



Bifunctional Amidophosphonate Molecules for Uranium Extraction in Nitrate Acidic Media

A. Artese, Sandrine Dourdain, N. Felines, Guilhem Arrachart, N. Boubals, P. Guilbaud, S Pellet-Rostaing

► To cite this version:

A. Artese, Sandrine Dourdain, N. Felines, Guilhem Arrachart, N. Boubals, et al.. Bifunctional Amidophosphonate Molecules for Uranium Extraction in Nitrate Acidic Media. Solvent Extraction and Ion Exchange, 2020, 38 (7), pp.703-718. <10.1080/07366299.2020.1790527>. <hal-03084432>

HAL Id: hal-03084432

<https://hal.science/hal-03084432v1>

Submitted on 22 Dec 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

1
2 **Bifunctional Amidophosphonate Molecules for Uranium Extraction in Nitric**
3 **Media**

4 ARTESE A.^{1,2}, DOURDAIN S.^{1*}, FELINES N.¹, ARRACHART G.¹, BOUBALS
5 N.², GUILBAUD P.², PELLET-ROSTAING S.¹

6 ¹ ICSM, Univ Montpellier, CEA, CNRS, ENSCM, Marcoule, France

7 ² CEA, DES, ISEC, DMRC, Univ Montpellier, Marcoule, France

8

1 *corresponding author: sandrine.dourdain@cea.fr

2

Bifunctional Amidophosphonate Molecules for Uranium Extraction in Nitric Media

Abstract

Bifunctional amidophosphonate derivatives, already known as efficient ligands in uranium extraction from phosphoric media, have been evaluated and compared to the conventional tri-n-butyl phosphate (TBP) for uranium extraction from nitric medium. The efficiency of U extraction and its selectivity towards competing elements such as Th, Zr, Mo, Fe and V was evaluated with various ligand structures. It was found that extractant molecules containing a monosaponified phosphonate moiety instead of phosphonate moieties are less effective and selective. Furthermore, it was observed that alkylation of the methylene bridge linking the two functional groups prevent the formation of precipitates during the uranium loading. Effects of acidity as well as ligand concentration were also investigated to estimate the loading capacity of the molecules. More detailed stoichiometry and transfer energy were further determined by the slope analysis method and a thermodynamic study. The possible uranium recovery from the organic phase has finally been demonstrated thanks to stripping steps at low nitric acid concentration.

Keywords: Solvent extraction, bifunctional extractant, uranium extraction, nitric media

Introduction

The refining plants of natural uranium concentrates rely on a solvent extraction process to produce uranium at so-called "nuclear" purity. Purification of uranium is obtained from yellow cake thanks to an organic phase containing the well-known extractant molecule tri-n-butyl phosphate (TBP).^[1] This organic phase is further washed to recover pure uranium which is exploited to produce 10% of the annual global electricity consumption.^[2] Despite the extensive application of TBP at industrial scale, it is still of research interest to find optimized and highly efficient systems. Higher selectivity towards Zr or Mo, optimized loading capacity, and a minimized extractant loss due to solubilization in aqueous phase are some of the targeted optimizations. Several research groups have proposed alternatives to TBP,^[3-5] among them

monoamide derivatives^[6-9] exhibit high potential as well as carbamides which have been studied very recently.^[10-11]

Another approach consists of designing multifunctional molecules, various multi-functional compounds have shown promising properties, for example, iminomethylenediphosphonic acids (phosphorus and nitrogen functions)^[12] or amidosulfoxide structures (sulfur and nitrogen functions)^[13] have been proposed for uranium extraction and purification from diluted or concentrated nitric acid solutions. Taking into account the potential of this approach, a new series of N, P bifunctional extractants was patented and showed excellent properties in nitric media in terms of affinity for uranium extraction.^[14]

N,P bifunctional extractants such as carbamoylalkylphosphonates involving an amido and a phosphorus functionality and especially the butyl-1-[N,N-bis(2-ethylhexyl)carbamoyl]nonyl phosphonic acid, called DEHCNPB, have shown unprecedented extraction properties for uranium from phosphoric media.^[15-19] So far, DEHCNPB efficiency has never been evaluated for uranium extraction from nitric media, and the patented N, P bifunctional family has not been investigated in the literature for this media. In the present study, two amidophosphonates, are therefore studied and compared to both DEHCNPB and TBP as reference extractants. As illustrated in Figure 1, these two molecules differ by the alkylation of the methylene bridge between the amido and the phosphonate functions:

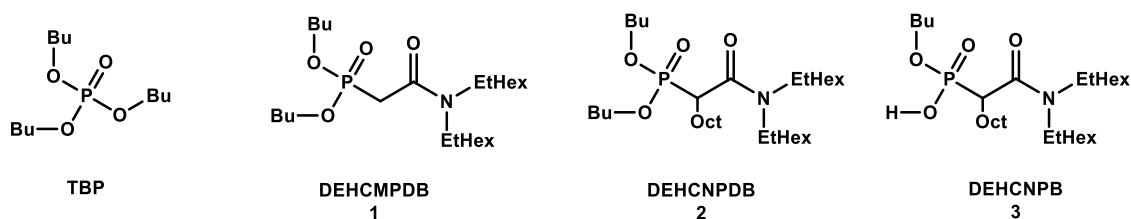


Figure 1. Structure of extractants TBP, DEHCMPDB (1), DEHCNPDB (2), and DEHCNPB (3) involved in this study.

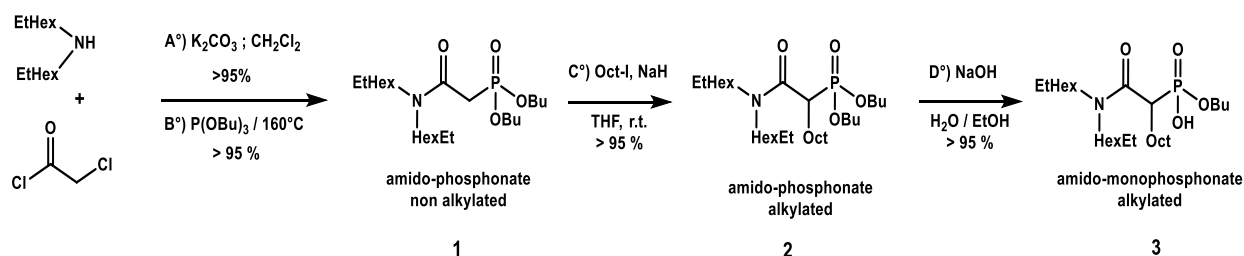
In this work, the influence of the molecular design of these N,P bifunctional molecules through the presence of alkyl chains, and the saponification of the phosphonate function are studied and correlated with their extraction efficiency. A comparative study was conducted on their selective extraction properties for U(VI) towards several competitors and the parameters of the

extraction processes (loading capacity, solubility in the aqueous phase, thermodynamic behavior and their back-extraction properties).

Materials and methods

Synthesis of amidophosphonate

Amidophosphonates were synthesized as described in references.^[15-16] The synthesis is illustrated in Scheme 1.



Scheme 1. Synthesis of amidophosphonate extractant involved in this study

Butyl-1-[N,N -bis(2-ethylhexyl)carbamoyl]nonyl phosphonic acid **3** (DEHCNPB) was synthesized in four steps with an overall yield of 81%.

- Amidation (step A) of N,N -ethylhexylamine with chloroacetyl chloride in the presence of K_2CO_3 in dichloromethane afforded an amide intermediate.
- Subsequently this intermediate is engaged in an Arbusev reaction (step B) with tributylphosphite to afford, with an overall yield of 90%, the Dibutyl N,N di(2-ethylhexyl)carbamoylmethylphosphonate (DEHCMPDB) named extractant **1** in the following.

- C-alkylation of extractant **1** (step C) using 1-iodooctane and sodium hydride in order to introduce an octyl group on the methylene bridge afforded the Dibutyl *N,N* di(2-ethylhexyl)carbamoylnonylphosphonate (DEHCNPDB) with an overall yield of 86% (extractant **2**).
- The corresponding amido-monophosphonate (extractant **3**) was finally obtained by mono-saponification with an aqueous sodium hydroxide solution (step D).

