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# Malonamides as New Extractants for Nuclear Waste Solutions

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## Abstract

A new class of extractants has been investigated: pentaalkylpropane diamides. Due to their chelating effect on metallic cations, they extract trivalent actinides such as $Am^{3+}$ and $Cm^{3+}$ from acidic nitrate nuclear waste solutions. These solvents are completely incinerable and do not generate large amounts of waste. A review is provided of their chemical properties, leading to the choice of the proper molecule. The results of a bench-scale experiment performed in a mixer–settler battery are presented.

## INTRODUCTION

Two alternatives are available in the nuclear fuel cycle: spent fuel reprocessing to recover uranium and plutonium followed by vitrification of the high activity wastes, or spent fuel disposal without any recovery of fissionable material.

Aside from political and safety considerations, the choice is mainly guided by economic factors. One way to improve the economics of reprocessing is to decrease the cost of waste treatment. The high toxicity of the waste is mainly due to long-lived actinides such as Pu, Np, and Am. Am and Cm are stable in the trivalent state in nitric acid solution and are therefore difficult to extract with conventional solvents. For two decades, bifunctional organophosphorus extractants have been investigated extensively in the United States (*1*, *2*), resulting in the development of the TRUEX process.

The main extractant is CMPO [octyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethylphosphine oxide], mixed with tributyl phosphate and diluted in an aliphatic or chlorinated diluent. In spite of their effectiveness, these solvents have some drawbacks, including the nonincinerable solid waste, due to phosphorus, obtained after complete degradation.

Research was conducted at Fontenay-aux-Roses on another class of bifunctional solvents containing no phosphorus, pentaalkylpropanediamides, formula $(RR'NCO_2)CHR''$, where R and R′ are alkyl radicals, and R″ is an alkyl or an oxyalkyl radical. Their chelating effect allows the extraction of trivalent cations $Am^{3+}$ and $Cm^{3+}$ from concentrated nitric acid solutions. The fact that they contain no phosphorus atoms is important; the solvents are hence completely incinerable and do not generate any new waste. Their degradation products are accordingly less harmful to the process.

This paper presents a systematic review of the chemical properties of the solvent, leading to the ideal choice of a molecule for practical applications. The nature of R, R′, and R″ greatly affects the extractive properties of the solvent (*3*, *4*) and its stability, and has an influence on the price and feasibility of the synthesis. Practical applications with given molecules are then described. The results obtained on a bench-scale experiment with a mixer–settler battery are then presented to show the possibility of using this solvent in a process comparable to the TRUEX process.

## EXPERIMENTAL

### Reagents

The diamides used in this study are not commercially available, and they were synthesized at IRCHA (Vert le Petit, France) by G. Thiollet. The synthesis is described in detail in Ref. *5* and can be summarized as follows. Two main steps are needed: 1) preparation of the unsubstituted malonamide $(RR'NCO)_2CH_2$ and 2) its alkylation or oxyalkylation with R″Br. If the latter is commercially unavailable, it has to be prepared too.

Other commonly used chemicals are Merck or Prolabo analytical grade reagents, without further purification. Radioactive metals were obtained from Cogema ($^{239}Pu$, $^{238}U$), STU Fontenay-aux-Roses ($^{244}Cm$, $^{239}Np$, $^{241}Am$), and ORIS Industrie Saclay ($^{99}Tc$, $^{152}Eu$).

### Methods and Analysis

Distribution coefficients were measured by contacting solvent, previously balanced with an aqueous phase at the same acidity, with an aqueous phase containing the metal (equal volumes were normally used and experiments performed at room temperature). Test tubes were agitated with a Vortex agitator for about 5 min. After centrifugation and separation, each phase was analyzed, mainly by radiometric ($\alpha$ or $\gamma$ spectrometry) methods. $\gamma$ spectrometry was used for $^{241}Am$, $^{152}Eu$, and $^{239}Np$. $\alpha$ spectrometry was used for $^{239}$Pu. Nitrate ions were titrated by Raman spectroscopy ($\nu$ = 1047 cm$^{-1}$). Free acid was titrated after addition of sodium oxalate to complex uranium. Colorimetric methods were used for iron, technetium, uranium, and phosphate. Iron was reduced to Fe(II) by hydroxylamine chlorhydrate and then complexed by orthophenanthroline in acidic medium. Technetium was titrated by spectrometry of the complex of Tc(V) and $SCN^-$ extracted in butyl acetate. Complexometry with dibenzoylmethane was used for U(VI). Phosphomolybdic complex extracted in hexone was used for phosphate titration.

