Inorganica Chimica Acta, 140 (1987) 197–206

Solvent Extraction for the Chemical Separations of the 5f Elements*

C. MUSIKAS

CEA-IRDI-DERDCA-DGR-SEP-SCPR, Centre d'Etudes Nucléaires, Fontenay-Aux-Roses 92265, France

Abstract

After a brief account of the needs for new extractants in actinide chemistry, interesting possibilities for *N,N*-dialkylamides and *N,N'*-tetraalkylmalonamides are discussed. Results dealing mainly with the properties of *N,N*-dialkylamides as an alternative to TBP in irradiated fuel reprocessing are presented. They are: the selection of amides of which the uranylnitrato adducts are soluble in alkanes; the extraction of: U(IV), Pu(IV) and fission products; the radiolytic and hydrolytic stability of amides and a bench-scale test of *N,N*-di(2-ethylhexyl)hexanamide in a first reprocessing cycle.

Extractive properties of the *N,N'*-tetra- or penta-alkyl malonamides are described. They indicate that these completely incinerable extractants are very promising for the recovery of actinides from radioactive wastes. The needs for basic research which could lead to a better understanding of actinide extraction chemistry are illustrated by some examples.

Introduction

Solvent extraction is universally used for chemical separations of the 5f elements. This paper directly follows that of Schulz and Horwitz at 'Actinides 85' [1]. It will try to propose some answers to questions arising at this conference: 'What kind and quantity of research should be done in separation chemistry of the actinides.' Since September 1985 the activities of the laboratories involved in this field have not changed and they can be divided into two main categories.

(i) Improvements in the practice and the understanding of the PUREX process used for the industrial reprocessing of irradiated nuclear fuels.

(ii) Basic chemistry of actinides extraction: synergism, new extractants, etc.

In this paper we will consider some ideas and new results which could have a significance in the future for chemical separations of the actinides at the industrial scale. The PUREX process will not be discussed as investigations dealing with tributyl phosphate (TBP), $(C_4H_9O)_3P{=}O$, have been presented at other conferences.

Organophosphorus extractants have played a major role in actinide extractions. This can be understood in view of the hard sphere acceptor of actinide ions which easily form bonds with the strongly polar P=O groups. These extractants are generally stable, cheap and commercially available. TBP is used for uranium purification in the mining industry and in the reprocessing of irradiated nuclear fuels.

Di(2-ethylhexyl)phosphoric acid (HDEHP), $(C_8H_{17}O)_2PO_2H$, is recommended for the trivalent actinide–lanthanide group separations in the TALSPEAK process [2]. More recently, bifunctional extractants such as dihexyl *N,N*-diethylmethylenecarbamoyl phosphonate (CMP) $(C_6H_{13}O)_2POCH_2CON(C_2H_5)_2$ or octylphenyl-*N,N*-diisobutylcarbamoylmethylene phosphine oxide (CMPO), $C_8H_{17}C_6H_5POCH_2CON(i\text{-}C_4H_9)_2$, have been recommended for the extraction of actinide(III), (IV) and (VI) from middle-range acidic wastes in order to convert them to non-α wastes, which can be stored inexpensively in near-surface disposals [3, 4]. A new process (TRUEX) has been devised for this purpose; CMPO is used as extractant [5]. However, as wastes management is an important part in the cost of nuclear energy, it is desirable to select extractants which will generate smaller amounts of wastes than the organophosphorus molecules.

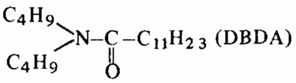
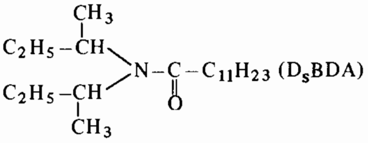
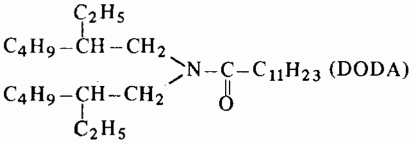
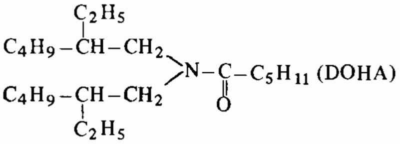
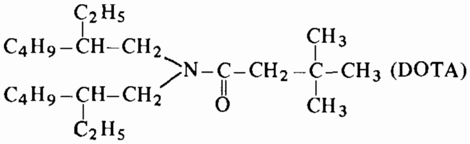
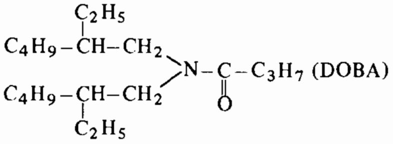
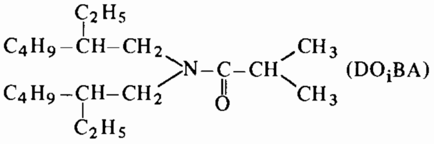
Among the common donor groups of completely incinerable organic molecules, carboxylic acid amides are especially interesting. The basicity of amides is higher than phosphates and they extract many nitrates of metallic ions by solvatation. Because of the rigidity of the $\underset{\underset{\displaystyle O}{\|}}{R{-}C{-}N(R'_2)}$ amide group, the nature of carbon and nitrogen substituents plays an important role in the steric hindrance around the metal, with the result that selectivities can be found by changing R or R' [6]. The prospects offered by *N,N*-dialkylamides as an alternative to TBP in the PUREX process, and the possible use of *N,N'*-tetraalkylmalonamides or *N,N'*-tetraalkyl-2-alkylpropanediamide for actinide(III), (IV) and (VI) extraction from wastes will be developed in the next paragraphs.

