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POTENTIALITY OF NONORGANOPHOSPHORUS EXTRACTANTS IN CHEMICAL SEPARATIONS OF ACTINIDES

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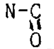
ABSTRACT

To limit the amounts of radioactive wastes coming from actinide separations by solvent extraction, completely incinerable extractants are desirable. This paper deals with the prospects offered by N,N-dialkylamides, as alternatives to TBP for irradiated nuclear fuels reprocessing and by N,N'-tetraalkyl 2-alkylpropane diamides as actinide extractants from radioactive wastes solutions. The selection of N,N'-dialkylamides based on the solubility of the nitrato-uranyl amide complexes in aliphatic hydrocarbons is presented. The extraction chemistry of the main metallic ions present in irradiated nuclear fuels nitrate solutions is discussed as well as the hydrolysis and radiolysis of these extractants. Results of a bench scale test for a first reprocessing cycle shows the reason for interest in the N,N-dialkylamides as substitutes for TBP. The extraction of the main metallic species contained in actinide wastes by N,N'-tetraalkylpropane diamide or by N,N'-tetraalkyl,2-alkylpropane diamide is presented. The results show that these diamides present good prospects, for removing the actinides contained in various wastes solutions.

INTRODUCTION

One way to limit the cost of reprocessing of irradiated nuclear fuels by wet processes would be to decrease the amounts of wastes and simplify the separations.

The extractant change seems a simple way of doing this since the organo phosphorus molecules (TBP, TOPO, HDEHP, CMP, CMPO...) generate large amounts of wastes because the extactants themselves and the numerous solvent regeneration cycles necessary to avoid the presence of altering radiolytic and hydrolytic products such as HDBP, all produce wastes that must be disposed of or incenerated. Among the completely incinerable nonorganophosphorus molecules those containing the amide moeity  $N-\underset{\underset{O}{\|}}{C}$ seem particularly interesting because of the donor properties of amides and their chemical stability.

It has already been reported that N,N-dialkylamides are good extractants for hexavalent and tetravalent actinides and selective towards fission products (1 to 5), but they must be diluted in an aromatic hydrocarbon in order to avoid third phase formation in the presence of large amounts of U(VI). The goals of our investigations were : 1/ to find N,N-dialkylamides of which the nitrato uranyl salts were sufficiently soluble in aliphatic hydrocarbons and 2/ to find simplifications of the reprocessing chemical processes. This paper is an up to date survey of the results obtained in our laboratory.

Trivalent actinides extractants from highly acidic wastes have been under investigations for more than two decades (5 to 10) and polyfunctionnal extractants like CMPO ($C_8H_{17}C_6H_5POCH_2CON$-$(iC_4H_9)_2$) have been found useful for the removal of α emitters from several type of wastes. In this paper we will present some chemical properties of the N,N'-tetraalkyl malonamides (RR' $NCOCH_2$ CON RR') where R and R' are alkyl radicals or N,N'-methylbutyl,2-alkyl propane diamide $(C_4H_9CH_3NCO)_2CHR$, where R is an alkyl or oxoalkyl radical. These bifunctionnal extractants are less known than the organophosphorus ones but they present the advantage of being completely incinerable and giving radiolytic and hydrolytic degradation products that perhaps alter the process less than the dialkylphosphoric acids.

EXPERIMENTAL

Reagents : The extractants used in this investigation were not commercially available. They were prepared by G.THIOLLET (IRCHA- Vert le Petit). The N,N-dialkylamides were obtained by reacting the corresponding acyl chloride with a secondary amine according to the reaction : $RCOCl + HNR'_2 \xrightarrow{(C_2H_5)_3N} RCONR'_2 + H(C_2H_5)_3NCl$.

The product amides were purified by vacuum distillation. After alkaline and acidic washings to remove small amounts of carboxylic acid and secondary amine, they were more than 99.5 % pure. The N,N'-tetraalkylmalonamides were obtained by the reaction of the corresponding secondary amine with malonylchloride according to: $2HNRR' + CH_2(COCl)_2 + 2(C_2H_5)_3N \rightarrow 2H(C_2H_5)_3NCl + CH_2(CONRR')_2$. The higher molecular weight tetralkylmalonamides were purified by chromatography on a silica gel column and the lighter ones by distillation under low pressure. The purity was checked by ^1H NMR, elemental analysis and acidimetry and found to be in the range 98.5 - 100 %.

