

RECENT PROGRESS IN ACTINIDE AND LANTHANIDE SOLVENT EXTRACTION :

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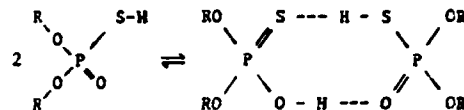
The development of future nuclear energy programs necessitates an improved knowledge of actinide solvent extraction. Short abstracts of what is done in the authors laboratory will be presented in this communication.

1) Interaction between organophosphorous extractants.

¹H and ³¹P NMR were used to elucidate several fundamental unsolved problems concerning organophosphorous extractants often used in actinides extraction.

a) Site of dialkylthiophosphate protonation.

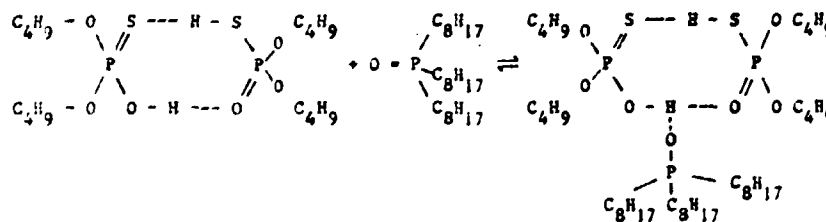
¹H NMR showed that in toluene the dialkylthiophosphatedimerization take place according to



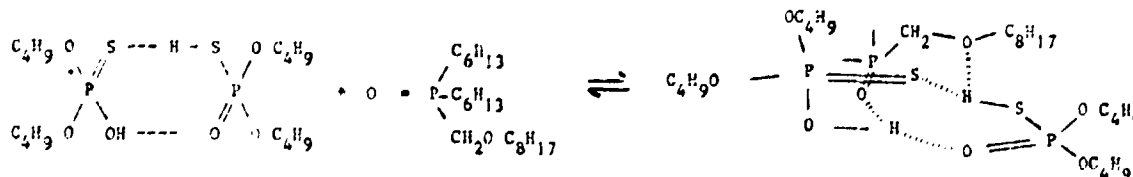
b) Addition of basic phosphine oxide to dibutylthiophosphoric acid dimer.

¹H and ³¹P NMR showed that TOPO (trioctylphosphine oxide) and POX 11 (dihexylmethoxyoctylphosphine oxide) react with dibutylmonothiophosphoric acid according to the reactions :

TOPO)



A second TOPO is fixed on the S - H --- S site when TOPO concentration increases (POX 11)



The oxygen ether interacts with the S --- HS group and a second POX 11 cannot be fixed by the acidic dimer.

2) Extraction of actinides from high radioactivity level wastes :

These last years interest has been focussed on carbamoylmethylene phosphonates as extractants of Ac(III) and Ln(III) from concentrated nitric acid. In spite of the advantages of this ligand over the classical TBP or HDEHP, it seems that use of completely incinerable solvents, if they exist, will be preferable in order to limit the amounts of radioactive wastes. Extraction of Am(III) and Eu(III) by tetrasubstituted methylene diamides was investigated (figure 1). These results illustrate the interest of diamides as actinides extractants from concentrated nitric acid.

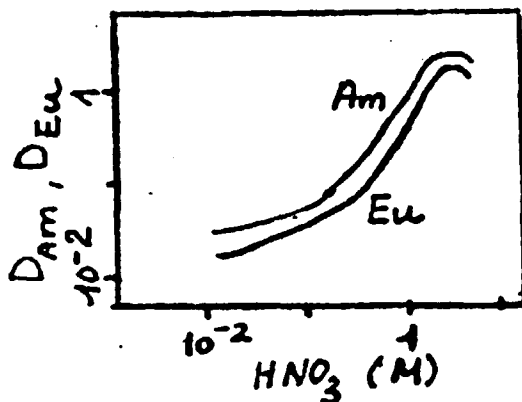


Figure 1 . Am(III) and Eu(III) distribution ratios as a function of aqueous HNO_3 concentration. Organic phase : NN' octylmethylmalonamide 1M in *t*-butylbenzene.

3) Trivalent actinide-lanthanide group separation :

Investigations of trivalent actinide and lanthanide aqueous complexes showed that rather soft donor ligands complexes of the 5f ions are more stable. Spectroscopic investigations indicated that this higher stability stem from higher covalent interactions in the actinide complexes. These differences can be used to separate the two trivalent ions families by solvent extraction, as illustrated by figure 2 and 3 :

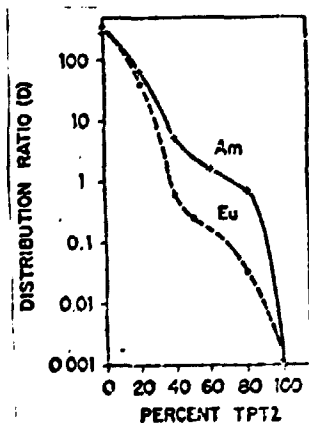


Fig.2 Distribution of Am and Eu between 0.1 M HNO_3 and 0.01 M (TPTZ + HDNNS) in *t*-butylbenzene.

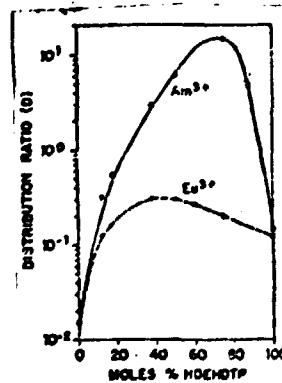


Fig.3 Am^{3+} - Eu^{3+} distribution between 0.05 M HNO_3 and 1 M HDEHDTP + TBP in dodecane.

4) Synergism in the trivalent and tetravalent actinide extraction.

Synergism for trivalent and tetravalent actinide has been observed mainly by using dicetones as the acidic extractants. Surprisingly mixtures of acidic and neutral organophosphorus extractants yield very small synergistic effects and most of the time antisynergism rather than synergism has been observed. We investigated the synergism of dinonylnaphtalene sulfonic acid (HDNNS) associated with several neutral donors like TBP, TOPO, amides.

Figure 5 and 6 illustrate the effects observed. It came out that HDNNS is the second acidic reagent for which strong synergism is observed for actinides and the first efficient in acidic media.

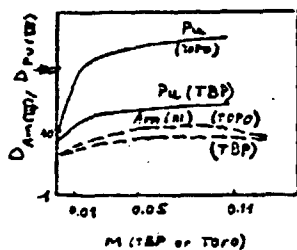


Fig.4
Distribution of
Pu(IV) and Am(III)
as a function of
TBP or TOPO.
Organic phase :
0.2 M HDNNS in
t-butylbenzene
Aqueous phase :
HNO₃ 1 N

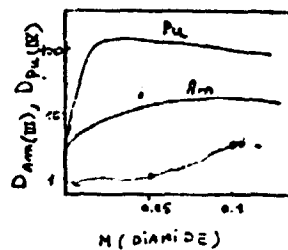


Fig.5
distribution ratios
of Pu(IV) and
Am(III) as a
function of diamide
concentration.
Organic phase :
0.2 HDNNS in
dodecane
Aqueous phase :
HNO₃ 1 N