EXTRACTION AND SEPARATION OF RARE EARTH ELEMENTS FROM CHLORIDE MEDIA USING TETRABUTYL DIGLYCOLAMIDE IN *1*-OCTANOL AND MODIFIED CARBON DIOXIDE

A Dissertation
Presented in Partial Fulfillment of the Requirements for the
Degree of Doctorate of Philosophy
with a
Major in Chemistry
in the
College of Graduate Studies
University of Idaho
by
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December 2017

Authorization to Submit Dissertation

This dissertation of Mary E. Case, submitted for the degree of Doctorate of Philosophy with a Major in Chemistry and titled "Extraction and Separation of Rare Earth Elements from Chloride Media Using Tetrabutyl Diglycolamide in *1*-Octanol and Modified Carbon Dioxide," has been reviewed in final form. Permission, as indicated by the signatures and dates below, is now granted to submit final copies to the College of Graduate Studies for approval.

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Abstract

Rare earth elements (REEs) are vital to energy-efficient modern technology and high-tech devices. Due to potential supply challenges for REEs, recycling these metals from post-consumer products, such as fluorescent lighting phosphors and neodymium iron boron magnets, has been proposed. Toward that end, liquid-liquid solvent extraction of various REEs was performed with tetrabutyl diglycolamide (TBDGA) in *1*-octanol and *1*-octanol modified carbon dioxide from chloride media. Hydrochloric acid, Cl^-, TBDGA concentrations were varied, and the thermodynamics of the extraction of REEs with TBDGA in *1*-octanol was explored. The extraction of REEs from phosphors and magnet materials using optimized conditions with TBDGA in *1*-octanol was performed. Stripping the metal from the metal-loaded TBDGA in *1*-octanol was investigated. HCl and an aqueous-soluble ligand, tetraethyl digylcolamide (TEDGA), were utilized for the back-extraction of the REEs into an aqueous phase. The concentrations of the HCl and the TEDGA were varied to determine if REEs could be selectively back-extracted and separated from one another.

Carbon dioxide is inert, has low cost, can be easily reused, and is readily available in a pure form. This means carbon dioxide is a better and “greener” diluent than traditional organic diluents for extraction. A system for extraction of REEs from chloride media with liquid carbon dioxide was optimized by varying mole percent *1*-octanol, pressure, temperature, metal concentration, TBDGA concentration, chloride concentration and H+ concentration. The effect of water concentration on the extraction with TBDGA into *1*-octanol modified $CO_{2(l)}$ was examined with UV-visible spectroscopy. Optimized $CO_{2(l)}$ extractions were performed on phosphor and magnet leachate solutions.

Acknowledgments

I would like to acknowledge my mentor at INL and committee member, Dr. Robert Fox, for his support throughout my academic graduate career. I am appreciative of his financial support, but he also was integral to every aspect of my degree. Without his help and advice I wouldn't be the researcher I have become.

I appreciate all of the staff I interacted with at INL. They were all kind and helpful. Especially thanks to Dr. Donna Baek and Dr. Bruce Mincher. Donna has been a friend and a mentor for many years. She has always been available for discussion and advice, and she always made an effort to help me become a better researcher. Bruce provided a lot of guidance throughout my academic career.

All of the University of Idaho Chemistry department staff and College of Graduate Studies deserve many thanks for all of their help with my degree. I especially would like to thank my major professor Dr. Chien Wai for seeing potential in me and supporting me throughout my undergraduate and graduate studies.

I would like to thank my other committee members, Dr. Bitterwolf and Dr. Rodriguez, for contributing their time and expertise to improving my work.

I would like to thank and acknowledge the Critical Material Institute, the Department of Energy, and Idaho National Laboratory for financially supporting my research. This research was supported by the Critical Materials Institute, an Energy Innovation Hub funded by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Advanced Manufacturing Office. Work was performed at the Idaho National Laboratory under DOE Idaho Operations Office Contract DE-AC07-05ID14517.

Dedication

To my parents for all of their support.

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%collection	collection efficiency
%E	percent extraction
<	less than
>	greater than
α	separation factor
ΔH	enthalpy of reaction
λ	wavelength
°C	degree Celsius
AA	acetylacetone
A^{n-}	counter ion
CEA	French Alternative Energies and Atomic Energy Commission
CRT	cathode ray tubes
CO_2	carbon dioxide
$CO_{2(l)}$	liquid carbon dioxide
Cyanex 301	bis(2,4,4-trimethylpentyl)dithiophosphinic acid
D	distribution ratio
DGA	diglycolamide
DMDOHEMA	2-(2-hexyloxy-ethyl)-N,N-dimethyldimethyl-N,N-dioctyl-malonamide
EXAFS	X-ray absorption fine structure
EXam	Extraction of Americium
FDDC	bis(trifluoroethyl)dithiocarbamate
FOD	2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedione
g	gram
HCl	hydrochloric acid
HDEHP	di(2-ethylhexyl) phosphoric acid
HEHEHP	2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester
HFA	hexafluoroacetylacetone

HNO_3	nitric acid
INL	Idaho National Laboratory
L	ligand
LED	light emitting diode
log	logarithm
M_o	metal in the organic phase
M_a	metal in the aqueous phase
mL	milliliter
mol	mole
mol%	mole percent
NIB	neodymium iron boron
REE	rare earth element
REO	rare earth oxide
P204	di(2-ethylhexyl) phosphoric acid
P507	2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester
P_c	critical pressure
psi	pound per square inch
PUREX	Plutonium Uranium Reduction Extraction
Sc-CO_2	supercritical carbon dioxide
SCF	supercritical fluid
TAA	trifluoroacetylacetone
T_c	critical temperature
TBDGA	N,N,N’N’-tetrabutyl diglycolamide
TBP	Tri-*n*-butyl phosphate
TEDGA	N,N,N’,N’-tetraethyl diglycolamide
TMDGA	N,N,N’,N’-tetramethyl diglycolamide
TODGA	N,N,N’N’-tetraoctyl digylcolamide
TPDGA	N,N,N’N’-tetrapropyl digylcolamide

TTA	thenoyltrifluoroacetone
USA	United States of America
UK	United Kingdom
V_a	volume of the aqueous phase
V_o	volume of the organic phase
XRD	X-ray diffraction

Chapter 1

Introduction

1.1. Objective

The focus of this work is analyzing the fundamental extraction behavior of rare earth elements (REEs) from chloride media with N’,N’,N,N-tetrabutyl digylcolamide (TBDGA) in conventional (*1*-octanol) and unconventional carbon dioxide (CO_2) solvents for the ultimate purpose of recovering and separating rare earth elements from end-of-life products such as magnets and fluorescent lighting phosphors. Examination of extraction behavior is followed by investigation of the stripping behavior of the metal from metal-loaded TBDGA/*1*-octanol into an aqueous chloride solution containing N’,N’,N,N-tetraethyl diglycolamide (TEDGA). End-of-life products contain a variety of valuable metallic materials in addition to REEs. Being able to remove and recover the REEs and other valuable metals using a “green” and effective solvent extraction method is important for the recycling/recovery of valuable materials.

This section begins with a discussion of the basics of rare earth containing phosphors and magnets, the basics of solvent extraction with traditional diluents, and extraction with the non-conventional diluent CO_2. The final section of this work contains a summary of what was learned.

1.2. Rare Earth Elements

The rare earth elements (REEs) are comprised of the 15 lanthanide elements (lanthanum-lutetium), plus yttrium and scandium.[1] These elements are commonly used in many modern technological applications such as phosphors, catalyst, and magnets. A summary of the applications for all of the REEs is found in Table 1-1. With the exception of Pm, the remaining 16 REEs are naturally occurring.[2-4] All isotopes of promethium are radioactive, and are formed from the decay of other radioactive elements.[5] The REEs are often divided into the following groups: light REEs, heavy REEs, and occasionally authors include reference to intermediate REEs. The light REEs are from lanthanum through gadolinium, and the heavy REEs are yttrium, and terbium through lutetium.[6] While there is disagreement within the literature as to the divide between light REEs and heavy REEs, dividing the series based on electron configuration is the most consistently used convention. The light REEs have 0-7 unpaired electrons (f^0-f^7), and the heavy lanthanides have 8-14 electrons (f^8-f^{14}) with some paired.[6] Yttrium is included in the heavy REEs as it often has traits similar to the heavy lanthanides. [7]

Although the name “rare” earth elements would indicate these metals are uncommon, the 16 naturally occurring REEs are actually quite abundant in the earth’s crust. The lighter REEs (La, Ce, Nd) are more abundant than common metals such as lead, copper, or tin.[8] The two least abundant REEs, Tm and Lu, are 200x more abundant than gold.[8] While REEs are abundant, they are not heavily concentrated in ore deposits; thus, negating the ability to efficiently mine REE ores. Within REE deposits lanthanum, cerium, praseodymium, and neodymium are the most concentrated and compose 80 – 99% of the total REEs. More valuable REEs such as yttrium, europium, and gadolinium through lutetium are less abundant or concentrated.[8]

Deposits containing only a single REE are uncommon and most ore bodies contain many REEs. Due to similar chemical and physical properties the REEs are difficult to separate from one another and require extensive processing to obtain pure rare earth oxides (REOs). One of the properties of REEs is called the "lanthanide contraction" which is evidenced by a very gradual decrease in ionic radii as the atomic number increases. Yttrium has an ionic radius similar to that of dysprosium.[9] Between two adjacent lanthanides the average difference in radius is 0.0152 Å.[2] Due to similarities in size and chemical properties, adjacent lanthanides are very difficult to separate.[10] The REEs are generally in the +3 oxidation state; other oxidation states are not easily obtained.[11-12] Therefore, a separation based on oxidation state behavior is difficult to achieve.

Table 1-1. Applications of REEs.[2-4]

Element	Application
Scandium	metal alloys, lighting, nuclear applications
Yttrium	metal alloys, phosphors, ceramics, simulated diamonds, lasers, temperature sensors
Lanthanum	fuel cracking catalyst, automotive catalyst, optical lenses, phosphors, lasers, X-ray film, super conductors, carbon arc lamps,
Cerium	phosphors, glass polishing powder, solar panels, catalyst, alloys, pigments, permanent magnets, lighter flints
Praseodymium	permanent magnets, CAT scan machines, fiber optics, alloys
Neodymium	phosphors, permanent magnets, hybrid engines, catalyst, glass colorant
Promethium	beta radiation source, portable X-ray sources
Samarium	permanent magnets, defense applications, medical devices, cancer pharmaceuticals, reactor control rods, electric motors
Europium	phosphors
Gadolinium	nuclear reactors, magnets, high strength alloys, phosphors
Terbium	magnets, phosphors, electric motors
Dysprosium	magnets, alloys, hybrid cars, nuclear reactors
Holmium	magnets, nuclear reactors, medical devices, fiber optics
Erbium	nuclear reactors, optical products, lasers
Thulium	lasers, X-ray sources, ceramics, fiber-optics
Ytterbium	alloys, health care
Lutetium	catalysts, X-ray phosphors

1.3. Phosphors

Phosphors are compounds that are capable of luminescence,[13] and are usually comprised of an inorganic matrix with impurities doped therein.[14] Rare earth elements have been used in many phosphors.[14] REE-containing phosphors are commonly used in fluorescent lighting, lasers, fiber optics, medical imaging, cathode ray tubes (CRTs), light emitting diodes (LEDs) and plasma displays.[3-4]

Fluorescent lighting was introduced to the consumer market in 1945,[15] but only recently with the introduction of the Compact Fluorescent Lamp (CFL) in 1985 has fluorescent lighting become the predominant form of lighting used in homes and commercial buildings. Since their commercial introduction in the late 1800's incandescent bulbs have dominated the US lighting market. Beginning around 2005 countries around the world have begun to phase-out incandescent bulbs due to the availability of more energy efficient lighting options.[16] In 2010 incandescent lighting was the most common lighting used in homes with ~85% of households using incandescent lighting as the primary lighting source.[17] In 2015 ~48% of homes were using incandescent bulbs and ~49% were using fluorescent lighting as their primary lighting source[17]. LEDs are rapidly advancing in the lighting market and by 2020 will eclipse both incandescent and fluorescent lamp usage. Fluorescent lamps use 25-35% of the energy used by incandescent lamps for the same lumens, and they last ~10x longer.[18] Even with the replacement of fluorescent lighting with LEDs, fluorescent lighting is still the primary light source in the USA as of 2017.[17]

Fluorescent bulbs use mixtures of red, blue, and green phosphors to generate the color of light that is desired. The specific phosphor compounds and the ratio of phosphors used will vary depending on the manufacturer and color of light wanted (i.e., soft white, daylight, etc.). While phosphors in fluorescent bulbs will vary between manufacturers, the more commonly used phosphors are listed in Table 1-2. The REEs commonly present in phosphors are Y, Eu, Ce, Tb, and La[19-20]. Yttrium, Ce, and Eu compose the majority of the REE content in fluorescent lamps.[21]

Table 1-2. Most common phosphors used in fluorescent lighting lamps.[19-20]

Phosphor Type	Common Compounds
Red phosphor	Y_2O_3:Eu^{3+}
Green Phosphor	$CeMgAl_{10}O_{17}$:Tb^{3+} $La(PO_4)$:Ce^{3+},Tb^{3+}; $(Ce,Tb)MgAl_{11}O_{19}$; $(Ce,Gd,Tb)MgB_5O_{10}$
Blue Phosphor	$BaMgAl_{10}O_{17}$:Eu^{2+} $(Sr, Ca,Ba)_5(PO_4)_3Cl$:Eu^{2+}

1.4. Magnets

Rare earth magnets are a critical component to clean energy technologies (e.g. wind turbines, electric vehicle motors) and high-tech devices (e.g. cell phones, computers, magnetic resonance imaging). There are two primary REE magnets types: samarium cobalt magnets and neodymium iron boron (NIB) magnets, $Nd_2Fe_{14}B$. Neodymium iron boron magnets are used more than samarium cobalt magnets because the NIB magnets are less expensive and are capable of achieving higher magnetic field strength. The samarium cobalt magnets have a higher curie temperature and are used in applications requiring high temperatures. NIB magnets are brittle and susceptible to corrosion and are often coated in copper, nickel, gold, zinc, tin, or epoxy to lend structural stability and to protect the magnet from oxidation and corrosion.

In 2010, use of REE in magnets comprised the single largest usage of the REEs (21% globally, 3.3% US).[22] It has been predicted that the use of REEs in magnets would continue to increase.[22]

1.5. Solvent Extraction Hydrometallurgy Basics

Solvent extraction is the partitioning of specific solutes between two immiscible phases. These two phases are typically an aqueous and an organic phase.[23] A basic schematic of a solvent extraction process is shown in Figure 1-1. The metal complexing ligand, L, is soluble in the organic phase (yellow top phase) and the REE metals are dissolved in the aqueous phase (blue bottom phase). The two phases are thoroughly mixed, which is shown as the green solution. This allows the ligands to interact with the REE ions and form complexes. If the metal-ligand complex is soluble in the organic phase it will partition from the aqueous phase to the organic phase. This allows some of the REEs to extract into the organic phase.

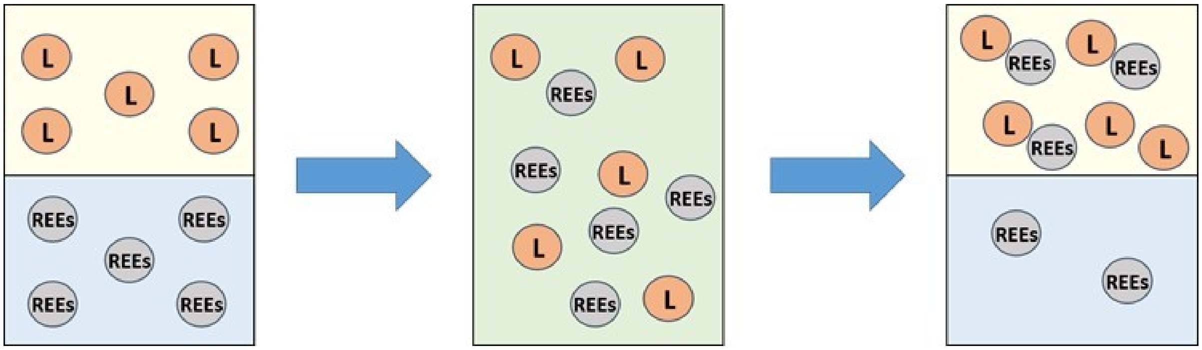

Figure 1-1. Basic solvent extraction schematic. The REEs are initially soluble in the aqueous phase (blue), and the complexing ligand *(l)* is soluble in the organic phase (yellow). After mixing (green) a portion of the REEs complex with the ligand and are now soluble in the organic phase. Some REEs may remain in the aqueous phase.

In solvent extraction processes, the efficiency of the extraction is determined by the distribution ratio (D), Eq. 1-1. The distribution ratio is defined as the concentration of the metal in the organic phase ($[M_o]$) divided by the concentration of the metal in the aqueous phase ($[M_a]$). The distribution ratio for a specific metal is dependent on the solvent extraction system which is composed of the ligand, organic diluent, aqueous phase, temperature, concentrations, and other factors.[24]

$$D = \frac{[M_o]}{[M_a]} \qquad \text{Eq. 1-1}$$

If the percent extraction (%E) is known, Eq. *1*-2 can be used to determine the D where V_a is the volume of the aqueous phase and V_o is the volume of the organic phase. When %E is 100 % the D is infinite, and if %E is 0 % the D is zero.

$$D = \frac{\frac{(V_a)}{(V_o)}\%E}{100-\%E} \qquad \text{Eq. 1-2}$$

The separation factor (α) between two elements (D_a and D_b) is the ratio of the distribution ratios. The greater the separation factor the fewer extraction steps required to separate the two elements from each other. This is shown in Eq. *1*-3.

$$\alpha = \frac{D_a}{D_b} \qquad \text{Eq. 1-3}$$

To recover the metals from the organic phase a stripping step is performed. This is done by contacting the metal-loaded organic with an aqueous stripping agent. The typical stripping agent is comprised of a small amount of acid in water (e.g., 0.01 – 0.1 M HNO_3 in water). However, the specific stripping agent used is determined by the ligands and conditions used in the solvent extraction process. Dilute, acidic aqueous strippers are not the only available stripping agents. Aqueous-soluble compounds can also be used for the stripping phase.[25] Not all metals can easily be stripped from the ligand in the organic phase, and this is the downside of some solvent extraction systems.

The PUREX process is the most well-known for traditional liquid-liquid extraction of f-orbital elements.[26] Spent nuclear fuel is first dissolved into nitric acid. That aqueous solution is contacted with 30% tri-*n*-butyl phosphate (TBP) in kerosene. The structure of TBP is shown in Figure 1-1. Uranium (UO_2^{2+}) and plutonium (Pu^{4+}) are extracted by the TBP into the organic phase. Following the extraction, plutonium is reduced to the +3 state with ferrous sulfamate. The change in oxidation state causes the plutonium to transfer into the aqueous phase, and the uranium remains in the organic phase. The uranium is then stripped from the TBP with dilute HNO_3 in water.[27-28] Expansion or improvements of the PUREX process have extended applicability of that solvent extraction process to include most of the f-elements, including REEs.

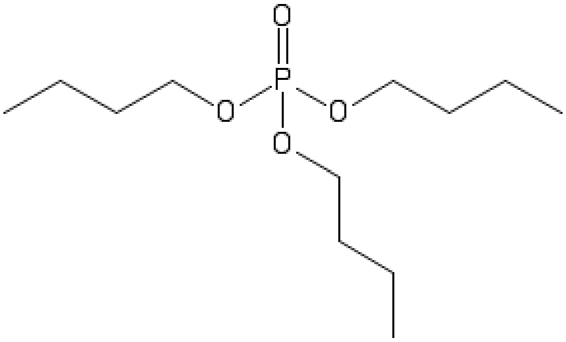

Figure 1-2. Structure of tri-*n*-butyl phosphate (TBP).

1.6. Diglycolamides

Diglycolamides (DGAs) were initially designed for use as a ligand in nuclear fuel reprocessing.[29] DGAs are novel and promising extractants that have the potential to replace phosphorus-based extractants that are often used in f-block element extractions.[25, 30] DGAs also have been shown to have superior extraction abilities when compared to other amide-based f-element extracting ligands.[29] The synthesis of DGAs is very easy compared to most phosphorus-based extractants.[31] The degradation products from DGAs are benign and can be easily washed from the organic phase.[32] DGAs are recyclable and completely incinerable which would reduce waste from an extraction process.

Figure 1-3 shows the basic structure of DGAs where the "R" groups can vary in chain length and degree of branching. The most commonly studied DGA is tetraoctyl diglycolamide (TODGA). The structure of TODGA is shown in Figure 1-5. However, there are a variety of other DGAs that have potential for f-element extraction and separation. Some of the more common DGAs under study, and their solubility behavior in water and *n*-dodecane are shown in Table *1*-3.[29] In general, as the chain length of the R groups on the DGA increases, the D for REEs decreases.[33] This will be expanded upon in Chapter 2.

Table 1-3. Commonly researched diglycolamides and their solubility in water and *n*-dodecane.[25, 29]

Diglycolamide	Solubility in Water (mM/L)	Solubility in *n*-dodecane
N,N,N',N'-Tetramethyl diglycolamide	>1000	Very poor
N,N,N',N'-Tetraethyl diglycolamide	>1000	Very poor
N,N,N',N'-Tetrapropyl diglycolamide	57.0	Very poor
N,N,N',N'-Tetrabutyl digylcolamide	2.3	Poor
N,N,N',N'-Tetrahexyl diglycolamide	0.11	Soluble
N,N,N',N'-Tetraoctyl diglycolamide	0.042	Freely soluble
N,N,N',N'-Tetradodecyl diglycolamide	0.040	Freely soluble

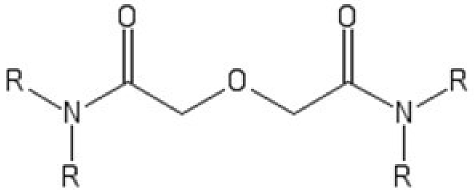

Figure 1-3. Basic structure of diglycolamides.

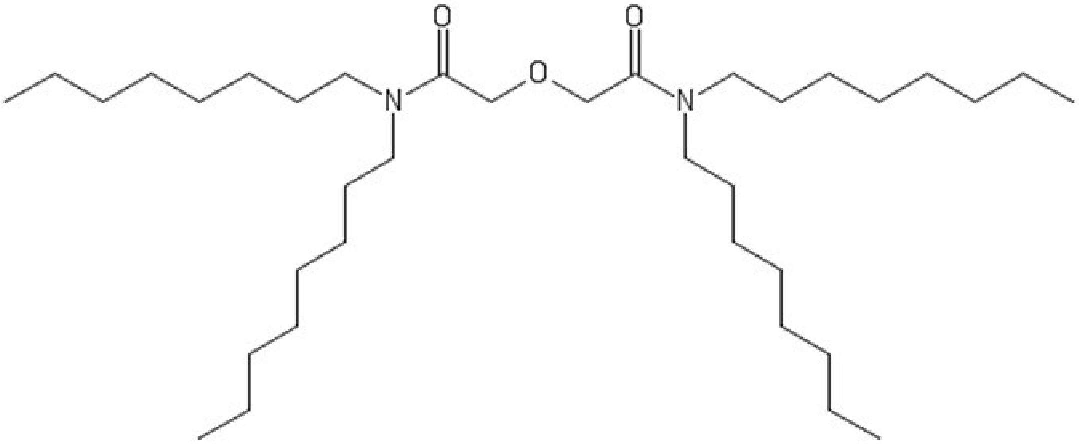

Figure 1-4. Structure of tetraoctyl diglycolamide.

The basic complexation reaction between TODGA and a metal is shown in equations Eq. 1-4, Eq. 1-5, Eq. 1-6.[34] It is thought this is a similar complexation reaction for most of the DGAs with metals.

$$M^{n+} + L \leftrightarrow M(L)^{n+} \quad \text{Eq. 1-4}$$

$$M(L)^{n+} + L \leftrightarrow M(L)_2^{n+} \quad \text{Eq. 1-5}$$

$$M(L)_2^{n+} + L \leftrightarrow M(L)_3^{n+} \quad \text{Eq. 1-6}$$

DGAs have been extensively studied in nitrate medium due to their potential use in the fuel cycle.[29] Chloride media has not been studied to the same extent.[35-38] Chloride studies are important for utilizing DGAs as REE extractants outside of the fuel cycle. The anion in the aqueous phase is what will be the counter ion to form a neutral extractable species. This complex is shown in Eq. 1-7. Where A^{n-} represents any counter ion and "x" is the stoichiometry needed to form a neutral complex. Common counter ions are NO_3^-, Cl^-, PO_3^{2-}, SO_4^{2-}, etc.

$$M(L)_3^{n+} + xA^{n-} \leftrightarrow ML_3A_x \qquad \text{Eq. 1-7}$$

If the ligand forms a strongly bonded complex with the metal, stripping with only dilute acidic aqueous solution can be difficult. The shorter chain DGAs (i.e., <propyl) are soluble in water[29, 39] and have potential use as masking agents and as a stripping agent. Often, carboxylic acids and aminocarboxylic acids are used as masking agents and strippents.[40] The benefit of short chain DGAs over other stripping agents is given below:[25]

- Ability to strip a variety of metals
- Ability to complex metals over a wide acidity range
- DGAs are neutral ligands that do not neutralize the charge of a cationic metal

1.7. Non-Conventional Solvent: Carbon Dioxide

Traditional solvent extraction is the primary process for the extraction and purification of rare earths. However, there are other non-traditional methods that can be utilized to improve an extraction process. Carbon dioxide can be used as the diluent for extraction of organic and inorganic complexes. This helps to eliminate or reduce the waste from traditional organic solvents such as kerosene, *n*-octanol, dichloromethane, dodecane, etc. CO_2 has many other benefits over traditional organic solvents: it is non-flammable, low cost, recyclable, and is high abundance.

Carbon dioxide as a solvent in an extraction process is most commonly used in its supercritical fluid phase. When a substance is at a pressure and temperature greater than its critical point's pressure and temperature the substance is in the supercritical phase, and it is considered a supercritical fluid (SCF). For CO_2 the critical pressure (P_c) is 1071 psi and the critical temperature (T_c) is 31.1 °C. The phase diagram for CO_2 and the pressure and temperature changes that occur during a sc-CO_2 extraction process is depicted in Figure 1-5. The phase diagram shows specific pressures and temperatures at which CO_2 is a solid, liquid, gas, or SCF. SCFs have properties of liquids and gases making them unique. SCFs have liquid-like densities, gas-like diffusivity, and low viscosity. This allows it to dissolve solutes like a liquid, and for easier mass transfer between the solute and the SCF.

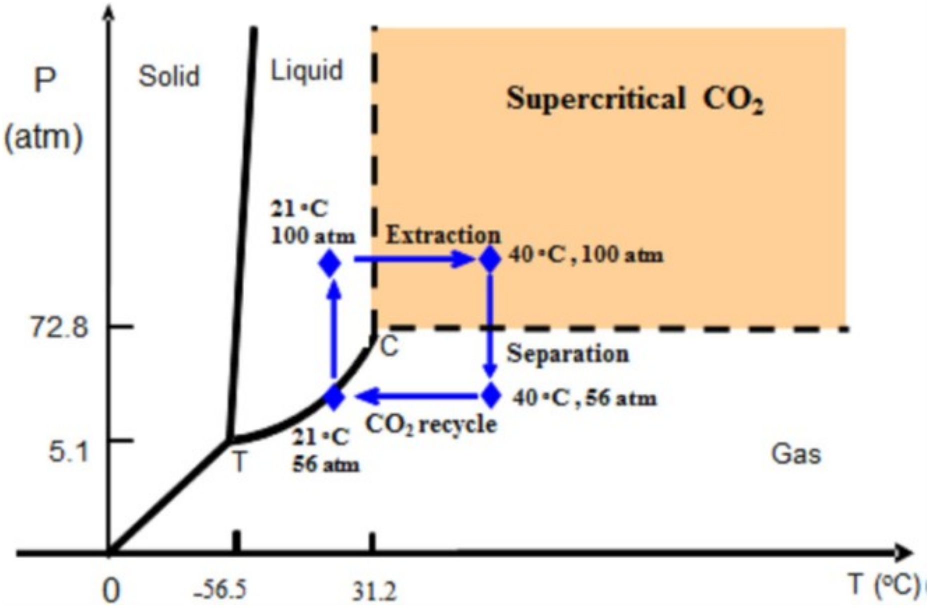

Figure 1-5. The phase diagram of carbon dioxide showing the pressure and temperatures at which carbon dioxide is a solid, liquid, gas, or supercritical fluid. This diagram shows how an extraction system with CO_2 would work with recycling the CO_2.

While sc-CO_2 is the most common phase of CO_2 used for extractions, liquid CO_2 ($CO_{2(l)}$) can also be used. Liquid CO_2 has been used as a diluent for organic compound extractions,[41] but no work has been published utilizing it for metal-complex extractions. Using $CO_{2(l)}$ instead of sc-CO_2 would require less energy by eliminating the heating of the system. The primary downside to using $CO_{2(l)}$ instead of sc-CO_2 is the loss of the diffusivity properties associated with sc-CO_2.[42] Diffusivity is important if extracting from solid samples, but with liquid samples diffusivity is not as vital.