In order to keep the cost of the extractant low, the N,N'-tetraalkyl, 2-alkyl, propane diamides were prepared by reacting N,N' -dimethyldibutylmalonamide (DMDBMA) with LiC_4H_9 and then with RX where R is an alkyl or oxoalkyl radical and X an halogen atom according to the reactions.

$$(CH_3C_4H_9NCO)_2\ CH_2 + C_4H_9Li \rightarrow (CH_3C_4H_9NCO)_2\ CHLi + C_4H_{10}$$

$$(CH_3C_4H_9NCO)_2\ CHLi + RX \rightarrow (CH_3C_4H_9NCO)_2\ CHR + LiX$$

DMDBMA was first prepared by the method described above. It is an advantageous starting material because of the commercial availability of N,N-methylbutylamine ($HNCH_3C_4H_9$) and the possibility to get high yields of pure DMDBMA by distillation under vacuum.

The radionuclides, ^{239}Pu, ^{233}U, ^{241}Am, and ^{106}Ru were provided by STU (Fontenay-aux-Roses) and ^{152}Eu, ^{141}Ce, ^{95}Zr, ^{59}Fe, ^{85}Sr, and ^{137}Cs were provided by ORIS (Saclay).

All the other chemicals were analytical grade RP Prolabo products and were used without further purification.

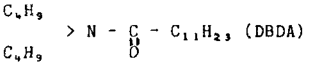
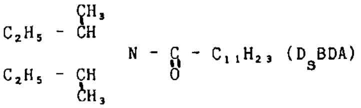
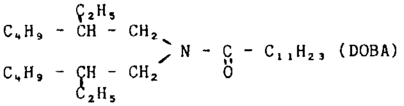
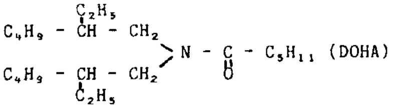
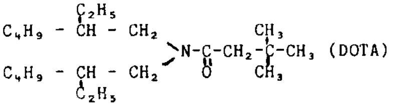
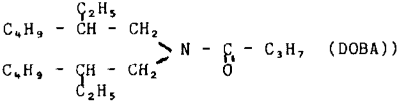
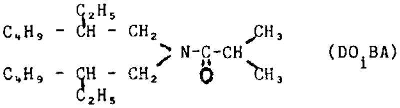
Procedures : The distribution ratios measurements were obtained by standard methods using radioactive tracers and quantitative γ or α spectrometric analysis. The irradiation tests were carried out in a ^{60}Co irradiator. Equal volumes of organic and HNO_3 aqueous phases were put together in the irradiator and shaken twice a day. The bench-scale first-reprocessing-cycle test has been carried out using small laboratory-scale mixer-settler batteries.

RESULTS- DISCUSSION

Extractive Properties of N,N-Dialkylamides

. Selection of N,N-dialkylamides based on the nitrato uranyl complex solubility into aliphatic hydrocarbons. The advantage of aliphatic hydrocarbons diluents over aromatic ones is well established for chemical processes performed in nitrate media. We first investigated the solubility of nitrato uranyl complexes with different N,N-dialkylamides having different nitrogen and carbonyl substituents in Hyfrane (a substituted aliphatic hydrocarbon with twelve carbon atoms). The results are contained in Table 1. It can be seen that amides with two 2-ethylhexyl substituents on the nitrogen are suitable for the separations since uranium solubilities higher than 100 g l^{-1} have been found. Further work was undertaken to gain insight into the carbonyl substituent influence, keeping the two 2-ethylhexyl as nitrogen substituents.

Table 1 : Solubility of $UO_2(NO_3)_2$ in various N,N-dialkylamide solutions (1M into hyfrane, θ = 25°C)

