

**The Itinerant Position of Yttrium as
Evidenced by Carboxylic Acid Extractions**

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The Doctor of Philosophy
Degree
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DEDICATION

To my family, especially my parents Melvin and Delores Collier, for their unconditional love, support, and encouragement throughout my life.

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ABSTRACT

The rare-earth elements Y and La-Lu share many similar physical and chemical properties. These similarities are reflected by the difficulty in the complete separation of the rare earths, often requiring hundreds to thousands of stages for the production of pure rare earths. Yttrium, traditionally known to be separated with Ho, has also been observed to be separated with other elements within the lanthanide series, and even outside the bounds of the lanthanide series itself. Previous publications by several authors have indicated that steric factors could influence the position of Y in solvent extractions of the rare earths using carboxylic acid extractants, and steric parameters such as E_s' could be used to rationalize the position of Y versus the overall steric bulk of these extractants.

The purpose of this research project was to build upon the primary findings of these previous investigations and to gain further insight into the structural characteristics that influence the position of Y in solvent extraction systems. Solvent extraction experiments were performed on nine-element rare-earth solutions using a total of 29 carboxylic acid extractants. Rare-earth concentrations were determined using inductively-coupled plasma-optical emission spectrometry (ICP-OES). The results of these experiments showed that $-E_s'$ values less than 2 placed Y in the light rare-earth region (La-Eu), while $-E_s'$ values greater than 2 placed Y in the heavy rare-earth region (Gd-Lu). Additionally, substitutions at the α -carbon atom relative to the carboxyl group in these extractants were found to have the greatest influences on the position of Y. It was found that extractants which possessed an α -carbon atom which was not a component of a phenyl or cyclohexyl ring placed Y in three distinct locations—Ce-Pr, Gd-Tb, and Ho-Er, depending on the number of hydrogen atoms located at the α -carbon. Extractants which had an α -carbon atom that was contained within a cyclohexyl or phenyl ring placed Y into two possible regions—Ce-Pr and Gd-Tb.

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Chapter 1: Introduction

The lanthanide elements, commonly referred to as the rare earths, lanthanum through lutetium, are a series of fifteen elements with atomic numbers 57-71 on the periodic table (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu). These lanthanide elements (Ln) tend to exhibit very similar physical and chemical properties. An important one of these properties, namely the crystal radius of the trivalent cations, tends to gradually decrease across the series from La to Lu. These values are listed in Table 1.1.

Many other physical and chemical properties of La^{+3} through Lu^{+3} follow this same trend with only slight differences from element to element. In aqueous solutions, the +3 oxidation state is the most stable cation formed by the lanthanides. Oxidation states of +2 and +4, however, are known to exist in aqueous solutions on two occasions, namely Ce^{+4} and Eu^{+2} . The chemical differences between rare-earth trivalent cations are so slight that mixtures of these elements have proven to be very difficult to separate. Early methods for the separation of these elements required upwards of 1000 stages for 99.9% separation (15,000 stages for separation of thulium),¹ while modern separation techniques require up to 100 stages for 99.999% separation.²

Yttrium, atomic number 39, (Y) also shares many of its physical and chemical properties with the lanthanide elements, and is classically included as a constituent of the rare earth group. The crystal radius of Y^{+3} , 104 pm,³ is the same as that of holmium. Rare earths occur naturally in two kinds of minerals: those that are rich in light rare earths (La-Eu), called cerium earths, and those that are rich in heavy rare earths (Gd-Lu), called yttrium earths. Yttrium is the major constituent of natural deposits which are rich in the heavy rare earths, reflecting its strong similarity to holmium. In the large majority of separation procedures, Y accompanies Ho. However, in a few rare instances involving special

Table 1.1: Names, symbols, and crystal radii of trivalent lanthanide cations³

Element Name	Symbol	Ln ⁺³ Radius (pm)
Lanthanum	La ⁺³	117
Cerium	Ce ⁺³	115
Praseodymium	Pr ⁺³	113
Neodymium	Nd ⁺³	112
Promethium	Pm ⁺³	111
Samarium	Sm ⁺³	110
Europium	Eu ⁺³	109
Gadolinium	Gd ⁺³	108
Terbium	Tb ⁺³	106
Dysprosium	Dy ⁺³	105
Holmium	Ho ⁺³	104
Erbium	Er ⁺³	103
Thulium	Tm ⁺³	102
Ytterbium	Yb ⁺³	101
Lutetium	Lu ⁺³	100

separation agents, Y is found to accompany other rare earths. This mysterious, itinerant behavior of Y is the basis of this investigation.

Rare-earth separation methods can be broadly divided into two main categories—classical and modern methods. The most significant classical methods for separation of rare-earth elements include fractional precipitation, fractional crystallization, volatilization, and decomposition. The most important modern industrial separation methods include ion exchange and liquid-liquid solvent extraction.

Fractional precipitation and fractional crystallization, among the earliest rare-earth separation techniques, have been used since the first half of the 19th century.⁴ Fractional precipitation is a technique in which a limited amount of precipitating agent is added to a mixture of trivalent rare earths in order to partially precipitate the rare-earth salts. Fractional crystallization, a similar technique, involves the induced partial crystallization of rare-earth salts. This induced crystallization commonly involves partial evaporation of the solvent or temperature variation to alter solubilities of the rare-earth salts in a particular solvent. These two methods utilize very slight differences in solubility between rare-earth compounds to separate mixtures of the trivalent elements. As a consequence of these slight differences, fractional precipitation and fractional crystallization involve a large number of repetitions to achieve significant separation between individual rare earths.

A general scheme for fractional precipitation and fractional crystallization is shown in Figure 1.1. In fractional crystallization, the original mixture of trivalent rare-earth compounds is first treated with a solvent in which the compound can be completely dissolved. The solution is then partially evaporated, allowing approximately half of the rare-earth content to crystallize from the solution. The crystals are then separated from the mother liquor, solvent is added to dissolve the isolated crystalline material, and each fraction is evaporated again and recrystallized, resulting in four fractions of

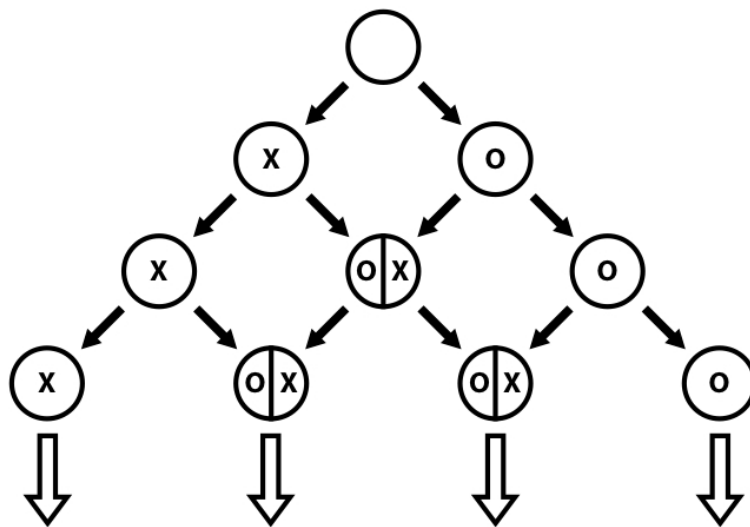


Figure 1.1: Fractional precipitation and fractional crystallization separation scheme⁵

material. The crystals obtained from the first liquor fraction are then combined with the liquor removed from the first crystal fraction. This process can be repeated many times, allowing relatively soluble rare earths to accumulate in the liquor portion of the fractions, and relatively insoluble rare earths to accumulate in the crystalline portion obtained from each fraction. Fractional precipitation methods follow this same sequence of steps, but these separations are often limited by the difficulty in the dissolution of precipitates and reprecipitation of these compounds.

Decomposition and volatilization separation methods, although used to a lesser extent than other early methods such as fractional precipitation and fractional crystallization, have also been historically used to separate rare-earth compounds.⁴ These methods make use of slight differences in decomposition and volatilization properties between individual rare-earth compounds to achieve partial separations between these elements. Decomposition of rare-earth compounds is typically accomplished by exposure of these compounds to elevated temperatures or application of electric current to solutions of these compounds. Both are generally very inefficient and are limited by the number of sequential steps that can be readily performed on these compounds.

Due to the numerous disadvantages of classical techniques for separation of rare-earth elements, modern separation techniques such as ion exchange and liquid-liquid solvent extraction have emerged as the most prominent industrial separation methods since the middle of the 20th century. Ion-exchange separation methods of rare-earth elements, first developed in the late 1940s,⁶ were among the earliest of these modern separation techniques. This separation method relies on the interaction of trivalent rare-earth cations or ionic rare-earth complexes with a stationary phase contained within a column in which these separations are carried out.

The stationary phase of a traditional ion-exchange column is typically comprised of a functionalized polymeric resin. These ion exchangers can be classified into two categories: anionic or

cationic resins. Cationic ion-exchange resins, containing protonated functional groups such as sulfonates or carboxylates, are commonly used to separate trivalent rare-earth cations or cationic rare-earth complexes. Anionic ion-exchange resins, possessing basic amine or quaternary ammonium functional groups with an attached anion, are generally used in separations of anionic rare-earth complexes.

A schematic of a typical ion-exchange separation column is shown in Figure 1.2. In separation processes employing cationic exchange resins, the column is first loaded with a solution of trivalent rare earths or cationic rare-earth complexes. The rare-earth cationic species bind to the deprotonated reaction sites located on the surface of the ion-exchange resin. An eluent, commonly containing chelating species such as citrate, tartrate, or ethylenediaminetetraacetate anions, is then passed through the column. The rare-earth cationic species are stripped from the ion-exchange resin by the chelating eluent and are removed sequentially from the ion-exchange column. In separation methods involving anionic exchange resins, the ion-exchange column is initially loaded with a solution containing anionic rare-earth complexes. These anionic complexes are then adsorbed by the cationic reaction sites of the ion-exchange resin. A concentrated eluent containing species such as chloride, nitrate, or carbonate anions is then used to remove these rare-earth complexes from the ion-exchange resin through interaction with the basic functional groups of the anion exchanger.

In both ion-exchange processes, individual rare-earth species exhibit different affinities for the ion-exchange resin. As the eluent is passed through the column, species possessing a lower affinity for the ion-exchange resin are first displaced by the eluent. Species with higher affinities for the ion exchanger are then successively eluted from the column. The differences in retention times of individual rare-earth species by the ion-exchange resin column allow resolution of these mixtures to occur.

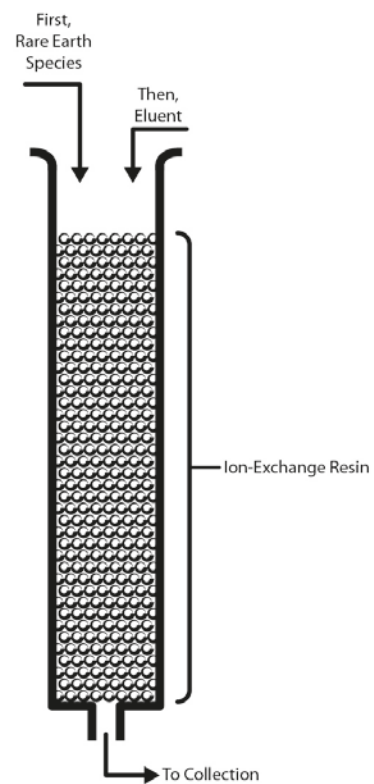


Figure 1.2: Simplified schematic of a typical small-scale ion-exchange column

Before an ion-exchange column is used for further separations, it must be treated with a regeneration agent to prepare the functional sites of the ion-exchange resin for future use. As a result of this regeneration step, industrial-scale separations by this method are limited to single batches of rare-earth solutions, as continuous operation is difficult to achieve.

Liquid-liquid solvent extraction techniques for the separation of rare-earth species were also first reported in the late 1930s and early 1940s.⁷ Utilized in both laboratory and industrial settings, these techniques have been one of the most highly-developed methods of rare-earth separations over the past 70 years.

Solvent extraction systems for the separation of rare-earth species usually contain two immiscible liquid phases— these phases typically consist of an aqueous phase and organic phase. The aqueous phase of the extraction system commonly carries a mixture of rare-earth trivalent cations or rare-earth ionic complexes. The selected organic diluent, exhibiting a low solubility in the aqueous phase of the extraction system, is loaded with an organic extractant. Organic extractants should possess slight solubilities in the aqueous phase and high solubilities in the organic phase of these extraction systems. These extractants must also possess considerable complexation abilities with the rare-earth species for which extraction is desired. Extractants used in rare-earth solvent extraction systems can be neutral, anionic, or cationic in nature.

When the two phases are placed in direct contact with each other, phase exchange of rare-earth species occurs at the interface of the two liquid phases. Hydrophilic rare-earth ions contained within the aqueous phase are then complexed by the hydrophobic organic extractant at this interface. This results in the formation of a neutral rare-earth complex that favors solubility in the organic phase of the extraction system. The organic phase, containing the complexed rare-earth species, can then be isolated from the aqueous phase. Due to the slight differences in chemical behavior of these rare-

earth species, the formation of these rare-earth complexes also follows a continuous trend, allowing some rare-earth species to be preferentially extracted into the organic phase of the extraction system. This process can be repeated multiple times to enhance the separation between individual rare-earth compounds.

Industrially, solvent extraction offers many advantages over other classical and modern rare-earth separation techniques. Unlike stationary ion-exchange resins, mobile extractants used in solvent extraction processes can be stripped from the rare-earth species in solution and reused without the need of a separate regeneration step. This allows solvent extraction separation processes to be operated on a continuous basis. The extent of separation between individual rare-earth species can also be enhanced by arrangement of solvent extraction systems in stages. Stages within industrial solvent extraction processes for the separation of rare earths commonly operate in a continuous, counter-current manner. An example of a continuous counter-current solvent extraction system is shown in Figure 1.3.

In this process, the aqueous phase, which contains the rare-earth ions to be separated, and an organic phase, containing the organic extractant, enter the extraction system as indicated on the diagram. Mixing of the two phases occurs in the center of each column, which possesses small plates to introduce turbulence as the phases traverse the column. This turbulence is often enhanced by mechanical shaking, stirring, or centrifugation of the column. After sufficient mixing of the two phases is complete, the phase with the lowest density (typically the organic phase) settles in the chamber at the very top of each column and is then routed to the next unit to the right. The phase with the highest density (typically the aqueous phase) settles in the chamber at the very bottom of each column and is then routed to the next unit to the left. This same process occurs in each solvent extraction unit in the series. By repetition of this process through multiple columns, each phase is

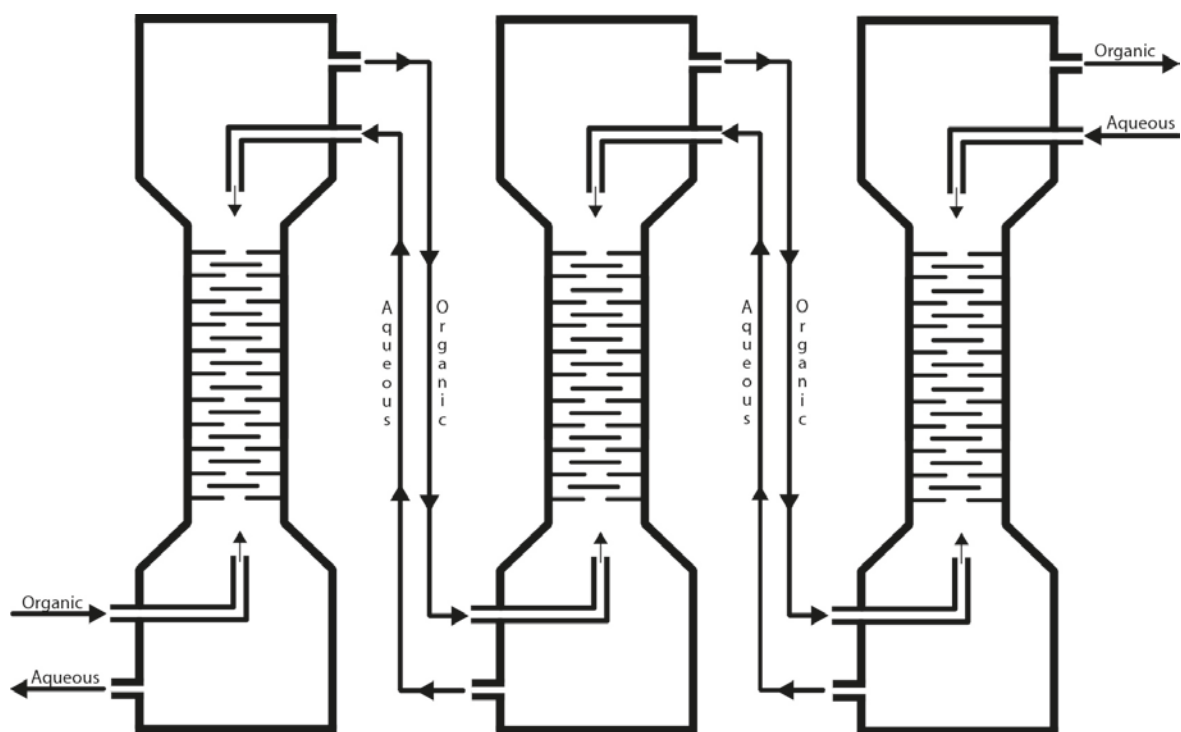


Figure 1.3: Multi-stage counter-current solvent extraction apparatus

subjected to several identical solvent extraction steps, increasing the separation between individual rare-earth species over a single solvent extraction step.

Since solvent extraction is the most widely used method for separation of rare earths, both in laboratory and industrial settings, this method has been selected for the following investigation.

Single solvent extraction separations, which are to be used, provide the basis for multi-staged separation methodologies.

Chapter 2: The Itinerant Behavior of Yttrium

Historical Considerations

Yttrium is found naturally with the lanthanide elements La-Lu and is the major constituent of ores with high concentrations of the heavy rare earths Gd-Lu. Reflecting this natural occurrence, significant interest has been placed on the chemical behavior of Y in combination with La-Lu—particularly concerning its separation from the other rare earths. Early attempts in the separation of Y from the rare earths using fractional crystallization, fractional precipitation, decomposition, and volatilization methods proved to be difficult, especially from Ho, which shares its crystal ionic radius with Y. However, it was observed that under special conditions, Y separated in positions with rare-earth elements other than its traditional position at Ho.

One of the earliest mentions of the itinerant behavior of Y was made in 1894 by Henry A. Rowland, who stated that Y could be separated from all other rare earths in gadolinite, fergusonite, and samarskite by a two-step process.⁸ First, separation of the Ce earths was effected by fractional crystallization of the sulfates. The remaining heavier rare earths were then subjected to fractional crystallization of the ferrocyanides, with Y remaining in the liquid phase. This reflects that Y acts as a heavy rare earth in the sulfate form and as a light rare earth in the ferrocyanide form.

Since this discovery, this phenomenon has been observed in several other rare-earth separation systems using techniques such as fractional precipitation, solvent extraction, ion exchange, and other similar chromatographic techniques. In Table 2.1, some examples of these systems are listed along with the position of Y relative to the lanthanide series and the separation agents used. The molecular structures associated with these separation agents are listed in Appendix A.

Table 2.1: The position of yttrium in selected systems

<	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	>
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17

Position Correlation Chart

Reference	Type	System	Position	Structure
9,10	Fractional Precipitation	Precipitation of potassium double ferrocyanide	1	-
11	Solvent Extraction	CMPO + Ammonium thiocyanate	1	1
12,13,14,15,16,17	Chromatography	Nitrates on γ -Al ₂ O ₃	1	-
18	Fractional Precipitation	Glycolates	1	2
19	Solvent Extraction	2-Bromodecanoic acid	1	3
19	Solvent Extraction	2-Bromo-3-cyclohexylpropanoic acid	1	4
19	Solvent Extraction	2-Bromo-3,5,5-trimethylhexanoic acid	1	5
20	Solvent Extraction	DIPSA + N,N,N',N'-tetraethylsuccinamide	1	6, 7
20	Solvent Extraction	DIPSA + N,N'-dibutyl-N,N'-dimethylsuccinamide	1	6, 8
20	Solvent Extraction	DIPSA + 1,2-bis(octylsulfinyl)ethane	1	6, 9
20	Solvent Extraction	DIPSA + Ethane-1,2-diylbis-(diisopropylphosphine oxide)	1	6, 10
20	Solvent Extraction	DIPSA + Methylenebis-(diisopropylphosphine oxide)	1	6, 11
21	Solvent Extraction	Hexanoic acid + Octanoic acid	2-3	12
21	Solvent Extraction	3-Cyclohexylpropanoic acid	2-3	13
21	Solvent Extraction	Cyclohexanecarboxylic acid	2-3	14
22	Ion Chromatography	Stationary: Iminodiacetic acid on SiO ₂ / Eluent: HNO ₃	2-3	-
22	Ion Chromatography	Stationary: Iminodiacetic acid on SiO ₂ / Eluent: Maleic acid	2-3	15

Table 2.1 (continued): The position of yttrium in selected systems

<	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	>
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17

Position Correlation Chart

Reference	Type	System	Position	Structure
23	Solvent Extraction	5- <i>n</i> -hexylsalicylic acid + N,N-di- <i>n</i> -pentylacetamide	2-3	16, 17
24	Solvent Extraction	Cekanoic acid	2-4	18
25	Solvent Extraction	Adogen-464SCN	1-8	19
26	Fractional Precipitation	Ammonium nitrate (presence of zinc)	2-4	-
27	Solvent Extraction	Tricaprylmethylammonium thiocyanate (Aliquat 336)	3-6	20
23	Solvent Extraction	DIPSA + N,N-di- <i>n</i> -pentylacetamide	3-4	6, 17
28	Ion Exchange	Stationary: Zerolit 225 / Eluent: Ammonium borate-acetate	<9	-
29	Solvent Extraction	Cyanex 925 + Ammonium Thiocyanate	2-6	21
24	Solvent Extraction	Naphthenic acid	3-4	22
19	Solvent Extraction	3,5,5-Trimethylhexanoic acid	4	23
23	Solvent Extraction	3,5- <i>tert</i> -butylsalicylic acid + N,N-di- <i>n</i> -pentylacetamide	3-5	24, 17
21	Solvent Extraction	Iso-nonanoic acid	4-5	25
23	Solvent Extraction	DIPSA + N,N-diethyl-2-ethyl-2-methylheptanamide	4-5	6, 26
19	Solvent Extraction	2-Bromo-2-ethylhexanoic acid	5	27
30	Ion Chromatography	Stationary: Bio-Rad AG 50W-X8 Eluent: Glycolic acid	5	2
31	Solvent Extraction	Pentanone	5-7	28
23	Solvent Extraction	3,5- <i>tert</i> -butylsalicylic acid + N,N-diethyl-2-ethyl-2-methylheptanamide	5-7	24, 26

Table 2.1 (continued): The position of yttrium in selected systems

<	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	>
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17

Position Correlation Chart

Reference	Type	System	Position	Structure
32	Solvent Extraction	sec-Nonylphenoxyacetic acid + EDTA or HEDTA	<12	29, 30, 31
22	Ion Chromatography	Stationary: Iminodiacetic acid on SiO ₂ / Eluent: Diglycolic acid	5-7	32
33	Ion Chromatography	Stationary: NTA Resin / Eluent: HNO ₃	4-8	-
34,9,10	Fractional Precipitation	Ferricyanide precipitation	5-11	-
35	Ion Chromatography	Stationary: Hitachi ODS #3056 / Eluent: NTA	7	33
36	Ion Chromatography	Stationary: Bio-Rad AG-50W X4 / Eluent: HEDTA	7	31
21	Solvent Extraction	2-Ethylhexanoic acid	8-9	34
21	Solvent Extraction	2-Butyl-2-ethylhexanoic acid	8-9	35
37	Solvent Extraction	HPMBP	8-10	36
38	Ion Exchange	Pyroracemic acid	<10	37
21	Solvent Extraction	Versatic 10 acid	9-10	38
21	Solvent Extraction	1-Methylcyclohexanecarboxylic acid	9-10	39
39	Solvent Extraction	Cyanex 925	9-10	40
40,41,42	Fractional Precipitation	Precipitation by ammonia in 0.1M solution	9-11	-
24	Solvent Extraction	Neo-heptanoic acid	9-11	41
43	Ion Exchange	Stationary: Amberlite IR-120 / Eluent: EDTA or Citric acid	10-11	30, 42
44	Capillary Electrophoresis	α -Hydroxyisobutyric acid / Acetic acid	10-11	43

Table 2.1 (continued): The position of yttrium in selected systems

<	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	>
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17

Position Correlation Chart

Reference	Type	System	Position	Structure
45	Precipitation	Peroxyarbonates	10-11	-
46	Capillary Electrophoresis	α -Hydroxyisobutyric acid / Oxalic acid	10-11	43, 44
47	Ion Chromatography	Stationary: Nucleosil 5 SA / Eluent: α -Hydroxyisobutyric acid	10-11	43
48	Ion Exchange	Stationary: Dowex 50-WX 8 / Eluent: α -Hydroxyisobutyric acid + Lactic acid	10-12	43, 45
49	Fractional Crystallization	Nitrate crystallization	11-12	-
50	Solvent Extraction	TBP	11-12	46
51	Ion Exchange	Stationary: Amberlite IR-1 or Dowex-50 / Eluent: Citric acid	11-12	42
52	Fractional Precipitation	Cacodylic acid	11-12	47
53	Solvent Extraction	HEHEHP + <i>sec</i> -Nonylphenoxyacetic acid (CA-100)	11-12	48, 29
54	Liquid Chromatography	Stationary: TSK Gel SP-2SW / Eluent: Ammonium lactate	11-12	45
55	Paper Chromatography	Stationary: SA-2 Paper / Eluents: NH_4 lactate + α -Hydroxy- α -methylbutyric acid	10-15	49
56	Ion Exchange	Stationary: Diaion SK-1 / Eluent: Ammonium thiocyanate	11-13	-
57	Solvent Extraction	EHEHPA + Cyanex 923	9-15	48, 50
58	Ion Chromatography	Stationary: Dowex CS5 Column / Eluent: Dipicolinic acid	12	51
59	Solvent Extraction	Cyanex 272	12-13	52
59	Solvent Extraction	Cyanex 272 + <i>sec</i> -Octylphenoxyacetic acid	12-13	52, 53

Table 2.1 (continued): The position of yttrium in selected systems

<	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	>
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17

Position Correlation Chart

Reference	Type	System	Position	Structure
⁵³	Solvent Extraction	2-Ethylhexylphosphonic acid mono-(2-ethylhexyl) ester (HEHEHP)	12-13	48
⁴⁹	Fractional Crystallization	Bromate crystallization	12-13	-
⁶⁰	Solvent Extraction	HTTA + TBPO	12-13	54, 55
⁶¹	Solvent Extraction	TBP + Potassium selenocyanate	13	46
⁶²	Fractional Leaching	Ammonium salts	>9	-
⁶³	Solvent Extraction	Ammonium nitrate	>9	-
⁶⁴	Ion Exchange	Stationary: Dowex I X-8 / Eluent: Potassium sulfate	14-15	-
⁶⁵	Fractional Precipitation	Precipitation by carbonate at 0°C	17	-
⁶⁶	Solvent Extraction	sec-Octylphenoxyacetic acid (CA-12)	17	53

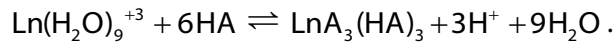
Over the past 70 years, several investigators have speculated about the factors involved in the migration of Y within the lanthanide series. In 1947, Joseph K. Marsh noted that Y fell between Nd and Sm when atomic radii were considered.⁶⁷ Assuming that atomic radii might be indicative of covalency, Marsh stated that a covalent contribution to bonding moved Y into the light rare-earth region, whereas chiefly ionic bonding placed it in the heavy rare-earth region. He then interpreted the placement of Y with the light rare earths in ferricyanide solubility separations as being due to a covalent contribution. To the contrary, the molecular volumes of these species show that the Y compounds resemble the heavy rare earths.

Siekierski, *et al.*, have also attributed the migratory phenomenon to variations in the degree of covalency in rare-earth to ligand bonding.⁶⁸ They assign this variation to covalent participation of the 4f electrons. Yttrium, possessing no 4f electrons, does not experience these effects. The effective atomic number of Y was then calculated from the unit cell volumes for a variety of rare-earth compounds containing ligands with variations in electronegativity. From these results, plots of the effective atomic number values versus the electronegativity of the atom directly bonded to Y suggest a correlation between these two values. The correlation indicates that ligands with lower electronegativities move Y from the heavier rare earths toward the lighter rare earths.

This behavior has also been investigated from the standpoint of hard-soft theory. In separations involving hard ligands such as nitrates, Y accompanies the heavy rare earths. The thiocyanates, which are softer, tend to place Y with the light rare earths. A 1973 patent by Gaudernack, *et al.*, utilizes this concept in a liquid-liquid solvent extraction process to remove Y from rare-earth mixtures.⁶³ In the first stage of this process, the light rare-earth nitrates are separated from the heavy rare-earth nitrates using tributyl phosphate (TBP) as the organic extractant. Yttrium, possessing hard nitrate ligands, accompanies the heavy rare earths. Next, Y and the heavy rare-earth

nitrate are treated with ammonium thiocyanate. The resulting rare-earth thiocyanates are then subjected to a second separation step using TBP. Yttrium, now behaving as a light rare earth with the softer thiocyanate ligands, can then be removed from the heavy rare earths. In 1994, Borkowski, *et al.*, attempted to discover other soft ligands which place Y with the light rare earths.⁶¹ The results of this investigation show that thiocyanate analogues, such as selenocyanates, do not cause the position of Y to deviate from its traditional position with the heavy rare earths.

Other attempts to explain this phenomenon suggest a connection between thermodynamic parameters and the position of Y within the lanthanide series. Consider the following reaction, which represents a solvent extraction system consisting of trivalent rare-earth cations (Ln^{+3}) and a carboxylic acid extractant (HA):



The overall Gibbs free energy of this reaction, $\Delta G^\circ(\text{rxn})$, represented by the equation

$$\Delta G^\circ_{\text{rxn}} = [\Delta G^\circ_{\text{LnA}_3(\text{HA})_3} + 3\Delta G^\circ_{\text{H}^+} + 9\Delta G^\circ_{\text{H}_2\text{O}}] - [\Delta G^\circ_{\text{Ln}(\text{H}_2\text{O})_9^{+3}} + 6\Delta G^\circ_{\text{HA}}] ,$$

is directly related to the Gibbs free energy of the individual species of this reaction. In mixed rare-earth solutions, the values of $\Delta G^\circ_{\text{H}^+}$, $\Delta G^\circ_{\text{HA}}$, and $\Delta G^\circ_{\text{H}_2\text{O}}$ remain constant for each rare-earth species.

As a result, the predominant free energy terms in rare-earth separation reactions correspond to the hydrated rare-earth complex, $\Delta G^\circ_{\text{Ln}(\text{H}_2\text{O})_9^{+3}}$ and the extracted complex $\Delta G^\circ_{\text{LnA}_3(\text{HA})_3}$. Some investigators have suggested that the free energy values corresponding to the formation of rare-earth complexes are the predominant terms in the $\Delta G^\circ_{\text{rxn}}$ equation shown above, but it is doubtful that the free energy value of the hydrated cation can be ignored. Other thermodynamic terms such as the enthalpy and

entropy for the complexation of rare earths in aqueous solutions have also been examined, but these values are known for very few rare-earth complexes.

Both the compositions of the hydrated cation and the extracted species can change the value of $\Delta G_{\text{rxn}}^{\circ}$. Considerations relating to coordination numbers, denticity of extractants, and solvent effects are of importance. It is generally known that rare-earth coordination numbers change from 9 to 8 as atomic number increases.^{69,70,71} However, there are exceptions to these numbers, even though a decrease in coordination number with atomic number is usually observed. When an extractant can exhibit more than one denticity, these ligands can attach to the rare-earth cation in varied ways. The result is differences in ΔG° of the extracted species. Solvent interactions with other species such as extractants and rare-earth complexes can also affect the ΔG° value of the extracted species and $\Delta G_{\text{rxn}}^{\circ}$.

In recent years, a few investigators have attempted to correlate the position of Y within the lanthanide series with the steric influence of the extractant, particularly carboxylic acid extractants. Although a steric influence on the position of Y has been suspected in the past, these investigations are the only systematic analyses of this phenomenon that have been made. A more detailed assessment of these studies, along with treatment of steric parameters and their possible correlations with the position of Y, will be given in the next section.