Potentiometry in nonaqueous medium was used for basicity and degradation measurements. Mono- and diamides were titrated in acetic anhydride by $HClO_4$ diluted in acetic acid, carboxylic acid in ethanol, with NaOH in ethanol and secondary amines with NaOH diluted in ethanol in an ethanol–benzene mixture. Improvements were achieved in basicity measurements by taking a separate reference calomel electrode filled with NaCl and adding 5% acetic acid to the acetic anhydride to forestall any effect of the variation in composition of the medium during titration. The cell was thermostated at 25°C. IR spectroscopy and $^{13}$C NMR were used in some cases. Irradiation tests were performed in a $^{60}$Co $\gamma$ irradiator. To simulate real conditions, the organic phase in contact with aqueous phases of varying acidity was shaken twice daily.

A bench-scale mixer–settler Pollux type battery was used for countercurrent experiment.

## RESULT AND DISCUSSION

### Selection of Extractant Molecule

The chemical properties of the solvent depend on the nature of R, R′, and R″. Among the major criteria are the extractive properties toward $Am^{3+}$ (and $Cm^{3+}$). As shown in Fig. 1 and Table 1, for unsubstituted malonamides, good results are obtained with R = methyl and R′ = butyl or octyl group (butyl is preferable for economical reasons despite weaker $D_{Am}$). Further enhancement of $Am^{3+}$ distribution coefficients is achieved by taking R″ as a long alkyl radical or, even better, an oxyalkyl radical. However, an optimal length of R″ appears to exist and a branched carbon chain has a weak effect.

In Fig. 1 the variation of $D_{Am^{3+}}$ with $HNO_3$ concentration exhibits a peak only for unsubstituted malonamides as $HNO_3$ increases. This is linked to the decrease in solvent basicity, which reduces the competition between $HNO_3$ and $Am^{3+}$ for bonding with the solvent. The basicities of various extractants were compared, and the results are given in Table 2. Mea-

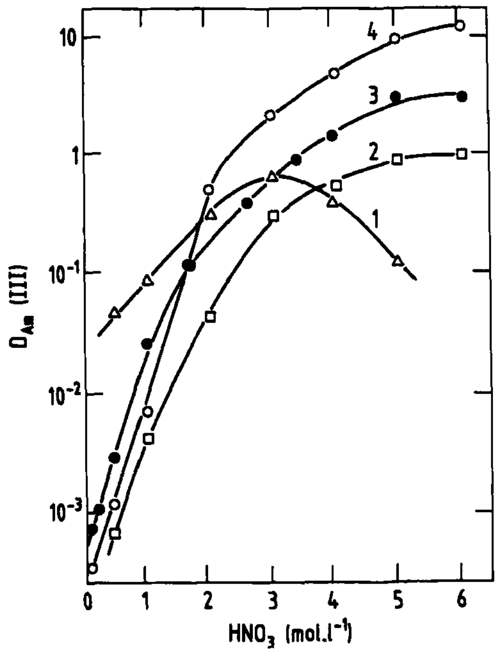


FIG. 1. Extraction of Am$^{3+}$ in nitric acid. (1) $R'' = H$, $R' = C_8H_{17}$. (2) $R'' = C_6H_{13}$. (3) $R'' = C_2H_4—O—C_2H_5$. (4) $R'' = C_2H_4—O—C_2H_4—O—C_6H_{13}$.

TABLE 1
Influence of Solvent Structure on the Distribution Coefficient of Americum ($D_{Am^{3+}}$) in $HNO_3$

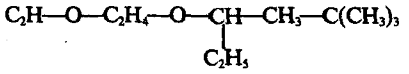
| R″ | R | R′ | $D_{Am3+}$ | Conditions |
|---|---|---|---|---|
| H | $C_6H_{11}$ | $C_2H_5$ | 0.11 | Solvent 0.5 *M* in benzene. *D* maximum. $HNO_3$ 2 to 4 *M* |
| H | $C_4H_9$ | $C_4H_9$ | 0.18 | |
| H | $C_3H_7$ | $C_8H_{17}$ | 0.45 | |
| H | $CH_3$ | $C_4H_9$ | 0.55 | |
| H | $CH_3$ | $C_8H_{17}$ | 1.18 | |
| $C_6H_{13}$ | $C_4H_9$ | $CH_3$ | 1.16 | Solvent 0.5 *M* in *t*-butylbenzene. $HNO_3$ 5 *M* |
| $C_2H_4—O—C_2H_5$ | $C_4H_9$ | $CH_3$ | 3.28 | |
| $C_2H_4—O—C_6H_{13}$ | $C_4H_9$ | $CH_3$ | 7.55 | |
| $C_2H_4—O—C_2H_4—O—C_8H_{17}$ | $C_4H_9$ | $CH_3$ | 9.43 | |
|  $C_2H—O—C_2H_4—O—\underset{\underset{\vert}{C_2H_5}}{CH}—CH_3—C(CH_3)_3$ | $C_4H_9$ | $CH_3$ | 10.38 | |
| $C_2H_4—O—C_2H_4—O—C_6H_{13}$ | $C_4H_9$ | $CH_3$ | 11.48 | |

