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Extraction Behavior of Selected Rare Earth Metals from Acidic Chloride Media Using Tetrabutyl Diglycolamide

(Extraction of Select REEs from Chloride Media Using TBDGA)

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Abstract

Rare earth elements (REEs) are vital to modern, high-tech devices. Recycling REEs from post-consumer electronics can potentially diminish supply chain risks. Toward that end, liquid-liquid solvent extraction of various REEs was investigated with tetrabutyl diglycolamide (TBDGA) in *1*-octanol from hydrochloric acid media. Metal partitioning to the organic phase was shown to increase as [Cl^-] increased. In contrast, increasing [H^+] did not improve extraction. The use of the polar diluent *1*-octanol provided high extraction efficiency, especially for the partition of heavy lanthanides from solutions of high chloride concentration. Although the polar diluent also extracted molar amounts of water and acid, it was concluded that a neutral metal/TBDGA complex as mainly the di-solvate was extracted, and that complexation was observed to be exothermic. These results indicate that REE extraction from aqueous chloride solutions can be efficient without the use of high acid concentrations.

Introduction

Rare earth elements are industrially important due to their appearance in energy-efficient electronic devices, magnets, lighting phosphors, solid-oxide fuel cells, catalysts, and advanced weapons systems. [1-4] Rare earth elements include the 15 elements in the lanthanide series plus scandium, and yttrium. Beginning in the mid-1980s rare earth ore production in southern China began to eclipse production from all other countries around the world. [2] Due to the internal policies in China, production of rare earth-laden ores and refined products was heavily subsidized, driving other global suppliers from the marketplace. In 2010, China produced >95% of the world supply of lanthanide ores and refined rare earth products.[5] As the electrification of society advances and high tech devices continue to be deployed into the world market, the need for “technology metals” will increase accordingly. Artificial materials shortages created by a single country that monopolizes supply could potentially have a significant negative effect world-wide on high-tech industrial sectors that rely heavily on rare earth materials.

To address potential rare earth materials supply challenges recycling strategies for recovery of critical materials have been proposed as a key component of a multi-faceted sustainability approach. An important step in the recycle/recovery process is the use of hydrometallurgical technologies for the recovery of rare earth materials from various streams (e.g., manufacturing scrap, end-of-life electronics, spent catalysts, etc). Kronholm *et al.* [6] recently published a primer on the essential aspects of hydrometallurgical processes for rare earth separations. Others have recently contributed to advancing the current state of hydrometallurgical technologies for recovering rare earths from consumer electronics, end-of-life products, and industrial waste containing rare earths.[7-16] The basic hydrometallurgical approach is to render an insoluble, solid form of the targeted metal into an aqueous soluble form by use of strong mineral acids. Once dissolved, ionic metal species are then extracted to an organic diluent phase via use of metal complexing agents. Metal is then commonly recovered from the organic phase through acid stripping, or back extraction into an aqueous acidic solution. Selection of the acid used for dissolution, and the ligand used for forming the organic soluble metal-ligand complex at the front-end of the hydrometallurgical process, can have profound effects on downstream separations and overall process efficiency and economics. Some matrices are highly recalcitrant, are not successfully attacked by nitric acid alone (e.g., phosphors, ores, catalysts), and require use of HCl to accomplish dissolution. It should also be noted that modern, industrial-scale chemistry used to leach and recover lanthanides from REE-rich ores is chloride-based.[17]

Recently, diglycolamide ligands (DGAs) have shown superior extraction properties for rare earth elements with the added advantage of the ligand being incinerable, [18-19] which is a problematic issue with regards to organophosphorus ligands. For example, our group previously reported data concerning the extraction of lanthanides and americium using tetrabutyl diglycolamide (TBDGA)/*1*-octanol extraction from HNO_3 solution.[20] Others have recently reported that DGAs have stated advantages for separations from HCl including improved separation factors between light and heavy lanthanides,[17-19, 21] exothermic complex formation reactions in a variety of diluent systems,[17, 19, 21] improved recovery of lanthanides from mixed metal liquors that contain high concentrations of transition metals (e.g., Fe, Ni, Co),[21] and even synergistic enhancement of lanthanide extraction in the presence of transition metals.[22]

Therefore, in this study we examine the extraction behavior of select rare earth metal ions from chloride media using the digylcolamide ligand, TBDGA. The structure of TBDGA is shown in Figure 1. Liquid-liquid solvent extraction was performed with TBDGA in *1*-octanol as the diluent. Pure *1*-octanol was chosen to provide the highest possible lanthanide extraction efficiency, given that polar diluents have been reported to provide high extraction efficiency as compared to the less polar but traditional dodecane/octanol mixtures. [23] The effects of [H^+], [Cl^-], [TBDGA], temperature, and equilibration time on extraction of various rare earth elements from chloride media were examined. Previous work has shown the effects of [HCl], [TBDGA], temperature, and diluent composition on the distribution ratios of Gd, Dy Er, Yb, Sm, and Nd.[17, 19] Work performed here expands the body of literature by studying additional REEs for which there are currently no data, by demonstrating the effects of varying [Cl^-] at constant [H^+], and by use of *1*-octanol as a diluent.

Materials and Methods

All liquid-liquid extractions were performed in 15 mL Corning conical tubes using equal volume contacts of the acid-pre-equilibrated organic phase with a metal loaded aqueous phase of the appropriate acid concentration. Removal of separated phases was performed with 2 mL glass Pasteur pipettes. A Centrific model 228 (Fisher Scientific, Hampton, NH) centrifuge was used to aid in phase separation. All ICP-MS analyses were performed on an Agilent model 7900 ICP-MS (Agilent, Santa Clara, CA). The following reagents from Sigma-Aldrich (Sigma-Aldrich, St. Louis, MO) were used as-received: hydrochloric acid (ACS grade), 1-octanol (≥99%), yttrium (III) chloride hexahydrate (99.9%), cerium (III) chloride heptahydrate (99.9%), neodymium (III) chloride hexahydrate (99.99%), samarium (III) chloride hexahydrate (≥99%), europium (III) chloride hexahydrate (99.99%), terbium (III) chloride hexahydrate (99.9%), dysprosium (III) chloride hexahydrate (99.9%), holmium (III) chloride hexahydrate (99.9%), lutetium (III) chloride hexahydrate (99.9%). Lanthanum (III) chloride heptahydrate (99.7%) was used as-received from J.T. Baker Chemical Company (J.T. Baker, Center Valley, PA). NaCl (≥99%) was used as-received from GFS Chemicals (GFS Chemicals, Powell, OH). N,N,N',N'-tetrabutyldiglycolamide (95%) (TBDGA) was used as-received from Tractus Chemical (Tractus Chemical, London, England).

