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Separation Studies of Uranium and Thorium Using Di-2-ethylhexyl Isobutyramide (D2EHIBA)

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ABSTRACT

The extraction behavior of di-2-ethylhexyl isobutyramide (D2EHIBA) in dodecane medium for U(VI), Th(IV), and fission products such as Zr, Ce, Eu, and Cs, and the structural material Fe, has been investigated over a wide range of nitric acid concentrations. It has been observed that whereas D_U varies from $< 10^{-3}$ (pH 2.0) to 4.4 (6 M HNO_3) with 1 M ligand, the corresponding D_{Th} values are 1.5×10^{-3} and 4×10^{-2}. In the presence of 250 g/L of Th, D_U values are 8.6 (pH 2.0) and 2.2 (6 M HNO_3). D2EHIBA has been found to be a promising extractant of trace concentrations of U in the presence of macro amounts of Th. The extraction of fission products and Fe is found to be negligible. D2EHIBA is found to extract nitric acid predominantly as a 1:1 species ($K_H = 0.156 \pm 0.048$). U(VI) is extracted as a disolvate $UO_2(NO_3)_2 \cdot 2D2EHIBA$ ($K_{ex} = 0.87 \pm 0.08$).

INTRODUCTION

With depleting uranium resources, several countries have intensified their efforts in recent years to investigate the thorium–uranium fuel cycle. ^{232}Th (a fertile material) when irradiated in a reactor leads to the formation of the fissile isotope ^{233}U:

$$^{232}\mathrm{Th} + \mathrm{n} \xrightarrow{\qquad} {}^{233}\mathrm{Th} \xrightarrow[23.5\ \mathrm{min}]{\beta^-} {}^{233}\mathrm{Pa} \xrightarrow[27.4\ \mathrm{days}]{\beta^-} {}^{233}\mathrm{U}$$

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Due to the high neutron yield (η) of ^{233}U in the thermal region (2.2), it is possible to breed ^{233}U sufficiently to achieve a self-sustained recycle system wherein no supplementary input of enriched material would be needed, i.e., thermal breeding is possible with the Th–U cycle. Reprocessing of irradiated thorium to separate and purify ^{233}U is an important part of the thorium fuel cycle and greatly influences the economics of the fuel cycle. Separation of uranium and thorium is rendered more difficult than separation of uranium and plutonium because thorium does not display variable oxidation states. Hence, one needs to exploit the difference in the complexation behavior of Th(IV) vis-à-vis U(VI) to arrive at experimental conditions where desired separation factors (S.F.) could be achieved. At present, the separation and purification of thorium and uranium is carried out by the THOREX process. It has many versions which can broadly be classified into two main categories: 1) both uranium and thorium are recovered using a high concentration (~40%) of tributyl phosphate (TBP) in a kerosene-type diluent, and 2) uranium alone is recovered using dilute TBP (5%) by rejecting thorium into the raffinate. The Th–TBP complex formed in the first case has low solubility in the organic phase, leading to the formation of a third phase. Use of 5% TBP in the second case restricts the loading of uranium and thus decreases the throughput.

There is a need, therefore, for the development of alternate extractants to TBP for the efficient separation of uranium from irradiated thorium. Organophosphorous extractants with sterically hindered alkyl groups, viz., tri-*sec*-butyl phosphate, tri-isobutyl phosphate, and tri-2-ethylhexyl phosphate, have been investigated in recent years toward this end (1, 2). These extractants behave either similarly to TBP or marginally better.

High molecular weight *N*,*N*-dialkyl aliphatic amides have been reported to be potential extractants of actinides and also have been considered as an alternate choice in place of TBP for the efficient reprocessing of plutonium from irradiated fuels (3). Apart from their desirable extraction behavior, amides offer certain distinct advantages: 1) the radiolytic and chemical degradation products of amides, mainly carboxylic acids and amines, are innocuous (4); 2) amides are completely incinerable, leading to a reduced volume of secondary waste [every liter of TBP introduced for reprocessing leaves behind ~20 vol% of phosphoric acid which has to be either neutralized and then bitumanized or converted into phosphate glass (5)], and 3) amides can easily be synthesized on a large scale.