TABLE 2
Influence of the Structure on Solvent Basicity[a]

| R = $C_4H_9$, R′ = $CH_3$, radicals R″ | p$K_A$ − p$K_{AR}$ | R = $C_4H_9$, R′ = $C_2H_5$, radicals R″ | p$K_A$ − p$K_{AR}$ |
|---|---|---|---|
| H | 3.43 | | |
| $CH_3$ | 3.10 | $C_2H_4$—O—$C_6H_{13}$ | 2.74 |
| $C_2H_5$ | 3.06 | *l*-$C_2H_4$—O—$C_8H_{17}$ | 2.67 |
| $C_6H_{13}$ | 3.17 | *r*-$C_2H_4$—O—$C_8H_{17}$ | 2.66 |
| *l*-$C_2H_4$—O—$C_8H_{17}$ | 2.66 | | |
| *r*-$C_2H_4$—O—$C_8H_{17}$ | 2.56 | | |
| *l*-$C_2H_4$—O—$C_2H_4$—O—$C_8H_{17}$ | 2.77 | | |
| *r*-$C_2H_4$—O—$C_2H_4$—O—$C_8H_{17}$ | 2.76 | | |

[a] *l* = linear; *r* = with branched carbon chain.

surements were carried out with the pH metric titration described above. Butyramide p$K_A$ was considered as the origin of the basicity scale, and it was mixed with the diamide to be measured. The following main conclusions can be drawn:

> The presence of a substitute on the central carbon decreases the basicity of the malonamide and a large oxyalkyl substitute more than an alkyl substitute.
>
> The effect of two oxygen atoms in the substitute is not clearly shown because of measurement accuracy (0.05 p$K_A$ units).
>
> R and R′ exert a weak effect on solvent basicity.

As shown by Fig. 1, a substituted malonamide with a large R″ displays improved extraction coefficients of $Am^{3+}$ at high acidities and low distribution coefficients than the unsubstituted compound at low acidity, leading to better extraction and easier back-extraction in dilute medium.

## Extraction of Acids

Extraction of nitric acid is an important parameter, and it was closely investigated for methylene unsubstituted malonamides (*3*, *6*). Three adducts are formed in the organic phase of increasing $HNO_3$ concentrations: $HNO_3$·diam$_2$, $HNO_3$·diam and $(HNO_3)_2$·diam. Research is under way to elucidate the mechanism of extraction with substituted malonamide. Oxalic acid offers a practical advantage to back-extract iron, Np(IV) or U(VI), or to separate $Am^{3+}$ from $Fe^{3+}$ or Zr(IV) (see below), and it was then useful to check its own extraction in the organic phase. The results in Table

TABLE 3
Extraction of $H_2C_2O_4$–solvent with $R'' = C_2H_4—O—C_6H_{13}$ 0.5 *M* in *t*-Butylbenzene: Initial $H_2C_2O_4$ 0.3 *M*

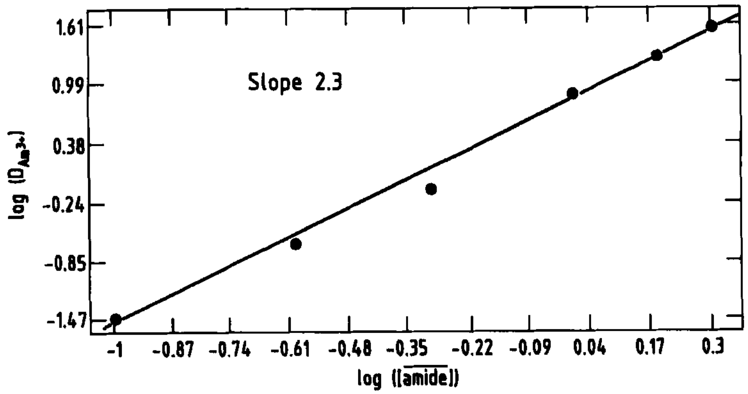
| $HNO_3$ (*M*) | $D_{H_2C_2O_4}$ |
|---|---|
| 0.05 | 0.08 |
| 0.1 | 0.14 |
| 1 | 0.04 |
| 6 | 0.06 |

3 show the weak extraction of $H_2C_2O_4$, contrary to what has been reported for organophosphorus molecules.

## Extraction of Metals

An IR study of Pr complexes (*7*) shows that both oxygen atoms are involved in the bonding with Pr, confirming the chelating nature of the extractant. The extraction stoichiometry seems different for simple and substituted maloamides. If R″ is a hydrogen, the slope of log $D_{Am}$ as a function of log $C_{diamide}$ has a value of 4 (*3*), and 2.3 if R″ is $C_6H_{13}$ (see Fig. 2), but the number of solvates has to be confirmed by other methods.

