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C. R. Chimie 7 (2004) 1201–1204



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# Application of phosphorus- and nitrogen-containing organic compounds for the isolation of actinides and technetium from acid or basic aqueous solutions

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Received 1 December 2003; accepted 11 May 2004

Available online 5 November 2004

## Abstract

The derivatives of ethers of phosphoric acid, namely *O*-(2-alkyl) (diethylcarbamoylmethyl) phenylphosphinates (O2ADECMP), were synthesized and tested for liquid–liquid extraction of transuranium elements, lanthanides and technetium in meta-nitrobenzotrifluoride or 1,2-dichloroethane from acidic solutions. The *O*-(ethylhexyl) (diethylcarbamoylmethyl) phenylphosphinate (O2EHDECMP) was used to prepare chelating granulated sorbents. The family of chelating fibrous ‘filled’ sorbents POLYORGS-type shows, according to preliminary experiments, that Pu and Tc at concentrations around  $10^{-5}$  M can be recovered almost completely. POLYORGS show fast kinetics for sorption processes. **To cite this article: G.V. Myasoedova et al., C. R. Chimie 7 (2004).**

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## Résumé

**Utilisation de réactifs phosphorés et azotés pour la séparation des actinides et du technétium de milieux acides et basiques.** Des dérivés de l'éther de l'acide phosphorique du type *O*-2-alkyl diéthylcarbamoylméthyl phénylphosphonates ont été préparés et testés pour extraire des éléments transuraniens, des lanthanides et du technétium dans le meta-nitrobenzène ou le 1,2-dichloroéthane, à partir de solutions aqueuses acides. Le dérivé *O*-éthylhexyl diéthylcarbamoylméthyl phénylphosphonate a été utilisé pour préparer des échangeurs solides par effet de chélation. La famille des chélatants fibreux Polyorgs montre, dans des expériences préliminaires, que Pu et Tc, à des concentration de l'ordre de  $10^{-5}$  M, peuvent être complètement récupérés à partir de milieux acides contenant d'autres éléments. Ces composés présentent des cinétiques de sorption très rapides. **Pour citer cet article : G.V. Myasoedova et al., C. R. Chimie 7 (2004).**

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**Keywords:** Actinides; Tc; Separation by chelating effect

**Mots clés :** Actinides ; Tc ; Séparation par effet de chélation

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## 1. Introduction

Chelating fibre sorbents have great advantages over liquid–liquid extraction for the recovery of elements in micro-amount (micro-elements) from natural and wastewater. They offer the possibility of selective sorption of microelement in the presence of elements in macro-amount, like alkali and alkaline-earth elements, with a high effective sorption [1,2]. Sorption capacity can be enhanced using ‘filled’ fibre chelating sorbents [3–5]. These materials are obtained by introducing the ‘filler’ (polymeric complexing sorbent) during the process of fibre formation. The content of the filler in the material amounts to 50% (mass) [5].

The basic aim of the present work is the preparation and the study of new nitrogen- and phosphorus-containing chelating fibre sorbents to be used for transuranium elements (TRU), lanthanides and technetium isolation from acidic or basic solutions. The goal of our researches was: (i) to synthesize the nitrogen-containing sorbents in the form of a fibrous ‘filled’ material for demonstration of their sorption and kinetic properties in the case of isolation of TRUs from complex acid systems; (ii) to select the one suitable for insertion into the polymeric matrix on the basis of liquid–liquid performance, and (iii) to prepare new sorbents.

## 2. Techniques

Composition, identification and purity monitoring of produced organic compounds were carried out using NMR spectrometry on the atoms of  $^{31}\text{P}$  (Bruker CXP-200) and on atoms of  $^1\text{H}$  in  $\text{C}_6\text{D}_6$  (Bruker AMX-400). For the identification of the oxidation state of element, spectrophotometry (Shimadzu UV-3100 PC) was used. Measurement of pH was performed using a standard electrode from Hanna Instruments (Hanna-4400). A liquid-to-liquid ratio of 1, and a liquid-to-solid ratio ( $V:m$ ) of  $100\text{ cm}^3\text{ g}^{-1}$  was used in liquid-liquid extraction and in batch experiment sorption. The contact time ranged from 5 min to 24 h at  $20\text{ }^\circ\text{C}$ . The distribution coefficients ( $D_M$ ,  $K_d$ ) of the elements have been determined by measuring the activity of the solution containing appropriate radionuclides before and after extraction or sorption. Isotopes of  $^{239}\text{Pu}$ ,  $^{241}\text{Am}$ ,  $^{233}\text{U}$ ,  $^{152}\text{Eu}$ ,  $^{137}\text{Cs}$ ,  $^{231}\text{Pa}$ ,  $^{237}\text{Np}$ , and  $^{99}\text{Tc}$  were used. The

range of the radionuclides concentrations was  $10^{-6}$ – $10^{-5}\text{ M}$ . The fibrous ‘filled’ sorbents of POLIORGS – a family of chelating materials produced at the Vernadsky Institute RAS – were used.

