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Synthesis and characterization of bisdiglycolamides for comparable extraction of Th^{4+}, UO_2^{2+} and Eu^{3+} from nitric acid solution

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Abstract The novel ligand N,N,N'''',N''''-tetrabutyl-N''',N'''-(N'',N''-diethyl)-ethidene bisdiglycolamide (TBEE-BisDGA) and other eight analogous extractants have been synthesized and characterized by NMR and HRMS. The solvent extraction of Th^{4+}, UO_2^{2+} and Eu^{3+} from nitric acid solution using the above BisDGA extractants was investigated in 1-dodecanol at 30 ± 1 °C. The extractants exhibited higher affinity toward Th^{4+} than UO_2^{2+} and Eu^{3+} in the present system. The maximum value of separation factor $SF_{Th(IV)/U(VI)}$ and $SF_{Th(IV)/Eu(III)}$ is 78.5 and 53.3 respectively for TBEE-BisDGA, 88.1 and 69.5 respectively in the case of TB^iPE-BisDGA at 3 M HNO_3 solution.

Keywords Bisdiglycolamides · Thorium (IV) · Uranium (VI) · Europium (III) · Separation factor

Introduction

Thorium originated from monazite which is coexisting with China's biggest rare earth ore mineral bastnasite in Baiyunebo mine. In comparison with uranium, thorium is far more abundant as well as much more energy-dense, and can provide a much safer and cheaper means of producing nuclear power. Therefore, thorium is considered as a potential nuclear fuel in the future field of nuclear power, because it may be used to make uranium–thorium dioxide fuels in the light water reactors (LWRs) [1]. Thorium and uranium are two of the main constituents in the nuclear spent fuels for the thorium-uranium fuel cycle process [2, 3]. In this process, one of the main concerns also is the management of the irradiated thorium-uranium fuel from the reactor. In view of their limited available resource and reducing their quantity for disposal as radioactive wastes [4–6], separation and recovery of the valuable thorium and uranium are vitally important. Furthermore, in the thorium-based nuclear energy system, due to uranium and thorium as blend fuel, it is also necessary to develop a method for separation of thorium and uranium.

Liquid–liquid extraction plays a fundamental role in the development of nuclear science and technology. During the extraction process, it is an extremely important task for synthesis and development valuable extractants to recover metal ions from industrial waste, laboratory waste and the high level radioactive waste [7, 8]. As we known, various organic compounds have been used for extraction of actinides and lanthanides from acidic wastes [7, 9–14]. Amongst them, the ligands based on diglycolamide (DGA) frame are quite famous due to their excellent extraction ability and high selectivity for actinides [15–19]. Compared with the phosphorus-based ligands used in the popular PUREX process [20] and the malonamide extractants used in the DIAMEX process [13], $N,N–N',N'$-tetraoctyl diglycolamide (TODGA) is particularly suitable for extracting actinides and lanthanides from nitric acid solution [21]. Furthermore, it was reported that two molecular diglycolamide (DGA) were attached by a suitable linker to offer the possibility of four or more oxygen donors, which indeed enhances

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the extraction efficiency of actinides and lanthanides from nitric acid aqueous solutions [22–24].

Following our previous works in synthesis of various extractants [25, 26], we attempted to combine two molecular diglycolamides by ethylenediamine-type linker to synthesize N,N,N''',N'''-tetrabutyl-N'',N''-ethidene bisdiglycolamide(TBE-BisDGA) and other eight analogous compounds including N,N,N''',N'''-tetrahexyl-N'',N''-ethidene bisdiglycolamide (THE-BisDGA), N,N,N''',N'''-tetraoctyl-N'',N''-ethidene bisdiglycolamide (TOE-BisDGA), N,N,N'''',N''''-tetrabutyl-N'',N''-(N'',N''-diethyl)-ethidene bisdiglycolamide (TBEE-BisDGA), N,N,N'''',N''''-tetrahexyl-N''',N''''-(N'',N''-diethyl)-ethidene bisdiglycolamide (THEE-BisDGA), N,N,N'''',N''''-tetraoctyl-N''',N''''-(N'',N''-diethyl)-ethidene bisdiglycol-amide (TOEE-BisDGA), N,N,N'''',N''''-tetrabutyl-N''',N''''-(N'',N''-diisopropyl)-ethidene bisdiglycolamide (TB^{i}PE-BisDGA), N,N,N'''',N''''-tetrahexyl-N''',N''''-(N'',N''-diisopropyl)-ethidene bisdiglycolamide (TH^{i}PE-BisDGA) and N,N,N'''',N''''-tetraoctyl-N''',N''''-(N'',N''-diisopropyl)-ethidene bisdiglycolamide (TO^{i}PE-BisDGA). In this research, we described the synthesis and characterization of different substituted BisDGA derivatives, and investigated their extraction properties for Th^{4+}, UO_2^{2+} and Eu^{3+} in nitric acid medium, and also evaluated the effect of various substituents either in the terminal or central nitrogen atoms on extractability to metal ions. Compared with the distribution ratio of UO_2^{2+} and Eu^{3+}, the better extraction efficiency was observed for tetravalent thorium ion using the present extractant. The high separation factors for both of Th^{4+}/UO_2^{2+} and Th^{4+}/Eu^{3+} were obtained, and suggested that these BisDGA extractants could be used in separation of lanthanides and actinides.