Metals are insoluble in CO_2.[43-44] This is due to weak solute-solvent interaction. Carbon dioxide is a linear, non-polar molecule with no dipole moment. Therefore, it is unable to solubilize a charged metal ion. A ligand must be used to form a CO_2-soluble complex.[45] For the metal-ligand complexes to be soluble in CO_2 three conditions must be met: the species must be charge neutral, the coordination needs of the metal must be satisfied, and the species must be non-polar (lipophilic). However, other factors can influence the efficiency of metal extraction. In addition, the parameters that will impact extraction when performing CO_2 extraction of metal are as follows:

(1) Solubility of the ligand in CO_2
(2) Solubility of the metal-ligand complex in CO_2
(3) The water and acid concentrations in the system
(4) The temperature and pressure of the system
(5) The matrix containing the metal being extracted (i.e., matrix effects)

The polarity of the carbon dioxide as a solvent can be altered with a modifier to allow for polar species to become soluble in the augmented CO_2. Acetone and methanol are frequently utilized, but any compound that is soluble in CO_2 can be used as a solvent modifier. Traditional modifiers such as acetone, ethanol, and methanol cannot be used with aqueous samples because they have a low partition-coefficient between the aqueous phase and the CO_2 phase.[46-47] This causes the metal-ligand complex to remain in the aqueous phase and not transport into the CO_2 phase.

There are two modes for an extraction: a static extraction or a dynamic extraction. A static extraction is performed by mixing the sample, ligands, any modifiers, and the CO_2 and allowing the components to mix for a set period of time in the same container with no solvent flow. A dynamic extraction involves continually flowing CO_2 over the sample while ligands, modifiers, etc. are also introduced and flow through the container. The ligand and modifiers can be mixed with the sample before contact with CO_2 or mixed and introduced with the CO_2.

1.8. Dissertation Overview

This study was initiated to understand some of the fundamental behavior related to the extraction of various REEs with TBDGA with a conventional organic diluent, *1*-octanol, and with a non-traditional diluent, CO_2. This investigation is divided into three sections with the goal being to examine the use of TBDGA as a ligand for REE extraction from chloride media. The following chapter will focus on the literature review of REE extraction from traditional solvents, REE extraction from CO_2, and previous work with DGAs. Chapter 3 examines extraction of REEs from chloride media with TBDGA in *1*-octanol. Chapter 4 examines the extraction of REEs from chloride media with TBDGA in CO_2. Chapter 5 explores the possibility of stripping REEs from loaded TBDGA in *1*-octanol with acid and TEDGA. The final chapter (Chapter 6) summarizes results obtained during this investigation and how those results relate to each other and to results found in the literature.

In Chapter 3, liquid-liquid solvent extraction of various rare earth elements with TBDGA in *1*-octanol from hydrochloric acid media is reported. The effects of $[H^+]$, $[Cl^-]$, and temperature on the extraction of REEs from chloride media were examined. A comparison of extraction from *1*-octanol to other diluents is provided. The extraction of rare earths from phosphor leachate and magnet dissolutions in HCl and NaCl solutions with TBDGA in *1*-octanol were studied.

In Chapter 4, conditions needed to optimize the extraction of europium from chloride media solutions with CO_2 were studied. Temperature, pressure, [Eu], [TBDGA], [HCl], $[H^+]$ were varied. The extraction of europium from 8 M HCl with TBDGA in *1*-octanol modified CO_2 was studied. The extraction of REEs with TBDGA in *1*-octanol modified $CO_{2(l)}$ from magnet and phosphor solutions at the optimized conditions was observed.

In Chapter 5, the stripping of the REE-loaded organic was studied with various [HCl] ranging from 1 M to 8 M. The aqueous ligand TEDGA in various [HCl] was used as a stripping agent. The [TEDGA]/[TBDGA] was varied to be [TEDGA]<[TBDGA], [TEDGA]=[TBDGA], and [TEDGA]>[TBDGA]. A basic REE stripping and separation process is shown.

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Chapter 2

Literature Review

2.1. Introduction

The extraction and separation of REEs from materials is commonly achieved with liquid-liquid solvent extraction. The disadvantages of a traditional solvent extraction process for REE processing is the use of high volumes of solvents and organic wastes. A “greener” REE processing method is desired, and is very relevant in the literature. This chapter will review the relevant literature to the topics researched in this dissertation: traditional rare earth solvents, diglycolamides, supercritical fluids and modifiers, CO_2 metal extraction, and stripping.

2.2. Traditional Rare Earth Solvent Extraction

The extraction of REEs with tributyl phosphate (TBP) was studied by Peppard *et al.* in the 1950s.[1-2] Extraction from chloride and nitrate media were studied. From both media the D_{REE} for lanthanides increased as atomic number increased. The reaction for the formation of neutral extractable species is given in equation Eq. 2-1.[1-2]

$$REE^{3+} + 3NO_3^- + 3TBP \leftrightarrow REE(NO_3)_3(TBP)_3 \qquad \text{Eq. 2-1}$$

With TBP and nitric acid it was possible to separate REEs lighter than Sm (III), but heavier REEs could not be separated.[1-2] In the 1960s in the UK, Thorium Limited, used TBP to separate light rare earths from nitrate media. That process was employed using a batch process instead of a continuous mode. The technique was found to be expensive and inefficient for a scaled-up operation.[3-5] Other solvent extraction ligands need to be utilized for an efficient, cost-effective separation process.

A variety of complexing ligands have been utilized commercially for REE solvent extraction: carboxylic acids, phosphorous acids, β-diketones, phosphorous esters, and amines. [6-7] The primary ligands used for commercial REE solvent extraction are di(2-ethylhexyl) phosphoric acid (aka HDEHP, or P204), and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (aka HEHEHP, or P507). [1-2] The structures of HDEHP and HEHEHP are given in Figure 2-1.

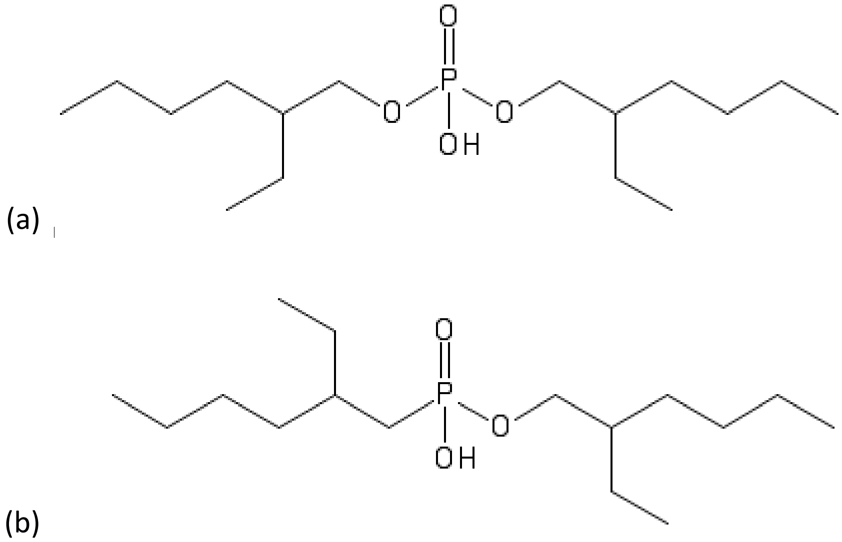

Figure 2-1. (a) The structure of HDEHP. (b) The structure of HEHEHP.

Extraction of Ln's from HCl media with HDEHP in toluene was reported by Peppard and Mason in 1961.[8] The selectivity with 0.75 M HDEHP in toluene from 0.5 M HCl was Lu > Yb > Y > Tm > Tb > Eu > Pm > Pr > Ce > La. HDEHP had a greater affinity for the heavy REEs than the light REEs. Between adjacent REEs the average separation factor observed was about 2.5. The extraction and separation efficiency varies depending on the acidity of the aqueous phase and the counter anion which forms a neutral metal-ligand complex. This was shown by Reddy *et al.* [9] who studied the extraction of REEs from nitrate media with HDEHP, and Pierce and Peck[10] who studied the extraction of Ln's from perchloric acid media.

In 1965, in the USA, Molycorp started using HDEHP to separate rare earth oxides (REOs) from bastnaesite ore. The REOs were leached from the ore via calcination and leaching with HCl to generate a ~100g/L REO chloride solution. That solution contains all REEs except cerium; Ce does not leach from the ore. Over five stages the REO chloride solution is contacted with 10% HDEHP in kerosene. That step extracts the intermediate and heavy REEs (Sm and greater) into the organic HDEHP solution. The REEs lighter than Sm remain in the aqueous raffinate.[11]

HEHEHP was then developed for the extraction of REEs because the REEs can be back-extracted into an aqueous solution, or stripped, easier than with HDEHP.[9] Sato *et al.* determined the selectivity for REEs with HEHEHP is Lu > Yb > Tm > Er > Ho > Y > Dy > Tb > Gd > Eu > Sm > Nd > Pr > Ce > La;[12] HEHEHP has a greater affinity for the heavier lanthanides. A process utilizing HEHEHP has been developed by Daihachi for REE extraction and separation, and has been used in the Chinese REE mining industry.[13-14]

2.3. Digylcolamides

Diglycolamides (DGAs) were first used for metal extraction in 1991 by Stephan *et al.*[15-16] It was discovered that open chain DGAs had very high D_{REE} values for extraction of REEs (D_{La}≈150 ,D_{Yb}≈316), but lower D values for the extraction of Ca (II) and Sr (II) (D_{Ca}≈15 ,D_{Sr}≈13). It was thought that the DGA's complex with the metals through the hard donor oxygen atoms and not with the nitrogen atoms because of Pearson's Hard and Soft Acid-Base concept.[17]

In 1998, Narita *et al.*[18] studied N,N-dimethyl-N',N'-diphenyl diglycolamide for extraction of various lanthanides from nitrate and chloride media. The distribution ratios were higher from HNO_3 than from HCl. This shows that the counter ion used influences the extraction of lanthanides with N,N-dimethyl-N',N'-diphenyl diglycolamide. In 2001, Narita *et al.*[19] used X-ray diffraction (XRD) and extended X-ray absorption fine structure (EXAFS) to determine that DGAs complex with metals in a tridentate fashion.

The effect of chain length of the DGA "R"-groups on extraction of actinide metals was further studied by Sasaki and coworkers.[20] Chain lengths from *n*-propyl to *n*-dodecyl were examined. The solubility of each DGA in water and dodecane, and the D_{Am} for each was studied. It was found that D_{Am} decreased as the chain length increased due to increased steric hindrance. The shorter chain DGAs were soluble in water and they had potential as masking agents during an extraction. The longer chain length DGA derivatives were soluble in dodecane and could be used as actinide extractant ligands. After that study the popularity of tetraoctyl diglycolamide (TODGA) as an actinide extractant increased. TODGA was selected due to its high solubility in paraffinic solvents, it's very low solubility in water, and its high D_{Am} value.

Mowafy *et al.*[21] also studied the extraction abilities of various DGAs in toluene from nitrate media. It was found that as the alkyl chain length decreased the D_{Ln} increased; N,N,N',N'-tetrabutyl diglycolamide (TBDGA) Figure 2-2, had the highest D_{Ln} (0.95-6.71) values of the DGAs examined. Branching of the R and R' groups leads to lower extraction efficiency. Those trends are due to steric hindrance of long and branched R-groups. For all DGAs, as the lanthanides increase in atomic mass, the extraction efficiency also increases.

From HNO_3, as the [HNO_3] increases from 0.1 M to about 1 M the D_{Ln} increases. From about 1 M to 5 M the D_{Ln} (D_{La}≈1, D_{Lu}≈10) and is stable.

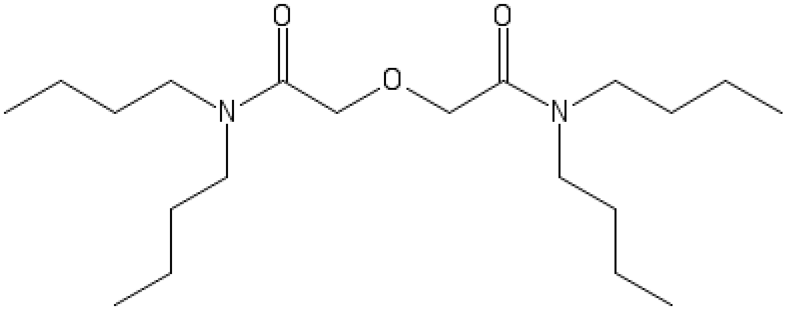

Figure 2-2. Structure of tetrabutyl diglycolamide.

Kannan *et al.* studied the complexation of DGAs with La (III) and U (VI).[22] The DGAs were reacted with $La(NO_3)\cdot 6H_2O$ in 1,2-dichloroethane (CH_2Cl_2) forming crystalized DGA-La (III) complex. The complexes were identified using single-crystal x-ray crystallography. It was shown that three of the tridentate DGAs surrounded La (III) with bonds occurring through the oxygen atoms (Figure 2-3). Bond lengths were also reported.

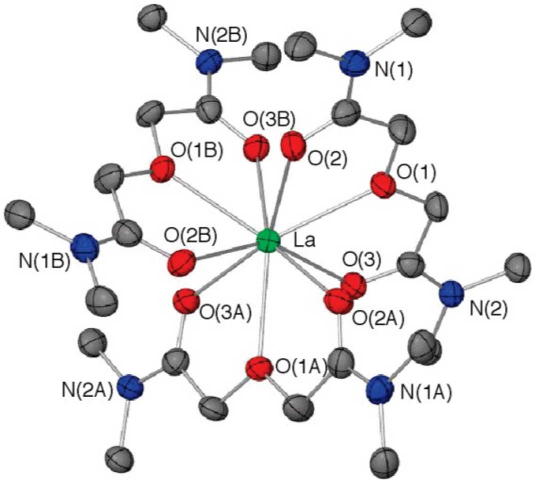

Figure 2-3. Lanthanum complexation with TBDGA. (Reprinted with permission from *Inorg. Chem.* **47**, 4691-4695. Copyright 2007 American Chemical Society. See Appendix A for documentation of permission to republish this material.) [22]

Yang *et al.*[23] studied TBDGA in 30% *1*-octanol in kerosene for extraction of Sm (III) and Nd (III) from chloride media. That diluent was chosen because the *1*-octanol will increase the polarity of the kerosene, and the kerosene is also an inexpensive diluent. It was found that for Sm (III) and Nd (III) the distribution ratios increase as the [HCl] increases in the range of 1.00 to 5.00 M. However, there was a peak in the D_{Sm} at about 3.5 M with a slight decline at higher [HCl]. This is not the trend observed from other TBDGA/HCl systems.[24] It was discovered that in HCl the TBDGA complex with Sm and Nd is $\mathrm{SmCl_3{\bullet}2TBDGA}$ and $\mathrm{NdCl_3{\bullet}2TBDGA}$ through the slope analysis method. The apparent equilibrium constants for Sm (III) and Nd (III) are in equations Eq. 2-2 and Eq. 2-3.

$$\mathrm{K_{ex1}} = \frac{c_{\mathrm{SmCl_3 \cdot 2TBDGA}}}{c_{\mathrm{Sm^{3+}}} c^{2}_{\mathrm{TBDGA}} c^{3}_{\mathrm{Cl^-}}} \qquad \text{Eq. 2-2}$$

$$\mathrm{K_{ex2}} = \frac{c_{\mathrm{NdCl_3 \cdot 2TBDGA}}}{c_{\mathrm{Nd^{3+}}} c^{2}_{\mathrm{TBDGA}} c^{3}_{\mathrm{Cl^-}}} \qquad \text{Eq. 2-3}$$

The extraction of Sm (III) and Nd (III) was exothermic, and as the temperature increased the D_{Ln} decreased. The enthalpy of reaction for Sm (III) and Nd (III) was reported as -68.54 kJ/mol and -35.70 kJ/mol respectively.

Cui *et al.*[24] studied the extraction of various REEs [Gd (III), Dy (III), Er (III), and Yb (III)] from HCl media with TBDGA. By varying the [HCl] from 1 M to 5 M it was found that for all REEs and all diluents studied the D_{REE} increased as the [HCl] increased. The extraction efficiency for the REEs studied with TBDGA was Yb (III) >Er (III) > Dy (III) > Gd (III). This shows that TBDGA has a greater affinity for heavy lanthanides. The authors noted this was similar to what has previously been seen in HNO_3 systems.[25] The effect of various diluents (toluene, *n*-octane, CCl_4, $CHCl_3$, *n*-octane:*n*-octanol (7:3)) on the D_{REE} values was studied. It was found that more polar diluents have a positive effect on the D_{REE} values. Cui also examined the species that is extracted through slope analysis of a log[TBDGA] vs log[D] plot. Such plots were used to estimate the stoichiometry of TBDGA in Eq. 2-4. The diluent did influence the stoichiometry. In toluene 3 TBDGA were in the complex with all REEs. *N*-octane and CCl_4 the REEs complexed with 1 TBDGA. $CHCl_3$ the REEs complexed with 2 TBDGA. In the *n*-octane:*n*-octanol mix the TBDGA in the complex varied: Gd required 2 TBDGA and the others required 3 TBDGA.

$$M^{3+}_{(a)} + 3Cl^{-}_{(a)} + nTBDGA_{(o)} \leftrightarrow MCl_3TBDGA_{n_{(o)}} \qquad \text{Eq. 2-4}$$

The effect of temperature was also studied. The enthalpy of reaction (ΔH) for the tested REEs in various diluents is shown in Table 2-1. The authors studied the effect of varying the ratio of *n*-octane/*n*-octanol as a diluent. The trend was similar for Gd (III), Er (III), and Yb (III). The diluent containing *1*-octanol resulted in higher D_{REE} values than the diluent with greater *n*-octane. This indicates a more polar diluent has greater extraction with TBDGA. When varying [HCl], it was found that as the [HCl] increased the D_{REE} values increased. Within that study the [HCl] never goes above 5 M.

Table 2-1. The enthalpy of reaction values for the extraction of Gd (III), Dy (III), Er (III)m Yb (III) with TBDGA from various diluents.[24]

Diluent	ΔH_r^{θ} (kJ/mol)			
	Gd	Dy	Er	Yb
Toluene	-30.83	-32.93	-29.10	-27.95
n-octane	-26.81	-27.57	-28.91	-39.44
CCl_4	-33.89	-34.08	-27.76	-28.15
$CHCl_3$	-56.48	-65.10	-52.27	-49.40
n-octane/*n*-octanol (V/V=7/3)	-62.99	-61.27	-65.47	-48.25

Sasaki *et al.*[26] studied the use of aqueous-soluble DGAs in nitric acid to back-extract actinides and other metals commonly found in the nuclear fuel cycle from TODGA in dodecane. The DGAs studied were N,N,N’,N’-tetramethyl diglycolamide (TMDGA), N,N,N’,N’-tetraethyl diglycolamide (TEDGA), and N,N,N’,N’-tetrapropyl diglycolamide (TPDGA). It was found those DGAs have stronger complexing abilities for Am (III) and Pu (IV) than the previous back-extraction complexing agents, carboxylic and aminopolycarboxylic acids. The complexing strength of those aqueous-soluble DGAs is TPDGA ≈ TEDGA > TMDGA. The longer chain of the TPDGA caused it to be partially soluble also in the dodecane, and there was a significant loss to the organic phase during the extraction. The authors came to the conclusion that TEDGA is the best of the studied ligands for back-extraction of metals of a variety of oxidation states: Am (III), Pu (IV), Ca (II), Sc (III), Y (III), Hf (IV), Bi (III).

Charbonnel *et al.*[27] studied the complexation of Ln (III) and Am (III) with TEDGA. TEDGA is an aqueous-soluble DGA that has been studied as a back-extraction ligand and has been introduced into the Extraction of Americium (EXam) process. The authors performed an extraction of La (III), Ce (III), Pr (III), Sm (III), Eu (III), and Gd (III) in 5 M HNO_3. The aqueous phase also contained ~0.6 M DMDOHEMA, ~0.3 M HDEHP in NPH diluent, and ~1.9 mM total concentration of the following lanthanides: La (III), Ce (III), Pr (III), Sm (III), Eu (III), and Gd (III). The extraction having no TEDGA present showed a constant D_M of about 10 across the series, indicating that each metal had approximately the same separation coefficient, which is not conducive to an effective intra-series separation. When 0.05 M TEDGA was used the D_M linearly increased across the lanthanide series from ~ 0.1 to ~3. This linearly changing and predictable response in D_M indicates that TEDGA is a promising ligand for a separation process for rare earths.

2.4. Supercritical fluids and modifiers

The first metal extraction with sc-CO_2 was reported by Laintz *et al.*[28] Copper was complexed with bis(trifluoroethyl)dithiocarbamate (FDDC), and subsequently that metal-ligand complex was extracted into sc-CO_2. In that report the copper was extracted from two different samples: an aqueous sample of $Cu(NO_3)_2$ and solid $Cu(NO_3)_2$ spiked onto silica. The extraction was performed by flowing the sc-CO_2 through solid LiFDDC; dissolving the LiFDDC into the sc-CO_2. That ligand loaded sc-CO_2 was then passed through either the aqueous or the solid sample. A UV-vis spectrometer was used to observe the formation of the $Cu(FDDC)_2$ complex, and Beer's law was used to determine to rate of extraction of Cu (II). A percent extraction (%E) of >99% copper was achieved from the aqueous solution, and >80% from the solid sample. The authors provided two reasons for the decrease in the extraction from the solid sample. A portion of the copper may have been in a different form in the solid sample compared to the Cu^{2+} in the aqueous sample. That copper species may not have formed a complex with the FDDC, or the formed complex was not observed at the 416 nm wavelength used for the UV-vis spectroscopy analysis.

Lin *et al.*[29] examined extraction of La (III), Eu (III), and Lu (III) from wet and dry filter paper with 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedione (FOD), a β-diketone, into sc-CO_2. The sample was prepared by spiking a solution containing the lanthanide nitrates onto the filter paper and allowed to dry. The FOD was directly pipetted onto the sample filter paper. A portion of the samples were spiked with water before the extraction. The system was pressurized to 2205 psi with sc-CO_2, or 5 mole percent methanol sc-CO_2, at 60°C for 10 minutes to allow the chelation to occur. That was followed by a 10 minute dynamic flush. The authors determined %E by what was remaining on the filter paper after the extraction. They showed that no extraction of any metal occurred without the FOD present. The percent extractions for the dry samples with FOD ranged from 5% to 12%, and the wet samples ranged from 10% to 19%. The authors attributed the increase in %E to water acting as a matrix modifier by reducing the interaction between the cellulose and the lanthanides. When 5 mole percent methanol was added to the sc-CO_2 the %E significantly increased from 54% to 99% with the highest E% being from the wet samples. Greater %E was observed for Lu (III) and Eu (III) over La (III).

The extraction of La (III), Eu (III), and Lu (III) from an aqueous sample into sc-CO_2 with fluorinated β-diketones and organophosphorus reagents was studied by Lin and Wai in 1994.[30] Extractions were performed at 60°C and 2204 psi with a 10 minute static extraction followed by a 20 minute dynamic extraction. The fluorinated β-diketones studied were: hexafluoroacetyllacetone (HFA), thenoyltrifluoroacetone (TTA), trifluoroacetylacetone (TAA), and 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedione (FOD). Extraction with TBP and acetylacetone (AA) was also studied. Single-ligand and duel-ligand extractions were studied. For some extractions methanol was used to modify the sc-CO_2. Percent extraction with a fluorinated β-diketone from filter paper with neat sc-CO_2 averaged 14%. When 5 mole % methanol was utilized as a modifier the E% average 85%, and for all ligands examined the %E increased. The dual-ligand systems showed greater E% than the single-ligand system. The average %E for extraction with fluorinated β-diketones with TBP into neat sc-CO_2 was 85%.

In all instances the AA had much lower E% than any of the β-diketones; that ligand had the lowest molecular weight and no fluorinated groups. The E% for the lanthanides with all examined ligands is in the order TTA ≈ FOD > HFA > TAA > AA > TBP.

Laintz and Tachikawa[31] studied the extraction of lanthanides from aqueous nitrate solutions (HNO_3 and $LiNO_3$) with TBP in sc-CO_2. Slope-analysis techniques were utilized to determine the Ln-TBP complex stoichiometry that was forming. They determined that the lighter lanthanides (La (III) through Eu (III)) formed the complex $Ln(TBP)_2$, and the heavier lanthanides (Gd (III) through Lu (III)) formed the complex $Ln(TBP)_3$. The authors theorized they have lower extraction with TBP than previous studies with β-diketones because of the ratio of complexing agents to the lanthanides. If the coordination of the metal isn't fulfilled it won't be effectively extracted.

Lagalante *et al.*[32] studied the solubility of Cu (II) complexes with β-diketones in sc-CO_2. Within that study the solubility of $Cu(HFA)_2$ and $Cu(HFA)_2{\bullet}H_2O$ were observed. Many metal-ligand are solvated when contacted with water. At 313 K and 2000 psi the solubility of $Cu(HFA)_2$ in sc-CO_2 is $3.211\text{x}10^{-3}$ mole fraction. The solubility of $Cu(HFA)_2{\bullet}H_2O$ under the same conditions is $1.741\text{x}10^{-3}$ mole fraction. The solubility is nearly half for the hydrated form of $Cu(HFA)_2$.

Duan *et al.*[33] examined the extraction of neodymium and cerium from their oxides with TBP-HNO_3 adduct and Cyanex 923-HNO_3 adduct in sc-CO_2. A dynamic extraction of Nd (III) and Ce (III) from the oxides with TBP-HNO_3 in sc-CO_2 resulted in %E of 95% and <1% respectively. Ce_2O_3 is very recalcitrant and is not easily dissolved with HNO_3. Extraction with Cyanex 923-HNO_3 in sc-CO_2 the %E of neodymium dropped significantly to <10%. The authors hypothesized the observed phenomena was due to the polarity of the Cyanex 923-HNO_3 complex being greater than the TBP-HNO_3 complex. The more polar complexes resulted in lower solubility in sc-CO_2.

Nejad *et al.*[34] optimized the extraction of La (III), Ce (IV), and Sm (III) from filter paper with bis(2,4,4-trimethylpentyl)dithiophosphinic acid (Cyanex 301) and TBP in sc-CO_2. The samples, nitrate REE salts in deionized water, were spiked on filter paper and dried. Cyanex 301 and TBP were spiked directly onto the filter paper samples. A static extraction was performed for 20 minutes followed by a 25 minute dynamic flush. A collection efficiency (%collection) value was determined from what was collected in a chloroform trap solution. The effects of pressure, temperature, amount of Cyanex 301, amount of TBP, and the flow rate of sc-CO_2 were studied. Cyanex 301 was varied from 0.07 g to 0.14 g. The %collection increased as the grams of Cyanex 301 increased. The flow rate of the sc-CO_2 was varied from 2 mL/min to 4 mL/min during the dynamic flush. As the flow rate increased the %collection increased. Temperature was varied from 313 K to 343 K, and the %collection increased with the increase in temperature. The authors hypothesized the saturated vapor pressure increased which allowed for greater solute dissolution into the sc-CO_2. The pressure was varied from 1740 psi to 3625 psi. An increase was observed in the %collection as the pressure increased. The authors hypothesized that in increase an density resulted in an increase in the solvating ability of the sc-CO_2. Increasing the moles of TBP increased the %collection showing a synergistic effect between TBP and Cyanex 301. The authors hypothesized that the TBP displaces water in the REE-Cyanex 301 complex allowing it to be more soluble in the sc-CO_2. Those data provided insight into optimizing CO_2 extractions.

Baek and coworkers[35] examined the extraction of Y (III), Ce (IV), Eu (III), Tb (III), and Dy (III) with TBP-HNO_3 adducts in sc-CO_2. Oxides of yttrium, cerium, europium, terbium, and dysprosium were packed into a column with salinized glass wool. Two different adducts were compared: $TBP(HNO_3)_{1.7}(H_2O)_{0.6}$ and $TBP(HNO_3)_{5.2}(H_2O)_{1.7}$. At a temperature and pressure of 338 K and 5000 psi, sc-CO_2 modified with adduct was passed through the extraction column and over the sample for 90 minutes. The sc-CO_2 flow rate was kept at ~ 3.0 mL/min. The mole ratio of $TBP(HNO_3)_{1.7}(H_2O)_{0.6}$ to sc-CO_2 was examined at 0.049 and 0.087, and for $TBP(HNO_3)_{5.2}(H_2O)_{1.7}$ the adduct/CO_2 mole ratios used were 0.019 and 0.05. These mole fractions were used based on the solubility of each adduct in sc-CO_2. The dynamic extraction was followed by a dynamic flush at 3.0 mL/min for 45 minutes. The trap solution was analyzed to determine E%. The $TBP(HNO_3)_{1.7}(H_2O)_{0.6}$ adduct had a greater E% than the $TBP(HNO_3)_{5.2}(H_2O)_{1.7}$ adduct. The 0.049 mole ratio resulted in the greatest extraction. With the $TBP(HNO_3)_{1.7}(H_2O)_{0.6}$ adduct at 0.049 mole ratio, Y (III) and Eu (III) were both extracted >99 %. Terbium (III) and Dy (III) were extracted to 92.1 % and 98.5 %, respectively. Cerium was minimally extracted at 0.12 %. The authors determined the Ce (IV) did not extract because in its oxide form it is in the +4 oxidation state; whereas the other REEs are +3. The $TBP(HNO_3)_{5.2}(H_2O)_{1.7}$ adduct resulted in lower extraction efficiency because TBP is the limiting reagent in the reaction and HNO_3 and water are in excess.

