PREDICTION OF EQUILIBRIA FOR RARE EARTH NITRATE-NITRIC ACID-TRIBUTYL PHOSPHATE SYSTEMS

by

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A Dissertation Submitted to the

Graduate Faculty in Partial Fulfillment of

The Requirements for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject: Chemical Engineering

Approved:

In Charge of Major Work

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Iowa State University
Of Science and Technology
Ames, Iowa

1959

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

SUMMARY

A study was made of the equilibrium extraction into tri-butyl phosphate of the neodymium nitrate-samarium nitrate-nitric acid system. The purpose of this study was not only to evaluate the extraction properties of this system, but also to develop methods of correlating and of predicting equilibrium phenomena which were reliable and also would be applicable to other rare earth nitrate-nitric acid systems.

The extraction properties of the neodymium nitrate-samarium nitrate-nitric acid system were evaluated by means of single stage equilibrium extractions performed on various mixtures of these solutes. From correlations of the equilibrium from these extractions based on the molar composition and the total molality of these solutes in the organic phase a general similarity was observed between the neodymium nitrate-nitric acid system and the samarium nitrate-nitric acid system. From this similarity it was concluded that the methods of data correlation used for these rare earth nitrate-nitric acid mixtures would also be applicable in the study of the extraction properties of the other trivalent light rare earth nitrates.

The equilibrium distribution of neodymium nitrate-nitric acid mixtures and of samarium nitrate-nitric acid mixtures was found to be approximated by the distribution of pure nitric

acid. The distribution coefficients for neodymium nitrate-nitric acid and for samarium nitrate-nitric acid mixtures were evaluated as a function of the composition and total molality of the organic phase. A method was shown for evaluating the distribution coefficients for neodymium nitrate-samarium nitrate-nitric acid mixtures from the distribution coefficients of the pure rare earth nitrate-nitric acid mixtures.

The variation of the samarium nitrate-neodymium nitrate separation factors was shown as a function of the total molality of the organic phase.

The variations of the nitric acid-neodymium nitrate and the nitric acid-samarium nitrate separation factors were shown as a function of the composition and total molality of the organic phase. The variations of these separation factors were explained by consideration of the mechanism by which the rare earths and nitric acid are extracted.

For neodymium nitrate-samarium nitrate-nitric acid mixtures it was found that the nitric acid-rare earth nitrate separation factors were different from the values of these separation factors observed with neodymium nitrate-nitric acid and samarium nitrate-nitric acid mixtures. These differences in the nitric acid-rare earth nitrate separation factors were shown to be a function of the composition of the

rare earth mixture (neglecting the nitric acid) in the organic phase and also of the samarium nitrate-neodymium nitrate separation factor.

A method was developed for the prediction of equilibrium phenomena for multicomponent extraction systems. This method was demonstrated by means of a sample calculation to predict the equilibrium concentration and composition of a hypothetical neodymium nitrate-samarium nitrate-nitric acid mixture using the equilibrium distribution and separation factor data for this rare earth nitrate-nitric acid system.

INTRODUCTION

In recent years there has been much interest in new metals and alloys because conventional materials have often not been suitable for use in nuclear reactors, missiles, space vehicles, etc. The rare earths represent almost a virgin territory for investigation and have been studied quite extensively in recent years. If a demand for a few of the rare earths develops, as appears certain, there will be considerable interest in finding the most economical method for separating and purifying them.

The rare earths are always found as mixtures in nature and, due to their chemical similarity, are difficult to separate. The various methods which have been devised for purifying the rare earths are reviewed by Vickery (21). Most of these methods require a series of slow and tedious operations, thus making them rather infeasible for the purification of large quantities of the rare earths.

Due to the efforts of Spedding and Powell (15) the ion exchange method for purifying the rare earths has been developed to the point that it is now possible to obtain rare earths of high purity in quantity. However, due to its semi-continuous nature and the low solubility of the rare earth chelates used, the ion exchange process has a low production rate per amount of capital investment.

Another method for purification of metals that has gained favor in recent years is the continuous solvent extraction process. This method has been successfully employed in the purification of uranium and plutonium to be used in nuclear reactors. It has also been employed in the separation of zirconium and hafnium, in the separation of niobium and tantalum, and in several other metal separations. It is thought that this method may also be applicable for the purification of the rare earths.

The solvent extraction technique involves the distribution of a solute or solutes between two immiscible phases (usually an aqueous and an organic phase). The distribution is such that at equilibrium the chemical potential is the same in each phase. The ratio of the concentration of a solute in the organic phase to its concentration in the aqueous phase at equilibrium is the distribution coefficient, k, for that solute. When two or more solutes are present, the ratio of the distribution coefficients for two of the solutes is the separation factor, β, between these solutes.

The separation factor is a measure of the ease of separation of two solutes. The more it differs from unity, the greater the ease of separation will be. For the extraction of rare earth nitrates with tributyl phosphate from an aqueous solution it has been found that the separation factors are

most favorable at high nitrate concentrations in the organic phase. Various means have been devised to attain these high concentrations.

Solutions of rare earth nitrates become very viscous at high concentrations making the operation of an extraction apparatus very difficult. Salting-out agents, which are not extractable into tributyl phosphate, may be added to the aqueous phase to increase the concentration of both phases. Separation of phases has been found to be slow in this case, however, and it is also necessary to remove the salting-out agent from the rare earths after the separation has been completed. Nitric acid also may be added to the system to increase the nitrate concentration of both phases. With this solute, high concentrations may be attained without an appreciable increase in the viscosity of the phases. Also, phase separation is very good in this case. This report deals with the separation of the rare earths in the presence of nitric acid.

To obtain rare earths of relatively high purity by solvent extraction it is necessary to repeat the extraction operation using a series of stages. This can be accomplished by passing the two phases countercurrent to each other in an extraction apparatus. The aqueous feed enters the extractor at one end of a series of stages while the solvent enters at the other end. In each stage the phases are mixed thoroughly

and then, after separating, are passed on to the adjoining
stages.

As the solvent passes countercurrent to the feed, it
preferentially extracts the more extractable components caus-
ing an enrichment in the aqueous phase of the less extract-
able components. Thus, the aqueous phase will be highly en-
riched in the less extractable components. For the organic
phase, however, the last mixture it comes in contact with is
the feed solution. Therefore, enrichment in this phase may
not be as great. If, however, this phase is passed counter-
current to an aqueous scrub solution, the solutes having the
lowest separation factors will be preferentially removed from
the organic phase, and thus an enrichment of the more ex-
tractable components will be attained in the organic phase.

In actual practice this is accomplished by use of a
countercurrent system with internal feed. Solvent and scrub
solutions enter at opposite ends of the extractor. The feed,
containing the solutes, enters at some internally located
stage. The extractor, then, is divided into two sections.
In one section, the extraction section, the organic solvent
will preferentially extract the more extractable components.
In the other section, the scrub section, the aqueous scrub
solution will remove the less extractable components from the
solvent phase and return them to the extraction section of
the extractor. The overall effect is an enrichment of the

less extractable components in the aqueous phase and the more extractable components in the organic phase.

To perform a systematic separation of the rare earths it is necessary to be able to predict the separation which is attainable under a given set of operating conditions. For a multicomponent system this usually requires that a method be available by which it is possible to calculate the stage-wise conditions in an extractor. Also, it is desirable to be able to predict the equilibrium and separation phenomena in each stage.

Since 1950, research has been conducted at the Ames Laboratory of the Atomic Energy Commission to develop a method for predicting the stage-wise conditions in an extraction operation. The groundwork for this was laid by Bochinski et al. (4) who developed a method for calculating stage-wise conditions from equilibrium and separation factor data and from the physical operating conditions in the extractor. Knapp et al. (11) continued the work of Bochinski. They obtained equilibrium and separation factor data for various rare earth mixtures both in acid and non-acid systems.

Using Knapp's data and the method for prediction of stage-wise conditions developed by Bochinski, an extraction run to process 1000 pounds of a Code 350 rare earth nitrate mixture from Lindsay Chemical Company was set up and performed. For this run the aqueous phase nitric acid concen-

tration was set at 5-normal in each stage and was expected to remain constant throughout the run. From stage-wise analyses at the completion of the run, however, the nitric acid concentration was found to vary appreciably throughout the extractor, and the concentrations and compositions of the rare earths in each stage were different from their predicted values.

The difference of the experimental results from the predicted values was attributable to the effect of nitric acid on extraction properties of the rare earths. Until this time it was thought that the nitric acid distribution could be considered independently and would not be appreciably affected by the presence of the rare earths. The results from the extraction run, however, indicated a definite interaction between the nitric acid and the rare earth nitrates. Therefore, efforts were directed toward evaluating the extent of this interaction.

In this report equilibrium and separation data are presented showing the interactions between neodymium nitrate, samarium nitrate, and nitric acid. Also, a method is presented for prediction of equilibrium phenomena for single stage multicomponent systems using equilibrium distribution and separation factor data.

LITERATURE REVIEW

The rare earths are one group of materials which may be classified among our untapped resources. Large quantities of them are available as by-products in the purification of uranium and thorium and in their own ores. The rare earths, however, are always found in nature as mixtures with each other, and are very difficult and costly to separate. Therefore, the development of uses for the rare earths has been slow, and commercial interest in them has been understandably limited.

In recent years, however, research has been in progress to develop economical methods for purifying the rare earths in quantity. One method in which considerable interest has been shown is continuous solvent extraction. Economical processes have been developed for the purification of uranium and for other metals separations using continuous solvent extraction, and it was thought that this method would also be applicable for the purification of the rare earths. Therefore, this method was investigated as a method of purifying the rare earths.

The first study of solvent extraction of the rare earths was reported in 1937 by Fischer et al. (8). They studied the distribution of rare earth chlorides between an aqueous phase and various organic phases, i.e., esters, alcohols, and

ketones. Their work indicated that the distribution coefficients for these systems were high enough for an economical solvent extraction process.

Appleton and Selwood (2) studied the fractionation of lanthanum and neodymium thiocyanates between water and butyl alcohol. They observed a separation factor between neodymium and lanthanum of 1.06, and noted that this could lead to a comparatively rapid separation if this process were put on a continuous basis.

Bock and Bock (5) studied the extraction of rare earths with various organic solvents. They found a high extractability of cerium IV nitrate into di-ethyl ether. They also found that, by saturation of the aqueous phase with other nitrate salts, the extraction of thorium nitrate was greatly increased. Their work indicated more effective extraction with esters, ketones, and alcohols than with ether.

Templeton (16) and Templeton and Peterson (17) studied the distribution of rare earth nitrates between water and hexyl alcohol. They found that, for all nitrates studied, the extractability of the rare earth nitrates increased with increasing atomic number. They obtained separation factors as high as 1.88 for neodymium nitrate-lanthanum nitrate mixtures.

The work of these early investigations was not very extensive and in some cases their conditions were not completely specified in their publications. Subsequent work in this

field has shown that solvents giving much higher distribution coefficients are available, and thus, the work of these early investigators is significant only in that it demonstrates the possibility of using the solvent extraction process as a method of extracting rare earths.

Tributyl phosphate has been found to give relatively high distribution coefficients and separation factors for the extraction of rare earth nitrates from aqueous solutions, and it also has other desirable solvent characteristics such as low volatility and, when pre-equilibrated with water, immiscibility with water. Therefore, in the past decade most extraction studies have been made using it as the organic solvent.

Weaver et al. (22) applied countercurrent liquid-liquid extraction to the separation of large quantities of rare earths using tributyl phosphate. Through a series of multi-stage countercurrent extractions they produced more than a kilogram of better than 95% pure gadolinium oxide from a mixture of this oxide with other rare earth oxides. This separation, however, was not performed under the optimum conditions, and it was realized at the time that a better knowledge of the system was necessary.

Bochinski et al. (4) demonstrated the feasibility of using continuous countercurrent multi-stage solvent extrac-

tion for separating rare earth mixtures. They developed a
method by which the stage-wise conditions could be evaluated
from equilibrium separation data and the physical operating
conditions in the extractor. Using this method they made a
simulated continuous countercurrent extraction run. The ex-
perimental results for this run compared favorably with the
predicted values.

Knapp et al. (11) determined equilibrium data for the
monazite rare earths. They found that, for both acid and
non-acid systems, the separation factors between the indi-
vidual rare earths increased with concentration.

Topp and Weaver (18) determined the distribution coeffi-
cients for samarium, gadolinium, dysprosium and yttrium
nitrates. On the assumption that the most effective separa-
tion could be obtained only when the distribution coefficient
remained constant throughout the extraction system, they con-
cluded that the optimum extraction conditions seemed to be
below 9-normal aqueous acid concentration.

Several investigators have studied the distribution of
the rare earths in the presence of nitric acid using tracer
quantities of rare earths. Using this method, Peppard et al.
(13) found that the extractability of the lanthanides in-
creased with increasing atomic number at moderate and high
acid concentration. At dilute acid concentrations the order
of extractability was inverted. The logarithm of the dis-

tribution coefficients was found to diverge with increasing acid concentration so that maximum separation would require the use of concentrated acid.

Scargill et al. (14), and Hesford et al. (9) verified and expanded on the work of Peppard. Using tracer quantities of rare earths in nitric acid, they found increasing extractability with increasing acidity and atomic number. For certain of the light rare earths, however, the extractability decreased between 4 and 7-normal aqueous phase nitric acid concentration and then increased at higher acid concentrations. For the higher lanthanides, Hesford et al. (9) found a general similarity to the lower lanthanides. However, they noted an appreciable difference between the lanthanides of even and odd atomic number.

In surveying the work of these investigators it was found that the information given was incomplete and could not be used effectively for evaluating the interaction between nitric acid and the rare earths. In the work at high rare earth concentrations in the presence of nitric acid the investigators failed to determine the nitric acid distribution at equilibrium or, if they did determine it, failed to take the nitric acid distribution into account in evaluating their equilibrium conditions. The work with tracer concentrations of the rare earths at high nitric acid concentrations, al-

though valuable in evaluating the relative extractability of the rare earths, could not be effectively applied in determining equilibrium phenomena for practical rare earth nitrate-nitric acid mixtures used in separating the rare earths. Therefore, research efforts were directed toward evaluating the interactions between neodymium nitrate, samarium nitrate, and nitric acid by determining the equilibrium phenomena for various mixtures of these components.

Neodymium and samarium were considered as being characteristic of the light rare earths, and thus, all correlations presented in this report for neodymium nitrate and samarium nitrate are thought to be applicable to the other trivalent light rare earth nitrates.

