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EXTRACTION OF ACTINIDE (III, IV, V, VI) IONS AND TcO_4^- BY N,N,N',N'-
TETRAISOBUTYL-3-OXA-GLUTARAMIDE

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ABSTRACT

The extraction behavior of U(VI), Np(V), Pu(IV), Am(III), and TcO_4^- with N, N, N', N'-tetraisobutyl-3-oxa-glutaramide (TiBOGA) were investigated. An organic phase of 0.2 mol/L TiBOGA in 40/60% (V/V) 1-octanol/kerosene showed good extractability for actinides (III, IV, V VI) and TcO_4^- from aqueous solutions of HNO_3 (0.1 to 4 mol/L). At 25 °C, the distribution ratio of the actinide ions (D_{An}) generally increased as the concentration of HNO_3 in the aqueous phase was increased from 0.1 to 4 mol/L, while the D_{Tc} at first increased, then decreased, with a maximum of 3.0 at 2 mol/L HNO_3 . Based on the slope analysis of the dependence of D_{M} (M = An or Tc) on the concentrations of reagents, the formula of extracted complexes were assumed to be $\text{UO}_2\text{L}_2(\text{NO}_3)_2$, $\text{NpO}_2\text{L}_2(\text{NO}_3)$, $\text{PuL}(\text{NO}_3)_4$, $\text{AmL}_3(\text{NO}_3)_3$, and $\text{HL}_2(\text{TcO}_4)$ where L = TiBOGA. The enthalpy and entropy of the corresponding extraction reactions, $\Delta_r H$ and $\Delta_r S$, were calculated from the dependence of D on temperature in the range of 15 – 55 °C.

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For U(VI), Np(V), Am(III) and TcO_4^- , the extraction reactions are enthalpy driven and disfavored by entropy ($\Delta_r H < 0$ and $\Delta_r S < 0$). In contrast, the extraction reaction of Pu(IV) is entropy driven and disfavored by enthalpy ($\Delta_r H > 0$ and $\Delta_r S > 0$). A test run with 0.2 mol/L TiBOGA in 40/60% 1-octanol/kerosene was performed to separate actinides and TcO_4^- from a simulated acidic high-level liquid waste (HLLW), using tracer amounts of $^{238}\text{U(VI)}$, $^{237}\text{Np(V)}$, $^{239}\text{Pu(VI)}$, $^{241}\text{Am(III)}$ and $^{99}\text{TcO}_4^-$. The distribution ratios of U(VI), Np(V), Pu(VI), Am(III) and TcO_4^- were 12.4, 3.9, 87, > 1000 and 1.5, respectively, confirming that TiBOGA is a promising extractant for the separation of all actinides and TcO_4^- from acidic HLLW. It is noteworthy that the extractability of TiBOGA for Np(V) from acidic HLLW ($D_{\text{Np(V)}} = 3.9$) is much higher than that of many other extractants that have been studied for the separation of actinides from HLLW.

INTRODUCTION

The safety and cost of treating and disposing of nuclear wastes is a serious concern in the development of advanced nuclear energy. One promising strategy for the treatment of nuclear wastes is the partitioning and transmutation process (the P-T process), in which small amounts of long-lived radionuclides such as the minor actinides (MAs: Np, Pu, Am, Cm) and fission products (FPs: ^{99}Tc , ^{90}Sr , ^{137}Cs) are first separated from the huge quantities of nuclear wastes so that the bulk of the high level wastes becomes low or intermediate level waste that can be disposed of in a subsurface repository. The separated long-lived radionuclides, including the MAs and ^{99}Tc , are converted into short-lived radioisotopes or stable isotopes by transmutation in nuclear reactors or in advanced accelerators. ^{90}Sr and ^{137}Cs can be used as radioactive sources or stored in a subsurface

repository. Thus, the P-T process can reduce the time scale and the risk of HLLW disposal.

To partition the long-lived nuclides, a few separation processes using various extractants have been developed including the TRUEX, DIAMEX, and TRPO processes [1-3]. They can almost completely recover most of the MAs and ^{99}Tc from the high level liquid waste (HLLW) generated from the PUREX process, but the recovery of Np is poor. There is an urgent need to develop new extractants and processes to improve the recovery of Np because ^{237}Np is a major radiation hazard in a long term due to its long half-life. Besides, to meet the increasingly higher demand of electricity, the nuclear power industry is expected to generate spent nuclear fuels with higher burn-up, in which the amount of ^{237}Np significantly increases. Thus, the development of new ligands that extract Np(V), along with other MAs and TcO_4^- , can improve the efficiency of partitioning processes and help advance the P-T strategy.

Extraction of actinides with a series of diglycolamides has been reported in the literature [4-11]. For example, tetraoctyl-3-oxapentane-1,5-diamide (TODGA) and N,N'-dimethyl-N,N'-dihexyl-3-oxa-pentanediamide (DMDHOPDA) show good extractabilities for some actinides, especially An(III) [4-11]. However, the extraction of Np(V) by TODGA is poor [11]. DMDHOPDA in nitrobenzene shows considerable extractability for Np(V) [6], but no further mechanistic studies on this system have been reported. Besides, nitrobenzene is not a desirable solvent in nuclear fuel reprocessing. In searching for better extractants for the P-T process, we have studied N, N, N', N'-tetrabutyl-3-oxa-

glutaramide (TiBOGA, Fig. 1). Preliminary experiments have shown that TiBOGA can extract actinides (III, IV, V, VI) and TcO_4^- from simulated HLLW [12], but the extraction mechanism remains unclear. In this paper, we report the results of mechanistic studies of the extraction of actinides (III, IV, V, VI) and TcO_4^- by TiBOGA.

