Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Application of N, N-Dialkyl Aliphatic amides in the Separation of Some Actinides

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To cite this Article Casparini, G. M. and Grossi, G.(1980) 'Application of N, N-Dialkyl Aliphatic amides in the Separation of Some Actinides', Separation Science and Technology, 15: 4, 825 — 844

To link to this Article: DOI: 10.1080/01496398008076273

URL: http://dx.doi.org/10.1080/01496398008076273

SEPARATION SCIENCE AND TECHNOLOGY, 15(4), pp. 825-844, 1980

APPLICATION OF N,N-DIALKYL ALIPHATIC AMIDES IN THE SEPARATION OF SOME ACTINIDES

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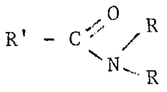
ABSTRACT

N,N-dialkyl substituted alkyl amides are known to be good extractants of some actinides such as U, Pu, and Th. Their stability is comparable to that of TBP, and their degradation products do not interfere as do the degradation products of TBP. On the other hand, the principal disadvantage of the amides is their tendency to form poorly soluble U adducts in organic diluents.

A systematic investigation has been carried out on the extractive behavior of two typical alkyl amides of different structures with respect to the actinide ions UO_2^{2+}, Th^{4+}, Np^{+4}, Pu^{+4}, NpO_2^{2+}, PuO_2^{2+}, Pu^{3+}, and Am^{3+}, as well as with respect to the most significant fission products. The results obtained have been compared with those obtained using TBP in the same experimental conditions, verifying the applicability of amides in the separation of U from Th.

INTRODUCTION

During the last twenty years different publications have pointed out the remarkable properties of N,N-dialkyl alkyl amides in the field of separations chemistry:



$R' = C_4 - C_8$
$R = C_3 = C_4$

These substances are able to form stable coordination compounds with different metallic ions (1-3).

N,N-disubstituted amides show an extracting capacity with regard to the tetravalent and hexavalent actinides so marked as to suggest the introduction of these compounds as alternative extractants to tributyl phosphate. This proposal could be particularly interesting when this so widely used extractant undergoes an elevated radiolytic degradation during the reprocessing of highly irradiated fuels, with the formation of dibutyl and monobutylphosphates (DBP and MBP) which might cause severe shortcomings. The principal advantage of these new compounds are easy preparation and an elevated stability with respect to chemical and radiolytic degradation. Furthermore, their degradation products (amines and carboxylic acids) do not affect the correct working of the extraction process (as do DBP and MBP) and can be easily washed out of the extractant.

On the other side, a negative characteristic of some amides is the tendency to form a third liquid phase or a precipitate with nitric acid and uranium above certain concentrations. Another pecularity of amides, pointed out in previous publications (4), is the influence of the molecular structure on the extracting capacity, especially with regard to the tetravalent actinides.

We have examined the preparation and the characterization of a series of amides to verify the effect of the aliphatic structure on their extracting capacity and on the formation of third phases. In this work we have compared the behavior of some of these amides with that of TBP, and at the same time we have tried to utilize the specific properties of these compounds in some original practical applications. Here we suggest an application of these compounds in a peculiar problem involved with the reprocessing of the irradiated fuels of the uranium-thorium cycle.

EXPERIMENTAL

The N,N-dialkyl amides were prepared by adding the corresponding acyl chloride to a cooled solution of the secondary amine in ether in the presence of triethylamine (5):

$$R'COCl + H\text{-}N{=}R_2 + (C_2H_5)_3N \rightarrow R'CONR_2 + (C_2H_5)_3NHCl.$$

The liquid amides were purified by distillation under vacuum. Only the N,N-dicyclohexyl derivatives are white solids. The amides were determined by potentiometric titration with perchloric acid in acetic anhydride solution or by gas chromatograph (2 m SS column with 20% E 301 in silanized Chromosorb W).

Detection of a third phase or a precipitate, as well as the determination of the distribution coefficient, was carried out by shaking equal volumes of the two phases in a test tube for 15 min and by centrifuging for 5 min. Unless otherwise specified, mesitylene was used as the diluent; mesitylene may be considered as a standard, single-structure organic diluent that is suitable also for employment on large scale. The organic solutions were always pre-equilibrated with nitric acid. Uranium was determined by the dibenzoyl methane method (6), and thorium was determined by the Thoron method (7). Uranium in the presence of thorium was determined by the ammonium thiocyanate method (8). Thorium in the presence of uranium was determined by a titration with EDTA (9). ^{233}U, ^{239}Pu, ^{237}Np, ^{234}Th, ^{95}Nb, ^{95}Zr, ^{106}Rh, and $^{152-154}Eu$ were used as tracers without the addition of stable or longer-lived isotopes. Pu(IV) (americium free) was stabilized with 0.02 M nitrous acid, Np(IV) and Pu(III) with 0.01 M ferrous sulfamate, Pu(VI) with silver peroxide, and Np(VI) with 0.1 M $KBrO_3$. The usual beta-gamma counting methods were utilized; when necessary a Ge intrinsic detector and a multichannel analyzer were used. A surface barrier detector with a multichannel analyzer was used for alpha counting. A ^{60}Co irradiator was utilized for the irradiation tests. The samples were irradiated at the same ratio $[HNO_3]_{org}$/[extractant]; in the amide tests the aqueous phase was present during the irradiation.