Experimental

General

The all reagents used for organic synthesis and all diluents were of analytical grade and without any further purification. $UO_2(NO_3)_2$ in HNO_3 solution was prepared from oxide U_3O_8. $Th(NO_3)_4$ in HNO_3 solution was prepared from $Th(NO_3)_4 \cdot 4H_2O$. $Eu(NO_3)_3$ in HNO_3 solution was prepared from oxide Eu_2O_3. TODGA was synthesized in our laboratory according to previous literature [17]. The synthesized extractants were characterized by ^1H NMR (400 M) and ^{13}C NMR (100 M) spectra. ^1H NMR and ^{13}C NMR were recorded on a Varian Mercury-400 spectrometer with $CDCl_3$ as a solvent and TMS as the internal standard. Purity of all the extractants was further characterized by a Bruker Esquire 6000 high-resolution mass spectrometer (HRMS).

### Synthesis of BisDGA and extraction experiment

TBEE-BisDGA and its eight analogous THEE-BisDGA, TOEE-BisDGA, TBE-BisDGA, THE-BisDGA, TOE-BisDGA, TB^{i}PE-BisDGA,TH^{i}PE-BisDGA and TO^{i}PE-BisDGA were synthesized in our laboratory as depicted in Scheme 1. First, the intermediate diglycolic acid monoamide **2** was synthesized from the commercially available diglycolic anhydride **1** as the starting material; subsequent reaction of the hemi-diglycolic acid **2** with an appropriate diamine, such as ethylenediamine or N,N'-diethylethylenediamine or N,N'-diisopropylethylenediamine afforded the expected BisDGA ligands in the presence of dicyclohexyl-carbodiimide (DCC), 1-hydroxybenzotriazole (HOBT) and triethylamine (TEA) in dichloromethane (DCM).

With the above extractants in hand, the corresponding TBE-BisDGA, THE-BisDGA, TOE-BisDGA, TBEE-BisDGA, THEE-BisDGA, TOEE-BisDGA, TB^{i}PE-BisDGA, TH^{i}PE-BisDGA and TO^{i}PE-BisDGA solutions of 5.0×10^{-2} mol/L were prepared by dissolving in organic solvent, which were employed for the further extraction experiments after proper dilution. Sodium nitrate, sodium sulfate and sodium chloride solutions of 3.0 mol/L were used for ionic-strength adjustment buffer. The solvents were pre-equilibrated with the desired concentration of nitric acid before use and the extraction was carried out at 30 ± 1 C in a 1:1 ratio of organic phase to aqueous solution in duplicate.

For a sample in each extraction experiment, 3.00 mL of diluent containing various concentration extractant (pre-equilibrated with an aqueous phase and no metal ion) was placed in a 10 mL plastic vial and mixed with 3.00 mL of aqueous metal solution at the desired pH value. After phase disengagement by centrifugation (2 min, 2000 rpm/min), duplicate 0.5–2.5 mL aliquots were taken from the aqueous phase. The remaining concentration of metal ions in the aqueous phase was determined by the appropriate methods. The concentration of metal ions in the organic phase was calculated by mass balance.

