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RECENT ADVANCES IN THE TREATMENT OF NUCLEAR WASTES BY THE USE OF DIAMIDE AND PICOLINAMIDE EXTRACTANTS

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ABSTRACT

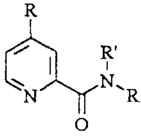
In the framework of the SPIN(ACTINEX) program for the partitioning and transmutation of actinides contained in effluents generated during the nuclear fuel reprocessing cycle, diamides and picolinamides, extractants which have the common characteristic of being totally combustible, were evaluated. Among the diamides, N,N'-dimethyl N,N'-dibutyl tetradecyl malonamide (DMDBTDMA) was chosen as the reference extractant. It has been shown that actinides(III) may be extracted from concentrated nitric acid effluent; the actinides(III) may be readily stripped from the loaded solvent. There is restricted third-phase formation. Long alkyl groups (R") and different R and R' on the amide nitrogen limit the extent of third-phase formation. The second class of extractants studied, the picolinamides, seem to have potential for the separation of An(III)/Ln(III).

INTRODUCTION

The separation of actinide(III, IV, VI) species from effluents generated during the nuclear fuel reprocessing cycle, specifically the PUREX process, and the transmutation of long-lived isotopes to short-lived ones is a promising strategy for improving the management of radioactive wastes. This strategy is the basis of the SPIN(ACTINEX) program which was launched recently (1). One of the objectives related to this program is the selection and the study of partitioning processes based on new extractants. Owing to their complete incinerability, amidic extractants has been considered. For several years, studies have been undertaken in Fontenay-aux-Roses with monoamides RCONR'R", [R, R', and R" are alkyl groups (2, 3)] or pentaalkyl -1,3 propanediamides $(RR'NCO)_2CHR"$ with R, R' alkyl and R" alkyl or oxyalkyl groups (4, 5). Monoamides are monodentate extracting agents that are only able to extract U(VI) and Pu(IV) nitrates. Owing to their chelating properties, diamides can extract all actinides, including tervalent actinides from acidic nitric solutions. Unfortunately, diamides also coextract tervalent lanthanides with tervalent actinides.

For the design of partitioning processes, two strategies were selected :

1. recovery of U(VI) and Pu(IV) via monoamides (6) (if necessary); extraction of actinides(III) and lanthanides(III) using diamides (4, 5); separation of actinides(III) from lanthanides(III) with soft donor atom ligands (7, 8). It should be mentioned that the second step of the above strategy corresponds to the DIAMEX process, which was the object of hot tests run successfully in June 1993 during the treatment of mixed oxide high level liquid effluent (9).

2. use of new extractants such as picolinamides 

(10). It was hoped that such compounds, owing to the presence of a soft donor nitrogen atom and an amide function, would be able to coextract all the actinides(III, IV, VI) but reject the lanthanides(III).

This paper provides a general survey of recent results concerning diamide and picolinamide extractants.

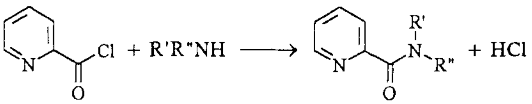
EXPERIMENTAL

Reagents

- Malonamides were provided by G. Thiollet (IRCHA, Vert le Petit, F); Y. Leguen (PANCHIM, Lisses, Evry, F); M. J. Hudson (University of Reading, U K). Acidimetric titrations with $HClO_4$ in acetic anhydride showed that one malonamide molecule is neutralized by one $HClO_4$ molecule.

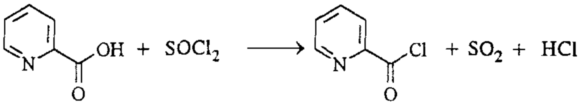
- Two kinds of picolinamides have been synthesized : substituted N-amide molecules and substituted pyridine ring molecules.

  - The substituted N-amide picolinamides were provided by G. Thiollet (IRCHA, Vert le Petit, F). They were obtained by reacting an acid chloride with a secondary amine, according to the following reaction (equation 1), in which R' and R" are alkyl groups (11).



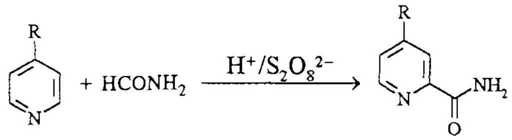
(1)

The acid chloride was prepared from pyridine 2-carboxylic acid by refluxing with excess thionyl chloride in the presence of few drops of N,N-dimethyl formamide catalyst (equation 2).



(2)

- The substituted pyridine ring molecules were provided by PROCHEM (Compiègne, F). They were obtained by reacting pyridine 4-alkyl with formamide in the presence of $Na_2S_2O_8$ according to equation 3. Abstraction hydrogen of $HCONH_2$ is promoted by thermal or redox decomposition of peroxydisulfate. This reaction is also used to synthesize quinoxaline and lepidine



(3)

- TPH (PROCHROM, Champignols, France), an abbreviation for tetrahydrogenated propene, is a commercial mixture of branched dodecanes and was used as the organic diluent.

- Benzene, 1,1,2,2-tetrachloro ethane, benzonitrile, tertiarybutylbenzene, and methanol were PROLABO or FLUKA reagents.
- U(VI) was obtained as $UO_2(NO_3)_2.6H_2O$ (PROLABO products).
- Lanthanides(III) nitrates were ALDRICH products. ^{152}Eu and ^{144}Ce radionuclides were provided by CIS-BIO industry.
- $^{239}Pu(IV)$ in nitric acid solution and ^{241}Am were provided by SPHA (CEA Fontenay-aux-Roses).
- Other products such as HNO_3, $LiNO_3$ were RP PROLABO or MERCK reagents.

Procedure and Apparatus

Prior to the studies, the solvents were preequilibrated with aqueous phases containing the same nitrate salt and nitric acid concentrations as the aqueous phase under study in order to prevent the coextraction of nitric acid during the distribution of metallic nitrates. Organic solutions (preequilibrated solvents) and aqueous solutions (equal volume) were shaken together for 5 min. Phase disengagement was achieved by centrifugation.

