Extraction of Europium(III) and Cobalt(II) by *N,N,N',N'*-Tetraoctyldiglycolamide and *N,N,N',N'*-Tetrahexyldiglycolamide from Aqueous Acid Solutions

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N,N,N',N'-tetraoctyldiglycolamide (TODGA) and *N,N,N',N'*-tetrahexyldiglycolamide (THDGA) were synthesized and characterized in order to further evaluate them as extracting agents for Eu(III) and Co(II) from nitric and hydrochloric acid solutions. Analysis of the dependence of metal distribution ratio, D_M, on concentrations of reagents indicated that the dominant extracted complexes are $Eu(TODGA)_3(NO_3)_3(HNO_3)$, $Eu(THDGA)_3(NO_3)_3(HNO_3)$, $Eu(THDGA)_3(NO_3)_3(HNO_3)_2$ and $Co(TODGA)Cl_2(HCl)$. In addition, TODGA was evaluated for partitioning of Eu(III). It was concluded that, with acidity adjustment, Eu(III) can be separated from Zr(IV), Nb(V), Co(II) and Cs(I) in nitric and hydrochloric acids.

1. Introduction

One of the main concerns related to the disposal of high–level radioactive liquid waste (HLLW) generated after reprocessing of spent nuclear fuel is related to the presence within this waste of long-lived radionuclides (LLRNs). The LLRNs in the spent nuclear fuels are mostly the so-called minor actinides (neptunium (Np), americium (Am) and curium (Cm)) and certain fission products. Transmutation of LLRNs to short-lived or stable isotopes represents a viable nuclear waste management strategy to drastically reduce the time and space requirements for a geological repository of the remaining waste. To be able to destroy LLRNs in a transmutation process they must be separated from the rest of the HLLW. Therefore, the concept of partitioning and transmutation (P&T) has been proposed for treatment of HLLW.[1-3] The P&T concept imposes highly-set demands on recovery yields and decontamination factors of the separated species. In this context, there has been considerable interest in amide extractants for the extraction of trivalent actinides and lanthanides from HLLW.[4-9] The amide reagents have the advantage that they can be completely decomposed to gaseous products, thus minimizing any residues for ultimate containment. Several studies have indicated that diglycolamide-based extractants show unusually effective extraction of actinides and lanthanides from nitric acid solutions.[10-14] Among diglycolamides, *N,N,N',N'*-tetraoctyldiglycolamide (TODGA) has shown the most favorable combination of properties.[15,16] and has been the focus of further studies. Sasaki and Choppin[13] have shown that the diglycolamide group is tridentate in configuration complexing trivalent metal ions through two carbonyl oxygen donors and an ether oxygen donor. Another interesting behavior of diglycolamide extraction systems is the hyperstoichiometric acid dependency. Yaita et al.[17] attributed it to acid – driven aggregation of diglycolamide which was studied by several authors.[18,19] On the other hand, Shimada et al.[20] and Sasaki et al.[21] attributed the hyperstoichiometric acid dependency of diglycolamide extraction to association of nitric acid molecules in metal - diglycolamide complexes.

In seek for partitioning of HLLW, Modolo et al.[22,23] investigated the efficiency of TODGA for extraction of trivalent actinides and lanthanides from raffinate of the PUREX process. They have also evaluated an extractant mixture of TODGA and tributylphosphate (TBP) for the separation of actinides(III) and lanthanides(III).[24-26] Extraction studies have demonstrated the efficiency of the TODGA + TBP extractant mixture for the recovery of minor actinides from genuine PUREX raffinate. Very high recovery and decontamination factors were obtained for Am and Cm. Ansari et al.[27] have evaluated a mixture of TODGA and *N,N*-dihexyloctanamide (DHOA) for lanthanides partitioning from simulated HLLW. Quantitative extraction (forward and backward) of trivalent lanthanides was achieved in four stages each.

In spite of the previous studies, the research continues for better understanding of the basic chemistry involved in diglycolamide extraction systems and for developing the process for potential full-scale operation. Additionally, only few studies have been reported on extraction of transition metal ions with diglycolamides. Therefore, our purpose in this research is to (i) study the extraction behavior of Eu(III) with diglycolamides, (ii) further evaluate TODGA as extractant for lanthanides partitioning and (iii) study the extraction behavior of Co(II) with TODGA and primarily identify the structure of Co – TODGA complexes.

2. Experimental

2.1. Synthesis of tetraalkyldiglycolamides. *N,N,N',N'*-tetraoctyldiglycolamide (TODGA) and *N,N,N',N'*-tetrahexyldiglycolamide (THDGA) were synthesized by the reaction of diglycolyl chloride with dialkylamines (dioctylamine or dihexylamine) and triethylamine.[28] All chemicals were purchased from Aldrich and used as received. The products of TODGA and THDGA were characterized by elemental analysis and nuclear magnetic resonance. The elemental analysis was performed on a Vario EL Elementar analyzer and the ^{1}H-NMR characterization was performed on a Varian Gemini 200 MHz NMR spectrometer. The chemical shift values are reported relative to trimethylsilane (TMS) standard and using $CDCl_3$ as solvent.