Formula and acronyum of the extractant	$[U(VI)]_{org}$ $g.l^{-1}$	$[HNO_3]_{aq}$ $mol\ l^{-1}$
 $\begin{matrix} C_4H_9 \\ C_4H_9 \end{matrix} > N - \underset{\overset{\Vert}{O}}{C} - C_{11}H_{23}$ (DBDA)	80	0
DBDA	71	4
 $\begin{matrix} C_2H_5 - \overset{CH_3}{CH} \\ C_2H_5 - \underset{CH_3}{CH} \end{matrix} N - \underset{\overset{\Vert}{O}}{C} - C_{11}H_{23}$ (D_sBDA)	64	0
D_sBDA	36	4
 $\begin{matrix} C_4H_9 - \overset{C_2H_5}{CH} - CH_2 \\ C_4H_9 - \underset{C_2H_5}{CH} - CH_2 \end{matrix} > N - \underset{\overset{\Vert}{O}}{C} - C_{11}H_{23}$ (DOBA)	>120	0 and 4
 $\begin{matrix} C_4H_9 - \overset{C_2H_5}{CH} - CH_2 \\ C_4H_9 - \underset{C_2H_5}{CH} - CH_2 \end{matrix} > N - \underset{\overset{\Vert}{O}}{C} - C_5H_{11}$ (DOHA)	>120	0 and 4
 $\begin{matrix} C_4H_9 - \overset{C_2H_5}{CH} - CH_2 \\ C_4H_9 - \underset{C_2H_5}{CH} - CH_2 \end{matrix} > N - \underset{\overset{\Vert}{O}}{C} - CH_2 - \overset{CH_3}{\underset{CH_3}{C}} - CH_3$ (DOTA)	>120	0 and 4
 $\begin{matrix} C_4H_9 - \overset{C_2H_5}{CH} - CH_2 \\ C_4H_9 - \underset{C_2H_5}{CH} - CH_2 \end{matrix} > N - \underset{\overset{\Vert}{O}}{C} - C_3H_7$ (DOBA))	>120	0 and 4
 $\begin{matrix} C_4H_9 - \overset{C_2H_5}{CH} - CH_2 \\ C_4H_9 - \underset{C_2H_5}{CH} - CH_2 \end{matrix} > N - \underset{\overset{\Vert}{O}}{C} - CH \begin{matrix} CH_3 \\ CH_3 \end{matrix}$ (DO_iBA)	>120	0 and 4

Extraction of metallic species : Uranium (VI) distribution ratios as a function of aqueous nitric acid and organic extractant concentrations are plotted in figures 1 and 2.

The extraction mechanism of U(VI) cannot be deduced from the slope of $\log D_{U(VI)}$ vs. log[Amide] (figure 2). It has been found (11) that the organic phase is saturated with uranium for the concentrations ratios [Amides]/[U(VI)] close to 2.0. There are no

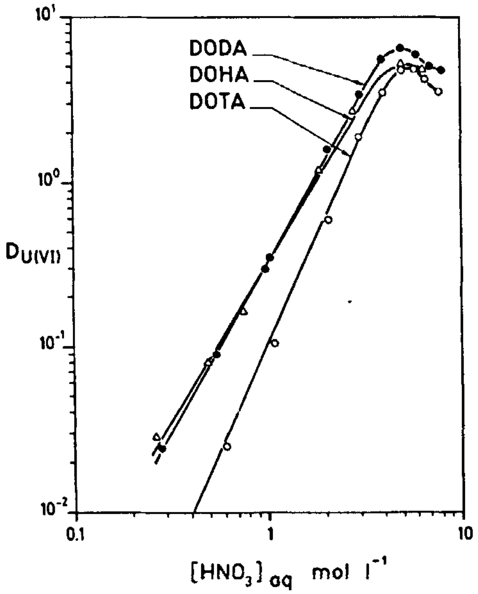


FIG.1.Distribution Ratios of U(VI) between 0.5M N,N-Dialkylamides into Hyfrane and Aqueous solutions as a function of Nitric acid concentration.

organic U V-spectrometric changes upon the organic phase loading, so the non-integer value of the slope can be attributed to highly non ideal behavior of amide extractants or to the formation of second sphere nitrato uranyl amide complexes with excess amide.

The U V-spectra of the organic phases and the slope values of log $D_{U(VI)}$ vs. log [extractant] (figure 2) showed that for high aqueous acidities the extraction equilibrium becomes

$UO_2^{2+} + 3NO_3^- + H^+ + \overline{L} \rightleftarrows \overline{UO_2(NO_3)_3 H^{+-}L}$ where L represents the extractant.