Tian *et al.*[36] studied the extraction of Nd (III) and Eu (III) with TBDGA-HNO_3 into sc-CO_2 and acetone modified sc-CO_2. It was found that in supercritical CO_2 no metals were extracted. When the sc-CO_2 was modified with acetone it resulted in an increase in the extraction of Nd (III) and Eu (III) to 85% and 95%, respectively, with a dynamic extraction.

Static extractions were also performed, and extraction efficiency was significantly lower than obtained with dynamic extractions. The reasons for that behavior were not apparent, and the authors did not speculate about the cause.

Water has an impact on the extraction of metals into CO_2. The solubility of water with supercritical and liquid CO_2 was studied by King *et al*., Coan and King, and Sabirzyanov *et al.*[37-39]. Temperatures from 25 to 100 °C and pressures from 17.1 to 50.8 psi have been examined. The CO_2 will be at a liquid or a sc-CO_2 phase depending on the pressure and temperature.

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Chapter 3

Extraction of REEs from Chloride Media with TBDGA in *1*-octanol

(Modified version of the following manuscript: Case, M. E.; Extraction behavior of selected rare earth metals from acidic chloride media using tetrabutyl diglycolamide, *Solvent Extr. Ion. Exc. 2017,* 1-11. Copyright 2017 Taylor & Francis) See Appendix A for documentation of permissions to republish this material.

3.1. 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 which 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 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 from HNO_3 solution using tetrabutyl diglycolamide (TBDGA)/octanol.[20] Others have recently reported that diglycolamide ligands 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 synergism.[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 3-1. Liquid-liquid solvent extraction was performed with TBDGA in *1*-octanol as the diluent. 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 (III), Dy (III), Er (III), Yb (III), Sm (III), and Nd (III).[17, 19] Work shown in this chapter 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. Optimized extraction of metals from magnet and phosphor materials are also discussed.

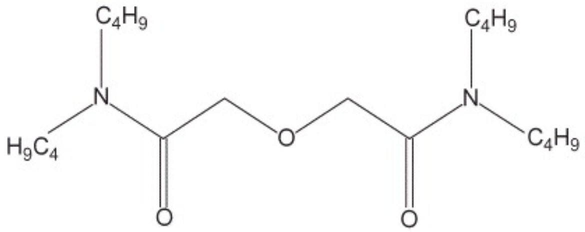

Figure 3-1. Structure of tetrabutyl diglycolamide.

3.2. Materials and Methods

All liquid-liquid extractions were performed in 15 mL Corning conical tubes. 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%), tri-chromatic phosphor powder. 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’-tetrabutyl diglycolamide (95%) was used as-received from Tractus Chemical (Tractus Chemical, London, England).

All aqueous solutions were made with water purified to a resistivity of at least 18 MΩ-cm. The concentration of the REEs in the aqueous phase was determined by ICP-MS; the concentration of the REEs in the organic phase was determined by the difference between the original aqueous solution concentration and the concentration in the final aqueous phase. The distribution ratio (D_{REE}) was calculated using Eq. 3-2 where the concentration of metal in the organic phase, $[M]_o$, is divided by the concentration of metal in the aqueous phase, $[M]_a$. The $[M]_o$ can be estimated by the concentration in the aqueous initially, $[M]_{ai,}$ minus the concentration of the metal in the aqueous post contact, $[M]_{af}$. An element is considered extracted with a D_{REE} of one or greater.

$$D = \frac{[M]_o}{[M]_a} \approx \frac{[M]_{ai} - [M]_{af}}{[M]_{af}} \qquad \text{Eq. 3-1}$$

3.2.1. *Kinetics*

8.0 M HCl pre-equilibrated 10 mM TBDGA 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.

3.2.2. *Effect of varying [HCl]*

Aqueous solutions were made with [HCl] of 0.1, 0.5, 1.0, 3.0, 5.0, and 8.0 M with, and without, rare earth elements added. Approximately 100 ppb of Y, La, Ce, Nd, Sm, Eu, Tb, Dy, Ho, and Lu were added to the HCl solutions as chloride salts. This adds about 21 µM Cl^- to the solutions. The organic phase consisted of 10 mM TBDGA in *1*-octanol. Equal volumes of the organic phase were pre-equilibrated by contact with the metal-free HCl solution for 15 minutes. This solution was then centrifuged for 5 minutes and the organic phase was removed. The pre-equilibrated organic was then contacted for 15 minutes with an equal volume of the appropriate metal-loaded aqueous phase. After the contact, 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.

3.2.3. *Effect of Varying [Cl$^-$]*

Aqueous solutions with 1.0 M [H$^+$] and varying [Cl$^-$] concentrations (2.0 M, 3.0 M, and 4.0 M), and a 5 M NaCl solution with no HCl added, with and without REE, were used. Approximately 100 ppb of Y (III), La (III), Ce (II), Nd (III), Sm (III), Eu (III), Tb (III), Dy (III), Ho (III), and Lu (III) were added to the solutions as a chloride salts. The distribution ratios were then determined by the same method as above.

3.2.4. *Extraction Behavior of Europium as a Function of [TBDGA]*

A concentration of 8.0 M HCl containing 0.65 mM Eu was contacted for 15 minutes with an equal volume of *1*-octanol with varying [TBDGA]. The [TBDGA] used were 0.065 mM, 0.33 mM, 0.66 mM, 0.99 mM, 1.3 mM, 2.0 mM, 2.6 mM, 3.3 mM, 5.3 mM, 9.9 mM. D_{Eu} were determined as described above.

3.2.5. *Thermodynamics*

A concentration of 8.0 M HCl was used to pre-equilibrate 10 mM TBDGA by contacting an equal volume of aqueous and organic for 15 minutes at about 2, 23, 35, 45, and 55 ^{o}C. The distribution ratios were then determined using 100 ppb Y, La, Ce, Nd, Sm, Eu, Tb, Dy, and Lu as above.

3.2.6. *[Water] and [H^+]*

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 18 MΩ-cm 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 burette. This was performed in triplicate for each sample.

3.2.7. *Extraction from phosphor leachate*

One gram of tri-chromatic phosphor powder were contacted with 50.0 mL 8 M or 4 M HCl for ~48 hours at room temperature. ICP-MS was performed to determine the metals that were leached from the powder.

This leachate was diluted 1:5 in either 8 M HCl or 5 M NaCl. Five milliliters of the diluted magnet leachate was contacted with 5.0 mL of pre-equilibrium 0.10 M TBDGA in *1*-octanol for 15 minutes at 23 °C. This was followed by a 5-minute centrifuge. The aqueous phase was collected to determine the metal concentrations by ICP-MS.

3.2.8. *Extraction from magnet dissolution*

The procedure from the section above was performed with 1.0 g demagnetized, ground NIB magnet material.

3.3. Results and Discussion

3.3.1. *Kinetics*

The kinetics of TBDGA in *1*-octanol for the extraction of Y (III), Eu (III), and Dy (III) from 8.0 M HCl are shown in Figure 3-2. Extraction kinetics were also examined for La (III), Ce (II), Nd (III), Sm (III), Tb (III), and Lu (III) (data not shown). Extraction kinetics for all of the examined REEs demonstrate a high degree of similarity. The D_{REE} increases slightly between 5 minutes and 10 minutes, after which it stabilizes. These results indicate that the contact time of 15 minutes used in all the experiments in this study provided equilibrium D_{REE} values.

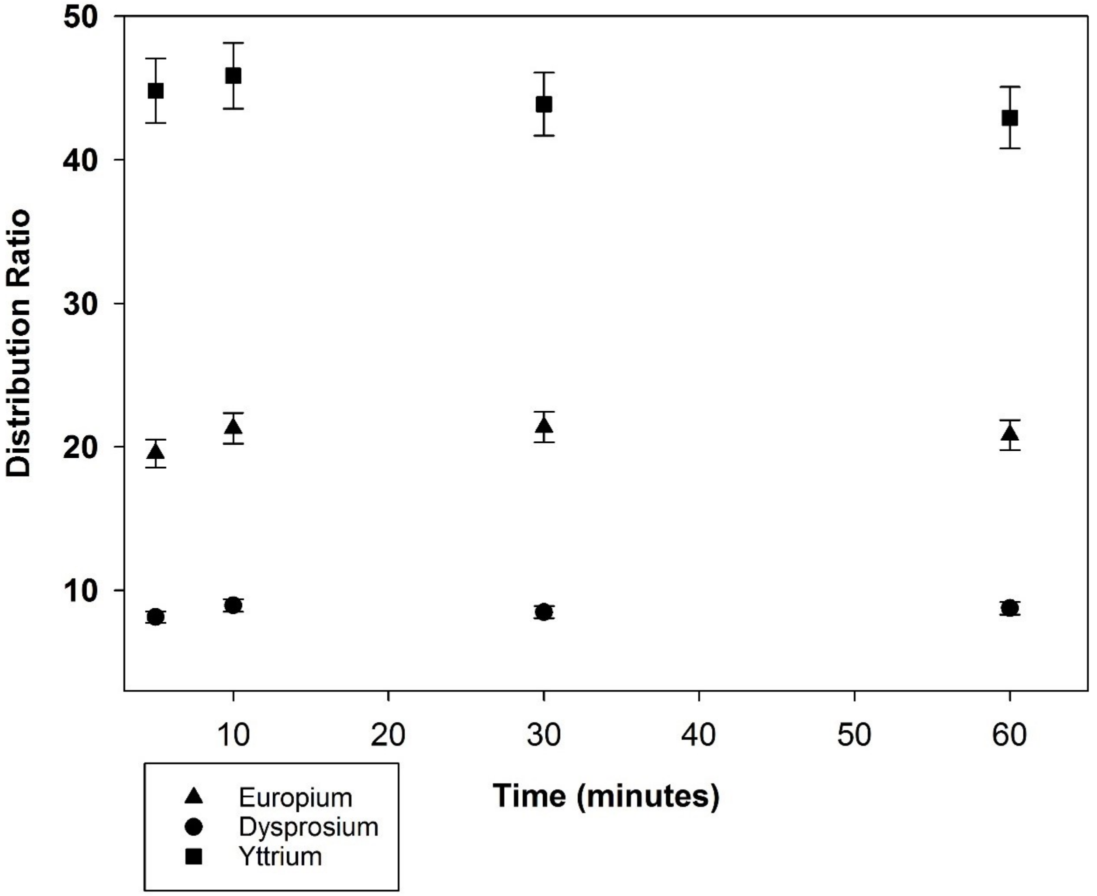

Figure 3-2. Kinetics of TBDGA extraction of 100 pbb each REE from 5 minutes to 60 minutes from 8.0 M HCl with 10 mM TBDGA.

3.3.2. *Effect of Varying [HCl]*

Data for the extraction of lanthanides from 1.0 M to 8.0 M HCl matrix using pre-equilibrated 10 mM TBDGA in *1*-octanol are graphically depicted in Figure 3-3. For all rare earths tested, as [HCl] increased in the aqueous phase the amount of REE extracted into the organic phase increased. This trend was also observed by Cui *et al.*[17, 19] An element is considered extractable for process application if the distribution ratio, D_{REE}, is greater than 1. From 0.1 to 1.0 M HCl none of the REEs examined are extractable. From 3.0 M HCl, Y (III), Tb (III), Dy (III), Ho (III), and Lu (III) are extractable with D_{REE} in the range of 1.5 to 4.1. All other elements were poorly extracted with $D_{REE} < 1$. As the acid concentration is increased, the heavy lanthanides Dy, Ho, and Lu, are highly extractable from 5.0 M HCl, with D_{REE} in the range 10.8 to 18.8. Samarium (III), Eu (III), Tb (III), and Y (III) are also extractable with lower D_{REE} in the range of 2.0 to 7.4. Lanthanum, Ce, and Nd are poorly extracted with $D_{REE} < 1$. Finally, from 8.0 M HCl only the light lanthanides, La and Ce, are poorly extracted with $D_{REE} < 1$. Neodymium and Sm are extractable with D_{REE} in the range 2.0 to 9.0. All other REEs examined are highly extractable from highly acidic solution with D_{REE} in the range of 15.1 to 141.9.

Increase in extraction efficiency as [HCl] increases is expected as the metal complex must be neutralized by the counter ion Cl^- for extraction into the organic phase to occur. To verify the increase in extraction efficiency is in fact due to the Cl^- and not the H^+, extraction at varying [Cl^-] was also performed and reported later in this chapter.

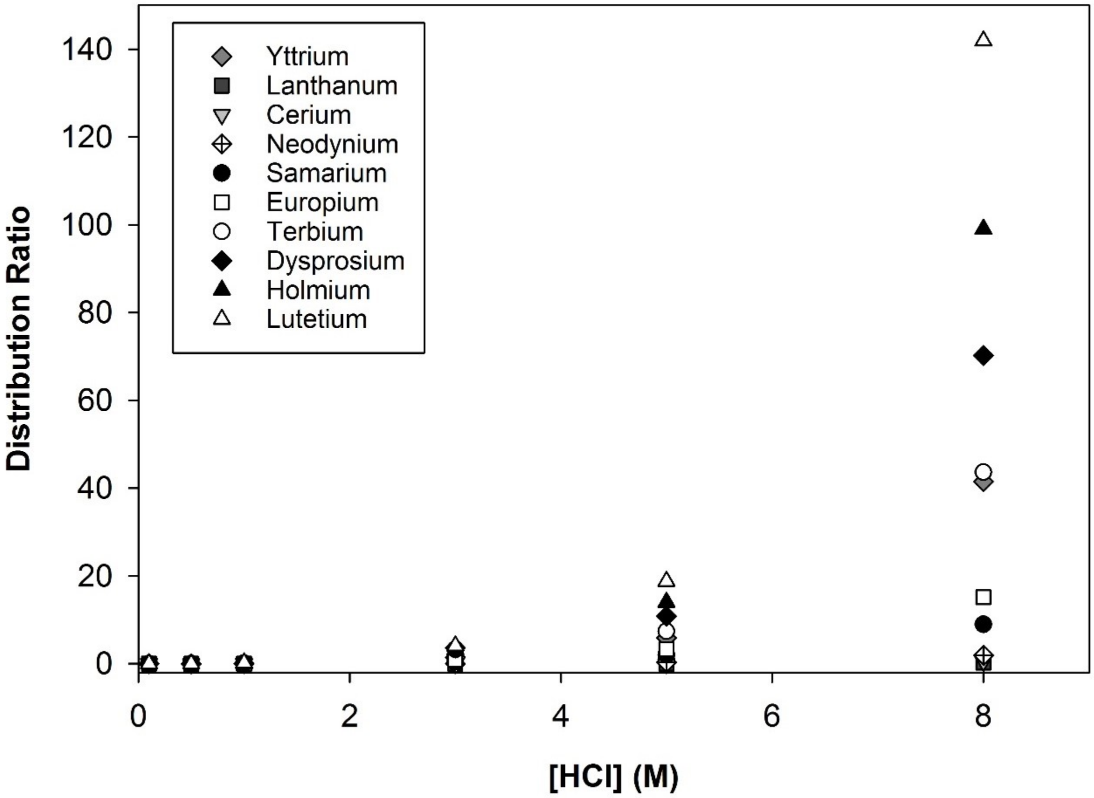

Figure 3-3. The solvent extraction profile of Y (III), La (III), Ce (II), Nd (III), Sm (III), Eu (III), Tb (III), Dy (III), Ho (III), and Lu (III) from hydrochloric acid media as a function of [HCl] using pre-equilibrated 0.010 M TBDGA in *1*-octanol. The aqueous phase consisted of ~100 ppb of each REE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

3.3.3. *Extraction Behavior as a Function of Ionic Radii*

Plotting ionic radii CN=6,[23] versus the distribution ratio, Figure 3-4 shows the general trend for the extraction of REEs with TBDGA from 8.0 M HCl. Overall, the relationship between ionic radii and D_{REE} is inversely proportional. As the ionic radii increase the D_{REE} decrease, suggesting that lanthanide ions of higher charge density are better complexed and extracted. The overall trend follows that observed by Cui *et al.* with TBDGA extraction from HCl using various diluents other than *1*-octanol.[17] This also is consistent with our previous report for the extraction of lanthanides from HNO_3 using TBDGA in *1*-octanol.[20] Those data are shown with the new data in Figure 3-4 for comparison. The light to intermediate lanthanides show similar extraction behavior from HNO_3 and HCl; however, the extraction efficiency is slightly improved in the HCl system over the HNO_3 system. The heaviest lanthanides Ho and Lu show higher extraction efficiency from HNO_3. The higher extraction efficiency overall from HCl does agree with the Hofmeister "salting out" series.[24]

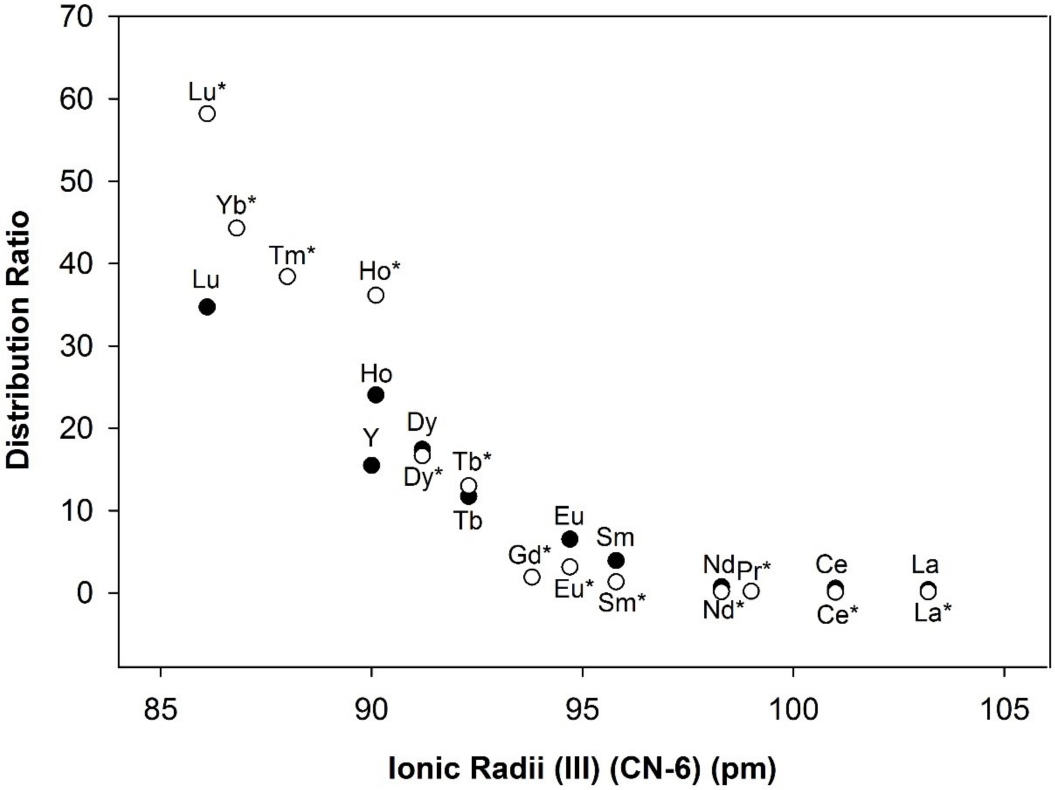

Figure 3-4. Ionic radii coordination number of 6 versus distribution ratio for the extraction of 0.007 M TBDGA in *1*-octanol from 8.0 M HCl (●) and from 8 M HNO_3[20] (○, labeled with *).

3.3.4. *Effect of Varying [Cl^-]*

Figure 3-5 shows the distribution ratios of REEs into the organic phase containing 10 mM TBDGA in *1*-octanol from an aqueous phase containing 1.0 M HCl and varying [Cl^-] ranging from 2.0 M to 4.0 M added Cl^- (total Cl^- range 2.0 M to 5.0 M). A similar trend was observed when compared to the previous experiment where [HCl] was varied. However, for these experiments, when [H^+] was kept constant at 1.0 M and [Cl^-] was varied, the magnitude of increase in D_{REE} was greater than when HCl alone was used. This indicates that $[H^+]$ can have a deleterious effect on metal extraction.

For extractions from HNO_3 it is often reported that D_{REE} reaches a maximum at intermediate acidity, followed by a decrease in extraction efficiency. This effect is usually attributed to competition for the ligand by undissociated HNO_3. However, this effect is not observed in Figure 3-5 for HCl, probably because less undissociated acid is available to complex the ligand. These results also introduce the concept that for potential process applications [HCl] may be kept at a minimum and D_{REE} for different REEs can be optimized by varying $[Cl^-]$ through use of a less expensive source of Cl^-, such as NaCl. The increased D_{REE} under this condition is attributed to salting out effect, in which a higher concentration of the anion facilitates charge neutralization of the metal-ligand complex.

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 in Figure 3-6. 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_{REE} values, indicating again that $[H^+]$ has a negative effect on the extraction of REE into the organic phase. The adverse effect of acidity indicates that protonation of the ligand, and thus creation of a positively charged metal complex, decreases the solubility of the metal complex in the organic phase which decreases extraction efficiency. By reducing [HCl] to 1.0 M, but keeping $[Cl^-]$ at 5.0 M the D_{REE} 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_{REE} increased about 2x to 9x when compared to the solution with 1.0 M HCl.

High [Cl^-] is required for extraction from aqueous media because the TBDGA metal complex must be neutral, requiring three Cl^- to satisfy the metal ion charge. Eq. 3-2 shows the complexation that occurs to form a charge neutral species, assuming no ligand protonation. The chloride ion poorly complexes with the metal ions.[17] A high chloride concentration thus drives the equilibrium toward the neutral species which is extractable into the organic phase.

$$REE^{3+} + n\mathrm{TBDGA} + 3\,Cl^- \leftrightarrow REE(\mathrm{TBDGA})_nCl_3 \qquad \text{Eq. 3-2}$$

The DGAs are basic compounds due to being oxygen donors.[25] It is logical to believe that under highly acidic conditions the protonated amide requires additional Cl- anions to achieve charge neutralization.

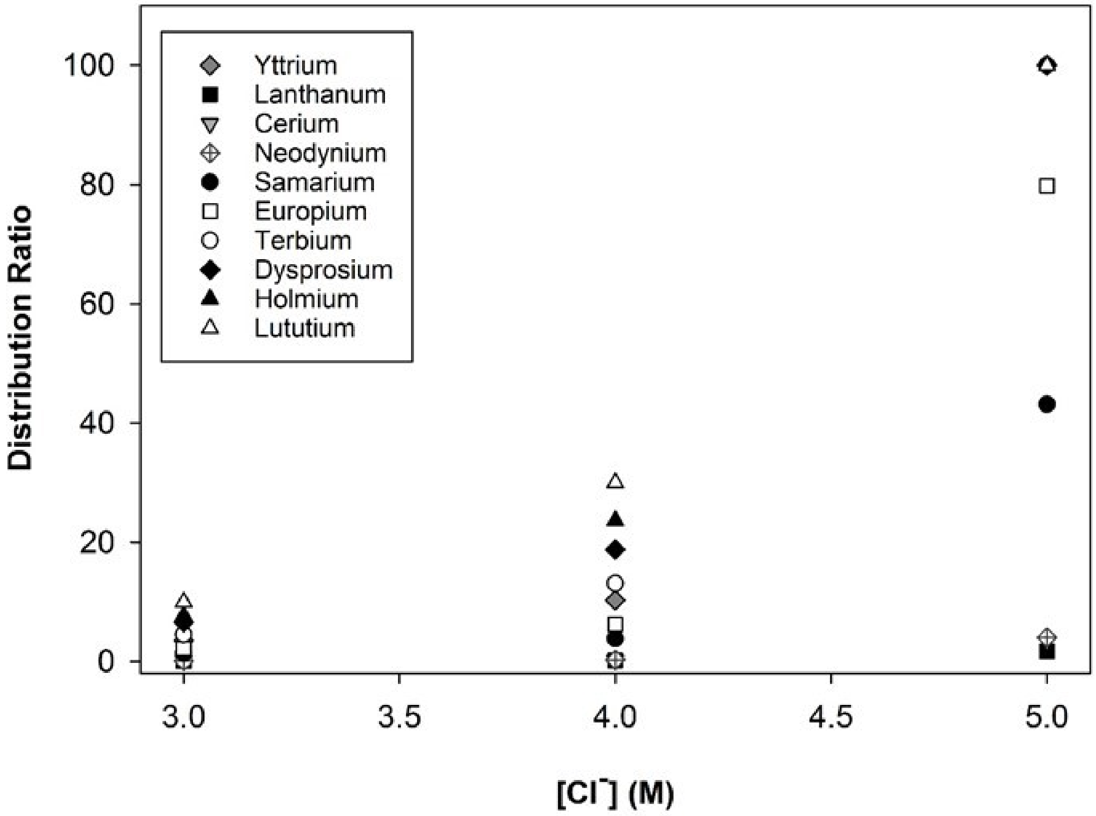

Figure 3-5. The solvent extraction profile of Y, La, Ce, Nd, Sm, Eu, Tb, Dy, Ho, Lu from aqueous media with 1.0 M HCl and 2.0 M - 4.0 M added NaCl with pre-equilibrated 10 mM TBDGA in *1*-octanol. The aqueous phase consisted of ~100 ppb of each REE resulting in a total REE concentration of about 7 µM.

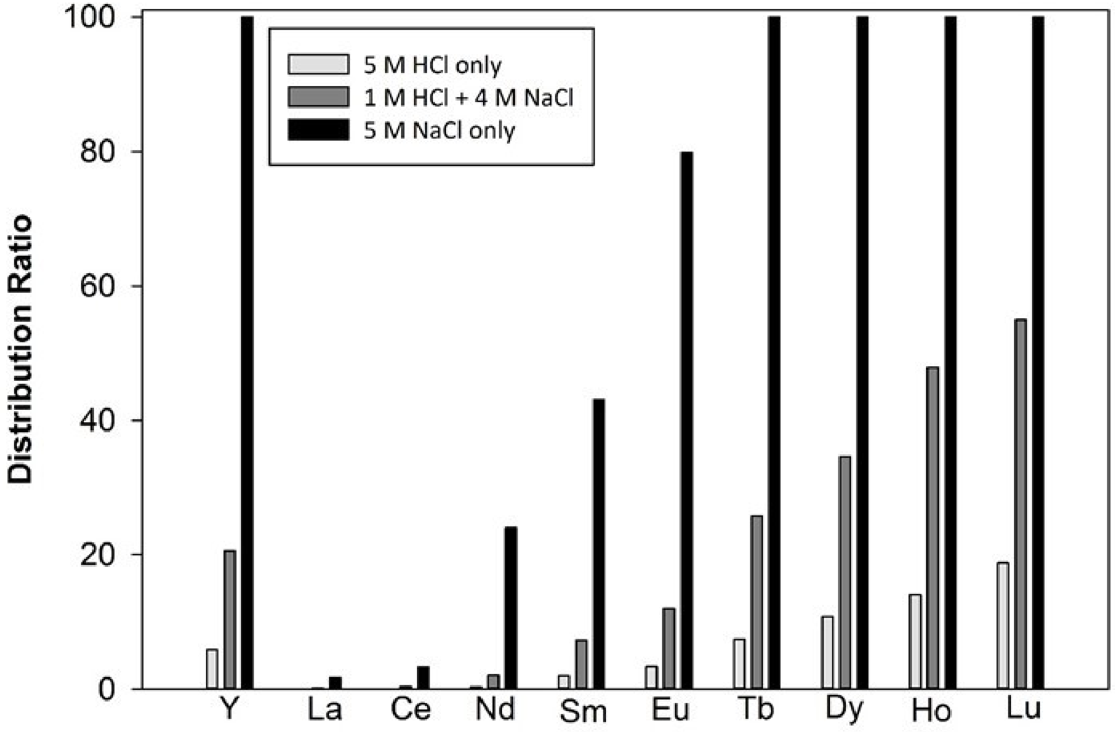

Figure 3-6. Distribution ratios for extraction of REE from 5.0 M Cl^- solutions with the Cl^- from either HCl, NaCl, or a mix of HCl and NaCl. Pre-equilibrated 10 mM TBDGA in *1*-octanol contacted with an aqueous phase containing Y, La, Ce, Nd, Sm, Eu, Tb, Dy, Ho, and Lu with a total REE concentration of about 7 µM with 5.0 M Cl^-. The black shows 5.0 M HCl, the light grey is 1.0 M HCl and 4.0 M NaCl, and the dark grey is 5.0 M NaCl.

3.3.5. *Extraction of H^+, water, and Eu by 1-octanol*

To evaluate the effects of the extraction of water and acid by the polar diluent and their possible effects on metal extraction, Eu solutions of HCl or NaCl were contacted with *1*-octanol and the post-contact organic solutions were analyzed 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). Data given in Table 3-1 indicate extraction of water was significant in all contacts, 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. Data trends are consistent with the lower water concentration found in high salinity 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 the 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 3-1, 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. 3-2 are the extracted metal species.