EXPERIMENTAL

TiBOGA was synthesized according to the procedures in the literature [13] in the Institute of Nuclear and New Energy Technology (INET), Tsinghua University. GC analysis indicated that its purity exceeded 98%. The melting point was measured to be 44 - 45 °C. Hydrogenated kerosene (#240) from Jinzhou Petroleum Refinery, China, was redistilled and the fraction between 180 and 220 °C was used in this work. Reagent grade 1-octanol from Beijing Chemical Co. was used without further purification. A solution of 40/60% (*V/V*) 1-octanol/kerosene was prepared and used as the diluent. Use of this mixed solvent was found to be effective in avoiding the formation of the third phase in the solvent extraction with TiBOGA [14]. Other reagents in this work were of analytical grade.

The stock solutions of TiBOGA were prepared by dissolving a precisely weighed amount of TiBOGA into 40/60% (*V/V*) 1-octanol/kerosene. Working solutions of TiBOGA were prepared by appropriate dilutions of the stock solutions prior to use. The aqueous phase solutions were prepared by adding appropriate amounts of the spiking nuclides into HNO_3 solutions.

Preparation of the solutions of $^{238}\text{U(VI)}$, $^{237}\text{Np(V)}$, $^{239}\text{Pu(IV)}$ and $^{241}\text{Am(III)}$ has been described elsewhere [15]. The concentrations of actinides in the stock solutions were determined by radiometric techniques, including γ -counting (1480 Wallac WIZARD 3" Automatic Gamma Counter, Perkin Elmer, US), liquid scintillation (Tri-Carb 2200CA, Packard, US), α -spectrometry (Alpha Spectrometer, S 407, Canberra, US), and ICP-AES (IRIS Advantage, Thermo Jarrell Ash, US). ^{99}Tc was analyzed by liquid scintillation counting.

The extraction was performed in 20ml glass-stoppered tubes in a constant-temperature water bath. All the extraction experiments were performed at 25 ± 0.2 °C except those of temperature dependence. The organic phase of TiBOGA in 40/60% (*V/V*) 1-octanol/kerosene was pre-equilibrated with corresponding HNO_3 solutions at least twice prior to use. In general, 5 ml of organic and 5 ml of aqueous phases were contacted for 10 minutes with magnetic stirring. Preliminary tests indicated that the contact time was sufficient to reach the equilibrium. After centrifugation, an aliquot of each phase was taken for the measurement of concentrations of the metal ions. The concentrations of U(VI), Np(V), Pu(IV), Am(III) and TcO_4^- were determined radiometrically, while the concentrations of non-radioactive components (e.g., Fe, Cr, etc.) were determined by ICP-AES. The distribution ratio of a solute M (D_M) was determined as a ratio of the concentrations of M between the organic phase and the corresponding aqueous phase. The extractions were run in triplicate.

RESULTS AND DISCUSSION

General Extraction Behavior of TiBOGA for An(III, IV, V, VI) and TcO_4^-

The distribution ratios of U(VI), Np(V), Pu(IV) and Am(III) (D_{An}) between 40/60% (V/V) 1-octanol/kerosene and aqueous solutions of different $[\text{HNO}_3]$ are shown in Fig. 2(a). For the extraction of U(VI), Np(V) and Pu(IV) by 0.2 mol/L TiBOGA, D_{An} increases as $[\text{HNO}_3]$ is increased from 0.1 to 4 mol/L. For the extraction of Am(III) with 0.02 mol/L TiBOGA, D_{An} increases as $[\text{HNO}_3]$ is increased from 0.1 to 2 mol/L but slightly decreases when $[\text{HNO}_3] > 2$ mol/L. The decrease of D_{An} can be attributed to the competition of HNO_3 that becomes more significant when $[\text{TiBOGA}]$ is low. In general, the extractability of TiBOGA for the actinide ions follows the order: $\text{Am(III)} \gg \text{Pu(IV)} > \text{U(VI)} > \text{Np(V)}$.

Data in Fig. 2(a) show that, even with a very dilute TiBOGA solution (0.02 mol/L) as the organic phase, Am(III) can be easily extracted ($D_{\text{Am}} > 10$ at $[\text{HNO}_3] = 2$ mol/L). The extractability of TiBOGA for Pu(IV) and U(VI) is lower than that for Am(III), but Pu(IV) and U(VI) can still be efficiently extracted by 0.2 mol/L TiBOGA at high $[\text{HNO}_3]$. The extractability of TiBOGA for Np(V) is the lowest among the four actinide ions (D_{Np} approaching 1 at $[\text{HNO}_3] > 3$ mol/L). To have higher extraction efficiency of Np(V), higher $[\text{TiBOGA}]$ in the organic phase and higher $[\text{HNO}_3]$ in the aqueous phase are necessary. Nevertheless, the extractability of TiBOGA for Np(V) is still stronger than that of many other extractants developed for the separation of MAs, including CMPO [1] and TRPO [3], with which little Np(V) is extracted at the same concentrations of the

extractant and acidity.

