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

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2

3 **Bifunctional Amidophosphonate Molecules for Uranium Extraction in Nitric** 4 **Media**

6 **Abstract**

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

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

23 **Introduction**

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

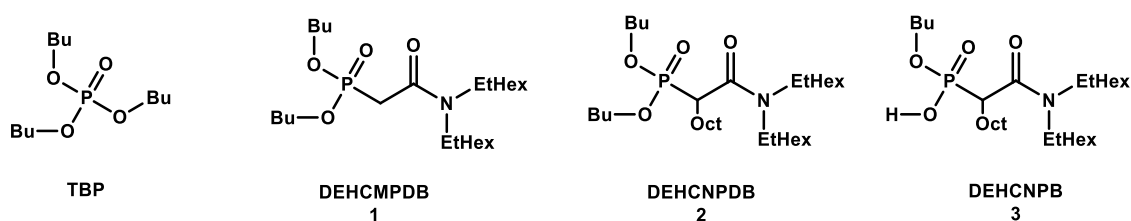
33 monoamide derivatives^[6-9] exhibit high potential as well as carbamides which have been studied
34 very recently.^[10-11]

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

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

51

52



53

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

55

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

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

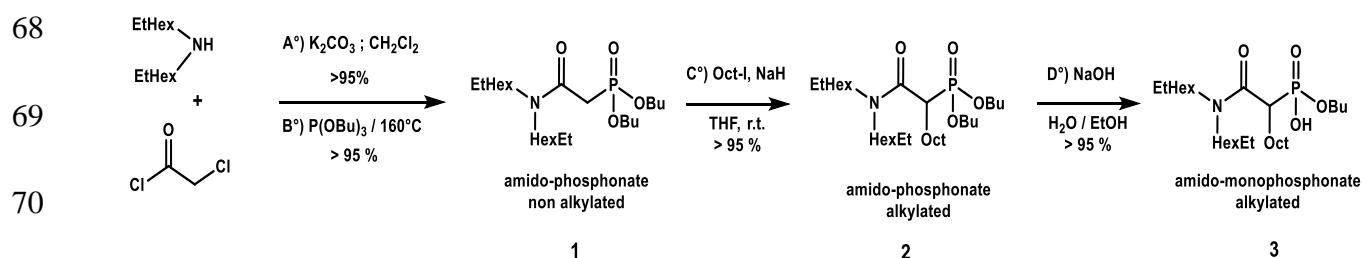
62 **Materials and methods**

63

64 **Synthesis of amidophosphonate**

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

67



75 **Scheme 1.** Synthesis of amidophosphonate extractant involved in this study

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

78

- 79
- Amidation (step A) of *N,N*-ethylhexylamine with chloroacetyl chloride in the presence
80 of K_2CO_3 in dichloromethane afforded an amide intermediate.
 - Subsequently this intermediate is engaged in an Arbuzov reaction (step B) with
81 tributylphosphite to afford, with an overall yield of 90%, the Dibutyl *N,N* di(2-
82 ethylhexyl)carbamoylmethylphosphonate (DEHCMPDB) named extractant **1** in the
83 following.
84

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

91

92 **Extraction experiments**

93 The organic phases were prepared by dissolving each extractant in n-dodecane. Aqueous
94 solutions at desired acidity were obtained using uranyl nitrate, thorium nitrate ($\text{Th}(\text{NO}_3)_4$), iron
95 nitrate ($\text{Fe}(\text{NO}_3)_3$), molybdenum oxide (MoO_3), zirconyl nitrate ($\text{ZrO}_2(\text{NO}_3)_2$) in their salt form
96 (from Sigma Aldrich), and vanadium from Inductively Coupled Plasma ICP standard from SCP
97 Science (aqueous solution of NH_4VO_3 1000 $\mu\text{g}/\text{mL}$ in HNO_3 4%). The desired concentrations
98 were prepared by dilution in ultrapure water (MilliQ, Millipore, $18 \text{ M}\Omega\cdot\text{cm}^{-1}$). Acidities (HNO_3
99 0.1 to 8 M) were adjusted with 69% nitric acid. Solvent extraction experiments were carried
100 out in 2 or 15 mL vials.

101 Organic phases were pre-equilibrated with an aqueous phase at the same acidity as the
102 extraction step without cations in a thermostated shaker (Infor-ht® ecotron) at 25°C and
103 400 rpm for 30 min. The volume ratio of organic to aqueous phases was $\text{O}/\text{A}=1/3$. The
104 concentration of nitric acid was kept constant for the extraction experiments carried out
105 thereafter. The aqueous and organic phases were separated by centrifugation at 19017 rcf for
106 10 min (Rotina 380R or Eppendorf centrifuge 5417R).