Analyses

- U(VI) was analyzed by spectrophotometry of its complex with dibenzoylmethane (DBM). The absorbance measured at 405 nm served for U(VI) determination.
- Total Pu was analyzed by α spectrometry (^{239}Pu) or by cerimetric titration.
- ^{241}Am was measured by γ counting.
- Lanthanide(III) ions were analyzed by EDTA titration. ^{144}Ce, ^{152}Eu were analyzed by counting (γ spectrometry).
- Iron(III) ions were analyzed by atomic absorption at 248.3 nm, and ^{59}Fe was analyzed by γ counting.
- Acidity measurements were performed by aqueous NaOH pHmetric titration.
- Raman spectra were recorded on a T800 Coderg spectrometer. A Rhodamine 6G dye laser tuned to 16667 cm^{-1} or 17268 cm^{-1} was used as the excitation beam for neodymium(III) and uranyl(VI) ions, respectively.
- UV-visible spectra were recorded with a Cary-2315 spectrophotometer.

NOTATIONS

Overlines indicate species in the organic layer.

C_X or $\overline{C_X}$: total concentrations of the species X in the aqueous or organic layers;

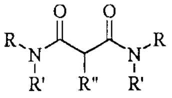
$[X]$ or $[\overline{X}]$: concentrations of species X at equilibrium in the aqueous or organic layers;

D_M : distribution coefficient of metal ion M : $D_M = \overline{C_M} / C_M$;

S_F : separation factor of two metal ions M_1 and M_2: $S_F = D_{M_1}/D_{M_2}$;
An and Ln represent actinides and lanthanides, respectively.

RESULTS AND DISCUSSION

Malonamides

The general formula of the malonamides, which are the diamides studied here, can be written :  . At the present time, (N,N'-dimethyl N,N'-dibutyl tetradecyl malonamide) (DMDBTDMA) is considered to be the reference extractant for the DIAMEX process. The diamide is able to extract trivalent actinides from nitric acidic solutions and may be used in aliphatic diluents such as TPH. It has been shown that americium(III) nitrate extraction is faster than iron(III) nitrate extraction and that hydrolytic degradation and aqueous-phase solubility are satisfactory for industrial-scale applications (12).

The extracting properties of DMDBTDMA have been investigated (12,13,14). It has been shown that, in non-acidic media, molecules associate to form aggregates (13) (equation 4; L represents DMDBTDMA). The degree of aggregation depends on the diluent and the diamide concentration. At low concentrations, in C_6D_6 or TPH, dimerization occurs, and for concentrated diamide solutions ($C > 5.5 \cdot 10^{-2}$ mol.l^{-1} in TPH and $C > 0.12$ mol.l^{-1} in C_6D_6) diamides combine to form larger aggregates $\overline{L_n}$ (n = 4 in TPH and n = 6 in C_6D_6).

$$n\overline{L} \rightleftarrows \overline{L_n} \qquad (4)$$

In nitric acid media, aggregate formation is negligible, but acidic adducts are formed for which the stoichiometries are $\overline{L_2.HNO_3}$, $\overline{L.HNO_3}$, $\overline{L.(HNO_3)_2}$ and $\overline{L.(HNO_3)_3}$.

From the extraction of metallic nitrates (12, 14), it can be concluded that :

- only one complex is formed with uranium(VI) nitrate. This is a non-ionic species, and the UV visible spectra are typical of a bidentate adduct (Figure 1) (15). The formula is $\overline{L.UO_2(NO_3)_2}$;

- two non-ionic species are formed with plutonium(IV) : $\overline{L_2.Pu(NO_3)_4}$ and $\overline{L.Pu(NO_3)_4}$;

- a mixture of nonacidic and acidic species is obtained with $Nd(NO_3)_3$ or $Am(NO_3)_3$. $\overline{L_2.M(NO_3)_3}$ and $\overline{L.M(NO_3)_3}$ in nonacidic media and further species $\overline{L_x.M(NO_3)_{3+y}.H_y}$ when the acidity is increased;

With a large excess of ligand compared to the metal species, outer-sphere complexes are formed in addition to inner-sphere complexes (14). Interactions occurs between the free or aggregated diamide molecule and the inner-sphere complex.

Interactions between diamides and lanthanides have been clarified by a crystallographic study of the (N,N,N',N'-tetraethyl malonamide) - $La(NO_3)_3$ system, which showed a complex with the stoichiometry : $\overline{L_2.La(NO_3)_3}$. From single crystal X-ray structural analysis, it has been shown that the lanthanum(III) ion is ten-coordinated with two bidentate diamide ligands and three bidentate nitrate groups (16).

Nevertheless, some properties of DMDBTDMA can be improved, especially the ability of the extractant, when diluted in aliphatic diluents, to form a third phase when extracting various solutes, such as HNO_3 or metallic nitrates; and the affinity for trivalent actinide nitrates from nitric acid solution into the organic layer. New diamides such as malonamides with modified R, R', and R" aliphatic groups were accordingly studied.

Selection of the New Molecule

The formulae of the new molecules are presented in Table 1.

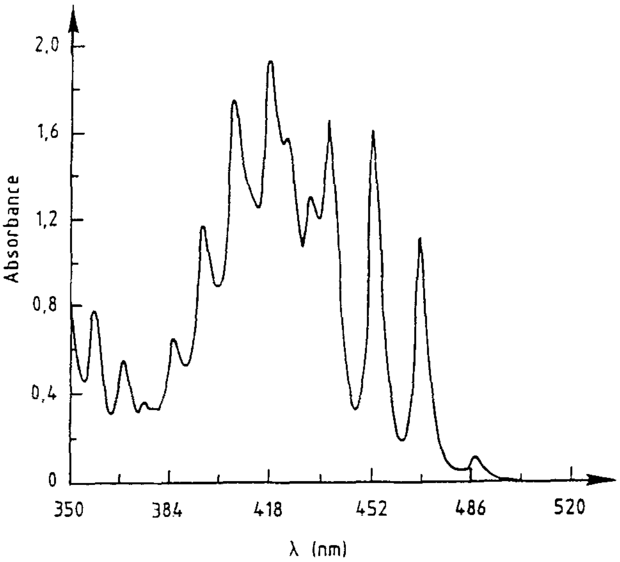


FIGURE 1. UV-visible spectra of uranyl nitrate-DMDBTDMA complex in tertiarybutylbenzene. [U(VI) nitrate was extracted from $LiNO_3$ medium]. $\overline{C_{amide}} = 0.132$ M, $\overline{C_U} = 0.134$ M.

