

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

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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 HNO₃ and TBDGA concentrations, and temperature, on extraction of lanthanide ions were studied. Stoichiometries of the main extracted species were HNO₃·TBDGA and M(NO₃)₃·3TBDGA (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 HNO₃ 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.

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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 HNO₃. 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 HNO₃, were of AR grade.

2.2 Extraction of HNO₃ 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 HNO₃ 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⁻³ 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

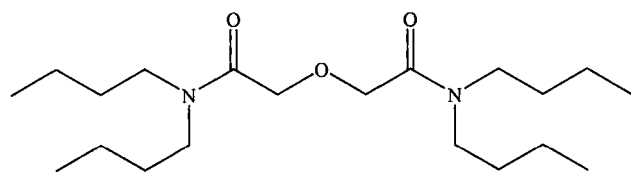


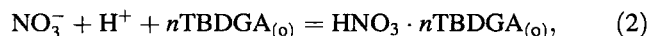
Fig. 1 Chemical structure of *N,N,N',N'*-tetrabutyl-3-oxa-diglycolamide (TBDGA)

wavenumber range of 400–4000 cm⁻¹, in 60 scan times and 2 cm⁻¹ resolution.

3 Results and discussion

3.1 Extraction of nitric acid

The extraction of HNO₃ 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 HNO₃·TBDGA. The K_H value was calculated at 0.35 ± 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⁻³ HNO₃ were in the following order: D2EHPVA (0.06 ± 0.002) < D2EHIBA (0.15 ± 0.04) < D2EHPRA (0.20 ± 0.01) < D2EHAA (0.28 ± 0.03) [19].

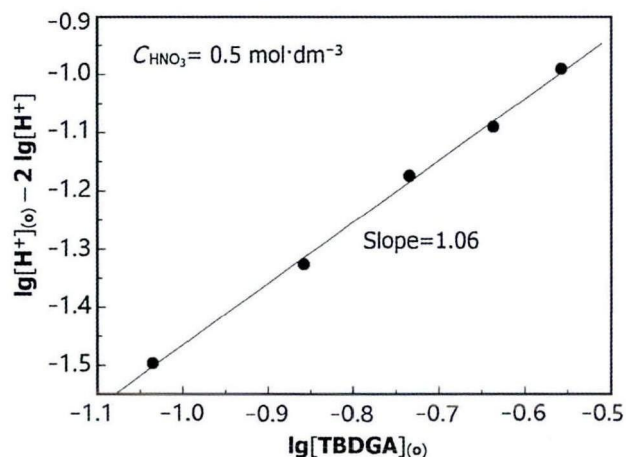


Fig. 2 Extraction of nitric acid with TBDGA

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 $\text{HNO}_3 \cdot \text{DHOA}$. In extraction of HNO_3 with diamide *N,N,N',N'*-dimethyl dibutyl tetradecyl malonamide, Nigond et al. [21] suggested the competing formation of four adducts: $\text{L}_2 \cdot \text{HNO}_3$, $\text{L} \cdot \text{HNO}_3$, $\text{L} \cdot (\text{HNO}_3)_2$, and $\text{L} \cdot (\text{HNO}_3)_3$, with their equilibrium constants for 0.72 mol dm^{-3} amide in TPH being 0.167 , 0.215 , 5.19×10^{-3} and 3.70×10^{-4} , respectively. These show that the basicity of TBDGA, indicated by the equilibrium constant for 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

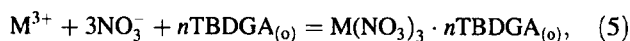
The extraction ratios of Er(III), Dy(III), La(III), Ce(III), Nd(III), Sm(III), Eu(III), Gd(III), and Tb(III) ions from aqueous solution at different concentrations of HNO_3 are shown in Fig. 3. The extraction distribution ratios of lanthanide ions increased with the HNO_3 concentration. This is in agreement with the result by Cuillerdier et al. [22]. 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 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].