---

*Paper presented at the Second International Conference on the Basic and Applied Chemistry of f-Transition (Lanthanide and Actinide) and Related Elements (2nd ICLA), Lisbon, Portugal, April 6–10, 1987.

0020-1693/87/$3.50

TABLE I. Solubility of $UO_2(NO_3)_2$ in Various *N,N*-Dialkylamide Solutions (1 M into hyfrane, Θ = 25 °C)

Formula and acronym of the extractant	Organic solubility of $UO_2(NO_3)_2$ ($g\,l^{-1}$)	Aqueous HNO_3 ($mol\,l^{-1}$)
	80	0
DBDA	71	4
	64	0
D_sBDA	36	4
	>120	0 and 4
	>120	0 and 4
	>120	0 and 4
	>120	0 and 4
	>120	0 and 4

Extraction of Actinides by *N,N*-Dialkylamides

Selection of N,N-Dialkylamides

N,N-Dialkylamides have been investigated as actinide extractants [6–8] because of their potential advantages over TBP. They are completely incinerable, and their degradation products do not alter the separation processes by forming insoluble salts, so solvent regeneration is not necessary at each extraction cycle. The U(VI) back-extraction is easier and higher fission product decontamination factors have been reported [9, 10]. However, these advantages are limited by the fact that *N,N*-dialkylamideonitratouranyls are poorly soluble in aliphatic hydrocarbons. We first investigated the solubility of the organic complexes of U(VI) into hyfrane 120 (a commercial substituted dodecane). The results of these investigations are contained in Table I. It can be seen that the nature of the nitrogen substituent is important to avoid precipitates or third-phase formation. The ethyl substitution in the β-position from the nitrogen is the more favourable. At present, the reasons for this increased solubility are not fully understood and should be the subject of further investigations. However, this finding suppresses one of the major draw-backs of *N,N*-dialkylamides.

Extraction of the Irradiated Nuclear Fuel Metallic Ions

Uranium(VI)

U(VI) distribution ratios between *N,N*-dialkylamides and aqueous nitric acid are plotted in Fig. 1. DOTA, which contains a tetra-substituted carbon in the position β from the C=O, extracts less U(VI) at low acidity. Saturation of the organic phase with $UO_2(NO_3)_2$ showed that the organic complex has the formula $UO_2(NO_3)_2L_2$ (where L represents the amidic extractant). However, the slope of the bilogarithmic representation of U(VI) distribution ratios as a function of the extractant concentration in the organic phase is not a straight line with slope 2. We observed slopes from 2.1 to 2.75. This feature indicates a strongly positive non-ideal behaviour (the acidity coefficients of amides vary sharply with concentration) or the existence of outer-sphere complexes like $[UO_2(NO_3)_2L_2]L_x$. At higher acidities there are changes in the UV–Vis spectra of the U(VI) organic complexes, as is shown in Fig. 2. These changes can be interpreted by the presence of $UO_2(NO_3)_3{}^{+-}HL$; the $UO_2(NO_3)_3{}^-$ anion has the typical spectrum shown in the Figure and has already been observed in $UO_2(NO_3)_3HR_3N$, where R_3N is a tertiary amine [11] and in solid $UO_2(NO_3)_3Cs$ [12]. The formation of $UO_2(NO_3)_3HL$ differentiates the amides from TBP and can be attributed to their higher basicity.

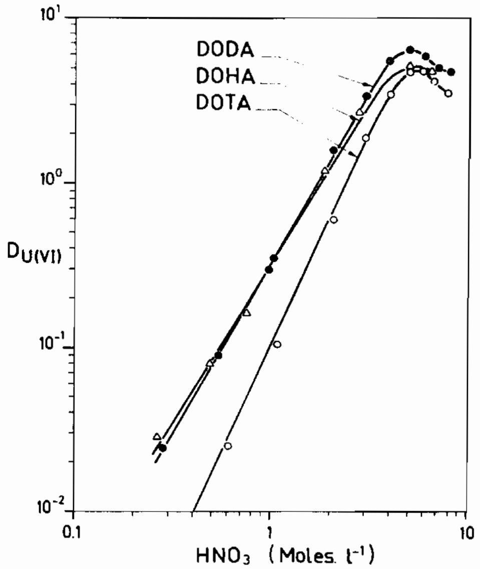


Fig. 1. Distribution ratios of U(VI) between 0.5 M *N,N*-dialkylamides into hyfrane and aqueous solutions as a function of nitric acid concentration.

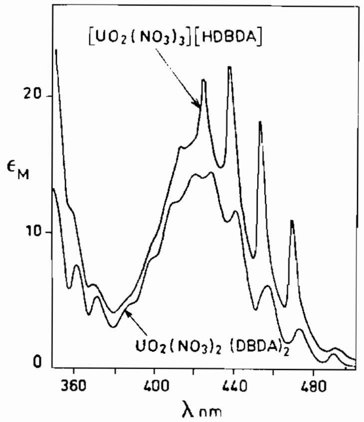


Fig. 2. UV–Vis spectra of U(VI) nitrato species in organic solution (0.5 M DBDA into t-butylbenzene). $UO_2(NO_3)_3(HDBDA)_2$ obtained by extraction from 9 N aqueous HNO_3.