EXPERIMENTAL PROCEDURE

The purpose of the experimental work was to obtain equilibrium data for various mixtures of neodymium nitrate, samarium nitrate, and nitric acid. The equilibrium data were obtained by use of single stage extractions. These extractions were made at room temperature, which was about $26^{\circ}C$. Aqueous feed solutions containing the rare earth nitrates and nitric acid were contacted with water equilibrated tributyl phosphate in a separatory funnel until equilibrium was attained. Thirty seconds of constant shaking gave the desired equilibration. For the extractions at high acid concentration, however, a marked rise in the temperature of the mixture was noted during mixing. Therefore, the samples for each extraction were allowed to stand for several hours and then shaken together again. Then, after the phases had separated, they were drawn off and prepared for analysis.

The solvent for these extractions was prepared by shaking commercial grade tributyl phosphate with water until equilibration was attained. The tributyl phosphate was kept in contact with water until it was used.

The feed solutions were prepared by dissolving the pure rare earth oxides in concentrated nitric acid. After the rare earth oxides had dissolved, the rare earth and nitric acid concentrations were adjusted to their desired values. This

was accomplished by evaporating the excess nitric acid from the mixture. Aliquots of the resulting rare earth nitrate solution were then mixed with various amounts of nitric acid so that feed solutions of varying rare earth and nitric acid compositions were obtained. Each of these feed solutions was then used to perform a series of extractions. The amount of feed solution used was varied so that the equilibrium results covered a range of concentration. In this way equilibrium data were obtained over a wide range of concentration and composition.

Equilibrium data were also obtained for saturated mixtures of neodymium nitrate and nitric acid and of samarium nitrate and nitric acid. For these extractions water equilibrated tributyl phosphate was contacted with varying amounts of nitric acid, and then rare earth nitrate crystals were added with constant mixing. Crystals were added and mixing was continued until saturation was apparent. The two liquid phases were then separated and analyzed. The analytical methods used are described in Appendix A.

To facilitate conversion of the analytical data to a molality basis, the samples for analysis were weighed on an analytical balance rather than measured volumetrically. Conversion of analyses of volumetric samples to molality required that the density of the samples be known. When weighed

samples were used, however, the conversion to molality could be performed directly from the analytical results. This resulted in an increase in the accuracy of the data since samples could be weighed more accurately than they could be measured volumetrically. Also, since the density was not required, the measurement of one less quantity was required.

DISCUSSION OF RESULTS

Basis for Reporting Concentrations

In the past concentration data for the rare earths have usually been expressed as grams of rare earth oxide per liter of solution because this was the common method of reporting the analytical results. However, upon consideration of the ultimate goal, which is the prediction of rare earth equilibria, it was found that more consistent data correlations could be obtained if the concentrations were reported on a molar basis rather than on a weight basis. Of the common methods for reporting molar concentrations, only molarity (moles of solute per liter of solution) and molality (moles of solute per 1000 grams of solvent) were considered. The choice of molality over molarity was dictated by solvent extraction theory.

From a consideration of solvent extraction theory it was found that, if the carrier solvents were insoluble in each other, the slope of the operating line was equal to the ratio of the volume flow rates of the phases when the concentration data were reported a molarity. However, when the concentration data were reported as molality, the slope of the operating line was equal to the ratio of the solvent flow rates.

The analysis of an extraction system was simplified if the slope of the operating line was constant. This was the

case only when the flow ratios were constant throughout the system. In rare earth extraction systems, where large concentration changes were obtained from stage to stage, volume changes as high as ten per cent were observed. In these cases, therefore, the volume flow rates and thus, the ratio of these flow rates did not remain constant through the extractor. Water and tributyl phosphate equilibrated with water, however, were practically immiscible so that for any extraction operation the solvent flow rates and thus, the ratio of these flow rates remained essentially constant.

From these arguments it was concluded that the slope of the operating line would be more constant if the concentration data were reported as molality rather than molarity. Therefore, in this report the concentration data have been reported on a molality basis.

This report involved a study of the interactions between nitric acid, and neodymium and samarium nitrate. Since nitric acid and the rare earth nitrates were both extracted, it was desirable to have a common basis for reporting the concentration data. The nitrate radical was common to both the rare earth nitrates and to nitric acid, and therefore, all concentration data were reported as the molality of the nitrate radical. On this basis the concentrations as reported were actually equal to the equivalents of solute per 1000 grams of

solvent.

Basis of Data Correlations

The equilibrium phenomena for the neodymium nitrate-
samarium nitrate-nitric acid extraction system discussed in
this report were evaluated from correlations of experimental
equilibrium data obtained for this system. To maintain con-
sistency in the correlation of the experimental data and
also in the use of these correlations in the prediction of
equilibrium phenomena for this system, it was desirable that,
in all cases, these correlations be based on the concentra-
tion and composition of only one of the phases. The choice
of the organic phase as the basis for these correlations was
made from a consideration of the argument presented below.

The magnitude of the separation factors between the rare
earths appeared to be controlled by the solute concentration
of the organic phase. This was observed from a comparison
of the separation factors between the rare earths in extrac-
tion systems in which salting-out agents were present in the
aqueous phase against the separation factors in extraction
systems in which no salting-out agents were present. In both
cases the separation factors at various organic phase concen-
trations and also the variation of the separation factors
with the organic phase concentration were found to be compar-
able. This was not found to be true in the case of the

aqueous phase. From this it was concluded that the organic phase was controlling the extractability of the rare earths, and therefore, the concentration and composition of the solutes in the organic phase were used as the basis for the correlations presented in this report.

Equilibrium Distribution Phenomena

Equilibrium data obtained by Knapp (10) for the pure light rare earths and for nitric acid were converted to a molality basis and plotted in Figure 1. This graph illustrates the general shape of the equilibrium curve when the data are reported on a molality basis. The positions of the equilibrium curves follow the order of extractability of these rare earths with lanthanum being the lowest and neodymium the highest. The extractability of nitric acid was greater than any of these rare earths.

For mixtures of these solutes it was expected that the overall distribution at a certain concentration was a function of the composition of the phases. In Figure 2 the distribution of various mixtures of neodymium nitrate and nitric acid was compared with the distribution of pure nitric acid. From Figure 2 it was observed that the distribution of neodymium nitrate-nitric acid mixtures was approximately the same as that of nitric acid, and thus the distribution of nitric acid alone could be used as a good approximation of
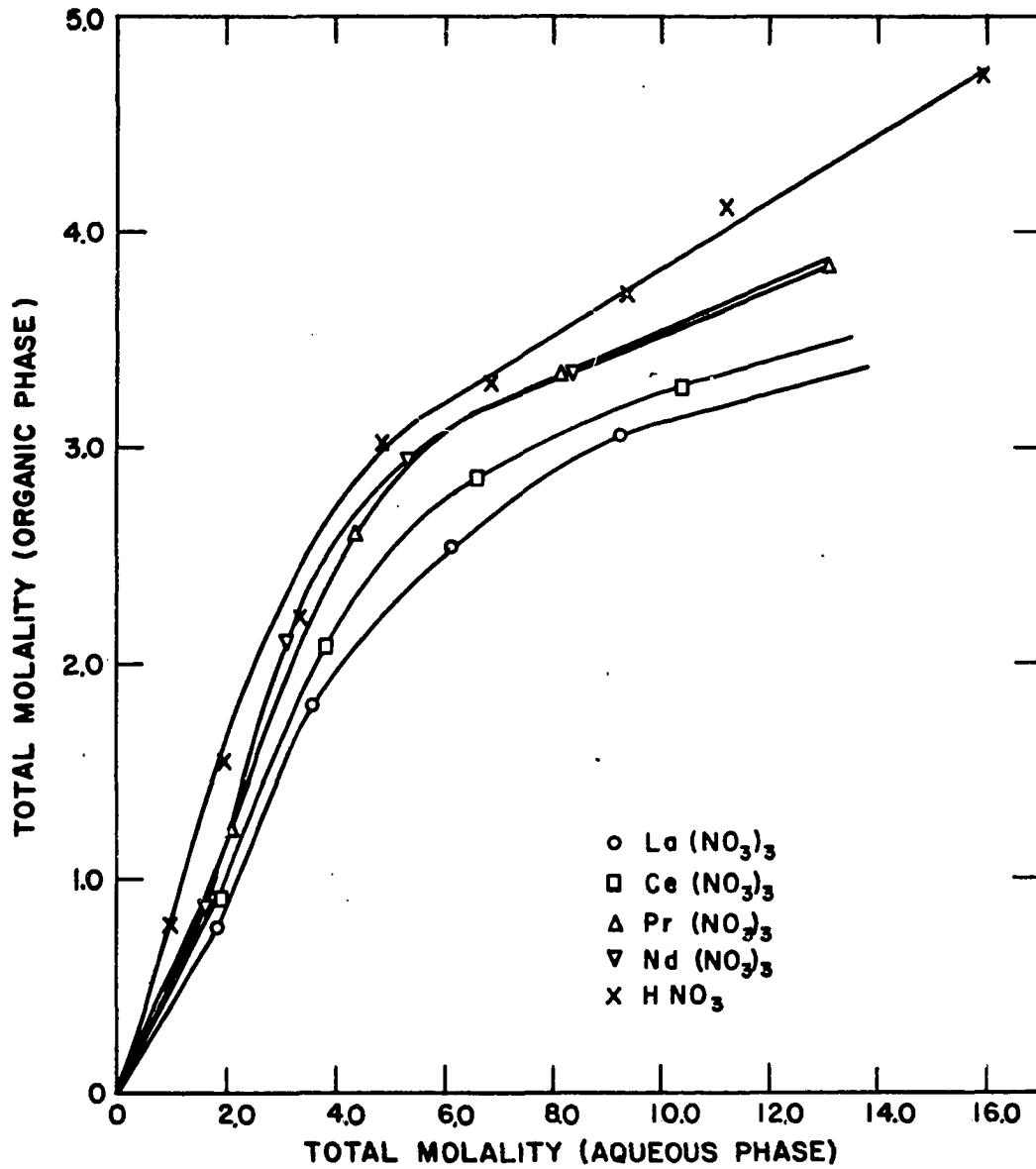
Figure 1. Equilibrium distribution of the pure light rare earths and of nitric acid between water and tributyl phosphate
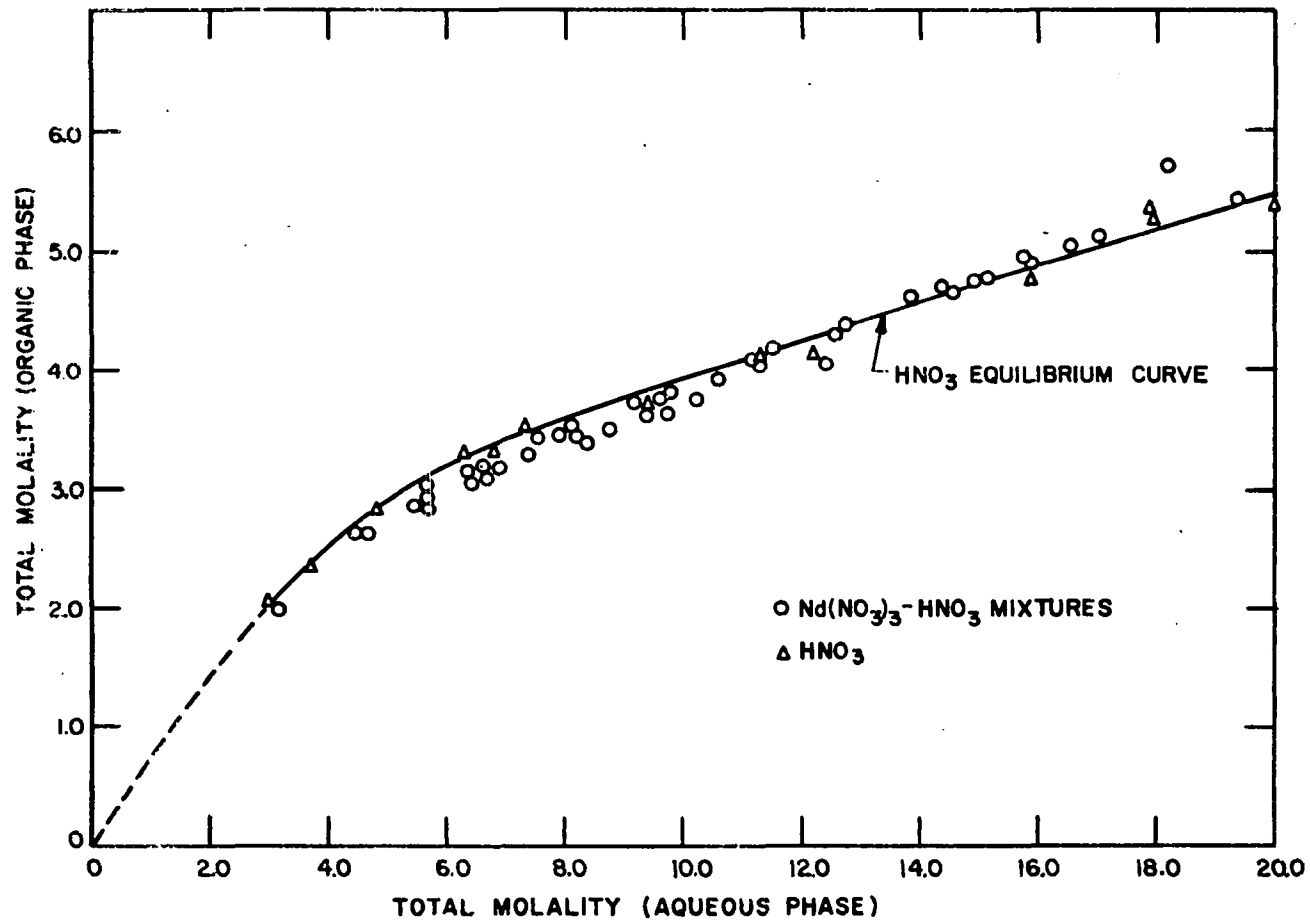
Figure 2. Comparison of the equilibrium distribution of neodymium
nitrate-nitric acid mixtures with that of pure nitric
acid

the distribution of neodymium nitrate-nitric acid mixtures.
This phenomenon was also observed for the distribution of mix-
tures of samarium nitrate and nitric acid (Figure 3), and the
conclusion drawn for neodymium nitrate-nitric acid mixtures
was also applicable for samarium nitrate-nitric acid mixtures.

