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# Lanthanide separations using rate-controlled solvent extraction

Angela Denise Brooks

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To the Graduate Council:

I am submitting herewith a thesis written by Angela Denise Brooks entitled "Lanthanide separations using rate-controlled solvent extraction." I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemistry.

George Schweitzer, Major Professor

We have read this thesis and recommend its acceptance:

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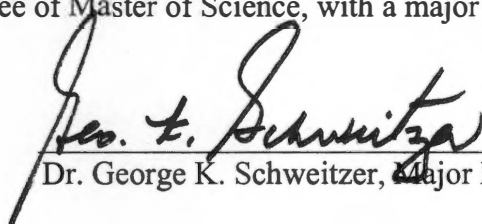
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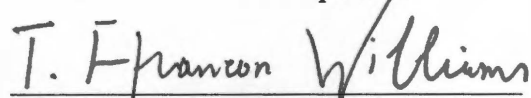
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To the Graduate Council:

I am submitting herewith a thesis written by Angela Denise Brooks entitled "Lanthanide Separations Using Rate-Controlled Solvent Extraction." I have examined the final paper copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemistry.

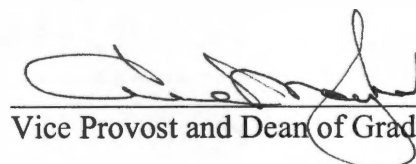
  
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We have read this thesis  
and recommend its acceptance:

  
Dr. T. Ffrancon Williams

  
Dr. John Turner

Accepted for the Council:

  
Vice Provost and Dean of Graduate Studies

**LANTHANIDE SEPARATIONS USING RATE-CONTROLLED  
SOLVENT EXTRACTION**

**A Thesis  
Presented for the  
Master of Science Degree  
The University of Tennessee, Knoxville**

**Angela Denise Brooks  
December 2003**

Thesis  
2003  
.B73

## DEDICATION

This thesis is dedicated to my parents Alice and James Brooks and to my wonderful husband Withers Morgan. They were always my biggest supporters, and I very much appreciate all of the assistance they have selflessly given in order to help me achieve my goals.

## ACKNOWLEDGEMENTS

I would like to thank all those who made this research possible. First I thank Dr. Rose Boll, whose excellent teaching gave me a real interest in chemistry as a major subject. My appreciation for my committee members Dr. George Schweitzer, Dr. Ffrancon Williams, and Dr. John Turner cannot be overstated. They are wonderful teachers and mentors, and they all make the learning experience an enjoyable one. I thank my many friends who gave seemingly endless support and encouragement. In particular I would like to thank my coworker and friend Wes Fellers for helpful discussions and for allowing me time away from the lab in order to finish the thesis. I would like to thank Rhodia for sending free samples of DEHPA that were used in the experiments. A special thanks goes to CTI Molecular Imaging for funding my degree and research. Last, but certainly not least, I thank my parents Alice and James Brooks for both monetary and emotional support and my husband Withers Morgan who did literally everything while I was so busy with school.

## ABSTRACT

In this study, certain trivalent lanthanide ions ( $\text{Nd}^{+3}$ ,  $\text{Sm}^{+3}$ ,  $\text{Eu}^{+3}$ ,  $\text{Dy}^{+3}$ ,  $\text{Tm}^{+3}$ , and  $\text{Yb}^{+3}$ ) along with  $\text{Sc}^{+3}$  and  $\text{Y}^{+3}$ , were complexed with DTPA (diethylenetriaminepentaacetic acid) and extracted into a water-immiscible kerosene layer containing DEHPA (di-2-ethylhexylphosphoric acid). Data were collected by measuring the cation content of the post-extraction aqueous phase via atomic emission. The purpose of this study was to investigate the kinetics and separation efficiencies in the extractions of binary mixtures via non-equilibrium solvent extraction and to compare these results with equilibrium results. In addition, mixture data were compared to results obtained from studies of extractions containing a single type of ion. In the single ion studies, the ions listed above were extracted in addition to  $\text{Lu}^{+3}$  and  $\text{Al}^{+3}$ .

The extraction speeds were found to decrease with decreasing cation radius, except for  $\text{Y}^{+3}$ .  $\text{Y}^{+3}$  extracted faster than expected from eight or nine coordinate size considerations. However, if the generally accepted change in coordination number from nine to eight occurs after  $\text{Sm}^{+3}$  in the lanthanide series, and if  $\text{Y}^{+3}$  is nine-coordinate in this system, then its size would fall in line with the observed kinetic series.

It was also observed that non-equilibrium extraction gives enhanced separation over equilibrium extraction in most binary mixtures. A mixing time of ten minutes seemed to give optimal separation of binary mixtures. For ions that extract at close to the same rate, a counter current non-equilibrium extraction system should require fewer stages than its equilibrium counterpart.



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# CHAPTER 1

## INTRODUCTION

### A. Background

Liquid-liquid solvent extraction is a well-established process that is frequently used to separate metal ions from one another. Solvent extraction systems can be simple or very complex, depending on the goals of the experimenter. A very simple solvent extraction method was employed to separate the metal ions in the research presented here. The following section is a brief history of solvent extraction as it relates to the procedures presented within the thesis.

For years people have used two phases in one type of metal-ion extraction system: an aqueous phase containing metal ions and a water-immiscible organic phase containing an extractant. The extractant moves metal ions from the aqueous phase into the organic phase via organic complex formation. In general, these extractions reach equilibrium within a few minutes.

The organophosphorus reagent DEHPA (di-2-ethylhexylphosphoric acid) is often chosen as an extractant, because it has been shown to be less prone to hydrolyze or to migrate into the aqueous phase than some other extractants<sup>[1]</sup>. The following is a generally accepted equation, describing the extraction of a trivalent metal cation ( $M^{+3}$ ) by the dimeric organic extractant DEHPA,  $(HR)_2$ <sup>[1-3]</sup>.

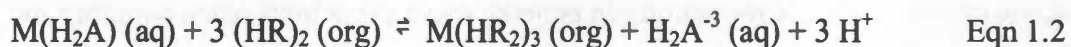


Because acid ( $H^+$ ) is liberated in the forward reaction, it is clear that the extent of the extraction depends on pH, and different metals usually extract at different pH values. Through pH control alone, metal ions can be separated from mixtures with varying degrees of efficiency. However, the separation of metal ions with identical charges and very similar sizes is usually inefficient.

Investigators began to add an aqueous complexing agent to their systems. The presence of two different complexing agents (aqueous and organic) creates a thermodynamic competition for metal ions, expressed as equilibrium constant K (see

equation 1.3). This competition often helps to increase the selectivity (separation coefficient,  $\beta$ ) as observed in many extractions. Aqueous complexing agents are sometimes referred to as “masking agents,” because they can mask certain ions from the organic complexing agent while leaving others open for more efficient extraction. In this way, the experimenter can either preferentially extract the desired ions into the organic phase or hold them in the aqueous phase and preferentially extract the impurity ions. Chelating agents are often used as masking agents in order to maximize thermodynamic stability of the aqueous complex through the additional feature of ring formation.

One aqueous chelating agent that has been used frequently to aid in separation via solvent extraction is DTPA (di-ethylenetriaminepentaacetic acid). This reagent has eight coordinating sites: three from amine nitrogens and five from acetate oxygens. Equation 1.2 represents an extraction of  $M^{+3}$ , complexed to DTPA (as  $H_2A^{-3}$ ).



Again, pH plays a crucial role in determining the extent of extraction, and most studies employ careful pH control at all times.

Experimenters noted that the addition of an aqueous complexing agent in some cases slowed the rate of extraction. This being observed, some investigators began to explore non-equilibrium extraction separations<sup>[4]</sup>. In this way, maximum selectivity might be reached by monitoring the change in separation coefficient as the reactions proceed. Non-equilibrium extraction exploits the kinetic competition between complexation with the organic extractant and complexation with the aqueous chelating agent in order to attain altered separation coefficients. In cases in which larger separation coefficients are observed, a smaller number of stages would be required for industrial counter-current extraction systems, and material and time costs would be reduced.

## B. Equations

### 1. **Equilibrium Expressions**

Equation 1.3 is the equilibrium constant expression for the system described in equation 1.2, where an overbar indicates that the species are present in the organic phase.

$$K = \left( \frac{[M(HR_2)_3]}{[M(H_2A)]} \right) \times \left( \frac{[H_2A^{-3}] \times [H^+]^3}{[(HR)_2]^3} \right) \quad \text{Eqn 1.3}$$

The first quotient in equation 1.3 is referred to as the distribution coefficient  $D$  and is very useful by expressing, via a number (unitless), the amount of metal ion ( $M^{+3}$ ) extracted versus that remaining in the aqueous phase.  $D$  can be written in terms of concentrations or extraction percentages, %E, into the organic phase.

$$D = \frac{[M(HR_2)_3]}{[M(H_2A)]} = \frac{\%E}{100 - \%E} \quad \text{Eqn 1.4}$$

In the case of binary mixtures of metal ions, the distribution coefficients from each extraction  $D_{M_1^{+3}}$  and  $D_{M_2^{+3}}$  can be divided to give another important quantity: the separation coefficient  $\beta$ , mentioned earlier in the context of selectivity.

$$\beta = \frac{D_{M_1^{+3}}}{D_{M_2^{+3}}} = \frac{\%E_{M_1^{+3}} (100 - \%E_{M_2^{+3}})}{\%E_{M_2^{+3}} (100 - \%E_{M_1^{+3}})} \quad \text{Eqn 1.5}$$

If  $\beta > 1$ , then  $M_1^{+3}$  extracts preferentially to  $M_2^{+3}$  and vice versa for  $\beta < 1$ . If  $\beta = 1$ , then no separation is achieved for the two metal ions with the chosen aqueous complexing agent and/or organic extractant.

## 2. Rate Expressions

### a. Irreversible Kinetics

If the rate of extraction was dependent solely upon the complexed aqueous metal ion concentration,  $[M(H_2A)]$ , and if the reverse reaction were too slow to be considered, then the extraction would be pseudo first order in  $[M(H_2A)]$ . The rate equation for the reaction expressed in equation 1.2 would be:

$$\frac{-d[M(H_2A)]}{dt} = k [M(H_2A)] \quad \text{Eqn 1.6.}$$

Integrating from zero to t gives equation 1.7, where  $[M(H_2A)]_o$  and  $[M(H_2A)]_t$  are the aqueous metal ion species initially and at time t, respectively.

$$\ln \left( \frac{[M(H_2A)]_o}{[M(H_2A)]_t} \right) = kt \quad \text{Eqn 1.7,}$$

Let  $a = [M(H_2A)]_o$ , and  $x = (EF)_t \times ([M(H_2A)]_o)$ , where  $EF_t$  is the extraction fraction at time t, then equation 1.7 becomes:

$$\ln \left( \frac{a}{a - x} \right) = kt \quad \text{Eqn 1.8.}$$

Equation 1.8 can be plotted with respect to time, forming a line through the origin. The slope is the rate constant k in units of  $\text{time}^{-1}$ .

#### b. Reversible Kinetics

If both forward and reverse reactions are considered (with the extraction rate dependent on the concentrations of both aqueous and organic metal ion species, but not DEHPA), the overall reaction remains pseudo first order in metal ion concentration. For this scenario, kinetic equations include the concentrations of both the aqueous and organic complexes as follows. Let  $[M(H_2A)] = [A_1]$  and  $[M(HR_2)_3] = [A_2]$ , and let  $k_f$  and  $k_r$  equal the forward and reverse rate constants, respectively. Equation 1.9 is the reversible rate equation:

$$\frac{-d[A_1]}{dt} = k_f [A_1] - k_r [A_2] \quad \text{Eqn 1.9.}$$

$$\Rightarrow \ln \left( \frac{k_f [A_1]_o}{(k_f + k_r) [A_1]_t - k_r [A_1]_o} \right) = (k_f + k_r) t \quad \text{Eqn 1.10}$$

For this research, the following substitutions were made for simplification of the rate expression:

$$[A_1]_t = [A_1]_o \times (1 - EF_t);$$

$$[A_2]_t = [A_1]_o \times EF_{eq}.$$

After algebraic manipulation, equation 1.11 was obtained and plotted, giving  $(k_f + k_r)$  the slope of the resulting line. Equation 1.12 was then used to solve for the individual forward and reverse rate constants.

$$\ln \left( \frac{EF_{eq}}{EF_{eq} - EF_t} \right) = (k_f + k_r) t \quad \text{Eqn 1.11.}$$

$$k_f [A_1]_{eq} = k_r [A_2]_{eq} \quad \text{Eqn 1.12.}$$

Rate constants obtained in the present researches are reported in chapter 3 and chapter 4, along with correlation coefficients (corr) and percentage errors ( $\epsilon$ ) associated with linear "goodness of fit"<sup>[5]</sup> Experimental data (average extraction percentages and standard deviations) are located in the Appendix. In addition to rate constants, separation coefficients and their standard deviations are presented in chapter 4.



## CHAPTER 2 APPARATUS AND TECHNIQUES

### A. Reaction Apparatus

The apparatus used for the rate studies described in this work was a custom-made, glass, cylindrical, lidded reaction vessel equipped with baffles and stopcock. (The stopcock is located on the bottom face of the cylinder.) The vessel is approximately 17 cm in height, 7.5 cm in diameter, and the baffles extend inward by approximately .5 cm. For stirring, a CPVC impeller (SX Kinetics, Inc.) and stirring motor (Arrow No. 1750) were employed, and all were attached to a stand with standard laboratory clamps (see Figure 1). Samples were removed during the solvent extractions for this research; 1 mL was drained at intervals of 5, 10, 30, 65, 100, 170, and 240 minutes during the course of each reaction. Samples were centrifuged for approximately 30 seconds in order to separate cleanly the aqueous and organic phases. The sample aqueous phase was then removed, diluted, and analyzed for metal content (see section D).



**Figure 1.** Reaction Apparatus Used For Solvent Extraction Experiments

## B. Solutions

### 1. **Aqueous Phase**

#### a. M(NO<sub>3</sub>)<sub>3</sub> Stock Solutions

All but one of the aqueous stock solutions were made by dissolving the appropriate metal oxide (Alfa, 99.9%) in concentrated nitric acid (Fisher, Certified ACS Plus) and diluting so that the solutions were 1.0 M in the appropriate metal ion. The one exception to this procedure occurred with the aluminum nitrate solution. Since Al<sub>2</sub>O<sub>3</sub> is a refractory and will not dissolve in nitric acid, the 1.0 M aluminum nitrate stock solution was made directly by dissolving solid aluminum nitrate (Merck, >99.5%) in deionized water.

#### b. DTPA Stock Solution

1.0 M DTPA (Diethylenetriaminepentaacetic acid, Aldrich, 97%) stock solution was made by dissolving 196.68 g solid DTPA in 169 mL of ammonium hydroxide (J. T. Baker, 28-30%) and diluting to 500 mL.

#### c. Feed Solutions

The aqueous solutions involved in the extractions (feed solutions) were made by taking approximately 700 mL of deionized water and adding 50 mL of the appropriate metal nitrate stock solution and 100 mL of 1.0 M DTPA solution while stirring. The pH was then brought to approximately 8 (Hydriion Papers 1-12) by adding drops of 28% NH<sub>4</sub>OH. This procedure forms solutions that are 0.050 M in metal ion and 0.10 M in DTPA and are hereafter referred to as "single-ion solutions." Binary mixtures were also 0.050 M in metal ion and were made by transferring, via repeater pipet, 25 mL each of two selected 0.050 M single-ion solutions (pH ≈ 8). In this case, each metal was present to the extent of 0.025 M, and DTPA was present at 0.10 M.

### 2. **Organic Phase**

Kerosene (Calumet) was the organic solvent used in this extraction system, and DEHPA, di-2-ethylhexylphosphoric acid (Rhodia), was the extractant. To make a 1.0 M DEHPA solution, a quantity of 83.1 mL of DEHPA was diluted to 250 mL with kerosene. The solution was then washed 3 times with 125 mL of 6 M HNO<sub>3</sub> and 3 times with 125 mL of deionized water and allowed to stand overnight.

### C. Solvent Extraction

Solvent extractions were carried out by the following procedure. First, a 100 mL quantity of the DEHPA/kerosene mixture was added to the reaction vessel. (In effort to achieve complete mixing, a stirring speed of 1420 rpm was chosen for all of the experiments.) Stirring commenced, and a 100 mL aliquot of the appropriate feed solution or solutions was added, giving a phase ratio of 1:1. A thick emulsion was formed (Figure 2) so that samples removed during the reaction contained approximately equal volumes of the aqueous and organic phases. In this way, the phase ratio in the reaction vessel remained virtually unchanged at 1:1 throughout the course of the reaction.

The pH was not adjusted during the extractions. As mentioned in section B, the feed-solution pH was set to approximately 8 before the extractions, and pH paper was used to monitor pH changes during the sampling intervals of the extraction. The pH in every case went to approximately 4 within five minutes and remained for the duration of the extraction.



**Figure 2.** Thick Emulsion Formed During Solvent Extraction

#### D. Spectroscopy

All aqueous metal ion concentrations, with the exception of aluminum(III), were determined via atomic emission spectroscopy. Aluminum(III) was analyzed via atomic absorption spectroscopy (Perkin Elmer, AAnalyst 100). Sample dilutions depended on the individual metal and its linear spectroscopic determination range, but in each case KCl (Fisher, Certified ACS) was added in order to reduce the possibility of interferences as recommended by Perkin Elmer<sup>[6]</sup>. All standards were diluted from 1000 ppm SpecPure AAS standards; each standard contained 0.1 mL of DTPA stock solution and was 1% in KCl.

## CHAPTER 3 SINGLE-ION RESULTS

Solvent extractions were performed on the trivalent cations of neodymium ( $\text{Nd}^{+3}$ ), samarium ( $\text{Sm}^{+3}$ ), europium ( $\text{Eu}^{+3}$ ), dysprosium ( $\text{Dy}^{+3}$ ), thulium ( $\text{Tm}^{+3}$ ), ytterbium ( $\text{Yb}^{+3}$ ), lutetium ( $\text{Lu}^{+3}$ ), scandium ( $\text{Sc}^{+3}$ ), aluminum ( $\text{Al}^{+3}$ ), and yttrium ( $\text{Y}^{+3}$ ). As described in chapter 1, each of these cations was complexed with DTPA and extracted into a kerosene layer containing DEHPA. The ions were extracted both from solutions containing a single cation and solutions containing binary mixtures of cations. Chapter 3 contains results from the single-ion study, and chapter 4 compares these results with those obtained from extractions of binary mixtures.