N,N,N',N'-tetraoctyldiglycolamide (TODGA) was obtained as yellow oil in 57% yield. The % composition found: C (73.52), H (12.24), N (5.03); calcd for $C_{36}H_{72}N_2O_3$: C (74.43), H (12.49), N (4.82). The chemical shift values (ppm): 4.185 (s), 3.175 (t), 3.069 (t), 1.153 (br) and 0.759 (br) are assigned to the

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protons of O-CH$^*_2$-CO, N-CH$^*_2$-(CH$_2$)$_6$-CH$_3$, N-CH$^*_2$-(CH$_2$)$_6$-CH$_3$, N-CH$_2$-(CH$^*_2$)$_6$-CH$_3$ and N-(CH$_2$)$_7$-CH$^*_3$, respectively. The structure of TODGA is presented in Figure 1(a).

N,N,N',N'-tetrahexyldiglycolamide (THDGA) was obtained as yellowish brown oil in 92% yield. The % composition found: C (70.78), H (11.64), N (6.34); calcd for C$_{28}$H$_{56}$N$_2$O$_3$: C (71.74), H (12.04), N (5.98). The chemical shift values (ppm): 4.205 (s), 3.199 (t), 3.087 (t), 1.426 (br), 1.187 (br) and 0.786 (m) are assigned to the protons of O-CH$^*_2$-CO, N-CH$^*_2$-(CH$_2$)$_4$-CH$_3$, N-CH$^*_2$-(CH$_2$)$_4$-CH$_3$, N-CH$_2$-CH$^*_2$-(CH$_2$)$_3$-CH$_3$, N-(CH$_2$)$_2$-(CH$^*_2$)$_3$-CH$_3$ and N-(CH$_2$)$_5$-CH$^*_3$, respectively. The structure of THDGA is presented in Figure 1(b).

2.2. Reagents. All the chemicals were of analytical grade and all water was bidistilled. The radionuclides $^{152+154}$Eu, ^{141}Ce, ^{95}Zr, ^{181}Hf, ^{95}Nb, ^{60}Co and ^{134}Cs were used as tracers for Eu, Ce, Zr, Hf, Nb, Co and Cs, respectively. $^{152+154}$Eu, ^{141}Ce, ^{95}Zr, ^{181}Hf, ^{60}Co and ^{134}Cs were prepared by neutron irradiation of suitable target materials in the Egyptian research reactor ET-RR-2. ^{95}Nb was obtained as the daughter of ^{95}Zr.

2.3. Extraction procedure. As an alkane diluent has usually been utilized in liquid – liquid extraction processes involving HLLW, the organic solutions were prepared by dissolving certain quantities of TODGA or THDGA in n-hexane. The organic solution was equilibrated with acid solution of desired concentration without metal ion. One mL of the pre-equilibrated organic solution was mixed with 1 mL of aqueous solution spiked with tracer amount(s) of radionuclide(s). The mixture was shaken mechanically in 5 mL glass vial in a thermostated water bath at 25 ± 1 °C. Preliminary experiments indicated that the reaction is fast and equilibrium is reached within 5 minutes, which is consistent with kinetics data reported for TODGA extraction systems.[21] The two phases were separated by centrifugation and suitable aliquots of both phases were withdrawn for activity measurement. The gamma activities of the radionuclides were measured using a hyper pure germanium (HPGe) detector connected to multi-channel analyzer operating under Genie-2000 software (Canberra Corp.). The distribution ratio, D_M, was calculated according to equation 1:

$$D_M = A_{org} / A_{aq} \tag{1}$$

where A_{org} and A_{aq} are the gamma activities of the radionuclide in the organic and aqueous phases, respectively.

3. Results and Discussion

3.1. Extraction of europium(III)

Extraction equilibrium: The extraction of radiotracer amount of $^{152+154}$Eu(III) was studied from nitric acid solutions. The nitric acid dependence of europium distribution ratio, D_{Eu}, was measured and the results are presented in Figure 2. The D_{Eu} increases with increasing HNO$_3$ concentration which indicates that NO$_3^-$ anion plays an important role in the extraction reaction. Since the diglycolamides are neutral ligands, it was expected that three NO$_3^-$ anions were associated in the extracted Eu – complexes in order to neutralize the charge of Eu^{3+} cation. However, the nitric acid dependency reaches the power of 4.4 and 6.6 for TODGA and THDGA, respectively. This hyperstoichiometric acid dependency has been observed in diglycolamide extraction systems and has been attributed to nitric acid - driven aggregation of diglycolamides [17] and/or participation of HNO$_3$ molecules in the extraction reactions.[20,21]