The actual variation of the distribution coefficients
for neodymium nitrate-nitric acid mixtures and for samarium
nitrate-nitric acid mixtures with the composition of the
organic phase is shown in Figure 4 (see Nomenclature). Al-
though the data given in Figure 4 are for mixtures of pure
neodymium nitrate and nitric acid and of pure samarium nitrate
and nitric acid, Figure 4 can be used to determine the dis-
tribution coefficients for neodymium nitrate-samarium nitrate-
nitric acid mixtures. To accomplish this a knowledge of the
composition and concentration of the organic phase is neces-
sary. The distribution coefficient in the above mixtures is
then evaluated in the following manner. First, evaluate the
distribution coefficient at the concentration and rare earth
composition (Y_{RE}) of the organic phase assuming that the rare
earths present are pure neodymium nitrate. Then repeat this
operation for samarium nitrate assuming that the rare earths
present are pure samarium nitrate. The distribution coeffi-
cient for the mixture is then determined by a linear inter-
polation between the above values according to the composi-
tion (y_{Nd} and y_{Sm}) of the rare earth mixture in the organic
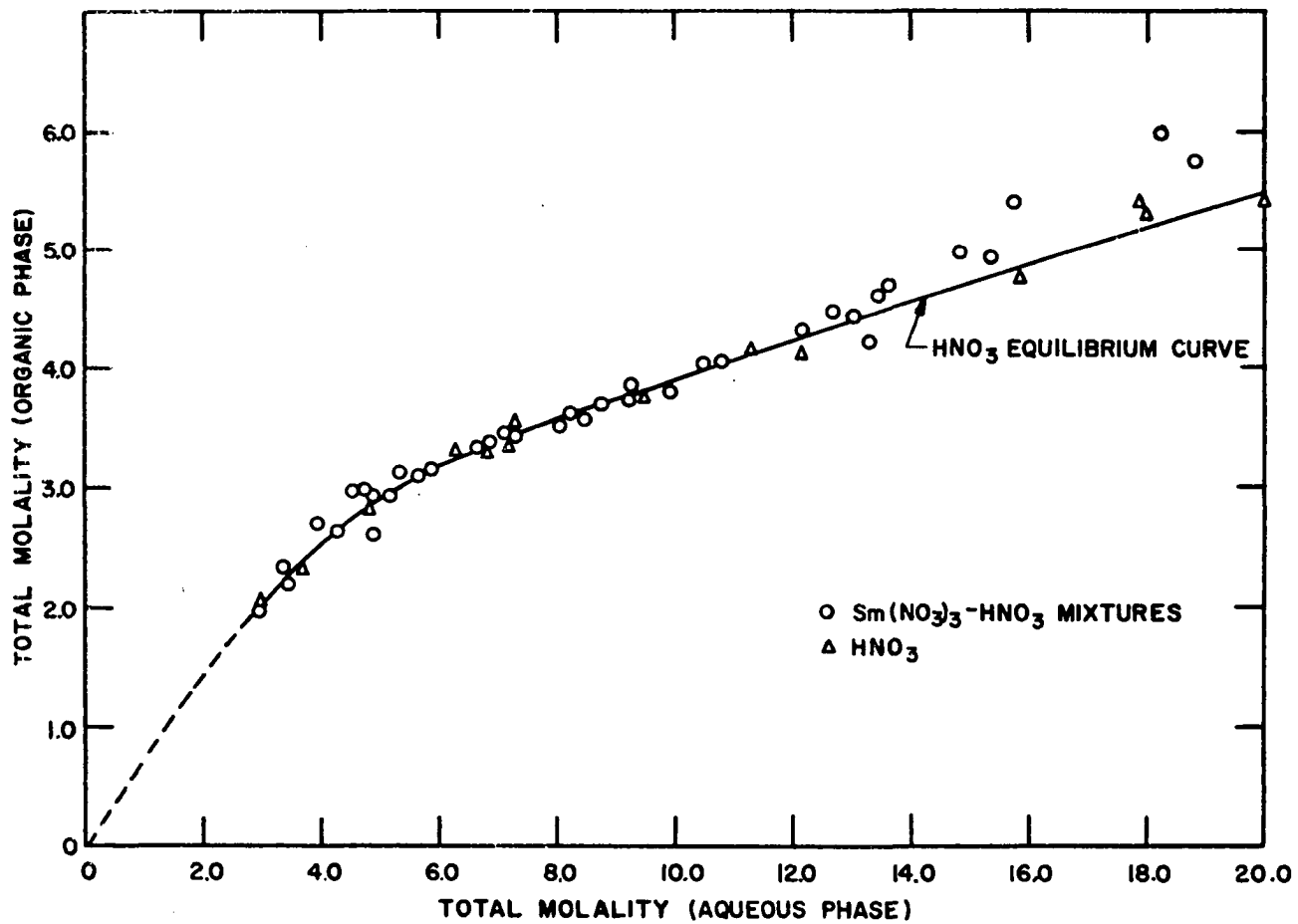
Figure 3. Comparison of the equilibrium distribution of samarium nitrate-nitric acid mixtures with that of pure nitric acid
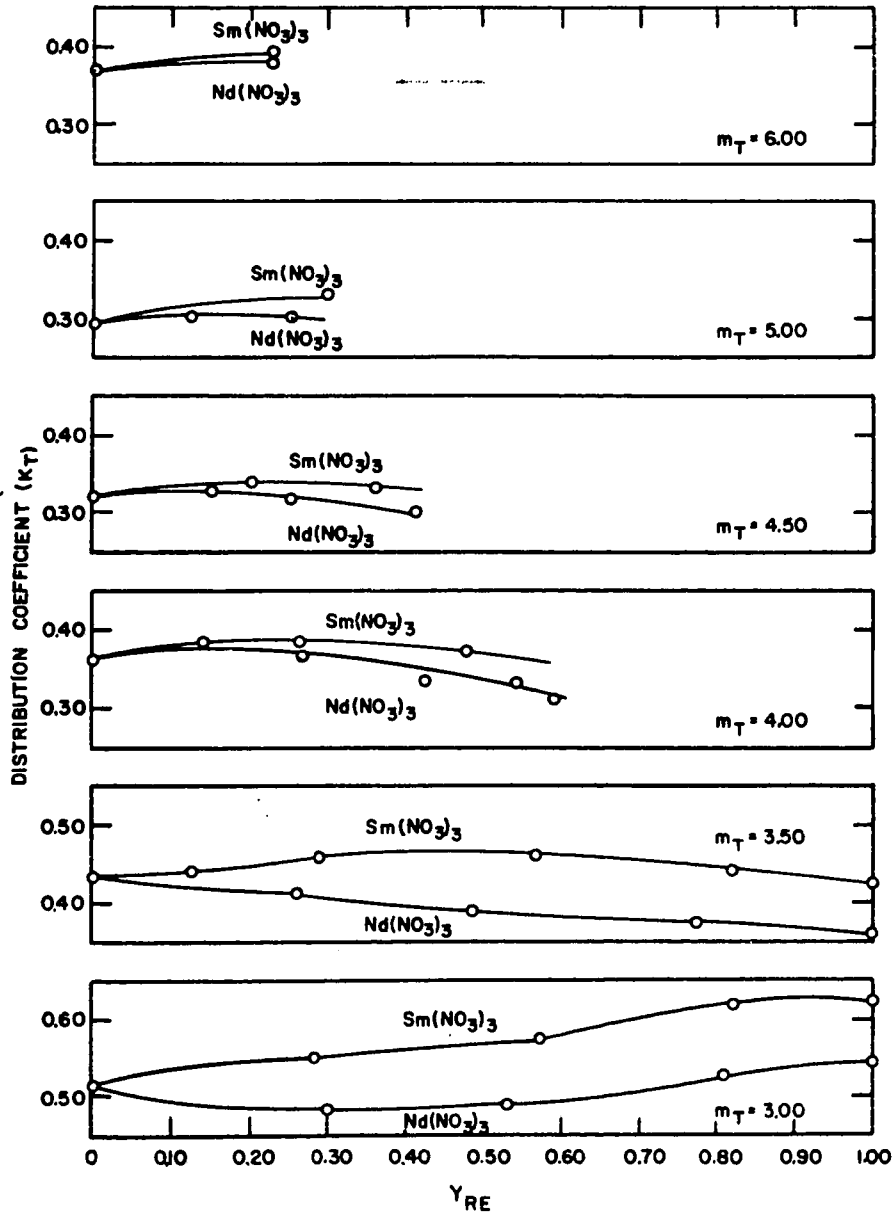
Figure 4. Distribution coefficient for neodymium nitrate-
nitric acid mixtures and samarium nitrate-nitric
acid mixtures as a function of the composition
and concentration of the organic phase

phase. The application of this method in the prediction of equilibria was demonstrated in another section of this report.

Separation Factors

The separation factors between samarium nitrate and neodymium nitrate were determined from single stage equilibrium extractions with various mixtures of neodymium nitrate, samarium nitrate and nitric acid. These separation factors are plotted in Figure 5 as a function of the total nitrate concentration of the organic phase. The position of the straight line in Figure 5 was determined by a least squares analysis of the experimental data.

It has been found that the separation factors between the rare earths increase with the total nitrate concentration of the organic phase and do not vary appreciably with the composition of the organic phase. This fact is borne out in Figure 5. The variations of the experimental data plotted on this graph are attributable to analytical deviations.

The separation factors between nitric acid and neodymium nitrate and between nitric acid and samarium nitrate were determined from single stage equilibrium extractions with neodymium nitrate-nitric acid mixtures and with samarium nitrate-nitric acid mixtures. These separation factors were found to vary both with the total concentration of the organic phase and with the composition of the organic phase.
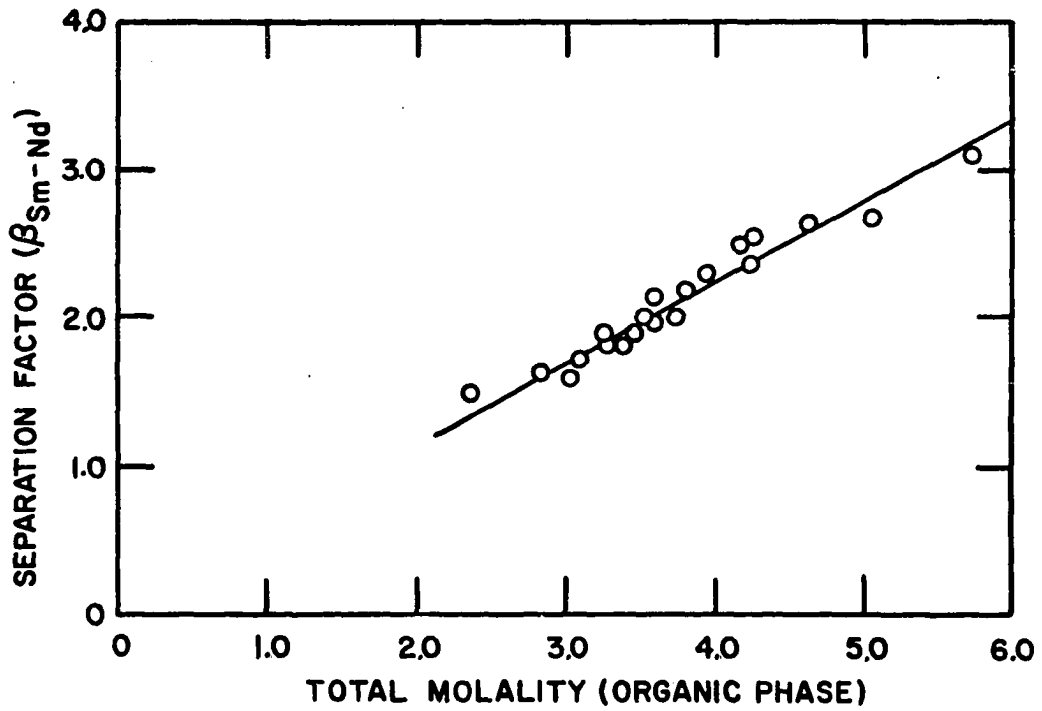
Figure 5. Separation factor between samarium nitrate and
neodymium nitrate as a function of the total
molality of the organic phase