Analytical method

The UO_2^{2+} and Th^{4+} in aqueous solution were measured by the Arsenazo-III spectrophotometric method using a 723 N model UV–Vis Spectrophotometer (Shanghai, China), which was equipped with a 1 cm path length quartz cell for the acquisition of visible spectra (wavelength range: 325–1000 nm). The absorption wavelength was set to 652 and 660 nm for the extraction of uranium and thorium respectively. The concentration of europium ions in the aqueous phase was determined by ICP-OES (PerkinElmer Optima 8000). The distribution ratio (D) was calculated from Eq. 1.
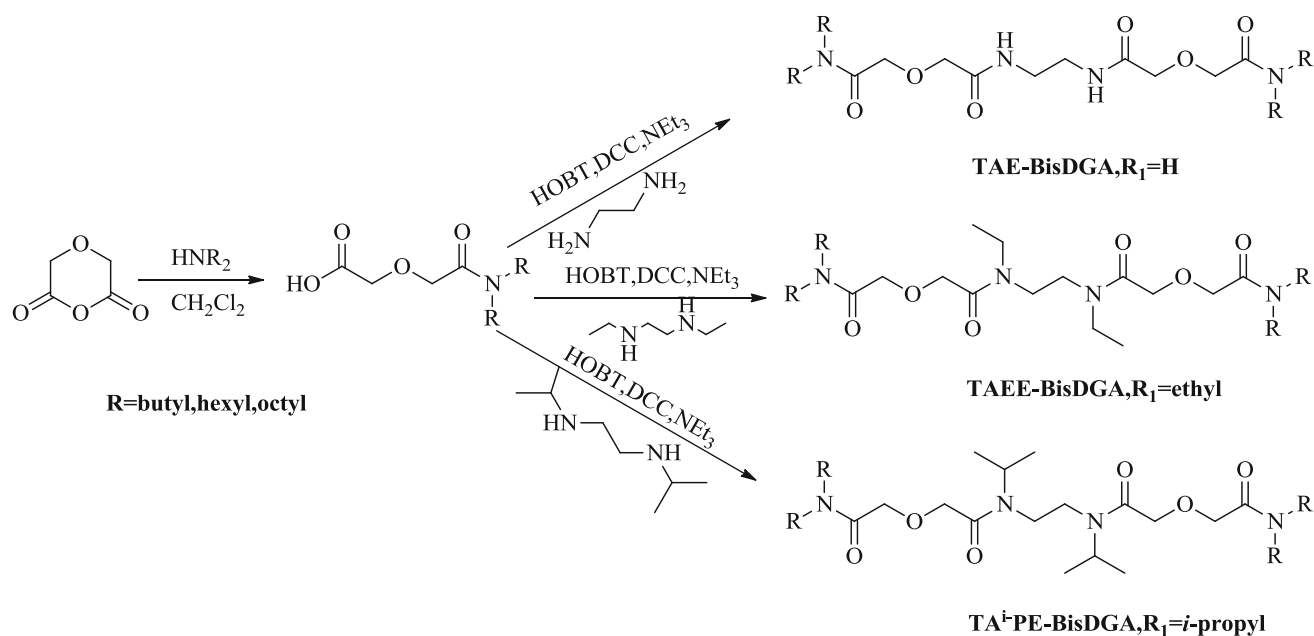
Scheme 1 Synthesis of BisDGAs from the starting diglycolic anhydride

$$D = \frac{C_i - C_f}{C_f} \quad (1)$$

where C_i and C_f represent the initial and final concentration of metal ions in the aqueous phase, respectively. The separation factor of Th^{4+} to UO_2^{2+} is calculated by the following Eq. 2. The corresponding separation factor of Th^{4+} to Eu^{3+} is calculated from Eq. 3.

$$SF_{Th(IV)/U(VI)} = D_{Th(IV)}/D_{U(VI)} \quad (2)$$

$$SF_{Th(IV)/Eu(III)} = D_{Th(IV)}/D_{Eu(III)} \quad (3)$$

Results and discussion

Extraction kinetics

The extraction kinetics of Th^{4+} was investigated by 1.0 mM Th^{4+} in aqueous 3 M HNO_3 solution contacting with 8 mM TBEE-BisDGA in 1-dodecanol. It is evident from Fig. 1 that the distribution ratios of Th^{4+} increase gradually with increasing of contacting time, and reached ca.17 after 25 min. Further extending time to 45 min, no obvious change in $D_{Th(IV)}$ is observed. The result exhibited that 25 min is sufficient up to equilibrium for the extraction process (Fig. 1). Though UO_2^{2+} and Eu^{3+} extraction kinetics was not studied, however, theirs extraction behavior could be predicted from the Th(IV) extraction data. In the present work, 30 min of equilibration time of two phases have been employed for all the extraction process in order to ensure the complete extraction.
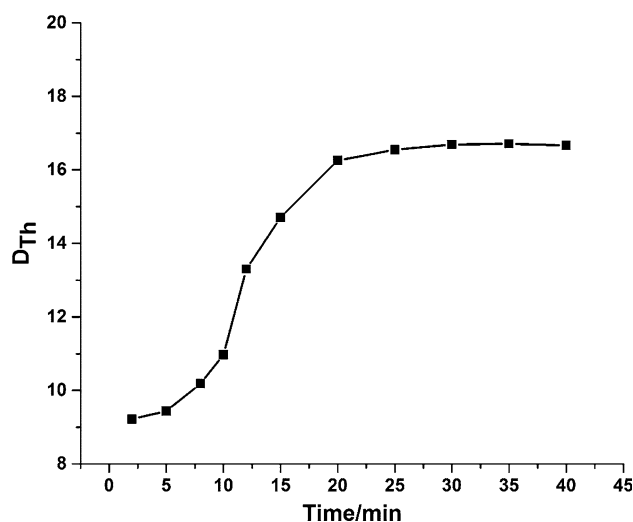
Fig. 1 Extraction kinetics of Th(IV) ions at 30 ± 1 °C from 3 M HNO_3 with 8 mmol TBEE-BisDGA in 1-dodecanol