TABLE 1. Formulae of Malonamides Studied $(RR'NCO)_2CHR''$

No.	R	R'	R"	Characteristic[a]
1	CH_3	C_4H_9	$C_{12}H_{25}$	yellow liquid
2[b]	CH_3	C_4H_9	$C_{14}H_{29}$	yellow liquid
3	CH_3	C_4H_9	$C_{16}H_{33}$	yellow liquid
4	CH_3	C_4H_9	$C_{18}H_{37}$	white solid
5	CH_3	C_4H_9	$C_2H_4OC_6H_{13}$	yellow liquid
6	CH_3	C_4H_9	$C_2H_4OC_8H_{17}$	yellow liquid
7	CH_3	C_4H_9	$C_2H_4OC_{12}H_{25}$	yellow liquid
8	CH_3	C_4H_9	$(CH_2)_3OC_{11}H_{23}$	yellow liquid
9	CH_3	C_4H_9	H	white solid
10	C_2H_5	C_2H_5	H	yellow liquid
11	C_2H_5	C_2H_5	$C_{18}H_{37}$	white solid
12	CH_3	CH_3	$C_{16}H_{33}$	white solid
13	CH_3	CH_3	$C_{20}H_{41}$	white solid

[a] *Ambient conditions.*

[b] *Reference diamide : DMDBTDMA.*

Solubilities of diamides in different diluents. Table 2 shows the solubilities of these compounds in different diluents. The solubilities at room temperature of malonamides vary according to the sequence TPH $<$ C_6H_6 $\approx$ $C_2H_2Cl_4$.

These results emphasize the fact that, for symmetric nitrogen groups, the solubilities of malonamides in aliphatic diluents such as TPH are low ($R=R'=C_2H_5$) or even very low ($R=R'=CH_3$). Thus, asymmetrical nitrogen alkyl substituents must be used to optimize malonamide solubility. As TPH-soluble diamides are required, the formation of the third phase was studied, and the results are presented below. The other diamide molecules, which are slightly soluble in TPH, are interesting for a more general understanding of diamide extracting properties.

Third-phase formation

The presentation of the experimental results on the determination of third phase boundaries is different for nitric acid and metallic nitrates :

- for the nitric acid boundary, the most interesting information concerns the aqueous phase, i. e. the highest aqueous nitric acid concentration compatible with a two phase liquid-liquid extraction system (cf. for example figure 2),

- for metallic nitrates, the most interesting information concerns the organic phase, i.e. the highest solvent extraction capacity for a particular metallic nitrate salt in specified experimental conditions ? (cf. for example figure 3).

Nitric acid : Table 3 shows the influence of nitric acid on third-phase formation. It is assumed (13) that the diamide is present in the organic phase as $\overline{(\text{diamide})_x.(\text{HNO}_3)_y}$. It appears that increasing the total number of carbons in the diamide molecule enhances the solubility of $\overline{(\text{diamide})_x.(\text{HNO}_3)_y}$ solvates (Figure 2). This also appears to apply to diamide extractants such as malonamides and glutaramides (17). For a constant number of carbon atoms, the presence of one oxygen in the R" group has no effect on third phase appearance, but the presence of two oxygen atoms lowers the solubility limit of the $\overline{(\text{diamide})_x.(\text{HNO}_3)_y}$ solvate in TPH (5).

TABLE 2. Solubilities of Malonamide Extractants (RR'NCO)$_2$CHR" in Various Diluents

No.	R	R'	R"	Diluent	Temperature (°C)	Solubility (M)
2	CH_3	C_4H_9	$C_{14}H_{29}$	TPH	22	>1.5
3	CH_3	C_4H_9	$C_{16}H_{33}$	TPH	22	>1.5
4	CH_3	C_4H_9	$C_{18}H_{37}$	TPH	23	2.2
7	CH_3	C_4H_9	$C_2H_4OC_{12}H_{25}$	TPH	22	>0.95
				C_6H_6	22.5	>1.1
				$C_2H_2Cl_4$	21	>1.1
8	CH_3	C_4H_9	$(CH_2)_3OC_{11}H_{23}$	TPH	22	>0.95
				C_6H_6	22	>1.1
				$C_2H_2Cl_4$	22	>1.1
9	CH_3	C_4H_9	H	TPH	22	>0.049
				C_6H_6	22.5	>1.0
				$C_2H_2Cl_4$	21	>1.0
10	C_2H_5	C_2H_5	H	TPH	22.5	>0.13
				C_6H_6	22	>1.44
				$C_2H_2Cl_4$	23	>1.37
11	C_2H_5	C_2H_5	$C_{18}H_{37}$	TPH	22	~0.21
				C_6H_6	22	~0.28
12	CH_3	CH_3	$C_{16}H_{33}$	TPH	23	~0.006
				C_6H_6	23	~0.28
				$C_2H_2Cl_4$	23	~0.6
13	CH_3	CH_3	$C_{20}H_{41}$	TPH	25	~0.02
				C_6H_6	25	0.26
				$C_2H_2Cl_4$	25	0.22