The mixer-settlers utilized were 6-stage and 16-stage CNEN models.

RESULTS AND DISCUSSION

Synthesis and Characterization of N,N-Dialkyl Alkyl Amides

For this study some amides of different structures have been taken into consideration, namely:

N,N-dicyclohexyl octanamide (DCHOA)
N,N-di-n-hexyl octanamide (DHOA)
N,N-dicyclohexyl acetamide (DCHAA)
N,N-di-*n*-butyl(2-ethyl)hexanamide (DBEHA)

DCHOA and DHOA having the same acyl radical differ in the radicals bonded to nitrogen; DCHAA and DCHOA having the same amine residue differ in the length of acyl radical; and DBEHA is a typical example of alpha-hindered (with respect to carbonyl) N,N-dialkyl amide. Their preparation from the acyl chloride and the secondary amine, as described in the experimental section, is easy and gives satisfactory yields. Table 1 shows the most significant results in this connection.

The solubility of these amides is generally extremely low in aqueous media and, except for the acetamide, very high in organic diluents (Table 2), thus showing a very promising behavior for application in liquid-liquid extraction.

Stability of Amides

The chemical stability of N,N-dialkyl amides seems to be very high, since samples of amides dissolved in mesitylene showed no trace of degradation even after some months of continuous contact with 3 *M* nitric acid.

In Fig. 1 the radiation stability of the system DHOA-nitric acid-diluent is compared with the stability of TBP and a tertiary amine under similar experimental conditions. The stability of this amide is at least similar to that of TBP and much better than that of the tertiary amine tested.

TABLE 1

Characteristics of Amides

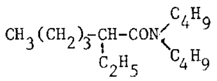
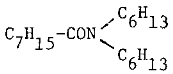
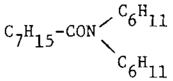
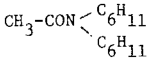
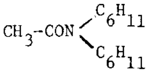
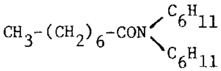
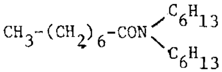
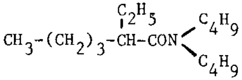
Amide	Structure	M.W.	Yields (%)	Density	n_D	b.p. (m.p.)	Neutralization equivalent
N,N'-di-butyl(2 ethyl) hexanamide	 $CH_3(CH_2)_3\text{-}\underset{C_2H_5}{CH}\text{-}CON{<}^{C_4H_9}_{C_4H_9}$	255	71	0.8607	1.4514	111-112°C (1 mm Hg)	264
N,N'-di-hexyl octanamide	 $C_7H_{15}\text{-}CON{<}^{C_6H_{13}}_{C_6H_{13}}$	311	80	0.8622	1.4510	150-180°C (23-24 mm Hg)	317
N,N'-di-cyclohexyl actanamide	 $C_7H_{15}\text{-}CON{<}^{C_6H_{11}}_{C_6H_{11}}$	307	60	-	-	m.p. 35-36°C (ethyl acetate)	308
N,N'-di-cyclohexyl acetamide	 $CH_3\text{-}CON{<}^{C_6H_{11}}_{C_6H_{11}}$	223	68	-	-	m.p.103-104°C (ethyl acetate)	223

TABLE 2

Solubility of Amides (moles/L)

	MW	T (°C)	n-dodecane ε=2.14(20°C)	Mesitylene ε=2.27(25°C)	Diethylbenzene	Toluene ε=2.38 (25°C)	1,1',2 trichloro-ethane ε=7.52 (20°C)	H_2O ε=78.5(25°C)
 $CH_3\text{-}CON\langle^{C_6H_{11}}_{C_6H_{11}}$	223	24 30	0.17 0.11	0.80 0.87	1.0021 1.0381	1.27 1.30	2.44 2.50	nd nd
 $CH_3\text{-}(CH_2)_6\text{-}CON\langle^{C_6H_{11}}_{C_6H_{11}}$	307	24	∞[a]	∞	∞	∞	∞	nd
 $CH_3\text{-}(CH_2)_6\text{-}CON\langle^{C_6H_{13}}_{C_6H_{13}}$	311	24	∞	∞	∞	∞	∞	nd
 $CH_3\text{-}(CH_2)_3\text{-}\overset{C_2H_5}{CH}\text{-}CON\langle^{C_4H_9}_{C_4H_9}$	255.5	21	-	∞	∞	∞	-	1.10^{-3}

[a] ∞: >3 moles/L.

