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ABSTRACT

N,N-Dialkyl amides have drawn the attention of radiochemists engaged in the development of alternate extractants to tri-*n*-butyl phosphate (TBP) for the reprocessing of irradiated fuels, particularly with high radiation fields and high plutonium content. Dihexyl hexanamide (DHHA) has been found to be a promising extractant in this direction. Log K_{ex} values for the extraction of $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{DHHA}$ and $\text{Pu}(\text{NO}_3)_4 \cdot 2\text{DHHA}$ in *n*-dodecane were found to be 1.43 and 3.62, respectively. At high nitric acid concentration (>5 M), the amide undergoes protonation and extracts U(VI) and Pu(IV) as ion pairs of the type $(\text{UO}_2(\text{NO}_3)_3^-)(\text{HDHHA}^+)$ and $(\text{Pu}(\text{NO}_3)_6^{4-})(\text{HDHHA}^+)_2$. At trace level concentrations, the distribution coefficient (D) of Pu(IV) and U(VI) with a 1 M solution of DHHA in *n*-dodecane at 3.5 M HNO_3 are 41.2 and 13.5, respectively. Similarly, at 50% uranium saturation of the organic phase the D values of Pu(IV) and U(VI) are 9.2 and 4.2, respectively. These results

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suggest the distinct advantages of DHHA over TBP in improved extraction of Pu and ease of stripping of uranium. The separation factors for 0.5 M DHHA at 30 Mrad are obtained as ~37 (U/Zr) and ~75 (Pu/Zr), suggesting that this extractant is particularly promising for the selectivity of Pu and U over Zr from irradiated solutions as compared to TBP. Results obtained during this work demonstrate the potential of amides in meeting the challenges posed by the large Pu content and high radiation fields encountered during the reprocessing of Pu-based fuels discharged from thermal as well as fast power reactors.

INTRODUCTION

The tri-*n*-butyl phosphate (TBP) based PUREX process has been the workhorse of the nuclear fuel reprocessing industry for the last four decades (1). Although it has been employed universally for reprocessing natural/enriched uranium fuels, a few drawbacks associated with the use of TBP have caused concern to separation scientists and technologists. The main disadvantages of TBP are 1) a lower distribution coefficient of Pu(IV) as compared to that of U(VI), resulting in increased losses of Pu to the raffinate stream and accumulation of plutonium in the extraction column; 2) its vulnerability to high radiation fields and the deleterious nature of degradation products (mainly H₂MBP and HDBP) affecting product recovery (2, 3); and 3) the nonincinerable nature of the spent solvent which yields large volumes of secondary radioactive waste (4–6). Therefore, there is a need for exploring alternate extractants.

In recent years, *N,N*-dialkyl aliphatic amides have received increasing attention as potential extractants for the reprocessing of spent nuclear fuels (7–10). The most interesting features of these extractants are 1) the innocuous nature of their degradation products [viz., carboxylic acids and amines (11)], and 2) the possibility to incinerate the used solvent without a large amount of inorganic residues as encountered for TBP (12). Most of the work reported so far on amides refers to either aromatic or substituted aliphatic hydrocarbons as diluents for the amides (9–11). The main hindrances to their use in the preferred process diluent, *n*-dodecane, are the tendency to form a three-phase system with nitric acid and the poor solubility of uranyl nitrate adducts. The aromatic and other diluents used are not suitable for commercial scale reprocessing due to their poor radiation and chemical stability in nitric acid. During the last few years we have synthesized a large number of *N,N*-dialkyl amides and investigated their extraction behavior in *n*-dodecane toward actinides and fission products (7). An attempt has been made in the present work to investigate the extraction behavior of U(VI) and Pu(IV) from nitric acid medium with *N,N*-dihexyl hexanamide (DHHA) in *n*-dodecane. The nature of extracted species formed in the organic phase, and the corresponding two-phase extraction constants, are evaluated. The influence of U/Pu loading on the distribution data has also been investigated.



EXPERIMENTAL

Materials

Uranium(VI) stock solution was prepared by dissolving nuclear-grade U_3O_8 powder (obtained from the Uranium Metal Plant, BARC) in 1:1 nitric acid. Plutonium was purified by an anion-exchange method (13). Plutonium nitrate solution at 7.5 M HNO_3 was loaded on a Dowex 1 \times 4 column pre-converted into the nitrate form. Pu(IV) was held on the column while impurities such as traces of uranium, fission products, americium, etc. passed through as washings. Elution was done with 0.3 M HNO_3 to get a purified Pu-stock solution. The radiochemical purity of the Pu was checked by alpha spectrometry. Plutonium in solution was adjusted and maintained in the tetravalent state by the addition of 0.03 M sodium nitrite and 0.005 M ammonium vanadate as holding oxidant (14). Commercial grade *n*-dodecane was purified by washing with 0.1 M NaOH, 0.1 M HNO_3 , and distilled water, and finally distilled after drying over anhydrous sodium sulfate. The middle fraction (boiling range 214–215°C) was used in the present work. All the chemicals used were of analytical reagent grade.

Synthesis and Characterization of DHHA

N,N-Dihexyl hexanamide (DHHA) was synthesized in our laboratory by the procedure described by Baldwin et al. (15) using hexanoyl chloride and dihexyl amine in the presence of triethyl amine. The purity of the vacuum-distilled product was ascertained by elemental analysis, IR spectra, and determination of the amide content. The amide content was determined by nonaqueous potentiometric titration in acetic anhydride using standard perchloric acid in dioxane as the titrant (16). The analytical data of the purified DHHA was obtained as % C, 75.8 (76.3); % H, 12.7 (13.2); % N, 5.2 (4.9); bp = 164–166°C (0.2 mm); $\nu_{>\text{C}=\text{O}}$ = 1645 cm^{-1} (numbers in parentheses for elemental analysis refer to the theoretical values.)