All aqueous solutions were prepared with water purified to a resistivity of at least 18 MΩ-cm^{-1}. The concentration of the REEs in the aqueous phase was determined by ICP-MS. Since it was not possible to perform ICP-MS on the organic phase using existing equipment, the concentration of the REEs in the organic phase was determined by the difference between the original aqueous solution concentration ($[\mathrm{Ln}]_{\mathrm{init}}$) and the concentration in the final aqueous phase ($[\mathrm{Ln}]_{\mathrm{post}}$). Because the organic phase concentration was determined by difference, no mass balance analysis was possible. The distribution ratio (D_{Ln}) was calculated using eq. 1 where the concentration of metal determined in the organic phase, ($[\mathrm{Ln}]_{\mathrm{init}} - [\mathrm{Ln}]_{\mathrm{post}}$), was divided by the concentration of metal in the aqueous phase, $[\mathrm{Ln}]_{\mathrm{post}}$. An element is considered extracted with a D_{Ln} of one or greater.

$$D_{\mathrm{Ln}} = \frac{[Ln]_{\mathrm{init}} - [Ln]_{\mathrm{post}}}{[Ln]_{\mathrm{post}}} \qquad (1)$$

To ensure that equilibrium distribution ratios were being measured, 8.0 M HCl pre-equilibrated 10 mM TBDGA/*1*-octanol was used to contact 8 M HCl containing about 100 ppb Y, La, Ce, Nd, Sm, Eu, Tb, Dy, Ho, and Lu added as chloride salts for contact times of 5, 10, 30, and 60 minutes. After the specified contact time the solution was centrifuged for 5 minutes and the aqueous phase was removed. The distribution ratios for the various contact times were then determined by the same method as above. These results indicated that the contact time of 15 minutes used in all the experiments in this study provided equilibrium D_{Ln} values. All contacts were performed at a temperature of 22 ± 1 °C.

Water concentrations were determined by duplicate Karl Fisher titration measurements for each extraction sample with a Metrohm 899 Coulometer (Metrohm USA, Riverview, FL). A sample size of 0.1 ± 0.02 g of the organic was used.

Acidity concentrations were determined by acid/base titration. One milliliter of the organic sample was contacted for 5 minutes with 5 mL of nanopure water. After centrifuging for 5 minutes the aqueous phase was collected. This was repeated for 5 total washes. The collected aqueous was diluted to about 100 mL and 2 drops of a phenolphthalein indicator (Idaho National Laboratory, Idaho Falls, ID) was added. This solution was titrated with 0.01 M standardized NaOH (Fisher Scientific, Hampton, NH) in a class A buret. This analysis was performed in triplicate for each sample.

Results and Discussion

Extraction Behavior as a Function of Ionic Radii

Plotting ionic radii CN=6,[24] versus the distribution ratio, Figure 2, shows the general trend for the extraction of REEs with TBDGA from 8.0 M HCl. Overall, the relationship between ionic radii and D_{Ln} is inversely proportional. As the ionic radii increase the D_{Ln} decrease, suggesting the expected trend of lanthanide ions of higher charge density being better complexed and extracted. The overall trend agrees with that observed by Cui et al., with TBDGA extraction from HCl using various diluents other than *1*-octanol.[17] Similar results have been reported for TODGA/dodecane extractions of both lanthanides and actinides by Sasaki et al., [25] This also is consistent with our previous report for the extraction of lanthanides from HNO_3 using TBDGA/*1*-octanol.[20] This HNO_3 data is shown along with our new HCl data in Figure 2, for comparison. The light lanthanides show better extraction behavior from HCl; the heaviest lanthanides Ho and Lu have high extraction efficiency from both acids. The better extraction of metals from HCl is in agreement with the Hofmeister "salting out" series for the extraction of a neutral species. [26]

Effect of Varying [HCl]

Data for the extraction of lanthanides from 1.0 M to 8.0 M HCl using pre-equilibrated 10 mM TBDGA/*1*-octanol are graphically depicted in Figure 3. For all rare earths tested, as [HCl] increased in the aqueous phase the amount of REE extracted into the organic phase also increased. This trend was also observed by Cui et al., [17, 19] for TBDGA extraction from HCl using several other diluents. An element is considered extractable for process application if the distribution ratio, D_{Ln}, is greater than one. From 0.1 to 1.0 M HCl none of the REEs examined were extractable. From > 3.0 M HCl, Y, Tb, Dy, Ho, and Lu were extractable with D_{Ln} in the range of 1.5 to 4.1. All other elements were poorly extracted with $D_{\mathrm{Ln}} < 1$. As the acid concentration was further increased, the heavy lanthanides Dy, Ho, and Lu, became highly extractable from 5.0 M HCl, with D_{Ln} in the range 10.8 to 18.8. Samarium, Eu, Tb, and Y were also extractable with lower D_{Ln} in the range of 2.0 to 7.4. Lanthanum, Ce, and Nd were still poorly extracted with $D_{\mathrm{Ln}} < 1$. Finally, from 8.0 M HCl only the light lanthanides, La and Ce, remained poorly extracted with $D_{\mathrm{Ln}} < 1$. Neodymium and Sm were extractable with D_{Ln} in the range 2.0 to 9.0. All other REEs examined were highly extractable from highly acidic solution with D_{Ln} in the range of 15.1 to 142. Thus, a separation of the REEs into light and heavy fractions can be envisioned under these conditions. Increasing extraction efficiency with increasing [HCl] is consistent with the requirement for charge neutralization of a metal complex by Cl^- anion prior to extraction. To separate the effect of acidity from [Cl^-], extraction at varying [Cl^-] with constant [HCl] was next performed.

