Selective extraction of Am(III) over Eu(III) in nitric acid solution by NTAamide(C8) using a novel water-soluble bisdiglycolamide as a masking agent

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Abstract

A novel water-soluble ligand of *N,N,N',N''*-tetraethyl-*N',N''*-ethidene bisdiglycolamide (TEE-BisDGA) was synthesized and used as a masking agent for selective extraction of Am(III) over Eu(III) from HNO₃ solution by *N,N,N',N',N'',N''*-hexaoctylnitrilotriacetamide (NTAamide(C8)) in kerosene. Influences of acidity, concentration of water-soluble ligands and extractant on the distribution ratios (*D*) and separation factors (*SF*) of Am(III) and Eu(III) were investigated. In the range of examined acidity from 0.001 to 0.2 mol/L, *D*_{Am} and *D*_{Eu} decreased with the increase of HNO₃ concentration. Using 0.1 mol/L NTAamide(C8) as an extractant, the maximum *SF*_{Am/Eu} of 26 can be obtained in the presence of 0.01 mol/L TEE-BisDGA in aqueous phase with pH of 3.0, which was significantly higher than that case with no TEE-BisDGA. Job's method and mole ratio method were employed for extraction mechanism research. It has been shown that Am(III) and Eu(III) formed di-solvated species with TEE-BisDGA and mono-solvated species with NTAamide(C8),

respectively. Moreover, the stability constants $\log\beta$ values were obtained from UV-vis adsorption spectroscopic titration for Nd(III) complexes with TEE-BisDGA and *N,N,N',N'*-tetraethyldiglycolamide (TEDGA), which indicated that TEDGA had a stronger complex ability than TEE-BisDGA.

Keywords: Water-soluble bisdiglycolamide; NTAamide; Lanthanides; Actinides; Solvent extraction.

1. Introduction

High level liquid waste (HLLW), generating in the process of the spent fuel reprocessing, is very harmful to the environment. Its long-lived radiotoxicity is dominated by actinides (An) such as Am and Cm. For reducing the long-term risks of HLLW, the transmutation strategy has been presented via the transformation of An into the short-lived radioactive or stable species using high-energy neutrons. However, because of the coexistence of lanthanides (Ln) having high thermal neutron cross-sections, the transmutation for An would be greatly hampered. Therefore, the separation of An from Ln is one of essential tasks to establish the transmutation technology [1–4].

In HLLW treatment process, Ln/An separation is commonly considered as one of the most challenging issues owing to the same valence state of +3, very close ionic radii and similar chemical behaviors [5]. In spite of this, according to hard and soft acids and bases principle, An(III) has stronger affinities with the soft ligands containing N- or S- donor in comparison to Ln(III). In other words, Ln(III)/An(III) separation can be performed using the N- or S- donor ligands [4], e.g., bis(2,4,4-

trimethyl-pentyl)dithiophosphinic acid (HBTMPDTP), *N,N,N',N'*-tetrakis(2-pyridylmethyl)ethylenediamine (TPEN), 2,6-bis(5,6-dialkyl-1,2,4-triazin-3-yl)pyridines (BTPs), 6,6-bis(5,6-dialkyl-1,2,4-triazin-3-yl)-2,2-bipyridine (BTBPs) (Fig. 1). Nevertheless, the above-mentioned typical ligands suffered from some problems, such as poor hydrolysis and irradiation stability, relatively slow extraction kinetics [6]. They still can not meet the practical needs of HLLW treatment. Consequently, it is very necessary to develop new ligands containing N- or S- donor.

Compared with S-bearing ligand, N-donor ligand consists only of C, H, O and N elements and can be completely incinerated to gases, meaning fewer secondary solid wastes. Thus, the research and development of N-bearing ligand attracts more attention. In recent years, it was found that NTAamide(C8) (Fig. 1), a kind of new N-donor ligand, could selectively separate Am(III) over Eu(III). The separation factor ($SF_{Am/Eu}$) could reach 9.67 in the case of the extraction by 0.1 mol/L NTAamide(C8) in n-dodecane from 0.2 mol/L HNO₃ solution [7], indicating an extraction selectivity for Am(III) to some extent. This could be ascribed to the coordination of soft N atom at the top of the tripod as well as the special tripod structure. As a matter of fact, this coordination interaction has been observed from x-ray crystal structure of the complex [Th(NTAamide(C4))(NO₃)₄] in our previous work [8]. In contrast to BTPs and BTBPs, the most important difference is that there is no N-heterocycle in NTAamide(C8) molecular structure, suggesting better hydrolysis and irradiation stability. However, due to the much lower $SF_{Am/Eu}$ value for NTAamide(C8) than that for BTPs or BTBPs whose $SF_{Am/Eu}$ is about 10²–10³ [9–12], the extraction system based on NTAamide(C8) still needs to be improved greatly.

