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DIAMEX PROCESS FOR MINOR ACTINIDE PARTITIONING: HYDROLYTIC AND RADIOLYTIC DEGRADATIONS OF MALONAMIDE EXTRACTANTS

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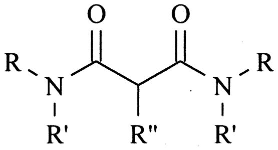
ABSTRACT

This paper deals with the hydrolysis and radiolysis of malonamides, which are used as extractants in the DIAMEX process for partitioning minor actinides from high-level liquid radioactive wastes. The general formula of the malonamides included in this study is as follows: $(R(R')NCO)_2CHR''$ (where R, R', and R'' are alkyl or oxyalkyl groups). Qualitative tests were carried out to identify malonamide degradation products using gas chromatography (GC) coupled to Fourier transform infrared spectroscopy (FTIR) or mass spectrometry (MS). The main degradation products were identified in organic phases after radiolysis or hydrolysis in the presence of the nitric acid aqueous phase and quantified using potentiometric titrations and gas chromatography. From the experimental data, a simplified degradation scheme for malonamide radiolysis and hydrolysis is proposed. The extracting properties of solvents made of malonamide solutions in an aliphatic diluent vs. actinide(III) and lanthanide(III) nitrates were determined after radiolysis and hydrolysis. The presence of malonamide degradation products leads to a decrease of the M(III) distribution ratios. Experiments carried out with synthetic organic solutions show that the decrease in solvent extraction properties can be explained by the decrease of the malonamide concentration and by the presence of the main malonamide degradation products. The hydrolytic and radiolytic stabilities of several malonamides are compared.

INTRODUCTION

To improve the management of radioactive wastes generated by spent nuclear fuel reprocessing, CEA (Commissariat à l'Energie Atomique) has launched the SPIN program, which has the objective, in particular, to separate the minor actinides [Am(III) and Cm(III)] from the high-level liquid waste. One separation strategy is based on a two-step process using incinerable extractants (made only with C, H, O, and N atoms). The first step consists in extracting trivalent minor actinides and lanthanides with a diamide (malonamide) molecule; this is the so-called DIAMEX process. The semideveloped formula of malonamide is,



, where *R, R',* and *R''* are alkyl or oxyalkyl groups. The optimization of a suitable extractant was undertaken, and numerous molecules were evaluated (1–4). The feasibility of the DIAMEX process has been shown in counter current "hot" tests with DMDBTDMA (*N*,*N*'- dimethyl, *N*,*N*'-dibutyl tetradecyl malonamide: $[C_4H_9(CH_3)NCO)_2CH(C_{14}H_{29})]$, which was the first reference molecule of the process (5). However, the formula of the extractant molecule has been further optimized and has led to DMDOHEMA (*N*,*N'*-dimethyl *N*,*N'*-dioctyl hexyloxyethyl malonamide: $[C_8H_{17}(CH_3)NCO)_2$ CH $(C_2H_4O$ $C_6H_{13})]$, which is the current reference molecule for the DIAMEX process (6,7).

This paper deals with the hydrolytic and radiolytic degradations of malonamide molecules, which were important criteria to take into account for extractant formulae optimization. Three molecules were studied: DMDBTDMA, *N*,*N'*-dimethyl *N*,*N'*-dibutyl dodecyloxyethyl malonamide DMDBDDEMA $[(C_4H_9(CH_3)NCO)_2CH(C_2H_4OC_{12}H_{25})]$ and DMDOHEMA.

Our objectives in this study were:

to identify the main malonamide degradation products and to measure the concentrations of diamide and the main degradation products in a biphasic system (the aqueous phase is a nitric acid solution) that simulate the liquid-liquid extraction step,

to identify the possible degradation pathways for diamides,

to correlate the concentration of the identified degradation species with the extracting properties of the spent solvents to point out the most problematic degradation products.

EXPERIMENTAL METHODS

Reagents

Malonamides and their degradation products (amide-acid, monoamide, and amine) were provided by Y. Leguen (PANCHIM, Lisses, Evry, F). DMDBTDMA and DMDBDDEMA were further purified by chromatographic treatment on a basic alumina column. Gas chromatographic analysis showed that the final purity of each diamide was $>98\%$.

n-dodecane (analytical grade, ALDRICH) and TPH (PROCHROM, Champignols, France), which is an industrial branched aliphatic diluent, were used as received.

Nitric acid was an RP PROLABO reagent.

Neodymium(III) nitrate was an ALDRICH product. The ^{241}Am was provided by SPHA (CEA Marcoule), whereas ^{152}Eu was provided by CEA/DAMRI/LMRI.

Solutions

All organic extractant solutions were prepared by dissolving weighed amounts of the desired compounds in the diluent (TPH or dodecane).

Nitric acid solutions were prepared by dilutions (in deionized water) of concentrated HNO_3. Metal nitrate solutions were prepared by dissolving weighed amounts of salt in the aqueous nitric acid solutions.

Degradation Experiments

Solvent Preequilibration before Degradation Studies

Prior to degradation studies, the solvents (volume V) were preequilibrated for 5 min with aqueous phases (volumes $4V$ and V) having the same nitric acid concentration as the aqueous phases to be used in the subsequent degradation studies.

Hydrolytic Degradation

A 10-mL sample of the preequilibrated organic phase was introduced with an equal volume of the aqueous phase (nitric acid) into a thermostated test tube (25°C or 60°C). The mixture was agitated for 5 min every day during the degradation experiment.

Radiolytic Degradation

An 8-mL sample of the preequilibrated organic phase was introduced with an equal volume of the aqueous phase (nitric acid) into a test tube. All tubes were placed in the ^{60}Co irradiation cell. Experiments were carried out at room temperature, and all the test tubes inside the irradiation cell were located at the same distance from the ^{60}Co source. The dose rate was about 4 kGy/h. The irradiations were done at the IPSN ^{60}Co irradiation facility (IRMA Cell, CEA Saclay).

After hydrolytic or radiolytic degradation of the solvents, the two clear phases were separated and stored for subsequent analyses.