Siddall (6), on the basis of data on the extraction of different actinides by various amides, has suggested that dialkyl amides with alkyl substitution on the α-carbon atom adjacent to the carbonyl group hold promise for the separation of hexavalent actinides from tetravalent actinides. Working on the extraction of actinides by various amides, Prabhu et al. (7) confirmed the above suggestion and reported that while di-2-ethylhexyl butyramide (D2EHBA) extracts both U(VI) and Pu(IV), the corresponding isobutyramide (D2EH

IBA) extracts uranium selectively. Amides with a branched chain on the acid side hold promise for uranium and plutonium separation from nitric acid medium. In view of the analogous nature of Th(IV) and Pu(IV) cations, it was interesting to investigate these amides as alternate extractants for the reprocessing of irradiated thorium.

EXPERIMENTAL METHODS

Materials

D2EHIBA used in the present work was synthesized by reacting di(2-ethylhexyl) amine and isobutyryl chloride in the presence of triethylamine in a 1:1:1 mole ratio in chloroform solvent. The reaction mixture was refluxed for 2 hours. The crude reaction mixture of amide was washed with aqueous alkali, hydrochloric acid, and then water followed by drying over anhydrous sodium sulfate. The amide was purified by vacuum distillation; bp = 160°C at 0.5 mm Hg; yield = 85%. The purity of the amide was checked by TLC, elemental analysis [% C = 77.7 (77.2), % N = 4.6 (4.5), % H = 13.4 (13.2)], and non-aqueous potentiometric titration [99.4% purity]. The IR spectrum of the product showed the 1640 cm^{-1} band characteristic of $\nu_{\mathrm{C=O}}$ in amides. The PMR spectrum was obtained in $CDCl_3$ using a Bruker FT-NMR (200 MHz). The observed chemical shifts (ppm), multiplicity, and intensity of various protons are shown in Table 1. The diluent *n*-dodecane used in the present study was freshly distilled before use. ^{233}U, used in the uranium extraction studies, was freshly purified by ion exchange. The absence of decay products after purification was ascertained by α-spectrometry. ^{234}Th was freshly milked from uranium loaded on Aliquat 336/$CHCl_3$ and purified as per the procedure described elsewhere (8). Tracers of fission products (^{95}Zr, ^{141}Ce, $^{152\text{–}154}$Eu, and ^{137}Cs) and structural material (^{59}Fe) were procured from BRIT, Mumbai, India. Natural uranium and thorium obtained from Uranium Metal Plant,

TABLE 1
^{1}H Chemical Shift Data of D2EHIBA

Proton type	Chemical shift (ppm)	Multiplicity	Number of protons
N—C**H**$_2$	3.16	Multiplet	4
O═C—C**H**	2.76	Multiplet	1
N—CH$_2$—C**H**	1.55	Multiplet	2
C—C**H**$_2$—C	1.21	Multiplet	16
C**H**$_3$—CH—C**H**$_3$	1.06	Doublet	6
C—C**H**$_3$	0.83	Multiplet	12

B.A.R.C., and from Indian Rare Earths Limited, Mumbai, India, respectively, were used wherever necessary.

Distribution Studies

Solutions of desired concentrations of D2EHIBA in *n*-dodecane were used as the organic phases after preequilibration twice with the respective nitric acid concentrations. Equal volumes (0.5 mL) of the preequilibrated organic phases and the aqueous phases containing metal ions at the desired nitric acid concentrations were shaken for equilibration in a water bath at 25°C for 30 minutes. The two phases were then centrifuged and assayed by taking known aliquots (100–200 μL) from both phases. In the case of ^{234}Th, ^{95}Zr, ^{141}Ce, $^{152-154}$Eu, ^{137}Cs, and ^{59}Fe tracers, the gamma peaks were counted using a single channel NaI(Tl) scintillation detector. ^{233}U was estimated by using a suitable liquid scintillator for measuring the α-activity. Toluene containing diethyl hexyl phosphoric acid (HDEHP) was used as the scintillator for the aqueous phase and a dioxane scintillator was used for the assay of the organic phase aliquot. The distribution ratio was calculated as the ratio of counts per minute per milliliter in the organic phase to that in the aqueous phase. However, the distribution ratio for uranium (D_U) in the presence of a macro concentration of Th was calculated after taking into account the counts contributed from ^{232}Th and its decay products. For this purpose, the total counts of ^{233}U were measured before the addition of thorium. The count rate of the organic phase after equilibration was measured, and from this the contribution due to the interference of counts of ^{232}Th and its decay products, determined experimentally, was substracted. The difference between the initial aqueous and the final organic phase activities of U was taken as the equilibrium aqueous phase activity of U. D_U values were also determined by computing ^{233}U(aq) activity from the aqueous phase activities of distribution experiments of ^{233}U + ^{232}Th and ^{232}Th alone. There was an excellent agreement ($\pm$5%) in the D_U values obtained by these two approaches.

