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An equilibrium study of the chloride and nitrate systems of praseodymium and neodymium with tributyl phosphate and acid

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AN EQUILIBRIUM STUDY OF THE CHLORIDE AND NITRATE SYSTEMS OF
PRASEODYMIUM AND NEODYMIUM WITH TRIBUTYL PHOSPHATE AND ACID

by

James Arthur Gray

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Approved:

Signature was redacted for privacy.
In Charge of Major Work

Signature was redacted for privacy.
Head of Major Department

Signature was redacted for privacy.
Dean of Graduate College

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Of Science and Technology
Ames, Iowa
1965
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M, N - trivalent rare-earth cations.
A - monovalent anion.
K - equilibrium constant.
\( (E^0)_{M} \) - distribution coefficient—the concentration of M-containing species in organic phase divided by the concentration of M-containing species in aqueous phase.
\( T(E^0)_{M} \) - thermodynamic distribution coefficient—activities rather than concentrations used in definition of distribution coefficient.
\( \beta_{M/N} \) - separation factor—ratio of distribution coefficients of M and N.
\( T\beta_{M/N} \) - thermodynamic separation factor—activities rather than concentrations used in definition of separation factor.
\( \beta_{iM} \) - stability constants, \( i = 1, 2, 3 \).
\( \gamma \) - activity coefficient of specie in subscript.
\( \gamma_{X^+} \) - average activity coefficient of aqueous phase species of M.
\( [\cdot]_o \) - activity of organic phase specie.
\( [\cdot]_a \) - activity of aqueous phase specie.
\( (\cdot)_o \) - concentration of organic phase specie.
\( (\cdot)_a \) - concentration of aqueous phase specie.
INTRODUCTION

The lanthanides, or rare earths, consist of elements 57-71 in the periodic table. Proceeding from lanthanum to lutetium, each new element is formed by the addition of a single electron to the 4f shell. Since the electrons are being added to an inner shell, rather than to an outer shell, many of the chemical properties of the rare earths are similar, especially in aqueous solutions.

Although called "rare earths", the lanthanides are more abundant than such common elements as copper, zinc, and lead, and many ores contain appreciable amounts of them in concentrated form. Because of their chemical similarity, the development of separation processes has long been a challenge to the chemist and chemical engineer.

The first rare earths were separated by a long tedious series of fractional crystallizations. Spedding and Powell (1) developed ion-exchange methods which are used to produce very pure lanthanides. Another possible method being developed is solvent extraction. Because solvent extraction has been successfully applied to separating many other metallic mixtures, it has also been considered as a technique for separating the rare earths.

This study was a part of an intensive effort in the Chemical Engineering Division of Ames Laboratory to understand better the technique of solvent extraction of the rare earths. The systems chosen to work with were \( \text{Nd(NO}_3\text{)}_3-\text{Pr(NO}_3\text{)}_3-\text{HNO}_3-\text{H}_2\text{O-TBP} \) and \( \text{NdCl}_3-\text{PrCl}_3-\text{HCl-} \text{H}_2\text{O-TBP} \) where TBP refers to tri-n-butyl phosphate. It is believed that neodymium and praseodymium represent two typical adjacent rare earths that are available.
in the necessary purity and quantity required for this work. TBP is probably the most common solvent used in previous research in this area, and it is also a very common solvent for industrial solvent extraction processes.

The purpose of this particular study was to use these rather specific rare-earth systems and accomplish the following:

1. obtain precise distribution coefficient and separation factor data,
2. investigate the reasons for success of the empirical approaches of Sharp (2) and Bochinski (3) who made the assumption that for the nitrate system the separation factor was a function of the total concentration of the rare earths present and was not dependent upon the ratios of the two rare earths,
3. compare the solvent extraction characteristics of similar chloride and nitrate systems,
4. attempt to determine the reasons why the separation factor changes with concentration.
LITERATURE REVIEW

Since the early 1940's, interest in the general field of solvent extraction has grown very rapidly. Diamond and Tuck (4) presented an excellent review of the general field of solvent extraction with 325 references in 1958. Marcus (5) extended Diamond and Tuck's review of the literature to 1962 in an article with 465 references.

Two of the earliest publications concerning solvent extraction of the rare earths were by Fischer et al. (6) in 1937 and by Appleton and Selwood (7) in 1941. Since then many varied approaches to rare-earth extraction have been reported in the literature.

Blake et al. (8) characterized the organophosphorus solvents as being either acidic or neutral compounds. They pointed out that the acidic organophosphorus compounds usually extract by a cation exchange between the metal ion being extracted and the hydrogen ion of the acidic solvent. The neutral organophosphorus compounds, on the other hand, extract a neutral specie from the aqueous phase and would be expected to be more efficient in concentrated aqueous solutions of rare earths where a greater fraction of the total rare earth present would be in the extractable neutral form. It also follows that the acidic organophosphorus compounds would be best in dilute aqueous solutions, since the ionic specie is being extracted. Hardy (9) and Peppard and Mason (10) presented more detailed studies of the extraction of various metals and acids by acidic organophosphorus solvents, and Burger (11) and Nikolaev et al. (12) surveyed some of the interesting properties of the neutral organophosphorus solvents.
Peppard (13) published a very good review of the extraction of the rare earths using both neutral and acidic organophosphorus solvents.

In 1952 Topp (14) made a preliminary study of the distribution of neodymium and samarium nitrates between 12 normal HNO$_3$ and TBP diluted with Varsol and observed that the distribution coefficient decreased with decreasing rare-earth concentration. He suggested that this was due to the decrease in total nitrate-ion concentration in the solution. Gray (15), using tracer methods in the rare-earth chloride-TBP system, noted that at high acid concentration the distribution coefficient increased with increasing atomic number, and, at lower acid concentrations, the distribution coefficients of the rare earths apparently converged.

Topp and Weaver (16) obtained distribution coefficient data for some pure rare-earth nitrates between TBP and HNO$_3$, with a HNO$_3$ concentration range of 8.5-17 normal and with a rare-earth concentration range of 3-80 grams of oxide per liter. They concluded that the dependency of the distribution coefficient on rare-earth concentration increases with increasing acidity and with increasing atomic number of the rare-earth. These conclusions were generalized for the rare-earth series based on data for samarium, gadolinium and dysprosium.

Knapp (17) investigated the distribution of the pure heavier rare-earth nitrates as well as the lighter rare-earth nitrates in the presence of no excess acid. Knapp's data, like Topp and Weaver's (16), showed that the extractability of the pure lighter rare earths increased with increasing atomic number. However, Knapp found that dysprosium exhibited the maximum extractability of the rare earths, and that rare earths with atomic numbers
greater than dysprosium had lower distribution coefficients. Knapp also investigated the influence of salting-out agents (non-extractable inorganic nitrates) and nitric acid on the distribution coefficient of rare-earth mixtures. He found that salting-out agents increased the distribution coefficients of the mixtures and had much the same effect on the separation factors as increasing the concentration of the rare earths. The effect of the salting-out agent was shown to be greater for salts and acids with higher ionic strengths. Up to five normal acid, the distribution coefficients for the rare earths decreased with addition of acid. Above five normal, further addition of acid increased the distribution coefficients.

Peppard et al. (18) carried out distribution studies, using tracer methods, on many of the rare-earth nitrates at several different levels of acidity. A plot of the logarithm of the distribution coefficient versus the atomic number was essentially two straight lines intersecting at atomic number 64 (gadolinium). The slope of the line for the heavier lanthanides was shown to change from negative to positive with increasing acid concentrations. They pointed out that the intersection of the two lines occurs at the point where the 4f electron shell is half-filled.

