

**COMPARATIVE SYNERGISTIC (TECHNETIUM-ACTINIDE)
EXTRACTION CHEMISTRY
BY TRIBUTYLPHOSPHATE AND SOME AMIDE EXTRACTANTS.**

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8 pages

FRANCOISE
DELMAU
1985

INTRODUCTION

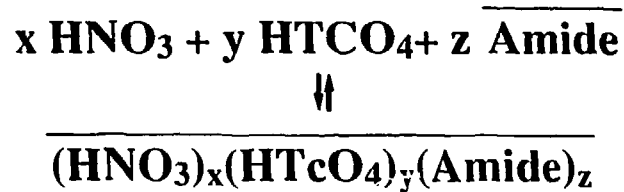
By now, nuclear fuel reprocessing is industrially performed by liquid-liquid extraction with tributylphosphate (TBP). We claim for several years [1,2,3] for the use of extractants N,N-dialkylamides known for their performances in Uranium-Plutonium purification and their ability to overcome TBP drawbacks as non-incinerable wastes formation, spurious degradation products disturbing ...

After a study of fundamental chemistry features of the actinides Uranium(VI) and Plutonium(IV) extraction by N,N-dialkylamides[3] we are interested in fission products extraction chemistry and especially in the technetium case. In PUREX process, technetium (TcO_4^-) leads to bad interferences in the extractions, being synergistically co-extracted with different actinide cations as Uranium(VI), Plutonium(IV) and Zirconium(IV) [4,5,6,7]. It destroys the hydrazine in the reductive partition of U and Pu, it decreases the decontamination of U and Pu from fission products. Thus, its extraction behaviour with new extractants as N,N-dialkylamides is useful to be known. We have first studied the behaviour of Tc in aqueous nitric acid and (uranyl nitrate-nitric acid) media.

EXTRACTION of TcO_4^- from HNO_3 MEDIA, FIRST RESULTS

* The influence of nitric acidity is tremendously related to the amides formula (figure 1).

*According to the general equilibrium:



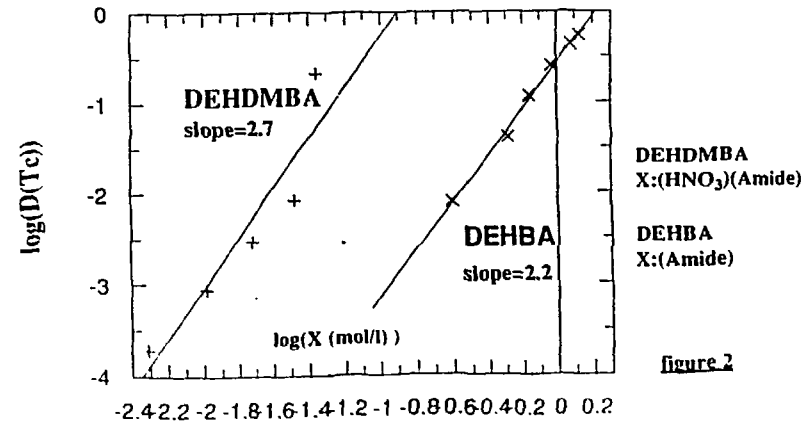
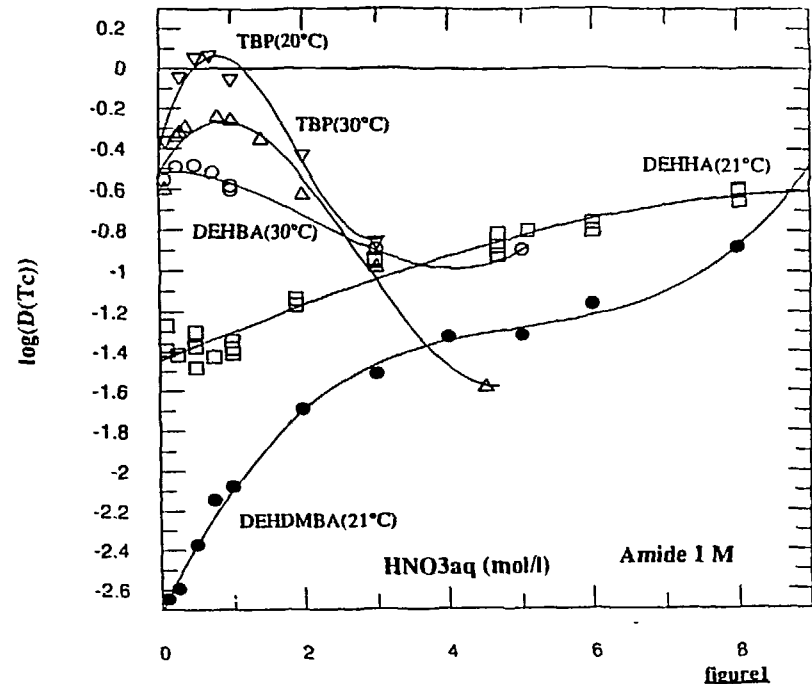
We suggest from figure 2:



*Further studies:

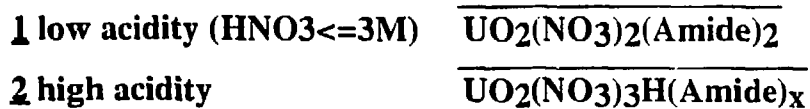
aims: to confirm the distribution coefficients data interpretation, to understand the nature of bounds and the influence of the carbonyl radical.

methods: spectrometric methods as IR spectroscopy.



**EXTRACTION of TcO_4^- from
(Uranyl nitrate-nitric acid) MEDIA**

*Amides form different organometallic species with U(VI) according to the acidity.



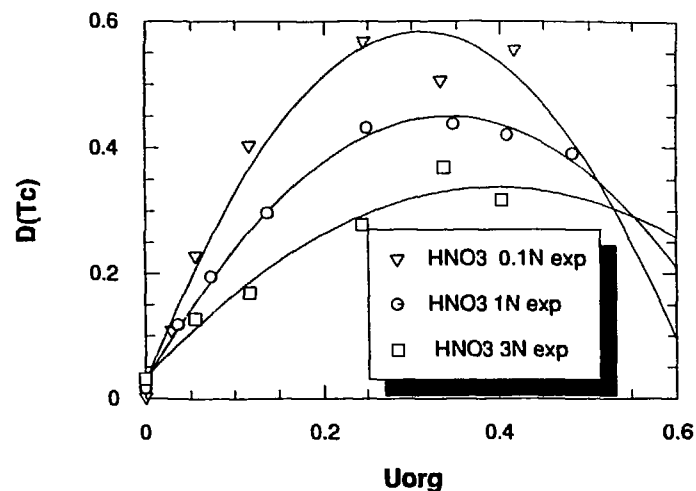
* TcO_4^- extraction has been studied in media of type 1 and 2.

*By now, we are interested in physicochemical conditions simulating PUREX process ($[TcO_4^-] \ll [UO_2^{2+}]$).

**EXTRACTION of TcO_4^- from LOW
ACID ($UO_2(NO_3)_2-HNO_3$) MEDIA**

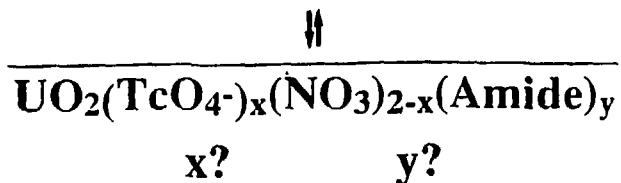
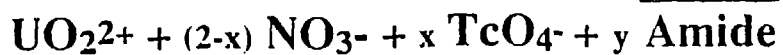
***SYNERGISTIC EXTRACTION?**

[DEHDMBA]=1 M, T=21°C



[UO_2^{2+}] increases, free amide available for $(HTcO_4)(HNO_3(DEHDMBA))_x$ decreases. $D(Tc)$ increases.