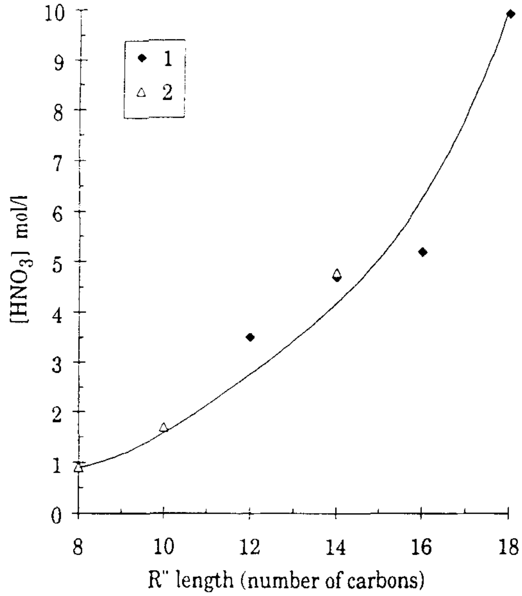


FIGURE 2. Third-phase boundary formed during the extraction of HNO_3 with various diamides of the type $(CH_3(C_4H_9)NCO)_2CHR"$ in TPH. Influence of the length of R" substituent at room temperature (21-23°C). $\overline{C_{amide}} = 0.5$ M in TPH.
1 : $R" = C_nH_{2n+1}$ 2 : $R" = C_2H_4OC_{(n-2)}H_{(2n-3)}$

Metallic nitrates : Data on third phase formation during the extraction of U(VI), Nd(III), and Fe(III) nitrates by malonamides at room temperature are given in Table 4. As shown in Figure 3, the maximum concentrations of U(VI), Nd(III), and Fe(III) nitrates in TPH malonamide solutions are related to the increase in the length of the R" central substituent.

From studies on third phase formation corresponding either to the data presented in Tables 3 and 4 and in figures 2 and 3, or to qualitative experimental observations not reported in this paper, the following conclusions may be proposed for solvates of nitric acid and of metallic nitrate-diamides :

- an increase in the amide concentration (Table 3, molecules Nos. 2 and 7), or in temperature (qualitative observations), increases the solubilities of the solvates of acid and metallic nitrate-diamides in diluent TPH;

TABLE 3. Third-Phase Formation During the Extraction of Nitric Acid by Some Malonamides $(RR'NCO)_2CHR''$ at room temperature (21-22 °) (ambient conditions).

No.	R	R'	R"	Diluent	$\left[\overline{\text{Diamide}}\right]$ (M)	Third phase boundary	
						$[HNO_3]$ (M)	$\left[\overline{HNO_3}\right]$ (M)
1	CH_3	C_4H_9	$C_{12}H_{25}$	TPH	0.5	3.5	-
2	CH_3	C_4H_9	$C_{14}H_{29}$	C_6H_6	0.65	11.8	3.1 [a]
				TPH	0.65	5.7	1.20
					0.5	4.7	-
3	CH_3	C_4H_9	$C_{16}H_{33}$	TPH	0.5	5.2	0.77
4	CH_3	C_4H_9	$C_{18}H_{37}$	TPH	0.51	9.9	1.56
5	CH_3	C_4H_9	$C_2H_4OC_6H_{13}$	TPH	0.5	0.9	-
6	CH_3	C_4H_9	$C_2H_4OC_8H_{17}$	TPH	0.5	1.7	-
7	CH_3	C_4H_9	$C_2H_4OC_{12}H_{25}$	TPH	0.5	4.8	0.34
					0.65	4.4	0.77
8	CH_3	C_4H_9	$(CH_2)_3OC_{11}H_{23}$	TPH	0.65	2.5	0.46
				C_6H_6	0.65	12.4	3.6 [a]
9	CH_3	C_4H_9	H	C_6H_6	0.65	6.34	1.4 [a]
10	C_2H_5	C_2H_5	H	TPH	0.1	14.6	0.012
				C_6H_6	0.5	6.33	0.08
11	C_2H_5	C_2H_5	$C_{18}H_{37}$	TPH	0.1	4.6	0.13
				C_6H_6	0.5	11.7	2.2

[a] *Such concentrations have been reached without third-phase formation.*

TABLE 4. Third-phase Formation During the Extraction of U(VI), Nd (III), and Fe(III) Nitrates from Nitric Acid Media, by Some Malonamides $(RR'NCO)_2CHR''$ at Room Temperature (21-22°C) (ambient conditions)

No.	R	R'	R"	[Diamide] (M)	Diluent	Third phase boundary for organic M in mol/l (corresponding aqueous nitric concentration in mol/l)		
						U(VI)	Nd(III)	Fe(III)
2	CH_3	C_4H_9	$C_{14}H_{29}$	0.5	TPH	0.02 (3.0)		
				0.65			0.041 (4.0)	
				0.67				0.026 (3.5)
3	CH_3	C_4H_9	$C_{16}H_{33}$	0.65		0.072 (3.5)	0.092 (4.0)	0.052 (3.6)
4	CH_3	C_4H_9	$C_{18}H_{37}$	0.5		0.12 (3.0)		
				0.65			0.15 (4.0)	0.088 (3.7)
7	CH_3	C_4H_9	$C_2H_4OC_{12}H_{25}$	0.65		0.053 (3.67)	0.050 (3.6)	0.036 (3.6)
2	CH_3	C_4H_9	$C_{14}H_{29}$	0.65	C_6H_6	0.76 (3.73) [a]	0.19 (3.4)[b]	0.24 (3.5) [c]
9	CH_3	C_4H_9	H	0.65		0.0088 (3.27)	0.026 (4.0)	0.0009 (4.1) [c]
10	C_2H_5	C_2H_5	H	0.65		0.0003 (3.44)	0.0041 (3.7) [b]	0.0001 (3.6) [c]
11	C_2H_5	C_2H_5	$C_{18}H_{37}$	0.65		0.79 (3.73) [a]	0.20 (3.4) [b]	0.24 (3.5) [c]
8	CH_3	C_4H_9	$(CH_2)_3OC_{11}H_{23}$	0.65		0.78 (3.65) [a]	0.21 (3.1) [b]	0.21 (3.4) [c]

[a][b][c] *Such concentrations have been reached without third-phase formation :*

[a] $C_U = 0.75\ \underline{M}$, [b] $C_{Nd} = 2\ \underline{M}$, [c] $C_{Fe} = 0.75\ \underline{M}$.