Table 3-1. 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	0.0029 ± 0.0004	< 0.01
0 M HCl-contacted	< 0.0002	2.40 ± 0.04	< 0.01
0.5 M HCl-contacted	0.14 ± 0.07	2.30 ± 0.04	0.029 ± 0.001
8 M HCl-contacted	0.13 ± 0.07	6.89 ± 0.06	2.15 ± 0.05
0.5 M NaCl-contacted	< 0.006	2.12 ± 0.04	< 0.01
5 M NaCl-contacted	< 0.004	1.31 ± 0.04	<0.01

3.3.6. *Extraction Behavior of Europium as a Function of [TBDGA]*

To better understand metal complex speciation, slope analysis can be used to determine the number of TBDGA molecules, n, in the metal-ligand complex (Eq. 3-2) extracted into the organic phase $M(TBDGA)_nCl_3$. The value of n is determined from a plot of the natural log of the distribution ratio versus the log of [TBDGA], Figure 3-7. Linear regression analysis yields a trend line through the data where the slope of the line, n, is equivalent to the number of TBDGA molecules involved in the formation of the metal-ligand complex. From this analysis a slope of 2.13 ± 0.05 for Eu in HCl was determined. For the extraction of Eu into *1*-octanol the Eu complex is di-solvate, i.e., $Eu(TBDGA)_2Cl_3$. This is comparable to values our group has measured for speciation from HNO_3 with TBDGA in *1*-octanol, shown also in Figure 3-7, which yielded a slope of 2.47 ± 0.08 for Eu, and 1.85 ± 0.04 for Ce also shown. It was determined by Cui *et al.*[17] that the number of TBDGA in the extracted complex changes based on the diluent used; the more polar the diluent the more TBDGA in the complex. From Figure 3-7 we can also surmise that as the concentration of TBDGA increases, the log distribution ratio also linearly increases.

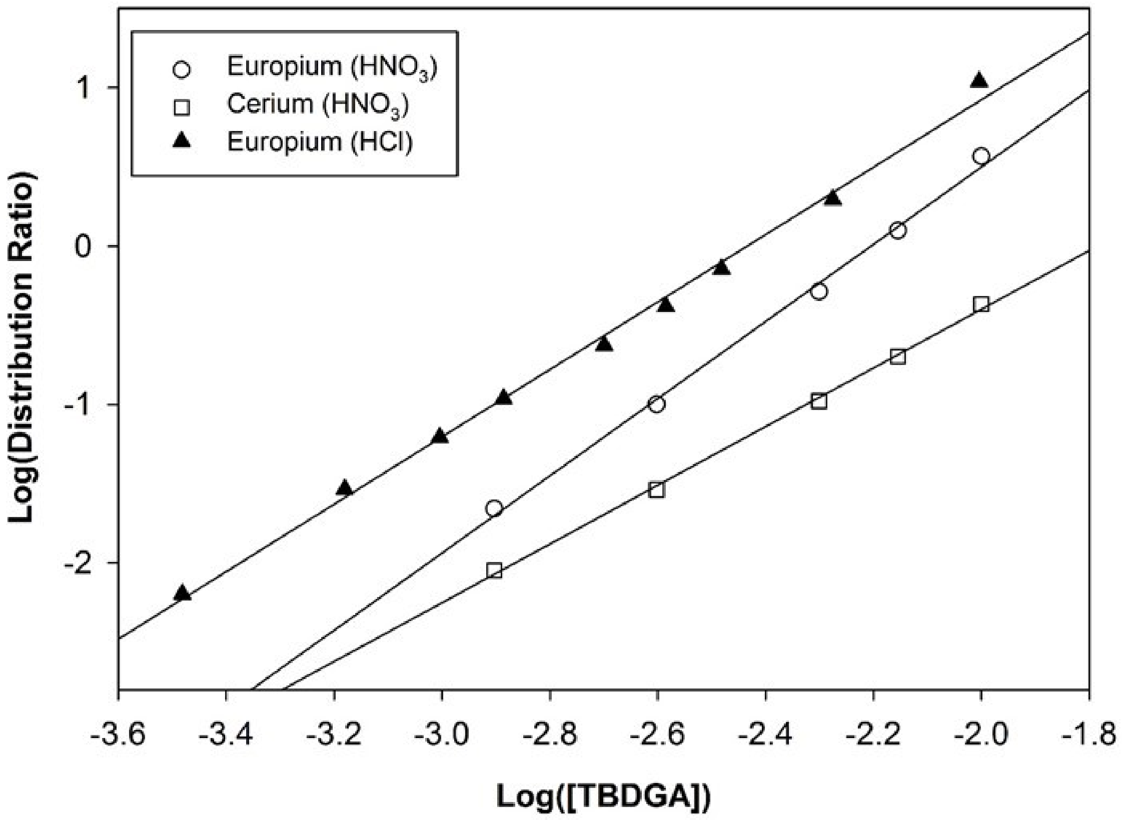

Figure 3-7. Log of the distribution ratio versus natural log varying concentration of TBDGA. The Eu concentration was 110 ppb in 8.0 M HCl with a contact time of 15 minutes (○). The slope of the linear trend line through the data indicates the number of TBDGA molecules participating in the extracted complex. Similar data for Eu (▲) and Ce (□) extracted from HNO_3 is also shown.[20]

3.3.7. *Thermodynamics*

The effect of temperature on the D_{REE} is shown in the Van't Hoff plot in Figure 3-8. 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. 3-3. The resulting enthalpy for Y (III), Sm (III), and Eu (III) are shown in Table 3-2. For all elements tested the extraction of rare earths from 8.0 M HCl with TBDGA is exothermic and the stability of the various REE(TBDGA)$_n$Cl$_3$ complexes decrease as the temperature increases. Almost no extraction was observed at 65 °C for all

REEs examined. The value obtained here for the enthalpy of Dy complex formation in *1*-octanol are compared to the values obtained by Cui *et al.*[17] using various diluents in Table 3-3. The enthalpy of reaction in octanol is about mid-range for the other diluents investigated. Enthalpy values may vary in diluents due to several factors, including viscosity, ease of solvation of the metal center, and ability to remove water coordinated to the metal center.

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

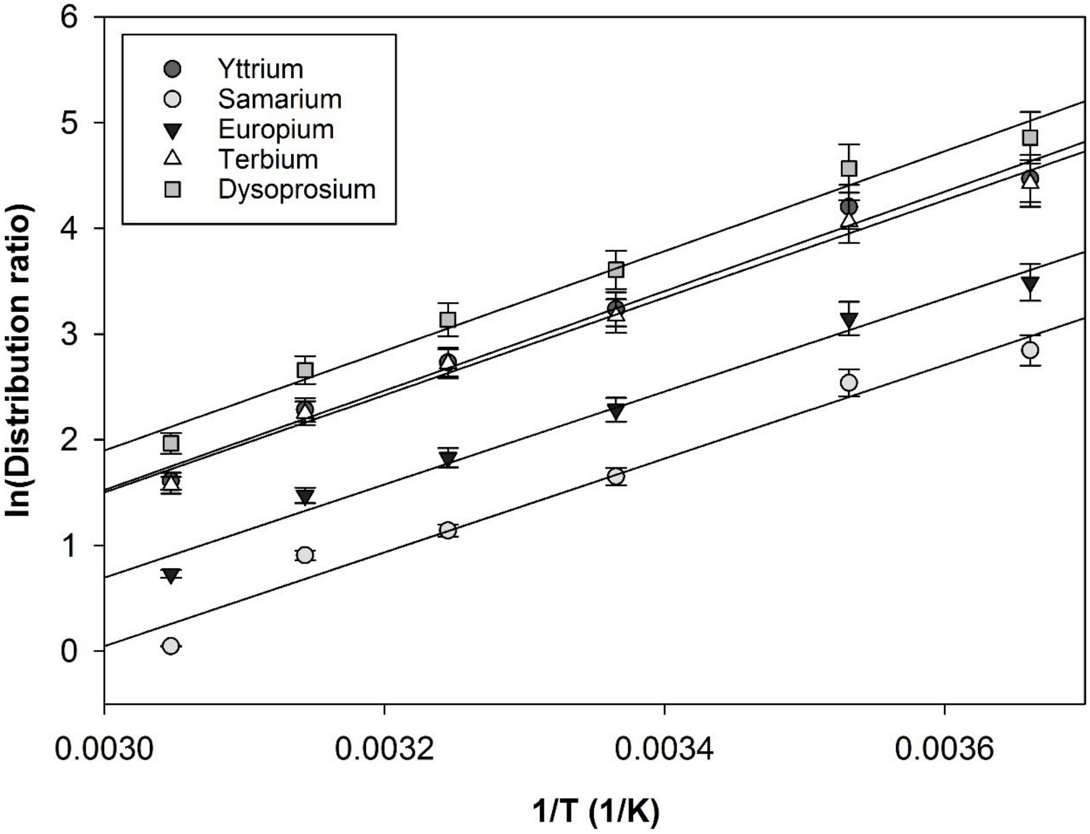

Figure 3-8. Effect of temperature on the extraction of several REEs from 8.0 M HCl with 0.010 M TBDGA in *1*-octanol.

Table 3-2. Enthalpy of reaction of the extraction of rare earth elements with TBDGA.

Element	Enthalpy of Reaction (kJ/mol)
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

Table 3-3. Comparison of the enthalpy of reaction for extraction of dysprosium with TBDGA into *1*-octanol to values obtained by Cui et al.[17] from various diluents.

Diluent	Enthalpy of reaction (kJ/mol)
Toluene	-32.93
n-octane	-27.57
CCl_4	-34.08
$CHCl_3$	-65.10
n-octane-*n*-octanol (V:V=7:3)	-61.27
1-octanol	-42.9 ± 2.6

3.3.8. *Effect of polarity of the diluent*

The effect of diluent on extraction of REEs from HCl with TBDGA was studied by Cui *et al.*[17] Their distribution ratios for the extraction of Dy with TBDGA from HCl for various diluents are depicted in Figure 3-9, along with our value for *1*-octanol. The observed trend is that D_{Dy} increases with diluent polarity. This suggests that the neutral metal complex itself has some polar character, perhaps not unexpected for the protonated DGA. However, toluene, encircled, is an outlier to this trend. Toluene is the only aromatic studied, and aromatics are common electron acceptors. The toluene interacts with electron donor oxygen groups in TBDGA. This likely causes for sequestration of TBDGA molecules, making less free-TBDGA available to complex with metals.

It can also be seen by comparing Figure 3-9 to Table 3-2 that the extraction efficiency is not strictly related to the enthalpy of reaction. This may indicate that entropy 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. There are 8-11 water molecules initially coordinated to the REE^{3+} metal in the aqueous phase,[26] and there are about 6 waters coordinated with the Cl^- anion.[27] These water molecules must be displaced for the 1-3 TBDGA molecules and the Cl^- anion to bind with the REE and form the $(REE)L_nCl_3$ complex. After the complex is formed, at the aqueous/organic interface the complex would have water molecules organized around it. As the complex transitions from the aqueous phase to the organic phase the water molecules will be released from an organized form. This displacement of water during complex formation and transition into organic phase translates to a more disordered system. Therefore, the change in entropy of the system would be positive.

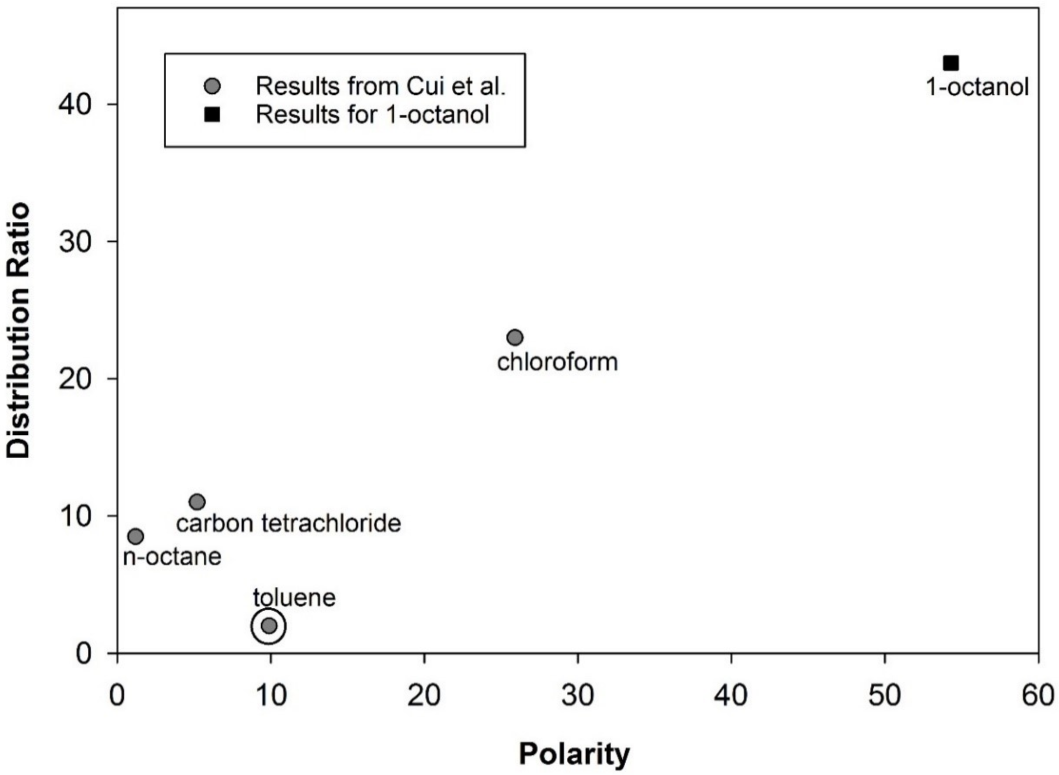

Figure 3-9**.** Distribution ratios for extraction of Dy from various diluent with TBDGA as reported by Cui et al[17] compared to extraction into *1*-octanol by polarity index (water = 100).[28]

3.3.9*. Extraction from phosphor dissolution*

The elemental composition of the Sigma-Aldrich trichromatic phosphor (wt%) examined in this work is given in Figure 3-10 (a). Approximately 35wt% of the phosphor is comprised of REEs. The majority of the inorganic phosphor matrix is comprised of O, Mg, Al, and Ba. As is shown in Figure 3-10 (b), of the 35wt% REEs found in the phosphor, Y is the most abundant (75wt%), with Ce, Eu, and Tb doped at smaller levels (11, 8, and 6wt%, respectively).

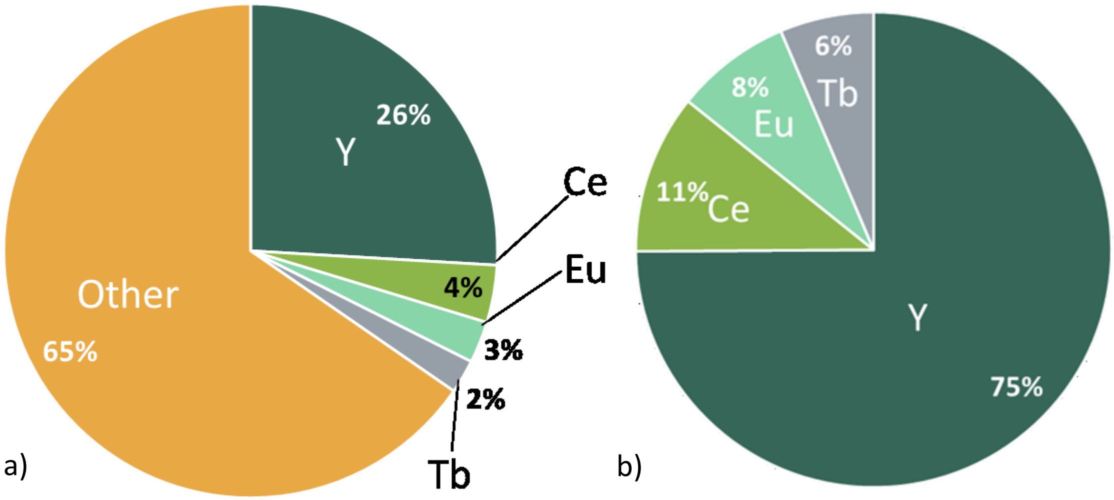

Figure 3-10. (a) Elemental composition of Sigma-Aldrich standard trichromatic phosphor by weight percent. (b) Weight percentages of the different REEs found in the Sigma-Aldrich trichromatic phosphor.

The recalcitrance of the phosphor was examined using 4 M and 8 M HCl at room temperature with a 48 hour contact. The results are summarized in Table 3-4. With both 4 M HCl and 8 M HCl minimal Ce (II) and Tb (III) were leached. Using 4 M HCl, 88.01% Y (III) and 64.10 % Eu (III)/(II) were leached; whereas contact with 8 M HCl, produced dissolution of 91.53% Y (III) and 65.53% Eu (III)/(II). The Y (III) and Eu (III)/(II) are contained in the $Y_2O_3:Eu^{3+}$ (red) and $BaMgAl_{10}O_{17}:Eu^{2+}$ (blue) phosphors. Ce and Tb are found in the $CeMgAl_{10}O_{17}:Tb^{3+}$ (green) phosphor. The green phosphor inorganic matrix is very recalcitrant and requires more extreme conditions to acid-leach the REEs.

Table 3-4. Percent REE leached by mass of REEs from Sigma-Aldrich trichromatic phosphor. 48 hour, ~23°C, 4 M HCl and 8 M HCl.

	Yttrium (%)	Cerium (%)	Europium (%)	Terbium (%)
4 M HCl Dissolution	88 ± 2	0.03 ± 0.01	64 ± 1	0.04 ± 0.01
8 M HCl Dissolution	91 ± 4	0.05 ± 0.01	66 ± 1	0.06 ± 0.01

Cerium, terbium, and barium were too low to detect in the aqueous phase. Distribution ratios of the 0.10 M TBDGA in *1*-octanol from the diluted phosphor leachates are shown in Figure 3-11. D_{REE}=2000 was assigned when the $[M]_a$ was less than the detection limits. Therefore, the *D* is infinite, but for the graphical display D was set to 2000. When extracting from phosphor solutions the Y (III) and the Eu (III) extract with both 8 M HCl and 5 M NaCl, 0.1 M HCl. However, the extraction efficiency of Y (III) does increase with 5 M NaCl. This was expected based on the previous extractions, Figure 3-6. While the D_Y is 1400 from HCl versus 2000 from NaCl, distribution ratios >99 are >99% extraction. Therefore, the difference between percent extraction at very high *D* values is minimal. Eu (III) extracts completely from both 8 M HCl and 5 M NaCl. From the extraction efficiency for the REEs examined in previous sections, it can be determined that Tb (III) would be extracted from the tri-chromatic phosphor in a chloride aqueous media if present in the leachate. The Mg shows no extraction from either solution.

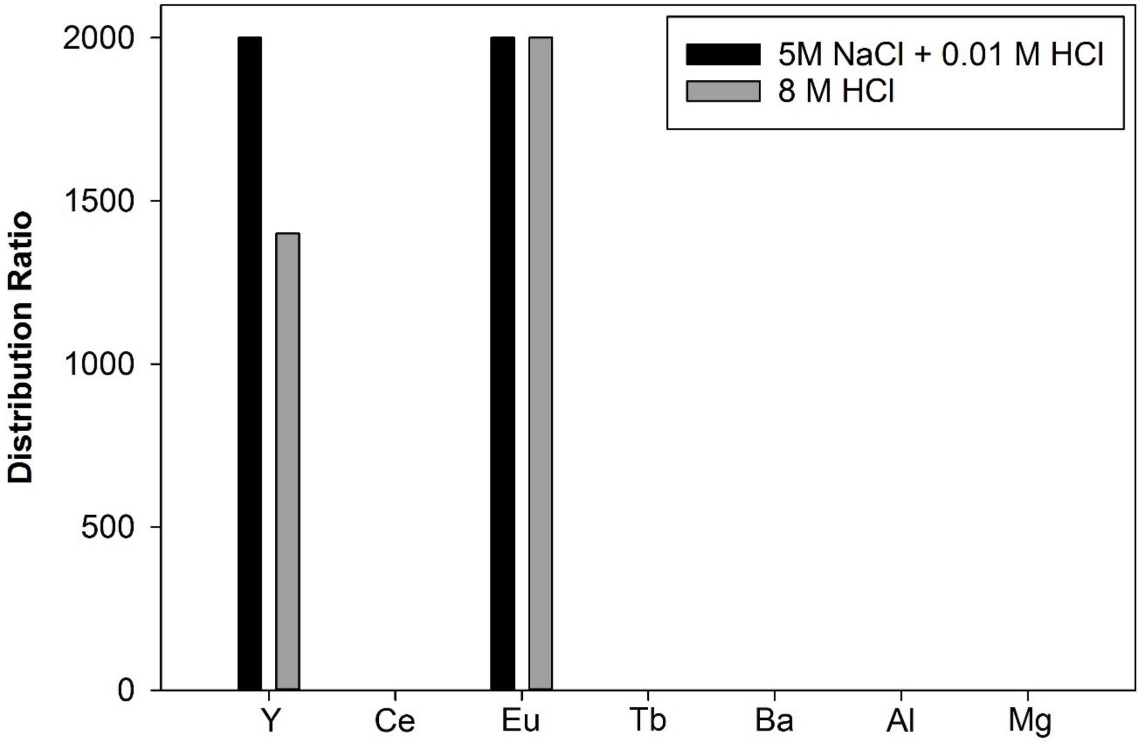

Figure 3-11. Distribution ratios based on extraction from diluted phosphor leachate in 8 M HCl and 5 M NaCl with 0.10 M TBDGA in *1*-octanol (TBDGA:M=5:1) at 23 °C.

3.3.10. *Extraction from magnet dissolution*

The composition by mass of the studied NaIB magnet material is shown in Figure 3-12. The magnet material primarily is composed of Fe. There is ~27% Nd (III), ~3% Pr (III), and ~1% Dy (III). The magnet also contains Ni, B, Al, and a small percentage of other metals. There was complete dissolution of the magnet material into 4 M and 8 M HCl at ~23 ˚C for 48 hours.

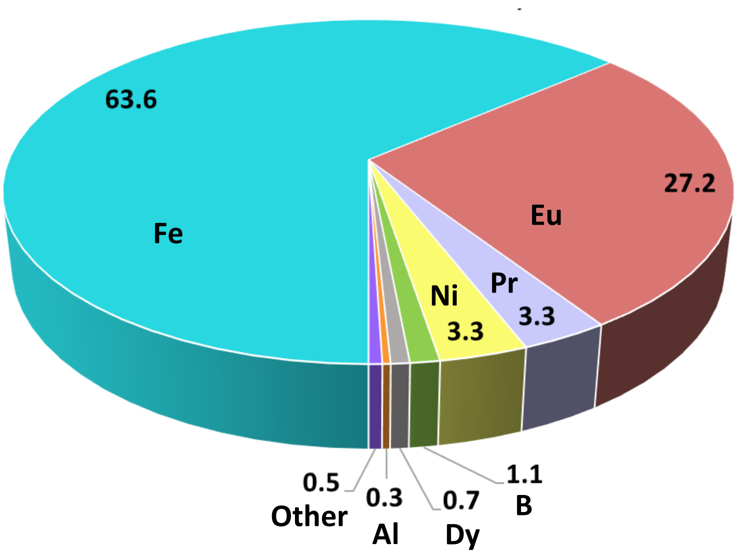

Figure 3-12. Composition of the studied NIB magnet by mass percentage.

D=300 was set at the maximum D_{REE} when the [$M^{3+}{}_a$] was less than the detection limits. The distribution ratios and the same values as percent extraction for the extraction of metals from 5 M NaCl and 8 M HCl with TBDGA are shown in Figure 3-13. The D_{Fe} dropped significantly when extracting from 5 M NaCl instead of HCl because the oxidation states of Fe would vary between (III) and (II) in different acidity media. The REEs (Pr (III), Nd (III), and Dy (III) has high extraction efficiency from both 8 M HCl and 5 M NaCl, but the extraction efficiency does increase from 5 M NaCl. Nickle does not extract from either 8 M HCl or 5 M NaCl.

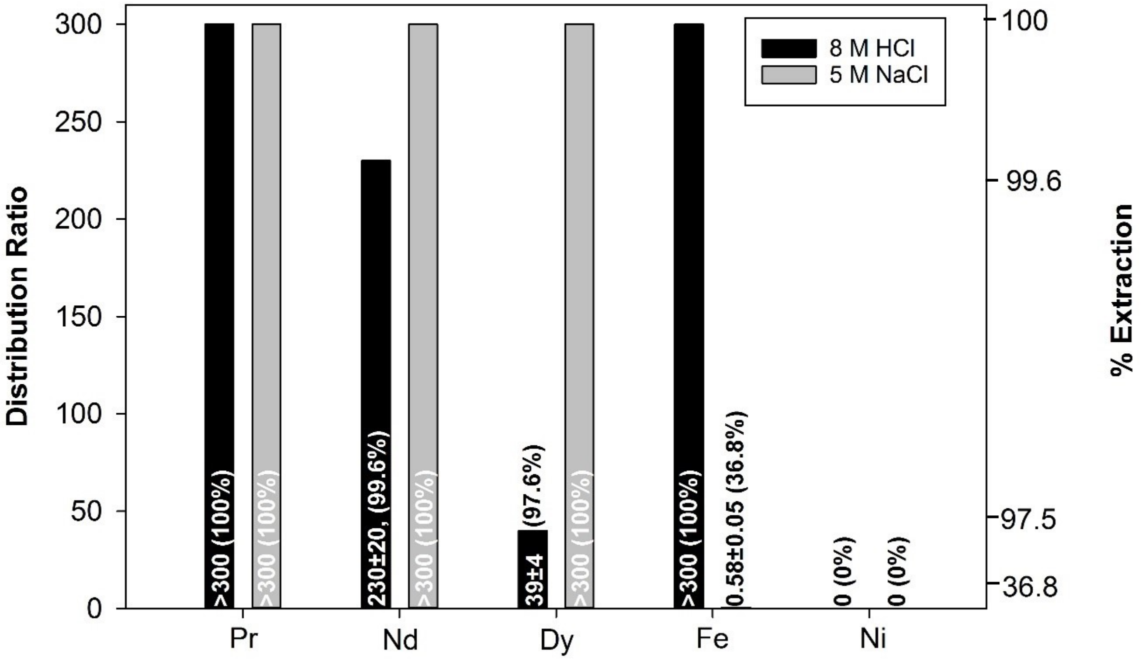

Figure 3-13. Distribution ratios and percent extractions based on extraction from diluted NIB magnet dissolution in 8 M HCl and 5 M NaCl with 0.10 M TBDGA in *1*-octanol (TBDGA:M=5:1) at 23 °C. Distribution Ratios are shown on the left axis and the percent extraction is shown on the right axis with the value in parenthesis.

3.4.Conclusions

Heavy and intermediate lanthanides and yttrium can be extracted from HCl solution using 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 protonation of the amide. When $[H^+]$ is decreased or removed by replacing HCl with NaCl to keep the Cl^- concentration constant, D_{REE} increases. As the $[Cl^-]$ increases D_{REE} increases due to the metal complex charge neutralization requirement. Lower temperatures are preferred for extraction due to the reaction being exothermic, and the $M(TBDGA)_nCl_3$ complexes therefore being heat labile. As temperature increases the distribution ratios consequently decrease, with almost no extraction occurring at about 65 ^oC. As the concentration of TBDGA is increased in the organic phase the distribution ratios increase. When comparing the diluent polarity effect found in this work with previous work it is seen that *1*-octanol provides very high extraction efficiency that is directly proportional to its polarity. When extracting REEs from phosphor leachate using TBDGA the Y (III) and Eu (III) almost completely extract. When extracting from NIB magnet dissolution the REEs exhibit >97% extraction from 8 M HCl, and there is a slight increase from 5 M NaCl. The percent extraction of Fe is ~100% from 8 M HCl, but the percent extraction decreases to ~38% from 5 M NaCl. The difference in percent extraction between REEs and Fe would allow for an efficient separation. This would be beneficial for a recycling process of NIB magnets.

3.5. References

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Chapter 4

Extraction of REEs from Chloride Media with TBDGA in Carbon Dioxide

4.1. Introduction

Rare earth elements (REEs) are important and essential for our modern world. REEs are the 15 lanthanides plus scandium and yttrium. Scandium and yttrium are included in the REEs due to their being found with the lanthanides during ore mining, and for having similar chemical properties as the lanthanides (only without the *f*-orbitals). Rare earth elements are used in micro-electronic devices (e.g. cell phones), magnets (used in wind turbines), lighting phosphors (e.g. fluorescent lighting; LEDs), solid-oxide fuel cells, catalysts, and advanced weapons systems.[1-4] Due to the widespread usage of the REEs there is high industrial demand, and the projected supply coming out of China cannot meet worldwide demand.[5] In 2010 China produced about 95% of the world supply of lanthanide ores and refined REE products.[6] China's monopoly on REEs allows it to dictate supply and export quotas as well as market price. While there are REE deposits in regions other than China, opening a mine in the United States requires significant financial investment,[7] a lengthy environmental assessment and permitting process (up to 10 years for the permitting process[8]), and additional time thereafter to actually build the mine and produce product. One way to expand the supply of REEs is through urban mining. Urban mining is "the systematic reuse of anthropogenic material from urban areas"[9]. Urban mining can be used to recycle REEs from end-of-life products. Through recycling, supply chain vulnerabilities can be minimized by narrowing the gap between REE supply and REE demand.