Relative Basicity of the Amide

The relative basicity of the amide was determined by the measurement of the equilibrium constant for the uptake of nitric acid by varying concentrations of the amide. The acidity of the organic phase was determined by alkalimetry using phenol red as indicator.

Distribution Experiments

Equal volumes (usually 2.0 mL) of the aqueous phase containing trace concentrations of Pu(IV) or U(VI) ions (10^{-6} to 10^{-3} M) in the desired concentrations of nitric acid and preequilibrated organic phase of the required concentration of the amide (in *n*-dodecane) were equilibrated mechanically in 20



mL capacity stoppered tubes for 10–15 minutes at room temperature. After equilibrium the phases were allowed to stand for half an hour and separated. Suitable aliquots of both the aqueous and organic phases were pipetted for U or Pu assay. Uranium was estimated by a spectrophotometric method using dibenzoylmethane (DBM) as a chromogenic reagent (17). Pu was assayed radiometrically using an alpha-liquid scintillation counting system. The distribution coefficient (D) was defined as

$$D = \frac{\text{concentration of metal ion in the organic phase}}{\text{concentration of metal ion in the aqueous phase}}$$

Experiments involving the extraction and stripping of U(VI) or Pu(IV) at concentration levels encountered during the reprocessing of spent fuels (U = 15–120 mg/mL and Pu = 0.5–5 mg/mL) were also carried out, in duplicate, and the agreement between them was found to be satisfactory ($\pm 5\%$).

RESULTS AND DISCUSSION

Extraction of Nitric Acid by DHHA

Amides extract nitric acid to readily form adducts of different stoichiometries. The distribution coefficient (D) for the extraction of nitric acid (2 M) by 0.5 M DHHA in *n*-dodecane is found to be 0.1. Third-phase formation in the HNO₃–DHHA–dodecane system occurs when nitric acid concentration in the aqueous phase approaches 7 M. This nitric acid concentration is much higher as compared to the nitric acid concentration (3–4 M) normally encountered in the PUREX process coextraction cycle. To evaluate the nature of the extracted species and the relative basicity of the amide, the uptake of nitric acid by varying the concentration of DHHA in *n*-dodecane (0.1–0.5 M) from 3.5 M HNO₃ was determined. Extraction of nitric acid by DHHA can be represented by the equation



Species without a subscript and with the subscript “o” refer to the aqueous and organic phase, respectively.

The equilibrium constant (K_H) for Eq. (1) can be written as

$$K_H = \frac{[\text{HNO}_3 \cdot n\text{DHHA}]_o}{[\text{H}^+][\text{NO}_3^-][\text{DHHA}]_o^n} \quad (2)$$

In Eq. (2), changes in the activity coefficients of the various species in the concentration range used were considered to be insignificant. Rearranging Eq. (2) in logarithmic form:

$$\log[\text{H}^+]_o - 2 \log[\text{H}^+] = \log K_H + n \log[\text{DHHA}]_o \quad (3)$$

where $[\text{H}^+]_o = [\text{HNO}_3 \cdot n\text{DHHA}]_o$ and $[\text{H}^+] = [\text{NO}_3^-]$.



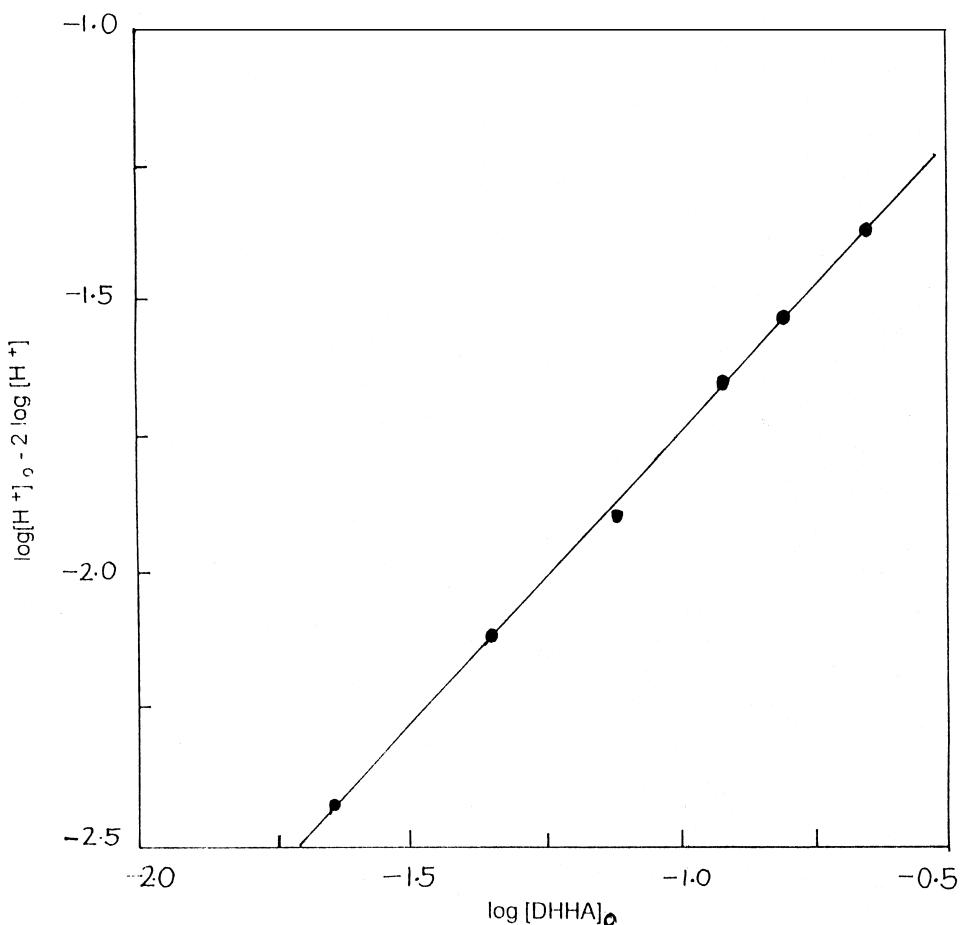


FIG. 1 Variation of $\log[H^+]_o - 2 \log[H^+]$ with $\log[DHHA]_o$.

