



# Solvent extraction study of actinide elements by *N,N'*-dimethyl-*N,N'*-dihexyl-3-oxapentanediamide and thenoyltrifluoroacetone

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## Abstract

We have studied the extraction of Eu(III), Am(III), Th(IV), U(VI) and Np(V) by 4 diamides (DMDHOPDA, *N,N'*-dimethyl-*N,N'*-dihexyl-3-oxapentanediamide; DHOPDA, *N,N'*-dihexyl-3-oxapentanediamide; DMDHTPDA, *N,N'*-dimethyl-*N,N'*-dihexyl-3-thiopentanediamide; DHTPDA, *N,N'*-dihexyl-3-thiopentanediamide) from perchlorate solutions. Synergistic extraction was observed with these diamides and thenoyltrifluoroacetone (TTA) in which the main extraction species determined are  $M(TTA)_3(DA)$  ( $M=Eu, Am$ ),  $Th(TTA)_3(DA)(X)$ ,  $UO_2(TTA)_2(DA)$  ( $DA$ : diamide,  $X^-: ClO_4^-$  or  $CH_2ClCOO^-$ ). The species,  $M(DA)_3(X)_3$ ,  $M(DA)_3(TTA)(X)_2$ ,  $M(DA)_2(TTA)_2(X)$  and  $M(DA)(TTA)_3$  are observed in the synergistic extraction of DMDHOPDA+TTA. © 1998 Elsevier Science S.A.

**Keywords:** Actinide; Solvent extraction; Diamide; Thenoyltrifluoroacetone; Synergistic extraction

## 1. Introduction

Diamides are neutral donor extractants [1] and show strong complexation with metal ions of III, IV and VI valence [2,3], providing good extraction of actinide ions from acidic solutions. Another useful feature is the easy of synthesis of diamides compared to that of organophosphorus compounds [3,4].

We have synthesized the diamides and tested them for extraction of actinide elements [5–8]. The synthesized diamides were *N,N'*-dimethyl-*N,N'*-dihexyl-3-oxapentanediamide (DMDHOPDA), *N,N'*-dihexyl-3-oxapentanediamide (DHOPDA), *N,N'*-dimethyl-*N,N'*-dihexyl-3-thiopentanediamide (DMDHTPDA), and *N,N'*-dihexyl-3-thiopentanediamide (DHTPDA); their chemical structures are shown in Fig. 1. These diamides contain either an ether oxygen or sulfur which can, with the oxygen in the amide group, complex with the metal ion to form a five-membered ring.

In this paper, we studied the extraction of Eu(III), Am(III), Th(IV), U(VI) and Np(V) with these diamides and thenoyltrifluoroacetone (TTA).

## 2. Experimental details

Solutions of  $10^{-3}$  M  $HClO_4$  containing the radioactive tracers,  $^{152+154}Eu$ ,  $^{241}Am$  and  $^{233}U$ , and 0.1 M  $HCl$  of  $^{237}Np$  were prepared.  $^{233}Pa$  in  $^{237}Np$  tracer was removed by extraction with di(2-ethylhexyl)phosphoric acid, as described in the previous papers [6,9].  $^{234}Th$  was separated from  $^{238}U$  using an anion exchange column with 8 M  $HCl$  eluent. The eluted solution was evaporated, and the  $^{234}Th$  was redissolved in  $10^{-2}$  M  $HClO_4$ . The chemical reagents, TTA (>98%, Wako Pure Chemical Industries) and chloroacetic acid (99%, Wako Pure Chemical Industries), were purified by recrystallization. All other chemicals were analytical grade.

The diamides were synthesized from diacetic acid and the amines in the presence of a condensing agent. After synthesis and purification, the yields of DMDHOPDA, DHOPDA, DMDHTPDA and DHTPDA were 70, 20, 40 and 30%, respectively. The results for the identifications of these diamides were described in previous reports [6–8].

