

# Extraction of lanthanide ions with *N,N,N',N'*-tetrabutyl-3-oxa-diglycolamide from nitric acid media

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Received: 28 October 2016/Revised: 18 December 2016/Accepted: 19 January 2017/Published online: 10 May 2017  
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**Abstract** Extractability and extraction mechanism of lanthanide ions were investigated by using a new extractant, *N,N,N',N'*-tetrabutyl-3-oxa-diglycolamide (TBDGA), in toluene from nitric acid media. The effects of HNO<sub>3</sub> and TBDGA concentrations, and temperature, on extraction of lanthanide ions were studied. Stoichiometries of the main extracted species were HNO<sub>3</sub>·TBDGA and M(NO<sub>3</sub>)<sub>3</sub>·3TBDGA (M = Er, Dy, Tb, Gd, La, Ce, Nd, Sm and Eu). The extracted species for metal ions were established to be ionic complex. In this complex, nitrate anion was not coordinated to the central ion. The extraction pattern increased gradually across the lanthanide ions series, showing enhanced affinity of TBDGA toward heavy lanthanide ions. Thermodynamic parameters were investigated for the exothermic extraction reaction.

**Keywords** Lanthanide ions · Extraction · *N,N,N',N'*-tetrabutyl-3-oxa-diglycolamide · Nitric acid · Toluene

## 1 Introduction

For the nuclear power industry, it is of great importance to develop the extraction and recovery process for lanthanide ions, actinide ions and minor radioactive elements from radioactive high-level liquid wastes (HLLW) [1], so as to minimize the disposal of HLLW by efficient extractants for actinide and lanthanide ions [2, 3]. Amide-based extractants are promising in this regard due to the easily processing of their radiolytic degradation products [4, 5]. Recently, the extraction of actinides, lanthanide, Zr(IV), Ca(II), Fe(III) and Nd(III) ions [6–10] by *N,N,N',N'*-tetraoctyldiglycolamide (TODGA) has attracted many researchers. As a kind of tridentate ligand, TODGA shows high affinity for actinide and lanthanide ions [11–13]. However, to our knowledge, extraction with an analogue of TODGA, *N,N,N',N'*-tetrabutyl-3-oxa-diglycolamide (TBDGA) was reported by a few groups. Mowafy and Mohamed [14] reported new diglycolamide extractants to extract trivalent lanthanide ions from HNO<sub>3</sub> solution. Sodaye et al. [2] and Moonsung et al. [15] described the extraction of uranium with TBDGA.

TBDGA is cheaper and more easily synthesized than TODGA. It can be well dissolved in diluents, and the water solubility is much lower in the extraction system, hence a good extractant especially using aromatic hydrocarbon diluent.

In this study, the extractability of TBDGA in toluene for lanthanide ions was investigated. The extractant was synthesized, and the interaction of lanthanide ions with TBDGA was studied by general extraction. The spectrophotometry technique was used to identify the structure of the extracted species.

This work was supported by the National Natural Science Foundation of China (21077044) and Natural Science Foundation of Shandong Province (ZR2015BM030).

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## 2 Materials and methods

### 2.1 Chemicals and reagents

TBDGA (purity >98%) was synthesized in our laboratory according to the procedure reported in Ref. [16]. Its chemical structure is given in Fig. 1. The rare earth oxides (>99.9%) were dissolved with concentrated HNO<sub>3</sub>. The working solution was prepared by diluting. TBDGA solutions were obtained by dissolving TBDGA in toluene. Other chemical reagents employed, such as the toluene and HNO<sub>3</sub>, were of AR grade.

### 2.2 Extraction of HNO<sub>3</sub> with TBDGA

The aqueous phase and organic TBDGA solution with phase ratio of 1:1 were vibrated at frequency for ten minutes. After separation by centrifugation, the acidities of each phase were measured by NaOH titration. The organic solution was diluted in ethanol before titration.

