MASTER

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EQUILIBRIUM OF THE SYSTEM LANTHANUM
NITRATE-PRASEODYMIUM NITRATE-NITRIC
ACID-WATER-TRIBUTYL PHOSPHATE

By
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November 1960

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NOMENCLATURE

- m_T - total molality of either phase; equivalents of total nitrate per 1000 grams of solvent
- m_{HNO_3} - molality of nitric acid in either phase
- m_{La} - molality of lanthanum nitrate in either phase given in terms of nitrate ion
- m_{Pr} - molality of praseodymium nitrate in either phase given in terms of nitrate ion
- K - distribution coefficient of any solute; concentration of solute in organic phase divided by concentration of same solute in aqueous phase
- K_{HNO_3} - distribution coefficient of nitric acid; $m_{HNO_3}(\text{org.})/m_{HNO_3}(\text{aq.})$
- K_{La} - distribution coefficient of lanthanum nitrate; $m_{La}(\text{org.})/m_{La}(\text{aq.})$
- K_{Pr} - distribution coefficient of praseodymium nitrate; $m_{Pr}(\text{org.})/m_{Pr}(\text{aq.})$
- K_T - total distribution coefficient; $m_T(\text{org.})/m_T(\text{aq.})$
- β_{A-B} - separation factor between A and B; K_A/K_B
- β_{Pr-La} - separation factor between praseodymium nitrate and lanthanum nitrate; K_{Pr}/K_{La}
- Y_{RE} - equivalents of rare earth nitrate per total equivalents of nitrate (organic phase)
- Y_{La} - equivalents of lanthanum nitrate per total equivalents of nitrate (organic phase)

- Y_{Pr} - equivalents of praseodymium nitrate per total equivalents of nitrate (organic phase)
- Y_{La} - equivalents of lanthanum nitrate per total equivalents of rare earth nitrate (organic phase)
- y_{Pr} - equivalents of praseodymium nitrate per total equivalents of rare earth nitrate (organic phase)
- X_{RE} - equivalents of rare earth nitrate per total equivalents of nitrate (aqueous phase)
- X_{La} - equivalents of lanthanum nitrate per total equivalents of nitrate (aqueous phase)
- X_{Pr} - equivalents of praseodymium nitrate per total equivalents of nitrate (aqueous phase)
- x_{La} - equivalents of lanthanum nitrate per total equivalents of rare earth nitrate (aqueous phase)
- x_{Pr} - equivalents of praseodymium nitrate per total equivalents of rare earth nitrate (aqueous phase)
- org. - abbreviation of organic phase
- aq. - abbreviation of aqueous phase

EQUILIBRIUM OF THE SYSTEM LANTHANUM NITRATE-PRASEODYMIUM NITRATE-NITRIC
ACID-WATER-TRIBUTYL PHOSPHATE*

by

Brooks Martin Sharp and Morton Smutz

ABSTRACT

The research project discussed in this paper consisted of a study of the extraction characteristics of the three systems lanthanum nitrate-nitric acid-water-tributyl phosphate, praseodymium nitrate-nitric acid-water-tributyl phosphate, and lanthanum nitrate-praseodymium nitrate-nitric acid-water-tributyl phosphate.

The experimental phase of the project consisted of the collection of equilibrium data for these systems. Single stage batch extractions of aqueous mixtures of the solutes with commercial grade tributyl phosphate were carried out. Each equilibrium phase was analyzed for rare earths and nitric acid.

The equilibrium data for the systems lanthanum nitrate-nitric acid-water-tributyl phosphate and praseodymium nitrate-nitric acid-water-tributyl phosphate were correlated graphically. A series of plots of the various distribution coefficients involved as a function of solute composition and total nitrate concentration of each equilibrium phase were prepared.

The separation factors between praseodymium and lanthanum for the system lanthanum nitrate-praseodymium nitrate-nitric acid-water-

*This report is based on an M.S. thesis by Brooks Martin Sharp, submitted November, 1960, to Iowa State University. This work was done under contract with the Atomic Energy Commission.

tributyl phosphate were shown to be a function of the total nitrate concentration of an equilibrium phase and practically independent of solute composition.

A method of predicting the concentrations of lanthanum nitrate, praseodymium nitrate, and nitric acid in an equilibrium phase of the system lanthanum nitrate-praseodymium nitrate-nitric acid-water-tributyl phosphate was presented. It is hoped that this prediction method will be of aid in the development of a design procedure of a solvent extraction process for the separation of the rare earths.

A comparison of the extraction characteristics of the system rare-earth nitrate-nitric acid-water-tributyl phosphate for the nitrates of lanthanum, praseodymium, neodymium, and samarium was made.

INTRODUCTION

The elements of atomic number 57 to 71 inclusive are commonly known as the rare earths or lanthanides. They occur in nature as rather complex mixtures and due to their chemical similarity are quite difficult to separate. The term rare earths is a misnomer, and these elements represent a potentially rich source of metals. The lanthanides as a group are estimated to be more abundant than such well known elements as copper, zinc, lead, tin, mercury, and platinum.

The earliest methods of separation were fractional crystallization and fractional precipitation. These methods are reviewed by Vickery (11). In general these techniques were slow, tedious, and costly. In recent years, primarily due to the work of Spedding and Powell (9) ion exchange methods have been developed for the separation of the rare earths into extremely pure fractions.

In the last decade much work has been done in an attempt to develop a solvent extraction separation process for the rare earths. If such a process could be developed it is thought that it would possess certain advantages over ion exchange, such as larger flow rates and truly continuous operation.