Plutonium(IV)

The distribution ratios of Pu(IV) between DOHA and DOTA solutions and aqueous nitric acid are plotted in Fig. 3. The steric hindrance due to the presence of the two CH_3 groups in the position β to C=O in DOTA favours U(VI)/Pu(IV) separation. As for $UO_2{}^{2+}$, the slope analysis of log $D_{Pu(IV)}$ as a function of log amide concentration is of little help for the speciation of the Pu(IV) organic complex formed by extraction from middle-acidity range aqueous solutions. At high acidity the UV–Vis spectrum of the organic phase indicates the presence of the $Pu(NO_3)_6{}^{2-}$ anion, as in $Pu(NO_3)_6(HR_3N)_2$ [13], suggesting that Pu(IV) forms the species $Pu(NO_3)_6(HL)_2$.

Ions of fission product elements

The distribution ratios of important fission products between 1 M DOHA or 1 M DOTA as a function of aqueous nitric acid concentration are plotted in Fig. 4. It can be seen that the two amides are convenient for the selective extraction of U(VI) plus Pu(IV) from solutions containing fission products. DOTA is ten times more efficient than DOHA for U(VI)/Zr(IV) separation. This behaviour is attributable to the steric hindrance promoted by the β quaternary carbon, as for U(VI)/Pu(IV) separation.

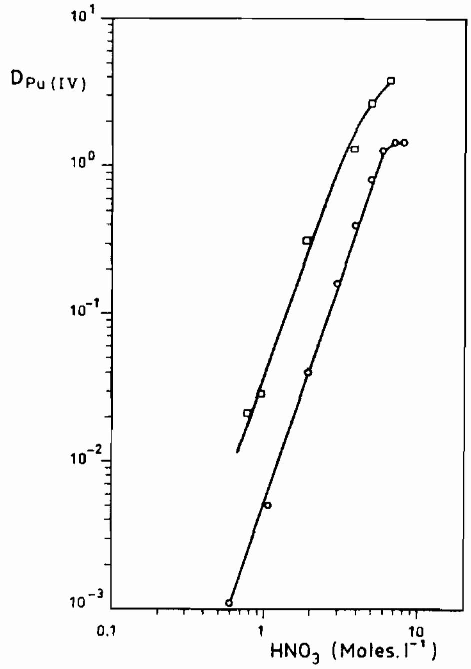


Fig. 3. Distribution ratios of Pu(IV) between 0.5 M *N,N*-dialkylamides into hyfrane and HNO_3 aqueous solutions as a function of HNO_3 concentration: DOHA, □; DOTA, ○.

Discussion and Conclusions Concerning N,N-Dialkylamides as Alternatives to TBP

The chemical investigations presented above show clearly the interest in *N,N*-dialkylamides for irradiated nuclear fuels reprocessing. However, to confirm this interest for the industry many points must be made more precise. The research efforts in extraction by amides represents a very small part of the efforts devoted to TBP in relation to the PUREX process. However, some practical aspects of the uses of *N,N*-dialkylamides have already been investigated; e.g., the synthesis of the extractants. They can be prepared easily by reacting a secondary amine with the appropriate carboxylic acid chloride according to the reaction:

$$RR'NH + ClCOR'' \longrightarrow HCl + RR'NCOR''$$

Good yields are obtained and the final products are easily purified by distillation and alkaline plus acidic washes, leading to purities as high as 99.5%. The extractant price is strongly dependent on the prices of the starting materials (RR'NH and ClOR″). Secondly, the behaviour of amides in counter current separations has been tested: first in Italy by Gasparini and Grossi [8] for U–Th separation, and shortly after [14] in a Pu–U bench-scale demonstration.

At Fontenay-Aux-Roses we investigated the behaviour of 1 M DOHA in TPH (a substituted dodecane) in a first cycle of irradiated nuclear fuel reprocessing. The flow sheet is given in Fig. 5. Although DOHA is less appropriate than DOTA for U(VI)–Pu(IV) separation, we calculated a flow sheet in order to separate U from Pu without Pu(IV) reduction. The results are summarized in Table II. It can be seen that U + Pu extraction was satisfactory. U(VI)–Pu(IV) partitioning was incomplete because of too short a residence time in the battery II mixers. Also U(VI) back-extraction did not follow the