### A. Rate Constant Determination: Single-Ion Summary

Figure 3 below shows the extraction rates as observed in the single-ion study. Note that the data corresponding to what is seen in the graph are found in the Appendix. Also included are standard deviations, calculated from extraction percentages. These standard deviations come from error within the system from atomic emission, dilution into volumetric flasks, pipet tips, etc. and were propagated in all calculations.

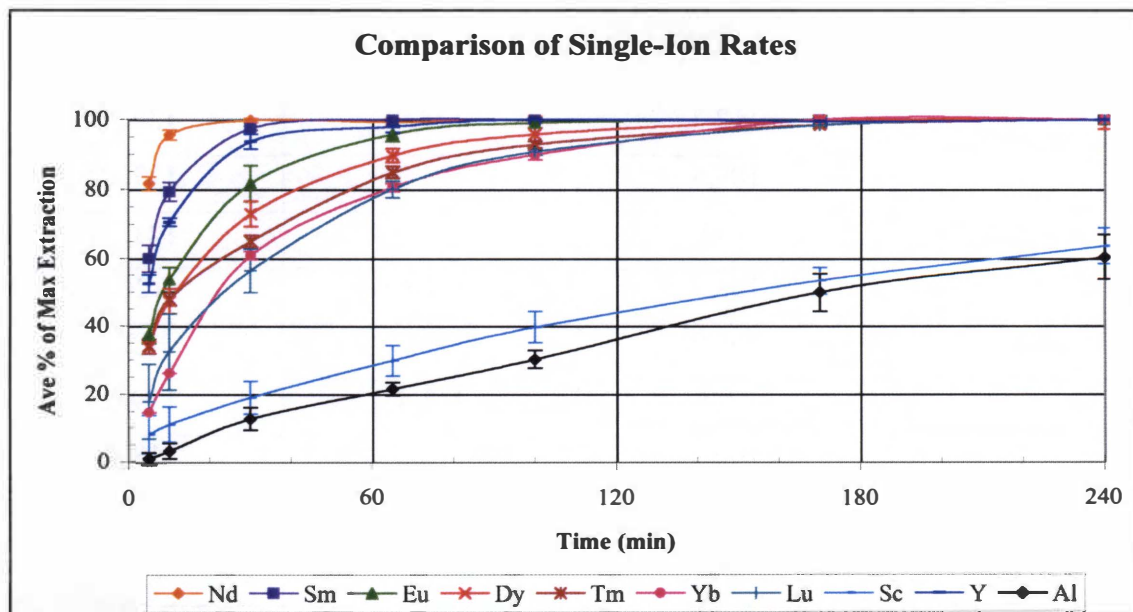


Figure 3. Comparison of Average Rates of Maximum Extraction: Single-Ion Study

Figure 3 illustrates how quickly each ion extracts relative to others and how quickly the reactions equilibrate. For the most part, the trend is with size (the smaller the ion, the slower the extraction). However the curve in Figure 3 for  $Y^{+3}$  is not in the order that one would predict for its extraction speed, if the prediction was based on ion size alone. One would expect it to fall between  $Dy^{+3}$  and  $Tm^{+3}$ , considering eight-coordinate ionic radii. Working backward from the curves to ion sizes, one would likely predict ion sizes to decrease in the following way:

$Nd^{+3} > Sm^{+3} > Y^{+3} > Eu^{+3} > Dy^{+3} > Tm^{+3} > Yb^{+3}, Lu^{+3} > Sc^{+3} > Al^{+3}$ . This is possible if  $Y^{+3}$  is 9-coordinate, and  $Eu^{+3}$  and  $Dy^{+3}$  are 8-coordinate as listed (observed series in bold) in Table 3.1. Note that these values come from reported theoretical considerations and experimental crystallographic data and so are not necessarily accurate for liquid coordination numbers.

### 1. Irreversible Kinetics

The first approximation for rate constants of the extractions represented in Figure 3 assumes extraction kinetics to be pseudo first order and irreversible in aqueous metal ion concentration,  $[M(H_2A)]$ . If true, this would mean that the reaction speed depends

**Table 3.1.** Trivalent Ion Sizes Depending On Coordination Number<sup>[7]</sup>

Ion (+3)	CN = 6	CN = 8	CN = 9
Nd	112.3	124.9	<b>130.3</b>
Sm	109.8	121.9	<b>127.2</b>
Y	104	115.9	<b>121.5</b>
Eu	108.7	<b>120.6</b>	126
Dy	105.2	<b>116.7</b>	122.3
Tm	102	<b>113.4</b>	119.2
Yb	100.8	<b>112.5</b>	118.2
Lu	100.1	<b>111.7</b>	117.2
Sc	<b>88.5</b>	101	-
Al	<b>67.5</b>	-	-

only upon aqueous metal ion concentration at time  $t$ , ( $[M(H_2A)]_t$ ). Results from this approximation vary as exemplified in Figure 4 and Figure 5 below. In general, it is the smaller ions ( $Al^{+3}$ ,  $Sc^{+3}$ ,  $Lu^{+3}$ ,  $Tm^{+3}$ , and  $Yb^{+3}$ ) that allow for relatively linear fit in the irreversible rate equation (Figure 4). The larger ions ( $Dy^{+3}$ ,  $Eu^{+3}$ ,  $Nd^{+3}$ ,  $Sm^{+3}$ , and  $Y^{+3}$ ) did not have good correlation in the irreversible regression analysis (Figure 5).

## 2. Reversible Kinetics

Because the linear fit for the larger lanthanides was so poor, rate constants were recalculated using the first order, reversible case. As discussed in chapter 1, the reversible rate equation is dependent on both species of metal ion: aqueous and organic. For smaller ions, the recalculated rate constants were very close or equal to the previously calculated ones from the irreversible case. Figure 6 shows a very good example of this with  $Lu^{+3}$ . The rate constant calculated for the extraction of  $Lu^{+3}$  under irreversible kinetics was  $0.023 \text{ min}^{-1}$ , the same as that calculated under reversible kinetic considerations.

The apparent increase in rate at  $t = 170$  minutes is a result of the fact that the

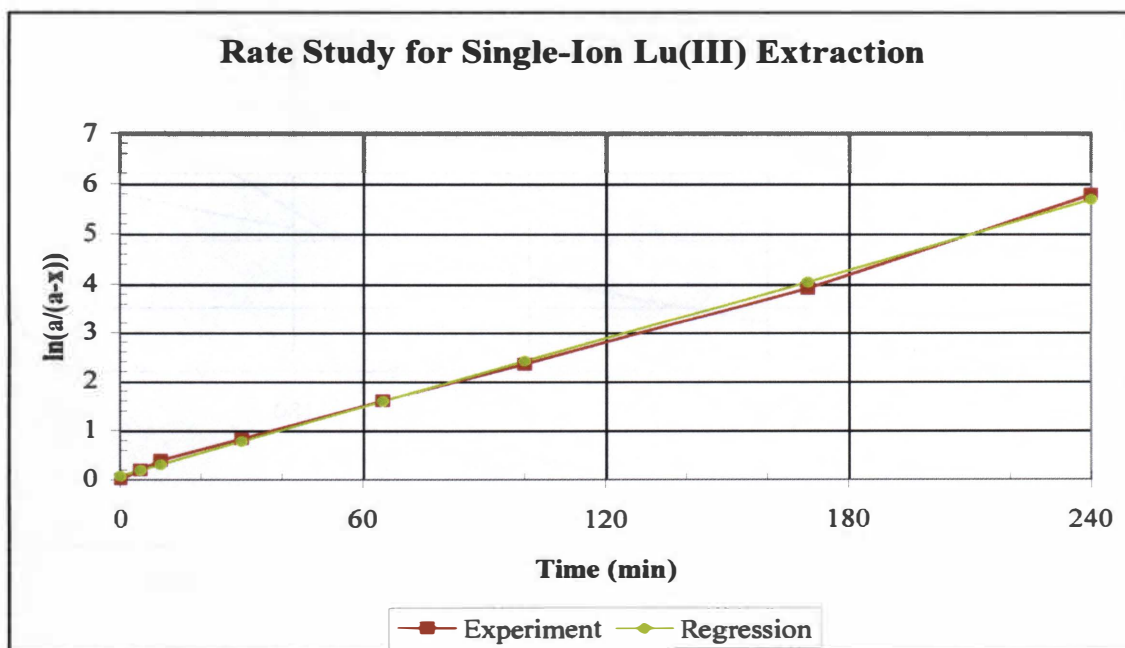


Figure 4.  $Lu^{+3}$  Extraction Rate Constant Determination: Irreversible

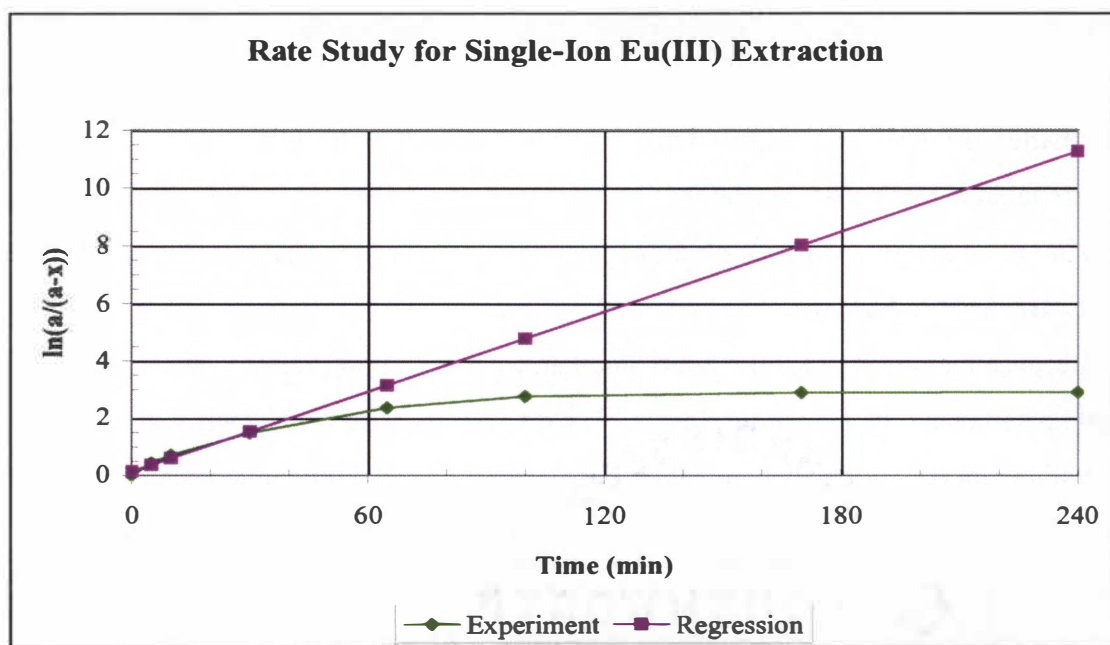


Figure 5. Rate Study For  $\text{Eu}^{+3}$  Extraction: Irreversible

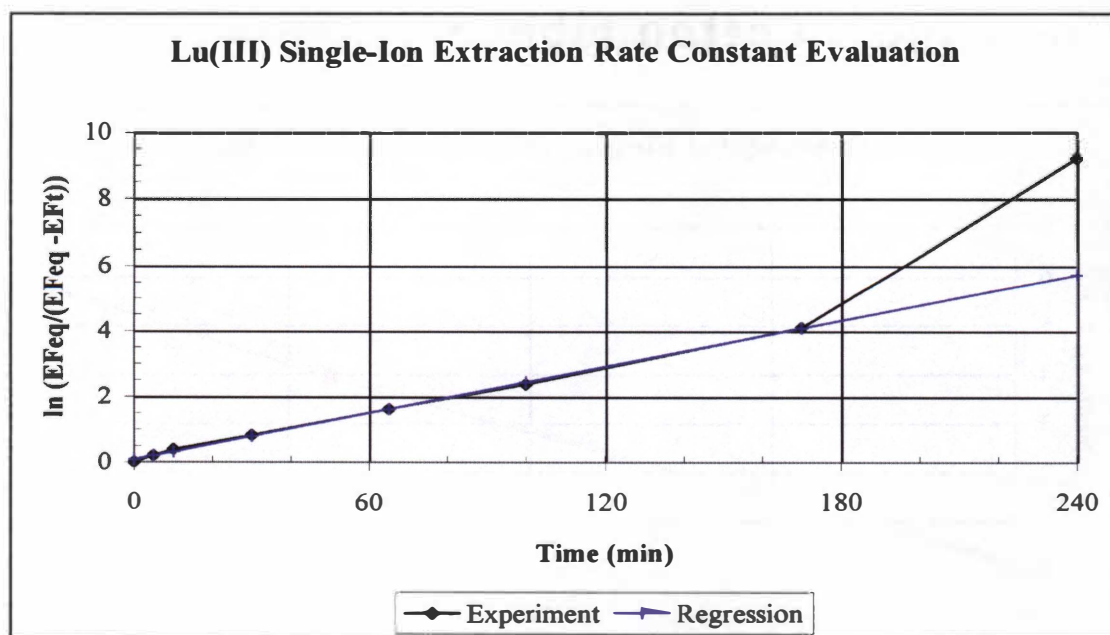


Figure 6.  $\text{Lu}^{+3}$  Extraction Rate Constant Determination: Reversible



extraction is coming to equilibrium. As this occurs, the extraction fraction at time  $t$  ( $EF_t$ ) is approaching the extraction fraction at equilibrium ( $EF_{eq}$ ), causing the denominator to become large ( $EF_t \rightarrow EF_{eq} \Rightarrow y \rightarrow \infty$ ). Another consequence is that the error on the  $t = 240$  point is also large. This eliminates  $t = 240$  as a regression data point for the reversible case, but that does not happen to increase its error relative to the error for the reversible case ( $\epsilon = 1.6\%$  in either case).

The recalculation of the rate constants for the larger lanthanides showed a much more dramatic change as exemplified by the case for  $Eu^{+3}$  (see Figure 7). In this case, the number of regression points considered increased from 4 to 8, and the rate constant approximation improved from  $0.046 \text{ min}^{-1}$  to  $0.035 \text{ min}^{-1}$ .

Using pseudo first-order, reversible kinetics, rate constants were recalculated for the single-ion extractions. These are shown in Figure 8, where slopes represent the sums of the rate constants ( $k_f + k_r$ ), and error bars represent percentage error from linearity. Note that the  $Al^{+3}$  and  $Sc^{+3}$  lines in Figure 8 lie on top of one another. This is also true for the  $Lu^{+3}$  and  $Yb^{+3}$  lines. Table 3.2 lists forward and reverse rate constants for all

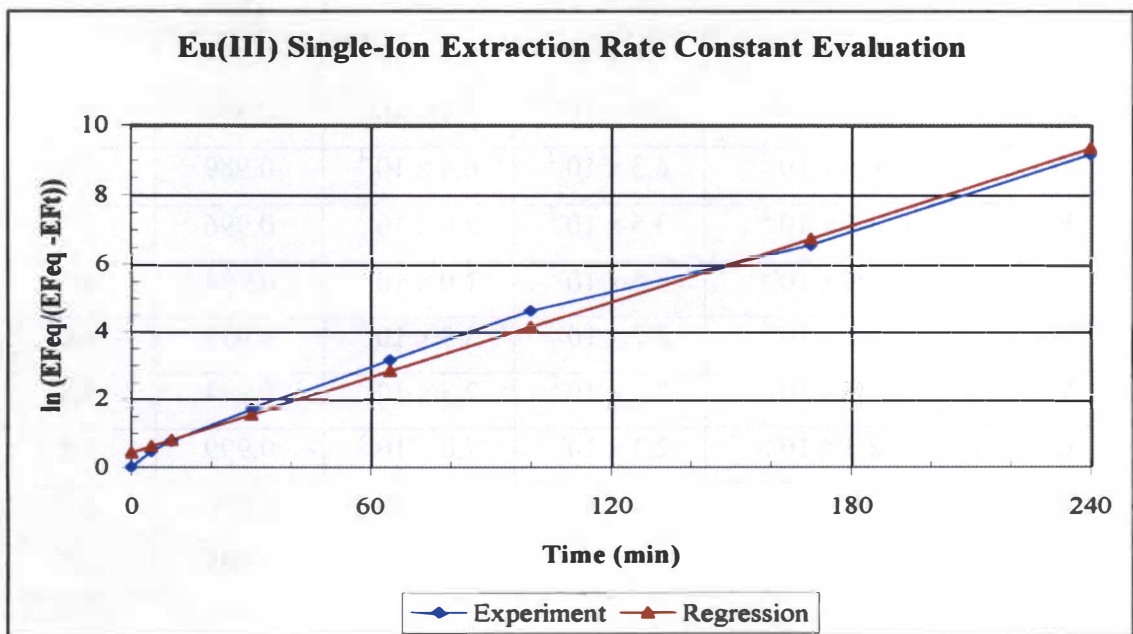


Figure 7.  $Eu^{+3}$  Extraction Rate Constant Evaluation: Reversible

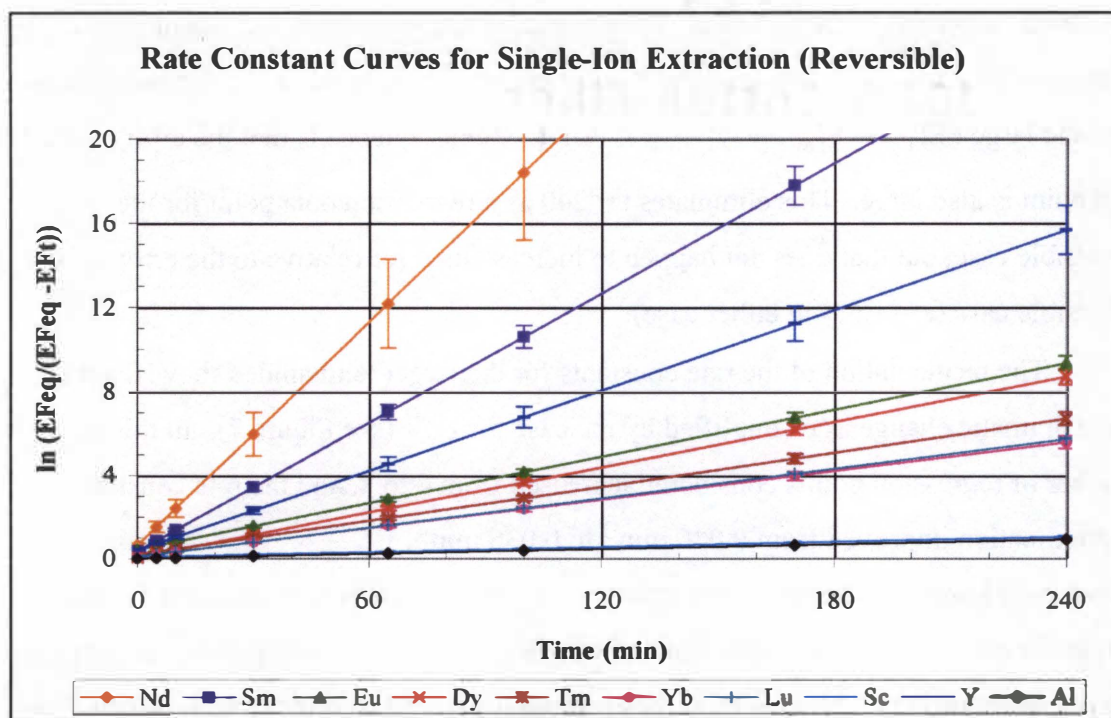


Figure 8. Summary of Single-Ion Rate Data

Table 3.2. Rate Constants For Single-Ion Extractions (Reversible, First-Order Kinetics)