It has been found that the extraction of aqueous solutions of nitric acid and rare-earth nitrates with tributyl phosphate offers promise as a possible separation system. Although nitric acid is not a necessary component of this system, certain advantages are realized with its inclusion. The separation factors between the individual rare-earth nitrates have been found to increase with increasing nitrate ion

concentration. The highly concentrated aqueous solutions of rare-earth nitrates are very viscous, and this high viscosity could cause handling and pumping problems in an extraction apparatus. The inclusion of nitric acid makes possible highly concentrated solutions with respect to nitrate ion without a great increase in viscosity. Phase separation is also somewhat faster in acidified systems.

Before a systematic design procedure can be applied to this system, it is necessary that the equilibrium conditions be known. Because of the large number of possible solutes, a systematic experimental determination of the equilibrium conditions covering the range of composition and concentration of interest in extractor design is practically impossible. Therefore, a method of predicting the equilibrium conditions for the rare-earth nitrate-nitric acid-water-tributyl phosphate system is a necessary prerequisite in selecting operating conditions for a desired separation. Schoenherr (8) has presented such a method for the neodymium nitrate-samarium nitrate-nitric acid-water-tributyl phosphate system and Dinnin (5) has presented a modification of this method for the system dysprosium nitrate-erbium nitrate-nitric acid-water-tributyl phosphate.

The purpose of this research project was to investigate the equilibrium of the systems lanthanum nitrate-nitric acid-water-tributyl phosphate, praseodymium nitrate-nitric acid-water-tributyl phosphate, lanthanum nitrate-praseodymium nitrate-nitric acid-water-tributyl phosphate, and to apply a prediction method to the equilibrium of the latter system.

Also, a comparison was to be made of the extraction characteristics of the light rare earths (lanthanum to samarium) as these are the most

abundant in nature and therefore of the most interest in the development of a solvent extraction separation process.

PREVIOUS WORK

The first study of solvent extraction separation of the rare earths was made in 1937 by Fischer, et al. (6). They studied the distribution of rare-earth chlorides between water and various alcohols, ethers, and ketones.

Appleton and Selwood (1) studied the distribution of lanthanum and neodymium thiocyanates between water and butyl alcohol. They reported a separation factor of 1.06 between neodymium and lanthanum.

Templeton (10) investigated the distribution of lanthanum, cerous, praseodymium, neodymium, and samarium nitrates between water and n-hexyl alcohol at 25°. He found a regular increase in extractability with atomic number for this system, excluding cerous nitrate which was found to be less extractable than lanthanum nitrate. He reported that separation factors between neodymium and lanthanum as high as 1.88 should be expected for this system under optimum conditions.

Tributyl phosphate, which has been found to give relatively high distribution coefficients and separation factors when used to extract rare-earth nitrates from aqueous solution, has been used almost exclusively as the organic solvent for separation studies in the last decade.

Weaver, et al. (12) produced better than a kilogram of 95 percent pure gadolinium oxide starting with a mixture of rare-earth oxides containing about 30 percent gadolinium oxide. They used a 60:40 mixture

of tributyl phosphate and Varsol¹ as the solvent and extracted a highly acidified aqueous mixture of the rare-earth nitrates many times in both batch extractions and countercurrent extractions in a York-Scheibel column. This separation was not preformed under the best conditions, and it was realized that a better knowledge of the system would be necessary before the operating conditions could be optimized.

Bochinski, et al. (4) demonstrated the partial separation of the monazite rare earths using continuous countercurrent extraction. They extracted acid free aqueous mixtures of the rare-earth nitrates with undiluted tributyl phosphate. The separation factors between the individual rare earths were found to increase with increasing concentration and to be practically independent of solute composition. They presented a calculation method for determining the stagewise conditions in a multistage continuous countercurrent extractor.

Knapp (7) studied the effect of process variables such as rare-earth concentration, acid concentration, and salting out agents on equilibrium phenomena of the rare-earth nitrate-tributyl phosphate-water system. He showed that the extractability of the pure rare-earth nitrates increases with increasing atomic number to a maximum at dysprosium and then diminishes with further increases in atomic number.

Atwood (2) investigated the effect of the addition of chelating agents on the equilibrium of the system rare-earth nitrate-water-tributyl phosphate. Salts of ethylenediaminetetraacetic acid were used.

¹Varsol is the trade name of a petroleum fraction similar to kerosene but purified from gasoline.

He found that the addition of these chelating agents increased the separation factors for all lanthanide mixtures in which the lanthanide which formed the most stable chelate was the least extractable component.

Schoenherr (8) investigated the equilibrium of the systems neodymium nitrate-nitric acid-water-tributyl phosphate, samarium nitrate-nitric acid-water-tributyl phosphate, and neodymium nitrate-samarium nitrate-nitric acid-water-tributyl phosphate. He reported the separation factor between samarium and neodymium to be practically independent of composition and dependent only on the total nitrate concentration. A maximum separation factor of about 3.0 between samarium and neodymium was reported. He presented a method of predicting the equilibrium conditions of the system neodymium nitrate-samarium nitrate-nitric acid-water-tributyl phosphate.

Dinnin (5) studied the equilibrium of the systems dysprosium nitrate-nitric acid-water-tributyl phosphate, erbium nitrate-nitric acid-water-tributyl phosphate, and dysprosium nitrate-erbium nitrate-nitric acid-water-tributyl phosphate. He presented a modification of the method of Schoenherr (8) for use in prediction of the equilibrium conditions of the latter system. The separation factors between erbium and dysprosium were significantly lower than those that have been reported for the lighter rare earths, the maximum value of the separation factor between erbium and dysprosium reported being about 1.1.