In order to investigate the role of nitrate ion in the extraction reaction more closely, the nitrate ion dependency of D_{Eu} was measured at constant concentration of H$^+$ ion. The concentration of NO$_3^-$ ion was adjusted with NaNO$_3$. The data presented in Figure 3 indicate that the relation between D_{Eu} and NO$_3^-$ ion concentration is a straight line relationship with slope equal to
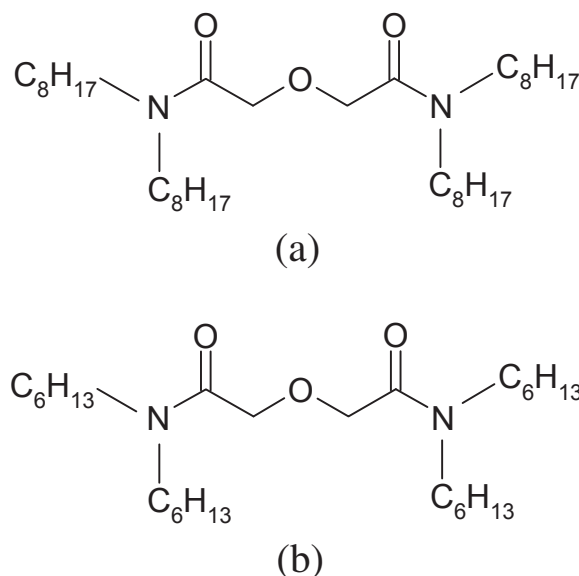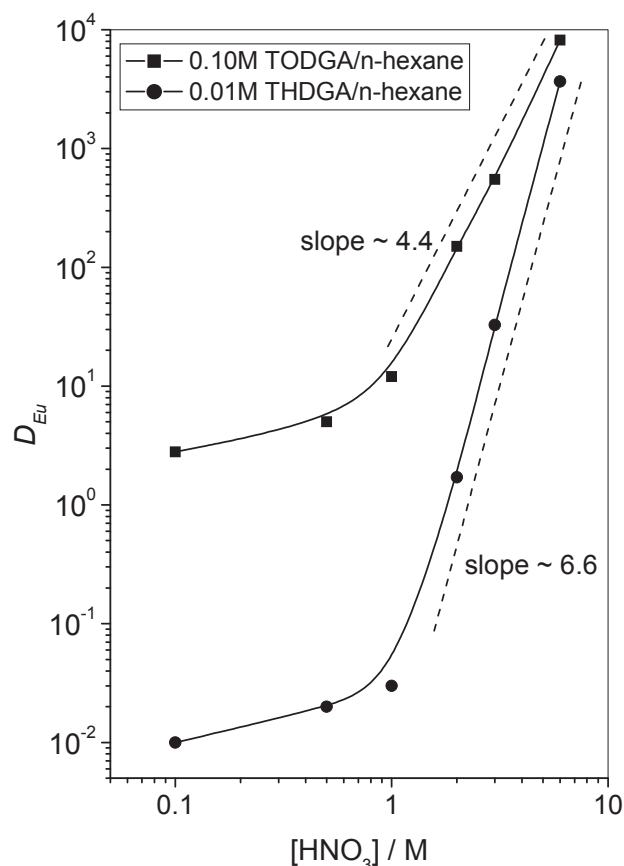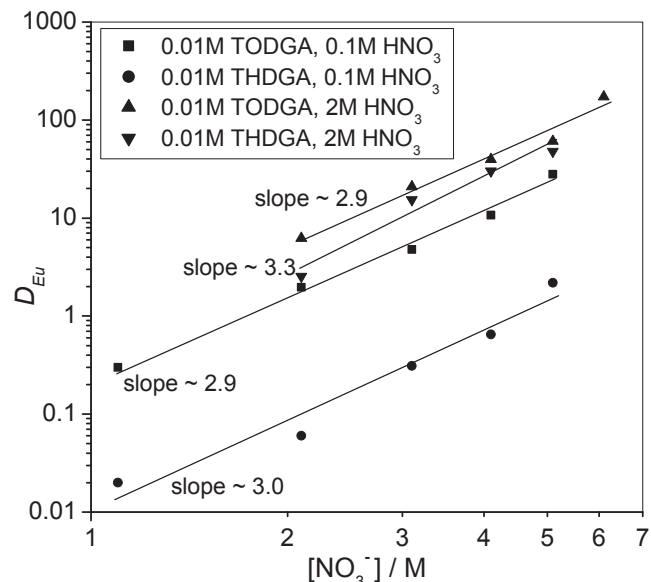

Figure 1. Structures of TODGA (a) and THDGA (b).

Figure 2. Effect of nitric acid concentration on distribution of radiotracer amount of Eu(III).

~ 3 for TODGA and THDGA. Therefore, three NO$_3^-$ anions participate in the extraction reaction of Eu(III).

Also, the acid dependency of Eu(III) distribution ratio, D_{Eu}, was measured at constant concentration of nitrate ion. The results are presented in Figure 4 which indicates that the relation between D_{Eu} and HNO$_3$ concentration is a straight line relationship with slopes equal to 0.8 ± 0.1 and 1.6 ± 0.2 for TODGA and THDGA, respectively. Therefore, one molecule of HNO$_3$ is associated in Eu - TODGA complexes, whereas Eu - THDGA complexes may contain one or two molecules of HNO$_3$. Sasaki et al.[21] also suggested the presence of either one or two HNO$_3$ molecules in metal(III) - diglycolamide complexes.

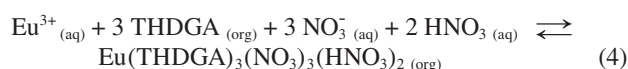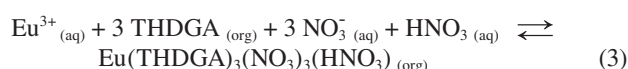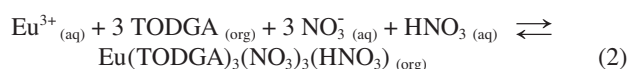In order to determine the stoichiometric number of extract-

Figure 3. Effect of nitrate ion concentration on distribution of radiotracer amount of Eu(III); $[HNO_3]$ = 0.1M.