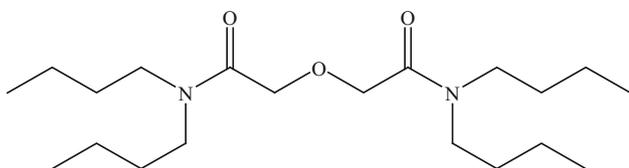
### 2.3 Extraction of lanthanide ions

TBDGA solutions were employed after pre-equilibration with HNO<sub>3</sub> solutions at acidities the same as that of aqueous phase. The organic phase and aqueous phase with equal volumes were shaken for 30 min at 25 °C. The two phases were then centrifuged and analyzed. The concentration of lanthanide ions in aqueous phase ( $C_e$ ) was detected by spectrophotometric method (Arsenazo-III). The concentration of lanthanide ions in organic phase ( $C_o$ ) was obtained by subtracting the  $C_e$  from the total initial aqueous concentration of lanthanide ions ( $C_i$ ). The distribution ratio ( $D$ ) was defined as

$$D = C_e/C_o = C_e/(C_i - C_e). \quad (1)$$

### 2.4 Preparation and characterization of the extracted species

0.20 mol dm<sup>-3</sup> TBDGA solution was shaken with saturated solution of gadolinium nitrate, centrifuged, and the organic phase separated. The samples were measured using liquid cells with KBr windows. FTIR spectrum was recorded with an FTS-165 spectrometer, over the



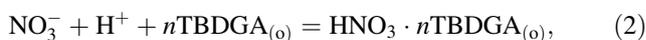
**Fig. 1** Chemical structure of *N,N,N',N'*-tetrabutyl-3-oxa-diglycolamide (TBDGA)

wavenumber range of 400–4000 cm<sup>-1</sup>, in 60 scan times and 2 cm<sup>-1</sup> resolution.

## 3 Results and discussion

### 3.1 Extraction of nitric acid

The extraction of HNO<sub>3</sub> with TBDGA can be represented by



where the subscript (o) denotes the organic phase. The conditional equilibrium constant ( $K_H$ ) can be expressed as

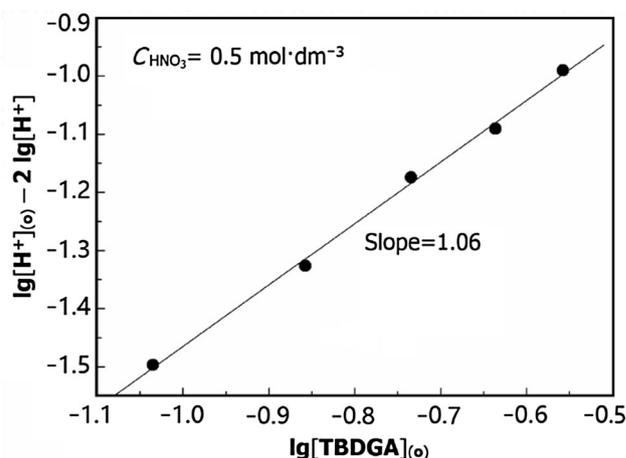
$$K_H = \frac{[\text{HNO}_3 \cdot n\text{TBDGA}]_{(o)}}{[\text{H}^+][\text{NO}_3^-][\text{TBDGA}]_{(o)}^n}, \quad (3)$$

where  $[\text{H}^+]$ ,  $[\text{NO}_3^-]$  and  $[\text{TBDGA}]_{(o)}$  are the equilibrium concentrations [17]. In Eq. (3), the activity coefficients were neglected under the studied conditions [2, 18]. The logarithmic expression of Eq. (3) is

$$\lg[\text{H}^+]_{(o)} - 2\lg[\text{H}^+] = \lg K_H + n\lg[\text{TBDGA}]_{(o)}, \quad (4)$$

where  $[\text{H}^+]_{(o)} = [\text{HNO}_3 \cdot n\text{TBDGA}]_{(o)}$  and  $[\text{H}^+] = [\text{NO}_3^-]$

A plot of  $\lg[\text{H}^+]_{(o)} - 2\lg[\text{H}^+]$  versus  $\lg[\text{TBDGA}]_{(o)}$  gives a straight line, and the slope value is 1.06 (Fig. 2). This shows that the stoichiometry of the main extracted specie is HNO<sub>3</sub>·TBDGA. The  $K_H$  value was calculated as  $0.35 \pm 0.02$ , being a little bigger than those of monoamide and diamide [16–20]. Pathak et al. studied the extraction of nitric acid with *N,N*-dialkyl amide and found that conditional acid uptake constant ( $K_H$ ) values for 1:1 species in 0.5–3 mol·dm<sup>-3</sup> HNO<sub>3</sub> were in the following order: D2EHPVA ( $0.06 \pm 0.002$ ) < D2EHIBA ( $0.15 \pm 0.04$ ) < D2EHPRA ( $0.20 \pm 0.01$ ) < D2EHAA ( $0.28 \pm 0.03$ ) [19].