Optimum of the diluent

Based on 8 mM TBEE-BisDGA concentration, different popular aliphatic and aromatic solvents (1-dodecanol, xylene, chloroform and kerosene) were explored for the extraction of Th^{4+} at different nitric acid concentration. As shown in Fig. 2, the concentration of HNO_3 has a significant impact on $D_{Th(IV)}$, the distribution ratio increases with the increase of nitric acid concentration for all the diluents used. Although there are high D values of Th^{4+} in xylene and kerosene solvent, the formation of third phase was also observed in extraction of Th^{4+} with TBEE-BisDGA ligand
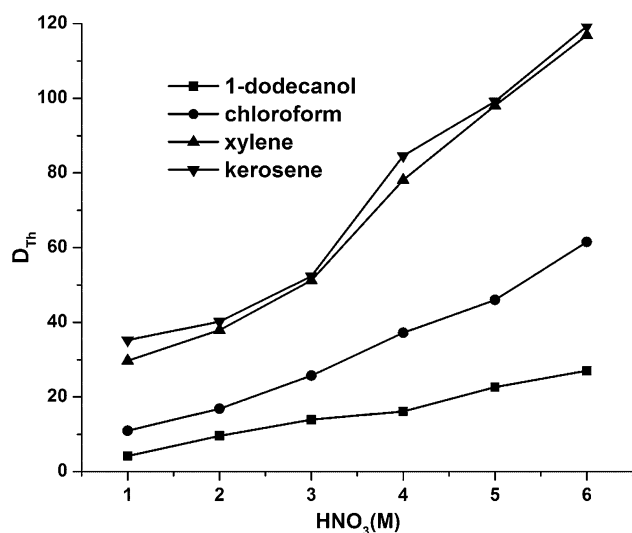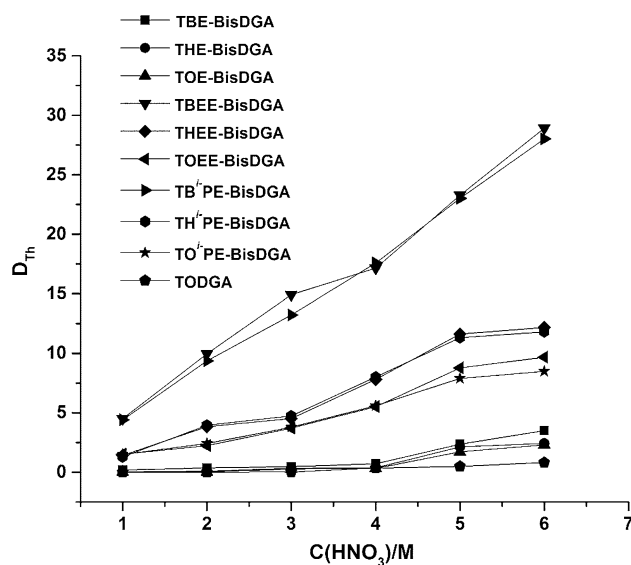
Fig. 2 Effect of different solvents on Th(IV) extraction; equilibration time: 30 min; Organic phase: 8 mM TBEE-BisDGA in 1-dodecanol; T: 30 ± 1 °C


Fig. 3 Effect of different structure of extractants on Th(IV) extraction; equilibration time: 30 min; Organic phase: 8 mM BisDGA in 1-dodecanol; T: 30 ± 1 °C

in high acidity. In addition, TBEE-BisDGA showed poor solubility in kerosene and xylene system. The volatility of chloroform limits its application in our experiment. Therefore, in view of the high compatibility, non-volatile, excellent solubility to BisDGA, and future industrial application as well as decent extractability, 1-dodecanol was chosen as the optimum diluent in this work.