Effect of Varying [Cl^-]

Figure 4 shows the distribution ratios of REEs into an organic phase containing 10 mM TBDGA/*1*-octanol from an aqueous phase containing 1.0 M HCl and varying [Cl^-] ranging from 2.0 M to 4.0 M, added as NaCl (total Cl^- range 3.0 M to 5.0 M). A similar trend was observed as was seen in the previous experiment where [HCl] was varied. However, for these experiments, when [H^+] was kept constant and [Cl^-] was varied, the magnitude of increase in D_{Ln} was greater for neutral Cl^-. This indicates that [H^+] can actually have a deleterious effect on metal extraction. This suggests that HCl competes for the ligand and that in this polar alcoholic diluent the amount of HCl extracted by TODGA is sufficient to interfere with lanthanide metal ion extraction.

Further evidence of the adverse effect of acidity on extraction is shown in Figure 5. The distribution ratios of different REEs from aqueous phases containing 0 M, 1.0 M, and 5.0 M [H^+] where [Cl^-] is held constant at 5.0 M are given. Distribution ratios are shown as 100 for elements that were below detection limit for the ICP-MS analysis of the aqueous phase indicating that almost all of the metal was extracted into the organic phase. It can be seen that for a constant chloride concentration, increasing acidity greatly decreased the D_{Ln} values, indicating again that HCl has a negative effect on the extraction of REE into the organic phase. By reducing [HCl] to 1.0 M, but keeping [Cl^-] at 5.0 M the D_{Ln} is increased by about 3.5x for most of the REEs. When there was no HCl in the aqueous solution, but the Cl^- was constant at 5.0 M, the D_{Ln} increased about 2x to 9x when compared to the solution with 1.0 M HCl. These results introduce the concept that for potential process applications [HCl] may be kept at a minimum and D_{Ln} for different REEs can be optimized by varying [Cl$^-$] through use of a less expensive source of Cl$^-$, e.g., NaCl.

If the extracted complex is indeed neutral, as is usually assumed for extraction into non-polar media, high [Cl$^-$] facilitates extraction from aqueous media because the TBDGA metal complex requires three Cl$^-$ to satisfy the metal ion charge. Equation 2 shows the complexation that occurs to form a charge neutral species. The chloride ion poorly complexes with the metal ions.[17] Thus, a high chloride concentration is needed to drive the equilibrium toward the neutral species which is extractable into the organic phase.

$$\mathrm{Ln}^{3+}_{(\mathrm{aq})} + n\mathrm{TBDGA}_{(\mathrm{o})} + 3\mathrm{Cl}^-_{(\mathrm{aq})} \leftrightarrow \mathrm{Ln(TBDGA)}_n\mathrm{Cl}_{3\,(\mathrm{o})} \quad (2)$$

A very polar diluent such as *1*-octanol can be assumed to extract acid and water, and thus possibly some metal ions, perhaps even in the absence of the DGA. In that case, metal may be extracted as species other than the neutral complex represented in Eq 2. This is discussed in more detail in the next section.

Extraction of acid and water by 1-octanol

To evaluate the effects of the extraction of water and acid by the polar diluent and their possible effect on metal extraction, Eu solutions of HCl or NaCl were contacted with *1*-octanol and the post-contact organic solutions were measured for their concentrations of water, HCl and Eu. The acidity measured in post-contact *1*-octanol was below detection limit (< ~0.01 M) following contact with pure water, or neutral NaCl solution, and only slightly elevated to 0.029

M following contact with 0.5 M HCl. However, the acid content of *1*-octanol after contact with 8 M HCl was significant, at 2.15 M ($D_{HCl} = 0.37$). These results are shown in Table 1. Geist[27] reported the extraction of similar amounts of HNO_3 by *1*-octanol. Also shown in Table 1 is that the extraction of water was significant in all cases, with approximately 3 M H_2O in the organic phase after contact with pure water, decreasing to 1.6 M at higher neutral chloride concentrations, consistent with the lower water concentration of very salty solutions. However, a greater amount of water was extracted from the 8 M HCl solution, possibly due to the equilibrium concentration of approximately 2 M HCl in that organic phase, creating a more polar solution than pure octanol alone. Finally, Eu distribution ratios for extraction into ligand-free *1*-octanol are also shown in Table 1, where only the solutions containing measurable acid extracted detectable Eu. However the D_{Eu} was low regardless of the acid concentration and therefore significant extraction of non-complexed metal cations can be ruled out even for polar *1*-octanol. This result provides greater confidence that neutral complexes such as that depicted in Eq. 2 are the extracted metal species.

Table 1. Equilibrium organic-phase concentrations of water and acid, and the distribution ratio of europium (D_{Eu}) into *1*-octanol following contact with various aqueous solutions.

Solution Composition	Distribution Ratio (Eu)	H_2O (M)	$[H^+]$ (M)
Blank *1*-octanol	Not measured	0.02 ± 0.0004	< 0.01
0 M HCl-contacted	< 0.0002	2.40 ± 0.043	< 0.01
0.5 M HCl-contacted	0.14 ± 0.07	2.30 ± 0.035	0.029 ± 0.001
8 M HCl-contacted	0.13 ± 0.07	6.89 ± 0.055	2.15 ± 0.05
0.5 M NaCl-contacted	< 0.006	2.12 ± 0.042	< 0.01
5 M NaCl-contacted	< 0.004	1.31 ± 0.039	<0.01

1-octanol as a Diluent; Effect on L:M Stoichiometry and Distribution Ratios

To further understand metal complex speciation in *1*-octanol, slope analysis was used to determine the number of TBDGA molecules, *n*, in the neutral metal-ligand complex (eq. 2) $M(TBDGA)_nCl_3$. The value of n is determined as the slope of the plot of the log of the distribution ratio D_M versus the log of [TBDGA], Figure 6. From this analysis a slope of 2.13 ± 0.05 for Eu TBDGA/*1*-octanol extraction from HCl was determined, suggesting that the complex is a di-solvate mixed-ligand species, e.g., $Eu(TBDGA)_2Cl_3$. We previously reported a slightly higher value of 2.47 ± 0.08 for Eu extraction from HNO_3 using TBDGA/*1*-octanol. [20]

