

Article

Enhanced Selective Separation of Pu(IV) and U(VI) Using Novel Diethylene Glycolamide Ligand

Xiaoyun Guo , Junli Wang *, Yao Liu, Haojun Zhao , Hui Wang, Wentao Wang, Baole Li and Taihong Yan *

Department of Radiochemistry, China Institute of Atomic Energy, P.O. Box 275-26, Beijing 102413, China; 17627812376@163.com (X.G.); ly18801256495@163.com (Y.L.); 18161317016@163.com (H.Z.); hwihwi@126.com (H.W.); wentaowang001@163.com (W.W.); libeanty@163.com (B.L.)

* Correspondence: jlwang92@163.com (J.W.); yanthcn@163.com (T.Y.)

Abstract: Developing a new efficient separation ligand based on the “CHON” principle to address the limitations of phosphorus containing extractants in nuclear fuel reprocessing can help further simplify the process flow and reduce the amount of secondary waste. Building upon this critical need, a novel ligand was developed through a strategic application of the Hard and Soft Acids and Bases (HSAB) theory, integrating a soft donor nitrogen atom into the linear architecture of bis-diglycolamide. This groundbreaking ligand, named N,N'-bis[2-(2-(N,N-dioctylcarbamoylethoxy)ethylacetamido]-N''-diethylenetriamine (TOMDEA-BisDGA), has demonstrated remarkable potential in the extraction of Pu(IV). The study unveils that the ligand demonstrates remarkable selectivity and separation efficiency towards Pu(IV) ions while maintaining an exceptionally low extraction capacity for U(VI) across a wide acidity spectrum of 0.1–6 mol/L. To explain the structure properties of complex formed by the ligand and Pu(IV), a systematic analysis was performed, including slope analysis, proton nuclear magnetic resonance (NMR) titration, and Fourier-transform infrared (FT-IR) spectroscopy. This study explores the coordination and separation behavior of diglycolamide ligands with actinide. This work is expected to provide important information and theoretical bases upon which advanced design and optimization of ligands for high-performance processes for the separation of plutonium might be carried out. Such findings will contribute to the understanding of actinide chemistry and further the design of improved separation methods for nuclear applications.

Keywords: plutonium; uranium; bis-diglycolamide; solvent extraction



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1. Introduction

Due to the rapid global expansion of nuclear power generation, spent nuclear fuel treatment and disposal are emerging as one of the most pressing safety and environmental challenges of our time [1,2]. Spent nuclear fuel constitutes a complex array of radioactive isotopes and, if not dealt with accordingly, poses serious risks to both human health and the environment [3–5]. Among the many different approaches to solving this problem, the PUREX (Plutonium uranium Reduction Extraction) process remains one of the most influential reprocessing technologies within the closed nuclear fuel cycle [6]. Based on solvent extraction, this process provides recovery and recycling of strategic components such as uranium and plutonium and certain other actinides for possible future use. However, the traditional tri-butyl phosphate (TBP) based PUREX process is not without its limitations [7]. It contradicts the desired “CHON” principle (which dictates that the waste should be composed of only carbon, hydrogen, oxygen, and nitrogen), produces caustic by-products during incineration relevant to its disposal, and generates a significant amount

of secondary waste. Moreover, the degradation of TBP during the process creates problematic by-products such as dibutyl phosphate (DBP) and monobutyl phosphate (MBP), which affect extraction efficiency and further complicated separation and purification procedures [8–10]. These constant challenges have led to the introduction of new extractant ligands, an area of active research in spent fuel reprocessing.

Over the past few decades, important developments in extractant design have come a long way, with researchers designing innovative ligands to address various separation needs [7,11–13]. Specific attention has been paid to the separation of U(VI) and Pu(IV) from spent fuel, as well as minor actinides and lanthanides from high-level liquid waste (HLLW) [14–16]. In this context, diglycolamide (DGA) extractants and their derivatives have garnered substantial attention due to their remarkable selectivity for actinides, attributed to their unique reverse micelle extraction mechanism [16–19]. With that recognition as green extractants, DGA-based extractants have been extensively studied, especially tetraoctyldiglycolamide (TODGA, Figure 1a), towards their abilities to coordinate and separate trivalent actinides and lanthanides effectively [19,20].

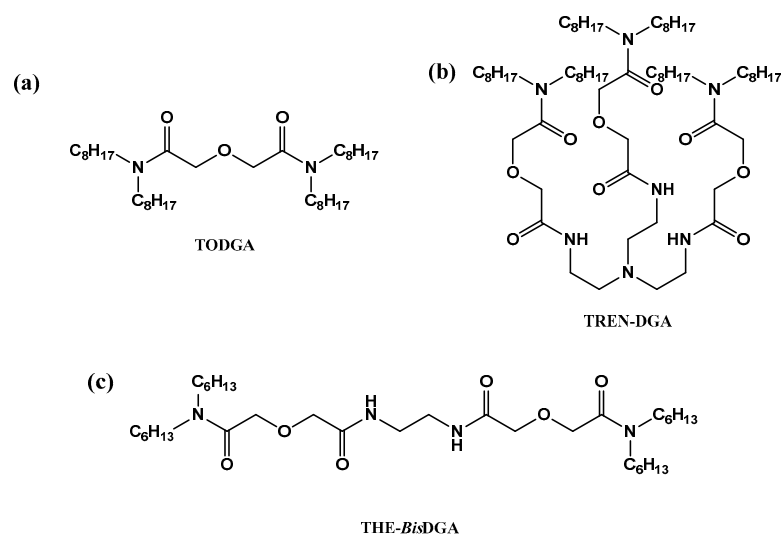


Figure 1. Structure of DGA ligands. (a) TODGA; (b) TREN-DGA; (c) THE-BisDGA.