The hydrogen ion concentration in the two phases was determined by titration with standard alkali using the weight burette method. The calculated difference between the initial and final aqueous acidity was in good agreement with the value obtained by direct titration of the organic phase in alcohol medium.

Speciation Studies

For speciation studies, ^{233}U tracer was taken in 2 M nitric acid and extracted with the amide. The concentration of amide was varied from 0.2 to 1 M in dodecane medium. Each amide solution was preequilibrated with 2 M HNO_3 twice. The amount of uranium in the aqueous phase and the organic phase after equilibration was determined radiometrically by α-liquid scintillation counting.

CALCULATIONS

Acid Uptake by Amide

Amides, being basic in nature, interact with acid according to the following mechanism.

$$H^+_{aq} + NO^-_{3\,aq} + nA_{org} \overset{K_H}{\rightleftharpoons} HNO_3\cdot nA_{org} \tag{1}$$

$$K_H = \frac{[HNO_3\cdot nA]_{org}}{[H^+]_{aq}[NO_3^-]_{aq}[A]^n_{org,free}} \tag{2}$$

Taking logarithm on both sides of Eq. (2) and rearranging;

$$\mathrm{Log}[H^+]_{org} - 2\,\mathrm{Log}[H^+]_{aq} = n\,\mathrm{Log}[A]_{org,free} + \mathrm{Log}\,K_H \tag{3}$$

where $[H^+]_{org} = [HNO_3\cdot nA]_{org}$ and $[H^+]_{aq} = [NO_3^-]_{aq}$. $[H^+]_{aq}$ was calculated from the titre value (T) and dissociation constant of HNO_3 (K_a).

$$K_a = \frac{[H^+]_{aq}[NO_3^-]_{aq}}{[HNO_3]_{aq}} = \frac{[H^+]^2_{aq}}{T - [H^+]_{aq}} \tag{4}$$

where $T = ([H^+]_{aq} + [HNO_3]_{aq})$ in the aqueous phase. Therefore,

$$[H^+]^2_{aq} + K_a[H^+]_{aq} - K_aT = 0 \qquad (K_a = 23.5, \text{ literature value}) \tag{5}$$

$[H^+]_{aq}$ was obtained from T by solving the above quadratic equation.

Assuming a 1:1 adduct of amide with HNO_3, the free amide concentration was obtained from $[H^+]_{org}$ as follows:

$$[A]_{org,free} = [A]_{initial} - [A]_{bound}$$

where $[A]_{bound} = [HNO_3\cdot A]_{org} = [H^+]_{org}$. Therefore,

$$[A]_{org,free} = [A]_{initial} - [H^+]_{org}$$

From Eq. (3) it can be seen that a plot of $\{\log[H^+]_{org} - 2\log[H^+]_{aq}\}$ against $\log[A]_{org,free}$ should give a straight line with slope n, i.e., the number of amide molecules bound to each HNO_3 in the adduct formed and the log K_H value can be found from the intercept (9). In view of the fact that the terms in Eq. (2) refer to concentrations, K_H should be referred to as the concentration acid uptake constant of D2EHIBA.

Uranium Extraction Constant

The extraction of U(VI) by D2EHIBA can be given by

$$UO^{2+}_{2\,aq} + 2NO^-_{3\,aq} + nA_{org} \overset{K_{ex}}{\rightleftharpoons} UO_2(NO_3)_2\cdot nA_{org} \tag{6}$$

where K_{ex} is the equilibrium constant for the biphasic extraction reaction (6).