Analysis

Potentiometric Analysis

The two types of liquid phases were analyzed by pH-metric titrations:

-Acidic functions in the aqueous phase were titrated by NaOH in water media.
-Acidic functions in the organic phase were titrated by NaOH in ethanol-water (60-40 vol%) media.
-Amide and amine functions were titrated by $HClO_4$ in anhydride acetic media.

Gas Chromatographic Analysis

Aliquots of the organic phases (volume *V*) were scrubbed with dilute nitric acid (5.10^{-2} mol/L HNO_3) (volumes 4*V* and *V* successively) to remove the extracted nitric acid. Several light compounds (i.e., butanoic acid, pentanoic acid, N-methyl N-butyl amine, . . .) soluble in aqueous phase were also eliminated with this pretreatment, but heavier degradation products (molecular weight upper than 170 g. mol^{-1}) had not been affected and had been further quantified. An aliquot of this organic scrubbed solution was then diluted with chloroform. The resulting sample was divided into two equal portions, one of which was treated with diazomethane (CH_2N_2) to convert organic acids to their methyl esters.

The chromatographic method was optimized to separated relatively heavy compounds (molecular weight upper than those of diluent: 170 g. mol^{-1}). A fused-silica-bonded phase column CPSIL5CB (CHROMPACK), 30 m x 0.25 mm Id, with 0.15-µm film thickness was employed. Helium was used as the carrier gas. The temperature program used was as follows: 100°C for 2 min, increased at 10°C/min to 220°C, increased at 5°C/min to 250°C, increased at 20°C/min to 270°C, and then held at 270°C for 25 min.

Qualitative Analysis by GC-MS and GC-IRTF

GC-MS studies were carried out in the electron-induced mode (EI, 70 eV) using a HP 5890 series II instrument equipped with a 5972 detector.

GC-IRTF studies were carried out using a HP 5890 series II instrument coupled to a NICOLET 5SXC IRTF spectrometer equipped with an MCT detector.

Quantitative Analysis

GC analyses of the samples were carried out using a VARIAN 3400 instrument equipped with a flame ionization detector and connected to a VARIAN 8200 autosampler. The STAR software was used to integrate chromatographic peaks.

Several internal standards were used for the different degraded solutions: DMDBDDEMA was chosen as an internal standard for degraded DMDBTDMA solution analysis**,** DMDOMA (*N*,*N'*-dimethyl *N*,*N'*-dioctyl malonamide) for degraded DMDBDDEMA solution, and DMDBHDEMA (*N*,*N'*-dimethyl *N*,*N'*-dibutyl hexadecyloxyethyl malonamide) for degraded DMDOHEMA solution.

Metal Nitrate Distribution Ratio Measurements

Before Solvent Degradation

One-milliliter aliquots of the organic solutions were preequilibrated twice (first with 4-mL aliquots then with 1-mL aliquots of the appropriate nitric acid solutions).

After Solvent Degradation

One-milliliter aliquots of the organic solutions were preequilibrated with the same volumes of the appropriate aqueous nitric acid solutions.

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Am(III) and Eu(III)

Each of the preconditioned organic phases was added to 1 mL nitric acid solution spiked with ^{241}Am(III) and ^{152}Eu(III). These solutions were thermostated at 25°C and mixed by vortex for 30 min, after which they were centrifuged and the phases separated. An aliquot of each phase was then taken for gamma counting (E = 59.64 keV for ^{241}Am and E = 121.8 keV for ^{152}Eu).

Nd(III)

The procedure described above was followed. In this case, the aqueous phase was prepared by 2×10^{-2} mol/L a neodymium in nitric acid solution. The Nd(III) concentrations in the two phases were determined by colorimetry using the arsenazo(III) method (see the experimental procedure described in [8]).

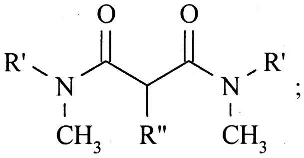
RESULTS AND DISCUSSION

Qualitative Analysis of the Degraded Solvents by GC-MS and GC-RTF

Qualitative studies of the degraded solvents were carried out using GC-FTIR or GC-MS to identify the diamide degradation products. Figure 1 presents, as an example, chromatograms of DMDOHEMA after radiolysis and hydrolysis in the presence of a nitric acid aqueous phase.

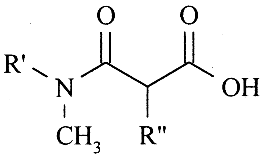
The main products identified in the organic phases of the three malonamides either in *n*-dodecane or TPH are the following:

Initial diamide:



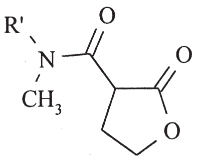
;

Bifunctional compounds: * amide-acid:



(*1*),

* amide-lactone:



(*2*),

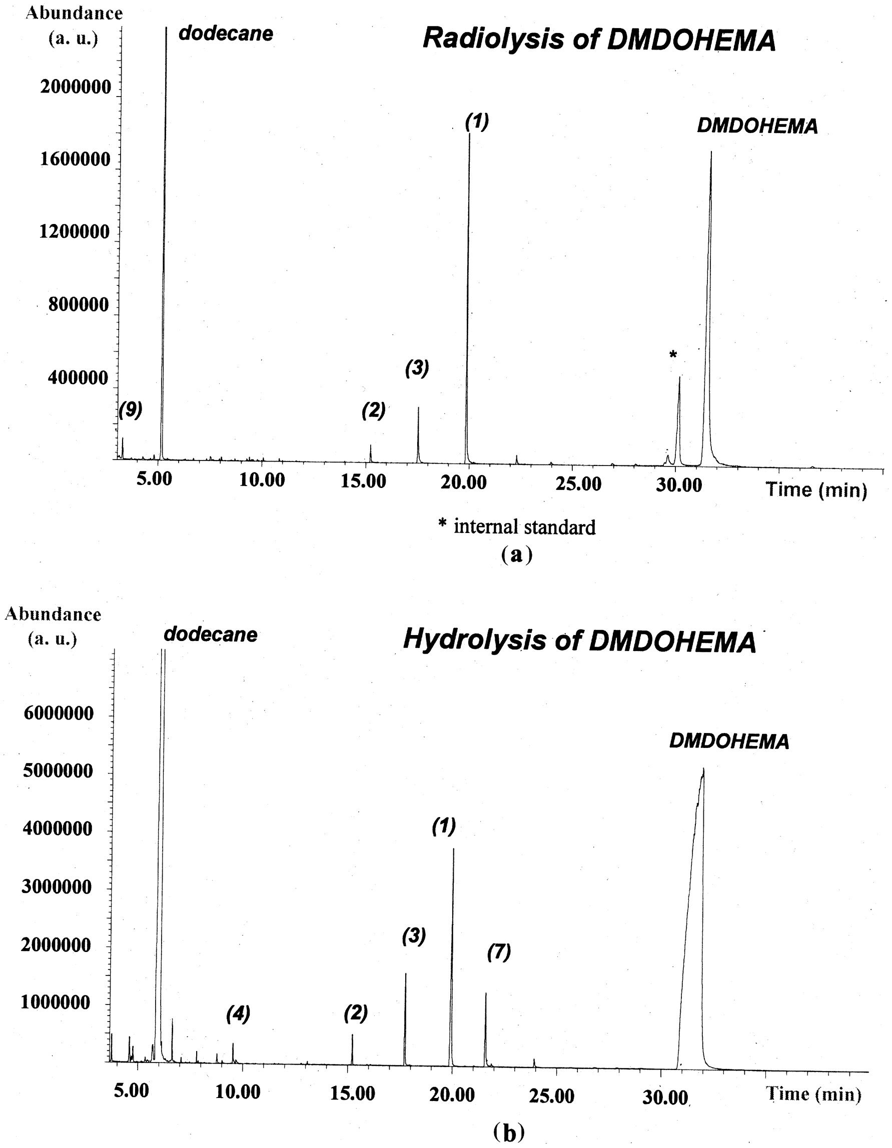
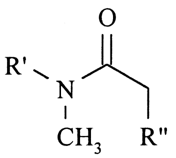
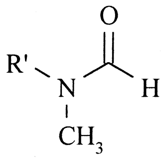
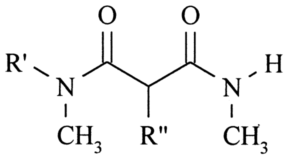
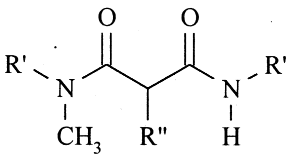
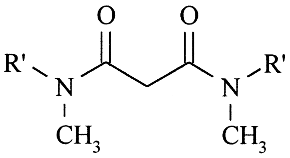
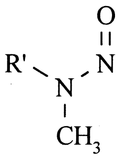


Figure 1. Chromatograms for degraded DMDOHEMA solutions in dodecane. For the nature of the species corresponding to numbered peaks, see text. a) DMDOHEMA, 1 mol/L in contact with nitric acid solution (HNO_3, 4 mol/L) after γ radiolysis (0.7 MGy) at room temperature. b) DMDOHEMA 0.65 mol/L in contact with nitric acid solution (HNO_3, 3 mol/L) after hydrolysis at 25°C for 1 month.

Monoamides:  (***3***) and  (***4***),

Diamides:  (***5***),

 (***6***), and  (***7***)

N-nitrosoamine:  (***8***),

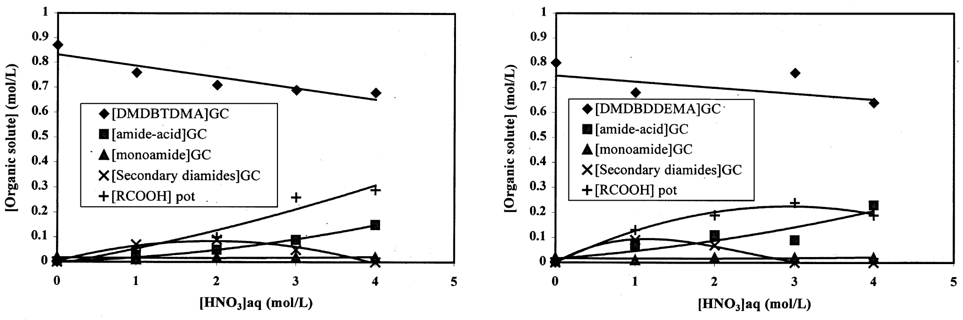
Carboxylic acids: RCOOH (with different R groups) (***9***).

Alcohol (only when an oxygen atom is present in the R” chain): $C_{12}H_{25}OH$ after degradation of DMDBDDEMA and $C_6H_{13}OH$ after degradation of DMDOHEMA.

The degradation products of the three diamides are similar in nature. The main difference between the behavior of DMDOHEMA and that of the other two molecules (DMDBTDMA and DMDBDDEMA) concerns the presence of significant quantities of formamide (***4***), *N*-nitrosamine (***8***), amide-lactone (***2***), and diamide (***7***) in the degraded organic phases (Fig. 1). These degradation products contain at least the $C_8H_{17}(CH_3)N$- group and thus are not aqueous solubles; an increasing alkyl chain length on the nitrogen atom (from C_4H_9 to C_8H_{17}) leads to an increasing lipophilicity of the malonamide degradation molecules and, in turn, to their increasing solubility in the organic phases.