**Fig. 2** Extraction of nitric acid with TBDGA

In their study on the uptake of nitric acid with *N,N*-dihexyloctanamide (DHOA) in *n*-dodecane, Gupta et al. [20] found  $K_H = 0.188$  for the extracted species of  $\text{HNO}_3$ -DHOA. In extraction of  $\text{HNO}_3$  with diamide *N,N,N',N'*-dimethyl dibutyl tetradecyl malonamide, Nigond et al. [21] suggested the competing formation of four adducts:  $\text{L}_2\text{HNO}_3$ ,  $\text{L}\cdot\text{HNO}_3$ ,  $\text{L}\cdot(\text{HNO}_3)_2$ , and  $\text{L}\cdot(\text{HNO}_3)_3$ , with their equilibrium constants for  $0.72 \text{ mol dm}^{-3}$  amide in TPH being  $0.167$ ,  $0.215$ ,  $5.19 \times 10^{-3}$  and  $3.70 \times 10^{-4}$ , respectively. These show that the basicity of TBDGA, indicated by the equilibrium constant for  $\text{HNO}_3$  extraction, is a little bit larger than those of monoamide and diamide. Based on HSAB (hard and soft acids and bases) theory, the enhanced basicity favors the coordination of TBDGA to lanthanide ions.

## 3.2 Extraction of lanthanide ions

### 3.2.1 Effect of nitric acid concentration on the extraction

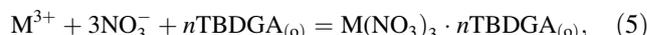
The extraction ratios of Er(III), Dy(III), La(III), Ce(III), Nd(III), Sm(III), Eu(III), Gd(III), and Tb(III) ions from aqueous solution at different concentrations of  $\text{HNO}_3$  are shown in Fig. 3. The extraction distribution ratios of lanthanide ions increased with the  $\text{HNO}_3$  concentration. This is in agreement with the result by Cuillerdier et al. [22].  $\text{NO}_3^-$  ion plays an important role due to its salt effect and common ion effect.

The order of extractability of TBDGA for the studied trivalent ions is  $\text{La(III)} < \text{Ce(III)} < \text{Nd(III)} < \text{Sm(III)} < \text{Eu(III)} < \text{Gd(III)} < \text{Tb(III)} < \text{Dy(III)} < \text{Er(III)}$ . In other words, the extraction pattern gradually ascends across the lanthanide ions series. Narita et al. [23] reported similar

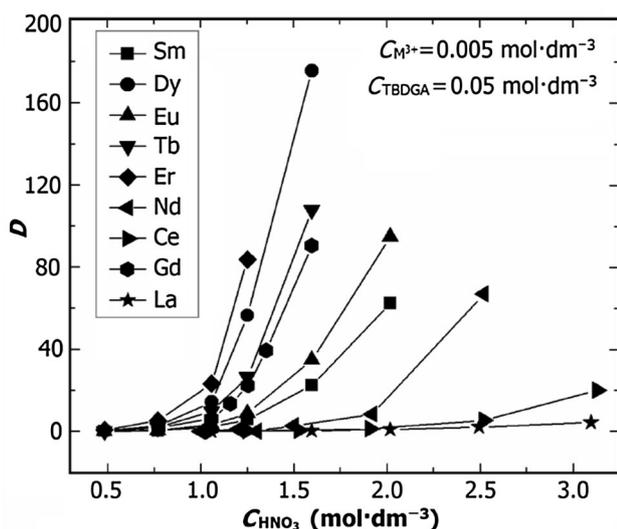
results using *N,N'*-dimethyl-*N,N'*-diphenyldiglycolamide as extractant. The reason may be that the charge densities of Ln(III) ions increase with a decreasing ionic radius. Therefore, the electrostatic interaction of the heavier Ln(III) ions with ligands is stronger than that of the lighter Ln(III) ions. The interaction results in the enhanced affinity of TBDGA toward heavy lanthanide ions. This ascending pattern is opposite to those obtained using diamide in Refs. [24, 25], where the degree of extractant basicity to dehydrate and the hydration energy of the Ln(III) ion were suggested to explain this phenomenon.