The value of K_{ex} can be given as

$$K_{ex} = \frac{[UO_2(NO_3)_2 \cdot nA]_{org}}{[UO_2^{2+}]_{aq}[NO_3^-]_{aq}^2[A]_{org,free}^n} \tag{7}$$

However in the aqueous phase, various species of U(VI) are present as UO_2^{2+}, $UO_2(NO_3)^+$, $UO_2(NO_3)_2$, etc. Therefore, the total concentration C_U of U(VI) in the aqueous phase at equilibrium can be shown as

$$C_U = [UO_2^{2+}](1 + \Sigma\beta_n[NO_3^-]^n) \qquad (n = 1, 2, 3, \text{etc.}) \tag{8}$$

where β_n is the overall concentration stability constant for complexes of the type $UO_2(NO_3)_n^{(2-n)+}$ and $[UO_2(NO_3)_2 \cdot nA]_{org}/C_U = D_U$.

Substituting the value of $[UO_2^{2+}]_{aq}$ from Eq. (8) into Eq. (7) and rearranging:

$$K_{ex} = \frac{[UO_2(NO_3)_2 \cdot nA]_{org}(1 + \Sigma\beta_n[NO_3^-]^n)}{C_U[NO_3^-]_{aq}^2[A]_{org,free}^n} \tag{9}$$

Substituting D_U as $[UO_2(NO_3)_2 \cdot nA]_{org}/C_U$ in Eq. (9):

$$K_{ex} = \frac{D_U(1 + \Sigma\beta_n[NO_3^-]^n)}{[NO_3^-]_{aq}^2[A]_{org,free}^n} \tag{10}$$

The value of $(1 + \Sigma\beta_n[NO_3^-]^n)$ has been reported by Pai et al. (10) as 1.64. At constant $[NO_3^-]_{aq}$, a plot of log D_U against $\log[A]_{org,free}$ should be linear with slope n, the number of amide molecules bound to each uranium atom in the extracted species.

RESULTS AND DISCUSSION

Time of Equilibration

In order to determine the time required to attain the equilibrium condition, the extraction studies were carried out at two nitric acid concentrations (3 and 6 M) using ^{233}U tracer. The contact time was varied from 2 to 125 minutes, and aliquots were taken from the two phases after each contact and assayed. It was observed that 5 minutes duration (Table 2) was good enough to achieve the equilibrium condition. However, it was decided to maintain an equilibration time of 30 minutes in all studies.

Speciation Experiments

It is important to know the type of species formed by the extractant in the organic phase in order to understand the extraction behavior. An attempt was made to find the number of amide molecules attached to each nitric acid molecule as well as to each uranium atom extracted into the organic phase.

TABLE 2
D_U as a Function of Time of Equilibration;
[D2EHIBA] = 1 M in Dodecane

	D_U	
Equilibration time (minutes)	3.0 M HNO_3	6.0 M HNO_3
2	1.95	3.77
5	2.01	4.08
15	2.13	4.01
30	2.22	4.18
60	2.16	4.18
125	2.24	4.21

Depending on their relative concentrations, amides interact with HNO_3 to form a variety of species of the type $(amide)_2 \cdot HNO_3$, $amide \cdot HNO_3$, $amide \cdot (HNO_3)_2$, etc. Equilibria governing the formation of these adducts influence the availability of the free ligand concentration as well as third-phase formation. It was therefore of interest to investigate amide–HNO_3 equilibrium under the experimental conditions chosen in the present work.

Acid uptake was studied in the following two ways.

(a) Fixed Amide Concentration with Varying Nitric Acid Concentration

From the plot of $\{\log[H^+]_{org} - 2\log[H^+]_{aq}\}$ against $\log[A]_{org,free}$ (Fig. 1), a slope of 1.05 ± 0.12 was obtained which suggested that one HNO_3 molecule is bound to each amide molecule in the acid-amide adduct in the 1 to 4 M concentration range. The K_H value was found to be 0.157 ± 0.016. The distribution ratio data of HNO_3 with varying nitric acid concentration are shown in Table 3. It can be seen that the $D_{nitric\ acid}$ values remain almost constant over the 2 to 6 M concentration range.

(b) Varying Amide Concentration at a Fixed Nitric Acid Concentration

The amide concentration was varied from 0.1 to 1.0 M at 2 M HNO_3. $\log[H^+]_{org} - 2\log[H^+]_{aq}$ was plotted against $\log[A]_{org,free}$. A slope of 1.01 ± 0.18 was obtained, suggesting that one HNO_3 molecule is bound to each amide in the adduct in the organic phase. The K_H value was found to be 0.155 ± 0.046.