Ion Extracted	$k_f + k_r$ ( $\text{min}^{-1}$ )	$k_f$ ( $\text{min}^{-1}$ )	$k_r$ ( $\text{min}^{-1}$ )	Corr.	$\epsilon$ (%)
$\text{Nd}^{+3}$	$1.8 \times 10^{-1}$	$1.6 \times 10^{-1}$	$2.1 \times 10^{-2}$	0.971	17.4
$\text{Sm}^{+3}$	$1.0 \times 10^{-1}$	$1.0 \times 10^{-1}$	$4.1 \times 10^{-3}$	0.996	5.1
$\text{Y}^{+3}$	$6.4 \times 10^{-2}$	$6.3 \times 10^{-2}$	$6.4 \times 10^{-4}$	0.989	7.4
$\text{Eu}^{+3}$	$3.7 \times 10^{-2}$	$3.5 \times 10^{-2}$	$2.0 \times 10^{-3}$	0.996	3.7
$\text{Dy}^{+3}$	$3.6 \times 10^{-2}$	$3.5 \times 10^{-2}$	$1.0 \times 10^{-3}$	0.994	4.3
$\text{Tm}^{+3}$	$2.7 \times 10^{-2}$	$2.7 \times 10^{-2}$	$3.3 \times 10^{-4}$	0.995	4.6
$\text{Yb}^{+3}$	$2.3 \times 10^{-2}$	$2.3 \times 10^{-2}$	$2.3 \times 10^{-5}$	0.994	5.4
$\text{Lu}^{+3}$	$2.3 \times 10^{-2}$	$2.3 \times 10^{-2}$	$7.0 \times 10^{-5}$	0.999	1.6
$\text{Sc}^{+3}$	$4.1 \times 10^{-3}$	$4.0 \times 10^{-3}$	$8.2 \times 10^{-5}$	0.996	3.7
$\text{Al}^{+3}$	$3.9 \times 10^{-3}$	$3.8 \times 10^{-3}$	$7.4 \times 10^{-5}$	0.999	2.2

single-ion extractions performed, along with correlation coefficients and error percentage data ( $\epsilon$ ) corresponding to calculation of the regression lines and their “goodness of fit”<sup>[5]</sup>. This error takes into account the number of regression data points (N) as well as the correlation coefficient r (see equation 3.1). Smaller N leads to larger  $\epsilon$  for the same correlation coefficient.

$$\epsilon = \frac{1}{r} \sqrt{\frac{1 - r^2}{N - 2}} \quad \text{Eqn 3.1}$$

### B. Scandium and Aluminum Results

It is evident from the previous section (see Figure 3) that extractions involving either  $\text{Sc}^{+3}$  or  $\text{Al}^{+3}$  do not come to equilibrium within four hours as the others do. In order to determine the extraction percentages for these two cases, their extraction times were extended. The results are shown in Figure 9 below. For aluminum(III), the equilibrium extraction percentage is close to 98%, and for scandium(III), it is around 99%.

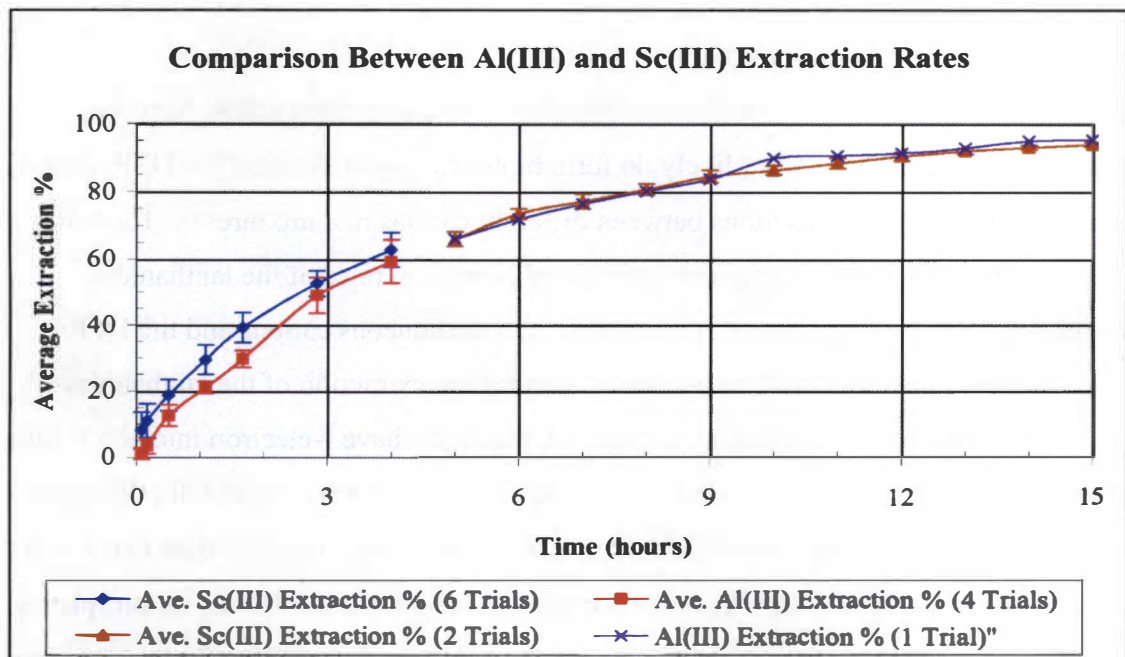


Figure 9. Comparison Between  $\text{Al}^{+3}$  and  $\text{Sc}^{+3}$  Extraction Rates

$$\left[\overline{\text{Al}^{+3}}\right]_{\text{eq}} = 0.98 \left[\text{Al}^{+3}\right]_0 \Rightarrow \left[\text{Al}^{+3}\right]_{\text{eq}} = 0.02 \left[\text{Al}^{+3}\right]_0 \quad \text{Eqn 3.2}$$

$$\left[\overline{\text{Sc}^{+3}}\right]_{\text{eq}} = 0.99 \left[\text{Sc}^{+3}\right]_0 \Rightarrow \left[\text{Sc}^{+3}\right]_{\text{eq}} = 0.01 \left[\text{Sc}^{+3}\right]_0 \quad \text{Eqn 3.3}$$

$\text{Al}^{+3}$  was studied as a comparison for the astonishingly slow rate observed with  $\text{Sc}^{+3}$ . These two ions are very small and have coordination numbers of six;  $\text{Y}^{+3}$  and the lanthanides are generally believed to have coordination numbers of eight and/or nine.

It has been shown that  $\text{Cu}^{+2}$  forms binuclear complexes with DTPA<sup>[8]</sup>. It has been alleged that it is the uncomplexed trivalent cation that is extracted by DEHPA into the organic phase in an “ $\text{S}_{\text{N}}1$ ” mechanism<sup>[2, 3, 9]</sup>. If these considerations are applicable to  $\text{Al}^{+3}$  and  $\text{Sc}^{+3}$ , then binuclear complex formation may account for the slow extraction rates observed with these ions compared with the other ions studied. If binuclear complexes of  $\text{Sc}^{+3}$  and  $\text{Al}^{+3}$  are formed, then there should be fewer free ions in the aqueous phase, relative to solutions in which binuclear complexes are not formed. If the species that extract are indeed the uncomplexed trivalent cations, a decrease in aqueous metal ion concentration ( $[\text{M}^{+3}]$ ) would result in a decrease in organic metal concentration ( $[\overline{\text{M}(\text{HR}_2)_3}]$ ) and therefore a decrease in  $\text{EF}_t$ . Smaller values of  $\text{EF}_t$  imply a lower rate of extraction as seen in equation 1.11.

It is believed that the lanthanides themselves do not to form stable binuclear complexes with DTPA<sup>[8, 10]</sup>, but likely do form binuclear intermediates ( $[\text{M}_1\text{DTPAM}_2]^+$ ) in the aqueous exchange reactions between different cations in a mixture<sup>[11]</sup>. Therefore, binuclear formation should not greatly affect the extraction rates of the lanthanides. Incidentally, it is the dissociation reaction between the aqueous cations and the DTPA anions that is thought to be the rate-limiting step for the extraction of the lanthanides<sup>[12]</sup>.

An additional consideration is that the lanthanides have f-electron interactions that  $\text{Al}^{+3}$ ,  $\text{Sc}^{+3}$ , and  $\text{Y}^{+3}$  do not. The bonding between the latter cations, especially the smaller (harder)  $\text{Al}^{+3}$  and  $\text{Sc}^{+3}$  ions, with DTPA is probably more ionic in nature than that for the lanthanides.  $\text{Al}^{+3}$  and  $\text{Sc}^{+3}$  also have the potential to have considerable solvation spheres, and that may mean that water exchange is an important rate-determining interaction.

However, whether or not these considerations have any effect on extraction rates is not answered by the research presented here.

### C. Variation in Extraction Rates

It was discovered that the rate of  $\text{Sc}^{+3}$  extraction appears to depend on whether or not the  $\text{Sc}(\text{H}_2\text{A})$  feed solution is freshly prepared. The extraction rate slowed dramatically for two trials in which the feed solution had been prepared immediately preceding the extraction (“fresh”) as seen in Figure 10. The forward rate constants observed are:  $4.0 \times 10^{-3} \text{ min}^{-1}$  for the older solution and  $1.7 \times 10^{-3} \text{ min}^{-1}$  for the fresh solution. (The “older” solutions were weeks or months old.)

Most of the other ions were not specifically tested for this behavior, however a test was performed on solutions of  $\text{Al}^{+3}$ ,  $\text{Lu}^{+3}$ , and  $\text{Yb}^{+3}$ , as they are the smallest ions studied and most “resemble”  $\text{Sc}^{+3}$  in extraction rate. Since  $\text{Al}^{+3}$  and  $\text{Sc}^{+3}$  extract at very close to the same rate with older solutions ( $3.8 \times 10^{-5} \text{ min}^{-1}$  and  $4.0 \times 10^{-5} \text{ min}^{-1}$  respectively), it would seem that  $\text{Al}^{+3}$  might also show a slowing of extraction rate with a fresh solution as  $\text{Sc}^{+3}$  does. Two trials of fresh  $\text{Al}^{+3}$  solutions were extracted, and results are in Figure 11 below. No rate difference was observed.

For  $\text{Lu}^{+3}$  and  $\text{Yb}^{+3}$ , single-ion rates were compared for fresh and older feed solutions by comparing the average of three trials on older solutions to a fresh extraction of only one trial on each metal ion. Figure 12 shows this comparison.  $\text{Yb}^{+3}$  appears to extract more quickly in a freshly prepared solution with a rate increase of  $0.023 \text{ min}^{-1}$  to  $0.034 \text{ min}^{-1}$ . Although it appears that there is no significant rate difference between the two  $\text{Lu}^{+3}$  solutions, the error bars on the first few data points are too large to allow for accurate determination of any possible rate differences. A “fresh vs older” experiment was performed on the  $\text{Lu}^{+3}/\text{Yb}^{+3}$  mixture system; see chapter 4 for these results.

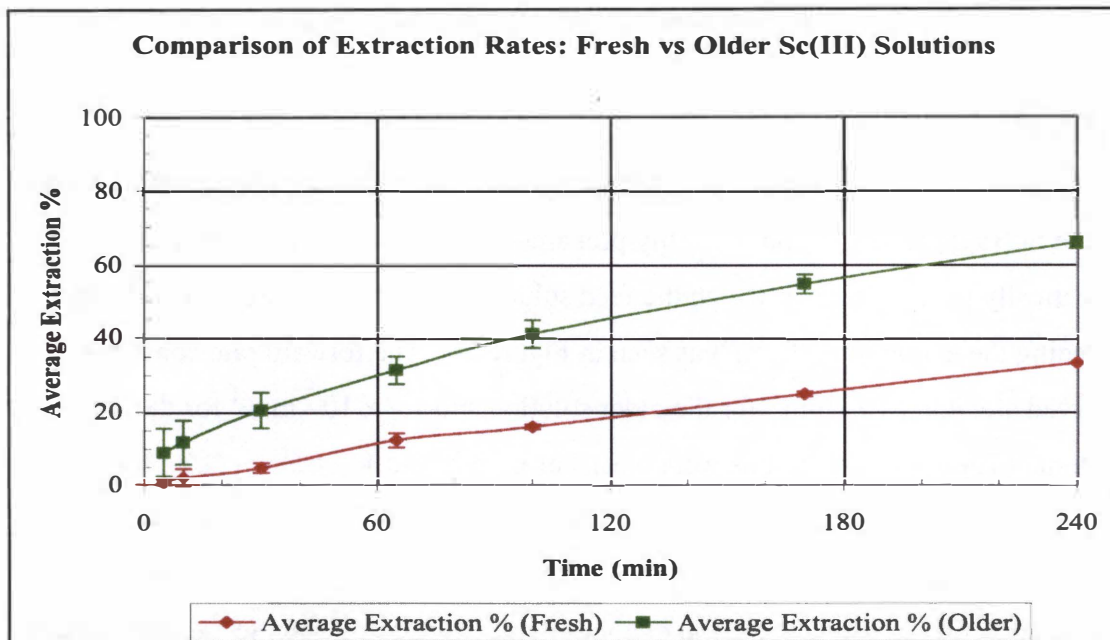


Figure 10. Comparison in Extraction Rates: Fresh vs Older Sc<sup>+3</sup> Feed Solutions

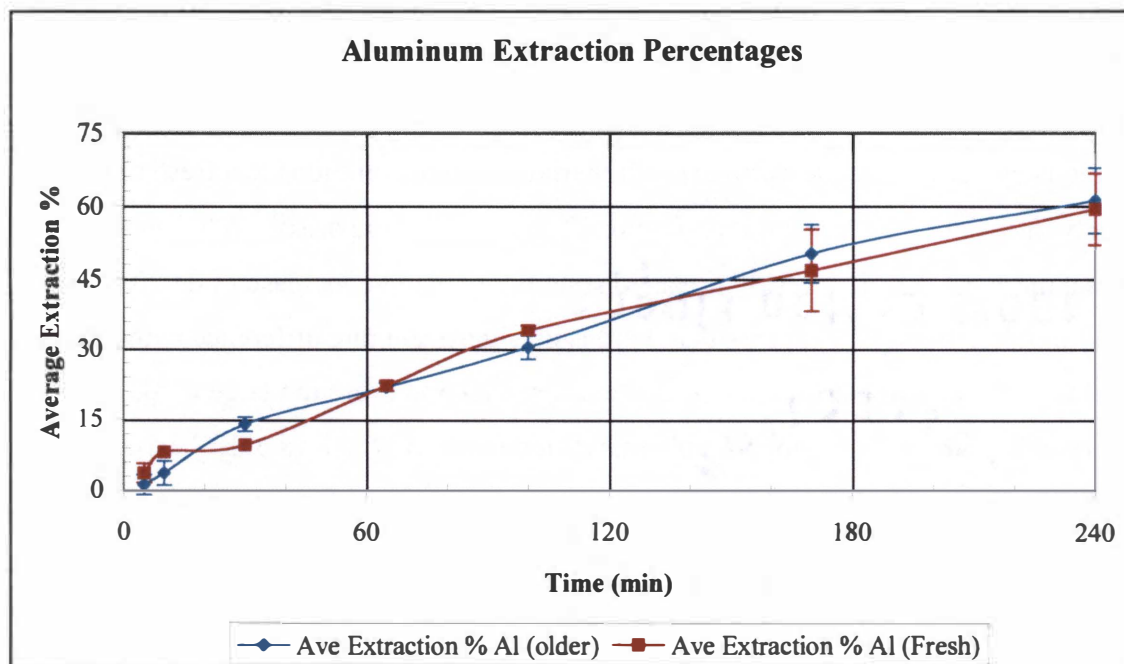
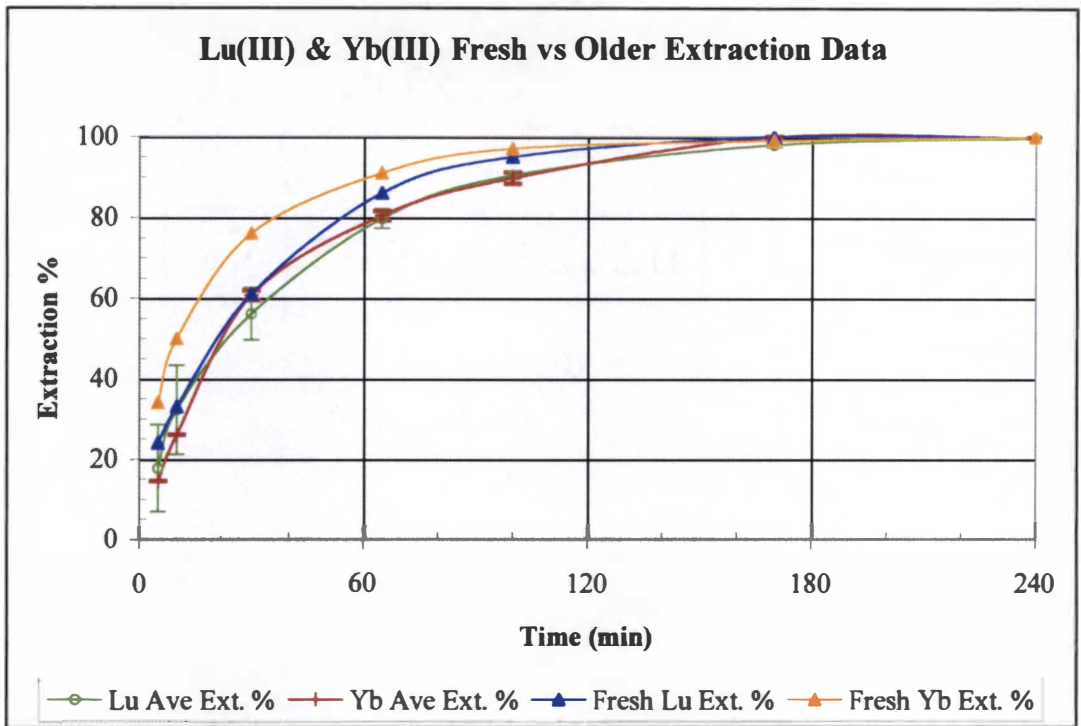


Figure 11. Comparison in Extraction Rates: Fresh vs Older Al<sup>+3</sup> Feed Solutions



**Figure 12.** Lu<sup>+3</sup> and Yb<sup>+3</sup> Single-Ion Study: Fresh vs Older Feed Solutions

## CHAPTER 4 MIXTURE RESULTS

Extractions were performed on binary mixtures of the following ions, each with one another:  $\text{Sc}^{+3}$ ,  $\text{Y}^{+3}$ ,  $\text{Nd}^{+3}$ ,  $\text{Sm}^{+3}$ ,  $\text{Eu}^{+3}$ ,  $\text{Dy}^{+3}$ ,  $\text{Tm}^{+3}$  and  $\text{Yb}^{+3}$ . In the following sections, mixture results will be given. Section A discusses the ion of least atomic number ( $\text{Sc}^{+3}$ ) and its mixtures with ions of larger atomic number. Section B discusses the ion of next larger atomic number ( $\text{Y}^{+3}$ ) and its mixtures with ions of yet larger atomic number. In this way mixture data are not repeated unnecessarily throughout the chapter. Recall that all experimental data are located in the Appendix.