Carboxylic Acids as Rare-Earth Extractants

Solvent extraction has used carboxylic acids in separations of the rare earths since the early stages of its development. Because of their ease of use in solvent extraction systems, low cost, and commercial availability, particular interest has been given to these reagents over the past several decades. Carboxylic acid extractants such as naphthenic acid and the Versatic acids have been used industrially to separate components of rare-earth ores,⁷² and a variety of these extractants have been used in small-scale, laboratory experiments. Contrary to their widespread usage in rare-earth separations, detailed investigations of the behavior of Y in rare-earth solvent extraction systems using carboxylic acid extractants did not appear until 1992.

In 1992, a series of experiments by Anna C. du Preez and John S. Preston were some of the first to systematically address the migratory behavior of Y using carboxylic acids as extractants.^{21,73} One primary focus of these experiments was on the effects of structural alterations of carboxylic acid extractants on the position of Y. Experimentally, du Preez and Preston placed a stirred aqueous solution of a rare earth nitrate in contact with a stirred xylene solution containing a carboxylic acid extractant. They adjusted the pH of the aqueous phase and measured the extraction of the rare earth as a function of pH, being careful to bring all systems to equilibrium. Such experiments, such as the example illustrated in Figure 2.1 for a single element, were conducted for each rare earth La-Lu (excluding Pm). Plots were then constructed of the atomic numbers of the rare earths against the pH values at which 50% of the rare earths were extracted. In other words, they were using the $\text{pH}_{0.5}$ as a value proportional to the distribution coefficient. An example of these graphs for a single carboxylic acid extractant, Versatic 10 acid, is shown in Figure 2.2. It is to be noted that du Preez and Preston are making the assumption that the rare earths act in a mixture the same as they do individually.

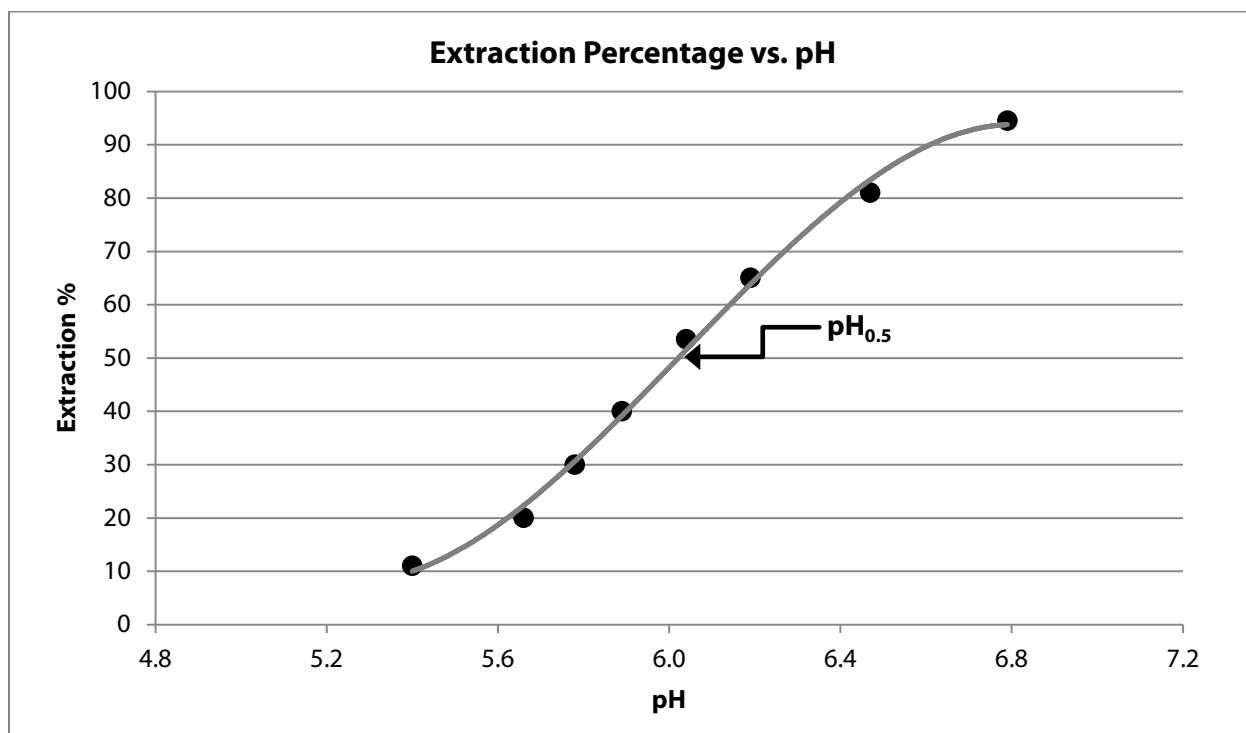


Figure 2.1: Determination of $\text{pH}_{0.5}$ value for a single rare earth (La)

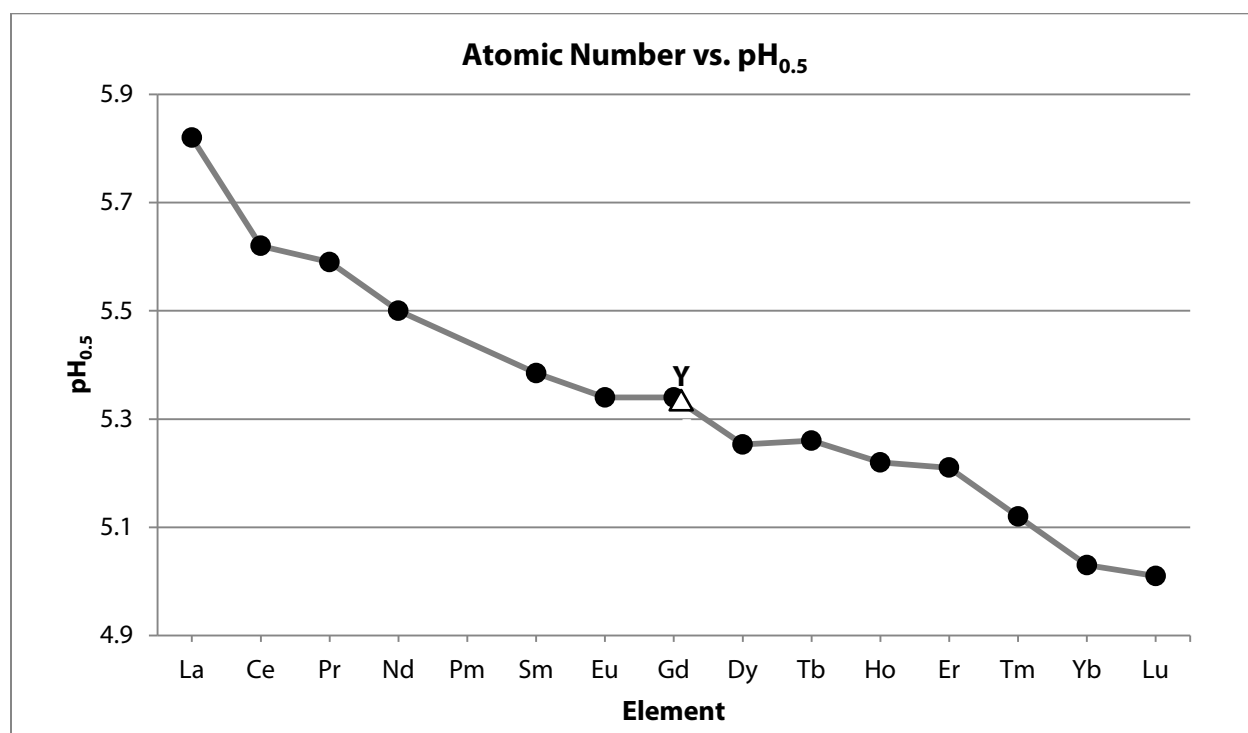
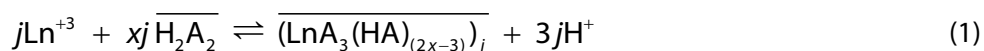


Figure 2.2: Values of $pH_{0.5}$ for lanthanide extractions using Versatic 10 acid

In a 1994 report by Preston, another series of individual solvent extractions using 2-bromoalkanoic acid extractants in xylene was also analyzed with similar general treatment of experimental data.¹⁹ In addition, inductively coupled plasma (ICP) methods were used for simultaneous detection of rare earths in multi-element solutions.

A similar study published in 2006 by Singh, *et al.*, also addressed the effect of structural changes in carboxylic acid extractants on the position of Y.²⁴ The authors used similar experimental conditions and techniques to determine extraction percentages of each rare earth with cekanoic acid, naphthenic acid, neo-heptanoic acid, and Versatic 10 acid in dodecane. Inductively coupled plasma-atomic emission spectrometry (ICP-AES) was used for analysis of binary rare-earth mixtures.

Both groups of authors interpreted the results of these separations using two major techniques—determination of the stoichiometry of extracted rare-earth species by slope analysis and the use of steric parameter values to rationalize the solvent extraction behavior of Y and the rare earths. Slope-analysis techniques rely on manipulation of equilibrium expressions to yield straight-line plots with slopes corresponding to values that determine the number of carboxylate anions and neutral carboxylic acid ligands attached to each extracted rare-earth species, and the degree of polymerization of the extracted species. A general equation representing the reaction between a rare-earth cation (Ln^{+3}) and a carboxylic acid dimer ($2\text{HA} \rightarrow \text{H}_2\text{A}_2$) can be written as



where the stoichiometric coefficient x determines the number of carboxylate anions and neutral carboxylic acid ligands attached to the rare earth and the variable j represents the degree of polymerization of the extracted species. Overlined terms indicate species contained in the organic

phase; all other species are assumed to exist in the aqueous phase. The equilibrium constant expression for this reaction can then be written as

$$K_{eq} = \frac{[(LnA_3(HA)_{(2x-3)})_j][H^+]^{3j}}{[Ln^{+3}]^j [H_2A_2]^{xj}} . \quad (2)$$

If the logarithm of this equation is then taken (for simplification, $[Ln_{org}] = j [(LnA_3(HA)_{(2x-3)})_j]$ and

$[Ln_{aq}] = [Ln^{3+}]$), the equation can be written and rearranged as

$$\log K_{eq} = \log [Ln_{org}] - \log j - 3j \text{ pH} - j \log [Ln_{aq}] - xj \log [H_2A_2] , \text{ or} \quad (3)$$

$$\log [Ln_{org}] = j (\log [Ln_{aq}] + 3 \text{ pH}) + (xj \log [H_2A_2] + \log K_{eq} + \log j) , \quad (4)$$

to produce a final equation with a linear form ($y = mx + b$). As shown in Equation 4, a plot of $\log [Ln_{org}]$ versus $(\log [Ln_{aq}] + 3 \text{ pH})$ at constant extractant concentration should yield a straight line with a slope equal to j , or the degree of polymerization of the extracted species. For ascertaining x , the equilibrium constant expression can be written in terms of the distribution ratio, D ,

$$D = \frac{[Ln_{org}]}{[Ln_{aq}]} , \quad (5)$$

to produce the equilibrium constant expression

$$K_{eq} = \frac{D [H^+]^{3j}}{j [Ln_{aq}]^{j-1} [H_2A_2]^{xj}} . \quad (6)$$

If the logarithm of Equation 6 is taken, this equation can now be expressed as

$$\log K_{eq} = \log D - 3j \text{ pH} - (j-1) \log [Ln_{aq}] - xj \log [H_2A_2] - \log j , \text{ or} \quad (7)$$

$$\log D - (j - 1) \log [Ln_{aq}] = x(j \log [\overline{H_2A_2}]) + (\log j + 3j \text{ pH} + \log K_{eq}). \quad (8)$$

According to Equation 8, a graph of $\log D - (j - 1) \log [Ln_{aq}]$ versus $j \log [\overline{H_2A_2}]$ should yield a straight line with a slope equal to x , indicating the number of carboxylate anions and neutral carboxylic acid ligands attached to the extracted species.

The second concept used by these authors was the steric influence of carboxylic acid extractants on the position of Y in rare-earth separations. Early publications by Ingold in the 1930s indicated that in esterification reactions of carboxylic acids and the hydrolysis of carboxylate esters, steric hindrance in proximity to the reaction site affected the rate of these two reactions.⁷⁴ In the early 1950s, Robert W. Taft proposed a mathematical equation designed to yield quantitative values to represent these steric effects.^{75,76} For esterification reactions of carboxylic acids and hydrolysis of carboxylate esters, the steric parameter E_s is defined as

$$\delta E_s = \log(k / k_o) \quad (9)$$

where δ represents a value which accounts for different experimental conditions, especially temperature and solvent, k represents the rate of reaction for substituted carboxylic acids and k_o represents the rate of reaction for a reference compound, generally defined as acetic acid. In the years following this initial report, Taft determined E_s values for carboxylic acids such as substituted benzoic acids and simple aliphatic carboxylic acids.

Some authors, however, have criticized the original E_s values calculated by Taft—most notably for the lack of standard experimental conditions used to calculate E_s values, contradictions in E_s values for some structurally similar carboxylic acids, and the limited range of E_s values that had been previously calculated. Beginning in 1978, a three-part series of publications by John A. MacPhee, *et al.*,

provided an extensive revision of the Taft steric parameter to address these issues.^{77,78,79} MacPhee first proposed the standardization of experimental conditions under which kinetic data were obtained. This revised steric parameter, E_s' , was to be calculated using only the rates of acid-catalyzed esterification of carboxylic acids in methanol at 40°C. Under these identical conditions, the value of δ is assumed to be unity, which simplifies the original expression to

$$E_s' = \log(k/k_o) \quad (10)$$

In order to maintain consistency in E_s' values for all substituted carboxylic acids, the authors recalculated existing steric parameter values which had previously been determined under nonstandard conditions. As a consequence of the standardization of experimental conditions, many contradictory steric parameter values appeared to be resolved.

MacPhee also calculated E_s' values for an additional 63 substituted carboxylic acids in an effort to expand upon the small number of preexisting E_s values originally reported by Taft. Due to the difficulties in direct calculations of esterification rates for carboxylic acids with high steric bulk, E_s' values for these carboxylic acids were determined from relative rates of esterification in binary mixtures of carboxylic acids.

Analysis of the E_s' values, listed in Table 2.2, for the 107 carboxylic acids reported by MacPhee revealed several important trends and observations. A plot of steric parameter values for branched alkyl carboxylic acids versus an increasing number of carbon atoms reveals three distinct regions of behavior. These three regions show an increase in E_s' values ($n=1$ to $n=7$), a decrease in E_s' values or “leveling effect” ($n=8$ to $n=9$), and an inversion of E_s' values ($n=10$) or “inversion effect”. A topological interpretation of these observations revealed that branched alkyl carboxylic acids that contained the same number of total carbon atoms also shared similar E_s' values.

Table 2.2: -E_s' values for selected carboxylic acids

<i>Abbreviations and Notes</i>			
Me = Methyl	Pr = Propyl	Bu = Butyl	Ph = Phenyl
An = Anthracenyl	Fl = Fluorenyl	^a = n > 1	^b = n > 2

R Group	-E _s '
H	-1.12
F-	-0.57
CH ₃ C(OH)H-	-0.08
HOCH ₂ -	-0.03
Me	0.00
Cl	0.02
cyclo-C ₄ H ₇	0.03
Et	0.06
CH ₂ C-	0.18
FH ₂ C-	0.20
Br	0.22
BrH ₂ C-	0.24
IH ₂ C-	0.30
Pr	0.31
n-Bu	0.31
n-C ₅ H ₁₁	0.31
(i-Bu)CH ₂ CH ₂ -	0.31
CH ₂ =CH-CH ₂ -	0.31
(i-Pr)CH ₂ CH ₂ -	0.32
F ₂ HC-	0.32
PhOCH ₂ -	0.32
(t-Bu)CH ₂ CH ₂ -	0.33
Ph(CH ₂) ₄ -	0.33
(cyclo-C ₆ H ₁₁)CH ₂ CH ₂ -	0.34
Ph(CH ₂) ₃ -	0.34
(2-furyl)CH ₂	0.34
PhCH ₂ CH ₂ -	0.35
CH ₃ (CH ₂) _n C(OH) ^a	0.35
(cyclo-C ₆ H ₁₁)(CH ₂) ₃ -	0.36

R Group	-E _s '
PhCH ₂ -	0.39
cyclo-C ₅ H ₉	0.41
CH ₂ =CH(CH ₂) _n ^b	0.43
PhCH ₂ MeCH-	0.44
i-Pr	0.48
I	0.50
CH ₃ (CH ₂) _n CO ^a	0.52
Cl ₂ HC-	0.58
cyclo-C ₆ H ₁₁	0.69
(3-furyl)CH ₂ -	0.74
Br ₂ HC-	0.76
F ₃ C-	0.78
(cyclo-C ₆ H ₁₁)CH ₂ -	0.89
NCCH ₂ -	0.89
PhMeCH-	0.90
cyclo-C ₇ H ₁₃	0.92
i-Bu	0.93
I ₂ HC-	0.93
(s-Bu)CH ₂ -	0.97
s-Bu-	1.00
(n-Pr)MeCH-	1.02
(n-Bu)MeCH-	1.06
cyclo-C ₃ H ₅	1.09
FICH-	1.13
PhEtCH-	1.32
AnCH-	1.35
CH ₃ (CH ₂) _n C(OMe)H ^a	1.39
t-Bu	1.43
Ph ₂ CH-	1.50

Table 2.2 (continued): -E_s' values for selected carboxylic acids

<i>Abbreviations and Notes</i>			
Me = Methyl	Pr = Propyl	Bu = Butyl	Ph = Phenyl
An = Anthracenyl	Fl = Fluorenyl	^a = n > 1	^b = n > 2

R Group	-E_s'
(t-Bu)CH ₂ -	1.63
Cl ₃ C-	1.75
BrMe ₂ C-	1.77
Me ₃ Si-	1.79
(t-Bu)CH ₂ MeCH-	1.81
FICMe	1.81
Br ₂ MeC-	1.92
PhC≡C-	1.97
Et ₂ CH-	2.00
PrEtCH-	2.00
(n-Pr) ₂ CH-	2.03
(n-Bu)EtCH-	2.03
(n-Bu) ₂ CH-	2.06
FICet	2.07
CH ₂ =CH-	2.07
Br ₃ C-	2.14
EtMe ₂ C-	2.28
Ph	2.31
3-furyl	2.33
(i-Bu) ₂ CH-	2.38
(t-Bu)CH ₂ Me ₂ C-	2.48
I ₃ C-	2.62
2-furyl	2.63
o-tolyl	2.82
(o-Et)C ₆ H ₄	2.97

R Group	-E_s'
(o-Ph)C ₆ H ₄	3.01
(o-Pr)C ₆ H ₄	3.04
[(t-Bu)CH ₂] ₂ CH-	3.06
(t-Bu)MeCH-	3.21
(i-Pr)EtCH-	3.23
FICPh	3.23
FICPr	3.46
(i-Pr)Me ₂ C-	3.54
Ph ₂ MeC-	3.73
FICBu-	4.32
Ph ₂ EtC-	4.55
Ph ₃ C-	4.91
(i-Pr) ₂ CH-	5.01
Et ₃ C-	5.29
(t-Bu)Me ₂ C-	5.40
(i-Pr)Et ₂ C-	6.20
(t-Bu)(i-Pr)CH-	6.53
(t-Bu)(i-Pr)EtC-	6.62
(i-Pr) ₃ C-	6.73
(t-Bu) ₂ CH-	6.97
(t-Bu)Et ₂ C-	7.21
(i-Pr) ₂ MeC-	7.38
(i-Pr) ₂ EtC-	7.38
(t-Bu)(i-Pr)MeC-	7.56

Another key observation made by MacPhee was the dependence of E_s' values on the substituents located at the α -position relative to the carboxyl group in substituted carboxylic acids. The magnitude of change in E_s' values corresponding to α -substitutions of carboxylic acids was found to be much higher than substitutions of the same group at β - or γ -positions. It is doubtful, however, that the E_s' values calculated by MacPhee are dependable to three significant figures due to the error introduced from the measurement of esterification rates. For this reason, E_s' values will be reported to only two significant figures throughout this discussion. Consider the two examples shown in Figure 2.3. In series "a", the substitution of a phenyl group at the α -carbon atom relative to the carboxyl group of propanoic acid gives rise to a much higher change in $-E_s'$ ($\Delta-E_s' = 0.8$) versus the substitution of the same group at the β -carbon atom ($\Delta-E_s' = 0.3$). In series "b", the value of $-E_s'$ increases substantially for each consecutive addition of phenyl groups to the α -carbon atom of propionic acid. Both of these examples demonstrate that α -substitution is key contributor to the overall steric bulk of these substituted carboxylic acids.

The results of the investigations by du Preez, Preston, and Singh revealed that some connections exist between the extraction position of Y and the overall steric bulk of carboxylic acid extractants used in rare-earth separations. These results are summarized in Table 2.3, which lists the reported positions of Y and $-E_s'$ values determined for some carboxylic acid extractants, and the associated structures of these extractants are listed in Appendix A. In the 1992 publication by du Preez and Preston, Y most closely resembled the rare earths Ce and Pr for carboxylic acid extractants of low steric hindrance, possessing $-E_s'$ values below 1, such as octanoic acid, hexanoic acid, 3-cyclohexylpropanoic acid, and cyclohexanecarboxylic acid. For extractants with $-E_s'$ values from 2-4, such as 2-ethylhexanoic acid and 1-methylcyclohexanecarboxylic acid, Y was extracted with the middle rare earths such as Gd and Tb. The same behavior of Y was observed for highly sterically

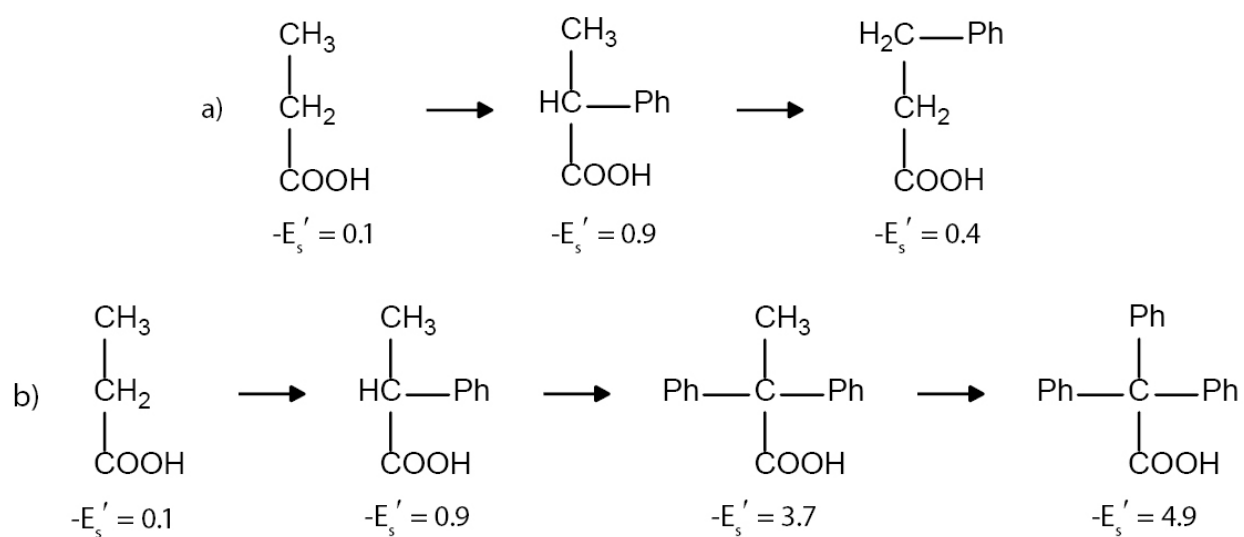


Figure 2.3: The effect of substitution location on the value of $-E'_s$

Table 2.3: Summary of literature results

Carboxylic Acid	-E _s '	Position of Y	Structure	Reference
Hexanoic acid	0.3	Ce	12	21
Octanoic acid	0.3	Ce	12	21
3-Cyclohexylpropanoic acid	0.3	Ce	13	21
Cyclohexanecarboxylic acid	0.7	Ce	14	21
Iso-nonanoic acid	1.0	Pr	25	21
Naphthenic acid	1.4	Nd	22	21
2-Ethylhexanoic acid	2.0	Eu	34	21
1-Methylcyclohexanecarboxylic acid	2.3	Tb	39	21
Versatic 10 acid	3.6	Gd	38	21
2-Butyl-2-ethylhexanoic acid	5.3	Gd	35	21
2-Bromodecanoic acid	1.3	< La	3	19
2-Bromo-3-cyclohexylpropanoic acid	1.3	< La	4	19
2-Bromo-3,5,5-trimethylhexanoic acid	1.9	< La	5	19
2-Bromo-2-ethylhexanoic acid	-	Nd	27	19
3,5,5-Trimethylhexanoic acid	-	Pr	23	19
Cekanoic acid	-	La-Pr	18	24
Naphthenic acid	1.4	Ce-Pr	22	24
Neo-heptanoic acid	-	Gd-Dy	41	24
Versatic 10 acid	3.6	Gd-Ho	38	24

hindered extractants with $-E_s'$ values greater than 4, such as 2-butyl-2-ethylhexanoic acid and Versatic 10 acid.

Characterization of extracted La, Gd, and Lu complexes using a slope-analysis technique showed that both the stoichiometry and the degree of polymerization of these species were also dependent on the extent of steric hindrance of the extractant. For extractants with high steric hindrance such as Versatic 10 acid ($-E_s' = 3.8$), the monomeric, 9-coordinate species $\text{LnA}_3(\text{HA})_3$ was found to be formed for all three rare earths. Rare-earth species formed with 3-cyclohexylpropanoic acid ($-E_s' = 0.3$), an extractant with low steric bulk, were determined to exist in dimeric form for all three rare earths. The stoichiometry, however, for each rare-earth complex was determined to be $(\text{LaA}_3(\text{HA})_3)_2$, $(\text{GdA}_3(\text{HA})_3)_2$, and $(\text{LuA}_3(\text{HA})_2)_2$, suggesting a coordination number change from 9 to 8 among the heavy rare earths.

Data analysis of systems containing 2-bromoalkanoic acids also indicated that steric factors influenced the extraction behavior of Y and the rare earths. A similar correlation was observed between the increase in $-E_s'$ values and the movement of Y toward the heavy rare earths. However, Y was found to occupy a position below La for the three extractants with the lowest $-E_s'$ values, such as 2-bromodecanoic acid ($-E_s' = 1.3$), 2-bromo-3-cyclohexylpropanoic acid ($-E_s' = 1.3$), and 2-bromo-3,5,5-trimethylhexanoic acid ($-E_s' = 1.9$). The most highly sterically hindered extractant, 2-bromo-2-ethylhexanoic acid, was found to place Y with Nd. Although the $-E_s'$ value for 2-bromo-2-ethylhexanoic acid could not be experimentally determined, it can be assumed that the steric hindrance caused by the 2-substituted (or α -substituted) ethyl group would result in a $-E_s'$ value higher than the other bromo-substituted carboxylic acids.

This publication also expanded on the characterization of extracted complexes using slope analysis from the 1992 article by du Preez and Preston. Preston determined the degree of

polymerization for all rare earths, including Y, in solvent extractions using 2-bromo-3,5,5-trimethylhexanoic acid and 2-bromodecanoic acid. In rare-earth complexes with 2-bromo-3,5,5-trimethylhexanoic acid, dimeric species were formed with the light rare earths, La-Eu, and monomeric species were formed with the heavy rare earths, Gd-Lu, and Y. The stoichiometry of the complexes of La and Lu were found to be $(\text{LaA}_3(\text{HA})_3)_2$ and $\text{LuA}_3(\text{HA})_3$, both with a coordination number of 9. The same transition between dimeric and monomeric species was observed in complexes containing 2-bromodecanoic acid. This transition, however, occurred at a point within the heavy rare earths, Tb and Dy. A similar analysis of complexes of La, Pr, Gd, Yb, and Y with 2-bromo-2-ethylhexanoic acid showed that monomeric complexes were formed for all rare earths.

The results of solvent extractions performed by Singh, *et al.*, were also in accordance with the observations reported by du Preez and Preston. Cekanonic acid and naphthenic acid, the two least sterically hindered extractants, were found to place Y in the region of La to Pr. Versatic 10 acid and neo-heptanoic acid, the most sterically hindered extractants, positioned Y with the heavy rare earths, Gd to Ho. Slope analysis treatment of data showed that monomeric complexes were extracted with these four carboxylic acids for all rare earths.

Chapter 3: Experimental

Introduction

As established in the previous chapter, the itinerant behavior of Y within the lanthanide series is a phenomenon which is presently not fully understood. Prior investigations have indicated that steric factors, particularly in rare-earth solvent extraction systems containing carboxylic acid extractants, can influence the position of Y. These studies were among the first systematic investigations to be performed in which the position of Y was examined for a variety of structurally different carboxylic acid extractants. Using steric parameter values such as E_s' , these investigators indicated a possible correlation between the position of Y and these values. It is to be noted, however, that a variety of carboxylic acid extractants still remain to be investigated, the ability to use steric parameter values to rationalize or predict the position of Y within the lanthanide series has not been fully explored, and the results obtained from systems containing multiple rare earths is very limited.

The goal of the following research is to expand upon the previous experiments performed by du Preez, Preston, and Singh. Through the use of a larger range of carboxylic acid extractants, a better understanding of the underlying structural factors that influence the position of Y in these solvent extractions might be achieved. These experiments were performed using mixtures of Y and multiple rare earths, along with simultaneous detection of rare-earth concentrations using inductively-coupled plasma-optical emission spectrometry (ICP-OES). The results of these experiments, along with considerations pertaining to steric influences on the position of Y, will also be outlined.

Materials and Reagents

Carboxylic acid extractants were obtained commercially and used as received. These extractants, along with the purity and commercial supplier of each extractant are listed in Table 3.1.

Table 3.1: Carboxylic acid extractants and suppliers

Name	Purity	Supplier
Octanoic acid	99%	Acros Organics
Decanoic acid	99+%	Acros Organics
Lauric acid	99.5+%	Acros Organics
2-Ethylbutyric acid	99%	Acros Organics
2,2-Dimethylbutyric acid	97%	Alfa Aesar
DL-2-methylbutyric acid	98%	Acros Organics
Trimethylacetic acid	99%	Acros Organics
o-Toluic acid	99%	Eastman Organic Chemicals
m-Toluic acid	99%	Acros Organics
p-Toluic acid	98%	Acros Organics
2,3-Dimethylbenzoic acid	98%	Acros Organics
2,4-Dimethylbenzoic acid	98%	Acros Organics
2,5-Dimethylbenzoic acid	98%	Acros Organics
2,6-Dimethylbenzoic acid	99%	Acros Organics
3,5-Dimethylbenzoic acid	99%	Acros Organics
Phenylacetic acid	99%	Sigma-Aldrich

Table 3.1 (continued): Carboxylic acid extractants and suppliers

Name	Purity	Supplier
Adamantane-1-carboxylic acid	99%	Alfa Aesar
1-Naphthoic acid	98%	Acros Organics
2-Naphthoic acid	98+%	Alfa Aesar
1-Naphthylacetic acid	96%	Alfa Aesar
2-Naphthylacetic acid	99%	Acros Organics
Cyclohexanecarboxylic acid	98+%	Acros Organics
Cyclohexylacetic acid	98+%	Acros Organics
Dicyclohexylacetic acid	99%	Sigma-Aldrich
1-Methylcyclohexanecarboxylic acid	99%	Alfa Aesar
1-Phenyl-1-cyclohexanecarboxylic acid	95%	Acros Organics
Anthranilic acid	≥98%	Sigma-Aldrich
2-Chlorobenzoic acid	98%	Acros Organics
2-Bromobenzoic acid	97%	Acros Organics
2-Iodobenzoic acid	98%	Acros Organics
α-Bromo-p-toluic acid	97%	Sigma-Aldrich
α-Bromophenylacetic acid	98%	Sigma-Aldrich

Aqueous solutions were prepared using high-purity water (Fisher Scientific, Optima LC/MS). Adjustment of pH was performed using sodium hydroxide (Fisher Scientific, Certified Grade) and ammonium hydroxide (J.T. Baker, Electronic Grade). Nitric acid (Fisher Scientific, TraceMetal Grade) was used for preparation of samples for analysis by ICP-OES and pH adjustments.