This anionic extraction is a consequence of the rather high basicity of N,N-dialkylamides in comparison with TBP. As already mentioned by Siddall (1) the distribution ratios of Pu(IV) are sensitive to the presence of branched chains on the carbonyl substituents. It can be seen from figure 3 plots that higher distributions coefficients are measured for DOHA (N,N di(2- ethylhexyl) hexanamide) ; than for DOTA (N,N-di(2-ethylhexyl), 3,3-dimethyl-

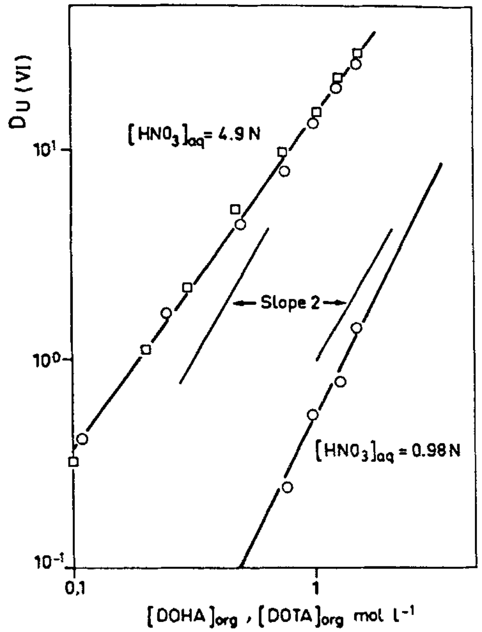


FIG.2.Distribution Ratios of U(VI) between Aqueous nitric acid solutions as a Function of N,N-Dialkylamide concentration in Hyfrane DOHA ◘ DOTA o

butyramide). The separations factors, $D_{U(VI)}/D_{Pu(IV)}$ increase with the carbonyl substituents branching and this feature can be used to advantage to design U/Pu partition flow sheets without Pu(IV) reduction.

The distribution ratios of ruthenium, nobium, and zirconium as a function of nitric acid concentration are plotted figure 4a and 4b. DOTA allows better Zr(IV) separations factors as already mentionned in previous work for branched N,N-dialkylamides (1).

Radiolysis and hydrolysis of N,N-dialkylamides : It is important for an extractant used in the nuclear field to be resistant to radiolysis and hydrolysis in the presence of nitric acid. Tests on N,N-dialkylamides radiolysis (4,12) or hydrolysis (2) have already been carried out showing that these extractants are fairly stable more or less like TBP. The DOHA radiolysis in the presence

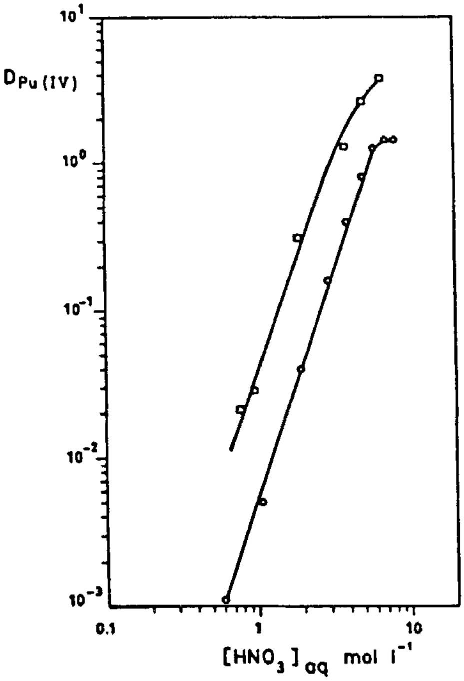


FIG.3.Distribution Ratios of Pu(IV) between 0.5M N,N-Dialkylamides into Hyfrane and HNO_3 Aqueous solutions as a Function of HNO_3 concentration.DOHA □ DOTA ○

of HNO_3 was investigated and its degradation is illustrated by the figure 5 plots. DOHA, hexanoic acid and N,N-di(2-ethylhexyl) amine were titrated in the radiolysed solutions by acido-basic reactions in non aqueous media. It can be pointed out that the missing DOHA corresponds roughly to the hexanoic acid formed whereas in the case of TBP, it is known that $G_{-TBP} > G_{HDBP}$. Surprisingly very small amounts of secondary amine have been detected ; probably because it disappears as fast as it appears. Since hexanoic acid is the primary degradation product, its effect on the distribution coefficients of Pu(IV) and U(VI) is shown figure 6. It can be seen that concentrations corresponding to radiation dose of respectively 10 M rad (HNO_3 4N) and 60 M rad ($HNO_3$0.5N) do not alter the extractive properties of the solvent. Some comparative G values for TBP and DOHA radiolysis are given in Table 2.

