

Synthesis and characterization of *N,N,N',N'*-tetraalkyl-4-oxaheptanediamide as extractant for extraction of uranium(VI) and thorium(IV) ions from nitric acid solution

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Abstract Tridentate ligand *N,N,N',N'*-tetraoctyl-4-oxaheptanediamide(TOOHA) and other three analogous diamides have been prepared and characterized by using NMR spectra and element analysis. The extraction of UO_2^{2+} and Th^{4+} with the present extractants was investigated at 293 ± 1 K from nitric acid solutions. *n*-Octane was found to be the most suitable diluent in the present study compared with other diluents tested. Extraction distribution ratios (*D*) of U(VI) and Th(IV) have been studied as a function of aqueous concentrations of HNO_3 , extractant concentrations. The results indicated that U(VI) is mainly extracted as $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TOOHA}$. In the case of Th^{4+} ion, the possible compositions of extracted species in organic phase were presumed to be $\text{Th}(\text{NO}_3)_4 \cdot 2\text{TOOHA}$ and $\text{Th}(\text{NO}_3)_4 \cdot 3\text{TOOHA}$. In addition, the influence of concentration of sodium nitrate as salting-out agent on the distribution ratio of U(VI) and Th(IV) with TOOHA was also evaluated.

Keywords 4-Oxaheptanediamide · Extraction · Uranium · Thorium · Separation

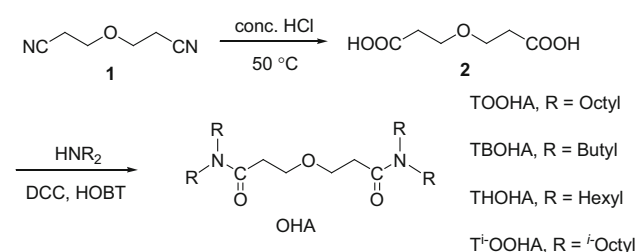
Introduction

In the past decades, extraction and separation of actinides and lanthanides using amide as an alternative to phosphorus-containing extractant has attracted interesting in the processes of extracting and refining nuclear fuel materials,

the treatment of radioactive wastes and radioanalytical chemistry [1–6]. It is due to the fact that amide ligand represents several outstanding advantages compared to phosphorus-containing extractant, such as facile preparation, high chemical and radiolytic stability, complete incineration which dramatically reduces the amounts of waste [7, 8]. The amide as extractant for the extraction of actinides was pioneered by Siddall in 1963 [9]. In contrast with monoamides, diamides have attracted extra attention due to strong complexation and better extraction ability. For instance, malondiamides were widely developed for the extraction of actinides during the 1980s [10]. Therefore, *N,N'*-dimethyl-*N,N'*-dioctylhexylethoxy malonamide (DIAMEX) ligand was ultimately found to have the best extraction behavior by further structural optimizations in the family of malondiamides. In the early 1990s, Stephan et al. [11] introduced an oxygen atom between both amide groups of malondiamide to synthesize diglycolamides (DGAs). The DGAs were assumed to associate with metal ions to form two bridged five-membered rings based on three oxygen atoms of one ether and two amide groups, and expected to increase the affinity with metal ions as tridentate ligands [12]. However, some important studies revealed that DGAs still are bidentate or imperfect tridentate ligands due to intrinsic property of chemical structure [13, 14]. In fact, as we all know, the two bridged five-membered rings are not as stable as two bridged six-membered rings due to the larger ring tension. For instance, naphthalene and quinoline are extremely common compounds, but similar species containing two bridged five-membered rings is rare.

Based on the above reason, we envisioned to synthesize *N,N,N',N'*-tetraoctyl-4-oxaheptanediamide(TOOHA) and its three analogous diamides *N,N,N',N'*-tetrabutyl-4-oxaheptanediamide(TBOHA), *N,N,N',N'*-tetrahexyl-4-oxa-

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Scheme 1 Synthesis of diamide extractants

heptanediamide (THOHA) and *N,N,N',N'*-tetra isooctyl-4-oxaheptanediamide ($\text{T}^i\text{-OOHA}$). These 4-oxaheptanediamide (OHA) ligands were assumed to be associated with the metal ion to form stable two bridged six-membered rings, and significantly increase extraction behavior to actinides. In this study, we described the synthesis and characterization of various substituted OHA derivatives, and their extraction properties for uranium(VI) and thorium(IV) ions from nitric acid solution.