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

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

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

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

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

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

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

128 The concentrations of the elements in the organic phase were also confirmed after a back-
129 extraction step. The previous organic phase loaded with cations was contacted with a stripping
130 aqueous solution typically a HNO₃ 0.05 M acidic solution. When the back-extraction is total,
131 the concentration of the element in the aqueous phase is equal to the concentration in the initial
132 loaded organic phase. The efficiency of the back-extraction was estimated thanks to ICP/AES.

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

136

137 **Results and discussion**

138

139 *Extraction studies*

140 *Separation factors*

141

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

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

151

152 **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

153

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

154

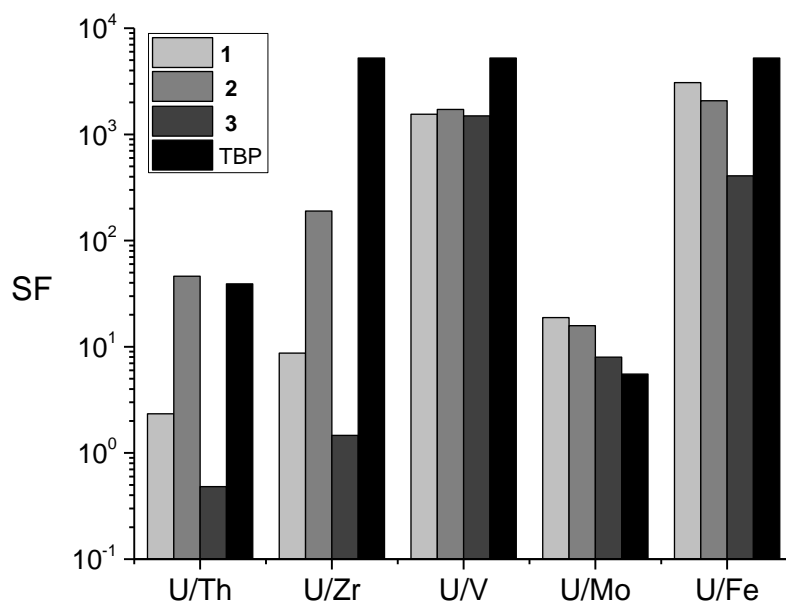


Figure 2. Extraction result for compounds **1**, **2**, **3** and TBP diluted at 0.2 M in dodecane - Aqueous phase:

$[U]=[Th]=[Zr]=[Mo]=[V]=[Fe]=1\text{mM}$, $[\text{HNO}_3]=4\text{ M}$ – separation factors

155
156
157
158

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

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

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

174

175 ***Extractant solubility in the aqueous phase***

176

177 Solubility of extractants **1** and **2** in aqueous phase was evaluated by contacting an organic phase
178 containing 0.5 M of the extractant in dodecane, with an aqueous phase of 4 M nitric acid with
179 A/O = 3. After centrifugation, the organic and aqueous phases were separated and the Total
180 Organic Carbon concentration (TOC) of the aqueous phase was measured by COT meter. Table
181 2 shows the mass percentages of carbon solubilized in the aqueous phase obtained from total
182 organic carbon concentration analysis. The solubility of each extractant was determined by
183 taking into account the volume ratio involved, the concentration and molar mass of the
184 extractant and by considering that dodecane solubility is negligible.

185

186

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

187 *data for TBP extrapolated from literature^[20]

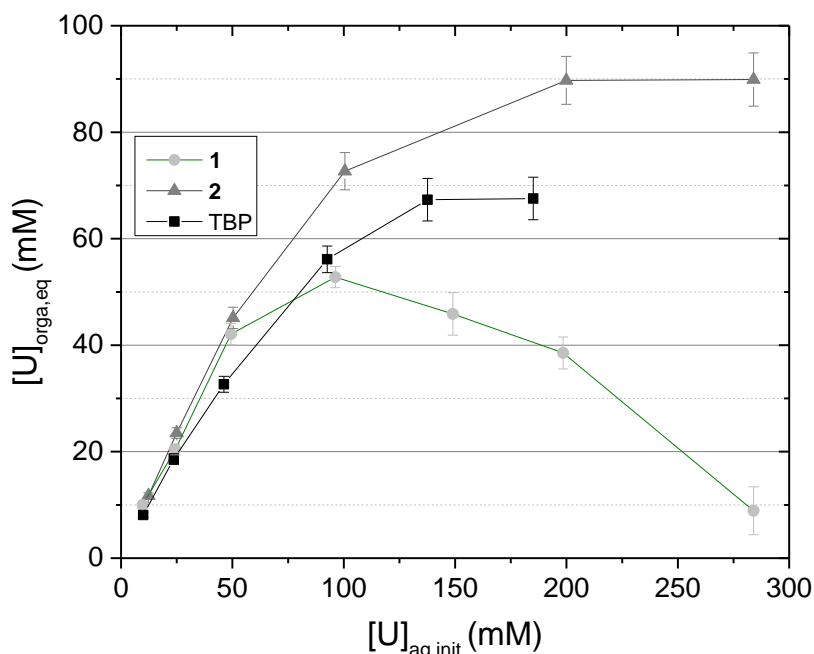
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189 As expected, due to the presence of a lipophilic alkyl chain on the methylene bridge it appears
190 that the mass loss of extractant **2** is lower than for extractant **1**. This difference in solubility is
191 coherent with higher lipophilicity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