$[H^+]$ was evaluated from the value of $[H^+]_o$ and the known dissociation constant (23.5) of nitric acid (18). $[DHHA]_o$ was computed from the initial total $[DHHA]$ and the value of $[H^+]_o$. The values of $\log[H^+]_o - 2 \log[H^+]$ were plotted against $\log [DHHA]_o$, and the plot thus obtained was a straight line (Fig. 1) with a slope of 1.0, confirming the stoichiometry of the extracted species as $HNO_3 \cdot DHHA$. The K_H value was evaluated as 0.174 from the intercept of the line.

Extraction of U(VI) and Pu(IV)

The extraction of U(VI) and Pu(IV) from varying concentrations of aqueous nitric acid (1–6 M) with 0.5 M DHHA was performed. The distribution coefficient (D) data are presented in Fig. 2. Pu(IV) is more efficiently extracted than U(VI) throughout the nitric acid concentration range investigated, unlike TBP. With an increase in nitric acid molarity in the aqueous phase, the extraction of U(VI) first increased, passed through a maxima in the range of 5



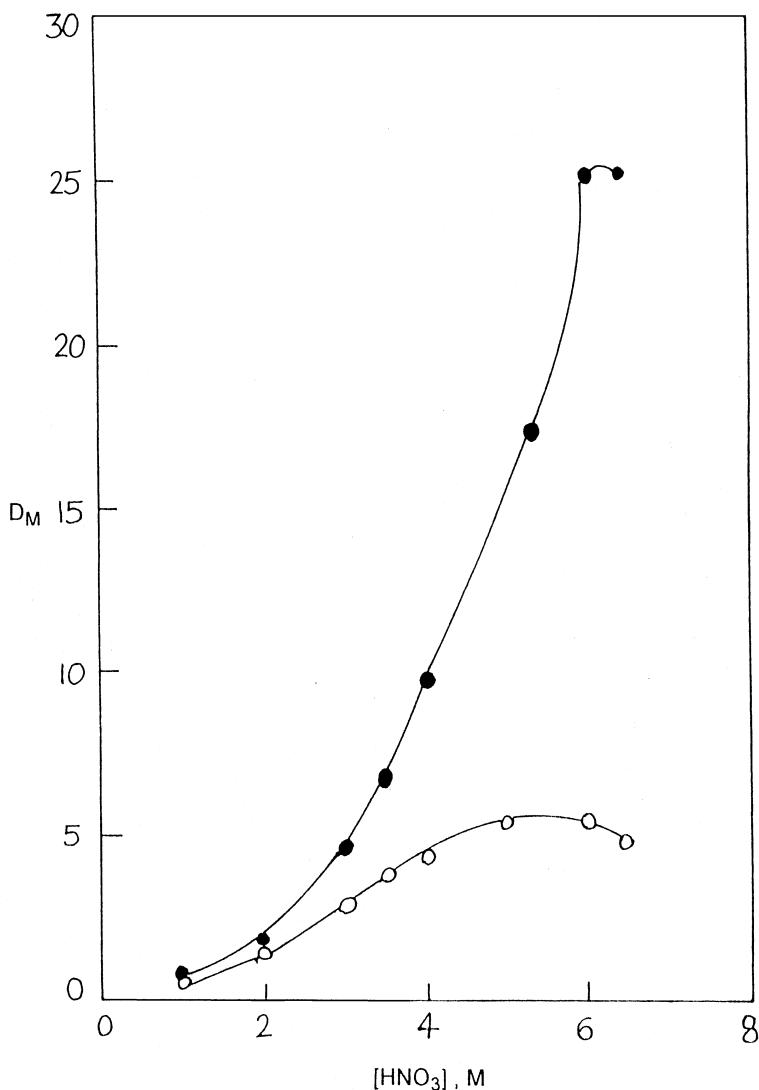


FIG. 2 Distribution ratios (D_M) of U(VI) and Pu(IV) as a function of nitric acid concentration.
(○): U(VI), (●): Pu(IV).

to 6 M HNO₃, and then decreased. The decrease in D value beyond 6 M HNO₃ is attributed to the competition between nitric acid and uranyl nitrate for the available DHHA. In the case of Pu(IV), the extraction increased steadily with increasing nitric acid concentration in the aqueous phase up to 6.5 M, and the third phase appeared at 7 M. Thus, the extraction behavior of Pu(IV) was different from that observed with TBP, which exhibited decreased extraction at higher acidities (beyond 5 M HNO₃) due to the formation of poorly extractable complexes of the type Pu(NO₃)₆²⁻, HPu(NO₃)₆⁻, and H₂Pu(NO₃)₆ (19, 20). Condamines and Musikas (21) reported that amides undergo protonation at higher nitric acid concentration and behave as anionic extractants

similar to tertiary amines, thereby extracting the hexanitrate species of Pu(IV) as $(Pu(NO_3)_6^{2-})(HDHHA^+)_2$ by ion-pair formation mechanism.