Cui et al., [17] reported stoichiometry for the extraction of Gd, Dy, Er, and Yb from HCl using TBDGA in several diluents. Their work indicated that mono-solvates were extracted into alkanes and CCl_4, di-solvates were extracted into $CHCl_3$, and that tri-solvates were extracted into toluene and *1*-octanol/octane mixtures. This was attributed to an effect of diluent polarity, with the lower stoichiometry associated with the non-polar diluents. (However, it must be noted that toluene is only of moderate polarity, in contrast to that conclusion.) This is in contrast to the di-solvate value reported in our work here for very polar *1*-octane as a diluent. As discussed below, most authors have reported higher L:M stoichiometry for polar diluents, which is consistent with our Eu result for *1*-octanol. [23, 24]

For example, based upon their similar ionic radii (1.01 Å for Am^{3+} vs. 0.950 Å for Eu^{3+}, coordination number = 6), [24] it might be expected that Am extraction by DGAs would be similar to Eu. A comprehensive study of Am extraction from HNO_3 by Sasaki et al., [29] using several DGAs over a wide range of alkane chain lengths concluded that a higher number of ligand molecules were required to solvate the extracted complex for extraction into non-polar diluents. This is the expected result, since additional solvation should enhance solubility of the metal complex in a non-polar solvent.

There are further examples. The most thoroughly studied DGA system is that of tetraoctyldiglycolamide (TODGA), in non-polar, long-chain alkane diluents. Wilden et al., [29] reported almost identical stiochiometry of 2.68 and 2.73 for the TODGA extraction of Eu and Am into the non-polar, kerosene-like alkane mixture hydrogenated tetrapropene (TPH) from nitric acid. Similarly, Ravi et al., [28] reported values for Am extraction using several unsymmetrical DGAs in dodecane from nitric acid with an average stiochiometry of 2.83 ± 0.04. The review by Ansari et al., [23] concluded that polar diluents such as *1*-octanol required only two TODGA molecules for solvation, while non-polar diluents such as dodecane required three to four TODGA molecules. Thus, most authors have reported lower stiochiometry for DGA metal complex extraction when using polar diluents. This is in agreement with our findings reported above for Eu extraction using TBDGA/*1*-octanol.

Finally, the effect of diluent polarity on the magnitude of the distribution ratio should be considered. The effect of diluent on extraction of REEs from HCl with TBDGA was studied by Cui et al.[17] Those authors reported that the extraction efficiency increased with polarity of the diluent, and when polar octanol was added to octane the extraction efficiency of the mixture increased. They also reported that moderately polar toluene was an exception and provided low distribution ratios under all conditions studied. Their distribution ratios for the extraction of Dy with TBDGA from HCl for various diluents are depicted in Figure 7, along with our value for *1*-octanol, where it is seen that *1*-octanol provided the highest distribution ratios and fit the trend reported by Cui et al. [17] very well. As mentioned previously, toluene, encircled in Figure 7, is an outlier to this trend. Sasaki et al., [25] also reported low distribution ratios for extraction into both toluene and benzene, and suggested that aromatic compounds might interact with the donor oxygens of the DGA, thus decreasing the activity of the ligand.

These results justify the use of *1*-octanol as a diluent in the study of REE extraction here, and strongly suggest that the neutral metal complex is the extracted species in this diluent.

Thermodynamics

The effect of temperature on the D_{Ln} is shown in the Van't Hoff plot in Figure 8. Linear regression analysis of the plot of natural log of the distribution ratio versus 1/T provides a slope that is the negative enthalpy (-ΔH) divided by the gas constant, R. The Van't Hoff equation is shown below as eq. 3. The resulting enthalpies for Y, Sm, Eu, Tb and Dy are shown in Table 2. For these REEs extraction from 8.0 M HCl with TBDGA/*1*-octanol is exothermic and the stability of the various $\mathrm{Ln(TBDGA)}_n\mathrm{Cl}_3$ complexes thus decrease as the temperature increases. Almost no extraction was observed at 65 °C for all REEs examined. The value obtained here of -42.9 ± 2.6 kJ $\mathrm{mol^{-1}}$ for Dy falls within the range of values reported by Cui et al., [17] using various diluents.

Table 2. Enthalpy of reaction of the extraction of rare earth elements with TBDGA.

Element	Enthalpy of Reaction (kJ $\mathrm{mol^{-1}}$)
Y	-42.9±2.6
Sm	-39.9±2.4
Eu	-39.3±2.4
Tb	-41.1±2.5
Dy	-42.9±2.6

Enthalpy values may vary in different diluents due to a number of factors, including viscosity, ease of solvation of the metal center, and ability to remove water coordinated to the metal center.

$$\frac{\Delta \ln(D)}{\Delta\frac{1}{T}} = \frac{-H_{tot}}{R} \qquad (3)$$

It can also be seen by comparing Figure 7 to Table 2 that the extraction efficiency is not strictly related to the enthalpy of reaction. This may indicate that entropy also plays a role in facilitating complex formation. Here, an increase in solvent polarity may enhance TBDGA complexation of the metal through solvation of the water molecules that must be removed from the metal prior to complex formation.

Conclusions

Heavy and intermediate lanthanides and yttrium are efficiently extracted from HCl using millimolar concentrations of TBDGA in *1*-octanol. The light lanthanides La and Ce are poorly extracted. For extraction to occur in HCl, at least 3.0 M HCl is required. However, H^+ itself negatively impacts the extraction, probably due to competition for the ligand by HCl extraction which decreases the amount of ligand available for metal ion complexation. When $[H^+]$ was decreased or removed by replacing HCl with NaCl to keep the Cl^- concentration constant, D_{Ln} increases. As the Cl^- concentration increased, D_{Ln} also increased due to the metal complex charge neutralization requirement. Although *1*-octanol is a polar diluent, and thus extracts significant amounts of water and acid, significant amounts of metal were not extracted in the absence of the ligand. The L:M stoichiometry for the extracted metal complex measured here is similar to the values reported by others for DGA extractants and thus it was concluded that the neutral complex is still the main extracted metal species in the polar diluent. Lower temperatures are preferred for extraction due to the reaction being exothermic and the $M(TBDGA)_nCl_3$ complexes therefore being heat labile. Thus, *1*-octanol is a an attractive diluent for REE extraction using TBDGA that provides high extraction efficiency for the intermediate and heavy lanthanides at low ligand concentration, is compatible with the chloride matrix used in industrial REE processing, and does not require extremely acidic conditions to be effective.