For the amide extractants (*8*, *9*) the wide variations in slopes show little correlation with the number of solvates in the extracted complexes. Strong nonideality has been claimed due to poorly oriented interactions between



log ([$\overline{amide}$]) with [$\overline{amide}$] in mol.l$^{-1}$ in organic phase

FIG. 2. Influence of the extractant ($R'' = C_6H_{13}$) concentration on $D_{Am^{3+}}$. Aqueous phase: $HNO_3$ 5 *M*. Organic: *t*-butylbenzene. Extractant: 10% decanol.

the coordinated amide and the free amide molecules. For the above diamides, saturation experiments combined with spectrophotometry showed that two or less molecules of extractants are present in the first coordination sphere. The difference between the two slopes can be explained by the steric hindrance close to the amide nitrogen arising from the $C_6H_{13}$ substitute and precluding bonded diamide–free diamide interaction.

The extraction of metallic cations present in nuclear wastes was measured.

## Trivalent Cations

Trivalent species such as $Am^{3+}$ and $Eu^{3+}$ are extracted in the same way. Some experiments were performed with $Cm^{3+}$, which displays weaker distribution coefficients than $Am^{3+}$ (roughly equal to $Eu^{3+}$ at the same acidity; see Table 4).

## Plutonium Extraction

Plutonium(IV) is well extracted in concentrated $HNO_3$ (see, for instance, Table 4); it needs a reducing medium, such as hydroxylamine in weak acid medium, and to be back-extracted at 45°C. Plutonium polymers are well extracted by diamides and are well back-extracted by $H_2C_2O_4$, HF, and even with hydroxylamine nitrate (for fresh polymers). Old polymers (>6 months) are also extracted, and stripping is possible with $H_2C_2O_4$, but precipitates sometimes occur. The results are given in Table 5. These studies were mainly carried out for practical purposes, so the complete

TABLE 4

Distribution Coefficients of Various Metals in $HNO_3$, O/A = 1; $t$ = 25°C; solvent 0.5 *M* in *t*-butylbenzene, R″ = $C_2H_4$—O—$C_6H_{13}$

| | [$HNO_3$] (*M*) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Metal | 0.5 | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| Tc(VII) | 0.72 | 1.09 | | 0.88 | 0.77 | 0.75 | | |
| Np(VI) | 3.81 | 5.20 | 7.91 | 15.11 | 73.0 | 81.6 | 131 | 26.5 |
| Np(V) | 0.019 | 0.029 | 0.430 | | | | | |
| Np(IV) | 5.12 | 15.03 | 55.2 | 58.5 | 67 | 266 | 151 | 113 |
| Am(III) | 0.0026 | 0.020 | 0.268 | 1.30 | 3.94 | 5.82 | 7.13 | 7.37 |
| Cm(III) | 0.0019 | 0.012 | 0.147 | 0.706 | 0.249 | 3.91 | 5.51 | 5.0 |
| Fe(III) | 0.0016 | 0.002 | 0.027 | 0.682 | 7.93 | 47.79 | 203 | 353 |
| Pu(IV) | 7.0 | 11.5 | 29.2 | 47.1 | 50 | 54 | 94 | |
| U(VI) | 5.5 | 7.3 | 37 | 67 | 69 | 72 | 75 | |

TABLE 5
Extraction of Stripping of Pu Polymer

| Extraction | | | Stripping | |
|---|---|---|---|---|
| | $D_{Pu}$ | | | |
| $[HNO_3]$ | Fresh polymer | Old polymer | Stripping conditions | $D_{Pu}$ |
| 1 | 11.4 | 1.1 | 0.2 $M$ NHA[a] | 0.8 |
| 2 | 49.2 | 9.6 | 0.1 $M$ $HNO_3$, 45°C | |
| 3 | 113 | 113 | 0.2 to 0.5 $M$ $H_2C_2O_4$ | 0.01 |
| 4 | 108 | 472 | 0.1 $M$ HF | 0.01 |
| 5 | 122 | 369 | 0.05 $M$ $HNO_3$ | |

[a] NHA = hydroxylamine nitrate.

mechanism was not clarified. For instance, the compositions of the precipitates were not determined.

## Neptunium Extraction

Neptunium(IV) and (VI) are well extracted in concentrated nitric acid solution (see Table 4). Np(V) is not extractable except in high nitric acid concentrations where disproportionation may occur and extraction shifts the equilibrium, leading to complete extraction of neptunium despite a rather short contact time (>10 min in the test tube under agitation). However, the valency state of neptunium in the organic phase has not been fully identified.