EXPERIMENTAL WORK

The purpose of the experimental phase of this research was to collect equilibrium data for the extraction with commercial grade tributyl phosphate of various aqueous mixtures of lanthanum nitrate, praseodymium nitrate, and nitric acid. To accomplish this, three series of single stage extractions were carried out. All extractions were carried out at room temperature, which was about 76° F. In these three series of extractions, equilibrium data were collected for the extraction of aqueous mixtures of lanthanum nitrate plus nitric acid, praseodymium nitrate plus nitric acid, and lanthanum nitrate plus praseodymium nitrate plus nitric acid.

The oxides of lanthanum and praseodymium, 99.9 percent pure, were obtained from the ion exchange group of the Ames Laboratory of the Atomic Energy Commission. The nitrate solutions were prepared by dissolving these oxides in boiling, concentrated nitric acid. After complete reaction, the excess nitric acid was boiled off and distilled water added. These solutions were then analyzed and stored.

Commercial grade tributyl phosphate, obtained from Commercial Solvents Corporation, was pre-equilibrated with water before use as the solvent. The tributyl phosphate was stored in contact with a water phase to ensure equilibrium.

The aqueous feeds for these extractions were prepared by mixing varying amounts of reagent grade concentrated nitric acid, distilled water, and a concentrated solution of one or both of the rare-earth nitrates. The amounts of each of the constituents were varied so as to ensure

coverage of a wide range of concentration and composition.

In carrying out the extractions, each constituent of the feed was added to a 60 ml. separatory funnel. Approximately 20 grams of tributyl phosphate were then added and the funnel was shaken vigorously for 30 seconds. The phases were allowed to separate and remain in contact for several hours, usually overnight. The funnel was then again shaken, the phases allowed to separate, and the heavier aqueous phase drawn off. The phases were stored in small glass stoppered volumetric flasks for analysis. The analytical procedures used are discussed in Appendix A. During this procedure, the separatory funnel was weighed on an analytical balance after each addition or depletion. The weights of each constituent added and the weight of each equilibrium phase thus obtained allowed solute material balances to be written over each extraction. These balances served as a good check on the analytical procedures.

EXPERIMENTAL RESULTS

The distributions of nitric acid, lanthanum nitrate, praseodymium nitrate, and samarium nitrate between water and tributyl phosphate are shown in Figure 1. These data were taken from the results of Knapp (7), supplemented by work of the author. In general, it is seen that the extractability of the light rare earths increases with atomic number. The shape of the equilibrium curves are similar, as would be expected from the chemical and physical similarity of the rare earths.

Throughout this paper, concentrations are reported as molality of nitrate ion associated with the solute in question. Since the nitrate radical is common to all the solutes involved, this method affords a common basis for reporting concentrations and allows direct comparison with the results of Schoenherr (8) and Dinnin (5).

The results of the extractions of aqueous mixtures of lanthanum nitrate plus nitric acid and praseodymium nitrate plus nitric acid are shown graphically in Figures 2 through 11.

Considering the final goal of this research, the prediction of equilibrium phenomena, it was thought that the results should be based on some function of an equilibrium phase, rather than, say, a function of the feed. Therefore, the graphical presentation decided upon was the plotting of the various distribution coefficients involved (K_{RE} , K_{HNO_3} , and K_T) versus the solute composition of an equilibrium phase with parameters of the total nitrate ion molality of that phase.

In order to reduce the data to this series of parametric plots it was necessary to interpolate between the data points obtained

Figure 1. Equilibrium distribution of the pure light rare-earth nitrates and of nitric acid between water and tributyl phosphate

Figure 2. Nitric acid distribution coefficient for the system lanthanum nitrate-nitric acid-water-tributyl phosphate as a function of the concentration and composition of the organic phase

Figure 3. Nitric acid distribution coefficient for the system lanthanum nitrate-nitric acid-water-tributyl phosphate as a function of the concentration and composition of the aqueous phase

Figure 4. Nitric acid distribution coefficient for the system praseodymium nitrate-nitric acid-water-tributyl phosphate as a function of the concentration and composition of the organic phase

Figure 5. Nitric acid distribution coefficient for the system praseodymium nitrate-nitric acid-water-tributyl phosphate as a function of the concentration and composition of the aqueous phase

Figure 6. Lanthanum nitrate distribution coefficient for the system lanthanum nitrate-nitric acid-water-tributyl phosphate as a function of the concentration and composition of the organic phase

Figure 7. Lanthanum nitrate distribution coefficient for the system lanthanum nitrate-nitric acid-water-tributyl phosphate as a function of the concentration and composition of the aqueous phase

Figure 8. Praseodymium nitrate distribution coefficient for the system praseodymium nitrate-nitric acid-water-tributyl phosphate as a function of the concentration and composition of the organic phase

Figure 9. Praseodymium nitrate distribution coefficient for the system praseodymium nitrate-nitric acid-water-tributyl phosphate as a function of the concentration and composition of the aqueous phase

Figure 10. Total distribution coefficient for the system lanthanum nitrate-nitric acid-water-tributyl phosphate and praseodymium nitrate-nitric acid-water-tributyl phosphate as a function of the concentration and composition of the organic phase

Figure 11. Total distribution coefficient for the systems lanthanum nitrate-nitric acid-water-tributyl phosphate and praesodymium nitrate-nitric acid-water-tributyl phosphate as a function of the concentration and composition of the aqueous phase

Figure 13. Separation factor between praseodymium nitrate and lanthanum nitrate for the system lanthanum nitrate-praseodymium nitrate-nitric acid-water-tributyl phosphate as a function of the total concentration of the aqueous phase

Figure 12. Separation factor between praseodymium nitrate and lanthanum nitrate for the system lanthanum nitrate-praseodymium nitrate-nitric acid-water-tributyl phosphate as a function of the total concentration of the organic phase

experimentally. Linear interpolation was used and this procedure undoubtedly introduced some error into the curves shown. However, by drawing smooth curves through the interpolated points, these errors should be minimized.