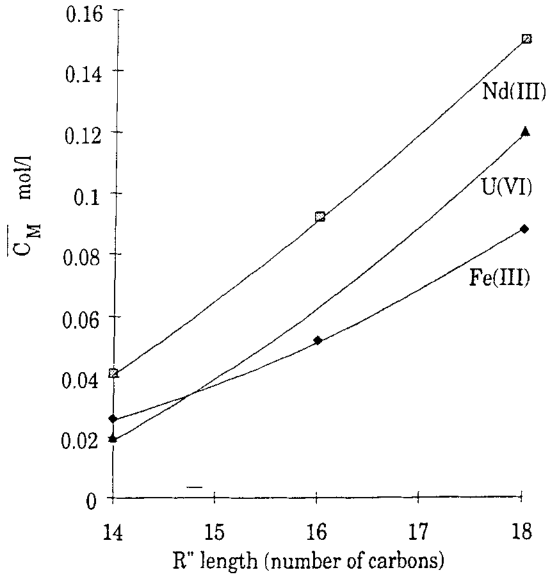


FIGURE 3. Third phase boundary formed during the extraction of U(VI), Nd(III) and Fe(III) nitrates with various malonamides (No. 1, 2, 3) $(CH_3(C_4H_9)NCO)_2CHR"$ in TPH at room temperature (21-23°).
U(VI) : $\overline{C_{amide}} = 0.5\ \underline{M}$ $C_{HNO_3} = 3\ \underline{M}$ (the 2 points are joined by a curve by analogy with the behaviour of the two other metallic ions) ;
Nd(III) : $\overline{C_{amide}} = 0.65\ \underline{M}$ $C_{HNO_3} = 3.6\ \underline{M}$;
Fe(III) : $\overline{C_{amide}} = 0.65\ \underline{M}$ $C_{HNO_3} = 4\ \underline{M}$.

- the use of aromatic diluents instead of aliphatic diluents shifts the third-phase boundary towards higher concentrations (Table 1, molecules 2 and 8 for HNO_3 and Table 4, molecule 2 for Nd(III), even if aqueous HNO_3 concentrations are not exactly the same for the two tests using TPH and benzene);
- increasing of the length of the R" alkyl substituent (for constant R and R' alkyl groups) shifts the third-phase boundary towards higher concentrations (e. g. figures 2 and 3). This effect is also observed on increasing the length of R or R' groups (for constant R" group), as demonstrated in experiments to be reported elsewhere (18);
- the introduction of an ether function in the γ place on the central group (CHR" with R" = $C_2H_4OC_{(n-2)}H_{(2n-3)}$) increases the concentration required for third phase formation. Investigations using benzene as a diluent show that an oxygen

in the δ place substitution (CHR" with R" = $C_3H_7OC_{(n-3)}H_{(2n-5)}$) has hardly any influence;

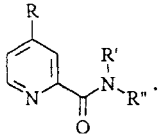
- loading capacities for diamides 2 and 3 in TPH solution are greatly improved by comparison with the reference diamide DMDBTDMA (No. 2) owing to their longer R" alkyl group.

Even, if we don't have any definite experimental proof, third-phase dependence on the length of the carbon chains of R", R, and R' can be tentatively attributed to the increase in the van der Waals-type interactions between these alkyl groups and the aliphatic chain of the diluent. Indeed, the third phase appearance (or non-miscibility of species in organic medium) had linked to amide-diluent interactions. These van der Waals interactons between aliphatic chains are essentially London forces (or dispersion force) (19) which increase with the size of the molecules (20) and with the length of the alkyl groups R", R or R'. These interactions counteract the effects of the polar moiety of these molecules which are active at the water-TPH interface.

Am(III) Extraction : Figure 4 shows the effect of the length of the central alkyl chain R" on the extraction of americium(III) nitrate by malonamide 0.5 M solutions in TPH. The best extraction for Am(III) nitrate from concentrated nitric solutions is obtained with 14 carbon atoms in the R" group. However, malonamide $(CH_3(C_4H_9)NCO)_2CHC_{18}H_{37}$ can be used over a larger range of acidities, although its extracting power is slightly lower.

Conclusion : These results confirm that the two substituents on the nitrogen atoms must be different, and that a sufficient number of carbon atoms is necessary in the nitrogen and the carbon bridge substituents to avoid third phase formation in the presence of metallic salts. The diamides $(CH_3(C_4H_9)NCO)_2CHR"$ with R" = $C_{18}H_{37}$ or $C_{16}H_{33}$ appear to be suitable molecules for further investigations.

Picolinamides

The general formula of picolinamides is . It has been found that nitrogen or sulfur donor ligands have higher affinities for trivalent actinides

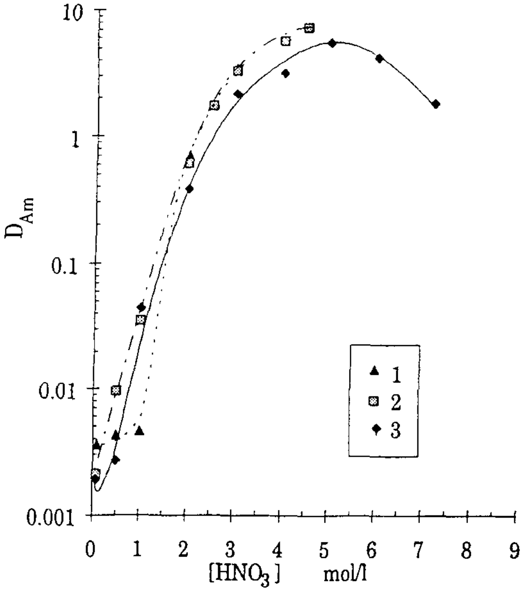


FIGURE 4. Extraction of Am(III) nitrate by various malonamides $(CH_3(C_4H_9)NCO)_2CHR"$ 0.5 M in TPH at room temperature.
1 : R" = $C_{12}H_{25}$,
2 : R" = $C_{14}H_{29}$,
3 : R" = $C_{18}H_{37}$.

than for trivalent lanthanide ions (7, 8). In fact, the soft N or S atoms form metal-ligand atom bonds with greater covalent character than is the case with oxygen. Combining the advantages of amides (O atom donors) with the selective properties of nitrogen atom donors, it was considered that the picolinamides with donor O and N atoms might have interesting properties for actinides separation.