Recently, using NTAamide(C8) as extractant, Sasaki *et al.* investigated the

separation of Am(III) over Cm(III) in the presence of TEDGA. It has been shown that $SF_{Am/Cm}$ value can be increased significantly from 1.66 to 6.5 with the presence of 10 mmol/L water-soluble TEDGA in aqueous phase [13–15]. It needs to be stressed that the separation of Am(III)/Cm(III) is more difficult than that of Am(III)/Eu(III). $SF_{Am/Cm}$ of 6.5 is also a very high value reported currently for the single stage extraction. The above results indicate that the introduction of water-soluble ligand can obviously improve the selectivity of NTAamide(C8) toward Am(III). In fact, the similar way has already been used in TALSPEAK process, in which di(2-ethylhexyl) phosphoric acid (HDEHP) and diethylenetriamine-*N,N,N',N',N''*-pentaacetic acid (DTPA) as extractant and actinide masking agent, respectively [16]. In view of this point, the addition of Eu(III) masking agent such as TEDGA can also enhance $SF_{Am/Eu}$ value of NTAamide(C8). Nevertheless, it is unfortunate that there is still no report on the selective extraction of NTAamide(C8) to Am(III) over Eu(III) in the presence of masking agent. So, the further study is necessary.

Not long ago, we found that $SF_{Eu/Am}$ value for *N,N,N''',N'''*-tetrabutyl-*N',N''*-ethidene bisdiglycolamide (TBE-BisDGA) could reach 10.0 in HNO₃ solution [17]. Compared with TODGA (*N,N,N',N'*-tetraoctyl diglycolamide, an oil-soluble homolog of TEDGA), TBE-BisDGA has higher selectivity to Eu(III) [18,19]. In other words, the water-soluble BisDGA maybe has better masking efficiency to Eu(III) than TEDGA. Therefore, it can be expected that $SF_{Am/Eu}$ value of NTAamide(C8) would be significantly improved in the presence of water-soluble BisDGA.

In the present paper, a novel water-soluble ligand of TEE-BisDGA was synthesized, and used as a masking agent for selective extraction of Am(III) over Eu(III) from HNO₃ solution by NTAamide(C8) in kerosene. Influences of acidity,

concentration of water-soluble ligands and extractant on the extraction of Am(III) and Eu(III) were investigated. The extraction mechanism was explored through Job's method and mole ratio method. Meanwhile, the effectiveness of TEE-BisDGA and TEDGA for selective extraction of Am(III) over Eu(III) were also compared.

2. Experimental

2.1. Reagents and measurements

The aqueous phase containing Eu(III) was prepared by dissolving the metallic oxide (99.99%, Aldrich, USA) in variable HNO₃ solution. Nd(NO₃)₃ in HNO₃ solution or acetonitrile was prepared from the oxides (99.99%, Aldrich, USA). The tracer stock solutions were obtained from the purified radionuclides ²⁴¹Am and provided by China Institute of Atomic Energy with radiochemical purity of 99.9%. Kerosene was purified by referring to the literature [20]. All the other reagents used in the experiments were of AR grade.

TEE-BisDGA and TEDGA were characterized by NMR, FT-IR and MS. ¹H NMR and ¹³C NMR were determined in CDCl₃ on a Varian Inova NMR spectrometer (¹H: 400 MHz; ¹³C: 100 MHz) (Bruker Inc., Switzerland) with tetramethylsilane as an internal solvent resonances reference. FT-IR spectra were recorded on a Nicolet 6700 Fourier transform infrared spectrometer (Thermo Fisher Scientific Inc., USA). MS were measured on a Bruker Amazon SL spectrometer (Bruker Inc., Switzerland).

2.2. Synthesis

NTAamide(C8) was prepared in our laboratory referring to the previous literature [8]. TEE-BisDGA and TEDGA were synthesized according to Scheme 1.

2.2.1. Synthesis of TEE-BisDGA

TEE-BisDGA was synthesized through the reaction of *N,N*-diethyl-3-oxa-glutaramic acid (DEOGA) with ethanediamine in the presence of 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI) as condensing agent and 1-hydroxybenzotriazole (HOBT) as catalyst, respectively. The diglycolic anhydride was prepared by the literature procedure [21], and the DEOGA was synthesized using the previous method [17].

The ethanediamine (0.70 mL, 10 mmol) and triethylamine (3.0 mL, 22mmol) were added slowly into a solution of DEOGA (4.7 g, 25 mmol) in 250 mL dichloromethane. After that, EDCI (4.8 g, 25 mmol) and HOBT (3.4 g, 25 mmol) were added sequentially and stirred for 10 h at ambient temperature. The reaction mixture was successively washed with 1.0 mol/L HCl (2 × 250 mL); 1.0 mol/L NaOH (2 × 250 mL) and deionized water (2 × 250 mL). The organic layer was dried with anhydrous Na₂SO₄ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel eluting with dichloromethane/methanol (v/v, 20:1) to give TEE-BisDGA (1.8 g, yield: 89%) as yellowish solid; m.p. 75.2-77.3 °C. ¹H NMR (400 MHz, CDCl₃, ppm) δ 1.18 (m, 12H, CH₃), 3.23 (q, 8H, CH₂), 3.41 (q, 4H, CH₂), 4.28 (s, 8H, CH₂), 8.12 (s, 2H, NH); ¹³C NMR (100MHz, CDCl₃, ppm) δ 12.9, 40.5, 41.0, 71.7, 76.7, 167.9, 170.1. IR (v/cm⁻¹): 3309(b,s), 2978(m), 2937(b,m), 1659(s), 1539(m), 1461(m), 1382(w), 1355(w), 1310(w), 1271(m), 1227(w), 1128(s), 1036(w), 981(w), 902(w). HRMS: m/z 403.2555, [M+H]⁺, calculated: 403.2556; 425.2309, [M+Na]⁺, calculated: 425.2376; 441.2013, [M+K]⁺, calculated: 441.2115.