The organic diluents toluene (Fisher Scientific, Laboratory Grade), methyl isobutyl ketone (MIBK, Fisher Scientific, Certified ACS), cyclohexanone (Fisher Scientific, Certified), p-xylene (Acros Organics, 99%), n-octane (Alfa Aesar, 98+%), 1-octanol (Alfa Aesar, 99%), chloroform (Fisher Scientific, Certified ACS), carbon tetrachloride (Acros Organics, 99%), and 2,6-dimethyl-4-heptanone (Sigma-Aldrich, 99%) were used in solvent extraction experiments as supplied.

Rare-earth oxides were used as the starting materials for all aqueous rare-earth stock solutions. Yttrium (III) oxide (Y_2O_3 , $\geq 99.99\%$) and lanthanum (III) oxide (La_2O_3 , 99.9%) were obtained from Sigma-Aldrich. Praseodymium (III) oxide (Pr_2O_3 , 99.9%), neodymium (III) oxide (Nd_2O_3 , 99.9%), samarium (III) oxide (Sm_2O_3 , 99.9%), europium (III) oxide (Eu_2O_3 , 99.9%), gadolinium (III) oxide (Gd_2O_3 , 99.9%), dysprosium (III) oxide (Dy_2O_3 , 99.9%), and holmium (III) oxide (Ho_2O_3 , 99.9%) were purchased from Alfa Aesar. Terbium (III, IV) oxide (Tb_4O_7 , 99.999%) was acquired from Acros Organics. Erbium (III) oxide (Er_2O_3 , 99.9%) was purchased from Pro Chem, Inc., and lutetium (III) oxide (Lu_2O_3 , 99.9%) was supplied by Rhône Poulenc.

Equipment and Instrumentation

Solvent extraction experiments were performed using 8-mL sample vials with Teflon-lined caps (National Scientific) and 20-mL scintillation vials with urea caps and poly-seal cone (Kimble). Measurement of pH was performed using an Accumet Basic pH meter (Fisher Scientific) equipped with an Accumet Microprobe Ag/AgCl combination electrode (Fisher Scientific). Samples were stirred

using a Variomag Poly 15 multipoint stirrer (Thermo Scientific). Measurements of rare-earth ppm concentrations were performed using an Optima 2100DV ICP-OES (PerkinElmer).

Preparation of Aqueous and Organic Phases

Rare-earth stock solutions were prepared individually by first dissolving weighed amounts of rare-earth (III) oxides in concentrated HNO_3 . Each solution was allowed to stir overnight until complete dissolution had occurred. This dissolution was also aided by gentle heating of the solution for some rare-earth oxides which did not readily dissolve. Each solution was then diluted to the appropriate level to yield a 2% HNO_3 concentration and 1000 ppm Ln^{+3} concentration.

Mixtures of trivalent rare earths used in solvent extraction experiments were prepared from the 1000-ppm stock solutions containing individual rare-earth species. All prepared mixtures were of equal ppm concentrations of rare earths.

Organic phases were prepared by dissolution of a weighed amount or known volume of carboxylic acid extractant in the chosen organic diluent for each solvent extraction sample.

Experimental Approach

Carboxylic acid extractants were used throughout all solvent extraction experiments in a tenfold molar excess of the total initial rare-earth molar concentration of the aqueous phase. Since the previously reported stoichiometries of extracted rare-earth carboxylate complexes indicated that 5 to 6 carboxylic acid ligands would be necessary to satisfy the coordination number of each rare-earth cation, this amount of extractant used for each solvent extraction should allow complete saturation of coordinating sites for each rare-earth cation to occur.

A preliminary series of solvent extraction experiments was performed to determine the optimum diluent and solvent extraction conditions to be used throughout the proposed research. To

validate that these experiments were consistent with previously reported data,^{21,73} octanoic acid in n-octane was selected for these initial experiments. Octane was chosen in an effort to minimize involvement of the organic diluent in the complexation of rare-earth cations during extraction.

In an 8-mL glass vial, 2 mL of aqueous solutions containing binary mixtures of 250 ppm Ln^{+3} (1.43×10^{-3} M to 1.80×10^{-3} M, depending on Ln^{+3}) and 250 ppm (2.75×10^{-3} M) Y^{+3} were placed in contact with 2 mL of octane. An excess of octanoic acid (4.15×10^{-2} M to 4.52×10^{-2} M concentrations in the organic phase, depending on Ln^{+3}) was added to the organic phase. The pH of the aqueous phase for each sample was then adjusted with dilute NaOH. Stabilization of pH values were observed at least 10 minutes after addition of base to the aqueous phase. Visual confirmation of this stabilization was often indicated by the gradual transition in appearance of the aqueous phase from cloudiness to a clear solution.

After each addition of base to the aqueous phase, the pH of the solution was determined. The concentrations and volumes of NaOH used to adjust pH levels were established on an individual basis. The volume of base added to the aqueous phase for each sample was also carefully recorded to take into account the effect of dilution on Ln^{+3} and Y^{+3} concentrations. Once pH adjustment was complete, each sample was allowed to stir for no less than 12 hours prior to analysis by ICP-OES.

Some difficulties were encountered in these initial experiments. The adjustment of pH to levels at which extraction was reported for previous solvent extractions of rare earths containing octanoic acid as an extractant resulted in the formation of precipitates at the interface between the organic and aqueous phases in several experiments. Centrifugation and increased stirring rate during pH adjustment prevented the formation of these precipitates in many cases. However, due to this instability and the difficulty involved in the inhibition of this precipitation, a search to find alternative organic diluents was conducted.

Initial tests to find more suitable organic diluents showed that solvents such as chloroform, MIBK, and 1-octanol each prevented this precipitation from occurring. Some diluents such as MIBK and 1-octanol, however, were known to act as adducting agents in the extraction of rare-earth species. These adducting agents can have the potential to participate in the complexation reaction through the replacement of neutral carboxylate ligands coordinated to the rare-earth cations. As a result, the observation of predominantly steric effects in the separation of these mixtures of rare earths could be affected by this interaction.

Nonpolar organic diluents, such as p-xylene and carbon tetrachloride, were used throughout the remainder of these experiments. Satisfactory results were obtained in these experiments, as these diluents seemed to prevent the precipitation issues encountered in the preliminary solvent extraction samples.

Another issue addressed in these first experiments was the difficulty in pH adjustment of the aqueous phase of these samples. Adjustments were made on a subjective basis—initial pH adjustments were performed using 6 M and 3 M NaOH solutions. As the pH of the aqueous phases approached the desired levels, NaOH solutions with concentrations of 1.0 M, 0.5 M, and 0.1 M were used to gradually increase the pH of these aqueous phases. However, adjustments performed with volumes of 1.0 μL to 10.0 μL of dilute NaOH often surpassed the target pH value, and the addition of dilute HNO_3 to lower the pH of these solutions resulted in the formation of precipitates in both the aqueous and organic phases.

To lessen the change in pH values resulting from each addition of NaOH to the aqueous phase, the volume of each phase was increased to 3.0 mL, maintaining consistent concentrations of octanoic acid in the organic phase and trivalent rare earths in the aqueous phase.

Additional experiments were performed to assess the behavior of rare earths in separations of mixtures of 2, 3, and 4 Ln^{+3} plus Y^{+3} . These experiments were conducted to ensure that the previously mentioned issues had been resolved before separations of several rare earths were attempted.

The second series of solvent extraction experiments was conducted using 20-mL glass vials containing 6.0 mL of a 125-ppm aqueous mixture of La^{+3} ($9.00 \times 10^{-4} \text{ M}$), Nd^{+3} ($8.63 \times 10^{-4} \text{ M}$), Eu^{+3} ($8.25 \times 10^{-4} \text{ M}$), Dy^{+3} ($7.75 \times 10^{-4} \text{ M}$), Lu^{+3} ($7.13 \times 10^{-4} \text{ M}$), and Y^{+3} ($1.38 \times 10^{-3} \text{ M}$) in contact with 6.0 mL of organic diluent and an excess of carboxylic acid extractant. The extractants chosen for this phase of research were o-toluic acid, m-toluic acid, and p-toluic acid, each with $5.45 \times 10^{-2} \text{ M}$ concentrations in the organic phase. The pH of each sample was adjusted with known volumes of dilute NaOH or NH_4OH , and these samples were stirred for no less than 12 hours prior to analysis by ICP-OES.

The volume of both aqueous and organic phases used in these solvent extractions was increased to improve the adjustment of pH levels, the availability of organic extractant at the aqueous-organic phase interface, and the ease of separation of the two phases prior to analysis. At this volume, minor increases in pH could be made using small additions of base to the aqueous phase.

Similar issues with diluents such as p-xylene and carbon tetrachloride were encountered during these solvent extractions. Precipitation was again observed at the interface between the two phases in many samples—this precipitation occurred in samples containing each of the three carboxylic acid extractants. The use of a similar diluent, toluene appeared to lessen the frequency of precipitation in samples containing these extractants. After this finding, toluene was used exclusively for all solvent extractions performed in this investigation.

Another important experimental improvement made during this phase of research was the replacement of NaOH with NH_4OH in the pH adjustment of the aqueous phase. Precipitates formed

during pH adjustments were significantly diminished as a result of the use of NH_4OH . Precipitation was observed only in samples with very high pH values, or samples in which pH adjustments were performed more aggressively than needed. An additional advantage of NH_4OH usage over NaOH was the reversibility of pH in samples which had surpassed the target pH for optimum separation between individual rare earths. No precipitation was observed upon addition of dilute HNO_3 to the aqueous phase, whereas addition of HNO_3 to samples in which pH had been adjusted using NaOH readily formed precipitates. Ammonium hydroxide concentrations of 6.0 M, 3.0 M, 1.0 M, 0.5 M, and 0.1 M were used in pH adjustments made throughout the remainder of these experiments.

Upon resolution of these experimental issues, other carboxylic acid extractants were used in separations of these six-element mixtures. These extractants are listed in Table 3.2. This stage of research was significant, as the pH at which extraction of Ln^{+3} and Y^{+3} occurred was established for systems containing these extractants. For many of these carboxylic acid extractants which little or no experimental data existed in past literature, these experiments were also used as a source of confirmation for results obtained in future rare-earth separations.

In the final series of experiments, 7.0 mL of a 125-ppm aqueous mixture of La^{+3} (9.00×10^{-4} M), Pr^{+3} (8.88×10^{-4} M), Nd^{+3} (8.63×10^{-4} M), Sm^{+3} (8.38×10^{-4} M), Gd^{+3} (8.00×10^{-4} M), Dy^{+3} (7.75×10^{-4} M), Er^{+3} (7.50×10^{-4} M), Lu^{+3} (7.13×10^{-4} M), and Y^{+3} (1.38×10^{-3} M) was placed in a 20-mL glass vial in contact with 7.0 mL of toluene and an excess of carboxylic acid extractant (7.91×10^{-3} M) was added to the mixture. The pH of each sample was then adjusted with a known volume of dilute NH_4OH , allowing at least 10 minutes between each addition. Each sample was then stirred for no less than 12 hours prior to analysis by ICP-OES. Each carboxylic acid extractant listed in Table 3.1 was used in this phase of research. Minor changes were required to the experimental procedure only in samples containing 2-

Table 3.2: Carboxylic acid extractants used in separations of La^{+3} , Nd^{+3} , Eu^{+3} , Dy^{+3} , Lu^{+3} , and Y^{+3}

Extractants	
Octanoic acid	Cyclohexanecarboxylic acid
Decanoic acid	Cyclohexylacetic acid
o-Toluic acid	Dicyclohexylacetic Acid
m-Toluic acid	1-Methylcyclohexanecarboxylic acid
p-Toluic acid	2,2-Dimethylbutyric acid
2,3-Dimethylbenzoic acid	2-Ethylbutyric acid
2,4-Dimethylbenzoic acid	Adamantane-1-carboxylic acid
3,5-Dimethylbenzoic acid	

chlorobenzoic acid, 2-bromobenzoic acid, and 2-iodobenzoic acid. In these solvent extractions, 10.0 μL of 1-octanol was added to the organic phase to suppress gel formation and increase solubility of these extractants in the organic phase.

Instrumental Analysis

All rare-earth concentrations in this investigation were determined using a PerkinElmer Optima 2100 DV ICP-OES instrument. Instrumental parameters used throughout all analyses are listed in Table 3.3. For the measurement of each rare-earth element, 6 replicates were performed and the instrument was set to use a total of 14 points to construct each peak.

Several preliminary analyses were conducted to assess the reproducibility of reported rare-earth concentrations by the ICP-OES instrument using aqueous mixtures of 1, 2, 3, 5, and 6 Ln^{+3} plus Y^{+3} of concentrations ranging from 5.0 ppm to 25.0 ppm. Measurements of rare-earth concentrations were first performed in replicates from the same sample. Rare-earth concentrations were also determined by the ICP-OES instrument across multiple samples prepared from the same original rare-earth stock solution. Standard deviations of the reported individual rare-earth concentrations were then calculated using the data obtained from both sets of measurements.

Standard deviations of individual rare-earth concentrations calculated from replicates of a single sample showed a maximum standard deviation of 0.3 ppm. Similarly, a maximum standard deviation of 0.3 ppm was calculated for individual rare-earth concentrations determined from samples prepared from the same stock solution. No correlation was observed between the magnitude of these calculated standard deviations and the total number of rare-earth elements in each mixture. Due to these findings, consistency in measurement of rare-earth concentrations was defined as no greater than 0.5 ppm reliable error (90% confidence level).

Table 3.3: Instrumental parameters used for ICP-OES analysis of rare earths

Parameter	Value
Plasma gas flow (L/min)	15
Auxillary gas flow (L/min)	0.20
Nebulizer gas flow (L/min)	0.80
Power (watts)	1300
Plasma view	Radial
Sample flow rate (mL/min)	1.50
Peak algorithm	Peak area
Points per peak	14
Replicates per sample	6

In addition, analysis of aqueous mixtures of rare earths in a 2% HNO₃ matrix was performed to assess the optimum concentrations and detection method for future solvent extraction samples. It was determined that rare-earth concentrations up to 30.0 ppm were reported consistently under radial plasma view conditions. Concentrations of 35.0 ppm and above proved to be inconsistent, as the reported rare-earth concentrations using the ICP-OES instrument deviated from the expected rare-earth concentrations. Due to the possibility of detector saturation under axial plasma view conditions, a radial plasma view was used for the duration of these analyses.

All standards used for ICP-OES analysis were prepared from the existing stock solutions containing mixtures of rare-earths in a 2% HNO₃ matrix. Calibration prior to each analysis was performed using standards with concentrations of 0.5 ppm, 1.0 ppm, 10.0 ppm, 20.0 ppm, and 30.0 ppm for each rare-earth element. Correlation coefficients of 0.999 or greater, as reported by the instrument, were obtained for all rare earths before analysis of solvent extraction samples was initiated.

Individual wavelengths, detection limits, and background equivalent concentrations for rare earths used throughout the course of ICP-OES analysis are listed in Table 3.4. Due to spectral overlaps between some rare-earth elements, changes in wavelengths used during analysis of some samples were necessary.

The preparation of solvent extraction samples for analysis using ICP-OES was completed after pH adjustment and sufficient stirring time was allowed for extraction to occur in each sample. In early solvent extraction samples containing mixtures of 1, 2, or 3 Ln⁺³ plus Y⁺³, a known volume of the aqueous phase was taken from each sample and placed inside a volumetric flask. This aliquot was then diluted to 10.0 mL using 2% HNO₃, resulting in a maximum concentration of 25.0 ppm if no extraction had taken place. This maximum concentration ensured that all reported rare-earth

Table 3.4: Wavelengths, detection limits, and background equivalent concentrations for rare earths used in ICP-OES analysis

Element	Wavelength (nm)	Detection Limit ⁸⁰ (ppm)	Background Equivalent Concentration ⁸¹ (ppm)
Y	371.029	0.0035	0.12
La	333.749	0.0100	0.33
	398.852	0.0110	0.37
Pr	390.844	0.0370	1.23
	422.293	0.0470	1.59
Nd	406.109	0.0960	3.23
Sm	359.260	0.0430	1.45
Eu	381.967	0.0027	0.09
	412.970	0.0043	0.14
Gd	376.839	0.0250	0.83
Tb	350.917	0.0230	0.77
Dy	353.170	0.0100	0.33
Ho	345.600	0.0057	1.00
Er	337.271	0.0100	0.34
	369.265	0.0180	0.63
Lu	261.542	0.0010	0.03

concentrations were in the appropriate concentration range determined during the preliminary analyses.

During the analysis of this first series of solvent extractions, it was apparent that some adjustments to the analytical procedure would be necessary. Due to the small volumes of aqueous and organic phases used to construct each solvent extraction sample, the removal of an aliquot from the aqueous phase was often difficult to achieve. The increases in volume for each phase outlined in the previous section were also designed to correct this problem.

In addition, signal intensities and reported rare-earth concentrations for individual elements during ICP-OES analysis of aqueous samples in the first series of solvent extractions often appeared to be much higher than expected. The presence of organic diluent and carboxylic acid extractant, both expected to be slightly soluble in the aqueous phase, was attributed to this observation. As a result, a method for the elimination of organic material contained in each sample was developed. This method was used prior to analysis of all solvent extractions performed in the second series (5 Ln^{+3} + Y^{+3} mixtures) and third series (8 Ln^{+3} + Y^{+3} mixtures) of experiments.

After the removal an aliquot of a known volume from the aqueous phase, these aliquots were placed into empty 20-mL glass vials. To liberate any complexed carboxylate ligands from the rare earths and precipitate these carboxylic acids from the aqueous solution, a small amount of 6.0 M HNO_3 was then added to each aliquot. This induced precipitation was found to expedite the elimination of organic materials during later steps.

Each glass vial was then placed inside an aluminum block which possessed small openings with a diameter slightly larger than the 20-mL glass vials used throughout this investigation. These aluminum blocks were then placed on a hot plate and each sample was heated at 70°C to dryness. For

many samples which contained carboxylic acid extractants with low volatilization temperatures, this step was also beneficial in the partial distillation of these acids during the course of evaporation.

After evaporation was complete, these sample vials were individually heated over a flame using a Bunsen burner. During this stage, initial heating was performed slowly at lower temperatures to prevent ignition of organic materials contained within each sample vial. As the decomposition or distillation of the organic materials progressed, flame temperatures were gradually increased. Because of the differences in flash points for each carboxylic acid extractant used throughout the course of investigation, the rate at which flame temperature was increased was established on an individual basis. During the final stages of heating at high temperatures, decomposition of remaining HNO_3 and any remaining traces of organic materials could be observed, resulting in the formation of rare-earth oxides at the bottom of each vial.

Early attempts to simultaneously eliminate organic material from multiple samples using a high-temperature furnace were problematic due to insufficient oxygen exposure to form rare-earth oxides and incomplete decomposition of organic materials contained within each sample. Direct heating of each sample by flame offered both visual confirmation of decomposition and the ability to direct heat to specific areas of each sample vial.

Upon cooling of each sample vial, approximately 5.0 mL of 2% HNO_3 was added to each vial, and these solutions were stirred until complete dissolution of rare-earth oxides had occurred. However, the use of NaOH during pH adjustment of the solvent extraction mixture in early experiments resulted in the presence of insoluble residues which appeared to be partially fused onto the surface of the glass vials during this phase of preparation. It was possible that occurrence was a result of the formation of Na_2O and its partial fusion to the glass vial at high temperatures. Through

the use of NH_4OH during pH adjustments, this issue was corrected, as NH_4OH readily decomposes upon heating during the previous stage of preparation.

When complete dissolution of rare-earth oxides contained in each sample had occurred, this solution was removed from the sample vial and placed into a volumetric flask. Each vial was rinsed with 2% HNO_3 three times to ensure complete transfer of any remaining rare earths, followed by dilution of each solution to an appropriate volume to yield a maximum concentration of 25.0 ppm for each rare-earth element. These solutions were then analyzed by ICP-OES to determine rare-earth concentrations which remained in the aqueous phase after extraction.

To ensure that no loss of rare earths occurred during the elimination of organic materials contained in each phase prior to analysis by ICP-OES, three sets of experiments were conducted to evaluate the agreement of reported rare-earth concentrations from each phase to the expected total rare-earth concentrations of both phases. In a 20-mL glass vial, 6.0 mL of a 125-ppm aqueous mixture of La^{+3} , Eu^{+3} , Lu^{+3} , and Y^{+3} was placed in contact with 6.0 mL of toluene and an appropriate excess of o-toluic acid, m-toluic acid, or p-toluic acid. The pH of the aqueous phase in each sample was adjusted using NH_4OH , and each sample was stirred for no less than 12 hours.

Next, 5.0 mL of the aqueous phase obtained from each sample was removed, placed in a separate 20-mL glass vial, and stored for later use. A 5.0-mL aliquot from the organic phase of each sample was then removed and placed in a separate 20-mL glass vial. To this organic aliquot, 5.0 mL of 2% HNO_3 was added to each aliquot, and each mixture was stirred for no less than 12 hours. The decrease in pH from the addition of HNO_3 resulted in the back extraction of the rare earths previously contained in the aliquots removed from the original organic phase into the aqueous 2% HNO_3 solution due to the protonation of the carboxylic acid extractants. This back-extraction method was preferred over direct analysis of the organic phases due to the minimization of organic materials to be

eliminated in later steps. After sufficient stirring time had elapsed, the 5.0-mL organic-extracted aqueous phases were removed and placed into a separate glass vials.

These organic-extracted aqueous phases and the 5.0-mL aliquots obtained from the aqueous phases of the original solvent extraction mixtures were then evaporated at 70°C and heated by flame to eliminate all remaining organic materials prior to analysis. The remaining rare-earth oxides contained in each vial were then dissolved in 2% HNO₃. Each solution was diluted to a total volume of 25.0 mL and analyzed by ICP-OES. For comparison to the reported rare-earth concentrations obtained from each phase, 5.0 mL of the original 125-ppm stock solution containing La⁺³, Eu⁺³, Lu⁺³, and Y⁺³ was also diluted to a total volume of 25.0 mL and analyzed by ICP-OES.

The results of these tests for samples containing o-toluic acid, m-toluic acid, and p-toluic acid revealed that no rare earth contents were lost during the elimination of organic materials. For each solvent extraction sample, the sum of rare-earth concentrations obtained from the aqueous phase and organic phase were in agreement with the previously established 0.5-ppm criterion when compared to total rare-earth concentrations obtained from analysis of the original, multi-element stock solution.

Due to these findings, it was determined that sampling of all solvent extraction mixtures would be performed by removal of the aqueous phase for analysis using ICP-OES. To determine the rare-earth concentrations extracted into the organic phase during each experiment, the reported rare-earth concentrations in the aqueous phase were then subtracted from the rare-earth concentrations obtained from analysis of an aliquot of the original, multi-element stock solution which had been diluted identically to the aliquot removed from the aqueous phase.

Chapter 4: Results

Preliminary Experiments

The results of selected preliminary experiments designed to assess the repeatability and reliable error (90%) of reported rare-earth concentrations using the ICP-OES instrument are shown in Table 4.1 and Table 4.2. Rare-earth concentrations shown in Table 4.1 were obtained from three sequential measurements of the same aqueous rare-earth solution after flushing with a 2% HNO₃ solution between each analysis. Reliable errors of reported concentrations for Y and La by ICP-OES in mixtures of 2, 3, 4, 6, and 7 rare earths are shown in Table 4.2. No changes in the reliable error of reported concentrations for these two elements were observed upon the introduction of additional rare-earth elements. These experiments, along with other similar experiments, were used to determine the error addressed in Chapter 3.

Table 4.3 demonstrates the effect of dissolved organic materials on rare-earth concentrations obtained using the ICP-OES instrument. The increase in these reported concentrations were inconsistent with the predetermined 0.5 ppm criterion for error, and the changes in concentration upon saturation of these aqueous solutions with organic diluents and carboxylic acid extractants varied significantly from element to element. For these reasons, it was determined that the elimination of dissolved organic materials would be performed in agreement with the procedure outlined in Chapter 3 for solvent extraction samples containing aqueous solutions of 6 rare-earth elements (5 Ln⁺³ + Y⁺³) and 9 rare-earth elements (8 Ln⁺³ + Y⁺³).

The results of experiments described in the previous chapter to determine if a mass balance could be achieved between the aqueous phase and organic phase in solvent extraction samples after the elimination of dissolved organic compounds are shown in Table 4.4. The total rare-earth concentrations in the aqueous and organic phases, in comparison to the reported rare-earth

Table 4.1: Rare-earth concentrations and reliable errors of measurements performed in replicates by ICP-OES

Sample Description	Rare-Earth Concentrations (ppm)					
	La	Nd	Dy	Er	Lu	Y
(5 Ln ⁺³ + Y ⁺³) in 2% HNO ₃ #1	12.7	12.7	12.7	12.6	12.8	12.5
(5 Ln ⁺³ + Y ⁺³) in 2% HNO ₃ #2	12.8	12.8	12.8	12.7	12.9	12.7
(5 Ln ⁺³ + Y ⁺³) in 2% HNO ₃ #3	12.8	12.8	12.8	12.8	13.0	12.7
Average Concentration	12.8	12.8	12.8	12.7	12.9	12.6
Reliable Error (90%)	0.2	0.2	0.2	0.2	0.2	0.3

Table 4.2: Reliable errors of La⁺³ and Y⁺³ concentrations reported by ICP-OES in aqueous solutions with increasing total number of rare-earth elements

Element	Reliable Error (90%)				
	Ln ⁺³ + Y ⁺³	2 Ln ⁺³ + Y ⁺³	3 Ln ⁺³ + Y ⁺³	5 Ln ⁺³ + Y ⁺³	6 Ln ⁺³ + Y ⁺³
Yttrium	0.3	0.2	0.2	0.3	0.2
Lanthanum	0.3	0.2	0.2	0.3	0.3

Table 4.3: Effect of organic materials present during ICP-OES analysis of rare earths

Sample Description	Rare Earth Concentrations (ppm)					
	La	Nd	Dy	Er	Lu	Y
(5 Ln ⁺³ + Y ⁺³) in 2% HNO ₃ Only	12.7	12.7	12.7	12.6	12.8	12.7
(5 Ln ⁺³ + Y ⁺³) in 2% HNO ₃ Saturated with MIBK, o-Toluic Acid	15.7	14.9	15.0	15.2	16.6	15.7
Δ Concentration	3.0	2.2	2.3	2.6	3.8	3.0

Sample Description	Rare Earth Concentrations (ppm)					
	La	Nd	Dy	Er	Lu	Y
(5 Ln ⁺³ + Y ⁺³) in 2% HNO ₃ Only	25.0	25.0	25.2	25.3	25.0	25.1
(5 Ln ⁺³ + Y ⁺³) in 2% HNO ₃ Saturated with Toluene, o-Toluic Acid	25.8	25.9	26.8	25.7	26.9	25.6
Δ Concentration	0.8	0.9	1.6	0.4	1.9	0.5

Table 4.4: Results of experiments to determine mass balance after destruction of organic materials in systems containing o-toluic acid, m-toluic acid, and p-toluic acid in toluene

Mass Balance in o-Toluic Acid / Toluene Solvent Extractions After Elimination of Organic Materials				
Concentration (ppm)	Element			
	La	Eu	Lu	Y
Aqueous Phase (ppm)	19.5	9.5	3.6	9.8
Organic Phase (ppm)	4.1	14.0	20.4	13.6
Total Concentration (ppm)	23.6	23.5	24.0	23.3
(3 Ln ⁺³ + Y ⁺³) Blank, Compensation for Addition of NH ₄ OH (ppm)	23.5	23.8	23.8	23.5
Δ Concentration	0.1	-0.3	0.2	-0.2

Mass Balance in m-Toluic Acid / Toluene Solvent Extractions After Elimination of Organic Materials				
Concentration (ppm)	Element			
	La	Eu	Lu	Y
Aqueous Phase (ppm)	17.0	8.2	2.7	9.1
Organic Phase (ppm)	6.7	15.4	20.9	14.6
Total Concentration (ppm)	23.7	23.6	23.6	23.7
(3 Ln ⁺³ + Y ⁺³) Blank, Compensation for Addition of NH ₄ OH (ppm)	23.5	23.8	23.8	23.6
Δ Concentration	0.2	-0.2	-0.2	0.1

Mass Balance in p-Toluic Acid / Toluene Solvent Extractions After Elimination of Organic Materials				
Concentration (ppm)	Element			
	La	Eu	Lu	Y
Aqueous Phase (ppm)	10.5	4.6	1.6	4.2
Organic Phase (ppm)	12.9	19.6	22.3	19.2
Total Concentration (ppm)	23.3	24.2	23.9	23.5
(3 Ln ⁺³ + Y ⁺³) Blank, Compensation for Addition of NH ₄ OH (ppm)	23.5	23.9	23.8	23.6
Δ Concentration	-0.2	0.3	0.1	-0.1

concentrations of a sample obtained from the original aqueous stock solution (with compensation for the volume of NH_4OH added during the adjustment of pH of solvent extraction samples) were within the 0.5 ppm error determined in prior experiments.

Extractions of aqueous solutions consisting of two rare earths ($\text{Ln}^{+3} + \text{Y}^{+3}$) and extractions of aqueous solutions consisting of four rare earths (La^{+3} , Eu^{+3} , Lu^{+3} , and Y^{+3}) were conducted in accordance with the experimental conditions described in Chapter 3. The results for extractions of binary mixtures of rare earths performed with octanoic acid as the selected carboxylic acid extractant are presented in Table 4.5. The results of these experiments suggest that Y is extracted similarly to Pr.

The results of solvent extractions performed with aqueous mixtures of La^{+3} , Eu^{+3} , Lu^{+3} , and Y^{+3} using the extractants o-toluic acid, m-toluic acid, p-toluic acid, cyclohexanecarboxylic acid, and 1-naphthoic acid in toluene are listed in Table 4.6. These results show that Y most closely resembles the middle to heavy rare earths in extractions using o-toluic acid, m-toluic acid, p-toluic acid, and 1-naphthoic acid, while Y lies somewhere in the region between La and Eu for extractions using cyclohexanecarboxylic acid.

It is important to note that the experiments outlined in Table 4.5 and Table 4.6 were performed prior to the addition of the step for elimination of organic materials before analysis by ICP-OES. Consequently, the results of these preliminary solvent extraction experiments only qualitatively indicate the position of Y relative to the other rare-earth components.

Solvent Extractions of ($5 \text{ Ln}^{+3} + \text{Y}^{+3}$) Mixtures

The results of solvent extraction experiments performed using aqueous solutions of La^{+3} , Nd^{+3} , Eu^{+3} , Dy^{+3} , Lu^{+3} , and Y^{+3} are shown in Figures 4.1 through 4.8.