Current REE ore mining practices include thermal roasting of the ore followed by leaching the REEs from the roasted ore with HCl. Soluble, leached REEs are then removed from the acidic liquor using a ligand in a multi-stage solvent extraction process. The common ligands used in the REE mining industry are di-2-ethylhexyl-phosphoric acid (P204) and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (P507).[10-12] Traditional multi-stage solvent extraction results in organic solvent byproduct waste. Extraction and recovery of REEs from end-of-life products is very similar to recovery of REEs from ore in that strong mineral acid usage to dissolve REEs from the various matrices is the most feasible approach as has been evidenced by the majority of reports in literature where end-of-life products are concerned.[13-22]

In this study, solvent extraction using CO_2 as the main extracting solvent is examined. The purpose for exploring use of carbon dioxide is to replace the main organic solvent used in conventional solvent extraction processes (e.g., dodecane, hexane, Isopar, etc.) with a solvent that is less expensive, easier to recycle and recover, and which has considerably less negative environmental side-effect. Carbon dioxide can be used for separations and extractions in a variety of physical forms. The gas can be heated and compressed into the supercritical fluid phase and used to extract metals, or the gas can be condensed into a dense liquid phase. Whereas many literature reports can be found for supercritical fluid metal extraction, few authors report on use of liquid CO_2, and no reports are available where liquid CO_2 is used in combination with diglycolamide ligands for recovery of REEs from acidic chloride media. The pressures and temperatures at which CO_2 is found in either a gas, liquid, or a supercritical fluid phase can be observed in the CO_2 phase diagram, Figure 4-1.

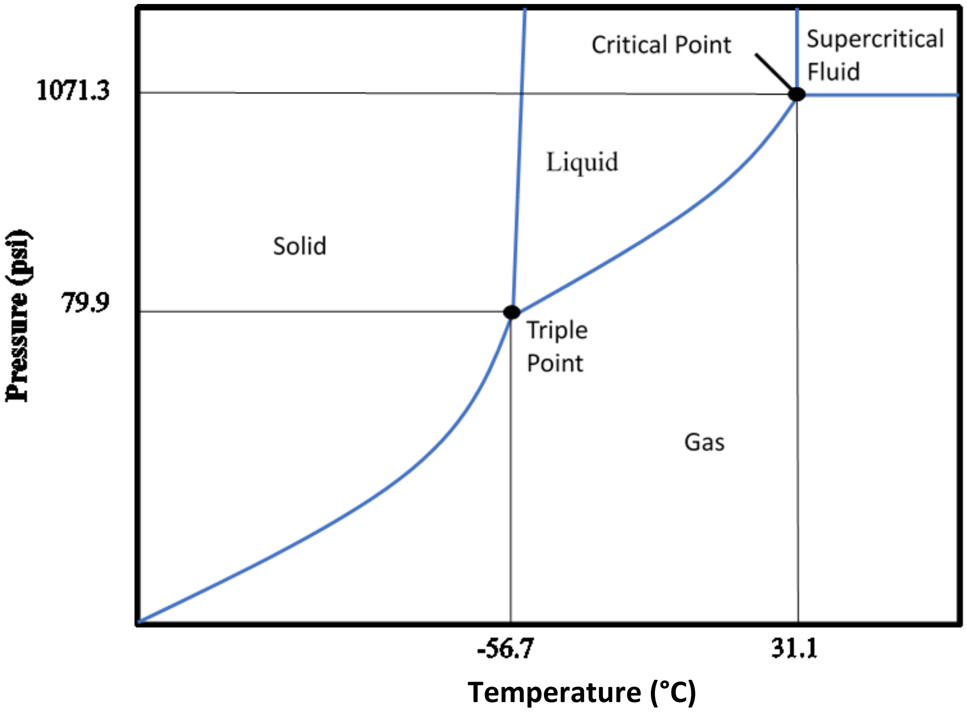

Figure 4-1. The phase diagram for carbon dioxide.

Carbon dioxide can be used as a diluent in varying applications; metal extraction[23-25], organic extraction[26], synthesis[27]. Carbon dioxide is considered to be a “green” alternative to traditional diluents because of its inherent waste-minimizing potential; it is recyclable and carbon-neutral in the environmental carbon cycle. Carbon dioxide is inert, inexpensive, can be easily reused, and is readily available in a pure form. Using CO_2 as a diluent minimizes the organic waste that is generated during solvent extraction. Metal ions are not soluble in CO_2. Thus, in order for solvent extraction of metal ions using CO_2 to occur the charge on the metal ion must be made neutral, the coordination requirements of the metal must be fulfilled, and the resulting metal-ligand complex must be CO_2 soluble.

A variety of chelating compounds can be used to complex metals which result in extractable metal-ligand complexes using CO_2 in either a supercritical or a liquid phase. Diglycolamides (DGAs) have attracted much study and attention recently for hydrometallurgical extraction and separation processes for actinides and the REEs. These ligands are composed of carbon, oxygen, and nitrogen, unlike traditional organophosphorus ligands such as tri-*n*-butyl phosphate (TBP) or the ligands used in the REE mining industry (P204 and P507). Diglycolamides are recyclable as well as completely incinerable. That property allows for decreased waste generated with a separation process. N,N,N',N'-tetrabutyl diglycolamide (TBDGA), Figure 4-2, is a DGA with shorter carbon chains than the more commonly researched diglycolamides such as tetraoctyl diglycolamide (TODGA). TBDGA has been shown to be effective at extraction of lanthanides from nitric acid media.[28-29] It has also been shown that TBDGA has potential for lanthanide extraction from hydrochloric acid media into a variety of organic solvents such as *1*-octanol, chloroform, *n*-octane, ect.[30-31]

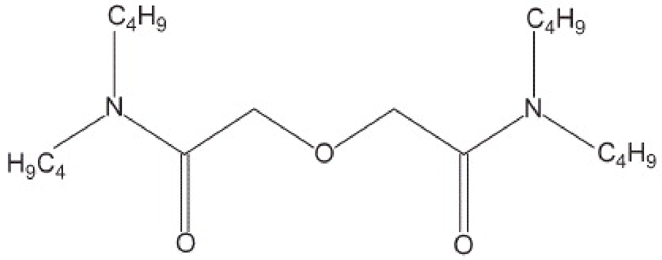

Figure 4-2. The structure of N,N,N',N'-tetrabutyl diglycolamide.

TBDGA has been studied for extraction of REEs in CO_2 previously. Tian *et al.* has studied the extraction of REEs with a TBDGA/HNO_3 adduct in supercritical CO_2.[32] They found that TBDGA/HNO_3 adduct could not extract Nd or Eu. However, when acetone was introduced to the CO_2 as a modifier about 85% and 90% of Nd (III) and Eu (III), respectively, were extracted in a dynamic extraction. Using acetone as a diluent modifier makes the diluent more polar, allowing for more polar metal-ligand complexes to have increased solubility in CO_2.

Extraction of REEs from HCl with TBDGA in CO_2 has not previously been studied, and no studies on the extraction of metals with a liquid CO_2 system have been published. This chapter examines and optimizes this extraction for pressure, temperature, mole percent *1*-octanol as a modifier, varying [TBDGA], and varying [metal]. This research will be beneficial to the development of a more environmentally friendly, more efficient method of extracting REEs from end-of-life products.

4.2. Materials and Methods

The following reagents from Sigma-Aldrich (Sigma-Aldrich, St. Louis, MO) were used as-received: Europium (III) Chloride hexahydrate (99.9%), *1*-octanol (≥99%), hydrochloric acid (ACS grade), nitric acid (trace-select grade), and hydrogen peroxide (trace-select grade). Methanol (ACS grade) was used as received from Fisher Scientific (Fisher Scientific, Waltham, MA). Liquid carbon dioxide was used as received from Norco Inc. (Boise, ID). N,N,N',N'-tetrabutyl diglycolamide (95%) was used as-received from Tractus Chemical (Tractus Chemical, London, England). All water used was purified to a resistivity of at least 18 MΩ-cm

All extractions were performed in the system shown in Figure 4-3. The system downstream of the pumps is constructed of Hastelloy C276 with the exception of the pressure transducer and the over-pressure relief valve. All pumps are controlled with a Teledyne ISCO D-Series controller (Teledyne, Lincoln, NE). Both CO_2 pumps are Teledyne ISCO model 500 HP syringe pumps and the ligand pump is a Teledyne ISCO model 260 D syringe pump. The pressure transducer is a HEISE digital pressure gauge (Ashcroft Inc., Stratford, CT). All valves are Autoclave Engineers (Erie, PA) and all tubing was received from Valvo Instruments Co. Inc. (Houston, TX). The equilibrium reaction cell is 54.35 mL and the sample cell is 64.47 mL. An example of the cells used in this work is shown in Figure 4-4. Both cells were machined at Idaho National Laboratory. The trap solution was 20 mL of *1*-octanol. For all extractions at about 23 °C the cells were kept uninsulated at room temperature and were not heated or cooled. For all extractions above 23 °C the temperature was measured using an RTD thermocouple, and controlled using a process control assembly comprised of Omega Engineering PID controllers, variacs, and Omega Engineering cartridge heaters. Cells were also insulated during runs above 23 °C. For extractions at 2 °C an ice bath was used to keep the equilibrium cell and the reaction cell at approximately 2 °C. After all extractions, a methanol flush was performed by filling the cells with methanol and running 3500 psi CO_2 through the system until no methanol remained in the cells.

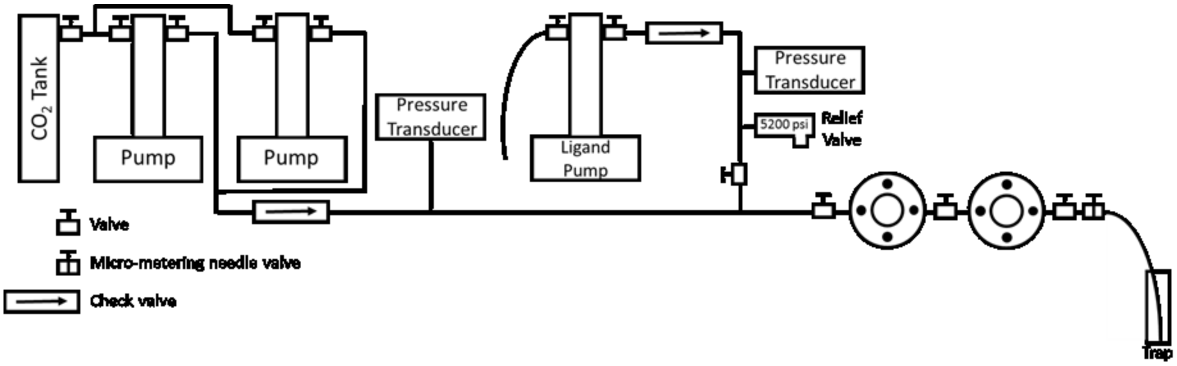

Figure 4-3. Diagram of the system used for CO_2 extractions.

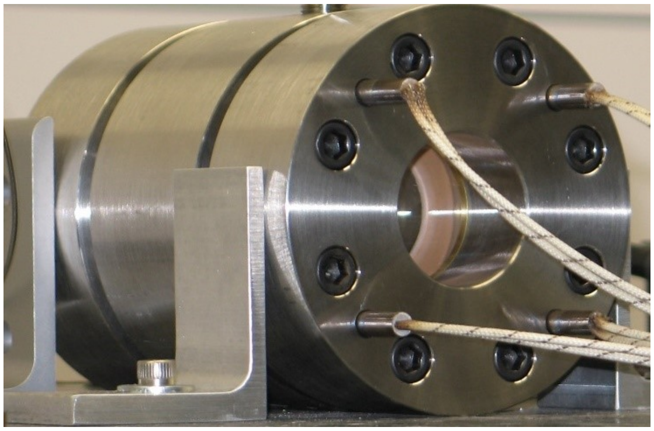

Figure 4-4. Example of reaction cell or equilibrium cell used.

The basic extraction procedure is as follows: Ten mL of an aqueous solution containing europium (III) chloride was pipetted into the sample cell with the upstream tubing dipping into the liquid. The solution was stirred continuously with a stir bar. The reaction cell and equilibrium cell were kept at a specific temperature. Liquid 10 °C CO_2 was pumped into the system, shown in Figure 4-3, and the system was kept at a constant pressure. A micro-metering needle valve heated to ~100 °C was used to keep the CO_2 flowrate at about 5.0 mL/min at the pump. Once the CO_2 flow rate was constant a *1*-octanol solution containing TBDGA was pumped into the system for 60 minutes. After 60 minutes the flow of *1*-octanol and TBDGA was stopped. The CO_2 continued to flush the system for 90 minutes. After 90 minutes the flow of CO_2 was stopped, and the system was depressurized. The contents remaining in the cell were collected and a water rinse of the cell was collected with the original sample. Extractions were performed in duplicate.

All samples were digested due to organics remaining in the cell. This digestion followed the EPA method 3052: Microwave Assisted Acid Digestion of Siliceous and Organically based Matrices. Some changes were made to the procedure to adapt it for current use. The samples were shaken before 0.500 mL was removed and put into a Teflon tube. To the sample 9.0 mL of concentrated nitric acid was added slowly. Drop-wise 1.0 mL of hydrogen peroxide was added. To avoid excessive pressure buildup during microwaving the samples a pre-reaction step was performed. The sample was heated in a hot water bath at about 90 °C for 30 minutes. Every 5 minutes 0.5 mL of hydrogen peroxide was added to the samples drop-wise. The samples were then loaded into a MARS CEM Microwave (CEM, Mathews, NC). The pre-programed setting 3052H-HP500 was used. After digestion the sample was removed and the tubes were rinsed with 10% HNO_3. The rinse was collected. The samples and rinses were diluted to 25.0 mL in a class A volumetric flask. This process was performed in triplicate. All sample analyses were performed on an Agilent model 7900 ICP-MS (Agilent, Santa Clara, CA).

4.2.1. *Phase equilibrium of 1-octanol at room temperature liquid CO_2*

Three mL of *1*-octanol was added to a 54.35 mL Hastelloy C-276 reaction cell with view window at about 23 °C. $CO_{2(l)}$ was pumped into the cell. The pressure at which there visibly was only one phase in the cell was recorded. This was repeated for 4 mL, 8 mL, 12 mL, and 16 mL of *1*-octanol in duplicate.

4.2.2. *Extraction of Eu from 8 M HCl varying mole percent 1-octanol*

The extraction procedure outlined above was followed. The sample was 1000 ppm europium in 8 M HCl. The pressure was kept constant at 5000 psi, and the temperature for the equilibrium and extraction cell was 23 °C. The mole ratio of TBDGA to Eu was kept at 5:1. The mole percent *1*-octanol was varied from 0.5 mol% to 3 mol%. The [TBDGA] and the flow rate of the *1*-octanol TBDGA solution for each mole percent studied is shown in Table 4-1.

Table 4-1. Mole percent solution and flowrates for the varying mole percent *1*-octanol.

Mole percent *1*-octanol in CO_2	[TBDGA] in *1*-octanol solution (M)	Flow rate of the *1*-octanol TBDGA solution (mL/min)
0.5	0.072	0.077
1	0.036	0.153
2	0.018	0.307
3	0.012	0.460

4.2.3. *Extraction of Eu from 8 M HCl varying temperature*

The extraction procedure above was followed with the temperature of the equilibrium and reaction cell being varied from 2 °C to 50 °C. The sample was 1000 ppm Eu in 8 M HCl. The pressure was kept constant at 5000 psi. The mole percent *1*-octanol was 2 %, and the 2 % *1*-octanol and TBDGA solution conditions are shown in Table 4-1. The temperature tested were 2 °C, 23 °C, 40 °C, and 50 °C. The equilibrium cell and the reaction cell were kept at about 2 °C with an ice bath, and heated to 40 °C and 50 °C with heating rods and insulation around the cells.

4.2.4. *Extraction of Eu in 8 M HCl varying pressure*

The extraction procedure above was followed, but the pressure was varied from 2000 psi to 5000 psi. The sample was 1000 ppm Eu in 8 M HCl. The temperature was kept constant at 23 °C, and the percent mole *1*-octanol was 2 %. The conditions of the TBDGA in *1*-octanol solution are shown in Table 4-1. Pressures tested were 2000 psi, 3000 psi, 3500 psi, 4000 psi, and 5000 psi.

4.2.5. *Extraction with varying [Eu]*

The extraction procedure above was followed, but the [Eu] in the sample was varied from 1000 ppm to 50,000 ppm in 8 M HCl. The pressure and temperature were kept constant at 5000 psi and 23 °C respectively. The mole percentage of *1*-octanol was 2 %. The conditions of the TBDGA in *1*-octanol solution are shown in Table 4-1. The mole ratio Eu:TBDGA and the [Eu] in each sample tested is shown in Table 4-2.

Table 4-2. Eu solutions, [Eu]:[TBDGA]

Eu:TBDGA mole ratio	Eu solution in 8 M HCl (ppm)
0.2	1,000
1	5,000
5	25,000
10	50,000

4.2.6. *Extraction of Eu from 8 M HCl with varying [TBDGA]*

The extraction procedure above was followed, but the [TBDGA] in the TBDA was varied from 1000 ppm to 50,000 ppm in 8 M HCl. The pressure and temperature were kept constant at 5000 psi and 23 °C respectively. The mole percentage *1*-octanol was 2 %. The flow rate of the *1*-octanol was 0.3067 mL/min. The ratio of mole TBDGA:Eu and the [TBDGA] for each test is shown in Table 4-3.

Table 4-3. TBDGA solutions, [Eu]:[TBDGA]

TBDGA:Eu mole ratio	[TBDGA] in *1*-octanol (M)
1	0.00281
0.4	0.00701
0.2	0.0140
0.1	0.0281

4.2.7. *Extraction of Eu from varying [HCl] and [Cl$^-$] solutions*

The extraction procedure above was followed, but the [HCl] and [Cl$^-$] of the solution were varied. All samples contained 1000 ppm Eu. The pressure and temperature were kept constant at 5000 psi and 23 °C respectively. The mole percentage *1*-octanol was 0.5 %. The conditions of the TBDGA in *1*-octanol solution are shown in Table 4-1. The solutions tested were: 5 M NaCl, 5 M HCl, 6 M HCl, 7 M HCl, 8 M HCl, 10 HCl, and 11 M HCl.

4.3. Results and Discussion

No Eu was extracted from 8 M HCl with TBDGA in CO_2. Similar results were seen by Tian *et al.* with a nitric acid/TBDGA adduct.[32] Tian used acetone as a modifier and saw improved extraction of Nd/TBDGA and Eu/TBDGA complexes. Both acetone and methanol modifiers were tried in this study, but minimal Eu/TBDGA extraction was observed with both of those modifiers. While acetone and methanol are common modifiers for CO_2 extraction, they both have low partition-coefficients between the aqueous phase and the CO_2 phase.[22] Therefore, as expected, neither acetone nor methanol work well as modifiers when aqueous solutions are used with CO_2 as the extracting solvent. *1*-octanol is a well-known diluent that has commonly been used for liquid-liquid solvent extraction. In this study, improved extraction of Eu/TBDGA complexes was observed with *1*-octanol as a co-solvent when compared against other modifiers previously studied[30]. CO_2 modified with *1*-octanol was used for all extractions conducted in this chapter for the intended purpose of modifying the polarity of the CO_2 and improving Eu/TBDGA complex solubility.

4.3.1. *Phase equilibria of 1-octanol in CO_2*

The phase equilibria of *1*-octanol in $CO_{2(l)}$ at 23 ^{o}C was determined by standard visual practices. As the $CO_{2(l)}$ was introduced into the cell the pressure increased. As the pressure increased the liquid *1*-octanol phase mixes with CO_2, expands, appeared to become less viscous, breaks into smaller droplets, and then forms into a single, homogenous phase. The liquid droplets of *1*-octanol could visually be seen to dissolve into the $CO_{2(l)}$ as pressure increased. At about 1300 psi the density of the *1*-octanol and the $CO_{2(l)}$ were approximately equal. As the pressure increased the density of $CO_{2(l)}$ increased to be greater than the density of the *1*-octanol. The pressure at which a single, homogenous phase appeared was determined. Each stage is shown in Figure 4-5. Figure 4-6 provides a graphic depiction of the phase equilibria given as the mole percent *1*-octanol varies from about 1.8mol% to 8.6mol%. The graphical region above the phase line indicates pressures at which the *1*-octanol/$CO_{2(l)}$ system is single phase; the region below the line indicates pressures at which the system is comprised of two liquid phases.

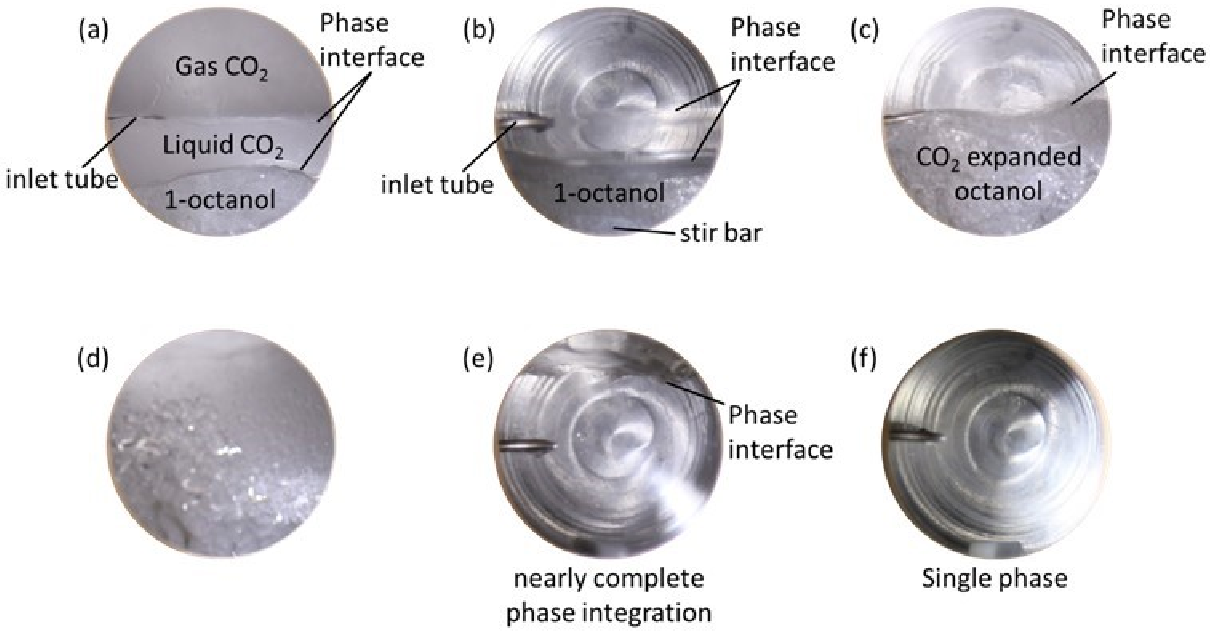

Figure 4-5. Phase equilibria of *1*-octanol with CO_2 as the pressure increases.

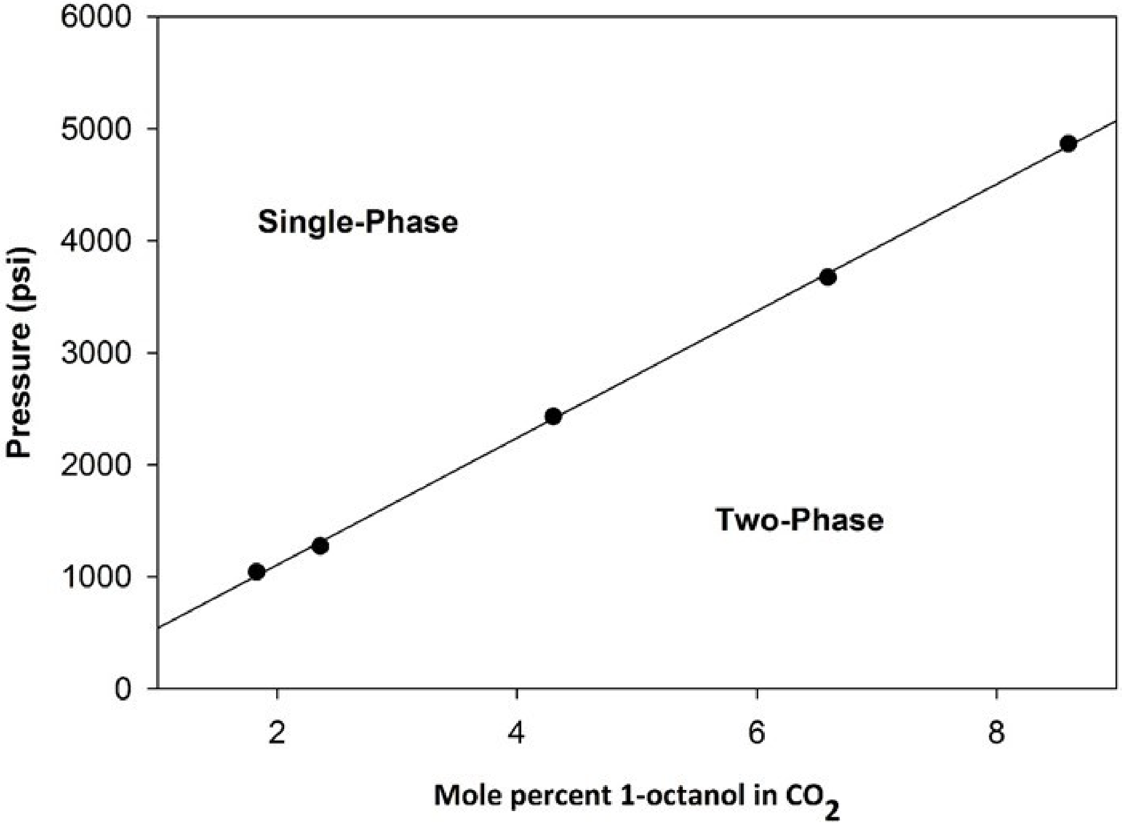

Figure 4-6. Phase equilibria of *1*-octanol with liquid $CO_{2(l)}$ at 23 °C.

4.3.2. *Effect of 1-Octanol Concentration on Eu Extraction Efficiency from Aqueous HCl Solution.*

The percent extraction of Eu from 8 M HCl with TBDGA in $CO_{2(l)}$ as a function of *1*-octanol concentration is shown in Figure 4-7. In this experiment the Eu originates as a 1000 ppm ionic form dissolved into 8 M HCl. A *1*-octanol solution containing TBDGA was mixed with CO_2 solvent and that mixture was then bubbled through the aqueous, acidic phase in the cell. The concentrations and flow rates of *1*-octanol/TBDGA solution for each experiment are given in Table 4-1. Pressure was kept at 5000 psi; temperature was kept at 23 °C; and vigorous phase mixing was applied using a magnetic stir bar during both the 60 minute extraction state and the 90 minute CO_2 flush stage of each run. As the mole percent *1*-octanol in CO_2 increased from 0.5 mol% to 3.0 mol% the extraction efficiency of the Eu-TBDGA complex into CO_2 decreased. As the mole percent *1*-octanol increased it becomes visually apparent that *1*-octanol partitions into the aqueous HCl phase and is not removed with the CO_2, both during the extraction and during the follow on 90 minute CO_2 flush cycle. As the experiment progresses the amount of organic (unbound TBDGA, Eu-TBDGA complex, and *1*-octanol) partitioned into the aqueous HCl phase increases, indicating the limit of the CO_2 solvent's ability to extract *1*-octanol/TBDGA out from the aqueous HCl phase occurs at fairly low levels of *1*-octanol/TBDGA dissolved into CO_2. At 5000 psi and 1 mol% *1*-octanol the aqueous HCl solution remaining in the cell is cloudy and contains visible unextracted organic, even after a 90 minute flush. The TBDGA-Eu complex appears to preferentially partition to the *1*-octanol phase remaining in the cell versus the $CO_{2(l)}$ phase.