Hesford and McKay, Hesford et al., and Scargill et al. in a series of articles (19-21) showed that all of the lanthanides appeared to form a trisolvated complex $M(NO_3)_3\cdot3\text{TBP}$ in the organic phase ($M$ represents any particular rare earth). Tracer methods were used and the solvent was one to five percent TBP in kerosene. The general reaction

$$q\text{TBP} + M^{3+} + 3NO_3^- \rightarrow M(NO_3)_3\cdot q\text{TBP}$$
was assumed. Assuming that the formation of the neutral rare-earth nitrate is a stepwise reaction, the following species would be present in the aqueous phase: $M^{+3}$, $M(NO_3)^{+2}$, $M(NO_3)^{+1}$, and $M(NO_3)_3$. The equilibrium constant for the general reaction, where the brackets refer to activities, is

$$K = \frac{[M(NO_3)_3 \cdot q TBP]_o}{[M^{+3}]_a [NO_3^{-3}]_a [TBP]^q}$$

or $[M(NO_3)_3 \cdot q TBP]_o = K [M^{+3}]_a [NO_3^{-3}]_a [TBP]^q$. The distribution coefficient is defined as

$$\left( E^0_a \right)_M = \frac{[M(NO_3)_3 \cdot q TBP]_o}{[M^{+3}]_a + [M(NO_3)^{+2}]_a + [M(NO_3)^{+1}]_a + [M(NO_3)_3]_a} = \frac{K [M^{+3}]_a [NO_3^{-3}]_a [TBP]^q}{[M^{+3}]_a + [M(NO_3)^{+2}]_a + [M(NO_3)^{+1}]_a + [M(NO_3)_3]_a}.$$  

Since the aqueous phase was very dilute, and the organic phase was also dilute, both phases were assumed ideal, and the activities were assumed to be equal to the concentrations. Letting $f_o$ represent the fraction of the aqueous metal species in the completely ionized form, i.e.,

$$f_o = \frac{[M^{+3}]_a}{[M^{+3}]_a + [M(NO_3)^{+2}]_a + [M(NO_3)^{+1}]_a + [M(NO_3)_3]_a},$$

the distribution coefficient becomes
\[(E^o)_a M = K f_o [NO_3^-]^3_a [TBP]^q_o\]

or

\[\log (E^o)_a M = \log K f_o [NO_3^-]^3_a + q \log [TBP]^q_o\]

Since the aqueous phase was kept at a constant but very dilute concentration, the term \(K f_o [NO_3^-]^3_a\) was constant. The slope of a log-log plot of the change in \((E^o)_a M\) with variation of \([TBP]^q_o\) indicates the TBP solvation number of three.

Both Knapp (17) and Hesford and McKay (19) found that for aqueous phase concentrations of approximately five to seven normal in HNO_3 the distribution coefficients reached a minimum, and then increased with increasing acid concentration.

Robinson and Topp (22) obtained equilibrium data for the La(NO_3)_3-Pr(NO_3)_3-TBP-H_2O system. The data covered the more concentrated ranges rather than the usual tracer levels. The data, obtained by liquid counting techniques, confirmed the fact that the separation factor increases with concentration. Several experiments were conducted keeping the total rare-earth concentration constant, but varying the mole fraction of rare earths. Some of the experimental runs indicated that the separation factor increased with the mole fraction of praseodymium nitrate in the aqueous phase.

Bostian and Smutz (23) investigated the mechanism of extraction by TBP in neodymium nitrate solutions up to saturation. Infrared studies indicated that the complexing occurs at the P=O bond of the TBP. It was also concluded that the complexing reaction was
\[
\text{Nd(NO}_3\text{)}_3 + 3 \text{TBP} \cdot \text{H}_2\text{O} \rightarrow \text{Nd(NO}_3\text{)}_3 \cdot 3 \text{TBP} + 3 \text{H}_2\text{O}.
\]

These results, combined with similar results for dilute solutions (19-21), indicated that the complex \(\text{M(NO}_3\text{)}_3 \cdot 3 \text{TBP}\) was the complex formed over the full range of concentrations.

Nadig and Smutz (24), using infrared methods, measured the P=O shift caused by the rare-earth complex as a function of the atomic number. They found that the degree of the shift decreased with increasing atomic number. This indicates that the strength of the complex decreases with increasing atomic number.

Several interesting studies of the aqueous phase have been made. Saeger (25) worked with aqueous solutions of rare-earth chlorides over the concentration range of 0.1 molal to saturation. Saeger pointed out that although the ionic radius of the rare earths decreases with increasing atomic number, solvation and coordination effects complicate the situation. As the ionic radius becomes smaller, it is possible for the rare-earth ion to have a smaller coordination number. Pikal\(^1\) shows that for the rare-earth chlorides, the partial molal volume decreases with increasing atomic number from lanthanum to neodymium and from terbium to ytterbium, however, it increases from neodymium to terbium. Since the volume in a solution of a free-water molecule is greater than the volume of a hydrated water molecule, a decrease in coordination number would cause an increase in the

\(^1\)Pikal, M. J., Ames Laboratory of the AEC, Ames, Iowa. Partial molal volumes of some rare-earth chlorides and nitrates and their relationships to the hydration numbers. Private communication. 1965.
partial molal volume. Assuming that a rare-earth ion can exist in equilibrium between two coordination numbers, Pikal postulates that between neodymium and terbium a gradual change in the coordination number takes place. Thus, Pikal believes that from lanthanum to neodymium a coordination number of nine is greatly favored, from neodymium to terbium a gradual displacement of the equilibrium toward the lower coordination number takes place, and between terbium and ytterbium a coordination number of eight is greatly favored.

In an effort to determine more quantitatively the species present in the aqueous phase, Peppard et al. (26) used acid-dependency studies to measure the stability constants for the reaction \( \text{M}^{3+} + \text{A}^- \rightarrow \text{MA}^{2+} \) for many of the lanthanide chlorides and nitrates. The chloride data showed that the stability constants were approximately constant for the lighter rare earths and decreased slightly for the heavier rare-earth chlorides.

Goto and Smutz (27) used a potentiometric method to determine the stability constant for \( \text{MCl}^{+2} \). The data showed that from a statistical viewpoint, there was no significant trend for the lighter rare-earth chlorides. Attempts to determine the stability constants of \( \text{MCl}_2^{+1} \) and \( \text{MCl}_3 \) were not successful.
EXPERIMENTAL PROCEDURE

Reagents

The rare earths used in this work were obtained as the oxides from the Rare-Earth Separation Group of Ames Laboratory of the Atomic Energy Commission. The purity of all rare-earth oxides was greater than 99.9 percent as determined by emission spectroscopy.

The TBP used was Fisher Scientific Company purified grade tri-n-butyl phosphate. All TBP used was washed three to four times with demineralized water, and stored in contact with water to insure saturation with water.

All acids used were reagent grade.

Preparation of Rare-Earth Stock Solutions

Both rare-earth chloride and nitrate solutions were prepared from the pure rare-earth oxides by reaction with an excess amount of hydrochloric or nitric acid. Because the preparation procedures for both rare-earth nitrate and chloride solutions are similar only the nitrate preparation will be discussed.

The general reaction is:

\[ \text{M}_2\text{O}_3 + 6\text{HNO}_3 \rightarrow 2\text{M(NO}_3)_2 + 3\text{H}_2\text{O} \]

The method is complicated by the following hydrolysis reaction:

\[ \text{M}^{+3} + \text{H}_2\text{O} \rightarrow \text{M(OH)}^{+2} + \text{H}^{+1} \]

When the excess acid is boiled off, the system is acid deficient due to the substitution of the hydroxide ion for the nitrate ion on some of the
rare-earth ions. In order to overcome this, the hydroxide is titrated with acid. The titration can be followed with a pH-meter, and the endpoint determined from a plot of pH versus milliliters of acid added. The endpoint of this titration, called the equivalence point, is where the ratio of rare earth to nitrate is 1:3.

After the solution has been adjusted to its equivalence point, it is heated to near its boiling point for several hours to react any colloidal oxide or hydroxide still present. If either of these reactions occur, the pH increases above the equivalence point, and the pH must be adjusted again. Usually after three or four cycles, the pH remains constant and a clear stable solution is obtained.

Separation Factor Studies

In order to determine if the separation factor was a function of only the total concentration of the rare earths present, and not dependent upon the ratio of the two rare earths, the following general type of run was performed. An initial aqueous phase total rare-earth concentration was chosen. Separate primary stock solutions of praseodymium and neodymium (chlorides or nitrates) were adjusted to the chosen rare-earth concentration. To determine the total rare-earth content of the stock solutions, the EDTA titration method of Fritz et al. (28) was used with hexamethylenetetramine as a buffer and xylenol orange as the indicator. These primary solutions were mixed to give secondary stock solutions of specified mole ratios of praseodymium to neodymium. In most runs the mole ratios used were 1:99, 20:80, 50:50, 80:20, and 99:1.
Specified volumes of these secondary stock solutions were weighed and added to a weighed amount of water-washed water equilibrated TBP in a separatory funnel. The phases were shaken vigorously for three minutes, allowed to stand a minimum of twelve hours, separated and sampled. The rare earth in the organic phase sample was back extracted into an acidified aqueous phase three to four times to remove all of the rare earth from the organic phase. The rare earths from both the aqueous and the organic phases were then precipitated with oxalic acid and ignited to the oxides in the usual method.