Quantitative Analyses of Degraded Solvents by Gas Chromatography and Potentiometric Titrations

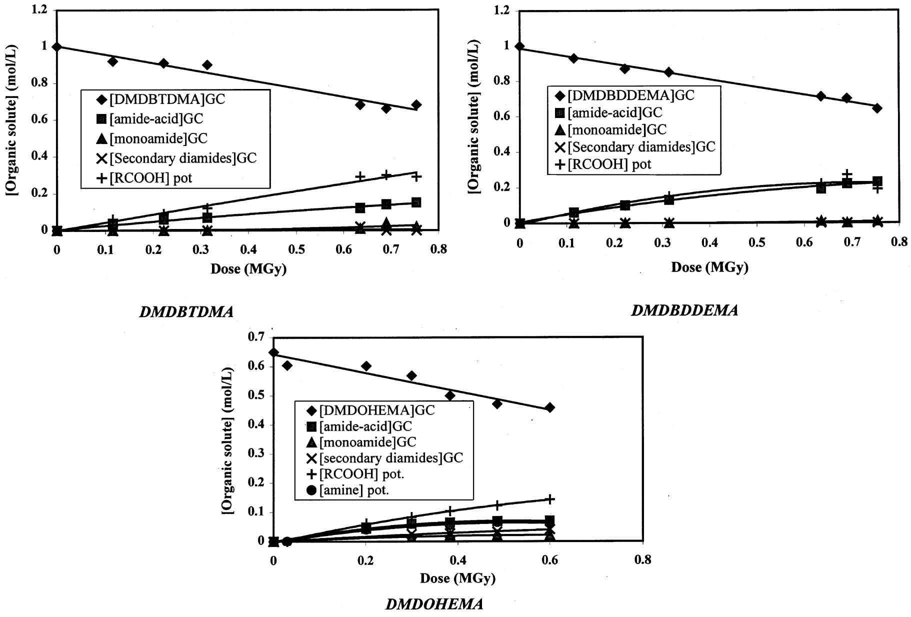
Figures 2 and 3 show the effects of the acidity and the integrated dose, and Figure 4 shows the effect of hydrolysis (at 25°C and 60°C) on the concentrations of the main products in the organic phases.



DMDBTDMA

DMDBDDEMA

Figure 2. Concentrations of the main solutes in the organic phases as determined by gas chromatography and potentiometric titration, after radiolysis of DMDBTDMA and DMDBDDEMA (1 mol/L in TPH) in contact with nitric acid (room temperature). Integrated dose = 0.75 MGy. Dose rate = 4.5 kGy/h. [HNO$_3$] = 0 corresponds to the radiolysis of diamide without aqueous phase.

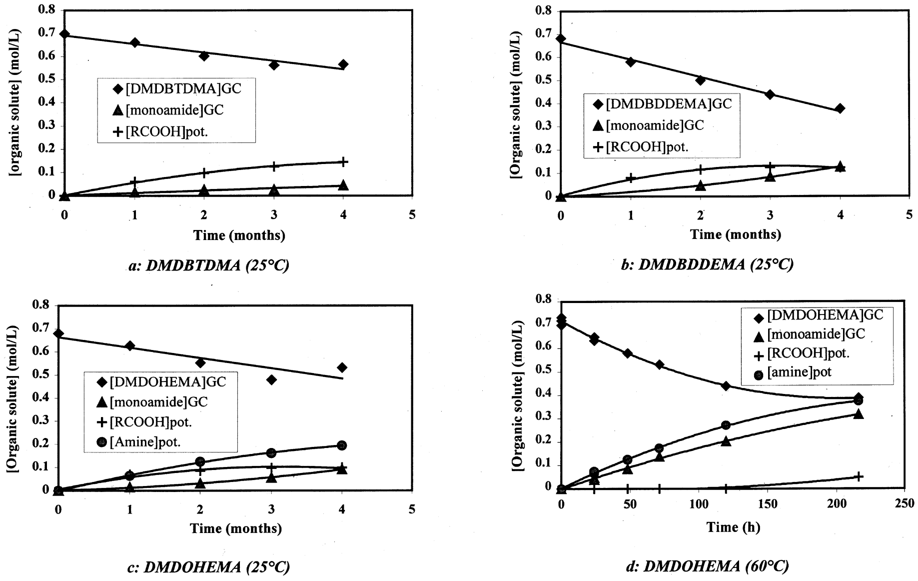


DMDBTDMA

DMDBDDEMA

DMDOHEMA

Figure 3. Concentrations of the main solutes in the organic phases as determined by gas chromatography and potentiometric titration after radiolysis of malonamide (room temperature). DMDBTDMA and DMDBDDEMA (1 mol/L in TPH) in contact with 4 mol/L nitric acid. DMDOHEMA (0.65 mol/L in TPH) in contact with 3 mol/L nitric acid.



a: DMDBTDMA (25°C)

b: DMDBDDEMA (25°C)

c: DMDOHEMA (25°C)

d: DMDOHEMA (60°C)

Figure 4. Concentrations of the main solutes in the organic phases as determined by gas chromatography and potentiometric titration after hydrolysis of malonamides in contact with nitric acid, 3 mol/L. a, b, c) Hydrolysis of 0.65 mol/L malonamide in dodecane at 25°C. d) Hydrolysis of 0.65 mol/L DMDOHEMA in TPH at 60°C.

Comparison of the results obtained by potentiometric titration and GC shows that all the degradation species formed are not detected by GC.

After radiolysis (Figs. 3 and 4), the concentration of carboxylic acid in the organic phase determined by potentiometric titration is higher than that determined by GC.

Moreover, one solute with a pKa equal to 9.7 (by NaOH titration in ethanol-water medium) assumed to be an amine was detected by pH titration and not by GC. We can explain this finding by the fact that the protonated form of the amine is not volatile in acidic media. The proposed formula for this amine is $CH_3(R')NH$ (***10***). This species is present only after the degradation of DMDOHEMA and not after the degradation of the two other diamides, probably because $CH_3(C_4H_9)NH$ (the degradation product of DMDBTDMA and DMDBDDEMA) is soluble in the aqueous phase, whereas $CH_3(C_8H_{17})NH$ (degradation product of DMDOHEMA) is not.

Quantitative studies of malonamide radiolytic and hydrolytic degradations using potentiometric titrations and gas chromatography show the following:

- The concentration of the extractant decreases strongly with the irradiation dose (the disappearance rate had been estimated to be 0.32

$mol.L^{-1}.(MGy)^{-1}$ for DMDOHEMA in the presence of 3 mol/L aqueous nitric acid ($G_{(DMDOHEMA)} = 3.7$) and to be 0.46 and 0.44 $mol.L^{-1}.(MGy)^{-1}$ for DMDBTDMA and DMDBDDEMA in the presence of 4 mol/L aqueous nitric acid ($G_{(DMDBTDMA)} = 5.2$ and $G_{(DMDBDDEMA)} = 5.5$), irrespective of the diluent used, i.e., *n*-dodecane or TPH. Nevertheless, as seen in Table 1, the "rate of radiolytic disappearance" of diamides in the presence of 4 mol/L aqueous nitric acid can be slightly different.