The extraction procedure was as follows: 5.00 ml of toluene containing diamide+TTA, 5.00 ml of the aqueous solution and 10  $\mu$ l of the radioactive tracer solution were introduced into the polyethylene vial. This organic solution was already preequilibrated by shaking with a non-radioactive aqueous solution for 2 h. The mixed solutions were shaken for 2 h at 25°C (the previous study had confirmed that 2 h for the shaking time is enough to ensure

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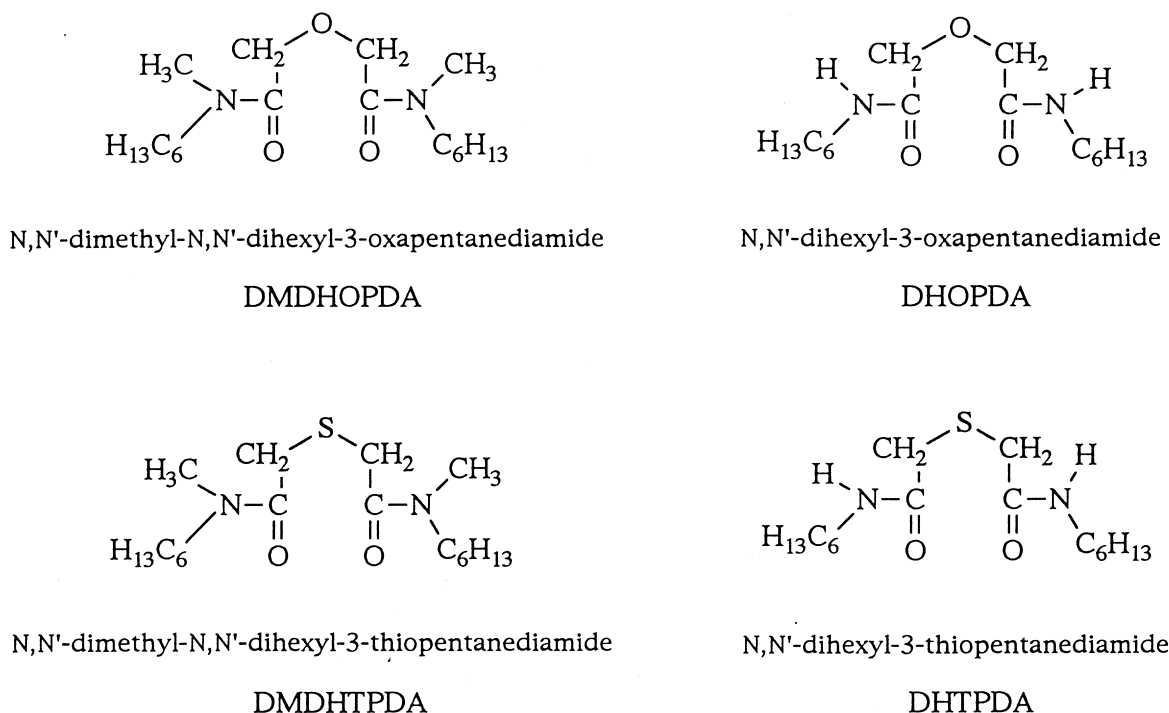


Fig. 1. The chemical structures of DMDHOPDA, DHOPDA, DMDHTPDA and DHTPDA.

equilibrium). After centrifugation, duplicate 1.00 ml aliquots were taken from both phases. The  $^{152+154}\text{Eu}$  and  $^{234}\text{Th}$  activities were measured with a NaI(Tl) counter (COBRA 5003, Packard Instrument), and the  $^{233}\text{U}$ ,  $^{237}\text{Np}$  and  $^{241}\text{Am}$  activities were measured by liquid scintillation counting (Tri-Carb 1600TR, Packard Instrument). The equilibrated pH values were measured after extraction. Each experiment for a particular set of conditions was repeated at least twice.