Extraction experiments

The organic phases were prepared by dissolving each extractant in n-dodecane. Aqueous solutions at desired acidity were obtained using uranyl nitrate, thorium nitrate ($\text{Th}(\text{NO}_3)_4$), iron nitrate ($\text{Fe}(\text{NO}_3)_3$), molybdenum oxide (MoO_3), zirconyl nitrate ($\text{ZrO}_2(\text{NO}_3)_2$) in their salt form (from Sigma Aldrich), and vanadium from Inductively Coupled Plasma ICP standard from SCP Science (aqueous solution of NH_4VO_3 1000 $\mu\text{g/mL}$ in HNO_3 4%). The desired concentrations were prepared by dilution in ultrapure water (MilliQ, Millipore, 18 $\text{M}\Omega\cdot\text{cm}^{-1}$). Acidities (HNO_3 0.1 to 8 M) were adjusted with 69% nitric acid. Solvent extraction experiments were carried out in 2 or 15 mL vials.

Organic phases were pre-equilibrated with an aqueous phase at the same acidity as the extraction step without cations in a thermostated shaker (Infor-ht® ecotron) at 25°C and 400 rpm for 30 min. The volume ratio of organic to aqueous phases was $\text{O/A}=1/3$. The concentration of nitric acid was kept constant for the extraction experiments carried out thereafter. The aqueous and organic phases were separated by centrifugation at 19017 rcf for 10 min (Rotina 380R or Eppendorf centrifuge 5417R).

The pre-equilibrated organic phases were then contacted with an equal volume of aqueous acidic stock solution of cations ($\text{O/A} = 1$) in a thermostated shaker at 25°C and 400 rpm for 1 h, (this time is sufficient to reach thermodynamic equilibrium).^[14] Phases were separated after centrifugation at 19017 rcf for 10 minutes. The acid concentration in the aqueous and organic phases before and after extraction was analyzed by titration with NaOH 0.1M or 0.01M (Fluka analytical) using a Metrohm 809 Titrando.

The concentrations of metals in aqueous phase were measured by inductively coupled plasma/atomic emission spectroscopy (ICP/OES Spectro Arcos - AMETEK Materials

Analysis). The ICP calibration samples were prepared from 1000 ± 4 mg/L uranium, thorium, iron, molybdenum, zirconium and vanadium standard solution (SCP Science PlasmaCal). Uncertainties relating to the metal concentration were determined by repeated measurement of different samples of the same concentration. These uncertainties were estimated to be of the order of $\pm 5\%$.

As commonly defined in liquid-liquid extraction, the distribution coefficient D_M of an element M corresponds to the ratio between the concentrations of this element in the organic and aqueous phases at equilibrium. The metal concentration in the organic phase, $[M]_{org}$, was estimated by the difference between the initial concentration in the aqueous phase, $[M]_{aq,ini}$, and the concentration at equilibrium, $[M]_{aq,eq}$, such as the following relation for a volume ratio of organic to aqueous phases $O/A=1$:

$$D_M = [M]_{org}/[M]_{aq} = ([M]_{aq,ini} - [M]_{aq,eq})/[M]_{aq,eq} \quad (1)$$

Additionally, the separation factor for a specific metal towards another metal is defined by the ratio of the distribution coefficient such as:

$$SF_{M1/M2} = D_{M1}/D_{M2} \quad (2)$$

The concentrations of the elements in the organic phase were also confirmed after a back-extraction step. The previous organic phase loaded with cations was contacted with a stripping aqueous solution typically a HNO_3 0.05 M acidic solution. When the back-extraction is total, the concentration of the element in the aqueous phase is equal to the concentration in the initial loaded organic phase. The efficiency of the back-extraction was estimated thanks to ICP/AES.

The amount of organic phase transferred in the aqueous phase was determined by measuring the Total Organic Content (TOC) using a Shimadzu TOCVCSH analyser based on a $680^\circ C$ combustion catalytic oxidation/NDIR method.

Results and discussion

Extraction studies

Separation factors

The efficiency of amidophosphonate **1**, **2** and **3** to selectively extract uranium from an aqueous phase containing competitive metals was compared to TBP. The extraction profile of the extractants was established for U(VI), Fe(III), Mo(VI), V(III), Zr(IV) and Th(IV), which are metals potentially present in uranium refining solutions.

Extraction experiments were carried out by contacting an equal volume ($V_{\text{org}} = V_{\text{aq}}$) of a 4 M nitric acid aqueous phase consisting of a 1 mM of each cation (U(VI), Fe(III), Mo(VI), V(III), Zr(IV) and Th(IV)) with an organic phase containing 0.2 M of extractants in dodecane. The results are summarized in Table 1 for the distribution coefficients and in Figure 2 for the separation factors for the extraction of U(VI).

Table 1. Distribution coefficients for **1**, **2**, **3** and TBP compound diluted at 0.2 M in dodecane

| | extractant | | | |
|-----------------|------------|------|------|-------|
| | 1 | 2 | 3 | TBP |
| D _U | 22 | 16 | 238 | 5.2 |
| D _{Th} | 9.4 | 0.35 | 492 | 0.13 |
| D _{Zr} | 2.5 | 0.08 | 162 | >0.01 |
| D _V | 0.01 | 0.01 | 0.16 | >0.01 |
| D _{Mo} | 1.2 | 1 | 30 | 0.95 |
| D _{Fe} | 0.01 | 0.01 | 0.58 | >0.01 |

Aqueous phase: [U]=[Th]=[Zr]=[Mo]=[V]=[Fe]=1 mM, [HNO₃]=4 M.

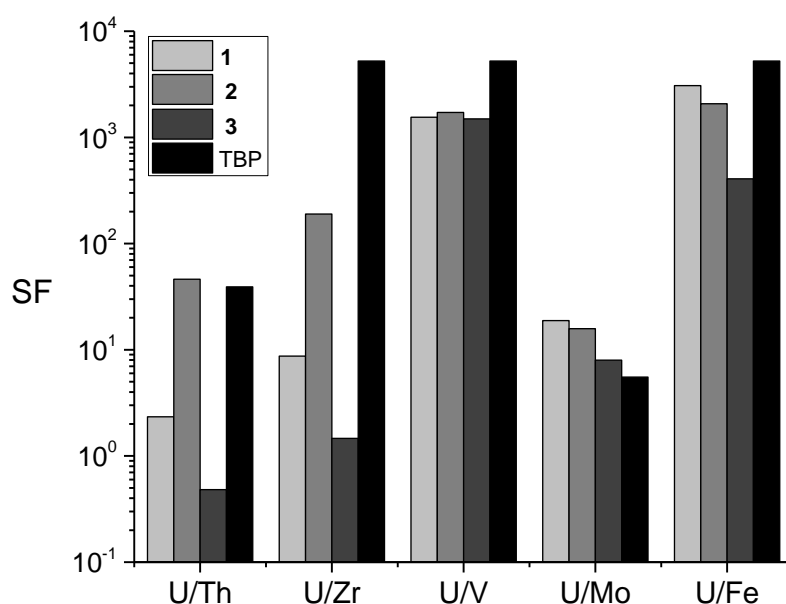


Figure 2. Extraction result for compounds **1**, **2**, **3** and TBP diluted at 0.2 M in dodecane - Aqueous phase:

$[U]=[Th]=[Zr]=[Mo]=[V]=[Fe]=1\text{mM}$, $[HNO_3]=4\text{ M}$ – separation factors

As shown in Table 1 and Figure 2, extractant **3** exhibits the highest distribution coefficients for all the elements, leading to poor separation factors for U towards Th, Zr and Mo. However, when the unsaponified amidophosphonates **1** and **2** are used, the extraction of competitive metals is much lower and comparable to those achieved with TBP, while the distribution coefficient for uranium is much higher ($D_U > 16$ for amidophosphonate compared to 5.24 for TBP).

These results show that the unsaponified amidophosphonates **1** and **2** display interesting features for the specific extraction of uranium (VI). At the same time, extractant **3** shows low separation factors and high distribution coefficients (which suggests potential issues for back extraction), indicating that it cannot be considered for a uranium refining process in nitric media.

Subsequently, the extraction capacities and the parameters of the extraction processes of the two amidophosphonates **1** and **2** have been compared to TBP. The influence of the alkyl chain grafted on the methylene bridge has been studied with regards to the solubility in the aqueous phase and the uranium loading capacity.

Extractant solubility in the aqueous phase

Solubility of extractants **1** and **2** in aqueous phase was evaluated by contacting an organic phase containing 0.5 M of the extractant in dodecane, with an aqueous phase of 4 M nitric acid with A/O = 3. After centrifugation, the organic and aqueous phases were separated and the Total Organic Carbon concentration (TOC) of the aqueous phase was measured by COT meter. Table 2 shows the mass percentages of carbon solubilized in the aqueous phase obtained from total organic carbon concentration analysis. The solubility of each extractant was determined by taking into account the volume ratio involved, the concentration and molar mass of the extractant and by considering that dodecane solubility is negligible.