The distribution ratio of TcO_4^- , D_{Tc} , between 0.2 mol/L TiBOGA in 40/60% (V/V) 1-octanol/kerosene and aqueous shows a different dependency on $[\text{HNO}_3]$ (Fig. 2(b)). D_{Tc} first increases with the increase of $[\text{HNO}_3]$, reaches the maximum at 2 mol/L HNO_3 , and then decreases. Such trend can be attributed to the opposing effects of H^+ and NO_3^- on the extraction of TcO_4^- : higher $[\text{H}^+]$ facilitates the extraction by forming neutral HTcO_4 species while higher $[\text{NO}_3^-]$ competes with TcO_4^- and suppresses its extraction. The maximum D_{Tc} is about 3 and occurs at 2 mol/L HNO_3 , sufficiently high to allow efficient extraction of TcO_4^- .

Extraction Equations of TiBOGA with An(III, IV, V, VI) and TcO_4^-

Because TiBOGA is a neutral extractant and all the extracted species in 1-octanol/kerosene are likely to be neutral [16], the extraction equations for actinide ions can be described by eq. (1), taken into consideration that NO_3^- is the only anion in the extraction system:



where L represents TiBOGA. Then the extraction equilibrium constant, K , can be described by eq. (2):

$$K = \frac{[\text{M}_m \text{L}_l (\text{NO}_3)_n]_{\text{org.}}}{[\text{M}^{n+}]_{\text{aq.}}^m [\text{NO}_3^-]_{\text{aq.}}^{m \times n} [\text{L}]_{\text{org.}}^l} = \frac{D_M \cdot Y_M^m}{C_M^{m-1} [\text{NO}_3^-]_{\text{aq.}}^{m \times n} [\text{L}]_{\text{org.}}^l} \quad (2)$$

where C_M is the total concentration of M in the aqueous phase. Y_M is the correction factor for the complexation of M with nitrate in the aqueous phase, $Y_M = (1 + \sum \beta_i [\text{NO}_3^-]^i)$ where

β_i is the formation constants of $M(\text{NO}_3)_i$ complexes in the aqueous phase. If the $[\text{NO}_3^-]$ is kept constant, eq.(2) can be rearranged into eq.(3) after taking the logarithm:

$$\log D_M = (m-1)\log C_M + l\log[\text{L}]_{\text{org.}} + \text{constant} \quad (3)$$

Thus, the stoichiometric coefficients of m and l can be determined from the slope analysis of the relationship between the distribution ratio and the concentrations of metal ions and/or the extractant.

The plots of $\log D_M$ vs. $\log [\text{L}]_{\text{org}}$ are shown in Fig. 3. The slopes of $\log D_M$ vs. $\log [\text{L}]_{\text{org}}$ are 1.83, 1.98, 0.98 and 3.10, suggesting the numbers of TiBOGA in the extracted complexes are 2, 2, 1, and 3, respectively for U(VI), Np(V), Pu(IV) and Am(III).

Fig. 4 shows the dependence of D_M on the concentration of metal ions. In these experiments, the concentrations of metal ions in the aqueous phase were low (tracer amounts) and varied by 1- 2 orders of magnitude, but D_M remained almost constant, i.e., the slope = $m - 1 = 0$ (Fig.4). These results indicate that all the extracted actinide complexes are mononuclear under these conditions. This information, in conjunction with the dependence of D_M on $[\text{L}]_{\text{org}}$ (Fig.3), suggests that the extracted complexes are $\text{NpO}_2\text{L}_2(\text{NO}_3)$, $\text{UO}_2\text{L}_2(\text{NO}_3)_2$, $\text{AmL}_3(\text{NO}_3)_3$ and $\text{PuL}(\text{NO}_3)_4$, respectively.

Similar experiments and data analysis were performed for the extraction of TcO_4^- by TiBOGA. The dependencies of D_{Tc} on $[\text{L}]_{\text{org}}$ and $[\text{TcO}_4^-]$ were found to be about 1.77 (Fig.3) and 0.02 (Fig.4), respectively. Therefore, $l \approx 2$ and $m \approx 1$, suggesting the extracted complex of TcO_4^- is $\text{HL}_2(\text{TcO}_4)$.