2.2.2. Synthesis of TEDGA

Thionyl chloride (44 mL, 620 mmol) was added dropwise to diglycol acid (DGAc) (6.9g, 50 mmol) with several drops of pyridine. The mixture was refluxed for 5 h at 78 °C. After cooling, thionyl chloride was evaporated via reduced pressure distillation. The residue was dissolved in 10 mL dichloromethane and then added dropwise into a mixture solution of diethylamine (15 mL, 140 mmol) and triethylamine (20 mL, 140 mmol) in 40 mL dichloromethane below 0 °C. Once the addition was finished, the reaction was continued for 2 h at 0 °C, and then warmed to room temperature for another 3 h. The obtained mixture was sequentially washed with 1.0 mol/L HCl (3 × 50 mL); 1.0 mol/L NaOH (3 × 50 mL) and deionized water (3 × 50 mL). The organic layer was dried with anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude product was purified through column chromatography on silica gel eluting with dichloromethane/methanol (v/v, 10:1) to provide TEDGA (5.9 g, yield: 49%) as reddish brown oil. ¹H NMR (400 MHz, CDCl₃) δ 1.18 (m, 12 H, CH₃), 3.30 (q, 8H, CH₂), 4.31 (s, 4H, CH₂); ¹³C NMR (100MHz, CDCl₃, ppm) δ 12.9, 14.2, 40.1, 41.1, 69.4, 168.0. IR (v/cm⁻¹): 2972(s), 2933(s), 2877(b,s), 1647(s), 1462(m), 1377(b,m), 1269(m), 1226(m), 1115(b,s), 953(m), 899(m), 798(m). HRMS: m/z 264.1558, [M+H]⁺, calculated: 264.1587.

2.3. Extraction

Using NTAamide(C8) in kerosene as the organic phase and HNO₃ solution containing TEE-BisDGA or TEDGA as the aqueous phase, the distributions of ²⁴¹Am and Eu(III) were investigated through measuring their concentrations in each phase at equilibrium. Firstly, the organic phases were pre-equilibrated three times with equal volume of HNO₃ solutions of the corresponding concentration, ensuring that the concentration of the aqueous electrolyte did not change during the equilibration with

the metal ion present. After that, equal volume (1.0 mL) of the organic phase and the aqueous phase were mixed in 10.0 mL stoppered glass tubes, stirring in water bath for 0.5 h at 25.0 ± 0.5 °C. The contents were then centrifuged and 0.50 mL aliquots were taken from the aqueous and organic phase for the concentration analysis of metal ion. The concentration of ^{241}Am in terms of radioactivity counts was detected by NaI(Tl) scintillation counter (China National Nuclear Inc., China). Eu(III) concentration in the aqueous phase were diluted to appropriate level and measured by ICP-AES (IRIS Advantage, Thermo Elemental Inc., America). The distribution ratio D of metal ion was defined as Eq. (1), where the subscripts (tot,org.) and (tot,aq.) represented the total concentration of metal ion in organic phase and aqueous phase, separately. The separation factor SF and extraction percentage ($E\%$) were expressed as Eq. (2) and Eq. (3), respectively.

$$D = [\text{M}]_{\text{tot,org.}} / [\text{M}]_{\text{tot,aq.}} \quad (1)$$

$$SF_{\text{Am/Eu}} = D_{\text{Am}} / D_{\text{Eu}} \quad (2)$$

$$E\% = \frac{[\text{M}]_{\text{tot,org.}}}{[\text{M}]_{\text{tot,org.}} + [\text{M}]_{\text{tot,aq.}}} \times 100\% \quad (3)$$

2.4. UV-vis spectra titration

UV-vis spectra titration was performed by means of the substitution of Nd(III) for Eu(III). The detailed explanations on this substitution will be given in the following section of "results and discussion".

The titration of Nd(III) was carried out on UV-vis spectrometer (Persee TU-1810PC). Quartz cells of 1.0 cm were used. The initial concentration of Nd(III)

was 0.05 mol/L in pH 4.0 HNO₃ solution or acetonitrile. In each titration, appropriate aliquots of the titrant (0.625 mol/L TEE-BisDGA, TEDGA and NTAamide(C8)) were added into the cell and with electromagnetic stirring for 2 min before the spectrum was detected. The absorption spectrum was collected from 560 to 605 nm at 0.1 nm interval. The stability constants of the Nd(III)-ligands complexes (on the molarity scale) were calculated by nonlinear least-squares regression using the *Hyperquad* program [22–24].