### A. Mixtures of $\text{Sc}^{+3}$

Figure 13 shows the variation in extraction rates of  $\text{Sc}^{+3}$  when mixed with the trivalent ions listed in the legend. Error bars represent the standard deviations observed from atomic emission analysis of aqueous metal ion concentration for each data point at time  $t$ . Extractions were repeated 3 or 4 times, depending on the precision of the results.

Under the experimental conditions, the extraction of  $\text{Sc}^{+3}$  takes approximately 30

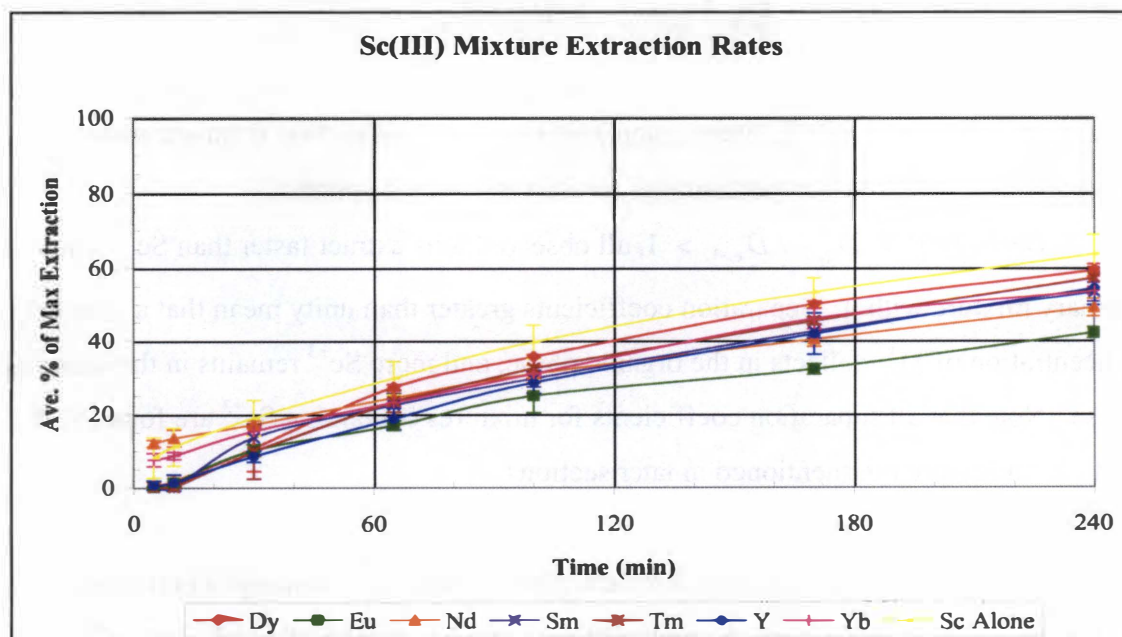


Figure 13. Average Percentages of Maximum Extraction:  $\text{Sc}^{+3}$  and Its Mixtures



hours to reach equilibrium, and so  $[\text{Sc}^{+3}]_{\text{eq}}$  was directly measured in only two experiments. The first was in its single-ion study and the other was in its mixture with  $\text{Sm}^{+3}$ . In both cases  $\text{Sc}^{+3}$  was found to extract to the extent of 99%. This value was used as an estimate in the remaining mixtures where  $[\text{Sc}^{+3}]_{\text{eq}}$  was needed to calculate  $k_r$ , as discussed in chapter 1. Forward and reverse rate constants are given in Table 4.1 along with correlation constants and error percentages.

Inherent in the mathematics behind extraction percentage (%E) are the following truths: as  $\%E \rightarrow 0$ ,  $D_{M^{+3}} \rightarrow 0$ , and as  $\%E \rightarrow 100$ ,  $D_{M^{+3}} \rightarrow \infty$  (see equation 1.4). The separation coefficients calculated for  $\text{Sc}^{+3}$  mixtures ( $\beta = D_{M^{+3}}/D_{\text{Sc}^{+3}}$ ) are found in Table 4.2. For  $t \geq 30$  min, some separation coefficients are very large because  $\%E_{M^{+3}} \rightarrow 100$ . Similarly, because  $D_{\text{Sc}^{+3}}$  values are small compared with  $D_{M^{+3}}$  values, some separation coefficients are very large for  $t = 5$  and 10 minutes (see equation 1.5).

As shown in Table 4.3, small  $D_{\text{Sc}^{+3}}$  values can also cause standard deviations on separation coefficients to be very large (see equation 4.1).

$$SD_{\beta} = (D_{M^{+3}}/D_{\text{Sc}^{+3}}) \times \sqrt{\left(\frac{SD_{D_{M^{+3}}}}{D_{M^{+3}}}\right)^2 + \left(\frac{SD_{D_{\text{Sc}^{+3}}}}{D_{\text{Sc}^{+3}}}\right)^2} \quad \text{Eqn 4.1}$$

Values presented in Table 4.3 were calculated via error propagation from standard deviations on the extraction percentages (presented in the Appendix).

Because  $\beta = D_{M^{+3}} / D_{\text{Sc}^{+3}} > 1$ , all observed ions extract faster than  $\text{Sc}^{+3}$  when in a binary mixture with it. Separation coefficients greater than unity mean that a greater concentration of  $M^{+3}$  collects in the organic phase, and more  $\text{Sc}^{+3}$  remains in the aqueous phase. Note that all separation coefficients for mixtures containing  $\text{Sc}^{+3}$  are found in this section, and so are not mentioned in later sections.

## B. Mixtures of $\text{Y}^{+3}$

The ion with second lowest atomic number in this study belongs to yttrium(III). Although like  $\text{Sc}^{+3}$ , it has a much smaller atomic number than the f-block ions,  $\text{Y}^{+3}$  extracts faster on average than almost all ions studied, except  $\text{Nd}^{+3}$  and  $\text{Sm}^{+3}$ . Figure 14

**Table 4.1. Rate Data For Sc<sup>+3</sup> Extractions In Various Mixtures.**

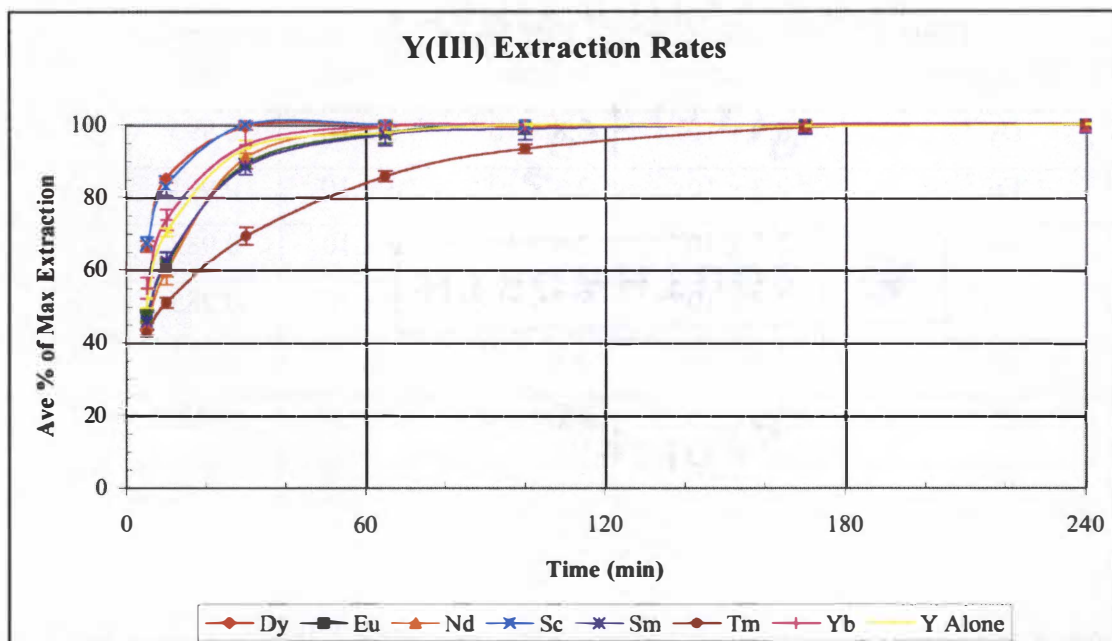
Ion Mixed with Sc <sup>+3</sup>	k <sub>f</sub> + k <sub>r</sub> (min <sup>-1</sup> )	k <sub>f</sub> (min <sup>-1</sup> )	k <sub>r</sub> (min <sup>-1</sup> )	Corr.	ε (%)
Dy <sup>+3</sup>	3.9 x 10 <sup>-3</sup>	3.8 x 10 <sup>-3</sup>	3.8 x 10 <sup>-5</sup>	0.995	4.3
Eu <sup>+3</sup>	2.3 x 10 <sup>-3</sup>	2.3 x 10 <sup>-3</sup>	2.3 x 10 <sup>-5</sup>	0.991	5.4
Nd <sup>+3</sup>	2.5 x 10 <sup>-3</sup>	2.5 x 10 <sup>-3</sup>	2.5 x 10 <sup>-5</sup>	0.982	7.8
Sm <sup>+3</sup>	3.8 x 10 <sup>-3</sup>	3.7 x 10 <sup>-3</sup>	3.8 x 10 <sup>-5</sup>	0.985	8.7
Tm <sup>+3</sup>	3.6 x 10 <sup>-3</sup>	3.6 x 10 <sup>-3</sup>	3.6 x 10 <sup>-5</sup>	0.997	3.0
Y <sup>+3</sup>	3.3 x 10 <sup>-3</sup>	3.3 x 10 <sup>-3</sup>	3.3 x 10 <sup>-5</sup>	1.000	1.2
Yb <sup>+3</sup>	3.1 x 10 <sup>-3</sup>	3.1 x 10 <sup>-3</sup>	3.1 x 10 <sup>-5</sup>	0.995	4.2

**Table 4.2. Separation Coefficients Involving Mixtures of Sc<sup>+3</sup>, Where β = D<sub>M<sup>+3</sup></sub> / D<sub>Sc<sup>+3</sup></sub>**

Time (min)	D <sub>Dy</sub> /D <sub>Sc</sub>	D <sub>Eu</sub> /D <sub>Sc</sub>	D <sub>Nd</sub> /D <sub>Sc</sub>	D <sub>Sm</sub> /D <sub>Sc</sub>	D <sub>Tm</sub> /D <sub>Sc</sub>	D <sub>Y</sub> /D <sub>Sc</sub>	D <sub>Yb</sub> /D <sub>Sc</sub>
5	9 x 10 <sup>1</sup>	~6 x 10 <sup>2</sup>	~2 x 10 <sup>2</sup>	~3 x 10 <sup>3</sup>	~4 x 10 <sup>2</sup>	1 x 10 <sup>1</sup>	5.4
10	7.5 x 10 <sup>1</sup>	9.6 x 10 <sup>1</sup>	3.2 x 10 <sup>1</sup>	~9 x 10 <sup>3</sup>	3 x 10 <sup>1</sup>	3.8 x 10 <sup>1</sup>	9.7
30	4.6 x 10 <sup>1</sup>	5.9 x 10 <sup>1</sup>	3.5 x 10 <sup>1</sup>	1.0 x 10 <sup>1</sup>	2.7	~10 <sup>5</sup>	2.3 x 10 <sup>1</sup>
65	7.0 x 10 <sup>1</sup>	~1 x 10 <sup>2</sup>	4.0 x 10 <sup>1</sup>	8.4	6.4 x 10 <sup>1</sup>	~10 <sup>5</sup>	6.5 x 10 <sup>1</sup>
100	~2 x 10 <sup>2</sup>	8.0 x 10 <sup>1</sup>	6.2	2.8 x 10 <sup>1</sup>	~2 x 10 <sup>2</sup>	~10 <sup>5</sup>	~2 x 10 <sup>2</sup>
170	~1 x 10 <sup>2</sup>	5.5 x 10 <sup>1</sup>	1.4 x 10 <sup>1</sup>	2.9 x 10 <sup>1</sup>	~10 <sup>4</sup>	~10 <sup>5</sup>	~4 x 10 <sup>2</sup>
240	~2 x 10 <sup>2</sup>	3.1 x 10 <sup>1</sup>	1.3 x 10 <sup>1</sup>	2.2 x 10 <sup>1</sup>	~10 <sup>4</sup>	~10 <sup>5</sup>	~1 x 10 <sup>3</sup>

**Table 4.3. Standard Deviations On Separation Coefficients of Scandium(III) Mixtures**

Time (min)	D <sub>Dy</sub> /D <sub>Sc</sub>	D <sub>Eu</sub> /D <sub>Sc</sub>	D <sub>Nd</sub> /D <sub>Sc</sub>	D <sub>Sm</sub> /D <sub>Sc</sub>	D <sub>Tm</sub> /D <sub>Sc</sub>	D <sub>Y</sub> /D <sub>Sc</sub>	D <sub>Yb</sub> /D <sub>Sc</sub>
5	~1 x 10 <sup>2</sup>	~1 x 10 <sup>3</sup>	5 x 10 <sup>1</sup>	~2 x 10 <sup>3</sup>	~4 x 10 <sup>2</sup>	2 x 10 <sup>1</sup>	1.3
10	7.6 x 10 <sup>1</sup>	~1 x 10 <sup>2</sup>	6	~6 x 10 <sup>3</sup>	5 x 10 <sup>1</sup>	5.8 x 10 <sup>1</sup>	1.3
30	2.7 x 10 <sup>1</sup>	9	2	3	2.0	~10 <sup>5</sup>	2
65	1.5 x 10 <sup>1</sup>	9	3	1.2	1.5 x 10 <sup>1</sup>	~10 <sup>5</sup>	5
100	7 x 10 <sup>1</sup>	1.7 x 10 <sup>1</sup>	0.5	3	5 x 10 <sup>1</sup>	~10 <sup>5</sup>	1 x 10 <sup>1</sup>
170	7 x 10 <sup>1</sup>	8	1	3	~10 <sup>4</sup>	~10 <sup>5</sup>	~1 x 10 <sup>2</sup>
240	~3 x 10 <sup>2</sup>	2	1	3	~10 <sup>5</sup>	~10 <sup>5</sup>	~1 x 10 <sup>3</sup>



**Figure 14.** Average Percentages of Maximum Extraction: Y<sup>+3</sup> and Its Mixtures

shows the extraction rates for Y<sup>+3</sup> in its mixtures. The rates exceed those seen with Sc<sup>+3</sup> mixtures by 10 to nearly 100 times. Forward and reverse rate constants are given in Table 4.4 below.

Tables 4.5 and 4.6 list separation coefficients and their standard deviations for mixtures of Y<sup>+3</sup>, except for those containing Sc<sup>+3</sup> (shown in the previous section). As is the case for mixtures containing Sc<sup>+3</sup>, some separation coefficients and standard deviations for Y<sup>+3</sup> mixtures are large. Fewer of these exist for Y<sup>+3</sup> and the other metal ions studied. One reason for this is that they do not have near-zero extraction percentages at some of the  $t \leq 10$  minute data points, as Sc<sup>+3</sup> mixtures do. In addition, when both metal ions approach 100% extraction,  $\beta \rightarrow 1$ , but if only one metal approaches 100% extraction, the  $\beta$  values and their standard deviations approach infinity. The latter is typically the case for faster-extracting ions mixed with Sc<sup>+3</sup> (including Y<sup>+3</sup>) and for Y<sup>+3</sup> when mixed with slower-extracting ions.