Experimental

Materials and instrumentation

All diluents and reagents were of analytical grades and used without any further purification. Analytical grade $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ and U_3O_8 were used. ^1H NMR (400 M) and ^{13}C NMR (400 M) spectra of extractants prepared were recorded with a Varian Mercury-400 spectrometer in CDCl_3 by using TMS as the internal standard. All the extractants were further characterized by Vario EL elemental analyzer. The concentration of UO_2^{2+} or Th^{4+} in aqueous phase was determined by a 723 N model UV-Vis Spectrophotometer (Shanghai Precision and Scientific Instruments Co., Ltd., Shanghai, China).

Synthesis of extractants

TOOHA and its three analogous TBOHA, THOHA, $\text{T}^i\text{-OOHA}$ were synthesized in our laboratory as depicted in Scheme 1. First, commercially available 3,3'-oxydipropionitrile **1** was treated with concentrated hydrochloric acid (HCl) to give the corresponding 3,3'-oxydipropionic acid **2** in excellent yield for 24 h; subsequent reaction of 3,3'-oxydipropionic acid **2** with an appropriate dialkylamine afforded the expected ligand TOOHA, TBOHA and THOHA, $\text{T}^i\text{-OOHA}$ in the presence of dicyclohexylcarbodiimide (DCC) and 1-hydroxybenzotriazole (HOBT) in dichloromethane.

TOOHA, TBOHA, THOHA and $\text{T}^i\text{-OOHA}$ solutions of 8.0×10^{-2} mol/mL were prepared by dissolving the

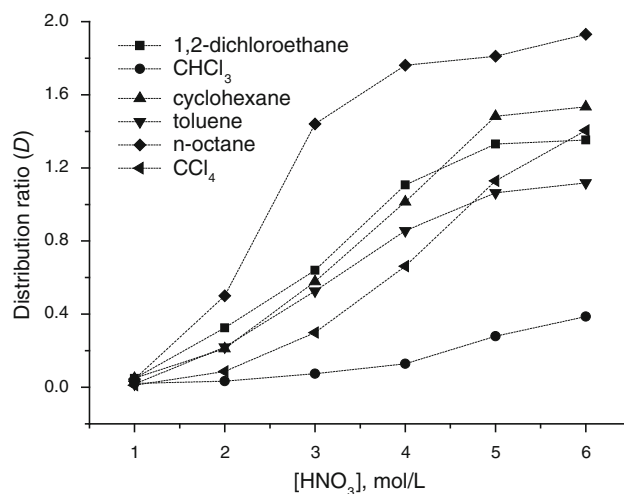


Fig. 1 Dependence of the distribution ratio (*D*) of U(VI) on various diluents using constant molar TOOHA from 1.0 to 6.0 M HNO_3 solution. $[\text{TOOHA}] = 0.05$ M, $[\text{UO}_2(\text{NO}_3)_2] = 6.301 \times 10^{-4}$ M, $T = 293 \pm 1$ K

required amount of the mentioned reagents in organic solvent, which were used for the distribution experiments after proper dilution. Sodium nitrate solution of 4.0 mol/mL was used for ionic strength adjustment. The solvents were pre-saturated before use in order to prevent volume changes of the phases during extraction. The extraction was carried out at room temperature.

For a sample in each extraction experiment, 3.00 mL of diluent containing 5–80 mM extractant (pre-equilibrated with an aqueous phase and no metal ion) was placed in a 10 mL plastic vial and mixed with 3.00 mL of $\text{UO}_2(\text{NO}_3)_2$ or $\text{Th}(\text{NO}_3)_4$ aqueous solution at the desired pH at 293 ± 1 K. In preliminary experiments, it had been found that the mixture was shaken for 30 min, and adequate to reach equilibrium. After phase disengagement by centrifugation (2 min, 2,000 rpm/min), duplicate 2.00 mL aliquots were taken from the aqueous phase. The remaining concentration of UO_2^{2+} or Th^{4+} in the aqueous phase was determined by the Arsenazo-III spectrophotometric method. The concentration of UO_2^{2+} or Th^{4+} in the organic phase was calculated by mass balance.