The landscape of DGA ligands has seen remarkable progress through various innovative designs. Arun Bhattacharyya and his team made significant advances by synthesizing tripodal diglycolamides (T-DGA) and N-pivot tripodal DGA (TREN-DGA, Figure 1b), which feature DGA-functionalized ligands with three to four DGA sidearms [21,22]. Their findings demonstrated these novel ligands' superior performance over traditional TODGA in extracting U(VI) and Pu(IV), with Pu(IV) extraction rates notably exceeding those of U(VI) under identical conditions. Although TREN-DGA exhibits high extraction capability in the ionic liquid $[C_4mim][Tf_2N]$, its extraction performance in molecular diluents is poor. In a parallel development, Chen and his collaborators achieved a breakthrough by introducing alkyl substituents into the central nitrogen atom between two DGA moieties, resulting in three innovative DGAs (N,N,N',N''-tetrahexyl-N'',N''-ethidene bisdiglycolamide, THE-BisDGA, Figure 1c; N,N,N',N''-tetrahexyl-N'',N''-(N'',N''-diethyl)-ethidene bisdiglycolamide, THEE-BisDGA; N,N,N',N''-tetrahexyl-N'',N''(N'',N''-diisopropyl)-ethidene bisdiglycolamide, THⁱ-PE-BisDGA) [23–25]. The ligands showed impressive Pu(IV) extraction capacity with less efficacy in extracting U(VI), even under higher acidity states. Though some developments show promise in the selective separation of Pu(VI) and U(IV), the actual separation mechanism remains unclear and needs further elucidation.

To better understand and improve the performance characteristics of bis-diglycolamide (Bis-DGA) ligands, this study proposes a strategic modification by introducing a soft donor nitrogen atom into the molecular backbone connecting the two DGA moieties (Figure 2). Using an extensive series of single-stage extraction experiments, the effects of varying acidity and ligand concentration on the extraction efficiencies of U and Pu were carefully studied. In this methodological approach, Ce(IV) was used as an analogue for Pu(IV) to conduct a more thorough mechanistic investigation [26,27]. Meanwhile, FT-IR and ^1H -NMR titration provided some of the advanced analytical techniques. These techniques encompassed an in-depth comprehension of the extraction process from the molecular and electronic size.

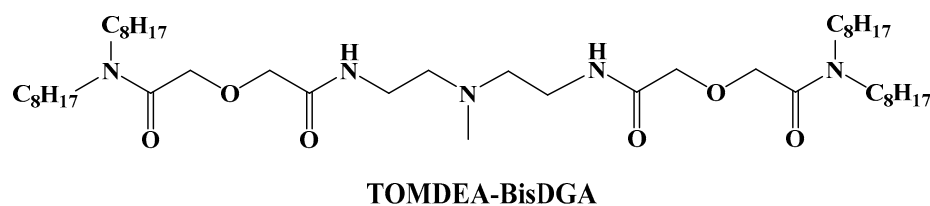


Figure 2. Structure of TOMDEA-BisDGA ligand.

2. Experimental Section

2.1. Materials

The chemicals used for ligand synthesis, including diglycolic anhydride, tetrahydrofuran, di-*n*-octylamine, dichloromethane, oxalyl chloride, triethylamine, and ethyl acetate, were supplied by Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China). Notably, 2,2-diamino-*N*-methyldiethylamine was obtained from Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). Additionally, the reagents used during the extraction, for instance, *n*-octanol, nitric acid, and ceric ammonium nitrate, were also provided by Macklin. All these reagents were of analytical reagent (AR) grade, ensuring high purity and reliability. The deuterated methanol used in nuclear magnetic resonance (NMR) titration experiments was also procured from Macklin and was of guaranteed reagent (GR) grade, matching the rigorous criteria of the NMR analyses.

Most of the radioactive solutions of uranium and plutonium were provided by the China Institute of Atomic Energy (Beijing, China), with the radiochemical purity of all isotopes being greater than 99.9%. All radioactive experiments were performed in licensed facilities and followed strict safety guidelines and regulations that ensure accuracy for these results and the personnel working on them.

2.2. Experimental Instruments

In this extraction procedure, the solution's acidity is precisely adjusted by utilizing the automated titration system (G20s, Mettler Toledo, Columbus, OH, USA). For plutonium concentration determination, a liquid scintillation spectrometer is used (Tri-Carb 2910 TR, PerkinElmer, Springfield, IL, USA), with three separate measurements per sample to ensure reliability, from which the average value is calculated. Uranium (VI) concentration analysis is conducted using a state-of-the-art inductively coupled plasma optical emission spectrometer (iCAP7400 Duo, Thermo Scientific, Waltham, MA, USA). Structural characterization is performed through advanced spectroscopic techniques: proton nuclear magnetic resonance (^1H NMR) spectra are acquired using a high-performance liquid NMR spectrometer (Bruker Ascend 400 MHz, Bruker, Waltham, MA, USA), while molecular vibrational analysis is carried out on a Fourier-transform infrared spectrometer (Bruker Alpha II FT-IR Spectrograph, Bruker, Waltham, MA, USA), providing comprehensive chemical fingerprint information.

2.3. Synthesis of TOMDEA-BisDGA

The synthetic pathway is meticulously illustrated in Figure 3, providing a clear blueprint for the experimental procedure. To initiate the process, 17.41 g of diglycolic anhydride was carefully dissolved in 200 mL of tetrahydrofuran, maintaining a precise temperature of 283 K under an argon atmosphere to ensure an inert environment. Following this, 24.15 g of di-*n*-octylamine was gradually introduced into the mixture via controlled dropwise addition to ensure a steady and complete reaction. The mixture was stirred at room temperature for 24 h to facilitate complete reaction. Post-reaction, the rotary evaporator removed the solvent under reduced pressure, after which dichloromethane was used to dissolve the resulting product. The solution underwent rigorous washing with deionized water for three consecutive washes to ensure purity. The organic phase was meticulously separated, dried over MgSO_4 , and filtered to yield intermediate A, identified as 2-[2-(*N,N*-dioctylcarbamoyl)ethoxy]acetic acid (yeild: 43%).