It should be pointed out that the actual extraction equilibrium may be more complicated than eq.(1). For example, the interaction of HNO_3 with TiBOGA is not considered in eq.(1). It is known that many neutral extractants are also moderately efficient in extracting mineral acids [16], TiBOGA may also extract HNO_3 , forming species such as $\text{L}_x(\text{HNO}_3)_y$. When this occurs, the free extractant concentration in the organic phase is reduced and the efficiency of metal ion extraction suffers [16]. We have made attempts to determine the dependency of D_M on $[\text{HNO}_3]$ by conducting extractions with $\text{HNO}_3/\text{NaNO}_3$ at constant $[\text{NO}_3^-]_{\text{total}}$, as well as extractions with $\text{HNO}_3/\text{HClO}_4$ at constant $[\text{H}^+]$. However, the data are inconclusive and no reliable dependency of D_M on $[\text{HNO}_3]$ has been determined. One of the complications involved in the experiments and data analysis results from the use of quite high concentrations of HNO_3 , NaNO_3 and/or HClO_4 . Under such conditions, calculation of the activities of reactants is difficult and highly uncertain. However, appropriate evaluation of the stoichiometric coefficients in the extracted complex by slope analysis requires using the activities or, as an approximation, the concentrations if the solution is dilute. Since we do not have conclusive evidence to support the inclusion or exclusion of HNO_3 in the extracted metal complexes with TiBOGA at present, we accept eq.(1) as a reasonable description of the extraction equilibrium.

Thermodynamic Parameters of the Extraction

The distribution ratios (D_M) of U(VI), Np(V), Pu(IV), Am(III) and TcO_4^- between 40/60% (V/V) 1-octanol/kerosene and an aqueous solution of 2 mol/L HNO_3 were determined at different temperatures (15, 25, 35, 45 and 55 °C). $[\text{L}]_{\text{org}}$ was 0.2 mol/L for the extraction of U(VI), Np(V), Pu(IV) and TcO_4^- , but 0.02 mol/L for Am(III). The equilibrium constants (K) of eq.(1) at different temperatures can be calculated from D_M by eq.(2), provided that the values of β_i (formation constants of $\text{M}(\text{NO}_3)_i$ complexes) at these temperatures are available for calculation of the correction factor for nitrate complexation ($Y_M = (1 + \sum \beta_i [\text{NO}_3^-]^i)$). Unfortunately, values of β_i are not available for 15, 35, 45 and 55 °C. Therefore, we have elected to use the value of β_i at 25 °C for all the temperatures as an approximation. In addition, we found it unnecessary to correct the nitrate complexation for Np(V) or TcO_4^- , because the Np(V)/ NO_3^- complexes are very weak and the anionic TcO_4^- is not expected to form nitrate complexes. For U(VI), Pu(IV) and Am(III), only the first nitrate complexes, MNO_3 , are considered so that $Y_M = 1 + \beta_1 [\text{NO}_3^-]$. Values of $\log \beta_1$ at $I = 2.0$ HNO_3 used in the correction were -0.44 , 0.49 and 0.06 for U(VI), Pu(IV) and Am(III), respectively. These values were calculated by the Specific Ion Interaction approach (SIT) [17-19] from the selected values of $\log \beta_1^0$ at $I = 0$ and associated ion interaction parameters in the literature [17-19]. Values of the extraction equilibrium constant, K , were calculated from D_M by eq.(2) and listed in Table 1.

The plots of $\ln K$ vs. $1/T$ are shown in Fig.5. For all the ions, the data were fit with linear correlations to obtain the enthalpy and entropy of extraction by the van't Hoff equation (4). The values are listed in Table 1.

$$\ln K = -\frac{\Delta H^0}{R} \left(\frac{1}{T} \right) + \frac{\Delta S^0}{R} \quad (4)$$

For U(VI), Np(V), Am(III) and TcO_4^- , the extraction processes are exothermic and driven by negative enthalpies. The distribution ratios decrease as the temperature is increased. The extraction processes are disfavored by the negative entropy, a result observed for most extraction processes in which a number of extractant molecules combine with metal ions and associated anions to form highly ordered extracted complexes in the organic phase.

On the contrary, the extraction process of Pu(IV) is endothermic and appears to be driven by the positive entropy. The “abnormal” behavior may probably be rationalized as follows. Due to its high ion potential and strong polarization ability, Pu^{4+} is much more strongly solvated in aqueous solutions than U(VI), Np(V) or Am(III). Thus more energy for dehydration of Pu^{4+} is needed and more water molecules are released when it is complexed and extracted by TiBOGA, resulting in more positive enthalpy and entropy of complexation.

Test Results for the Separation of An(III, IV, V, VI) and TcO_4^- from Simulated HLLW

To test the extraction of actinide ions and TcO_4^- with TiBOGA from high level liquid waste (HLLW), a simulated HLLW was prepared, containing 2 mol/L HNO_3 and tracer amounts of ^{238}U , ^{237}Np , ^{239}Pu , ^{241}Am and ^{99}Tc , as well as non-radioactive components such as the nitrates of Fe(III), Cr(III), Ni(II), Al(III), Cs(I) and Na(I). This simulated

HLLW is chosen because it has been systematically studied [3] and it offers convenient comparison with other studies such as the separation of Sr(II) [14]. Extraction experiments were performed by using 0.2 mol/L TiBOGA in 40/60% 1-octanol/KO as the organic phase. The volumes of aqueous and organic phases are both 5.0 mL. The composition of the simulated HLLW and the observed distribution ratios are shown in Table 2.