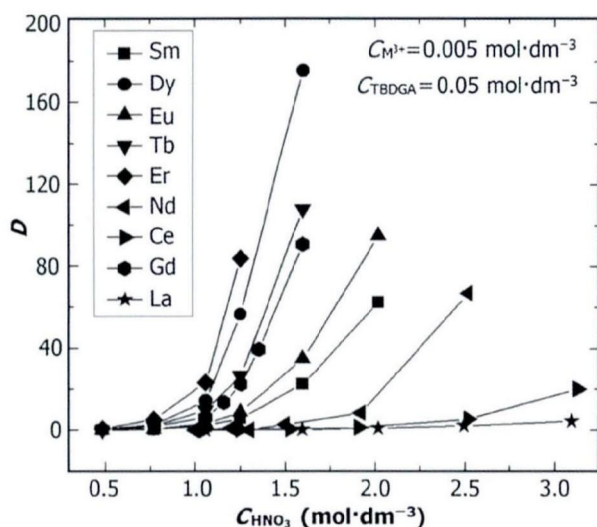


Fig. 3 Distribution of lanthanide ions as a function of HNO_3 concentration

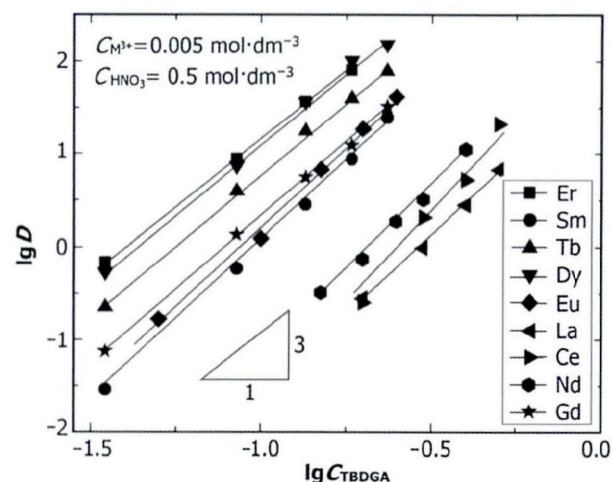


Fig. 4 Influence of TBDGA concentration on the distribution of lanthanide ions

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

$$K_{\text{ex}} = \frac{a_{\text{M}(\text{NO}_3)_3 \cdot 3\text{TBDGA}(\text{o})}}{a_{\text{M}^{3+}} a_{\text{NO}_3^-}^3 a_{\text{TBDGA}}^3} = \frac{C_{\text{M}(\text{NO}_3)_3 \cdot 3\text{TBDGA}(\text{o})}}{\gamma_{\text{M}^{3+}} C_{\text{M}^{3+}} \gamma_{\text{NO}_3^-}^3 C_{\text{NO}_3^-}^3 C_{\text{TBDGA}}^3}, \quad (6)$$

where γ 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

$$C_{\text{M}} = C_{\text{M}^{3+}} (1 + \beta_1 C_{\text{NO}_3^-}). \quad (7)$$

The γ values of NO_3^- and lanthanide ions, calculated by Debye–Hückel formula [27], were 0.9025 and 0.3974, respectively. β_1 is the first-order stability constant of lanthanide ions with nitrate, and the data $\text{La}^{3+}(1.3 \pm 0.3)$, $\text{Ce}^{3+}(1.3 \pm 0.3)$, $\text{Nd}^{3+}(0.77 \pm 0.1)$, $\text{Sm}^{3+}(0.95)$, $\text{Eu}^{3+}(1.8 \pm 0.4)$, $\text{Gd}^{3+}(2.33 \pm 0.02)$, $\text{Tb}^{3+}(1.13 \pm 0.05)$, $\text{Er}^{3+}(0.54)$ were reported by other authors [28–30] (the γ value of Dy^{3+} has not been reported).

The distribution ratio D is

$$D = \frac{C_{\text{M}(\text{o})}}{C_{\text{M}}} = \frac{C_{\text{M}(\text{NO}_3)_3 \cdot 3\text{TBDGA}(\text{o})}}{C_{\text{M}^{3+}} (1 + \beta_1 C_{\text{NO}_3^-})}. \quad (8)$$

Therefore, K_{ex} can be written as

$$K_{\text{ex}} = \frac{D(1 + \beta_1 C_{\text{NO}_3^-})}{C_{\text{NO}_3^-}^3 C_{\text{TBDGA}(\text{o})}^3 \gamma_{\text{M}^{3+}} \gamma_{\text{NO}_3^-}} = K \frac{(1 + \beta_1 C_{\text{NO}_3^-})}{\gamma_{\text{M}^{3+}} \gamma_{\text{NO}_3^-}}, \quad (9)$$

where K is the conditional extraction constant defined as

$$K = \frac{D}{C_{\text{NO}_3^-}^3 C_{\text{TBDGA}(\text{o})}^3}. \quad (10)$$

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

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

M^{3+}	$\lg K$	$\lg K_{\text{ex}}$
La^{3+}	2.52 ± 0.11	3.27 ± 0.11
Ce^{3+}	2.79 ± 0.20	3.54 ± 0.20
Nd^{3+}	2.97 ± 0.17	3.65 ± 0.17
Sm^{3+}	3.96 ± 0.22	4.63 ± 0.22
Eu^{3+}	4.16 ± 0.16	4.98 ± 0.16
Gd^{3+}	4.23 ± 0.08	5.10 ± 0.08
Tb^{3+}	4.69 ± 0.07	5.42 ± 0.07
Dy^{3+}	5.03 ± 0.08	–
Er^{3+}	5.06 ± 0.05	5.70 ± 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 ($\Delta_r H_m^\theta$) of the extraction reaction [19].