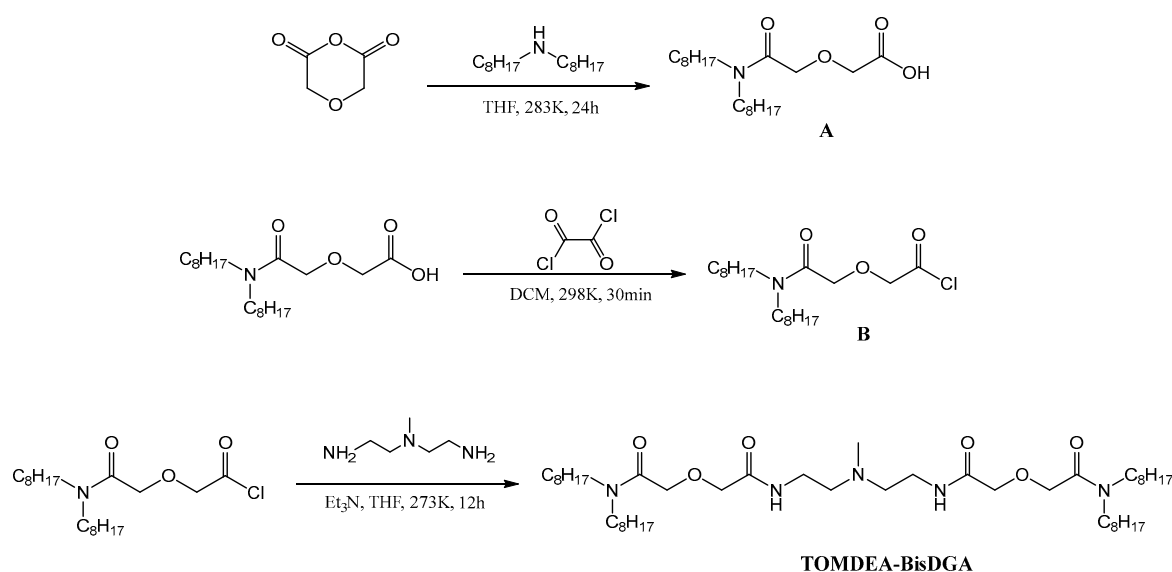


Figure 3. Synthesis pathway of TOMDEA-BisDGA ligand.

In the subsequent phase of the synthesis, 13.42 g of intermediate A was dissolved in 100 mL of dichloromethane, and 5.72 g of oxalyl chloride was slowly added dropwise at room temperature during a stirring time of 30 min to ensure the completion of the whole process. To eliminate any excess oxalyl chloride, argon gas was bubbled through the solution for 15 min, resulting in a purified dichloromethane solution of intermediate B, specifically 2-[2-(*N,N*-dioctylcarbamoyl)ethoxy]acetyl chloride.

Then, 2.00 g of 2,2-diamino-*N*-methyldiethylamine was dissolved in 100 mL of tetrahydrofuran, to which triethylamine 4.31 g was added while keeping the temperature at 273 K. The dichloromethane solution of intermediate B was added dropwise to the reaction mixture at a slow rate, ensuring a controllable and uniform reaction. The reaction mixture was stirred for 12 h to get complete interaction. Finally, the mixture was filtered, and the filtrate was evaporated to dryness. The residue was dissolved in ethyl acetate and washed three times with deionized water for impurity removal. The mixture was carefully separated, dried over anhydrous magnesium sulfate, filtered, and thoroughly dried to obtain the final product, *N,N'*-bis[2-(2-(*N,N*-dioctylcarbamoyl)ethoxy)ethylacetamido]-*N'',N''*-diethylenetriamine, abbreviated as TOMDEA-BisDGA (yeild: 36%). Finally, the mixture was filtered and the filtrate allowed to dry to a residue. The residue was dissolved in ethyl acetate and searched three times with deionized water to remove any impurities. The

characterization data (^1H NMR, ^{13}C NMR, and ESI-MS spectra) of TOMDEA-BisDGA are provided in Figures S1–S3.

2.4. Solvent Extraction Experiments

The ligand was dissolved and diluted in n-octanol to a concentration of 0.05 M based on its polarity and solubility. To facilitate experimental operations and accommodate instrumental measurement ranges, the aqueous phase consisted of nitrate solutions containing the following radionuclides: 5 mg/L Pu(IV) and 5 mg/L U(VI). The nitric acid concentration in the aqueous phase was maintained at 3 M to closely simulate actual spent nuclear fuel reprocessing environments. All experiments, except those involving temperature variations, were conducted under controlled conditions at 298 K.

Before starting the extraction, the organic phase goes through two pre-equilibrations with an equal volume of nitric acid aqueous solution matching the same concentration to obtain uniformity and reproducibility. The organic and aqueous phases were mixed in a vortex mixer at 2000 rpm for 30 min for each extraction run to achieve the best contact between the phases inside the test tubes. Separation of the phases was performed by centrifugation at 2000 rpm for 3 min after mixing.

To ensure reliability, each set of experiments was performed in duplicate. Post-extraction, the organic and aqueous phases were carefully sampled for concentration determination. The radionuclide concentrations in each phase were measured using liquid scintillation counting, a precise and sensitive analytical technique. The extraction distribution ratio formula is shown in Equation (1):

$$D_M = \frac{C_0 - C_{aq}}{C_{aq}} \quad (1)$$

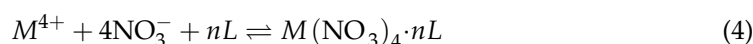
In the given equation, C_0 denotes the initial concentration of metal ions, while C_{aq} represents their aqueous-phase concentration. The extraction and separation efficiency of ligands for metals A and B can be expressed through the Separation Factor (SF), which is formulated as shown in Equation (2):

$$SF_{A/B} = \frac{D_A}{D_B} \quad (2)$$

To derive the reaction's thermodynamic parameters, the Van't Hoff equation was employed, establishing a clear correlation between $\log K$ and $1000/T$, which is formulated as shown in Equation (3):

$$\log K = \frac{-\Delta H}{2.303R} \cdot \frac{1}{T} + \frac{\Delta S}{2.303R} \quad (3)$$

The extraction reaction equation for the ligands with $M(IV)$ as shown in Equation (4):



The apparent equilibrium constant of the extraction reaction and the extraction partition ratio are in Equations (5) and (6):

$$K = \frac{[M(\text{NO}_3)_4 \cdot nL]}{[M^{4+}][\text{NO}_3^-]^4[L]^n} \quad (5)$$

$$D_M = \frac{[M]_{org}}{[M]_{aq}} \quad (6)$$

From this, the relationship between $\log D$ and $\log L$ is obtained in Equation (7):

$$\lg D_M = \lg K + 4\lg[\text{NO}_3^-] + n\lg[L] \quad (7)$$

2.5. FT-IR Spectrum

To investigate the coordination behaviors of plutonium (Pu(IV)), tetravalent cerium (Ce(IV)) was utilized as a non-radioactive surrogate, owing to their striking similarities in physical, chemical, and coordination properties [26,27]. This approach enabled the safe and effective simulation of Pu(IV) interactions in controlled experiments. The coordination process was monitored by systematic infrared spectroscopy analysis of organic phase samples prior and post-pre-equilibrium and then after Ce(IV) extraction. Such comprehensive analysis gave detailed information regarding the coordination dynamics and the involved extraction mechanisms.

