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ACTINIDES COMPLEXES IN SOLVENT EXTRACTION. THE AMIDE TYPE OF  
EXTRACTANTS

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1. Introduction : The N,N-dialkylamides (1 to 4) and the N,N'-tetraalkyl 2-alkyl 1,3-diamide propane (5) are two promising classes of extractants which could replace advantageously the organophosphorus molecules for the separations of the actinide. The main advantages of the amides lie in their complete incinerability and the small interference of their radiolytic and hydrolytic degradation products for the processes. The actinide extraction chemistry with various amides will be reviewed in this paper.

## 2. N,N-dialkylamides (RRNCOR') actinides nitrate complexes

2.1. Hexavalent ions : We observed two kinds of U(VI) complexes in organic media  $UO_2(NO_3)_2(amide)_2$  and  $UO_2(NO_3)_2H(amide)_x$ . The second species is favored by high aqueous  $HNO_3$  concentrations and high dielectric constant of the organic phase. It has been characterized by U-V visible spectrophotometry. The same technique allows (figure 1) the observation of a mixed complex  $UO_2(NO_3)_2DOBA$ .  $DO_2BA$  being the acronym of respectively N,N-di(2-ethyl hexyl) butyramide and N,N-di(2-ethyl hexyl)iso butyramide.

2.2. Tetravalent ions : Pu(IV) forms also neutral and acidic complexes  $Pu(NO_3)_4(DOEA)_2$  and  $Pu(NO_3)_4H_2(DOBA)_x$ . With the more sterically hindered  $DO_2BA$ , the neutral complex is hardly formed and has the formula  $Pu(NO_3)_4(DO_2BA)_2$ , when the acidic complex is the same as the DOBA one. No mixed DOBA,  $DO_2BA$  complex is observed.

2.3 Trivalent and pentavalent ions : The actinide (V) and (III) ions are not extracted by N,N-dialkylamides from acidic nitrate solutions.

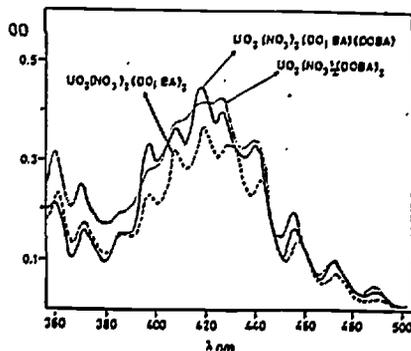


Fig. 1 : U(VI) complexes into 1M DOBA,  $DO_2BA$  and 1/1 DOBA/ $DO_2BA$  into dodecan ( $\frac{C_{12}H_{26}}{U(VI)} = 0.03$ )

3. Actinides complexes formed by the diamides : The extraction chemistry of the diamides is governed by the number of  $CH_2$  separating the two amides function. Hexavalent and tetravalent ions are extracted by all the diamides when trivalent ions are only extracted by the malonamides ( $(RR'NCO)_2CH_2$ ) and pentavalent ions are not extracted.  $UO_2^{3+}$  forms the species  $UO_2(NO_3)_2TBGA$  and  $UO_2(NO_3)_2H TBGA$  with N,N'-tetrabutylglutaramide ( $TBGA = ((C_4H_9)_2NCO)_2CH_2$ ). In the solid  $UO_2(NO_3)_2TBGA$  (figure 2)  $UO_2^{3+}$  ions are linked by TBGA molecules. This solid is insoluble in toluene, but an excess of TBGA solubilizes the complex probably by forming species like  $UO_2(NO_3)_2TBGA \cdot (TBGA)_x$  where some TBGA are in the second coordination sphere of the complex. In both

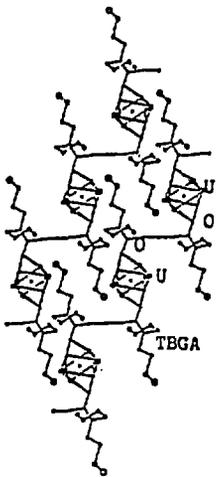


Fig. 2 : Chain structure in  $UO_2(NO_3)_2$ , TBGA

complexes of  $UO_2^{2+}$  it has been observed that the order of stability is :  $UO_2(NO_3)_2 \cdot H(TBGA)_x > UO_2(NO_3)_2 \cdot H(DOBA)_x > UO_2(NO_3)_2 \cdot H(Malonamide)_x$  when the order of basicity is  $TBGA > Malonamide > DOBA$ .

Table 1 -  $pH_{1/2}$  of various weak bases neutralization by  $HClO_4$  into acetic anhydride-acetic acid

Base and acronym	$pH_{1/2}$	pKa
Isobutyramide (iBA)	-5.45	0
N,N-di(S-butyl)dodecanamide(D <sub>2</sub> BDA)	-4.15	1.3
N,N'-dimethyldibutylmalonamide (DMDBDA)	-2.0	3.45
N,N'-dimethyldibutylsuccinamide (DMDBSA)	-1.6	3.85
N,N'-tetrabutylglutaramide (TBGA)	-1.55	3.90
Trioctylphosphine oxide (TOPO)	-2.95	2.5
Tributylphosphate (TBP)	< -5.45	< 0

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$UO_2(NO_3)_2$ , TBGA and  $Th(NO_3)_4$ , TBGA the two C=O are linked to the metal as shown by IR spectroscopy. Actinides (III) ions are extracted by the malonamides. With DMDOMA ( $(CH_3)_2C_4H_9NCO_2$ ,  $CH_3$ ) one observed Am ( $NO_3$ )<sub>2</sub>(DMDOMA)<sub>2</sub> (DMDOMA)<sub>2</sub>, with probably two DMDOMA molecules in the second coordination sphere.

4. Conclusion : The actinide extraction chemistry of amides differ by many aspects from the organo phosphorus extractants. Two main points must be stressed out. The stronger influence of the C=O and N substituents upon the metal ligand interaction ; because of the steric hindrance due to the rigidity of the partial  $\pi$  character of the amide bond. The formation of acidic complexes  $M(NO_3)_n H_m (Amide)_x$  due to the higher basicity of amides when compared with most of the organophosphorus extractants (see Table 1). For the acidic