutions containing U(VI) and lanthanides. In addition, light scattering measurements showed no nano-sized aggregates in the extracts after $L^2 + \text{TOA}$ (1 mmol/L podand in DCE) was in contact with 0.025 mmol/L thorium nitrate solution in 0.04 mol/L HNO_3 , as opposed to L^2 (1,5-bis[*o*-(oxyethoxyphosphoryl)-4-phenoxy]-3-oxapentane, acid sesquiester) [26].

The U(VI) distribution ratio versus nitric acid concentration plot for extraction by $L^2 + \text{TOA}$ (Fig. 2) has a peak. The distribution ratio increases while nitric acid concentrations are low (up to 1 mol/L). However, the extraction capacity decays as the nitric acid concentration increases further.

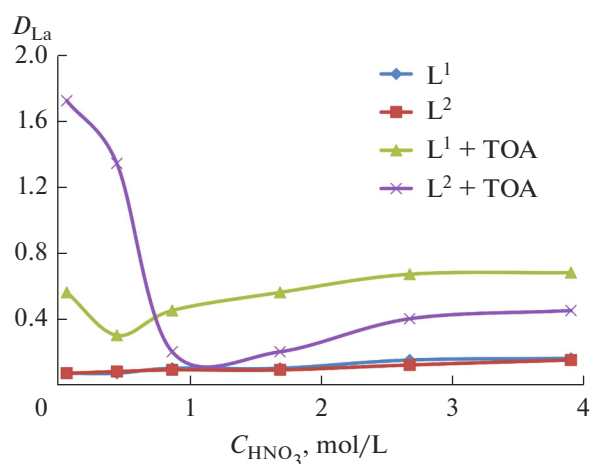


Fig. 3. La(III) distribution ratio versus nitric acid concentration in extraction by L^1 , L^2 , $L^1 + \text{TOA}$, and $L^2 + \text{TOA}$ (0.001 mol/L ligand) solutions in DCE.

Table 1. Stripping of thorium(IV), uranium(VI), and lanthanum(III) by 5.15 mol/L HNO₃ from the saturated organic phase obtained after extraction from 0.56 mol/L HNO₃ by 1 mmol/L L² + TOA in 1,2-dichloroethane

Element	Equilibrium concentration in aqueous phase (after extraction), mmol/L	Equilibrium concentration in organic phase (after extraction), mmol/L	Concentration after stripping in aqueous phase, mmol/L	Recovery, %
Th(IV)	~0	0.25	0.20	80
U(VI)	0.0042	0.246	0.224	91
La(III)	0.11	0.14	0.133	95

A similar situation is observed for La(III) extraction capacity of this compound (Fig. 3). A considerable rise in extraction capacity of trivalent elements compared to the values provided by L² is observed within a narrow range of low nitric acid concentrations. At higher nitric acid concentrations, however, the La(III) extraction capacity lowers, as well as for U(VI) extraction, too.

Noteworthy, in Th(IV), U(VI), and La(III) extraction capacities, binary extractant L² + TOA is not exterior to such an efficient extractant as tetraphenylmethylene diphosphine dioxide [35].

Stripping of actinides and lanthanides by nitric acid solutions. The next task was to find stripping conditions for lanthanides and actinides and to recover and reuse the studied binary extractants.

From the data gained from studies of thorium(IV), uranium(VI), and lanthanum(III) extraction by salts L¹ + TOA and L² + TOA, we recognized that efficient recovery is possible in the range of nitric acid concentrations up to 2 mol/L. At higher HNO₃ concentrations, the extraction efficacy decays dramatically both for lanthanides and actinides, so we could suggest that stripping of actinides and lanthanides would become possible at higher HNO₃ concentrations. We checked this suggestion; the saturated organic phase was once washed with 5.15 mol/L nitric acid (Table 1).

The uranium(VI) and lanthanum(III) recovery from the saturated organic phase under these condi-

tions reaches ~90%, and the thorium(IV) recovery amounts to 80%; so, the metals are almost completely stripped from the organic phase.

After the metals are stripped by 5.15 mol/L nitric acid, the organic phase is likely a solution of podand L² in the form of unionized acid and trioctylamine nitrate in DCE. In order for binary extractant to be regenerated, L² should be converted to the completely ionized species (L²)⁴⁻ and the TOA salt to the free amine.

According to the distribution diagram of ionized L² species as a function of pH, L² exists in solution as four-charged anion (L²)⁴⁻ at pH > 10 (Fig. 4). In view of this, we used consecutive washing of the organic phase by 0.05 mol/L sodium carbonate solution (pH 11) and distilled water to restore the extraction capacity of the binary extractant. When thorium(IV), uranium(VI), and lanthanum(III) were repeatedly extracted from 0.56 mol/L nitric acid, the distribution ratios were virtually the same.

CONCLUSIONS

We have studied U(VI), Th(IV), and La(III) extraction from nitric acid solutions in DCE by the binary extractants that were prepared by mixing L¹ or L² with TOA in the ratio 1 : 4. The new selective binary extractant (L² + TOA) has been found to quantitatively recover Th(IV) from solutions containing U(VI) and La(III). We have developed a method for efficiently stripping Th(IV), U(VI), and La(III) from the saturated organic phase via washing with 5.15 mol/L nitric acid solution. We have found conditions for regenerating the studied binary extractants after stripping to make them reusable.

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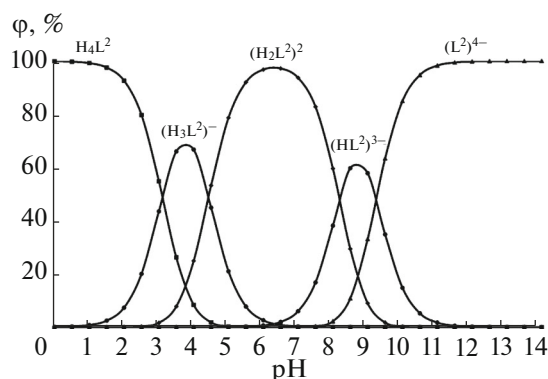


Fig. 4. Ionized species distribution diagram for phosphoryl podand L² versus pH.

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