2.6. ^1H -NMR Titration

To investigate the coordination reaction process between Ce(IV) and TOMDEA-BisDGA, the experiment employed a stepwise titration method combined with NMR technology for monitoring [28,29]. First, a 0.1 M ammonium ceric nitrate/ CD_3OD solution was precisely prepared as the titration reagent. Next, a TOMDEA-BisDGA solution of approximately 0.01 M was prepared using CD_3OD as the solvent, and 0.5 mL of this solution was placed in an NMR tube as the initial reaction system. Ce(IV) solution was added stepwise using a microsyringe, with 10 μL added each time. The mixture was then rigorously shaken for 30 min after each addition to make sure that equilibrium was established in the reaction system. After allowing the solution to stand for 2 min, ^1H NMR spectra were collected under constant temperature conditions. By continuously monitoring the changes in the characteristic peaks of various coordination intermediates until the positions and intensities of all characteristic peaks in the NMR spectrum remained unchanged, it was concluded that the reaction had reached complete equilibrium.

2.7. Stripping

The stripping experiments for Pu(IV)-loaded organic phases were systematically conducted using three distinct aqueous solutions: low-acidity solution (0.2M HNO_3), complexing agent solutions ($\text{H}_2\text{C}_2\text{O}_4$, EDTA- HNO_3), and reducing agent solutions (DMHAN-MMH, AHA- HNO_3). To evaluate ligand reusability, five consecutive extraction-back-extraction cycles were meticulously performed under 0.2M HNO_3 conditions. The experimental protocol employed a standardized procedure with both organic and aqueous phases maintained at 1 mL volumes. Phase contact was ensured through vigorous mixing in a vortex mixer for precisely 30 min, followed by effective phase separation via centrifugation. Each experimental condition was replicated to ensure data reliability, with concentrations in both phases being independently quantified to validate system behavior and extraction efficiency.

3. Results and Discussion

3.1. The Influence of Contact Time

To ascertain the equilibrium time of the extraction reaction, extraction experiments were carried out by varying the contact time between the two phases (Figure 4). It was discovered that the extraction equilibrium time of the TOMDEA-BisDGA ligand for Pu(IV) or U(VI) was 10–15 min. To ensure that the extraction reaches equilibrium, all subsequent extraction experiments were conducted at a contact time of 30 min.

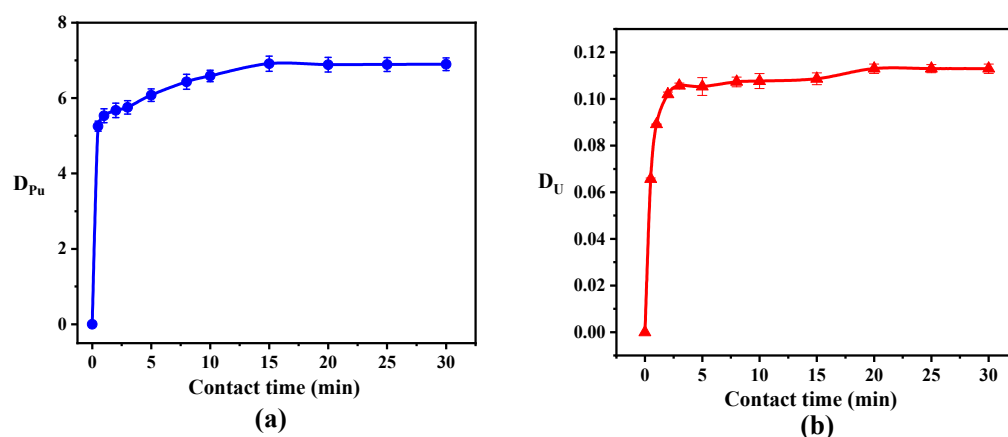


Figure 4. Effect of contact time on Pu (IV) or U(VI) extraction distribution Ratio. Organic phase: 0.05 M TOMDEA-BisDGA in n-octanol; aqueous phase: 3 M HNO₃; temperature: 298 K. (a) Effect of contact time on Pu (IV) extraction distribution Ratio. 5 mg/L Pu(IV); (b) Effect of contact time on U(VI) extraction distribution Ratio. 5 mg/L U(VI).

3.2. Effect of Acidity

Figure 5 delineates the extraction efficiencies of Pu(IV) and U(VI) using TOMDEA-BisDGA across varying HNO₃ concentrations in n-octanol medium. As the nitric acid concentration escalates from 0.2 to 6 M, there is a notable augmentation in the distribution ratios for both Pu(IV) and U(VI). Specifically, in 3 M HNO₃, the distribution ratio for Pu(IV) reaches approximately 9.0, while that of U(VI) remains closed to 10^{-2} – 10^{-1} . Moreover, the TOMDEA-BisDGA ligand demonstrates a remarkable separation factor for Pu(IV)/U(VI), which exceeds other reported neutral phosphorus extractants and amide extractants (Table 1). This enhancement in separation factor is particularly significant when compared to other bis-diglycolamide ligands devoid of soft donor nitrogen atoms. Consequently, the TOMDEA-BisDGA ligand exhibits considerable promise for the effective separation of Pu(IV) and U(VI) in environments characterized by high nitric acid concentrations.

Table 1. Extraction of Pu (IV) and U (VI) by TOMDEA-BisDGA and other extractants in 3M HNO₃.