The method of Adams and Campbell (29) was used to determine the acidity of the aqueous phase for the runs in which a large excess of acid was present. The method consists of passing the rare-earth solution through a column of Dowex 50W-X-8 cation exchange resin in the hydrogen form. The effluent from the column was titrated with a standardized solution of NaOH. The acidity of the initial sample was obtained after making proper allowance for the rare earth in the sample.

Spectrophotometric Methods of Analysis

Spectrophotometric methods were used to analyze the praseodymium and neodymium oxide mixtures from the organic and aqueous phases. The general spectrophotometric method of Banks and Klingman (30) was used for the oxide samples from the experimental runs with initial aqueous mole ratios of 20:80, 50:50, and 80:20.

The analysis of the oxides from the runs with an initial aqueous phase mole ratio of 1:99 and 99:1 was somewhat more complex, and will be
discussed in detail. The procedure is a modification of the differential spectrophotometric method of Banks et al. (31). This method consists of comparing the absorbance of the unknown sample with the absorbancies of a set of standard solutions on a Beckman DU spectrophotometer. Linear interpolation is used to obtain the concentration of the unknown. The procedures used for praseodymium and neodymium are discussed in the following paragraphs.

The praseodymium absorbancies were read at a wavelength of 445 μm and a slit width of 0.04 mm on the spectrophotometer. Each standard and unknown was also read at 400 μm. At 400 μm neither praseodymium nor neodymium should absorb light. If any reading was obtained, it was assumed to be a constant background over the wavelength range used, and this reading was subtracted from the absorbancy of the solution at 445 μm. It was also found that neodymium has a slight absorbancy at 445 μm, and if a large amount of neodymium was present, as was the case in the lPr:99Nd samples, the neodymium absorbancy also had to be taken into account.

The neodymium absorbancy was read at 795 μm and a slit width of 0.03 mm. Here again, the constant background was measured at 700 μm and subtracted from the absorbancy of the solution at 795 μm. It was found that praseodymium had no absorbancy at 795 μm.
EXPERIMENTAL RESULTS

A summary of the initial conditions for all of the experimental runs performed is shown in Table 1. The first set of experimental runs was designed to evaluate statistically whether the following analysis variables were important:

1. the order of analysis of the samples on the spectrophotometer,
2. the day of analysis on the spectrophotometer,
3. the set of experiments from which the sample was taken (for instance, comparing samples from sets A and B, where A and B were duplicate experiments),
4. which sample was taken from a specific set of experiments (for instance, comparing samples 1 and 2 which were taken from the same solution).

Each of the above variables was found to be unimportant.

Five runs were made with the Pr(NO$_3$)$_3$-Nd(NO$_3$)$_3$-HNO$_3$-H$_2$O-TBP system. Three runs were made in which the initial feed solution contained no excess acid, the pertinent variable being the initial rare-earth concentration. The results of these three runs are shown in Tables 2, 3 and 4. In order to determine the effect of the acid concentration for the nitrate system, a medium- and a high-acid run were completed at the intermediate level of rare-earth concentration. The results of these two runs are shown in Tables 5 and 6.

The PrCl$_3$-NdCl$_3$-HCl-H$_2$O-TBP system results are shown in Tables 7 thru 12. Runs 6 and 7 shown in Tables 7 and 8 had exactly the same initial
Table 1. Summary of runs performed

<table>
<thead>
<tr>
<th>Run</th>
<th>Rare earths used</th>
<th>Anion</th>
<th>Initial rare-earth concentration moles HA₃ per liter</th>
<th>Initial acid concentration</th>
<th>Mole ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Nd,Pr</td>
<td>NO₃⁻</td>
<td>2.97</td>
<td>0</td>
<td>1:99, 50:50, 99:1</td>
</tr>
<tr>
<td>2</td>
<td>Nd,Pr</td>
<td>NO₃⁻</td>
<td>0.30</td>
<td>0</td>
<td>1:99, 50:50, 99:1</td>
</tr>
<tr>
<td>3</td>
<td>Nd,Pr</td>
<td>NO₃⁻</td>
<td>0.99</td>
<td>0</td>
<td>1:99, 20:80, 50:50, 80:20, 99:1</td>
</tr>
<tr>
<td>4</td>
<td>Nd,Pr</td>
<td>NO₃⁻</td>
<td>0.99</td>
<td>5.85N HNO₃</td>
<td>1:99, 20:80, 50:50, 80:20, 99:1</td>
</tr>
<tr>
<td>5</td>
<td>Nd,Pr</td>
<td>NO₃⁻</td>
<td>0.97</td>
<td>10.9N HNO₃</td>
<td>1:99, 20:80, 50:50, 80:20, 99:1</td>
</tr>
<tr>
<td>6</td>
<td>Nd,Pr</td>
<td>Cl⁻</td>
<td>3.22</td>
<td>0</td>
<td>1:99, 20:80, 50:50, 80:20, 99:1</td>
</tr>
<tr>
<td>7</td>
<td>Nd,Pr</td>
<td>Cl⁻</td>
<td>3.22</td>
<td>0</td>
<td>1:99, 20:80, 50:50, 80:20, 99:1</td>
</tr>
<tr>
<td>8</td>
<td>Nd,Pr</td>
<td>Cl⁻</td>
<td>3.22</td>
<td>pH=1.35</td>
<td>1:99, 20:80, 50:50, 80:20, 99:1</td>
</tr>
<tr>
<td>9</td>
<td>Nd,Pr</td>
<td>Cl⁻</td>
<td>3.22</td>
<td>pH=0</td>
<td>1:99, 20:80, 50:50, 80:20, 99:1</td>
</tr>
<tr>
<td>10</td>
<td>Nd,Pr</td>
<td>Cl⁻</td>
<td>0.53</td>
<td>0</td>
<td>1:99, 20:80, 50:50, 80:20, 99:1</td>
</tr>
<tr>
<td>11</td>
<td>Nd,Pr</td>
<td>Cl⁻</td>
<td>2.0</td>
<td>0</td>
<td>20:80, 50:50, 80:20</td>
</tr>
<tr>
<td>12</td>
<td>Nd,Pr</td>
<td>Cl⁻</td>
<td>2.0</td>
<td>1.05N HCl</td>
<td>20:80, 50:50, 80:20</td>
</tr>
<tr>
<td>13</td>
<td>Nd,Pr</td>
<td>Cl⁻</td>
<td>2.0</td>
<td>2.9N HCl</td>
<td>20:80, 50:50, 80:20</td>
</tr>
<tr>
<td>14</td>
<td>Sm,Nd</td>
<td>Cl⁻</td>
<td>2.0</td>
<td>1.05N HCl</td>
<td>20:80, 50:50, 80:20</td>
</tr>
</tbody>
</table>
Table 2. Run 1—Pr(NO$_3$)$_3$-Nd(NO$_3$)$_3$-TBP-H$_2$O system with initial aqueous phase concentration of 2.97 moles M(NO$_3$)$_3$/liter and no acid

<table>
<thead>
<tr>
<th>Mole ratios</th>
<th>Separation factor with 95% confidence interval</th>
<th>Average distribution coefficient</th>
<th>Average final concentrations moles M(NO$_3$)$_3$/1000 Gms solution</th>
<th>Number of duplications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr:Nd</td>
<td>$\frac{\beta_{Nd/Pr}}{}$</td>
<td>$(E^0)<em>{Pr}$ $(E^0)</em>{Nd}$</td>
<td>$(Pr)_a$ $(Nd)_a$ $(Pr)_o$ $(Nd)_o$</td>
<td></td>
</tr>
<tr>
<td>1:99</td>
<td>1.48±0.02</td>
<td>0.359</td>
<td>0.0170</td>
<td>1.614</td>
</tr>
<tr>
<td>50:50</td>
<td>1.52±0.01</td>
<td>0.418</td>
<td>0.828</td>
<td>0.816</td>
</tr>
<tr>
<td>99:1</td>
<td>1.50±0.02</td>
<td>0.521</td>
<td>1.615</td>
<td>0.0165</td>
</tr>
</tbody>
</table>
Table 3. Run 2—Pr(NO$_3$)$_3$-Nd(NO$_3$)$_3$-TBP-H$_2$O system with initial aqueous phase concentration of 0.30 moles M(NO$_3$)$_3$/liter and no acid

