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Separation studies of uranium and thorium using tetra(2-ethylhexyl) diglycolamide (TEHDGA) as an extractant

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The extraction behavior of uranium, thorium and nitric acid has been investigated for the TEHDGA/isodecyl alcohol/n-dodecane solvent system. Conditional acid uptake constant (K_H) of TEHDGA/n-dodecane and the ratio of TEHDGA to nitric acid were obtained as 1.72 and 1 : 0.96, respectively. The extracted species of uranium and thorium in the organic phase were found to be $UO_2(NO_3)_2 \cdot 2TEHDGA$ and $Th(NO_3)_4 \cdot 2TEHDGA$. A workable separation factor (D_{Th}/D_U) of the order of 300 was observed between thorium and uranium in the nitric acid range of 0.5M to 1.5M. Similar separation factor was also achieved at higher acidity when thorium was present in large concentration compared to uranium. These results indicate that TEHDGA solvent system could be a potential candidate for separation of thorium from uranium.

Introduction

Nuclear power generation program based on thorium fuels necessitates the effective separation of uranium and thorium from each other.[1,2] In this regard there has been considerable interest in developing new and improved solvent systems for effective separation of these actinides from each other. Various extractants of the class of organophosphorous and monoamides have been investigated for this purpose.[3,4] However, a very important extractant of the diglycolamide class which has been extensively investigated for minor actinide partitioning, has not been exclusively studied for the separation of uranium and thorium. For diglycolamide based solvents, it has been observed that the extractability for various actinides at 1M nitric acid were in the order of An(III), An(IV)>An(VI)>An(V),[5] indicating a higher extraction of Th(IV) over U(VI). The diglycolamide family, tetra(2-ethylhexyl)diglycolamide (TEHDGA) has been extensively studied by us,[6] therefore, this ligand was chosen for the present study as well.

In this paper the extraction behavior of thorium, uranium and nitric acid in the TEHDGA/30% isodecyl alcohol/n-dodecane were studied to investigate the possibility of separation of uranium and thorium and to understand the acid uptake properties of this solvent system. Attempts were also made to investigate the separation of trace amount of uranium from macro amount of thorium at higher acidity to explore the application of TEHDGA solvent system in the reprocessing of irradiated Th-U fuel.[3]

Experimental

Chemicals, reagents and instrumentation

TEHDGA was synthesized by the condensation of diglycolylchloride and bis (2-ethylhexyl) amine in presence of triethyl amine by a known procedure.[6]

The product was characterized by GC-MS and elemental analyzer. GC-MS was performed on Thermo Finnigan Trace DSQ GC-MS instrument with a single quadrupole mass spectrometer at 70 eV using 15 m×0.25 mm DB5 fused silica capillary column. Helium was the carrier gas and the temperature program was 100 °C for 1 minute, increased to 280 °C at 10 °C per minute rise and held at 280 °C for 20 minutes. The injector temperature was 300 °C. Elemental analysis was performed on Thermo Finnigan Flash EA TM1112 analyzer.

The results are as follows: GC-MS: 9.05 min, 1.89%, *m*/*z* 241 calculated for $HN(C_8H_{17})_2$; 22.00 min, 28.13 min, 98.11%, *m*/*z* 582 calculated for $O[CH_2C(O)N(C_8H_{17})_2]_2$.

Elemental analysis: C: 74.471%, H: 12.488%, N: 5.108%, and O: 8.0%; calculated C: 74.41%, H: 12.5%, N: 4.82% and O: 8.28%.

AR grade n-dodecane and isodecyl alcohol were obtained from local market and were used as such. The standard stock solutions of metal ions and nitric acid were prepared by dissolving requisite amounts of AR grade $UO_2(NO_3)_2 \cdot 6H_2O$, $Th(NO_3)_4 \cdot 5H_2O$ and nitric acid in deionized water and were standardized by known methods.

Distribution studies

The solvent extraction experiments were carried out at ambient temperature by batch extraction method at equal volume of organic to aqueous phase. The contact time for all the batch extraction studies was 10 minutes.

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The distribution coefficient D_M of a metal was determined as a ratio of concentration of the metal in organic phase to aqueous phase. The separation factor was calculated by determining D_{Th} and D_U in the presence of each other and defined as D_{Th}/D_U.