-----> **SYNERGISM** and possibility of $UO_2(NO_3)_x(TcO_4)_{2-x}(Amide)_y$



x?



$$\log(D(\text{Tc})) = \text{constant} + (x-1) [\text{TcO}_4^-]$$



0.21M

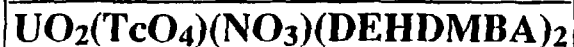
(* aqueous acidity)

[TcO ₄ ⁻](M)	D(Tc)(*0.1M)	D(Tc)(*1M)	D(Tc)(*3M)
1.86E-4	5.19E-1	3.75E-1	2.47E-1
3.79E-4	5.20E-1	3.80E-1	2.50E-1
1.14E-3	5.83E-1	3.75E-1	2.50E-1
1.89E-3	4.06E-1	3.94E-1	2.67E-1

[TcO₄⁻] increases, D(Tc)=constant,

x=1

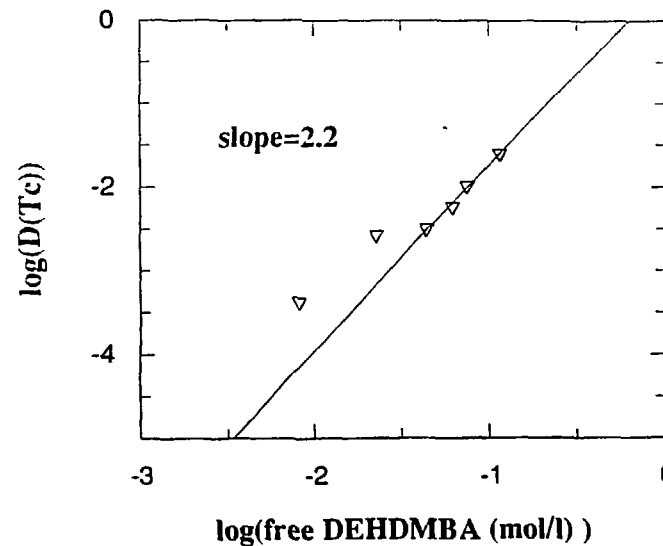
Low acidity



y?

[TcO₄⁻] << [UO₂²⁺], constant ionic strength.
low amide concentration, ideal organic medium.

