

EXTRACTION OF LANTHANIDES AND ACTINIDES (III) BY DI-2 ETHYL
DITHIOPHOSPHORIC ACID AND DI-2 ETHYL HEXYL MONOTHIOPHOSPHO-
RIC ACID.
STRUCTURE OF THE COMPLEXES IN THE ORGANIC PHASE.

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Communication présentée à : INTERNATIONAL SOLVENT EXTRACTION CONFERENCE
(ISEC 86)

Muenchen (Germany, FR)

11-16 Sep 1986

Extraction of lanthanides and actinides (III) by di-2 ethyl hexyl dithiophosphoric acid and di-2 ethyl hexyl monothiophosphoric acid.

Structure of the complexes in the organic phase.

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To operate a trivalent actinide-lanthanide (III) group chemical separation from low pH nitric solutions we studied the extractive properties of the di-2 ethyl hexyl dithiophosphoric acid (HDEHDTP) ; this bidentate ligand which possesses a sulfur donor atom is a good extractant of soft acids [1]. We so expect a better selectivity for the actinides(III) extraction : 5f electrons have a better ability to delocalization than 4f electrons and form more covalent bounds as it has already been demonstrated by previous works in this laboratory [2].

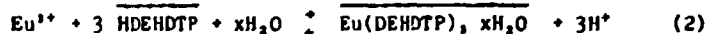
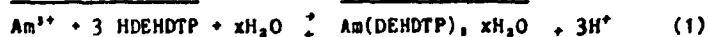
As the di-2 ethyl hexyl monothiophosphoric acid (HDEHTP) is the main by-product of the synthesis of HDEHDTP and is also the main degradation product of HDEHDTP by a phenomenon of hydrolysis [3] we also have investigated its extractive properties for trivalent actinides and lanthanides ; HDEHTP is a bidentate ligand with one oxygen donor atom and so is a better extractant for hard acids like actinides and lanthanides (III) ; but its selectivity is weak.

The addition of TBP (tri-n butyl phosphate) to HDEHDTP deals to strong synergistic organic complexes with a great selectivity for Am(III). We explicited this phenomenon. When the metal is macroconcentrated the organic complexes aggregate and form inverted micelles.

1. Extraction of Am(III) and Eu(III) trace concentrations by HDEHDTP and HDEHTP

a - extraction by the purified acid HDEHDTP

We first plotted the distribution ratio of the metals versus the pH of the aqueous phase (fig. 1) at constant concentration of the extractant. The slope is very close to 3. Then we plotted the distribution ratio of the metals versus the concentration of the extractant at constant pH. The slope is also 3 (figure 2). So the mechanism of extraction is :



$$\begin{aligned} \text{Log } K_{\text{ex}} \text{ Am(III)} &= - 7,87 \pm 0,52 \\ \text{Log } K_{\text{ex}} \text{ Eu(III)} &= - 8,28 \pm 0,4 \end{aligned}$$

The constants of extraction are weak and it confirms the lack of affinity of trivalent actinides and lanthanides for a soft base like DEHDTP[⊖]. But the weak selectivity is in favour of Am(III)