### 3. Results and discussion

In Fig. 2, the relationship between  $\log D$  of Eu(III), Am(III), Th(IV), U(VI) and Np(V) and  $\log [\text{DMDHOPDA}]$  are given. Here, the extraction involves the ion pairs formed by the metal ions, the neutral diamide donor and the counter anion ( $\text{ClO}_4^-$  or  $\text{CH}_2\text{ClCOO}^-$ ). The linear regression analysis of the data in Fig. 2 yielded the equations:  $y=2.89x+10.4$  for Eu,  $y=3.07x+10.09$  for Am,  $y=1.31x+3.96$  for Th,  $y=2.45x+5.22$  for U and  $y=1.93x+2.29$  for Np ( $y: \log D$ ;  $x: \log [\text{DMDHOPDA}]$ ). The main extracted species of these cations were determined to be  $\text{Eu}(\text{DA})_3(\text{X})_3$ ,  $\text{Th}(\text{DA})(\text{X})_4$ ,  $\text{UO}_2(\text{DA})_2(\text{X})_2$ ,  $\text{Am}(\text{DA})_3(\text{X})_3$ , and  $\text{NpO}_2(\text{DA})_2(\text{X})$  ( $\text{DA}=\text{DMDHOPDA}$ ,  $\text{X}^-=\text{ClO}_4^-$  or  $\text{CH}_2\text{ClCOO}^-$ ).

In extraction of actinide elements solely by the diamides DHOPDA, DMDHTPDA and DHTPDA, only negligibly small amounts were extracted. Hydrogen bonding in these diamides [10] and the soft sulfur donor probably decrease their complexation strength.

The results of the synergistic extractions with diamide and TTA are summarized in Table 1. The  $\log D$  values were calculated for the same TTA concentration and pH. The calculated values are plotted in Figs. 3–5 for Eu(Am),

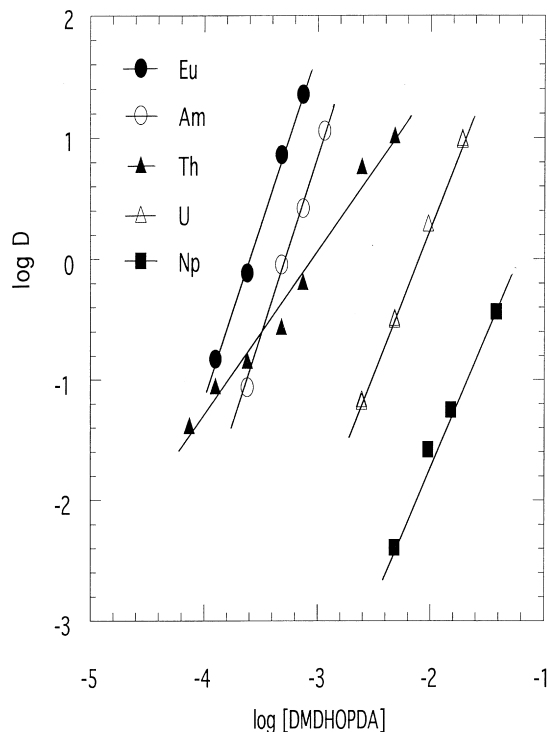


Fig. 2. The extraction behavior of Eu(III), Am(III), Th(IV), U(VI) and Np(V) by DMDHOPDA. Aqueous phase: for Eu and Am, 1 M  $\text{NaClO}_4$ , pH=3.0; for U and Th, 1 M  $\text{NaClO}_4$ , pH=-0.1; for Np, 2 M  $\text{NaClO}_4$ , pH=0.7; organic phase: [DMDHOPDA] in toluene.

Table 1

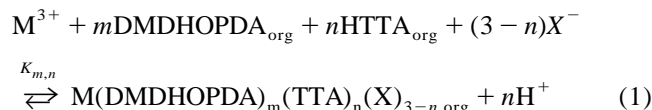
The main extraction species of Eu(III), Th(IV), U(VI), Np(V) and Am(III) with HTTA and/or diamide