### C. Mixtures of Nd<sup>+3</sup>

Continuing to move to ions with increasing atomic number, the next ion studied was Nd<sup>+3</sup>. Below is the chart containing the average percentage of maximum extraction

**Table 4.4. Rate Data For Mixtures Containing Y<sup>+3</sup>**

Ion Mixed with Y <sup>+3</sup>	k <sub>f</sub> + k <sub>r</sub> (min <sup>-1</sup> )	k <sub>f</sub> (min <sup>-1</sup> )	k <sub>r</sub> (min <sup>-1</sup> )	Corr.	ε (%)
Dy <sup>+3</sup>	1.4 x 10 <sup>-1</sup>	1.4 x 10 <sup>-1</sup>	1.4 x 10 <sup>-4</sup>	0.993	6.7
Eu <sup>+3</sup>	5.9 x 10 <sup>-2</sup>	5.8 x 10 <sup>-2</sup>	5.9 x 10 <sup>-4</sup>	0.996	4.4
Nd <sup>+3</sup>	7.3 x 10 <sup>-2</sup>	7.2 x 10 <sup>-2</sup>	2.9 x 10 <sup>-4</sup>	0.999	2.9
Sc <sup>+3</sup>	3.2 x 10 <sup>-1</sup>	3.1 x 10 <sup>-1</sup>	3.2 x 10 <sup>-4</sup>	0.990	10.1
Sm <sup>+3</sup>	5.0 x 10 <sup>-2</sup>	4.9 x 10 <sup>-2</sup>	7.0 x 10 <sup>-4</sup>	0.990	6.4
Tm <sup>+3</sup>	2.6 x 10 <sup>-2</sup>	2.6 x 10 <sup>-2</sup>	2.6 x 10 <sup>-5</sup>	0.995	4.7
Yb <sup>+3</sup>	8.9 x 10 <sup>-2</sup>	8.8 x 10 <sup>-2</sup>	7.1 x 10 <sup>-4</sup>	0.999	2.6

**Table 4.5. Separation Coefficients For Y<sup>+3</sup> Mixtures:  $\beta = D_{Y^{+3}} / D_{M^{+3}}$ ; M ≠ Nd<sup>+3</sup>**

Time (min)	D <sub>Y</sub> /D <sub>Dy</sub>	D <sub>Y</sub> /D <sub>Eu</sub>	D <sub>Nd</sub> /D <sub>Y</sub>	D <sub>Y</sub> /D <sub>Sm</sub>	D <sub>Y</sub> /D <sub>Tm</sub>	D <sub>Y</sub> /D <sub>Yb</sub>
5	4.6	1.8	5.9	1.3	2.9	4.8
10	9.2	2.3	5.7	1.3	2.4	6.2
30	~9 x 10 <sup>2</sup>	7.0	0.8	1.5	1.8	9.7
65	~1 x 10 <sup>3</sup>	1.9 x 10 <sup>1</sup>	0.1	2.5	1.6	2.1 x 10 <sup>1</sup>
100	~1 x 10 <sup>3</sup>	6.1 x 10 <sup>1</sup>	0.1	3.7	1.7	1.4 x 10 <sup>1</sup>
170	3.9	5.2 x 10 <sup>1</sup>	0.0	6.5	3.0	2.7
240	2.8	9.0 x 10 <sup>1</sup>	0.0	6.8	3.8	0.5

**Table 4.6. Standard Deviations On Separation Coefficients of Yttrium(III) Mixtures**

Time (min)	D <sub>Y</sub> /D <sub>Dy</sub>	D <sub>Y</sub> /D <sub>Eu</sub>	D <sub>Nd</sub> /D <sub>Y</sub>	D <sub>Y</sub> /D <sub>Sm</sub>	D <sub>Y</sub> /D <sub>Tm</sub>	D <sub>Y</sub> /D <sub>Yb</sub>
5	0.4	0.1	0.2	0.3	0.1	0.7
10	0.8	0.3	0.6	0.1	0.2	0.9
30	~1 x 10 <sup>3</sup>	1.7	0.1	0.2	0.3	1.0 x 10 <sup>1</sup>
65	~2 x 10 <sup>3</sup>	1.4 x 10 <sup>1</sup>	0.1	1.4	0.2	2.8 x 10 <sup>1</sup>
100	~8 x 10 <sup>2</sup>	8.8 x 10 <sup>1</sup>	0.1	3.2	0.4	2.4 x 10 <sup>1</sup>
170	7.6	9.1 x 10 <sup>1</sup>	0.1	8.7	2.6	4.0
240	5.2	~2 x 10 <sup>2</sup>	0.0	7.0	6.8	0.7

curves for  $\text{Nd}^{+3}$  when alone and when mixed with the other trivalent cations listed in the chart's legend (see Figure 15). Clearly  $\text{Nd}^{+3}$  extracts fastest when compared with  $\text{Sc}^{+3}$  and  $\text{Y}^{+3}$ , and it turns out that it is the fastest-extracting ion of all ions included in this study, coming to equilibrium within a few minutes. It is notable that  $\text{Nd}^{+3}$  is also the largest metal ion in this study.

Table 4.7 lists rate constants for  $\text{Nd}^{+3}$  extraction in the presence of other ions. Striking are two aspects of Table 4.7: first are the speeds of both the forward and reverse reactions compared with the other ions, and second are the enormous error percentages  $\epsilon$  (see equation 3.1). Because the  $\text{Nd}^{+3}$  extraction reaches equilibrium so quickly, fewer data points can be considered in regression, increasing the size of  $\epsilon$ . For  $\text{Nd}^{+3}$ , the maximum number of data points available for regression is generally three ( $N = 3$ ), including the origin ( $EF_0 = 0 \Rightarrow y = 0$ ).

For many measurements involving the larger ions ( $\text{Nd}^{+3}$ ,  $\text{Sm}^{+3}$ , and  $\text{Y}^{+3}$ ), the concentrations of ions extracted at equilibrium are slightly less than the maximum attained in the system ( $EF_{\text{eq}} < EF_{\text{max}}$ ). In these cases, the maximum value was used in

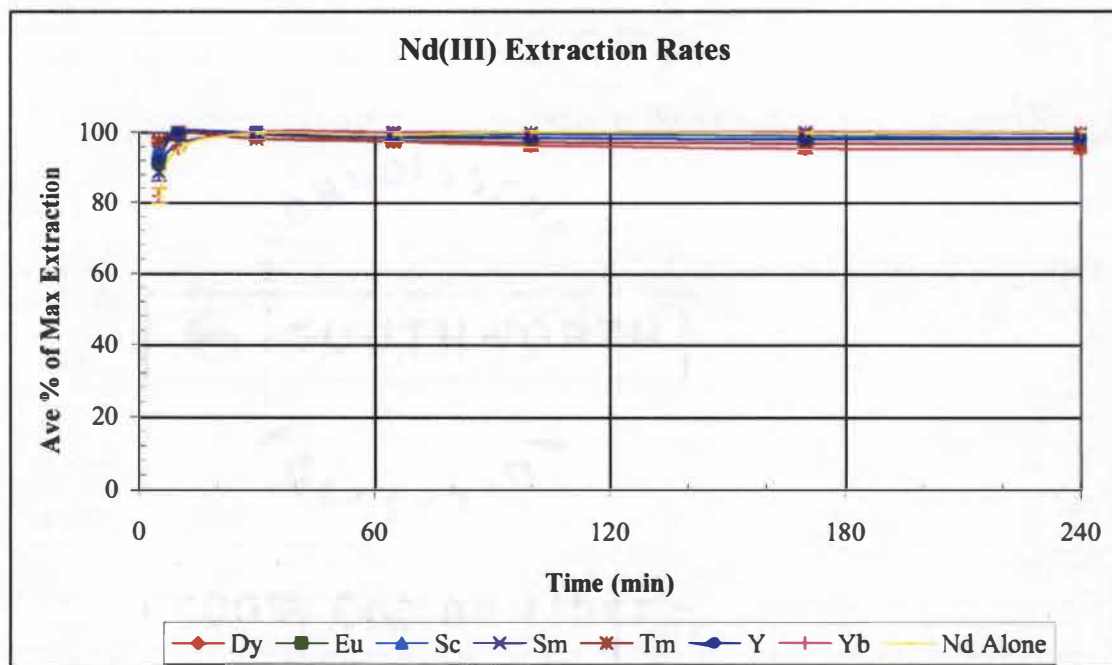


Figure 15. Average Percentages of Maximum Extraction:  $\text{Nd}^{+3}$  and Its Mixtures

**Table 4.7. Rate Data For Mixtures of Nd<sup>+3</sup>**

Ion Mixed with Nd <sup>+3</sup>	k <sub>f</sub> + k <sub>r</sub> (min <sup>-1</sup> )	k <sub>f</sub> (min <sup>-1</sup> )	k <sub>r</sub> (min <sup>-1</sup> )	Corr.	ε (%)
Dy <sup>+3</sup>	9.1 x 10 <sup>-1</sup>	8.3 x 10 <sup>-1</sup>	7.9 x 10 <sup>-2</sup>	0.978	21.2
Eu <sup>+3</sup>	2.9 x 10 <sup>-1</sup>	2.6 x 10 <sup>-1</sup>	2.7 x 10 <sup>-2</sup>	0.967	18.7
Sc <sup>+3</sup>	9.1 x 10 <sup>-1</sup>	8.6 x 10 <sup>-1</sup>	5.7 x 10 <sup>-2</sup>	0.983	18.5
Sm <sup>+3</sup>	1.3 x 10 <sup>-1</sup>	1.2 x 10 <sup>-1</sup>	1.3 x 10 <sup>-2</sup>	0.963	16.1
Tm <sup>+3</sup>	9.1 x 10 <sup>-1</sup>	8.6 x 10 <sup>-1</sup>	5.4 x 10 <sup>-2</sup>	0.994	11.4
Y <sup>+3</sup>	9.1 x 10 <sup>-1</sup>	8.1 x 10 <sup>-1</sup>	9.7 x 10 <sup>-2</sup>	0.970	24.9
Yb <sup>+3</sup>	6.8 x 10 <sup>-1</sup>	6.2 x 10 <sup>-1</sup>	6.1 x 10 <sup>-2</sup>	0.983	18.5

order to get a more accurate representation of the rate approaching equilibrium. Once extractions are at equilibrium, the slopes generated by the data change; the lines tend to level off (see Figure 16). Because Nd<sup>+3</sup> extracts most slowly when mixed with Sm<sup>+3</sup>, Figure 16 is an atypical example for Nd<sup>+3</sup> mixtures in that N = 5 rather than three.

Tables 4.8 and 4.9 give the separation coefficients  $\beta = D_{Nd^{+3}} / D_{M^{+3}}$ , where M<sup>+3</sup> represents the heavier metals not yet discussed: Dy<sup>+3</sup>, Eu<sup>+3</sup>, Sm<sup>+3</sup>, Tm<sup>+3</sup>, and Yb<sup>+3</sup>. Separation coefficients for those Nd<sup>+3</sup> mixtures with Sc<sup>+3</sup> and Y<sup>+3</sup> are reported in the previous two sections. Unlike those for Sc<sup>+3</sup> and Y<sup>+3</sup>, the separation coefficients for Nd<sup>+3</sup> mixtures are not enormous nor are their standard deviations, despite the fact that Nd<sup>+3</sup> itself extracts much more quickly than any of the other ions present in its mixtures. The reason for this is simply that Nd<sup>+3</sup> does not reach 100 % extraction. As seen in the Appendix, it only extracts to the extent of  $\approx 90\%$ , so distribution coefficients and therefore separation coefficients do not approach infinity.

#### D. Mixtures of Sm<sup>+3</sup>

Samarium(III) is the second largest of the ions studied, and on average it is also the second fastest extracting ion studied next to Nd<sup>+3</sup> and tied with Y<sup>+3</sup>. Figure 17 shows the rates at which Sm<sup>+3</sup> extracts when in binary mixtures with the trivalent ions listed. Forward and reverse rate constants and percentage error data are found in Table 4.10.

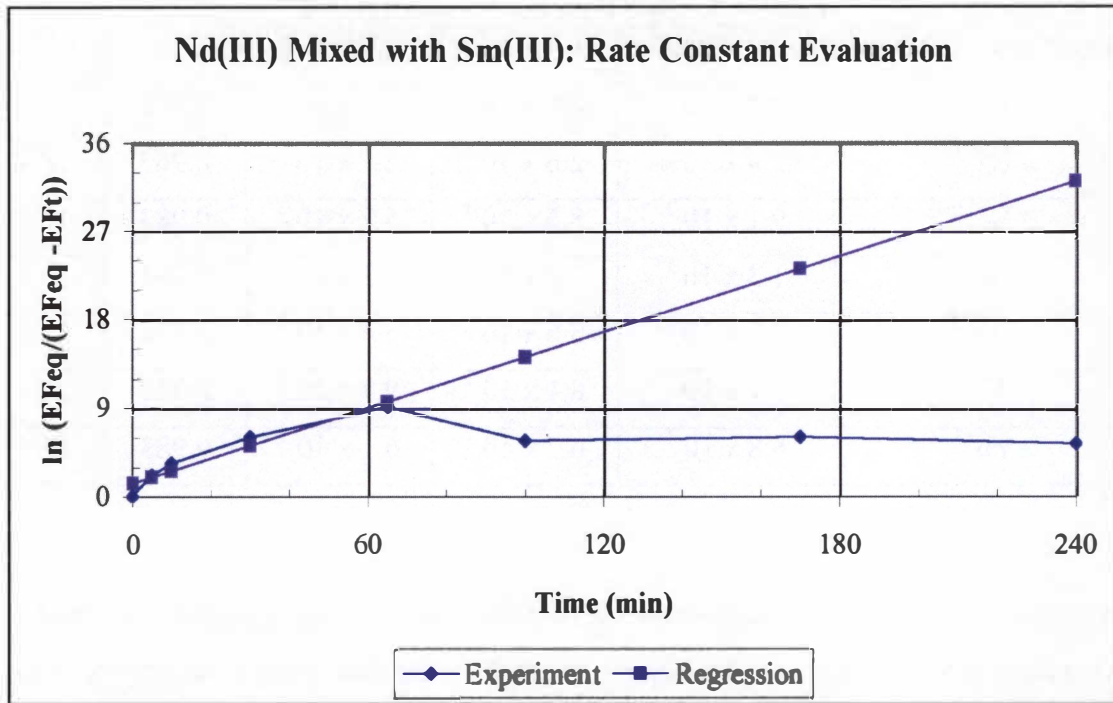


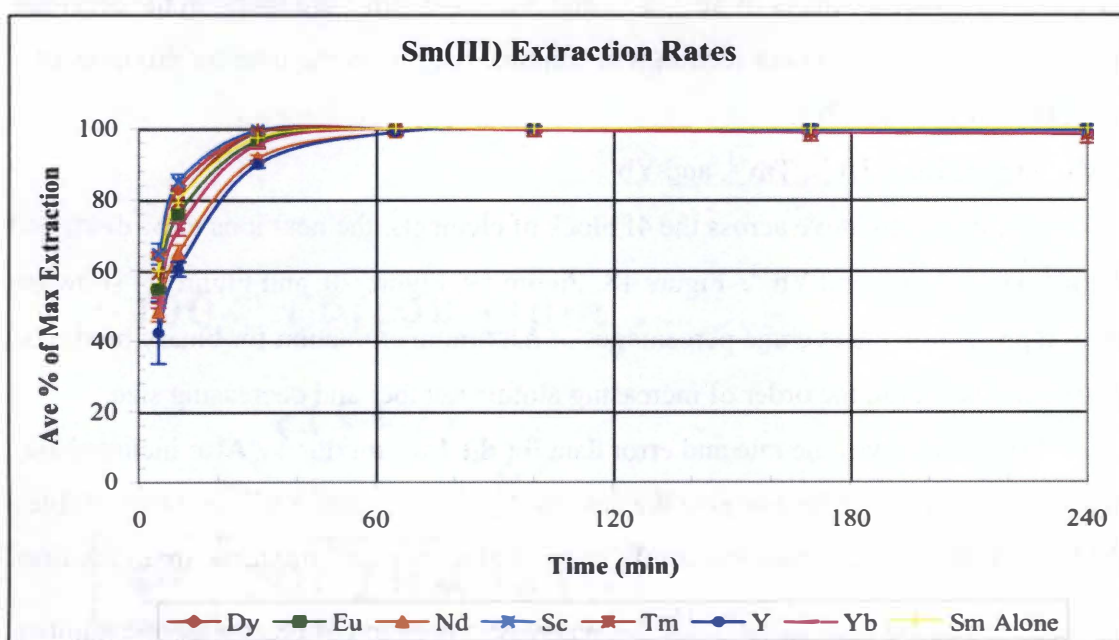
Figure 16. Typical Regression For Mixtures

Table 4.8. Separation Coefficients Involving Mixtures of  $Nd^{+3}$ , Where  $\beta = D_{Nd^{+3}}/D_{M^{+3}}$

Time (min)	$D_{Nd}/D_{Dy}$	$D_{Nd}/D_{Eu}$	$D_{Nd}/D_{Sm}$	$D_{Nd}/D_{Tm}$	$D_{Nd}/D_{Yb}$
5	40.2	9.8	4.8	40.8	24.5
10	12.9	1.9	4.5	24.4	32.2
30	3.7	0.4	1.5	3.6	9.3
65	0.4	0.3	0.8	0.5	4.1
100	0.4	0.1	0.6	0.1	2.1
170	0.0	0.2	0.6	0.0	0.5
240	0.0	0.8	0.6	0.0	0.2

**Table 4.9. Standard Deviations On Separation Coefficients of Nd<sup>+3</sup> Mixtures**

Time (min)	D <sub>Nd</sub> /D <sub>Dy</sub>	D <sub>Nd</sub> /D <sub>Eu</sub>	D <sub>Nd</sub> /D <sub>Sm</sub>	D <sub>Nd</sub> /D <sub>Tm</sub>	D <sub>Nd</sub> /D <sub>Yb</sub>
5	8.7	0.7	0.7	3.7	5.4
10	4.0	0.2	0.5	2.2	5.9
30	0.3	0.0	0.1	0.4	1.1
65	0.1	0.1	0.0	0.1	0.8
100	0.1	0.0	0.0	0.0	0.5
170	0.0	0.0	0.0	0.0	0.3
240	0.0	0.0	0.0	0.0	0.1



**Figure 17. Average Percentages of Maximum Extraction: Sm<sup>+3</sup> and Its Mixtures**



**Table 4.10. Rate Data For Mixtures of Sm<sup>+3</sup>**

Ion Mixed with Sm <sup>+3</sup>	k <sub>f</sub> + k <sub>r</sub> (min <sup>-1</sup> )	k <sub>f</sub> (min <sup>-1</sup> )	k <sub>r</sub> (min <sup>-1</sup> )	Corr.	ε (%)
Dy <sup>+3</sup>	1.4 x 10 <sup>-1</sup>	1.3 x 10 <sup>-1</sup>	1.1 x 10 <sup>-2</sup>	0.999	2.7
Eu <sup>+3</sup>	1.4 x 10 <sup>-1</sup>	1.3 x 10 <sup>-1</sup>	1.1 x 10 <sup>-2</sup>	0.994	6.1
Nd <sup>+3</sup>	5.4 x 10 <sup>-2</sup>	5.1 x 10 <sup>-2</sup>	3.6 x 10 <sup>-3</sup>	0.988	7.1
Sc <sup>+3</sup>	1.4 x 10 <sup>-1</sup>	1.3 x 10 <sup>-1</sup>	7.3 x 10 <sup>-3</sup>	0.994	6.5
Tm <sup>+3</sup>	1.4 x 10 <sup>-1</sup>	1.3 x 10 <sup>-1</sup>	8.7 x 10 <sup>-3</sup>	0.999	2.1
Y <sup>+3</sup>	5.4 x 10 <sup>-2</sup>	4.9 x 10 <sup>-2</sup>	4.7 x 10 <sup>-3</sup>	0.993	5.2
Yb <sup>+3</sup>	1.4 x 10 <sup>-1</sup>	1.3 x 10 <sup>-1</sup>	1.0 x 10 <sup>-2</sup>	0.992	7.5

Tables 4.11 and 4.12. list separation coefficients ( $\beta = D_{Sm^{+3}} / D_{M^{+3}}$ ) and standard deviations for mixtures of Sm<sup>+3</sup> with ions of higher atomic number: Dy<sup>+3</sup>, Eu<sup>+3</sup>, Tm<sup>+3</sup>, and Yb<sup>+3</sup>. (Data for mixtures of Sc<sup>+3</sup>, Y<sup>+3</sup>, and Nd<sup>+3</sup> with Sm<sup>+3</sup> are found in the previous three sections.) The following section will combine the remaining data for mixtures of Eu<sup>+3</sup>, Dy<sup>+3</sup>, Tm<sup>+3</sup>, and Yb<sup>+3</sup>.