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

200 ***Influence of uranium (VI) loading on uranium extraction***

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



204
205 **Figure 3.** Loading uranium extraction isotherm- Aqueous phase: [U] = 10 mM to 300 mM, [HNO₃] = 4 M; Organic phase:
206 **1**, **2** or TBP extractant at 0.2M in dodecane; (V_{org} = V_{aq}).
207

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

212 As plotted in Figure 3 up to 90 mM (> 21 g/L) of uranium(VI) can be loaded into the organic
213 phase when the extractant **2** is used. At its maximum loading capacity with 0.2M of extractant
214 **2** in dodecane, neither third-phase nor precipitate formation were observed. From these results,
215 an extractant/U molar ratio of about two is estimated at saturation in these conditions, which
216 suggests that two molecules of extractant **2** are necessary to extract uranium(VI) into the organic
217 phase at saturation. This result was correlated by applying the slope analysis method which
218 enables determining complementary information regarding the number of extractant molecules
219 in the extracted complex.

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

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

223
224 where Y represents the concentration of uranium saturation in g/L and X the volume percentage
225 of TBP in the organic phase. From this equation and considering our operating conditions, a
226 uranium saturation concentration of 77 mM in the organic phase can be assumed.

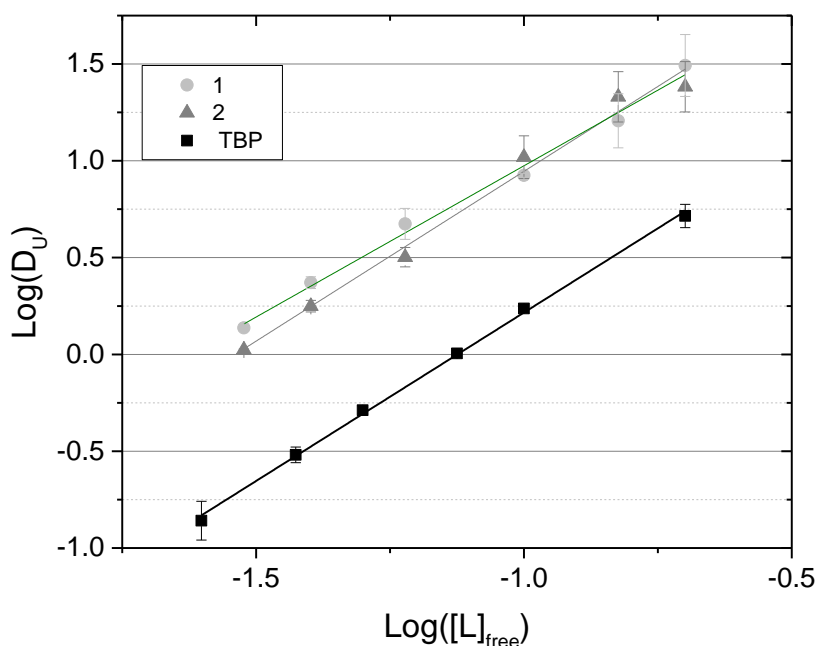
227

228 *Thermodynamic studies*

229 *Slopes analysis*

230

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



237

238

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

239

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

240

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

241

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

242

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

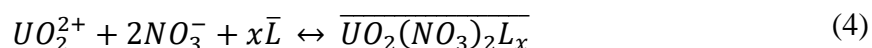
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Aqueous phase: $[U] = 1 \text{ mM}$, $[HNO_3] = 4 \text{ M}$; Organic phase: **1**, **2** or TBP extractant from 0.025 to 0.2 M in dodecane; ($V_{org} = V_{aq}$), 25°C.

244

245

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



248

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

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

252

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

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

256
 257 Considering a constant nitrate concentration, log-log plots of distribution ratios vs. total
 258 concentration of the extractant indicate the number of free extractants in the extracted complex
 259 (Figure 4).