3. Results and discussion

3.1. Influence of HNO₃ and NTAamide(C8) concentration

In the presence of 0.01 mol/L TEE-BisDGA or TEDGA in aqueous phase, the influence of HNO₃ concentration on D_{Am} and D_{Eu} is shown in Fig. 2. Both D_{Am} and D_{Eu} decreased with the increase of HNO₃ concentration, which was similar to that reported by Sasaki [7]. When HNO₃ concentration exceeds 0.01 mol/L, the downward trend is more obvious. This can be ascribed to the competition extraction of HNO₃ [8], especially at high acidity. The separation factors of Am(III) and Eu(III) under different concentrations of HNO₃ were calculated and listed in Table 1. A decrease of $SF_{Am/Eu}$ for both TEE-BisDGA and TEDGA was observed with increasing HNO₃ concentration in the examination of acidity ranging from 0.001 to 0.2 mol/L. Nevertheless, $SF_{Am/Eu}$ of TEE-BisDGA was remarkably higher than that of TEDGA. TEE-BisDGA had the maximum $SF_{Am/Eu}$ of 26 at 0.001 mol/L HNO₃, whilst TEDGA gave only $SF_{Am/Eu}$ of 9.6 under the same conditions. This result indicated that the former exhibited higher selectivity for Eu(III) over Am(III). The influence of NTAamide(C8) concentration on D is given in Fig. 3. It can be seen that D_{Am} and D_{Eu} increased with increasing the concentration of NTAamide(C8). The separation factors

were summarized in Table 2. $SF_{Am/Eu}$ values of TEE-BisDGA were obviously higher than those of TEDGA. This also showed better selectivity of TEE-BisDGA than TEDGA toward Eu(III) over Am(III) [17,19]. Meanwhile, $SF_{Am/Eu}$ increased with the increase of NTAamide(C8) concentration, which is also in agreement with that from literatures [7,14]. In addition, all D_{Am} and D_{Eu} values of TEE-BisDGA are higher than the counterpart values of TEDGA, meaning that the latter has stronger complexation ability with Am(III) and Eu(III) than the former [19].

3.2. Influence of masking agent concentration

Keeping the concentrations of NTAamide(C8) and HNO_3 as constants, we investigated the influence of masking agent concentration on D and $SF_{Am/Eu}$. The results are shown in Fig. 4 and Table 3, respectively. It can be seen clearly that both D_{Am} and D_{Eu} decreased with increasing the concentration of TEE-BisDGA and TEDGA. This can be attributed to the masking effect of the water-soluble ligand. Nevertheless, the downtrend of D_{Am} and D_{Eu} was different to some extent. A considerable reduction of D_{Eu} occurred as the concentration of water-soluble ligand approached 0.01 mol/L. And then the reduction became moderate in excess of this concentration. However, D_{Am} decreased smoothly within 0.01 mol/L of the start, then becoming sharply with the further increase of masking agents. $SF_{Am/Eu}$ increased at first with the increase of water-soluble ligand concentration until up to 0.01 mol/L and then decreased. This phenomenon can be explained as follows. Both TEE-BisDGA and TEDGA showed higher affinity toward Eu(III) than Am(III), the initial addition of masking agent resulted in the faster decrease of D_{Eu} than D_{Am} . But, due to the enhancement of masking effect to Am(III), the further increase of masking agent led a significant decrease of D_{Am} . As a result, the highest $SF_{Am/Eu}$ for both TEE-

BisDGA and TEDGA were obtained at the concentration of 0.01 mol/L. Moreover, as listed in Table 3, $SF_{Am/Eu}$ values of TEE-BisDGA were obviously higher than those of TEDGA, it also showed that the former has better selectivity for Eu(III) over Am(III) than the latter. That is to say, TEE-BisDGA is more favorable for the separation of Am(III) and Eu(III) than TEDGA.

3.3. Extraction mechanism

NTAamide(C8), TEE-BisDGA and TEDGA belong to neutral chelating agents. In general, the main extraction reaction of metal ions by NTAamide(C8) and masking reaction by water-soluble ligand in HNO_3 solution can be expressed severally as follows:

Where M, L and Y denote metal ions, extractant and masking agent, respectively, n and m are the the coordination numbers.

K_{ex} and β represent the reaction equilibrium constants. They can be defined as:

$$K_{ex} = \frac{[M(NO_3)_3 \cdot nL]_{(org.)}}{[M^{3+}]_{(aq.)}[NO_3^{-}]^3_{(aq.)}[L]^n_{(org.)}} \quad (6)$$

$$\beta = \frac{[M(NO_3)_3 \cdot mY]_{(aq.)}}{[M^{3+}]_{(aq.)}[NO_3^{-}]^3_{(aq.)}[Y]^m_{(aq.)}} \quad (7)$$

And the distribution ratio of metal ions can be represented as:

$$D = \frac{[M(NO_3)_3 \cdot nL]_{(org.)}}{[M^{3+}]_{(aq.)}} \quad (8)$$

Substituting D values in Eq. (8) into Eq. (6) and taking the logarithm of the

rearranged equation:

$$\log K_{\text{ex}} = \log D - 3 \log [\text{NO}_3^-]_{(\text{aq.})} - n \log [\text{L}]_{(\text{org.})} \quad (9)$$

Generally speaking, a plot of $\log D$ vs $\log [\text{L}]_{(\text{org.})}$ can give a straight line. However, due to the introduction of masking agent into the aqueous phase, the extraction system become more complex. Thus, the most commonly used slope analysis is not suitable for determining the ratio between the extractant molecule and metal ion. In the present work, the plot of $\log D$ vs $\log [\text{L}]_{(\text{org.})}$ can not obtain a straight line with good linear relationship. In this case, the other methods such as Job's method and mole ratio method are needed to determine the stoichiometry of extracted complexes.