Effect of the structure of BisDGA extractants

In order to pick out the optimum extractant, extraction of Th^{4+} with various substituted BisDGAs in 1-dodecanol system from aqueous nitric acid solution was investigated. In general, the pre-organized BisDGA extractants exhibited higher extraction ability to Th^{4+} compared with simple DGAs, such as the popular TODGA (Fig. 3). In some cases ($TB^{i}PE$-BisDGA and TBEE-BisDGA), the extractability of Th^{4+} by BisDGA and TODGA shows the difference of magnitude in $D_{Th(IV)}$. It is clear that introduction of ethylenediamine-type linker to combine two-molecular diglycolamides leads to better extractability. The extractability of BisDGA ligands towards Th^{4+} follows the following sequence: TOE-BisDGA < THE-BisDGA < TBE-BisDGA ≪ $TO^{i}PE$-BisDGA ≈ TOEE-BisDGA < $TH^{i}PE$-BisDGA ≈ THPE-BisDGA ≪ $TB^{i}PE$-BisDGA ≈ TBEE-BisDGA. It indicates that substituents on the both center and terminal nitrogen atoms (R and R_1 groups, Scheme 1) play a vital role in extraction of thorium (IV) using BisDGAs. It is worthy of note that Sasaki et al. [17]. Investigated D values of Am^{3+} and Eu^{3+} using diglycolamide extractants as a function of the length of an amidic alkyl chain (corresponding to the present R groups). The

results revealed that the longer alkyl chain suppresses the extraction ability for metal ions due to steric hindrance around carbonyl groups, which shows good agreement with our results.

On the other hand, we assumed that ethyl or isopropyl bonded to the central nitrogen atoms act as electron donating groups, which could effectively improve the extractability of BisDGA. As shown in Fig. 3, the D value of Th^{4+} increased with the sequence of TAE-Bis-DAG < $TA^{i}PE$-BisDGA ≈ TAEE-BisDGA (A represents alkyl on the terminal nitrogen atom). This is due to the fact that the favorable electronic effect generally increases in the order: Hydrogen < Me (methyl) < Et (ethyl), and the substituents longer than ethyl have practically the same electronic property as ethyl, and probable stronger steric effect.

Distribution behavior of Th^{4+}, Eu^{3+} and UO_2^{2+}

Figure 4 shows the effect of HNO_3 concentration on the distribution ratios of Th^{4+}, Eu^{3+} and UO_2^{2+} based on 8 mM of TBEE-BisDGA or $TB^{i}PE$-BisDGA extractants. It was found that the D values of Th^{4+} increased with the increase of HNO_3 concentration for both TBEE-BisDGA and $TB^{i}PE$-BisDGA in 1-dodecaol. However, nitric acid concentration has only lightly influence on the distribution ratios of UO_2^{2+} and Eu^{3+} for both TBEE-BisDGA and $TB^{i}PE$-BisDGA in the same system. It indicates that both TBEE-BisDGA and $TB^{i}PE$-BisDGA exhibited rather higher affinity toward Th^{4+} than UO_2^{2+} and Eu^{3+}. Table 1 listed the separation factor of Th^{4+}, Eu^{3+} and UO_2^{2+} at nitric acid concentration range from 1.0 to 6.0 M, it was
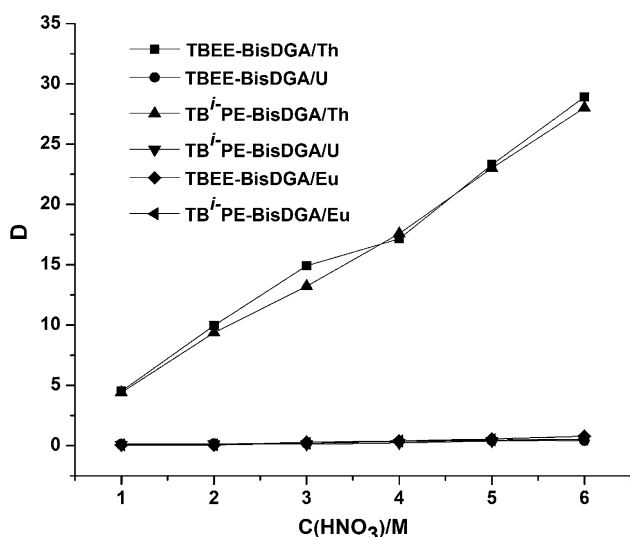
Fig. 4 The distribution ratio of Th(IV), Eu(III) and U(VI) as a function of the concentration of nitric acid. Organic phase: 8 mM TBEE-BisDGA or TB^{i-}PE-BisDGA in 1-dodecanol; [Th(IV)] = 1.0 mM, [Eu(III)] = 1.0 mM, [U(VI) = 1.0 mM]; T: 30 ± 1 °C

found that the $SF_{Th(IV)/U(VI)}$ and $SF_{Th(IV)/Eu(III)}$ increased with the increase of nitric acid concentration, and reached a maximum value at 3 mol/L, and followed by decreased in SF values. The maximum separation factor $SF_{Th(IV)/U(VI)}$ reached 78.5 for TBEE-BisDGA and 88.1 for TB^{i-}PE-BisDGA at 3.0 M HNO$_3$, respectively. The maximum separation factor $SF_{Th(IV)/Eu(III)}$ was up to 53.3 for TBEE-BisDGA and 69.5 for TB^{i-}PE-BisDGA at 3.0 M HNO$_3$, respectively. The excellent separation factor for Th(IV)/U(VI) and Th(IV)/Eu(III) shows the potential value of these BisDGA extractants in separation of Ln/An and different valence state of actinides.