Element	HTTA	DMDHOPDA	HTTA +			
			DMDHOPDA	DHOPDA	DMDHTPDA	DHTPDA
Eu	Eu(TTA) <sub>3</sub>	Eu(DA) <sub>3</sub> (X) <sub>3</sub>	Eu(TTA) <sub>3</sub> (DA)	N.D. <sup>b</sup>	Eu(TTA) <sub>3</sub> (DA)	Eu(TTA) <sub>3</sub> (DA)
Th	Th(TTA) <sub>3</sub> (X)	Th(DA)(X) <sub>4</sub>	Th(TTA)(DA)(X) <sub>3</sub>	N.D.	Th(TTA) <sub>3</sub> (DA)(X)	Th(TTA) <sub>3</sub> (DA)(X)
U	UO <sub>2</sub> (TTA) <sub>2</sub>	UO <sub>2</sub> (DA) <sub>2</sub> (X) <sub>2</sub>	UO <sub>2</sub> (TTA) <sub>2</sub> (DA)	UO <sub>2</sub> (TTA) <sub>2</sub> (DA)	UO <sub>2</sub> (TTA) <sub>2</sub> (DA)	UO <sub>2</sub> (TTA) <sub>2</sub> (DA)
Np	N.E. <sup>c</sup>	NpO <sub>2</sub> (DA) <sub>2</sub> (X)	N.D.	N.D.	N.D.	N.D.
Am	Am(TTA) <sub>3</sub>	Am(DA) <sub>3</sub> (X) <sub>3</sub>	Am(TTA) <sub>3</sub> (DA)	N.D.	Am(TTA) <sub>3</sub> (DA)	Am(TTA) <sub>3</sub> (DA)

<sup>a</sup> DA, diamide; X<sup>−</sup>, ClO<sub>4</sub><sup>−</sup> or CH<sub>2</sub>ClCOO<sup>−</sup>.<sup>b</sup> N.D., Not Determined.<sup>c</sup> N.E., Not Extracted.

Th and U, respectively, where the dotted lines in these figures indicate the extraction behaviors by DMDHOPDA alone. Log *D* values for TTA extraction were calculated to be −3.0 for Eu, −0.5 for Th, and −0.3 for U, respectively. The following order of log *D* values were obtained: DMDHOPDA+TTA>DMDHOPDA, DMDHTPDA+TTA>DHTPDA+TTA for Eu (and Am); DMDHOPDA+TTA>DHTPDA+TTA>DMDHTPDA+TTA>DMDHOPDA for Th; DMDHOPDA+TTA>DHOPDA+TTA, DMDHTPDA+TTA, DHTPDA+TTA>DMDHOPDA for U.

A previous study [11] proposed several Eu and Am species in the synergistic extraction of DMDHOPDA+TTA. The extraction reactions were defined as (M=Eu or Am):



We investigated the dependence of the species on pH at a constant concentration of [DMDHOPDA] and [TTA]. The experimental conditions, the extraction species, and the calculated extraction constants, log *K*<sub>*m,n*</sub>, are listed in Table 2. The total distribution coefficients, *D*, can be calculated from the equation:

$$D = D_{3,0} + D_{3,1} + D_{2,2} + D_{1,3} \\ = ([M(\text{DA})_3(\text{X})_3]_{\text{org}} + [M(\text{DA})_3(\text{TTA})(\text{X})_2]_{\text{org}} \\ + [M(\text{DA})_2(\text{TTA})_2(\text{X})]_{\text{org}})$$

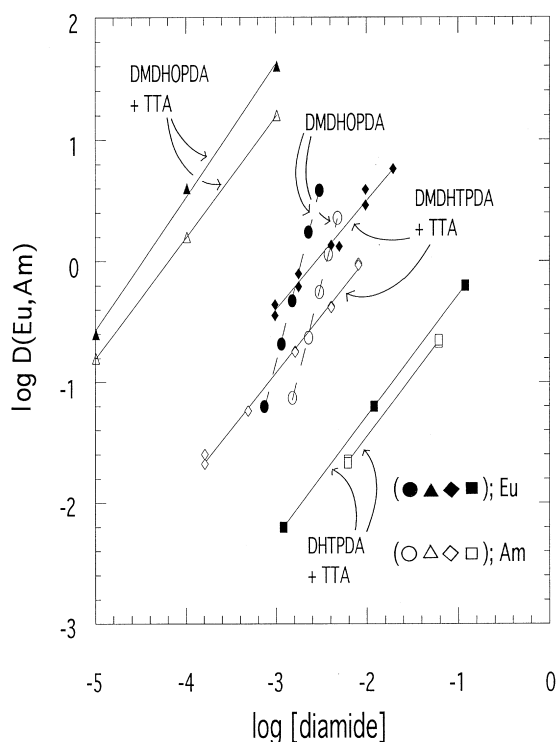


Fig. 3. The log *D* values of Eu(III) and Am(III) calculated in the synergistic extraction system. Aqueous phase: 0.1 M NaClO<sub>4</sub>, pH=3.0; organic phase: 12 mM [TTA]+[diamide] in toluene.