3.3.1. Job's method

Job's method was established by Job in 1928 [25]. In the early stage, this method was often used in the fields of analytical chemistry for determining the stoichiometry of two interacting components [26–29]. Afterwards, it was also widely applied in the solvent extraction chemistry [30–33]. As commonly practiced, Job's method is conducted in a hatch mode by mixing aliquots of two equimolar stock solutions of metal and ligand. These solutions are prepared in such a way that the total concentration of metal and ligand is maintained constant while the the concentration ratio between ligand and metal varies from flask to flask, that is:

$$C_{\text{M}} + C_{\text{L}} = k \quad (10)$$

where C_{M} and C_{L} are the concentrations of metal and ligand, respectively, and k is a constant.

The mole fraction of ligand χ_{L} is defined as:

$$\chi_L = \frac{C_L}{C_M + C_L} \quad (11)$$

A measurable parameter such as distribution ratio D and extraction percentage E is plotted against χ_L to generate a broken line. The stoichiometry of the two components can be reflected from the intersection projection values [28].

In our experiments, the concentration of masking agent was kept as 1.0×10^{-2} mol/L. The total concentration of the initial metal ion in aqueous phase and NTAamide(C8) in organic phase was maintained as a constant of 2.0×10^{-2} mol/L, The plot of the concentration of Am(III) and Eu(III) in the organic phase against the molar fraction of NTAamide(C8) are shown in Fig. 5 (a) and Fig. 5 (b), severally. The maximum values of metal ions extracted by NTAamide(C8) were obtained at the extractant molar fraction of 0.5, revealing that the mono-solvated species are produced. Analogously, the stoichiometry of TEE-BisDGA and TEDGA with metal ion are 2:1 and 3:1, according to the intersection projection values of the masking agent fraction of 0.65 and 0.74 in Fig. 5 (c) and Fig. 5 (d), respectively.

3.3.2. Mole ratio method

Mole ratio method is also used to discuss the extraction mechanism. This method is based upon considerations of a type of reaction as follows:

Both Eq. (4) and Eq. (5) belong to this type reaction. If the product of reaction is very little dissociated, a plot of extraction percentage E against the mole ratio of component L to component M (also known as the relative concentration), with the concentration of M held constant, rises steeply from the origin as a straight line and then breaks sharply. The corresponding value of L/M at the break in the curve

represents the mole ratio in the product [30,34,35].

Like the previous Job's method, both metal ion concentration and masking agent concentration were maintained as constants of 1.0×10^{-2} mol/L. The plot of extraction percentage E of Am(III) and Eu(III) against the relative concentration are given in Fig. 6 (a) and Fig. 6 (b), respectively. It can be seen that L/M values at the breaks were close to 1.0, representing that 1:1 type complexes were formed. That is to say, both Am(III) and Eu(III) were extracted by NTAamide(C8) as mono-solvated species. Similarly, keeping the concentrations of both metal ion and NTAamide(C8) as 1.0×10^{-2} mol/L, the approximate values of inflection point projection on the X-axis shown in Fig. 6 (c) and Fig. 6 (d) are 2.0 and 3.0 for TEE-BisDGA and TEDGA, separately. This indicated that TEE-BisDGA and TEDGA complexed with metal ion at the molar ratios of 2:1 and 3:1, respectively.

Both Job's method and mole ratio method gave the conclusion that Am(III) and Eu(III) formed di-solvated complexes with TEE-BisDGA and tri-solvated complexes with TEDGA, severally. This may be attributed to the much larger molecule of TEE-BisDGA than TEDGA, which results in a fewer molecules coordinated with metal ion for the former.

On the basis of the results obtained from Job's method and mole ratio method, the stoichiometric relation of the extraction reaction with NTAamide(C8) and masking process with water-soluble ligands can be proposed as follows:

(13)

(14)

(15)

3.4. UV-vis spectra titration

For a deep insight into the complexation behavior of the ligand with Eu(III), UV-visible spectra titration was carried out. Unfortunately, Eu(III) in HNO₃ solution has almost no ultraviolet absorption in a wide range of wavelength from 300 nm to 900 nm (Fig. S13). Nevertheless, Nd(III) as the most similar f-element to Eu(III) has the very good ultraviolet absorption (Fig. S13). Consequently, it can be employed Nd(III) as a substitution for Eu(III) to investigate the complexation behavior. In fact, as far as Am, Eu and Nd be concerned, they have the very similar ionic radii (0.099Å, 0.095Å and 0.100Å, respectively) and the same oxidation state of +3 in aqueous solution, leading to very similar chemical behavior. Thus, Nd(III) is also usually used as a representative of lanthanides for study on Ln(III)/An(III) separation and absorption spectroscopy [22,36–38]. In the following experiments, UV-visible spectra titrations for Nd(III) with TEE-BisDGA, TEDGA and NTAamide(C8) were investigated.