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

where constant $R=8.314$. The enthalpy changes (in kJ mol^{-1}) of the extraction reactions of $\text{Ln}(\text{III})$ with TBDGA are: La^{3+} , -69.34 ± 5.82 ; Ce^{3+} , -59.28 ± 2.37 ; Nd^{3+} , -69.87 ± 2.34 ; Eu^{3+} , -96.90 ± 2.51 ; Gd^{3+} , -93.00 ± 3.12 ; Tb^{3+} , -106.2 ± 6.20 ; Dy^{3+} , -97.86 ± 3.06 ; and Er^{3+} , -91.7 ± 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 $\text{Gd}(\text{III})$ extracted species are shown in Fig. 6. The $\text{C}=\text{O}$ stretching vibration of free TBDGA appears at 1652 cm^{-1} . After extraction of $\text{Gd}(\text{III})$, the absorption band of $\text{C}=\text{O}$ shifts to 1605 cm^{-1} . The shift of the $\text{C}=\text{O}$ frequency for TBDGA before and after extraction is up to 47 cm^{-1} , suggesting a strong binding of TBDGA with $\text{Gd}(\text{III})$ 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

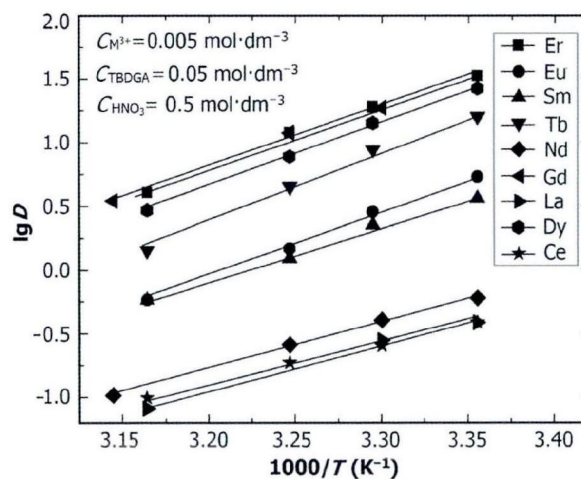


Fig. 5 Extraction of lanthanide ions with TBDGA in toluene at different temperatures

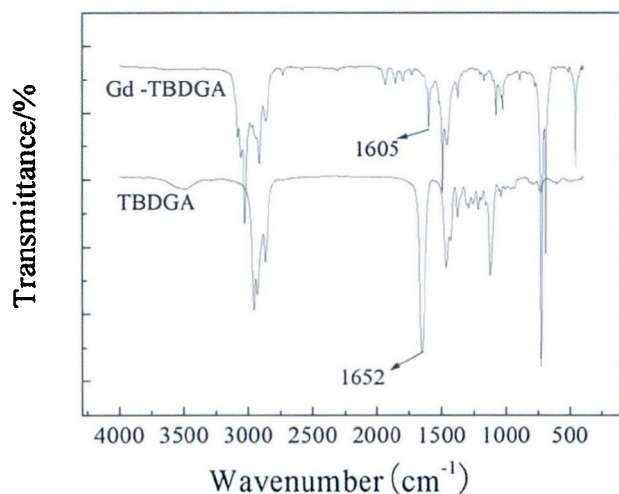


Fig. 6 IR spectra of TBDGA and Gd-TBDGA extracted species

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 HNO_3 media have been studied. TBDGA extracts 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 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.