<table>
<thead>
<tr>
<th>Mole ratios</th>
<th>Separation factor with 95% confidence interval</th>
<th>Average distribution coefficient</th>
<th>Average final concentrations moles M(NO$_3$)$_3$/1000 Gms solution</th>
<th>Number of duplications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr:Nd</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1:99</td>
<td>$1.07 \pm 0.02$</td>
<td>0.142 0.152</td>
<td>0.00244 0.236 0.000347 0.0358</td>
<td>8</td>
</tr>
<tr>
<td>50:50</td>
<td>$1.08 \pm 0.01$</td>
<td>0.143 0.154</td>
<td>0.119 0.120 0.0170 0.0185</td>
<td>8</td>
</tr>
<tr>
<td>99:1</td>
<td>$1.09 \pm 0.02$</td>
<td>0.141 0.154</td>
<td>0.235 0.00239 0.0332 0.00368</td>
<td>8</td>
</tr>
</tbody>
</table>
Table 4. Run 3—Pr(NO$_3$)$_3$-Nd(NO$_3$)$_3$-TBP-H$_2$O system with initial aqueous phase concentration of 0.99 moles M(NO$_3$)$_3$/liter and no acid

<table>
<thead>
<tr>
<th>Mole ratios</th>
<th>Separation factor with 95% confidence interval</th>
<th>Average distribution coefficient</th>
<th>Average final concentrations moles M(NO$_3$)$_3$/1000 Gms solution</th>
<th>Number of duplications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr:Nd</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1:99</td>
<td>$\beta_{Nd/Pr}$ = 1.15±0.06</td>
<td>$E_a^{O}<em>{Pr}$ = 0.642 $E_a^{O}</em>{Nd}$ = 0.741</td>
<td>(Pr)$<em>a$ = 0.00661 $N_d$ = 0.613 $E_a^{O}</em>{Pr}$ = 0.00424 $E_a^{O}_{Nd}$ = 0.454</td>
<td>3</td>
</tr>
<tr>
<td>20:80</td>
<td>$\beta_{Nd/Pr}$ = 1.15±0.01</td>
<td>$E_a^{O}<em>{Pr}$ = 0.655 $E_a^{O}</em>{Nd}$ = 0.753</td>
<td>(Pr)$<em>a$ = 0.1305 $N_d$ = 0.494 $E_a^{O}</em>{Pr}$ = 0.0855 $E_a^{O}_{Nd}$ = 0.372</td>
<td>4</td>
</tr>
<tr>
<td>50:50</td>
<td>$\beta_{Nd/Pr}$ = 1.14±0.01</td>
<td>$E_a^{O}<em>{Pr}$ = 0.669 $E_a^{O}</em>{Nd}$ = 0.765</td>
<td>(Pr)$<em>a$ = 0.320 $N_d$ = 0.310 $E_a^{O}</em>{Pr}$ = 0.214 $E_a^{O}_{Nd}$ = 0.237</td>
<td>4</td>
</tr>
<tr>
<td>80:20</td>
<td>$\beta_{Nd/Pr}$ = 1.15±0.02</td>
<td>$E_a^{O}<em>{Pr}$ = 0.690 $E_a^{O}</em>{Nd}$ = 0.792</td>
<td>(Pr)$<em>a$ = 0.507 $N_d$ = 0.122 $E_a^{O}</em>{Pr}$ = 0.350 $E_a^{O}_{Nd}$ = 0.0966</td>
<td>4</td>
</tr>
<tr>
<td>99:1</td>
<td>$\beta_{Nd/Pr}$ = 1.13±0.02</td>
<td>$E_a^{O}<em>{Pr}$ = 0.694 $E_a^{O}</em>{Nd}$ = 0.784</td>
<td>(Pr)$<em>a$ = 0.624 $N_d$ = 0.00626 $E_a^{O}</em>{Pr}$ = 0.433 $E_a^{O}_{Nd}$ = 0.00491</td>
<td>4</td>
</tr>
</tbody>
</table>
Table 5. Run 4—Pr(NO$_3$)$_3$-Nd(NO$_3$)$_3$-HNO$_3$-H$_2$O-TBP system with initial aqueous phase concentration of 0.99 moles M(NO$_3$)$_3$/liter and 5.85N HNO$_3$

<table>
<thead>
<tr>
<th>Mole ratios</th>
<th>Separation factor with 95% confidence interval</th>
<th>Average distribution coefficient</th>
<th>Average final concentrations moles M(NO$_3$)$_3$/1000 Gms solution</th>
<th>Final aqueous acidity</th>
<th>Moles HNO$_3$ Liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr: Nd</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1:99$^a$</td>
<td>1.45±0.02</td>
<td>0.180 0.262</td>
<td>0.00715 0.663 0.00129 0.174</td>
<td>4.77</td>
<td></td>
</tr>
<tr>
<td>20:80$^a$</td>
<td>1.42±0.01</td>
<td>0.189 0.268</td>
<td>0.141 0.537 0.0267 0.144</td>
<td>4.80</td>
<td></td>
</tr>
<tr>
<td>50:50$^a$</td>
<td>1.41±0.01</td>
<td>0.197 0.277</td>
<td>0.345 0.334 0.0678 0.0926</td>
<td>4.71</td>
<td></td>
</tr>
<tr>
<td>80:20$^a$</td>
<td>1.43±0.03</td>
<td>0.204 0.292</td>
<td>0.548 0.130 0.112 0.0380</td>
<td>4.66</td>
<td></td>
</tr>
<tr>
<td>99:1$^a$</td>
<td>1.40±0.02</td>
<td>0.210 0.295</td>
<td>0.666 0.00664 0.140 0.00196</td>
<td>4.68</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Number of duplications = 4.
Table 6. Run 5—Pr(NO₃)₃-Nd(NO₃)₃-HNO₃-H₂O-TBP system with initial aqueous phase concentration of 0.97 moles M(NO₃)₃/liter and 10.9N HNO₃

<table>
<thead>
<tr>
<th>Mole ratios</th>
<th>Separation factor with 95% confidence interval</th>
<th>Average distribution coefficient</th>
<th>Average final concentrations moles M(NO₃)₃/1000 Gms solution</th>
<th>Final aqueous acidity</th>
<th>Molar HNO₃/Liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr:Nd</td>
<td>βNd/Pr</td>
<td>(E°)ₐPr (E°)ₐNd</td>
<td>(Pr)ₐ (Nd)ₐ (Pr)₀ (Nd)₀</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1:99</td>
<td>1.67±0.05</td>
<td>0.214 0.357</td>
<td>0.00662 0.599 0.00142 0.214</td>
<td>9.48</td>
<td></td>
</tr>
<tr>
<td>20:80</td>
<td>1.60±0.04</td>
<td>0.232 0.370</td>
<td>0.132 0.486 0.0306 0.180</td>
<td>9.40</td>
<td></td>
</tr>
<tr>
<td>50:50</td>
<td>1.57±0.04</td>
<td>0.253 0.397</td>
<td>0.317 0.300 0.0803 0.119</td>
<td>9.41</td>
<td></td>
</tr>
<tr>
<td>80:20</td>
<td>1.58±0.03</td>
<td>0.269 0.424</td>
<td>0.509 0.118 0.137 0.050</td>
<td>9.48</td>
<td></td>
</tr>
<tr>
<td>99:1</td>
<td>1.57±0.05</td>
<td>0.280 0.441</td>
<td>0.621 0.00610 0.174 0.00269</td>
<td>9.41</td>
<td></td>
</tr>
</tbody>
</table>

a Number of duplications = 8.

b Number of duplications = 4.
Table 7. Run 6—PrCl₃-NdCl₃-TBP-H₂O system with initial aqueous phase concentration of 3.22 moles MCl₃/liter and no acid

<table>
<thead>
<tr>
<th>Mole ratios</th>
<th>Separation factor with 95% confidence interval</th>
<th>Average distribution coefficient</th>
<th>Average final concentrations moles MCl₃/1000 Gms solution</th>
<th>Number of duplications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr:Nd</td>
<td>$\beta_{Nd/Pr}$</td>
<td>$(e^{0})<em>{Pr}$ $(e^{0})</em>{Nd}$</td>
<td>$(Pr)<em>{a}$ $(Nd)</em>{a}$ $(Pr)<em>{o}$ $(Nd)</em>{o}$</td>
<td></td>
</tr>
<tr>
<td>1:99</td>
<td>$0.91 \pm 0.03$</td>
<td>0.0831 0.0753</td>
<td>0.0189 1.846 0.00157 0.139</td>
<td>4</td>
</tr>
<tr>
<td>20:80</td>
<td>$0.91 \pm 0.01$</td>
<td>0.0820 0.0743</td>
<td>0.367 1.494 0.0301 0.111</td>
<td>5</td>
</tr>
<tr>
<td>50:50</td>
<td>$0.90 \pm 0.01$</td>
<td>0.0783 0.0704</td>
<td>0.923 0.939 0.0723 0.0661</td>
<td>5</td>
</tr>
<tr>
<td>80:20</td>
<td>$0.90 \pm 0.02$</td>
<td>0.0767 0.0691</td>
<td>1.474 0.369 0.113 0.0255</td>
<td>5</td>
</tr>
<tr>
<td>99:1</td>
<td>$0.92 \pm 0.02$</td>
<td>0.0765 0.0705</td>
<td>1.857 0.0193 0.142 0.00136</td>
<td>4</td>
</tr>
</tbody>
</table>
Table 8. Run 7—PrCl$_3$-NdCl$_3$-TBP-H$_2$O system with initial aqueous phase concentration of 3.22 moles MCl$_3$/liter and no acid