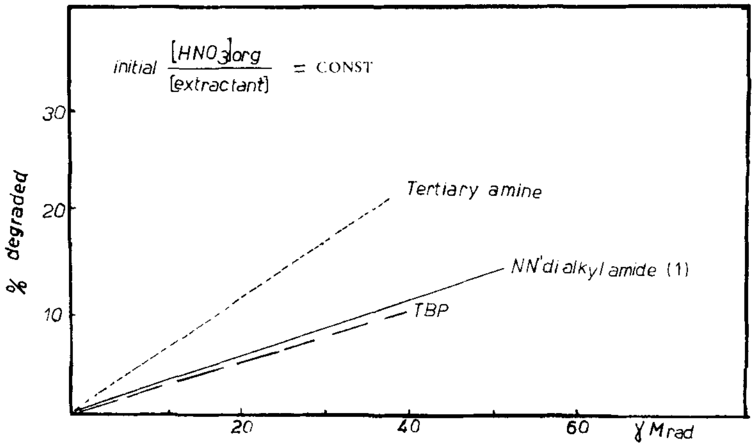


FIGURE 1. Comparison of the radiolytic stability of an N,N-disubstituted amide (DHOA), a tertiary amine, and TBP. (1) Irradiated in the presence of nitric acid.

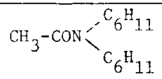
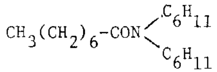
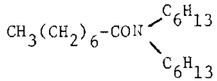
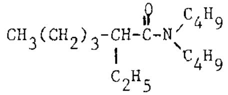
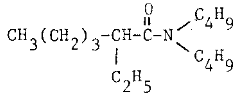
Third Phase Formation

N,N-dialkyl aliphatic amides, dissolved in hydrocarbon diluents and contacted with nitric acid-uranyl nitrate solutions, may give rise to the formation of a third phase, like some other very well investigated systems such as tertiary amines and quaternary ammonium compounds (10). The structure of the amide, the nature of the diluent, the temperature, the concentration of amide, nitric acid, and uranium, and the phase ratio may strongly affect this tendency. Table 3 shows the results obtained for the different amides prepared, dissolved in mesitylene, at room temperature, for different concentrations of amides, nitric acid, and uranyl nitrate. Only DHOA shows an excellent behavior for all the experimental conditions tested; furthermore, it shows the same behavior even if dissolved in dodecane. The dicyclohexyl amides, showing unsatisfactory general performance, were dropped from further experiments. The alpha-substituted amide shows an intermediate behavior. Because of the interest of

TABLE 3

The Presence of Third Phase or Precipitate as a Function of Amide, Nitric Acid, Uranyl Nitrate Concentration

Diluent: Mesitylene T = 21 to 23°C

Phase ratio	Organic Phase		Aqueous phase (Initial concentration)		Results of test
	Amide	Molarity	HNO_3 (M)	Uranyl nitrate	
1:1	 $CH_3\text{-}CON<^{C_6H_{11}}_{C_6H_{11}}$	0.25	4	-	OK
		0.25	6	-	Third phase
		0.25	3	10	OK
		0.25	3	25	Precipitation
1:1	 $CH_3(CH_2)_6\text{-}CON<^{C_6H_{11}}_{C_6H_{11}}$	1 (dodecane)	6	-	Third phase
		1	12	-	OK
		1	3	5	Third phase
		1	3	10	Small precipitation
		1	3	25	Precipitation
1:1	 $CH_3(CH_2)_6\text{-}CON<^{C_6H_{13}}_{C_6H_{13}}$	1	12	-	OK
		1	3	500	OK
1:1	 $CH_3(CH_2)_3\text{-}\underset{C_2H_5}{CH}\text{-}\overset{O}{C}\text{-}N<^{C_4H_9}_{C_4H_9}$	0.5	1	15	OK
		0.5	2	15	Third phase
		1	1	15	Third phase
3:1	 $CH_3(CH_2)_3\text{-}\underset{C_2H_5}{CH}\text{-}\overset{O}{C}\text{-}N<^{C_4H_9}_{C_4H_9}$	1	6	15	OK
		1	2	15	OK
		1	2	50	Third phase
		2	1	15	Third phase

verifying the influence of the structure on the actinide extraction, it has been further investigated, using always an organic-to-aqueous phase ratio of 3 in order to reduce the risk of third-phase formation.

Further studies are now in progress aimed at clarifying, with a systematic investigation using a great number of different new amides, the role of the molecular structure of the amide with respect to the problem of third phase formation.

Extraction of Actinides

As mentioned before, for all solvent extraction experiments only DHOA (a typical straight chain N,N-dialkyl aliphatic amide) and DBEHA (a typical alpha-branched N,N-dialkyl aliphatic amide) have been used. The results obtained with these two different amides have been compared with those obtained, at the same experimental conditions, with TBP. A concentration of 1 M of the amides in the selected diluent (mesitylene) was chosen, corresponding closely to the molarity of 30% TBP.

Figures 2, 3, and 4 collect the results obtained for the distribution coefficients of some actinide ions at different aqueous nitric acid concentrations. Data concerning the most significant fission products and the nitric acid itself are also presented. The following considerations can be deduced:

Nitric acid - The extractive behavior is essentially the same with the two amides and TBP.

Uranium(VI) - The extracting capacity is essentially the same with the two amides, and very similar to that of TBP. The uranium loading capacity (Figures 5 and 6) is high with DHOA (about 80 g/ℓ) and not very high with DBEHA (8 g/ℓ); for the hindered amide, the loading value is referred to the saturated organic solution, before the formation of the third phase. The best acidity for extraction is 3 M HNO_3; very low values of distribution coefficients are obtained at acidities lower than 0.2 M HNO_3, thus permitting very easy stripping of uranium. This is a remarkable advantage over TBP.