$$\frac{D \text{ Am(III)}}{D \text{ Eu(III)}} = 2.55$$

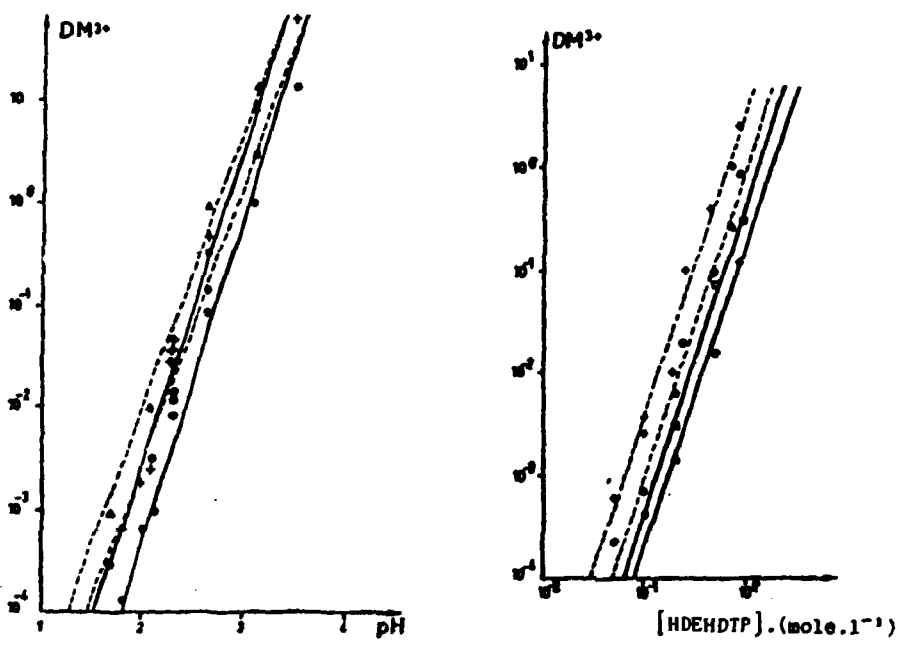


FIGURE 1 : VARIATIONS OF THE DISTRIBUTION RATIO DM^{3+} VERSUS pH.
- Aqueous phase : $[KNO_3] = [HNO_3]$ at $I = 1$.
 $[Eu(III)] : 5 \text{ g of } [HDEHTP]_1$

- Organic phase :
 + Am³⁺ [HDEHTP]₁ = 0,5 N
 ● Eu³⁺
 △ Am³⁺ [HDEHTP]₁ = 0,75 N
 ○ Eu³⁺

FIGURE 2 : VARIATIONS OF THE DISTRIBUTION RATIO OF DM^{3+} VERSUS THE CONCENTRATION OF THE EXTRACTANT HDEHTP

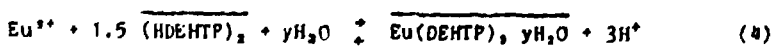
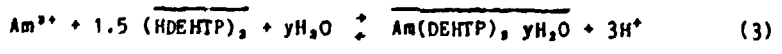
- Aqueous phase : $[KNO_3] = [HNO_3]$ at 1, $[Eu(III)] : 5 \text{ g of } [HDEHTP]_1$

- Organic phase : diluent : dodecane
 ● Eu³⁺ pH = 2,8
 + Am³⁺
 ○ Eu³⁺ pH = 2,5
 ○ Am³⁺

b - Extraction by the purified acid HDEHTP (metals as traces).

The distribution ratio of the metals versus pH at constant concentration of the extractant are plotted. Figure 3, we also plotted the distribution ratio of the metals versus the concentration of HDEHTP at constant pH, figure 4.

As the extractant is dimerized [3] the slope analysis of these curves indicates the following extraction mechanism :



Log Kex Am(III) = - 2,32 ± 0.05
 Log Kex Eu(III) = - 2,27 ± 0.05

The constants are stronger than those obtained with HDEHDTP because the hard acids Am(III) and Eu(III) have a better affinity for DEHTP[⊖] which possesses a hard oxygen donor atom. But there is no selectivity

$$\frac{D_{Am(III)}}{D_{Eu(III)}} = 0.89$$

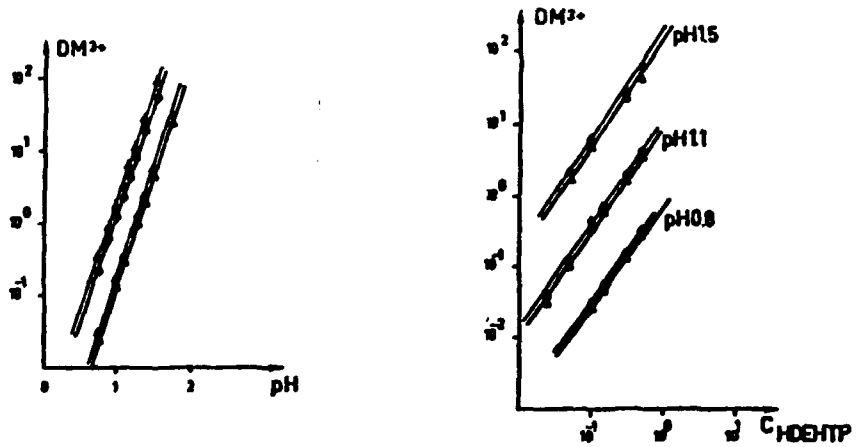


FIGURE 3 : VARIATIONS OF THE DISTRIBUTION RATIO OF DM²⁺ VERSUS pH.