Table 2. Solubility of the extractant molecules in the aqueous phase

| Extractant | [C] _{aq} (g/L) | Mass loss (%) | [L] _{aq} (mM) |
|---|-------------------------|---------------|------------------------|
| TBP (0.5 M in dodecane)* | | | 0.6* |
| Extractant 1 (0.5 M in dodecane) | 0.141 ± 0.007 | 0.27 | 0.45 ± 0.01 |
| Extractant 2 (0.5 M in dodecane) | 0.044 ± 0.002 | 0.065 | 0.11 ± 0.01 |

*data for TBP extrapolated from literature^[20]

As expected, due to the presence of a lipophilic alkyl chain on the methylene bridge it appears that the mass loss of extractant **2** is lower than for extractant **1**. This difference in solubility is coherent with higher lipophilicity due to the alkylation of the molecule, log P = 11 vs. 7.63, respectively, for extractants **2** and **1** (log P estimated from ACDlab2015 - Percepta software). In comparison to data obtained from literature^[20], extractants **1** and **2** have lower solubility than TBP, with an interesting result for extractant **2**.

It should be noticed that the carbon concentration measured in the aqueous phase may come from degradation products of the extractants as well as from impurities. However, the analyses after pre-equilibration and/or successive contact suggests that the carbon concentration probably does not come from impurities. A degradation study of the molecules **1** and **2** as well as of the solubility of the possible degradation products should be performed in the future.

Influence of uranium (VI) loading on uranium extraction

The uranium (VI) loading capacity of the extractants was investigated by extraction experiments carried out contacting the organic phases (0.2 M of extractant **1**, **2** or TBP in dodecane) with increasing concentrations of uranium from 10 to 300 mM in 4 M nitric acid.

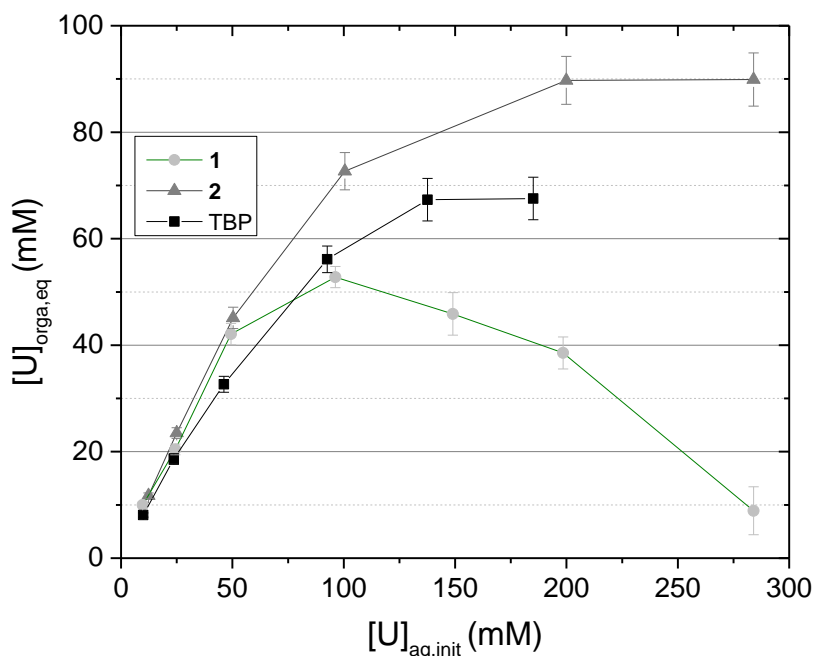


Figure 3. Loading uranium extraction isotherm- Aqueous phase: [U] = 10 mM to 300 mM, [HNO₃] = 4 M; Organic phase: **1**, **2** or TBP extractant at 0.2M in dodecane; (V_{org} = V_{aq}).

The loading capacity of extractant **1** in dodecane reached 52 mM when the aqueous phase used had a concentration of 100 mM in uranium and decreased for higher concentration because of the formation of precipitates. This result demonstrates the importance of the alkyl chain in order to prevent the apparition of precipitates.

As plotted in Figure 3 up to 90 mM (> 21 g/L) of uranium(VI) can be loaded into the organic phase when the extractant **2** is used. At its maximum loading capacity with 0.2M of extractant **2** in dodecane, neither third-phase nor precipitate formation were observed. From these results, an extractant/U molar ratio of about two is estimated at saturation in these conditions, which suggests that two molecules of extractant **2** are necessary to extract uranium(VI) into the organic phase at saturation. This result was correlated by applying the slope analysis method which enables determining complementary information regarding the number of extractant molecules in the extracted complex.

Therefore, extractant **2** allows a higher loading capacity than TBP (70 mM in the same conditions). This measured value is also consistent with the relationship experimentally found by *B. Narasimha Murty et al.* with TBP diluted in kerosene^[21] :

$$Y = 3.9753 X + 0.10143 \quad (3)$$

where Y represents the concentration of uranium saturation in g/L and X the volume percentage of TBP in the organic phase. From this equation and considering our operating conditions, a uranium saturation concentration of 77 mM in the organic phase can be assumed.

Thermodynamic studies

Slopes analysis

To analyze the effect of the concentration on the extraction efficiency, a range of extractant concentrations was engaged in the same extraction conditions. The concentration in extractant **1**, **2** or TBP was varied from 0.025 to 0.2 M. The organic phase was subsequently contacted with an aqueous phase containing 1 mM of U(VI) in 4 M nitric acid media. The logarithm of the distribution coefficient of uranium is plotted as a function of the logarithm of free extractant concentration in Figure 4.

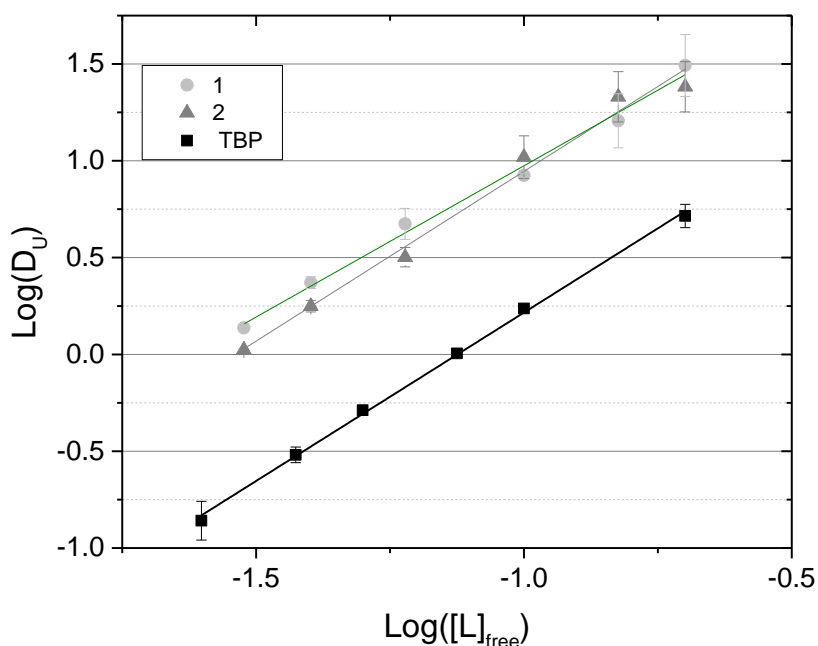


Figure 4. Slopes analysis of uranium extraction as a function of free ligand concentration

Logarithm of the distribution ratio of uranium (VI) as a function of free extractant $[L]_{\text{free}}$:

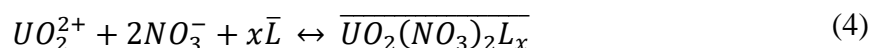
$$\log D_U = f(\log[1]): y = 1.505(\pm 0.026)x + 2.432(\pm 0.033), R^2 = 0.999$$

$$\log D_U = f(\log[2]): y = 1.736(\pm 0.063)x + 2.667(\pm 0.096), R^2 = 0.995$$

$$\log D_U = f(\log[\text{TBP}]): y = 1.726(\pm 0.036)x + 1.947(\pm 0.041), R^2 = 0.998$$

Aqueous phase: $[U] = 1 \text{ mM}$, $[\text{HNO}_3] = 4 \text{ M}$; Organic phase: **1**, **2** or TBP extractant from 0.025 to 0.2 M in dodecane; ($V_{\text{org}} = V_{\text{aq}}$), 25°C.