Results in Table 2 can be summarized as follows. 1) The extraction of Fe(III), Cr(III), Ni(II), Al(III), Cs(I) and Na(I) is minimal and insignificant. 2) TiBOGA extracts the actinide ions and TcO_4^- quite well from the simulated HLLW. This is as expected from the results of extraction experiments with individual radionuclides. However, it is interesting to notice that the distribution ratios for the actinide ions in the test with simulated HLLW are higher than those in the individual extraction experiments (both with 2 mol/L HNO_3). This is probably due to the strong salting-out effect of nitrate in the simulated HLLW, in which the concentration of nitrate is about 6 mol/L. In contrast, the distribution ratio for TcO_4^- in the test with simulated HLLW is somewhat lower than that in the extraction experiments with only TcO_4^- in 2 mol/L HNO_3 . This can be interpreted as the result of a strong competition of nitrate with anionic TcO_4^- for the extraction by TiBOGA, in excellent agreement with the results in Fig. 2. 3) It is worthwhile mentioning that the extraction of Np(V) by TiBOGA from the simulated HLLW is quite good, $D_M \approx 4$, and better than other extractants used for separation of actinides from HLLW [1-3].

CONCLUSION

Mechanistic studies have been conducted to derive the compositions of the extracted complexes and the mechanism of the extraction of U(VI), Np(V), Pu(IV), Am(III) and TcO_4^- by TiBOGA in 40/60% 1-octanol/KO. The extraction of these radionuclides is strongly dependent on the concentrations of HNO_3 and TiBOGA. Extraction experiments with individual radionuclides and a simulated high level liquid waste have demonstrated that, from 2.0 mol/L HNO_3 solutions, 0.2 M TiBOGA in 40/60% 1-octanol/KO has good ability to extract TcO_4^- and actinide ions including Np(V) that is usually difficult to extract by many extractants. Under these conditions, the extractability for the actinides follows the order: Am(III) \gg Pu(IV) $>$ U(VI) $>$ Np(V). The extractability of Tc(VII) is slightly higher than that of U(VI) from the 2.0 M mol/L HNO_3 solution, but lower than that for all the four actinide ions from the simulated high-level liquid waste where the total concentration of nitrate is about 6 mol/L.

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Captions of Figures

Fig. 1. N, N, N', N'-tetraisobutyl-3-oxa-glutaramide.

Fig. 2. The dependence of D_M on $[\text{HNO}_3]$ in the equilibrated aqueous phase. Organic phase: 0.02 mol/L TiBOGA for Am(III), 0.2 mol/L TiBOGA for U(VI), Np(V), Pu(IV) and TcO_4^- ; aqueous phase: tracer amounts of metal ions in HNO_3 . The errors associated with D_M are $\pm 5\%$ for $0.01 < D_M < 100$; $\pm 10\%$ for $D_M > 100$.

Fig. 3. The dependence of D_M on $[\text{L}]_{\text{org}}$. Organic phase: TiBOGA in 40/60% 1-octanol/KO; aqueous phase: tracer amounts of metal ions in 2 mol/L HNO_3 . The errors associated with D_M are $\pm 5\%$ for $0.01 < D_M < 100$; $\pm 10\%$ for $D_M > 100$.

Fig. 4. The dependence of D_M on the concentration of metal ions. Organic phase: TiBOGA in 40/60% 1-octanol/KO, $[\text{L}]_{\text{org}} = 0.02$ mol/L for Am(III), 0.2 mol/L for U(VI), Np(V), Pu(IV) and TcO_4^- ; aqueous phase: tracer amounts of metal ions in 2 mol/L HNO_3 . The errors associated with D_M are $\pm 5\%$ for $0.01 < D_M < 100$; $\pm 10\%$ for $D_M > 100$.

Fig. 5. The effect of temperature on the extraction equilibrium constant ($\ln K$ vs. $1/T$). Organic phase: TiBOGA in 40/60% 1-octanol/KO, $[\text{L}]_{\text{org}} = 0.02$ mol/L for Am(III), 0.2 mol/L for U(VI), Np(V), Pu(IV) and TcO_4^- ; aqueous phase: tracer amounts of metal ions in 2 mol/L HNO_3 . The errors associated with D_M are $\pm 5\%$ for $0.01 < D_M < 100$; $\pm 10\%$ for $D_M > 100$.

Table 1. The equilibrium constants, $\Delta_r G$, $\Delta_r H$ and $\Delta_r S$ of the extraction.

Reaction	K	$\Delta_r G$	$\Delta_r H$	$\Delta_r S$
		kJ/mol	kJ/mol	J/(K mol)
$\text{UO}_2^{2+}(\text{aq}) + 2\text{NO}_3^-(\text{aq}) + 2\text{L}(\text{o}) = \text{UO}_2(\text{L})_2(\text{NO}_3)_2(\text{o})$	19 ± 5	-7.3 ± 0.8	-25.8 ± 5.0	-62 ± 16
$\text{NpO}_2^+(\text{aq}) + \text{NO}_3^-(\text{aq}) + 2\text{L}(\text{o}) = \text{NpO}_2(\text{L})_2(\text{NO}_3)(\text{o})$	3.4 ± 0.4	-3.1 ± 0.3	-11.9 ± 3.0	-30 ± 10
$\text{Pu}^{4+}(\text{aq}) + 4\text{NO}_3^-(\text{aq}) + \text{L}(\text{o}) = \text{PuL}(\text{NO}_3)_4(\text{o})$	36 ± 13	-8.9 ± 0.8	30.1 ± 7.7	130 ± 25
$\text{Am}^{3+}(\text{aq}) + 3\text{NO}_3^-(\text{aq}) + 3\text{L}(\text{o}) = \text{Am}(\text{L})_3(\text{NO}_3)_3(\text{o})$	$(2.8 \pm 0.3) \times 10^6$	-37 ± 3	-82.8 ± 2.7	-155 ± 10
$\text{TcO}_4^-(\text{aq}) + \text{H}^+(\text{aq}) + \text{L}(\text{o}) = \text{HTcO}_4\text{L}(\text{o})$	39 ± 15	-9.1 ± 0.9	-30.2 ± 7.9	-71 ± 26