References

1. R.F. Li, C.X. Liu, H.G. Zhao et al., Di-1-methyl heptyl methylphosphonate (DMHMP): a promising extractant in Th-based fuel reprocessing. *Sep. Purif. Technol.* **173**, 105–112 (2017). doi:10.1016/j.seppur.2016.07.035

2. H. Sodaye, S. Nisan, C. Poletiko et al., Extraction of uranium from the concentrated brine rejected by integrated nuclear desalination plants. *Desalination* **235**, 9–32 (2009). doi:10.1016/j.desal.2008.02.005
3. S. Sayin, M. Yilmaz, Preparation and uranyl ion extraction studies of calix[4]arene-based magnetite nanoparticles. *Desalination* **276**, 328–335 (2011). doi:10.1016/j.desal.2011.03.073
4. Y. Cui, X.F. Yang, C. Yang et al., Solvent extraction of U(VI) by *N,N*-dimethyl-*N',N'*-dioctylsuccinylamide and *N,N*-dimethyl-*N',N'*-didecylsuccinyl amide in cyclohexane. *Nucl. Sci. Tech.* **27**, 59 (2016). doi:10.1007/s41365-016-0056-z
5. G.J. Sun, J.H. Yang, H.X. Yang et al., Extraction study of rare earth elements with *N,N'*-dibutyl-*N,N'*-di(1-methylheptyl)-diglycolamide from hydrochloric acid. *Nucl. Sci. Tech.* **27**, 75 (2016). doi:10.1007/s41365-016-0055-0
6. Y. Sasaki, P. Rapold, M. Arisaka et al., An additional insight into the correlation between the distribution ratios and the aqueous acidity of the TODGA system. *Solvent Extr. Ion Exch.* **25**, 187–204 (2007). doi:10.1080/07366290601169345
7. S.A. Ansari, P.K. Mohapatra, V.K. Manchanda, Recovery of actinides and lanthanides from high-level waste using hollow-fiber supported liquid membrane with TODGA as the carrier. *Ind. Eng. Chem. Res.* **48**, 8605–8612 (2009). doi:10.1021/ie900265y
8. Y. Sasaki, Z.X. Zhu, Y. Sugo et al., Extraction of various metal ions from nitric acid to *n*-dodecane by diglycolamide (DGA) compounds. *J. Nucl. Sci. Techn.* **44**, 405–409 (2007). doi:10.1080/18811248.2007.9711301
9. Z.X. Zhu, S. Yuji, S. Hideya et al., Cumulative study on solvent extraction of elements by *N,N,N',N'*-tetraoctyl-3-oxapentanediamide (TODGA) from nitric acid into *n*-dodecane. *Anal. Chim. Acta* **527**, 163–168 (2004). doi:10.1016/j.aca.2004.09.023
10. X.C. Cai, B. Wei, J.X. Han et al., Solvent extraction of iron(III) from hydrochloric acid solution by *N,N,N',N'*-tetra-2-ethyl-hexyldiglycolamide in different diluents. *Hydrometallurgy* **164**, 1–6 (2016). doi:10.1016/j.hydromet.2016.04.010
11. A. Sengupta, S.M. Ali, K.T. Shenoy, Understanding the complexation of the Eu^{3+} ion with TODGA, CMPO, TOPO and DMDBDMA: extraction, luminescence and theoretical investigation. *Polyhedron* **117**, 612–622 (2016). doi:10.1016/j.poly.2016.06.037
12. M.K. Jha, A. Kumari, R. Panda et al., Review on hydrometallurgical recovery of rare earth metals. *Hydrometallurgy* **165**, 2–26 (2016). doi:10.1016/j.hydromet.2016.01.035
13. M. Wehbie, G. Arrachart, I. Karamé et al., Triazole Diglycolamide Cavitan for lanthanide extraction. *Sep. Purif. Technol.* **169**(17–24), 2016 (2016). doi:10.1016/j.seppur.2016.06.003
14. E.A. Mowafy, D. Mohamed, Extraction behavior of trivalent lanthanides from nitric acid medium by selected structurally related diglycolamides as novel extractants. *Sep. Purif. Technol.* **128**, 18–24 (2014). doi:10.1016/j.seppur.2014.03.005
15. K. Moon Sung, Y. Jaeryong, P. Yong et al., Supercritical CO_2 extraction of uranium(VI) from HNO_3 solution using *N,N,N',N'*-tetrabutyl-3-oxapentanediamide. *Ind. Eng. Chem. Res.* **45**, 5308–5313 (2016). doi:10.1021/ie050992n
16. L.N. Zhang, Y.Q. Wang, G.X. Sun et al., Synthesis of *N,N'*-dimethyl-*N,N'*-didecyl-3-oxa-diglycolamide for extraction of lanthanides. *Nucl. Sci. Tech.* **25**, 24–27 (2014). doi:10.13538/j.1001-8042/nst.25.040301
17. A.N. Turanov, V.K. Karandashev, V.E. Baulin, Effect of anions on the extraction of lanthanides (III) by *N,N'*-dimethyl-*N,N'*-diphenyl-3-oxa-pentanediamide. *Solvent Extr. Ion Exch.* **26**, 77–99 (2008). doi:10.1080/07366290801904871
18. E.A. Mowafy, H.F. Aly, Synthesis of some *N,N,N',N'*-tetraalkyl-3-Oxa-Pentane-1,5-diamide and their applications in solvent extraction. *Solvent Extr. Ion Exch.* **25**, 205–224 (2007). doi:10.1080/07366290601169352