- The stability of the malonamides varies slightly with the acidity of the aqueous phase.
- The amide-acid compound (***1***) is only found in acidic media and at moderate temperatures. Its concentration increases with aqueous nitric acidity and irradiation dose. At high temperatures, it decomposes, leading to the formation of a corresponding monoamide (**3**).
- After hydrolysis, the concentration of amide-acid (***1***) is equal to the concentration of carboxylic acid determined by potentiometric titration, whereas after radiolysis, more acidic species are present.
- The quantity of monoamide (***3***) produced is important after hydrolysis and small after radiolysis owing to competitive reactions between the formation of (***3***) and its degradation.
- When the alkyl group R' represented by the malonamides is long enough, the quantity of amine ($R'CH_3NH$: (***10***)) formed in the organic phase is important.

From these data, we propose the malonamide degradation pathways. The example illustrated in Figure 5 is the case of a malonamides bearing an ether function within the R" group. In this scheme, the first step is the attack on the amide group by hydrolysis, resulting in the formation of a carboxylic acid (***1***) and a secondary amine (***10***). The resulting carboxylic acid is thermally unstable and decarboxylates to form monoamide (***3***). Another reaction is the hydrolysis of the ether function of the central oxy-alkyl chain leading to alcohols. From these two successive breaks, an acid-alcohol is formed and an intramolecular reaction between the alcohol function and the acid function leads to a lactone (***2***). In the same way, new attacks on the amide groups of compounds (**3**) and (**2**) result in the formation of the same carboxylic acid (***9***). All these species are distributed between the 2 phases (organic and aqueous).

Extracting Properties of the Solvent After Radiolytic and Hydrolytic Degradation

Figures 6 and 7 present the distribution ratios of Am(III), Eu(III), or Nd(III) after radiolysis or hydrolysis of diamides. It appears that the malonamide degradation leads to a decrease in the distribution coefficients.

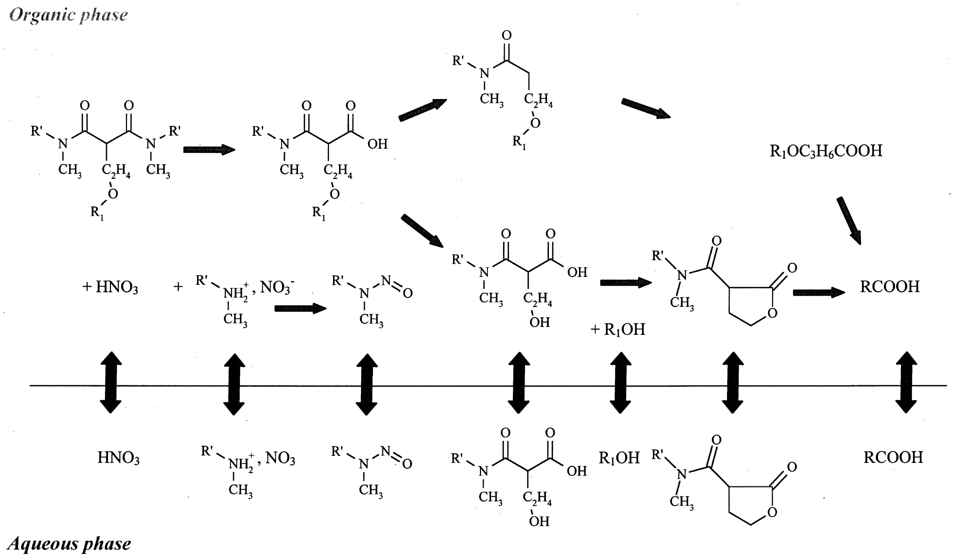


Figure 5. Proposed simplified scheme for the hydrolytic and radiolytic degradation of malonamides with an ether group in R''. (In the case of DMDBTDMA, the scheme is the same except that cleavage around the oxygen atom in the central chain of the malonamide does not exist.)

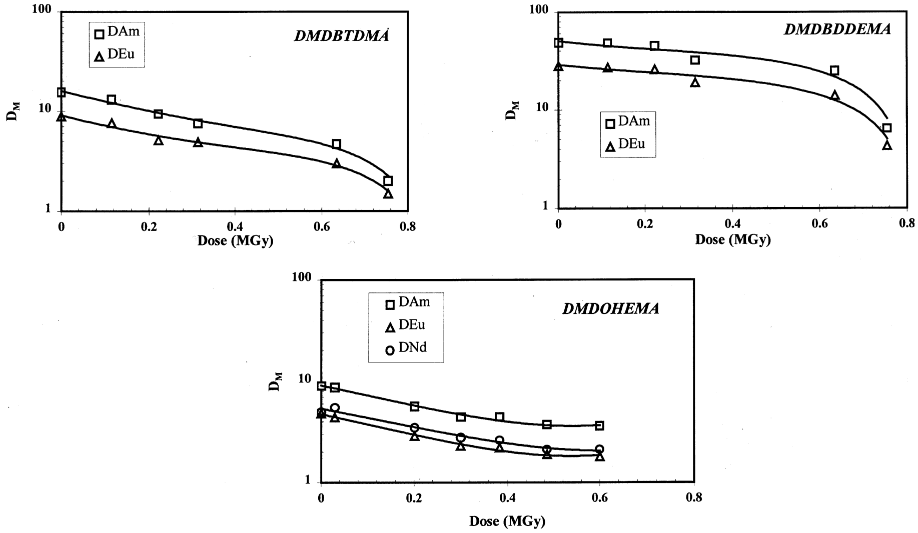
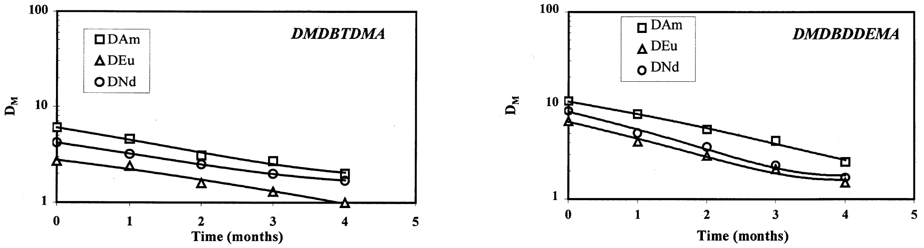
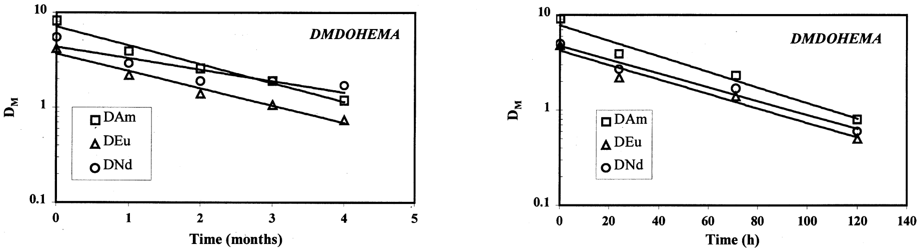