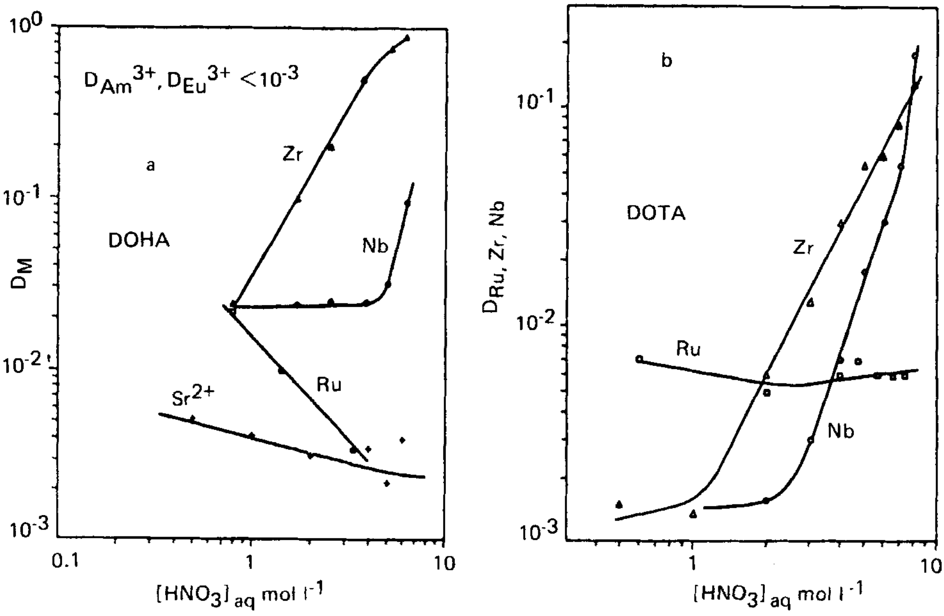


FIG.4.Distribution Ratios of Fission products between 1M DOHA (a) or 1M DOTA (b) into Hyfrane as a Function of Nitric acid concentration.

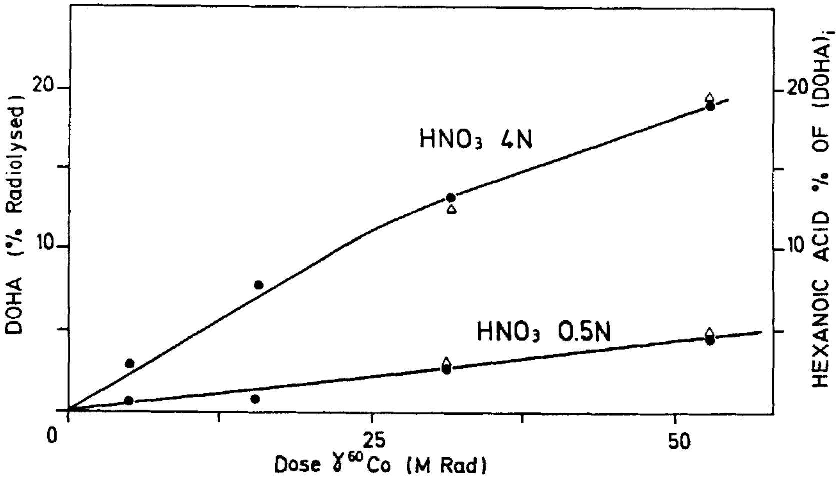


FIG.5. % of DOHA radiolysed or % of Hexanoic acid yield as a function of irradiation dose.
Initial organic solutions : 1M DOHA into TPH.Initial aqueous solutions : HNO_3 as indicated Temperature : 40° C