Table 4.5: Rare-earth concentrations in the aqueous phase for solvent extractions performed using octanoic acid in p-xylene at pH=5.2

Element Rare-Earth Concentrations (ppm)	System #1		System #2		System #3		System #4	
	La	Y	Pr	Y	Ho	Y	Lu	Y
	12.2	10.0	15.0	14.9	16.0	18.0	15.1	16.7

Table 4.6: Rare-earth concentrations in the organic phase for solvent extractions performed using o-toluic acid, m-toluic acid, p-toluic acid, cyclohexanecarboxylic acid, and 1-naphthoic acid

Extractant	pH	Rare-Earth Concentrations in the Organic Phase (ppm)			
		La	Y	Eu	Lu
o-Toluic acid	6.4	3.1	12.2	12.4	18.4
m-Toluic acid	6.2	3.4	8.4	8.8	11.8
p-Toluic acid	6.2	5.1	8.0	8.2	10.4
Cyclohexanecarboxylic acid	5.8	11.0	12.2	13.3	18.8
1-Naphthoic acid	5.0	15.7	21.6	21.7	21.6

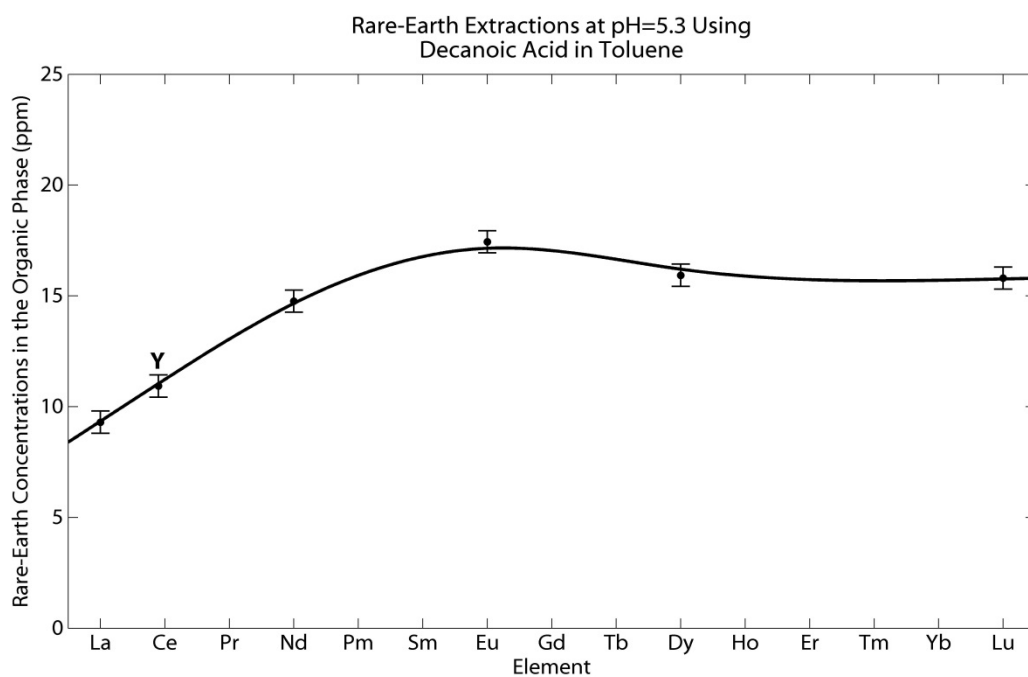
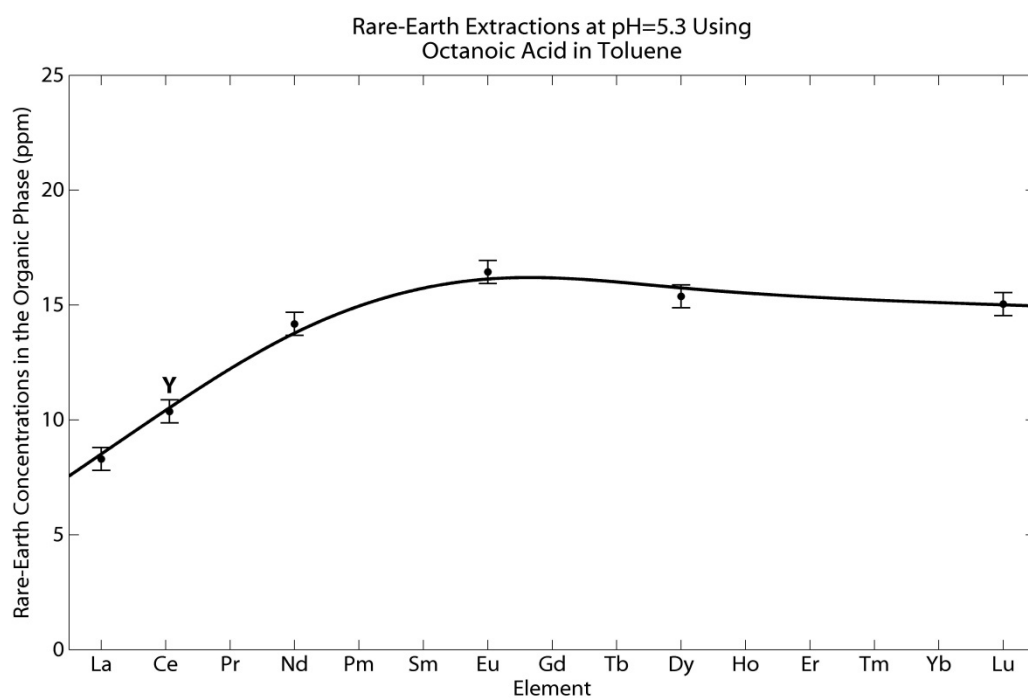


Figure 4.1: Extraction curves for $(5 \text{ Ln}^{+3} + \text{Y}^{+3})$ systems containing octanoic acid (top) and decanoic acid (bottom) in toluene

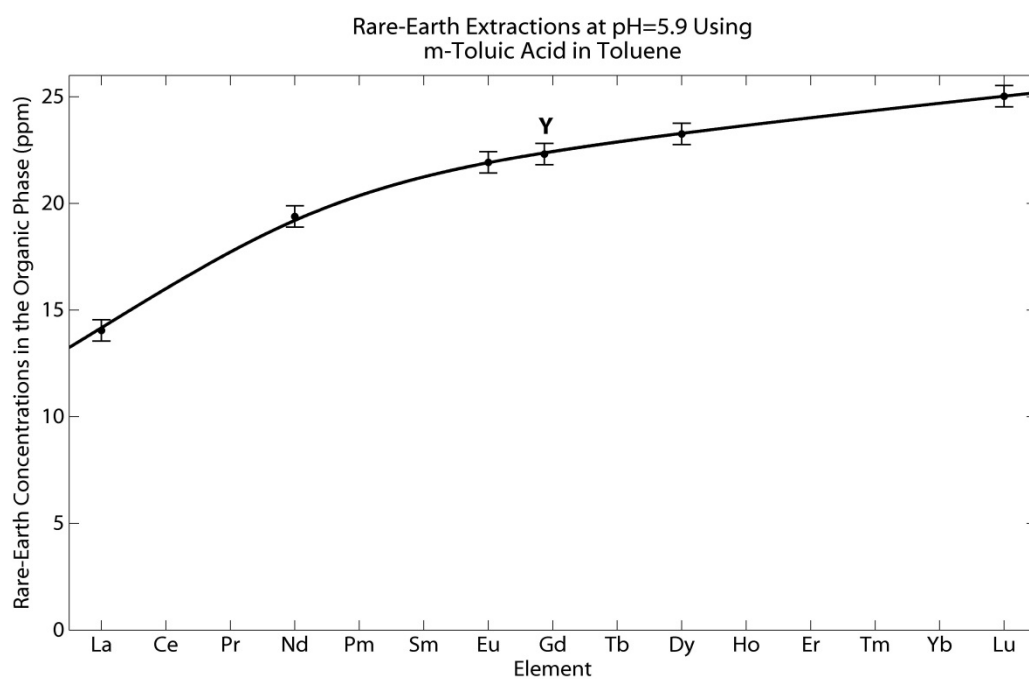
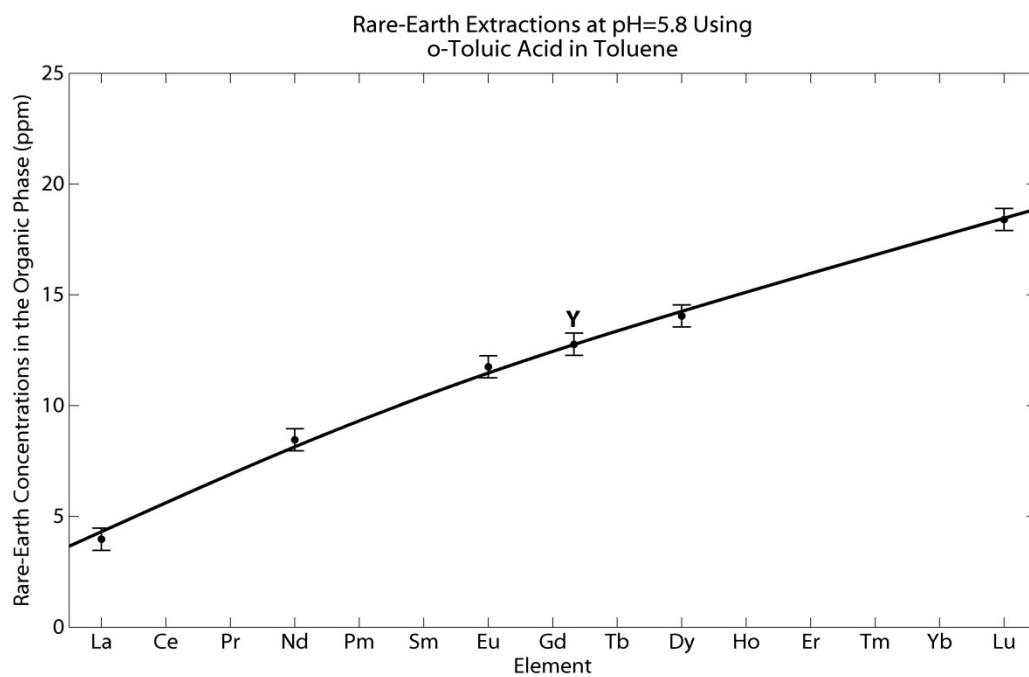


Figure 4.2: Extraction curves for (5 Ln⁺³ + Y⁺³) systems containing o-toluic acid (top) and m-toluic acid (bottom) in toluene

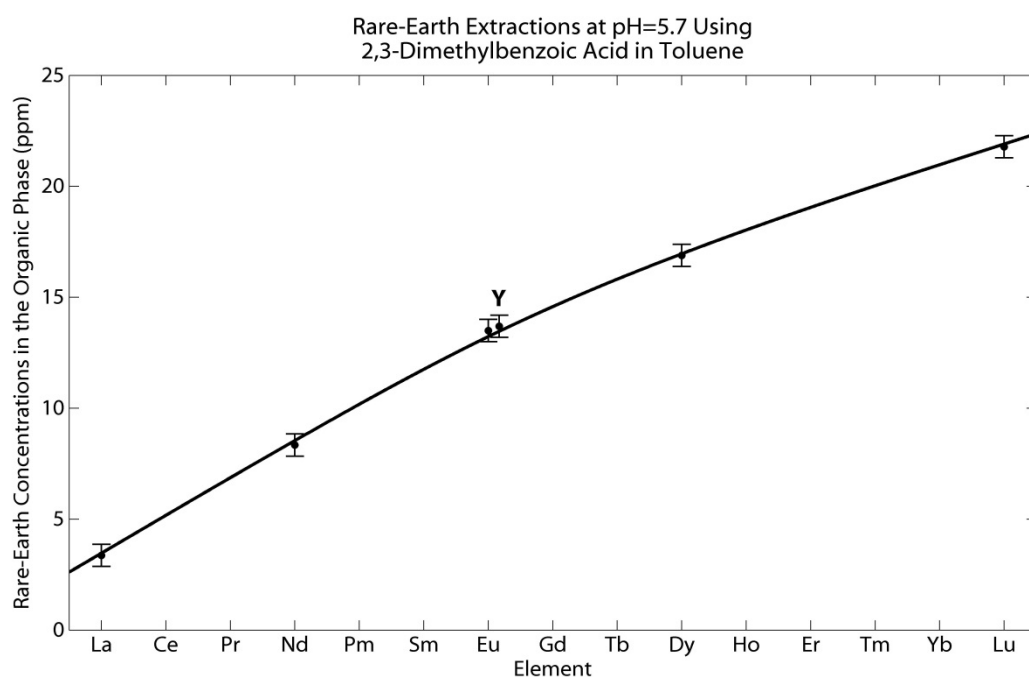
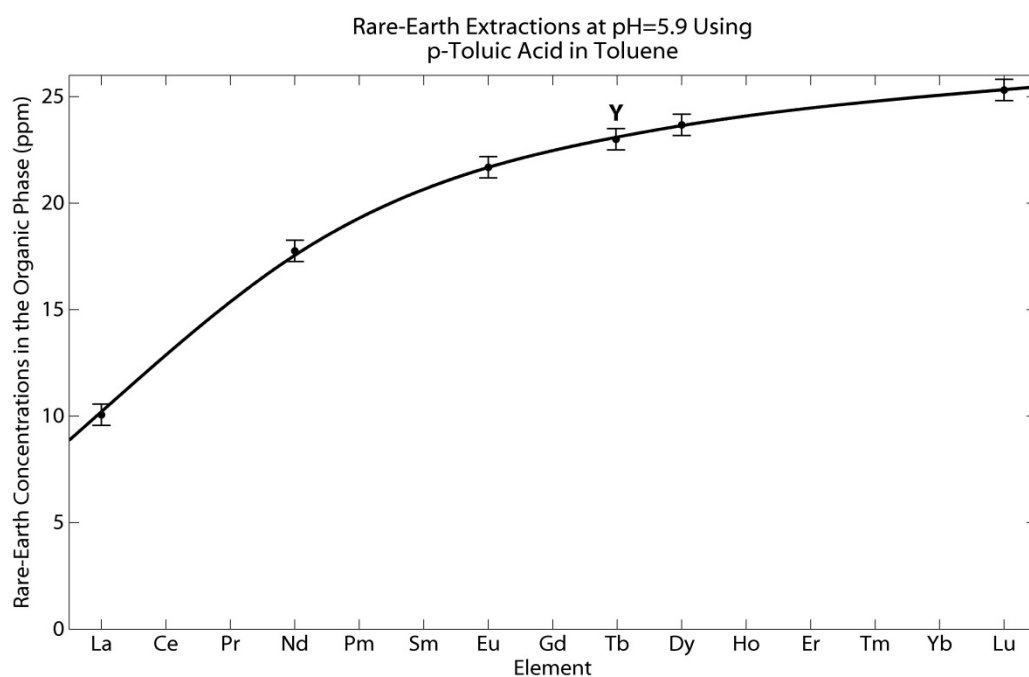


Figure 4.3: Extraction curves for (5 Ln^{+3} + Y^{+3}) systems containing p-toluic acid (top) and 2,3-dimethylbenzoic acid (bottom) in toluene

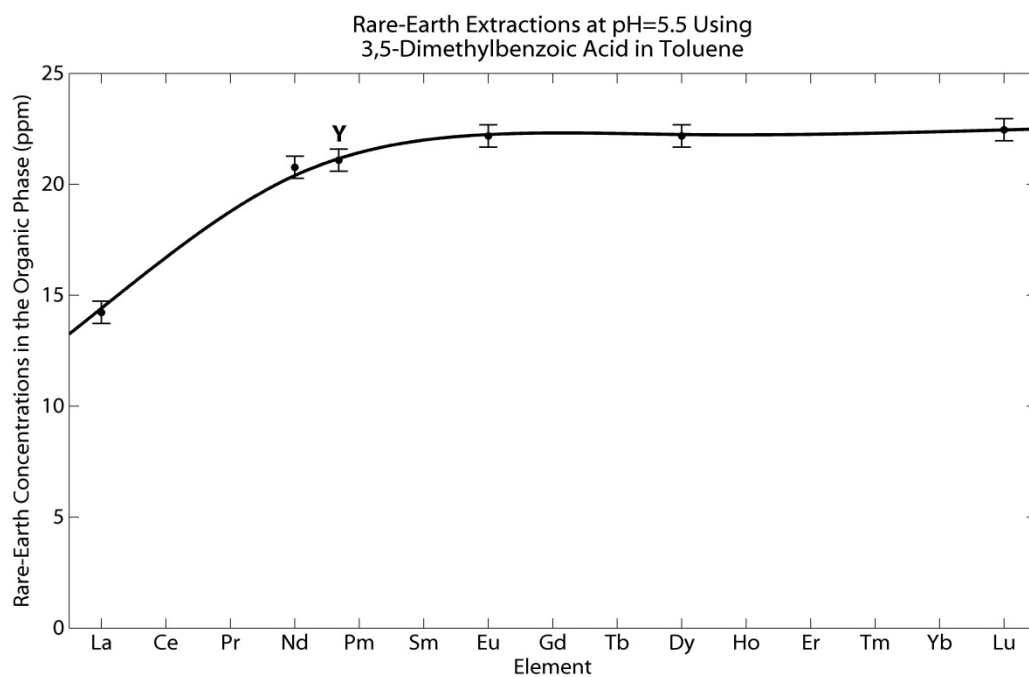
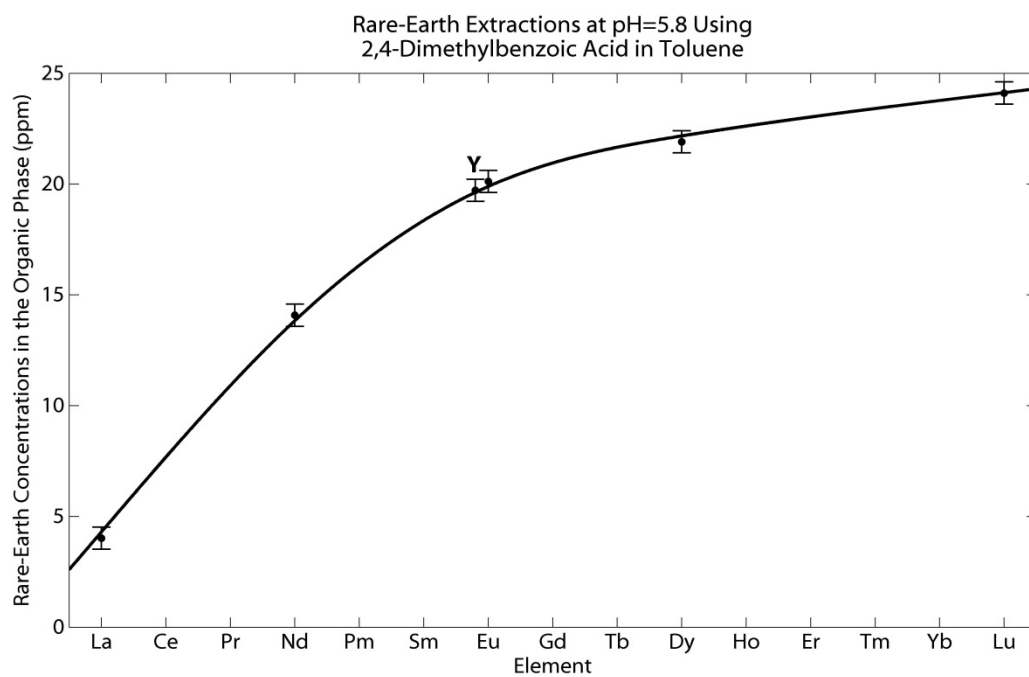


Figure 4.4: Extraction curves for (5 $\text{Ln}^{+3} + \text{Y}^{+3}$) systems containing 2,4-dimethylbenzoic acid (top) and 3,5-dimethylbenzoic acid (bottom) in toluene

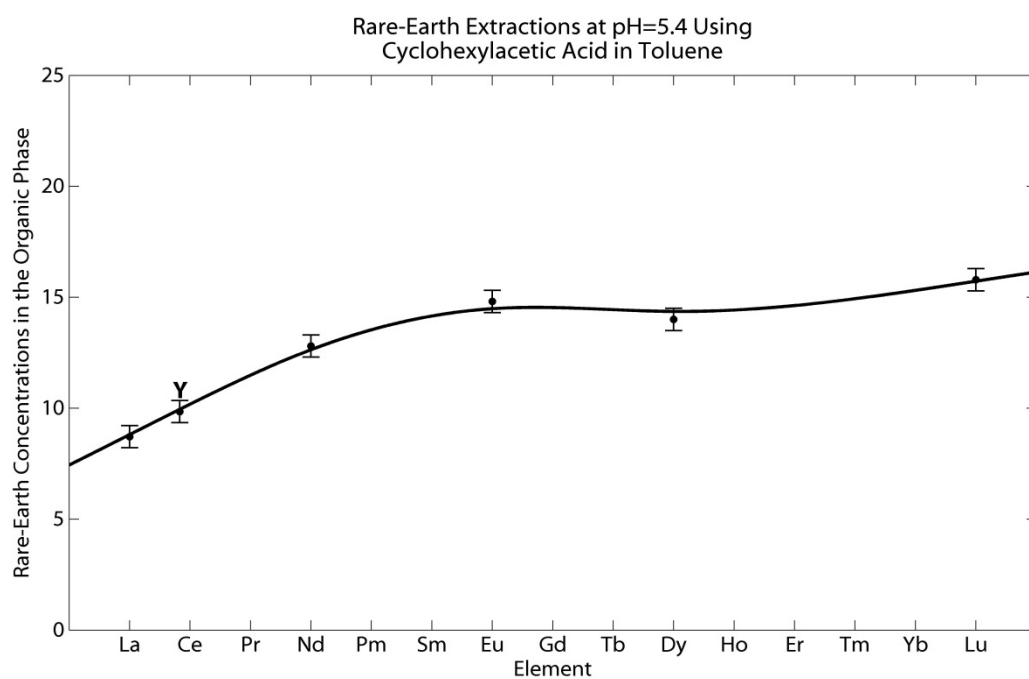
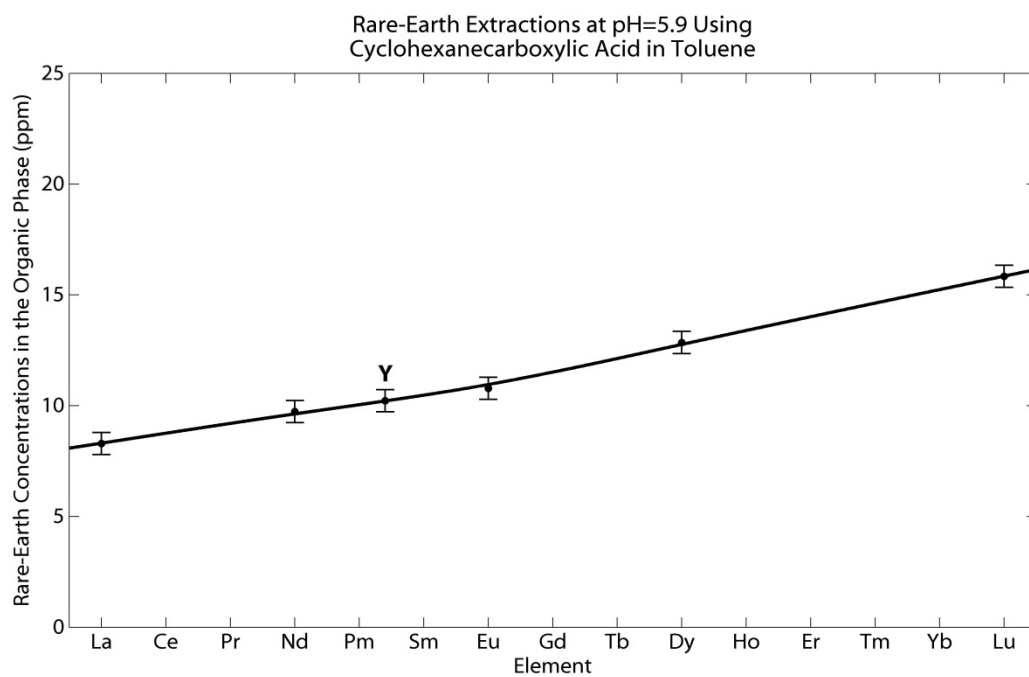


Figure 4.5: Extraction curves for $(5 \text{ Ln}^{+3} + \text{Y}^{+3})$ systems containing cyclohexanecarboxylic acid (top) and cyclohexylacetic acid (bottom) in toluene

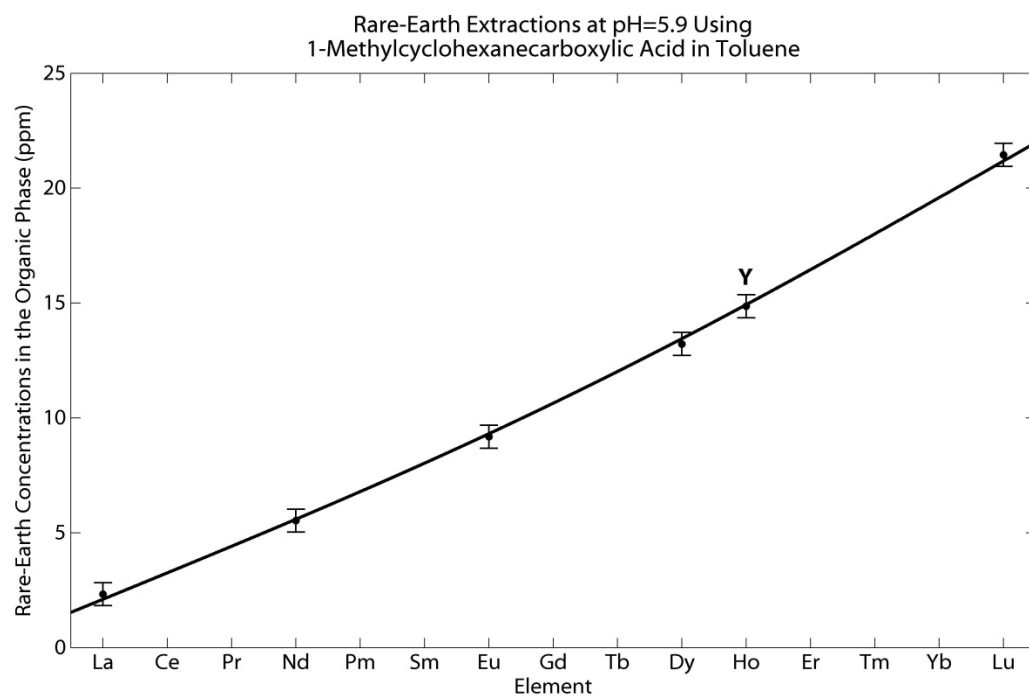
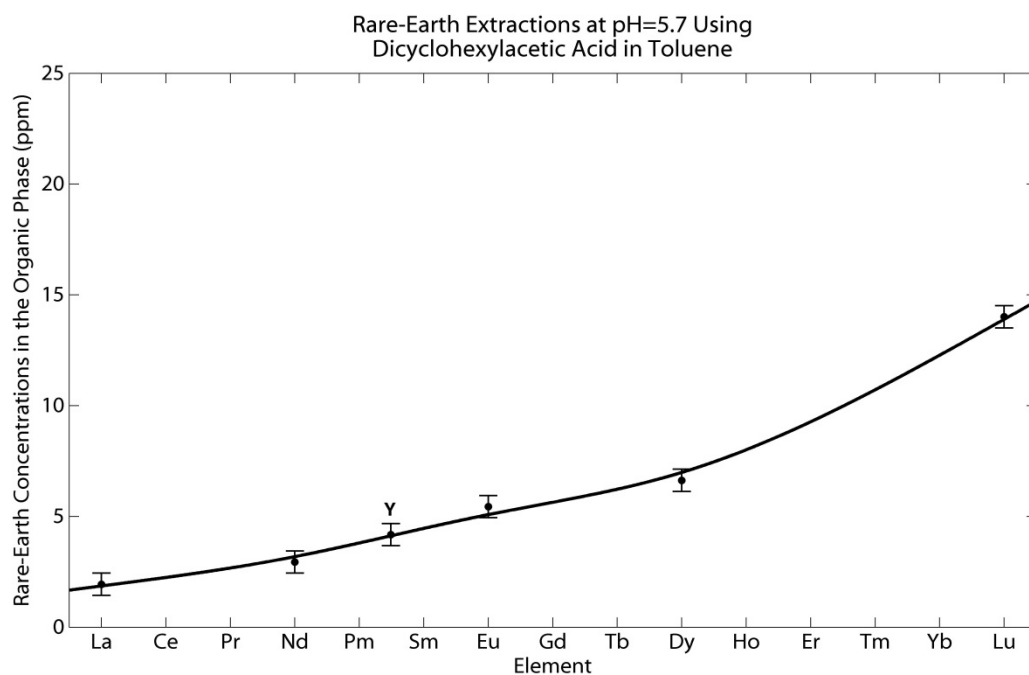


Figure 4.6: Extraction curves for ($5 \text{ Ln}^{+3} + \text{Y}^{+3}$) systems containing dicyclohexylacetic acid (top) and 1-methylcyclohexanecarboxylic acid (bottom) in toluene

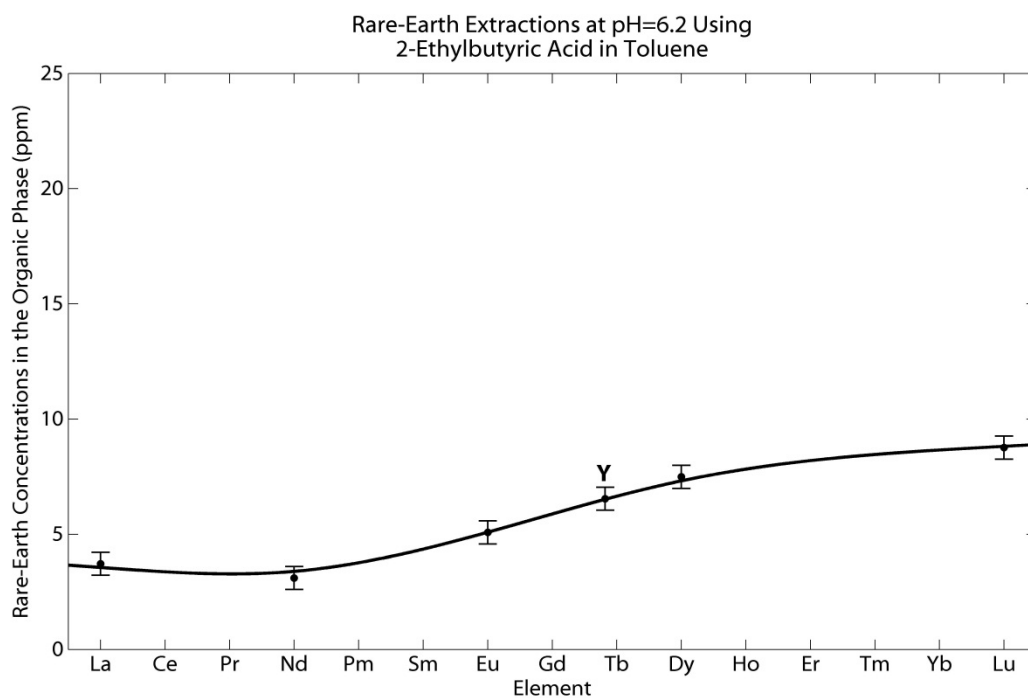
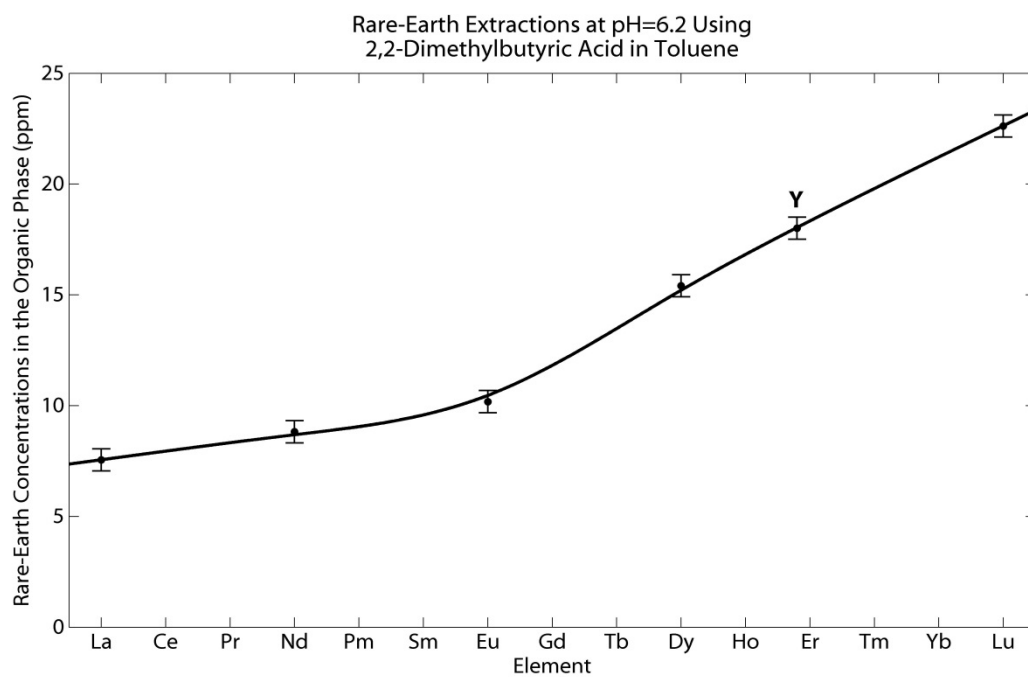


Figure 4.7: Extraction curves for ($5 \text{ Ln}^{+3} + \text{Y}^{+3}$) systems containing 2,2-dimethylbutyric acid (top) and 2-ethylbutyric acid (bottom) in toluene

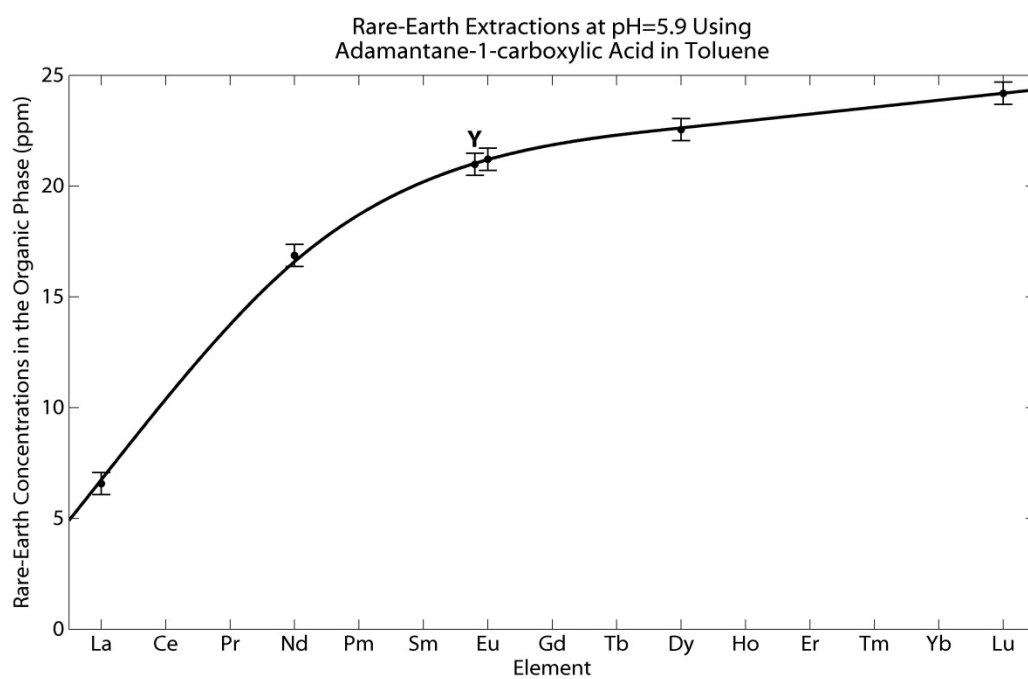


Figure 4.8: Extraction curves for $(5 \text{ Ln}^{+3} + \text{Y}^{+3})$ systems containing adamantane-1-carboxylic acid in toluene

Solvent Extractions of (8 Ln⁺³ + Y⁺³) Mixtures

The results of solvent extraction experiments performed using aqueous solutions of La⁺³, Pr⁺³, Nd⁺³, Sm⁺³, Gd⁺³, Dy⁺³, Er⁺³, Lu⁺³, and Y⁺³ are shown in Figures 4.9 through 4.23. Of the carboxylic acid extractants listed in Table 3.1 that were used in this investigation, satisfactory results were not obtained for trimethylacetic acid and 2,6-dimethylbenzoic acid, due to high solubility in the aqueous phase and gel formation issues encountered during experimentation, respectively.