In general, the graphical portrayal of the results of the extractions of aqueous mixtures of lanthanum nitrate plus praseodymium nitrate plus nitric acid was quite difficult. Qualitatively, the increase of extractability from lanthanum nitrate to praseodymium nitrate to nitric acid was reflected in these data. The most important conclusion derived from these extractions was the fact that, to a reasonably good approximation, the separation factor between praseodymium nitrate and lanthanum nitrate could be assumed independent of composition and dependent only on the total nitrate ion concentration of an equilibrium phase. This observation is in accord with the observation Schoenherr made when considering the extraction of mixtures of neodymium nitrate, samarium nitrate, and nitric acid. Bochinski, et al. (4) also made the same observation when considering the acid free system.

Graphs of $\beta_{\text{Pr-La}}$ versus the total nitrate ion molality of the equilibrium phases are shown in Figures 12 and 13. Each group of points represents a wide variation in total solute composition.

APPLICATION OF EXPERIMENTAL RESULTS TO PREDICTION OF EQUILIBRIA

As stated in the Introduction, the primary purpose of this research project was to develop a method of predicting equilibrium phenomena for the lanthanum nitrate-praseodymium nitrate-nitric acid-water-tributyl phosphate system. For this purpose, a modification of the method used by Schoenherr (8) was developed. Using this method, the concentration of each solute and the total concentration of an equilibrium phase of the system under consideration were predicted assuming the total concentration and composition of the solutes in the other equilibrium phase were known.

The equations that were used are the defining equations for K_{HNO_3} , K_T , $m_T(\text{org.})$, $m_T(\text{aq.})$, and β_{Pr-La} which are:

$$K_{HNO_3} = m_{HNO_3}(\text{org.})/m_{HNO_3}(\text{aq.}) , \quad (1)$$

$$K_T = m_T(\text{org.})/m_T(\text{aq.}) , \quad (2)$$

$$m_T(\text{org.}) = m_{HNO_3}(\text{org.}) + m_{La}(\text{org.}) + m_{Pr}(\text{org.}) , \quad (3)$$

$$m_T(\text{aq.}) = m_{HNO_3}(\text{aq.}) + m_{La}(\text{aq.}) + m_{Pr}(\text{aq.}) , \quad (4)$$

$$\beta_{Pr-La} = K_{Pr}/K_{La} = \frac{m_{Pr}(\text{org.})/m_{Pr}(\text{aq.})}{m_{La}(\text{org.})/m_{La}(\text{aq.})} . \quad (5)$$

Since the problem as stated was to determine the unknown concentrations of one equilibrium phase with the other equilibrium phase completely defined, it is seen that either $m_{HNO_3}(\text{org.})$, $m_T(\text{org.})$, $m_{La}(\text{org.})$, and $m_{Pr}(\text{org.})$ or $m_{HNO_3}(\text{aq.})$, $m_T(\text{aq.})$, $m_{La}(\text{aq.})$, and $m_{Pr}(\text{aq.})$ will be known

for each prediction of this type. Therefore, if K_{HNO_3} , K_T , and β_{Pr-La} can be determined from the known composition and concentration of a specified equilibrium phase, the Equations 1, 2, 5, and either 3 or 4 reduce to four equations in the four unknown concentrations of the unspecified equilibrium phase.

Assuming an organic equilibrium phase containing the three solutes nitric acid, lanthanum nitrate, and praseodymium nitrate is specified, values of the nitric acid distribution coefficient, the total distribution coefficient, and the separation factor between praseodymium nitrate and lanthanum nitrate may be determined graphically in the following manner.

Assuming that all the rare-earth nitrates present are lanthanum nitrate, that is, assuming $Y_{RE} = Y_{La}$, values of K_{HNO_3} and K_T may be obtained from Figures 2 and 10 respectively by linear interpolation between the parameters of $m_T(org.)$ according to the specified total molality of the organic phase. Next, assuming that all the rare-earth nitrates present are praseodymium nitrate values of K_{HNO_3} and K_T are determined similarly utilizing Figures 4 and 10. The values of K_{HNO_3} and K_T for the three solute extraction under consideration are then determined by interpolation between the two values of K_{HNO_3} and the two values of K_T according to the rare-earth nitrate composition (y_{La} and y_{Pr}).

Utilizing the approximation that the praseodymium nitrate-lanthanum nitrate separation factor is independent of composition, a value of β_{Pr-La} may be taken from Figure 12 at the specified total molality of the organic phase.

For a specified equilibrium aqueous phase, values of K_T , K_{HNO_3} , and β_{Pr-La} may be determined in exactly the same manner utilizing the graphical representation of these variables based on the total molality of the aqueous phase. The interpolation between the two values of K_T and the two values of K_{HNO_3} obtained graphically would be carried out according to the rare-earth nitrate composition in the aqueous phase (x_{La} and x_{Pr}).