Considering a solvation mechanism of extraction with TBP, **1** and **2**, uranium extraction can be described by the following equation:



where x represents the number of extractants required for the transfer of one uranyl from the aqueous phase to the organic phase. The overbar refers to species in the organic phase, and the absence of the overbar denotes aqueous species.

$$K_{ex} = \frac{[\overline{UO_2(NO_3)_2L_x}]}{[NO_3^-]^2 \cdot [UO_2^{2+}] \cdot [\bar{L}]^x} \cdot \frac{\bar{\gamma}_{UO_2(NO_3)_2L_x}}{\bar{\gamma}_L^x \cdot \gamma_{UO_2^{2+}} \cdot \gamma_{NO_3^-}^2} \quad (5)$$

If the ratio of activity coefficients is considered constant (which is acceptable in such diluted solutions and with a constant nitric acid concentration), the following equation can be established:

$$[\bar{L}]_{free}^x = D_U \cdot \frac{1}{K_{ex} \cdot [NO_3^-]^2} \quad (6)$$

Considering a constant nitrate concentration, log-log plots of distribution ratios vs. total concentration of the extractant indicate the number of free extractants in the extracted complex (Figure 4).

$$\log(D_U) = x \log([\bar{L}]_{free}) + \log(K_{ex}) + 2\log([NO_3^-]) \quad (7)$$

The $[\bar{L}]_{free}$ can be calculated from the ligand concentration after subtracting the part of extractant complexed with uranium and the part of ligand complexed with nitric acid:

$$[\bar{L}]_{free} = [\bar{L}]_{ini} - x \cdot [U]_{orga} - [HNO_3]_{orga} \quad (8)$$

Acid titration demonstrated that very little nitric acid was extracted into the organic phase, therefore the free ligand concentration was obtained from the following equation:

$$[\bar{L}]_{free} = [\bar{L}]_{ini} - x \cdot [U]_{orga} \quad (9)$$

Concentrations of free extractants were calculated by iteration considering x values from 1 to 5 with the assumption that the fraction of extractants protonated or associated with nitric acid can be neglected.

The plot of the logarithm of distribution ratio is linear with the logarithm of the concentration of extractant with a slope between 1.5 and 1.75. It suggests that uranium is similarly extracted by the three molecules investigated. The stoichiometry of complexation between the extractant and uranium is expected to be 2:1. For extractant **2**, this result is consistent with the molar ratio obtained at saturation. Also, these values are similar to those that can be encountered in the literature for this type of bifunctional molecule in the context of the extraction of uranium from phosphoric acid.^[22] The value found for TBP is also in agreement with that reported by Stas and coworkers.^[23]

Temperature dependency of uranium extraction

Uranium distribution ratio was determined for various temperatures from 25 to 55°C at 4 M of nitric acid containing 1 mM of U(VI) and with 0.2 M of extractant in dodecane. The results point out the exothermic nature of the extraction process with a decreasing D-value with increasing temperature for each extractant.

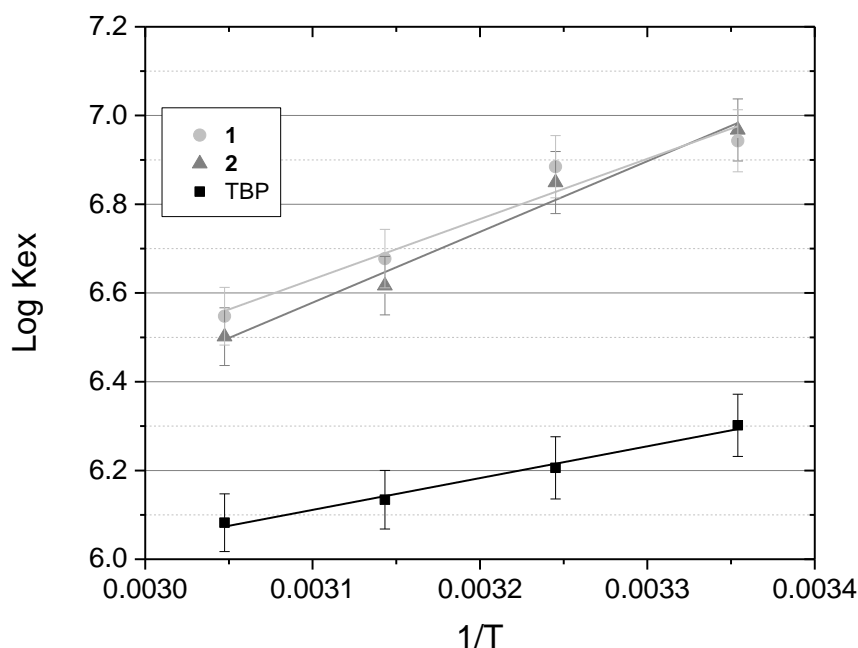


Figure 5. Influence of the temperature on uranium extraction (25 – 55 °C).

Logarithm of the distribution ratio D_U as a function of the reverse of the temperature T :

$$\log K_{ex}(1) = f(1/T): y = 1364(\pm 202) x + 2.400(\pm 0.647); R^2 = 0.958$$

$$\log K_{ex}(2) = f(1/T): y = 1594(\pm 161) x + 1.635(\pm 0.514); R^2 = 0.980$$

$$\log K_{ex}(TBP) = f(1/T): y = 714(\pm 53) x + 3.898(\pm 0.170); R^2 = 0.989$$

Aqueous phase: $[U] = 1 \text{ mM}$, $[HNO_3] = 4 \text{ M}$; Organic phase: **1**, **2** or TBP extractant at 0.2 M in dodecane; ($V_{org} = V_{aq}$).

Uranium extraction was measured for various temperatures to estimate different thermodynamic parameters, which can provide trends regarding the complexation of U with the various extractants.

If we consider the direct proportionality between D_U and K_{ex} , van't Hoff's law enables calculation of the different free enthalpies related to the extraction of uranium.

$$\ln K_{ex} = -\frac{\Delta H_{ext}^0}{R} \cdot \frac{1}{T} + \frac{\Delta S_{ext}^0}{R} \quad (10)$$

The logarithm plot of the distribution coefficient vs. the inverse of the absolute temperature (Figure 5) produces a straight line function, from which enthalpy can be calculated with the slope of the linear regression plot. The value of the thermodynamic parameters (ΔH , ΔS , and ΔG) are provided in the Table 3.

Table 3. Thermodynamic parameters (ΔH , ΔS , and ΔG) for the extraction of uranium with **1**, **2** and TBP extractants

| | ΔH (kJ/mol) | ΔS (J/mol/K) | ΔG (kJ/mol) | | |
|------------|---------------------|----------------------|---------------------|-------------------|-------------------|
| | | | 313 K | 323 K | 333 K |
| 1 | -11.34 ± 1.68 | 19.95 ± 5.38 | -17.59 ± 3.36 | -17.79 ± 3.42 | -17.98 ± 3.47 |
| 2 | -13.25 ± 1.34 | 13.59 ± 4.27 | -17.51 ± 2.68 | -17.64 ± 2.72 | -17.78 ± 2.76 |
| TBP | -5.94 ± 0.44 | 32.41 ± 1.41 | -16.08 ± 0.88 | -16.40 ± 0.90 | -16.73 ± 0.91 |

Aqueous phase: [U] = 1 mM, [HNO₃] = 4 M; Organic phase: **1**, **2** or TBP extractant at 0.2 M in dodecane; (V_{org} = V_{aq}).

Negative values of free enthalpies indicate that each compound reacts spontaneously to extract uranium through an exothermic reaction. Also, the Gibbs free energy values ($-\Delta G$) for the extractants follow the order: $-\Delta G(\mathbf{1}) \geq -\Delta G(\mathbf{2}) > -\Delta G(\text{TBP})$, which suggests that uranium extraction is thermodynamically more favorable for the amidophosphonates than for TBP. Furthermore, the similar values obtained for the amidophosphonates **1** and **2** show that the complexes formed with the two bifunctional extractants have a similar stability.

Stripping of uranium

Influence of the nitric acid concentration in the aqueous phase

The effect of nitric acid concentration on the uranium extraction was investigated for all three extractants. Extractions were carried out using organic phases containing 0.2 M of extractants and with aqueous phases containing 5 mM of uranium(VI) at nitric acid concentrations ranging from 0.1 to 8 M.

Figure 6 shows uranium distribution ratio as a function of nitric acid concentration. For the three extractants tested, distribution values increase sharply with low nitric acid concentrations and reach a saturation plateau. No difference is observed between extractants **1** and **2**, and both amido-phosphonates exhibit higher distribution ratios than TBP over the whole range of nitric acid tested. Figure 6 also shows a clear correlation between nitric acid concentration and

extraction efficiency, which is in accordance with a solvating mechanism during the extraction. At low acidity the distribution coefficient of uranium is lower than one, suggesting a possible efficient back-extraction with a decrease of concentration in nitric acid.