Results and discussion

Effect of nitric acid concentration in various diluents

Based on constant molar TOOHA concentration, different aliphatic and aromatic diluents were evaluated for the extraction of U(VI) with the increase of nitric acid concentration. As shown in Fig. 1, for same concentration of nitric acid, the values of distribution ratios are different in

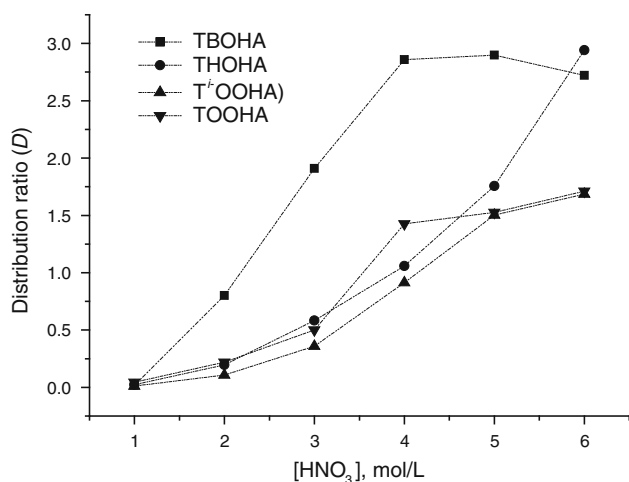


Fig. 2 The dependences of the extraction of U(VI) on different extractants from 1.0 to 6.0 M HNO₃ solution. Organic phase, [OHA] = 0.05 M in *n*-octane; aqueous phase, [UO₂(NO₃)₂] = 6.301 × 10⁻⁴ M, T = 293 ± 1 K

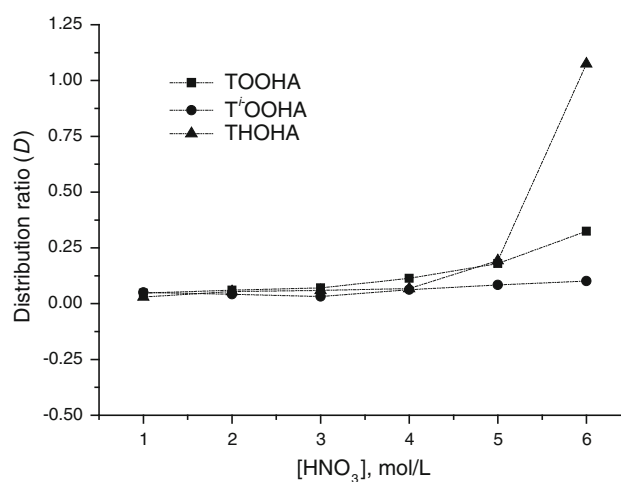


Fig. 3 The dependences of the extraction of Th(IV) on different extractant from 1.0 to 6.0 M HNO₃ solution. Organic phase, [OHA] = 0.05 M in *n*-octane; aqueous phase, [Th(NO₃)₄] = 4.310 × 10⁻⁴ M, T = 293 ± 1 K

various diluents although the tendency of the change in extraction distribution is similar for all diluents. In all the range of concentrations tested, as the concentration of nitric acid increases, the distribution ratio also increases. It indicates that no obvious competing extraction of nitric acid appeared in the range of 1.0–6.0 M of nitric acid in the proposed condition. Compared to other solvents investigated, *n*-octane demonstrated excellent extraction behavior in nitric acid solution of relatively high acidity. Therefore, *n*-octane was considered as preferable diluent for further extraction study.

Optimization of extractant in various HNO₃ concentration

Figures 2 and 3 show the effect of nitric acid concentration on the distribution ratio (*D*) of U(VI) and Th(IV) between the two phases based on 0.05 mol/L of the above mentioned extractants. In general, the *D*_{U(VI)} increases with increasing the concentration of HNO₃ from 1.0 to 6.0 M in exception with TBOHA. In the case of TBOHA, the *D*_{U(VI)} reaches a maximum value at about 5.0 M HNO₃, after which *D*_{U(VI)} slightly decreases. This decrease can be attributed to competition of U(VI) ions and HNO₃ for the coordination sites of TBOHA. It is also noted that the distribution ratio of Th(IV) slightly increases with increasing nitric acid concentration up to 6.0 M. However, the Th(IV) extraction was always significantly lower than that of U(VI). In addition, although the extractant of TBOHA always show better characteristic extraction behavior in extraction of uranyl ion compared to other three extractants, unfortunately, TBOHA has a strong