## 3. Experimental results

### 3.1. Extraction studies

The derivatives of ethers of phosphoric acid, namely *O*-(2-alkyl) (diethylcarbamoylmethyl) phenylphosphinates (O2ADECMP) were synthesized and examined for the liquid–liquid extraction of elements M ( $M = \text{TRU}, \text{Ln}$  and  $\text{Tc}$ ) from nitric acid solutions. There is a non-linear increase of  $D_M$  as a function of the carbon radical extension on these phosphoric-acid ethers when meta-nitrobenzotrifluoride (Ftoropol-723) or 1,2-dichlorethane was used as solvent. Maximums of  $D_M$  are found at  $n = 9$  ( $R = \text{C}_n\text{H}_{2n+1}$ ) for all elements used. However, in all further experiments, the easily available and equally efficient O2EHDECMP reagent was used ( $n = 8$ ). The maximums of  $D_M$  for Am(III) and Eu(III) extraction by O2EHDECMP in 1,2-dichlorethane were observed at  $[\text{HNO}_3] = 3\text{ M}$  for  $[\text{E}] = 0.1\text{ M}$  (with E = extractant),  $D_{\text{Am}} = 1.45$  and  $D_{\text{Eu}} = 1.02$ . For Pu(IV), and U(VI) extraction, the increase in the  $\text{HNO}_3$  concentration in the range 0.1–5 M leads to an increase in  $D_M$  and, at  $[\text{E}] = 0.01\text{ M}$ , the values of  $D_{\text{Pu}}$  change from 0.48 to 35, and those of  $D_{\text{U}}$  change from 0.057 to 4.8. On the contrary, for Tc(VII) extraction by O2EHDECMP in 1,2-dichlorethane, the increase in the  $\text{HNO}_3$  concentration causes a noticeable decrease in  $D_{\text{Tc}}$ . In the  $[\text{HNO}_3]$  range from 0.1M to 5 M,  $D_{\text{Tc}}$  decreases from 9.6 to 0.013 ( $[\text{E}] = 0.1\text{ M}$ ).

Dependencies of the distribution coefficients for TRU's, Ln and Tc(VII) on  $[\text{E}]$  were measured for 3 M  $\text{HNO}_3$ . For Am(III), Eu(III), and Tc(VII), the increase in reagent concentration in the range 0.025–0.1 M leads to an increase in  $D_{\text{Am}}$  from 0.057 to 1.45, in  $D_{\text{Eu}}$  from 0.055 to 1.02, and in  $D_{\text{Tc}}$  from 0.01 to 0.12. In logarithmic coordinates, the dependence slope of  $D_{\text{Am}}$  and  $D_{\text{Eu}}$  versus  $[\text{E}]$  is close to 2, upon which we considered that the composition of the extracted complexes is:  $\text{Am}\cdot 2\text{E}$  and  $\text{Eu}\cdot 2\text{E}$ . For Tc(VII) extraction, the solvate number in similar conditions is about 1.5. Probably, in the extraction system, two different Tc

complexes (mono- and bi-coordinated species) were formed. For Pu(IV) and U(VI), the increase in the reagent concentration in the [E] range from  $10^{-4}$  to 0.01 M leads to an increase in the  $D_M:D_{Pu}$  ratio from 0.08 to 11, and in  $D_U$  from 0.02 to 3.2. Values of the solvate number calculated from the slopes of these bi-logarithmic plots for Pu(IV) and U(VI) are close to 1, and we considered that the composition of the extracted complex is: M·E.

### 3.2. Sorption studies

#### 3.2.1. Granulated sorbents

On the basis of the O2ADECMP compounds, new chelating granulated sorbents were synthesized, which were tested with respect to Pu(IV) isolation from nitric acid solutions. The immobilization of O2EHDECMP was realized using two methods: impregnation and chemical fixation of the phosphinate-groups on the solid matrix. The impregnate was prepared using the so-called 'dry method'. For this purpose, aliquots of O2EHDECMP were brought into contact with the XAD-7<sup>TM</sup> pattern in chloroform solutions during 4 h under mixing. The mixture obtained was streamed and dried. The phosphorus content of the impregnate was 0.85% (mass) – (sorbent 1). The chemical fixation was provided using: (i) the Mekhaelis–Bekker reaction using the chloromethylated copolymer of styrene with divinylbenzene – the phosphorus content in the interaction reagent was 3.4% (in mass) (sorbent 2) –; (ii) the Arbousov reaction – the content of phosphorus in the product was 7% (in mass) (sorbent 3). Pu(IV) sorption on sorbent 1 in nitric acid gives the larger values of  $K_d$  ( $K_d^{\max} = 1760 \text{ cm}^3 \text{ g}^{-1}$  in 5 M  $\text{HNO}_3$ ). The  $K_d$  values for Sorbents 2 and 3 changed from 1250 and  $850 \text{ cm}^3 \text{ g}^{-1}$  (in 0.03 M  $\text{HNO}_3$ ) to 850 and  $750 \text{ cm}^3 \text{ g}^{-1}$  (in 5 M  $\text{HNO}_3$ ), respectively. Complete isolation of Pu(IV) ions by phosphorus sorbents 1–3 is obtained after 2 h.