For acid distribution studies, organic phase were contacted with HNO_3 at varying initial acid concentrations (0.1 to 5.0M). The acidity of the aqueous as well as the organic phase was determined by using standard acid-base titration methods.[7] The solvent for acid distribution studies was constituted without phase modifier.

For metal ion distribution studies, the organic phase was equilibrated with an aqueous phase containing uranium and thorium at various nitric acid concentrations. Two phases were separated and the aqueous phase was analyzed for metal ions by ICP-ES (JY-238, Emission Horiba Group, France). For extractant dependency studies, the organic phase was prepared by keeping the isodecyl alcohol concentration of 30% (v/v) unchanged for all the different extractant concentrations.

Results and discussion

Extraction of nitric acid

To investigate the acid extraction behavior of TEHDGA, it is important to have quantitative knowledge of their basicity in terms of conditional acid uptake constant (K_H)[8–10] of these extractants under similar conditions.

The extraction of nitric acid by diglycolyl based ligands involves the protonation of the carbonyl group according to the following equation:

$$E\,(\text{org.}) + nH^+(\text{aq.}) + nNO_3^-(\text{aq.}) \rightleftarrows E\cdot nHNO_3(\text{org.}) \qquad (1)$$

where E is the neutral diglycolyl extractant and n is the number of nitric acid molecule involved in the formation of adduct. The acid uptake constant K_H is given by:

$$K_H = \frac{[E\cdot nHNO_3]_{org.}}{[E]_{org.}[H^+]^n_{aq.}[NO_3^-]^n_{aq.}} \qquad (2)$$

where $[E]_{org.}$ is the concentration of free organic extractant and calculated as:

$$[E]_{org.} = [E]_{initial} - [E\cdot nHNO_3]_{org.}$$

As the data for the activities of HNO_3 and free TEHDGA in the organic phase are not available, therefore, the concentration terms have been used and the equilibrium constant is referred as conditional acid uptake constant. Since in aqueous medium $[H^+] = [NO_3^-]$, the above equation can be written as:

$$K_H = \frac{[E\cdot nHNO_3]_{org.}}{[E]_{org.}[H^+]^{2n}_{aq.}} \qquad (3)$$

Taking logarithm on the both sides of Eq. (3) and rearranging:

$$\log[E\cdot nHNO_3]_{org.} - \log[E]_{org.} = \log K_H + 2n\log[H^+]_{aq.} \qquad (4)$$

where $[E\cdot nHNO_3]$ denotes the concentration of H^+ in the organic phase, therefore Eq. (4) can be written as:

$$\log[H^+]_{org.} - \log[E]_{org.} = \log K_H + 2n\log[H^+]_{aq.} \qquad (5)$$

where $[H^+]_{aq.}$ can be calculated from the titre value (T)[8] and the dissociation constant of HNO_3 ($K_a = 23.5$).[8]

$$K_a = \frac{[H^+]_{aq.}[NO_3^-]_{aq.}}{[HNO_3]_{aq.}} \qquad (6)$$

where the titre value (T) is the total acidity in aqueous phase comprising of dissociated and undissociated nitric acid, hence, $T = [HNO_3]_{aq.} + [H^+]_{aq.}$.

Thus, from Eq. (5), the plot of $\log[H^+]_{org.} - \log[E]_{org.}$ vs. $\log[H^+]_{aq.}$ gives a straight line with intercept of $\log K_H$ and slope of $2n$.

The slope value obtained from the graphic is 1.918±0.106 (Fig. 1), suggesting that the stoichiometry of the extracted molecule being 1 : 0.96 for TEHDGA : HNO_3. The basicity (K_H) of TEHDGA as calculated from the intercept is 1.72±0.2. This indicates that basicity of TEHDGA is comparable to CMPO ($K_H = 2.0$)[9] and less than its straight chain isomer namely N,N,N',N'-tetraoctyl diglycolamide (TODGA).[8] The lower basicity of TEHDGA could be attributed to the branching of alkyl group attached to nitrogen atom of the molecule. As discussed earlier[6,11] lower basicity results in lower uptake of metal ions, resulting in more selectivity during extraction.