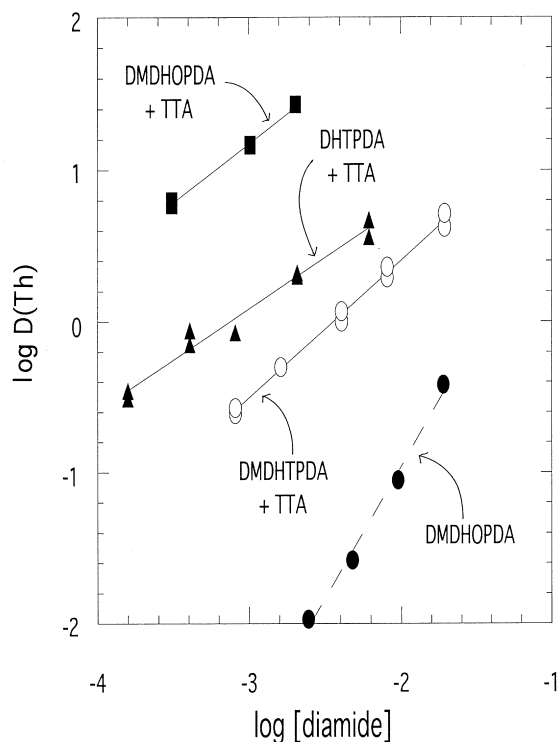


Fig. 4. The log *D* values of Th(IV) calculated in the synergistic extraction system. Aqueous phase: 0.1 M NaClO<sub>4</sub>, pH=1.0; organic phase: 12 mM [TTA]+[diamide] in toluene.

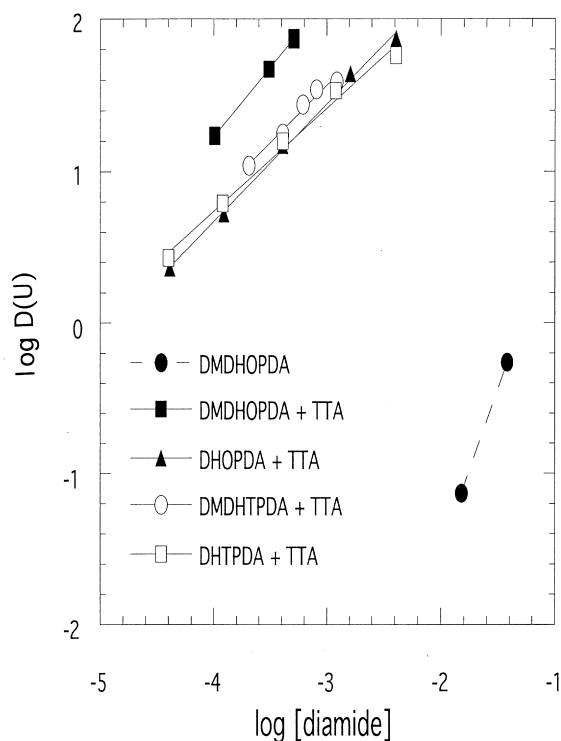


Fig. 5. The log  $D$  values of U(VI) calculated in the synergistic extraction system. Aqueous phase: 0.1 M NaClO<sub>4</sub>, pH = 3.0; organic phase: 12 mM [TTA] + [diamide] in toluene.