Using this method, two series of prediction calculations were carried out. For each series several of the extractions of aqueous mixtures of lanthanum nitrate plus praseodymium nitrate plus nitric acid covering a wide range of composition and concentration were selected. In the first series the experimentally determined concentrations of the organic phases were assumed to be known, and the concentrations of the aqueous phases were predicted. For the second series the experimentally determined concentrations of the aqueous phases were assumed to be known, and the concentrations of the organic phases were predicted. The results of these calculations are shown in Tables 1 and 2.

Sample Calculation

A sample calculation is now given to illustrate this method. Numerical values for this example were taken from the equilibrium data for extraction number 4 in Table 1. It was assumed that the experimental results for the analysis of the organic phase were specified and the concentrations of the aqueous phase were to be determined. Therefore for the organic phase:

Table 1. Comparison of predicted and experimental values of concentrations of aqueous equilibrium phases of the system lanthanum nitrate-praseodymium nitrate-nitric acid-water-tributyl phosphate

Extraction number	Experimental aqueous concentrations				Predicted aqueous concentrations			
	m_T	m_{La}	m_{Pr}	m_{HNO_3}	m_T	m_{La}	m_{Pr}	m_{HNO_3}
1	2.79	0.66	1.11	1.02	2.85	0.68	1.09	1.08
2	2.72	0.32	0.62	1.79	2.66	0.34	0.60	1.73
3	2.64	0.63	0.30	1.71	2.67	0.65	0.32	1.70
4	5.57	1.72	2.95	0.90	5.60	1.75	2.93	0.92
5	5.62	3.38	1.41	0.83	5.69	3.42	1.39	0.88
6	5.36	1.18	2.07	2.11	5.47	1.24	2.06	2.18
7	5.38	2.31	1.01	2.06	5.63	2.37	1.04	2.21
8	5.32	0.68	1.04	3.61	5.50	0.68	1.12	3.70
9	5.32	1.20	0.52	3.60	5.44	1.26	0.57	3.61
10	11.11	2.33	4.28	4.50	10.85	2.18	4.11	4.56
11	10.94	4.54	2.04	4.36	10.86	4.48	1.95	4.43
12	10.85	1.17	2.22	7.47	10.63	1.20	2.03	7.40

Table 2. Comparison of predicted and experimental values of concentrations of organic equilibrium phases of the system lanthanum nitrate-praseodymium nitrate-nitric acid-water-tributyl phosphate

Extraction number	Experimental organic concentrations				Predicted organic concentrations			
	m_T	m_{La}	m_{Pr}	m_{HNO_3}	m_T	m_{La}	m_{Pr}	m_{HNO_3}
1	1.65	0.27	0.73	0.65	1.64	0.28	0.74	0.63
2	1.62	0.57	0.37	0.68	1.59	0.57	0.39	0.64
3	1.70	0.15	0.37	1.18	1.66	0.13	0.34	1.19
4	1.67	0.28	0.19	1.21	1.60	0.26	0.18	1.16
5	2.69	0.36	1.23	1.10	2.68	0.35	1.22	1.11
6	2.62	0.82	0.67	1.13	2.57	0.80	0.66	1.10
7	2.69	0.19	0.64	1.87	2.65	0.18	0.64	1.83
8	2.67	0.38	0.34	1.95	2.59	0.38	0.34	1.87
9	2.81	0.08	0.27	2.47	2.76	0.08	0.27	2.41
10	2.76	0.15	0.14	2.47	2.73	0.16	0.15	2.42
11	3.75	0.31	1.54	1.90	3.73	0.35	1.48	1.91
12	3.70	0.78	0.93	1.99	3.63	0.81	0.87	1.96
13	3.84	0.16	0.77	2.92	3.90	0.17	0.82	2.91
14	3.79	0.37	0.42	3.00	3.83	0.40	0.47	2.96
15	3.89	0.07	0.30	3.52	3.97	0.06	0.32	3.58
16	4.59	0.16	0.88	3.54	4.64	0.15	0.85	3.64
17	4.46	0.38	0.49	3.59	4.51	0.35	0.46	3.70

$$m_{La} = 0.36 ,$$

$$m_{Pr} = 1.23 ,$$

$$m_{HNO_3} = 1.10 ,$$

$$m_T = 2.69 .$$

From these data Y_{RE} , y_{La} , and y_{Pr} were calculated as

$$Y_{RE} = \frac{m_{La}(\text{org.}) + m_{Pr}(\text{org.})}{m_T(\text{org.})} = \frac{0.36 + 1.23}{2.69} = 0.59 ,$$

$$y_{La} = \frac{m_{La}(\text{org.})}{m_{La}(\text{org.}) + m_{Pr}(\text{org.})} = \frac{0.36}{0.36 + 1.23} = 0.23 ,$$

$$y_{Pr} = \frac{m_{Pr}(\text{org.})}{m_{La}(\text{org.}) + m_{Pr}(\text{org.})} = \frac{1.23}{0.36 + 1.23} = 0.77 .$$

Utilizing Figures 2, 4 and 10, and the method described previously in this section values of the nitric acid distribution coefficient and the total distribution coefficient were then determined to be

$$K_T = 0.48 ,$$

$$K_{HNO_3} = 1.20 .$$

From Figure 12 a value of β_{Pr-La} was taken at the total molality of the organic phase. This value was

$$\beta_{Pr-La} = 2.05 .$$

The unknown values of $m_{La}(\text{aq.})$, $m_{Pr}(\text{aq.})$, $m_{HNO_3}(\text{aq.})$, and $m_T(\text{aq.})$

were then determined using Equations 1, 2, 4, and 5.