<table>
<thead>
<tr>
<th>Mole ratios</th>
<th>Separation factor with 95% confidence interval</th>
<th>Average distribution coefficient</th>
<th>Average final concentrations moles MCl$_3$/1000 Gms solution</th>
<th>Number of duplications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr: Nd</td>
<td>$\frac{\beta}{Nd/Pr}$</td>
<td>$(E^o)<em>{Pr}$ (E$^o)</em>{Nd}$</td>
<td>$(Pr)_a$ $(Nd)_a$ $(Pr)_o$ $(Nd)_o$</td>
<td></td>
</tr>
<tr>
<td>1:99</td>
<td>0.90±0.03</td>
<td>0.0883 0.0797</td>
<td>0.0180 1.844 0.00159 0.147</td>
<td>4</td>
</tr>
<tr>
<td>20:30</td>
<td>0.91±0.04</td>
<td>0.0843 0.0768</td>
<td>0.376 1.498 0.0317 0.115</td>
<td>4</td>
</tr>
<tr>
<td>50:50</td>
<td>0.90±0.01</td>
<td>0.0831 0.0751</td>
<td>0.937 0.935 0.0779 0.0702</td>
<td>4</td>
</tr>
<tr>
<td>80:20</td>
<td>0.93±0.03</td>
<td>0.0814 0.0757</td>
<td>1.498 0.371 0.122 0.0281</td>
<td>4</td>
</tr>
<tr>
<td>99:1</td>
<td>0.92±0.03</td>
<td>0.0796 0.0729</td>
<td>1.859 0.0192 0.148 0.0014</td>
<td>4</td>
</tr>
</tbody>
</table>
Table 9. Run 8—PrCl₃-NdCl₃-HCl-H₂O-TBP system with initial aqueous phase concentration of 3.22 moles MCl₃/liter and pH = 1.35

<table>
<thead>
<tr>
<th>Mole ratios Pr:Nd</th>
<th>Separation factor with 95% confidence interval</th>
<th>Average distribution coefficient</th>
<th>Average final concentrations moles MCl₃/1000 Gms solution</th>
<th>Final aqueous pH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>β₀Nd/Pr</td>
<td>(E_a)₀Pr, (E_a)₀Nd</td>
<td>(Pr)ₐ, (Nd)ₐ, (Pr)₀, (Nd)₀</td>
<td></td>
</tr>
<tr>
<td>1:99</td>
<td>0.89±0.01</td>
<td>0.0824, 0.0729</td>
<td>0.0193, 1.352, 0.00159, 0.135</td>
<td>1.86</td>
</tr>
<tr>
<td>20:80</td>
<td>0.90±0.01</td>
<td>0.0807, 0.0723</td>
<td>0.369, 1.493, 0.0298, 0.108</td>
<td>1.85</td>
</tr>
<tr>
<td>50:50</td>
<td>0.90±0.01</td>
<td>0.0788, 0.0709</td>
<td>0.924, 0.937, 0.0728, 0.0664</td>
<td>1.86</td>
</tr>
<tr>
<td>80:20</td>
<td>0.90±0.01</td>
<td>0.0764, 0.0686</td>
<td>1.479, 0.370, 0.113, 0.0254</td>
<td>1.83</td>
</tr>
<tr>
<td>99:1</td>
<td>0.92±0.02</td>
<td>0.0741, 0.0682</td>
<td>1.862, 0.0192, 0.138, 0.00131</td>
<td>1.83</td>
</tr>
</tbody>
</table>

*aNumber of duplications = 8.*
Table 10. Run 9—PrCl₃-NdCl₃-HCl-H₂O-TBP system with initial aqueous phase concentration of 3.22 moles MCl₃/liter and pH = 0.0

<table>
<thead>
<tr>
<th>Mole ratios of Pr:Nd</th>
<th>Separation factor with 95% confidence interval</th>
<th>Average distribution coefficient</th>
<th>Average Final concentrations moles MCl₃/1000 Gms solution</th>
<th>Final aqueous pH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>βNd/Pr</td>
<td>(E⁰a)Pr (E⁰a)Nd</td>
<td>(Pr)ₐ (Nd)ₐ (Pr)₀ (Nd)₀</td>
<td></td>
</tr>
<tr>
<td>1:99ᵃ</td>
<td>0.90±0.02</td>
<td>0.0762 0.0686</td>
<td>0.0193 1.838 0.00147 0.126</td>
<td>0.55</td>
</tr>
<tr>
<td>20:80ᵃ</td>
<td>0.90±0.01</td>
<td>0.0772 0.0692</td>
<td>0.373 1.489 0.0288 0.103</td>
<td>0.57</td>
</tr>
<tr>
<td>50:50ᵃ</td>
<td>0.91±0.01</td>
<td>0.0785 0.0714</td>
<td>0.932 0.929 0.0732 0.0663</td>
<td>0.61</td>
</tr>
<tr>
<td>80:20ᵃ</td>
<td>0.92±0.02</td>
<td>0.0783 0.0718</td>
<td>1.494 0.369 0.117 0.0265</td>
<td>0.60</td>
</tr>
<tr>
<td>99:1ᵃ</td>
<td>0.94±0.04</td>
<td>0.0789 0.0745</td>
<td>1.863 0.0188 0.147 0.00140</td>
<td>0.62</td>
</tr>
</tbody>
</table>

ᵃNumber of duplications = 4.
Table 11. Run 12—PrCl₃-NdCl₃-HCl-H₂O-TBP system with initial aqueous phase concentration of 2.0 moles MCl₃/liter and 1.05N HCl

<table>
<thead>
<tr>
<th>Mole ratios</th>
<th>Separation factor with 95% confidence interval</th>
<th>Average distribution coefficient</th>
<th>Average final concentrations moles MCl /1000 Gms solution</th>
<th>Final aqueous acidity Moles HCl/Liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr:Nd</td>
<td>β</td>
<td>(E₀)ₚr</td>
<td>(E₀)ₐNd</td>
<td>(Pr)ₐ</td>
</tr>
<tr>
<td>20:80ᵃ</td>
<td>1.00±0.03</td>
<td>0.00616</td>
<td>0.00618</td>
<td>0.289</td>
</tr>
<tr>
<td>50:50ᵃ</td>
<td>0.98±0.02</td>
<td>0.00659</td>
<td>0.00649</td>
<td>0.709</td>
</tr>
<tr>
<td>80:20ᵃ</td>
<td>1.00±0.08</td>
<td>0.00635</td>
<td>0.00638</td>
<td>1.134</td>
</tr>
</tbody>
</table>

ᵃNumber of duplications = 4.
Table 12. Run 13—PrCl₃-NdCl₃-HCl-H₂O-TBP system with initial aqueous phase concentration of 2.0 moles MCl₃/liter and 2.9N HCl

<table>
<thead>
<tr>
<th>Pr:Nd</th>
<th>Separation factor with 95% confidence interval</th>
<th>Average distribution coefficient</th>
<th>Average final concentrations moles MCl₃/1000 Gms solution</th>
<th>Final aqueous acidity</th>
<th>Moles HCl/Liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>20:80</td>
<td>$0.98 \pm 0.03$</td>
<td>0.0131 0.0128</td>
<td>0.295 1.158 0.00385 0.0148</td>
<td>2.02</td>
<td></td>
</tr>
<tr>
<td>50:50</td>
<td>$0.98 \pm 0.02$</td>
<td>0.0129 0.0126</td>
<td>0.729 0.727 0.00938 0.00917</td>
<td>2.04</td>
<td></td>
</tr>
<tr>
<td>80:20</td>
<td>$0.99 \pm 0.02$</td>
<td>0.0129 0.0128</td>
<td>1.164 0.286 0.0150 0.00365</td>
<td>2.05</td>
<td></td>
</tr>
</tbody>
</table>

a Number of duplications = 4.
conditions and were made to determine the reproducibility of results for the chloride system. The results of runs 8 and 9, shown in Tables 9 and 10, along with the results of the duplicate runs 6 and 7, were used to determine whether the formation of a small amount of non-extractable specie would appreciably affect the separation factor. As with the nitrate system, runs were made to determine the effect of rare-earth concentration when no acid was present and the effect of the initial acidity of the aqueous phase. The results of these runs are shown in Tables 10 thru 13.