Construction of Figures

Figures 4.1 through 4.23 were constructed using MATLAB software and MATLAB Curve Fitting Toolbox. All data points were plotted as a standard scatter plot, with the previously established 0.5 ppm reliable error included for each data point. Curve fitting was performed using a smoothing spline fit, with smoothing parameters determined on an individual basis. The parameter for each fitted line was adjusted to the point at which each extraction curve was at its smoothest, while still existing within the bounds of the error bars of each data point. This approach to curve fitting was preferred to minimize the presence of any features of these extraction curves which could not be accurately verified without consideration to the reliable error.

The position of Y noted in each solvent extraction curve was determined using the concentration of Y in the organic phase calculated from experimental data and the relative atomic number of Y, Z_Y, which can be calculated using the equation

$$Z_Y = Z_{Ln}' + (Z_{Ln}'' - Z_{Ln}') \left(\frac{C_{Ln}' - C_Y}{C_{Ln}' - C_{Ln}''} \right)$$

Where Z_{Ln}' and Z_{Ln}'' are the atomic numbers of a rare-earth element to the left and a rare-earth element to the right of Y, and C_Y, C_{Ln}', and C_{Ln}'' are the concentrations of the respective elements.

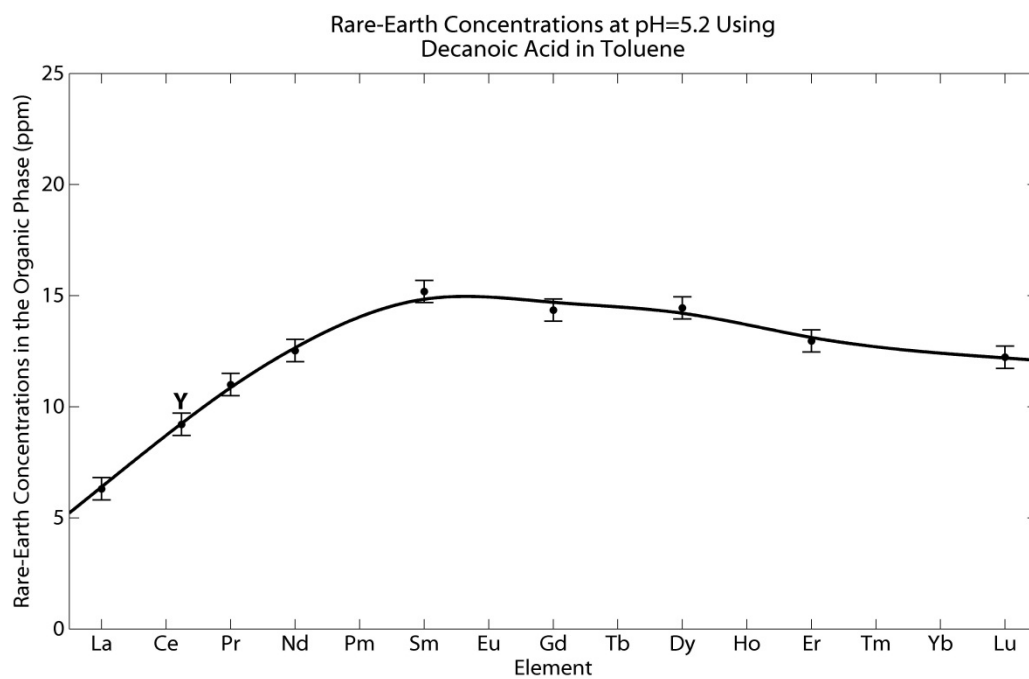
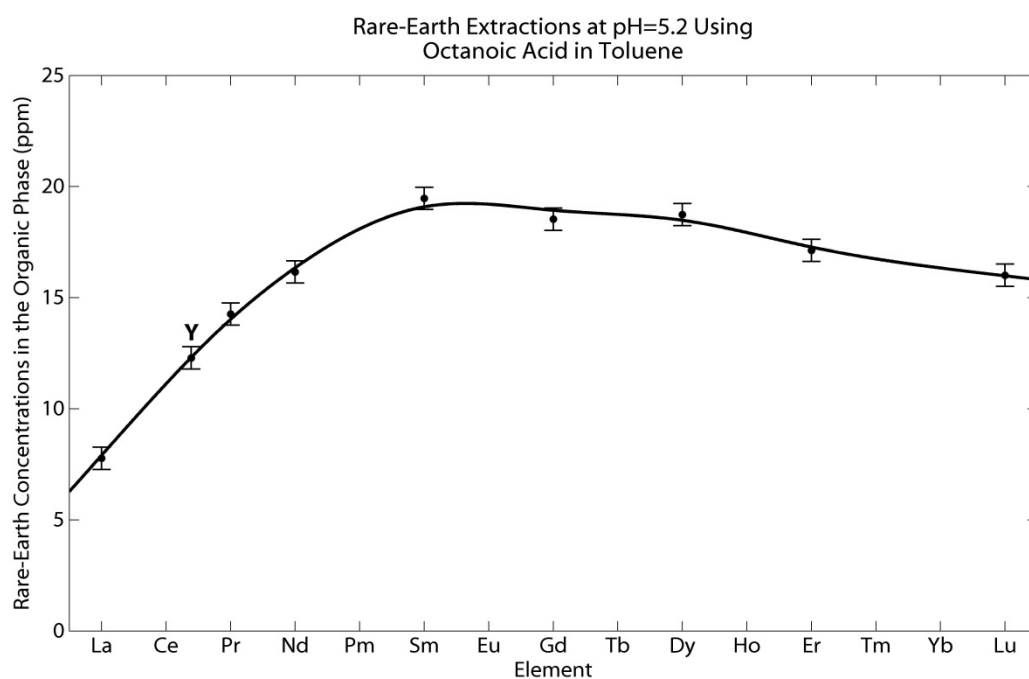


Figure 4.9: Extraction curves for (8 Ln⁺³ + Y⁺³) systems containing octanoic acid (top) and decanoic acid (bottom) in toluene

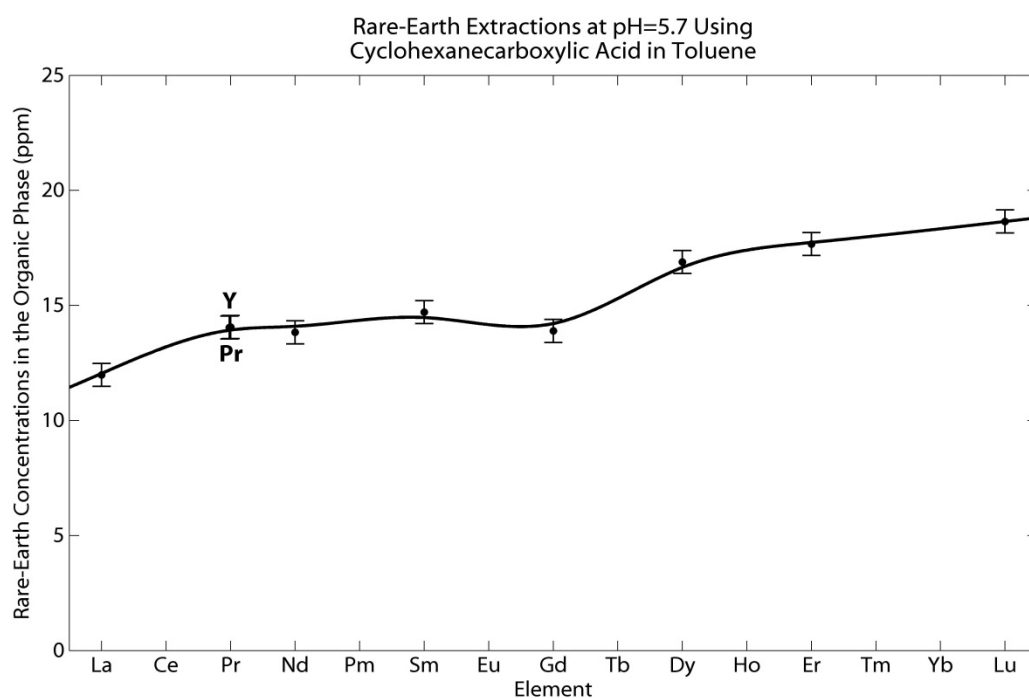
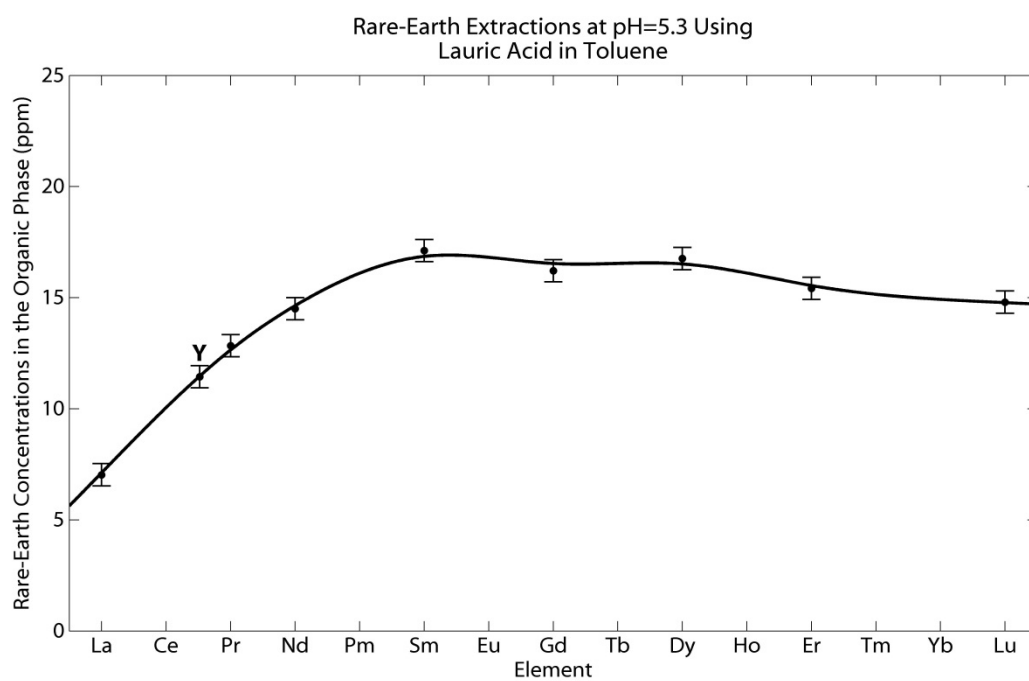


Figure 4.10: Extraction curves for (8 $\text{Ln}^{+3} + \text{Y}^{+3}$) systems containing lauric acid (top) and cyclohexanecarboxylic acid (bottom) in toluene

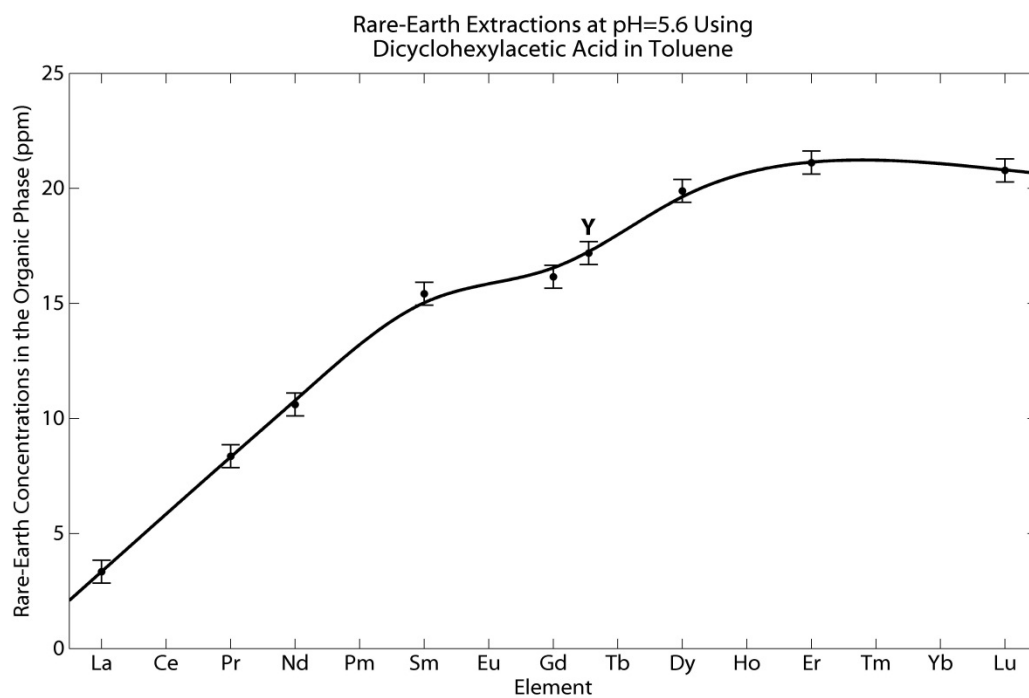
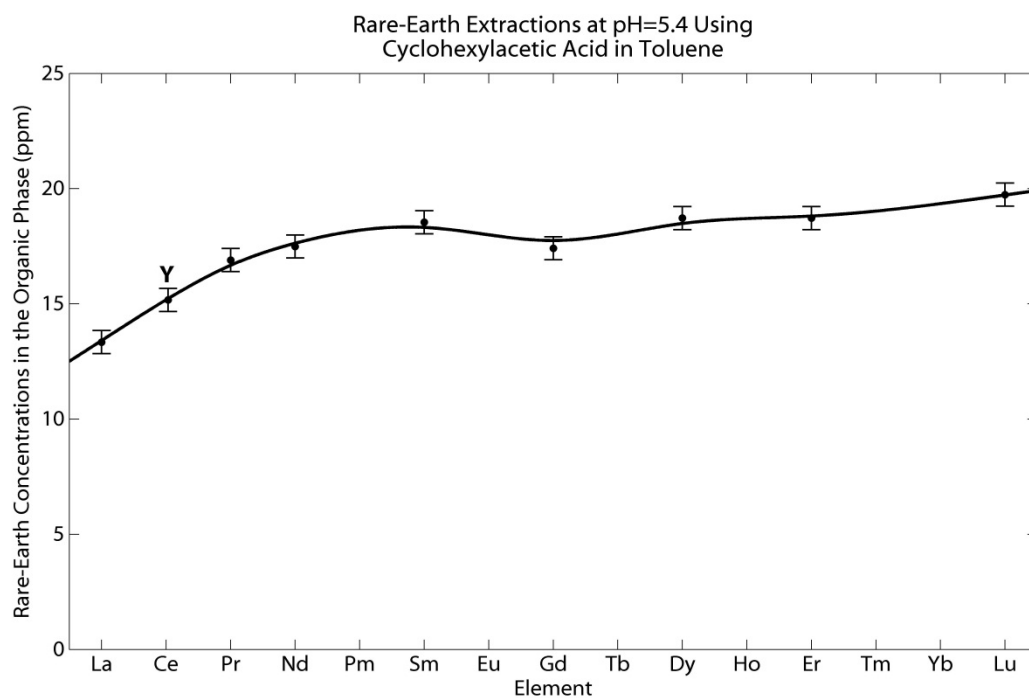


Figure 4.11: Extraction curves for (8 $\text{Ln}^{+3} + \text{Y}^{+3}$) systems containing cyclohexylacetic acid (top) and dicyclohexylacetic acid (bottom) in toluene

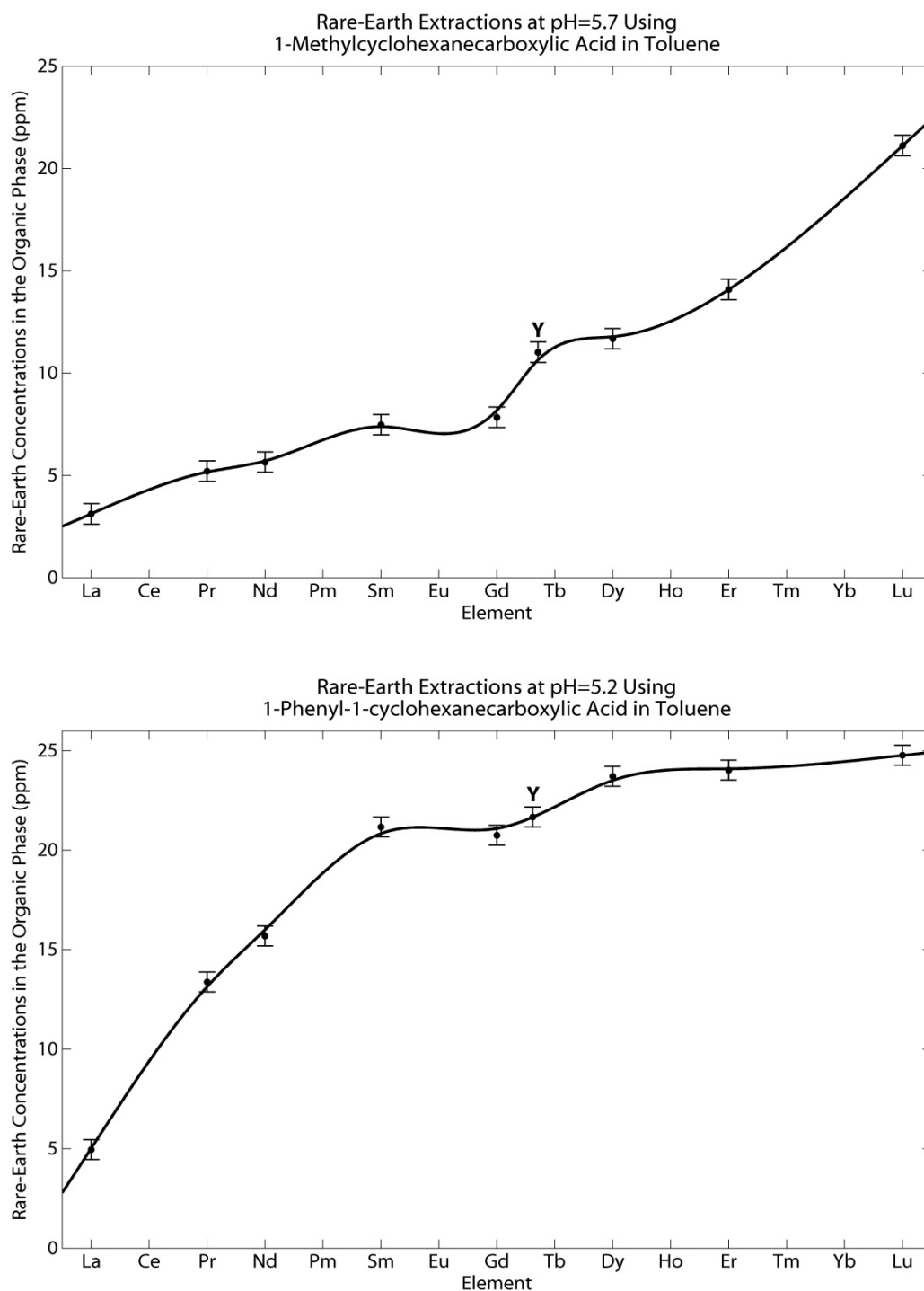


Figure 4.12: Extraction curves for (8 Ln⁺³ + Y⁺³) systems containing 1-methylcyclohexanecarboxylic acid (top) and 1-phenyl-1-cyclohexanecarboxylic acid (bottom) in toluene

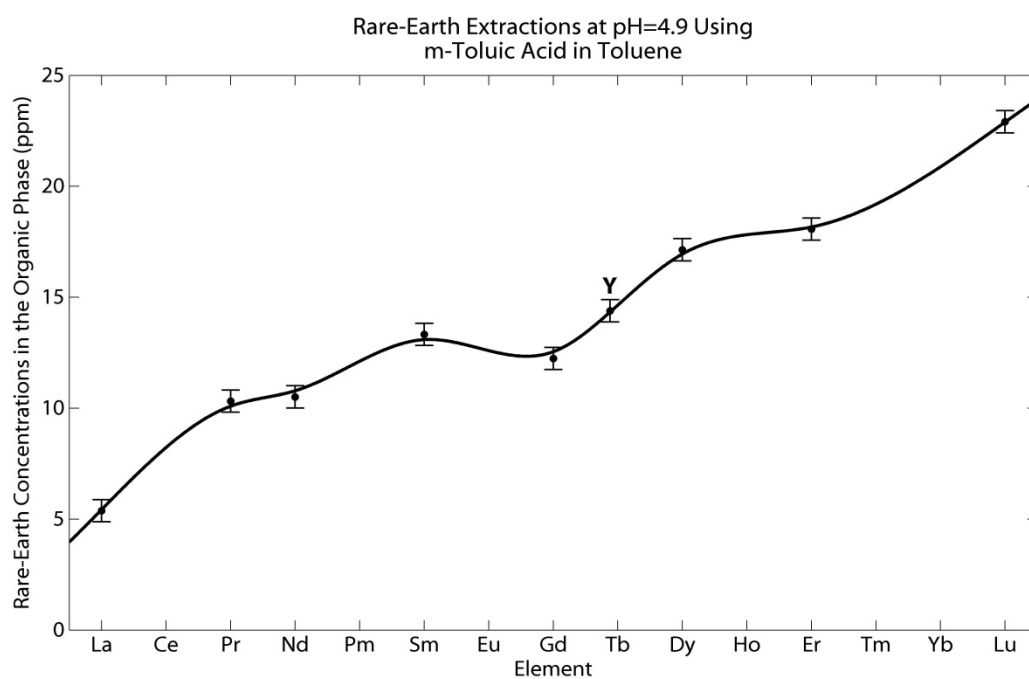
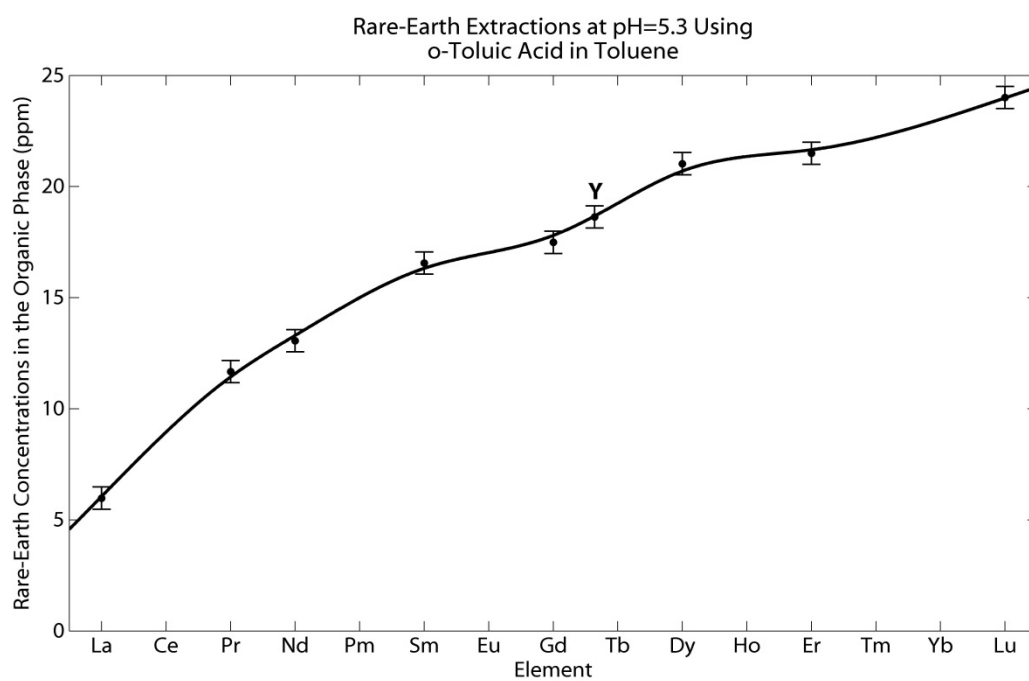


Figure 4.13: Extraction curves for (8 Ln^{+3} + Y^{+3}) systems containing o-toluic acid (top) and m-toluic acid (bottom) in toluene

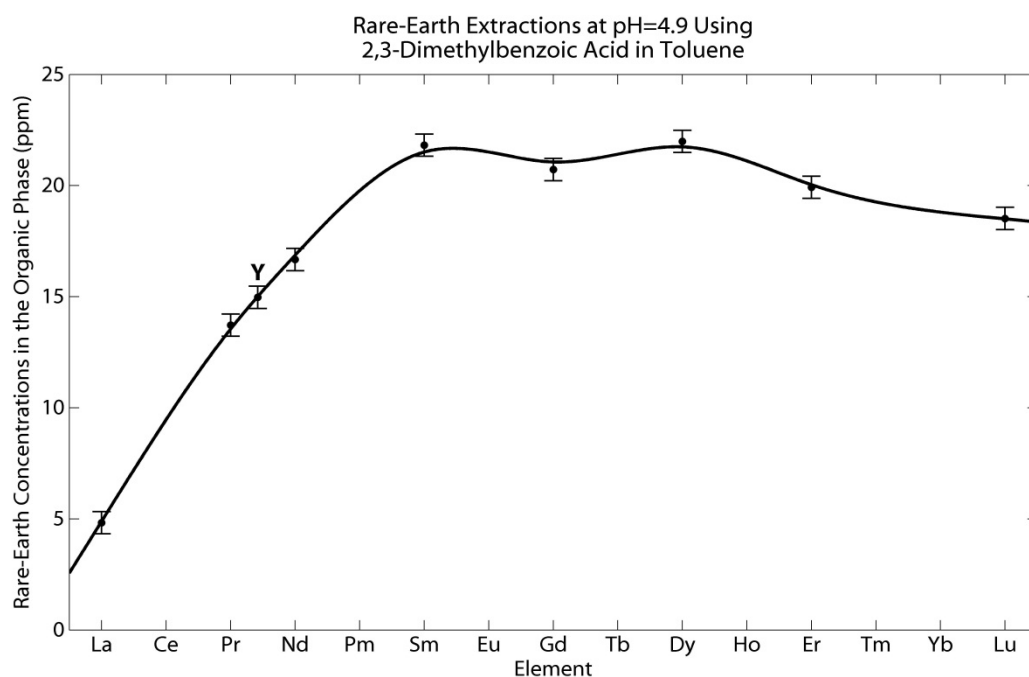
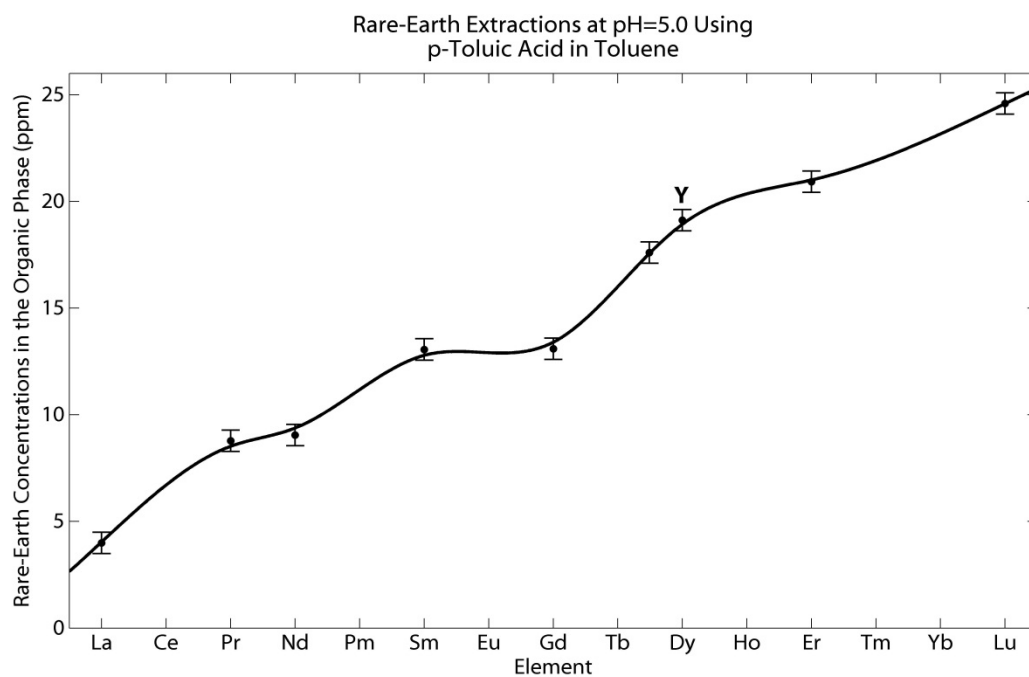


Figure 4.14: Extraction curves for (8 Ln^{+3} + Y^{+3}) systems containing p-toluic acid (top) and 2,3-dimethylbenzoic acid (bottom) in toluene