In order to ascertain the nature of the species extracted, the dependence of D for both U(VI) and Pu(IV) on DHHA concentration was determined by keeping the nitric acid concentration constant in the aqueous phase. The plot of $\log D$ versus $\log [DHHA]_0$ gave straight lines (Figs. 3 and 4) with slopes equal to 2 when the extraction was performed from 3.5 M HNO_3 . This indicated that both U(VI) and Pu(IV) were extracted as disolvates similar to TBP. The absorption spectra of U(VI) and Pu(IV) species (Figs. 5 and 6) extracted with DHHA in *n*-dodecane from 3.5 M HNO_3 were found similar to that of TBP extract. Also, bathochromic shifts of the peaks in the spectra of U(VI) (415.8 \rightarrow 425.4 nm) and Pu(IV) (476 \rightarrow 497 nm) were observed as compared to their aqueous spectra. From spectral studies it appeared that the two amide ligands in the extracted species existed in the primary coordination sphere of the metal ion and were linked through oxygen atoms of the carbonyl groups (21).

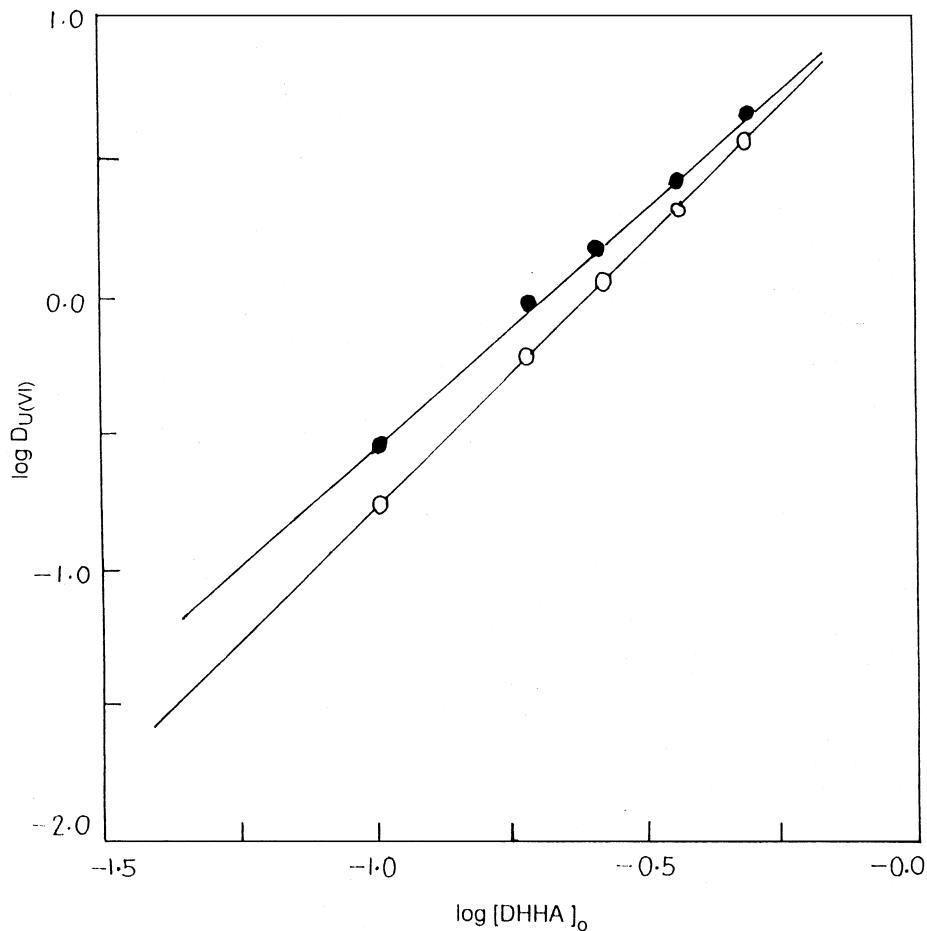


FIG. 3 Variation of $\log D_{U(VI)}$ with $\log [DHHA]$. (○): 3.5 M HNO_3 , (●): 6.5 M HNO_3 .