In runs 10 and 11 no data were obtained because not enough rare earth was extracted into the organic phase to perform the necessary analytical work.

The data from run 14, shown in Table 13, was obtained with the NdCl$_3$-SmCl$_3$-HCl-H$_2$O-TBP system to compare the separation factor for this system with the PrCl$_3$-NdCl$_3$-HCl-H$_2$O-TBP system.
Table 13. Run 14—NdCl$_3$-SmCl$_3$-HCl-H$_2$O-TBP system with initial aqueous phase concentration of 2.0 moles MCl$_3$/liter and 1.05N HCl

<table>
<thead>
<tr>
<th>Mole ratios</th>
<th>Separation factor with 95% confidence interval</th>
<th>Average distribution coefficient</th>
<th>Average final concentrations moles MCl$_3$/1000 Gms solution</th>
<th>Final aqueous acidity</th>
<th>Final HCl moles/Liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd:Sm</td>
<td>$\beta_{Sm/Nd}$</td>
<td>$(E_a^O)_{Nd}$</td>
<td>$(E_a^O)_{Sm}$</td>
<td>$(Nd)_a$</td>
<td>$(Sm)_a$</td>
</tr>
<tr>
<td>20:80$^a$</td>
<td>1.41±0.02</td>
<td>0.00690</td>
<td>0.00971</td>
<td>0.281</td>
<td>1.133</td>
</tr>
<tr>
<td>50:50$^a$</td>
<td>1.47±0.04</td>
<td>0.00643</td>
<td>0.00943</td>
<td>0.691</td>
<td>0.707</td>
</tr>
<tr>
<td>80:20$^b$</td>
<td>1.54±0.07</td>
<td>0.00607</td>
<td>0.00936</td>
<td>1.117</td>
<td>0.280</td>
</tr>
</tbody>
</table>

$^a$Number of duplications = 6.

$^b$Number of duplications = 10.
DISCUSSION OF RESULTS

It is generally assumed (19,26,27) that the rare-earth containing species present in an aqueous rare-earth solution are $M^{+3}$, $MA^{+2}$, $MA_{2}^{+1}$, and $MA_{3}$, where $M$ refers to the rare earth and $A$ is a ligand such as chloride or nitrate. There is also the possibility of various forms of rare-earth hydroxides (25,32) however, these are present only in solutions whose pH is above its equivalence point, and will not be considered to be present in this work. Based on these assumptions, the following reactions occur in the aqueous phase:

\[ M^{+3} + A^{-1} \rightleftharpoons MA^{+2} \] \hspace{1cm} (1)

\[ M^{+3} + 2A^{-1} \rightleftharpoons MA_{2}^{+1} \] \hspace{1cm} (2)

\[ M^{+3} + 3A^{-1} \rightleftharpoons MA_{3} \] \hspace{1cm} (3)

Using these equations, the following stability constants can be written for $M$:

\[ \beta_{1M} = \frac{[MA^{+2}]_{a}}{[M^{+3}]_{a}[A^{-}]_{a}} \] \hspace{1cm} (4)

\[ \beta_{2M} = \frac{[MA_{2}^{+1}]_{a}}{[M^{+3}]_{a}[A^{-}]^{2}_{a}} \] \hspace{1cm} (5)

\[ \beta_{3M} = \frac{[MA_{3}]_{a}}{[M^{+3}]_{a}[A^{-}]^{3}_{a}} \] \hspace{1cm} (6)
From the mechanism of extraction proposed by Hesford and McKay, Hesford et al., and Scargill et al. (19-21) and Bostian and Smutz (23),

\[ \text{MA}_3 + 3\text{TBP} \rightarrow \text{MA}_3 \cdot 3\text{TBP}, \] (7)

the following equation for the equilibrium constant for M can be written:

\[ K_M = \frac{[\text{MA}_3 \cdot 3\text{TBP}]}{[\text{MA}_3]_a [\text{TBP}]_o^3}. \] (8)

Using an approach similar to that of Hesford and McKay (19), when two rare earths, M and N, are present in a solution simultaneously, the expression for the thermodynamic separation factor is, by definition:

\[ T_{B_{M/N}} = \frac{(E_a^0)_M}{(E_a^0)_N} = \frac{\left(1 + \frac{[\text{MA}_3 \cdot 3\text{TBP}]}{[\text{MA}_3]_a} \right)}{\left(1 + \frac{[\text{NA}_3 \cdot 3\text{TBP}]}{[\text{NA}_3]_a} \right)} \] (9)

\[ = \frac{[\text{MA}_3 \cdot 3\text{TBP}]}{[\text{NA}_3 \cdot 3\text{TBP}]} \frac{[\text{N}^2_a + [\text{N}^2_a]_a + [\text{N}^3_a]_a + [\text{N}^3_a]_a]}{[\text{M}^3_a + [\text{M}^2_a]_a + [\text{M}^1_a]_a + [\text{M}^3_a]_a} \] (10)

Using the stability constants of equations 1, 2, and 3, for both M and N, to represent the aqueous species, the following equation results:

\[ T_{B_{M/N}} = \frac{[\text{MA}_3 \cdot 3\text{TBP}]}{[\text{NA}_3 \cdot 3\text{TBP}]} \frac{[\text{N}^2_a + [\text{N}^2_a]_a + [\text{N}^3_a]_a + [\text{N}^3_a]_a]}{[\text{M}^3_a + [\text{M}^2_a]_a + [\text{M}^1_a]_a + [\text{M}^3_a]_a} \] (11)
Insertion of the equilibrium constant of equation 8 for both M and N gives
the following result after cancellation of like terms:

\[ T^\beta_{M/N} = \frac{K_M [MA_3]^a [N^{+3}]a \{1 + \beta_{1N} [A^-]^a + \beta_{2N} [A^-]^2 + \beta_{3N} [A^-]^3\}}{K_N [NA_3]^a [M^{+3}]a \{1 + \beta_{1M} [A^-]^a + \beta_{2M} [A^-]^2 + \beta_{3M} [A^-]^3\}.} \]  

(12)

Using equation 6 to obtain

\[ \frac{[MA_3]^a}{[N^{+3}]a} = \beta_{3M} [A^-]^3, \]  

and likewise for N, and combining with equation 12 gives the following result:

\[ T^\beta_{M/N} = \frac{K_M \beta_{3M} \{1 + \beta_{1N} [A^-]^a + \beta_{2N} [A^-]^2 + \beta_{3N} [A^-]^3\}}{K_N \beta_{3N} \{1 + \beta_{1M} [A^-]^a + \beta_{2M} [A^-]^2 + \beta_{3M} [A^-]^3\}.} \]  

(13)

A slightly different approach yields another interesting equation.

Using equation 8 for both M and N in equation 9, gives the following result:

\[ T^\beta_{M/N} = \frac{\left\{ \frac{K_M [MA_3]^a}{[M^{+3}]a + [MA_2]^a + [MA_3]^a} \right\}}{\left\{ \frac{K_N [NA_3]^a}{[N^{+3}]a + [NA_2]^a + [NA_3]^a} \right\}.} \]  

(14)
The fractions in the numerator and denominator of equation 15 represent the fraction of the extractable specie of M and N in the aqueous phase.