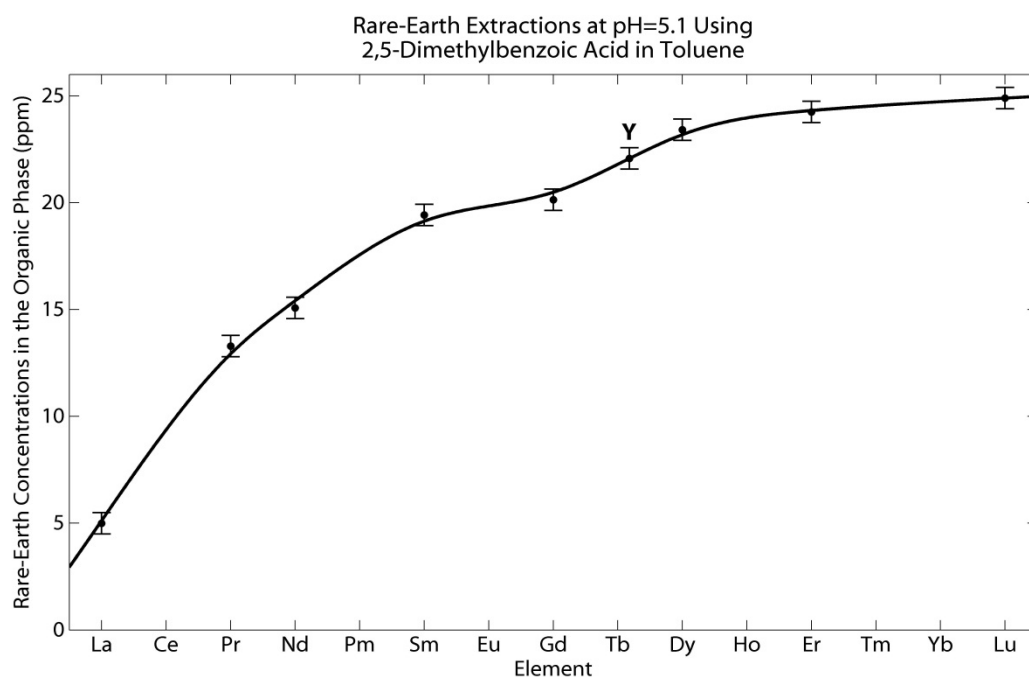
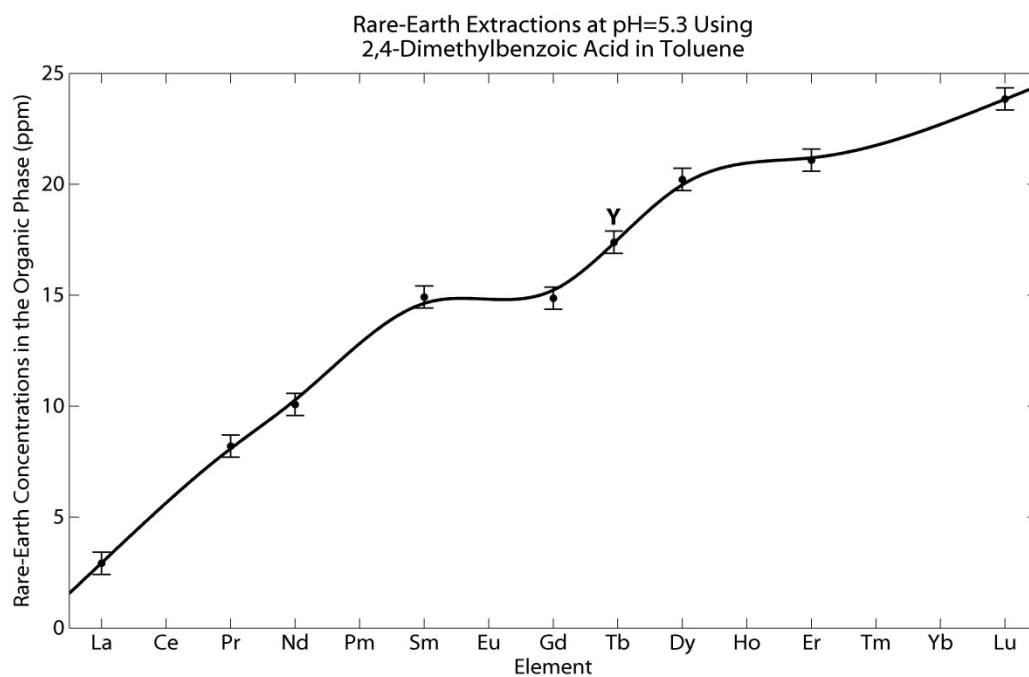


Figure 4.15: Extraction curves for (8 Ln^{+3} + Y^{+3}) systems containing 2,4-dimethylbenzoic acid (top) and 2,5-dimethylbenzoic acid (bottom) in toluene

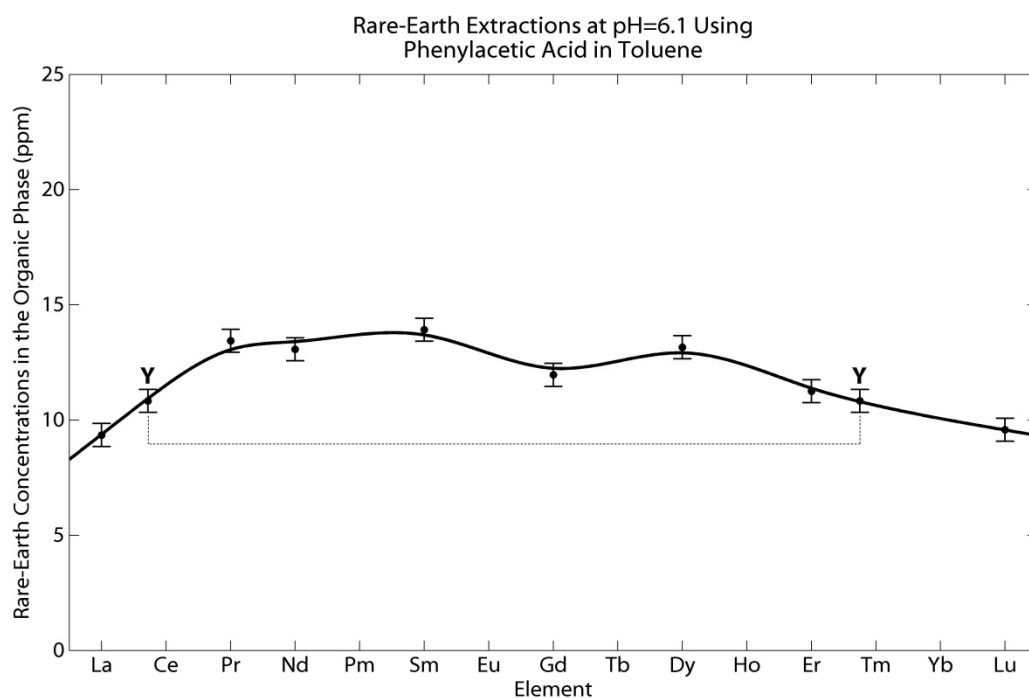
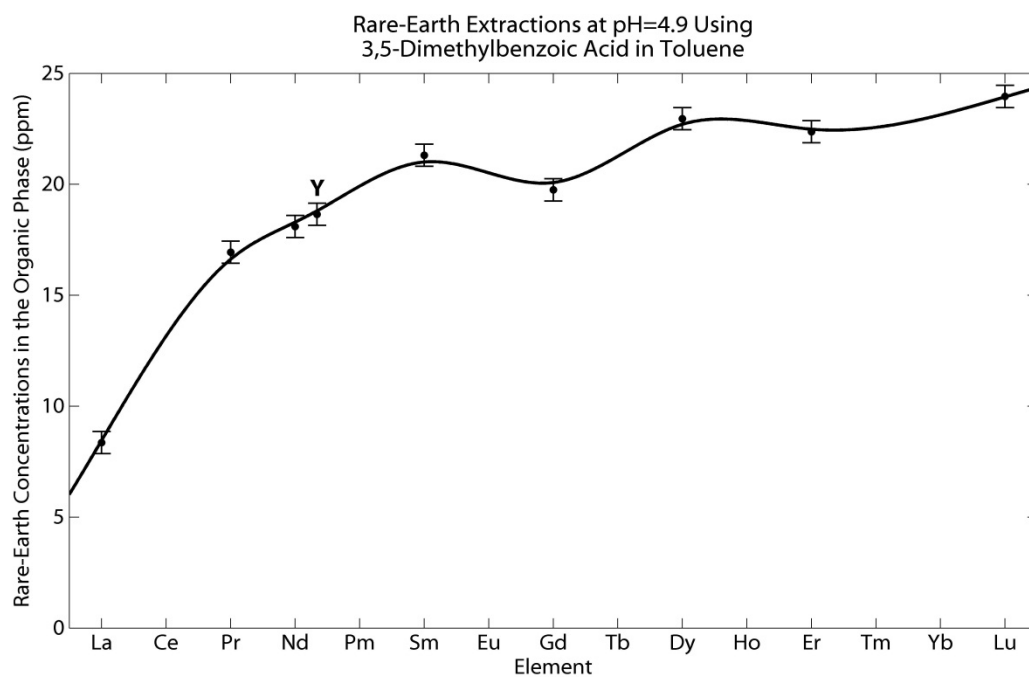


Figure 4.16: Extraction curves for (8 Ln^{+3} + Y^{+3}) systems containing 3,5-dimethylbenzoic acid (top) and phenylacetic acid (bottom) in toluene

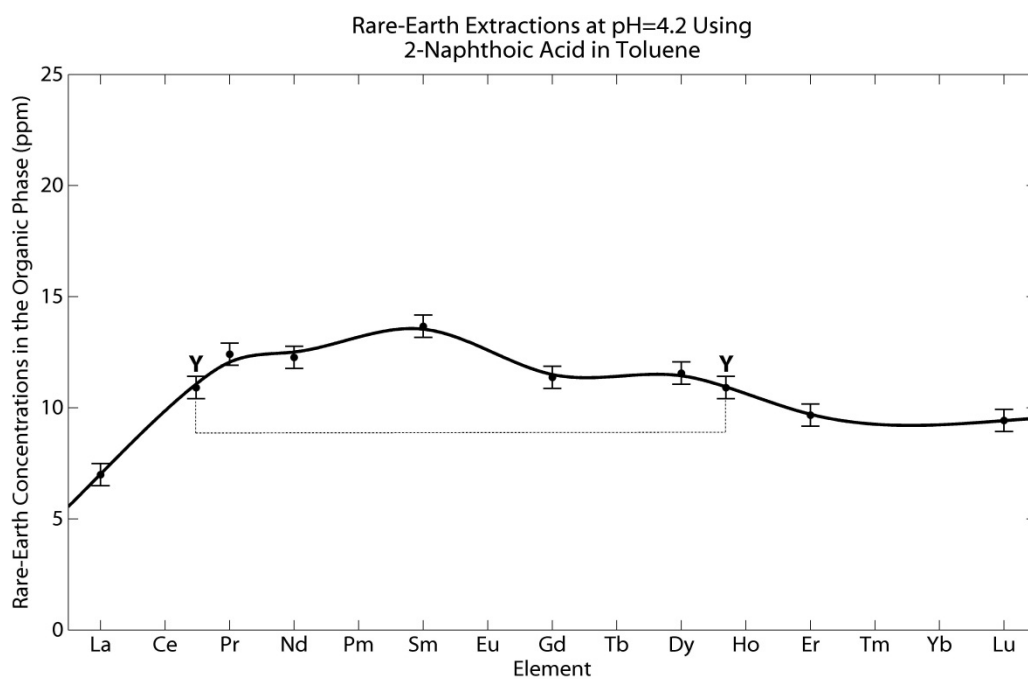
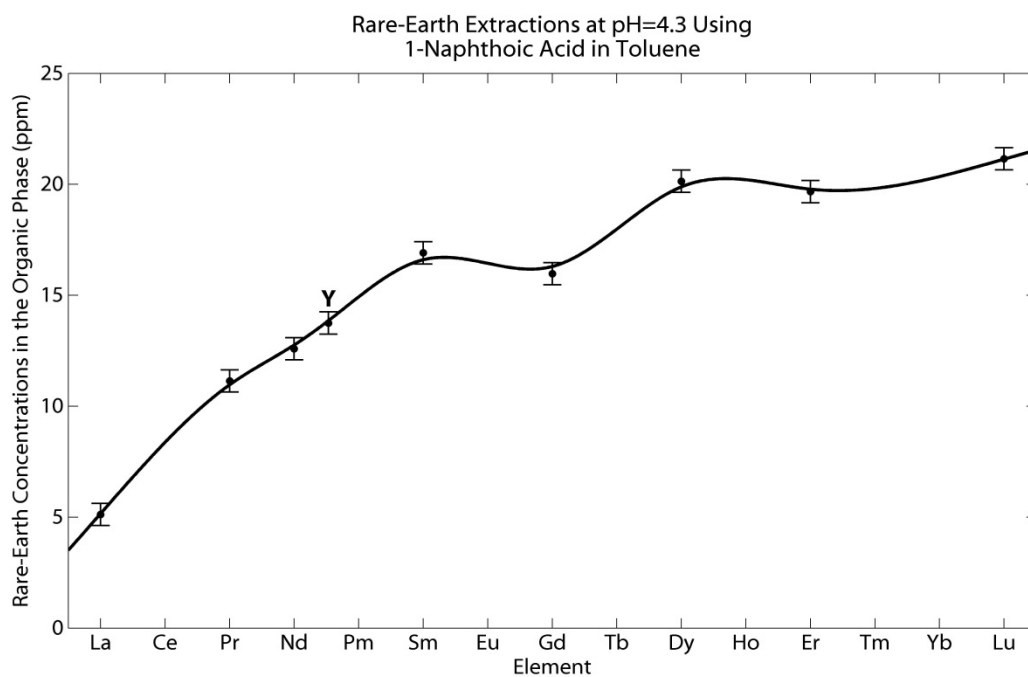


Figure 4.17: Extraction curves for (8 Ln⁺³ + Y⁺³) systems containing 1-naphthoic acid (top) and 2-naphthoic acid (bottom) in toluene

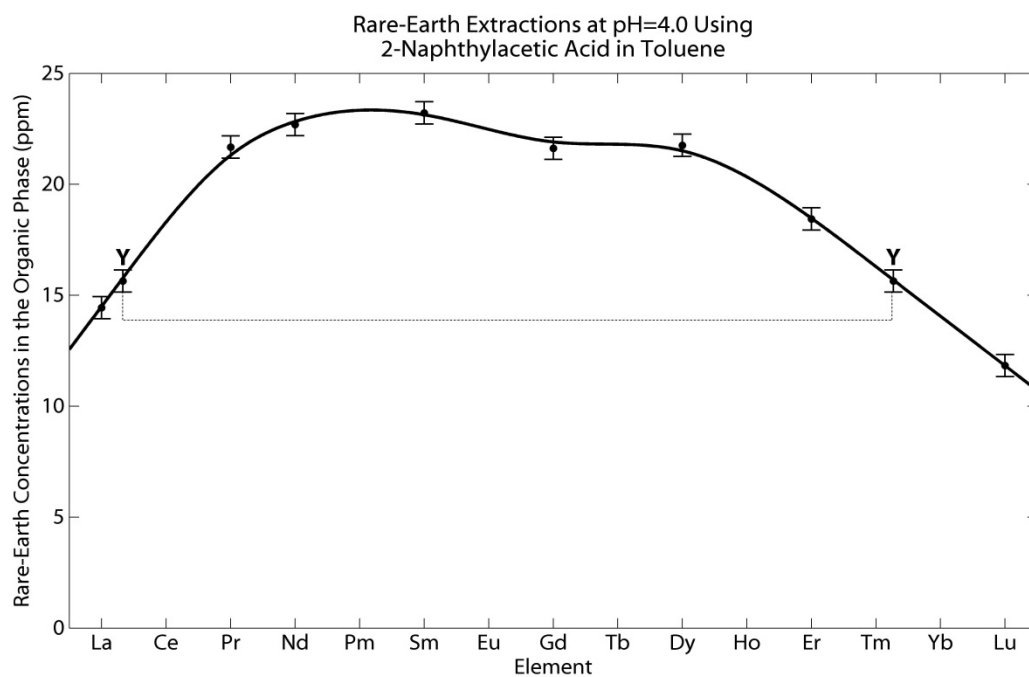
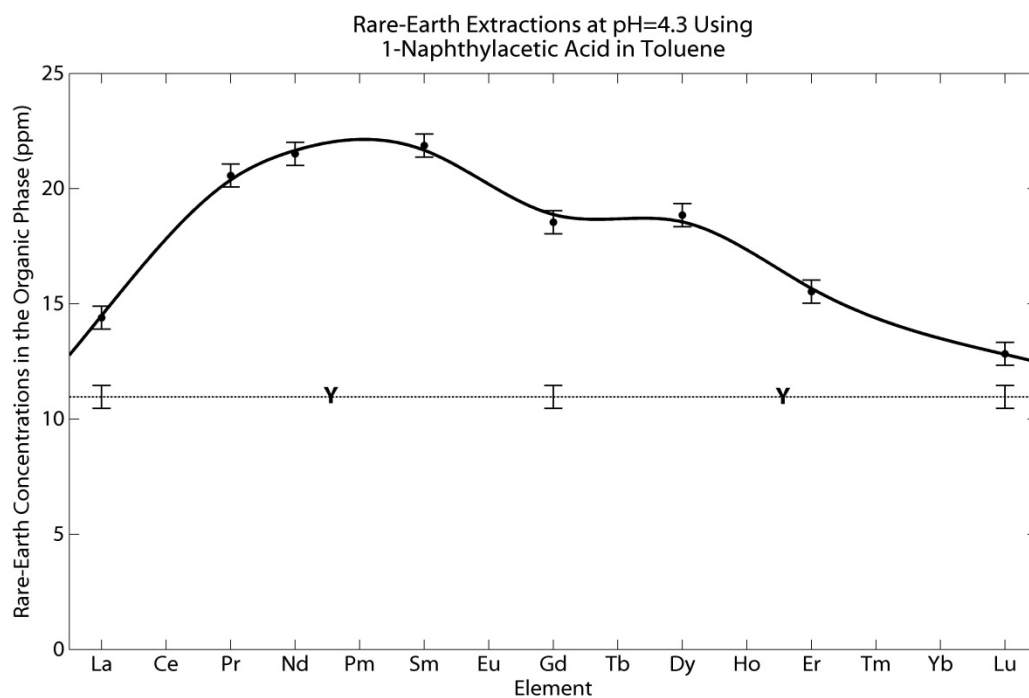


Figure 4.18: Extraction curves for (8 $\text{Ln}^{+3} + \text{Y}^{+3}$) systems containing 1-naphthylacetic acid (top) and 2-naphthylacetic acid (bottom) in toluene

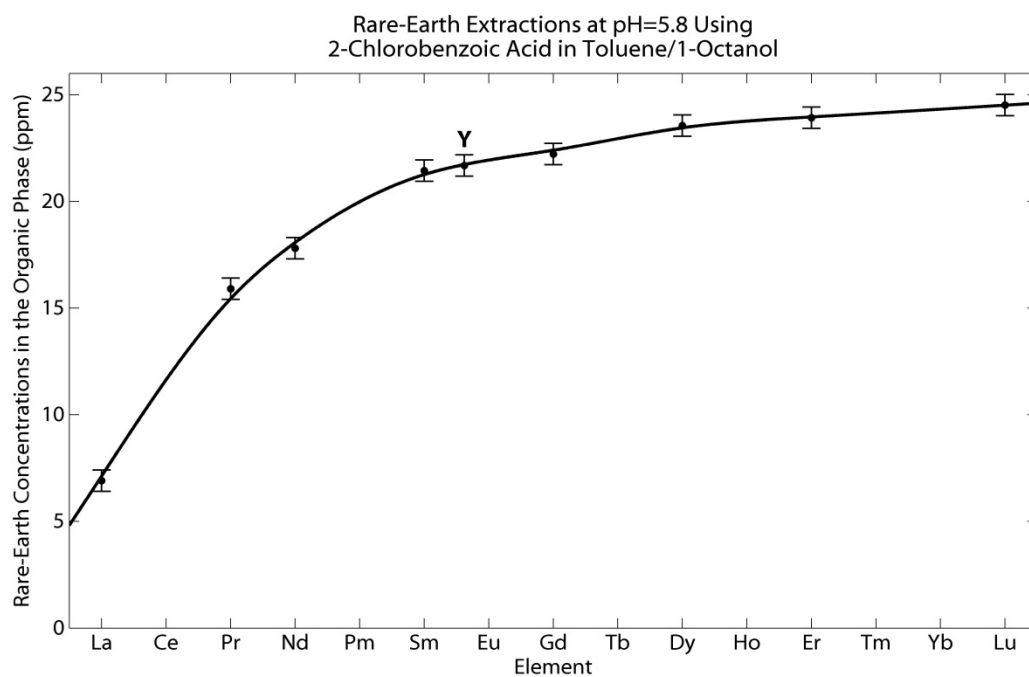
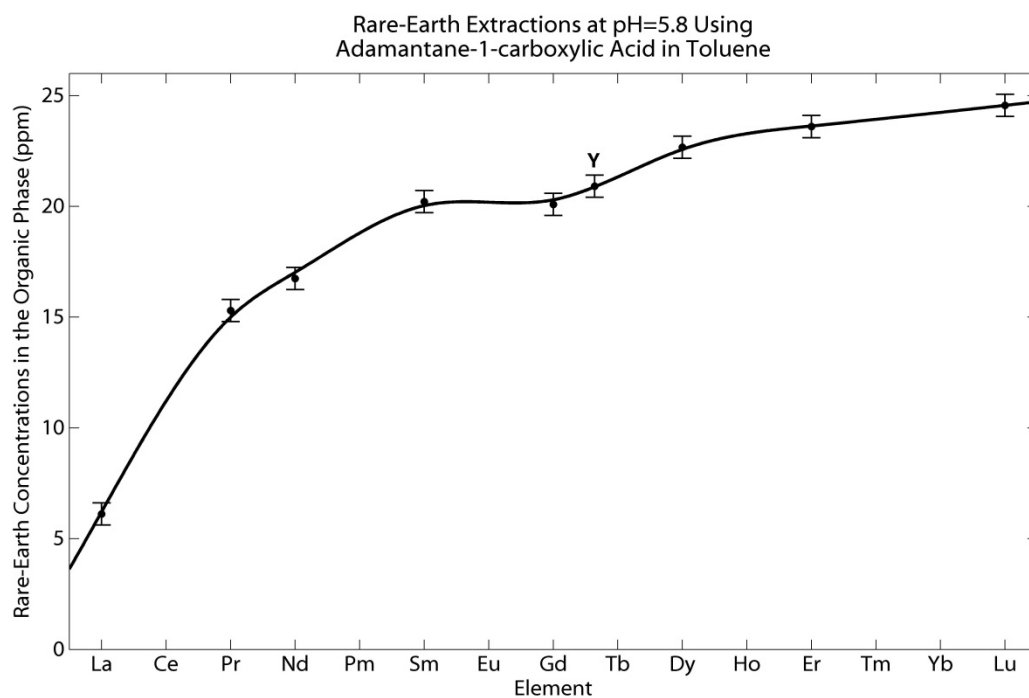


Figure 4.19: Extraction curves for (8 $\text{Ln}^{+3} + \text{Y}^{+3}$) systems containing adamantane-1-carboxylic acid (top) in toluene and 2-chlorobenzoic acid (bottom) in toluene/1-octanol

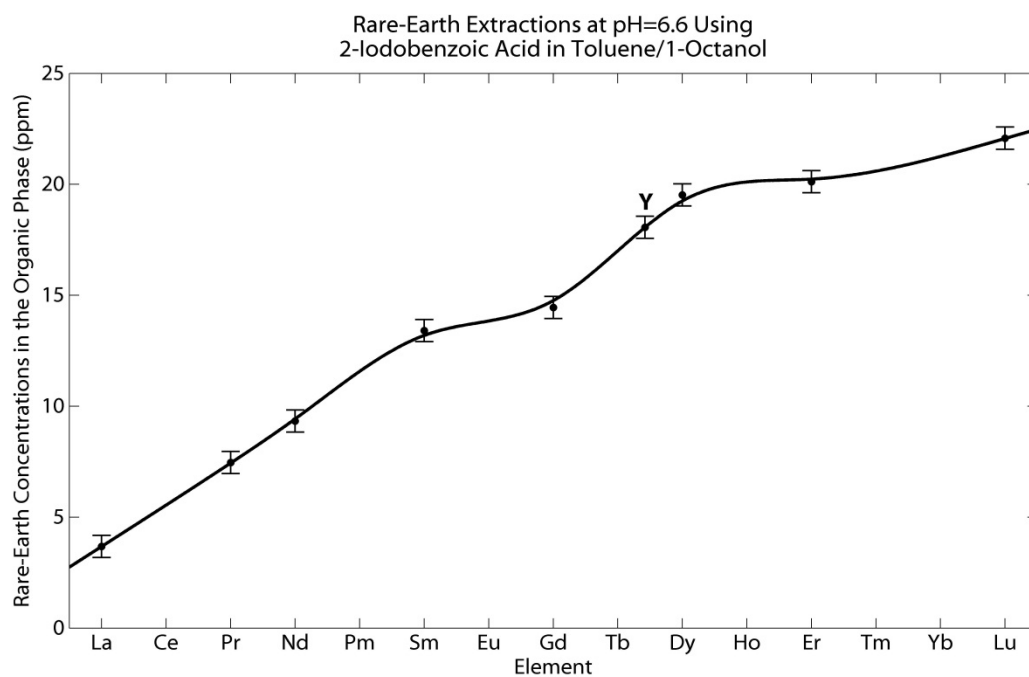
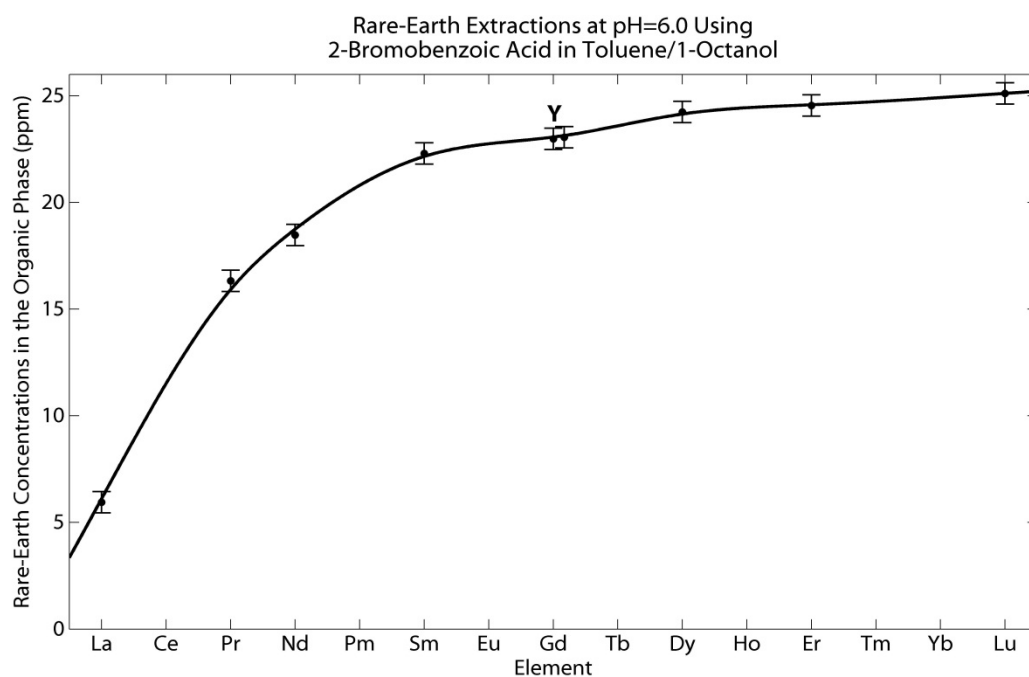


Figure 4.20: Extraction curves for (8 Ln⁺³ + Y⁺³) systems containing 2-bromobenzoic acid (top) and 2-iodobenzoic acid (bottom) in toluene/1-octanol

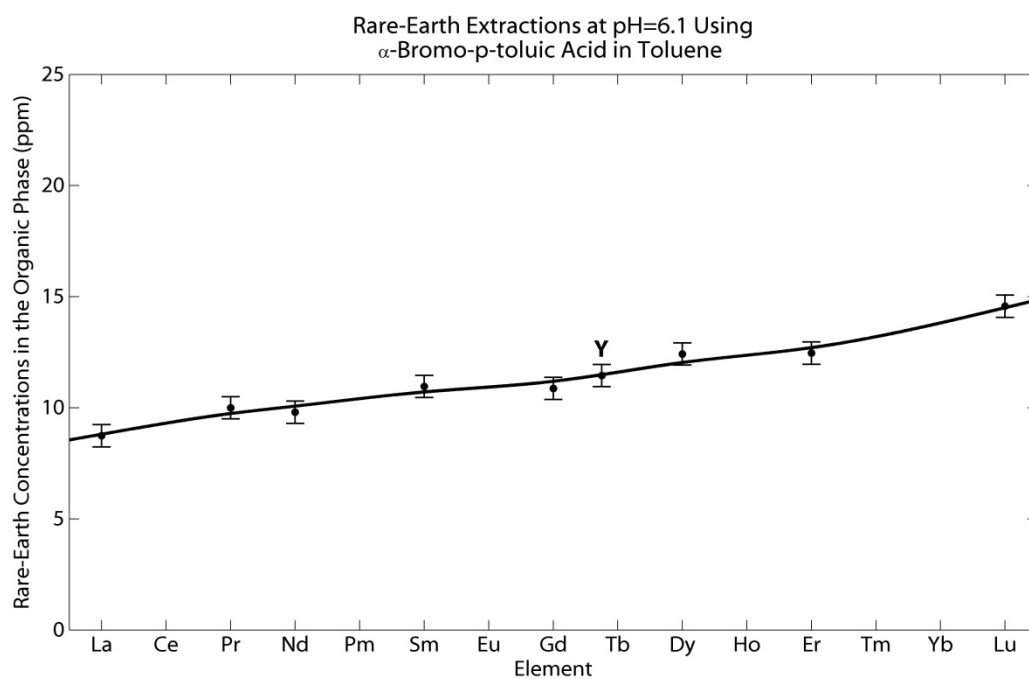
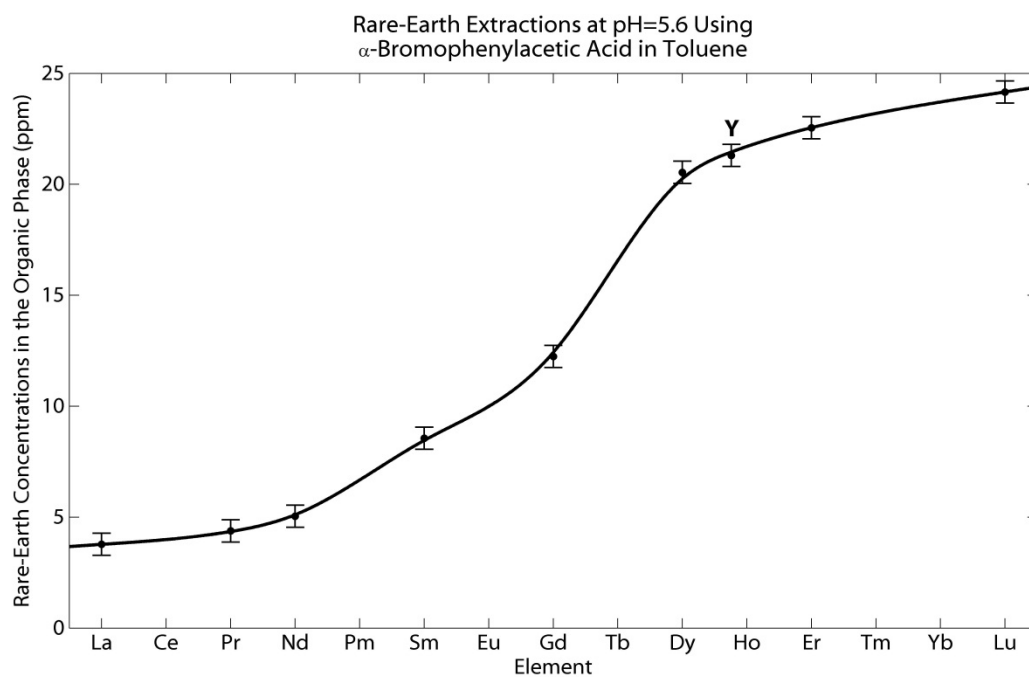


Figure 4.21: Extraction curves for $(8 \text{ Ln}^{+3} + \text{Y}^{+3})$ systems containing α -bromophenylacetic acid (top) and α -bromo-p-toluic acid (bottom) in toluene