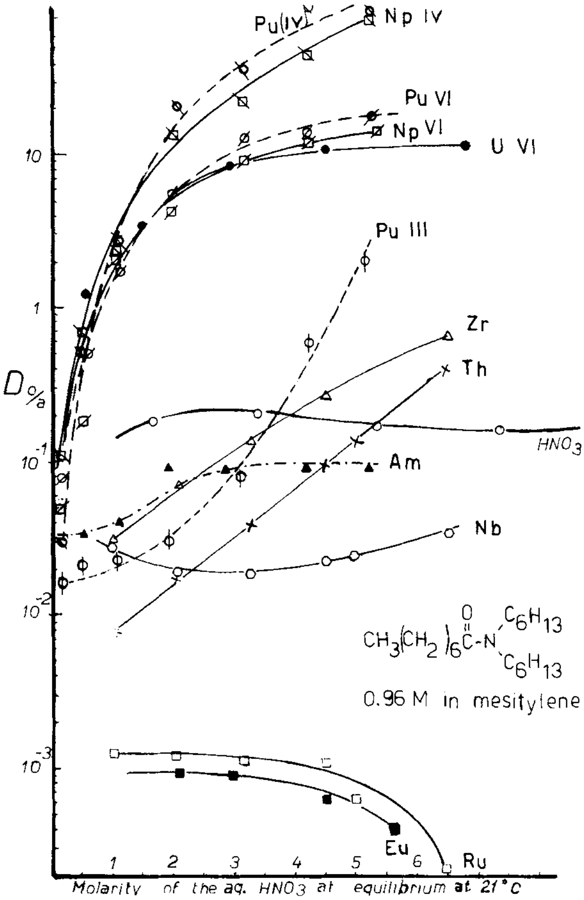


FIGURE 2. Extraction coefficients for the actinides, fission products, and nitric acid as a function of the aqueous nitric acid concentration at 21°C: DHOA.

<u>Hexavalent actinides</u> - With DHOA, U(VI), Np(VI), and Pu(VI) show practically identical extractive behavior, in contrast to TBP systems where Pu(VI) is much less extracted than U(VI) (11). With DBEHA, there is an evident difference in behavior, the extracting capacity following the order U(VI) >

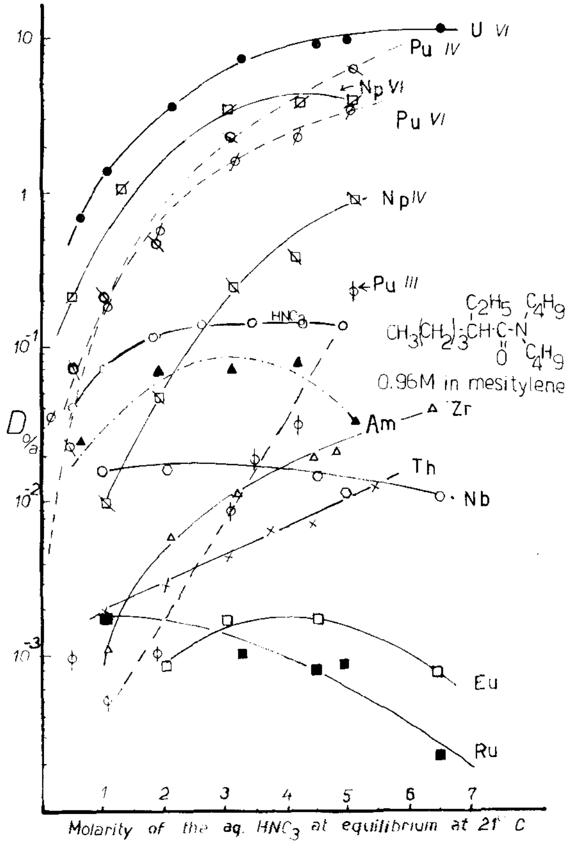


FIGURE 3. Extraction coefficients for the actinides, fission products, and nitric acid as a function of the aqueous nitric acid concentration at 21°C: DBEHA.

Np(VI) > Pu(VI), and a separation of uranium(VI) from plutonium(VI) appears to be possible.

Tetravalent actinides - With DHOA, Np(IV) and Pu(IV), showing an essentially identical behavior, exhibit the highest values of distribution coefficients with respect to all ions tested. In the acidity range explored, they are better