It is very interesting to note at this point, that a similar approach for the system \( \text{MA}_3, \text{NA}_3, \text{H}_2\text{O}, \) and di-(2-ethylhexyl) phosphoric acid (D2EHPA), where the mechanism of extraction is by an ion exchange, rather than neutral molecule extraction, yields the expression

\[
\frac{K'_M}{K'_N} = \frac{\left( \frac{[\text{MA}_3]^a}{[\text{M}^{+3}]^a + [\text{MA}^{+2}]^a + [\text{MA}_2^{+1}]^a + [\text{MA}_3]^a} \right)}{\left( \frac{[\text{NA}_3]^a}{[\text{N}^{+3}]^a + [\text{NA}^{+2}]^a + [\text{NA}_2^{+1}]^a + [\text{NA}_3]^a} \right)}.
\]  

(15)

where again the fractions in the numerator and denominator of equation 16 represent the fraction of extractable specie of M and N in the aqueous phase (see Appendix for complete derivation). It should be noted that in both equations 15 and 16, the ratios of the equilibrium constants are dependent on the organic solvent, and the ratios of the fractions are dependent on the aqueous phase. This illustrates the dependency of the separation factor on both the organic and the aqueous phases.
Equations 13 and 15 are exact treatments of the systems, i.e., activities were used in the development of all equations. Since activity data are often very difficult to obtain, it is of more practical interest to consider the equations as a function of concentrations. Inserting the proper activity coefficients, equation 9 becomes

\[
T_{B_{M/N}} = \frac{\left\{ (M_{A3} \cdot 3TBP)_y \gamma_{Mo} \right\}}{\left( (M^{+3})_a \gamma_{M^{+3}} + (M^{+2})_a \gamma_{M^{+2}} + (M^{+1})_a \gamma_{M^{+1}} + (M_{A3})_a \gamma_{MA3} \right)}
\]

(17)

\[
= \frac{\left\{ (NA_{A3} \cdot 3TBP)_o \gamma_{No} \right\}}{\left( (NA^{+3})_a \gamma_{NA^{+3}} + (NA^{+2})_a \gamma_{NA^{+2}} + (NA^{+1})_a \gamma_{NA^{+1}} + (NA_{A3})_a \gamma_{NA3} \right)}
\]

(18)

where the parenthesis refer to concentrations and \( \gamma_{M^{+}} \) and \( \gamma_{M^{-}} \) are average activity coefficients of the aqueous phase species of M and N respectively. Equation 18 may also be written as

\[
T_{B_{M/N}} = B_{M/N} \frac{\left\{ \gamma_{No} \gamma_{M^{+}} \right\}}{\left\{ \gamma_{No} \gamma_{M^{+}} \right\}}
\]

(19)

where \( B_{M/N} \) is the usual expression reported for separation factors.
Equations 13 and 15 can be rewritten in terms of \( b_{M/N} \) rather than \( T_{b_{M/N}} \) as follows:

\[
\beta_{M/N} = \frac{K_M \beta_{3M} \left(1 + \beta_{1N} [A^-]_a + \beta_{2N} [A^-]^2_a + \beta_{3N} [A^-]^3_a\right)}{K_N \beta_{3N} \left(1 + \beta_{1M} [A^-]_a + \beta_{2M} [A^-]^2_a + \beta_{3M} [A^-]^3_a\right)} \cdot \frac{\gamma}{\gamma} \cdot \frac{No}{Mo} \frac{M^+}{N^+} \tag{20}
\]

and

\[
\beta_{M/N} = \frac{K_M}{K_N} \left(\frac{[M^{+3}]_a + [MA^{+2}]_a + [MA_2^{+1}]_a + [MA_3]_a}{[N^{+3}]_a + [NA^{+2}]_a + [NA_2^{+1}]_a + [NA_3]_a}\right) \cdot \frac{\gamma}{\gamma} \cdot \frac{No}{Mo} \frac{M^+}{N^+} \tag{21}
\]

Since the separation factor increases with increasing concentration of rare earths, consideration of equation 20 shows that either (1) the ratio of equilibrium constants and stability constants increases, (2) the ratio of the terms in braces increases, (3) the activity coefficient term increases, or (4) a combination of these. Since the equilibrium constants and stability constants are based on activities, they are true constants, and their ratio would be independent of the concentration. In the lighter rare earths, with atomic number of \( M > N \), it would be expected that since the ionic radius of \( M \) is smaller than that of \( N \), \( M \) would tend to hold the ligand tighter than \( N \), due to its greater charge density. This would indicate that \( \beta_{M/N} > \beta_{N/M} \) for \( i = 1, 2, \) and \( 3 \). This indicates that the ratio
of the terms in braces in equation 20 is less than or equal to unity for all concentrations. Since at infinite dilution this term would be equal to 1.0, a decrease in this term with increasing concentration is indicated. Since the separation factor, $\frac{\beta_{Nd}}{Pr}$, in the nitrate system increases with increasing concentration, and the other terms in equation 20 are constant or decreasing with increasing concentration, the ratio involving the activity coefficients must increase with increasing concentration. Petheram and Spedding's (33) data indicate that the ratio of the mean molal activity coefficients of neodymium to praseodymium increases with increasing concentration. Although the average activity coefficients in equations 18-21 are not the same as the mean molal activity coefficients found by isopiestic measurements, they should vary in a similar manner.

In the derivation of equation 13, and ultimately equation 20, it should be noted that activities of TBP and nitrate ion appeared in both the numerator and denominator and were canceled. These terms can be validly canceled only when both rare earths are present in the same solution. When distribution coefficient data are obtained for the individual rare earths in separate solutions, the ratio of the distribution coefficients does not necessarily represent the separation factor because the activities of the TBP and nitrate ion can not be shown to be identical in both solutions. In order to obtain separation factors from such data one must be able to take into account the variation in the activities of the TBP
and nitrate ion in both solutions. These effects cannot be quantitatively determined at the present time.

Both equations 20 and 21 are consistent with much of the data presented by earlier workers in the field. In equation 20, the average activity coefficient terms would be very dependent upon the free-ligand concentration in the aqueous phase. The observation of Knapp (17) that addition of salting-out agents to the nitrate system had much the same effect on the separation factor as increasing the concentration of the rare earths is consistent with equation 20.

Knapp's (17) data also indicate that for the nitrate system as the concentration of rare earths decreases, the separation factor approaches unity. Consideration of equation 20 shows that

$$\lim_{[A^-]_d \to 0} \beta_{M/N} = \frac{K_M \beta_{3M}}{K_N \beta_{3N}} \cdot \frac{\gamma_{No} \gamma_{M^+}}{\gamma_{Mo} \gamma_{N^+}} = 1.$$  \hspace{1cm} (22)

At infinite dilution, the activity coefficients approach unity, so therefore

$$\frac{K_M \beta_{3M}}{K_N \beta_{3N}} = 1.$$  \hspace{1cm} (23)

As stated previously, $\beta_{3M} > \beta_{3N}$ or $\beta_{3M}/\beta_{3N} > 1$, as M has a greater charge density than N. Nadig and Smutz's (24) data indicate qualitatively that $K_M < K_N$ or $K_M/K_N < 1$. These two hypotheses are qualitatively consistent with equation 23.
Both Sharp (2) and Bochinski (3) assumed that the separation factor was only a function of the total solute, i.e., the total nitrate present in an equilibrium stage. As seen in equation 20, this assumption would be more exact if the free-nitrate ion were the independent variable rather than the total nitrate present. The fact that successful correlations were obtained indicates that the free-nitrate ion concentration in the aqueous phase must have been proportional to the total nitrate in the concentration ranges used. Figure 1 gives a comparison of the data of this research with the data of Sharp. Figure 1 is based on data from the 50:50 mole ratio in each run.

The most direct way of demonstrating that the separation factor is a function of the free-ligand concentration would be to measure the separation factor and the free-ligand concentration in the aqueous phase. However, no satisfactory analytical methods are available for determining the free-nitrate ion in the aqueous phase. It is possible to determine the free-chloride ion concentration in dilute chloride solutions with a Ag-AgCl electrode, but since this work is concerned only with more concentrated chloride solutions, this approach would not be successful, due to the formation of a silver chloride complex ion.

The data for the experimental runs with the rare-earth nitrates shown in Tables 2 thru 6 indicate that in the runs in which the initial feed solution contained no excess acid, i.e., the feed solution was at its equivalence point, the separation factor did not depend on the mole ratio of the two rare earths. The data for the runs in which the initial feed solution contained an excess amount of acid showed a slight increase in
Figure 1. Comparison of nitrate system data of this research with Sharp's data.
separation factor at very high mole ratios of neodymium. However, it is believed that this slight increase in separation factor would not cause a large error in an empirical correlation such as that done by Sharp (2) and Bochinski (3).