Extraction mechanism

In order to determine the fundamental stoichiometry of extracted complexes, slope analysis method was carried out using TBEE-BisDGA extractant in 1-dodecanol system at different temperature, where D values of the Th^{4+} were plotted as a function of the equilibrium concentration of

TBEE-BisDGA in 1-dodecanol at 3.0 M HNO$_3$. As seen in Fig. 5, the linear relationships of log$D$ and log[TBEE-BisDGA] were obtained in a slope of ca.1 at the different
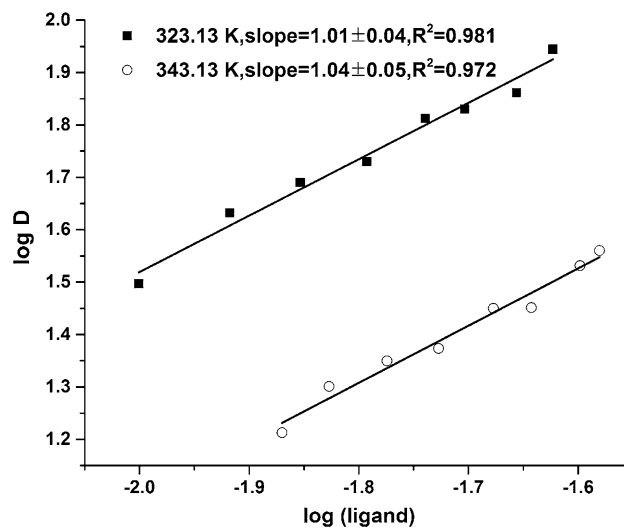
Fig. 5 Plots of log$D$ versus log[ligand], [Th^{4+}] = 1.0 mM
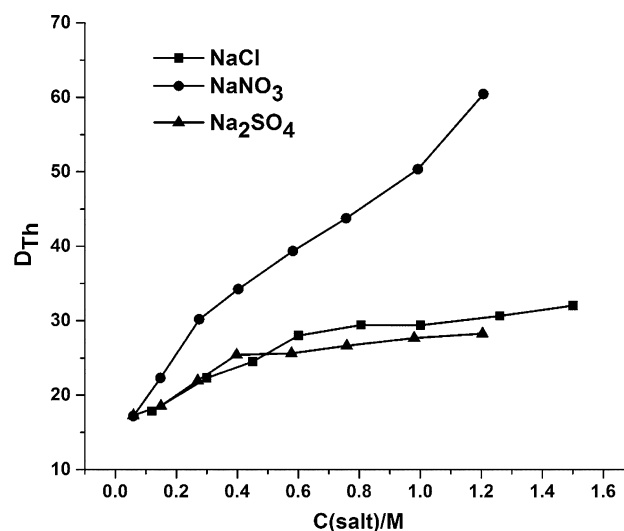
Fig. 6 Influence of NaNO$_3$, NaCl and Na$_2$SO$_4$ on the extraction of Th(IV) from 3.0 M HNO$_3$ solution by TBEE-BisDGA (8 mM) in 1-dodecanol. [Th(IV)] = 1.0 mM; T: 30 ± 1 °C

Table 1 Effect of HNO$_3$ concentration on the separation factor, Organic phase: TBEE-BisDGA or TB^{i-}PE-BisDGA in 1-dodecanol; Aqueous solution: 1.0 mM Th(IV) or Eu(III) or U(VI) in nitric acid solution; Temperature: 30 ± 1 °C	[HNO$_3$]/M	TBEE-BisDGA		TB^{i-}PE-BisDGA	
		$SF_{Th(IV)/U(VI)}$	$SF_{Th(IV)/Eu(III)}$	$SF_{Th(IV)/U(VI)}$	$SF_{Th(IV)/Eu(III)}$
	1.0	37.5	45.4	48.9	43.0
	2.0	66.4	50.3	78.1	58.1
	3.0	78.5	53.3	88.1	69.5
	4.0	50.4	44.0	54.9	47.6
	5.0	56.8	45.6	60.6	48.5
	6.0	65.7	47.5	63.0	50.1

temperature. It suggests that one molecular ligand could be associated with Th^{4+} to form 1:1 complex during the extraction process.