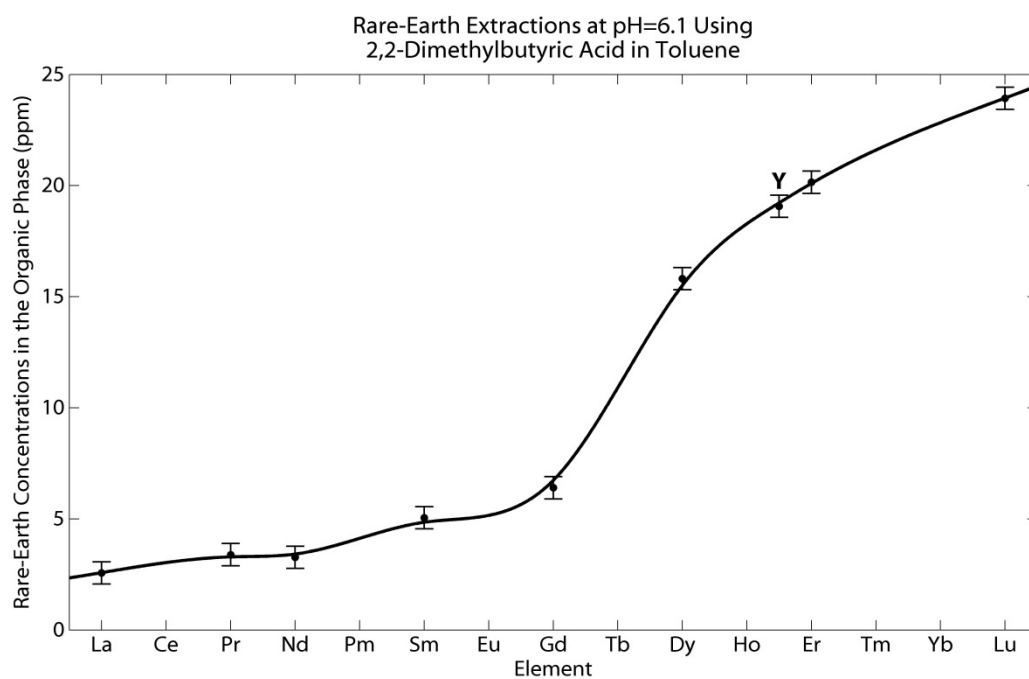
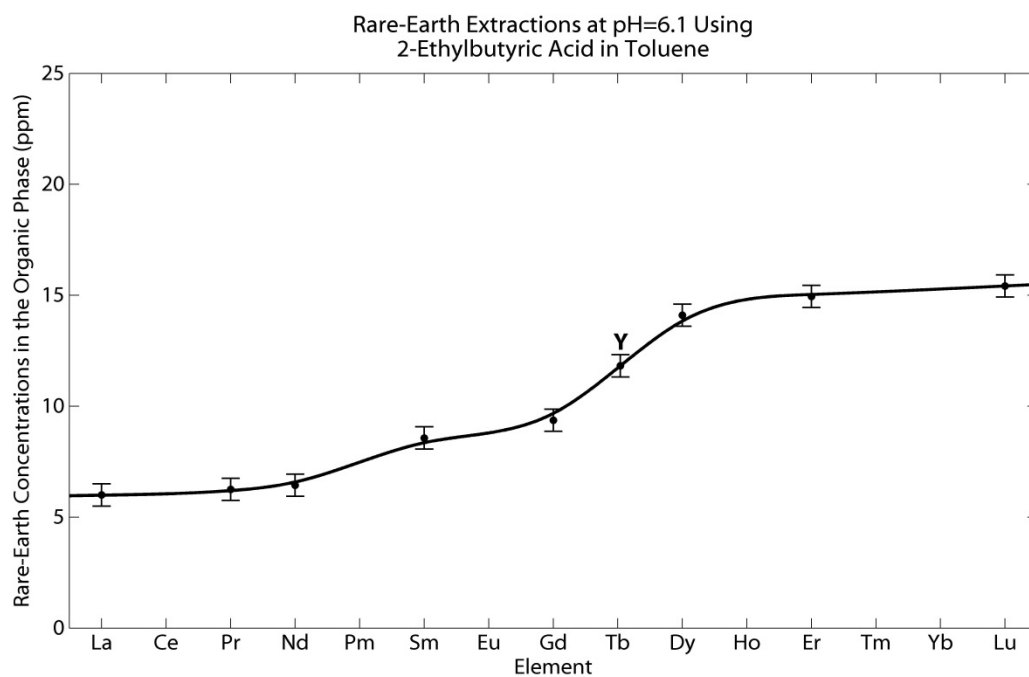


Figure 4.22: Extraction curves for (8 Ln^{+3} + Y^{+3}) systems containing 2-ethylbutyric acid (top) and 2,2-dimethylbutyric acid (bottom) in toluene

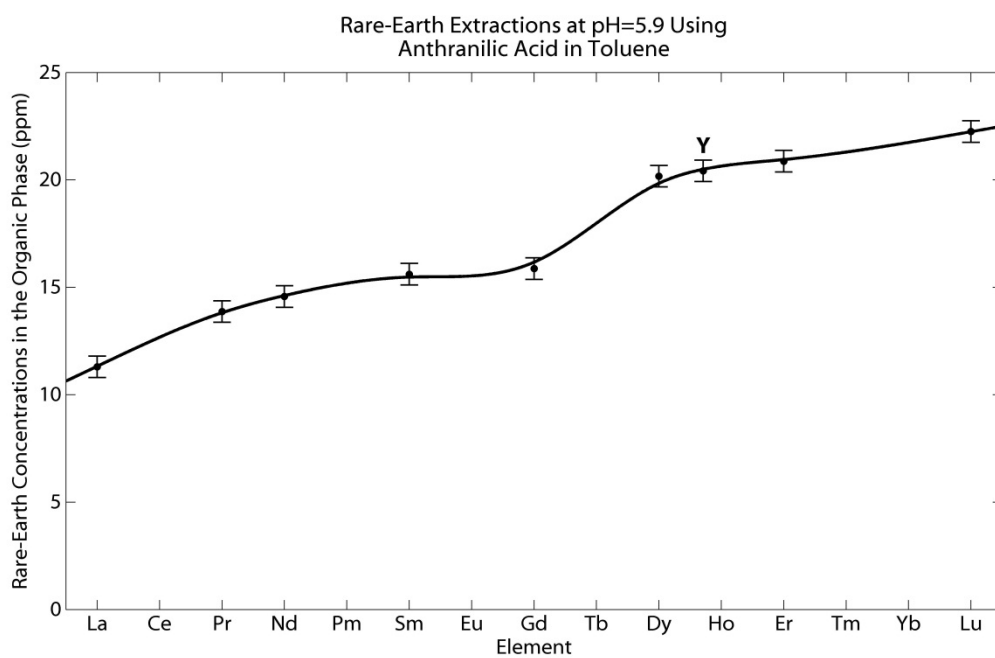


Figure 4.23: Extraction curves for (8 Ln⁺³ + Y⁺³) systems containing anthranilic acid in toluene

Chapter 5: Discussion and Conclusions

Discussion of Results

Based upon the findings of the research conducted by du Preez and Preston, and Singh, *et al.*,^{21,19,24} the research presented in Chapter 4 was designed to offer additional insight into the structural influences of carboxylic acid extractants on the position of Y in rare earth solvent extraction systems. The primary goal of this investigation is to determine if the steric-hindrance assertions made by these authors can be applied to a larger range of carboxylic acid extractants, or if any additional structural relationships can be found from these experimental results.

As a measure of overall steric hindrance exhibited by substituted carboxylic acids, the steric parameter E_s' has previously been used to rationalize the behavior of Y in rare-earth solvent extraction systems. These steric parameter values were calculated using the ratio of rates of acid-catalyzed esterification of the substituted carboxylic acids at 40°C versus the rate of acid-catalyzed esterification of a standard reference compound, acetic acid, at 40°C. These authors indicated a possible correlation with the values of E_s' and the position of Y within the lanthanide series. This assertion will also be analyzed in more detail in this chapter.

The experimental results shown in the previous chapter are summarized in Table 5.1 for solvent extractions containing aqueous ($5 \text{ Ln}^{+3} + \text{Y}^{+3}$) mixtures and Table 5.2 for aqueous ($8 \text{ Ln}^{+3} + \text{Y}^{+3}$) mixtures. The position of Y for each carboxylic acid extractant was determined by selecting the maximum range which Y can be placed within the bounds of the reliable error included at each data point and each table is sorted according to increasing values of Z_Y , or the relative atomic number of Y, discussed in the previous chapter. Values of $-E_s'$ listed in each table (if known) were obtained from literature sources. The position of Y for solvent extractions performed using iso-nonanoic acid and

Table 5.1: The position of Y and values of $-E_s'$ for carboxylic acid extractants in solvent extractions of $(5 \text{ Ln}^{+3} + \text{Y}^{+3})$ mixtures

Extractant	Position	Z_Y	$-E_s'$	Structure
Decanoic acid	Ce	58	0.3	56
Cyclohexylacetic acid	Ce	58	0.3	57
Octanoic Acid	Ce	58	0.9	12
3,5-Dimethylbenzoic acid	Nd-Pm	61	-	58
Cyclohexanecarboxylic acid	Nd-Sm	61	0.7	14
Dicyclohexylacetic acid	Pm-Sm	62	-	59
Adamantane-1-carboxylic acid	Sm-Eu	63	-	60
2,4-Dimethylbenzoic acid	Eu	63	-	61
2,3-Dimethylbenzoic acid	Eu-Gd	63	-	62
m-Toluic acid	Eu-Tb	64	-	63
o-Toluic acid	Gd-Tb	64	2.8	64
2-Ethylbutyric acid	Gd-Dy	65	2.0	65
p-Toluic acid	Gd-Tb	65	-	66
1-Methylcyclohexanecarboxylic acid	Ho	67	2.3	39
2,2-Dimethylbutyric acid	Ho-Er	68	2.3	67

Table 5.2: The position of Y and values of $-E_s'$ for carboxylic acid extractants in solvent extractions of $(8 \text{ Ln}^{+3} + \text{Y}^{+3})$ mixtures

Extractant	Position	Z_Y	$-E_s'$	Structure
1-Naphthylacetic acid	< La-Lu	<57	-	68
2-Naphthylacetic acid	La-Ce and Tm-Yb	57, 69	-	69
Phenylacetic acid	Ce and Er-Tm	58, 67	0.4	70
Cyclohexylacetic acid	Ce-Pr	58	0.9	57
Decanoic acid	Ce-Pr	58	0.3	56
Octanoic acid	Ce-Pr	58	0.3	12
2-Naphthoic acid	Ce-Pr and Dy-Ho	59, 67	-	71
Lauric acid	Ce-Pr	59	0.3	72
Cyclohexanecarboxylic acid	Ce-Sm	59	0.7	14
Iso-nonanoic acid	Pr	59	1.1 ^a	25
2,3-Dimethylbenzoic acid	Pr-Nd	59	-	62
Naphthenic acid	Nd	60	1.4 ^a	22
3,5-Dimethylbenzoic acid	Nd	60	-	58
1-Naphthoic acid	Nd-Pm	61	-	73
2-Chlorobenzoic acid	Sm-Eu	63	-0.2 ^b	74
2-Bromobenzoic acid	Sm-Tb	64	0.0 ^b	75
Dicyclohexylacetic acid	Gd-Tb	65	-	59
1-Phenyl-1-cyclohexanecarboxylic acid	Gd-Tb	65	-	76
o-Toluic acid	Gd-Tb	65	0.0 ^b / 2.8	64
Adamantane-1-carboxylic acid	Gd-Tb	65	-	60
1-Methylcyclohexanecarboxylic acid	Tb	65	2.3	39
α -Bromo-p-toluic acid	Eu-Dy	65	-	77
m-Toluic acid	Tb	65	-	63
2,4-Dimethylbenzoic acid	Tb	65	-	61
2-Ethylbutyric acid	Tb	65	2.0	65
2,5-Dimethylbenzoic acid	Tb	65	-	78
2-Iodobenzoic acid	Tb-Dy	65	0.2 ^b	79
p-Toluic acid	Tb-Dy	66	-	66
Anthranilic acid	Dy-Ho	67	-	80
α -Bromo-phenylacetic Acid	Dy-Ho	67	-	81
2,2-Dimethylbutyric acid	Ho-Er	68	2.3	67

^{a, b} See text for further explanation

naphthenic acid, along with their corresponding $-E_s'$ values, were obtained from experimental results reported by du Preez and Preston (denoted by a superscript "a" in Table 5.2).²¹ Structures of all carboxylic acids listed in Table 5.1 and Table 5.2 can be found in Appendix A.

In solvent extractions of $(5 \text{ Ln}^{+3} + \text{Y}^{+3})$ mixtures and $(8 \text{ Ln}^{+3} + \text{Y}^{+3})$ mixtures, Y can be placed into two main regions. For $-E_s'$ values less than 2.0, which correspond to extractants with a lower amount of steric bulk, Y most closely resembles the light rare earths, Ce-Sm. In solvent extractions performed using carboxylic extractants with considerably higher steric bulk, or $-E_s'$ values greater than or equal to 2.0, Y most closely resembles the heavy rare earths, Gd-Er.

The values of E_s listed for o-toluic acid, 2-chlorobenzoic acid, 2-bromobenzoic acid, and 2-iodobenzoic acid (denoted by the superscript "b" in Table 5.2) were obtained from early publications by R. W. Taft.⁸² Using o-toluic acid as a standard reference compound, the relative steric parameter values of E_s for 2-chlorobenzoic acid, 2-bromobenzoic acid, and 2-iodobenzoic acid differ only slightly from o-toluic acid. This similarity in E_s values for these carboxylic acids is reflected by the very slight variation in the position of Y for solvent extractions performed using these extractants.

As a predictor of the position of Y in solvent extraction systems containing carboxylic acid extractants, the steric parameter E_s' has been shown to roughly determine the region of the lanthanide series in which Y should be extracted, such as the light rare earths and heavy rare earths. However, it appears that E_s' offers little specificity in terms of the exact position at which Y extracts. These observations are in agreement with those made by the authors of the original investigations, in which no further resolution could be achieved using E_s' values.

A somewhat more refined structural correlation can, however, be drawn from these experimental results between the position of Y and substitutions at the α -carbon atom relative to the

carboxyl group. The extractants used throughout this investigation can be classified into two structural categories—those which possess an α -carbon atom which is not contained within a phenyl or cyclohexyl ring, and those which possess an α -carbon atom which is a component of a phenyl or cyclohexyl ring.

For the first group of extractants, or those containing an α -carbon atom which is not a component of a phenyl or cyclohexyl ring, three primary locations of Y can be observed. For carboxylic acid extractants which possess two hydrogen atoms at the α -carbon atom, Y most closely resembles Ce-Pr, as demonstrated by the results of extractions performed using octanoic acid, phenylacetic acid, and cyclohexylacetic acid. Carboxylic acid extractants which possess one hydrogen atom at the α -carbon atom and an additional substituent, such as an ethyl group, appear to shift the position of Y to the region of Gd-Tb. This shift in the position of Y is demonstrated in extractions performed using 2-ethylbutyric acid. It is to be noted, however, that extractants which possess a single hydrogen atom and a halogen atom at the α -carbon atom, such as α -bromophenylacetic acid, appear to shift the position of Y slightly further to the region of Dy-Ho. This finding is contradictory to the results reported by Preston in which extractants that contained a bromine atom at the α -carbon placed Y with the light lanthanide elements or outside the lanthanide series itself. Finally, an additional shift in the position of Y is observed in the use of extractants which possess no hydrogen atoms at the α -carbon atom. These extractants, such as 2,2-dimethylbutyric acid, place Y at its highest position of all carboxylic acids used throughout this investigation, near Ho-Er.

In the second group of carboxylic acid extractants, or those in which the α -carbon is a component of a phenyl or cyclohexyl ring, the behavior of Y upon substitution of the α -carbon atom differs slightly from the first group of extractants. Extractions performed using cyclohexanecarboxylic acid, which has a single hydrogen atom at the α -carbon which is contained within the cyclohexyl ring,

results in a position of Y near Ce-Sm. This behavior is somewhat similar to extractants of the first group, which possess two hydrogen atoms at the α -carbon atom. Extractants such as 1-methylcyclohexanecarboxylic acid and 1-phenyl-1-cyclohexanecarboxylic acid, which both contain an α -carbon atom within the cyclohexyl ring and no hydrogen atom at the α -carbon atom, place Y in the region of Gd-Tb. In this circumstance, the behavior of Y is most similar to that of the first group of extractants which contain a single hydrogen atom at the α -carbon. In addition, it is to be noted that both 1-methylcyclohexanecarboxylic acid and 1-phenyl-1-cyclohexanecarboxylic acid appear to place Y in similar positions within the lanthanide series. This finding suggests that the position of Y is independent of the type of substituted group located at the α -carbon atom which is a component of a cyclohexyl ring.

Carboxylic acid extractants which contain an α -carbon atom that is a component of a phenyl ring also exhibit different behavior from the first group of extractants. In these structures, the position of Y is commonly found to be near Gd-Tb. This behavior is similar to that of extractants that belong to the first group of extractants which possess one hydrogen atom at the α -carbon. The α -carbon atom of these extractants, however, cannot undergo further substitution. This characteristic is reflected by the similar behavior of Y in solvent extractions performed using many of these extractants.

Solvent extractions performed using substituted benzoic acid derivatives which possessed two methyl groups on the phenyl ring yielded inconclusive results. In some cases, such as extractions performed using 2,4-dimethylbenzoic acid and 2,5-dimethylbenzoic acid as extractants, Y was found to occupy a position near Tb. The extractants 3,5-dimethylbenzoic acid and 2,3-dimethylbenzoic acid, however, were found to place Y in a position near Nd for $(8 \text{ Ln}^{+3} + \text{Y}^{+3})$ mixtures. In $(5 \text{ Ln}^{+3} + \text{Y}^{+3})$ mixtures, 2,3-dimethylbenzoic acid appeared to place Y in a position near Eu-Gd. Further

investigations into the use of these extractants are needed before any definitive steric relationships could be determined.

The naphthoic and naphthylacetic acids constitute another class of carboxylic acid extractants not pursued during the course of the previously cited research. These extractants exhibited some interesting behavior which was not observed in solvent extractions with other carboxylic acids used during this investigation. In extractions performed using 1-naphthylacetic acid, Y was consistently extracted into the organic phase to a lesser extent than all other rare earths in solution. The related extractants 2-naphthylacetic acid, 1-naphthoic acid, and 2-naphthoic acid, however, did not appear to place Y outside the lanthanide series. Because the values of E_s' are not presently known for these carboxylic acids, further investigation would be necessary before any conclusions could be drawn.

Conclusions

Complete separations of the rare-earth elements Y and La-Lu have traditionally been difficult to achieve, often requiring hundreds to thousands of separation stages for the production of pure rare earths. In many instances, Y is found to be separated with Ho, which shares its crystal cationic radius with Y. However, reports as early as 1891 indicated that in certain instances, Y could be separated in other positions along the lanthanide series. This itinerant behavior of Y was to be the foundation of this research project.

Since the earliest declarations of this phenomenon, Y has been shown to occupy many positions within the lanthanide series, ranging from La to Lu and even outside the bounds of the lanthanide series itself. The position of Y reported in previous literature sources varies greatly between separation systems, and this occurrence has been observed in rare-earth separations using techniques such as fractional crystallization, fractional precipitation, decomposition, volatilization, ion exchange, and solvent extraction. Although many investigators have speculated on the reasons

behind this behavior, this phenomenon is not completely understood and few systematic studies of this behavior have been conducted.

Beginning in the mid-1990s, publications by du Preez and Preston, and Singh, *et al.*, indicated that a possible correlation exists between the position of Y and the overall steric bulk of carboxylic acid extractants used in rare-earth solvent extraction systems. These investigators carried out rare-earth extractions using a variety of extractants, ranging from carboxylic acids with low steric bulk to those with high steric bulk. As a quantitative means of representing the steric hindrance of these extractants, the authors used the steric parameter E_s' , a value determined from the rates of acid-catalyzed esterification of carboxylic acids in methanol at 40°C.

The results of the studies conducted by these authors showed that in extractions performed using extractants with $-E_s'$ values less than 1, Y was found to be extracted with the light rare earths, typically in the region from La-Nd. In solvent extractions performed using extractants with $-E_s'$ values greater than 2, Y was extracted with the middle to heavy rare earths, Gd to Ho. These extractions, however, were primarily conducted using solutions of individual rare-earths, and the range of carboxylic acid extractants used in these experiments was very limited.

The primary goal of the research outlined in the preceding chapters was to elaborate upon the findings of these authors and to determine if any further correlations between the position of Y and the steric bulk of carboxylic acid extractants, as indicated by the steric parameter E_s' , can be found. To more accurately reflect the behavior of Y in competition with other rare earth elements, these solvent extractions were to be performed using an aqueous phase consisting of rare-earth mixtures.

The results summarized in this chapter show that the values of E_s' can only be used to roughly determine the location of Y in these solvent extraction systems. For $-E_s'$ values less than 2, Y is

extracted with the light rare earths, La-Eu. Extractants with $-E_s'$ values greater than 2 tend to place Y with the heavy rare earths, Gd-Lu. No further refinement of this correlation between steric parameter values and the position of Y, however, can be achieved from these experimental results. The lack of available values of E_s' for carboxylic acids which can be commercially obtained—particularly those which have a high degree of steric bulk—limits the ability to readily obtain a full range of extractants which have preexisting steric parameter values. Although E_s' values have been calculated for numerous carboxylic acids, many of these compounds also possess significant solubility in aqueous solutions. As a result, these acids are not suitable for use as extractants in solvent extraction systems.

One significant observation made this study is the importance of α -substitution in the shift of the position of Y from the light rare earths to heavy rare earths. It was found that extractants which possess an α -carbon atom which is not a component of a phenyl or cyclohexyl ring place Y in three distinct regions—Ce-Pr, Gd-Tb, and Ho-Er, depending on the number of hydrogen atoms located at the α -carbon atom. Extractants which contain an α -carbon atom that is contained within a cyclohexyl ring place Y in two regions—Ce-Pr and Gd-Tb, depending on the number of hydrogen atoms located at the α -carbon atom. Carboxylic acid extractants which contain an α -carbon atom which is a component of a phenyl ring primarily place Y in the region of Gd-Tb. These extractants exhibit similar extraction behavior due to the inability to place substituted groups at the α -carbon atom.

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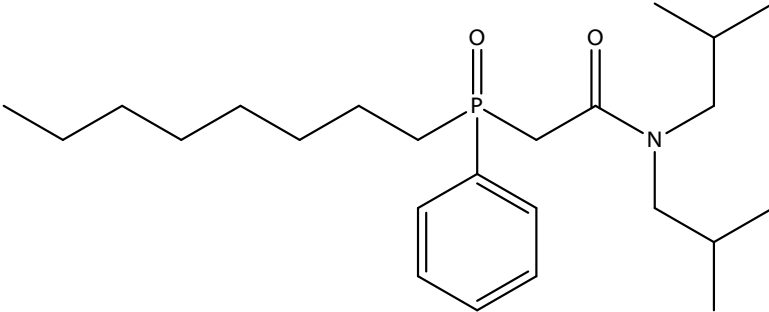
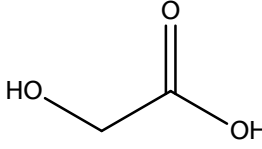
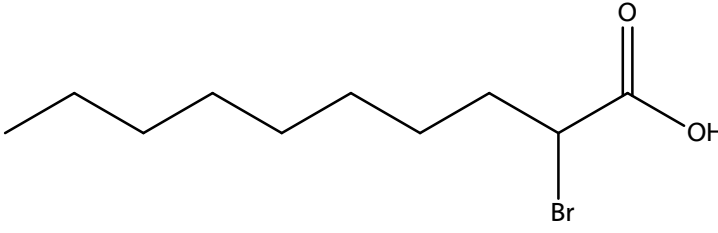
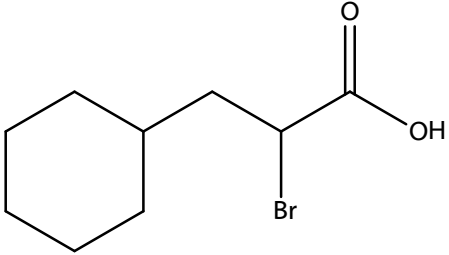
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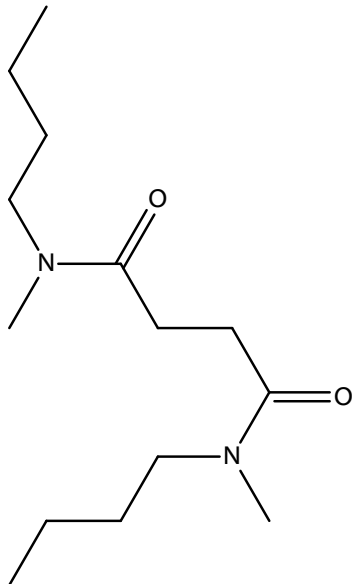
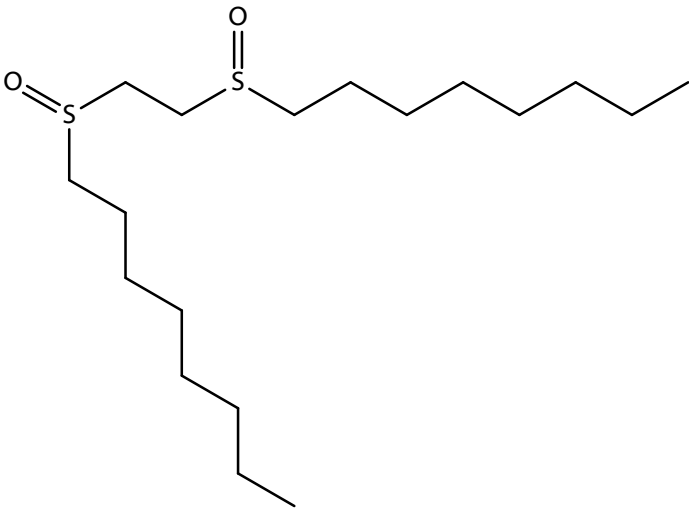
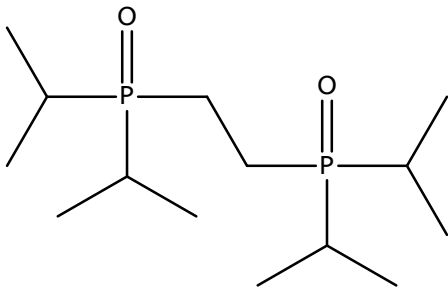
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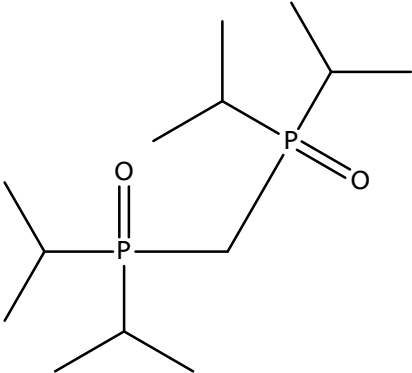
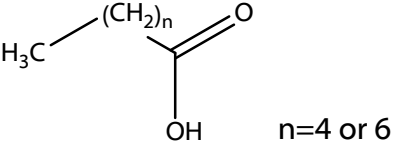
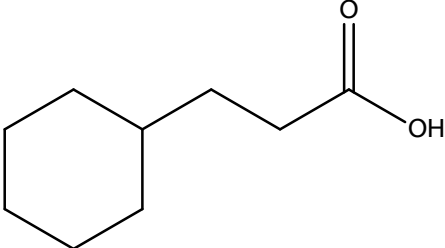
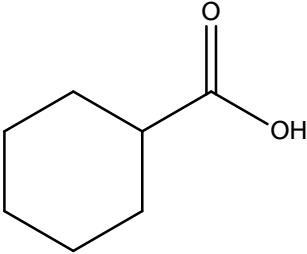
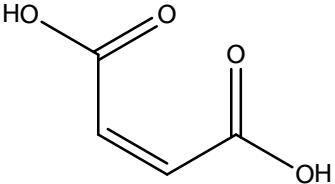
APPENDIX

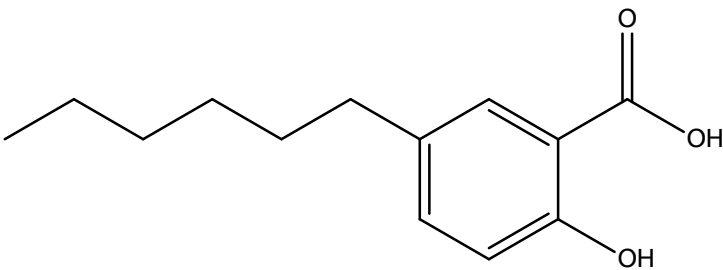
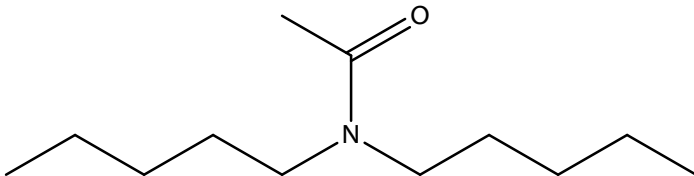
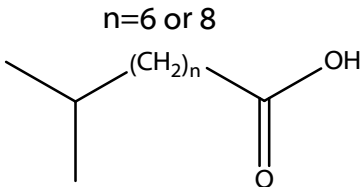
Appendix A: Structures of Selected Separation Agents

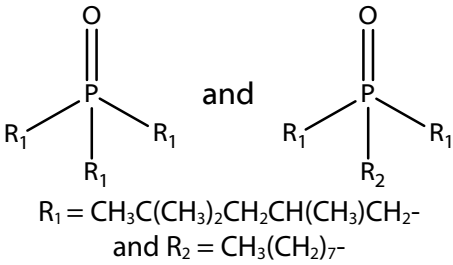
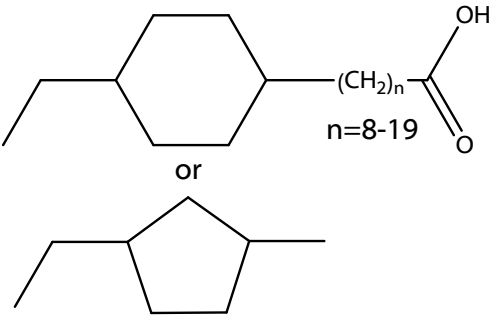
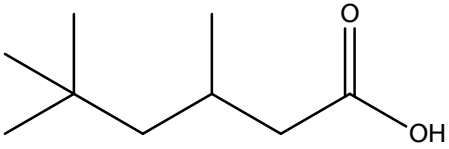
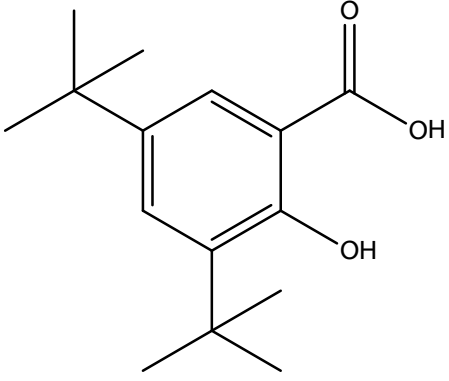
Structure Number	Trade/Chemical Name Or Abbreviation	Chemical Structure
1	CMPO / Octyl-(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide	
2	Glycolic acid	
3	2-Bromodecanoic acid	
4	2-Bromo-3-cyclohexylpropanoic acid	