Table 2. The composition of the simulated HLLW (2 mol/L HNO₃) and the distribution ratios ($t = 25\text{ }^{\circ}\text{C}$, $V_{\text{org}}/V_{\text{aq}} = 5\text{ mL}/5\text{ mL}$, organic phase: 0.2 mol/L TiBOGA in 40/60% 1-octanol/KO).

Metal ion	Fe ³⁺	Al ³⁺	Cr ³⁺	Ni ²⁺	Na ⁺	Cs ⁺	U(VI)	Np(V)	Pu(IV)	Am(III)	TcO ₄ ⁻
C(mol/L)	0.6	0.25	0.025	0.1	1.0	0.01	tracer	tracer	tracer	tracer	tracer
D_M	2×10^{-3}	$<10^{-3}$	$<10^{-3}$	$<10^{-3}$	$<10^{-3}$	$<10^{-3}$	12.4	3.9	87	$>10^3$	1.5

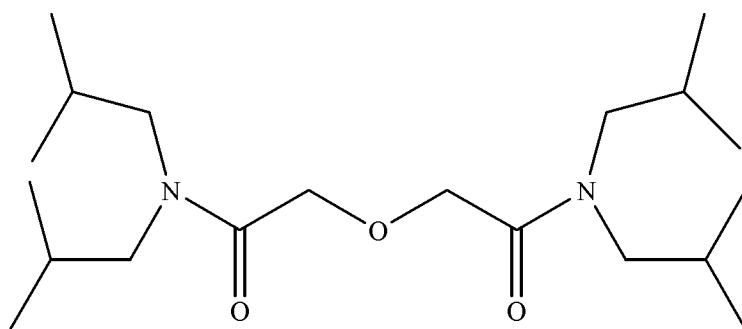


Fig. 1. N, N, N', N'-tetraisobutyl-3-oxa-glutaramide.

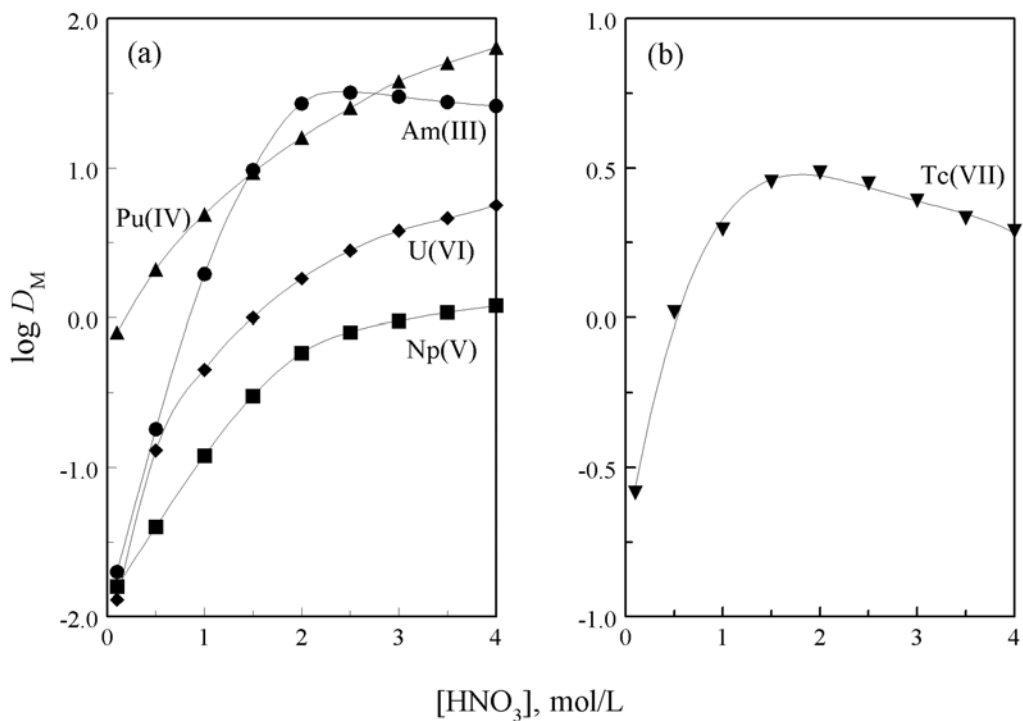


Fig. 2. The dependence of D_M on $[HNO_3]$ in the equilibrated aqueous phase. Organic phase: 0.02 mol/L TiBOGA for Am(III), 0.2 mol/L TiBOGA for U(VI), Np(V), Pu(IV) and TcO_4^- ; aqueous phase: tracer amounts of metal ions in HNO_3 . The errors associated with D_M are $\pm 5\%$ for $0.01 < D_M < 100$; $\pm 10\%$ for $D_M > 100$.