Extraction of uranium and thorium

At various extractant concentration: The extraction of uranium and thorium at 1.0 g/L, each in 3.0M nitric acid, was investigated at various extractant concentrations. Separate experiments were carried out for uranium and thorium. The dependency of D_{Th} and D_U on TEHDGA concentrations is shown in Fig. 2. The slopes were analyzed to be 2.00425±0.13849 for uranium and 2.20071±0.21751 for thorium. Therefore, under these conditions the extracted species could be written as $UO_2(NO_3)_2\cdot 2TEHDGA$ and $Th(NO_3)_4\cdot 2TEHDGA$. These stoichiometries were also determined by saturating the organic phase with uranium and thorium at 3M nitric acid. For 0.1M TEHDGA and 0.2M TEHDGA in 30% isodecyl alcohol/n-dodecane, the saturation loading values for uranium were obtained as 9.2 g/L and 18.8 g/L. These values for thorium were 11.2 g/L and 24.4 g/L, respectively. The stoichiometries obtained from both the above approaches were found to be comparable. This could be due to the fact that slope analysis experiments were carried out in the presence of significantly higher concentration of metal ion in the aqueous phase compared to usual practice where these experiments are performed with trace concentrations of metal ions. No third phase formation was observed during all these studies.

At various nitric acid concentrations: The extraction behavior of uranium and thorium present together at concentrations of 1.0 g/L each in the aqueous phase was studied using 0.2M TEHDGA/30% isodecyl alcohol/n-dodecane as a function of nitric acid concentrations (Fig. 3). A workable separation factor of the order of 300 was observed in the nitric acid range of 0.5 to 1.5M which gradually decreases with increase in nitric acid concentration.