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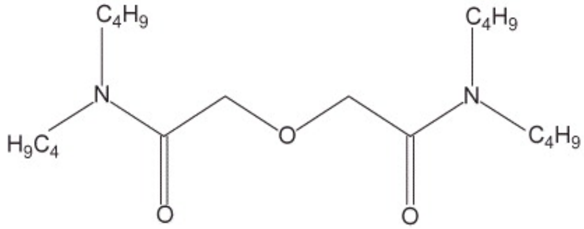

Figure 1. Structure of tetrabutyl diglycolamide (TBDGA)

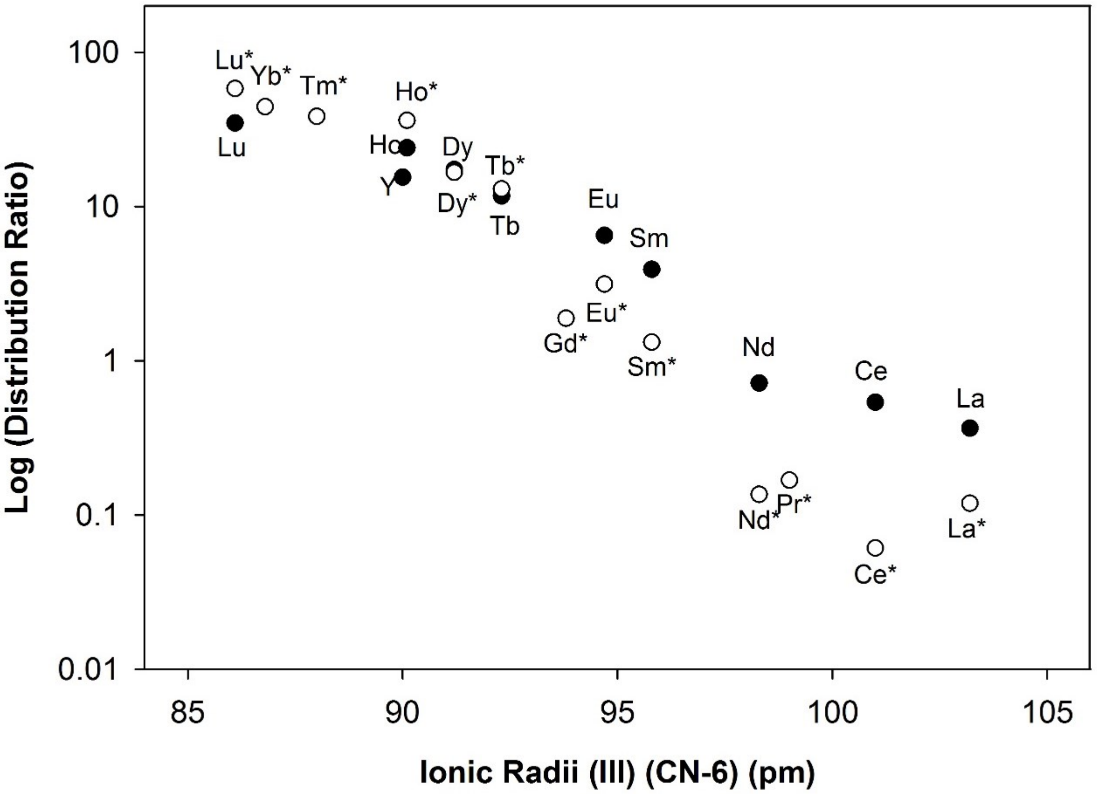

Figure 2. Ionic radii (coordination number=6) versus log of the distribution ratio for the extraction of REEs using 0.007 M TBDGA in *1*-octanol from 8.0 M HCl (black closed circles) and from 8 M HNO_3 [20] (open white circles, labeled with *).