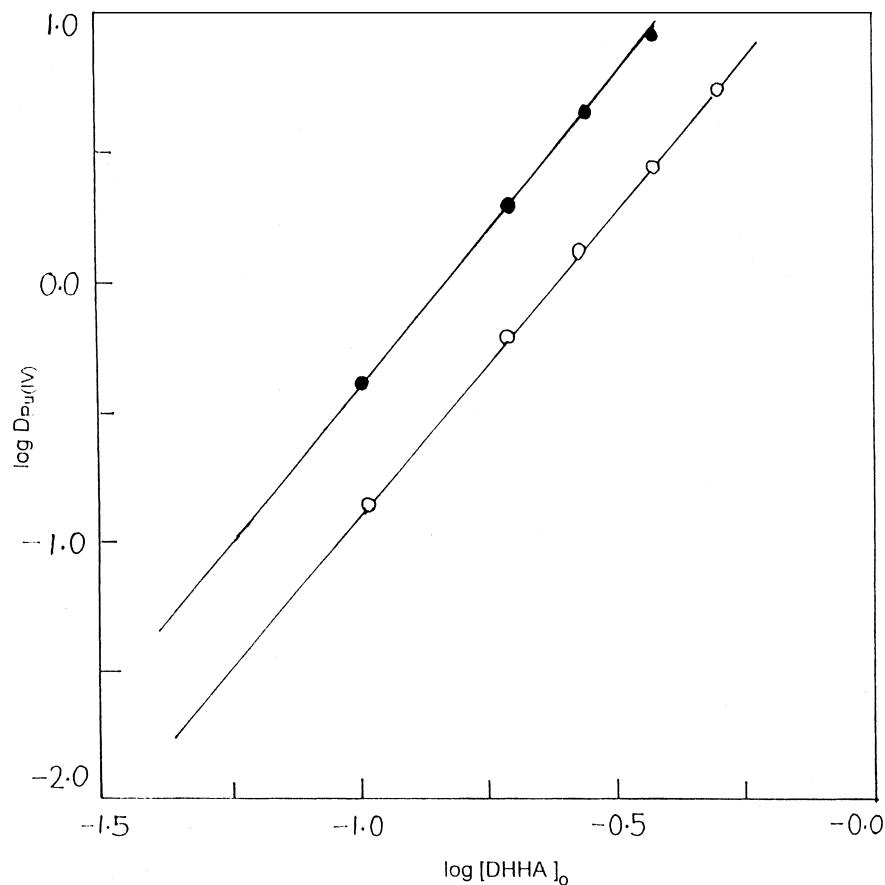


FIG. 4 Variation of $\log D_{Pu(IV)}$ with $\log [DHHA]$. (○): 3.5 M HNO_3 , (●): 6.5 HNO_3 .

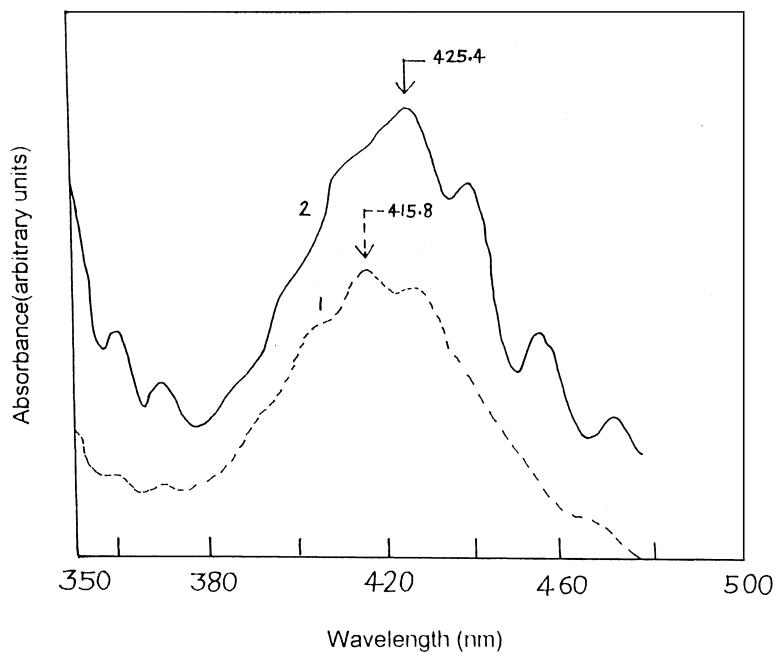


FIG. 5 Absorption spectrum of U(VI). (1): in 3.5 M HNO_3 , (2): in 0.5 M DHHA-*n*-dodecane.

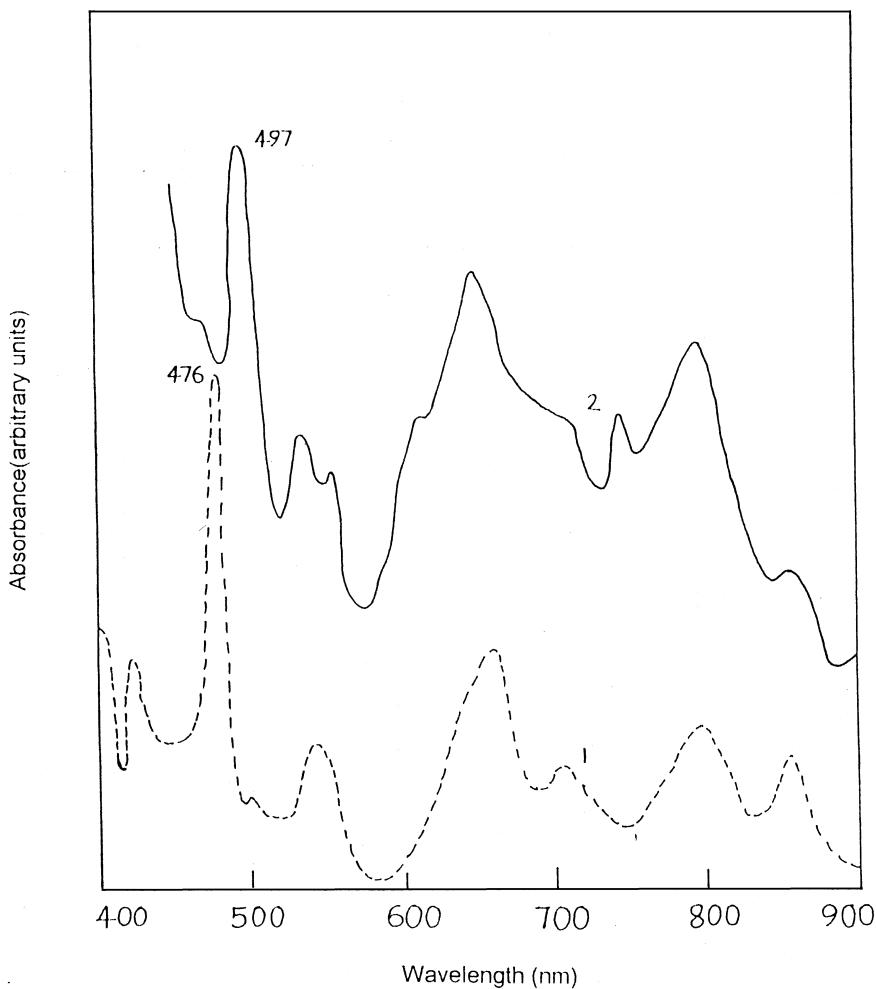


FIG. 6 Absorption spectrum of Pu(IV). (1): in 3.5 HNO₃, (2): in 0.5 M DHHA-*n*-dodecane.