Back-extraction of neptunium is more complicated. If neptunium is extracted as neptunium(VI), back-extraction is possible with hydroxylamine, which reduces Np(VI) to Np(V). If iron is present in the solution, $Fe^{3+}$ can be reduced to $Fe^{2+}$, leading to the reduction of Np(VI) to Np(IV), which then remains in the organic phase. Np(IV) can be back-extracted with oxalic acid. Several experiments conducted to separate neptunium from plutonium were not completely successful. Hydrogen peroxide and butyraldehyde were tried out, but for $H_2O_2$ the $HNO_3$ concentration range which can be used is very narrow, and for butyraldehyde the reduction is too slow.

## Technetium Extraction

Technetium is a serious problem in effluents produced by LWR fuels reprocessing. As shown in Table 4, the distribution coefficients are close to unity and it is hence difficult to keep all the technetium in one phase. In weak acidic medium, $Am^{3+}$ is coextracted with technetium, as shown in Fig. 3. Technetium as $TcO_4^-$ is expected to behave like $ClO_4^-$, leading

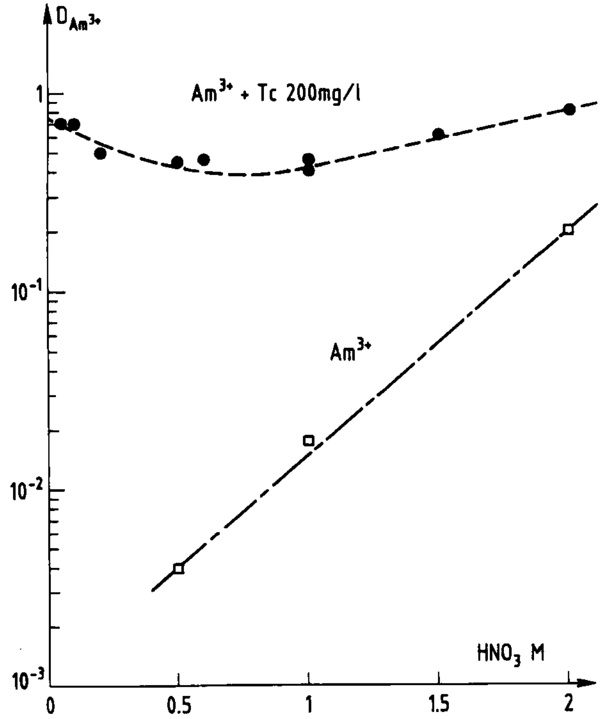


FIG. 3. Influence of Tc on Am extraction.

to enhancement of $D_{Am^{3+}}$ which is higher in $HClO_4$ than in $HNO_3$ (*3*). This fact may explain the behavior of americium during the back-extraction step in the countercurrent experiment in mixer–settlers (see below). Some experiments were conducted to reduce technetium with hydrazine, but the reduction reaction is too slow for a back-extraction process.

## Zirconium and Iron Extraction

Both Zr(IV) and Fe(III) are well extracted from 5 *M* $HNO_3$ (see Table 4). They can be separated from the actinides by adding $H_2C_2O_4$ to the aqueous phase; see Tables 6A and 6B.

## Extractant Hydrolysis and Radiolysis

Several experiments were performed to check extractant resistance to hydrolysis by nitric acid and radiolysis (under irradiation). The purpose was to estimate the percentage degradation as a function of several pa-

TABLE 6A
Separation of $Fe^{3+}$–$Am^{3+}$ in the Presence of Oxalic Acid; Solvent with R″ = $C_2H_4$—O—$C_6H_{13}$ 0.5 *M* in *t*-Butylbenzene; Aqueous $HNO_3$ 3 *M*

| $[H_2C_2O_4]$ (*M*) | $[Fe^{3+}]$ (*M*) | $D_{Am}$ | $D_{Fe}$ |
|---|---|---|---|
| 0.213 | 0.05 | 0.93 | 0.04 |
| 0.213 | 0.1 | 1.06 | 0.09 |
| 0.213 | 0.2 | 1.05 | 0.23 |
| 0.5 | 0.2 | 1.2 | 0.12 |

TABLE 6B
Distribution Ratios of Zr(IV) in the Presence of Oxalic Acid; Solvent with R″ = $C_2H_4$—O—$C_2H_4$—O—$C_6H_{13}$ 0.5 *M* in *t*-Butylbenzene

| $[HNO_3]$ (*M*) | $[H_2C_2O_4]$ (*M*) | $D_{Zr(IV)}$ |
|---|---|---|
| 1 | 0 | 0.092 |
| 1 | 0.1 | 0.02 |
| 2 | 0 | 7.86 |
| 2 | 0.1 | 0.12 |
| 3 | 0 | 170.2 |
| 3 | 0.1 | 1.46 |

rameters, such as $HNO_3$ concentration, temperature, time, absorbed dose of γ, and solvent structure. Identification of the main degradation products was also an objective. For practical applications it was useful to test the behavior of a degraded solvent for extraction and actinides back-extraction, and to identify potential practical problems such as plutonium retention and slow phase disengagement.