The molality of the nitric acid in the aqueous phase was determined from Equation 1 to be

$$m_{\text{HNO}_3}(\text{aq.}) = m_{\text{HNO}_3}(\text{org.})/K_{\text{HNO}_3} = 1.10/1.20 = 0.92 .$$

The total molality of the aqueous phase was determined from Equation 2 to be

$$m_{\text{T}}(\text{aq.}) = m_{\text{T}}(\text{org.})/K_{\text{T}} = 2.69/0.48 = 5.60 .$$

Equations 4 and 5 were then solved simultaneously to obtain $m_{\text{Pr}}(\text{aq.})$ and $m_{\text{La}}(\text{aq.})$. Equation 4 was rearranged to give

$$m_{\text{La}}(\text{aq.}) = m_{\text{T}}(\text{aq.}) - m_{\text{HNO}_3}(\text{aq.}) - m_{\text{Pr}}(\text{aq.}) . \quad (4-a)$$

Equation 4-a was then substituted into Equation 5 which was then solved for $m_{\text{Pr}}(\text{aq.})$ to give

$$m_{\text{Pr}}(\text{aq.}) = \frac{[m_{\text{T}}(\text{aq.}) - m_{\text{HNO}_3}(\text{aq.})] \times m_{\text{Pr}}(\text{org.})}{\beta_{\text{Pr-La}} \times m_{\text{La}}(\text{org.}) + m_{\text{Pr}}(\text{org.})} . \quad (6)$$

Known values were then substituted into Equation 6 to obtain

$$m_{\text{Pr}}(\text{aq.}) = \frac{(5.60 - 0.92) \times 1.23}{2.05 \times 0.36 + 1.23} = 2.93 .$$

Equation 4-a was then used to calculate the concentration of the lanthanum nitrate in the aqueous phase.

That is:

$$m_{\text{La}}(\text{aq.}) = 5.60 - 0.92 - 2.93 = 1.75 .$$

This completes the calculation of the equilibrium aqueous concentrations for the specified organic phase.

If an aqueous equilibrium phase had been specified and it was desired to calculate the equilibrium organic phase concentrations the procedure would have been completely similar, the final step being the simultaneous solution of Equations 3 and 5 to obtain the concentrations of lanthanum nitrate and praseodymium nitrate in the organic phase.

DISCUSSION

In general, the agreement between the experimental and calculated values of equilibrium phase concentrations was considered reasonably good. The average percent differences between experimental and calculated values are given in Table 3.

Table 3. Average percent differences between experimental and calculated concentrations of equilibrium phases of the system lanthanum nitrate-praseodymium nitrate-nitric acid-water-tributyl phosphate

	m_T	m_{La}	m_{Pr}	m_{HNO_3}
Percent differences organic phases	1.6	5.9	4.5	2.3
Percent differences aqueous phases	2.1	3.2	4.3	2.9

A combination of the data collected by the author for the systems lanthanum nitrate-nitric acid-water-tributyl phosphate and the data collected by Schoenherr (8) for the systems neodymium nitrate-nitric acid-water-tributyl phosphate and samarium nitrate-nitric acid-water-tributyl phosphate allows a comparison of the extraction characteristics of the light rare earth nitrates in acidified systems.

This comparison excludes cerium and promethium, which are not of interest in the development of a solvent extraction process for the

Figure 14. Nitric acid distribution coefficient for the systems lanthanum nitrate-nitric acid-water-tributyl phosphate, praseodymium nitrate-nitric acid-water-tributyl phosphate, neodymium nitrate-nitric acid-water-tributyl phosphate, and samarium nitrate-nitric acid-water-tributyl phosphate as a function of the composition of the aqueous phase at m_T (aq.) equal to 7.0

Figure 16. Total distribution coefficient for the systems, lanthanum nitrate-nitric acid-water-tributyl phosphate, praseodymium nitrate-nitric acid-water-tributyl phosphate, neodymium nitrate-nitric acid-water-tributyl phosphate, and samarium nitrate-nitric acid-water-tributyl phosphate as a function of the composition of the aqueous phase at m_T (aq.) equal to 7.0

Figure 15. Rare-earth nitrate distribution coefficient for the systems lanthanum nitrate-nitric acid-water-tributyl phosphate, praseodymium nitrate-nitric acid-water-tributyl phosphate, neodymium nitrate-nitric acid-water-tributyl phosphate, and samarium nitrate-nitric acid-water-tributyl phosphate as a function of the composition of the aqueous phase at m_T (aq.) equal to 7.0

separation of the rare earths. No stable isotope of promethium occurs in nature and cerium may exist in the tetravalent state in aqueous solution. In this tetravalent state, cerium possesses chemical properties significantly different from the other rare earths, and these properties have been exploited in the separation and purification of cerium.

In Figure 14, the variation of the nitric acid distribution coefficient with solute composition at a single total molality of the aqueous phase is shown. Figures 15 and 16 depict the variation of the rare-earth nitrate distribution coefficient and the total distribution coefficient with solute composition at this same total molality of the aqueous phase. These plots reflect the increasing extractability with increasing atomic number that is characteristic of the light rare earths.

Considering the similarity of the extraction characteristics of the rare earths as shown in these plots, it seems reasonable to conclude that a graphical prediction of the total distribution coefficient and the nitric acid distribution coefficient for a system containing the five solutes lanthanum nitrate, praseodymium nitrate, neodymium nitrate, samarium nitrate, and nitric acid would give a good approximation of the actual distribution coefficients for this system.