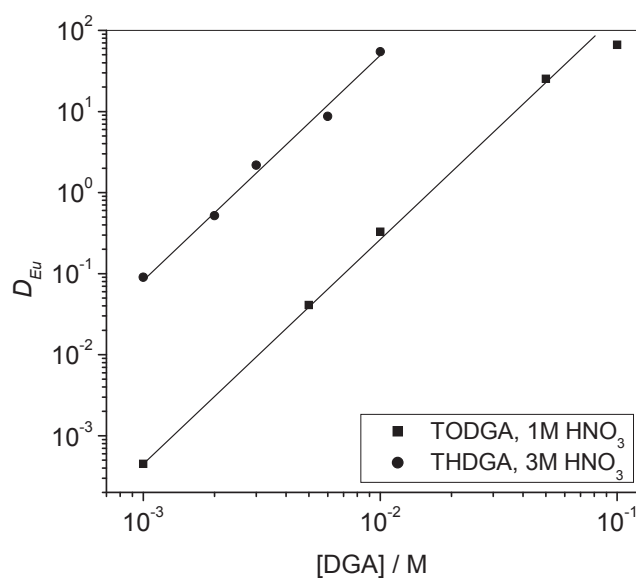**Figure 5.** Effect of diglycolamide concentration on distribution of radiotracer amount of Eu(III).
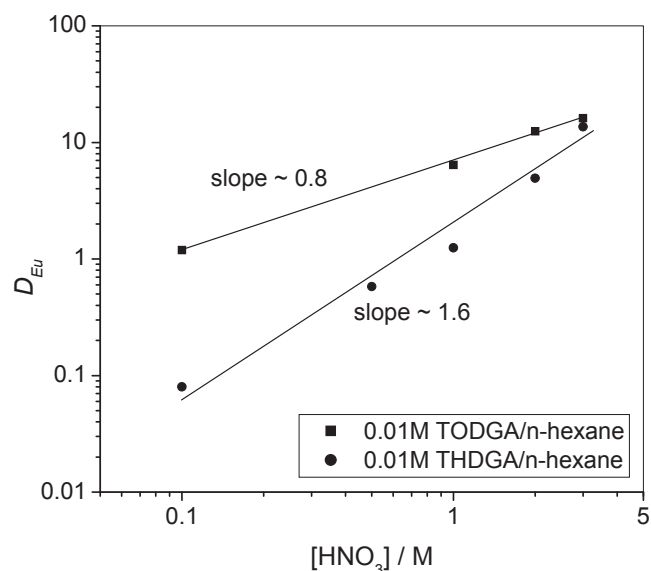
Figure 4. Effect of nitric acid concentration on distribution of radiotracer amount of Eu(III); $[(H,Na)NO_3]$ = 3M.

ant molecules participating in the extraction reaction, the dependence of europium distribution ratio, D_{Eu}, on extractant concentration was investigated. The values of D_{Eu} were plotted against extractant concentration ($[TODGA]$ and $[THDGA]$) in Figure 5. Straight lines were obtained with slopes equal to 2.8 ± 0.1. Therefore, three molecules of extractant (TODGA or THDGA) participate in the extraction reaction. Based on the previous results, the most predominant extraction reactions of Eu(III) could be represented by equations 2-4:

$$Eu^{3+}_{(aq)} + 3\ TODGA_{(org)} + 3\ NO_3^{-}_{(aq)} + HNO_{3\ (aq)} \rightleftarrows$$
$$Eu(TODGA)_3(NO_3)_3(HNO_3)_{(org)} \quad (2)$$

$$Eu^{3+}_{(aq)} + 3\ THDGA_{(org)} + 3\ NO_3^{-}_{(aq)} + HNO_{3\ (aq)} \rightleftarrows$$
$$Eu(THDGA)_3(NO_3)_3(HNO_3)_{(org)} \quad (3)$$

$$Eu^{3+}_{(aq)} + 3\ THDGA_{(org)} + 3\ NO_3^{-}_{(aq)} + 2\ HNO_{3\ (aq)} \rightleftarrows$$
$$Eu(THDGA)_3(NO_3)_3(HNO_3)_{2\ (org)} \quad (4)$$

As described above, the proposed Eu - complexes contain 3 molecules of tridentate diglycolamide, 3 NO_3^{-} anions and 1 ~ 2 molecules of HNO_3. Since Eu^{3+} cation, with coordination number of 8 or 9, cannot accommodate all these ligands, it appears

that some of these ligands reside in the outer coordination sphere of Eu^{3+} cation.[19-21]

The equilibrium concentration constant of the extraction reaction 2, K_2, is expressed as follows:

$$K_2 = \frac{[Eu(TODGA)_3(NO_3)_3(HNO_3)]}{[Eu^{3+}]\ [TODGA]^3\ [NO_3^{-}]^3\ [HNO_3]}$$

The distribution ratio of Eu^{3+}, D_{Eu}, is defined by

$$D_{Eu} = \frac{[Eu(TODGA)_3(NO_3)_3(HNO_3)]}{[Eu^{3+}]}$$

Hence,

$$K_2 = \frac{D_{Eu}}{[TODGA]^3\ [NO_3^{-}]^3\ [HNO_3]} \quad (5)$$

Similarly, the equilibrium concentration constant of the extraction reaction 4, K_4, is expressed as:

$$K_4 = \frac{[Eu(THDGA)_3(NO_3)_3(HNO_3)_2]}{[Eu^{3+}]\ [THDGA]^3\ [NO_3^{-}]^3\ [HNO_3]^2}$$