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

260
 261 The $[\bar{L}]_{free}$ can be calculated from the ligand concentration after subtracting the part of
 262 extractant complexed with uranium and the part of ligand complexed with nitric acid:

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

263
 264 Acid titration demonstrated that very little nitric acid was extracted into the organic phase,
 265 therefore the free ligand concentration was obtained from the following equation:

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

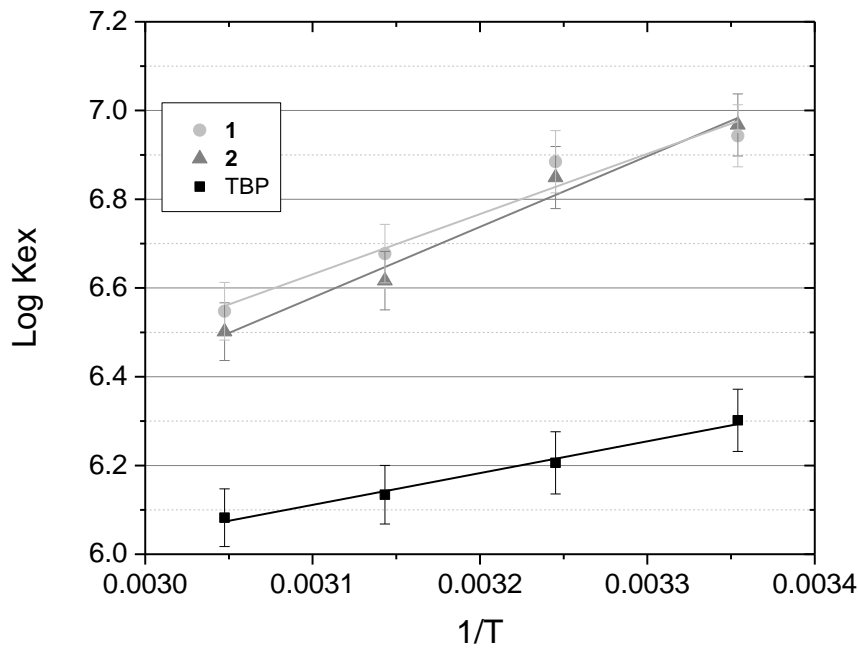
266
 267 Concentrations of free extractants were calculated by iteration considering x values from 1 to 5
 268 with the assumption that the fraction of extractants protonated or associated with nitric acid can
 269 be neglected.

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

278

279 *Temperature dependency of uranium extraction*

280 Uranium distribution ratio was determined for various temperatures from 25 to 55°C at
281 4 M of nitric acid containing 1 mM of U(VI) and with 0.2 M of extractant in dodecane. The
282 results point out the exothermic nature of the extraction process with a decreasing D-value with
283 increasing temperature for each extractant.



284

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

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

287 $\log K_{ex}(1) = f(1/T): y = 1364(\pm 202)x + 2.400(\pm 0.647); R^2 = 0.958$

288 $\log K_{ex}(2) = f(1/T): y = 1594(\pm 161)x + 1.635(\pm 0.514); R^2 = 0.980$

289 $\log K_{ex}(TBP) = f(1/T): y = 714(\pm 53)x + 3.898(\pm 0.170); R^2 = 0.989$

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

291

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

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

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

297

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

302

303 **Table 3.** Thermodynamic parameters (ΔH , ΔS , and ΔG) for the extraction of uranium with **1**, **2** and TBP
304 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

305 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}).

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

312 *Stripping of uranium*

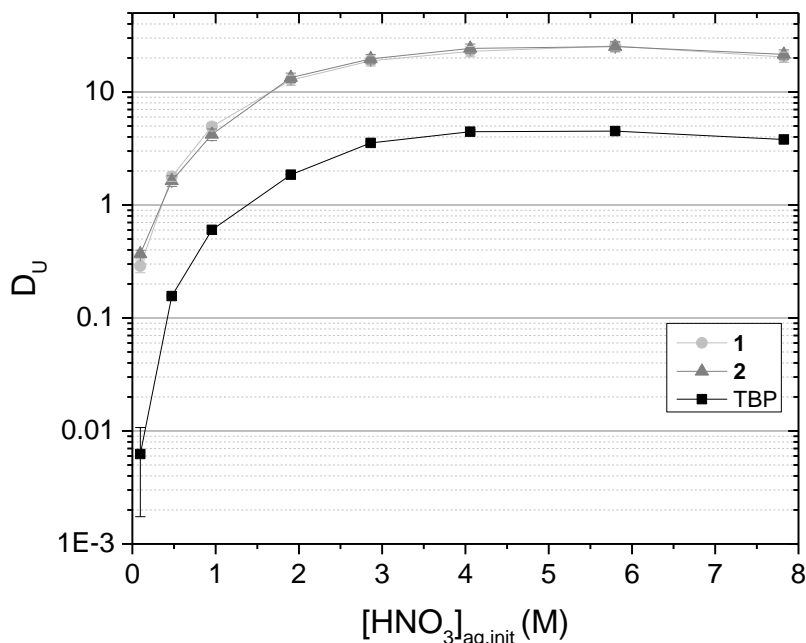
313 *Influence of the nitric acid concentration in the aqueous phase*