The other necessary step in the prediction of equilibria for this five solute system is a method of predicting the separation factors between the individual rare-earth nitrates present. Since Bochinski, et al. (4) observed that the separation factors between the rare earths could be assumed independent of solute composition in acid free systems, regardless of the number of rare-earth nitrates present, it would be hoped that this assumption is also possible in the acidified system. It is recommended

that this possibility be checked in future work.

In conclusion, as brought out in the Introduction, this research project is not considered an end in itself, but only one necessary step in the development of a systematic design procedure of a solvent extraction process for the separation of the rare earths.

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APPENDIX A. ANALYTICAL PROCEDURES

Weighed samples of each equilibrium phase were taken for analysis. The solutes in the organic samples were transferred to aqueous solution prior to analysis. This was accomplished by contacting the organic samples three times with water. The three aqueous phases were combined and analyzed in the same manner as the aqueous phase samples.

For the determination of total rare earths, the aqueous sample was diluted to approximately 200 ml. with distilled water, brought to a boil on a hot plate, and the rare earths completely precipitated with a saturated solution of oxalic acid. The oxalates were filtered and converted to the oxides at 800° C in a muffle furnace. The weight of the oxides was determined on an analytical balance.

For the extractions in which both lanthanum and praseodymium were present, the composition of the rare earths was determined by the spectrophotometric method developed by Banks and Klingman (3).

To determine the nitric acid content, the samples were diluted to approximately 200 ml. and the rare earths present were precipitated by addition of an excess of saturated potassium ferrocyanide. The nitric acid content was then determined by titration with standardized sodium hydroxide. An automatic titrator was used and the end point was taken at a pH of 8.7.

It was found that the nitric acid content of aqueous solutions of nitric acid and potassium ferrocyanide diminishes with time. This was thought to be due to oxidation by the acid. To obtain satisfactory analyses for

the nitric acid, it was necessary to titrate the aqueous solutions of nitric acid, potassium ferrocyanide, and precipitated rare-earth ferrocyanides within about 15 minutes after addition of the potassium ferrocyanide solution.

APPENDIX B. EQUILIBRIUM DATA

Table 4. Equilibrium data for the system lanthanum nitrate-nitric acid-water-tributyl phosphate

	Aqueous phase			Organic phase		
	Grams of $\text{La}(\text{NO}_3)_3$ per gram of solution	Grams of HNO_3 per gram of solution	Grams of solvent per gram of solution	Grams of $\text{La}(\text{NO}_3)_3$ per gram of solution	Grams of HNO_3 per gram of solution	Grams of solvent per gram of solution
1	0.127	0.065	0.808	0.026	0.075	0.899
2	0.170	0.087	0.743	0.035	0.095	0.871
3	0.204	0.112	0.684	0.037	0.113	0.849
4	0.258	0.147	0.595	0.037	0.143	0.820
5	0.309	0.173	0.519	0.035	0.161	0.804
6	0.169	0.036	0.796	0.051	0.054	0.896
7	0.214	0.050	0.736	0.061	0.070	0.869
8	0.278	0.064	0.658	0.074	0.087	0.839
9	0.351	0.082	0.567	0.078	0.112	0.810
10	0.419	0.093	0.488	0.078	0.134	0.788
11	0.070	0.099	0.831	0.011	0.090	0.899
12	0.089	0.131	0.781	0.014	0.115	0.871
13	0.111	0.173	0.716	0.015	0.140	0.845
14	0.142	0.229	0.629	0.013	0.170	0.817
15	0.162	0.283	0.555	0.012	0.191	0.798
16	0.032	0.126	0.842	0.004	0.097	0.898
17	0.046	0.166	0.789	0.006	0.121	0.873
18	0.055	0.232	0.713	0.005	0.154	0.841
19	0.072	0.288	0.640	0.006	0.177	0.817
20	0.089	0.343	0.568	0.005	0.194	0.801
21	0.211	0.013	0.776	0.094	0.027	0.880
22	0.272	0.020	0.709	0.114	0.037	0.849
23	0.342	0.025	0.633	0.131	0.049	0.819
24	0.432	0.031	0.537	0.145	0.066	0.789
25	0.226	0.006	0.768	0.116	0.014	0.869

Table 4. (Continued)

	Aqueous phase			Organic phase		
	Grams of $\text{La}(\text{NO}_3)_3$ per gram of solution	Grams of HNO_3 per gram of solution	Grams of solvent per gram of solution	Grams of $\text{La}(\text{NO}_3)_3$ per gram of solution	Grams of HNO_3 per gram of solution	Grams of solvent per gram of solution
26	0.287	0.009	0.704	0.140	0.021	0.839
27	0.360	0.010	0.631	0.169	0.024	0.807
28	0.457	0.012	0.531	0.191	0.034	0.776
29	0.091	0.399	0.510	0.006	0.195	0.799
30	0.102	0.444	0.454	0.008	0.213	0.779
31	0.180	0.332	0.488	0.016	0.209	0.775
32	0.195	0.363	0.443	0.020	0.223	0.757
33	0.110	0.507	0.383	0.016	0.267	0.717
34	0.338	0.210	0.453	0.038	0.187	0.775
35	0.511	0.036	0.453	0.143	0.089	0.768
36	0.531	0.019	0.450	0.177	0.061	0.763
37	0.457	0.111	0.432	0.071	0.156	0.773
38	0.529	0.051	0.420	0.120	0.115	0.765
39	0.358	0.229	0.413	0.042	0.198	0.760
40	0.461	0.138	0.402	0.065	0.170	0.765
41	0.208	0.432	0.360	0.035	0.253	0.712