From the above two set of experiments it could be seen that 1) the concentration of HNO_3 in the aqueous phase was altered significantly due to acid up-

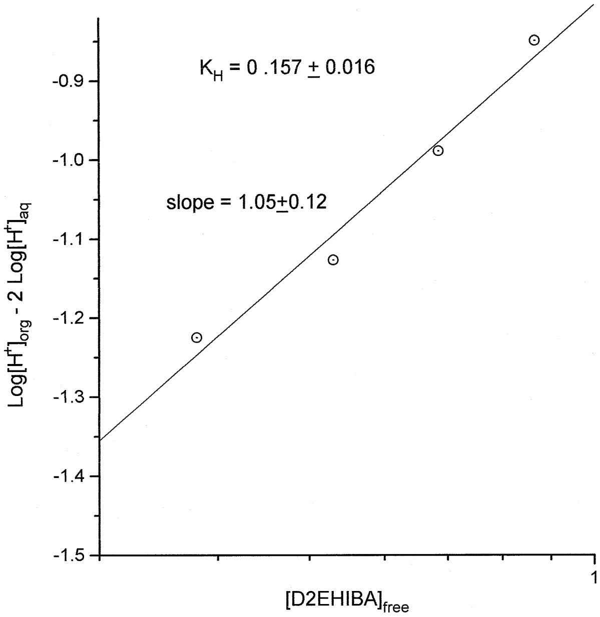

FIG. 1 Determination of K_H by varying HNO_3 concentration ($1\ M \leq [HNO_3] \leq 4\ M$); [D2EHIBA] = 1 M; diluent = *n*-dodecane.

take by amide, 2) with an increase in aqueous acid concentration, the fraction of free amide in the organic phase dropped sharply, and 3) the average K_H value for the dominating 1:1 adduct was 0.156 ± 0.048.

The number of amide molecules attached to each uranium atom extracted in the organic phase was evaluated using 2 M HNO_3 as the aqueous medium. As seen in Fig. 2, a slope with a value of 2.13 ± 0.08 was obtained, suggesting that two amide molecules are bound per UO_2^{2+} species extracted. So the species extracted in the organic phase is $UO_2(NO_3)_2 \cdot 2A$ where A = D2EHIBA, and the extraction constant (K_{ex}) is 0.87 ± 0.08.

TABLE 3
Distribution of Nitric Acid in the Two-Phase System; [D2EHIBA] = 1 M in Dodecane

No.	Initial $[HNO_3]$ (M)	Equilibrium $[HNO_3]_{aq}$ (M)	Equilibrium $[HNO_3]_{org}$ (M)	$D_{\text{nitric acid}}$
1	1.14	1.01	0.13	0.13
2	2.22	1.90	0.32	0.17
3	3.25	2.78	0.47	0.17
4	4.29	3.67	0.62	0.17
5	5.42	4.65	0.77	0.17
6	6.30	5.40	0.90	0.17

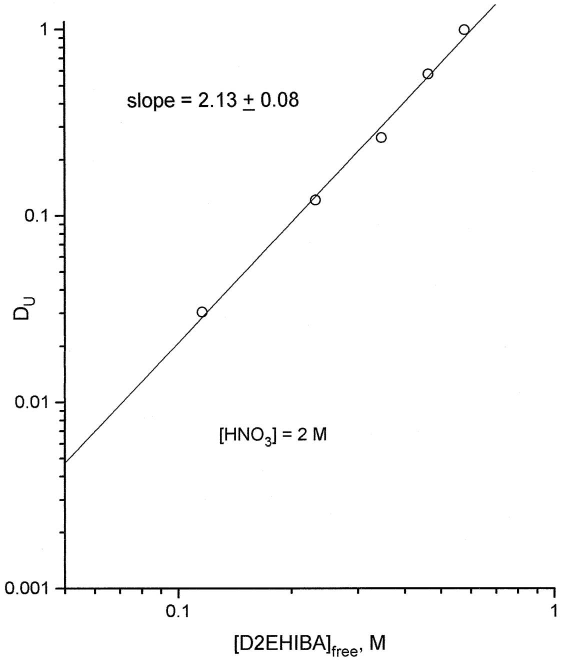

FIG. 2 Variation of D_U with D2EHIBA concentration (0.2 M ≤ [D2EHIBA] ≤ 1.0 M); [HNO$_3$] = 2 M.