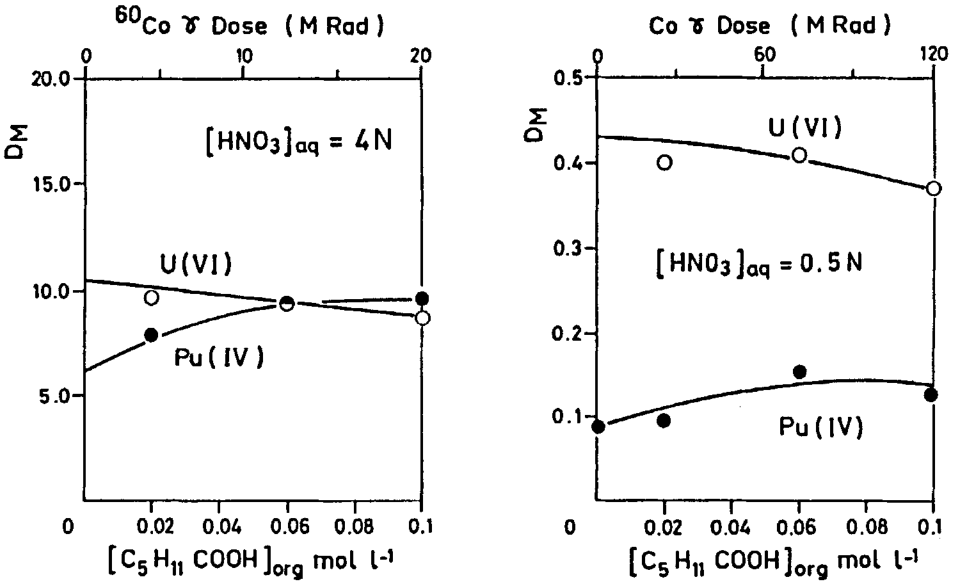


FIG.6. Effect of Hexanoic Acid Concentration Upon the U(VI) Traces Distribution Ratios Between 1M DOHA into Hyfrane and Aqueous 4N HNO_3 (Extraction Step) or 0.5N HNO_3 (Partition Step). The upper abcissae numbers indicate the γ dose which produces equivalent amounts of hexanoic acid.

Table 2 : Comparaison of DOHA 1M in TPH and TBP 30 % in dodecan radiolysis. (11)

Doses Wh.l^{-1}	Aqueous phase	G ($^{-}$DOHA)	G HA	G (HDBP)
147	HNO_3 4N	3.6	3.6	
147	HNO_3 0.5N	0.9	0.9	
200	HNO_3 2N			0.77
416	HNO_3 5N			0.86
45	HNO_3 1N			1.82

The hydrolysis of the two extractants are compared in Table 3.

Table 3 : Hexanoic acid (HA) and N,N-di(2-ethyl)hexylamine (DEA) yields in the hydrolysis of DOHA at 110° - 115° in contact with aqueous HNO_3 (stirred solutions) and comparison with TBP hydrolysis (Extractants diluted in aliphatic hydrocarbons).

HNO_3 (mol l^{-1})	Contact time (hours)	DOHA (mol l^{-1})	HA (mol l^{-1})	DEA (mol l^{-1})	TBP (mol l^{-1})	HDBP (mol l^{-1})
0.5	4	0.95	0	0		
4	1	0.95	0	0		
4	4	0.94	0.015	0		
0.5	4				1.08	0.0008
5	4				1.08	0.0047

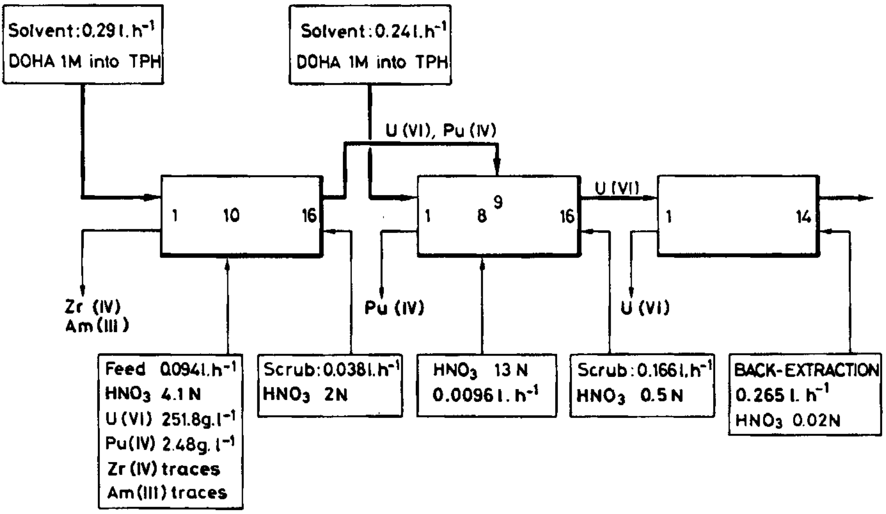


FIG.7. Flow sheet for a First reprocessing cycle using 1M DOHA into TPH as Solvent and no Reductive partition

Table 4 : Result of a mixer settler first cycle reprocessing separation using 1M DOHA in TPH as a solvent.