The variations of the nitric acid-neodymium nitrate separation factors with the organic phase composition and concentration are shown in Figures 6 and 7. From Figure 7 it was observed that, at constant organic phase concentration, the nitric acid-neodymium nitrate separation factors increased linearly with the neodymium nitrate composition of the organic phase. From Figure 6 it was observed that, at constant organic phase composition, the nitric acid-neodymium nitrate separation factors increased with the organic phase concentration to a maximum value at a concentration in the vicinity of 3.7-molal and then decreased with the organic phase concentration at higher concentrations. The concentration at which the maximum value of the separation factors was obtained was dependent upon the composition of the organic phase. When Y_{Nd} was equal to zero, the maximum separation factor was obtained at a concentration of approximately 3.4-molal. When Y_{Nd} was equal to 0.20, the maximum value of the separation factor was obtained at a concentration of approximately 4.2-molal. A comparison of the nitric acid molalities for these two cases showed that they were approximately equal, and therefore, it was concluded that the maximum value of the separation factor between nitric acid and neodymium nitrate was obtained at approximately the same nitric acid concentration of the organic phase regardless of the composition of the organic phase.
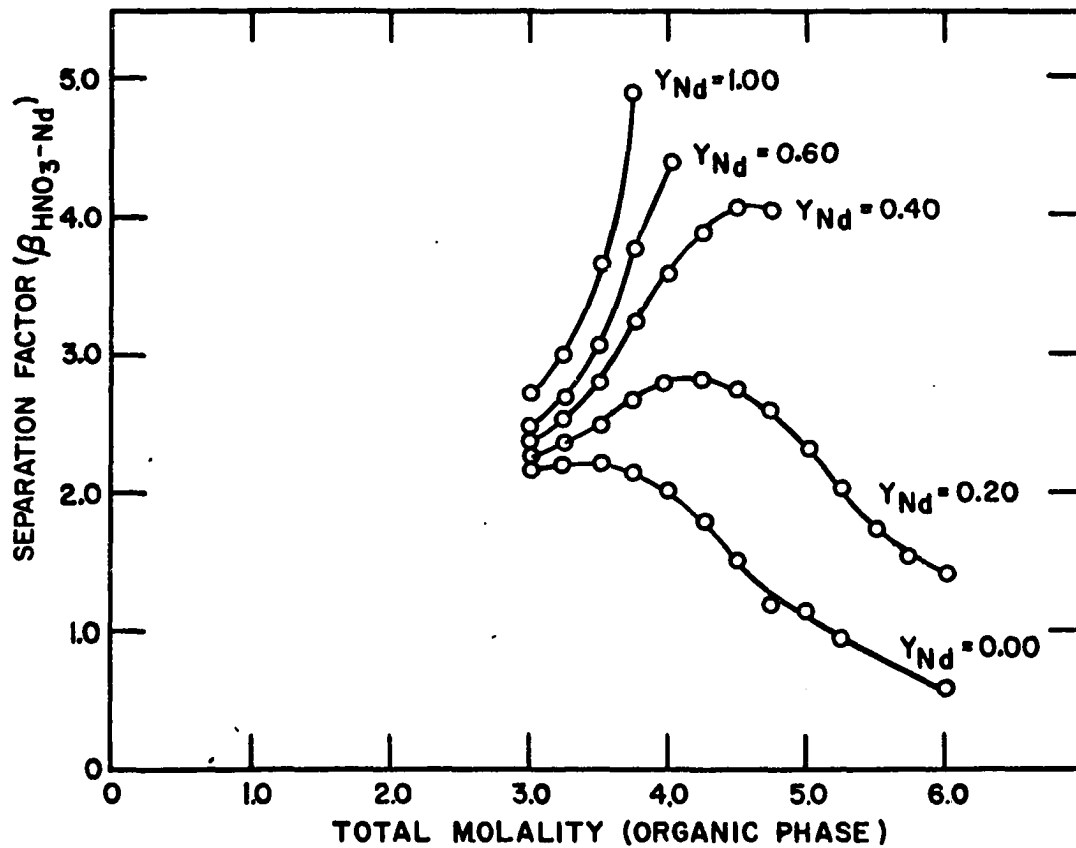
Figure 6. Separation factor between nitric acid and
neodymium nitrate as a function of the total
molality of the organic phase
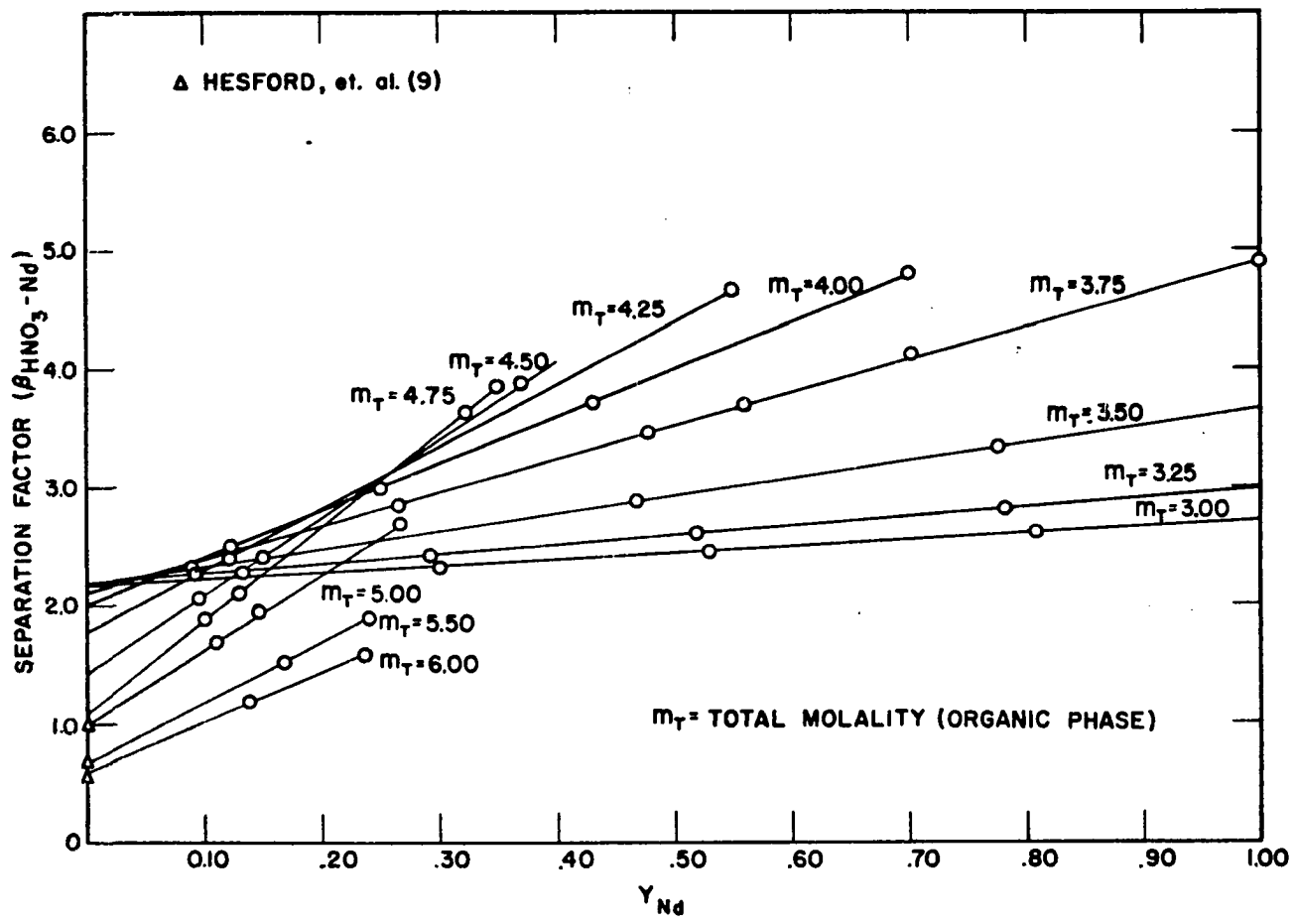
Figure 7. Separation factor between nitric acid and neodymium nitrate as a function of the composition of the organic phase

The variations of the separation factors between nitric acid and samarium nitrate are shown in Figures 8 and 9. Comparison of Figures 8 and 9 with Figures 6 and 7 indicates a general similarity in the interactions between these rare earths and nitric acid. By extrapolating this similarity to the other trivalent light rare earths it was concluded that the methods used to correlate the separation factor data for neodymium nitrate and samarium nitrate were also applicable in the study of the interactions of the other light rare earths with nitric acid.

Further observation of the data on the separation factors between nitric acid and neodymium nitrate and between nitric acid and samarium nitrate showed that the ratio of these separation factors extrapolated to zero per cent rare earths compared closely with the observed separation factors between samarium nitrate and neodymium nitrate. That is:

$$\beta_{Sm-Nd} \text{ (observed)} = \frac{\beta_{HNO_3-Nd} \text{ (0\% Nd)}}{\beta_{HNO_3-Sm} \text{ (0\% Sm)}} . \qquad (1)$$

Also, data were obtained by Hesford et al. (9) on the distribution of tracer quantities of neodymium nitrate and samarium nitrate at various nitric acid concentrations. Using these data the separation factors between nitric acid and these rare earths were calculated (see Appendix C), and then the ratios of these separation factors were calculated
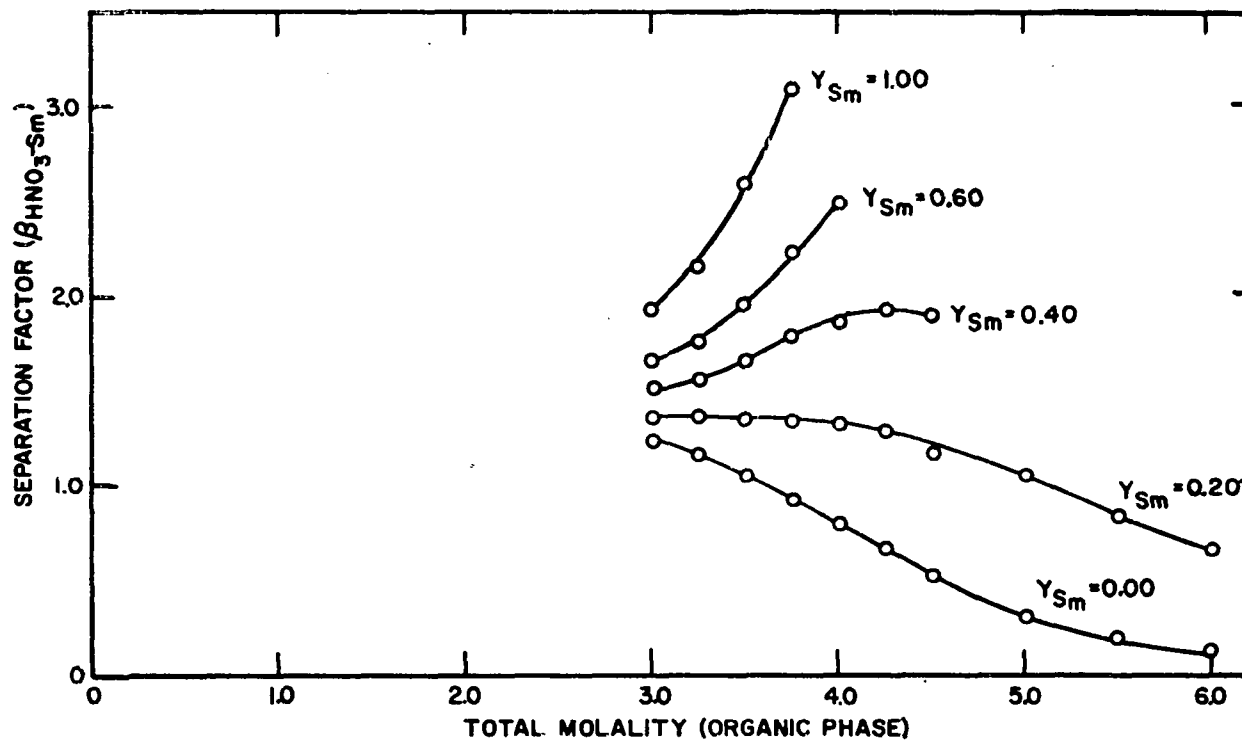
Figure 8. Separation factor between nitric acid and samarium nitrate as a function of the total molality of the organic phase
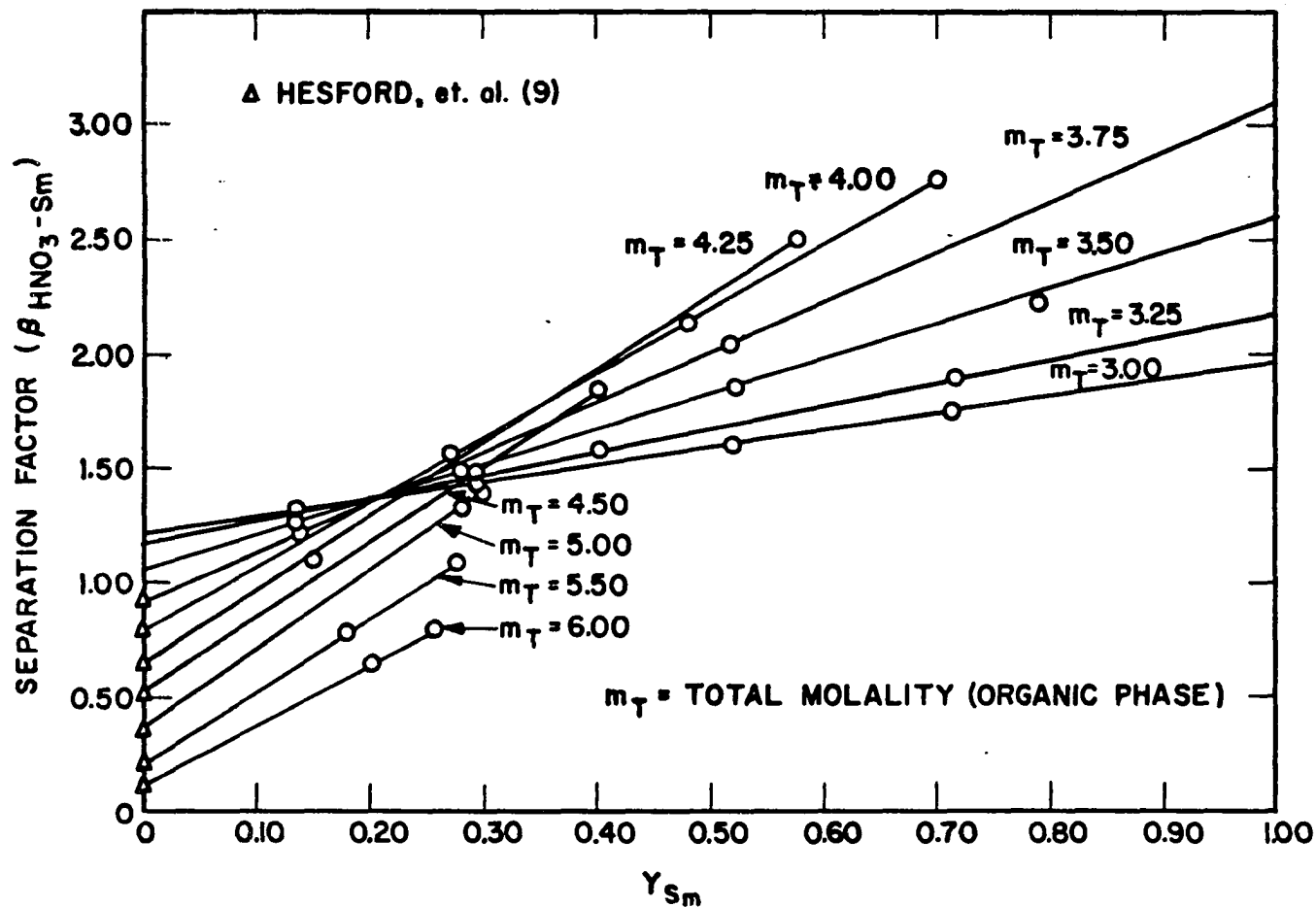
Figure 9. Separation factor between nitric acid and samarium nitrate as a function of the composition of the organic phase

by Equation 1.

The comparison of these methods for determining the separation factors between neodymium nitrate and samarium nitrate is shown in Table 1. These data indicated that it was possible to evaluate the separation factors between the rare earths from equilibrium data obtained with mixtures of nitric acid and the individual pure rare earth nitrates.

Using the data reported above on the nitric acid-rare earth nitrate separation factors for mixtures of nitric acid and the pure rare earth nitrates, it was possible to evaluate the nitric acid-rare earth nitrate separation factors when both rare earths were present provided that the composition and concentration of the organic phase were known.