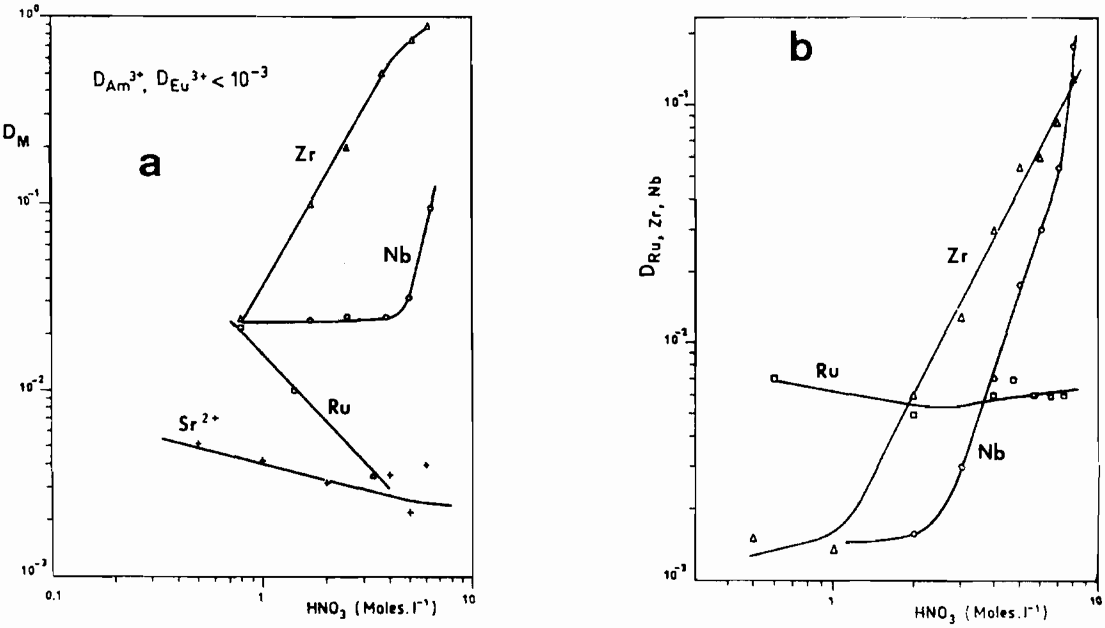


Fig. 4. Distribution ratios of fission products between (a) 1 M DOHA or (b) 1 M DOTA into hyfrane as a function of nitric acid concentration.

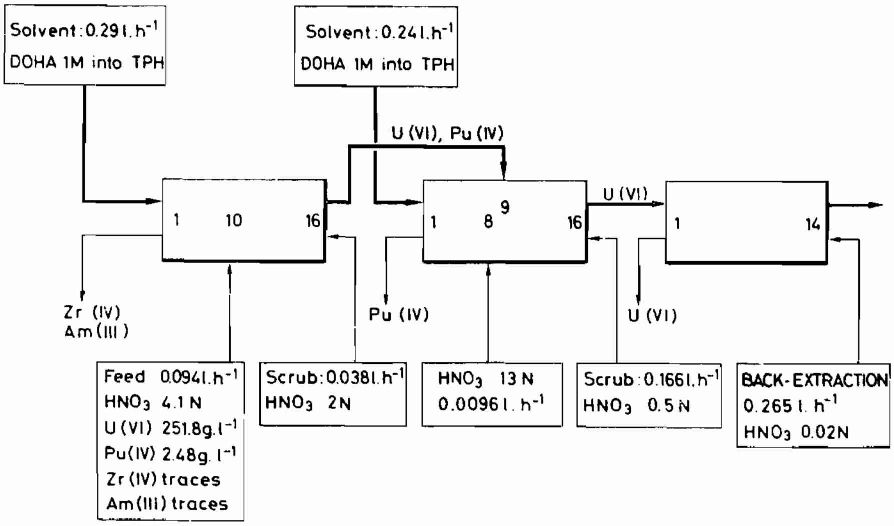


Fig. 5. Flow sheet for a first reprocessing cycle using 1 M DOHA into TPH as solvent and no reductive partition.

TABLE II. Results of a Mixer Settler First Cycle Reprocessing Separation using 1 M DOHA in TPH as Solvent

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

predictions because of too short a residence time in battery III. Phase disengagements were satisfactory and no deleterious effects were observed. The kinetic problems were easy to overcome and it must be concluded that this test is encouraging for technological investigations of amide extractants. Another important point is the chemical radiolytical stability of *N*,*N*-dialkylamides. Previous workers [8, 9] pointed out that the stability of amides was sufficient for practical applications. Gasparini *et al.* [8, 14] reported that dibuyloctanamide is more resistant than a tertiary amine to radiolysis, but is slightly more degraded than TBP. These findings were confirmed at Fontenay-Aux-Roses. Table III contains some results of hydrolysis of DOHA and TBP.

The degradation rate of DOHA as a function of the irradiation time is shown in Fig. 6. It can be seen that acidity plays an important role in the degradation rate. The TBP and DOHA radiolysis are compared in Table IV.

To go further in technological investigations it is now necessary to select a particular *N*,*N*-dialkylamide which will be the best alternative for TBP. Economic reasons must play an important role in the selection. The most important factors are: simplification of the solvent regeneration with as small as possible amounts of radioactive wastes; suppression of the reductive partition; higher selectivity regarding the fission products; cost of the solvent, etc. At present this

TABLE III. Hexanoic acid (HA) and *N*,*N*-Di(2-ethyl)hexylamine (DEA) Yields in the Hydrolysis of DOHA at 110–115 °C in the Presence of Aqueous HNO_3 (Stirred Solutions) and Comparison with TBP Hydrolysis

C_{HNO_3} (mol l^{-1})	Time (h)	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 [16]
5	4				1.08	0.0047 [16]