The distribution ratio of Eu^{3+}, D_{Eu}, is defined by

$$D_{Eu} = \frac{[Eu(THDGA)_3(NO_3)_3(HNO_3)_2]}{[Eu^{3+}]}$$

Hence,

$$K_4 = \frac{D_{Eu}}{[THDGA]^3\ [NO_3^{-}]^3\ [HNO_3]^2} \quad (6)$$

Thermodynamic Parameters: The extraction of Eu(III) with TODGA and THDGA was studied at different temperatures (30 – 50 °C). The equilibrium constants of reactions 2 and 4 were calculated using equations 5 and 6. The obtained values of ln K and the corresponding values of standard deviation (σ) are presented in Table 1. The values of ln$K$ are plotted against $1/T$ in Figure 6. The data were fit with linear regres-

TABLE 1: Equilibrium constants of Eu(III) extraction reactions and standard deviation values

Temperature (K)	Eu(III)–TODGA–HNO$_3$		Eu(III)–THDGA–HNO$_3$	
	ln K_2	σ	ln K_4	σ
303	14.92	0.19	12.01	0.30
308	14.73	0.21	11.53	0.29
313	14.42	0.22	11.26	0.34
318	14.04	0.19	10.45	0.40
323	13.68	0.27	10.63	0.37
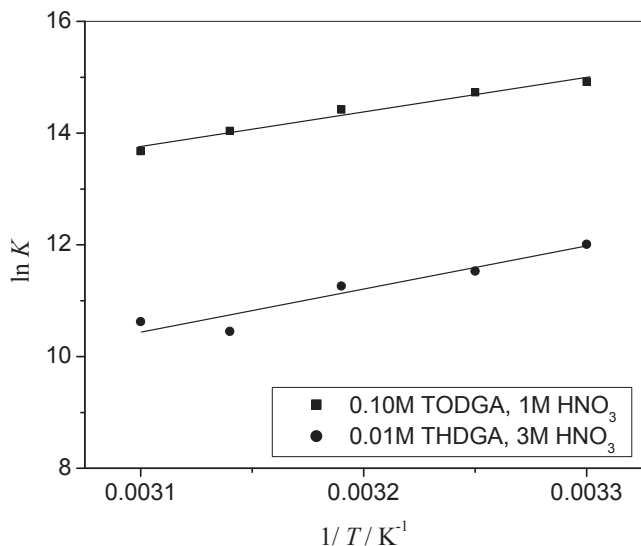
Figure 6. Effect of temperature on distribution of radiotracer amount of Eu(III).

sion to calculate the enthalpy and entropy of the extraction process according to van't Hoff equation 7:

$$\ln K = -\frac{\Delta H}{R}\left[\frac{1}{T}\right] + \frac{\Delta S}{R} \tag{7}$$

where T is absolute temperature and R is the general gas constant.

The calculated values of the thermodynamic parameters are given in Table 2. The obtained results indicate that the extraction processes are exothermic and driven by the relatively large and negative enthalpy. On the other hand, the extraction processes are disfavored by the negative entropy, resulting from combining the metal ion with extractant molecules, associated anions and acid molecules to form highly ordered extracted complexes in the organic phase. These results are consistent with those previously reported for diglycolamide extraction systems.[29,30]

3.2. Extraction of cobalt(II)

The extraction of radiotracer amount of ^{60}Co(II) with TODGA was studied from hydrochloric acid solutions. The hydrochloric acid dependence of Co(II) distribution is shown in Figure 7. The distribution ratio of Co(II), D_{Co}, is low and does not show much change up to 1M HCl. Beyond 1M HCl, D_{Co} increases with increasing HCl concentration up to 8M HCl.
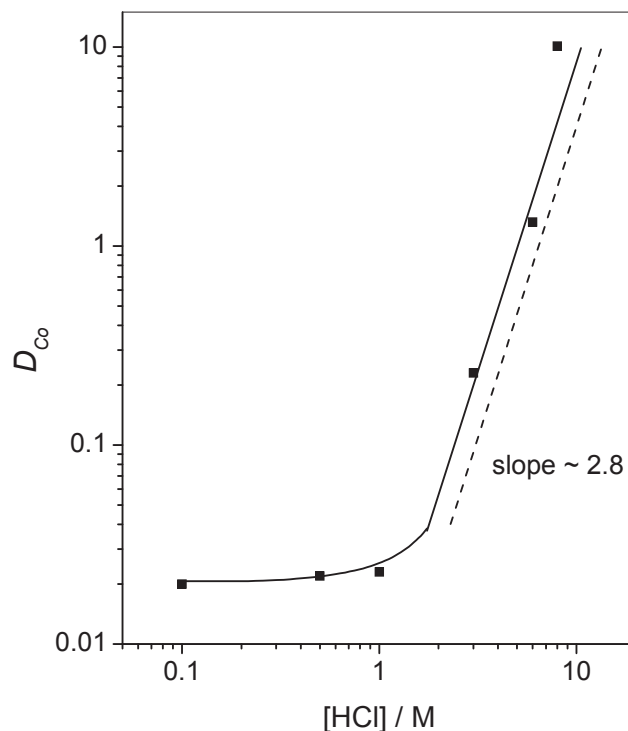
Figure 7. Effect of hydrochloric acid concentration on distribution of radiotracer amount of Co(II); [TODGA] = 0.1M.