Figure 6. Distribution ratios of Am(III), Eu(III), and Nd(III) at 25°C after radiolysis of malonamide. Am and Eu: trace level concentration; $[\mathrm{Nd}]_{\mathrm{initial}} = 2\mathrm{x}10^{-2}$ mol/L. DMDBTDMA and DMDBDDEMA: $[\mathrm{diamide}]_{\mathrm{initial}} = 1$ mol/L in TPH in contact with nitric acid (4 mol/L). DMDOHEMA: $[\mathrm{diamide}]_{\mathrm{initial}} = 0.65$ mol/L in TPH in contact with nitric acid (3 mol/L).



a: DMDBTDMA (25°C)

b: DMDBDDEMA (25°C)



c: DMDOHEMA (25°C)

d: DMDOHEMA (60°C)

Figure 7. Distribution ratios of Am(III), Eu(III), and Nd(III) at 25°C after hydrolysis of malonamides in contact with 3 mol/L nitric acid aqueous solutions. Am and Eu: trace level concentration ; $[\mathrm{Nd}]_{\mathrm{initial}} = 2\mathrm{x}10^{-2}$ mol/L. a, b, c) Hydrolysis at 25°C; $[\mathrm{diamide}]_{\mathrm{initial}} = 0.65$ mol/L in dodecane in contact with nitric acid (3 mol/L). d) Hydrolysis at 60°C; $[\mathrm{diamide}]_{\mathrm{initial}} = 0.65$ mol/L in TPH in contact with nitric acid (3 mol/L).

For all diamides, the decrease of the diamide concentration cannot alone explain the observed decrease in the extraction properties, except for DMDOHEMA after radiolysis. Indeed, for this malonamide, M(III) nitrate distribution ratios after radiolysis in the presence of 3 mol/L nitric acid are similar to distribution ratios obtained with a corresponding concentration of diamide alone in the diluent.

Comparison of the Three Malonamides

Stability

Table 1 presents the concentrations of the main solutes in the organic phases after gamma radiolytic and hydrolytic degradation under identical conditions for the three malonamides studied.

It appears that the three diamides have the same generic behavior. The stability of diamides bearing an ether function in their R” groups (DMDBDDEMA and DMDOHEMA) is slightly lower than that of DMDBTDMA. After

Table 1. Concentrations of Main Solutes in Organic Solutions After Radiolysis of Diamide in the Presence of a Nitric Acid Aqueous Phase

	[Diamide][b] (mol/L)	[Amide-acid][b] (mol/L)	[Monoamide][b] (mol/L)	[Carboxylic acids][c] (mol/L)	[Amine][c] (mol/L)
Radiolysis in *n*-dodecane (***A***)[a]					
DMDBTDMA	0.74	0.08	0	0.24	0
DMDBDDEMA	0.69	0.11	0.02	0.22	0.03
DMDOHEMA	0.59	0.09	0.01	0.25	0.11
Radiolysis in TPH (***B***)[a]					
DMDBTDMA	0.68	0.15	0.02	0.29	0
DMDBDDEMA	0.64	0.23	0.01	0.28	0
DMDOHEMA	0.57	0.08	0	0.33	0.13
Hydrolysis in *n*-dodecane (***C***)[a]					
DMDBTDMA	0.66	0.06	0.01	0.06	0
DMDBDDEMA	0.58	0.10	0	0.08	0
DMDOHEMA	0.63	0.07	0.01	0.07	0.06

[a] (***A***) $[\text{diamide}]_{\text{initial}} = 1$ mol/L in *n*-dodecane; aqueous phase: HNO_3 4 mol/L; integrated dose: 0.69 MGy; (***B***) $[\text{diamide}]_{\text{initial}} = 1$ mol/L in TPH; aqueous phase: HNO_3 4 mol/L; integrated dose: 0.75 MGy; (**C**) $[\text{diamide}]_{\text{initial}} = 0.68$ mol/L in *n*-dodecane; aqueous phase: HNO_3 3 mol/L; after one month at 25°C.

[b] Concentration determined by GC.

[c] Concentration determined by pHmetry.

radiolysis or hydrolysis under similar conditions, the concentration of carboxylic acids present in the organic phases is about the same for all the diamides. The main difference between these three diamides involves the presence of the amine (R^1CH_3NH: (***10***)), which was only observed after degradation of DMDOHEMA, probably because of the high lipophilicity of $CH_3(C_8H_{17})NH$ (***10***). For the two other malonamides, compound (***10***) is $CH_3(C_4H_9)NH$, and experiments realised with a synthetic solution had shown that it is soluble in the nitric acid aqueous phase.