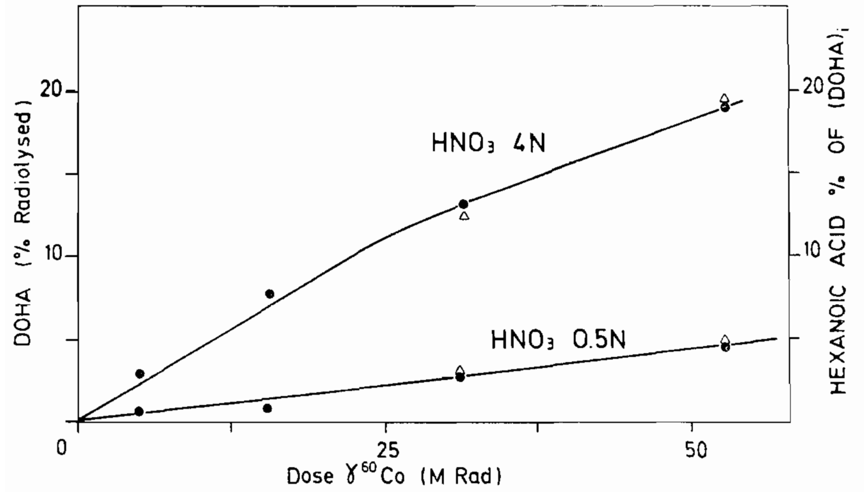


Fig. 6. Percent of DOHA radiolysed or percent of hexanoic acid yield as a function of irradiation dose: initial organic solutions = 1 M DOHA into TPH; initial aqueous solutions = HNO_3 as indicated; temperature = 40 °C.

TABLE IV. Comparison of DOHA 1 M in TPH and TBP 30% Radiolysis [17]

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

selection is not possible because of insufficient data but continuous investigations will clarify this point in the near future.

Separation of the Actinides Contained in Highly Radioactive Wastes

Another field of actinide separations by amides is the treatment of highly radioactive wastes before storage. As mentioned in the introduction, efficient purification of those wastes from the long lived α-emitters simplifies the requirements for their storage. Over the past five years considerable progress has been made. The TRUEX process [5, 15], in which the CMPO + TBP mixture is used as solvent, has received considerable attention; several U.S. laboratories are involved in its research and development. The key to its success lies mainly in the fact that the extractant is comparable to the PUREX one. At Fontenay-Aux-Roses we investigated the extractive properties of tetraalkylmalonamides and tetraalkyl-2-alkylpropanediamide with the generic formulae $RR'NCOCO_2CONRR'$ and $RR'NCOCHR''$-$CONRR'$ (where R, R' and R'' are alkyl or oxyalkyl radicals). This choice was guided by the desire to avoid organophosphorus molecules which generate important amounts of wastes by themselves, their degradation products and the alkaline regeneration cycles necessary in the PUREX process.

Selection of Suitable Diamides

Trivalent actinides are extracted less than other actinide ions, so we selected diamides by measuring the distribution ratios of trivalent ions. Siddall [15] failed to extract trivalent lanthanides by *N,N'*-tetrabutyloxalamide and *N,N'*-tetrabutylsuccinamide.

In order to gain insight into the alkyl group influence upon Am(III) extraction, we collected the data contained in Table V. It can be seen that the best extraction is obtained with with disymmetric N,N'-substituents like C_8H_{17} and CH_3(DMDOMA). This feature is probably due to the steric hindrance prevailing when the four N,N'-substituents are longer than these. IR and NMR spectroscopy showed that the two C=O groups in malonamides are bonded to the trivalent lanthanide ions.

Extraction of Metallic Ions

Distribution ratios of Am(III) and Eu(III) as a function of aqueous HNO_3 are plotted in Fig. 7. The presence of one alkyl group on the central

TABLE V. Influence of the Substituents R, R′ upon Am(III) Distribution Ratios between HNO_3 Solutions and 0.5 M Malonamide $\left(\begin{matrix}R\\R'\end{matrix}\!\!>N-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-N\!\!<\!\begin{matrix}R\\R'\end{matrix}\right)$ into Benzene

Malonamide acronym	R	R′	$D_{Am(III)}$[a]
DCHDEMA	C_6H_{11}	C_2H_5	0.11
TBMA	C_4H_9	C_4H_9	0.18
DPDOMA	C_3H_7	C_8H_{17}	0.45
DMDBMA	CH_3	C_4H_9	0.55
DMDOMA	CH_3	C_8H_{17}	1.18

[a] Distribution ratios at the maximum of the curve $D_{Am(III)}$ as a function of aqueous HNO_3.

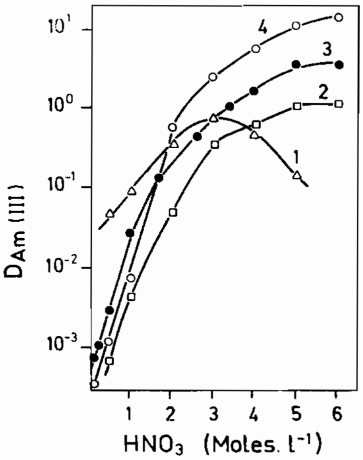
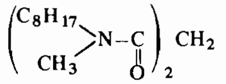
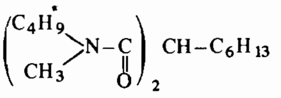


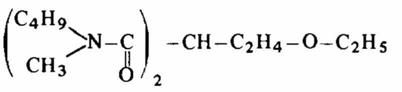
Fig. 7. Distribution ratios of Am(III) between 0.5 M malonamide solutions into t-butylbenzene and HNO_3 solutions as a function of aqueous HNO_3:

(1)


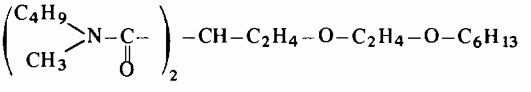
$$\left(\begin{matrix}C_8H_{17}\\CH_3\end{matrix}\!\!>N-\underset{\underset{O}{\|}}{C}\right)_2 CH_2$$