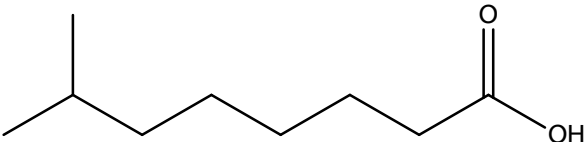
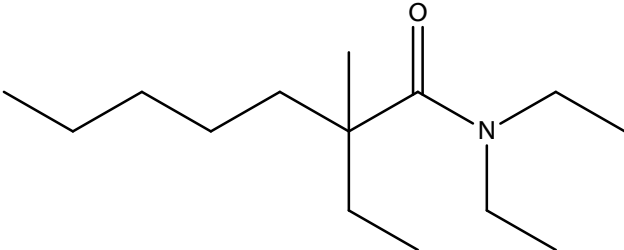
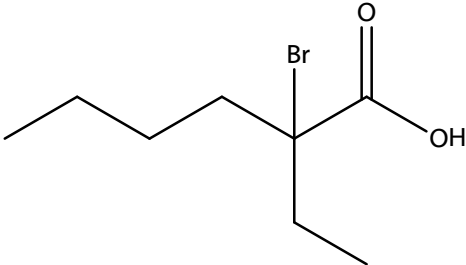
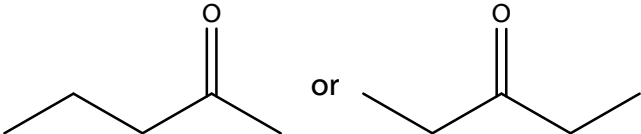
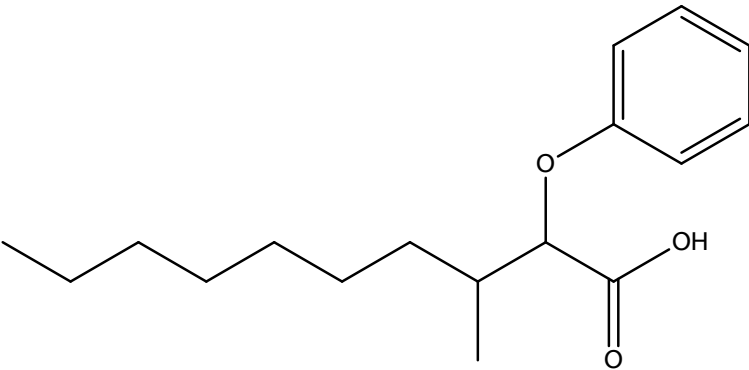
Structure Number	Trade/Chemical Name Or Abbreviation	Chemical Structure
5	2-Bromo-3,5,5-trimethylhexanoic acid	<chem>CC(C)(C)C(Br)CC(=O)O</chem>
6	DIPSA / 3,5-Diisopropylsalicylic acid	<chem>CC(C)c1cc(C(C)C)c(C(=O)O)c(O)c1</chem>
7	N,N,N',N'- tetraethylsuccinamide	<chem>CCN(CC)C(=O)CC(=O)N(CC)CC</chem>

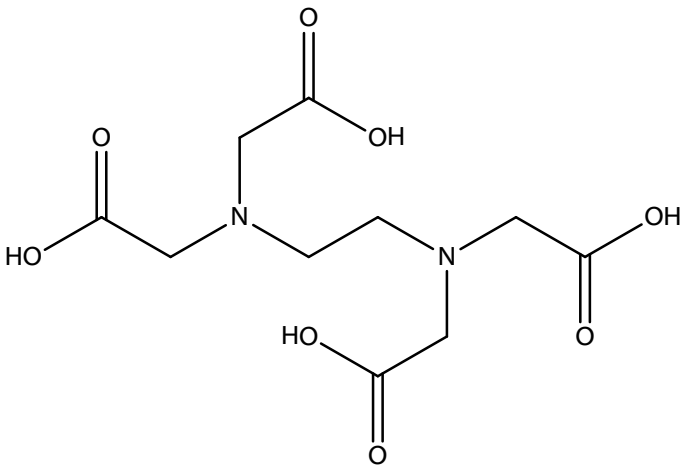
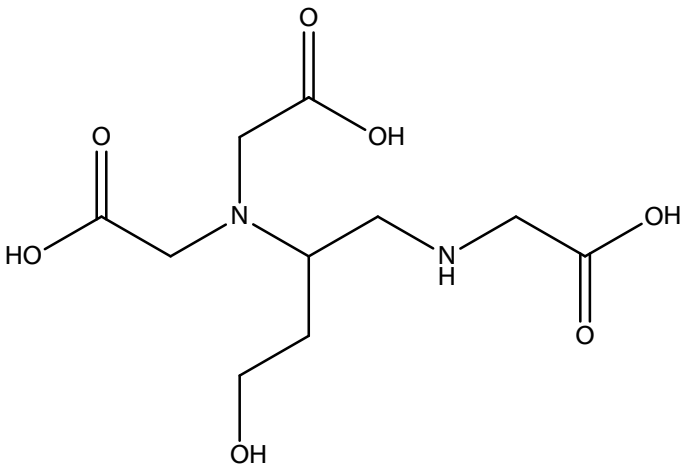
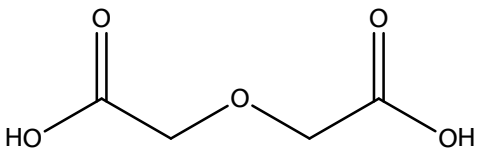
Structure Number	Trade/Chemical Name Or Abbreviation	Chemical Structure
8	N,N'-dibutyl-N,N'-dimethylsuccinamide	
9	1,2-bis-(octylsulfinyl)ethane	
10	Ethane-1,2-diylbis-(diisopropylphosphine oxide)	

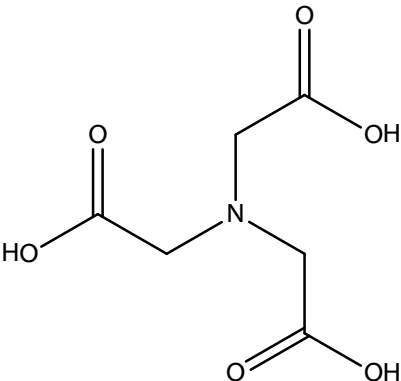
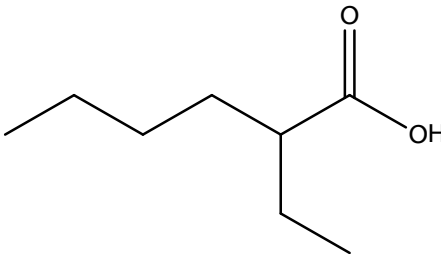
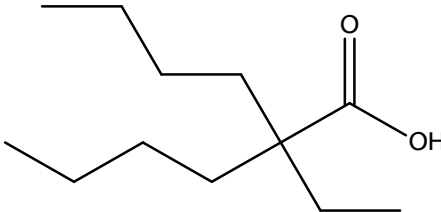
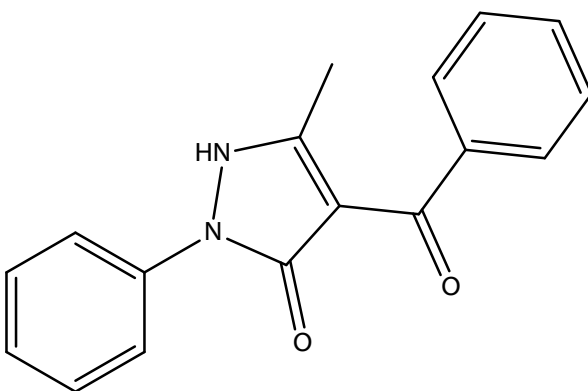
Structure Number	Trade/Chemical Name Or Abbreviation	Chemical Structure
11	Methylenebis-(diisopropylphosphine oxide)	
12	Hexanoic acid/ Octanoic acid	
13	3-Cyclohexylpropanoic acid	
14	Cyclohexanecarboxylic acid	
15	Maleic acid	

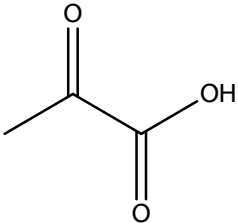
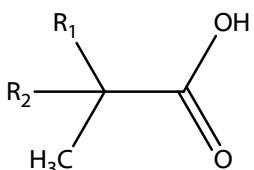
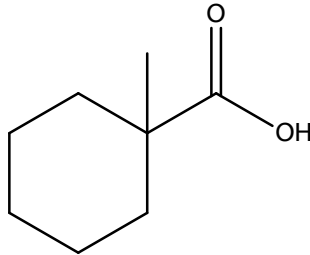
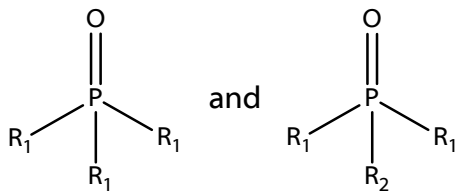
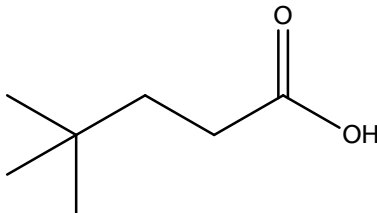
Structure Number	Trade/Chemical Name Or Abbreviation	Chemical Structure
16	5- <i>n</i> -Hexylsalicylic acid	
17	N,N-di- <i>n</i> -pentylacetamide	
18	Cekanoic acid	
19	Adogen-464 SCN / Methyltrialkyl(C ₈ -C ₁₀)-ammonium thiocyanate	$ \begin{array}{c} \text{R} \\ \\ \text{R}-\text{N}^+-\text{CH}_3 \\ \\ \text{R} \end{array} \text{SCN}^- $ R = CH₃(CH₂)_nCH₂- where n = 6, 7, or 8
20	Aliquat 336 / Tricaprylmethyl-ammonium thiocyanate	$ \begin{array}{c} \text{R} \\ \\ \text{R}-\text{N}^+-\text{CH}_3 \\ \\ \text{R} \end{array} \text{SCN}^- $ R = CH₃(CH₂)_nCH₂- where n = 6

Structure Number	Trade/Chemical Name Or Abbreviation	Chemical Structure
21	Cyanex 925	 $\text{R}_1 = \text{CH}_3\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2-$ $\text{and R}_2 = \text{CH}_3(\text{CH}_2)_7-$
22	Naphthenic acid	 $\text{n} = 8-19$
23	3,5,5-Trimethylhexanoic acid	
24	3,5-di- <i>tert</i> -butylsalicylic acid	

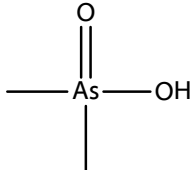
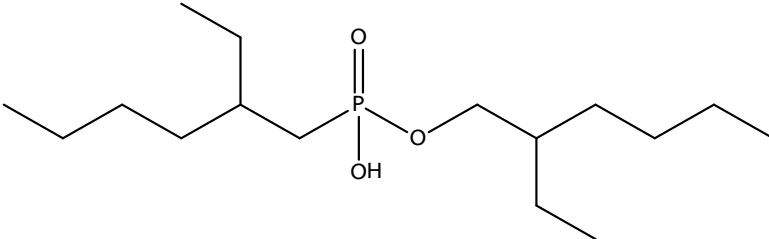
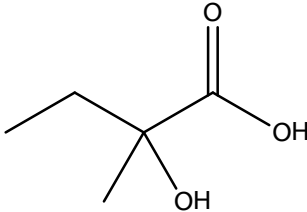
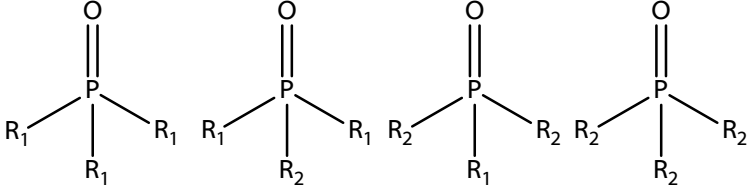
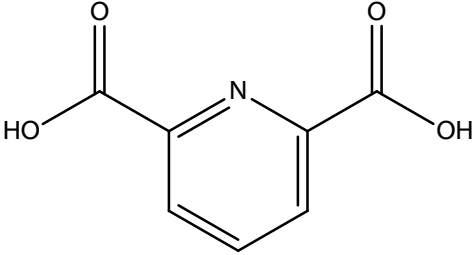
Structure Number	Trade/Chemical Name Or Abbreviation	Chemical Structure
25	Iso-nonanoic acid	
26	N,N-diethyl-2-ethyl-2-methylheptanamide	
27	2-Bromo-2-ethylhexanoic acid	
28	Pentanone (ambiguous)	
29	CA-100 / <i>sec</i> -Nonylphenoxyacetic acid	

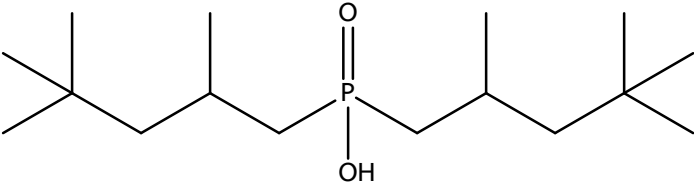
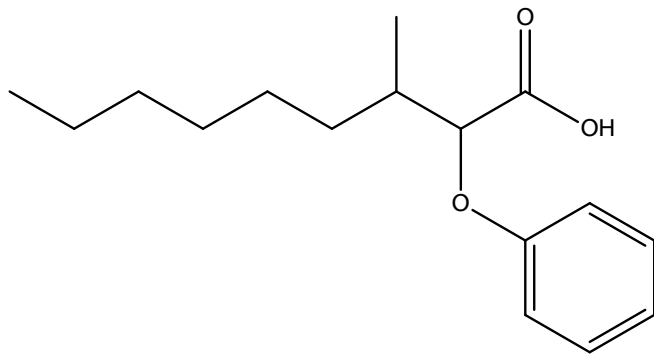
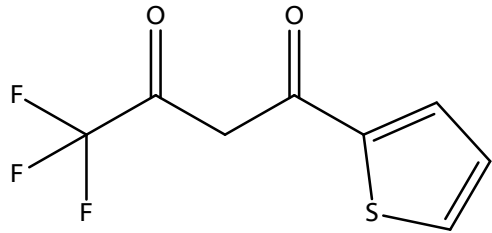
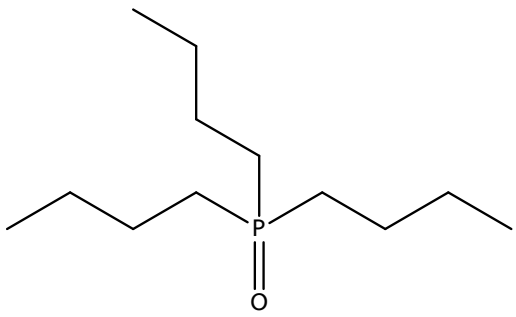
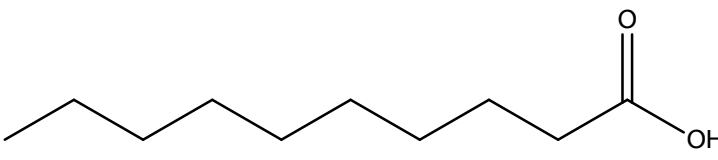
Structure Number	Trade/Chemical Name Or Abbreviation	Chemical Structure
30	EDTA / Ethylenediamine-tetraacetic acid	
31	HEDTA / N-(hydroxyethyl)-ethylenediamine-triacetic acid	
32	Diglycolic acid	

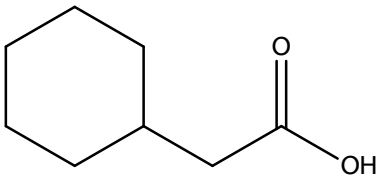
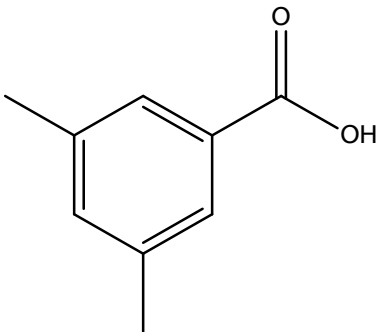
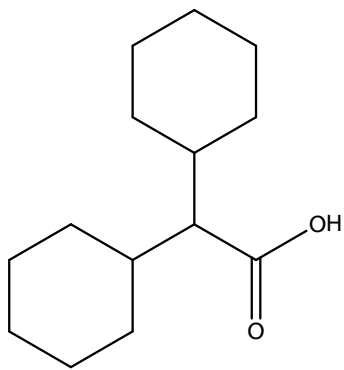
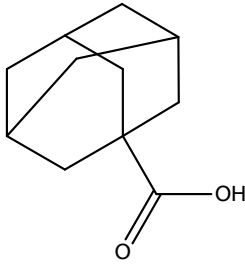
Structure Number	Trade/Chemical Name Or Abbreviation	Chemical Structure
33	NTA / Nitrilotriacetic acid	
34	2-Ethylhexanoic acid	
35	2-Butyl-2-ethylhexanoic acid	
36	HPMBP / 1-phenyl-3-methyl-4-benzoyl-pyrazolone-5	

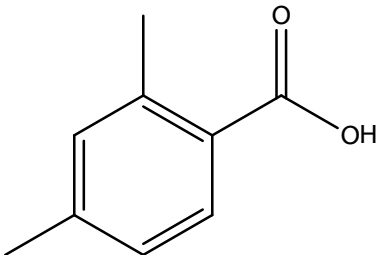
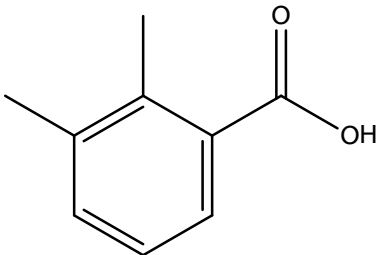
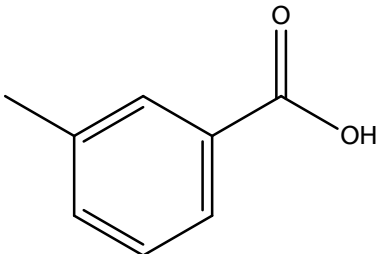
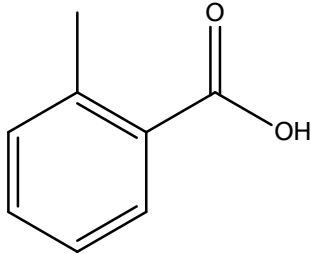
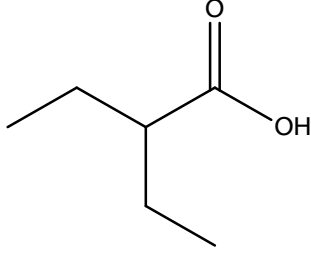
Structure Number	Trade/Chemical Name Or Abbreviation	Chemical Structure
37	Pyroracemic acid / Pyruvic acid	
38	Versatic 10 acid	 R₁ and R₂= Alkyl groups Total carbon atoms = 10
39	1-Methylcyclohexane-carboxylic acid	
40	Cyanex 925	 R₁ = CH₃C(CH₃)₂CH₂CH(CH₃)CH₂- and R₂ = CH₃(CH₂)₇-
41	Neo-heptanoic acid	

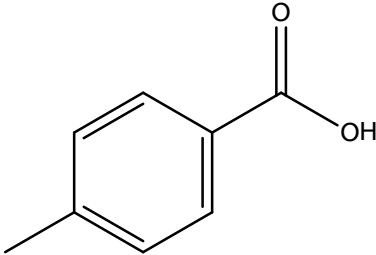
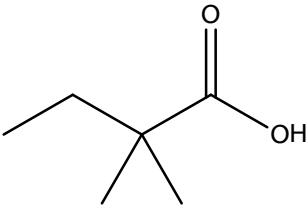
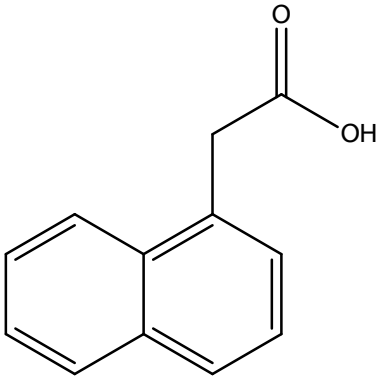
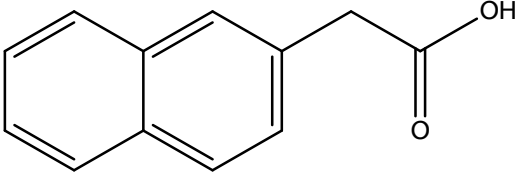
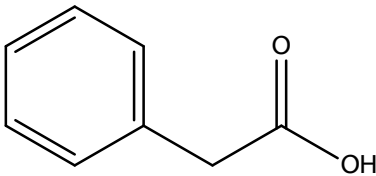
Structure Number	Trade/Chemical Name Or Abbreviation	Chemical Structure
42	Citric acid	<chem>OC(=O)CC(O)(CC(=O)O)CC(=O)O</chem>
43	HIBA / α-Hydroxyisobutyric acid	<chem>CC(C)(O)C(=O)O</chem>
44	Oxalic acid	<chem>OC(=O)C(=O)O</chem>
45	Lactic acid	<chem>CC(O)C(=O)O</chem>
46	TBP / Tributyl phosphate	<chem>CCCCOP(=O)(OCCCC)OCCCC</chem>

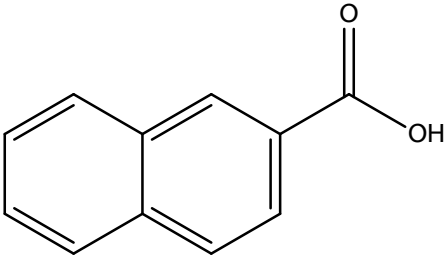
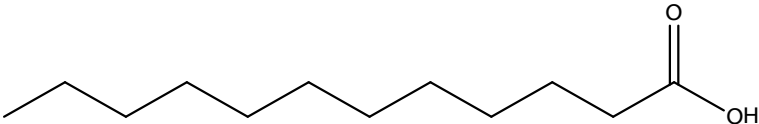
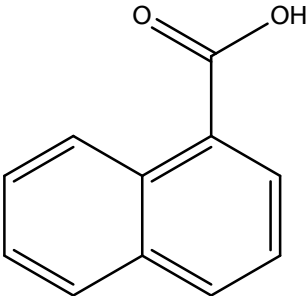
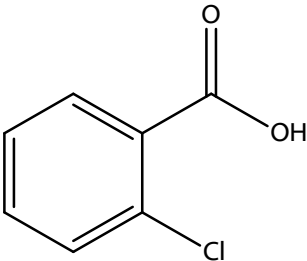
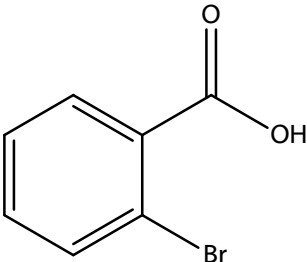
Structure Number	Trade/Chemical Name Or Abbreviation	Chemical Structure
47	Cacodylic acid	
48	HEHEHP / EHEHPA / 2-Ethylhexylphosphonic acid mono-(2-ethylhexyl) ester	
49	α -Hydroxy- α -methylbutyric acid	
50	Cyanex 923	 $R_1 = n\text{-hexyl-}$ and $R_2 = n\text{-octyl-}$
51	Dipicolinic acid	

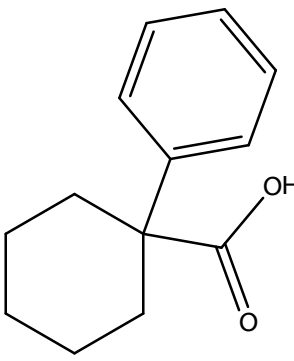
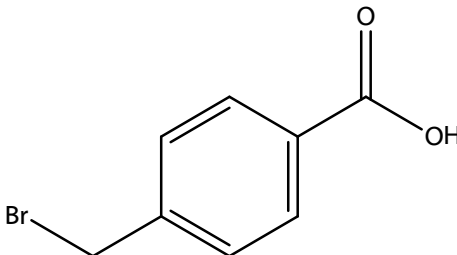
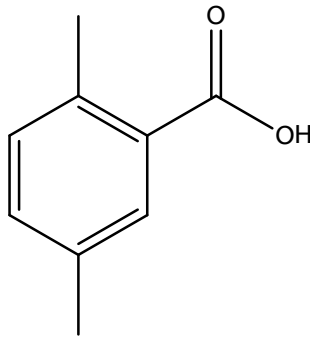
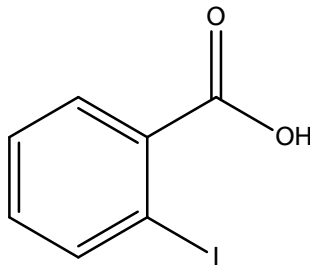
Structure Number	Trade/Chemical Name Or Abbreviation	Chemical Structure
52	Cyanex 272 / bis(2,4,4-trimethylpentyl)-phosphinic acid	
53	CA-12 / <i>sec</i> -Octylphenoxyacetic acid	
54	HTTA / 2-Thenoyl-trifluoroacetylacetone	
55	TBPO / Tributylphosphine oxide	
56	Decanoic acid	

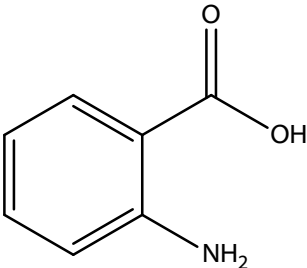
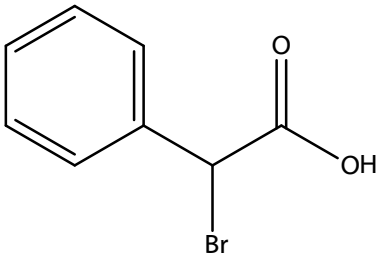
Structure Number	Trade/Chemical Name Or Abbreviation	Chemical Structure
57	Cyclohexylacetic acid	
58	3,5-Dimethylbenzoic acid	
59	Dicyclohexylacetic acid	
60	Adamantane-1-carboxylic acid	

Structure Number	Trade/Chemical Name Or Abbreviation	Chemical Structure
61	2,4-Dimethylbenzoic acid	
62	2,3-Dimethylbenzoic acid	
63	m-Toluic acid	
64	o-Toluic acid	
65	2-Ethylbutyric acid	

Structure Number	Trade/Chemical Name Or Abbreviation	Chemical Structure
66	p-Toluic acid	
67	2,2-Dimethylbutyric acid	
68	1-Naphthylacetic acid	
69	2-Naphthylacetic acid	
70	Phenylacetic acid	

Structure Number	Trade/Chemical Name Or Abbreviation	Chemical Structure
71	2-Naphthoic acid	
72	Lauric acid	
73	1-Naphthoic acid	
74	2-Chlorobenzoic acid	
75	2-Bromobenzoic acid	

Structure Number	Trade/Chemical Name Or Abbreviation	Chemical Structure
76	1-Phenyl-1-cyclohexanecarboxylic acid	
77	α -Bromo-p-toluic acid	
78	2,5-Dimethylbenzoic acid	
79	2-Iodobenzoic acid	

Structure Number	Trade/Chemical Name Or Abbreviation	Chemical Structure
80	Anthranilic acid	 <chem>Nc1ccccc1C(=O)O</chem>
81	α -Bromo-phenylacetic acid	 <chem>BrC(c1ccccc1)CC(=O)O</chem>

Appendix B: Solvent Extraction Data for (5 Ln⁺³ + Y⁺³) and (8 Ln⁺³ + Y⁺³) Systems

Data Used for Construction of (5 Ln⁺³ + Y⁺³) Extraction Curves

Extractant	Rare-Earth Concentrations in the Organic Phase (ppm)					
	La	Nd	Eu	Dy	Lu	Y
Octanoic acid	8.3	14.2	16.4	15.4	15.0	10.4
Decanoic acid	9.3	14.8	17.4	15.9	15.8	10.9
o-Toluic acid	4.0	8.5	11.8	14.1	18.4	12.8
m-Toluic acid	14.1	19.4	21.9	23.3	25.0	22.3
p-Toluic acid	10.1	17.8	21.7	23.7	25.3	23.0
2,3-Dimethylbenzoic acid	3.4	8.3	13.5	16.9	21.8	13.7
2,4-Dimethylbenzoic acid	4.0	14.1	20.1	21.9	24.1	19.7
3,5-Dimethylbenzoic acid	14.2	20.8	22.2	22.2	22.5	21.1
Cyclohexanecarboxylic acid	8.3	9.7	10.8	12.9	15.8	10.2
Cyclohexylacetic acid	8.7	12.8	14.8	14.0	15.8	9.9
Dicyclohexylacetic acid	1.9	2.9	5.4	6.6	14.0	4.2
1-Methylcyclohexanecarboxylic acid	2.3	5.5	9.2	13.2	21.5	14.9
2,2-Dimethylbutyric acid	7.6	8.8	10.2	15.4	22.6	18.0
2-Ethylbutyric acid	3.7	3.1	5.1	7.5	8.8	6.5
Adamantane-1-carboxylic acid	6.6	16.9	21.2	22.6	24.2	21.0

Data Used for Construction of (8 Ln⁺³ + Y⁺³) Extraction Curves

Extractant	Rare-Earth Concentrations in the Organic Phase (ppm)								
	La	Pr	Nd	Sm	Gd	Dy	Er	Lu	Y
Octanoic acid	7.8	14.3	16.2	19.5	18.5	18.7	17.1	16.0	12.3
Decanoic acid	6.3	11.0	12.5	15.2	14.4	14.5	13.0	12.2	9.2
Lauric acid	7.0	12.8	14.5	17.1	16.2	16.8	15.4	14.8	11.4
2-Ethylbutyric acid	6.0	6.3	6.4	8.6	9.4	14.1	15.0	15.4	11.8
2,2-Dimethylbutyric acid	2.6	3.4	3.3	5.1	6.4	15.8	20.2	23.9	19.1
o-Toluic acid	6.0	11.7	13.1	16.6	17.5	21.0	21.5	24.0	18.6
m-Toluic acid	5.4	10.3	10.5	13.3	12.2	17.1	18.1	22.9	14.4
p-Toluic acid	4.0	8.8	9.1	13.1	13.1	19.1	20.9	24.6	17.6
2,3-Dimethylbenzoic acid	4.8	13.7	16.7	21.8	20.7	22.0	19.9	18.5	15.0
2,4-Dimethylbenzoic acid	2.9	8.2	10.1	14.9	14.9	20.2	21.1	23.8	17.4
2,5-Dimethylbenzoic acid	5.0	13.3	15.1	19.4	20.1	23.4	24.3	24.9	22.1
3,5-Dimethylbenzoic acid	8.4	16.9	18.1	21.3	19.8	23.0	22.4	24.0	18.7
Phenylacetic acid	9.4	13.4	13.1	13.9	12.0	13.2	11.3	9.6	10.8
Adamantane-1-carboxylic acid	6.1	15.3	16.7	20.2	20.1	22.7	23.6	24.6	20.9
1-Naphthoic acid	5.1	11.1	12.6	16.9	16.0	20.1	19.7	21.2	13.8

Data Used for Construction of (8 Ln⁺³ + Y⁺³) Extraction Curves (continued)

Extractant	Rare-Earth Concentrations in the Organic Phase (ppm)								
	La	Pr	Nd	Sm	Gd	Dy	Er	Lu	Y
2-Naphthoic acid	7.0	12.4	12.3	13.7	11.4	11.6	9.7	9.4	10.9
1-Naphthylacetic acid	14.4	20.6	21.5	21.9	18.5	18.9	15.5	12.8	11.0
2-Naphthylacetic acid	14.4	21.7	22.7	23.2	21.6	21.8	18.4	11.8	15.6
Cyclohexanecarboxylic acid	12.0	14.1	13.8	14.7	13.9	16.9	17.7	18.7	14.0
Cyclohexylacetic acid	13.3	16.9	17.5	18.5	17.4	18.7	18.7	19.7	15.2
Dicyclohexylacetic acid	3.3	8.4	10.6	15.4	16.2	19.9	21.1	20.8	17.2
1-Methylcyclohexanecarboxylic acid	3.1	5.2	5.7	7.5	7.8	11.7	14.1	21.1	11.0
1-Phenyl-1-cyclohexanecarboxylic acid	5.0	13.4	15.7	21.2	20.7	23.7	24.0	24.8	21.7
Anthranilic acid	11.3	13.9	14.6	15.6	15.9	20.2	20.9	22.3	20.4
2-Chlorobenzoic acid	6.9	15.9	17.8	21.4	22.2	23.6	23.9	24.5	21.7
2-Bromobenzoic acid	6.0	16.3	18.5	22.3	23.0	24.2	24.5	25.1	23.0
2-Iodobenzoic acid	3.7	7.5	9.3	13.4	14.5	19.5	20.1	22.1	18.1
α-Bromo-p-toluic acid	8.7	10.0	9.8	11.0	10.9	12.4	12.5	14.6	11.5
α-Bromo-phenylacetic Acid	3.8	4.4	5.0	8.6	12.2	20.5	22.5	24.2	21.3

Vita

Dustin Courtney Collier was born in Huntington, WV on January 26, 1982. He grew up in Gate City, VA and graduated from Gate City High School in May 2000. In August 2000, he enrolled at the University of Virginia in Charlottesville, VA. He graduated with a Bachelor of Science degree in chemistry with a specialization in materials science in May 2004. He then enrolled at the University of Tennessee—Knoxville in the Department of Chemistry where he began his pursuit of a doctoral degree in inorganic chemistry in August 2004. He graduated in May 2012.