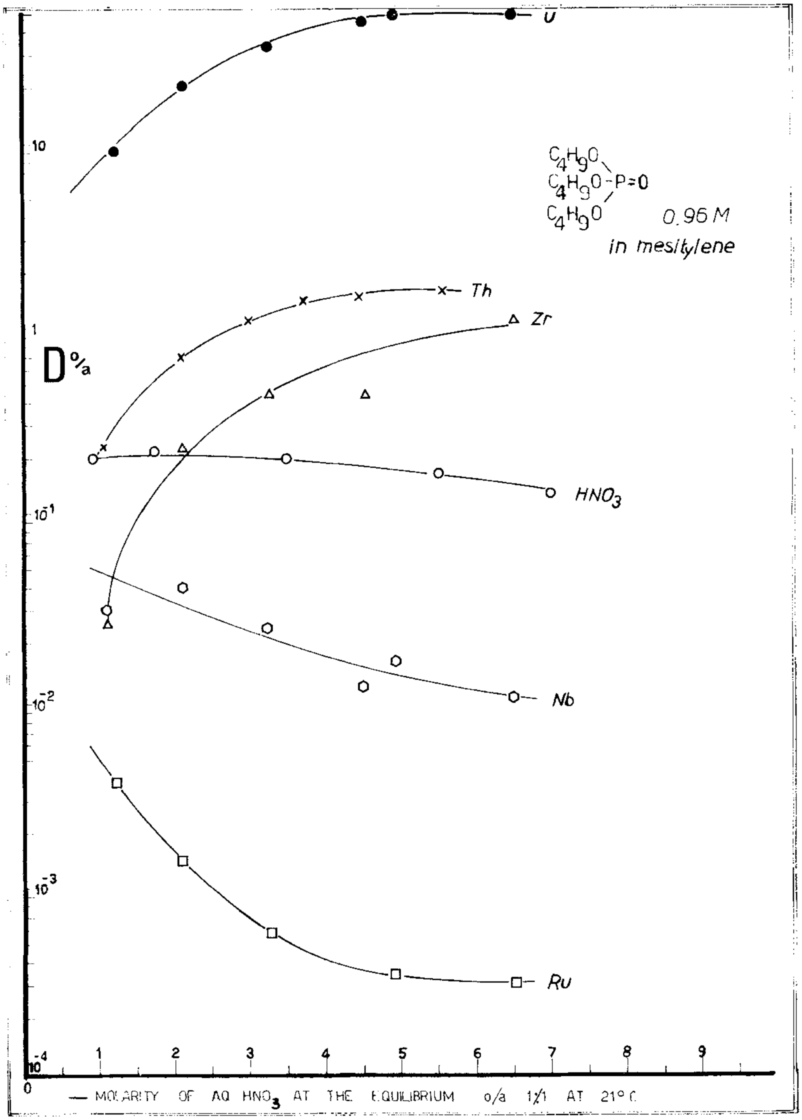


FIGURE 4. Extraction coefficients for the actinides, fission products, and nitric acid as a function of the aqueous nitric acid concentration at 21°C: TBP.

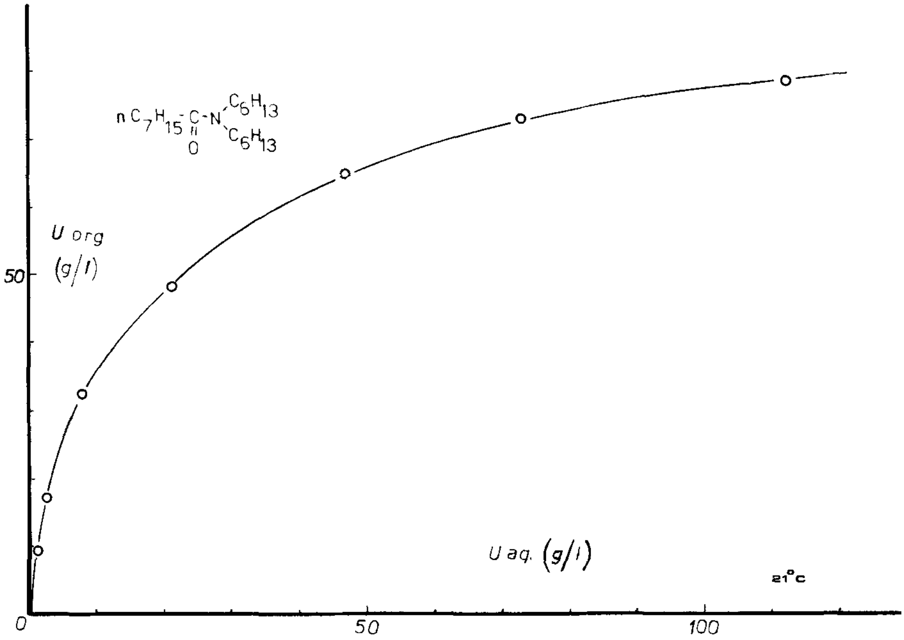


FIGURE 5. Equilibrium isotherm of uranium(VI) extraction by 1 $\underline{M}$ N,N-dihexyl octanamide in mesitylene preequilibrated with 3 $\underline{M}$ nitric acid.

extracted than U(VI), in contrast to TBP, by which Pu(IV) and especially Np(IV) are much less extracted than U(VI). The extraction of Th is always very low, especially if compared with the extraction in TBP systems. At 2 $\underline{M}$ HNO_3, the ratio R of the distribution coefficients with DHOA to those with DBEHA is

$$R_{(Th)} = 6 \qquad R_{(NP\ IV)} = 230 \qquad R_{(Pu\ IV)} = 14$$

The same ratio for uranium(VI) is 1.6. As a consequence, hindered amides seem to be very promising for the separation