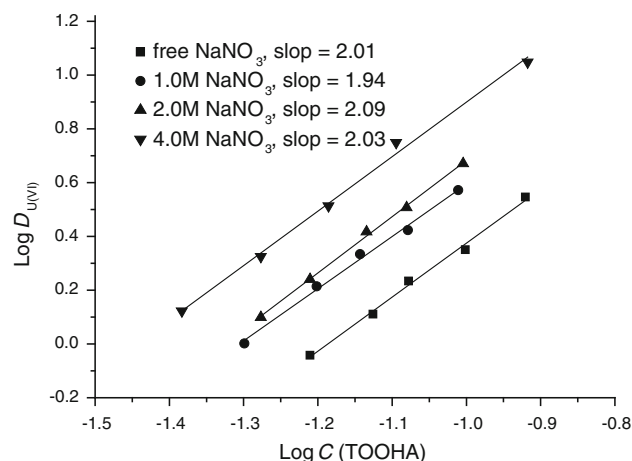


Fig. 4 Effect of TOOHA concentrations in the organic phase on the distribution ratios of UO₂²⁺ in the presence of salting-out agent; [HNO₃] = 4.0 M, [UO₂(NO₃)₂] = 6.301 × 10⁻⁴ M, T = 293 ± 1 K, [NaNO₃] = 0, 1, 2, 4 M

tendency to form a third phase in aliphatic solvents. In our experiments, to form a third phase was often observed in TBOHA extraction system. Therefore, as a compromise of distribution ratio (*D*) and extraction behavior, TOOHA as a preferable extractant was chosen for the following extraction experiments. In addition, based on the above large difference of distribution ratios, we must conclude that a better U–Th separation could be achieved for the extraction of U(VI) and Th(IV). To compare *D*_{U(VI)} values in Fig. 2 with ones in Fig. 3, the best separation of U(VI) from Th(IV) can be proceeded from 4.0 M HNO₃ with TOOHA as a preferable extractant.

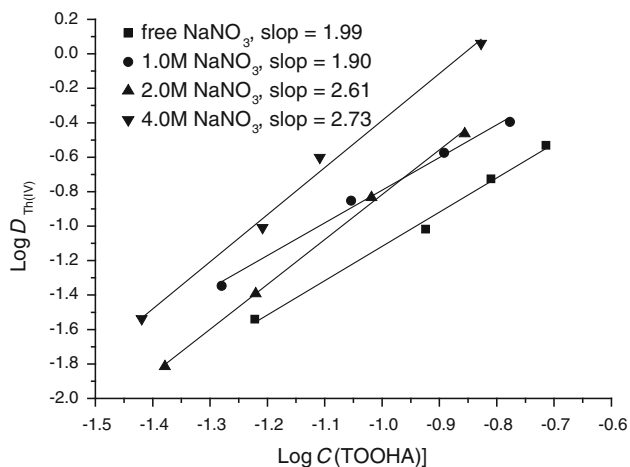
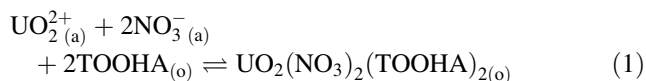


Fig. 5 Extraction dependence of Th^{4+} on TOOHA concentration in the presence of salting-out agent. $[\text{HNO}_3] = 4 \text{ M}$, $[\text{Th}(\text{NO}_3)_4] = 4.310 \times 10^{-4} \text{ M}$, $T = 293 \pm 1 \text{ K}$, $[\text{NaNO}_3] = 0, 1, 2, 4 \text{ M}$

Effect of extractant and salting-out agent concentrations

The extraction of uranium(VI) and thorium(IV) from 4.0 mol/L nitric acid solution with TOOHA increases with increasing extractant and salting-out agent (NaNO_3) concentrations (Figs. 4, 5).