Extractants	$D_{Pu(IV)}$	$D_{U(VI)}$	$SF_{Pu(IV)/U(VI)}$	Source
0.05M TOMDEA-BisDGA	9.0	0.1	72.8	This work
1.1M TBP	15.0	17.2	0.9	[30]
1.1M TiAP ¹	18.1	18.9	1.0	[30]
30% TRPO ²	3316.1	432.0	7.7	[31]
0.2M CMPO ³	68.0	17.1	4.0	[32]
0.1M TODGA + 0.5M dihydroxyoctylamide	124.8	9.5	13.2	[33]
0.01M THE-BisDGA	15.4	0.2	66.3	[23]
0.01M THEE-BisDGA	4.4	0.7	5.9	[23]
0.01M TH ⁱ -PE-BisDGA	24.2	0.6	41.7	[23]

¹ TiAP is tri-isoamyl phosphate. ² TRPO is trialkylphosphine oxide. ³ CMPO is octyl(phenyl)N,N-diisobutylcarbamoylmethylphosphine oxide.

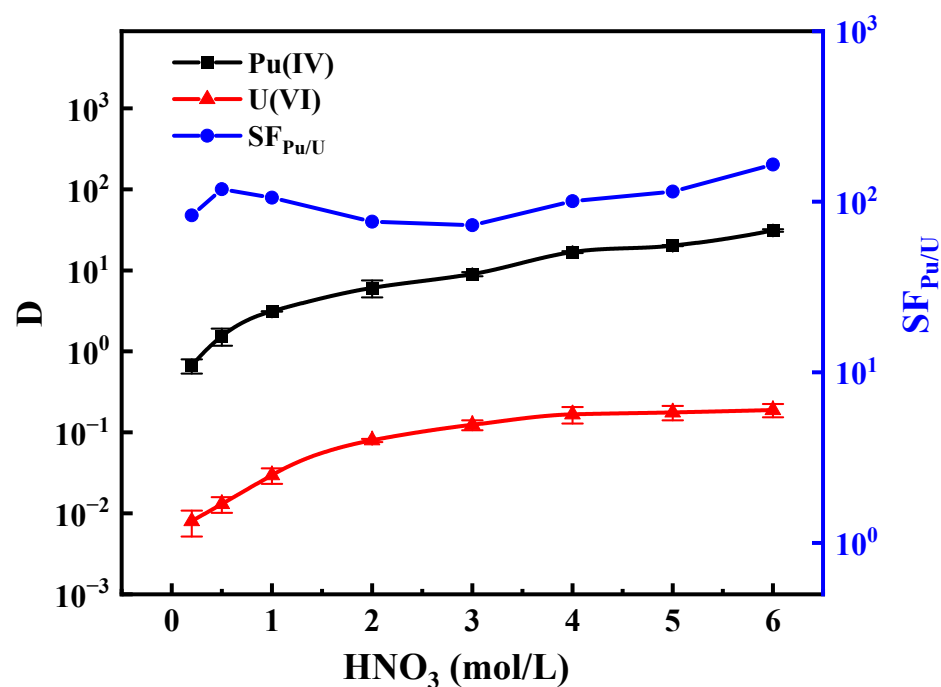


Figure 5. The effect of HNO₃ concentration on extraction distribution ratio and extraction separation factor. Organic phase: 0.05 M TOMDEA-BisDGA in n-octanol; aqueous phase: 5 mg/L Pu(IV), 5 mg/L U(VI); temperature: 298 K; contact time: 30 min.

3.3. The Effect of Temperature

Due to the excessively low distribution ratio of U(VI) by the ligand, the associated relative error became unacceptably large, rendering the data inadequate to accurately reflect the influence of temperature variations on the extraction efficiency. Consequently, the temperature dependence of U(VI) extraction was excluded from further discussion. A complete thermodynamic study has been realized on the extraction reaction of Pu(IV) from 300 K to 330 K. Figure 6 clearly illustrates a crucial trend: as the temperature rises, the distribution ratio of the ligand to Pu (IV) exhibits a significant decline. This inverse relationship strongly suggests that elevated temperatures hinder the extraction efficiency, implying the exothermic nature of the process. To further validate this observation and derive the reaction's thermodynamic parameters, the Van't Hoff equation was employed, establishing a clear correlation between $\log K$ and $1000/T$. At the standard temperature of 298.15 K, the following thermodynamic data were obtained: $\Delta H = -20.32 \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta S = -54.36 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. The ΔG of this reaction was determined as $-4.11 \text{ kJ}\cdot\text{mol}^{-1}$, demonstrating thermodynamic spontaneity for the extraction process. The $\Delta H < 0$ indicates an exothermic nature of the reaction, which can be attributed to the energy release during coordinate bond formation. This enthalpy reduction effectively lowers the total system energy, thermodynamically favoring the forward reaction. Concurrently, the $\Delta S < 0$ suggests a net decrease in system disorder. This phenomenon arises from two counteracting effects: while partial liberation of water molecules from the aqueous phase occurs during complexation, their contribution to system randomness appears insufficient to offset the entropy loss caused by the highly ordered arrangement of metal-ligand complexes in the organic phase.

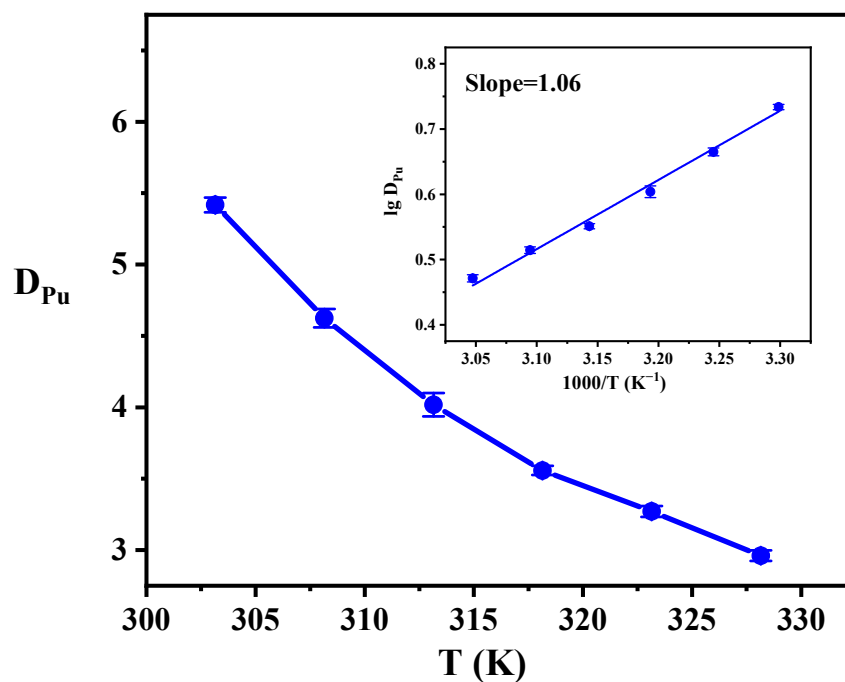


Figure 6. The Effect of Extraction Temperature on the Distribution Ratio of Pu (IV) Extraction. Organic phase: 0.05 M TOMDEA-BisDGA in n-octanol; aqueous phase: 3 M HNO₃, 5 mg/L Pu(IV); contact time: 30 min.