Distribution of Uranium

The distribution ratio values of uranium (D_U) at various nitric acid concentrations were determined at the tracer level as well as under low loadings of U (1 g/L) and Th (1 g/L) employing 1 M D2EHIBA in *n*-dodecane (Fig. 3). The extraction of uranium was dependent on the concentration of nitric acid as well as that of uranium. When the nitric acid concentration was increased, nitrate ions formed extractable complex species with uranium and higher D_U values resulted. At higher nitric acid concentrations (>5 M) a plateau was observed in D_U values due to the interaction of the ligand with nitric acid and also because of the formation of metal anionic species, viz., $UO_2(NO_3)_3^-$, in aqueous phase (3, 4). Table 4 shows that with an increase of HNO$_3$ concentration, [D2EHIBA]$_{free}$ decreases significantly. As a consequence, the effect of U loading on contact with 1 g/L of U (though limited at lower acidity) is manifested much more at higher acidity. The experimentally observed decrease in D_U values (ΔD_U) is much more than what can be explained due to U loading alone. The reason for this abnormal decrease is not clear.

Figure 3 also shows that the presence of Th (1 g/L) does not influence D_U significantly. When the Th concentration was increased to 10 or 100 g/L, the salt effect was manifested clearly (Fig. 4). The distribution profile of U was influenced significantly when the Th concentration increased to 250 g/L. The

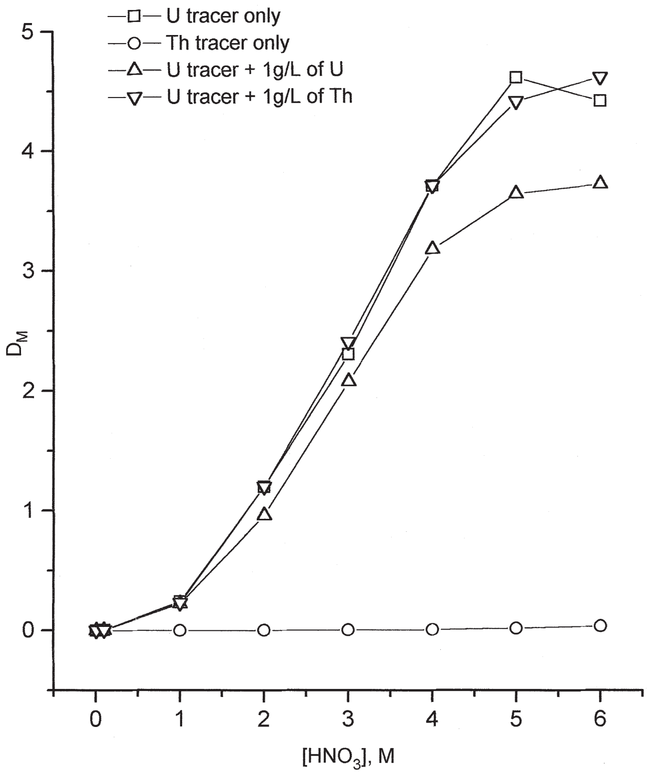

FIG. 3 Extraction behavior of uranium and thorium (at tracer concentration and at 1 g/L of the respective metal ions) under varying nitric acid concentrations.

extraction maximum shifted from ~5 M HNO_3 to pH 2.0. It appeared that the presence of 4.3 M NO_3^- ion resulted in the maximum D_U, which was otherwise attainable only at ~5 M HNO_3. Relatively larger values of the distribution ratio were explained on the basis of 1) decreased water activity of the aqueous phase due to a salt effect and 2) a larger ligand concentration at lower acidity. Preston et al. (11) also observed that the percent extraction of U(VI)

TABLE 4
Effect of U Loading on D_U

		D_U		
$[HNO_3]$ (M)	$[D2EHIBA]^*_{free}$ (M)	Tracer only	1 g/L of U	ΔD_U
1.0	0.88	0.24	0.22	0.02
2.0	0.65	1.19	0.96	0.23
3.0	0.47	2.37	2.08	0.29
4.0	0.35	3.69	3.17	0.48
5.0	0.26	4.60	3.63	0.97