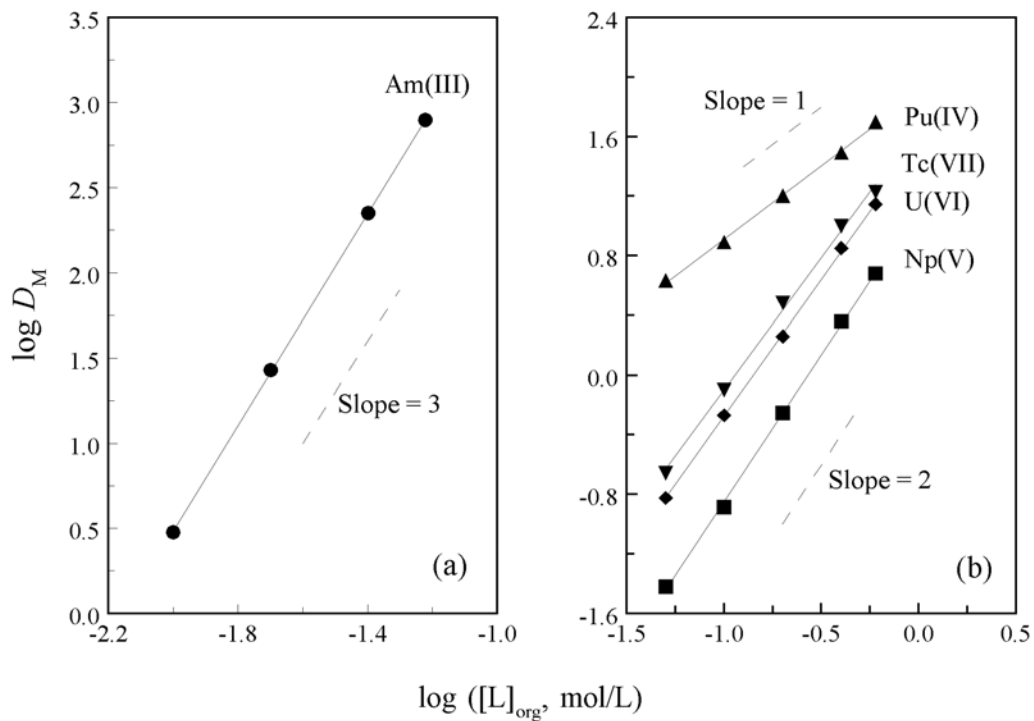


Fig. 3. The dependence of D_M on $[L]_{\text{org}}$. Organic phase: TiBOGA in 40/60% 1-octanol/KO; aqueous phase: tracer amounts of metal ions in 2 mol/L HNO_3 . The errors associated with D_M are $\pm 5\%$ for $0.01 < D_M < 100$; $\pm 10\%$ for $D_M > 100$.