Extracting Properties

Figure 8 presents the distribution ratios of Am(III) and Nd(III) measured after hydrolytic degradation under identical conditions for the three malonamides studied. Comparison of Figure 8 and Table 1 shows that:

Although the stabilities of DMDBTDMA and DMDOHEMA are similar, the extracting properties of DMDOHEMA are more sensitive to hydrolysis than those of DMDBTDMA.

The more important decrease of the extracting properties of DMDBDDEMA as compared with those of DMDBTDMA can be explained by the lower stability of DMDBDDEMA.

Effect of Malonamide Degradation Products on M(III) Extraction

In the case of DMDOHEMA, it was shown that synthetic solutions containing the diamide and all its identified degradation products (diamide, amide-acid, monoamide, and amine) reproduce the solvent extracting properties after hydrolysis (see following).

In an effort to understand the role played by each degradation product for solvent extraction properties, synthetic organic solutions containing the initial diamide and their degradation products identified after hydrolysis or radiolysis were prepared. The Nd(III) and Am(III) distribution ratios measured with these synthetic organic solutions indicate the effect of the presence of these products on the solvent extraction properties (Fig. 9).

Figure 9 shows that:

The distribution ratios measured with trace level concentrations of metal (D_{Am}) are modified to a greater extend by the presence of degradation products than those measured with macro amounts of metal (D_{Nd}).

The presence of all the degradation products considered leads to a decrease in the solvent extracting properties.

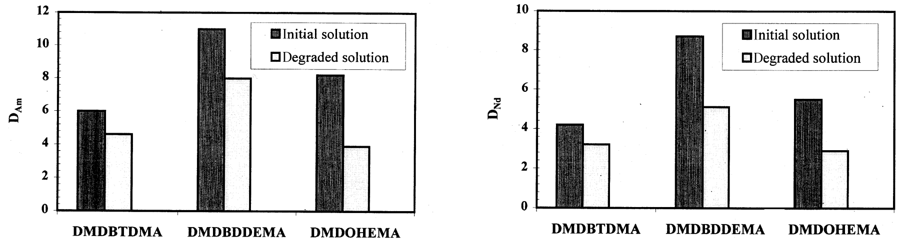


Figure 8. Effect of the hydrolysis of malonamide during 1 month on distribution ratios of Am(III) and Nd(III) at 25°C. $[\text{diamide}]_{\text{initial}} = 0.65$ mol/L in dodecane in contact with nitric acid (3 mol/L) at 25°C. Am: trace level concentration ; $[\text{Nd}]_{\text{initial}} = 2 \times 10^{-2}$ mol/L.

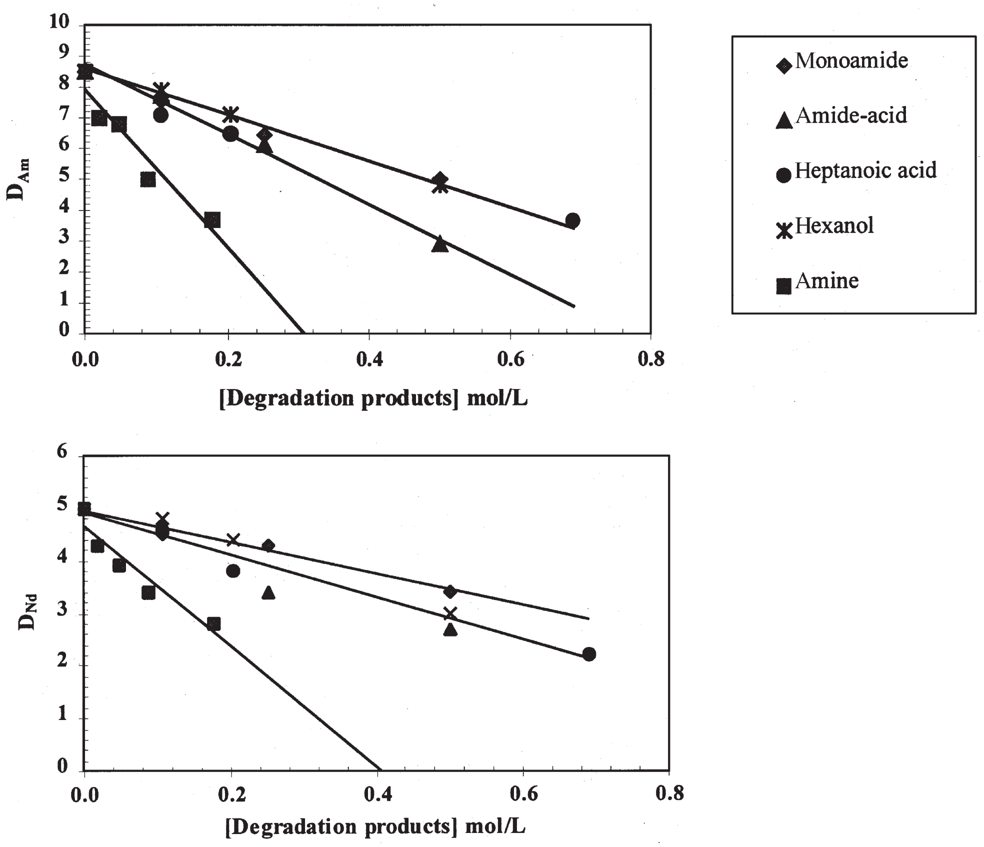


Figure 9. Distribution ratios of Am(III) and Nd(III) as a function of the degradation product concentration in a synthetic DMDOHEMA solution. [DMDOHEMA] = 0.65 mol/L in TPH in contact with nitric acid (3 mol/L) at 25°C. Am(III): trace level concentration and $[\mathrm{Nd}]_{\mathrm{initial}} = 2.10^{-2}$ mol/L. Three differents behaviors can be observed: 1. Effect of the amine, 2. Effect of the acid (amide-acid and heptanoic acid), and 3. Effect of monoamide or hexanol.

The degradation compounds lead to a decrease in the solvent extracting properties in the following order: amine > carboxylic acid > monoamide ≈ hexanol. These effects can possibly be explained by the occurrence of interactions between these compounds and the malonamide extractant.