3.4.1. UV-visible spectra titration for Nd(III)/TEE-BisDGA

Fig. 7 showed the representative series of absorption spectra of Nd(III) with TEE-BisDGA. Increasing the concentration of TEE-BisDGA is accompanied by a slight decrease in absorption and a red-shift of the spectra. Besides that, two shoulder bands appeared at 574.3 nm and 584.4 nm with the addition of titrant [39,40]. Analysis by *Hyperquad* program revealed that there were two new absorbing species of Nd(III), namely, NdY³⁺ and NdY₂³⁺ forming in the titration (Y represents TEE-BisDGA). Meanwhile, the complexation stability constant logβ values were calculated to be 0.80 ± 0.02 and 1.32 ± 0.05 for NdY³⁺ and NdY₂³⁺, respectively.

3.4.2. UV-visible spectra titration for Nd(III)/TEDGA

Significant changes in the absorption spectra of representative titration for Nd(III) and TEDGA was shown in Fig. 8. It can be seen that sharp branches of the band were

appeared in the region of 574.0–589.0 nm with the addition of TEDGA. Similarly to Nd(III)/TEE-BisDGA system, a red-shift of curve and two shoulder peaks were obviously appeared, suggesting the formation of new species. The best fit of the spectra by *Hyperquad* program indicated that there were three compounds generated successively: NdY^{3+} , NdY'_2^{3+} and NdY'_3^{3+} (Y' represents TEDGA). $\log\beta$ values of the corresponding complexes were 2.07 ± 0.03 , 3.81 ± 0.04 and 5.35 ± 0.06 , severally. In comparison with TEE-BisDGA, $\log\beta$ values of TEDGA were obviously larger, showing the stronger affinity of TEDGA than TEE-BisDGA. This result was in accordance with that of the extraction experiments.

3.4.3. UV-visible spectra titration for Nd(III)/NTAamide(C8)

Due to the indissolubility for NTAamide(C8) in aqueous solution, UV-visible spectra titration for Nd(III)/NTAamide(C8) system had to be performed in acetonitrile solution. As shown in Fig. 9, the intensity of absorption band increased with the addition of NTAamide(C8) until up to 1.0 equivalent, and then decreased with the further increase of titrant. It is noteworthy that the spectra shape of Nd(III) in acetonitrile solution was different from that in HNO_3 solution. This phenomenon may be ascribed to the solvent effect. An isosbestic point observed at 581.3 nm suggested the presence of two absorbing Nd(III) species including $\text{Nd}(\text{NO}_3)_3$. The stability constant of NdL^{3+} (L represents NTAamide(C8)) was calculated as 8.27 ± 0.06 [41].

4. Conclusions

It has been shown that Am(III) and Eu(III) can be separated effectively in HNO_3 solution using NTAamide(C8) as extractant and TEE-BisDGA as masking agent, severally. TEE-BisDGA has better masking efficiency than TEDGA. Extraction mechanism research revealed that TEE-BisDGA, TEDGA and NTAamide(C8) with

metal ion formed the complexes at the mole ratio of 2:1, 3:1 and 1:1, respectively. UV-vis adsorption spectral analyses confirmed the existence of these complexed species. Meanwhile, the complexation stability constants for TEDGA are obviously larger than those for TEE-BisDGA, indicating the stronger affinity of the former than the latter. As a novel water-soluble agent, TEE-BisDGA may be used to be not only a masking agent, but also a stripping agent for Ln(III)/An(III) separation in HLLW treatment.

Acknowledgments

The authors are very grateful for the financial support by the National Science Foundation of China (Grant Nos. 91426302, 11675115 and 11475120). Analytical & Testing Center of Key Laboratory of Green Chemistry & Technology (Sichuan University) of Education Ministry of China is acknowledged for NMR, MS and ICP-AES analyses.

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Figures captions

Scheme 1. Synthesis route of TEE-BisDGA and TEDGA.

Fig. 1. Chemical structures of the representative N- or S- donor ligands for Ln(III)/An(III) separation.

Fig. 2. Influence of HNO₃ concentration on the distribution ratios of Am(III) and Eu(III). Organic phase: 0.1 mol/L NTAamide(C8) in kerosene; Aqueous phase: tracer amount Am(III) or 200 ppm Eu(III) and 0.01 mol/L water-soluble ligand in different concentrations of HNO₃; Temperature: 25.0 ± 0.5 °C.

Fig. 3. Influence of extractant concentration on the distribution ratios of Am(III) and Eu(III). Organic phase: different concentrations of NTAamide(C8) in kerosene; Aqueous phase: tracer amount Am(III) or 200 ppm Eu(III) and 0.01 mol/L water-soluble ligand in 0.2 mol/L HNO₃; Temperature: 25.0 ± 0.5 °C.

Fig. 4. Influence of masking agent concentration on the distribution ratios of Am(III) and Eu(III). Organic phase: 0.1 mol/L NTAamide(C8) in kerosene; Aqueous phase: tracer amount Am(III) or 200 ppm Eu(III) and different concentrations of water-soluble ligand in 0.2 mol/L HNO₃; Temperature: 25.0 ± 0.5 °C.