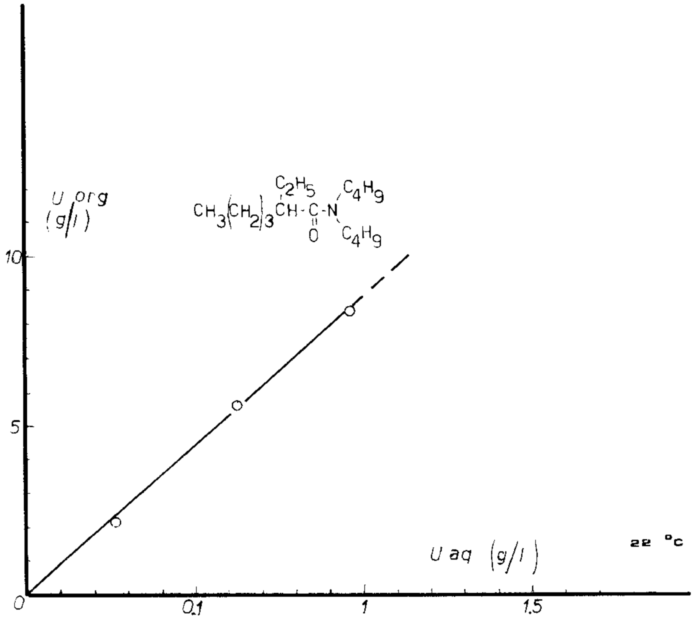


FIGURE 6. Equilibrium isotherm of uranium(VI) extraction by 1 M N,N-dibutyl 2-ethylhexanamide in mesitylene preequilibrated with 3 M nitric acid.

of uranium from tetravalent actinides, and in this respect they should be much more effective than TBP.

Trivalent actinides - The extraction of Pu(III) and Am(III) with amides is low in all experimental conditions tested, following a similar behavior with TBP. The increase of the distribution coefficient of Pu(III) at high acidity values is probably due to the tendency of oxidation of Pu(III) to Pu(IV) at high nitric acid concentration.

Fission products - The results obtained for the extraction of Zr, Nb, Ru, and Eu with amides are similar to those obtained with TBP. However, with DBEHA, the extraction of

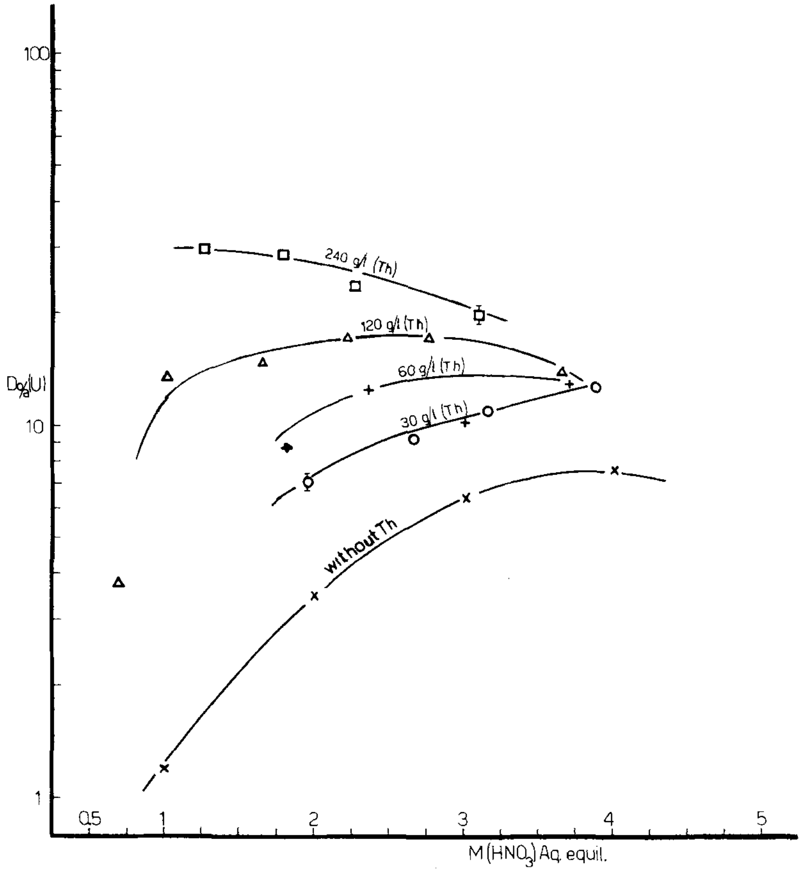


FIGURE 7. Extraction coefficients of uranium(IV) with 1 M N,N-dibutyl 2-ethylhexanamide in mesitylene as a function of the aqueous acidity and in the presence of different amounts of $Th(NO_3)_4$. O/A = 3. Contact time: 15'.

zirconium drops to lower values (at 2 M HNO_3, R_{Zr} = 13), thus confirming the general behavior of hindered amides with tetravalent ions.