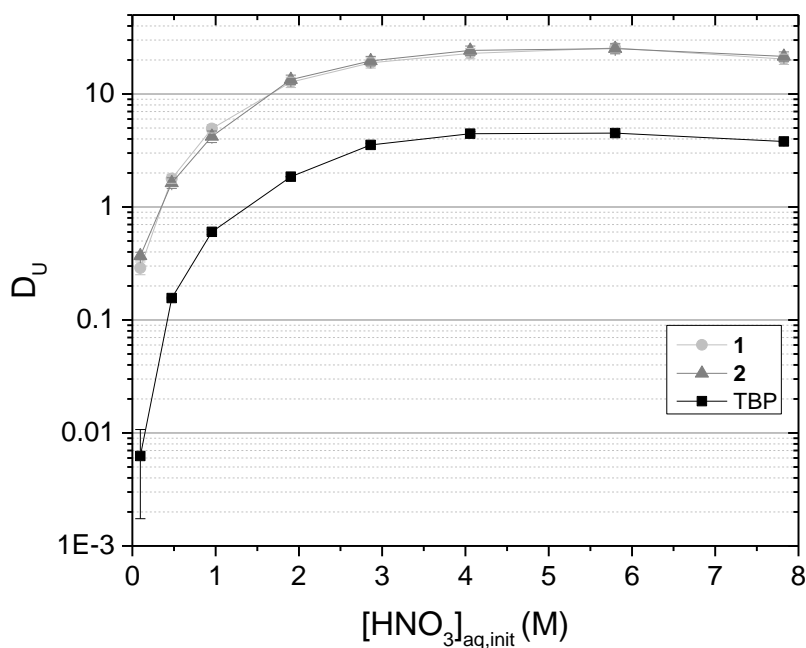


Figure 6. Uranium distribution coefficient versus the initial acidity in aqueous phase – aqueous phase: [U] = 5 mM with 0.1 M to 8 M of nitric acid; organic phase **1**, **2** or TBP extractant at 0.2 M in dodecane.

Uranium back-extraction by nitric acid

Given the low extraction performance of the compounds at low nitric acid concentration, the possibility of carrying out the back-extraction step was investigated for the purpose of quantitatively stripping uranium from the organic phases. After the extraction step (0.2 M of extractant in dodecane was contacted with 4 M nitric acid solution containing 5 mM of uranium) the loaded organic solution was then engaged in the back-extraction step which was performed by three successive contacts of the organic phase with 0.05 M HNO₃. Figure 7 shows the uranium concentration in organic phase as a function of the number of nitric acid back-extractions. The results highlight that the uranium concentrations in organic phases gradually decrease after the different back-extraction steps from uranium concentration of 5 mM to less

than 2 mM. Back-extraction of uranium appears possible with a simple $[\text{HNO}_3]$ decrease, however at least two back-extraction contacts are required.

Uranium stripping appears less efficient with extractant **1** and **2** than with TBP, suggesting that the uranium complexes in the organic phase may be more stable with the amidophosphonates than with TBP. This behavior is coherent with the thermodynamic study described earlier.

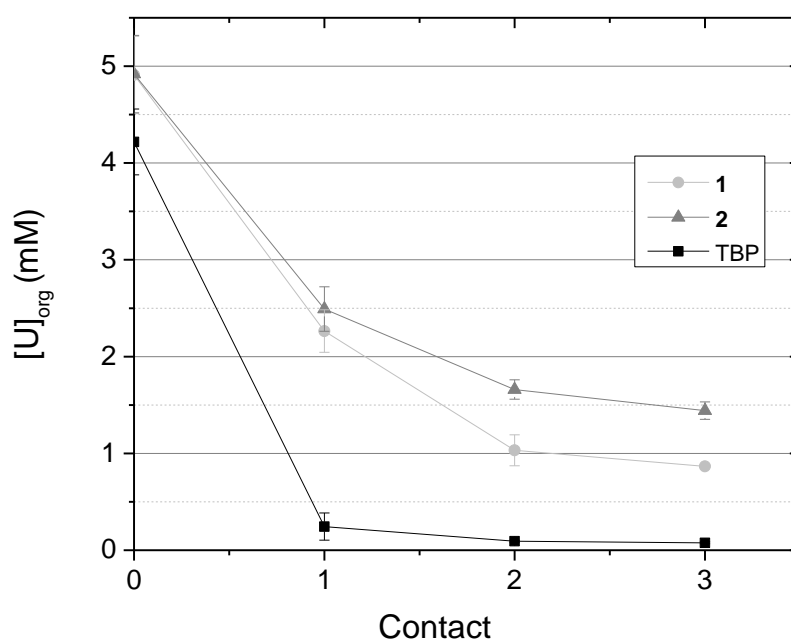


Figure 7. Back-extraction of uranium — aqueous phases: $[\text{HNO}_3]=0.05\text{M}$ O/A=1 ; organic phase: **1**, **2** or TBP extractant at 0.2 M in dodecane loaded with $[\text{U}]=5\text{ mM}$.

Conclusion

Amidophosphonates as bifunctional extractants were evaluated and compared to TBP for uranium extraction from nitric media. To exhibit high extraction efficiency and selective properties, the importance of the presence of biphosphonate moiety instead of monophosphonate was demonstrated as well as the increase of the separation factors. Indeed, it was found that the monosaponified amidophosphonate DEHCNPB (named **3**) gives poor separation factors ($\text{SF}_{\text{U/Th}}=0.5$; $\text{SF}_{\text{U/Zr}}=1.5$) compared to the unsaponified molecules, DEHCNPDB **1** and DEHCMPDB **2**. The latter molecules, which only differ by an octyl chain on their methylene bridge between their two functions, gave promising performance for the specific extraction of uranium (VI) in nitric media and were therefore studied in more detail in

this work. Preliminary extraction studies and mechanistic investigations have been performed, such as the feed acidity and extractant concentration dependencies.

It was shown for extractant **1** and **2** that the octyl chain on the methylene bridge between the functions implies a decrease of the extractant solubility in the aqueous phase and a significant increase of uranium loading capacity. This alkylation also prevents the appearance of the third phase and precipitate formation at high uranium concentration. In comparison to TBP, it was also found that the bifunctional extractant **2** improves uranium loading capacity by a factor of *ca* 1.3 and presents a slightly lower solubility in the aqueous phase.

As for TBP, uranium extraction is favored for high nitric acid concentrations, which suggests also that a back extraction at low acidity would be possible. This was confirmed in this study that up to 80% of uranium can be back extracted after 3 contacts of an organic phase (loaded with 5 mM of uranium) with an aqueous phase of 0.05 M nitric acid. The stoichiometry of the extracted complex has been determined by the slope method. As for TBP, two bifunctional molecules are necessary to extract one uranyl. The free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) were estimated showing an exothermic and spontaneous reaction for the extraction process. Extractions at different temperatures showed that the bifunctional molecules form slightly more stable complexes, which is consistent with the easier stripping of uranium in TBP.

All these results demonstrate the potential use of the alkylated amidophosphonate **2** for the selective extraction of uranium from nitric acid solution. This extractant molecule has interesting extraction properties. Indeed, it extracts more uranium than TBP, induces a very low extractant loss due to its solubility in the aqueous phase, provokes no third-phase nor precipitate problems and allows a possible back-extraction of uranium by $[\text{HNO}_3]$ decrease.

Additional experiments, in particular on real solutions, would be useful to validate such promising ligand for uranium extraction at the front end of the nuclear fuel cycle. Complementary experiments such as a study on the degradation of the extractant, on the impact of degradation products on the extraction performance, the development of a process diagram and a study on a semi-industrial scale, would however be necessary before proposing amidophosphonate **2** as an alternative to TBP for the industrial process.

Acknowledgement

This research was supported financially by CEA. We thank Beatrice Baus Lagarde, Fabrice Giusti and Bruno Corso for the help in ICP, synthesis and SAXS experiments.