The values of the nitric acid-neodymium nitrate and the nitric acid-samarium nitrate separation factors in mixtures of neodymium nitrate, samarium nitrate and nitric acid were found to be different from the values of these separation factors in mixtures of nitric acid with the pure rare earth nitrates. The amount of the difference in these separation factors was found to be a function of the composition $(y_{Nd}$ and $y_{Sm})$ of the rare earth mixture in the organic phase. Therefore, it was possible to be able to evaluate the nitric acid-neodymium nitrate separation factor or the nitric acid-samarium nitrate separation factor for two different nitric acid-rare earth nitrate mixtures and then to interpolate

Table 1. Comparison of separation factors between samarium
nitrate and neodymium nitrate (observed versus
calculated)

Total molality (organic phase)	β_{Sm-Nd} (observed)	β_{Sm-Nd} (calculated by extrapolation to 0% rare earths)	β_{Sm-Nd} (calculated from the data of Hesford et al. (9))
3.015	1.59	1.78	1.48
3.080	1.71	1.78	1.50
3.260	1.87	1.89	1.66
3.353	1.79	1.97	1.73
3.454	1.87	2.03	1.82
3.514	1.99	2.06	1.84
3.587	1.96	2.15	1.86
3.735	1.99	2.26	2.10
3.820	2.17	2.31	2.14
3.929	2.27	2.41	2.18
4.158	2.48	2.53	2.26
4.221	2.52	2.60	2.77
4.243	2.35	2.59	2.37
4.638	2.63	2.93	2.61
5.045	2.67	3.42	2.94
5.715	3.091	3.53	3.41

between these values according to the composition of the
organic phase in the nitric acid-rare earth nitrate mixture
for which the values of the separation factors were desired.
The method used to evaluate these various separation factors
is described in detail below. From Figure 5 the separation
factor between samarium nitrate and neodymium nitrate was
evaluated at the total concentration of the organic phase.

The separation factor between nitric acid and samarium
nitrate was evaluated from Figure 9 at the composition and
concentration of the organic phase. The composition of
samarium nitrate for this determination was assumed equal to
the composition of the rare earths (Y_{RE}) in the organic phase.

The separation factor between nitric acid and neodymium
nitrate was evaluated from Figure 7 at the concentration and
composition of the organic phase. The composition of neodym-
ium nitrate for this determination was assumed equal to the
composition of the rare earths (Y_{RE}) in the organic phase.

The nitric acid-neodymium nitrate separation factor was
also determined for a mixture of neodymium nitrate, samarium
nitrate and nitric acid in which the rare earth nitrate com-
position (Y_{RE}) was equal to the composition of the desired
mixture, but the composition of neodymium nitrate (y_{Nd}) in the
rare earth mixture was essentially equal to zero. In this
rare earth nitrate-nitric acid mixture the separation factor
between nitric acid and samarium nitrate was not affected by

the presence of the small amount of neodymium nitrate, and thus, this separation factor was equal to its pure component value. The neodymium nitrate, however, was distributed so as to satisfy the samarium nitrate-neodymium nitrate separation factor. Therefore, the nitric acid-neodymium nitrate separation factor for this mixture was determined by the equation,

$$\beta_{HNO_3-Nd} = \beta_{HNO_3-Sm} \times \beta_{Sm-Nd} \cdot \qquad (2)$$

Thus, the nitric acid-neodymium nitrate separation factor had been determined for two different rare earth nitrate-nitric acid mixtures in which the rare earth composition (Y_{RE}) was the same as the rare earth composition in the original proposed mixture. The composition of neodymium nitrate (y_{Nd}) in the rare earth mixture in one case was 1.0 and in the other case was zero. The nitric acid-neodymium nitrate separation factor was then determined for the desired mixture by a linear interpolation between these two values according to the composition of neodymium nitrate (y_{Nd}) in the desired mixture.

The nitric acid-samarium nitrate separation factor in the desired rare earth nitrate-nitric acid mixture was then determined by use of Equation 2. The nitric acid-rare earth nitrate separation factors determined by the above method compared very closely with the values for these separation

factors observed in the single stage extractions with neo-
dymium nitrate, samarium nitrate and nitric acid. The appli-
cation of this method in the prediction of equilibrium phenom-
ena is shown in another section of this report.

PREDICTION OF EQUILIBRIUM PHENOMENA

The value of equilibrium and separation data for multi-component systems lies in their use in the prediction of equilibrium phenomena for any mixture of these components. A method was developed for the prediction of equilibrium phenomena for a multi-component single stage extraction. This method incorporated a series of equilibrium and material balance calculations by which the concentration of each solute was determined for each phase. This method is demonstrated here by means of a sample calculation to predict the equilibrium concentrations for a mixture of neodymium nitrate, samarium nitrate and nitric acid using the equilibrium data for these components given in the Discussion of Results section.

Sample Calculation

It was assumed that 1000 grams of tributyl phosphate (S) and a feed solution (F) containing 1000 grams of water, five equivalents of nitric acid, five equivalents of neodymium nitrate and five equivalents of samarium nitrate were fed into a vessel as shown in Figure 10.

The equilibrium concentration and composition of each phase for this system were evaluated by a trial and error procedure. To determine the distribution coefficients and sep-
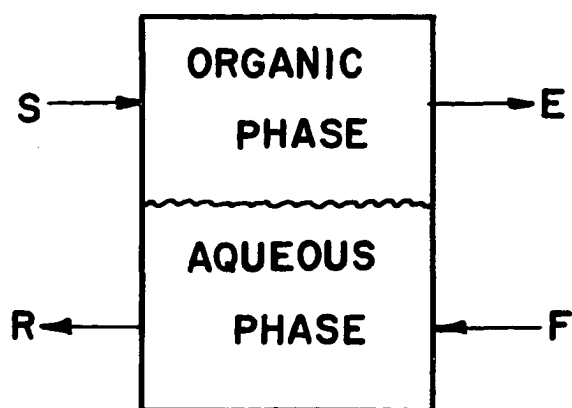
S=SOLVENT STREAM
F=FEED STREAM
R=RAFFINATE STREAM
E=EXTRACT STREAM

Figure 10. Illustration of a single stage extraction system

aration factors for this system it was first necessary to estimate the composition, and concentration of the organic phase. Using these distribution coefficients and separation factors it was then possible to calculate the composition and concentration of the organic phase and then to compare these calculated values with the estimated values. If agreement was obtained, the solution was correct. If agreement was not obtained, however, the calculated values of the composition and concentration of the organic phase were used as the new estimated values, and the procedure was repeated. The calculations given here were for the final trial on this system.

Procedure: The material balance for the solutes in this system was

$$Fm_F + Sm_S = Rm_R + Em_E, \tag{3}$$

where F and R were the weight of water (kilograms) in the feed and raffinate streams, respectively, S and E were the weight of tributyl phosphate (kilograms) in the solvent and extract streams, respectively, and m was the total molality of each stream as indicated by the subscript. m_E and m_R are related by the distribution coefficient, K_T, in the equation,

$$K_T = m_E/m_R . \tag{4}$$

Equation 4 was substituted into Equation 3 to obtain

$$Fm_F + Sm_S = (R/K_T + E)m_E . \tag{5}$$

From the statement of the problem, F and S were equal

to one kilogram of water and one kilogram of tributyl phosphate, respectively. Due to the immiscibility of the solvents, S and E were also equal to one kilogram of water and one kilogram of tributyl phosphate, respectively. Also, from the statement of the problem, m_F was equal to 15-molal, and m_S was zero. These values were substituted into Equation 5 to obtain

$$(1/K_T + 1)m_E = 15 . \tag{6}$$

This equation was rearranged to obtain m_E as a function of K_T. That is:

$$m_E = 15K_T/(1 + K_T) . \tag{7}$$

In Figure 4 the distribution coefficient, K_T, was plotted as a function of the composition and concentration of the organic phase. Therefore, from a knowledge of the relative extractability of the components present, it was necessary to estimate the composition of the organic phase, and then, by the method described in the Discussion of Results section, evaluate K_T as a function of m_E for this composition. Various combinations of these values were then substituted into Equation 7 until an equality was obtained. This, then, gave the value of m_E for this calculation based on the estimated composition of the organic phase. For this calculation the composition of the organic phase was estimated to be 49 per cent rare earths and 51 percent nitric acid. The rare earths in

the organic phase were estimated to be 35 per cent neodymium

nitrate (y_{Nd}) and 65 per cent samarium nitrate (y_{Sm}). From

Figure 4 the distribution coefficient, K_T, was then determined

at various values of concentration, m_E, using the estimated

composition values. K_T was then plotted against m_E in Figure

11. Using combinations of these variables from Figure 11 and

substituting them into Equation 7, an equality was obtained

when m_E was equal to 3.92, and K_T was equal to 0.354. That

is:

$$m_E = 15K_T/(1 + K_T);\qquad(7)$$

$$3.92 = 15 \times 0.354/(1 + 0.354) = 3.922 \ .$$

The concentration of the aqueous phase was then determined

to be 11.08-molal from a material balance on the total solutes

in the system.

Thus, the total concentration of each phase based on the

estimated composition of the organic phase was established.

It was then necessary to determine the separation factors be-

tween the various solutes and, using these separation factors,

to calculate the composition of each phase. The calculated

composition of the organic phase was then compared with the

estimated composition of the organic phase.

The samarium nitrate-neodymium nitrate and the nitric

acid-neodymium nitrate separation factors were determined by

the following method described in the Discussion of Results

section.
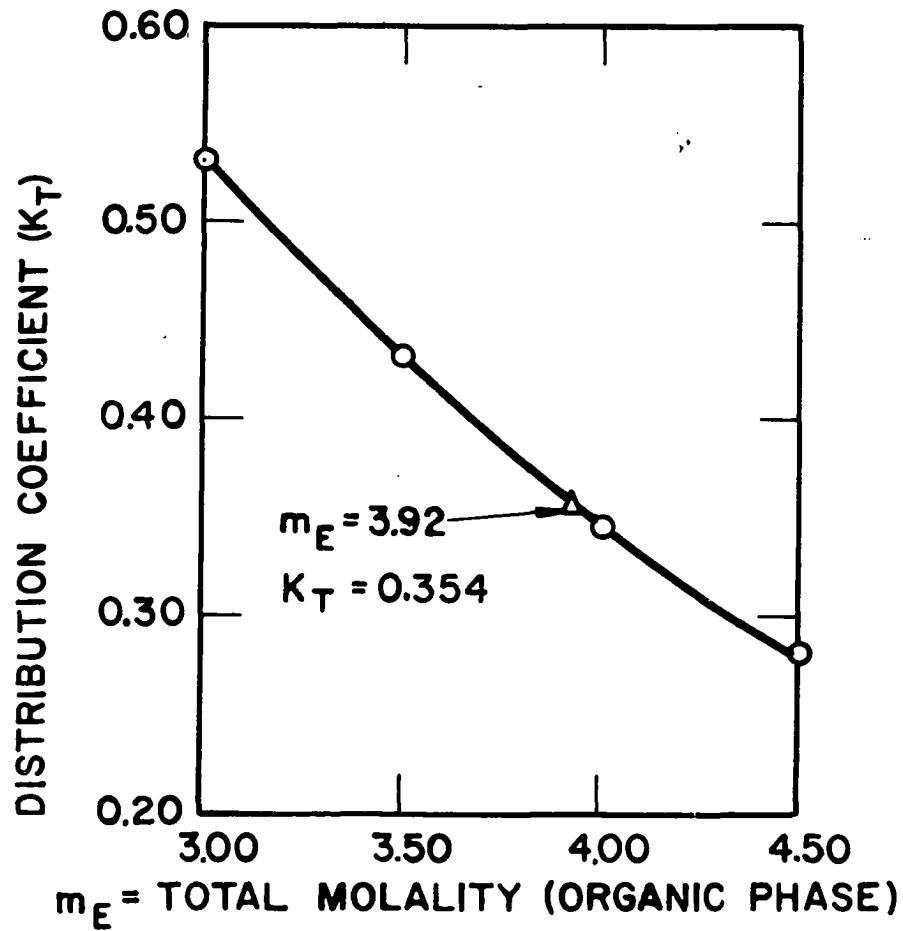
Figure 11. Distribution coefficient as a function of the total molality of the organic phase for neodymium nitrate-samarium nitrate-nitric acid mixtures evaluated at Y_{RE} = 0.49 and y_{Nd} = 0.35

The separation factor between samarium nitrate and neodymium nitrate was determined from Figure 5 to be equal to 2.13 at the concentration of the organic phase.

The separation factor between nitric acid and samarium nitrate, assuming that the rare earths present in the organic phase were pure samarium nitrate, was determined from Figure 9 by evaluating this separation factor at various concentrations in the vicinity of m_E equal to 3.92, and at Y_{Sm} equal to 0.49. These separation factors were then plotted versus m_E (Figure 12). The nitric acid-samarium nitrate separation factor was then determined from Figure 12 to be equal to 2.13.

The separation factor between nitric acid and neodymium nitrate, assuming the rare earths present were pure neodymium nitrate, was determined from Figure 7 by the method described above for determining the nitric acid-samarium nitrate separation factor. The nitric acid-neodymium nitrate separation factors were also plotted versus m_E in Figure 12. The separation factor between nitric acid and neodymium nitrate was then determined from Figure 12 to be equal to 3.79.