- Aqueous phase : KNO₃ + HNO₃ at I = 1

Eu(III) : 5 % of [HDEHTP]₁

- Organic phase : diluent : dodecane

Δ Eu³⁺ [HDEHTP]₁ = 0,1 M.
 Δ Am³⁺

Δ Eu³⁺ [HDEHTP]₁ = 0,5 M.
 Δ Am³⁺

FIGURE 4 : VARIATIONS OF THE DISTRIBUTION RATIO OF DM²⁺ VERSUS THE CONCENTRATION OF THE EXTRACTANT

- Aqueous phase : [KNO₃] + [HNO₃] at I = 1

Eu(III) : 5 % of [HDEHTP]₁

- Organic phase : diluent : dodecane

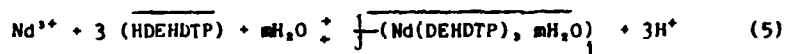
Δ Am³⁺
 Δ Eu³⁺

2. Extraction of Nd(III) in macro concentrations by raw HDEHDTP

This raw material contained at least 10 % of HDEHTP. So we plotted log D - 3 log ([HDEHTP]₀ - 3 [Nd(DEHDTTP)]₀) versus pH (figure 5). The slope indicates the number of exchanged protons [3].

The first part of the curve is the extraction of Nd(III) by HDEHTP (figure 6). The second part of the curve is the extraction of Nd(III) by HDEHTP (figure 7). The last part of the curve is the extraction by KDEHTP which does not depend on the pH.

The slope of the intermediate part of the curve very close to 3.5 (figure 5) indicates that another phenomenon takes place during the extraction. We supposed and verified that it is the aggregation of Nd(DEHTP), according to :



$$\text{with } \log D = \log K_{\text{ex}} + 3 \log([\text{HL}]_1 - 3[\text{Nd}]_{\text{org}}) + \frac{1}{j} \log J + \frac{j-1}{j} \log[\text{Nd}]_{\text{org}} + 3\text{pH} \quad (6)$$

We determined $j \approx 5$ $\log K_{\text{ex}} \approx -7$ and $m = 25$

The aggregation of the organic complex stabilizes it.

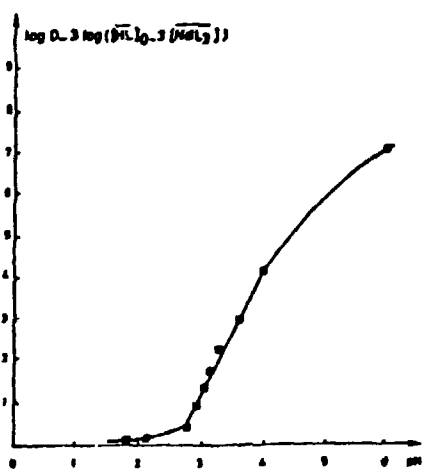


FIGURE 5 : VARIATION OF LOG D VERSUS pH
- Aqueous phase : $[\text{Nd(III)}] = 0,27 \text{ M}$

- Organic phase : $\text{con} [\text{HDEHTP}] = 0,595 \text{ M/dodecane}$

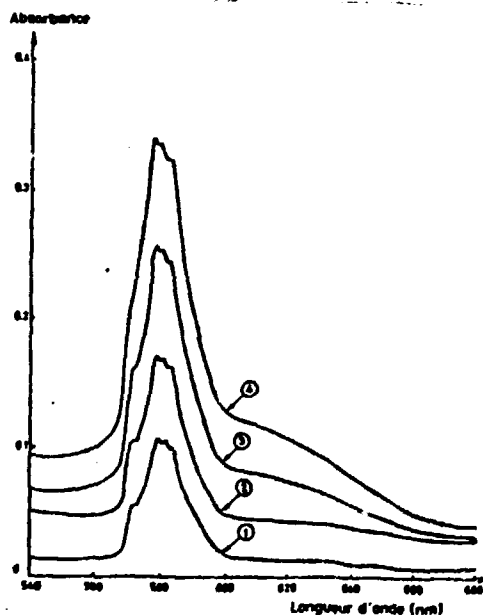


FIGURE 6 : U.V-visible spectra of the organic phase after extraction (pH aq. < 3)
before extraction ; aqueous phase : $[\text{Nd(III)}] = 0,27 \text{ M.l}^{-1}$

organic phase : $\text{con} [\text{HDEHTP}] = 0,595 \text{ M.l}^{-1}$ / dodecane

after extraction : aqueous phase : pH = 1,45 (1), 1,82 (2), 2,13 (3), 2,95 (4).