The relation between D_{Co} and HCl concentration could be represented in the later range by a straight line with slope equal to 2.8 ± 0.4. Therefore, it is suggested that three chloride anions participate in the extraction reaction.

The chloride ion dependence of Co(II) distribution ratio was measured at constant concentration of H$^+$ ion. The concentration of chloride ion was adjusted with LiCl. The data are presented in Figure 8. The relation between D_{Co} and chloride ion concentration is a straight line relationship with slope equal to 3.1 ± 0.1, which confirms the suggestion that three chloride anions participate in the extraction reaction.

Figure 9 represents the extraction of Co(II) from aqueous solutions containing various concentrations of H$^+$ ion. The concentration of chloride ion was kept constant using LiCl. The distribution ratio of Co(II), D_{Co}, increases with increasing H$^+$ ion concentration. Beyond 2M H$^+$, the relation could be represented by a straight line with slope equal to 0.9 ± 0.1. Therefore, one hydrogen ion participates in the extraction reaction of Co(II).

The distribution ratio of Co(II), D_{Co}, was measured as a

TABLE 2: Thermodynamic parameters for extraction of Eu(III) with TODGA and THDGA

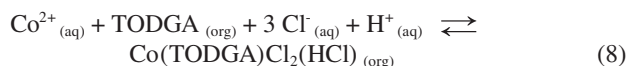| System	K (25 °C)	ΔH (kJ/mol)	ΔS (J/K.mol)	ΔG (kJ/mol)
Eu(III)–TODGA–HNO$_3$	(4.6 ± 0.9) × 10^6	-49.6 ± 1.3	-39.1 ± 4.3	-38.0 ± 0.5
Eu(III)–THDGA–HNO$_3$	(2.5 ± 0.7) × 10^5	-62.5 ± 2.1	-106.6 ± 6.7	-30.8 ± 0.8
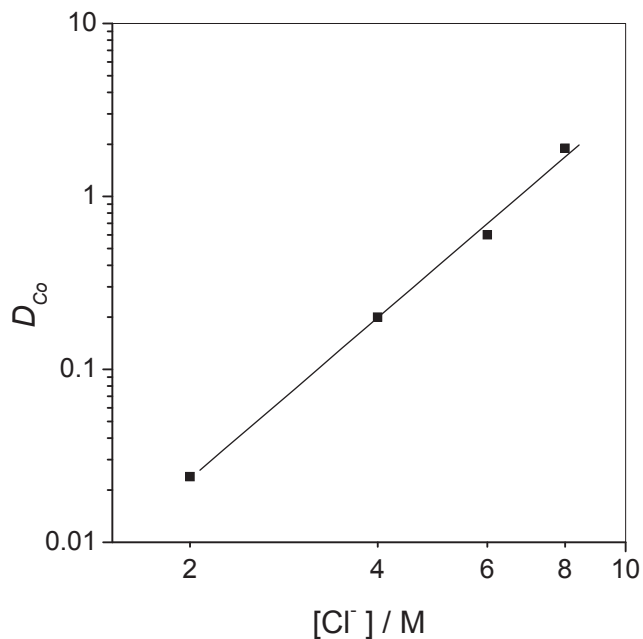
Figure 8. Effect of chloride ion concentration on distribution of radiotracer amount of Co(II); [HCl] = 0.2M, [TODGA] = 0.1M.
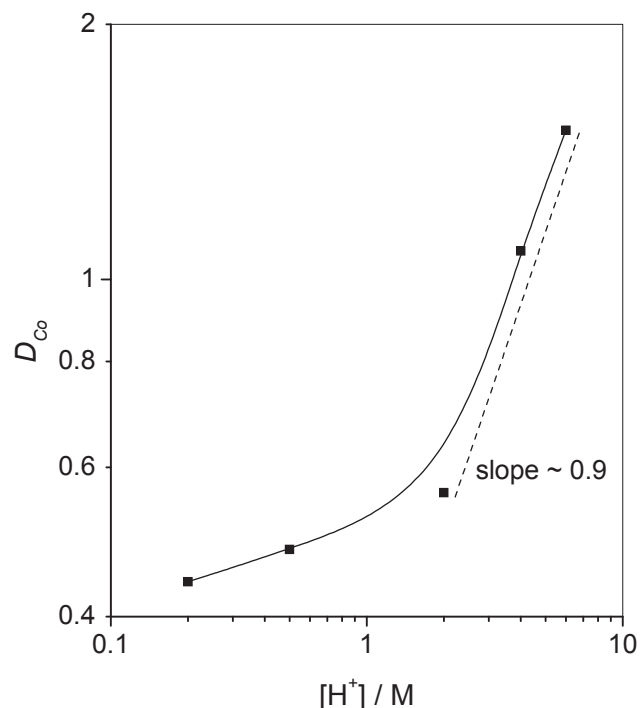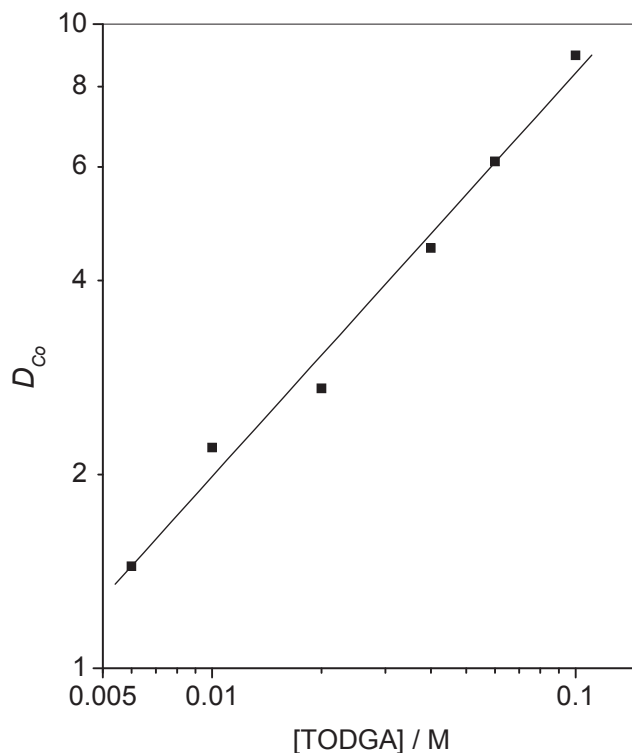