(2)


$$\left(\begin{matrix}C_4H_9\\CH_3\end{matrix}\!\!>N-\underset{\underset{O}{\|}}{C}\right)_2 CH-C_6H_{13}$$

(3)


$$\left(\begin{matrix}C_4H_9\\CH_3\end{matrix}\!\!>N-\underset{\underset{O}{\|}}{C}\right)_2 -CH-C_2H_4-O-C_2H_5$$

(4)


$$\left(\begin{matrix}C_4H_9\\CH_3\end{matrix}\!\!>N-\underset{\underset{O}{\|}}{C}-\right)_2 -CH-C_2H_4-O-C_2H_4-O-C_6H_{13}$$

carbon raises the Am(III) distribution ratios by a factor of ten, probably because it favours the conformations with the two C=O groups in the *cis* position. The distribution ratios of other metallic ions between 0.5 M *N,N′*-dimethyldibutyl-2-(3,6-dioxadodecyl)propane diamide,

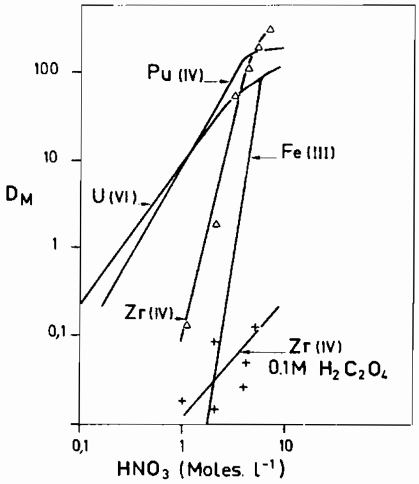
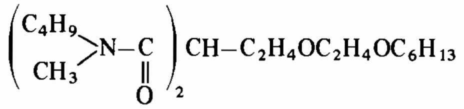


Fig. 8. Distribution ratios of metallic ions between 0.5 M $\left(\begin{matrix}C_4H_9\\CH_3\end{matrix}\!\!>N-\underset{\underset{O}{\|}}{C}\right)_2 -CH-C_2H_4OC_2H_4OC_6H_{13}$ into t-butylbenzene and aqueous nitric acid solutions as a function of nitric acid concentration.



$$\left(\begin{matrix}C_4H_9\\CH_3\end{matrix}\!\!>N-\underset{\underset{O}{\|}}{C}\right)_2 CH-C_2H_4OC_2H_4OC_6H_{13}$$

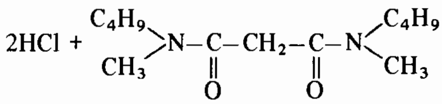
into t-butylbenzene and aqueous nitric acid solutions as a function of nitric acid are plotted in Fig. 8. It can be seen that U(VI) and Pu(IV) are well extracted.

U(VI) back-extraction can be performed with water. Pu(IV) back-extraction needs some supplementary data because of its hydrolysis near pH 1. As with the bidentate organophosphorus extractants, Zr(IV) is well extracted at high acidities, but the addition of 0.1 M oxalic acid allows its retention in the aqueous phase.

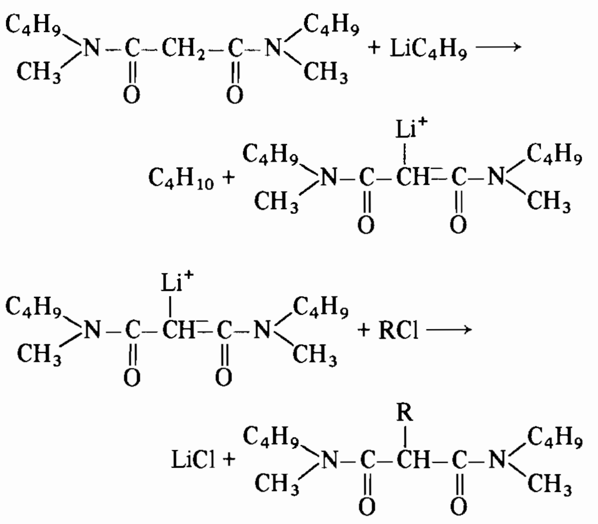
Future Developments for Substituted Malonamides

From the surveys presented above, it is clear that the amount of research necessary to confirm the interest in substituted malonamides for the practical separations of actinides is larger than that necessary for *N,N*-dialkylamides. Chemical and radiolytical stabilities are unknown. The degradation products must be identified. However, a strong point for these new extractants is their easy synthesis and purification. They were obtained [18] by the following reactions.

$$(CO)_2CH_2Cl_2 + 2CH_3C_4H_9NH \longrightarrow$$



$$2HCl + \begin{matrix}C_4H_9\\CH_3\end{matrix}\!\!>N-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-N\!\!<\!\begin{matrix}C_4H_9\\CH_3\end{matrix}$$



At the present time it appears that *N,N'*-tetraalkyl-2-alkylpropane diamides are more interesting than the simpler *N,N*-tetraalkyldiamides.