395 **References**

- 396 [1] Kumar, J. R.; Kim, J. S.; Lee, J. Y.; Yoon, H. S., A Brief Review on Solvent Extraction
397 of Uranium from Acidic Solutions. *Separation and Purification Reviews* **2011** 40 77-125. DOI:
398 10.1080/15422119.2010.549760.
- 399 [2] OECD; NEA *Uranium 2016: Resources, Production and Demand* NEA No. 7301;
400 Organisation for Economic Co-operation and Development / Nuclear Energy Agency: Paris,
401 France, 2017.
- 402 [3] Shen, C. H.; Bao, B. R.; Bao, Y. Z.; Wang, G. D.; Qian, J.; Cao, Z. B., Extraction of
403 U(VI), TH(IV) and some fission-products from nitric-acid medium by sulfoxides and effect of
404 gamma-irradiation on the extraction. *Journal of Radioanalytical and Nuclear Chemistry-*
405 *Articles* **1994** 178 91-98. DOI: 10.1007/BF02068660.
- 406 [4] Wang, Y. S.; Sun, G. X.; Xie, D. F.; Bao, B. R.; Cao, W. G., Extraction of uranium(VI)
407 and thorium(IV) ions from nitric acid solutions by N,N,N',N'-tetrabutyladipicamide. *Journal of*
408 *Radioanalytical and Nuclear Chemistry-Letters* **1996** 214 67-76. DOI: 10.1007/bf02165059.
- 409 [5] Han, J. T.; Sun, G. X.; Fang, J. H.; Bao, B. R., Solvent extraction of uranium (VI) by
410 N-octanoylpyrrolidine in toluene. *Journal of Radioanalytical and Nuclear Chemistry* **1999** 241
411 215-217. DOI: 10.1007/BF02347316.
- 412 [6] Manchanda, V. K.; Pathak, P. N., Amides and diamides as promising extractants in the
413 back end of the nuclear fuel cycle: an overview. *Separation and Purification Technology* **2004**
414 35 85-103. DOI: 10.1016/j.seppur.2003.09.005.
- 415 [7] McCann, K.; Drader, J. A.; Braley, J. C., Comparing Branched versus Straight-chained
416 Monoamide Extractants for Actinide Recovery. *Separation & Purification Reviews* **2018** 47
417 49-65. DOI: 10.1080/15422119.2017.1321018.
- 418 [8] Pathak, P. N., N,N-Dialkyl amides as extractants for spent fuel reprocessing: an
419 overview. *Journal of Radioanalytical and Nuclear Chemistry* **2014** 300 7-15. DOI:
420 10.1007/s10967-014-2961-0.
- 421 [9] Condamines, N.; Musikas, C., The Extraction by N,N-Dialkylamides. II. Extraction of
422 Actinide Cations. *Solvent Extraction and Ion Exchange* **1992** 10 69-100. DOI:
423 10.1080/07366299208918093.
- 424 [10] Berger, C.; Marie, C.; Guillaumont, D.; Tamain, C.; Dumas, T.; Dirks, T.; Boubals, N.;
425 Acher, E.; Laszczyk, M.; Berthon, L., Coordination Structures of Uranium(VI) and
426 Plutonium(IV) in Organic Solutions with Amide Derivatives. *Inorganic Chemistry* **2020** 59
427 1823-1834. DOI: 10.1021/acs.inorgchem.9b03024.
- 428 [11] Berger, C.; Marie, C.; Guillaumont, D.; Zekri, E.; Berthon, L., Extraction of
429 Uranium(VI) and Plutonium(IV) with Tetra-Alkylcarbamides. *Solvent Extraction and Ion*
430 *Exchange* **2019** 37 111-125. DOI: 10.1080/07366299.2019.1630095.

- 431 [12] Bouhoun Ali, M.; Badjah Hadj Ahmed, A. Y.; Attou, M.; Elias, A.; Didi, M. A.,
 432 Synthesis under Microwave Irradiation, Characterization and Application of
 433 Alkyliminodimethylenediphosphonic Acids in Solvent Extraction of Uranium (VI). *Journal of*
 434 *Applied Sciences* **2011** 11 284-291. DOI: 10.3923/jas.2011.284.291.
- 435 [13] Gamare, J. S.; Chetty, K. V.; Mukerjee, S. K.; Kannan, S., Extraction Studies of
 436 Uranium(VI), Plutonium(IV) and Americium(III) from Nitric Acid Using the Bi-functional
 437 Carbamoyl Methyl Sulfoxide Ligands. *Analytical Sciences* **2009** 25 1167-1170. DOI:
 438 10.2116/analsci.25.1167.
- 439 [14] Pellet-Rostaing, S.; Arrachart, G.; Leydier, A.; Turgis, R.; Chapron, S. Use of
 440 bifunctional compounds with phosphonic acid / phosphonate and amino functions for extracting
 441 uranium (VI) from aqueous nitric acid solutions. FR3072824A1, 2017.
- 442 [15] Turgis, R.; Leydier, A.; Arrachart, G.; Burdet, F.; Dourdain, S.; Bernier, G.;
 443 Miguirditchian, M.; Pellet-Rostaing, S., Uranium extraction from phosphoric acid using
 444 bifunctional amido-phosphonic acid ligands. *Solvent Extraction and Ion Exchange* **2014** 32
 445 478-491. DOI: 10.1080/07366299.2014.898435.
- 446 [16] Turgis, R.; Leydier, A.; Arrachart, G.; Burdet, F.; Dourdain, S.; Bernier, G.;
 447 Miguirditchian, M.; Pellet-Rostaing, S., Carbamoylalkylphosphonates for Dramatic
 448 Enhancement of Uranium Extraction from Phosphates Ores. *Solvent Extraction and Ion*
 449 *Exchange* **2014** 32 685-702. DOI: 10.1080/07366299.2014.951279.
- 450 [17] Turgis, R.; Leydier, A.; Arrachart, G.; Burdet, F.; Dourdain, S.; Bernier, G.;
 451 Miguirditchian, M.; Pellet-Rostaing, S., Carbamoylalkylphosphonates type ligand for uranium
 452 extraction from phosphates ores. *Procedia Engineering* **2016** 138 258-266. DOI:
 453 10.1016/j.proeng.2016.02.083.
- 454 [18] Miguirditchian, M.; Bernier, G.; Pacary, V.; Balaguer, C.; Sorel, C.; Berlemont, R.;
 455 Fries, B.; Bertrand, M.; Cames, B.; Leydier, A.; Turgis, R.; Arrachart, G.; Pellet-Rostaing, S.;
 456 Mokhtari, H., Development of a new solvent extraction process based on butyl-1- N,N-bis(2-
 457 ethylhexyl)carbamoyl nonyl phosphonic acid for the selective recovery of uranium(VI) from
 458 phosphoric acid. *Solvent Extraction and Ion Exchange* **2016** 34 274-289. DOI:
 459 10.1080/07366299.2016.1169147.
- 460 [19] Leydier, A.; Arrachart, G.; Turgis, R.; Bernier, G.; Marie, C.; Miguirditchian, M.;
 461 Pellet-Rostaing, S., Recovery of uranium (VI) from concentrated phosphoric acid using
 462 bifunctional reagents. *Hydrometallurgy* **2017** 171 262-266. DOI:
 463 10.1016/j.hydromet.2017.05.008.
- 464 [20] Velavendan, P.; Ganesh, S.; Pandey, N. K.; Geetha, R.; Ahmed, M. K.; Mudali, U. K.;
 465 Natarajan, R., Studies on solubility of TBP in aqueous solutions of fuel reprocessing. *Journal*
 466 *of Radioanalytical and Nuclear Chemistry* **2013** 295 1113-1117. DOI: 10.1007/s10967-012-
 467 1945-1.
- 468 [21] Murty, A. N.; Rao, B. S. P.; Lingaiah, L.; Yadav, R. B.; Gopalan, B.; Syamsunder, S.,
 469 Determination of percentage saturation of uranium in TBP samples from uranium extraction

470 plant. *Journal of Radioanalytical and Nuclear Chemistry* **2001** 247 329-334. DOI:
471 10.1023/A:1006753618076.

472 [22] Pecheur, O.; Guillaumont, D.; Dourdain, S.; Berthon, L.; Turgis, R.; Fillaux, C.;
473 Arrachart, G.; Testard, F., Uranium Extraction by a Bifunctional Amido-Phosphonic Acid:
474 Coordination Structure and Aggregation. *Solvent Extraction and Ion Exchange* **2016** 34 260-
475 273. DOI: 10.1080/07366299.2016.1169146.

476 [23] Stas, J.; Dahdouh, A.; Shlewit, H., Extraction of uranium (VI) from nitric acid and
477 nitrate solutions by tributylphosphate/kerosene. *Periodica Polytechnica: Chemical*
478 *Engineering* **2005** 49 3-18.

List of Figures

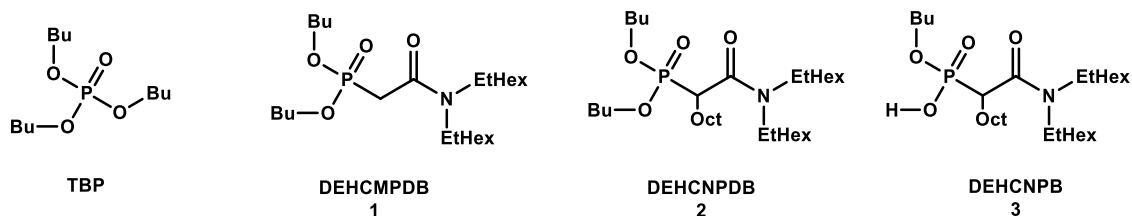


Figure 8. Structure of extractants TBP, DEHCOMPDB (1), DEHCNPDB (2), and DEHCNPB (3) involved in this study.