Degradation of the diamides under hydrolysis or radiolysis is expected to yield carboxylic acids, secondary amines, other diamides, monoamides, and various products such as alcohols, ketones, etc.

Measurements were taken by the potentiometric methods described earlier. These methods are not sufficient to identify all the degradation products. It is impossible to distinguish precisely between several products with similar basicities (for instance, two or more diamides or monoamides). Any gaseous products formed were not analyzed. Depending on the mechanism, the total percentage degradation is underestimated if measured only by a potentiometric method. For these reasons, $^{13}C$ NMR was used to clarify some mechanisms.

Concerning hydrolysis, qualitative studies showed that nitric acid concentration and temperature are the most important parameters, and that chemical degradation appears to be correlated with aqueous solubility. Hydrolysis of the diamide with R″ = $C_2H_4—O—C_8H_{17}$ was monitored by $^{13}C$ NMR.

The solvent was diluted in benzene and contacted with 5 *M* nitric acid for 6 days at 40°C and 10 hours at boiling temperature (≃ 103°C) to obtain a sufficient quantity of degradation products. The analytical results are given in Table 7.

Figure 4 shows the $>C{=}O$ region of the product $^{13}C$-NMR spectrum before and after degradation. In Fig. 4(a) the $N—C{=}O$ band of the diamide is split into three if the solvent is contacted with 5 *M* nitric acid because of the formation of several types of solvent acid complex in the organic phase, as described previously. After degradation (10 h boiling in contact with 5 *M* $HNO_3$), several other peaks appear (Fig. 4b) in the $C{=}O$ region, showing monoamides and other diamides.

The ether function of the radical R″ can be expected to be a weak point in the molecule. In fact, it appears that the molecule is mainly cut at the oxygen bridge, yielding an alcohol and another diamide. Octanol was identified on the NMR spectrum and titrated by comparison with isopropanol. At boiling temperature the molecule exhibits other possibilities of degradation on the $>N—\underset{\underset{O}{\|}}{C}$ or $C—\underset{\underset{O}{\|}}{C}$ bonds, leading to light monoamides, carboxylic acids, or bifunctional products. If the degraded product is washed with 2 *M* NaOH and then with dilute nitric acid, only two amides still appear on the NMR spectrum: one monoamide and the initial diamide, which was found to be 0.35 *M*. All the other products were washed out, confirming either their hydrophilic character (small alkyl chains) or their bifunctional nature (carboxylic acid function). The NMR spectrum of the

TABLE 7

Results of Degradation under Hydrolysis of Solvent (R″ = $C_2H_4—O—C_8H_{17}$) 1.044 *M* in Benzene Contacted with 5 *M* $HNO_3$

| Time | *T* (°C) | Potentiometry | $^{13}C$ NMR |
|---|---|---|---|
| 6 days | 40 | Diamide, 1 *M*<br>Monoamide, $5 \times 10^{-2}$ *M* | Octanol only, 0.1 *M* |
| 10 hours | 103 | Diamide, 0.634 *M*<br>Monoamide, $5.8 \times 10^{-2}$ *M* | Octanol, 0.355 *M*<br>Monoamide, 0.155 *M*<br>Diamide, 0.525 *M* |

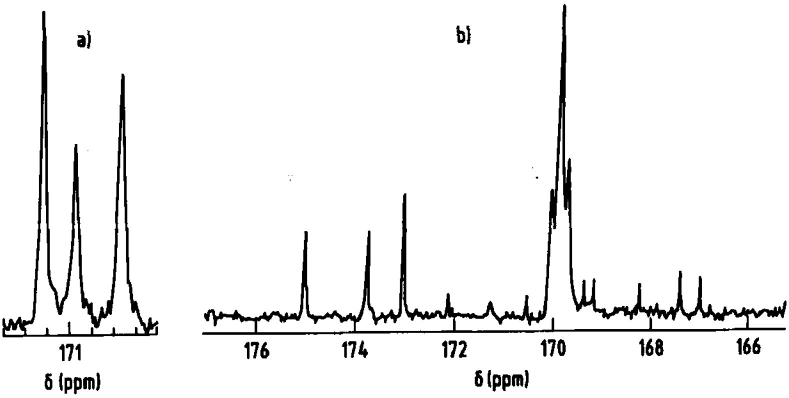


FIG. 4. C=O region of the NMR spectrum of the solvent.

aqueous phase contacted with the solvent during boiling shows only monoamides and carboxylic acids. Light diamides with small alkyl chains, which have a hydrophilic character, are probably destroyed in that medium.

At 40°C after 6 days, degradation is weak, and only a small concentration of octanol is seen on the NMR spectrum (roughly 10%), which means that only the "main" mechanism of degradation occurs (cutting the molecule at the oxygen bridge in R″). We are now trying to elucidate the mechanism under different conditions and to validate the methods of titration.