In general, the extraction process in conventional organic solvent proceeded by neutral extraction mechanism. As shown in Figs. 3 and 5, the D values of Th^{4+} increased with increase of nitric acid concentration. It suggests that nitrate ion has a significant effect on the extraction of thorium ion, and the extraction is more efficient in high concentration of HNO_3 sollution. In order to obtain a detailed insight into the role of the nitrate ion in the extraction process, the effect of the inorganic salt on the
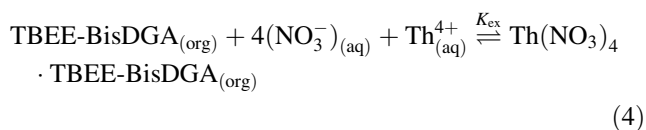
distribution ratio of Th^{4+} was investigated by adding $NaNO_3$, $NaCl$ and Na_2SO_4 into aqueous solution during the extraction process while keeping the initial constant Th^{4+} concentration in the aqueous solution (Fig. 6). The results demonstrated that the distribution ratios increased with increase of inorganic salt concentration for all cases. It is worthy of note that loading of $NaNO_3$ into aqueous phase has a more powerful impact on D values of Th^{4+} than adding $NaCl$ and Na_2SO_4 into aqueous solution. The evidence indicated that $NaNO_3$ is a very strong salting-out reagent for the present extraction system. Only adding

Fig. 7 ESI-MS spectrum after extraction of Th(IV) ion with TBEE-BisDGA in 1-dodecanol
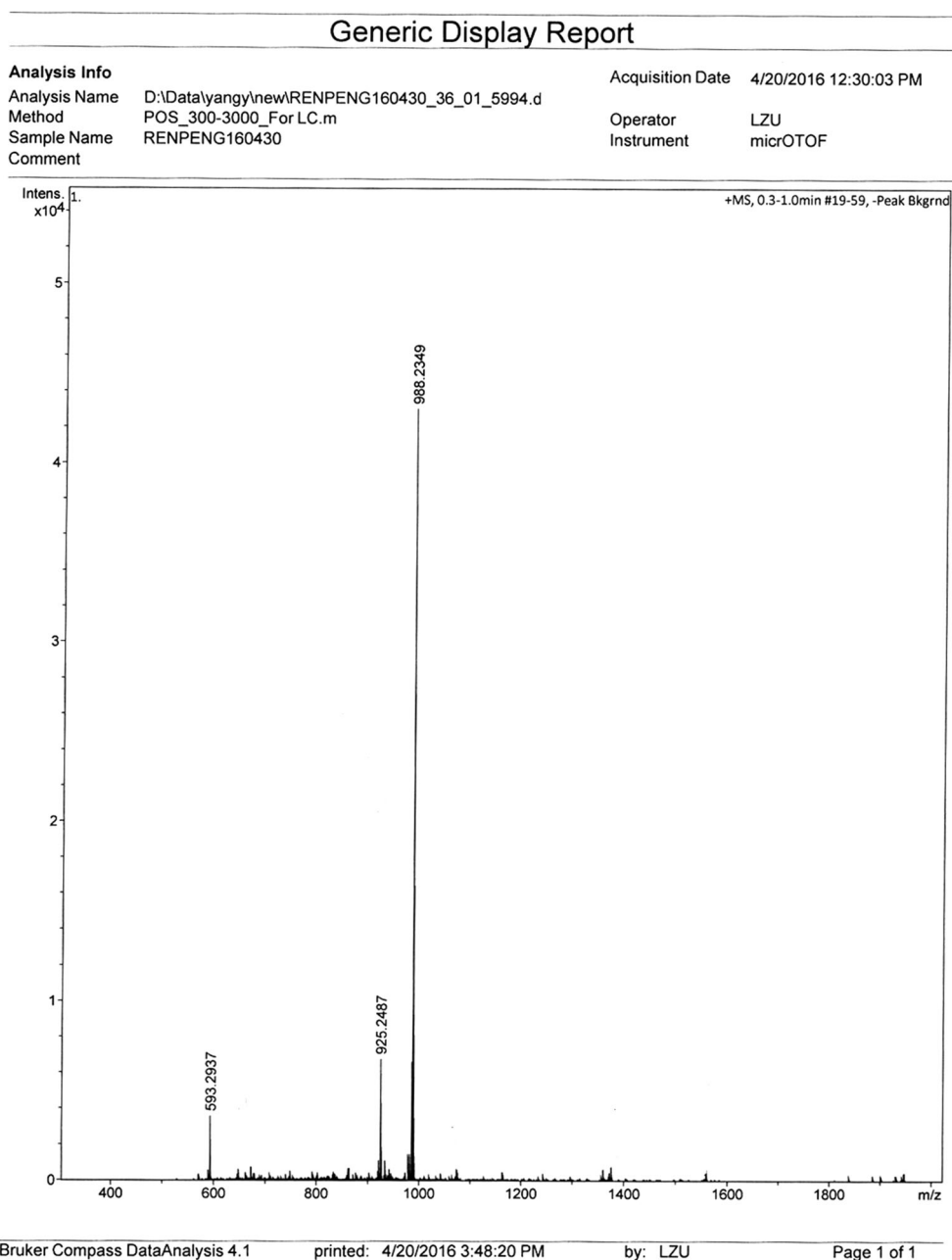
1 mol L^{-1} NaNO$_3$ to the aqueous phase resulted in a significant increase of $D_{Th(IV)}$.