The extraction of UO_2^{2+} in Fig. 4 shows the linear relations of $\log D_U$ versus $\log[\text{TOOHA}]_{(o)}$ at the different ionic strengths (the plots in figures are the averages of two experiments). The calculated slopes are about two in case of U(VI). As we known, the coordination number of U in UO_2^{2+} manner is 6 [11]. Thus, the present result suggests TOOHA functions as a tridentate ligand, which is in good agreement with our expectation (see “Introduction” section), and is distinct with diglycolamide extractants reported [9]. The plots of $\log D_U$ versus $\log[\text{TOOHA}]_{(o)}$ also indicates that the extracted complex can be described as $\text{UO}_2(\text{NO}_3)_2(\text{TOOHA})_2$, the extraction reaction can be expressed as follows:



For the above extraction reaction, the equilibrium constant K_{ex} can be written as:

$$K_{\text{ex}} = \frac{[\text{UO}_2(\text{NO}_3)_2(\text{TOOHA})_{2(o)}]}{[\text{UO}_2^{2+}]_{(a)}[\text{NO}_3^-]_{(a)}^2[\text{TOOHA}]_{(o)}^2}, \quad (2)$$

where subscripts (a) and (o) stand for the presence of the species in the aqueous and organic phase, respectively. In view of the tracer metal extracted, the distribution ratio D is described as:

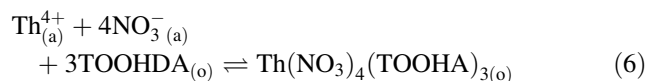
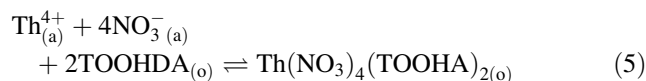
$$D = \frac{[\text{UO}_2(\text{NO}_3)_2(\text{TOOHA})_{2(o)}]}{[\text{UO}_2^{2+}]_{(a)}} \quad (3)$$

Introducing distribution ratio to the equilibrium Eq. 2, which can be rewritten by taking the logarithm and rearranged as:

$$\log D = \log K_{\text{ex}} + 2\log [\text{NO}_3^-]_{(a)} + 2\log [\text{TOOHA}]_{(o)} \quad (4)$$

Thus, instead of activities with molar concentrations, values of equilibrium constants of U(VI) can be easily determined by using the slope method according to Eq. 4.

The linear relations of $\log D_{\text{Th}}$ with $\log[\text{TOOHA}]$ are illustrated in Fig. 5. The calculated slopes are within the range from 1.90 to 2.73. As we known, Th^{4+} has a coordination number of 8 or 9 [11]. Based on these non integral data, so we can assume at least two following reactions for Th^{4+} extraction:



The above data suggest that the dominating compositions of extracted species in organic phase is $\text{Th}(\text{NO}_3)_4 \cdot 2\text{TOOHA}$ in low nitrate ion; But, it has a tendency to form $\text{Th}(\text{NO}_3)_4 \cdot 3\text{TOOHA}$ species with increasing nitrate ion concentrations or stronger salting-out effect. Because Th^{4+} has a coordination number of 8 or 9, the present results suggested that $\text{Th}(\text{NO}_3)_4 \cdot 2\text{TOOHA}$ species must have inner sphere hydration under low ionic strength.

Figures 4 and 5 also show the effect of sodium nitrate concentrations (salting-out agent) on the distribution ratios of U(VI) and Th(IV) while keeping constant acid concentration at 4.0 M. It is clear that the distribution ratios of U(VI) dramatically increase as initial nitrate ion concentrations increase. Due to D_{Th} only slightly increase accompanying with increasing concentrations of salting-out agent. Therefore, a maximum U–Th separation could be completed for the extraction of U(VI) and Th(IV). The separation factor for $D_{\text{U(VI)}}/D_{\text{Th(IV)}} > 10$ shows the potential value of TOOHA extractant in U(VI)/Th(IV) separations.

Spectroscopic data

After purification and identification, the yields of TOOHA, TBOHA, THOHA and $\text{T}^i\text{-OOHA}$ are 75.8, 64.3, 73.0 and

74.2 %, respectively, and the purity of all the ligands was found to be >97 %. For TOOHA, ^1H NMR(CDCl_3 , 400 MHz): δ 3.78 (t, $J = 7.2$ Hz, 4H), 3.28 (t, $J = 7.6$ Hz, 4H), 3.20 (t, $J = 7.6$ Hz, 4H), 2.59 (t, $J = 6.8$ Hz, 4H), 1.50–1.59 (m, 8H), 1.19–1.31 (m, 40H), 0.86–0.90 (q, 12H) ppm; ^{13}C NMR(CDCl_3 , 100 MHz): δ 170.11, 67.28, 47.91, 45.80, 33.30, 31.66, 29.26, 29.14, 29.00, 27.66, 26.96, 26.83, 22.51, 13.96. $\text{C}_{38}\text{H}_{76}\text{N}_2\text{O}_3$ (609.02): calcd. C 74.94 %, H 12.58 %, N 4.60 %, O 7.88 %; found C 74.63 %, H 12.54 %, N 4.61 %, O 7.90 %.