Figure 9. Effect of hydrogen ion concentration on distribution of radiotracer amount of Co(II); [(H,Li)Cl] = 6M, [TODGA] = 0.1M.

Figure 10. Effect of TODGA concentration on distribution of radiotracer amount of Co(II); [HCl] = 8M.

Figure 11. Effect of HNO_3 concentration on distribution of radiotracer amounts of Eu(III), Ce(III), Zr(IV), Hf(IV), Nb(V), Co(II) and Cs(I) with 0.1M TODGA/n-hexane solution.
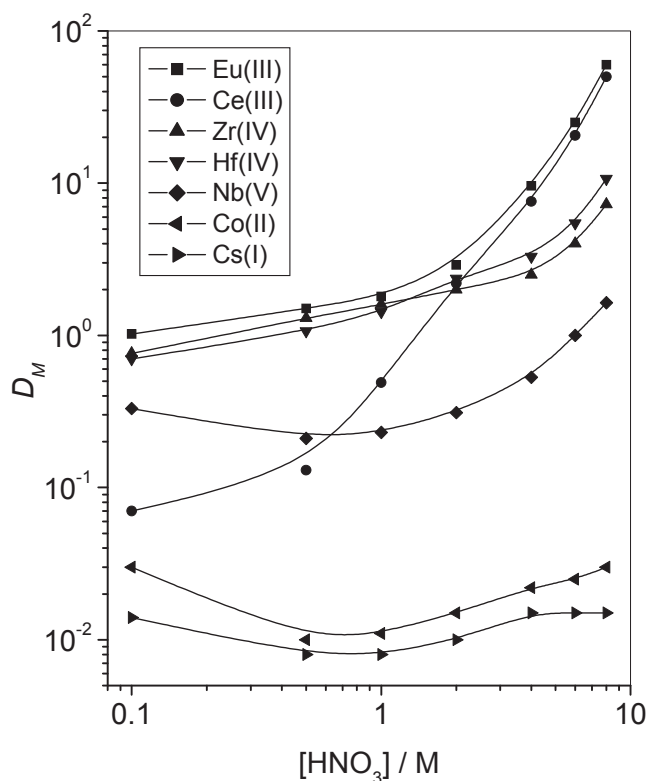
function of TODGA concentration in the organic phase. Figure 10 shows that the relation between D_{Co} and TODGA concentration is a straight line relationship with slope equal to 0.7 ± 0.1 which indicates that almost one molecule of TODGA participates in the extraction reaction. Therefore, the most predominant extraction reaction of Co(II) could be represented by equation 8:

$$Co^{2+}_{(aq)} + TODGA_{(org)} + 3\,Cl^-_{(aq)} + H^+_{(aq)} \rightleftharpoons$$
$$Co(TODGA)Cl_2(HCl)_{(org)} \quad (8)$$

Finally, the extraction of Co(II) with TODGA was studied at different temperatures (20 ~ 50 °C). It was found that the extraction reaction is nearly temperature independent in the studied range of temperature.