3.4. The Effect of Ligand Concentration

To determine the stoichiometry of the complexes formed between the ligands and Pu(IV) and U(VI), extraction experiments were conducted within the ligand concentration range of 0.01–0.10 M, and the obtained experimental data were subjected to slope analysis. As shown in Figure 7, the D_{pu} values of the TOMDEA-BisDGA ligand increased with the rise in ligand concentration.

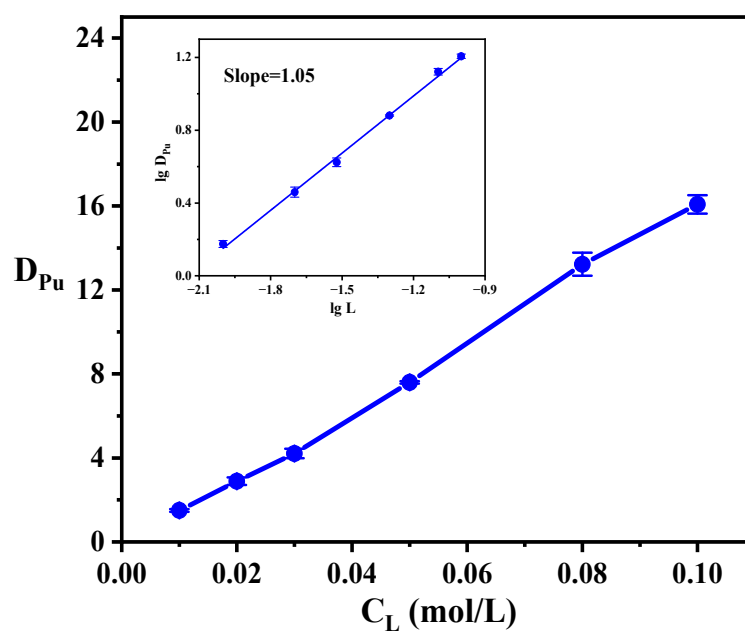


Figure 7. The Effect of ligand concentration on extraction partition ratio of Pu (IV). Organic phase: TOMDEA-BisDGA in n-octanol; aqueous phase: 3 M HNO₃, 5 mg/L Pu(IV); temperature: 298 K; contact time: 30 min.

Based on Equation (7) and the slope of 1.05 in the $\lg D_{Pu}$ - $\lg L$ plot in Figure 7, it is inferred that the stoichiometric ratio of Pu(IV) to the ligand in the formed complex is approximately 1:1, with the primary complex being $Pu(NO_3)_4 \cdot L$, consistent with those reported for the three BisDGA derivatives (THE-BisDGA, THEE-BisDGA, THⁱ-PE-BisDGA) in the literature [23]. Similarly, with a slope of 1.07 in the $\lg D_U$ - $\lg L$ plot in Figure 8, it is deduced that the predominant complex formed is $UO_2(NO_3)_2 \cdot L$.

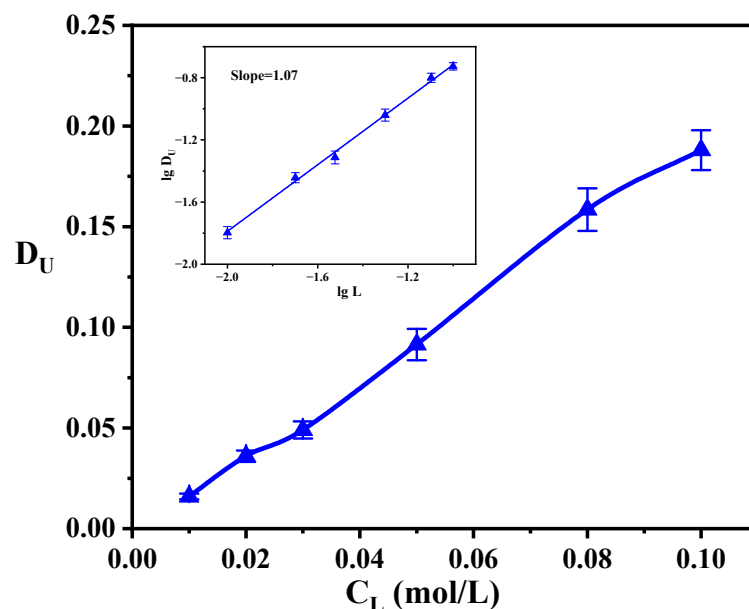


Figure 8. Effect of ligand concentration on extraction partition ratio of U (VI) Organic phase: TOMDEA-BisDGA in n-octanol; aqueous phase: 3 M HNO_3 , 5 mg/L U (VI); temperature: 298 K; contact time: 30 min.

3.5. Stripping Experiment Analysis

To investigate the recyclability of the TOMDEA-BisDGA ligand, a back-extraction experiment was conducted. However, due to the ligand's extremely low distribution ratio for U, the concentration of U extracted into the organic phase was insufficient for stripping experiments. Consequently, only the back-extraction of Pu(VI) was investigated. From the results of the extraction experiment, it was found that the D_{Pu} of the TOMDEA-BisDGA ligand is smaller under conditions of low nitric acid concentration, thus a low-acidity aqueous phase can be used as the back-extractant. Additionally, aqueous complexing agents and reducing back-extractants were employed to back-extract Pu(IV) from the organic phase. The results are shown in Figure 9. The primary back-extraction rates of Pu(IV) by the five back-extractants were all above 85%. After three back-extractions, nearly all Pu(IV) was transferred to the aqueous phase. When using 0.2M HNO_3 as the back-extractant, the back-extraction rate reached 98% after three extractions, indicating that the extraction and back-extraction of Pu(IV) can be achieved simply by adjusting the acidity without the need for introducing additional back-extractants.