The nitric acid-neodymium nitrate separation factor was also determined for a mixture of neodymium nitrate, samarium nitrate and nitric acid in which the rare earth nitrate composition (Y_{RE}) was equal to 0.49, but the composition of neodymium nitrate (y_{Nd}) was essentially equal to zero. This separation factor was evaluated by Equation 2. That is:
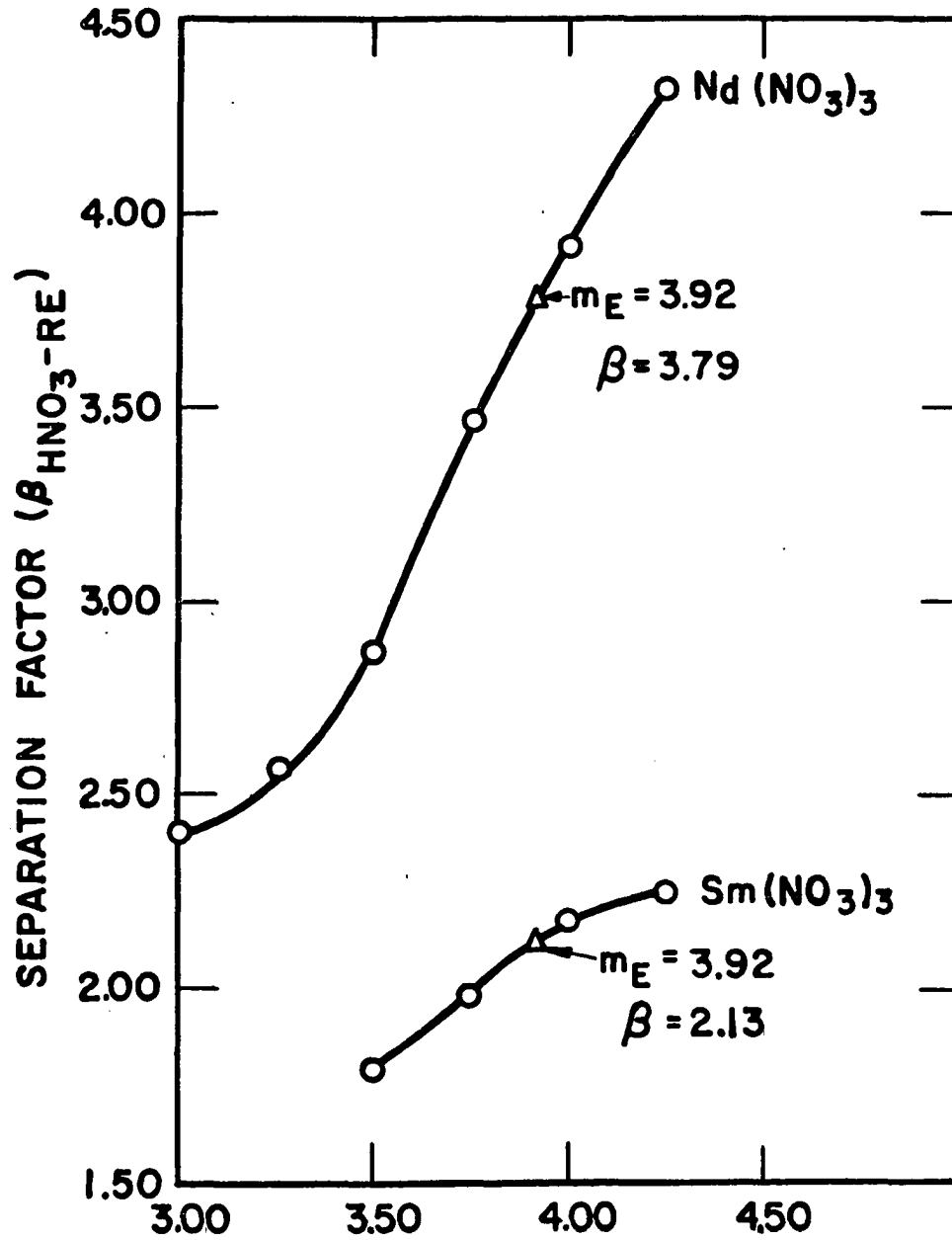
Figure 12. Separation factor between nitric acid and the
indicated rare earth nitrates as a function
of the total molality of the organic phase
evaluated at $Y_{RE} = 0.49$

$$\beta_{HNO_3-Nd} = \beta_{HNO_3-Sm} \times \beta_{Sm-Nd} ; \qquad (2)$$

$$\beta_{HNO_3-Nd} = 2.13 \times 2.13 = 4.537 .$$

Thus, the nitric acid-neodymium nitrate separation factor when Y_{RE} was equal to 0.49, and y_{Nd} was equal to 1.00 was determined to be 3.79, and the nitric acid-neodymium nitrate separation factor when Y_{RE} was equal to 0.49, and y_{Nd} was equal to zero was determined to be 4.537. The value of this separation factor when Y_{RE} was equal to 0.49, and y_{Nd} was equal to 0.35 was then determined by a linear interpolation between the calculated values to be equal to 4.275. This is the nitric acid-neodymium nitrate separation factor in the proposed mixture based on the assumed composition for this mixture. This separation factor and the samarium nitrate-neodymium nitrate separation factor determined above were then used to calculate the concentration of each component in each of the phases.

The concentration of neodymium nitrate in the organic phase was calculated from the assumed composition of the organic phase and the calculated concentration of the organic phase. That is:

$$m_{Nd} \, (org.) = 3.92 \times 0.49 \times 0.35 ;$$

$$m_{Nd} \, (org.) = 0.672 .$$

The concentration of neodymium nitrate in the aqueous phase

was then determined by a material balance on neodymium nitrate. Since five equivalents of neodymium nitrate were originally fed to the extractor,

$$m_{Nd}(aq.) = 5.0 - m_{Nd}(org.) \ . \tag{8}$$

Therefore,

$$m_{Nd}(aq.) = 5.0 - 0.672 = 4.328 \ .$$

The distribution coefficient for neodymium nitrate was then calculated as

$$k_{Nd} = m_{Nd}(org.)/m_{Nd}(aq.) \ ; \tag{9}$$

$$k_{Nd} = 0.672/4.238 = 0.1553 \ .$$

The distribution coefficients for samarium nitrate and for nitric acid could then be calculated since

$$k_{Sm} = k_{Nd} \times \beta_{Sm-Nd} \ , \tag{10}$$

and

$$k_{HNO_3} = k_{Nd} \times \beta_{HNO_3-Nd} \ . \tag{11}$$

Therefore,

$$k_{Sm} = 0.1553 \times 2.13 = 0.3308,$$

and

$$k_{HNO_3} = 0.1553 \times 4.275 = 0.6647 \ .$$

Thus, the distribution coefficient was determined for each solute. The concentrations of samarium nitrate and nitric acid were then determined by consideration of the distribution coefficient and a material balance for each

solute. That is:

$$m_{Sm}(aq.) + m_{Sm}(org.) = m_{Sm}(feed) \; ; \qquad (12)$$

$$m_{Sm}(org.) = k_{Sm} \times m_{Sm}(aq.) \; . \qquad (13)$$

Equation 13 was substituted into Equation 12 to obtain

$$m_{Sm}(aq.) = m_{Sm}(feed)/(1 + k_{Sm}) \; . \qquad (14)$$

For this system the molality of samarium nitrate in the feed

solution was five equivalents per kilogram of water. There-

fore, by Equation 14

$$m_{Sm}(aq.) = 5.0/(1 + 0.3308) = 3.757 \; ,$$

and by Equation 12

$$m_{Sm}(org.) = 5.0 - 3.757 = 1.243 \; .$$

This same analysis (Equation 12 through Equation 14)

was used for nitric acid to determine the concentration of

nitric acid in each phase. The molality of nitric acid in

the feed solution was five equivalents per kilogram of water.

Therefore, by Equation 14 for nitric acid

$$m_{HNO_3}(aq.) = 5.0/(1 + 0.6647) = 3.004 \; ,$$

and by Equation 12 for nitric acid

$$m_{HNO_3}(org.) = 5.0 - 3.004 = 1.996 \; .$$

Thus, the concentration of each component was evaluated

for each phase. It was then necessary to calculate the com-

position of the solutes in the organic phase and compare these

with the original assumed composition. It was also necessary

to determine the total concentration of the organic phase and compare this against the value of the concentration calculated from the overall equilibrium based on the assumed compositions. If agreement was obtained for both comparisons, the calculated compositions and concentration were correct.

The total concentration of the organic phase was equal to the sum of the concentrations of each component. That is:

$$m_{Nd}(org.) + m_{Sm}(org.) + m_{HNO_3}(org.) = m_E ; \qquad (15)$$

$$0.672 + 1.243 + 1.996 = 3.911 = m_E .$$

This compared very favorably with the value of $m_E(3.92)$ calculated originally.

The composition of the rare earths (Y_{RE}) in the organic phase was

$$Y_{RE} = (m_{Nd} + m_{Sm})/m_E ; \qquad (16)$$

$$Y_{RE} = (0.672 + 1.243)/3.911 = 0.4896 .$$

The composition of neodymium nitrate (y_{Nd}) in the rare earth nitrate mixture was

$$y_{Nd} = m_{Nd}/(m_{Nd} + m_{Sm}) ; \qquad (17)$$

$$y_{Nd} = 0.672/(0.672 + 1.243) = 0.3509 .$$

These calculated values also compared very favorably with the estimated values. Therefore, the calculations were correct, and the composition and concentration of each phase for a neodymium nitrate-samarium nitrate-nitric acid system was effectively predicted.

A further comment should be made concerning the material balances used in this sample calculation. These material balances applied only when the amount of water and tributyl phosphate in the system were equal. Equal amounts of water and tributyl phosphate were used for this sample calculation to provide more clarity in the demonstration of the method of predicting equilibrium phenomena. If the amount of water and tributyl phosphate had not been equal, it would have been necessary to take this into account in the performance of the material balance calculations.

DISCUSSION

As is shown by the experimental results, the rare earth nitrate-nitric acid system is rather complex. In the evaluation of the nitric acid-rare earth nitrate separation factors, variations were seen both with the composition and with the concentration of the organic phase. The reason for these variations in the separation factors can be explained qualitatively from a consideration of the mechanism by which the extraction of the rare earths and nitric acid takes place.

It was shown (6) that pure water was extracted into tributyl phosphate in a ratio of approximately one mole of water per mole of tributyl phosphate, and it was postulated that this extraction occurred by addition at the strongly polar P=O group of the tributyl phosphate molecule. It was found (6) that the rare earth nitrates were also extracted into water equilibrated tributyl phosphate by addition at the P=O group with the subsequent replacement of one mole of water per equivalent of rare earth nitrate extracted (see also Table 3, Appendix B).

A similar mechanism has been proposed for the extraction of nitric acid into tributyl phosphate (1, 7, and 20). These investigators proposed that the nitric acid was extracted into tributyl phosphate by addition at the P=O group up to the concentration (approximately 3.7-molal) at which a one

to one molar tributyl phosphate-nitric acid complex was formed. This complex then acted as a solvent to extract additional nitric acid either through direct solubility or by addition at some other group of the tributyl phosphate molecule. In the case of nitric acid extraction, however, it was found (1) that not all the water was displaced from the tributyl phosphate phase (see also Table 2, Appendix B). Therefore, it was proposed that the water which remained in the organic phase formed a hydrate with the tributyl phosphate-nitric acid complex.

A consideration of this proposed mechanism for nitric acid extraction in explaining the shape of the nitric acid equilibrium curve (see Figure 3) brings out a discrepancy in this mechanism. In the region of the proposed one to one molar tributyl phosphate-nitric acid complex (3.7-molal) there is continuity in the nitric acid equilibrium curve that would not be expected if the mechanism of extraction changed at this point. This discrepancy can be resolved, however, through a modification of the mechanism proposed above. Continuity of the nitric acid equilibrium curve would be more likely if both modes of extraction occurred simultaneously. This would mean that, at concentrations well below 3.7-molal, the nitric acid would be extracted both by addition at the P=O group and also by addition at some other group of the tributyl

phosphate molecule or through direct solubility. Extraction
by both mechanisms would then continue at higher concentra-
tions.

By this modified mechanism the water that was in the
organic phase was not all complexed in the same manner. Part
of the water was present as a complex at the P=O group of the
tributyl phosphate molecule, and the remainder was present as
a hydrate of the tributyl phosphate-nitric acid complex.
From Table 2, Appendix B, it was observed that the water
present in the organic phase was a minimum at approximately
3.7-molal nitric acid concentration. Therefore, it was pro-
posed that the increase in the amount of water above 3.7-molal
was due both to hydration of the tributyl phosphate-nitric
acid complex and also to the replacement of nitric acid by
water at the P=O group in the tributyl phosphate-nitric acid
complex. As a consequence of this proposal the concentration
of the tributyl phosphate-water complex would be a minimum
at 3.7-molal.

Considering this modified mechanism for nitric acid ex-
traction and also the mechanism for rare earth extraction, a
possible explanation for the variations of the nitric acid-
rare earth nitrate separation factors would be as follows.
In the rare earth nitrate-nitric acid extraction system the
rare earths are extracted mainly by displacement of the water

in the tributyl phosphate-water complex. The tributyl phos-phate-nitric acid complex is affected only slightly by the rare earth nitrate extraction. The extractability of the rare earth nitrates is therefore a function of the concentration of the tributyl phosphate-water complex. Since this concentration is a minimum at approximately 3.7-molal, it would be expected that the extractability of the rare earth nitrates would be a minimum in the vicinity of this concentration. This was found to be the case for the variation of the nitric acid-neodymium nitrate separation factor with the total solute concentration of the organic phase at constant composition (Figure 6). The nitric acid-neodymium nitrate separation factor in this case was observed to exhibit a maximum (indicating minimum extractability of neodymium nitrate) in the vicinity of 3.7-molal total nitrate concentration. This was also observed in the variation of the nitric acid-monazite rare earth nitrate separation factors with the total nitrate concentration of the organic phase when the rare earths were present in tracer concentrations (Figure 13). For this case the nitric acid-rare earth nitrate separation factors also exhibited a maximum in the vicinity of 3.7-molal total nitrate concentration.

The increase in the nitric acid-neodymium nitrate separation factor with an increase in the neodymium nitrate-nitric acid ratio at constant total nitrate concentration

(Figure 7) can be explained by the analysis presented above. As the neodymium nitrate-nitric acid ratio increases, the concentration of the tributyl phosphate-water complex will decrease, and thus, the extractability of neodymium nitrate will decrease causing an increase in the nitric acid-neodymium nitrate separation factor. This analogy is also applicable in the case of the nitric acid-samarium nitrate separation factor.

The rare earth nitrate-nitric acid system is probably much more complex than is indicated here, and other factors should be taken into account. However, the analysis presented above serves to give at least a qualitative explanation of the data obtained for the rare earth nitrate-nitric acid extraction system.

CONCLUSIONS

1. The equilibrium distribution of neodymium nitrate-nitric acid mixtures and of samarium nitrate-nitric acid mixtures is approximated by the equilibrium distribution of nitric acid. The actual distribution of these mixtures may be represented as a function of the composition and concentration of the organic phase. The distribution coefficients for neodymium nitrate-samarium nitrate-nitric acid mixtures can be determined using the data given for neodymium nitrate-nitric acid and for samarium nitrate-nitric acid mixtures.

2. The samarium nitrate-neodymium nitrate separation factors can be represented as a function of the concentration of the organic phase and can be evaluated from equilibrium data obtained with mixtures of each pure rare earth nitrate with nitric acid.

3. The nitric acid-neodymium nitrate separation factors and the nitric acid-samarium nitrate separation factors vary with both the composition and total concentration of the organic phase. From a consideration of the mechanism by which the extraction of these species was thought to occur, it was found that the variations of these separation factors correlated with variation of the concentration of the tributyl phosphate-water complex in the organic phase.

4. For neodymium nitrate-samarium nitrate-nitric acid

mixtures the nitric acid-rare earth nitrate separation factors are different from their values in neodymium nitrate-nitric acid and in samarium nitrate-nitric acid mixtures. This difference in the separation factors is a function of both the samarium nitrate-neodymium nitrate separation factor and the composition of the rare earth mixture (y_{Nd} and y_{Sm}) in the organic phase.

5. Neodymium nitrate and samarium nitrate were chosen for these extraction studies because of their ease of analysis. However, a general similarity was noted in the extraction properties of these rare earths. Extrapolating this similarity to the other trivalent light rare earth nitrates, it is thought that the correlations presented in this report will also be applicable in equilibrium studies with other nitric acid-light rare earth nitrate mixtures.