Table 5. Equilibrium data for the system praseodymium nitrate-nitric acid-water-tributyl phosphate

	Aqueous phase			Organic phase		
	Grams of $\text{Pr}(\text{NO}_3)_3$ per gram of solution	Grams of HNO_3 per gram of solution	Grams of solvent per gram of solution	Grams of $\text{Pr}(\text{NO}_3)_3$ per gram of solution	Grams of HNO_3 per gram of solution	Grams of solvent per gram of solution
1	0.079	0.134	0.787	0.022	0.108	0.870
2	0.099	0.179	0.721	0.027	0.133	0.841
3	0.130	0.237	0.634	0.028	0.160	0.812
4	0.158	0.287	0.554	0.030	0.179	0.792
5	0.173	0.332	0.495	0.034	0.195	0.771
6	0.146	0.087	0.766	0.050	0.087	0.864
7	0.187	0.113	0.700	0.061	0.103	0.836
8	0.245	0.150	0.605	0.067	0.130	0.803
9	0.294	0.184	0.522	0.065	0.153	0.782
10	0.328	0.211	0.461	0.069	0.168	0.763
11	0.230	0.041	0.729	0.102	0.055	0.842
12	0.268	0.065	0.667	0.108	0.075	0.817
13	0.336	0.085	0.579	0.116	0.095	0.789
14	0.409	0.101	0.489	0.116	0.117	0.768
15	0.455	0.115	0.430	0.116	0.133	0.752
16	0.467	0.143	0.390	0.113	0.151	0.736
17	0.258	0.022	0.720	0.137	0.036	0.828
18	0.328	0.027	0.646	0.167	0.040	0.793
19	0.416	0.032	0.552	0.185	0.050	0.765
20	0.491	0.040	0.470	0.183	0.067	0.750
21	0.536	0.051	0.412	0.170	0.088	0.742
22	0.269	0.011	0.720	0.164	0.020	0.816
23	0.343	0.012	0.645	0.198	0.021	0.781
24	0.437	0.019	0.544	0.211	0.032	0.747
25	0.522	0.018	0.459	0.219	0.038	0.743

Table 5. (Continued)

	Aqueous phase			Organic phase		
	Grams of $\text{Pr}(\text{NO}_3)_3$ per gram of solution	Grams of HNO_3 per gram of solution	Grams of solvent per gram of solution	Grams of $\text{Pr}(\text{NO}_3)_3$ per gram of solution	Grams of HNO_3 per gram of solution	Grams of solvent per gram of solution
26	0.184	0.372	0.444	0.043	0.209	0.749
27	0.349	0.241	0.410	0.081	0.180	0.739
28	0.195	0.401	0.404	0.055	0.220	0.725
29	0.352	0.270	0.378	0.091	0.192	0.717
30	0.064	0.103	0.834	0.017	0.094	0.889
31	0.124	0.066	0.809	0.040	0.072	0.888
32	0.172	0.039	0.789	0.069	0.054	0.877
33	0.208	0.014	0.778	0.113	0.026	0.860
34	0.224	0.007	0.770	0.139	0.014	0.847
36	0.201	0.424	0.375	0.068	0.226	0.706

Table 6. Equilibrium data for the system lanthanum nitrate-praseodymium nitrate-nitric acid-water-tributyl phosphate

	Aqueous phase				Organic phase			
	Grams of $\text{La}(\text{NO}_3)_3$ per gram of solution	Grams of $\text{Pr}(\text{NO}_3)_3$ per gram of solution	Grams of HNO_3 per gram of solution	Grams of solvent per gram of solution	Grams of $\text{La}(\text{NO}_3)_3$ per gram of solution	Grams of $\text{Pr}(\text{NO}_3)_3$ per gram of solution	Grams of HNO_3 per gram of solution	Grams of solvent per gram of solution
1	0.075	0.130	0.019	0.776	0.025	0.069	0.036	0.870
2	0.142	0.065	0.019	0.774	0.054	0.035	0.037	0.873
3	0.057	0.096	0.051	0.796	0.014	0.036	0.046	0.885
4	0.106	0.049	0.049	0.797	0.027	0.018	0.067	0.887
5	0.029	0.055	0.093	0.824	0.005	0.015	0.087	0.893
6	0.057	0.027	0.089	0.827	0.010	0.008	0.087	0.895
7	0.119	0.205	0.036	0.639	0.031	0.108	0.056	0.805
8	0.233	0.098	0.033	0.636	0.072	0.059	0.058	0.811
9	0.086	0.152	0.089	0.673	0.017	0.058	0.098	0.828
10	0.168	0.074	0.087	0.671	0.034	0.031	0.102	0.833
11	0.052	0.080	0.161	0.707	0.007	0.024	0.131	0.838
12	0.092	0.040	0.160	0.707	0.013	0.013	0.131	0.843
13	0.178	0.300	0.054	0.468	0.026	0.127	0.091	0.757
14	0.334	0.145	0.050	0.471	0.064	0.078	0.096	0.763
15	0.126	0.233	0.142	0.500	0.013	0.065	0.143	0.779
16	0.247	0.112	0.138	0.503	0.031	0.036	0.148	0.785
17	0.069	0.132	0.256	0.544	0.006	0.026	0.176	0.792
18	0.144	0.273	0.176	0.407	0.013	0.072	0.167	0.748
19	0.289	0.130	0.171	0.409	0.031	0.041	0.171	0.757
20	0.086	0.154	0.328	0.433	0.007	0.039	0.203	0.752
21	0.167	0.076	0.325	0.433	0.015	0.021	0.207	0.756