After five cycles of extraction with 3M HNO_3 and back-extraction with 0.2M HNO_3 , the D_{Pu} of Pu(IV) by the TOMDEA-BisDGA ligand did not show significant changes (Figure 10), demonstrating that the TOMDEA-BisDGA ligand has certain reusability.

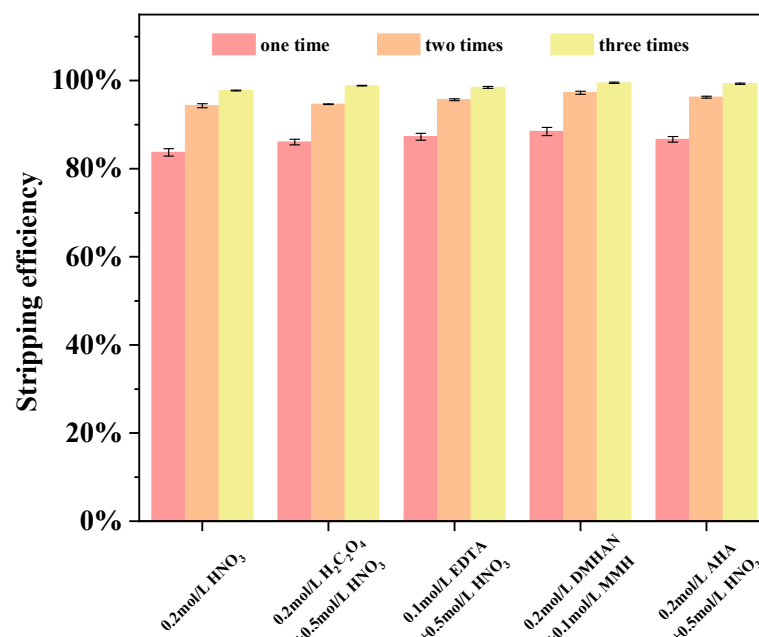


Figure 9. The extraction rate of Pu(IV) from the loaded organic phase using five different stripping agents. Organic phase: 0.05 M TOMDEA-BisDGA in n-octanol; temperature: 298 K; contact time: 30 min.

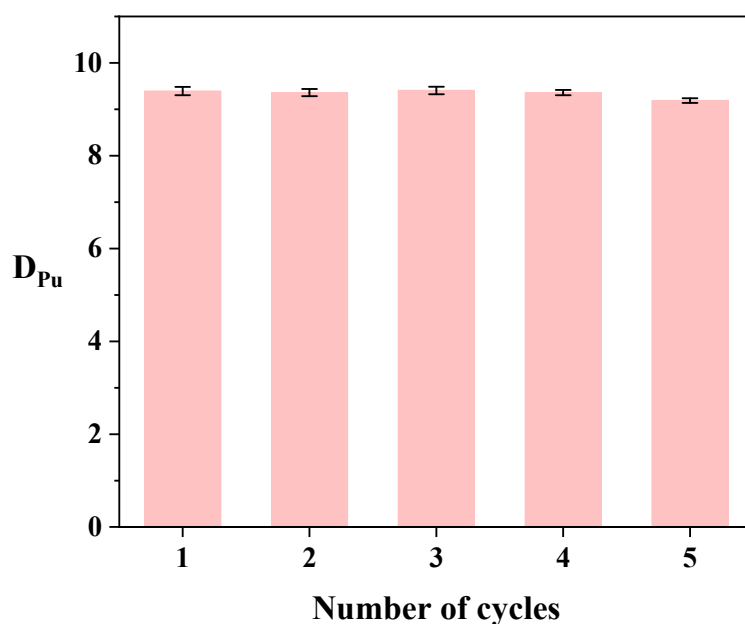


Figure 10. The impact of five extraction-stripping cycles on the extraction ability of plutonium. (Extraction conditions: 0.05 M ligand; 3M HNO₃; stripping conditions: 0.2 M HNO₃; temperature: 298 K; contact time: 30 min).

3.6. The Coordination Mechanism of TOMDEA-BisDGA Towards Pu(IV)

Due to the similarity in the coordination properties of Ce(IV) and Pu(IV), tetravalent cerium was employed to simulate the radioactive element plutonium for FT-IR studies. The major features, which are well defined for TOMDEA-BisDGA at the carbonyl stretching vibrational peak, are 1652 cm⁻¹ (Figure 11). When the ligand comes into contact with the aqueous solution, the oxygen atom of the carbonyl group participates in coordination, whereupon the strong carbonyl absorption peak, due to vibrational coupling interaction, further splits into two minor peaks. The peak at 1128 cm⁻¹ corresponds to the stretching vibration of the ether oxygen bond. Upon contact of the ligand with nitric acid, this peak undergoes a slight redshift, which further redshifts upon the addition of metal, indicating

that the ether oxygen bond is involved in coordination. After the extraction reaction, a new peak emerges at 1377 cm^{-1} , which should be the stretching vibration peak of the N-O bond in NO_3^- . This shows that NO_3^- also participates in the reaction. Therefore, the coordination of the ligand with Ce(IV) occurs through the C=O and C-O-C bonds in the ligand, accompanied by the involvement of NO_3^- .