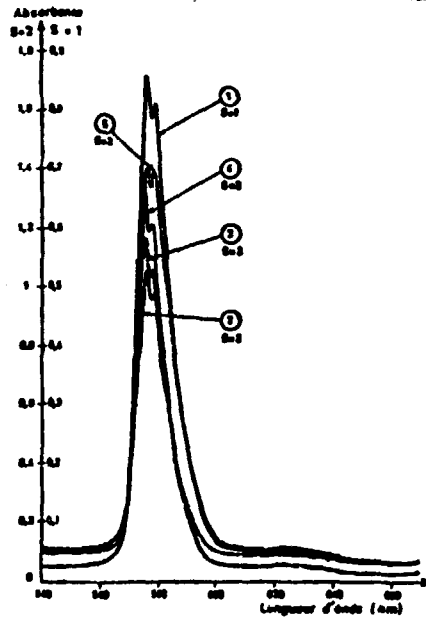


FIGURE 7 : U.V. VISIBLE SPECTRUM OF THE ORGANIC PHASE AFTER Ni(III) EXTRACTION
 (pH aq > 3)
 before extraction : aqueous phase : [Ni(III)] = 0,27 M.l⁻¹
 organic phase : raw [Ni(III)] = 0,585 M.l⁻¹ / dodecane
 after extraction : aqueous phase : pH 3,1 (1), 3,3 (2), 3,5 (3), 3,6 (4), 3,8 (5).

3. Extraction of 4f and 5f ions by a synergistic mixture

When the complex $[\overline{\text{Nd}(\text{DEHDTP})}_2]_j$ is formed we add one equivalent of TBP to the organic phase. We can observe two phenomena (see also figure 8).

- no NO_3^- ion is extracted
- water is expelled from the organic phase
- the U V-visible spectrum shows a fine electronic structure with a strong nephelauxetic effect and a strong enhancement of the molar absorption coefficient ($\epsilon = 5$ (575 nm) $\rightarrow \epsilon = 22,5$ (585 nm)).

M

M

This phenomenon has already been observed with the charge transfer complex of Eu(III) with HDEHDTP [4] it is well explained by the substitution and the elimination of water molecules from the inner coordination sphere of Nd(III); this induces a shortening of the S-metal bond; this shortening [5] [6] reveals the better ability of 5f electrons to form covalent bonds; consequently we can observe the higher stability of the organic complex Am(DEHDTP),TBP compared to Eu, complex (see figure 9) $\frac{D_{Am(III)}}{D_{Eu(III)}} = 25$

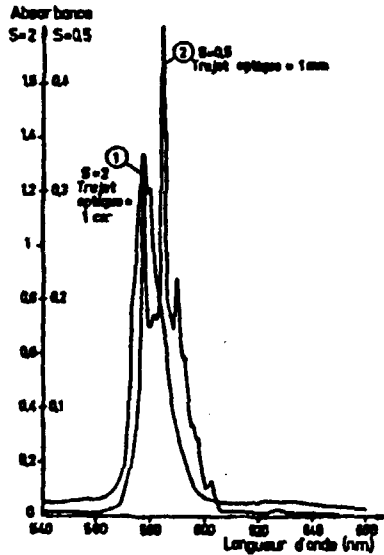


FIGURE 8 : U.V.-VISIBLE SPECTRUM OF THE ORGANIC PHASE AFTER EXTRACTION.

before extraction Aqueous phase : Nd(III) = 0,27 N. l.⁻¹
 Organic phase : [HDEHDTP] = 0,585 N. l.⁻¹
 + TBP = 0,2 N. l.⁻¹

after extraction Aqueous phase : pH = 5,6

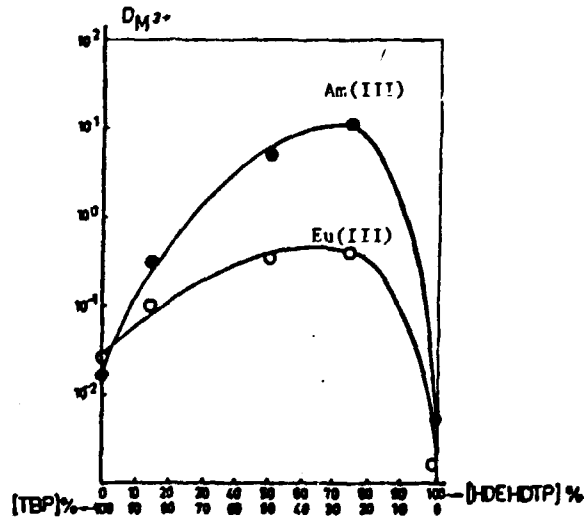


FIGURE 9 : VARIATIONS OF THE DISTRIBUTION RATIO OF $D_{M^{3+}}$ VERSUS THE PERCENTAGE OF HDEHDTP

Aqueous phase : $\frac{[M^{3+}]_0 \cdot [NO_3^-]}{[Eu(III)]_0 \cdot 10^5} \cdot \frac{1}{[HDEHDTP]_1} = 1$