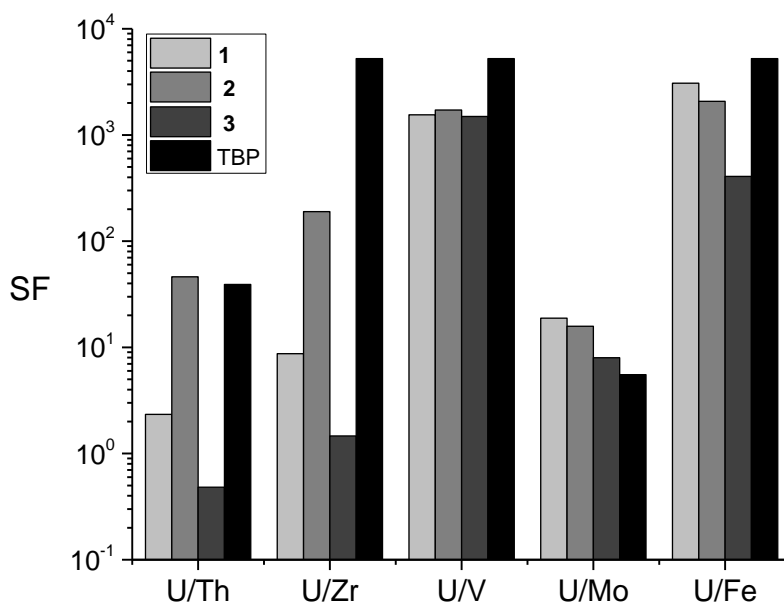


Figure 9. Extraction result for compounds 1, 2, 3 and TBP diluted at 0.2 M in dodecane - Aqueous phase:
 $[U]=[Th]=[Zr]=[Mo]=[V]=[Fe]=1\text{mM}$, $[\text{HNO}_3]=4\text{ M}$ – separation factors

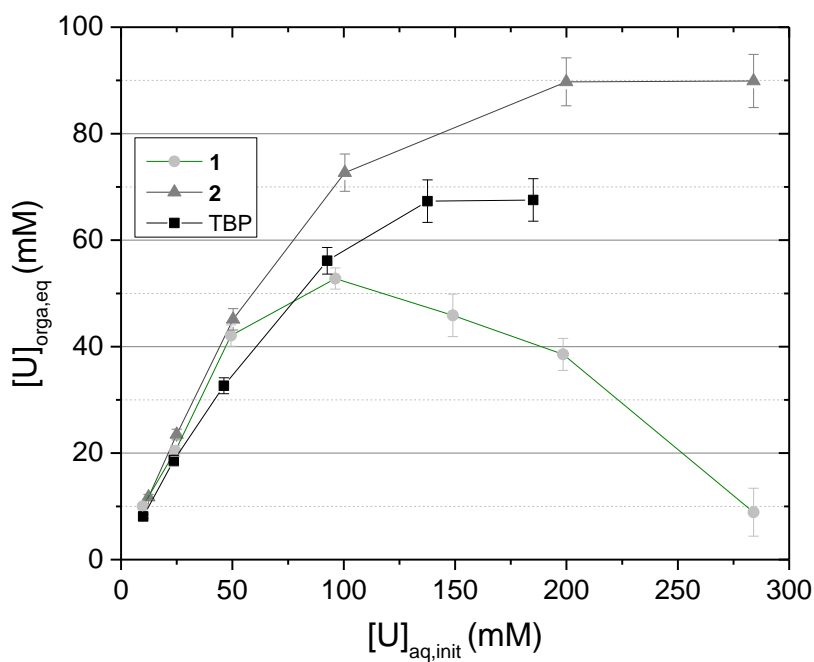


Figure 10. Loading uranium extraction isotherm- Aqueous phase: [U] = 10 mM to 300 mM, [HNO₃] = 4 M; Organic phase: 1, 2 or TBP extractant at 0.2M in dodecane; (V_{org} = V_{aq}).

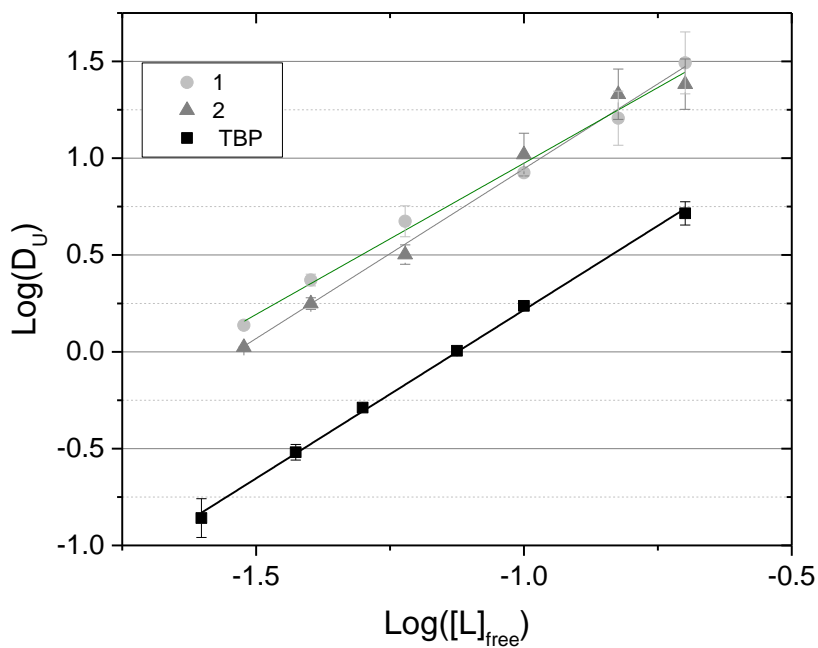


Figure 11. Slopes analysis of uranium extraction as a function of free ligand concentration

Logarithm of the distribution ratio of uranium (VI) as a function of free extractant [L]_{free}:

$$\log D_U = f(\log[1]): y = 1.505(\pm 0.026)x + 2.432(\pm 0.033), R^2 = 0.999$$

$$\log D_U = f(\log[2]): y = 1.736(\pm 0.063)x + 2.667(\pm 0.096), R^2 = 0.995$$

$$\log D_U = f(\log[\text{TBP}]): y = 1.726(\pm 0.036)x + 1.947(\pm 0.041), R^2 = 0.998$$

Aqueous phase: [U] = 1 mM, [HNO₃] = 4 M; Organic phase: 1, 2 or TBP extractant from 0.025 to 0.2M in dodecane; (V_{org} = V_{aq}), 25°C.

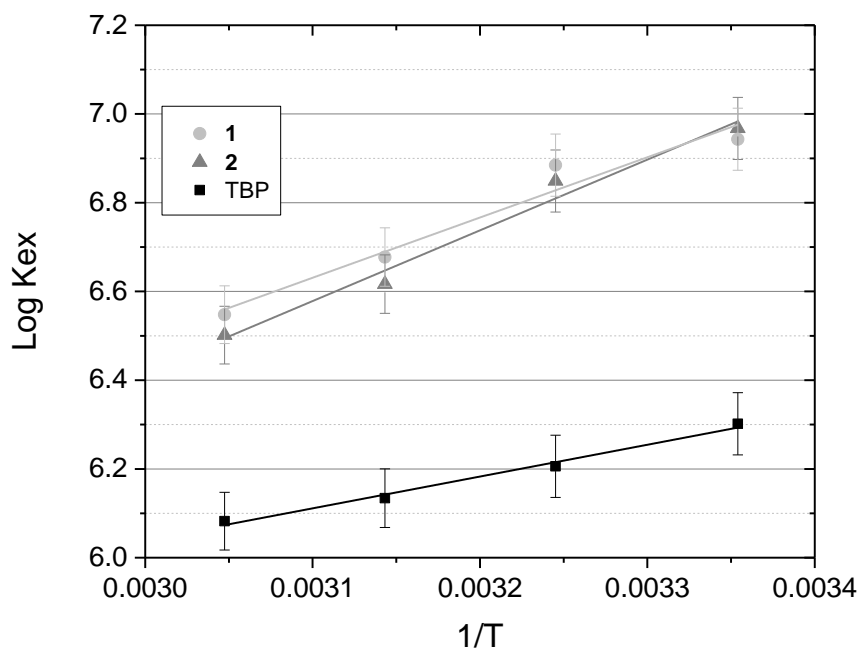


Figure 12. Influence of the temperature on uranium extraction (25 – 55 °C).