#### E. Mixtures of Eu<sup>+3</sup>, Dy<sup>+3</sup>, Tm<sup>+3</sup>, and Yb<sup>+3</sup>

Continuing to move across the 4f block of elements, the next ions to be discussed are Eu<sup>+3</sup>, Dy<sup>+3</sup>, Tm<sup>+3</sup>, and Yb<sup>+3</sup>. Figure 18, Figure 19, Figure 20, and Figure 21 show the curves representing the average percentages of maximum extraction for binary mixtures of Eu<sup>+3</sup> and the rest in the order of increasing atomic number and decreasing size.

Table 4.13 gives the rate and error data for the Eu<sup>+3</sup> mixtures. Also included are Tables 4.14, 4.15, and 4.16 that give the data for Dy<sup>+3</sup>, Tm<sup>+3</sup>, and Yb<sup>+3</sup> mixtures. Table 4.17 lists the remaining separation coefficients. Values for Eu<sup>+3</sup> mixtures are in the first three columns of the table as  $\left(\beta = \frac{D_{Eu^{+3}}}{D_{M^{+3}}}\right)$ , where M<sup>+3</sup> is an ion of greater atomic number than Eu<sup>+3</sup>.  $\beta$  values calculated from mixtures of Dy<sup>+3</sup> are given in the fifth and sixth columns, and the last column contains those for the Yb<sup>+3</sup>/Tm<sup>+3</sup> mixture. The last three columns of Table 4.17 show the difficulty in separating the heavy lanthanides. If  $\beta \approx 1$ ,

**Table 4.11.** Separation Coefficients Involving Mixtures of  $\text{Sm}^{+3}$ , Where  $\beta = D_{\text{Sm}^{+3}}/D_{\text{M}^{+3}}$ 

Time (min)	$D_{\text{Sm}}/D_{\text{Dy}}$	$D_{\text{Sm}}/D_{\text{Eu}}$	$D_{\text{Sm}}/D_{\text{Tm}}$	$D_{\text{Sm}}/D_{\text{Yb}}$
5	3.8	1.7	3.8	3.4
10	4.9	1.8	6.7	4.3
30	5.7	1.9	13.9	6.2
65	2.2	1.0	6.5	3.5
100	0.9	0.7	2.6	1.6
170	0.1	0.7	0.8	0.4
240	0.1	0.7	0.2	0.1

**Table 4.12.** Standard Deviations On Separation Coefficients of  $\text{Sm}^{+3}$  Mixtures

Time (min)	$D_{\text{Sm}}/D_{\text{Dy}}$	$D_{\text{Sm}}/D_{\text{Eu}}$	$D_{\text{Sm}}/D_{\text{Tm}}$	$D_{\text{Sm}}/D_{\text{Yb}}$
5	0.2	0.1	0.5	0.5
10	0.3	0.1	0.9	0.6
30	0.7	0.4	6.7	0.7
65	0.2	0.1	1.4	0.2
100	0.1	0.1	0.7	0.2
170	0.1	0.0	0.2	0.1
240	0.0	0.0	0.1	0.0

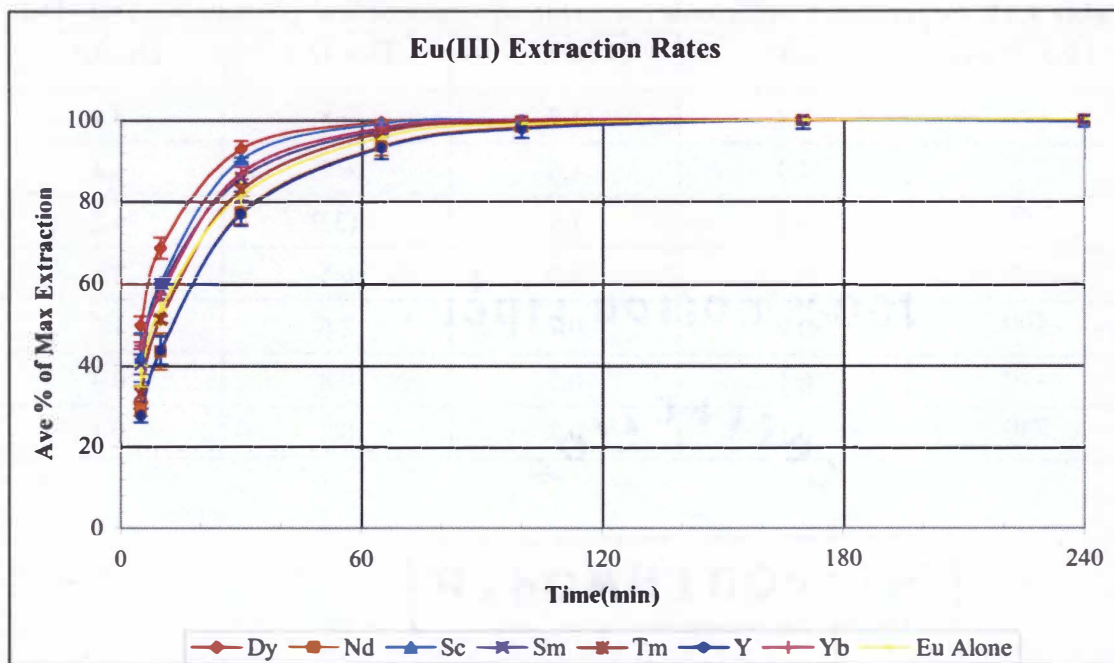


Figure 18. Average Percentages of Maximum Extraction:  $\text{Eu}^{+3}$  and Its Mixtures

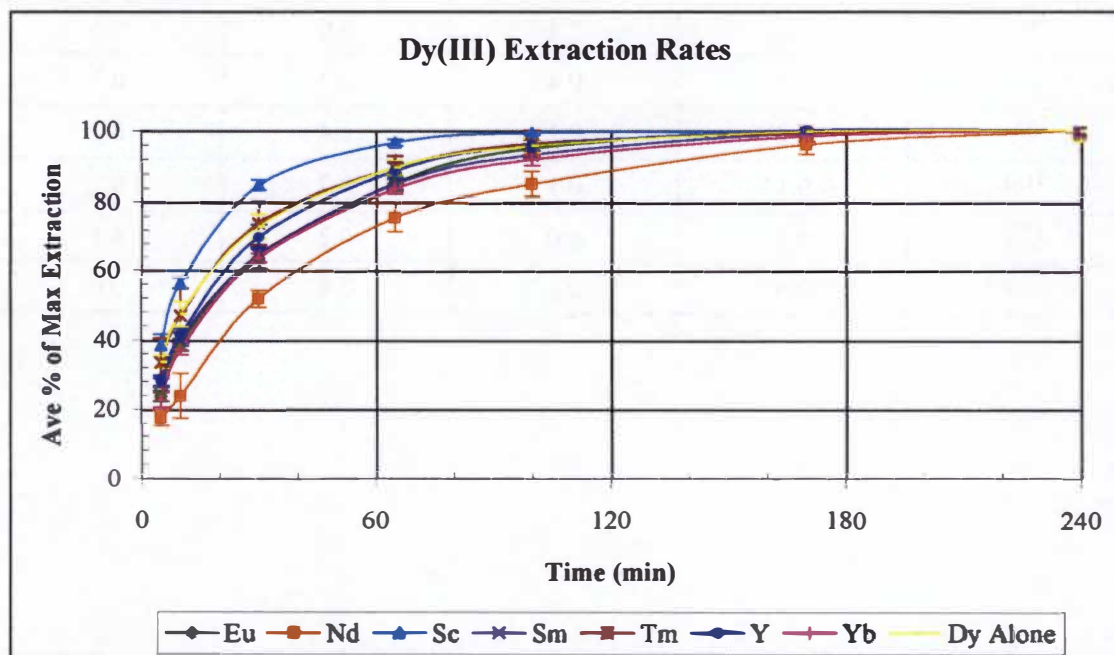
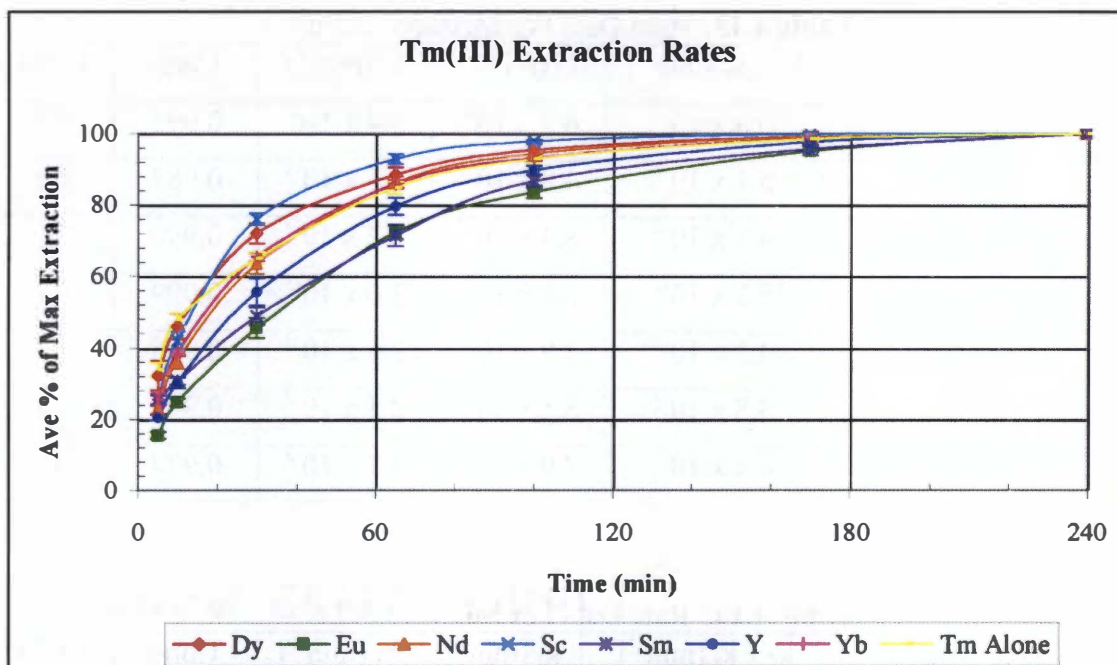
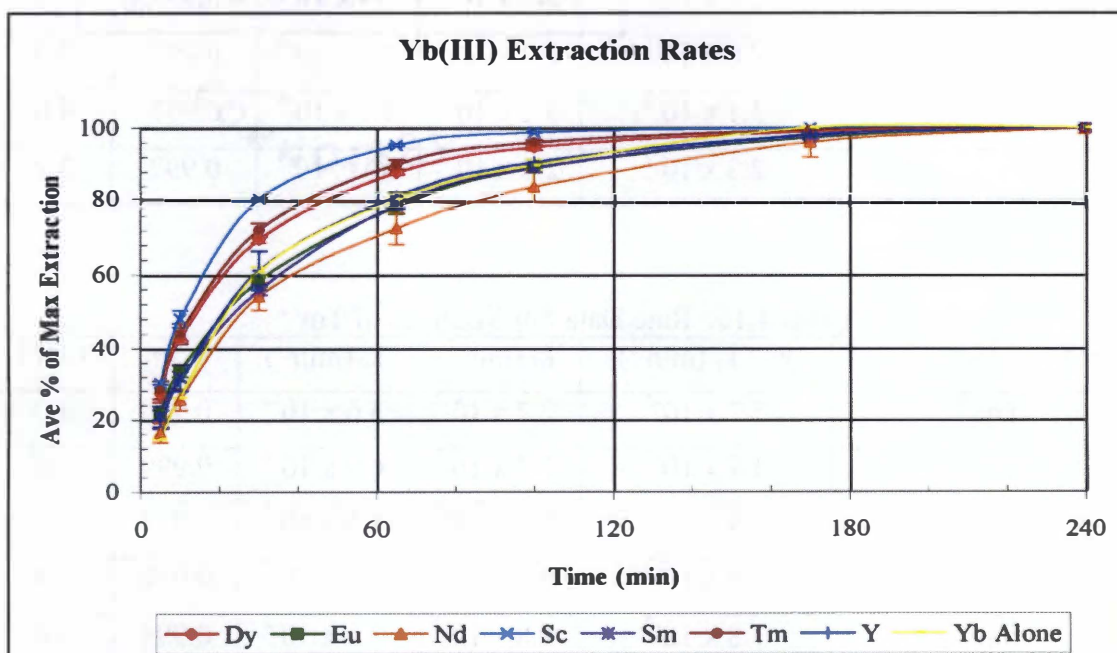


Figure 19. Average Percentages of Maximum Extraction:  $\text{Dy}^{+3}$  and Its Mixtures



**Figure 20.** Average Percentages of Maximum Extraction:  $Tm^{+3}$  and Its Mixtures



**Figure 21.** Average Percentages of Maximum Extraction:  $Yb^{+3}$  and Its Mixtures

**Table 4.13. Rate Data For Mixtures of Eu<sup>+3</sup>**

Ion Mixed with Eu <sup>+3</sup>	k <sub>f</sub> + k <sub>r</sub> (min <sup>-1</sup> )	k <sub>f</sub> (min <sup>-1</sup> )	k <sub>r</sub> (min <sup>-1</sup> )	Corr.	ε (%)
Dy <sup>+3</sup>	6.8 x 10 <sup>-2</sup>	6.4 x 10 <sup>-2</sup>	3.4 x 10 <sup>-3</sup>	0.995	5.1
Nd <sup>+3</sup>	5.1 x 10 <sup>-2</sup>	4.8 x 10 <sup>-2</sup>	3.1 x 10 <sup>-3</sup>	0.987	7.2
Sc <sup>+3</sup>	8.7 x 10 <sup>-2</sup>	8.4 x 10 <sup>-2</sup>	3.2 x 10 <sup>-3</sup>	0.990	7.1
Sm <sup>+3</sup>	5.3 x 10 <sup>-2</sup>	5.0 x 10 <sup>-2</sup>	3.0 x 10 <sup>-3</sup>	0.999	1.7
Tm <sup>+3</sup>	4.2 x 10 <sup>-2</sup>	3.9 x 10 <sup>-2</sup>	2.5 x 10 <sup>-3</sup>	0.985	7.7
Y <sup>+3</sup>	3.8 x 10 <sup>-2</sup>	3.5 x 10 <sup>-2</sup>	2.5 x 10 <sup>-3</sup>	0.999	1.8
Yb <sup>+3</sup>	8.4 x 10 <sup>-2</sup>	7.9 x 10 <sup>-2</sup>	4.7 x 10 <sup>-3</sup>	0.974	11.7

**Table 4.14. Rate Data For Mixtures of Dy<sup>+3</sup>**

Ion Mixed with Dy <sup>+3</sup>	k <sub>f</sub> + k <sub>r</sub> (min <sup>-1</sup> )	k <sub>f</sub> (min <sup>-1</sup> )	k <sub>r</sub> (min <sup>-1</sup> )	Corr.	ε (%)
Eu <sup>+3</sup>	2.9 x 10 <sup>-2</sup>	2.9 x 10 <sup>-2</sup>	2.9 x 10 <sup>-5</sup>	0.998	3.1
Nd <sup>+3</sup>	1.9 x 10 <sup>-2</sup>	1.8 x 10 <sup>-2</sup>	2.8 x 10 <sup>-4</sup>	0.998	2.7
Sc <sup>+3</sup>	4.7 x 10 <sup>-2</sup>	4.7 x 10 <sup>-2</sup>	1.4 x 10 <sup>-4</sup>	0.996	4.5
Sm <sup>+3</sup>	2.8 x 10 <sup>-2</sup>	2.8 x 10 <sup>-2</sup>	1.9 x 10 <sup>-4</sup>	0.997	3.3
Tm <sup>+3</sup>	2.8 x 10 <sup>-2</sup>	2.7 x 10 <sup>-2</sup>	2.8 x 10 <sup>-4</sup>	0.997	2.9
Y <sup>+3</sup>	3.1 x 10 <sup>-2</sup>	3.1 x 10 <sup>-2</sup>	3.1 x 10 <sup>-5</sup>	0.997	4.0
Yb <sup>+3</sup>	2.3 x 10 <sup>-2</sup>	2.3 x 10 <sup>-2</sup>	6.1 x 10 <sup>-4</sup>	0.997	3.2

**Table 4.15. Rate Data For Mixtures of Tm<sup>+3</sup>**

Ion Mixed with Tm <sup>+3</sup>	k <sub>f</sub> + k <sub>r</sub> (min <sup>-1</sup> )	k <sub>f</sub> (min <sup>-1</sup> )	k <sub>r</sub> (min <sup>-1</sup> )	Corr.	ε (%)
Dy <sup>+3</sup>	2.7 x 10 <sup>-2</sup>	2.7 x 10 <sup>-2</sup>	3.6 x 10 <sup>-4</sup>	0.996	4.0
Eu <sup>+3</sup>	1.7 x 10 <sup>-2</sup>	1.7 x 10 <sup>-2</sup>	6.9 x 10 <sup>-4</sup>	0.999	1.9
Nd <sup>+3</sup>	2.9 x 10 <sup>-2</sup>	2.9 x 10 <sup>-2</sup>	1.5 x 10 <sup>-4</sup>	0.997	4.5
Sc <sup>+3</sup>	3.8 x 10 <sup>-2</sup>	3.8 x 10 <sup>-2</sup>	3.8 x 10 <sup>-5</sup>	0.999	1.8
Sm <sup>+3</sup>	1.8 x 10 <sup>-2</sup>	1.8 x 10 <sup>-2</sup>	3.1 x 10 <sup>-4</sup>	0.998	3.0
Y <sup>+3</sup>	2.1 x 10 <sup>-2</sup>	2.1 x 10 <sup>-2</sup>	1.1 x 10 <sup>-4</sup>	0.999	2.1
Yb <sup>+3</sup>	2.6 x 10 <sup>-2</sup>	2.6 x 10 <sup>-2</sup>	2.6 x 10 <sup>-5</sup>	0.994	5.3