#### 3.2.2. Filled fibrous sorbents

The 'filled' fibrous complexing sorbents POLYORGS 4-n with 3(5)-methylpyrazole groups and POLYORGS 17-n with 1,3(5)- dimethylpyrazole groups, which possess the anion exchanger properties, were tested for the Pu solution. We used also an anion exchanger with quaternary ammonium groups in the form of 'filled' fibrous material (AV-17-n). Only Pu

Table 1  
Separation factors of Pu(IV) from other elements ( $V:m = 100 \text{ cm}^3 \text{ g}^{-1}$ ;  $\tau_c = 2 \text{ h}$ ; 5 M  $\text{HNO}_3$ )

Radionuclides	Separation factors of Pu(IV) from other elements	
	POLYORGS-4-n	POLYORGS-17-n
Am(III)	$10^6$	$10^6$
Eu(III)	$10^6$	$10^2$
U(VI)	$10^6$	$0.75 \times 10^2$
Pa(V)	$0.92 \times 10^2$	$10^2$
Np(V)	$0.57 \times 10^2$	$0.58 \times 10^2$
Tc(VII)	$0.92 \times 10^2$	$0.74 \times 10^2$
Cs(I)	$10^6$	$3 \times 10^2$

among other actinide elements is completely sorbed by these 'filled' fibre sorbents from nitric acid solutions at 1–5 M within 10-min contact at 20 °C. The distribution coefficients of Pu (IV) ( $K_d^{\text{Pu}}$ ) were determined as  $1.5 \times 10^3$ ,  $10^3$ , and  $9 \times 10^2 \text{ cm}^3 \text{ g}^{-1}$  by POLYORGS 17-n, 4-n and AV-17-n, respectively. The values of  $K_d^{\text{Pu}}$  were not changed in the presence of  $\text{NaNO}_3$  concentration up to 1 M. For stripping of Pu(IV), we used 0.5–1.0M  $\text{HNO}_3$  solutions. Species of Am(III), Eu(III), U(VI), Pa(V), Np(V), Tc(VII), and Cs(I) were badly or not sorbed at all by these materials. The separation factors of Pu(IV) from other elements ( $f = K_d^{\text{Pu}}/K_d^{\text{M}}$ ) are listed in Table 1.

The distribution coefficients concerning the pertechnetate ion Tc(VII) for sorption by fibrous 'filled' sorbents from acid, neutral and basic solution were measured. AV-17-n and POLYORGS-17-n quantitatively isolates Tc from low acidic as well as from neutral and alkaline media. Investigation of the sorption degree as a function of time showed that the sorption process is almost finished in 10–20 min at room temperature. Technetium (VII) desorbed with 3 M  $\text{HNO}_3$  solutions. The measured  $K_d^{\text{Tc}}$  are listed in Table 2. The maximum of Tc sorption by fibrous sorbents AV-17-n and POLYORGS 17-n takes place for solutions with pH about 3–5 and in 0.1 M NaOH. Distribution coefficients are decreasing with increasing the acid concentration in the solution from 0.001 to 0.5 M  $\text{HNO}_3$  and from 0.1 to 1 M NaOH.

## 4. Conclusion

The results obtained show that 'filled' fibrous sorbents POLYORGS can be used for the isolation of plutonium from nitric acid solutions and for its separa-

Table 2  
Distribution coefficients ( $K_d$ ) for Tc(VII) sorption from solutions  
( $V:m = 100 \text{ cm}^3 \text{ g}^{-1}$ ;  $\tau_c = 2 \text{ h}$ )

Solution	Sorbents	
	AV-17-n	POLYORGS-17-n
HNO <sub>3</sub> (M)		$K_d$
10 <sup>-3</sup>	$3.7 \times 10^{-4}$	$1.0 \times 10^{-3}$
10 <sup>-2</sup>	$1.3 \times 10^{-4}$	$2.5 \times 10^{-3}$
0.1	$1.2 \times 10^{-3}$	$2.2 \times 10^{-3}$
0.2	670	300
0.5	380	200
3.0	< 1	< 1
[NaOH] (M)		$K_d$
0.1	$1.0 \times 10^{-3}$	300
1.0	900	–
[NaNO <sub>3</sub> ] (M)		$K_d$
0.1	860	450

tion from other elements. POLYORGS can be used also for concentration of technetium from low acidic and alkaline solutions. ‘Filled’ fibrous sorbents possess good filter capacity and fast kinetic properties provided by fibrous properties and by small-size filler particles.

For TRU elements, in comparison with the extraction capacity of O2ADECMP and well-known phosphorous-containing compounds, the following ratio has been obtain:  $D_{Am}(\text{TBP}):D_{Am}(\text{dialkylmethylphosphanates}):D_{Am}(\text{O2ADECMP}):D_{Am}(\text{diphenyldibutyl(carbamoylmethyl) phosphine oxide}) = 1:5 \times 10^1:2.5 \times 10^4:5 \times 10^4$ . For Tc(VII), the best extractant is O2ADECMP.

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