Fig. 5. Job's method for determining the composition of metal complexes formed with extractant or masking agent.

(a) Organic phase: 2.0×10^{-3} to 1.8×10^{-2} mol/L NTAamide(C8) in kerosene; Aqueous phase: tracer amount ²⁴¹Am mixed with 2.0×10^{-3} to 1.8×10^{-2} mol/L Eu(III) and 1.0×10^{-2} mol/L water-soluble ligands in 0.001 mol/L HNO₃; Total concentration of metal ion and NTAamide(C8) was 2.0×10^{-2} mol/L.

(b) Organic phase: 2.0×10^{-3} to 1.8×10^{-2} mol/L NTAamide(C8) in kerosene; Aqueous phase: 2.0×10^{-3} to 1.8×10^{-2} mol/L Eu(III) and 1.0×10^{-2} mol/L water-soluble ligands in 0.001 mol/L HNO₃; Total concentration of Eu(III) and NTAamide(C8) was 2.0×10^{-2} mol/L.

(c) Organic phase: 1.0×10^{-2} mol/L NTAamide(C8) in kerosene; Aqueous phase: tracer amount of ²⁴¹Am mixed with 2.0×10^{-3} to 1.8×10^{-2} mol/L Eu(III) and $2.0 \times$

10^{-3} to 1.8×10^{-2} mol/L water-soluble ligands in 0.001 mol/L HNO_3 ; Total concentration of metal ion and water-soluble ligands was 2.0×10^{-2} mol/L.

(d) Organic phase: 1.0×10^{-2} mol/L NTAamide(C8) in kerosene; Aqueous phase: 2.0×10^{-3} to 1.8×10^{-2} mol/L Eu(III) and 2.0×10^{-3} to 1.8×10^{-2} mol/L water-soluble ligands in 0.001 mol/L HNO_3 ; Total concentration of Eu(III) and water-soluble ligands is 2.0×10^{-2} mol/L.

Fig. 6. Mole ratio method for determining the composition of metal complexes formed with extractant or masking agent.

(a) Organic phase: 2.0×10^{-3} to 2×10^{-2} mol/L NTAamide(C8) in kerosene; Aqueous phase: tracer amount of Am(III) mixed with 1.0×10^{-2} mol/L Eu(III) and 1.0×10^{-2} mol/L water-soluble ligands in 0.001 mol/L HNO_3 .

(b) Organic phase: 2.0×10^{-3} to 2.0×10^{-2} mol/L NTAamide(C8) in kerosene; Aqueous phase: 1.0×10^{-2} mol/L Eu(III) and 1.0×10^{-2} mol/L water-soluble ligands in 0.001 mol/L HNO_3 .

(c) Organic phase: 1.0×10^{-2} mol/L NTAamide(C8) in kerosene; Aqueous phase: 2.0×10^{-3} to 4.0×10^{-2} mol/L water-soluble ligands and tracer amount ^{241}Am mixed with 1.0×10^{-2} mol/L Eu(III) in 0.001 mol/L HNO_3 .

(d) Organic phase: 1.0×10^{-2} mol/L NTAamide(C8) in kerosene; Aqueous phase: 2.0×10^{-3} to 4.0×10^{-2} mol/L water-soluble ligands and 1.0×10^{-2} mol/L Eu(III) in 0.001 mol/L HNO_3 .

Fig. 7. UV-visible spectra titration of Nd(III) with TEE-BisDGA at 25 °C. Initial solution: $V_0 = 2.50$ mL, $C_{\text{Nd(III)}} = 0.05$ mol/L in pH = 4.0 HNO_3 ; Titrant: 0.625 mol/L TEE-BisDGA in pH = 4.0 HNO_3 , each 20 μL titrant, as 0.1 times equivalent of Nd(III) was added.

Fig. 8. UV-visible spectra titration of Nd(III) with TEDGA at 25 °C. Initial solution: $V_0 = 2.50$ mL, $C_{\text{Nd(III)}} = 0.05$ mol/L in pH = 4.0 HNO_3 ; Titrant: 0.625 mol/L TEDGA in pH = 4.0 HNO_3 , each 20 μL titrant, as 0.1 times equivalent of Nd(III) was added.

Fig. 9. UV-visible spectra titration of Nd(III) with NTAamide(C8) at 25 °C. Initial solution: $V_0 = 2.50$ mL, $C_{\text{Nd(III)}} = 0.05$ mol/L in acetonitrile; Titrant: 0.625 mol/L NTAamide(C8) in acetonitrile, each 20 μL titrant, as 0.1 times equivalent of Nd(III) was added.

HBMPT

HBTMPDTP

HBCPDTP

TPEN

TPTZ

BTPs

BTBPs

BTPhens

NTAamide(C8)

Table 1 Influence of HNO₃ concentration on the separation factors of Am(III) and Eu(III)^a.