Besides the slope analysis method, the determining ESI-MS of organic phase was performed after extraction of 50 mM Th^{4+} with 50 mM TBEE-BisODGA in 1-dodecanol. The data were acquired on a Bruker Model maXis4G system. In positive ion mode of mass spectrometry (Fig. 7), peaks at m/z 988.2349 can be observed, which is corresponding to the representative extracted species ([Th(NO$_3$)$_3$·TBEE-BisDGA)]$^+$, calcd. m/z: 988.4372). The ESI-MS data further confirmed that Th^{4+} ion was coordinated with TBEE-BisDGA ligand in 1:1 coordination mode. Thus, the extraction reaction of Th^{4+} from nitric acid solution with TBEE-BisDGA in 1-dodecanol was written as Eq. 4.

$$\text{TBEE-BisDGA}_{(org)} + 4(NO_3^-)_{(aq)} + Th^{4+}_{(aq)} \overset{K_{ex}}{\rightleftharpoons} Th(NO_3)_4 \cdot \text{TBEE-BisDGA}_{(org)}$$

$$(4)$$

Representative spectroscopic data

After purification and identification, the purity of all the extractants was identified to be >97.0%. Spectroscopic data of the optimum extractants in the present study were given as follows. For TBEE-BisDGA extractant, ^{1}H NMR (CDCl$_3$, 400 MHz): δ 4.34 (s, 4H), 4.32 (s, 4H), 3.41–3.50 (t, J = 7.2 Hz, 4H), 3.30–3.37 (m, 4H), 3.19–3.23 (m, 8H), 1.51–1.59 (m, 8H), 1.28–1.36 (m, 8H), 1.23–1.29 (t, J = 7.2 Hz, 6H), 0.89–0.95 (m, 12H) ppm; ^{13}C NMR (CDCl$_3$, 100 MHz): δ 169.00, 69.04, 46.66, 45.51, 44.16, 30.99, 29.68, 14.27, 13.84 ppm; HRMS (ESI, C$_{30}$H$_{58}$N$_4$O$_6$): Calcd. m/z: 593.4254 [M + Na]$^+$; Found m/z: 593.4230 [M + Na]$^+$.

For TB^{i}PE-BisDGA extractant, ^{1}H NMR (CDCl$_3$, 400 MHz): δ 4.36 (s, 4H), 4.31 (s, 4H), 3.97–3.89 (m, 2H), 3.36–3.34 (t, J = 3.2 Hz, 4H), 3.33–3.27 (t, J = 6.8 Hz, 4H), 3.20–3.16 (t, J = 6.8 Hz, 4H), 1.53–1.51 (m, 8H), 1.36–1.28 (m, 8H), 1.33–1.29 (m, 12H), 0.95–0.89 (m, 12H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 168.78, 168.4, 69.48, 69.39, 47.65, 46.94, 45.75, 31.58, 22.59, 20.92, 14.02; HRMS (ESI, C$_{32}$H$_{62}$N$_4$O$_6$): Calcd. m/z: 621.4567 [M + Na]$^+$; Found m/z: 621.4543 [M + Na]$^+$.

Conclusions

In conclusion, the nine novel extractants based on the BisDGAs frame have been synthesized. TBEE-BisDGA and TBB^{i}PE-BisDGA were chosen as the preferable extractants for extraction of Th^{4+}, UO$_2^{2+}$ and Eu^{3+} in 1-dodecanol from nitric acid solution. The results revealed that distribution ratios of Th^{4+} using TBEE-BisDGA increased with the increase of nitric acid concentration and extractant concentration. Slope analysis and ESI-MS data revealed that Th^{4+} was extracted as mono-solvated species by TBEE-BisDGA. Both of the TBEE-BisDGA and TB^{i}PE-BisDGA show a higher affinity toward Th^{4+} than UO$_2^{2+}$ and Eu^{3+}, and excellent separation factors suggest that TBEE-BisDGA is a good candidate for the separation of Th^{4+} from UO$_2^{2+}$ and Eu^{3+}.

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