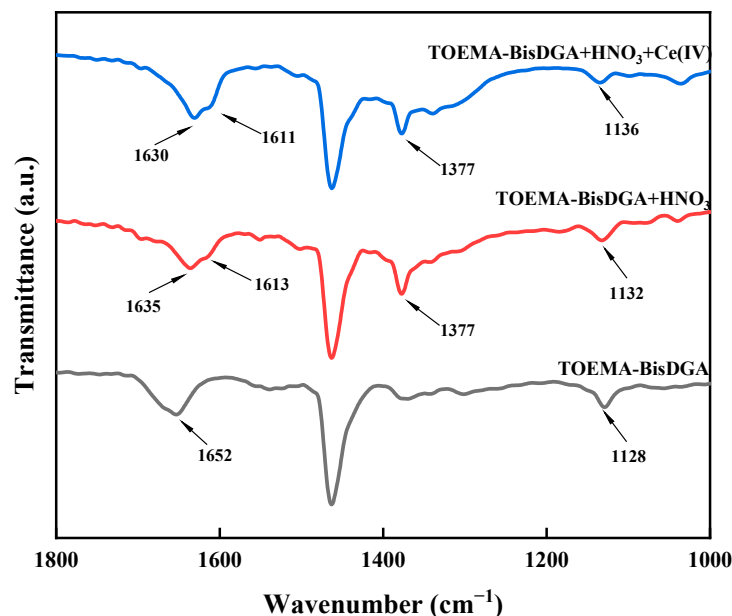


Figure 11. FT-IR spectra of complexation of TOMDEA-BisDGA with Ce(IV).

To analyze the coordination mode of the complex, an ^1H NMR titration experiment was conducted using the diamagnetic tetravalent metal element Ce(IV) with the TOMDEA-BisDGA ligand. As shown in Figure 12, the peaks at 4.36 ppm and 4.07 ppm correspond to the protons (H1, H2) on the carbon atoms adjacent to the ether bond in the initial ligand ($\text{M/L} = 0.0$). Upon the addition of Ce(IV), the peaks of H1 and H2 rapidly diminished, indicating the coordination between Ce(IV) and the ligand, which occurred between the two carbonyl oxygens and the ether oxygen. New peaks appeared at 4.25 ppm and 3.16 ppm (marked by black arrows), and when $\text{M/L} \geq 1.0$, the peak positions stabilized. This suggests that the stoichiometric ratio of the resulting complex should be 1:1.

The coordination modes were preliminarily investigated through FT-IR and NMR titration studies of the ligand with Ce(IV). The oxygen atoms of the two carbonyl groups in the ligand, acting as hard base electron-donating groups, form strong coordination bonds with the highly charged and small-radius Ce(IV) ion via lone pair electrons, which aligns with the Hard and Soft Acid-Base (HSAB) theory. Concurrently, the oxygen atoms of the ether groups participate in coordination through their lone pair electrons, leading to weakened bond strength and increased bond length, as evidenced by a red shift in vibrational frequency. This further confirms their role as auxiliary coordination sites. Multidentate chelation involving both carbonyl and ether oxygen groups enables the formation of a stable cyclic structure, thereby enhancing the thermodynamic stability of the coordination complex. Additionally, nitrate ions occupy the remaining coordination sites and participate in the formation of complexes. These experiments provide both experimental and theoretical foundations for simulating the coordination behavior of Pu(IV).

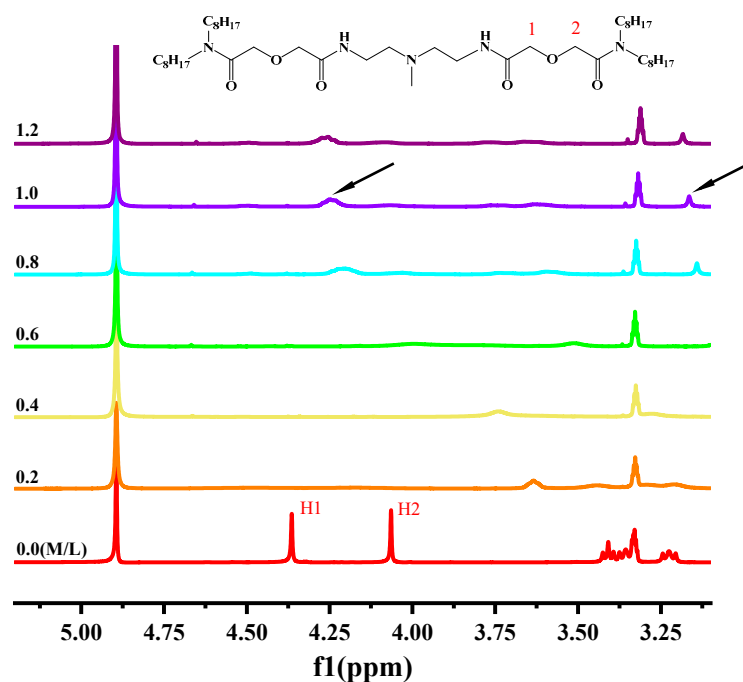


Figure 12. ^1H NMR titration profile of TOMDEA-BisDGA with Ce(IV). Diluent: CD_3OD .

4. Conclusions

In this study, we successfully designed and synthesized a novel diglycolamide-based ligand, TOMDEA-BisDGA, which demonstrates exceptional performance in the selective extraction and separation of Pu(IV) and U(VI) from nitric acid solutions. Our findings reveal that TOMDEA-BisDGA exhibits remarkable extraction efficiency for Pu(IV) across a wide range of nitric acid concentrations (2–6 M), while showing minimal affinity for U(VI). Significantly, the separation factor between Pu(IV) and U(VI) reaches approximately 10^2 , indicating excellent selectivity. Thermodynamic investigations demonstrate that the extraction process is exothermic and spontaneously occurs at ambient temperatures, highlighting its practical applicability. A complete slope analysis and ^1H NMR titration experiments confirmed a preferential 1:1 stoichiometry on the extracted complex between the ligand and tetravalent metal ions. Stripping experiments further revealed the ligand's excellent recyclability and reusability, which are crucial for potential industrial applications. Additionally, FT-IR spectroscopy provided preliminary insights into the complex's coordination mode. The strategic incorporation of a soft donor nitrogen atom into the bis-diglycolamide scaffold represents a significant advancement in ligand design. This modification enables superior Pu(IV)/U(VI) separation performance without the need for oxidation state manipulation, setting it apart from conventional ligands. This work not only extends the application scope of DGA-like ligands but also offers valuable mechanistic insights into the extraction behavior and coordination chemistry of diglycolamide-based compounds. These findings contribute to both fundamental research and practical applications in the nuclear fuel cycle and environmental management of actinides.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/separations12050106/s1>, Figure S1: ^1H -NMR spectrum of TOMDEA-BisDGA; Figure S2: ^{13}C NMR spectrum of TOMDEA-BisDGA; Figure S3: ESI-MS spectrum of TOMDEA-BisDGA.

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