19. P.N. Pathak, L.B. Kumbhare, V.K. Manchanda, Structural effects in *N,N*-dialkyl amides on their extraction behavior toward uranium and thorium. *Solvent Extr. Ion Exch.* **19**, 105–126 (2001). doi:10.1081/SEI-100001377
20. K.K. Gupta, V.K. Manchanda, M.S. Subramanian et al., Solvent extraction studies on U(VI), Pu(IV), and fission products using *N,N*-dihexyloctanamide. *Solvent Extr. Ion Exch.* **18**, 273–292 (2000). doi:10.1080/07366290008934681
21. L. Nigond, C. Musikas, C. Cuillardier, Extraction by *N,N,N',N'*-tetraalkyl-2-alkyl propane -1,3-diamides I. *Solvent Extr. Ion Exch.* **12**, 261–296 (1994). doi:10.1080/07366299408918212
22. C. Cuillardier, C. Musikas, P. Hoel et al., Malonamides as new extractants for nuclear waste solutions. *Sep. Sci. Technol.* **26**, 1229–1244 (1991). doi:10.1080/01496399108050526
23. H. Narita, T. Yaita, K. Tamura et al., Solvent extraction of trivalent lanthanoid ions with *N,N'*-dimethyl-*N,N'*-diphenyl-3-oxapentanediamide. *Radiochim. Acta* **81**(4), 223–226 (1998). doi:10.1524/ract.1998.81.4.223
24. Y. Sasaki, S. Tachimori, Extraction of actinides (III), (IV), (V), (VI), and lanthanides (III) by structurally tailored diamides. *Solvent Extr. Ion Exch.* **20**(1), 21–34 (2002). doi:10.1081/SEI-100108822
25. E.A. Mowafy, H.F. Aly, Extraction behaviors of trivalent lanthanides from nitrate medium by selected substituted malonamides. *Solvent Extr. Ion Exch.* **24**, 677–692 (2006). doi:10.1080/07366290600762322
26. P.N. Pathak, S.A. Ansari, S.V. Godbole et al., Interaction of Eu^{3+} with *N,N,N',N'*-tetraoctyl diglycolamide: a time resolved luminescence spectroscopy study. *Spectrochim. Acta Part A* **73**, 348–352 (2009). doi:10.1016/j.saa.2009.02.040
27. J.A. Dean, *Lange's Handbook of Chemistry*, 12th edn. (McGraw-hill, New York, 1978)
28. D.F. Peppard, M.G. Wason, I. Hucher, Stability constants of certain lanthanide(III) and actinide(III) chloride and nitrate complexes. *J. Inorg. Nucl. Chem.* **24**, 881–888 (1962). doi:10.1016/0022-1902(62)80109-2
29. G.R. Choppin, W.F. Strazik, Complexes of trivalent lanthanide and actinide ions I. outer-sphere ion pairs. *Inorg. Chem.* **4**, 1250–1254 (1965). doi:10.1021/ic50031a003
30. Y. Cui, S.X. Sun, R.Q. Xu et al., Extraction of Ce(III) with *N,N,N',N'*-tetrabutylmalonamide from nitrate media chinese. *J. Inorg. Chem.* **19**, 669–672 (2013). doi:10.3321/j.issn:1001-4861.2003.06.024
31. G.X. Tian, J.C. Wang, Y.F. Shen et al., Extraction of strontium from HLLW using *N,N,N',N'*-tetraisobutyl 3-oxa-glutaramide. *Solvent Extr. Ion Exch.* **23**, 519–528 (2005). doi:10.1021/ic50031a003
32. S. Kannan, M.A. Moody, B.C. Larnes et al., Lanthanum(III) and uranyl(VI) diglycolamide complexes: synthetic precursors and structural studies involving nitrate complexation. *Inorg. Chem.* **47**, 4691–4695 (2008). doi:10.1021/ic7025076
33. M. Hirata, P. Guilbaud, M. Dobler et al., Molecular dynamics simulations for the complexation of Ln^{3+} and UO_2^{2+} ions with tridentate ligand diglycolamide (DGA). *Phys. Chem. Chem. Phys.* **5**, 691–695 (2003). doi:10.1039/B205127N