**Table 4.16. Rate Data For Mixtures of Yb<sup>+3</sup>**

Ion Mixed with Yb <sup>+3</sup>	k <sub>f</sub> + k <sub>r</sub> (min <sup>-1</sup> )	k <sub>f</sub> (min <sup>-1</sup> )	k <sub>r</sub> (min <sup>-1</sup> )	Corr.	ε (%)
Dy <sup>+3</sup>	2.6 x 10 <sup>-2</sup>	2.6 x 10 <sup>-2</sup>	7.8 x 10 <sup>-5</sup>	0.995	4.3
Eu <sup>+3</sup>	2.1 x 10 <sup>-2</sup>	2.0 x 10 <sup>-2</sup>	2.5 x 10 <sup>-4</sup>	0.998	2.8
Nd <sup>+3</sup>	1.8 x 10 <sup>-2</sup>	1.8 x 10 <sup>-2</sup>	3.6 x 10 <sup>-4</sup>	0.998	3.2
Sc <sup>+3</sup>	3.7 x 10 <sup>-2</sup>	3.7 x 10 <sup>-2</sup>	3.7 x 10 <sup>-5</sup>	0.996	3.4
Sm <sup>+3</sup>	2.1 x 10 <sup>-2</sup>	2.1 x 10 <sup>-2</sup>	1.9 x 10 <sup>-4</sup>	0.999	2.1
Tm <sup>+3</sup>	2.9 x 10 <sup>-2</sup>	2.8 x 10 <sup>-2</sup>	5.7 x 10 <sup>-5</sup>	0.996	4.1
Y <sup>+3</sup>	2.2 x 10 <sup>-2</sup>	2.2 x 10 <sup>-2</sup>	1.1 x 10 <sup>-4</sup>	0.998	2.7

**Table 4.17. Separation Coefficients Involving Mixtures of Eu<sup>+3</sup>, Dy<sup>+3</sup>, Tm<sup>+3</sup>, and Yb<sup>+3</sup>**

Time (min)	D <sub>Eu</sub> /D <sub>Dy</sub>	D <sub>Eu</sub> /D <sub>Tm</sub>	D <sub>Eu</sub> /D <sub>Yb</sub>	D <sub>Dy</sub> /D <sub>Tm</sub>	D <sub>Yb</sub> /D <sub>Dy</sub>	D <sub>Yb</sub> /D <sub>Tm</sub>
5	2.9	2.6	2.7	1.1	1.3	1.2
10	3.0	3.0	2.4	1.0	1.3	1.2
30	4.3	4.5	3.4	1.1	1.4	1.4
65	2.9	4.5	3.6	1.1	1.6	1.5
100	1.0	3.5	2.3	1.3	2.0	1.6
170	0.0	1.5	0.7	1.2	3.2	1.7
240	0.0	0.6	0.2	1.3	9.5	0.7

many stages in a counter current solvent extraction system are required to achieve reasonable purity. Table 4.18 lists the standard deviations on the separation coefficients.

#### F. Miscellaneous Mixture Experiments

##### **1. Nd<sup>+3</sup>/Yb<sup>+3</sup> Low Temperature Study**

An additional study was performed on a mixture of 9-coordinate Nd<sup>+3</sup> and 8-coordinate Yb<sup>+3</sup> in which the reaction vessel was jacketed, and ice water flowed through to keep the reaction temperature from increasing. One might expect this act to slow the reaction, but it appeared to have no effect on the observed extraction rates (see Figure 22.)

##### **2. Yb<sup>+3</sup>/Lu<sup>+3</sup> Mixture (Fresh vs Older Study)**

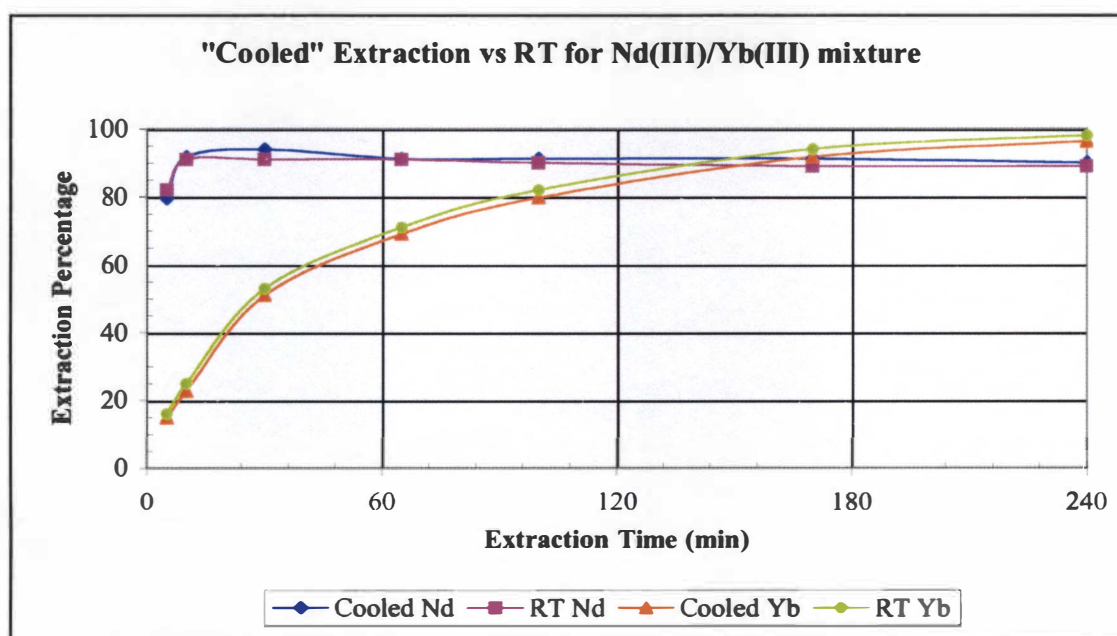
Recall from chapter 3 (section C), that while studying single-ion solutions of Yb<sup>+3</sup>, it appeared that Yb<sup>+3</sup> extracted faster when the feed solution had been freshly prepared. In addition, Lu<sup>+3</sup> did not seem to show this tendency, so a “fresh vs older” study was performed on a mixture of the two to determine whether or not any exploitable rate difference actually exists. One extraction was performed, and results were obtained via ICP-OES from Galbraith Laboratories. Due to the expense of the measurements, only the 30-minute sample was submitted to see if any difference could be detected. The 30-minute sample was chosen, because it was expected to be the sample with the maximum separation between the two ions based on observed single-ion rates. It was found that in the mixture of Lu<sup>+3</sup> and Yb<sup>+3</sup>, regardless of whether the solution was fresh or older, both ions extracted to same extent after 30 minutes. Because there were no detectable rate differences in this sample, no further samples were studied.

##### **3. Nd<sup>+3</sup>/Yb<sup>+3</sup> Mixture (Varied DEHPA Concentration)**

It is desirable to know exactly how the extraction rates are affected by the extractant concentration. Equation 1.9 shows that increased concentration of DEHPA in the organic phase, leading to increased  $\left[\overline{M(HR_2)_3}\right]$ , slows the forward reaction while increasing the rate of the reverse reaction. Extractions were carried out on a mixture of Nd<sup>+3</sup> and Yb<sup>+3</sup>, because they are at opposite ends of the 4f block and so have different coordination numbers (9 and 8, respectively). Experiments were run with DEHPA concentrations of 0.15M, 0.30M, 0.45M, 0.60M, 0.75M, and 1.0M. Since three DEHPA molecules are

**Table 4.18. Separation Coefficient Standard Deviations for Remaining Ion Mixtures**

Time (min)	$D_{Eu}/D_{Dy}$	$D_{Eu}/D_{Tm}$	$D_{Eu}/D_{Yb}$	$D_{Dy}/D_{Tm}$	$D_{Yb}/D_{Dy}$	$D_{Yb}/D_{Tm}$
5	0.3	0.2	0.2	0.3	0.2	0.1
10	0.3	0.1	0.2	0.2	0.1	0.1
30	0.8	0.5	0.3	0.3	0.1	0.1
65	0.5	0.4	0.5	0.4	0.1	0.2
100	0.2	0.3	0.3	1.0	0.3	0.3
170	0.0	0.2	0.1	1.6	1.0	0.6
240	0.0	0.1	0.0	1.6	6.0	0.6



**Figure 22. Low vs Room Temperature Extraction Results For  $Nd^{+3}/Yb^{+3}$  Mixture**

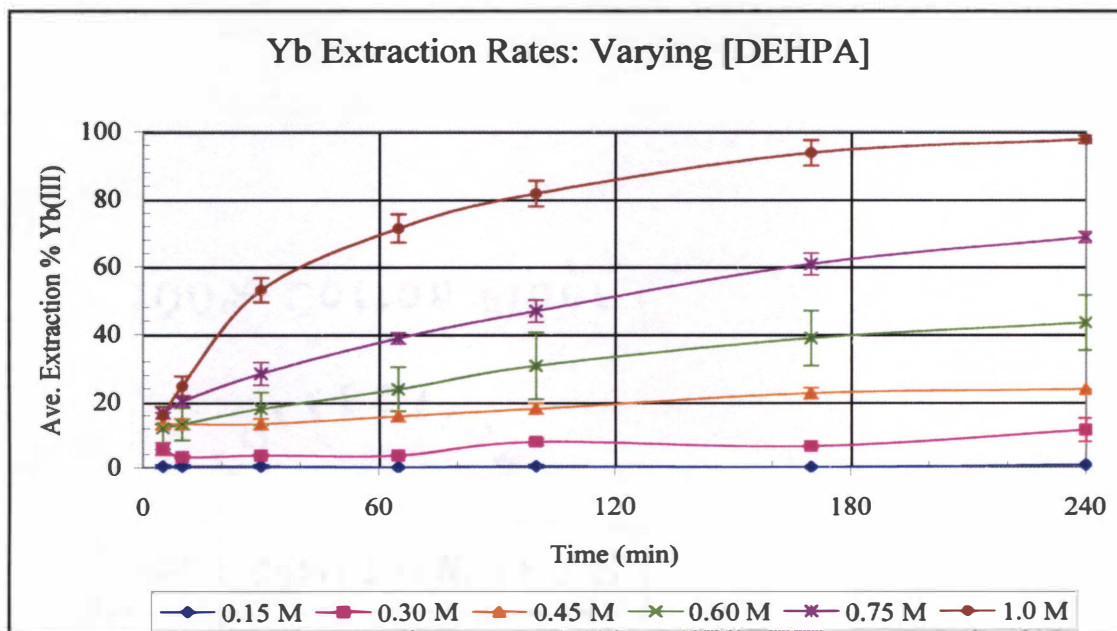


required to extract one metal ion (see equation 1.1), 0.15 M DEHPA is the minimum amount required theoretically to extract all aqueous metal ions ( $[M^{+3}] = 0.05M$ ). At the remaining DEHPA concentrations, there are 2, 3, 4, 5, and ~7 times as many DEHPA molecules, and the rates increase as seen in Table 4.19 below. It appears to require at least 0.45 M DEHPA to attain appreciable rate constant magnitudes.

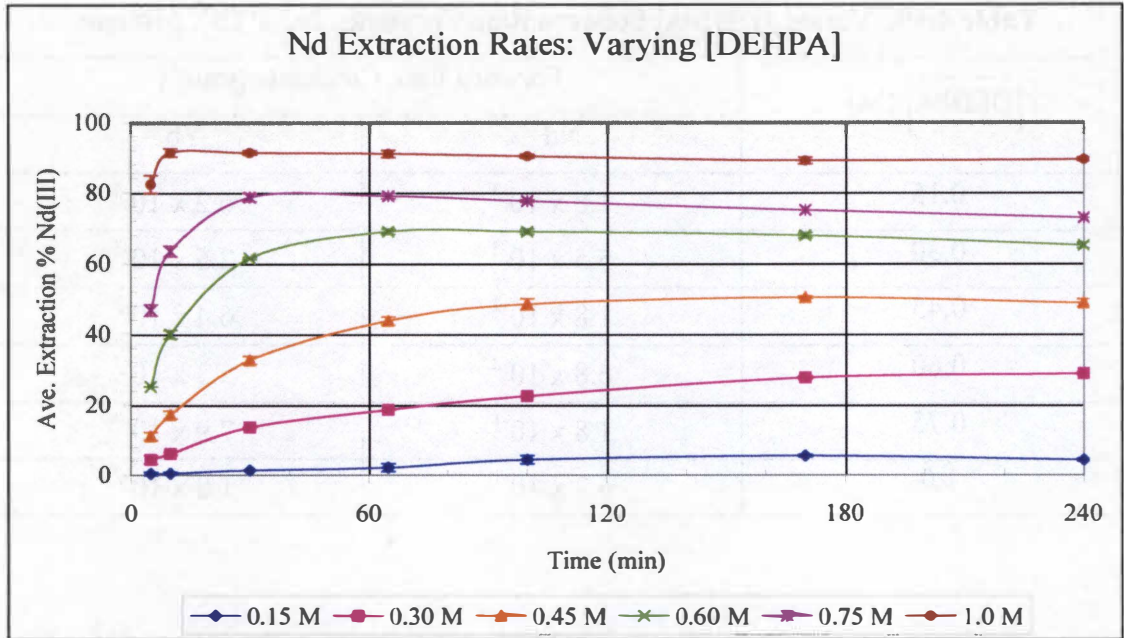
Figure 23 and Figure 24 show the average extraction percentages of each metal at the various DEHPA concentrations. Error bars represent the standard deviations from two trials each except for the 1.0 M experiment that is from three trials.

**Table 4.19. Varied [DEHPA] Forward Rate Constants: Nd<sup>3+</sup>/Yb<sup>3+</sup> Mixture**

[DEHPA] (M)	Forward Rate Constants (min <sup>-1</sup> )	
	Nd <sup>3+</sup>	Yb <sup>3+</sup>
0.15	1.8 x 10 <sup>-3</sup>	6.2 x 10 <sup>-5</sup>
0.30	5.5 x 10 <sup>-3</sup>	2.5 x 10 <sup>-3</sup>
0.45	1.8 x 10 <sup>-2</sup>	6.4 x 10 <sup>-3</sup>
0.60	6.8 x 10 <sup>-2</sup>	5.3 x 10 <sup>-3</sup>
0.75	1.8 x 10 <sup>-1</sup>	7.9 x 10 <sup>-3</sup>
1.0	6.2 x 10 <sup>-1</sup>	1.8 x 10 <sup>-2</sup>



**Figure 23. Yb<sup>3+</sup> Extraction Rates With Varied Concentrations of Organic DEHPA**



**Figure 24.** Nd<sup>3+</sup> Extraction Rates With Varied Concentrations of Organic DEHPA

## CHAPTER 5 CONCLUSION

Solvent extractions of many of the trivalent lanthanide ions,  $\text{Sc}^{+3}$ , and  $\text{Y}^{+3}$  have been carried out. These cations were complexed with DTPA (diethylenetriaminepentaacetic acid) in an aqueous phase and were extracted with DEHPA (di-2-ethylhexylphosphoric acid) in an organic phase (kerosene). The experiments were designed to measure the rates of extraction in the hope that separation coefficients might be enhanced under non-equilibrium conditions, as has been determined in some prior experiments<sup>[3,4,13]</sup>. Rates of extraction for  $\text{Sc}^{+3}$ ,  $\text{Y}^{+3}$ ,  $\text{Nd}^{+3}$ ,  $\text{Sm}^{+3}$ ,  $\text{Eu}^{+3}$ ,  $\text{Dy}^{+3}$ ,  $\text{Tm}^{+3}$ ,  $\text{Yb}^{+3}$ , and  $\text{Lu}^{+3}$  were determined. Similar determinations were made for  $\text{Al}^{+3}$  in order to compare the above with a representative element cation. Then extraction rates and separation coefficients were measured for binary mixtures of all combinations of  $\text{Sc}^{+3}$ ,  $\text{Y}^{+3}$ ,  $\text{Nd}^{+3}$ ,  $\text{Sm}^{+3}$ ,  $\text{Eu}^{+3}$ ,  $\text{Dy}^{+3}$ ,  $\text{Tm}^{+3}$ , and  $\text{Yb}^{+3}$ .

In most experiments, the DEHPA concentration in the organic phase was held constant at a twenty-fold excess over the moles of metal ion. Under these conditions, the data for the extraction rates were found to be in accordance with pseudo first order kinetics assuming the extraction reaction to be:



The rate constants calculated from the extractions showed a decrease with ionic size, with the exception of  $\text{Y}^{+3}$ . This is true if all the eight-coordinate or all the nine coordinate radii are employed. The  $\text{Y}^{+3}$  cation extracts much faster than would be predicted from its eight-coordinate or its nine-coordinate ionic radius. However, if one assumes that the lanthanide coordination number changes from nine to eight following  $\text{Sm}^{+3}$ , the  $\text{Y}^{+3}$  nine-coordinate radius falls into place. It is generally accepted that the lanthanide coordination number changes somewhere along the series, but there is disagreement as to exactly where. Perhaps it changes differently under different conditions.

In some other cases, the behavior of  $Y^{+3}$  with respect to the lanthanides is found to be out of order with respect to ionic radii trends. This shows up in some separation techniques, particularly ion exchange and solvent extraction<sup>[9, 14]</sup>. The stability constants of  $Y^{+3}$  and the trivalent lanthanide ions with DTPA also show trends that evidence a displaced  $Y^{+3}$  with regard to ionic size. The present rate constant data along with DTPA complex stability constant data are presented in Table 5.1 below.

Enhanced separation coefficients were found in many cases. In most cases the optimal separation coefficients are found at an aqueous/organic contact time of ten minutes. For these cases, non-equilibrium extractions would be more efficient than equilibrium extractions. This could be valuable in industrial separations.