The chemical properties of picolinamides depend on the nature of the R, R', and R" alkyl groups. A potential extractant for better reprocessing must satisfy several points :

- extraction of An(III), (IV) and (VI) nitrates;
- minimal extraction of Ln(III) nitrates;
- compatibility with concentrated nitric acidic solutions;

- compatibility with the industrial diluent (TPH); and
- a low solubility in the aqueous phase.

Two kinds of studies were performed : complexation studies using picolinamides soluble in the aqueous phase ; and extraction studies with more lipophilic molecules. The formulae of these molecules are presented in Tables 5 and 6.

Each picolinamide was tested, in particular, the complexation behavior of the water- soluble picolinamide pyridine 2-carboxamide (No. 1) was especially studied.

Optimisation of the Picolinamide Formula

The main requirement is the An(III)/Ln(III) separation. The formation constants of light picolinamide complexes with Am(III) and Nd(III) ions are given in the Table 7. These constants are determined by monitoring the hypersensitive absorption band by UV-visible spectrophotometry of Am(III) and Nd(III) at 503.5 and 580 nm respectively.

Several trends can be observed. The replacement of H atoms by alkyl groups is associated with a decrease of the complex formation constant. This can probably be explained by a steric effect which hindered the cation-ligand approach.

The influence of R, R', and R" substituents on the distribution ratios between lipophilic picolinamides and aqueous lithium nitrate solutions are reported in the Table 8 and shown in figure 5.

In the same experimental conditions, the separation factors do not depend on the length of R". Nevertheless, a maximum of the extraction of M(III) nitrates is observed with R" = C_8H_{17}. Further increasing R" length decreases the extracting power of picolinamide but, conversely, increases the solubility of the molecule in the diluent (21).

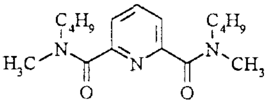
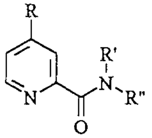
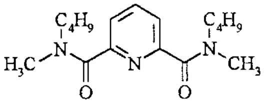
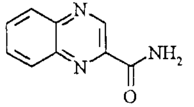
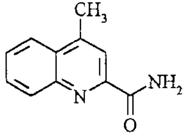
The molecule  with two amidic functions was tested. It possesses a nitrogen donor atom (the pyridinic one) and two amidic functions. The molecule displays comparable affinity for Am(III) and Eu(III) nitrates and far lower affinity for Ce(III) nitrate (Table 9).

TABLE 5. Formulae of the Picolinamides Studied



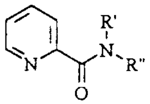
No.	R	R'	R"	Nature of the Study
1	H	H	H	complexation
2	H	H	C_4H_9	complexation and extraction
3	H	CH_3	C_4H_9	complexation
4	H	H	C_8H_{17}	extraction
5	H	H	$C_{12}H_{25}$	extraction

TABLE 6. Other Studied Picolinamides

No.	Formula	Nature of the Study
6		extraction
7		extraction
8		extraction

The difference between the extraction of Am(III) and Eu(III) is very slight. Picolinamides are probably coordinated to metal cations by the oxygens of the two amidic groups, but the nitrogen atom may not be bound to the metal ion. The difference between the extraction behavior of Eu(III) and Ce(III) can be explained by differences in ionic radii (Eu^{3+} : 0.95 Å and Ce^{3+} : 1.01 Å). The radius contraction with constant ionic charge increases the charge density

TABLE 7. Stability constants of Am(III) and Nd(III)-Picolinamide



Complexes at Room Temperature (21, 22).

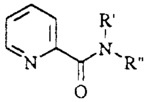
No.	R'	R"	Medium	β_{11} Nd(III) (l.mol^{-1})	β_{11} Am(III) (l.mol^{-1})	β_{12} Am(III) (l^2.mol^{-2})
1	H	H	H_2O[a]	2.5	75	250
			MeOH[b]	18	-	-
2	H	C_4H_9	MeOH[b]	6	54	-
3	CH_3	C_4H_9	MeOH[b]	0.1	-	-

[a] *Ionic Strength = 1 ($NaNO_3$), pH = 4;*

[b] *Methanol medium with 3 % water;*

- not determined.

TABLE 8. Eu(III) and Am(III) Extraction from Lithium Nitrate Media by



at Room Temperature.

No.	R'	R"	$LiNO_3$ (M	C_{amide} (M	Diluent	$D_{Eu(III)}$	$D_{Am(III)}$	S_F Am/Eu*
2	H	C_4H_9	5	2	C_6H_6	0.42	1.86	4.4
			5	pure	none	0.94	2.53	2.7
4	H	C_8H_{17}	5	2	C_6H_6	0.7	3.22	4.6
			3	pure	none	3.8	29.8	7.7
5	H	$C_{12}H_{25}$	5	1.8	C_6H_6	0.16	0.74	4.6
			3	1.5	C_6H_5CN	0.26	1.95	7.5

* S_F *Am/Eu* = $D_{Am(III)}/D_{Eu(III)}$.

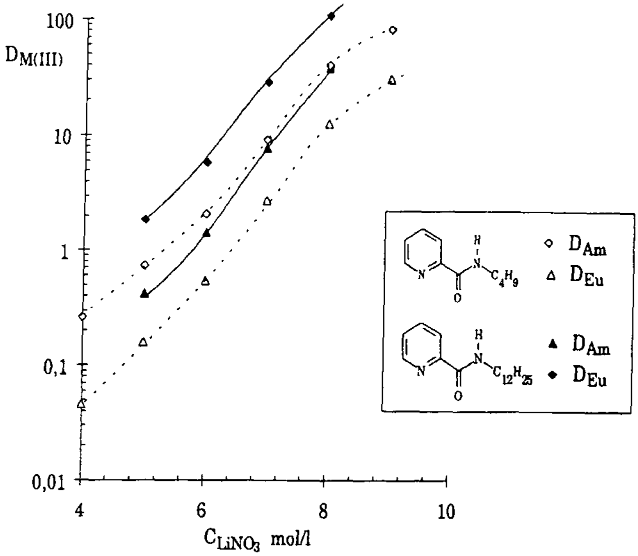
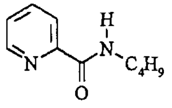
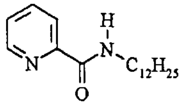


FIGURE 5. Extraction of Am(III) nitrate and Eu(III) nitrate by picolinamides. Aqueous phase contained HNO_3 (0.01 M) and $LiNO_3$ at room temperature (ambient conditions).