On the other hand, straight lines with slopes equal to 1.5 and 2.0, respectively, for U(VI) and Pu(IV) were obtained when the extraction was carried out from 6.5 M HNO₃. This anomalous behavior of the amide at higher acidities was attributed to the change in extraction mechanism. As mentioned earlier, amides undergo protonation and act as anionic extractants similar to tertiary alkyl amines at higher acidities, thereby extracting metal nitrate as anionic species by ion-pair formation (21). Modification in the UV-VIS spectra of U(VI)-DHHA and Pu(IV)-DHHA complexes (Figs. 7 and 8) in the organic phase at higher acidities and their close resemblance to U(VI)-tri-*n*-octyl amine and Pu(IV)-tri-*n*-octyl amine species provided further evidence for the presence of (UO₂(NO₃)₃⁻) and (Pu(NO₃)₆²⁻) anions (22, 23).

These studies suggest that DHHA extracts U(VI) and Pu(IV) as UO₂(NO₃)₂·2DHHA and Pu(NO₃)₄·2DHHA, respectively, by solvation from



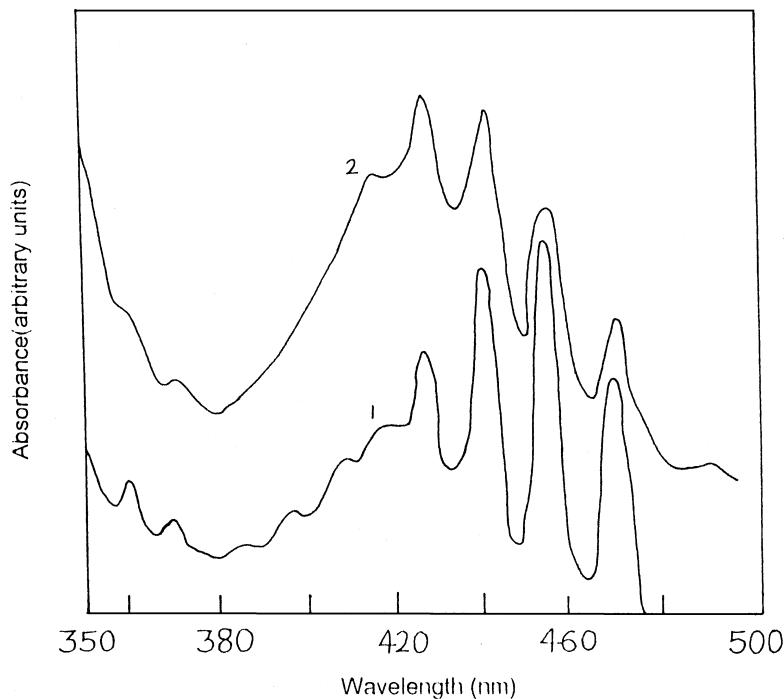


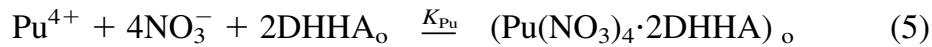
FIG. 7 Absorption spectrum of U(VI) species extracted from 6.5 M HNO₃. (1): with 0.5 M TOA-xylene, (2): 0.5 M DHHA-*n*-dodecane.

moderate nitric acid solutions. At high nitric acid concentrations (> 5 M), the amide undergoes protonation and extracts U(VI) and Pu(IV) as ion-pairs of the type (UO₂(NO₃)₃⁻)(DHHA⁺) and (Pu(NO₃)₆⁴⁻)(DHHA⁺)₂.

The extraction equilibria of U(VI) and Pu(IV) with DHHA from moderate nitric acid solutions (3.5 M) can be represented by



and



The equilibrium constants for the two reactions are written as

$$K_U = \frac{[\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{DHHA}]_o}{[\text{UO}_2^{2+}][\text{NO}_3^-]^2[\text{DHHA}]_o^2} \quad (6)$$

and

$$K_{\text{Pu}} = \frac{[\text{Pu}(\text{NO}_3)_4 \cdot 2\text{DHHA}]_o}{[\text{Pu}^{4+}][\text{NO}_3^-]^4[\text{DHHA}]_o^2} \quad (7)$$

respectively. However, UO₂²⁺ and Pu⁴⁺ in aqueous solution were present as equilibrium mixtures of UO₂(NO₃)⁺-UO₂(NO₃)₂, Pu(NO₃)³⁺-Pu(NO₃)₂²⁺,