Separation of Eu³⁺ with TODGA: *N,N,N',N'*-tetraoctyldiglycolamide (TODGA) has been examined for the separation of europium and some selected elements. Europium was selected as a representative of trivalent f–elements. The other selected elements are those that could be present in matrices of nuclear waste. Figures 11 and 12 show the distribution ratios of tracer amounts of ¹⁵²⁺¹⁵⁴Eu, ¹⁴¹Ce, ⁹⁵Zr, ¹⁸¹Hf, ⁹⁵Nb, ⁶⁰Co and ¹³⁴Cs with TODGA/n-hexane solution as a function of nitric
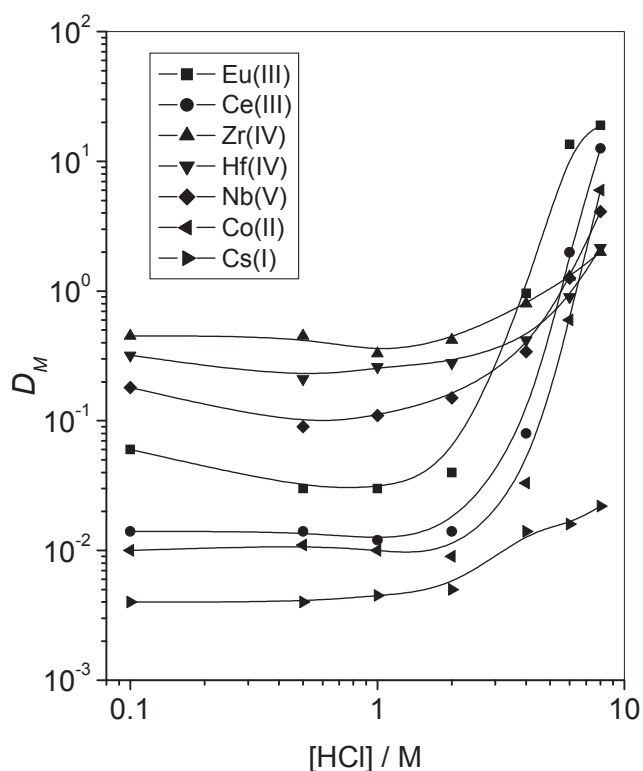
Figure 12. Effect of HCl concentration on distribution of radiotracer amounts of Eu(III), Ce(III), Zr(IV), Hf(IV), Nb(V), Co(II) and Cs(I) with 0.1M TODGA/n-hexane solution.

TABLE 3: Separation factors of Eu(III) in the extraction system: 0.1M TODGA/n-hexane – HNO$_3$

[HNO$_3$] (M)	D_{Eu}/D_{Zr}	D_{Eu}/D_{Nb}	D_{Eu}/D_{Co}	D_{Eu}/D_{Cs}
0.1	1.3	3.1	34	73
0.5	1.2	7.1	150	188
1	1.1	7.8	164	225
2	1.5	9.4	193	290
4	3.8	18	437	641
6	6.3	25	1002	1670
8	8.3	37	2000	4000

TABLE 4: Separation factors of Eu(III) in the extraction system: 0.1M TODGA/n-hexane – HCl

[HCl] (M)	D_{Eu}/D_{Zr}	D_{Eu}/D_{Nb}	D_{Eu}/D_{Co}	D_{Eu}/D_{Cs}
0.1	0.13	0.33	6.0	15
0.5	0.07	0.33	2.7	7.5
1	0.09	0.27	3.0	6.7
2	0.1	0.27	4.4	8.0
4	1.2	2.8	29	69
6	11.0	11.0	23	845
8	9.5	4.6	3.2	864

and hydrochloric acid concentrations, respectively. Figure 11 indicates that Eu(III) and Ce(III) are extracted quite well from concentrated nitric acid solutions. The extraction of Zr(IV), Hf(IV) and Nb(V) is intermediate and that of Co(II) and Cs(I) is insignificant. Generally, the order of extractability at ≥ 3M HNO$_3$ is M(III) > M(IV) > M(V) >> M(II) ~ M(I). In addition, it can be observed that the values of D_{Eu} in Fig. 11 are lower than those in Fig. 2 which is probably due to competition between Eu(III) ion and other metal ions for the extractant molecules. This competition is more significant at higher HNO$_3$ concentrations where Ce(III), Zr(IV) and Hf(IV) are highly extractable.

Figure 12 indicates that the extraction of Eu(III), Ce(III) and Co(II) from hydrochloric acid solutions is low till 2M HCl and then increases drastically up to 8M HCl. Except for Co(II), the extraction of the studied metal ions from hydrochloric acid solutions is generally lower than that from nitric acid solutions.

The separation factors of Eu(III) were calculated from nitric and hydrochloric acid media. The values are given in Tables 3 and 4. It is concluded that with adjustment of acid concentration, Eu(III) can be separated from Zr(IV), Nb(V), Co(II) and Cs(I) in both HNO$_3$ and HCl media.

4. Conclusion

N,N,N',N'-tetraoctyldiglycolamide (TODGA) and *N,N,N',N'*-tetrahexyldiglycolamide (THDGA) show effective extraction of Eu(III) from nitric acid solutions. However, TODGA is preferred to THDGA because TODGA has higher lipophilicity than THDGA. The structures of the extracted Eu-complexes are suggested to be Eu(TODGA)$_3$(NO$_3$)$_3$(HNO$_3$), Eu(THDGA)$_3$(NO$_3$)$_3$(HNO$_3$) and Eu(THDGA)$_3$(NO$_3$)$_3$(HNO$_3$)$_2$. The extraction reactions of Eu(III) are exothermic processes driven by the relatively large and negative enthalpy and disfavored by the negative entropy. By acidity adjustment, TODGA could potentially be used for separation of Eu(III) from Nb(V),

Zr(IV), Co(II) and Cs(I) in nitric and hydrochloric acid solutions. Generally, the order of metal ions extractability from concentrated nitric acid solution is M(III) > M(IV) > M(V) >> M(II) ~ M(I) and the extractabilities are generally higher from nitric acid solutions than hydrochloric acid solutions. TODGA also shows effective extraction of Co(II) from concentrated hydrochloric acid solutions and the structure of the extracted complex is suggested to be Co(TODGA)Cl$_2$(HCl).

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