General Conclusions

These results show that new separation methods can stem from the introduction of new extractants. The needs for actinide extractants have been discussed, as well as their important properties, such as their resistance to hydrolysis, radiolysis and the nature of their degradation products. However, actinide chemistry has given few examples and the basis for the actinide extractant choice has not been presented extensively. Some guidelines will be given here. As extraction is a complexation phenomenon, the general 'a' hard sphere acceptor of the 5f or 4f series ions must be taken into account. This is shown clearly in the actinide extraction by acidic extractants such as the dialkylphosphoric acids, for which the extraction mechanism is:

$$M^{3+} + 3(HA)_2 \rightleftharpoons 3H^+ + MA_3(AH)_3$$

$$\text{with } K_{ex} = \frac{(MA_3(AH)_3)(H^+)^3}{(M^{3+})((HA)_2)^3}$$

It is interesting to compare the extraction constants by thio- and oxophosphoric acids of 4f or 5f trivalent ions with Tl(III), which has a comparable ionic radius. The 'a' and 'b' character of the f and Tl(III) ions is shown by the higher extraction constants of the latter with thiophosphates and the higher 4f and 5f constants with phosphates (Table VI). For neutral extractants the phenomena are not as simple because the aqueous phase anions A^- play an important role, as shown by the mechanism

$$M^{3+} + 3A^- + nS \rightleftharpoons MA_3S_n$$

$$\text{with } K_{ex} = \frac{(MA_3S_n)}{(S)^n(A^-)^3(M^{3+})}$$

To be stable, the complex MA_3S_n must have the following characteristics: M^{3+} has a good affinity for A^- and S; A^- has a sufficient lipophilic character; the geometry of MA_3S_n must be harmonious. That is to say the coordination sphere of M^{3+} must be fitted with $3A^-$ anions and nS molecules. These conditions can be extended to the synergistic extraction with the mechanism:

$$M^{3+} + nS + 3HA \longrightarrow 3H^+ + MA_3S_n$$

where AH is an acidic extractant; that is to say, A^- is lipophilic; the requirements are the same as the extraction by neutral molecules. The complex MA_3S_n is particularly stable compared to the complexes MA_3 and $MS_mX_3{\cdot}xH_2O$, where X^- is an anion of the aqueous phase, and water molecules which can be replaced by the more lipophilic S molecules to complete the coordination sphere of MA_3 in the organic phase. These simple considerations indicate what kind of factors must be taken into account to preselect an organic complexant for a peculiar separation. They also suggest investigations which would identify the important features of an extractant. The main investigations would be:

(i) Measurement of distribution ratios as a function of the concentration of each species intervening in the extraction, all the others being maintained at constant concentrations. The slope of the straight line $\log D_M$ as a function of $\log C_S$ generally gives

TABLE VI. Comparison of the Extraction Constants of Trivalent 4f or 5f Elements with Other Trivalent Cations for One 'b' and One 'a' Type Acidic Extractant

Ions	Am(III)	Eu(III)	Bi(III)	Tl(III)	In(III)	References
Ionic radius (Å)	1.06	1.03	1.2	0.95	0.81	
HDEDHTP into CCl_4						
from HCl (extraction constant)	$10^{-7.9}$	$10^{-8.3}$	10^{6a}	$10^{3.7a}$	$10^{6.1a}$	19, 20
HDEHP into toluene						
from HCl (extraction constant)	$10^{-2.4}$	$10^{-0.95}$	$10^{-1.2}$	10^{-4}	$10^{-0.1}$	21, 22

[a] Dibutyldithiophosphoric acid [20].

the number of S molecules in the organic complex MS_nA. However, care must be taken because sometimes the variation of concentration of a species introduces so many changes in the organic phase properties that its activity coefficient varies faster than its concentration.

For example, the slope analysis of the log of the U(VI) distribution ratios as a function of the log of *N,N'*-di(2-ethylhexyl)isobutyramide (i-DOBA) concentration in dodecane at constant aqueous acidity (8 N) yields a value of 1.8, indicating that probably two i-DOBA molecules are present in the extracted complex. The identification of the complex in the organic phase by UV–Vis spectrophotometry indicated that at low concentrations in i-DOBA, $UO_2(NO_3)_2$(i-DOBA)$_2$ occurs, but at high concentrations $UO_2(NO_3)_3H$(i-DOBA) predominates. So the slope in this case is due to several factors of which the principal is the higher dissociation of HNO_3 at high extractant concentration which favours the reaction:

$$UO_2(NO_3)_2L_2 + 2HNO_3 \rightleftharpoons UO_2(NO_3)_3^{-+}HL + LHNO_3$$

The increase in the dielectric constant of a solution containing the same $UO_2(NO_3)_2L_2$, HNO_3 and total L concentrations displaces the equilibrium from the left to the right, showing the effect of the HNO_3 higher dissociation [23].

The presence or not of water in the metallic organic complexes is important because it indicates if the extractant will give large synergistic effects or not.

Structural information is necessary to improve the design of the extractants. However, it is often difficult to correlate the structure found in solids with the structure in solutions. A striking example is given by $UO_2(C_4H_9)_2NCO(CH_2)_3CON(C_4H_9)_2(NO_3)_2$ •(uranyldinitratotetrabutylglutaramide), for which UO_2 are linked in the solid (Fig. 9) by tetrabutylglutaramide (TBGA) molecules forming infinite chains [24]. The slope analysis of the log of the U(VI) distribution ratios as a function of log TBGA indicates that two TBGA molecules are present in the complex formed in toluene solutions. In addition, there is no indication of a uranyl polymeric species ($D_{U(VI)}$ is constant in a wide range of U(VI) concentrations [25]). It is likely that an important change in UO_2^{2+} coordination occurs when the solid is dissolved in TBGA–toluene.