**Table 5.1 Average Rate Constants and Standard Deviations From the Single-Ion and Mixture Studies As Well As Stability Constants Observed For the M-DTPA Complex**

Ion	Nd <sup>+3</sup>	Sm <sup>+3</sup>	Y <sup>+3</sup>	Eu <sup>+3</sup>	Dy <sup>+3</sup>	Tm <sup>+3</sup>	Yb <sup>+3</sup>	Sc <sup>+3</sup>
Ave $k_f$ (min <sup>-1</sup> )	0.57	0.11	0.10	0.054	0.030	0.025	0.024	0.0032
S.D. $k_f$ (min-1)	0.33	0.04	0.09	0.020	0.009	0.007	0.006	0.0006
log $K_{M-DTPA}$ <sup>[10]</sup>	21.60	22.34	22.05	22.39	22.82	22.72	22.62	-
Log $K_{M-DTPA}$ <sup>[8]</sup>	22.24	22.84	22.40	22.91	23.46	22.97	23.01	-

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## APPENDIX



## APPENDIX: EXPERIMENTAL DATA

### Average Single-Ion Extraction Percentages

Time (min)	Al <sup>+3</sup>	Sc <sup>+3</sup>	Y <sup>+3</sup>	Nd <sup>+3</sup>	Sm <sup>+3</sup>	Eu <sup>+3</sup>	Dy <sup>+3</sup>	Tm <sup>+3</sup>	Yb <sup>+3</sup>	Lu <sup>+3</sup>
5	1.1	8.1	52.0	72.0	57.5	35.2	32.6	33.7	14.5	17.7
10	3.3	10.9	70.0	84.3	76.0	50.6	45.9	47.5	26.0	32.2
30	12.5	18.7	93.0	88.0	93.5	77.1	70.8	64.7	60.7	56.1
65	21.1	29.3	97.3	87.7	96.0	90.5	87.1	84.3	80.4	79.7
100	29.6	39.0	99.4	88.3	96.0	93.6	93.0	92.3	89.7	90.4
170	48.9	52.5	98.9	88.0	96.0	94.4	96.9	98.0	99.9	98.0
240	59.2	62.7	99.3	88.3	96.0	94.5	97.2	99.5	99.9	99.7

### Standard Deviations from Single-Ion Extraction Percentages

Time (min)	Al <sup>+3</sup>	Sc <sup>+3</sup>	Y <sup>+3</sup>	Nd <sup>+3</sup>	Sm <sup>+3</sup>	Eu <sup>+3</sup>	Dy <sup>+3</sup>	Tm <sup>+3</sup>	Yb <sup>+3</sup>	Lu <sup>+3</sup>
5	1.7	5.5	2.6	1.7	3.9	2.4	1.6	2.1	0.0	10.8
10	2.2	5.1	1.1	1.2	2.6	3.5	3.4	1.8	0.0	11.1
30	3.2	4.7	2.1	0.0	0.6	4.8	3.3	1.7	1.2	6.5
65	1.8	4.4	1.6	0.6	0.0	1.8	0.9	1.7	1.2	2.4
100	2.5	4.5	0.3	0.6	0.0	1.1	0.3	1.0	1.4	0.8
170	5.5	4.0	0.8	0.0	0.0	0.9	1.0	0.5	0.2	0.6
240	6.5	5.1	0.5	0.6	0.0	0.8	1.9	0.2	0.0	0.1

### Average Extraction Percentages for Sc<sup>+3</sup> in Its Mixtures

Time (min)	Average Sc <sup>+3</sup> Extraction Percentages in Mixtures With:						
	Dy <sup>+3</sup>	Eu <sup>+3</sup>	Nd <sup>+3</sup>	Sm <sup>+3</sup>	Tm <sup>+3</sup>	Y <sup>+3</sup>	Yb <sup>+3</sup>
5	0.7	0.1	11.9	0.01	0.01	0.7	7.5
10	1.7	1.4	13.3	0.01	0.1	1.4	8.6
30	10.6	10.1	17.0	13.5	9.8	8.4	15.2
65	27.0	16.7	24.1	22.2	23.2	18.5	22.9
100	35.2	24.7	30.6	29.3	32.1	28.2	30.6
170	49.3	31.8	39.8	42.0	44.8	41.3	45.4
240	58.7	41.6	48.4	52.7	56.7	53.8	53.1

Standard Deviations for Sc<sup>+3</sup> Extraction Percentages

Time (min)	Standard Deviations on Sc <sup>+3</sup> Extraction Percentages in Mixtures With:						
	Dy <sup>+3</sup>	Eu <sup>+3</sup>	Nd <sup>+3</sup>	Sm <sup>+3</sup>	Tm <sup>+3</sup>	Y <sup>+3</sup>	Yb <sup>+3</sup>
5	0.9	0.2	0.9	0.0	0.0	1.2	1.8
10	1.7	2.2	2.3	0.0	0.2	2.2	1.0
30	6.2	1.6	1.0	3.7	7.4	1.5	1.0
65	0.7	1.3	1.4	3.1	2.9	2.8	1.0
100	0.4	4.6	2.4	2.2	2.7	2.9	0.0
170	0.7	1.4	1.9	1.8	0.9	5.6	2.7
240	1.6	1.4	2.4	2.6	2.7	4.7	1.0

Average Extraction Percentages for Y<sup>+3</sup> in Its Mixtures

Time (min)	Average Y <sup>+3</sup> Extraction Percentages in Mixtures With:						
	Dy <sup>+3</sup>	Eu <sup>+3</sup>	Nd <sup>+3</sup>	Sc <sup>+3</sup>	Sm <sup>+3</sup>	Tm <sup>+3</sup>	Yb <sup>+3</sup>
5	66.5	46.9	44.5	67.3	45.4	42.7	54.7
10	85.2	61.0	59.5	83.2	61.6	51.1	73.3
30	99.4	88.5	90.6	99.9	87.4	69.4	93.8
65	99.9	96.8	98.8	99.9	95.9	85.9	98.9
100	99.9	98.8	99.1	99.9	97.4	93.3	99.2
170	99.9	99.0	99.5	99.9	98.6	99.0	99.1
240	99.9	99.0	99.6	99.9	98.6	99.9	99.0

Standard Deviations for Y<sup>+3</sup> Extraction Percentages

Time (min)	Standard Deviations on Y <sup>+3</sup> Extraction Percentages in Mixtures With:						
	Dy <sup>+3</sup>	Eu <sup>+3</sup>	Nd <sup>+3</sup>	Sc <sup>+3</sup>	Sm <sup>+3</sup>	Tm <sup>+3</sup>	Yb <sup>+3</sup>
5	1.5	1.6	1.0	1.9	2.3	1.0	2.7
10	0.9	3.2	3.6	2.7	2.3	1.4	2.7
30	0.9	2.5	1.2	0.2	1.4	2.4	6.3
65	0.2	2.3	2.0	0.0	2.3	1.4	1.5
100	0.0	1.7	0.9	0.0	2.2	1.2	1.3
170	0.0	1.7	0.8	0.0	1.9	0.8	1.4
240	0.0	1.3	0.6	0.0	1.5	0.2	1.1

Average Extraction Percentages for Nd<sup>+3</sup> in Its Mixtures

Time (min)	Average Nd <sup>+3</sup> Extraction Percentages in Mixtures With:						
	Dy <sup>+3</sup>	Eu <sup>+3</sup>	Sc <sup>+3</sup>	Sm <sup>+3</sup>	Tm <sup>+3</sup>	Y <sup>+3</sup>	Yb <sup>+3</sup>
5	86.2	82.7	89.6	79.9	91.7	82.6	82
10	91.3	90.2	93.8	87.2	94.1	89.3	91
30	90.6	90.7	93.8	90.0	92.4	88.9	91
65	88.9	89.9	93.5	90.2	91.7	87.9	91
100	87.9	89.3	93.2	89.9	91.5	87.8	91
170	87.1	88.8	92.8	90.0	91.1	87.5	89
240	86.9	88.8	92.2	89.8	91.0	87.9	89

Standard Deviations for Nd<sup>+3</sup> Extraction Percentages

Time (min)	Standard Deviations on Nd <sup>+3</sup> Extraction Percentages in Mixtures With:						
	Dy <sup>+3</sup>	Eu <sup>+3</sup>	Sc <sup>+3</sup>	Sm <sup>+3</sup>	Tm <sup>+3</sup>	Y <sup>+3</sup>	Yb <sup>+3</sup>
5	2.4	0.7	2.5	2.3	0.6	0.3	2.5
10	0.9	0.2	0.3	1.0	0.3	0.3	1.2
30	0.2	0.1	0.2	0.3	0.3	0.3	0.6
65	0.2	0.4	0.3	0.2	0.3	0.2	1.0
100	0.7	0.2	0.1	0.3	0.2	0.3	0.6
170	0.6	0.2	0.3	0.6	0.3	0.3	1.0
240	0.4	0.2	0.6	0.2	0.4	0.3	0.6

Average Extraction Percentages for Sm<sup>+3</sup> in Its Mixtures

Time (min)	Average Sm <sup>+3</sup> Extraction Percentages in Mixtures With:						
	Dy <sup>+3</sup>	Eu <sup>+3</sup>	Nd <sup>+3</sup>	Sc <sup>+3</sup>	Tm <sup>+3</sup>	Y <sup>+3</sup>	Yb <sup>+3</sup>
5	59.1	50.2	45.0	61.3	55.5	38.7	47.1
10	76.5	69.5	60.5	80.5	74.3	55.1	66.3
30	91.1	88.6	85.6	94.3	92.8	82.1	88.5
65	92.1	91.8	92.4	94.8	93.8	90.3	92.6
100	91.6	91.7	93.3	94.6	93.8	91.1	92.1
170	91.0	91.5	93.4	94.2	92.6	91.3	91.5
240	90.8	91.5	93.2	94.1	92.2	91.2	91.3

Standard Deviations for  $\text{Sm}^{+3}$  Extraction Percentages

Time (min)	Standard Deviations on $\text{Sm}^{+3}$ Extraction Percentages in Mixtures With:						
	$\text{Dy}^{+3}$	$\text{Eu}^{+3}$	$\text{Nd}^{+3}$	$\text{Sc}^{+3}$	$\text{Tm}^{+3}$	$\text{Y}^{+3}$	$\text{Yb}^{+3}$
5	1.0	0.6	2.4	2.8	4.0	8.1	1.4
10	0.8	1.1	2.2	2.1	3.3	1.9	1.7
30	0.8	1.7	0.9	0.2	3.5	0.8	1.1
65	0.2	0.3	0.2	0.1	1.2	0.1	0.3
100	0.3	0.2	0.3	0.3	1.5	0.7	0.3
170	0.4	0.3	0.2	0.4	1.6	0.4	0.5
240	0.4	0.3	0.1	0.7	1.9	0.3	0.3

Average Extraction Percentages for  $\text{Eu}^{+3}$  in Its Mixtures

Time (min)	Average $\text{Eu}^{+3}$ Extraction Percentages in Mixtures With:						
	$\text{Dy}^{+3}$	$\text{Nd}^{+3}$	$\text{Sc}^{+3}$	$\text{Sm}^{+3}$	$\text{Tm}^{+3}$	$\text{Y}^{+3}$	$\text{Yb}^{+3}$
5	47.2	27.3	40.3	37.9	31.0	25.8	42.3
10	65.1	40.7	57.9	55.2	48.1	40.7	54.0
30	88.2	72.5	86.9	80.8	77.8	71.7	82.1
65	94.4	87.8	95.4	91.8	91.0	86.9	92.5
100	95.0	92.2	96.3	93.8	93.5	91.2	94.4
170	94.7	93.9	96.2	94.2	94.0	93.2	94.4
240	94.7	93.9	95.6	94.2	93.8	93.3	94.4

Standard Deviations for  $\text{Eu}^{+3}$  Extraction Percentages

Time (min)	Standard Deviations on $\text{Eu}^{+3}$ Extraction Percentages in Mixtures With:						
	$\text{Dy}^{+3}$	$\text{Nd}^{+3}$	$\text{Sc}^{+3}$	$\text{Sm}^{+3}$	$\text{Tm}^{+3}$	$\text{Y}^{+3}$	$\text{Yb}^{+3}$
5	2.1	1.4	5.7	2.3	1.8	1.6	0.8
10	2.4	4.2	0.0	2.3	0.8	3.2	1.4
30	1.9	2.7	0.4	3.1	1.5	2.5	1.4
65	0.3	2.1	0.1	0.8	0.7	2.3	0.8
100	0.3	1.0	0.3	0.4	0.3	1.7	0.3
170	0.5	0.3	0.5	0.3	0.2	1.7	0.3
240	0.1	0.1	0.2	0.3	0.1	1.3	0.3

**Average Extraction Percentages for Dy<sup>+3</sup> in Its Mixtures**

Time (min)	Average Dy <sup>+3</sup> Extraction Percentages in Mixtures With:						
	Eu <sup>+3</sup>	Nd <sup>+3</sup>	Sc <sup>+3</sup>	Sm <sup>+3</sup>	Tm <sup>+3</sup>	Y <sup>+3</sup>	Yb <sup>+3</sup>
5	23.7	17.0	38.2	27.3	33.0	28.1	22.0
10	38.5	23.4	56.0	39.8	46.3	41.1	36.1
30	63.4	50.9	84.4	64.1	73.0	69.7	61.8
65	85.2	74.3	96.3	84.4	88.7	88.6	81.5
100	94.9	83.7	98.9	92.5	95.3	95.7	89.4
170	99.9	94.6	99.3	98.6	98.3	99.9	95.8
240	99.9	98.5	99.7	99.3	99.0	99.9	97.4

**Standard Deviations for Dy<sup>+3</sup> Extraction Percentages**

Time (min)	Standard Deviations on Dy <sup>+3</sup> Extraction Percentages in Mixtures With:						
	Eu <sup>+3</sup>	Nd <sup>+3</sup>	Sc <sup>+3</sup>	Sm <sup>+3</sup>	Tm <sup>+3</sup>	Y <sup>+3</sup>	Yb <sup>+3</sup>
5	1.5	2.2	3.1	1.2	7.0	1.5	2.1
10	1.8	6.4	1.7	1.9	7.8	1.9	1.4
30	3.0	2.3	1.4	2.2	6.2	3.6	1.1
65	2.2	3.8	0.8	1.5	3.1	2.2	1.0
100	1.0	3.2	0.5	1.2	3.5	1.6	1.1
170	0.0	2.3	0.3	0.6	2.1	0.1	1.0
240	0.0	1.7	0.3	0.4	1.0	0.1	1.1

**Average Extraction Percentages for Tm<sup>+3</sup> in Its Mixtures**

Time (min)	Average Tm <sup>+3</sup> Extraction Percentages in Mixtures With:						
	Dy <sup>+3</sup>	Eu <sup>+3</sup>	Nd <sup>+3</sup>	Sc <sup>+3</sup>	Sm <sup>+3</sup>	Y <sup>+3</sup>	Yb <sup>+3</sup>
5	31.7	14.8	22.7	25.4	25.0	20.3	25.4
10	45.2	23.8	36.1	41.8	30.2	30.1	38.6
30	71.0	43.7	63.2	75.9	47.9	55.3	65.4
65	87.1	69.4	85.7	92.7	70.2	79.2	85.8
100	94.1	80.4	93.9	97.6	85.1	89.2	93.1
170	97.8	91.4	98.7	99.8	94.1	97.1	98.6
240	98.6	96.1	99.5	99.9	98.3	99.5	99.9

Standard Deviations for Tm<sup>+3</sup> Extraction Percentages

Time (min)	Standard Deviations on Tm <sup>+3</sup> Extraction Percentages in Mixtures With:						
	Dy <sup>+3</sup>	Eu <sup>+3</sup>	Nd <sup>+3</sup>	Sc <sup>+3</sup>	Sm <sup>+3</sup>	Y <sup>+3</sup>	Yb <sup>+3</sup>
5	4.1	1.0	1.3	1.7	1.2	0.7	1.7
10	3.5	1.0	2.1	2.5	1.0	1.5	1.0
30	2.7	2.7	2.9	1.6	2.5	3.8	1.3
65	2.0	1.8	1.8	1.5	3.0	2.4	1.0
100	1.3	1.6	1.0	0.5	1.9	1.3	0.8
170	1.2	1.0	0.6	0.2	1.1	0.8	0.4
240	0.9	0.6	0.3	0.1	0.4	0.3	0.1

Average Extraction Percentages for Yb<sup>+3</sup> in Its Mixtures

Time (min)	Average Yb <sup>+3</sup> Extraction Percentages in Mixtures With:						
	Dy <sup>+3</sup>	Eu <sup>+3</sup>	Nd <sup>+3</sup>	Sc <sup>+3</sup>	Sm <sup>+3</sup>	Tm <sup>+3</sup>	Y <sup>+3</sup>
5	27.1	21.6	16	30.2	20.6	28.2	20.0
10	42.5	33.3	25	47.9	31.4	43.9	30.6
30	69.4	57.6	53	80.3	55.3	71.9	60.7
65	87.4	77.5	71	95.1	78.2	89.8	80.7
100	94.3	87.9	82	98.6	88.3	95.7	90.1
170	98.6	96.2	94	99.7	96.8	99.1	97.5
240	99.7	98.8	98	99.9	99.1	99.8	99.5

Standard Deviations for Yb<sup>+3</sup> Extraction Percentages

Time (min)	Standard Deviations on Yb <sup>+3</sup> Extraction Percentages in Mixtures With:						
	Dy <sup>+3</sup>	Eu <sup>+3</sup>	Nd <sup>+3</sup>	Sc <sup>+3</sup>	Sm <sup>+3</sup>	Tm <sup>+3</sup>	Y <sup>+3</sup>
5	2.3	1.8	2.6	0.5	2.8	2.5	2.6
10	0.6	1.8	2.9	2.3	3.6	2.7	2.8
30	1.0	1.5	3.6	0.3	1.3	1.9	5.2
65	0.6	1.9	4.2	0.3	0.9	1.3	0.7
100	0.8	1.3	3.8	0.1	1.1	0.7	0.6
170	0.3	0.7	3.8	0.1	0.9	0.2	0.3
240	0.1	0.3	1.2	0.1	0.4	0.0	0.3

## VITA

Angela Denise Brooks was born in Knoxville, TN on November 22, 1968. She was raised in Knoxville, attending Cedar Bluff School through grade seven and switched to Bearden for grades eight through eleven. She graduated from Farragut High School in 1987 and began attending the University of Tennessee, Knoxville in the fall of 1987. She received a B.S. degree in mathematics in 1995. From there she tutored for several years before beginning chemistry classes in 1998, and this led to a Master of Science degree in chemistry in 2003.

Angela currently works for PETNET Pharmaceuticals, Inc. in Knoxville, Tennessee.

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