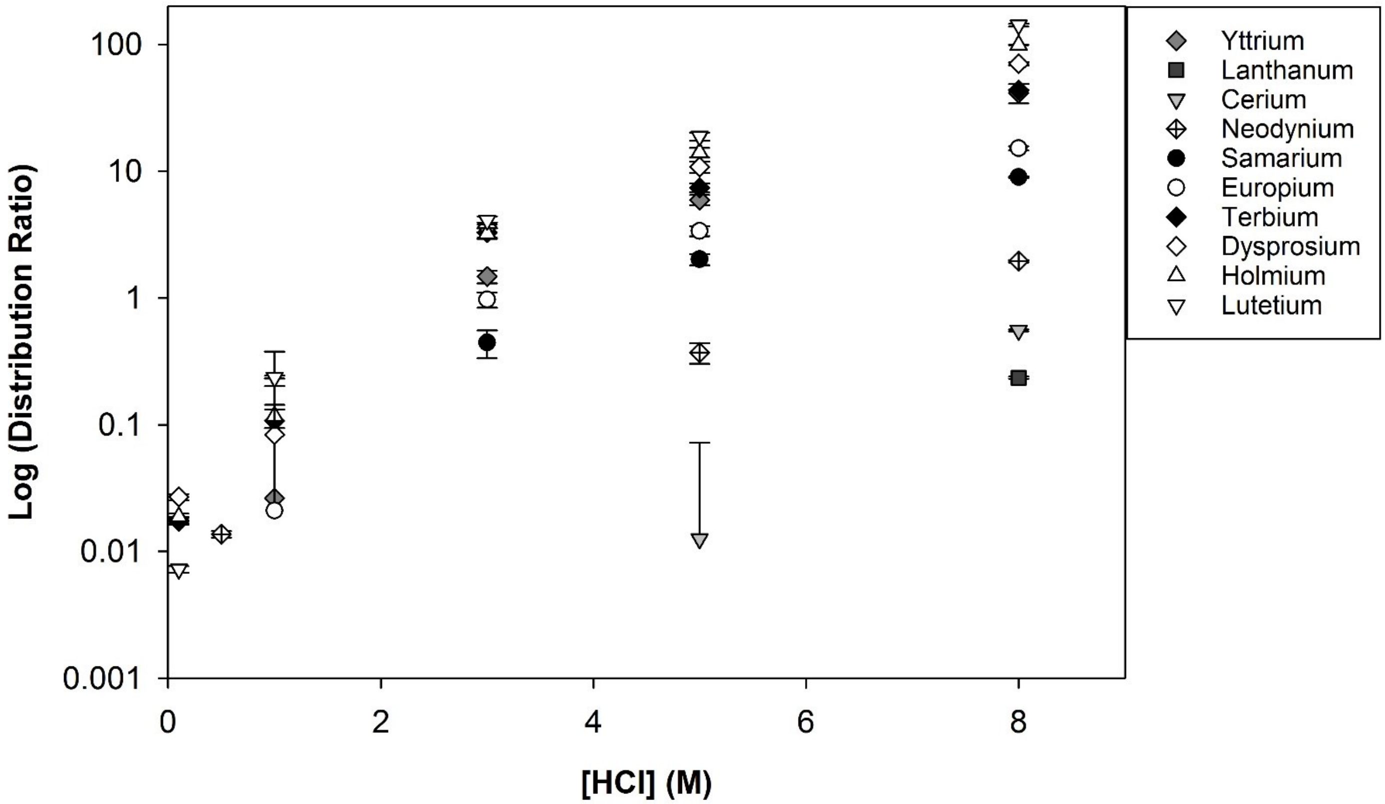

Figure 3. The solvent extraction profiles of Y, La, Ce, Nd, Sm, Eu, Tb, Dy, Ho, and Lu from hydrochloric acid media as a function of [HCl] using pre-equilibrated 0.010 M TBDGA in *1*-octanol. The aqueous phase consisted of ~100 ppb of each REE resulting in a total REE concentration of about 7 μM.

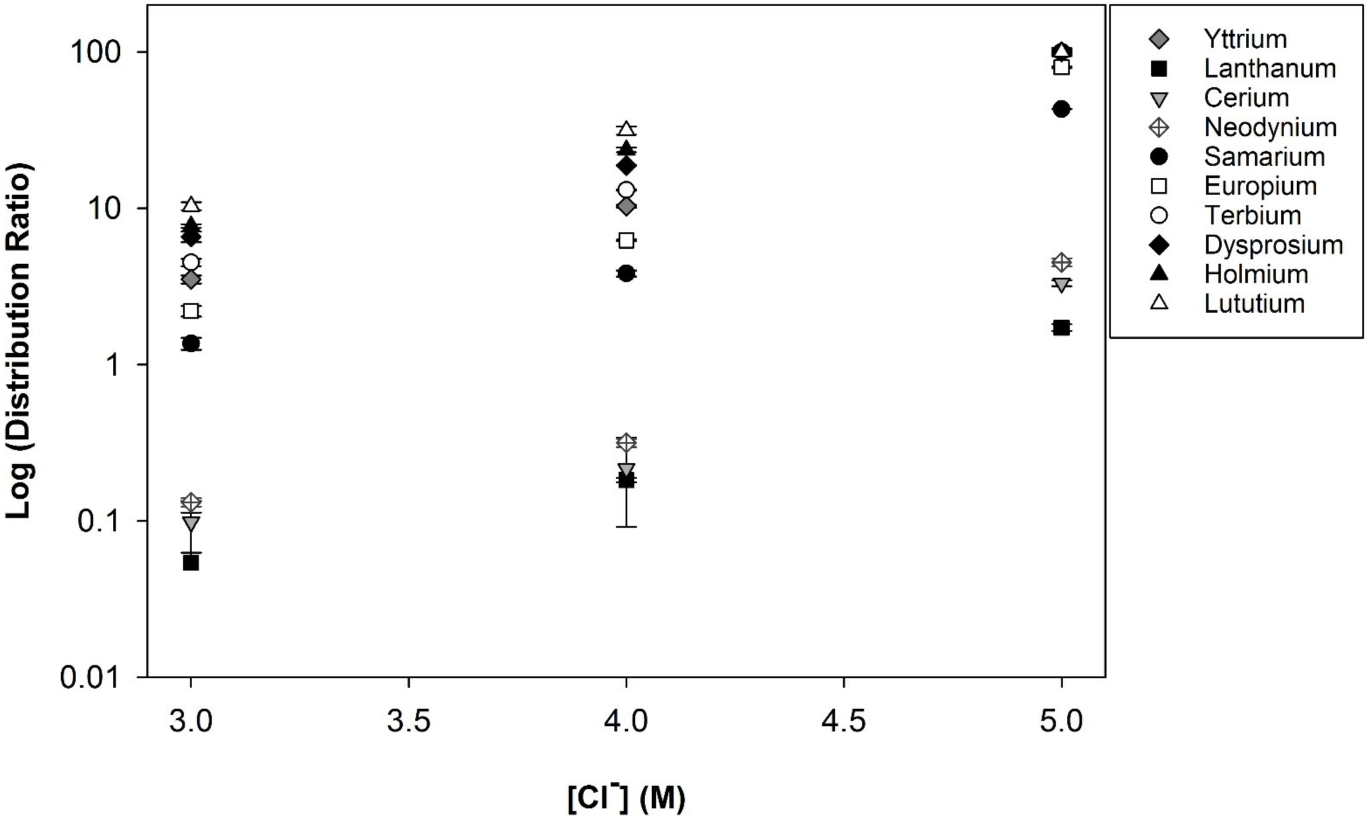

Figure 4. The solvent extraction profile of Y, La, Ce, Nd, Sm, Eu, Tb, Dy, Ho, and Lu from aqueous media with 1.0 M HCl and 2.0 M - 4.0 M added NaCl using pre-equilibrated 10 mM TBDGA in *1*-octanol. The aqueous phase consisted of ~100 ppb of each REE resulting in a total REE concentration of about 7 µM.