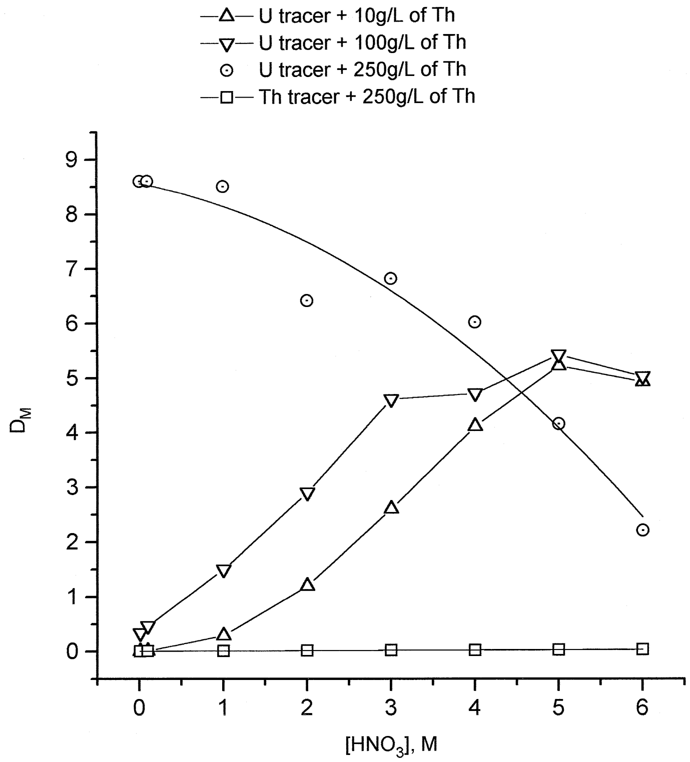

FIG. 4 Extraction behavior of uranium and thorium at higher concentrations of thorium under varying nitric acid concentrations.

by 0.5 M *N*,*N*-diethyl-*tert*-nonyl amide at 0.02 M HNO_3 increased from 12 to 50.9% when the sodium nitrate concentration was increased from 2.0 to 4.0 M. Similarly, Stevenson et al. (12) showed that D_U increased with 52% TBP from 2.3 (0.26 M HNO_3) to 7.0 [0.26 M HNO_3 + 0.125 M $Th(NO_3)_4$]. Lowering of D_U at higher acidity (>2.0 M HNO_3) is due to the formation of an anionic species, viz., ≥6.0 M NO_3^-. This was independently verified by measuring D_U values in ^{233}U tracer studies performed at various HNO_3 concentrations of 6–10 M: 4.4 (6.0 M), 3.8 (7.0 M), 3.3 (8.0 M), and 2.4 (10.0 M).

Distribution of Thorium

These studies have been carried out for two thorium concentrations, viz., carrier-free tracer ($\sim 10^{-11}$ M) and 250 g/L of thorium (1.08 M), at various nitric acid concentrations. It was observed from Figs. 3 and 4 that there was almost negligible extraction of thorium in comparison to uranium. D_{Th} varied from 1.5×10^{-3} to 4.0×10^{-2} for pure tracer and from 4.5×10^{-3} to 3.7×10^{-2} in the presence of 250 g/L of thorium. The poor extraction of thorium arose because of the role of steric factors in accommodating bulky branched

TABLE 5
Distribution Ratio Values (*D*) of Different Fission Products
in the Presence of 250 g/L of Thorium at Various Nitric Acid Concentrations.
Organic Phase: 1 M D2EHIBA in *n*-Dodecane

$[HNO_3]$ (M)	D_{Cs} $\times 10^4$	D_{Zr} $\times 10^2$	D_{Eu} $\times 10^4$	D_{Fe} $\times 10^3$	D_{Cs} $\times 10^3$	$D_{Ce}{}^a$ $\times 10^4$	$D_{Zr}{}^a$ $\times 10^3$
0.01	2.5	< 0.01	1.9	1.8	2.3	4.0	—
0.1	5.8	0.06	1.2	2.1	3.0	3.0	10
1.0	5.2	4.5	2.1	1.1	2.4	2.9	1.8
2.0	6.0	4.8	1.0	1.3	2.4	7.2	1.5
3.0	3.0	5.8	2.8	4.7	2.1	4.3	1.9
4.0	5.1	4.8	3.6	1.3	2.7	6.1	28
5.0	5.5	3.7	7.7	9.2	3.0	5.2	78
6.0	5.0	2.5	7.1	9.2	1.4	3.1	100

[a] For tracers only.

chain ligands like D2EHIBA in the thorium nitrate complex. Interestingly, distribution ratio values of thorium did not show a significant enhancement as a consequence of a salt effect. In contrast to U(VI), the small size of Th(IV) surrounded by four nitrate radicals hindered the interaction of D2EHIBA molecules essential for the solvation of $Th(NO_3)_4$ species and thereby the extraction. It appears that the steric effect is dominant over the salting effect.