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

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

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

326



327
328 **Figure 6.** Uranium distribution coefficient versus the initial acidity in aqueous phase – aqueous phase: [U] = 5 mM with 0.1
329 M to 8 M of nitric acid; organic phase 1, 2 or TBP extractant at 0.2 M in dodecane.

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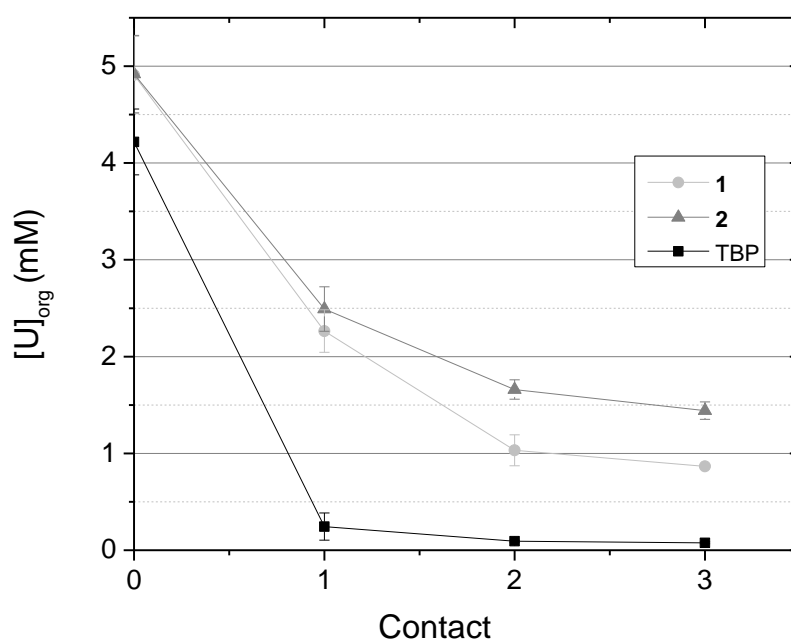
332 *Uranium back-extraction by nitric acid*

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

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

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

347



348

349 **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
350 0.2 M in dodecane loaded with $[\text{U}]=5$ mM.

351

352 Conclusion

353 Amidophosphonates as bifunctional extractants were evaluated and compared to TBP
354 for uranium extraction from nitric media. To exhibit high extraction efficiency and selective
355 properties, the importance of the presence of biphosphonate moiety instead of
356 monophosphonate was demonstrated as well as the increase of the separation factors. Indeed, it
357 was found that the monosaponified amidophosphonate DEHCNPB (named **3**) gives poor
358 separation factors ($\text{SF}_{\text{U/Th}}=0,5$; $\text{SF}_{\text{U/Zr}}=1,5$) compared to the unsaponified molecules,
359 DEHCNPDB **1** and DEHCMPDB **2**. The latter molecules, which only differ by an octyl chain
360 on their methylene bridge between their two functions, gave promising performance for the
361 specific extraction of uranium (VI) in nitric media and were therefore studied in more detail in

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

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

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

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

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

390

391 **Acknowledgement**

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393 Giusti and Bruno Corso for the help in ICP, synthesis and SAXS experiments.