### 3.2.2 Effect of TBDGA concentration on distribution ratio

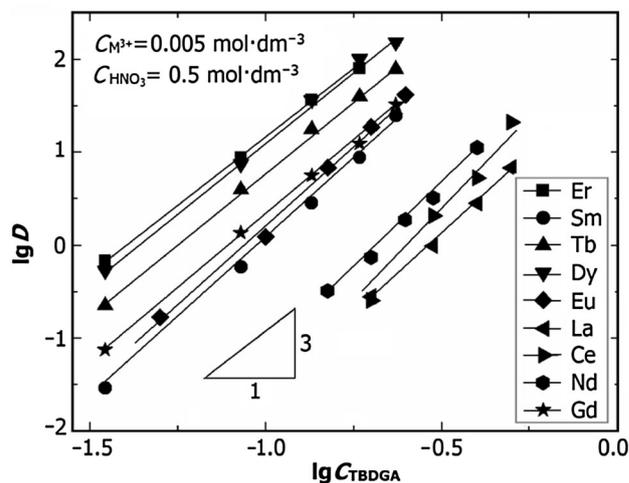
The reaction occurred in extracting lanthanide ions from aqueous nitrate medium by TBDGA in toluene can be expressed as



where  $\text{M}^{3+}$  is lanthanide ions. The slope analysis method was used to determine the “*n*” value of the predominant extracted species. Under the studied conditions, TBDGA is in large excess to lanthanide ions, so the TBDGA concentration can be regarded as constant. The distribution ratios as a function of the TBDGA concentration are shown in Fig. 4. Solvate numbers of different lanthanide ions obtained by slope analysis are approaching 3, suggesting that lanthanide ions may be extracted as an extracted species of tri-solvates. This is similar to that obtained with TODGA, where the extracted complex was  $\text{M}(\text{TODGA})_4(\text{NO}_3)_3$  or  $\text{M}(\text{TODGA})_3(\text{NO}_3)_3$ . The metal complex needs 3 or more TODGA molecules to keep stable in non-polar solvents [26].



**Fig. 3** Distribution of lanthanide ions as a function of  $\text{HNO}_3$  concentration



**Fig. 4** Influence of TBDGA concentration on the distribution of lanthanide ions

The extraction equilibrium constant,  $K_{ex}$ , is defined as

$$K_{ex} = \frac{a_{M(NO_3)_3 \cdot 3TBDGA(o)}}{a_{M^{3+}} a_{NO_3^-}^3 a_{TBDGA}^3} = \frac{C_{M(NO_3)_3 \cdot 3TBDGA(o)}}{\gamma_{M^{3+}} C_{M^{3+}} \gamma_{NO_3^-}^3 C_{NO_3^-}^3 C_{TBDGA}^3}, \quad (6)$$

where  $\gamma$  represents the activity coefficients of  $NO_3^-$  and lanthanide ions. The species activity in organic phase was suggested to be equal to its concentration due to the poor interaction in organic phase. The total concentration of ions in aqueous solution,  $C_M$ , can be written as

$$C_M = C_{M^{3+}} (1 + \beta_1 C_{NO_3^-}). \quad (7)$$

The  $\gamma$  values of  $NO_3^-$  and lanthanide ions, calculated by Debye–Hückel formula [27], were 0.9025 and 0.3974, respectively.  $\beta_1$  is the first-order stability constant of lanthanide ions with nitrate, and the data  $La^{3+}(1.3 \pm 0.3)$ ,  $Ce^{3+}(1.3 \pm 0.3)$ ,  $Nd^{3+}(0.77 \pm 0.1)$ ,  $Sm^{3+}(0.95)$ ,  $Eu^{3+}(1.8 \pm 0.4)$ ,  $Gd^{3+}(2.33 \pm 0.02)$ ,  $Tb^{3+}(1.13 \pm 0.05)$ ,  $Er^{3+}(0.54)$  were reported by other authors [28–30] (the  $\gamma$  value of  $Dy^{3+}$  has not been reported).