6. The method presented for prediction of equilibrium phenomena may be applied to many other multicomponent systems. This method may also be applied to the prediction of stage-wise equilibria in multi-stage systems although, in this case, the calculations involved could become rather cumbersome.

NOMENCLATURE

k	– distribution coefficient of any solute
k_{HNO_3}	– distribution coefficient of nitric acid
k_{Nd}	– distribution coefficient of neodymium nitrate
k_{Sm}	– distribution coefficient of samarium nitrate
k_T	– distribution coefficient based on the total molality of each phase
β_{A-B}	– separation factor between A and B; k_A/k_B
β_{Sm-Nd}	– separation factor between samarium nitrate and neodymium nitrate
β_{HNO_3-Nd}	– separation factor between nitric acid and neodymium nitrate
β_{HNO_3-Sm}	– separation factor between nitric acid and samarium nitrate
β_{HNO_3-RE}	– separation factor between nitric acid and either rare earth nitrate
m_T	– equivalents of total nitrate/1000 grams of solvent (either phase)
Y_{RE}	– equivalents of rare earth nitrate/total equivalents of nitrate (organic phase)
Y_{Nd}	– equivalents of neodymium nitrate/total equivalents of nitrate (organic phase)
Y_{Sm}	– equivalents of samarium nitrate/total equivalents of nitrate (organic phase)

y_{Nd} — equivalents of neodymium nitrate/equivalent of rare earth nitrate (organic phase)

y_{Sm} — equivalents of samarium nitrate/equivalent of rare earth nitrate (organic phase)

F — weight of water in feed (kilograms)

S — weight of tributyl phosphate in solvent (kilograms)

R — weight of water in raffinate (kilograms)

E — weight of tributyl phosphate in extract (kilograms)

m_F — equivalents of solute per 1000 grams of water (feed)

m_S — equivalents of solute per 1000 grams of tributyl phosphate (solvent)

m_R — equivalents of solute per 1000 grams of water (raffinate)

m_E — equivalents of solute per 1000 grams of tributyl phosphate (extract)

m_{Nd} — equivalents of neodymium nitrate per 1000 grams of solvent

m_{Sm} — equivalents of samarium nitrate per 1000 grams of solvent

m_{HNO_3} — equivalents of nitric acid per 1000 grams of solvent

org. — abbreviation of organic phase

aq. — abbreviation of aqueous phase

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ACKNOWLEDGEMENT

APPENDIX A. ANALYTICAL METHODS

Before analysis of the organic phase could be performed, it was necessary to transfer the solutes from the organic phase into water. This was accomplished by contacting a known amount of the organic phase three times with water. To improve the separation of phases, an inert diluent (heptane) was added to the organic phase. The aqueous solutions from the three contacts were then combined, and analyses were performed on these samples the same as for the aqueous phase samples.

The rare earth concentrations were determined by precipitating the rare earths with oxalic acid. The resulting oxalates were filtered and then ignited to rare earth oxides at 800 to $1000^{\circ}C$ in a muffle furnace. The weight of the oxides were then determined on an analytical balance.

The composition of the rare earths for the runs with mixtures of rare earth nitrates was determined by the spectrophometric method developed by Banks and Klingman (3).

For the nitric acid determinations the rare earths in the samples were first precipitated by addition of an excess of potassium ferrocyanide. The nitric acid concentration was then determined by titration against standard sodium hydroxide. An automatic titrator was used for the titrations, and the end point was taken at a pH of 8.7.

APPENDIX B. EQUILIBRIUM DISTRIBUTION OF WATER

Upon extraction of neodymium nitrate or nitric acid, it was found that a certain amount of water was displaced from water equilibrated tributyl phosphate to the aqueous phase. The amount of water transferred to the aqueous phase was determined by means of a series of single stage extractions. To evaluate the water transfer the weights of the feed and solvent solutions were determined accurately for each extraction. This was accomplished in the following manner. The separatory funnel to be used for each extraction was weighed on an analytical balance. Then the tributyl phosphate was added, and the separatory funnel was again weighed. After addition of the feed solution, a third weighing was performed. The weights of the solvent and feed solutions could then be determined. The mixture was then shaken until equilibrium was attained, and the phases were separated and analyzed to determine the solute concentrations.

The weights of the equilibrium phases were determined by consideration of the analytical results and also material balance calculations for the runs. By writing a total material balance and a solute balance for each run, the weights of the equilibrium phases could be determined by the simultaneous solution of the following equations obtained.

$$M_a + M_o = M_t \; ; \qquad\qquad (1)$$

$$xM_a + yM_o = M_x \; , \qquad\qquad (2)$$

where M_a, M_o and M_t were the weight of the aqueous phase,
the weight of the organic phase and the total weight, re-
spectively, x and y were the composition, by weight, of the
solute in the aqueous and organic phases, respectively, and
M_x was the weight of solute in the feed. The amount of water
in the aqueous phase could then be evaluated. The amount of
water transferred was determined as the difference between
the amount of water in the aqueous phase at equilibrium and
the amount of water in the feed. These results are given in
Tables 2 and 3.

It was also attempted to use this method for mixtures
of neodymium nitrate and nitric acid. However, due to the
small amount of water transfer and the decreased precision
in the analytical results when both solutes were present, it
was impossible to obtain consistent data for this system.

Table 2. Distribution of water in the extraction of nitric acid

Molality HNO$_3$ (aqueous phase)	Molality HNO$_3$ (organic phase)	Molality H$_2$O (organic phase)	Moles H$_2$O transferred per mole HNO$_3$ extracted	% H$_2$O transferred from organic phase
1.517	1.325	3.330	0.320	11.3
1.698	1.441	3.176	0.392	15.1
1.906	1.575	3.127	0.416	17.4
2.187	1.731	3.196	0.340	15.7
2.479	1.801	3.463	0.271	13.8
3.000	2.048	2.976	0.363	20.8
3.392	2.224	2.977	0.335	20.8
3.693	2.343	2.721	0.424	27.6
4.794	2.884	2.469	0.448	34.3
5.116	2.998	2.358	0.468	37.3
5.475	3.096	2.328	0.469	38.0
5.748	3.177	2.111	0.519	43.9
6.277	3.320	2.013	0.527	46.5
6.815	3.460	1.931	0.529	48.7
7.302	3.541	1.613	0.604	57.0
8.594	3.801	1.685	0.546	55.2
17.982	5.364	2.135	0.305	43.4
20.182	5.781	2.400	0.229	36.0
22.602	6.226	2.616	0.171	30.3
25.330	6.815	2.832	0.132	24.1

Table 3. Distribution of water in the extraction of
neodymium nitrate

Molality $Nd(NO_3)_3$ (aqueous phase)	Molality $Nd(NO_3)_3$ (organic phase)	Molality H_2O (organic phase)	Moles H_2O transferred per equivalent of $Nd(NO_3)_3$ extracted	% H_2O transferred from organic phase
1.507	0.692	2.91	1.23	22.6
2.840	1.999	1.76	0.999	53.3
3.077	2.168	1.67	0.963	55.6
4.203	2.746	1.17	0.945	68.9
4.990	2.969	0.90	0.962	76.0
5.653	3.142	0.82	0.935	78.4

APPENDIX C. NITRIC ACID-RARE EARTH NITRATE SEPARATION FACTORS (TRACER RARE EARTH CONCENTRATIONS)

Data were obtained by Scargill et al. (14), and Hesford et al. (9) on the distribution of tracer quantities of the monazite rare earth nitrates in the presence of nitric acid at various acid concentrations. The data given were the normality of nitric acid in the aqueous phase and the distribution coefficients of the rare earths.

The concentration of nitric acid in the organic phase was determined by assuming that the small amount of rare earths present did not appreciably affect the distribution of nitric acid. The organic phase nitrate concentrations and thus, the distribution coefficient of nitric acid could then be determined from equilibrium data for pure nitric acid. The nitric acid-rare earth nitrate separation factors were then determined as the ratio of the distribution coefficient of nitric acid to the distribution coefficient of the rare earth nitrates. The total concentration of the organic phase was taken as the concentration of the nitric acid since the slight amount of rare earths present would not change the total concentration appreciably. These data are plotted in Figure 13. Due to the method used in calculating these data, certain inaccuracies will be present. However, these data

serve to illustrate the complexity of the rare earth nitrate-
nitric acid system.
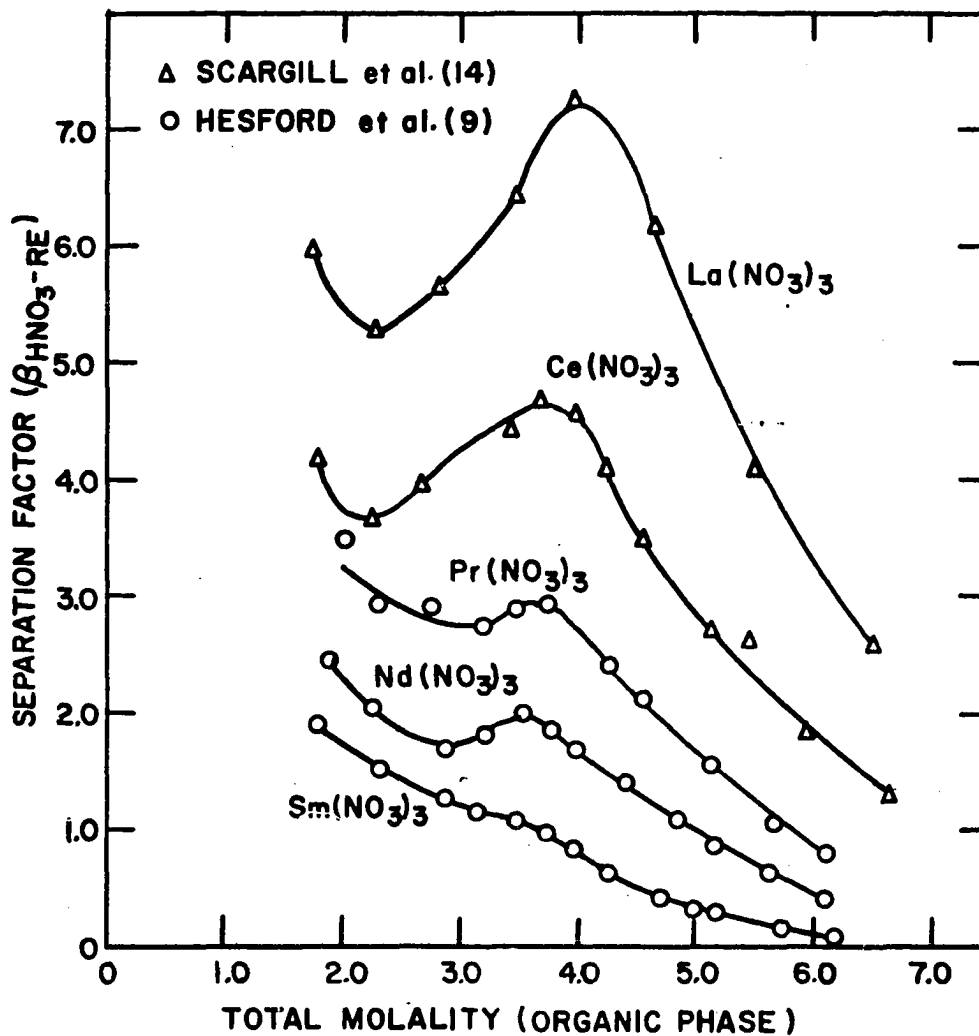
Figure 13. Separation factor between nitric acid and the indicated rare earth nitrates at tracer rare earth concentrations as a function of the total molality of the organic phase

APPENDIX D. DISTRIBUTION COEFFICIENTS

Table 4. Equilibrium distribution of neodymium nitrate-nitric acid and samarium nitrate-nitric acid mixtures as a function of the composition and total concentration of the organic phase (from Figure 4)

Y_{RE}	Distribution coefficient of $Nd(NO_3)_3$-HNO_3 mixtures	Distribution coefficient of $Sm(NO_3)_3$-HNO_3 mixtures
	Molality (organic phase) = 3.00	
0.00	0.515	0.515
0.15	0.496	0.541
0.30	0.485	0.552
0.45	0.486	0.560
0.60	0.498	0.581
0.75	0.517	0.605
0.90	0.534	0.625
1.00	0.543	0.625
	Molality (organic phase) = 3.50	
0.00	0.435	0.435
0.15	0.420	0.441
0.30	0.410	0.455
0.45	0.396	0.465
0.60	0.381	0.460
0.75	0.373	0.448
0.90	0.368	0.432
1.00	0.359	0.423

Table 4. (Continued)

Y_{RE}	Distribution coefficient of $Nd(NO_3)_3$-HNO_3 mixtures	Distribution coefficient of $Sm(NO_3)_3$-HNO_3 mixtures
	Molality (organic phase) = 4.00	
0.00	0.364	0.364
0.10	0.373	0.379
0.20	0.371	0.382
0.40	0.347	0.379
0.60	0.316	0.363
	Molality (organic phase) = 4.50	
0.00	0.322	0.322
0.10	0.333	0.335
0.20	0.330	0.337
0.30	0.318	0.335
0.45	0.290	0.325
	Molality (organic phase) = 5.00	
0.00	0.295	0.295
0.15	0.305	0.320
0.27	0.300	0.327
	Molality (organic phase) = 6.00	
0.00	0.266	0.266
0.10	0.277	0.282
0.22	0.280	0.290

APPENDIX E. NITRIC ACID-RARE EARTH NITRATE
SEPARATION FACTORS

Table 5. Separation factor between nitric acid and neodymium
nitrate as a function of the composition and con-
centration of the organic phase (from Figure 7)

Molality of organic phase	Y_{Nd}				
	0.00	0.20	0.40	0.60	1.00
	Nitric acid-neodymium nitrate separation factor				
3.00	2.17	2.26	2.37	2.48	2.71
3.25	2.18	2.35	2.51	2.67	2.97
3.50	2.20	2.46	2.76	3.05	3.65
3.75	2.12	2.67	3.23	3.78	4.90
4.00	2.00	2.79	3.58	4.38	
4.25	1.77	2.82	3.86		
4.50	1.45	2.74	4.05		
4.75	1.10	2.65			
5.00	1.10	2.25			
5.50	0.67	1.67			
6.00	0.60	1.42			

Table 6. Separation factor between nitric acid and samarium
nitrate as a function of the composition and total
concentration of the organic phase (from Figure 9)