[HNO ₃], mol/L	$SF_{Am/Eu}$	
	TEE-BisDGA	TEDGA
0.001	26.0 ± 1.7	9.6 ± 0.9
0.01	16.2 ± 1.3	8.5 ± 1.1
0.10	15.4 ± 1.1	7.3 ± 0.9
0.20	14.1 ± 1.1	7.0 ± 0.7

^a Organic phase: 0.10 mol/L NTAamide(C8) in kerosene; Aqueous phase: tracer amount Am(III) or 200 ppm Eu(III) and 0.01 mol/L water-soluble ligand in different concentrations of HNO₃; Temperature: 25.0 ± 0.5 °C.

Table 2 Influence of extractant concentration on the separation factors of Am(III) and Eu(III)^a.

[NTAamide(C8)], mol/L	$SF_{Am/Eu}$	
	TEE-BisDGA	TEDGA
0.05	10.2 ± 0.9	3.3 ± 0.3
0.10	14.1 ± 1.1	7.0 ± 0.7
0.20	14.9 ± 1.1	7.4 ± 0.5
0.30	20.4 ± 0.9	7.6 ± 0.6
0.40	22.8 ± 1.0	7.8 ± 0.6
0.50	26.9 ± 1.2	12.3 ± 0.7

^a Organic phase: different concentrations of NTAamide(C8) in kerosene; Aqueous phase: tracer amount Am(III) or 200 ppm Eu(III) and 0.01 mol/L water-soluble ligand in 0.20 mol/L HNO₃; Temperature: 25.0 ± 0.5 °C.

Table 3 Influence of masking agent concentration on the separation factors of Am(III) and Eu(III)^a.

[Masking agent], mol/L	$SF_{Am/Eu}$	
	TEE-BisDGA	TEDGA
0	6.8 ± 0.4	6.8 ± 0.7
0.005	5.3 ± 0.6	5.8 ± 0.6
0.01	14.1 ± 1.1	7.0 ± 0.7
0.02	8.9 ± 0.9	1.8 ± 0.5
0.03	1.9 ± 0.3	1.7 ± 0.3
0.04	1.4 ± 0.1	1.5 ± 0.2

^a Organic phase: 0.10 mol/L NTAamide(C8) in kerosene; Aqueous phase: tracer amount Am(III) or 200 ppm Eu(III) and different concentrations of water-soluble ligand in 0.20 mol/L HNO₃; Temperature: 25.0 ± 0.5 °C.

Table 4 Influence of nitrate concentration on the extraction of Am(III) and Eu(III)^a.

[NO ₃ ⁻], mol/L	TEE-BisDGA			TEDGA		
	D_{Am}	D_{Eu}	$SF_{\text{Am/Eu}}$	D_{Am}	D_{Eu}	$SF_{\text{Am/Eu}}$
0.20	0.70 ± 0.14	0.05 ± 0.01	14.1 ± 1.1	0.15 ± 0.03	0.02 ± 0.01	7.0 ± 0.7
0.50	1.61 ± 0.52	0.15 ± 0.04	11.2 ± 0.8	0.47 ± 0.11	0.07 ± 0.01	6.7 ± 1.2
1.0	2.73 ± 0.54	0.25 ± 0.06	11.4 ± 0.8	0.79 ± 0.26	0.12 ± 0.04	6.6 ± 0.9
2.0	7.10 ± 0.42	0.58 ± 0.14	11.8 ± 1.1	1.82 ± 0.38	0.24 ± 0.05	7.5 ± 0.8
3.0	13.32 ± 0.61	0.89 ± 0.23	14.7 ± 1.2	2.82 ± 0.56	0.38 ± 0.07	7.4 ± 1.0

^a Organic phase: 0.10 mol/L NTAamide(C8) in kerosene; Aqueous phase: tracer amount Am(III) or 200 ppm Eu(III), 0.01mol/L water-soluble ligand and different concentrations of NaNO₃ in 0.20 mol/L HNO₃; Temperature: 25.0 ± 0.5 °C.

Table 5 Back-extraction of Am(III) and Eu(III) from the loaded organic phase^a

Stripping reagent		Stripping percentage, %		
		Stage I	Stage II	Stage III
Deionized water	Am(III)	3.1 ± 0.5	6.1 ± 0.7	9.0 ± 1.2
	Eu(III)	3.8 ± 0.6	7.4 ± 1.2	11.2 ± 2.1
0.10 mol/L HNO ₃	Am(III)	13.2 ± 2.3	24.2 ± 2.4	33.7 ± 3.4
	Eu(III)	11.9 ± 2.2	21.8 ± 2.4	32.3 ± 3.3
1.0 mol/L HNO ₃	Am(III)	68.0 ± 3.8	89.8 ± 4.0	96.6 ± 4.7
	Eu(III)	66.3 ± 3.7	88.0 ± 4.0	96.1 ± 4.6
3.0 mol/L HNO ₃	Am(III)	91.4 ± 3.1	99.1 ± 4.9	100.0 ± 4.0
	Eu(III)	88.2 ± 3.1	98.3 ± 4.7	100.0 ± 4.0
0.10 mol/L Oxalic acid	Am(III)	74.7 ± 3.5	94.2 ± 3.4	98.2 ± 4.8
	Eu(III)	74.2 ± 3.4	92.9 ± 3.3	98.0 ± 4.8

^a Organic phase: 0.10 mol/L NTAamide(C8)/kerosene solution loaded with Am(III) or Eu(III); Aqueous phase: different stripping reagents.