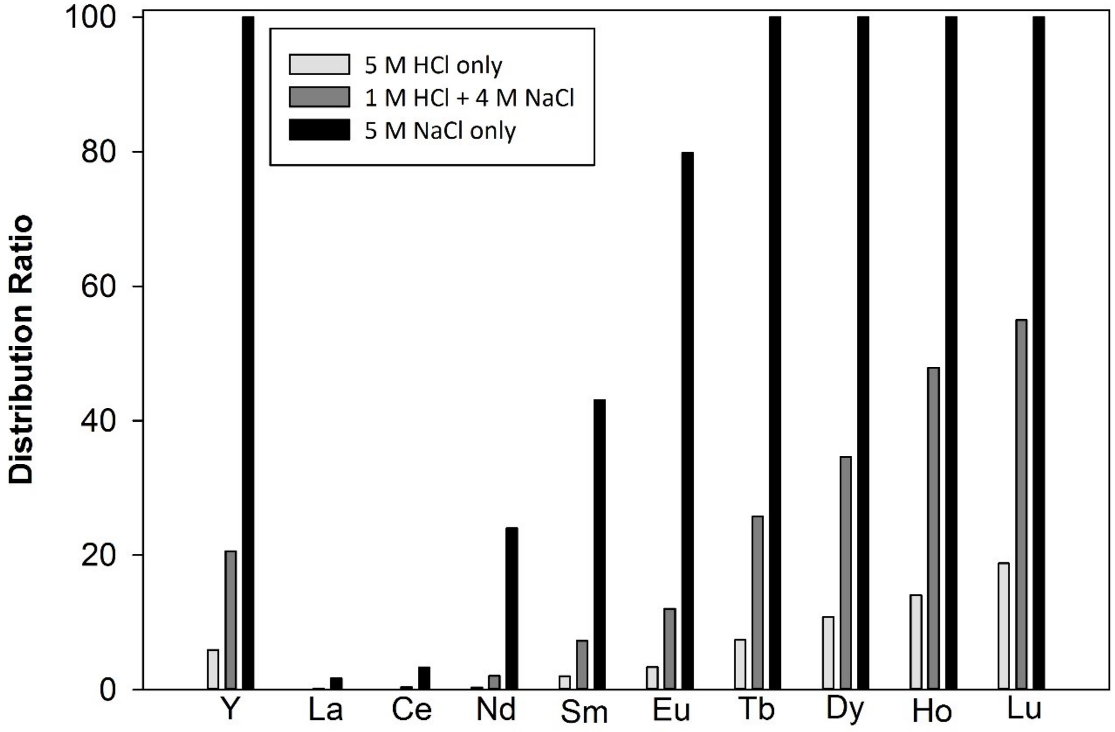

Figure 5. Distribution ratios for extraction of REEs from 5.0 M Cl^- solutions of varying acidity. Pre-equilibrated 10 mM TBDGA in *1*-octanol was contacted with an aqueous phase containing Y, La, Ce, Nd, Sm, Eu, Tb, Dy, Ho, and Lu with a total REE concentration of about 7 µM. The light grey bars shows 5.0 M HCl, the dark grey shows 1.0 M HCl + 4.0 M NaCl, and the black bars shows 5.0 M NaCl.

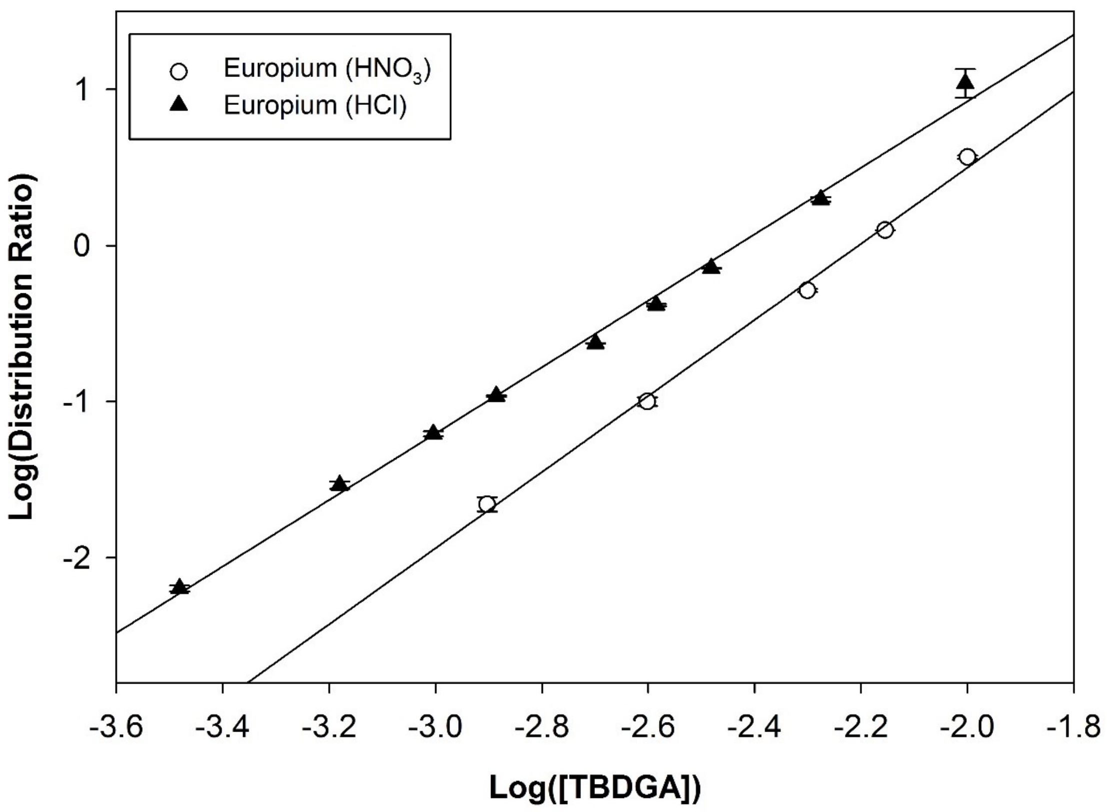

Figure 6. Log of the distribution ratio versus log [TBDGA], for the determination of the L:M stoichiometry for Eu extraction from HCl. The Eu concentration was 110 ppb in 8.0 M HCl with a contact time of 15 minutes (open circle). Similar data from reference [20] are shown for HNO_3 (black triangle).