For TBOHA, ^1H NMR(CDCl_3 , 400 MHz): δ 3.77 (t, $J = 7.2$ Hz, 4H), 3.28 (t, $J = 7.6$ Hz, 4H), 3.21 (t, $J = 7.6$ Hz, 4H), 2.59 (t, $J = 6.8$ Hz, 4H), 1.44–1.55 (m, 8H), 1.24–1.33 (m, 8H), 0.88–0.96 (m, 12H) ppm; ^{13}C NMR(CDCl_3 , 100 MHz): δ 170.45, 67.36, 47.82, 45.72, 33.40, 31.15, 29.86, 20.22, 20.10, 13.84. $\text{C}_{22}\text{H}_{44}\text{N}_2\text{O}_3$ (384.60): calcd. C 68.70 %, H 11.53 %, N 7.28 %, O 12.48 %; found C 68.93 %, H 11.55 %, N 7.26 %, O 12.51 %.

For THOHA, ^1H NMR(CDCl_3 , 400 MHz): δ 3.77 (t, $J = 6.8$ Hz, 4H), 3.28 (t, $J = 7.6$ Hz, 4H), 3.21 (t, $J = 7.6$ Hz, 4H), 2.59 (t, $J = 6.4$ Hz, 4H), 1.49–1.59 (m, 8H), 1.19–1.31 (m, 24H), 0.86–0.91 (q, 12H) ppm; ^{13}C NMR(CDCl_3 , 100 MHz): δ 170.20, 67.30, 47.97, 45.85, 33.36, 31.49, 28.99, 27.64, 26.61, 26.48, 22.51, 13.91. $\text{C}_{30}\text{H}_{60}\text{N}_2\text{O}_3$ (496.81): calcd. C 72.53 %, H 12.17 %, N 5.64 %, O 9.66 %; found C 75.79 %, H 12.20 %, N 4.61 %, O 9.68 %.

For Tⁱ-OOHA, ^1H NMR(CDCl_3 , 400 MHz): δ 3.77 (t, $J = 6.8$ Hz, 4H), 3.23–3.33 (m, 4H), 3.14–3.21 (m, 4H), 2.51 (t, $J = 6.8$ Hz, 4H), 1.60–1.65 (m, 4H), 1.24–1.27 (m, 32H), 0.84–0.90 (q, 24H) ppm; ^{13}C NMR(CDCl_3 , 100 MHz): δ 171.11, 67.47, 51.85, 48.55, 38.30, 36.86, 33.72, 30.45, 30.36, 28.66, 23.73, 23.66, 22.93, 13.93, 10.74, 10.57. $\text{C}_{38}\text{H}_{76}\text{N}_2\text{O}_3$ (609.02): calcd. C 74.94 %, H 12.58 %, N 4.60 %, O 7.88 %; found C 75.14 %, H 12.63 %, N 4.60 %, O 7.89 %.

Conclusion

In conclusion, different types of structurally modified 4-oxaheptanediamide ligands have been prepared. TOOHA was chosen as a new chelating ligand for extracting U(VI) and Th(IV) in *n*-octane. $\text{UO}_2(\text{NO}_3)_2(\text{TOOHA})_2$ was determined as predominant extracted species by comparing the distribution ratios (D_{U}) of uranium(VI), in the concentration ranges of TOOHA and HNO_3 between the aqueous and organic phases. The extraction of UO_2^{2+} into *n*-octane by strong complexation with TOOHA from nitric acid aqueous solution indicates 4-oxaheptanediamides probably functions as a true tridentate ligand in extraction process, rather than bidentate chelation like diglycolamide extractant. Excellent separation factors for $D_{\text{U}}/D_{\text{Th}} > 10$

show the potential value of present extractant in U–Th separation. Further work to extend the extraction of Eu^{3+} , NpO_2^+ , Am^{3+} and other actinides and lanthanides using 4-oxaheptanediamide ligands is ongoing in our laboratory.

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