Application of Amides in the Separation of U from Th

The preceding results emphasize the potential utilization of amides, especially if alpha hindered, in the separation of uranium

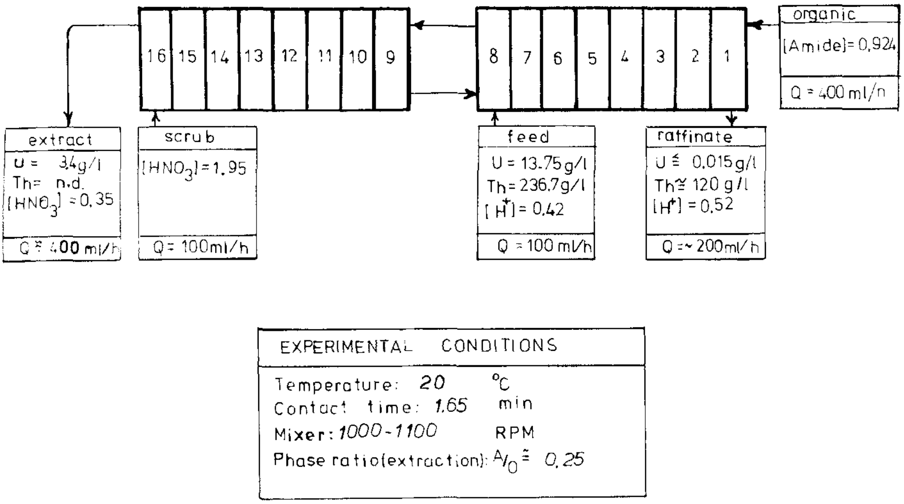


FIGURE 8. Demonstration of a flowsheet for the separation of uranium from thorium with 1 M N,N-dibutyl 2-ethylhexanamide in mesitylene (extracting section).

from tetravalent actinides. Therefore the separation of uranium from thorium with DBEHA has been investigated in connection with the hot runs at CNEN ITREC (Impianto Trattamento Elementi Combustibili) pilot reprocessing plant (12), in which the reprocessing of irradiated thorium fuels is now carried out by a TBP (Thorex) flowsheet.

The aim of this investigation is to propose the use of amides as an alternative to TBP for the separation of ^{233}U from the thorium matrix. Figure 7 shows the influence of different amounts of thorium on the extractive behavior of uranium with 1 M DBEHA. The salting-out effect of thorium is clearly shown, and the strong increase of the extraction of uranium should make the separation even easier. Laboratory mixer-settler runs have been carried out with simulated solutions containing U and Th in the same

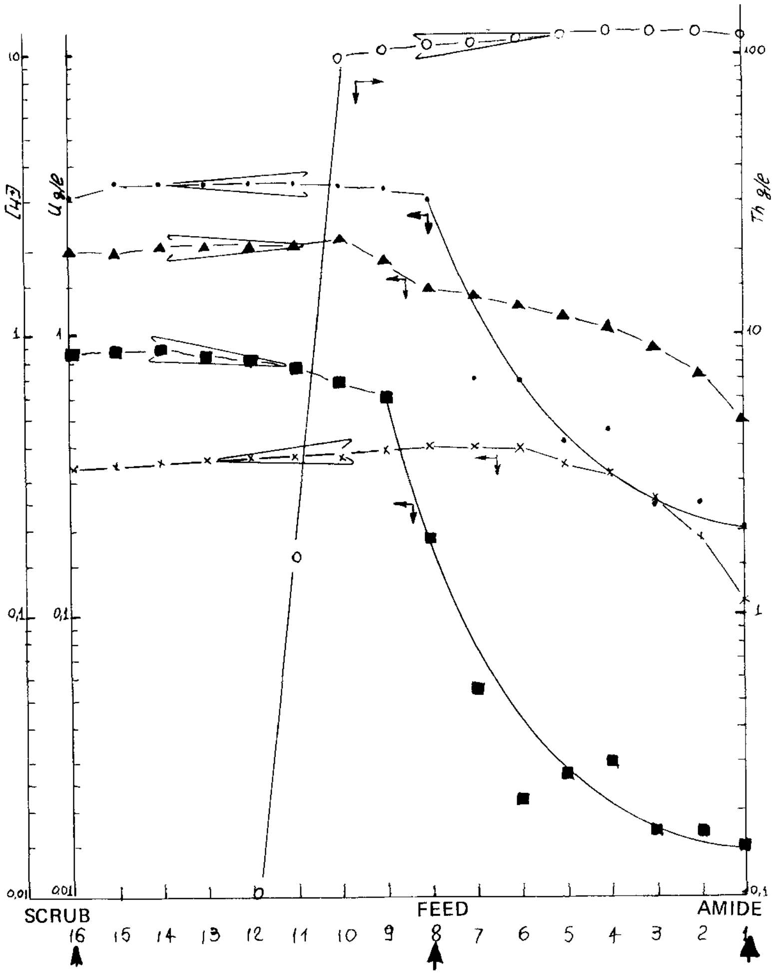


FIGURE 9. Concentration profile in the extraction section at steady state.