Qualitatives studies have shown that a long oxyalkyl R″ improves the stability of the molecule.

Concerning radiolysis, only qualitative conclusions can be drawn because measurements were taken only by potentiometric methods. Irradiation was carried out for periods ranging from 1 to 9 days (0.33 *M* rd/h, 40°C). Since the solvents were in contact with nitric acid, these values are in fact the sum of [hydrolytic + radiolytic] degradation. The main results are:

Stability as a function of R″ increases in the order $H < C_2H_5 < C_2H_4{-}O{-}C_6H_{13} \simeq C_2H_4{-}O{-}C_2H_4{-}O{-}C_6H_{13}$.

Stability seems to vary roughly with aqueous solubility as for hydrolysis.

A long oxyalkyl radical appears to protect the molecule from degradation.

There is no significant difference between one or two oxygens in R″.

Evidence exists for the formation of carboxylic acids and of bifunctional molecules such as amide-acid. The amides formed as primary degradation products are further degraded, as only small amounts were found.

Distribution coefficients of some metals ($Am^{3+}$, $Eu^{3+}$, $Pu^{4+}$, $UO_2^{2+}$) were measured in degraded solvents (diamide with R″ = $C_2H_4$—O—$C_2H_4$—O—$C_6H_{13}$ diluted to 0.5 *M* in *t*-butylbenzene). Some results are given in Table 8. Extractions of trivalent cations and of U and Pu remain possible after irradiation of 71.3 Mrd. Back-extraction is also possible in dilute medium for trivalent cations. Plutonium(IV) can be stripped by reduction, and uranium in very dilute $HNO_3$, as in nondegraded solvents.

These results clearly reveal one of the advantages of diamides: the degradation products do not cause retention of actinides or precipitates.

## Separation of Actinides Contained in Waste in Mixers–Settlers

As stated previously, the nature of R″ influences the extractive properties and the price of the diamide. A compromise was found when a diamide with R″ = $C_2H_4$—O—$C_6H_{13}$ was chosen for practical application in a mixer–settler battery. R″ is sufficiently long to allow good separation of trivalent species and good solvent stability, and the synthesis is not too expensive or difficult. This molecule was used at a concentration of 0.5 *M* diluted in *t*-butylbenzene. An aromatic diluent was chosen to prevent third-phase formation (the third phase appears at an acidity of 0.9 *N* with an aliphatic diluent, hydrogenated tetrapropylene, and at 9 *N* with *t*-butylbenzene). The solvent was found to be pure (>95%) and to display good aptitude for coalescence.

The waste solution to be treated was a solution from the pulsed column facility at Fontenay-aux-Roses. The composition of this solution is given in Table 9. As it did not contain curium, $^{152}$Eu was added to mimic its behavior (the distribution coefficients are identical). Neptunium was added at 50 mg/L and analytically followed by $^{239}$Np traces.

The flow sheet of the experiment is shown in Fig. 5. The first battery is designed to extract α emitters (10 stages) and scrub to diminish solvent acidity. The second battery serves to back-extract actinides and lanthanides. Uranium is systematically stripped with dilute $HNO_3$, and neptunium is stripped, if necessary, with oxalic acid.

TABLE 8

Distribution Coefficients of Some Metals ($D_M$) in Degraded Solvent (R″ = $C_2H_4$—O—$C_2H_4$—O—$C_6H_{13}$) 0.5 *M* in *t*-butylbenzene, *t* = 40°C, dose 71.3 Mrd

| Aqueous $HNO_3$ (*M*) | $D_{Am}$ | $D_{Eu}$ | $D_{Pu}$ | $D_U$ |
|---|---|---|---|---|
| 5 | 9.6 | 5.8 | 209 | 30 |
| 0.5 | 0.16 | 0.07 | — | — |

TABLE 9
Composition of Aqueous Phase Used in the Bench-Scale Mixer–Settler Separation

| Element | Content | Element | Content |
|---|---|---|---|
| $H^+$ | 5 *M* | Fe | 500 mg/L |
| $NO_3^-$ | 5.5 *M* | $P_{total}$ | 270 mg/L |
| Pu | 110 mg/L | $^{237+239}Np$ | 50 mg/L |
| Am | 0.91 mg/L | $^{152}Eu$ | Traces |
| U | 5.9 g/L | $\alpha_{activity}$ | 50 mCi/L |
| Tc | 134 mg/L | | |

## Results

The decontamination factors found for each element are given in Table 10. Hydraulic behavior of the solvent was satisfactory during the experiment. Radiolytic and hydrolytic degradation did not occur during the time of the experiment (42 h) and was checked by NMR and potentiometry. As shown in Table 9, extraction of α emitters was fairly good. The experimental profile of americum follows the calculated profile (acidity at equilibrium was 5.5 *M* in the aqueous phase, see Fig. 6).