T = 21°C, [TcO₄⁻] = 3.79E-5M, [UO₂²⁺]_{aq} = 0.805M,
[HNO₃]_{aq} = 0.1M



$\log(D(\text{Tc})) = \text{constant} + y [\text{Amide}]$

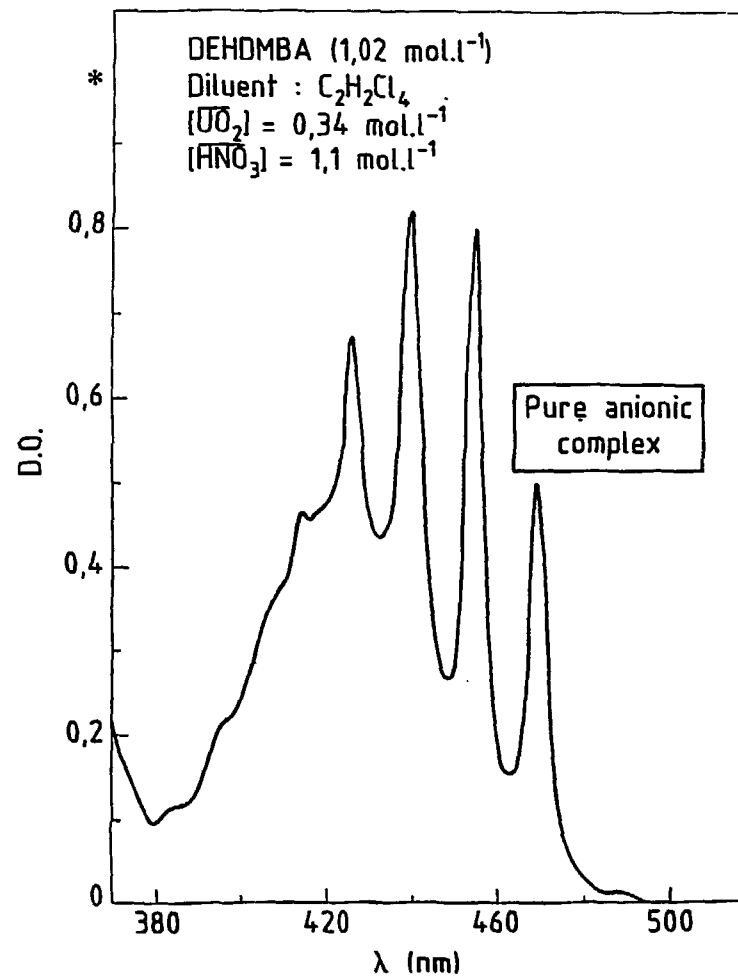
y=2

**Insertion of TcO_4^- in the anionic
 $\text{UO}_2(\text{NO}_3)_3\text{H}(\text{DEHDMBA})_x$
 complex ?**

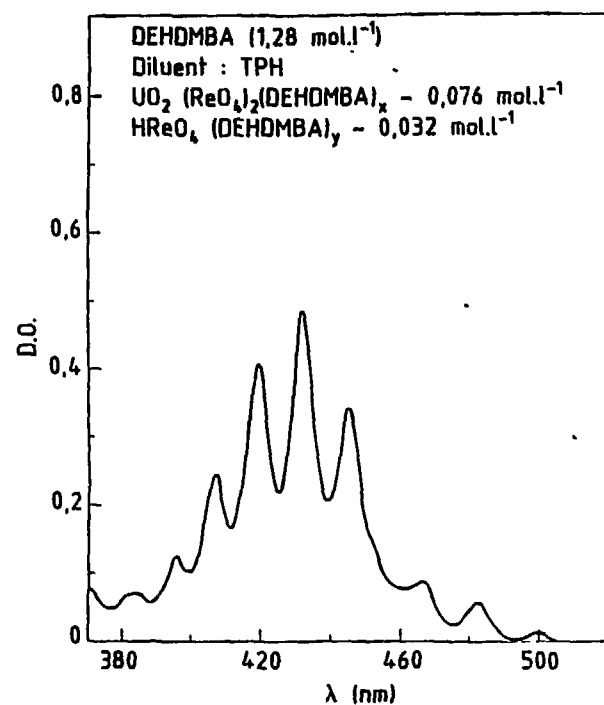
Comparison	<u>1</u>	<u>2</u> *
DEHDMBA	1.28 M	1.28 M
HNO_3 aq	8.22 M	8.29 M
UO_2 aq	0 M	0.73 M
UO_2 org	0 M	0.34 M
D(Tc)	0.68	0.52

$$D(\text{Tc})_1 > D(\text{Tc})_2$$

No synergistic behaviour
 TcO_4^- cannot enter in the inner-sphere of
 $\text{UO}_2(\text{NO}_3)_3\text{H}(\text{amide})_x$.



Possibility of
 $\text{UO}_2(\text{TcO}_4)_2(\text{Amide})_y$?



TcO_4^- is simulated by ReO_4^- .

A complex

**$\text{UO}_2(\text{ReO}_4)_2(\text{DEHDMBA})_y$
 is pointed out.**

EXTRACTANTS FORMULA

TBP



AMIDES

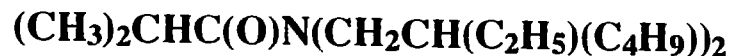
DEHDMBA



DEHBA



DEHiBA



DEHHA



extractants are diluted in TPH (mixture of branched dodecanes)

CONCLUSION

Like TBP, N,N-dialkylamides are liable to form mixed complexes between actinides cations and technetium, substituting a nitrate anion by TcO_4^- in the inner-sphere of coordination of the usual (actinide-amide) species.

We intend to pursue our study by considering the effect of plutonium and zirconium on TcO_4^- extraction by N,N-dialkylamides.

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