x = $[H^+]_{org}$ Δ = $[H^+]_{aq}$ ○ = $[Th]_{aq}$

□ = $[U]_{aq}$ ● = $[U]_{org}$

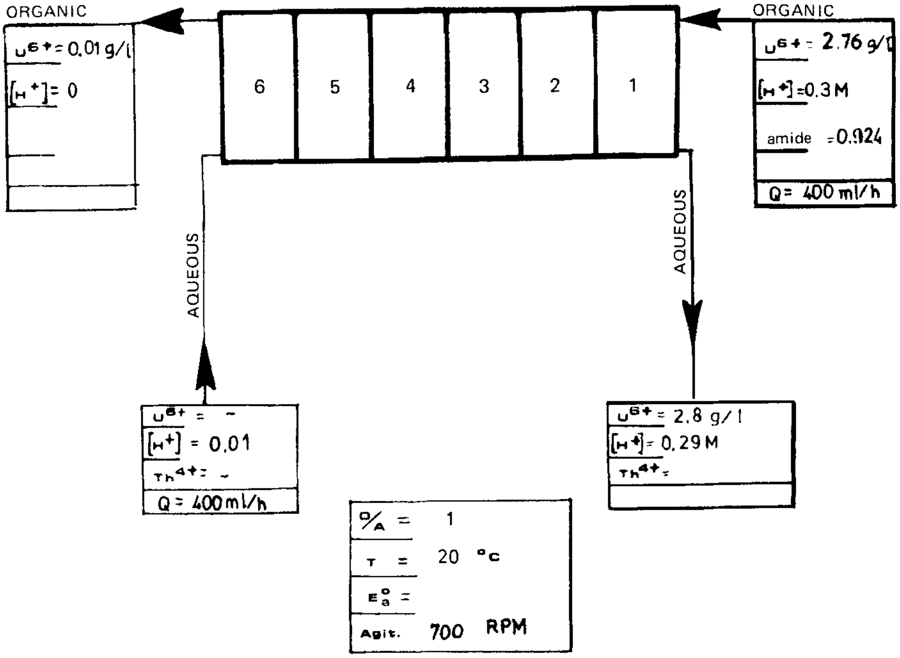


FIGURE 10. Demonstration of a flowsheet for the separation of uranium from thorium with N,N-dibutyl 2-ethylhexanamide in mesitylene (stripping section).

amounts as in the concentrated first cycle final product of the ITREC plant. As shown by Figures 8-11, both the separation of U from thorium and the stripping of uranium from loaded amide by diluted nitric acid are very easy and effective.

CONCLUSIONS

N,N-dialkyl aliphatic amides proved to be very promising as a new category of extracting agents for actinides.

Their preparation at a high degree of purity is easy and cheap. The performance of the amides examined, in regard to solubility, stability, and extraction behavior, supports the

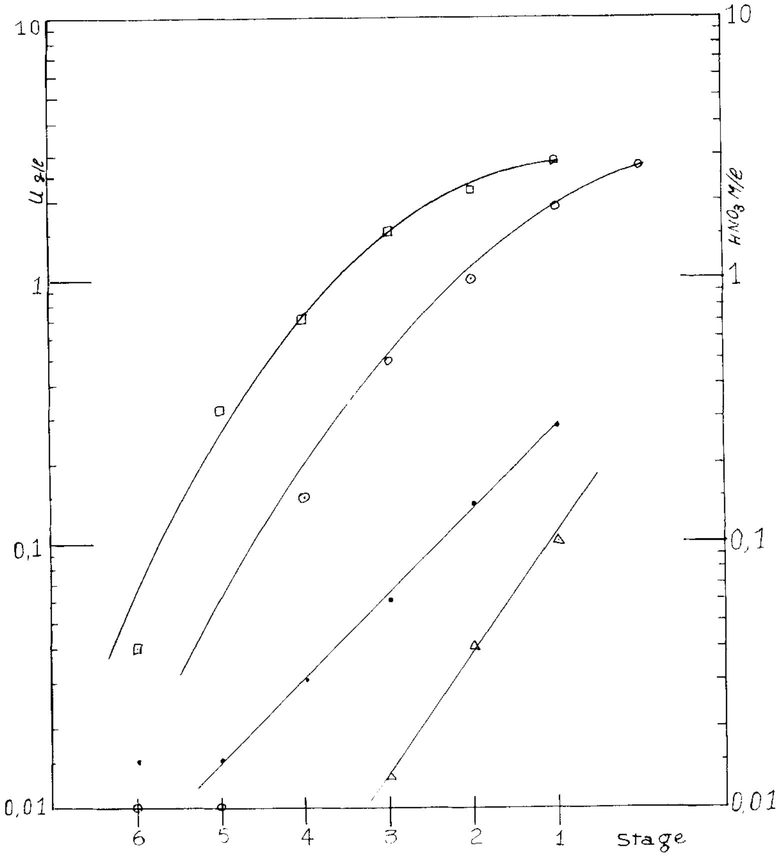


FIGURE 11. Concentration profile in the stripping section at steady state.

● = $[HNO_3]_{aq}$ Δ = $[HNO_3]_{org}$ ○ = $[U]_{org}$ □ = $[U]_{aq}$.

possibility of their use in the field of recovery and separation of actinides even on an industrial scale.

In this connection, it is important to point out that both DHOA and DBEHA show behaviors at least similar to and often even better than TBP: better decontamination of uranium from some fission products, better U-Th separation, better stability, and less-deleterious degradation products.

Research is now in progress to clarify the problem of third phase formation, and several mixer-settler runs will be carried out in order to support the proposal of amides for Purex-type and even for coprocessing flowsheets.

ACKNOWLEDGMENTS

The authors are indebted to Mrs. D. Carlini, M. Guerra, G. Puzzuoli, and S. Torcini for their valuable help and skillful technical cooperation in the experimental work.

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