Organic phase : diluent : dodecane $\frac{[HDEHDTP]_1 \cdot [TBP]_1}{[M^{3+}]_1} = 10^3$

4. Structure of the organic complexes

The evidence of the micellisation of the organic complexes has been provided by (H_2O 1H NMR) and low angle X-Ray diffraction.

a - NMR results :

In our previous work [3] [7] we demonstrated that NaDEHDP forms inverted micelles in benzene and cyclohexane ; we used the mass action law model and applied the hypothesis that the chemical shift of the proton δ is a level-headed average between the chemical shift of water bound to the monomere δ_1 and the chemical shift of the water bound to the n-mer δ_n (see fig. 9 and 10). This leads to the following equation :

$$\log c (\delta - \delta_1) = n \log c (\delta_n - \delta) + \log nK - (n-1) \log (\delta_n - \delta_1) \quad (6)$$

$$\text{with } c = c_1 + c_n \quad \text{and } \delta = \frac{c_1}{c} \delta_1 + \frac{c_n}{c} \delta_n$$

$$\text{and } nM_1 \frac{K}{z} M_n \quad \text{and } K = \frac{C_n}{n(C_1)^n}$$

We can determine n and K by a linear regression on the equation (6) where $x = \log c(\delta_n - \delta)$ and $y = \log c(\delta - \delta_1)$.

With this model we determined for $La(DEHDP)_2, TBP$ $n = 2$ and $K = 188,3$ before the c.m.c. (critical micellar concentration) and $n = 8,4$ and $K = 5,29 \cdot 10^{18}$ after the c.m.c.

c.m.c. = $7.5 \cdot 10^{-3} M$.

For $La(DEHDP)_2$, the c.m.c. was determined on the plot because the experimental points cannot be interpreted by the previous model. We determined c.m.c. = $1.5 \cdot 10^{-3} M$. (see figure 10).

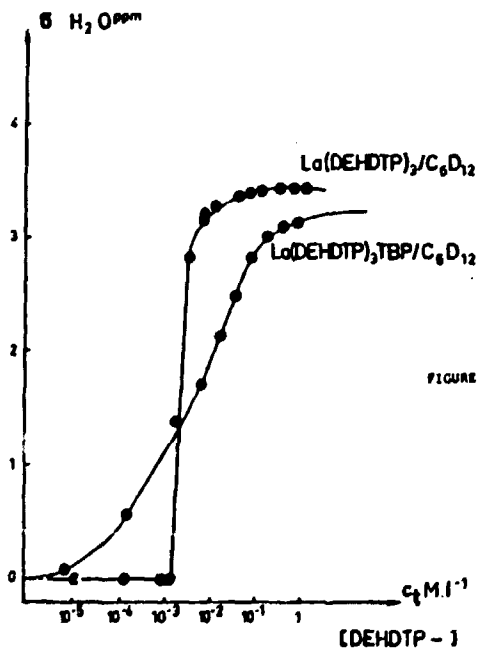


FIGURE 10 : VARIATIONS OF 1H WATER THE CHEMICAL SHIFT VERSUS THE CONCENTRATION OF [DEHDP⁻] DILUENT C₆D₁₂ (CYCLOHEXANE).

b - low angle X ray diffraction :

The experiments confirmed the aggregation of $\text{La}(\text{DEHDTP})$, and $\text{La}(\text{DEHDTP})_2\text{IBP}$. The inverted micelles have the form of hollow shells where the La^{3+} ions are strongly tied to the ligands. For $\text{La}(\text{DEHDTP})$, the pool is filled with water ($m = 25$ molecules of water by molecule of salt). For $\text{La}(\text{DEHDTP})_2\text{IBP}$ the quantity of water is weak ($m < 5$).

Conclusion

We investigated the extractive properties of HDEHDTP and HDEHTP for trivalent actinides and lanthanides. We found that HDEHDTP is able to operate lanthanide/actinide group separation in presence of IBP. IBP expels water from the complex so that the S-metal bond is shortened and the selectivity Am(III)/Eu(III) is enhanced.

The organic complexes form inverted micelles with high metal concentrations.

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