$$\begin{aligned}
 &+ [\text{M}(\text{DA})(\text{TTA})_3]_{\text{org}} / [\text{M}^{3+}] = K_{3,0} [\text{DA}]_{\text{org}}^3 [\text{X}]^3 \\
 &+ K_{3,1} [\text{DA}]_{\text{org}}^3 [\text{HTTA}]_{\text{org}} [\text{X}]^2 / [\text{H}^+] \\
 &+ K_{2,2} [\text{DA}]_{\text{org}}^2 [\text{HTTA}]_{\text{org}}^2 [\text{X}] / [\text{H}^+]^2 \\
 &+ K_{1,3} [\text{DA}]_{\text{org}} [\text{HTTA}]_{\text{org}}^3 / [\text{H}^+]^3 \quad (2)
 \end{aligned}$$

Using the extraction constants,  $K_{m,n}$  in Table 2 with Eq. (2), the total  $D$  values were calculated. Each  $D_{m,n}$  value was divided by the total  $D$  value, to obtain the fractional concentration of each extraction species. The pattern of fractional variation of the Eu and Am species as a function of pH is illustrated in Fig. 6. The curves indicate that this extraction system does not provide a useful separation of Eu and Am.

Table 2

The species in the synergistic extraction with DMDHOPDA and HTTA ([DMDHOPDA] = 0.748 mM, [HTTA] = 5 mM)

Element	pH	Main species	Extraction constant
Eu	<2	Eu(DA) <sub>3</sub> (X) <sub>3</sub>	8.03 (log $K_{3,0}$ )
Eu	2.2–2.7	Eu(DA) <sub>3</sub> (TTA)(X) <sub>2</sub>	8.34 ± 0.11 (log $K_{3,1}$ )
Eu	2.7–3.3	Eu(DA) <sub>2</sub> (TTA) <sub>2</sub> (X)	4.32 ± 0.03 (log $K_{2,2}$ )
Eu	>3.3	Eu(DA)(TTA) <sub>3</sub>	0.03 ± 0.17 (log $K_{1,3}$ )
Am	<2	Am(DA) <sub>3</sub> (X) <sub>3</sub>	7.29 (log $K_{3,0}$ )
Am	2.2–2.7	Am(DA) <sub>3</sub> (TTA)(X) <sub>2</sub>	7.81 ± 0.02 (log $K_{3,1}$ )
Am	2.7–3.3	Am(DA) <sub>2</sub> (TTA) <sub>2</sub> (X)	4.48 ± 0.05 (log $K_{2,2}$ )
Am	>3.3	Am(DA)(TTA) <sub>3</sub>	0.18 ± 0.06 (log $K_{1,3}$ )

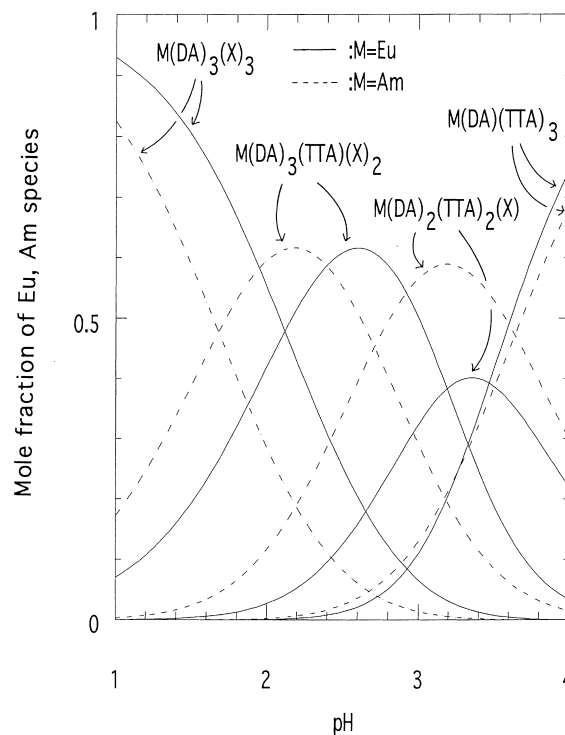


Fig. 6. The relationship between the fractional concentration of the species of Eu and Am and pH at the synergistic extraction of DMDHOPDA and TTA. Aqueous phase: 0.1 M NaClO<sub>4</sub>; organic phase: 0.748 mM [DMDHOPDA] + 5 mM [TTA] in toluene.

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