From these data, it is possible to calculate predicted distribution ratios for Am(III) and Nd(III), taking into account both the decrease of diamide concentration and the presence of degradation products. It appears then that these calculated $D_{M(III)}$ values correspond to the experimental distribution ratios. Therefore, the decrease in extraction properties can be explained by the decrease of the malonamide concentration and by the presence of the main degradation products (***1***, ***3***, ***10***).

Removal of Degradation Products from the Spent Solvents

In an effort to eliminate the degradation products from the degraded solvents, we performed acid washings of the degraded solvents with 3 mol/L HNO_3 solution (twice with an O/A volume ratio equal to 0.25) to remove basic products [amine (***10***), for example] followed by water scrubbing to remove the extracted nitric acid and by basic washing with a 0.5 mol/L Na_2CO_3 solution (with O/A = 1) to remove acidic products [amide-acid (***1***) for example]. The Am(III) distribution ratios after this solvent treatment show that the extracting properties are similar to those of a solution containing the diamide as the only solute (Fig. 10).

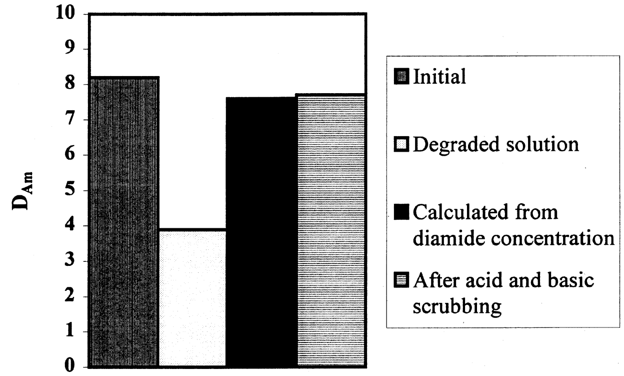


Figure 10. Effect of scrubbing of the spent solvent on Am(III) distribution ratio after hydrolysis of 0.65 mol/L DMDOHEMA in dodecane in contact with nitric acid solution (HNO_3, 3 mol/L) at 25°C during one month. Extraction conditions: Am(III): trace level concentration, aqueous phase: nitric acid, 3 mol/L, temperature: 25°C. Initial: D_{Am} before degradation. Degraded solution: D_{Am} after hydrolysis in contact with nitric acid solution during one month at 25°C. Calculated: D_{Am} calculated from the amide concentration measured by GC after hydrolysis. After scrubbing: D_{Am} after acidic (twice four volume of HNO_3, 3 mol/L) and basic scrubbing (one volume of Na_2CO_3 0.5 mol/L).

Table 2. Concentrations of Main Solutes in Organic Solutions After Radiolysis of Diamide and TBP in Presence of Nitric Acid Aqueous Phase

Extractant[a]	[Extractant][b] (mol/L)	[Acids][c] (mol/L)	[Amine][c] (mol/L)
DMDBTDMA	0.68	0.29	0
DMDOHEMA	0.57	0.33	0.13
TBP	0.95	0.04[b,d]	—

[a] $[\text{Extractant}]_{\text{initial}} = 1$ mol/L in TPH, aqueous phase: HNO_3 4 mol/L, integrated dose: 0.7 MGy.

[b] Concentration determined by GC.

[c] Concentration determined by pHmetry.

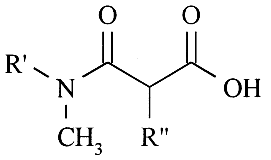
[d] After degradation of TBP, the main degradation species in the organic phase is HDBP (di-*n*-butyl phosphoric acid).

Comparison Between Malonamides and TBP Stabilities

To compare the stability of malonamide extractant with that of tri-*n*-butyl phosphate (TBP), the extractant of the PUREX process used in spent nuclear fuel reprocessing, gamma radiolytic degradation tests were carried out with the two types of extractant (diamide and TBP) under identical conditions. Table 2 presents the concentrations of the main solutes in the organic phases after radiolysis with an integrated dose equal to 0.7 MGy.

Table 2 shows that the stability of each malonamide is lower than that of TBP by a factor of 6 to 9. However, it appears that the influence of degradation products on the solvent extracting properties is less acute for malonamides than that for TBP, and that cleanup of spent solvent by aqueous washings seems somewhat easier for malonamides than for TBP. Moreover, malonamide degradation products are totally C H O N molecules, which obviously is not the case for HDBP; thus, no secondary solid waste is expected to be produced from the subsequent management of the malonamide degradation products.

CONCLUSIONS

Malonamide extractants degrade by hydrolysis or radiolysis, mainly to the amide-acid  (*1*) and a secondary amine ($R'CH_3NH$: (***10***)

If the R' alkyl group of the malonamides is long enough, the quantity of amine found in organic phase is important; however if this R' group is short (for example, the butyl group), the amine species is soluble in the aqueous phase. The amide-acid formed is thermally unstable and decarboxylates to form a monoamide (***3***). These compounds (***1***, ***10***, ***3***) are the main ones generated by degradation. Other reactions exist and lead to compounds whose concentrations in the organic phase are lower than those for compounds ***1***, ***10***, and ***3***. This is the case for amide-lactone (***2***), diamides (***5***, ***6***, ***7***), carboxylic acids (***9***), and alcohol.

The extracting properties of solvents comprising malonamide solutions in an aliphatic diluent vs. actinides(III) and lanthanides(III) nitrates were determined after radiolysis and hydrolysis. The degradation of the solvent leads to a decrease of the M(III) distribution ratios. Experiments carried out with organic synthetic solutions show that the decrease in solvent extraction properties can be explained by a decrease in the malonamide concentration and by the presence of the main degradation products [amide-acid (***1***), monoamide (***3***), and amine (***10***)].

Acidic and basic solvent washings seem to be promising approaches to remove these degradation products from the spent solvents.

Even if it can be said that malonamides are less stable, for comparable conditions, than the TBP (the extractant employed for the PUREX process), their stabilities vs. radiolysis and hydrolysis appear to be sufficient to allow an efficient industrial implementation of the DIAMEX process.

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