Some hydrodynamic problems occurred in the second battery, creating an increase of acidity, which may explain the weaker back-extraction performance. The effect of technetium can also be expected. In dilute nitric medium, americium is normally well back-extracted and no retention occurs under degradation of the solvent. If technetium is still present during

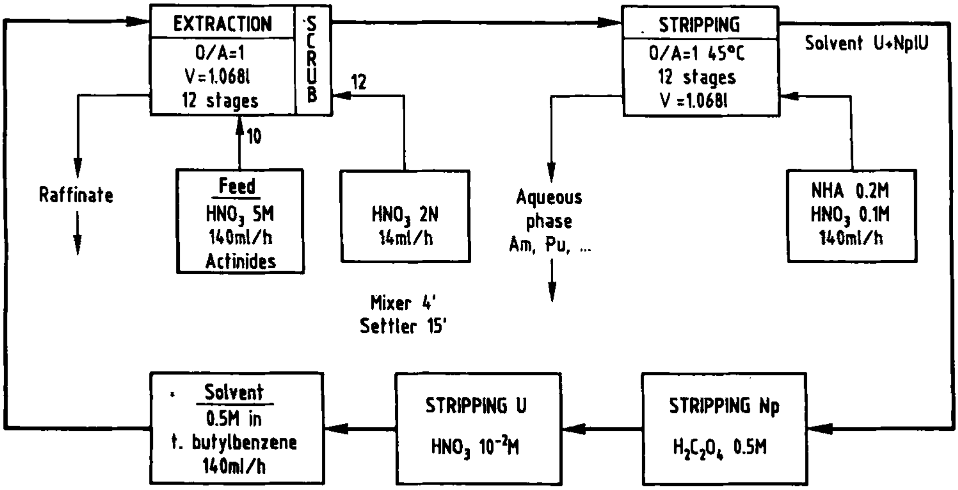


FIG. 5. Schematic flow sheet for the bench-scale separation of actinides.

TABLE 10
Decontamination Factors Obtained in the Mixer–Settler Batteries

| Element | DF extraction | DF stripping |
|---|---|---|
| Am | $1.26 \times 10^4$ | 800 |
| | $5 \times 10^{4a}$ | |
| Eu | $6.7 \times 10^3$ | 250 |
| $\alpha_{total}$ | $1.1 \times 10^4$ | 125 |
| Pu | $>10^5$ | 274 |
| | $>10^{5a}$ | |
| Np | 144 | 400 |
| U(VI) | >1000 | |
| | $>10^{5a}$ | |
| Fe | >1000 | |

[a] From TRUEX literature (*1*, *2*).

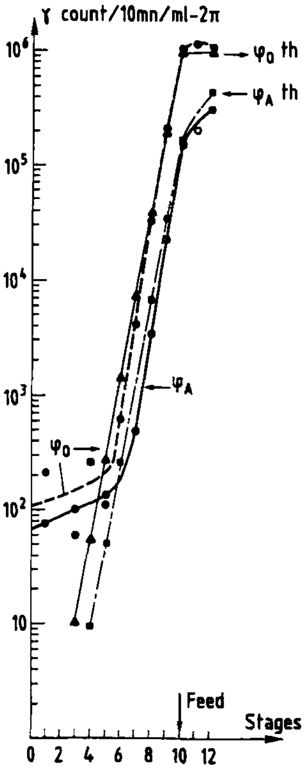


FIG. 6. Am repartition in the extraction battery compared to calculation.

the back-extraction stages, it can increase the distribution coefficient of americium to roughly 1, preventing proper back-extraction.

## CONCLUSION

Substituted malonamides can extract α emitters from radioactive solutions in concentrated nitric acid. All the actinides (III, IV, VI) are well extracted and can be easily back-extracted. Some problems remain, especially the presence of Tc, in all the process streams. It is difficult to state exact prices for the solvents if they are produced on an industrial scale due to the lack of large-scale development, but they are estimated to be inexpensive because of the simple reactions involved in synthesis and purification. For industrial purposes, the synthesis must be optimized, and a proper choice of commercial basic products can lower the cost. The solvent obtained on a pilot scale (1 kg) was found to be pure enough and needed no additional treatment. Degradation under hydrolysis or radiolysis is not significant in practical experimental conditions ($t \leq 45°C$). Degradation products can be washed with NaOH (carboxylic acids) and do not yield precipitates or emulsions, as shown by a proper choice of diluents and R″, R, and R′. Considering their lack of industrial development, diamides seem to be promising extractants mainly because of their incinerability and behavior under degradation.

In fact, degradation is significant at high acidity in addition to high temperature, but extraction processes are conducted at room temperature and $HNO_3 \simeq 5\ M$. Back-extraction, which requires 40°C, is achieved with a dilute nitric medium.

Further research is underway in two main directions: 1) optimizing the synthesis and 2) using aliphatic diluents.

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