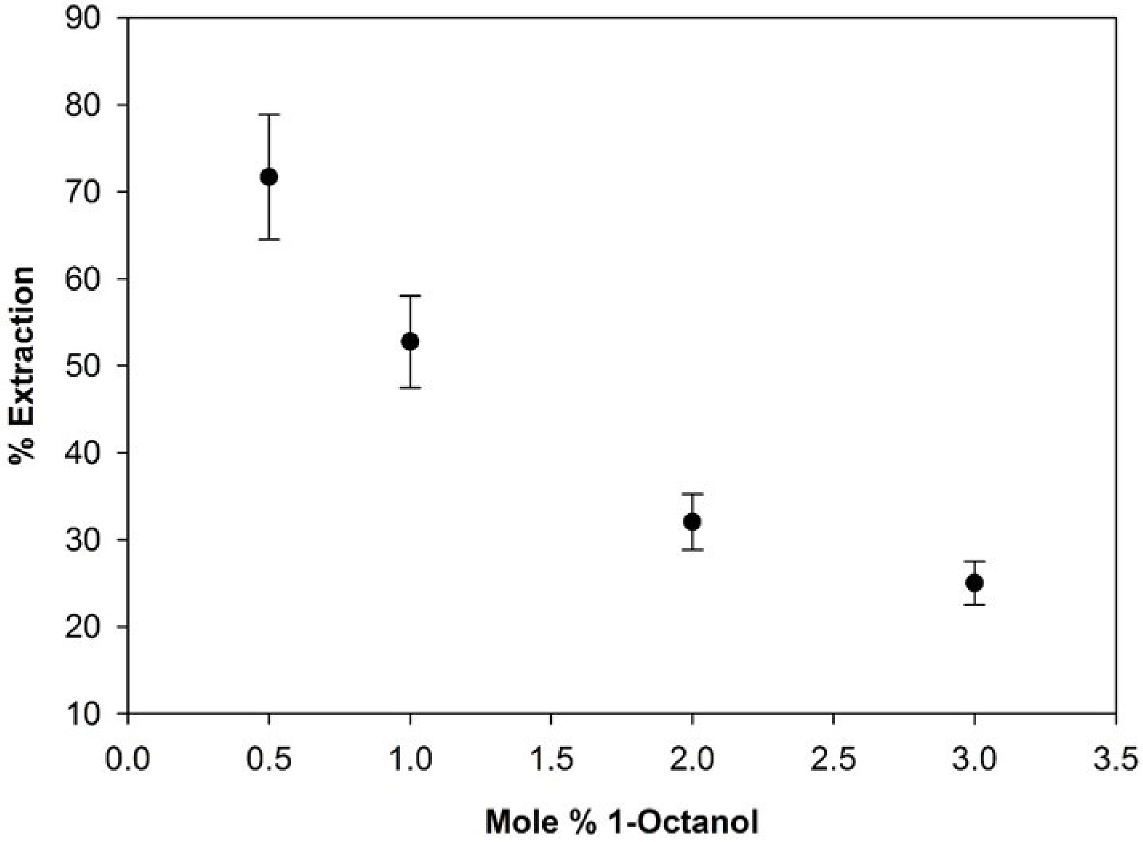

Figure 4-7. The percent extraction Eu from 10 mL 1000 ppm Eu in 8 M HCl with 0.018 M TBDGA at 23 °C and 5000 psi in $CO_{2(l)}$ modified with varied mole percent *1*-octanol.

4.3.3. *The Effect of Temperature on 1-Octanol/TBDGA-Mediated Extraction of Eu from HCl Solution*

The percent extraction of Eu from 8 M HCl using TBDGA in *1*-octanol modified CO_2 as a function of temperature ranging from 2 °C to 50 °C is shown in Figure 4-8. This series of dynamic extraction experiments was conducted using 1000 ppm Eu in 8 M HCl. A 2 mol% *1*-octanol/TBDGA mixture was added to CO_2 solvent, and the mixture was bubbled through the acidic, aqueous phase at temperatures ranging from 2 °C to 50 °C at 5000 psi with vigorous mixing. From 2 °C to 23 °C there is an increase in extraction efficiency. The increase is attributed to solubility differences of *1*-octanol into CO_2 vs. solubility of *1*-octanol into 8 M

HCl at those temperatures and is not a function of complex stability or reaction kinetic. After 60 minutes of extraction at 2 °C it was noted there was organic remaining partitioned to the aqueous phase. That organic remained even after the 90 minute CO_2 flush. At 23 °C there was very little organic partitioned to the aqueous phase. When the extraction temperature was increased to >40 °C there is a significant drop in extraction; transitioning from 75% Eu extracted at 23 °C to approximately 13% Eu extracted at 40 °C. At temperatures higher than 50 °C there was little to no organic remaining in the aqueous phase, but due to thermodynamic instability of the Eu-TBDGA metal-ligand complex very little Eu was extracted out of the HCl. It was previously shown that the complexation between TBDGA and lanthanides is exothermic in chloride media.[30]

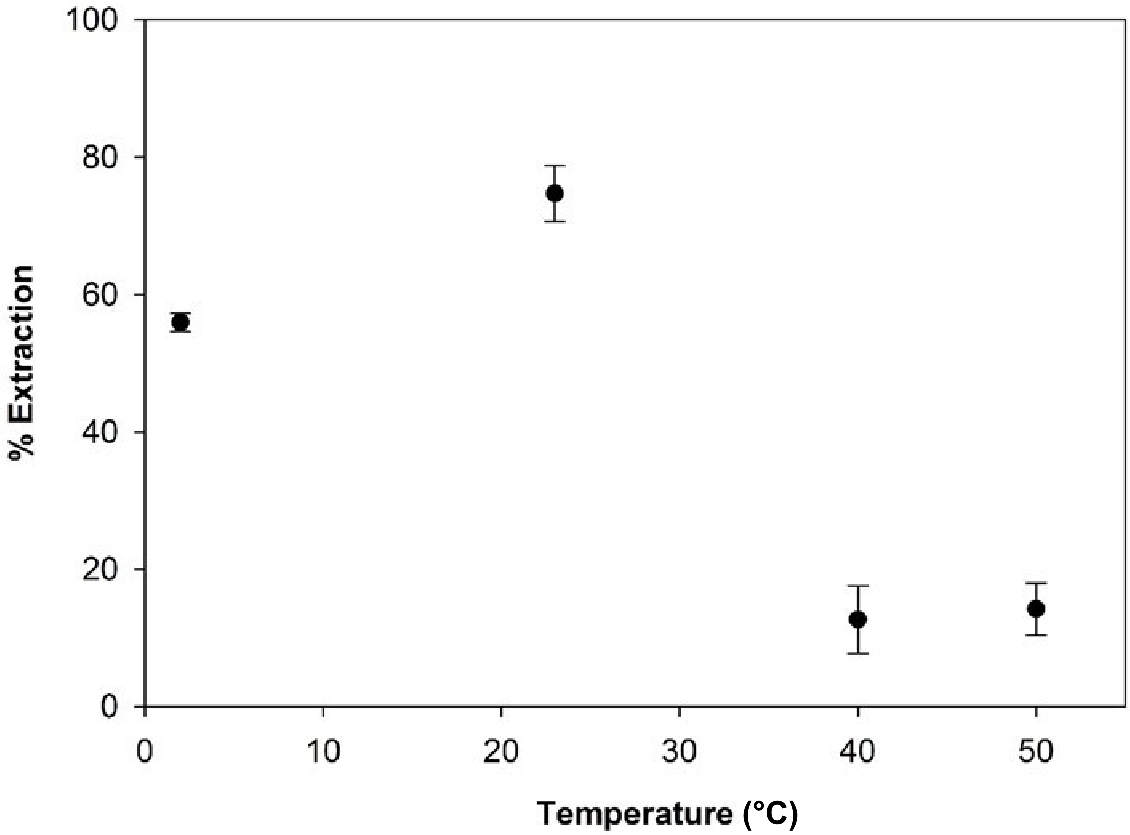

Figure 4-8. The percent extraction of Eu with TBDGA in CO_2 modified with 2 mol% *1*-octanol as the temperature is varied from 2 °C – 50 °C at 5000 psi.

4.3.4. *The Effect of Pressure on Eu Extraction from HCl Media Using 1-Octanol/TBDGA in CO_2*

The effects of varying the pressure was studied. The extractions were performed on 1000 ppm Eu in 8 M HCl. The dynamic extractions were performed by bubbling $CO_{2(l)}$ containing TBDGA and 2mol% *1*-octanol through the aqueous phase with mixing at 23 °C. Data showing percent extraction of Eu from 8 M HCL using the *1*-octanol/TBDGA system in $CO_{2(l)}$ as the pressure varies from 2000 psi to 5000 psi at approximately 23 °C are given in Figure 4-9. As the pressure increased from 2000 psi to 3500 psi the percent extraction of Eu also increased. As the pressure increased from 3500 psi to 5000 psi the percent extraction of Eu decreases. There is a maximum in the extraction at 3500 psi with a percent Eu extraction of 75%. Although there is higher solubility of *1*-octanol at higher pressures, as shown in Figure 4-6, less organic is remaining in the cell at 3500 psi than at 5000 psi. It is hypothesized this behavior is attributed to the increased solubility of water into CO_2 at higher pressures. King et al.[33] showed that as the pressure increases the solubility of water into the CO_2 also increases. As the solubility of H_2O in the $CO_{2(l)}$ increases the solubility of *1*-octanol and the TBDGA-Eu complex in the $CO_{2(l)}$ would decrease. The effect of water was investigated later in this chapter. This would lead to lower recovery of Eu at higher pressures. However, there may be an increase until 3500 psi due to the extraction requiring a high solubility of *1*-octanol in the $CO_{2(l)}$.

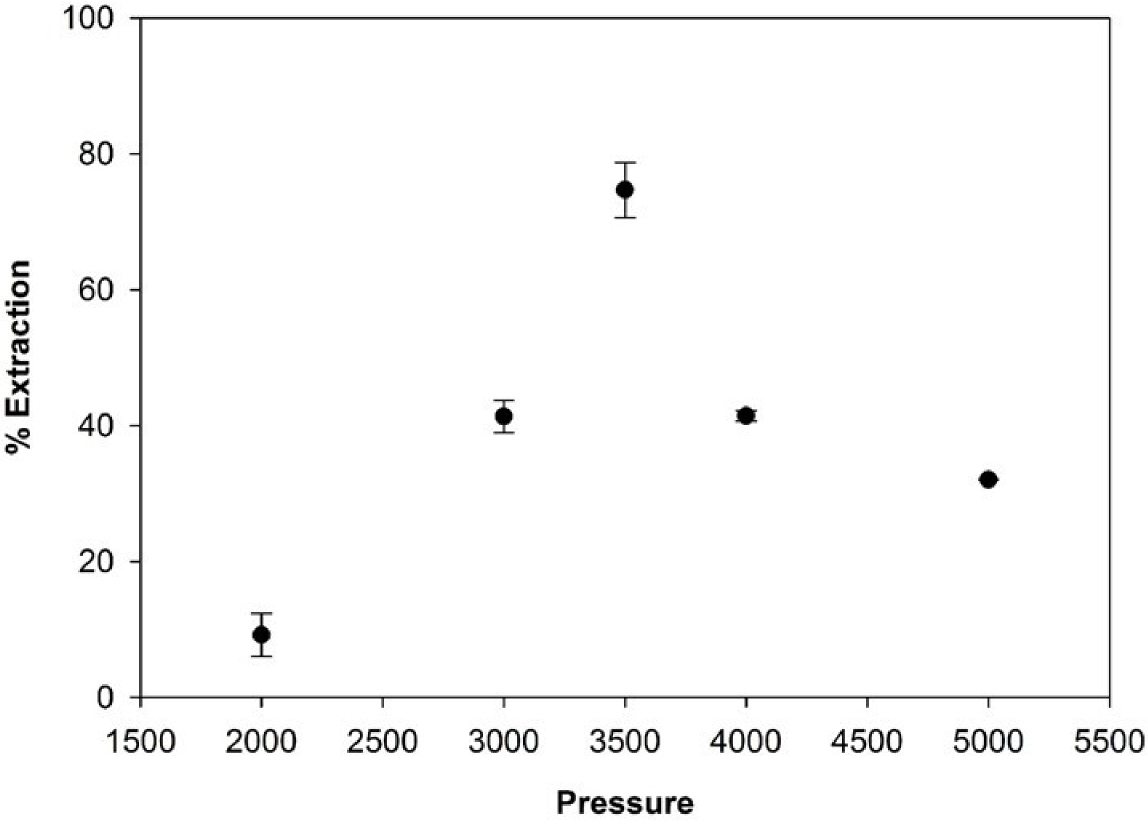

Figure 4-9. The percent extraction of Eu from 8 M HCl with TBDGA in $CO_{2(l)}$ modified with 2 mol% *1*-octanol as a function of pressure at 23°C.

4.3.5. *The Effect of Initial [Eu] In the HCl Phase on Extraction Efficiency*

In this series of dynamic extraction experiments the concentration of Eu initially present in the 8 M HCl is varied from 1,000 ppm to 50,000 ppm. CO_2 modified with 2 mol% 1-octanol/TBDGA is bubbled through the HCl phase for 60 minutes with vigorous stirring to achieve effective phase mixing. Each dynamic extraction is conducted at 23 °C and 5000 psi followed by a 90 minute CO_2 flush afterwards. Percent Eu extraction as a function of [Eu]:[TBDGA] mole ratio is shown in Figure 4-10. At high starting concentrations of Eu in the HCl phase the molar ratio of Eu to incoming TBDGA ligand is ~10:1; there is 10X more Eu than there is ligand. In that condition nearly all of the ligand is being pulled from the incoming solvent and complexing the large pool of excess Eu present in the HCl phase. As such, very little complete, charge-neutral, CO_2-soluble TBDGA-Eu complexes are being made in the 60 minute run, resulting in low extraction efficiency. At a [Eu]:[TBDGA] molar ratio of 0.2 (i.e., 5X more TBDGA than Eu) the extraction efficiency is at its highest for the given conditions. These results indicate that regardless the starting concentration of Eu in the aqueous phase an optimum ratio of TBDGA to metal is required for the formation of complete metal-ligand complexes which leads to efficient extraction.

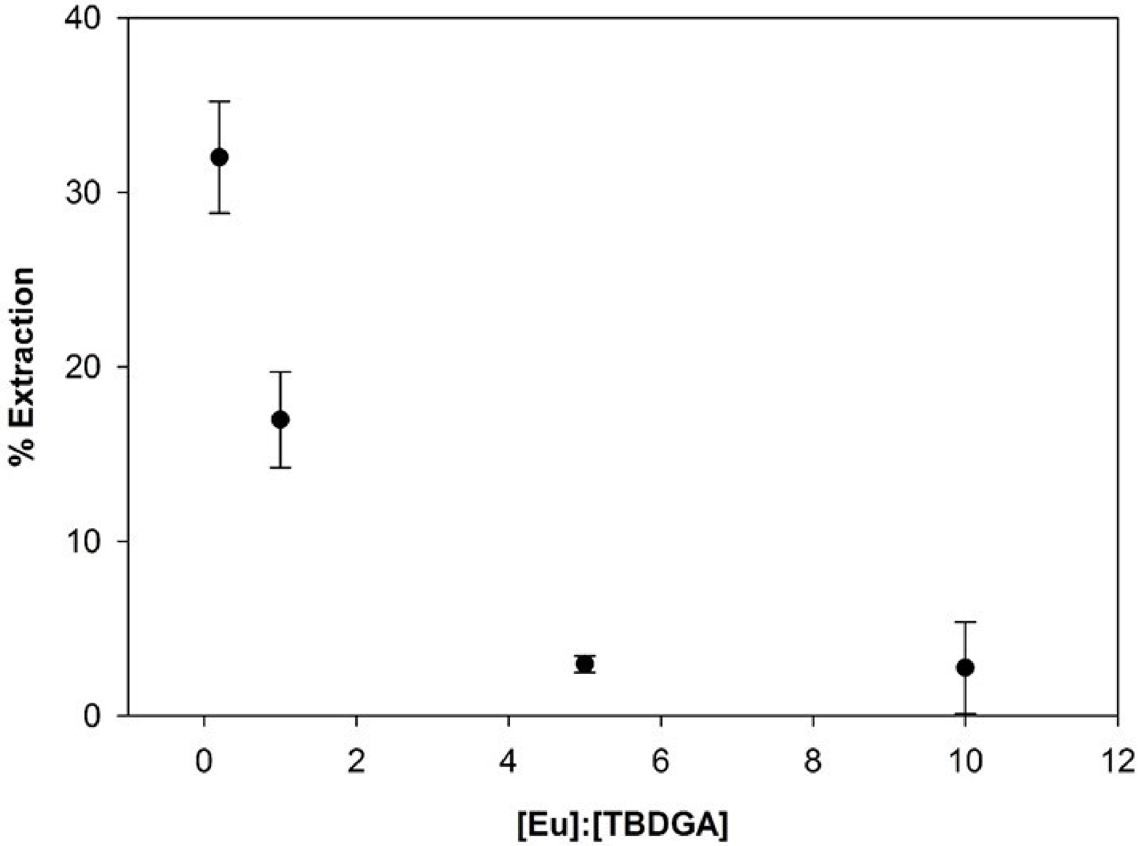

Figure 4-10. The percent extraction Eu from 8 M HCl with TBDGA in $CO_{2(l)}$ modified with 2 mol% *1*-octanol at 5000 psi and 23 °C where the starting [Eu] in the HCl phase is varied.

4.3.6. *Effect of [TBDGA] on Eu Extraction Efficiency from 8 M HCl*

This series of dynamic extractions was accomplished using a 2 mol% *1*-octanol modified CO_2 solvent that was bubbled through 8 M HCl at 23 C and 5000 psi for 60 minutes followed by a 90 minute CO_2 flush. The initial concentration of Eu in the 8 M HCl was kept at a fixed value for each experiment, but the incoming concentration of TBDGA in the modified CO_2 solvent was varied from 1000 ppm to 50,000 ppm. Data in Figure 4-11 show that as the molar ratio of Eu:TBDGA goes from 0.1 to 1 (i.e., ligand-rich conditions to equal molar amounts of ligand to metal) the Eu extraction efficiency drops significantly. As TBDGA ligand enters the HCl phase it complexes with Eu and forms TBDGA-Eu complexes. As intact complexes are made which are charge-neutral those complex are CO_2 soluble and dissolve into the CO_2 phase and are swept out of the contact vessel. A larger amount of TBDGA would therefore result in more CO_2-soluble complexes.

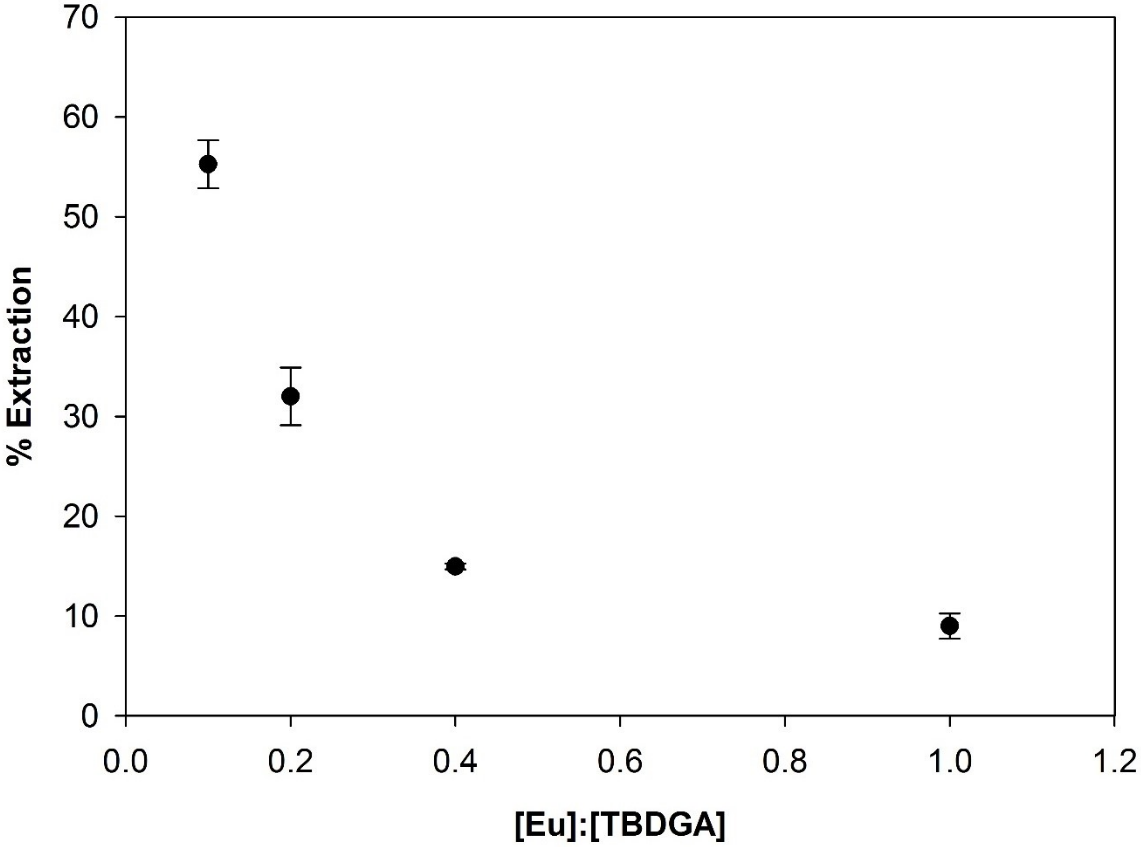

Figure 4-11. The percent extraction of Eu 8 M HCl with varied TBDGA in $CO_{2(l)}$ modified with 2 mol% *1*-octanol at 5000 psi and 23 °C.

4.3.7. *Effect of Varying [HCl] and [H$^+$] on Eu Extraction Efficiency from Chloride Solution*

Although previous extractions were performed from 8 M HCl, varying the [HCl] or extracting from NaCl could impact the extraction efficiency as was observed with the *1*-octanol system. The effect of [HCl] and [H$^+$] on the extraction of Eu was studied at the optimum conditions of 23 °C, 3500 psi, and 0.5 mol% 1-octanol. This was performed as a dynamic extraction for 60 minutes followed by a 90 minute $CO_{2(l)}$ flush. The [HCl] was varied from 5 M to 11 M, and the maximum [NaCl] achievable of 5 M was studied. Results for percent extraction of Eu from each [HCl] and [NaCl] solution studied in this work is given in Table 4-4. When varying the [HCl] no extraction of Eu is observed from 5 M HCl through 7 M HCl. When the [HCl] reaches ≥8 M the percent extraction of Eu reaches levels ≥95%. When extracting from ≤7M [Cl^-] the flow rate of the $CO_{2(l)}$ significantly fluctuated from ~0 mL/min to ~10 mL/min with an average of ~5 mL/min. whereas, with ≥8 M [HCl] few flow rate fluctuations were experienced and flow rate was maintained at about 5.00 mL/min±0.25 mL/min throughout the extraction. This is from dissolution of water into the $CO_{2(l)}$ phase, and transport of water downstream. At the point where the pressurized liquid would expand (the micro-metering valve orifice) the cooling of expansion would freeze the water in the line causing a flow obstruction. King *et al.*[33] At 25 °C and 2930 psi it was observed that the solubility of water in $CO_{2(l)}$ is 0.378 mol%. Based on their observed trends, at 3500 psi and 23 °C the solubility of water in $CO_{2(l)}$ would be approximately 0.379 mol%. With *1*-octanol being added as a modifier and shifting the polarity of the $CO_{2(l)}$ toward being more polar it can be expected that the solubility of H_2O would be greater than with pure $CO_{2(l)}$. As the [HCl] or [NaCl] decreases the concentration of water increases which allows for greater solubility into $CO_{2(l)}$. The solubility of H_2O into the $CO_{2(l)}$ is causing the extraction of Eu to significantly decrease.

Table 4-4**.** The percent extraction of Eu from various HCl and NaCl aqueous solutions with 0.5 mole percent *1*-octanol, 3500 psi, 23 °C, and 5x TBDGA:Eu by mole.

Aqueous Solution	Percent Extraction
5 M NaCl	0 %E
5 M HCl	0 %E
6 M HCl	0 %E
7 M HCl	0 %E
8 M HCl	95±2 %E
10 M HCl	97±2 %E
11 M HCl	99±3 %E

4.3.8. *CO_2 vs 1-octanol*

The *1*-octanol modified $CO_{2(l)}$ can be compared to the neat 1-octanol system. A comparison of the reagents used and the percent extraction achieved in each system in summarized in Table 4-5. Both system were extracting ionic Eu from 8 M HCl at 23 °C. For the $CO_{2(l)}$ system the pressure was kept at 3500 psi. In the $CO_{2(l)}$ system to achieve 95% extraction Eu a mole ratio Eu:TBDGA of 0.2 is required, and to achieve a 94% extraction Eu in the 1-octanol system a Eu:TBDGA of ~7.99×10^{-5} is necessary. The $CO_{2(l)}$ system uses 53.8% less *1*-octanol than the *1*-octanol system to achieve similar percent extractions. When the Eu:TBDGA mole ratio is increased to 0.2 in the *1*-octanol the extraction of Eu is reduced to 42%. The $CO_{2(l)}$ system is more efficient at utilizing less reagent (*1*-octanol and TBDGA) for extracting Eu. The *1*-octanol system avoids using pressurized $CO_{2(l)}$.

Table 4-5. Comparison of extraction with TBDGA in *1*-octanol to TBDGA in *1*-octanol modified $CO_{2(l)}$. In parenthesis the percent extraction at an equal moles TBDGA:Eu as in the $CO_{2(l)}$ is stated.

	1-octanol	CO_2 modified with *1*-octanol
Percent Extracted Eu	94% (42%)	95%
Moles Eu : Moles TBDGA	~$7.99X10^{-5}$ (~0.2)	~0.2
mL *1*-octanol : mL aqueous	1	0.462

2. Solubility of Ho-TBDGA in 1-octanol modified CO_2

Solubility of the TBDGA\Ho complex was observed in three $CO_{2(l)}$ systems: water saturated single-phase system, water saturated two-phase system with a dry $CO_{2(l)}$ phase over, and dry *1*-octanol. This was performed on Ho-TBDGA with UV-visible spectroscopy of the upper $CO_{2(l)}$ phase at 3500 psi, 23 °C, 0.5 mol% 1-octanol. The Ho-TBDGA complex was used due to Ho having a higher molar extinction coefficient than Eu. For this experiment, the molar extinction coefficient was determined from the integrated vibrionic band from 529 nm to 555 nm. This is shown in Eq. 4-1 which is a modification of Beer's Law. Where A is the absorption, λ is the wavelength, ε Is the extinction coefficient, and b is the cell path length.

$$\int_{\lambda_{555}}^{\lambda_{529}} \mathrm{A}\, \mathrm{d}\lambda = \varepsilon \mathrm{b}[\mathrm{Ho}] \qquad \text{Eq. 4-1}$$

The UV-visible spectra of a dry system, a single-phase water saturated system, and a two-phase water saturated system is shown in Figure 4-12. The peak area for the wet systems is less than the peak area for the dry systems. This indicates that the solubility of water in $CO_{2(l)}$ has an deleterious effect on the solubility of a REE-TBDGA complex in $CO_{2(l)}$.

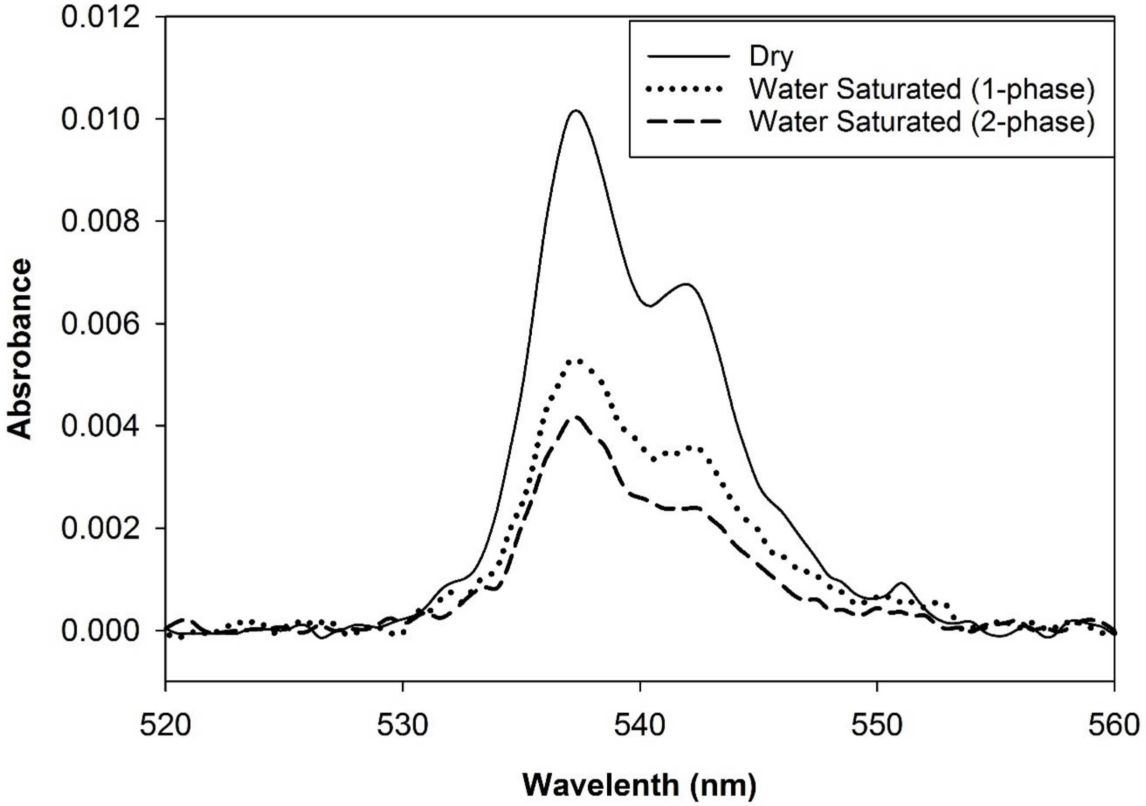

Figure 4-12. UV-visible spectra from 520 nm to 560 nm of Ho-TBDGA complex in 0.5 mole percent *1*-octanol modified $CO_{2(l)}$ at 23°C and 3500 psi. By integrating the area under the peak the [Ho] was determined. The integrated molar extinction coefficient or the peak from 529 nm to 554.5 is 26.6 $A \cdot nm \cdot M^{-1} \cdot cm^{-1}$. The dry system (a solid black line) has a [Ho] in the $CO_{2(l)}$ of 2.57 mM. The water saturated $CO_{2(l)}$ 1-phase wet system (dotted black line) had 4 µL of water added, and the [Ho] in the $CO_{2(l)}$ was determined to be 1.45 mM. The 2-phase wet system (dashed black line) had 100 µL of water added, and the [Ho] in the $CO_{2(l)}$ of 1.04 mM.