Operation	Element	Feed ($g.l^{-1}$)	% of feed in effluent
Extraction		Aqueous phase	Aqueous phase
	U(VI)	251.8	0.015
	Pu(IV)	2.48	0.14
	Zr(IV)	TRACES	99.5
	Am(III)	TRACES	99.5
Partition		Organic phase	Aqueous phase
	U(VI)	81.7	0.37
	Pu(IV)	0.805	95.5
Back-Extraction		Organic phase	Aqueous phase
	U(VI)	44.7	99.9
	Pu(IV)	0.0198	95.2

Counter current test of DOHA in mixer-settler: A counter current test of DOHA mimicking a first cycle of irradiated nuclear fuels cycle has been carried out in laboratory mixer-settlers. Although DOHA is not the best amide extractant for U-Pu partition without reduction, the flow sheet was designed to avoid the Pu(IV)-Pu(III) reductive step. The flow sheet diagram is shown in figure 7 and the main results of the test are contained in Table 4

The efficiency of the extraction battery was satisfactory, in spite of the high temperature, 41° C, at which this run was carried out. It must be remembered that U(VI) distribution ratios decrease with the temperature. The partition in the second battery, was not quite complete and did not verify the flow sheet calculations.

Pu(IV) distribution coefficients measured afterwards with the mixer settler solutions indicated that for the conditions used the efficiency of each stage was 75 %. This rather poor efficiency is probably due to slow Pu(IV) back extraction together with too high fluids flow rates. The U(VI) back extraction was complete at room temperature. In this battery rather low stage efficiency was also observed. Nevertheless the chemical factors (low $D_{U(VI)}$ distribution ratios) were so favourable that a U(VI) concentration was made at U(VI) back-extraction. Some Pu(IV) remain in the solvent, probably because of the low acidity used in U(VI) stripping.

Extractive Properties of N,N'-Tetraalkylmalonamides and N,N'-Tetraalkylpropane Diamides.

As mentioned above N,N-dialkylamides do not extract the trivalent actinide ions, so if one wants to remove all the α emitters

Table 5 : Main extractive properties of DMDOMA

Extracted species	Species in the organic phase	Extraction constants
HNO_3	$HNO_3(DMDOMA)_2$	0.64
	HNO_3 DMDOMA	0.11
	$HDMDOMA^{+-}NO_3.HNO_3$	0.075
$HClO_4$	$HDMDOMA^{+-}ClO_4$	4.15
Am^{3+}, Eu^{3+} from HNO_3	$[Am(NO_3)_3(DMDOMA)_2](DMDOMA)_2$	263 and 229

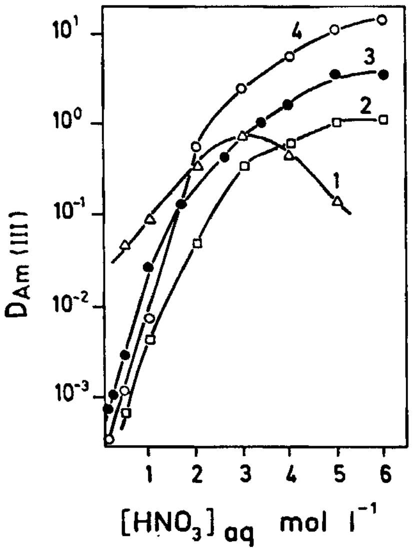


FIG.8. Distribution Ratios of Am(III) between 0.5M Malonamides Solutions into t-butylbenzene and HNO_3 Solutions as a Function of Aqueous HNO_3

1 : $(C_8H_{17}CH_3NCO)_2CH_2$

2 to 4 : $(C_4H_9CH_3NCO)_2CHR$

with R = $-C_6H_{13}(2)$, $-C_2H_4OC_2H_5(3)$, $- C_2H_4OC_2H_4OC_6H_{13}$ (4)