Comparison of the data in Tables 7 thru 12 for the NdCl\textsubscript{3}-PrCl\textsubscript{3}-HCl-H\textsubscript{2}O-TBP system shows no dependence of the separation factor on the mole ratio of the two rare earths. Tables 7 thru 10 present data for the chloride system at a constant total rare-earth concentration. The pertinent variable in this set of experiments was the initial pH of the aqueous phase. The purpose of this set of experiments was to determine if a significant amount of the non-extractable Nd(OH)\textsuperscript{+2} is formed when the pH of the aqueous phase is adjusted to a point between the equivalence points of praseodymium chloride and neodymium chloride. Gildseth\textsuperscript{1} reported that the equivalence points of neodymium and praseodymium chlorides at this concentration to be 1.66 and 1.85 respectively. The final aqueous phase pH's for the tests reported in Tables 8, 9, and 10, were 1.85, 1.85, and 0.6 respectively. When the pH of the aqueous solution is 1.85, there would be some tendency for the neodymium to hydrolyze and form the non-extractable Nd(OH)\textsuperscript{+2} since the system is on the basic side of the neodymium equivalence point. Since the pH of the aqueous solution is at the equivalence point of praseodymium, there will be no tendency for the praseodymium to hydrolyze. The fact that the separation factors showed no significant changes in the three experiments indicates that the amount of the hydrolysis product formed is negligible.

\textsuperscript{1}Gildseth, W. M., Ames Laboratory of the AEC, Ames, Iowa. Equivalence points of some of the rare-earth chlorides. Private communication, 1964.
From a comparison of the order of magnitude of the distribution coefficients for the chloride and nitrate systems it can be seen that the nitrates extract into the organic phase much better than the chlorides. The fact that the separation factor, $\beta_{\text{Nd/Pr}}$, in the NdCl$_3$-PrCl$_3$-HCl-H$_2$O-TBP system was less than unity was very surprising. No separation factors over this range of conditions have been reported previously for this system. It is interesting to note that the data in Table 13 for the system SmCl$_3$-NdCl$_3$-HCl-H$_2$O-TBP show that for this system the separation factor, $\beta_{\text{Sm/Nd}}$, is greater than unity. This reversal in separation factor for the chloride systems can not be fully explained, however, the work done by Saeger (25) and Pikal is very helpful in postulating an explanation. Saeger's and Pikal's work indicate that the hydration number for neodymium in an aqueous solution is essentially nine, and that for samarium, an equilibrium exists between rare-earth ions having coordination numbers of eight and nine. It seems logical, from energy requirements, that an ion with a lower number of water molecules closely associated with it, would have a greater tendency to form the neutral, extractable specie. Thus, the Sm$^{+3}$ ion would have a greater tendency to form the neutral, extractable specie than the Nd$^{+3}$ ion and cause a separation factor greater than unity. However, since praseodymium and neodymium both have essentially the same hydration number, both ions would have the same number of hydrated water molecules, so both ions would have about the same tendency to form the neutral specie.

$^1$Pikal, op. cit.
It was found that the organic phases from the chloride system became unstable after standing several weeks and formed a crystalline precipitate. Carbon and hydrogen analyses and infrared data obtained by the Analytical Chemistry Group I of Ames Laboratory of the Atomic Energy Commission showed that the precipitated specie was \([(C_{4}H_{9}O)_{2}PO_{2}]M\), which is a rare-earth salt formed from the hydrolysis product of TBP. This finding was verified in the literature by Kertes and Halpern (34) who reported that HCl promotes the hydrolysis of TBP and by Baldwin and Higgins (35) who have studied rare-earth complexes of dibutyl phosphoric acid. Although the formation of this salt did not hinder this work, it could be a problem in a large-scale extraction process.
CONCLUSIONS

The experimental and theoretical work in this study are consistent with the following conclusions:

1. A rigorous expression for the separation factor contains three terms. One term contains aqueous phase stability constants and equilibrium constants for the reactions between solute and solvent. The second term involves the aqueous phase stability constants and the free-ligand concentrations. The third term involves activity coefficients of species in the two phases. It is concluded that in the nitrate system the increase in separation factor with increasing concentration of solute in the aqueous phase is caused by an increase in the activity coefficient term.

2. A smooth curve results when the separation factor, $\frac{\beta_{Nd/Pr}}{\beta_{Nd/Pr}'}$, for the Nd(NO$_3$)$_3$-Pr(NO$_3$)$_3$-HNO$_3$-H$_2$O-TBP system is plotted versus the equivalents of nitrates per 1000 grams solvent in the organic phase. This correlation holds well even though the Nd/Pr mole ratio was varied from 1:99 to 99:1 and the nitric acid concentration varied from 0 to 10.9 normal. At very high acid concentrations, the separation factor increases slightly for very high mole ratios of neodymium to praseodymium.

3. In the system NdCl$_3$-PrCl$_3$-HCl-H$_2$O-TBP the separation factor, $\frac{\beta_{Nd/Pr}}{\beta_{Nd/Pr}'}$, is not dependent upon the ratio of the two rare earths.

4. The separation factors, $\frac{\beta_{Nd/Pr}}{\beta_{Nd/Pr}'}$, for the system NdCl$_3$-PrCl$_3$-HCl-H$_2$O-TBP are less than unity, whereas the separation factors,
$\beta_{\text{Sm/Nd}}$ for the system $\text{SmCl}_3-\text{NdCl}_3-\text{HCl-}H_2O-TBP$ are greater than unity. It is concluded that this reversal in separation factor is caused by the samarium ion having a lower coordination number than the neodymium and praseodymium ions.

5. It is concluded from a comparison of data for the $\text{NdCl}_3-\text{PrCl}_3-\text{HCl-}H_2O-TBP$ and $\text{Nd(NO}_3)_3-\text{Pr(NO}_3)_3-\text{HNO}_3-H_2O-TBP$ systems, that the nitrate system has larger rare-earth distribution coefficients than the chloride system.
SUMMARY

An equilibrium study has been made of the solvent extraction systems \( \text{Nd(NO}_3\text{)}_3-\text{Pr(NO}_3\text{)}_3-\text{HNO}_3-\text{H}_2\text{O-TBP} \) and \( \text{NdCl}_3-\text{PrCl}_3-\text{HCl-H}_2\text{O-TBP} \). Comparison of a rigorous expression for the separation factor with available data, indicates that for the nitrate system the increase in the separation factor with increasing concentration is caused by an activity coefficient term. It is shown that a good separation factor correlation for the nitrate system is obtained when the separation factor, \( \beta_{\text{Nd/Pr}} \), is plotted versus equivalents of nitrate per 1000 grams solvent in the organic phase. The separation factor for the nitrate system was found to be a function of the ratio of the two rare earths only at very high acid concentrations and at very high mole ratios of neodymium to praseodymium.

The separation factors, \( \beta_{\text{Nd/Pr}} \), for the chloride system were less than unity, and not ratio dependent, for all concentrations and acidities used. The fact that for the system SmCl\(_3\)-NdCl\(_3\)-HCl-H\(_2\)O-TBP the separation factor, \( \beta_{\text{Sm/Nd}} \), was greater than unity was attributed to samarium having a lower hydration number than neodymium and praseodymium.


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APPENDIX

Derivation of Separation Factor Equation for the System MA$_3$-NA$_3$-D2EHPA-H$_2$O

The derivation of the separation factor equation for the MA$_3$-NA$_3$-
D2EHPA-H$_2$O system is very similar to the derivation for the MA$_3$-NA$_3$-TBP-
H$_2$O system. Equations 1-6 are applicable to both systems. The mechanisms
of extraction are the main difference. The mechanism with D2EHPA is

\[ M^{+3} + 3(HG)_2 \rightarrow M(HG)_3^+ + 3H^+ \]  \hspace{1cm} (24)

and likewise for Na. The equilibrium constant, $K_M^*$, is

\[ K_M^* = \frac{[M(HG)_3]^3}{[M^{+3}][HG]^3} \]  \hspace{1cm} (25)

and a similar equation can be written for Na. The thermodynamic separation
factor is, by definition:

\[ T_{M/N} = \frac{(E_{aM}^0)}{(E_{aN}^0)} = \frac{\left( \frac{[N(HG)_3]^3}{[M^{+3}][MA] + [MA] + [MA] + [MA]} \right)}{\left( \frac{[N(HG)_3]^3}{[N^{+3}][MA] + [MA] + [MA] + [MA]} \right)} \]  \hspace{1cm} (26)

Plugging in equation 24 for both M and Na into equation 25 and canceling
like terms, gives the desired equation 16:
\[ T_{M/N}^{\beta} = \frac{K_M^{\prime}}{K_N^{\prime}} \cdot \frac{\left[ \frac{[M^+^3]_a}{[N^+^3]_a + [N^+^2]_a + [M^+^2]_a + [M^+]_a} \right]}{\left[ \frac{[N^+^3]_a}{[N^+^3]_a + [N^+^2]_a + [N^+^1]_a + [N^+]_a} \right]} \]