4.3.9. *Extraction from Phosphor Material Leachate*

Extraction from a simulant mixture of REEs found in phosphors was examined. This simulant was created from a mixture of 250 ppm each Y, Ce, Eu, and Tb from the chloride forms in 8 M HCl. A 90 minute dynamic extraction was performed with TBDGA in 0.5 mol% *1*-octanol modified $CO_{2(l)}$ followed by a 60 minute $CO_{2(l)}$ flush. The percent extraction for the REEs is shown in Figure 4-13. The extraction efficiency is similar to what was observed in the liquid-liquid *1*-octanol system (Figure 3-2). Cerium did not extract well at 8.27%, and the other REEs did extract >84% with Tb>Eu>Y. Cerium is low due to its larger ionic radii. These results are similar to what was observed in the *1*-octanol system in Figure 3-4. The percent extraction for Eu was lower than the previous extractions of previous single-element with optimized conditions. There is an effect from the competition with the other REEs for the TBDGA complex to form.

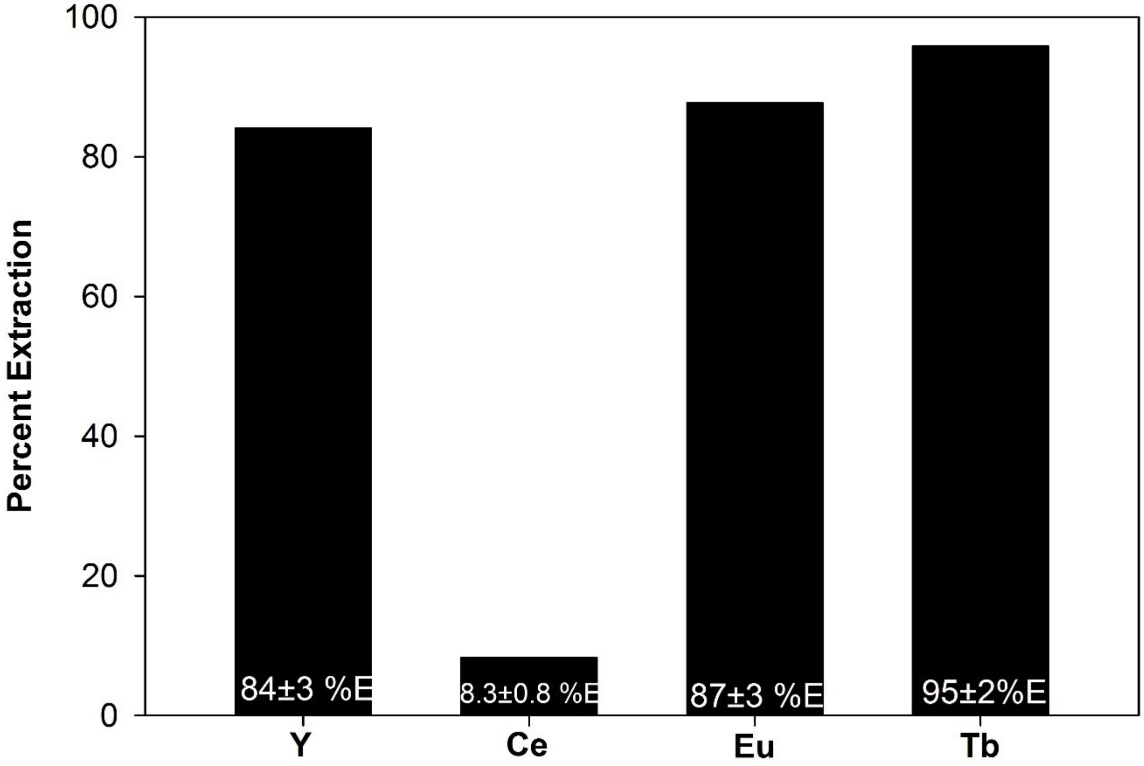

Figure 4-13. Extraction of 250 ppm each Y (III), Ce (IV), Eu (III), and Tb (III) in 8 M HCl with 5:1 TBDGA:REE, 0.5 mole % *1*-octanol, 23 °C, 5 mL/min, 3500 psi.

Next, extraction was performed on the phosphor leachate from Chapter 3. Extraction from the phosphor leachate with TBDGA in 0.5 mole percent *1*-octanol in $CO_{2(l)}$ at room temperature and 3500 psi was performed. The percent extraction is shown in Figure 4-14. Due to the Ce and Tb not leaching into the HCl at quantifiable concentrations by ICP-MS there is no extraction shown. The Y and Eu are very effectively separated from the Ba, Mg, and Al that did leach into the HCl. The percent extraction of Eu at 95% was similar what was observed previously in Table 4-4. In this extraction compared to the phosphor REE simulant extraction, Figure 4-13, the Y and Eu percent extraction was higher than observed in the simulant material. There was less competition from the Tb, or one of the other elements in the leachate had a synergistic effect on the extraction.

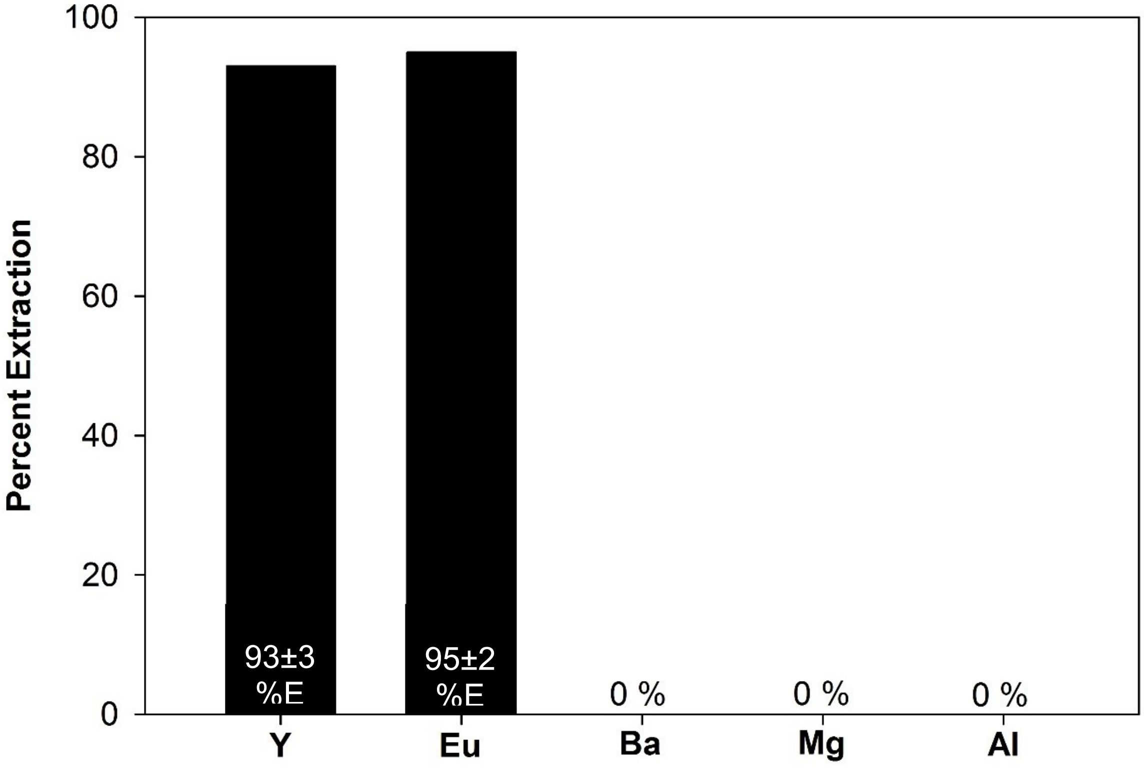

Figure 4-14. Extraction from phosphor leachate that was used in Chapter 3 in 8 M HCl with 5:1 TBDGA:REE, 0.5 mole % *1*-octanol, 23 °C, 5 mL/min, 3500 psi.

4.3.10. *Extraction from Magnet Material Leachate*

The extraction of metals from NIB magnet dissolution in 5 M NaCl and 8 M HCl with TBDGA in *1*-octanol modified $CO_{2(l)}$ was performed. The REEs and Fe were extracted >97% From 8 M HCl. As the mass of the REEs increase there is an increase in the extraction efficiency, Dy>Nd>Pr. This was also observed in the liquid-liquid *1*-octanol extraction system, Chapter 3, Figure 3-4. There was no extraction of any metals from the 5 M NaCl. This is expected based on the results of varying the chloride media summarized in Table 4-4. This is due to increased water extraction. TBDGA in *1*-octanol modified $CO_{2(l)}$ is effective at extracting the REEs, but all of the Fe is also extracted. There would be a need to perform post-extraction purification of the REEs to separate the Fe.

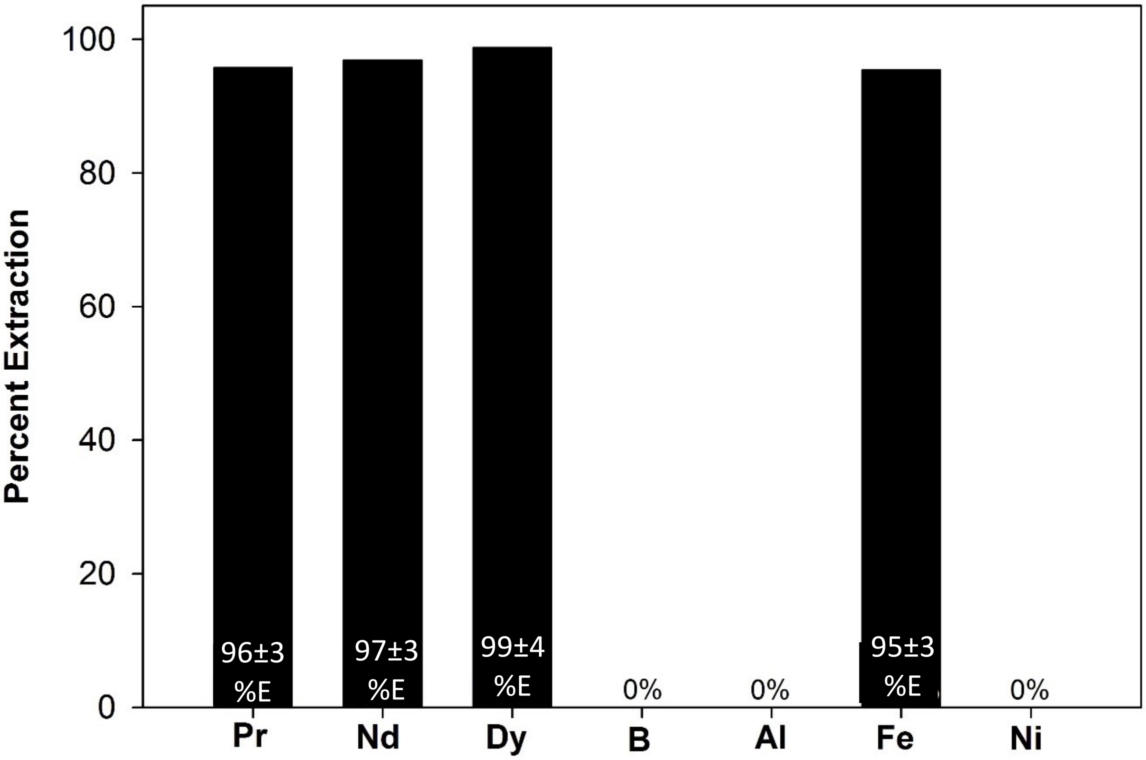

Figure 4-15. 0.5 mole % *1*-octanol in $CO2_{(l)}$, 5:1 TBDGA:M by mole, 23 ˚C, 3500 psi, and a flow rate of 5±0.5 mL/min.

4.4. Conclusion

When extracting Eu from 8 M HCl with TBDGA in *1*-octanol certain conditions will optimize the extraction. When temperature is varied the highest percent extraction is observed at 23 °C. By varying the pressure a peak is seen in the percent extraction at 3500 psi. The percent extraction increases as the ratio of TBDGA:Eu increases. As the mole percent

1-octanol used to modify the system is decreased the percent extraction is increased; the highest percent extraction was observed at 0.5 mole percent *1*-octanol. By optimizing this extraction of Eu from 8 M HCl with 0.5 mole percent *1*-octanol approximately 95±2% Eu can be extracted when using a [Eu]:[TBDGA] of 0.2, and keeping the system at 3500 psi and 23 °C. Yttrium and Eu can be effectively extracted and separated from other elements from phosphor HCl leachate with TBDGA in *1*-octanol modified $CO_{2(l)}$. Praseodymium, Nd, Dy, and Fe are extracted >97 % from NIB magnet HCl dissolution with TBDGA in *1*-octanol modified $CO_{2(l)}$.

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Chapter 5

Stripping REEs from TBDGA in *1*-octanol with HCl and TEDGA

5.1.Introduction

Recovery of the REEs from any extraction process is a vital step to the success of a new process. Stripping the extracted REEs from the loaded organic is one of the more common recovery methods.[1] This step involves contacting the metal-loaded organic with an aqueous solution. The stripping step can also be utilized to selectively separate the various metals that had been extracted.[2-3] One method for selectively stripping is to use a stripping or masking ligand.[4-6] These are ligands that are water soluble, and they compete with the organic soluble extracting ligand to complex the metal.

The novel diglycolamide ligands can be easily varied by chain length and branching of the R and R' groups. By varying the chain length the DGAs will be soluble in different liquids. Specifically, shorter chain length DGAs (<ethyl) are very soluble in aqueous solutions. This was shown in Table 1-3[6-7] in Chapter 1. N',N',N,N-tetraethyl diglycolamide (TEDGA), Figure 5-1, has high solubility in water and has poor solubility in dodecane.

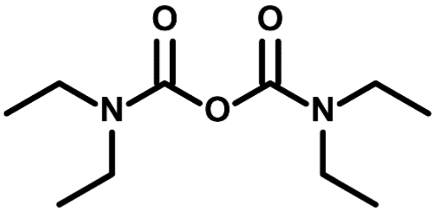

Figure 5-1. Structure of N’,N’,N,N-tetraethyl diglycolamide (TEDGA)

This makes it ideal as a stripping or masking ligand. TEDGA has been utilized in the Extraction of Americium (EXAm) process.[8] The EXAm process has been developed by the French Alternative Energies and Atomic Energy Commission (CEA) for reducing radionuclide waste.[9] TEDGA’s purpose in this process is to selectively complex curium and the heavy lanthanides. These TEDGA-M complexes will form in the aqueous phase. Americium and the light lanthanides would be extracted into the organic phase by 2-(2-hexyloxy-ethyl)-N,N-dimethyl N,N-dioctyl-malonamide (DMDOHEMA).[8] This allows for the long lived Am isotope to be removed from the high level radioactive waste. This will reduce the timeline of the radiotoxicity of this waste while allowing the use of the Am in a fast reactor.[8-9]

Most of the research involving TEDGA is for its use in the nuclear fuel cycle. The available publications for TEDGA reports use in nitric acid media and focuses on actinides. The published data shows TEDGA has potential as a selective stripping agent for lanthanides.[6, 10-11] No published data exist for the stripping of TBDGA metal-loaded from a chloride media followed by stripping with HCl or TEDGA. In this chapter HCl and TEDGA in HCl will be examined for having potential to selectively stripping REEs from TBDGA.

5.2. Materials and Methods

The contact procedure followed for all contacts in this chapter involved mixing equal volume phases for 15 minute in 12 mL conical tubes by hand. After the 15 minute contact, the solution was centrifuged using a Centrific model 228 (Fisher Scientific, Hampton, NH) for 5 minutes. The organic and aqueous phases were separated. The aqueous phase was analyzed by ICP-MS on an Agilent model 7900 ICP-MS (Agilent, Santa Clara, CA). The [REEs] in the organic phase were determined by subtracting the final aqueous [REE] from the starting aqueous [REE].

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) choride 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′-tetrabutyl diglycolamide (95%) was used as-received from Tractus Chemical (Tractus Chemical, London, England). N,N,N′,N′-tetraethyl diglycolamide (95%) was used as-received from NewChem Technologies Limited (NewChem Technologies Limited, Durham, United Kingdom) All aqueous solutions were made with water purified to a resistivity of at least 18 MΩ-cm.

To pre-equilibrate the organic phase equal volumes of *1*-octanol containing 0.010 M TBDGA and 8 M HCl were contacted. The pre-equilibrated organic phase was removed qand then contacted with 8 M HCl containing ~100 ppb each Y (III), La (III), Ce (III), Nd (III), Sm (III), Eu (III), Eu(III), Tb (III), Dy (III), Ho (III), and Lu (III) following the same contact and analysis steps above.

The metal-loaded organic was then contacted with varying [HCl] (0 M, 1 M, 2 M, 3 M, 5 M, and 8 M HCl) following the contacts and analysis procedure above.

The metal-loaded organic was contacted with varying [HCl] containing TEDGA. The TEDGA concentrations studied were 0.050 M, 0.010 M, 0.005 M. For each [HCl] and each [TEDGA] the contact and analysis procedure above were followed.

5.3. Results and Discussion

5.3.1*. Stripping from REE loaded TBDGA in 1-octanol with HCl*

An organic comprised of 0.01 M TBDGA in *1*-octanol was loaded with REEs by contacting it with an 8 M HCl containing Y, La, Ce, Nd, Sm, Eu, Tb, Dy, Ho, Lu from their chloride salts. This metal-loaded organic was then contacted with varying [HCl] from 1 M – 8 M to determine what [REEs] would be back-extracted into the aqueous. When a D value is less than 1, then by convention >50% of the REE is in the aqueous phase. The stripping of REE loaded TBDGA in *1*-octanol with varying [HCl] is shown in Figure 5-2. The same plot with the scale of the y-axis set to 0 to 2 is shown in Figure 5-3. When the metal concentration was below the detection limit of the ICP-MS the maximum D=100 based on the detection limits. A D value <1 indicates that a metal is strippable from the organic phase. A line was placed at D=1 as a guise showing whether or not a REE is stripped. When stripping with HCl, as the [HCl] decreases the [REEs] stripped into the aqueous phase increases. La (III) and Ce (III) are stripped at all [HCl]. Nd is stripped with <3 M HCl. Sm (III) and Eu (III) are stripped with <1 M

HCl. All other elements are not stripped with any [HCl] studied. La (III) is almost completely stripped at all [HCl].

When using HCl as a stripping agent a basic separation process could be developed. The La and Ce are removed from the organic with 8 M HCl while most of the remaining REEs remain in the organic phase. When the organic phase is them contacted with 1 M HCl the Nd, Sm, and Eu would be stripped. Afterwards, Y, Tb, Dy, Ho, and Lu will remain in the organic phase.

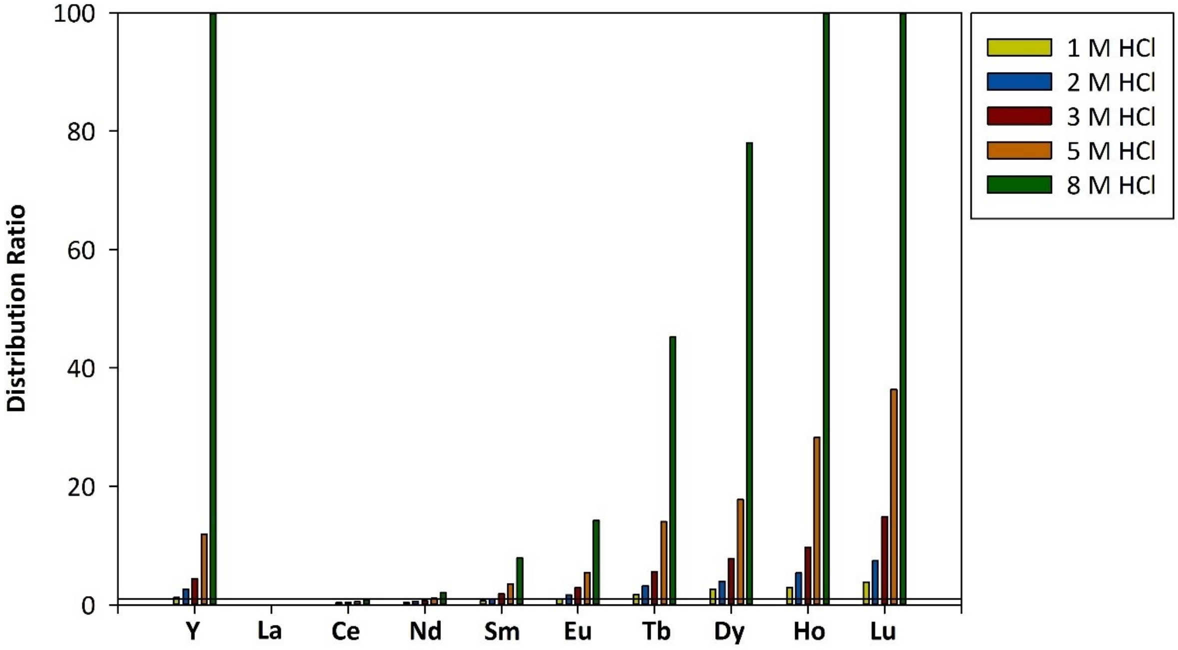

Figure 5-2. Stripping of a REE loaded 0.01 M TBDGA in *1*-octanol with and equal volume of varying [HCl]. D_{REE} was set to 100 when [REE] was below detection limit in the aqueous phase.

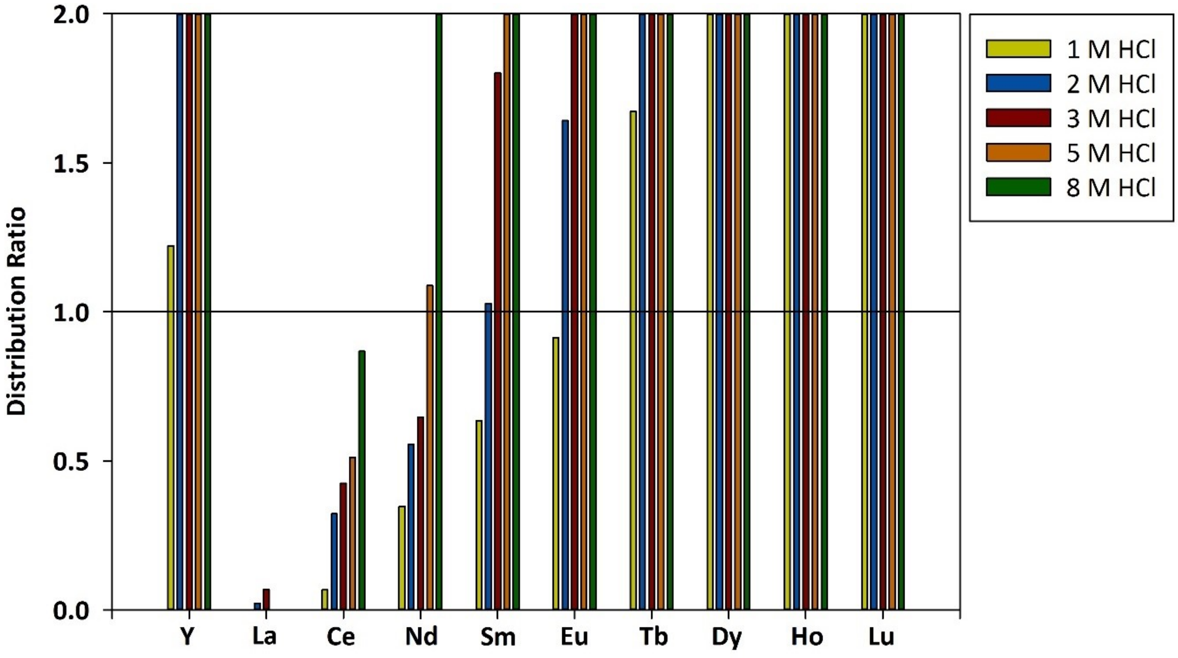

Figure 5-3. Stripping of a REE loaded 0.01 M TBDGA in *1*-octanol with and equal volume of varying [HCl] with the Y-axis set to show D=0 to D=2.

Select data was plotted as ionic radii (CN=6)[12] versus the distribution ratio, Figure 5-4, shows the stripping trend for the REEs from TBDGA in *1*-octanol with 1 M. The trend was similar for the other [HCl] studied. For all [HCl] as the ionic radii increases the D_{REE} decreases. The point that does not follow the trend is D_Y. While Y usually reacts similarly to lanthanides, it does not always perfectly fit lanthanide trends. The trend observed for D vs ionic radii when stripping is very similar to what was observed with the extraction of REEs with TBDGA, Figure 3-4. When extracting with TBDGA the D_Y value is lower than would be expected based on its ionic radius.

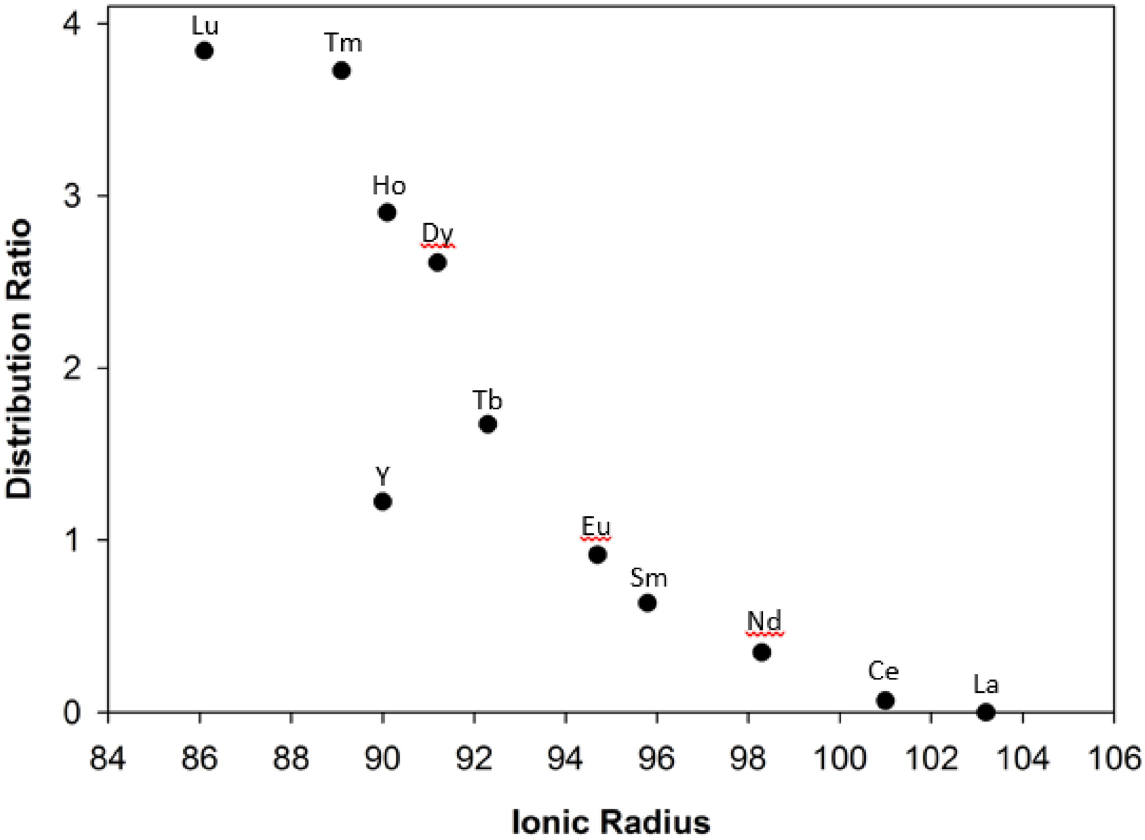

Figure 5-4. Ionic radii (CN=6)12 vs distribution ratio for the stripping of REEs from 0.010 M TBDGA in *1*-octanol with 1 M HCl.

5.3.2. *Stripping from REE loaded 0.010 M TBDGA in 1-octanol with 0.05 M TEDGA at varying [HCl]*

Next, the aqueous-soluble masking ligand TEDGA was studied to observe the effect it has on stripping REEs from TBDGA in *1*-octanol into varying [HCl]. The [TEDGA] was first introduced at concentrations greater than the [TBDGA]. The [HCl] was varied from 1 M - 8 M. The stripping of REEs from REE loaded 0.010 M TBDGA in *1*-octanol into 0.05 M TEDGA was performed with equal volume phases at 23°C. The results are shown in Figure 5-6. With the TEDGA/TBDGA=5 all the REEs were stripped from the organic phase into the aqueous phase. There is no consistent trend within the D_{REE} values. This is because the D_{REE} values are small causing greater error in the analysis.