The distribution ratio  $D$  is

$$D = \frac{C_{M(o)}}{C_M} = \frac{C_{M(NO_3)_3 \cdot 3TBDGA(o)}}{C_{M^{3+}} (1 + \beta_1 C_{NO_3^-})}. \quad (8)$$

Therefore,  $K_{ex}$  can be written as

$$K_{ex} = \frac{D(1 + \beta_1 C_{NO_3^-})}{C_{NO_3^-}^3 C_{TBDGA(o)}^3 \gamma_{M^{3+}} \gamma_{NO_3^-}} = K \frac{(1 + \beta_1 C_{NO_3^-})}{\gamma_{M^{3+}} \gamma_{NO_3^-}}, \quad (9)$$

where  $K$  is the conditional extraction constant defined as

$$K = \frac{D}{C_{NO_3^-}^3 C_{TBDGA(o)}^3}. \quad (10)$$

The calculated  $\lg K_{ex}$  and  $\lg K$  values are given in Table 1.

**Table 1**  $\lg K$  and  $\lg K_{ex}$  values for extraction of lanthanide ions with TBDGA

$M^{3+}$	$\lg K$	$\lg K_{ex}$
$La^{3+}$	$2.52 \pm 0.11$	$3.27 \pm 0.11$
$Ce^{3+}$	$2.79 \pm 0.20$	$3.54 \pm 0.20$
$Nd^{3+}$	$2.97 \pm 0.17$	$3.65 \pm 0.17$
$Sm^{3+}$	$3.96 \pm 0.22$	$4.63 \pm 0.22$
$Eu^{3+}$	$4.16 \pm 0.16$	$4.98 \pm 0.16$
$Gd^{3+}$	$4.23 \pm 0.08$	$5.10 \pm 0.08$
$Tb^{3+}$	$4.69 \pm 0.07$	$5.42 \pm 0.07$
$Dy^{3+}$	$5.03 \pm 0.08$	–
$Er^{3+}$	$5.06 \pm 0.05$	$5.70 \pm 0.05$

### 3.2.3 The temperature effect on the distribution

As shown in Fig. 5, the distribution ratios of lanthanide ions decrease with increasing temperatures, indicating that the extraction reaction is exothermic.

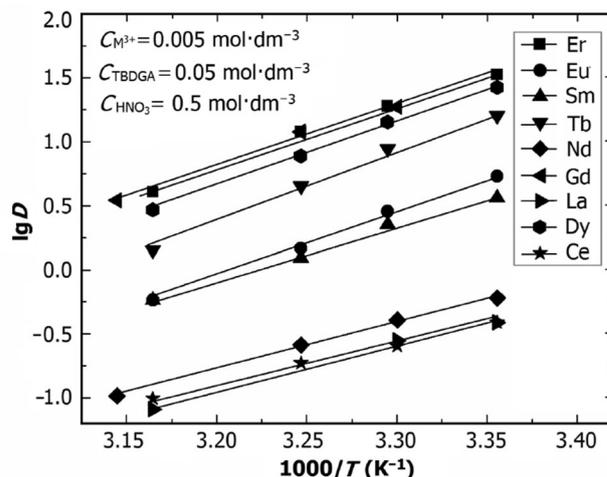
The following thermodynamic equation was employed to calculate enthalpy change ( $\Delta_r H_m^0$ ) of the extraction reaction [19].