Extraction of Fission Products

The distribution of certain fission products, viz., $^{152-154}$Eu, ^{137}Cs, ^{141}Ce, ^{95}Zr, and ^{59}Fe (for structural material Fe), in the system was studied. Fe, Cs, Ce, and Eu were not extracted ($D < 10^{-2}$) (Table 5) at the tracer level as well

TABLE 6
Comparison of D_U / D_{Zr} for 30% TBP and
1 M D2EHIBA Diluent: *n*-Dodecane

	D_U / D_{Zr}	
$[HNO_3]$ (M)	30% TBP[a]	1 M D2EHIBA
1.0	333	134
2.0	222	793
3.0	75	1247
4.0	50	131
5.0	23	59
6.0	6	44

[a] Ref. 13.

TABLE 7
Separation Factor Values for Uranium and Thorium Diluent: *n*-Dodecane

	S.F. (D_U/D_{Th})	
[HNO_3] (M)	30% TBP	1 M D2EHIBA
1	17	120
2	10	343
3	10	315
4	10	370
5	9	230
6	8	110

as in the presence of 250 g/L Th in the 0.01 to 6 M HNO_3 range. However, in the presence of 250 g/L, Zr was extracted to the extent of 2–6%. Extraction of Zr increased with nitric acid concentration. Table 6 shows that D2EHIBA is better than TBP for fission product decontamination in the 2–6 M HNO_3 acidity range. Extraction studies of fission products generally revealed that significant uranium decontamination can be achieved using D2EHIBA (Table 5).

Comparison of Separation Factors Values of D2EHIBA with TBP

The U(VI)/Th(IV) separation factor (S.F.) values for 1 M D2EHIBA were an order of magnitude better than those obtained for 30% TBP in the 1–6 M HNO_3 acidity range (13) (Table 7). This is a consequence of the poorer extraction of thorium in the present work.

It was interesting to observe that the S.F. values were uniformly larger (~30 times) with the amide than with TBP in the 2–4 M HNO_3 acidity range. Thus, D2EHIBA is particularly promising for application in uranium–thorium separation. It is imperative to investigate the effect of uranium loading, radiation field, and distribution behavior of Pa(V) to assess the suitability of this ligand for any large-scale application.

CONCLUSIONS

D2EHIBA extracts nitric acid to form a 1:1 species of the type $HNO_3 \cdot D2EHIBA$. The concentration equilibrium constant for acid extraction (K_H) has been evaluated as 0.156 ± 0.048.

When uranium is extracted by D2EHIBA, the extracted species is found to conform to $UO_2(NO_3)_2 \cdot 2D2EHIBA$ with a concentration extraction constant, K_{ex}, of 0.87 ± 0.08.

Distribution studies with uranium have shown that uranium extraction is enhanced by an increase in NO_3^- concentration caused by either 1) increasing the HNO_3 concentration or 2) increasing the $Th(NO_3)_4$ concentration, with the extraction maxima at 4.3 M NO_3^-.

The extraction of Th(IV) by D2EHIBA is very poor ($D_{Th} < 5 \times 10^{-2}$) even at higher HNO_3 or nitrate ion concentrations leading to high separation factor values. In comparison to the THOREX process (S.F. = 10 for TBP), S.F. values are significantly larger in the present work (>100).

The extraction of fission products and Fe by D2EHIBA is very poor. Thus, this amide displays better extraction behavior than TBP for fission product decontamination.

Finally, on the basis of better (U/Th) separation factor values and fission product decontamination, D2EHIBA appears to be a very promising alternative to TBP for the recovery and purification of ^{233}U from irradiated ^{232}Th. However, the acceptability of D2EHIBA depends on other aspects such as its chemical and radiolytic degradation behaviors and the limiting organic phase concentration of uranium.

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