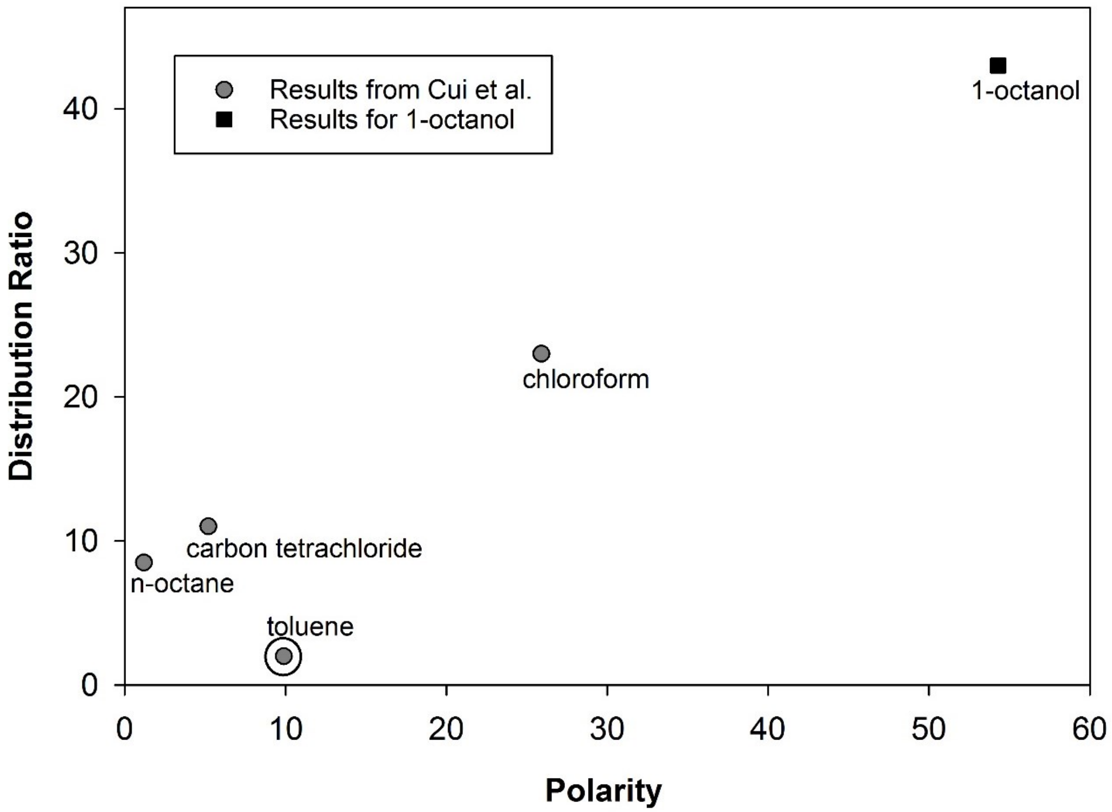

Figure 7. Distribution ratios for extraction of Dy from HCl using various TBDGA in various diluents as reported by Cui et al. ([Dy^{3+}]=4.00x10^{-3} M, [TBDGA]=0.20 M, [HCl]=5 M), [17] compared to the results for extraction into *1*-octanol of this study versus the polarity index of the diluent (water = 100).[30]

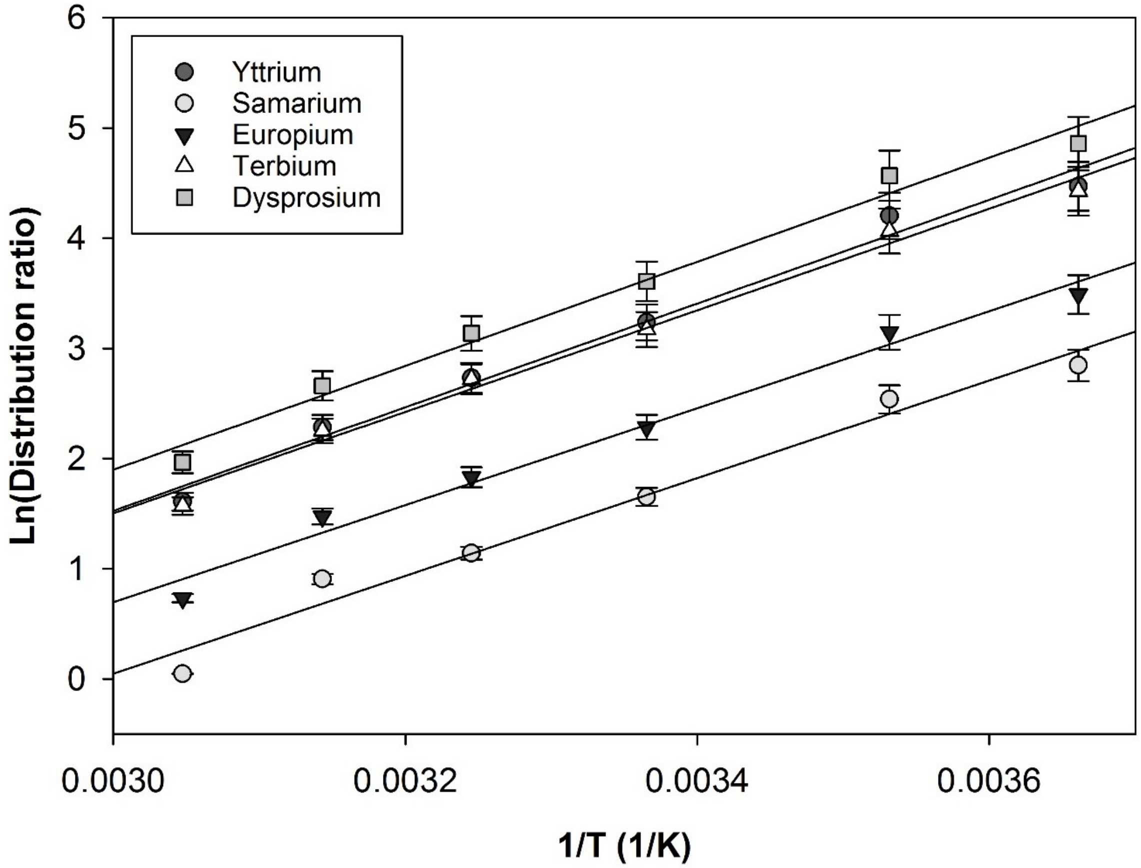

Figure 8. Effect of temperature on the extraction of several REEs from 8.0 M HCl with 0.010 M TBDGA in *1*-octanol.