(ii) In solid $UO_2(NO_3)_2$(DBDA)$_2$, (where DBDA is *N,N*-dibutyldodecanamide) there are considerable chain–chain interactions, as shown by the structure in Fig. 10 [26]. Here again, it appeared that the cloth structure is broken by dissolution in dodecane but the tendency to form such a structure is probably responsible for the low solubility of $UO_2(NO_3)_2$(DBDO)$_2$ in alkanes.

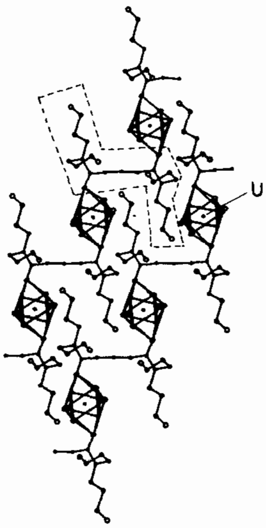


Fig. 9. Packing of $UO_2(NO_3)_2$TBGA, viewed down the [010] axis (ORTEP-JOHNSON, 1976). The dotted line delimits one TBGA molecule.

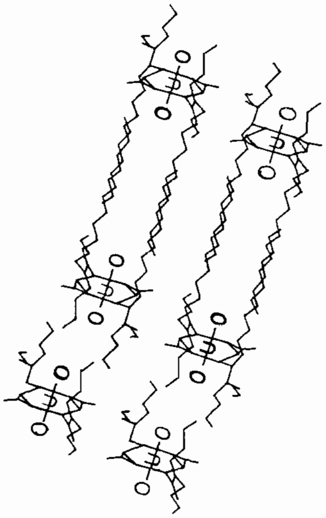


Fig. 10. Projection of the $UO_2(NO_3)_2$(DBDA)$_2$ structure along the [010] direction (ORTEP-JOHNSON, 1965).

Finally, it must be pointed out that the investigation methods used in coordination chemistry are not very often applied to solvent extraction. Their introduction in the field will increase tremendously the understanding of the chemical reactions involved in liquid–liquid transfer.

References

1 W. W. Schulz and E. P. Horwitz, 'Proceedings of Actinides 85', *J. Less-Common Met.*, *122*, 125 (1986).

2 B. Weawer and F. A. Kappelmann, *J. Inorg. Nucl. Chem.*, *30*, 263 (1968).

3 W. W. Schulz and J. D. Navratil, in N. W. Li (ed.), 'Recent Developments in Separation Science', Vol. VI, CRC Press, Boca Raton, Fl., 1982, p. 31.

4 E. P. Horwitz, K. A. Martin, H. Diamond and L. Kaplan, *Solv. Extr. Ion Exch., 4*(3) 449 (1986).

5 E. P. Horwitz, D. G. Kalina, H. Diamond, G. F. Vandergrift and W. W. Schulz, *Solv. Extr. Ion Exch., 3*(1), 75 (1985).

6 T. H. Siddall, III, *J. Phys. Chem., 64*, 1863 (1960).

7 'New Extractants: Amides', *U.S. AEC Chem. Tech. Div. Ann. Rep. ORNL 3452*, 1963, p. 178.

8 G. M. Gasparini and G. Grossi, *Sep. Sci. Technol., 15*(4), 825 (1980).

9 T. H. Siddall, III, *DP 541* (1961).

10 G. M. Gasparini and G. Grossi, *Solv. Extr. Ion Exch. 4*(6) 1233 (1986).

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

12 L. Kaplan, R. A. Hildebrandt and M. Ader, *ANL 4520* (1959); *ANL 4521* (1951).

13 J. L. Ryan, *J. Phys. Chem., 64* 1375 (1960).

14 D. Carlini, M. Casarci, G. M. Gasparini, G. Grossi and A. Moccia, *Proc. Fuel Reprocessing and Wastes Management*, Jackson Hole, Wyo., 1984.

15 T. H. Siddall, III, *J. Inorg. Nucl. Chem., 25*, 883 (1963).

16 Z. Nowak and M. Nowak, *Radiochem. Radioanal. Lett. 14*, 161 (1973).

17 W. Davis, Jr., in W. W. Schulz and J. D. Navratil (eds.), 'Science and Technology of TBP', CRC Press, Boca Raton, Fla., 1984, p. 221.

18 *French Patent 85 11706* (1985) to G. Thiollet, L. Lafosse, C. Musikas, P. Höel.

19 D. Pattée, C. Musikas, A. Faure and C. Chachaty, *Proc. ISEC 86, International Solvent Extraction Conference*, Vol. I, Munich, 1986, p. 267.

20 T. H. Handley, *Talanta, 12*, 893 (1965).

21 C. F. Baes, Jr., *J. Inorg. Nucl. Chem., 24*, 707 (1962).

22 Y. Marcus and A. S. Kertes, 'Ion Exchange and Solvent Extraction. Appendices Distribution Chart,' Wiley Interscience, New York, p. 945.

23 N. Condamines, personal communication.

24 P. Charpin, M. Lance, M. Nierlich, D. Vigner, M. C. Charbonnel and C. Musikas, *Acta Crystallogr., Sect. C, 43*, 442 (1987).

25 M. C. Charbonnel and C. Musikas, *Proc. ISEC 86, International Solvent Extraction Conference*, Vol. I, Munich, 1986, p. 261.

26 P. Charpin, M. Lance, M. Nierlich, D. Vigner, N. Descouls and C. Musikas, *Acta Crystallogr., Sect. C, 42*, 560 (1986).