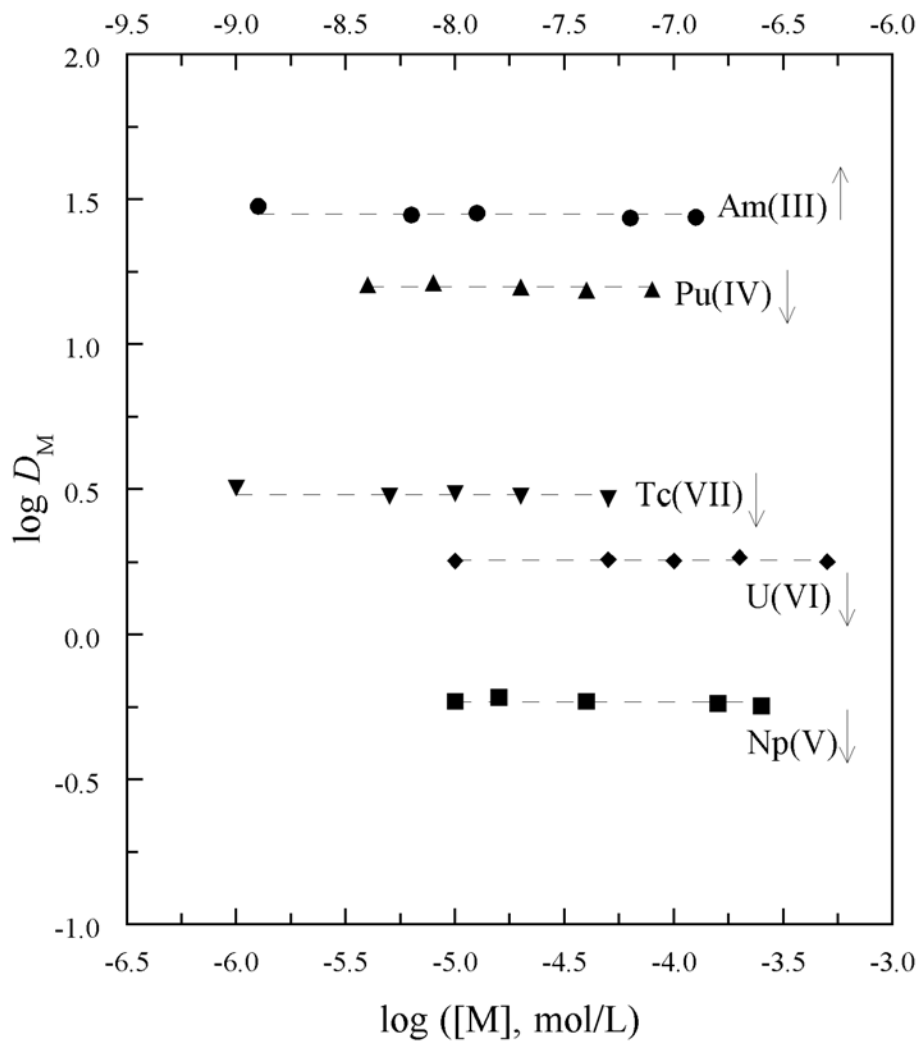


Fig. 4. The dependence of D_M on the concentration of metal ions. Organic phase: TiBOGA in 40/60% 1-octanol/KO, $[L]_{\text{org.}} = 0.02$ mol/L for Am(III), 0.2 mol/L for U(VI), Np(V), Pu(IV) and TcO_4^- ; aqueous phase: tracer amounts of metal ions in 2 mol/L HNO_3 . The errors associated with D_M are $\pm 5\%$ for $0.01 < D_M < 100$; $\pm 10\%$ for $D_M > 100$.

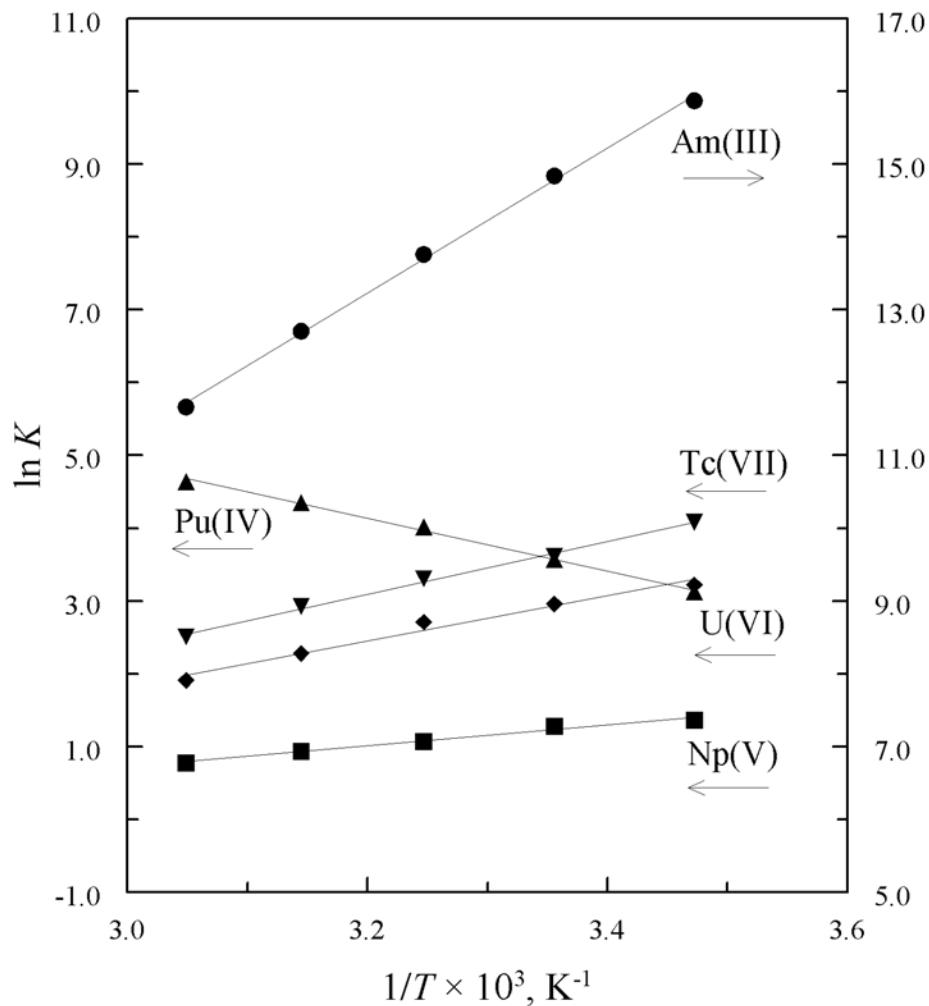


Fig. 5. The effect of temperature on the extraction equilibrium constant ($\ln K$ vs. $1/T$). Organic phase: TiBOGA in 40/60% 1-octanol/KO, $[L]_{\text{org.}} = 0.02$ mol/L for Am(III), 0.2 mol/L for U(VI), Np(V), Pu(IV) and TcO_4^- ; aqueous phase: tracer amounts of metal ions in 2 mol/L HNO_3 . The errors associated with D_M are $\pm 5\%$ for $0.01 < D_M < 100$; $\pm 10\%$ for $D_M > 100$.