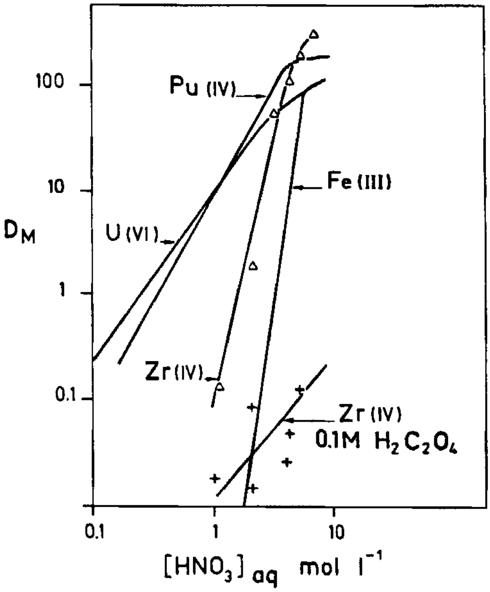


FIG.9. Distribution Ratios of Metallic ions between 0.5M $(C_4H_9\ CH_3\ N\ CO)_2\ CH\ C_2H_4OC_2H_4\text{-}OC_6H_{13}$ into t-butylbenzene and aqueous nitric acid solutions as a function of nitric acid concentration.

from nitrate solutions without using organophosphorus extractants some new extractants must be proposed. The donating properties of $>$N C=O group suggest that it would be useful to investigate diamides. The pioneer work of Siddall indicated that N,N'-tetrabutyloxalamide, N,N'-tetrabutylmalonamide and N,N'-tetrabutylsuccinamide are poor Ce(III) extractants(15). In preliminary work (16) we demonstrated that the nature of the N substituents have a great influence upon the Am(III) distribution ratios between nitric acid solutions and organic solutions of N,N'-tetraalkylmalonamides. The best extractions were obtained with N,N'-dimethyldialkylmalonamides. The presence of two CH_2 groups between the two C=O provokes a drastic decreasing of the distribution ratios for the 4f and 5f trivalent ions showing that favorable chelation occurs only with malonamides. Systematic investigations of acids (17) and metals (18) extraction have been carried out with N,N'-dimethyldioctylmalonamide (DMDOMA- $-CH_3NCOCH_2\text{-}CONCH_3C_8H_{17}\text{-}C_8H_{17}$). The main results are summarized Table 5.

It can be pointed out that U(VI), Pu(IV), Pu(VI), Np(IV), Np(VI) are well extracted by DMDOMA. Zr(IV) and Fe(III) are extracted at high aqueous acidities ; their extraction can be avoided by the addition of small amounts of oxalic acid. Further improvements of Am(III) and Eu(III) extraction were obtained by placing a branched alkyl group or an oxyalkyl group on the central methylene ; as shown by the data in figure 8. It can be seen that a C_6H_{13} radical allows one to obtain a higher Am(III) distribution ratio at high acidities and lower ones at low acidities, features which are favorable in a chemical separation. The presence of one or two oxygens in the chains increases the distribution coefficients at high acidities without increasing too much the extraction at low acidities. At first glance such effects can be explained by the malonamides basicity sequence as a function of the central CH_2 substituents $C_6H_{13} > C_2H_4OC_2H_5 > C_2H_4OC_2H_4OC_6H_{13}$. Nitric acid competes less strongly with Am(III) for the C=O coordination sites as the basicity decreases. For DMDOMA the nitrogen substituents are different ; however, it seems that this compound has a higher basicity because of the higher Am(III) extraction at low acidity and the lower at high acidity due to the competition between HNO_3 and Am(III) for the coordination sites of the ligand. The presence of oxygens in the alkyl chain decreases the C=O basicity because of the electronic affinity of oxygen.

Distribution ratios of several metallic ions, often present with the actinides in the wastes, are plotted as a function of nitric acid concentration on figure 9. It is poosible to back extract U(VI) with HNO_3. Like for DMDOMA it is necessary to add oxalic acid in order to avoid Zr(IV) extraction.

CONCLUSION

N,N-dialkylamides and N,N'-tetraalkyl,2-alkylmalonamides are promising actinide extractants. The first class could be an alternative to TBP in chemical separation processes which resemble the PUREX process with the following potential advantages.

- Lower amounts of wastes.
- Simpler process because of the reductive step suppression in the U-Pu partition.
- Possibilities of limiting the number of purification cycles.
- Easier U(VI) back-extraction.
- Easier solvent regeneration.

This paper indicates that these improvements can be realized with some additional investigations which are necessary to confirm the interest of N,N-dialkylamides for industrial applications. For example the solvent regeneration has not yet been studied in details and it is important to test during long time experiments the efficiency of this step.

With the diamides, the situation is worse because mixer settler and stability tests have not yet been carried out. However the easy synthesis and purification of the extractants and their extractive properties regarding the most important metallic species incite us to pursue the investigations.

ACKNOWLEDGMENT

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