$$[\partial(\lg D)/\partial(1/T)]_p = -\Delta_r H_m^0 / (2.303R), \quad (11)$$

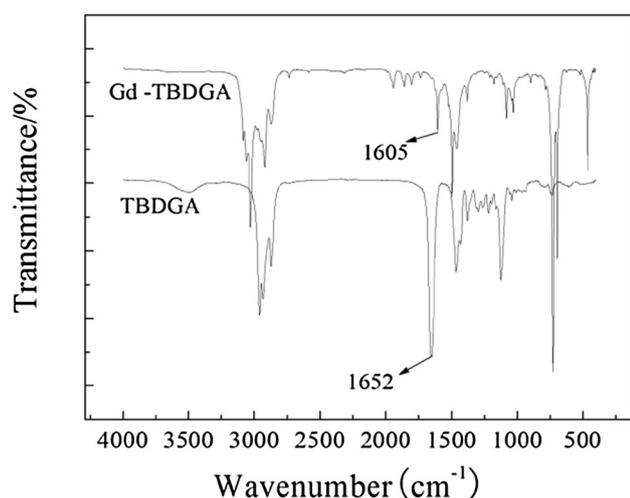
where constant  $R=8.314$ . The enthalpy changes (in  $\text{kJ mol}^{-1}$ ) of the extraction reactions of Ln(III) with TBDGA are:  $La^{3+}$ ,  $-69.34 \pm 5.82$ ;  $Ce^{3+}$ ,  $-59.28 \pm 2.37$ ;  $Nd^{3+}$ ,  $-69.87 \pm 2.34$ ;  $Eu^{3+}$ ,  $-96.90 \pm 2.51$ ;  $Gd^{3+}$ ,  $-93.00 \pm 3.12$ ;  $Tb^{3+}$ ,  $-106.2 \pm 6.20$ ;  $Dy^{3+}$ ,  $-97.86 \pm 3.06$ ; and  $Er^{3+}$ ,  $-91.7 \pm 6.34$ . It indicates that the enthalpy change benefits extraction reaction [2]. This is in accordance with common reports for most extraction processes [18, 31].

### 3.3 IR spectra study on the extracted species

The IR spectra of extractant and Gd(III) extracted species are shown in Fig. 6. The C=O stretching vibration of free TBDGA appears at  $1652 \text{ cm}^{-1}$ . After extraction of Gd(III), the absorption band of C=O shifts to  $1605 \text{ cm}^{-1}$ . The shift of the C=O frequency for TBDGA before and after extraction is up to  $47 \text{ cm}^{-1}$ , suggesting a strong binding of TBDGA with Gd(III) in the extracted species. This indicates that lanthanide ions are coordinated to the oxygen of the carbonyl group of TBDGA. The band shift of the etheric bond is not obvious. Considering the distinct extractability of TBDGA for trivalent lanthanide ions, the etheric oxygen atom must be coordinated to lanthanide ions in the extracted species. That



**Fig. 5** Extraction of lanthanide ions with TBDGA in toluene at different temperatures



**Fig. 6** IR spectra of TBDGA and Gd-TBDGA extracted species

is to say, three oxygen atoms of each TBDGA molecule binding with lanthanide ion form two five-cycle chelate rings, hence the stability of the extracted species. The tridentate coordination of diglycolamide to the lanthanide ions has been established already by X-ray diffraction and molecular dynamics simulation studies [32]. It is therefore possible that the three ligands in one extracted species completely enclose the metal and form a nine-coordinated complex that provides a hydrophobic exterior. An ion-pair mechanism involving the formation of  $[\text{Ln}(\text{TBDGA})_3]^{3+}$  for lanthanide ions extraction seems to occur [33].

#### 4 Conclusion

Extraction properties of TBDGA in toluene for lanthanide ions in  $\text{HNO}_3$  media have been studied. TBDGA extracts  $\text{HNO}_3$  to form  $\text{HNO}_3\cdot\text{TBDGA}$  under the studied conditions. TBDGA shows high extraction capability toward lanthanide ions, especially heavy lanthanide ions. The distribution ratio increase with the atomic number under the same extraction conditions. The increase in TBDGA and  $\text{HNO}_3$  concentration is favor of the extraction. The extraction reactions of lanthanide ions are exothermic processes. The predominant composition of the extracted species is  $\text{M}(\text{NO}_3)_3\cdot 3\text{TBDGA}$ , and an ion-pair extraction mechanism is suggested.

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