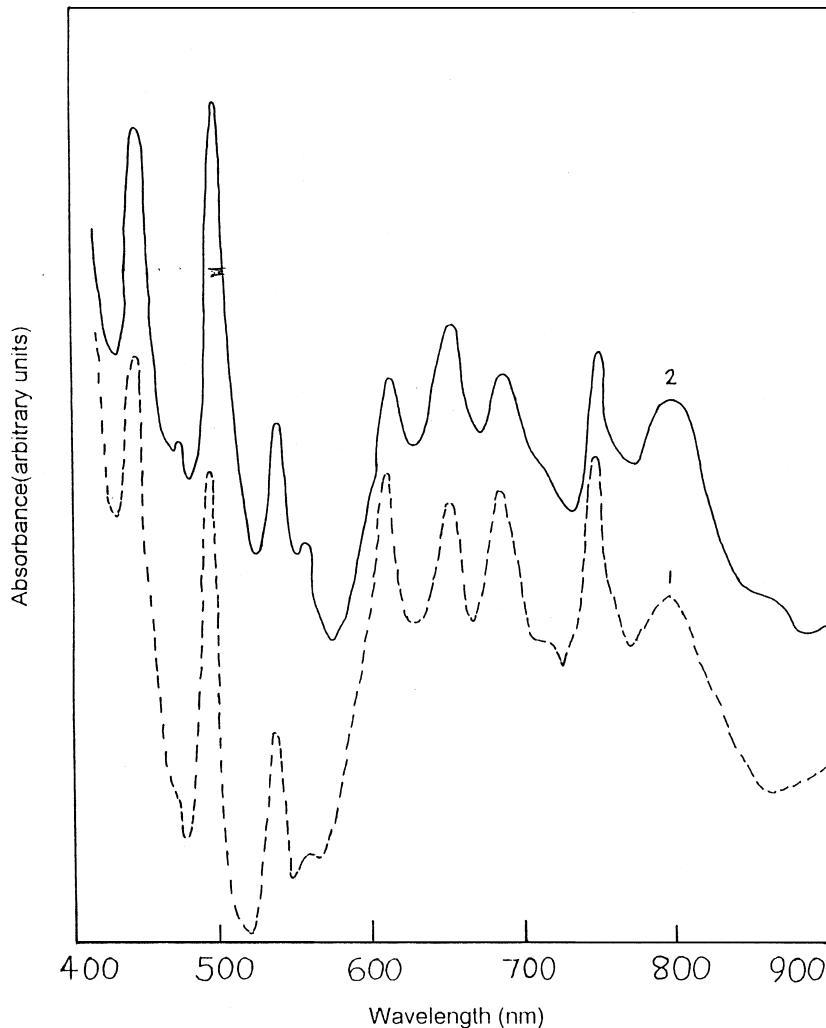


FIG. 8 Absorption spectrum of Pu(IV) species extracted from 6.5 M HNO₃. (1): with 0.5 M. TOA-xylene, (2): 0.5 M DHHA-*n*-dodecane.

etc. Thus, if *C* was the total concentration of the actinide ion and *D* was the distribution ratio,

$$C_U = [UO_2^{2+}](1 + \sum \beta_n [NO_3^-]^n)$$

and

$$C_{Pu} = [Pu^{4+}](1 + \sum \beta_n [NO_3^-]^n)$$

from which it follows that

$$K_U = \frac{D_U(1 + \sum \beta_n [NO_3^-]^n)}{[NO_3^-]^2 [DHHA]_0^2} \quad (8)$$

$$K_{\text{Pu}} = \frac{D_{\text{Pu}}(1 + \sum \beta_n [\text{NO}_3^-]^n)}{[\text{NO}_3^-]^4 [\text{DHHA}]_0^2} \quad (9)$$

Partitioning of the DHHA toward the aqueous phase (3.5 M HNO₃) was neglected. [DHHA]₀ refers to the uncomplexed concentration at equilibrium. It was computed using a modified form of Eq. (2). The correction factor, 1 + $\sum \beta_n [\text{NO}_3^-]^n$, for the nitrate complexation of UO₂²⁺ from 3.5 HNO₃ was determined by a cation-exchange method and that for Pu⁴⁺ by a 2-thenoyl trifluoroacetone (TTA) extraction method. The values obtained are 2.23 ± 0.03 and 2093 ± 72 respectively for UO₂²⁺ and Pu⁴⁺. The equilibrium constant values (log K_U and log K_{Pu}) evaluated from the data were 1.43 ± 0.008 and 3.62 ± 0.20 for U(VI) and Pu(IV) respectively.

Extraction of Macro Concentrations of U(VI) and Pu(IV)

The extraction behavior of U(VI) and Pu(IV) with DHHA was investigated at concentration levels likely to be encountered during reprocessing. The distribution ratios of U(VI) and Pu(IV) between 1 M DHHA in *n*-dodecane and 3.5 M HNO₃ were determined as a function of uranium(VI) and plutonium(IV) concentration (U: 10⁻³ to 0.5 M; Pu: 10⁻⁵ to 0.02 M). As can be seen from Tables 1 and 2, the *D* value for U(VI), as well as for Pu(IV), decreased with uranium and plutonium concentrations, respectively, due to the increased loading of organic phase. The *D* value ranges from 13.52 (trace level) to 2.25 (120 mg/mL) for U(VI), and 41.2 (trace level) to 19.36 (5 mg/mL) for Pu(IV). The percentage extraction (O/A = 1) varies from 93 to 69 for U(VI) and >97 to 95 for Pu(IV). Plutonium concentrations up to 10

TABLE 1
Distribution Data of Uranium(VI) as a Function of Uranium Concentration:
[HNO₃] = 3.5 M, [DHHA] = 1 M (stripping agent = 0.01 M HNO₃)

U total (mg/mL)	D _U	% Extraction	% Stripping (in two steps)		
			I	II	Total
Tracer	13.52	93.1	54	36	90
15.0	10.70	91.4	58	35	93
30.0	8.76	89.7	59	34	93
45.0	6.96	87.4	63	33	96
60.0	5.63	84.9	64	34	98
75.0	4.18	80.7	66	33	99
100.0	2.81	73.7	67	32	99
120.0	2.25	69.2	68	32	100



TABLE 2

Distribution Data of Plutonium(IV) as a Function of Plutonium Concentration:
 $[HNO_3] = 3.5\text{ M}$, $[DHHA] = 1\text{ M}$ (stripping agent = $0.5\text{ M }HNO_3 + 0.05\text{ M }NH_2OH \cdot HCl$)