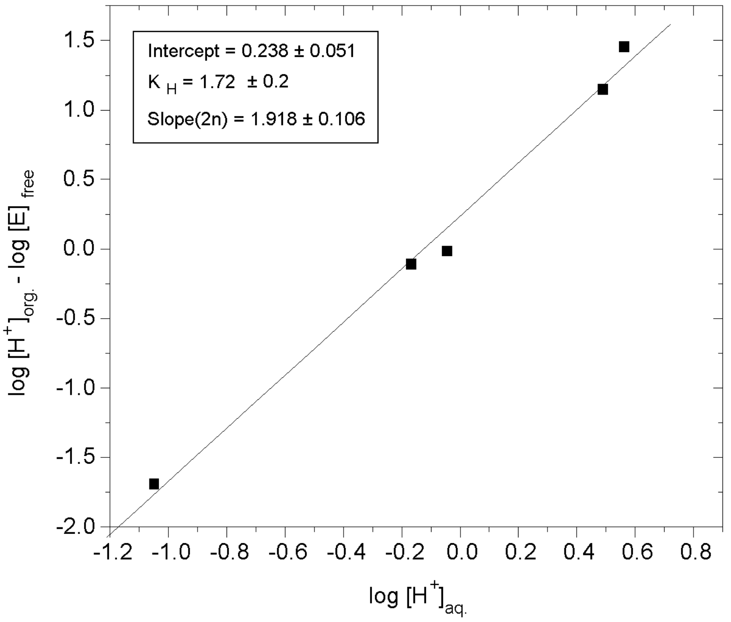

Fig. 1. Extraction of HNO_3 from aqueous solution by 0.2M TEHDGA/n-dodecane

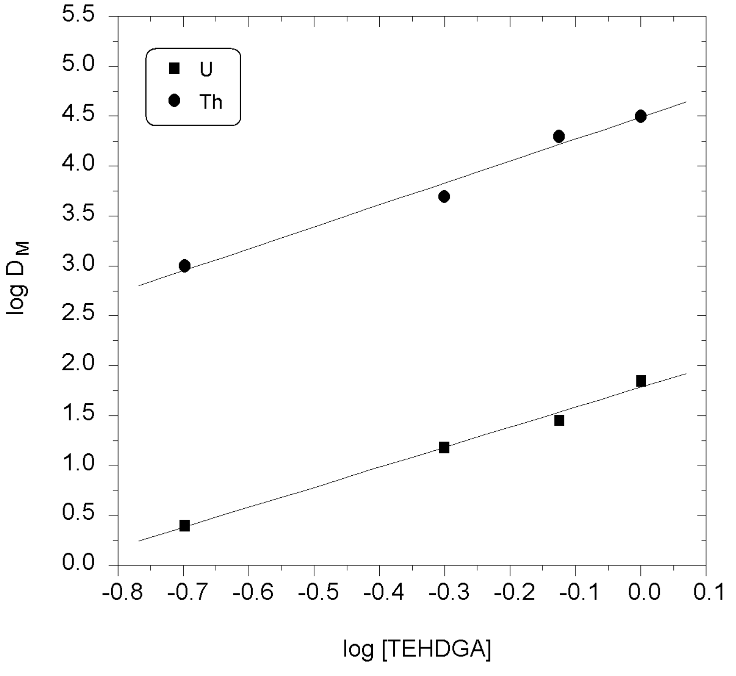

Fig. 2. Dependence of D_{Th} and D_U on TEHDGA concentration. Aqueous phase: 3.0M nitric acid (initial concentration)

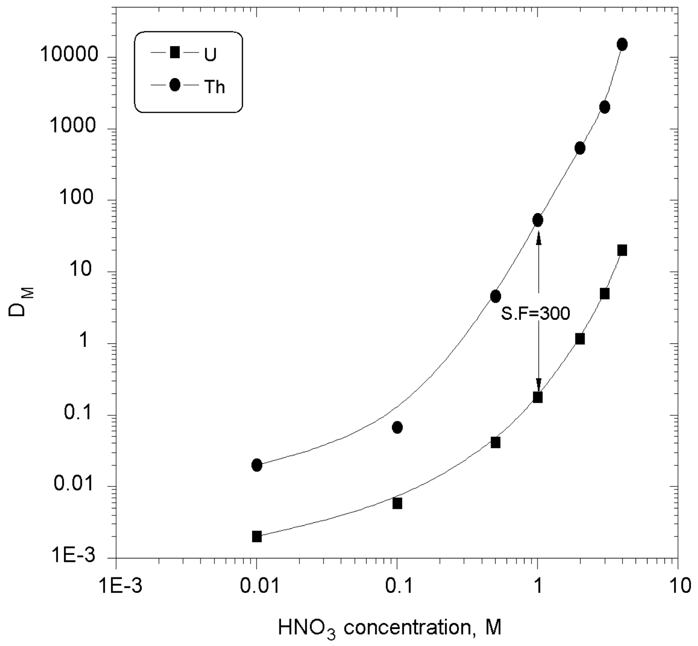

Fig. 3. Extraction of thorium and uranium by 0.2M TEHDGA/30% isodecyl alcohol/n-dodecane as a function of nitric acid concentration

At various metal ion concentrations

0.2M TEHDGA/30% isodecyl alcohol/n-dodecane was used to investigate the extraction of thorium and uranium as a function of nitric acid. The concentration of thorium was in the range of 1.0 g/L to 30 g/L in the presence of 200 ppm of uranium. The separation factors at various amount of thorium are listed in Table 1. It is observed that separation factor increases with the increase of the thorium concentration in the aqueous medium. This may be attributed to a higher extractability of thorium over that of uranium which results in rejection of uranium from the organic phase in the presence of large concentration of thorium.

Table 1. Separation factor (S.F. = D_{Th}/D_U) of uranium and thorium at 200 ppm uranium and various thorium concentrations

HNO_3, M	Initial concentration of Th(IV)		
	1.0 g/L	15.0 g/L	30.0 g/L
0.1	7.4	8.57	10
0.5	15	95	110
1.0	50	130	172
2.0	75	200	257
3.0	130	272	300
4.0	140	285	317

[TEHDGA] = 0.2M TEHDGA/30% isodecyl alcohol/n-dodecane.

Conclusions

TEHDGA extracts nitric acid to form a 1 : 1 species of the type TEHDGA : HNO_3. The basicity of TEHDGA in term of conditional acid uptake constant (K_H) has been evaluated as 1.72. Separation of thorium from uranium at low concentrations is feasible using TEHDGA in the nitric acid range of 0.5 to 1.5M. At higher acidity this separation is achieved by using macro amount of thorium with respect to uranium. As dissolution of the irradiated Th–U fuel generate solutions containing macro amount of thorium compared to uranium in high nitric acid concentration, this solvent system, therefore, appears to be a potential candidate for reprocessing of such type of solutions. Further continuous counter current extraction studies are in progress to process the feed solutions under simulated conditions.

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