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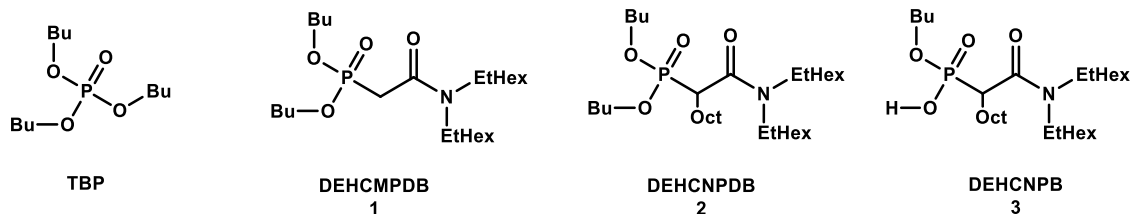
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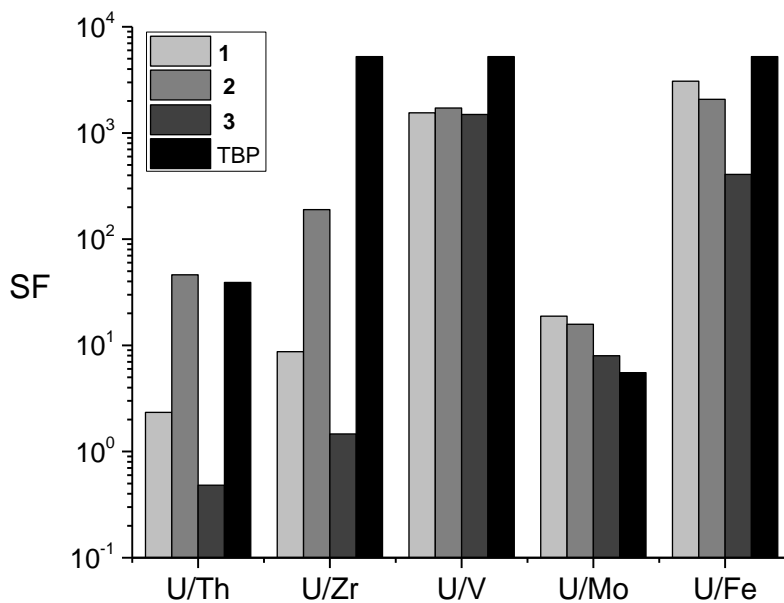
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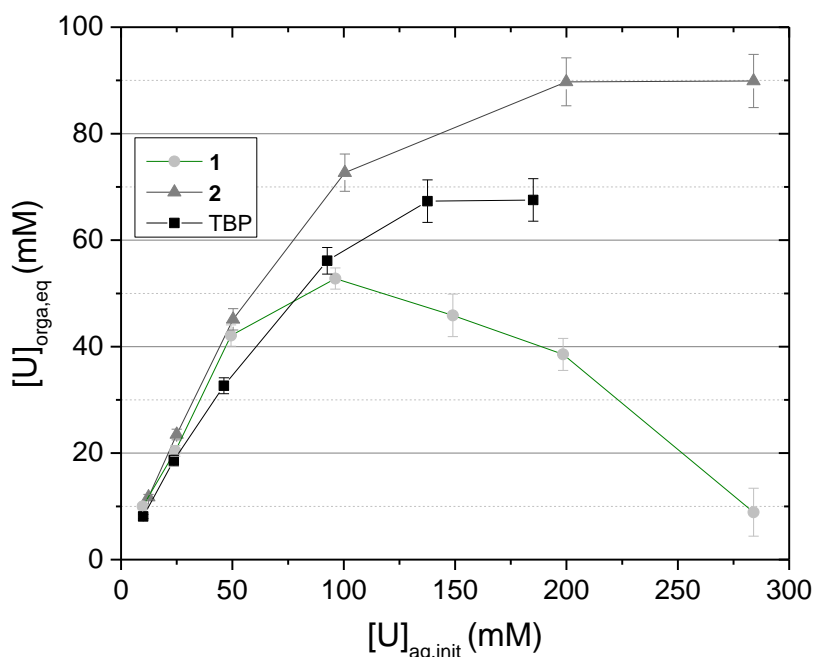
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Figure 8. Structure of extractants TBP, DEHCOMPDB (1), DEHCOMPDB (2), and DEHCOMPDB (3) involved in this study.



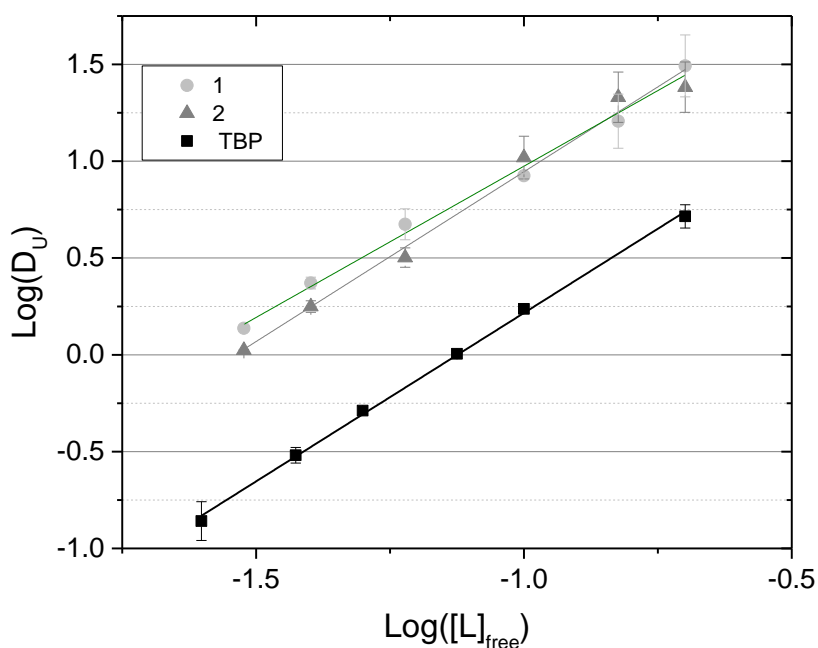
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Figure 9. Extraction result for compounds 1, 2, 3 and TBP diluted at 0.2 M in dodecane - Aqueous phase:
[U]=[Th]=[Zr]=[Mo]=[V]=[Fe]=1mM, [HNO₃]=4 M – separation factors