Pu total (mg/mL)	D_{Pu}	% Extraction	% Stripping (in two steps)		
			I	II	Total
Tracer	41.20	97.6	83.0	14.6	97.6
0.5	35.69	97.3	59.6	38.9	98.5
1.0	34.92	97.2	66.4	32.9	99.3
1.5	34.53	97.2	65.6	32.5	98.1
2.0	33.21	97.0	68.3	31.9	100.2
2.5	32.06	96.9	66.3	33.3	99.6
3.0	26.30	96.3	67.3	31.6	98.9
3.5	25.12	96.2	64.6	35.3	99.9
4.0	23.17	95.9	68.9	31.7	100.6
4.5	21.85	95.6	69.2	30.5	99.7
5.0	19.36	95.0	67.6	31.3	98.9

mg/mL were loaded into 1 M DHHA at 3.5 M HNO_3 without encountering the formation of a third phase. Uranium loading capacity of 1 M DHHA at 3.5 HNO_3 was evaluated as 82.6 g/L.

Uranium is present in a much higher concentration as compared to that of plutonium during reprocessing, therefore the effect of aqueous phase U(VI) concentration on the extraction of Pu(IV) (10 $\mu\text{g/mL}$) was studied. The distribution ratios of Pu(IV) between 1 M DHHA and 3.5 M HNO_3 were measured as a function of uranium(VI) concentration (0–75 mg/mL). The D value as well as the percentage extraction decreased with uranium concentration (Table 3). The D value ranged from 41.2 (in the absence of uranium) to 9.2 at 50% uranium saturation of the organic phase. The corresponding D values of Pu(IV) for 1 M TBP in *n*-dodecane were found to be 19.2 and 1.8 (24), which are much lower compared to DHHA. It is evident from these data that DHHA extracts Pu(IV) more efficiently than TBP at trace level concentrations as well as under uranium loading conditions. As a result of this, during the co-extraction of U(VI) and Pu(IV) with the amide the losses of Pu toward the aqueous raffinate stream could be reduced considerably, especially in processing fuels with a high plutonium content. This is a distinct advantage of DHHA over TBP.

Table 1 shows the distribution data of U(VI) at 3.5 M HNO_3 as a function of total uranium concentration using 1 M DHHA. As expected D_U decreases with uranium loading from 13.52 (tracer) to 2.25 (120 g/L) due to the decreased availability of free ligand. % U saturation for 120 g/L of total uranium is ~70, which is close to that encountered in the PUREX process. Extracted



TABLE 3
Distribution Data of Plutonium(IV) as a Function of Uranium Concentration:
[HNO₃] = 3.5 M, [DHHA] = 1 M (stripping agent: 0.5 M HNO₃ + 0.05 M NH₂OH·HCl)

Aqueous phase U concentration (mg/mL)	Organic phase U saturation (%)	<i>D</i> _{Pu}	%	% Stripping (in two steps)		
				Extraction (single step)	I	II
00	—	41.20	97.6	83	14	97
15.0	11.4	29.70	96.7	86	12	98
30.0	22.4	22.54	95.7	85	13	98
45.0	32.8	18.40	94.8	87	12	99
60.0	42.45	16.50	94.3	87	11	98
75.0	50.44	9.17	90.2	91	9	100

uranium from the loaded organic phase was stripped quantitatively using 0.01 M HNO₃ (O/A = 1). Recoveries of 90 to 100% were obtained in two steps (Table 1). Table 2 summarizes the Pu(IV) extraction data as a function of Pu concentration in the range from tracer to 5.0 g/L. Extraction data of a single stage and stripping data of two stages suggest that >94% of Pu could be separated in one cycle even up to 5 g/L of Pu. Plutonium from the loaded organic phase was stripped quantitatively by using a mixture of 0.5 M HNO₃ and 0.05 M hydroxylamine hydrochloride which reduced Pu(IV) to inextractable Pu(III). Backextraction in the 97 to 100% range was obtained in two steps (O/A = 1). Table 3 summarizes the tracer Pu(IV) extraction data in the presence of varying amounts of uranium (up to 75 g/L). The organic phase loaded with U and Pu was stripped using a mixture of 0.5 M HNO₃ and 0.05 M hydroxylamine hydrochloride. As expected, the % extraction decreases but the % stripping increases with uranium loading of the organic phase. No attempt was made to assay the uranium stripped toward the aqueous phase.

The separation factors for U and Pu with respect to Ru and Zr (fission products) with 0.5 M DHHA irradiated at 30 Mrad were obtained as ~37 (U/Zr) and ~75 (Pu/Zr), which were distinctly larger than the corresponding values of ~7 (U/Zr) and ~12 (Pu/Zr) with 30% TBP (25, 26). However, there was little difference in the behavior of DHHA and TBP for Ru decontamination. It corroborates the view that Ru distribution is influenced by degradation of the diluent rather than degradation of the extractant.

CONCLUSIONS

DHHA extracts U(VI) and Pu(IV) as UO₂(NO₃)₂·2DHHA and Pu(NO₃)₄·2DHHA, respectively, at 3.5 M HNO₃ with the corresponding log



K_{ex} values as 1.43 and 3.62. At HNO_3 concentration $> 5 \text{ M}$, the predominating species for U is $(\text{UO}_2(\text{NO}_3)_3^-)(\text{HDHHA}^+)$ and for Pu is $(\text{Pu}(\text{NO}_3)_6^{2-})(\text{HDHHA}^+)_2$. Results obtained during the present work demonstrate the potential of *N,N*-dihexyl hexanamide in meeting the challenges posed by the large Pu content and high radiation field encountered during the reprocessing of Pu-based fuels discharged from thermal as well as fast reactors.

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