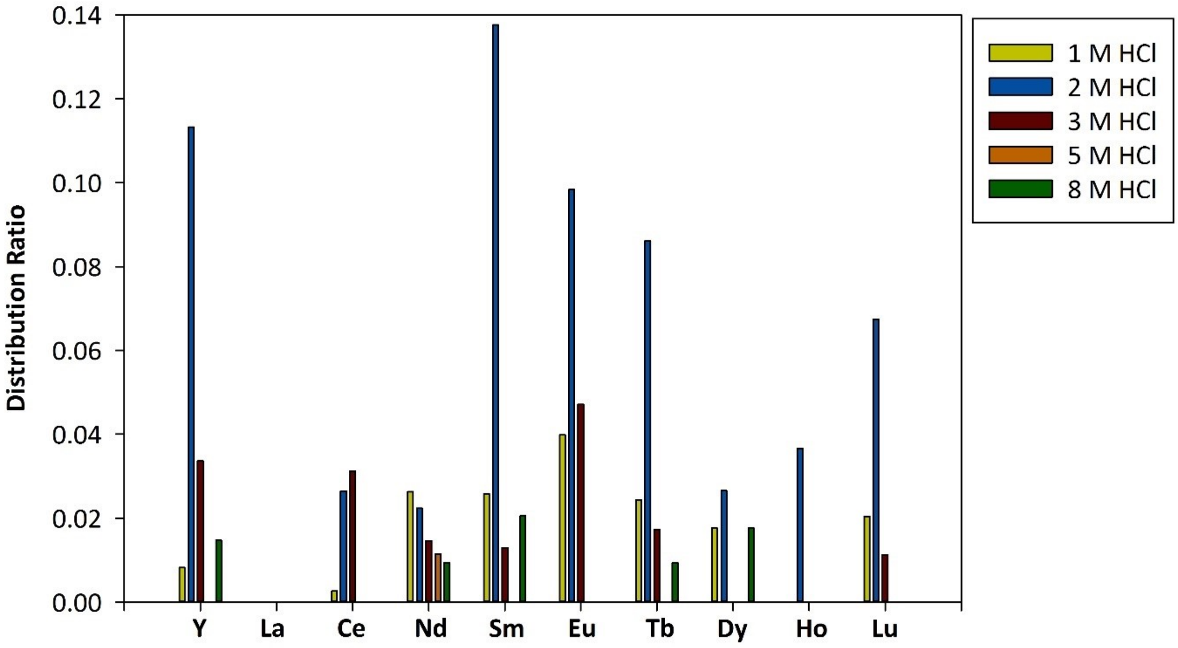

Figure 5-5. Stripping of a REE loaded 0.010 M TBDGA in *1*-octanol with and equal volume of varying [HCl] containing 0.05 M TEDGA.

5.3.3. *Stripping from REE loaded 0.010 M TBDGA in 1-octanol with 0.010 M TEDGA at varying [HCl]*

Next, the [TEDGA] was lowered to determine if there is potential for selective stripping. The [TEDGA] was decreased to 0.010 M, which is equal to the [TBDGA]. The stripping of REEs from REE-loaded 0.010 M TBDGA in *1*-octanol with 0.010 M TEDGA in HCl ranging from 0.1 M to 8 M at 23°C is shown in Figure 5-7. When the [TEDGA]=[TBDGA] all of the D_{REE} are <1. A majority of each REE is back-extracted into the aqueous phase, and all REEs are strippable at all [HCl]. This shows that TEDGA has a greater affinity for REEs than TBDGA. The D_{REEs} is greater with higher [HCl] indicating that TEDGA is less effective at displacing TBDGA and forming the TEDGA-REE complex at higher [HCl].

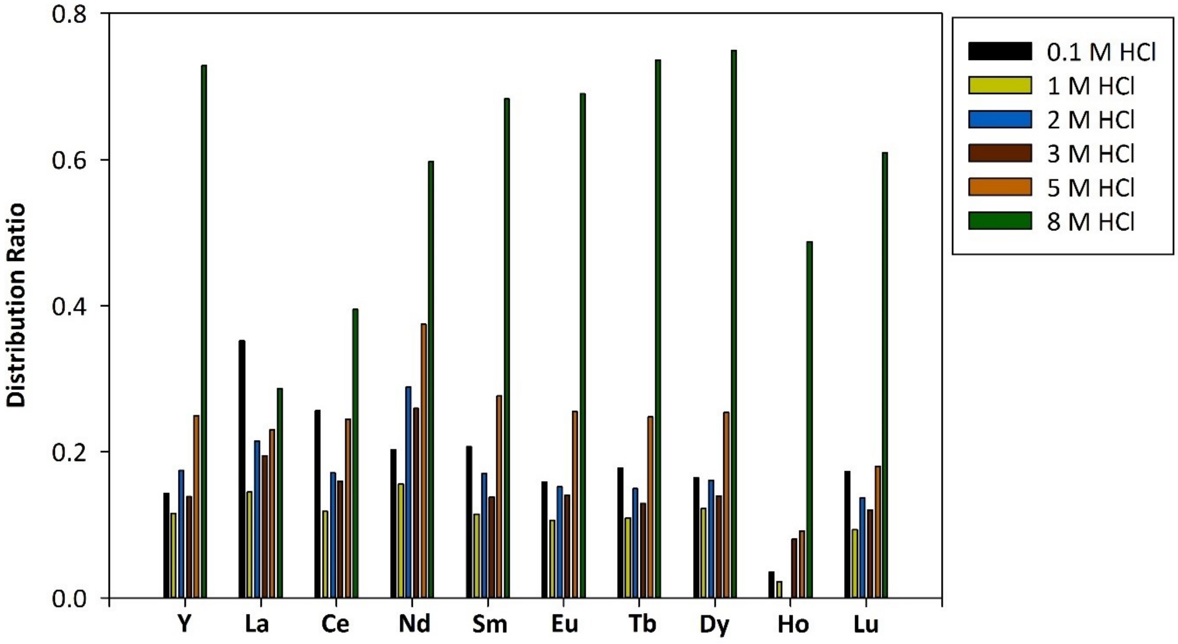

Figure 5-6. Stripping of a REE loaded 0.010 M TBDGA in 1-octanol with and equal volume of varying [HCl] containing 0.010 M TEDGA.

5.3.4 *Stripping from REE loaded TBDGA in 1-octanol with 0.005 M TEDGA at varying [HCl] 0.005 M TEDGA*

Finally, the back-extraction of REEs was studied when the [TEDGA] is lower than the [TBDGA]. Equal volume phases of *1*-octanol containing 0.010 M TBDGA that had been previously loaded with REEs, and an aqueous phase ranging from 0.1 M to 8 M HCl with 0.0050 M TEDGA were contacted. This contact was performed at 23 °C. With 8 M HCl Y (III), Eu (III), Tb (III), Dy (III), Ho (III), and Lu (III) were not stripped into the aqueous phase. At [HCl] < 8 M all the REEs were stripped into the aqueous phase. This shows that even when [TEDGA]<[TBDGA] the TEDGA still has a greater affinity for the REEs than the TEDGA at [HCl] < 8 M.

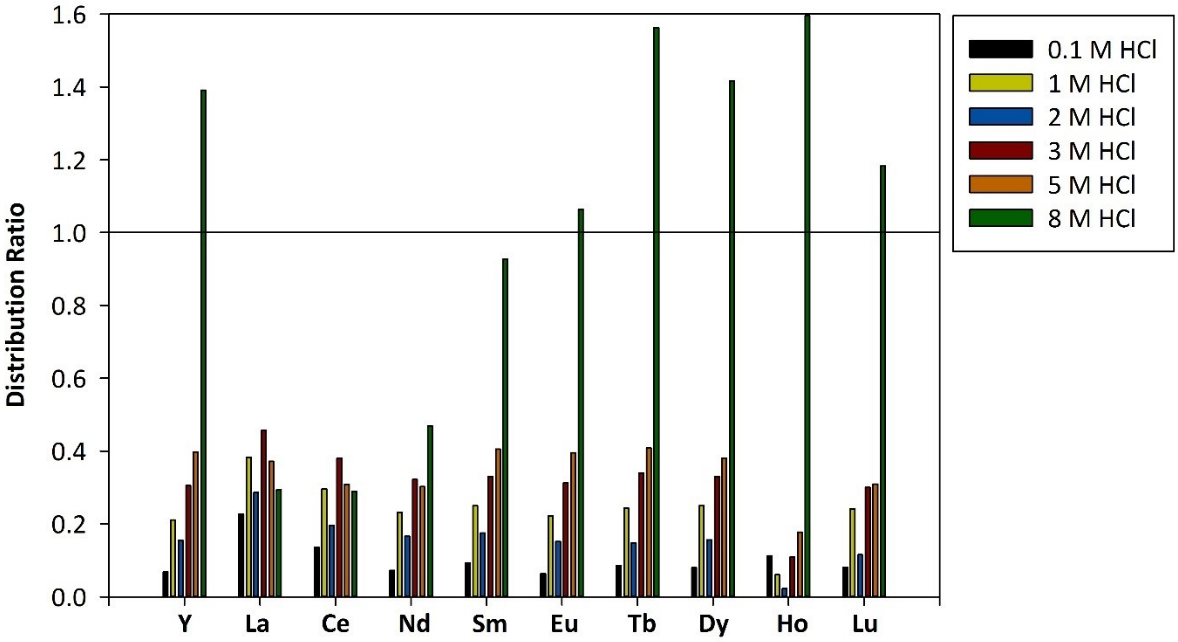

Figure 5-7. Stripping of a REE loaded 0.010 M TBDGA in *1*-octanol with and equal volume of varying [HCl] containing 0.005 M TEDGA.

5.3.5. *Comparisons of varying [TEDGA] stripping REEs from TBDGA at vary [HCl]*

A comparison of the three different [TEDGA] (0.05 M, 0.01 M, 0.005 M) studied for stripping REEs from 0.01 M TBDGA in *1*-octanol is shown in Figure 5-9 for Dy (III). The [HCl] varied from 1 M to 8 M for each is also shown. Distribution ratio vs [HCl] for the three [TEDGA] are similar for all REEs that were examined. As the [TEDGA] increases the D_{REE} decreases due to the high affinity TEDGA has for the REEs. When [TEDGA] ≤ [TBDGA] as the [HCl] increases the D_{REE} increases. As the [HCl] increases the D_{REE} increases because TBDGA has a preference to complex with REEs at high [HCl].

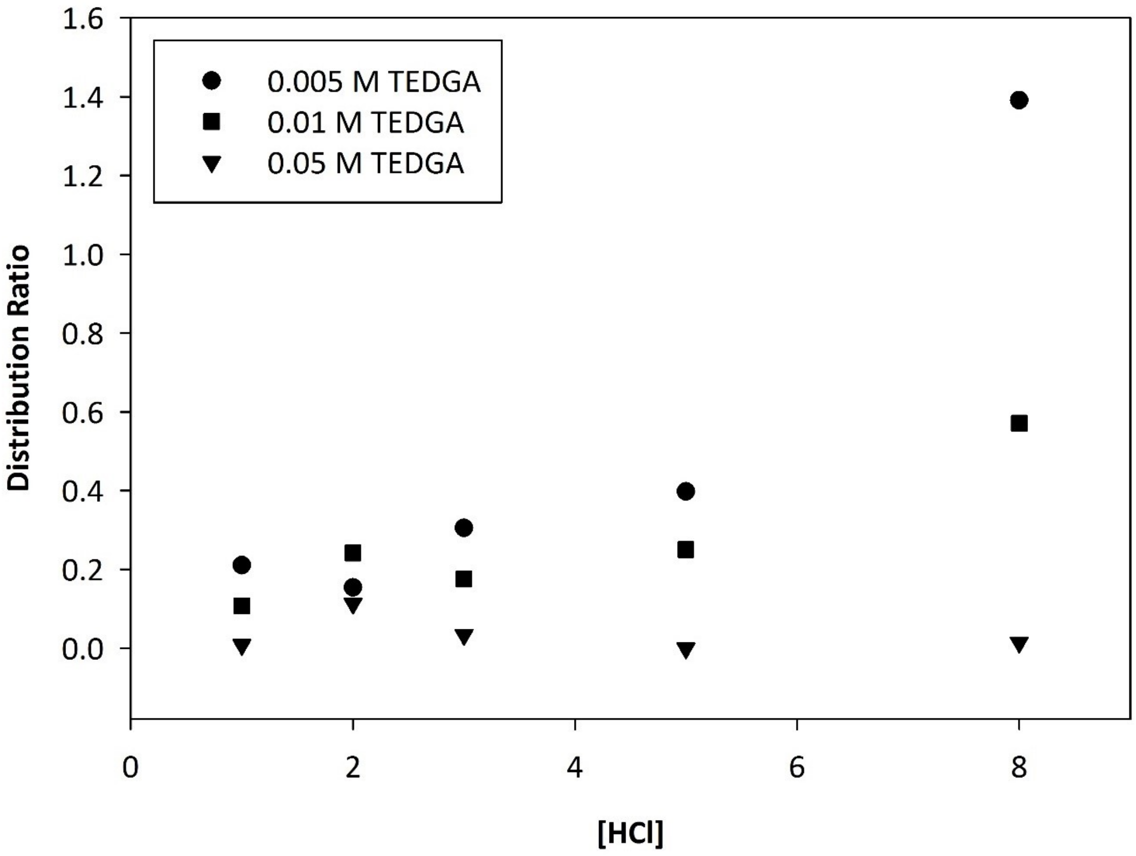

Figure 5-8. Comparison of 0.005 M, 0.010 M, and 0.05 M TEDGA in [HCl] from 1 M to 8 M for stripping REEs from 0.010 M TBDGA in 1-octanol.

5.4. Conclusions

HCl and TEDGA in HCl were studied as potential stripping agents for REEs from TBDGA. When stripping with HCl, the heaver REEs (Tb (III), Dy (III), Ho (III), Lu (III)) were not stripped at any of the [HCl] studied. The light REEs examined were stripped with ≤5 M HCl. The La (III) and Ce (III) could be removed from the organic phase with 8 M HCl while most of the remaining REEs will remain in the organic phase. 1 M HCl could then strip the Nd (III), Sm (III), and Eu (III). After the 8 M and 1 M HCl strip steps, the Y (III), Tb (III), Dy (III), Ho (III), and Lu (III) will remain in the organic phase. When the [TEDGA]≥[TBDGA] all the REEs were stripped into the aqueous phase. When [TEDGA]<[TBDGA] by 2x in 8 M HCl the REEs Y (III), Eu (III), Tb (III), Dy (III), Ho (III), and Lu (III) are not stripped, but all the remaining REEs are stripped. At all other [HCl] studied all the REEs were stripped. After the 1 M HCl strip step, stripping with TEDGA would remove the remaining REEs in the HCl. TEDGA does help with stripping the REEs from the TBDGA, but it is not very selective in the TBDGA/HCl system. A stripping processes combining an 8 M HCl, 1 M HCl, and a 1 M HCl containing TEDGA would allow for a light/intermediate/heavy REE separation. A schematic of this process is shown in Figure 5-9.

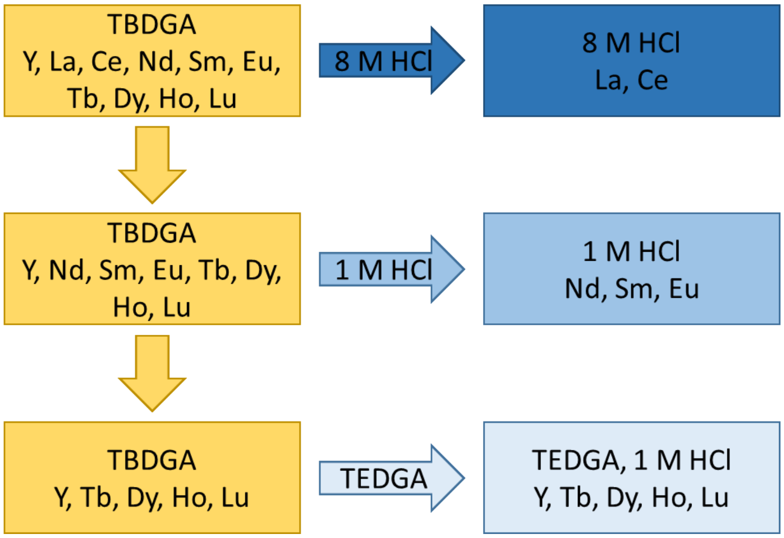

Figure 5-9. Basic REE separation process for the separation of light/intermediate/heavy REEs. The yellow is the starting metal-loaded TBDGA organic phase. The first step is to remove any La and Ce that did extract into TBDGA with 8 M HCl. Next, by contacting the organic with a 1 M HCl Nd, Sm, and Eu can be stripped. Finally, a 1 M HCl containing TEDGA strip would remove the Y, Tb, Dy, Ho, and Lu.

5.5. References

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Chapter 6

Summary

Reducing waste while increasing efficiency is important to improving REE solvent extraction. Two methodologies for achieving increased efficiency were studied: diglycolamides as extracting ligands and carbon dioxide as an alternative solvent. Diglycolamides are novel ligands that were introduced for extraction of actinides and lanthanides in the nuclear fuel cycle. They have primarily been of interest due to their recyclability and being elementally comprised of C-H-O-N making them completely incinerable. Carbon dioxide has been explored as a non-traditional solvent due to it being non-toxic, non-flammable, reusable, and inherently waste minimizing compared to a traditional extraction system. In this work, the extraction of REEs with TBDGA in *1*-octanol and *1*-octanol modified CO_2 from chloride media was studied. The stripping of REEs from TBDGA in *1*-octanol into HCl with and without TEDGA was also examined.

Initially, the ability of TBDGA in *1*-octanol to extract REEs from various chloride media was examined. A number of conditions were varied to determine the optimized conditions for the greatest extraction efficiency. When varying the $[Cl^-]$ in the aqueous phase it was shown that an increase in $[Cl^-]$ directly leads to an increase in extraction efficiency. The Cl^- anions are required to neutralize the REE cations to form a neutrally charged, extractable species, $M(TBDGA)_nCl_3$. However, when comparing extraction from NaCl, HCl, and NaCl/HCl it was observed that as the $[H^+]$ increased it had a deleterious effect on the extraction of REEs with TBDGA. Extraction temperature was varied from 2°C to 65°C and enthalpy of reaction values were obtained for extraction with TBDGA in *1*-octanol for Y, Sm, Eu, Tb, and Dy in 8 M HCl. The highest extraction efficiency occurred at 2°C, and there was no detectable extraction at 65°C. By constructing a Van't Hoff plot, the entropies of reactions for the REEs tested were found to be in the range of -39.9 to -42.9 kJ/mol. Indicating the reactions are exothermic. The light REEs, La and Ce, were not extractable with TBDGA. The intermediate REES (Nd, Sm, and Eu) were extractable under specific conditions. The heavy REEs (Y, Tb, Dy, Ho, and Lu) are extractable with TBDGA. When creating an extraction process from chloride media with TBDGA in *1*-octanol it is feasible to achieve basic separation between light and heavy REEs.

Next, leaching and dissolutions from trichromatic phosphor and neodymium iron boron magnet samples with TBDGA in *1*-octanol from 8 M HCl and 5 M NaCl was performed. 8 M and 4 M HCl were used to leach from the trichromatic phosphor. About 90% Y and 65% of the Eu were leached, but Ce and Tb were minimally leached at about 0.05% of each. The analysis performed on this extraction showed Ba, Al, and Mg were not extracted. Y and Eu were extracted >99.9% from both 5 M NaCl and 8 M HCl. The magnet material was fully dissolved into HCl. Pr, Nd, Dy, and Fe were extractable from 8 M HCl. When extracting from 5 M NaCl, the extraction efficiency of the REEs increased, but the extraction of Fe decreased significantly. The oxidation state of Fe would vary when in HCl and NaCl solutions which does have an effect on extractability of a metal. This would allow for a separation of Fe/REEs when extracting from NaCl. The REEs would extract while leaving behind the Fe bulk of the NIB magnet.

Carbon dioxide was examined as a potential solvent for extraction from chloride media. Optimizing the extraction conditions for TBDGA-mediated extraction of REEs was performed on Eu in chloride media. No extraction of Eu was observed with TBDGA in CO_2. A solvent modifier had to be added to shift the polarity of the CO_2 for the TBDGA-Eu complex to be soluble. *1*-octanol was used as the modifier. It was found that the conditions to achieve ≥95% extraction Eu are 23°C, 3500 psi, Eu:TBDGA≥0.2, ≥8M HCl, 0.5 mol% *1*-octanol. Temperature has a significant impact on the extraction of REEs with TBDGA. This was observed in both the *1*-octanol and the CO_2 systems. When extracting with CO_2, the percent extraction of Eu dropped from about 75% at 23°C to 13% when the temperature was increased to 40°C. This meant that at the optimal temperature the CO_2 is in the liquid phase and not the SCF phase. There is no literature available showing use of CO_2 for liquid CO_2 being used for metal extraction. The solubility of an Ho-TBDGA complex in $CO_{2(l)}$ at 23°C, 3500 psi, 0.5 mol% *1*-octanol was examined by UV-vis spectroscopy in a dry system and a wet system to verify the effect of water on extraction of REEs. When water was added to the sample cell there was a decrease in the solubility of the Ho-TBDGA into the $CO_{2(l)}$. This indicates that water in the system has a deleterious effect on the extraction of REEs with TBDGA in *1*-octanol modified $CO_{2(l)}$. When the pressure was varied the extraction profile had a peak in percent extraction at 3500 psi. As the pressure increased the solubility of water in CO_2 increases which decreased the solubility of the Eu-TBDGA complex. When the [HCl] was <8 M HCl or a NaCl solution was used the percent extraction of Eu was ~0%. These solutions introduced more water into the system resulting is a decrease in percent extraction.

The extraction from the phosphor leachate in 8 M HCl with 0.5 mol% *1*-octanol modified $CO_{2(l)}$, M:TBDGA=0.2, 23 °C, and 3500 psi resulted in extraction of the Y and Eu >93%. Ba, Mg, and Al were not extracted. The Ce and Tb were not leached into the HCl and remained in the phosphor material. Extracting from magnet dissolution under the same conditions resulted in extraction of Pr, Nd, Dy, and Fe >95%. The B, Al, and Ni were not extracted. Further processes would be needed to separate the Fe from the REEs.

When comparing the *1*-octanol system and the *1*-octanol modified $CO_{2(l)}$ system similar percent extractions can be achieved for Eu, 94% and 95% respectively. However, The $CO_{2(l)}$ system uses less TBDGA and *1*-octanol. Approximately 2860x more TBDGA and 2.2x more *1*-octanol is needed in the *1*-octanol system compared to the $CO_{2(l)}$ system.

When stripping the TBDGA with HCl the heavy REEs (Tb, Dy, Ho, and Lu) were not removed from the organic at any [HCl] studied. La and Ce were extracted into the aqueous at all [HCl] examined, and the remaining intermediate REEs were stripped from the organic with ≤5 M HCl. The aqueous-soluble ligand TEDGA was added to the various [HCl] solutions to determine if it has potential for selective back extraction of REEs. When [TEDGA]≥[TBDGA] all the REEs were stripped at all [HCl]. When the [TEDGA]<[TBDGA] by 2x the intermediate to heavy REEs (Y, Eu, Tb, Dy, Ho, and Lu) had $D_{REE}>1$ so a majority of these REEs remained in the organic phase. The other REEs partitioned into the aqueous phase. Using a combination of the HCl and TEDGA in steps a basic separation between the light, intermediate, and heavy REEs could be achieved.

The results shown in this study indicate that TBDGA and CO_2 can be used for the extraction of REEs from chloride media to reduce the waste of traditional solvent extraction.

Although CO_2 with TBDGA was not successful for extraction of Eu without the addition of *1*-octanol, less *1*-octanol can be used than a traditional process. The conditions required for TBDGA to extract REEs into $CO_{2(l)}$ with high efficiency are very specific, but extraction of intermediate and heavy REEs can be achieved. Separation between light, intermediate, and heavy REEs is possible with TBDGA and TEDGA in chloride media, but further research would be required to further develop a separation process. Extraction of REEs with TBDGA in *1*-octanol and *1*-octanol modified $CO_{2(l)}$ was found to be successful from both trichromatic phosphor powder and NIB magnet material. Other materials are not extracted from the phosphor leachate, but Fe is extracted from the NIB magnet solution when HCl is used. In the *1*-octanol system extraction from magnet material in NaCl aqueous solution selectively extracts the REEs while not extracting the other materials including Fe. Further work can be performed by varying the conditions of the CO_2 extraction process to determine if separation of Fe/REEs from NIB magnet material could be achieved.

Appendix A

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Title: Extraction behavior of selected rare earth metals from acidic chloride media using tetrabutyl diglycolamide

Author: M. E. Case, R. V. Fox, D. L. Baek, et al

Publication: Solvent Extraction and Ion Exchange

Publisher: Taylor & Francis

Date: Sep 21, 2017

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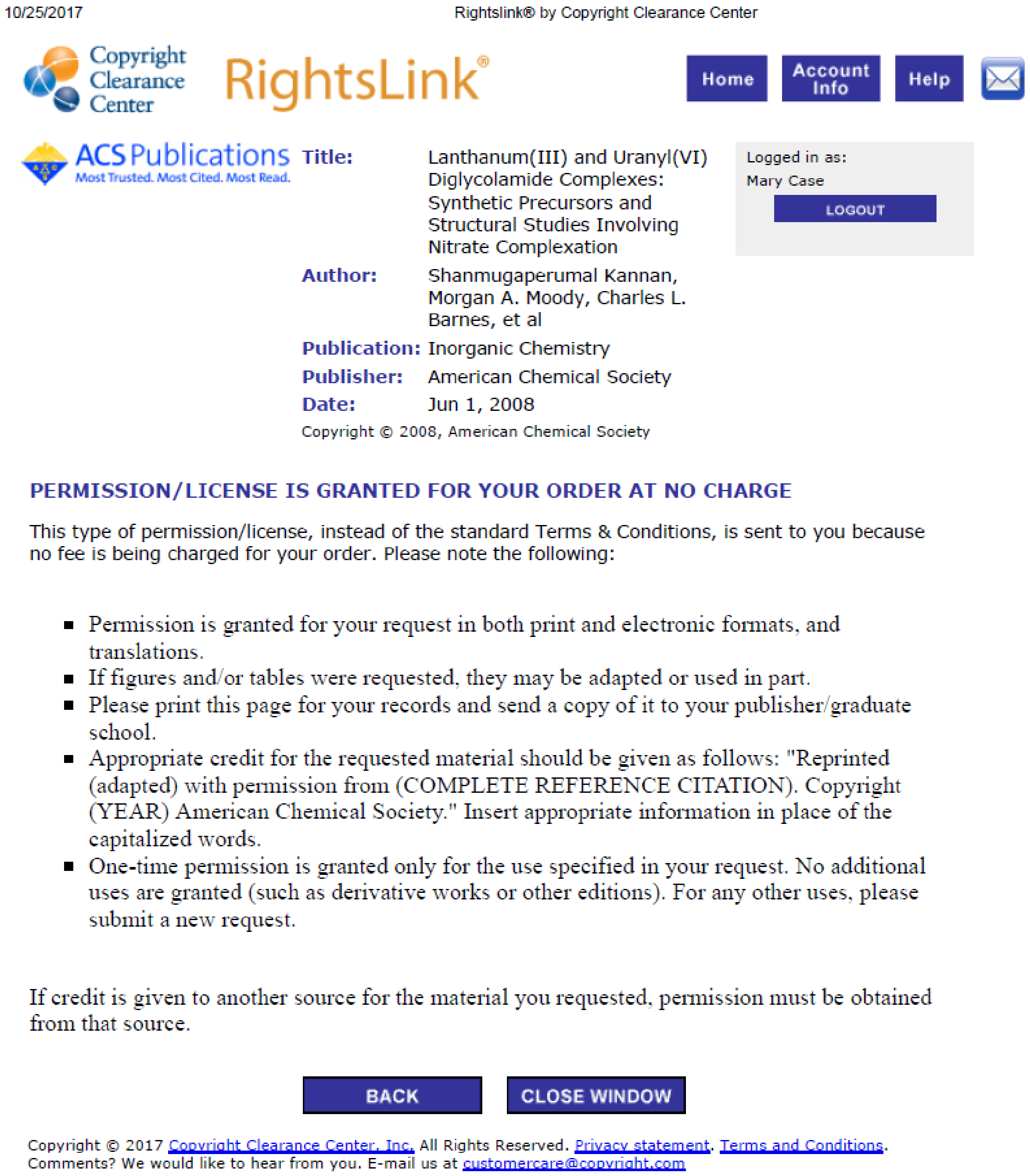

Title: Lanthanum(III) and Uranyl(VI) Diglycolamide Complexes: Synthetic Precursors and Structural Studies Involving Nitrate Complexation

Author: Shanmugaperumal Kannan, Morgan A. Moody, Charles L. Barnes, et al

Publication: Inorganic Chemistry

Publisher: American Chemical Society

Date: Jun 1, 2008

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