Logarithm of the distribution ratio D_U as a function of the reverse of the temperature T :

$$\log Kex(1) = f(1/T): y = 1364(\pm 202)x + 2.400(\pm 0.647); R^2 = 0.958$$

$$\log Kex(2) = f(1/T): y = 1594(\pm 161)x + 1.635(\pm 0.514); R^2 = 0.980$$

$$\log Kex(TBP) = f(1/T): y = 714(\pm 53)x + 3.898(\pm 0.170); R^2 = 0.989$$

Aqueous phase: $[U] = 1\text{mM}$, $[HNO_3] = 4\text{ M}$; Organic phase: **1**, **2** or TBP extractant at 0.2 M in dodecane; ($V_{org} = V_{aq}$).

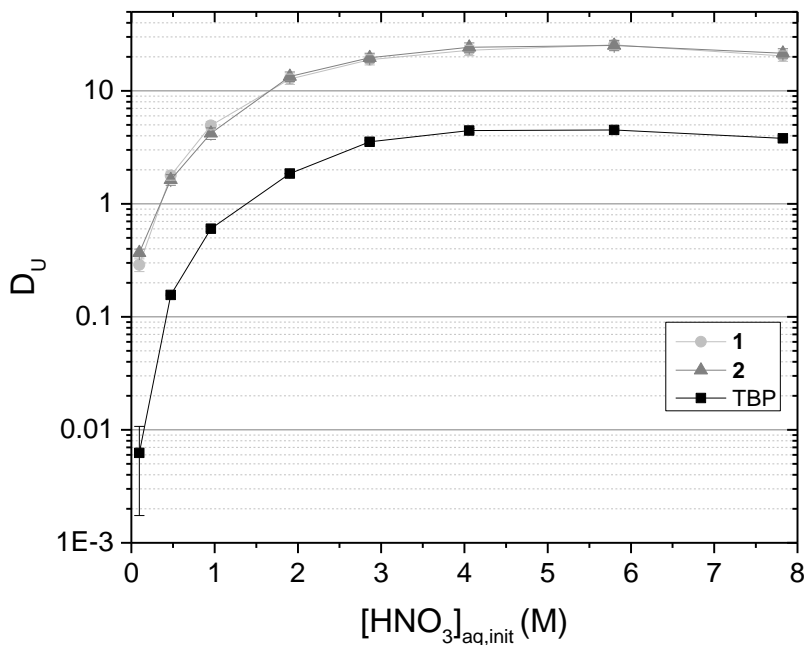
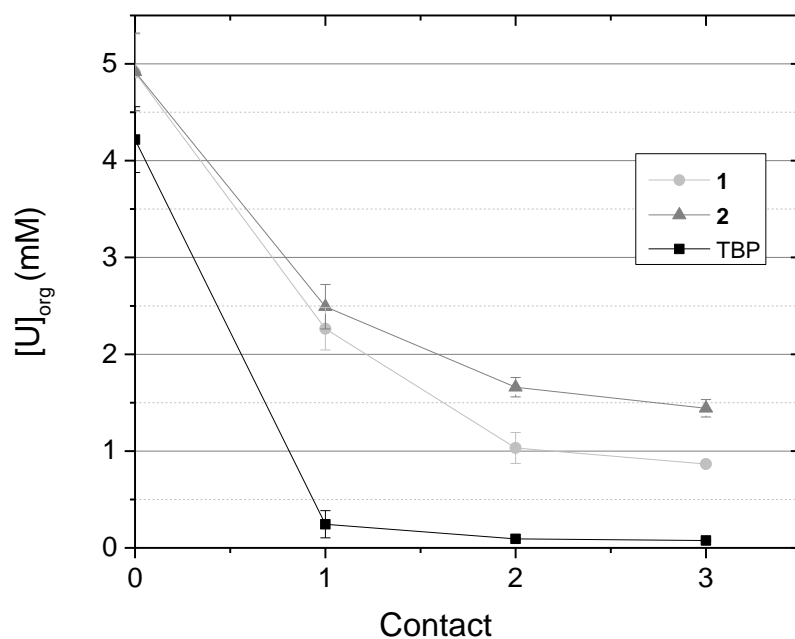


Figure 13. Uranium distribution coefficient versus the initial acidity in aqueous phase – aqueous phase: $[U] = 5\text{ mM}$ with 0.1 M to 8 M of nitric acid; organic phase **1**, **2** or TBP extractant at 0.2 M in dodecane.

518



519

520

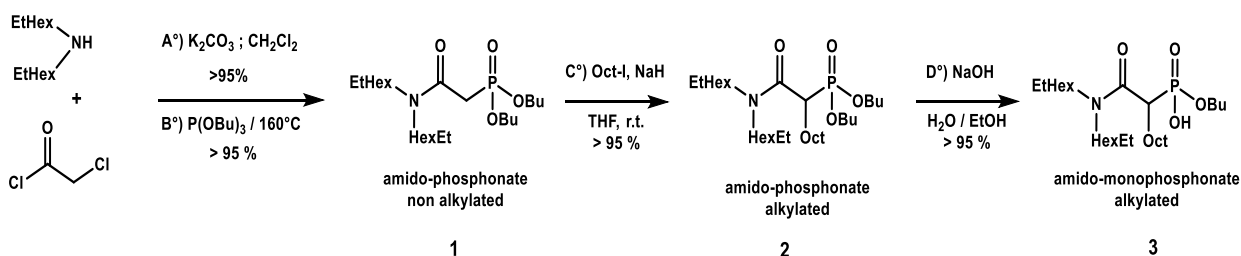
521

522

523

Figure 14. Back-extraction of uranium — aqueous phases: $[\text{HNO}_3]=0.05\text{M}$ O/A=1 ; organic phase: 1, 2 or TBP extractant at 0.2 M in dodecane loaded with $[\text{U}]=5\text{ mM}$.

List of Schemes



Scheme 1. Synthesis of amidophosphonate extractant involved in this study

List of Tables

Table 4. Distribution coefficients for **1**, **2**, **3** and TBP compound diluted at 0.2 M in dodecane

| | extractant | | | |
|-----------------|------------|------|------|-------|
| | 1 | 2 | 3 | TBP |
| D _U | 22 | 16 | 238 | 5.2 |
| D _{Th} | 9.4 | 0.35 | 492 | 0.13 |
| D _{Zr} | 2.5 | 0.08 | 162 | >0.01 |
| D _V | 0.01 | 0.01 | 0.16 | >0.01 |
| D _{Mo} | 1.2 | 1 | 30 | 0.95 |
| D _{Fe} | 0.01 | 0.01 | 0.58 | >0.01 |

Aqueous phase: [U]=[Th]=[Zr]=[Mo]=[V]=[Fe]=1 mM, [HNO₃]=4 M.

Table 5. Solubility of the extractant molecules in the aqueous phase

| Extractant | [C] _{aq} (g/L) | Mass loss (%) | [L] _{aq} (mM) |
|---|-------------------------|---------------|------------------------|
| TBP (0.5 M in dodecane)* | | | 0.6* |
| Extractant 1 (0.5 M in dodecane) | 0.141 ± 0.007 | 0.27 | 0.45 ± 0.01 |
| Extractant 2 (0.5 M in dodecane) | 0.044 ± 0.002 | 0.065 | 0.11 ± 0.01 |

*data for TBP extrapolated from literature^[20]

Table 6. Thermodynamic parameters (ΔH , ΔS , and ΔG) for the extraction of uranium with **1**, **2** and TBP extractants

| | ΔH (kJ/mol) | ΔS (J/mol/K) | ΔG (kJ/mol) | | |
|------------|---------------------|----------------------|---------------------|-------------------|-------------------|
| | | | 313 K | 323 K | 333 K |
| 1 | -11.34 ± 1.68 | 19.95 ± 5.38 | -17.59 ± 3.36 | -17.79 ± 3.42 | -17.98 ± 3.47 |
| 2 | -13.25 ± 1.34 | 13.59 ± 4.27 | -17.51 ± 2.68 | -17.64 ± 2.72 | -17.78 ± 2.76 |
| TBP | -5.94 ± 0.44 | 32.41 ± 1.41 | -16.08 ± 0.88 | -16.40 ± 0.90 | -16.73 ± 0.91 |

Aqueous phase: [U] = 1mM, [HNO₃]=4 M; Organic phase: 1, 2 or TBP extractant at 0.2 M in dodecane; (V_{org} = V_{aq}).