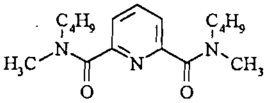


2.0 M in benzene,



1.78 M in tertiarybutylbenzene.

TABLE 9. Distribution Coefficients of Trivalent Metallic Nitrates for

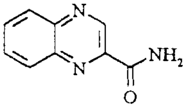
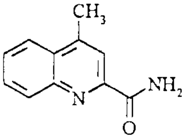


in C_6H_5CN (0.4 M) at Room Temperature.

[The aqueous phase contains HNO_3 (0.04 M) and $LiNO_3$ (5 M)].

Cation	$D_{M(III)}$	S_F Am/Eu
Am(III)	8.82	-
Eu(III)	6.39	1.4
Ce(III)	0.75	11.8

and hence the ionic association. The complexation being mainly ionic, this is in agreement with an increase of the extraction from Ce(III) to Eu(III).

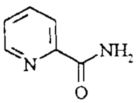
Two other molecules were tested :  (quinoxaline 2-carboxamide N°7) and  (lepidine 2-carboxamide No. 8). The main drawback for the use of these molecules is their limited solubility in common diluents. For example, the solubility in $CHCl_3$ at 26°C is only 0.1 M for quinoxaline 2-carboxamide and 0.6 M for lepidine 2-carboxamide. The use of such organic solutions for the extraction of Am(III) or Ln(III) nitrates led to negligible distribution ratios of these metallic species.

Conclusion

From the first results obtained, several trends for the definition of an optimum picolinamide molecule have been established:

- picolinamides with a double ring (e.g. quinoxaline 2-carboxamide) do not extract An(III) and Ln(III) nitrates;
- picolinamides with 2 amide functions (e.g. pyridine 2,6-dicarboxamide) have properties similar to those of malonamides. They do not allow An(III)/Ln(III) group separation (see for example the poor S_F Am/Eu in Table 5);
- molecules with long alkyl group on the nitrogen of the amide appear to be attractive.

In the future, the extracting properties of 4-alkyl 2-carboxamido pyridine will also be considered.

Properties of 

Protonation : The protonation of the pyridine 2-carboxamide molecule was studied by UV-visible spectroscopy and Raman spectroscopy.

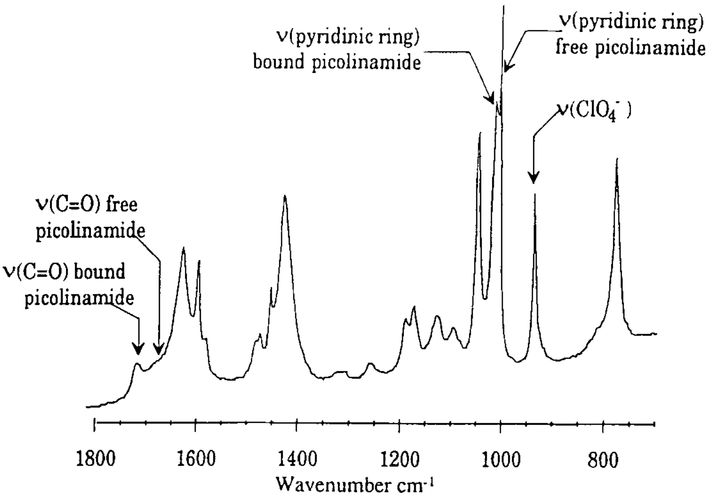
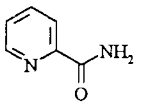


FIGURE 6. Raman spectra of  in acidic media. $\overline{C_{amide}} = 0.5$ M, $C_{HCl} = 0.134$ M, $C_{NaClO_4} = 0.1$ M.

- For aqueous solutions of pyridine 2-carboxamide with hydrochloric acid concentrations lower than 1 M, the modification of the UV-visible and Raman spectra indicated N-pyridinic protonation. A shift of the carbonyl stretching vibration from 1675 cm^{-1} to 1714 cm^{-1} and of the pyridinic ring vibration from 1000 cm^{-1} to 1012 cm^{-1} (Figure 6) agree with only a protonation of the pyridine ring nitrogen.

- For hydrochloric acid concentrations over 1 M, a slight shift of the pyridinic ring vibration from 1012 cm^{-1} to 1014 cm^{-1} and a regular increase of the intensity of that band with acid concentration, suggests a second protonation, probably on the amidic nitrogen.

The pKa of pyridine 2-carboxamide for the protonation of the pyridine ring nitrogen was determined from UV-visible and Raman spectroscopic data. The different values obtained are reported in Table 10.

TABLE 10. pKa of Pyridine 2-carboxamide in Aqueous Phase at Room Temperature (Ionic Strength = 1 (NaCl)).

Method used	pKa	Reference
UV-visible spectroscopy	1.83	(21)
Raman spectroscopy	1.87	(23)

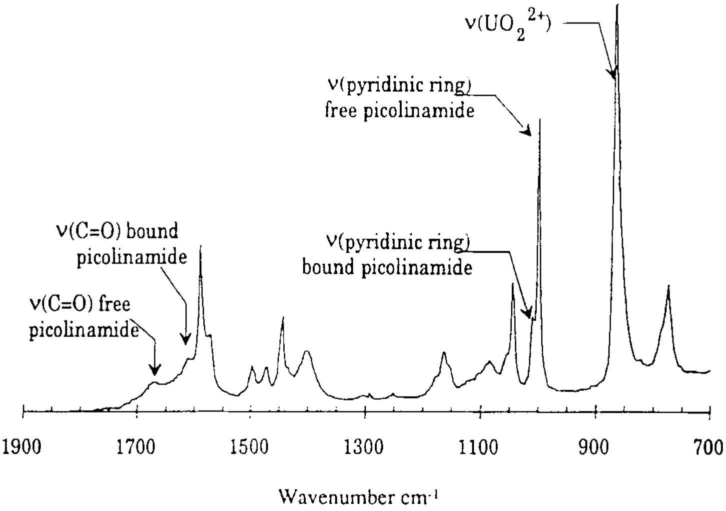


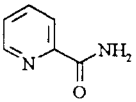
FIGURE 7. Raman spectra of UO_2^{2+} -  complex. $\overline{C_{amide}} = 0.5$ M, $C_{UO_2Cl_2} = 0.25$ M.