Molality of organic phase	Y_{Sm}				
	0.00	0.20	0.40	0.60	1.00
	Nitric acid-samarium nitrate separation factor				
3.00	1.23	1.36	1.51	1.67	1.95
3.25	1.17	1.37	1.56	1.76	2.17
3.50	1.05	1.36	1.66	1.97	2.60
3.75	0.92	1.35	1.80	2.23	3.10
4.00	0.80	1.34	1.87	2.48	
4.25	0.67	1.30	1.94		
4.50	0.52	1.17	1.91		
5.00	0.32	1.06			
5.50	0.20	0.84			
6.00	0.12	0.66			

APPENDIX F. EQUILIBRIUM DATA

Table 7. Equilibrium data for neodymium nitrate-nitric acid
systems

	Aqueous phase			Organic phase		
	Grams of Nd(NO$_3$)$_3$ per gram of solution	Grams of HNO$_3$ per gram of solution	Grams of solvent per gram of solution	Grams of Nd(NO$_3$)$_3$ per gram of solution	Grams of HNO$_3$ per gram of solution	Grams of solvent per gram of solution
1	0.3014	0.0172	0.6814	0.1854	0.0249	0.7897
2	0.3517	0.0209	0.6274	0.2011	0.0286	0.7703
3	0.3774	0.0225	0.6001	0.2069	0.0316	0.7615
4	0.3551	0.0185	0.6264	0.2052	0.0279	0.7669
5	0.4578	0.0229	0.5193	0.2217	0.0367	0.7416
6	0.4831	0.0256	0.4913	0.2181	0.0434	0.7385
7	0.4539	0.0925	0.4536	0.1422	0.1095	0.7483
8	0.4268	0.0756	0.4976	0.1513	0.0913	0.7574
9	0.3966	0.0814	0.5220	0.1443	0.0914	0.7643
10	0.3704	0.0740	0.5556	0.1460	0.0811	0.7729
11	0.3476	0.0712	0.5812	0.1447	0.0777	0.7776
12	0.3246	0.0681	0.6073	0.1409	0.0731	0.7860
13	0.2949	0.0599	0.6452	0.1351	0.0679	0.7970
14	0.2868	0.0600	0.6532	0.1337	0.0680	0.7983
15	0.3496	0.2068	0.4436	0.0927	0.1634	0.7439
16	0.3457	0.1783	0.4760	0.0931	0.1500	0.7569
17	0.3122	0.1783	0.5095	0.0852	0.1471	0.7677

Table 7. (Continued)

	Aqueous phase			Organic phase		
	Grams of Nd(NO$_3$)$_3$ per gram of solution	Grams of HNO$_3$ per gram of solution	Grams of solvent per gram of solution	Grams of Nd(NO$_3$)$_3$ per gram of solution	Grams of HNO$_3$ per gram of solution	Grams of solvent per gram of solution
18	0.2949	0.1638	0.5913	0.0866	0.1377	0.7757
19	0.2843	0.1588	0.5569	0.0850	0.1346	0.7804
20	0.2615	0.1523	0.5862	0.0833	0.1242	0.7925
21	0.2378	0.1342	0.6280	0.0836	0.1129	0.8035
22	0.2252	0.1304	0.6444	0.0815	0.1093	0.8092
23	0.2043	0.3844	0.4113	0.0726	0.2056	0.7218
24	0.1997	0.3411	0.4592	0.0590	0.1975	0.7435
25	0.1831	0.3244	0.4925	0.0486	0.1906	0.7608
26	0.1718	0.2903	0.5379	0.0432	0.1787	0.7781
27	0.1686	0.2863	0.5451	0.0422	0.1772	0.7806
28	0.1541	0.2644	0.5815	0.0395	0.1668	0.7937
29	0.1423	0.2356	0.6221	0.0401	0.1564	0.8035
30	0.1330	0.2268	0.6402	0.0384	0.1523	0.8093
31	0.1505	0.4455	0.4040	0.0639	0.2274	0.7087
32	0.1511	0.3979	0.4510	0.0495	0.2106	0.7399
33	0.1396	0.3755	0.4849	0.0398	0.2024	0.7578
34	0.1340	0.3430	0.5230	0.0338	0.1919	0.7743
35	0.1285	0.3309	0.5406	0.0316	0.1871	0.7813
36	0.1187	0.3058	0.5755	0.0288	0.1789	0.7923

Table 7. (Continued)

	Aqueous phase			Organic phase		
	Grams of $Nd(NO_3)_3$ per gram of solution	Grams of HNO_3 per gram of solution	Grams of solvent per gram of solution	Grams of $Nd(NO_3)_3$ per gram of solution	Grams of HNO_3 per gram of solution	Grams of solvent per gram of solution
37	0.1113	0.2768	0.6119	0.0284	0.1680	0.8036
38	0.1004	0.2544	0.6452	0.0276	0.1615	0.8110
39	0.1440	0.3530	0.5030	0.0363	0.1953	0.7684
40	0.2700	0.2360	0.4940	0.0662	0.1669	0.7669
41	0.3301	0.1913	0.4786	0.0843	0.1517	0.7640
42	0.4633	0.0567	0.4800	0.1731	0.0780	0.7489
43	0.4533	0.0549	0.4918	0.1756	0.0773	0.7471
44	0.3672	0.1253	0.5075	0.1121	0.1238	0.7641
45	0.2649	0.2173	0.5178	0.0682	0.1598	0.7720
46	0.1428	0.3305	0.5267	0.0357	0.1889	0.7754
47	0.5354	0.0619	0.4027	0.1787	0.0955	0.7258
48	0.4679	0.1378	0.3943	0.1325	0.1437	0.7238
49	0.4044	0.1825	0.4131	0.1204	0.1546	0.7250
50	0.2114	0.4226	0.3660	0.0910	0.2258	0.6832
51	0.2384	0.4745	0.2871	0.1320	0.2502	0.6178
52	0.5960	0.0046	0.3994	0.2728	0.0074	0.7198
53	0.5115	0.0548	0.4337	0.1818	0.0853	0.7329
54	0.4363	0.1469	0.4168	0.1206	0.1461	0.7333
55	0.2729	0.3390	0.3881	0.0914	0.2046	0.7040

Table 7. (Continued)

	Aqueous phase			Organic phase		
	Grams of $Nd(NO_3)_3$ per gram of solution	Grams of HNO_3 per gram of solution	Grams of solvent per gram of solution	Grams of $Nd(NO_3)_3$ per gram of solution	Grams of HNO_3 per gram of solution	Grams of solvent per gram of solution
56	0.2310	0.4407	0.3283	0.1116	0.2351	0.6533
57	0.3351	0.2567	0.4082	0.0956	0.1815	0.7229
58	0.4734	0.1150	0.4116	0.1402	0.1322	0.7276
59	0.5288	0.0469	0.4243	0.1940	0.0792	0.7268
60	0.2230	0.4780	0.2990	0.1253	0.2420	0.6327

Table 8. Equilibrium data for samarium nitrate-nitric acid mixtures

	Aqueous phase			Organic phase		
	Grams of Sm(NO$_3$)$_3$ per gram of solution	Grams of HNO$_3$ per gram of solution	Grams of solvent per gram of solution	Grams of Sm(NO$_3$)$_3$ per gram of solution	Grams of HNO$_3$ per gram of solution	Grams of solvent per gram of solution
1	0.4872	0.0285	0.4843	0.2261	0.0469	0.7270
2	0.4465	0.0302	0.5233	0.2284	0.0368	0.7348
3	0.3857	0.0271	0.5872	0.2246	0.0313	0.7441
4	0.3409	0.0225	0.6366	0.2173	0.0267	0.7560
5	0.3074	0.0202	0.6724	0.2068	0.0259	0.7673
6	0.3129	0.0221	0.6650	0.2083	0.0259	0.7658
7	0.2771	0.0180	0.7048	0.1937	0.0233	0.7830
8	0.2479	0.0156	0.7365	0.1769	0.0179	0.8052
9	0.4002	0.1082	0.4916	0.1601	0.0980	0.7419
10	0.3756	0.0961	0.5283	0.1633	0.0856	0.7511
11	0.3239	0.0867	0.5894	0.1593	0.0756	0.7651
12	0.2819	0.0720	0.6461	0.1537	0.0658	0.7805
13	0.2605	0.0634	0.6761	0.1478	0.0629	0.7893
14	0.2585	0.0714	0.6701	0.1456	0.0634	0.7910
15	0.2340	0.0590	0.7070	0.1355	0.0570	0.8075
16	0.1783	0.0427	0.7790	0.1019	0.0486	0.8495
17	0.2688	0.2829	0.4483	0.1129	0.1610	0.7261
18	0.2605	0.2600	0.4795	0.1039	0.1561	0.7400

Table 8. (Continued)

	Aqueous phase			Organic phase		
	Grams of Sm(NO₃)₃ per gram of solution	Grams of HNO₃ per gram of solution	Grams of solvent per gram of solution	Grams of Sm(NO₃)₃ per gram of solution	Grams of HNO₃ per gram of solution	Grams of solvent per gram of solution
19	0.2299	0.2280	0.5421	0.0922	0.1418	0.7660
20	0.2047	0.1959	0.5994	0.0880	0.1287	0.7833
21	0.1882	0.1786	0.6332	0.0875	0.1226	0.7899
22	0.1758	0.1744	0.6498	0.0828	0.1202	0.7976
23	0.1618	0.1586	0.6796	0.0807	0.1128	0.8065
24	0.1416	0.1402	0.7182	0.0723	0.1022	0.8255
25	0.1289	0.4317	0.4394	0.0896	0.1969	0.6574
26	0.1227	0.4020	0.4753	0.0743	0.1894	0.6839
27	0.1192	0.3439	0.5369	0.0557	0.1760	0.7683
28	0.1026	0.2938	0.6036	0.0470	0.1637	0.7893
29	0.0991	0.2833	0.6176	0.0458	0.1598	0.7944
30	0.0936	0.2707	0.6357	0.0438	0.1534	0.8028
31	0.0851	0.2426	0.6723	0.0414	0.1480	0.8106
32	0.0547	0.1415	0.8038	0.0260	0.1077	0.8693
33	0.2218	0.2913	0.4869	0.0966	0.1645	0.7389
34	0.2170	0.2804	0.5026	0.0934	0.1597	0.7469
35	0.2130	0.2687	0.5183	0.0894	0.1564	0.7542
36	0.2020	0.2452	0.5528	0.0846	0.1468	0.7686
37	0.2222	0.2920	0.4858	0.0952	0.1660	0.7388

Table 8. (Continued)

	Aqueous phase			Organic phase		
	Grams of Sm(NO$_3$)$_3$ per gram of solution	Grams of HNO$_3$ per gram of solution	Grams of solvent per gram of solution	Grams of Sm(NO$_3$)$_3$ per gram of solution	Grams of HNO$_3$ per gram of solution	Grams of solvent per gram of solution
38	0.2190	0.2845	0.4965	0.0919	0.1620	0.7461
39	0.2142	0.2701	0.5157	0.0878	0.1579	0.7543
40	0.2042	0.2443	0.5533	0.0821	0.1506	0.7673
41	0.1286	0.5262	0.3452	0.1261	0.2216	0.6532
42	0.1997	0.3827	0.4176	0.1137	0.1884	0.6979
43	0.2778	0.2684	0.4538	0.1162	0.1613	0.7225
44	0.4219	0.1300	0.4481	0.1562	0.1159	0.7279
45	0.4837	0.0642	0.4521	0.2021	0.0728	0.7251
46	0.5409	0.0428	0.4163	0.2224	0.0649	0.7127
47	0.5786	0.0068	0.4164	0.2768	0.0093	0.7139
48	0.1010	0.5968	0.3022	0.1378	0.2482	0.6142

Table 9. Equilibrium data for neodymium nitrate-samarium nitrate-nitric acid mixtures

	Aqueous phase				Organic phase			
	Grams of $Nd(NO_3)_3$ per gram of solution	Grams of $Sm(NO_3)_3$ per gram of solution	Grams of HNO_3 per gram of solution	Grams of solvent per gram of solution	Grams of $Nd(NO_3)_3$ per gram of solution	Grams of $Sm(NO_3)_3$ per gram of solution	Grams of HNO_3 per gram of solution	Grams of solvent per gram of solution
1	0.2317	0.1842	0.1253	0.4588	0.0495	0.0924	0.1177	0.7404
2	0.2174	0.1714	0.1031	0.5081	0.0540	0.0924	0.0988	0.7547
3	0.1998	0.1607	0.1068	0.5327	0.0539	0.0864	0.0955	0.7602
4	0.1919	0.1482	0.0983	0.5616	0.0556	0.0855	0.0903	0.7886
5	0.1790	0.1412	0.0930	0.5868	0.0562	0.0828	0.0893	0.7717
6	0.1670	0.1316	0.0883	0.6131	0.0556	0.0799	0.0842	0.7803
7	0.1521	0.1209	0.0796	0.6474	0.0557	0.0757	0.0789	0.7897
8	0.1362	0.1123	0.0718	0.6797	0.0536	0.0713	0.0735	0.8017
9	0.0892	0.0585	0.4160	0.4363	0.0285	0.0577	0.2061	0.7077
10	0.0837	0.0596	0.3973	0.4594	0.0229	0.0435	0.1967	0.7369
11	0.0787	0.0584	0.3697	0.4933	0.0194	0.0378	0.1882	0.7547
12	0.0753	0.0559	0.3365	0.5323	0.0170	0.0317	0.1781	0.7732

Table 9. (Continued)

	Aqueous phase				Organic phase			
	Grams of Nd(NO₃)₃ per gram of solution	Grams of Sm(NO₃)₃ per gram of solution	Grams of HNO₃ per gram of solution	Grams of solvent per gram of solution	Grams of Nd(NO₃)₃ per gram of solution	Grams of Sm(NO₃)₃ per gram of solution	Grams of HNO₃ per gram of solution	Grams of solvent per gram of solution
13	0.0725	0.0538	0.3234	0.5503	0.0161	0.0294	0.1778	0.7767
14	0.0662	0.0511	0.2972	0.5856	0.0155	0.0271	0.1707	0.7868
15	0.0602	0.0455	0.2632	0.6311	0.0149	0.0239	0.1584	0.8028
16	0.0510	0.0402	0.2272	0.6816	0.0146	0.0215	0.1473	0.8166
17	0.2910	0.2148	0.0048	0.4927	0.1128	0.1609	0.0075	0.7188
18	0.2478	0.1735	0.0030	0.5757	0.1172	0.1472	0.0047	0.7309
19	0.2034	0.1490	0.0023	0.6453	0.1137	0.1329	0.0029	0.7505
20	0.1490	0.1074	0.0023	0.7413	0.0973	0.1037	0.0034	0.7956