495

496 **Figure 10.** Loading uranium extraction isotherm- Aqueous phase: [U] = 10 mM to 300 mM, [HNO₃] = 4 M; Organic phase:
 497 1, 2 or TBP extractant at 0.2M in dodecane; (V_{org} = V_{aq}).
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500 **Figure 11.** Slopes analysis of uranium extraction as a function of free ligand concentration

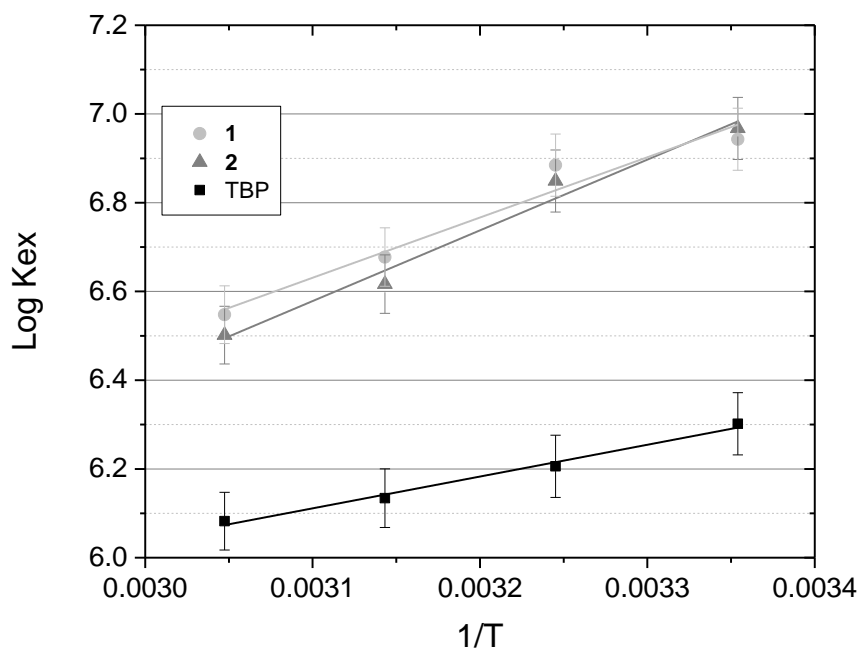
501 Logarithm of the distribution ratio of uranium (VI) as a function of free extractant [L]_{free}:

502 $\log D_U = f(\log[1]): y = 1.505(\pm 0.026)x + 2.432(\pm 0.033), R^2 = 0.999$

503 $\log D_U = f(\log[2]): y = 1.736(\pm 0.063)x + 2.667(\pm 0.096), R^2 = 0.995$

504 $\log D_U = f(\log[\text{TBP}]): y = 1.726(\pm 0.036)x + 1.947(\pm 0.041), R^2 = 0.998$

505 Aqueous phase: [U] = 1mM, [HNO₃] = 4 M; Organic phase: 1, 2 or TBP extractant from 0.025 to 0.2M in dodecane; (V_{org} =
 506 V_{aq}), 25°C.
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Figure 12. Influence of the temperature on uranium extraction (25 – 55 °C).