TABLE 11. Stability Constants of Metallic Ion-Picolinamide 1-1 Complexes at Room Temperature.

Metallic Ion	β_{11}	Reference
Nd(III)	2.5[a]	(22)
Nd(III)	9.5[b]	(23)
U(VI)	5.3[b]	(23)
Th(IV)	> 100[b]	(23)

[a] *determined by UV-visible spectroscopy in nitrate media.*
Ionic strength = 1 ($NaNO_3$), pH = 4.
[b] *determined by Raman spectroscopy in chloride media.*
Ionic strength = 3.

The value of pKa showed that picolinamide has a weak basic character. Thus, proton complexation will be in competition with metallic ion complexation.

Metallic cation complexation : In the Raman spectra of Nd(III), U(VI), and Th(IV) - pyridine 2-carboxamide complexes [see for example Figure 7 for the U(VI) complex], the following were observed :

- a shift of the pyridinic ring stretching vibration from 1000 to 1011 cm^{-1};
- a shift of the carbonyl stretching vibration from 1675 to 1615 cm^{-1}.

These features imply the formation of a bidentate complex. The metal-picolinamide bonds arise through the oxygen of the carbonyl group and the nitrogen of the pyridinic ring. The stability constants determined by Raman spectroscopy are reported in Table 11.

The following complex stability scale is U(VI) < Ln(III) < Th(IV).

The values of the stability constants of the Nd(III)-picolinamide complex, determined by Raman and UV-visible spectroscopies, are different. The difference between complexation constants of lanthanide by nitrate and chloride ligand agrees with the variation of β_{11} M(III)-picolinamide in the two media (for example : $\beta_{PrCl^{2+}} = 0.9$ and $\beta_{PrNO_3^{2+}} = 1.7$ at pH = 3 (24)) but does not fully explain the variation. Moreover, the experimental conditions (ionic strength and pH) are not exactly the same. To explain that, and to confirm either one value or the other, further studies will be needed using other techniques (e. g., NMR spectroscopy).

CONCLUSIONS

We have seen that malonamides are able to extract actinides(III, IV and VI) from nitric acid solutions. It has been demonstrated that while DMDBTDMA is a satisfactory molecule, its properties can be improved substantially, especially concerning the third-phase boundary when extracting solutes like nitric acid or metallic nitrates. Picolinamides have potential for the separation of An(III) and Ln(III).

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REFERENCES

1. J.M. Adnet, L. Nigond, N. Condamines, J. Bourges and C. Madic, Proceedings of SAFEWASTE 93 International Conference 13-16 June 1993 Avignon (FRANCE) Vol 2, 323 SFEN Ed.
2. N. Condamines and C. Musikas, Solvent Extr. Ion Exch., 6 (6) 1007 (1988).
3. N. Condamines and C. Musikas, Solvent Extr. Ion Exch., 10 (1) 69 (1992).
4. C. Cuillerdier, C. Musikas, P. Hoel, L. Nigond and X. Vitart, Sep. Sci. Technol. 26 (9) 1229 (1991).

5. C. Cuillerdier, C. Musikas and L. Nigond, Sep. Sci. Technol., 28 (1-3) 155 (1993).

6. C. Musikas, Proceedings of "ISEC 90" Kyoto 1990.

7. C. Musikas, Actinide-lanthanide separations, G.R. Choppin, J.D. Navratil, W.W. Schultz, Eds, Word Scientific, (1984).

8. K.L. Nash, Solvent Extr. Ion Exch., 11 (4) 728 (1993).

9. C. Madic, and al., Procedings of RECOD'94, Volume III, (London, U K)

10. C. Cuillerdier, C. Musikas and C. Coutin, 22èmes Journées des Actinides, Méribel, April 1992.

11. C. Cuillerdier, C. Musikas, French Patent FR. 2.684.670 (1991).

12. L. Nigond, Thèse de Doctorat de l'Université Blaise Pascal, (1992). Published as CEA-R-5610.

13. L. Nigond, C. Musikas and C. Cuillerdier, Solv. Extr. Ion Exch., 12 (2) 261 (1994).

14. L. Nigond, C. Musikas and C. Cuillerdier, Solv. Extr. Ion Exch., 12 (2) 297 (1994).

15. T.H. Siddall. III, R.L. McDonald and W.E. Stewart, J. Mol. Spectrosc., 28, 243 (1968).

16. P. Byers, M.G.B. Drew, M.J. Hudson, N.S. Isaacs and C. Madic, Polyhedron, 13 (3) 349 (1994).

17. M.C. Charbonnel, Thèse de Doctorat de l'Université Blaise Pascal (1988). Published as CEA-R-5469.

18. N. Condamines and al., to be published (1995).

19. Y. Marcus, Principles and practices of solvent extraction, J. Rydberg, C. Musikas, G.R. Choppin, M Dekker, New York, Basel, Hong Kong, 21 (1992)

20. J.A.A. Ketelaar, Liaisons et propriétés chimiques, Translated by M. Fayard, Dunod, Paris, 294 (1960).

21. P.Y. Cordier, personal communication.

22. C. Coutin, personal communication.

23. J. Livet, P.Y. Cordier and N. Condamines, 23èmes Journées des Actinides, Schwarzwald (April 1993).

24. D.F. Peppard, G.W. Mason and I. Hucher, J. Inorg. Nucl. Chem., 24, 881 (1962).