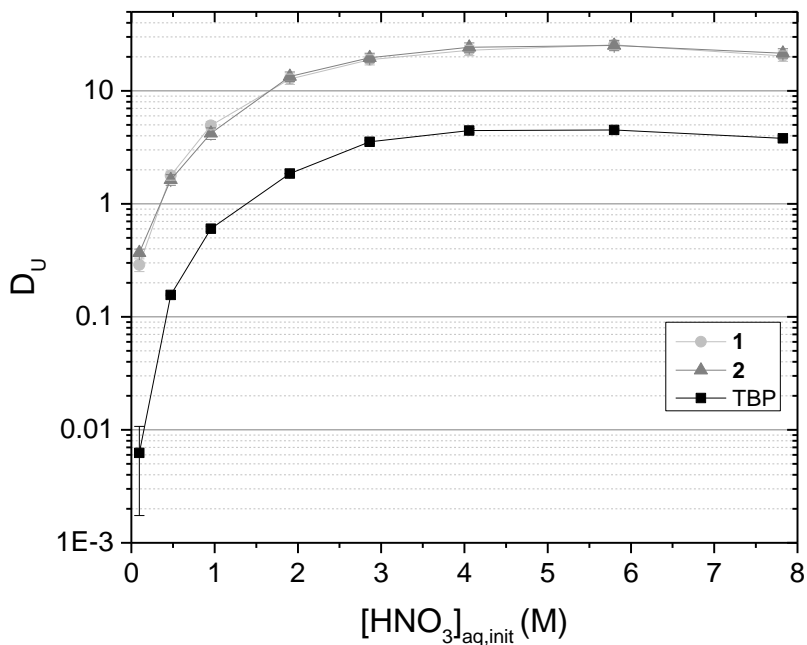
Logarithm of the distribution ratio D_U as a function of the reverse of the temperature T:

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

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

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

Aqueous phase: $[U] = 1\text{mM}$, $[\text{HNO}_3] = 4\text{M}$; Organic phase: **1**, **2** or TBP extractant at 0.2 M in dodecane; (Vorg = V_{aq}).



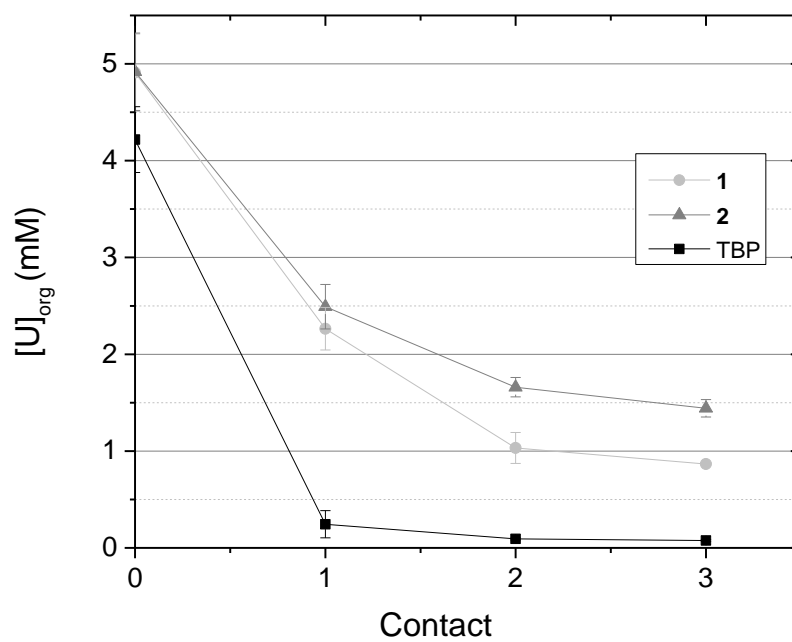
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Figure 13. Uranium distribution coefficient versus the initial acidity in aqueous phase – aqueous phase: $[U] = 5\text{mM}$ with 0.1 M to 8 M of nitric acid; organic phase **1**, **2** or TBP extractant at 0.2 M in dodecane.

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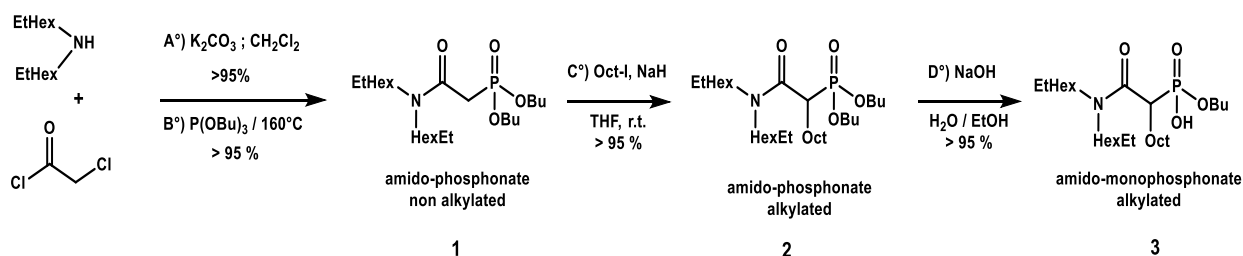
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Figure 14. Back-extraction of uranium — aqueous phases: $[\text{HNO}_3]=0.05\text{M}$ O/A=1 ; organic phase: 1, 2 or TBP extractant at 0.2 M in dodecane loaded with $[\text{U}]=5$ mM.

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]

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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

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550

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