PREDICTIVE THERMODYNAMIC MODELS FOR
LIQUID-LIQUID EXTRACTION OF SINGLE, BINARY
AND TERNARY LANTHANIDES AND ACTINIDES

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Predictive thermodynamic models for
liquid-liquid extraction of single, binary
and ternary lanthanides and actinides

by

Ying-Chu Hoh

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NOMENCLATURE

$\bar{a}_i$	activity of particular specie
α_i	degree of formation of a particular ion
B	ligand
E	overall electrode voltage (millivolts)
E_a	reference electrode voltage (millivolts)
F	Farady's electrochemical constant
f_i	fugacity of a particular specie
I	ionic strength of solution
k_i	stoichiometric overall stability constant
K_d	distribution coefficient
K_e	liquid-liquid extraction equilibrium constant
K_1	effective liquid-liquid extraction equilibrium constant
K'_1	K_1 / K_e
K_{M-N}	K_M / K_N
K'_{M-N}	K'_M / K'_N
K_r	activity coefficient quotient
k_x	selective constant
M	metallic ion
m	molarity of a particular species in solution
$\bar{n}$	ligand number
ϕ	the ratio of the organic concentration to the ligand concentration in the aqueous phase

r_i	activity coefficient of a particular specie
R	ideal gas constant
S_{M-N}	separation factor for species M and N
T	absolute temperature, °K
T_{kn}	thermodynamic overall stability constant
T_{sn}	thermodynamic stepwise stability constant
x_i	mole fraction of particular specie
Z_i	charge of particular ion

Subscripts

A	refers to the aqueous phase
i	refers to ith species
n	number of ligand ions in a complex
O	refers to organic phase
R	refers to resin phase
$\pm$	refers to mean

Superscripts

E	refers to equilibrium conditions
I	refers to initial conditions
o	refers to standard state
T	refers to total
$ $	refers to activity
$()$	refers to concentration

INTRODUCTION

The lanthanide and actinide elements constitute two families of metals which often exhibit very similar chemical behavior. The similarity is most easily observed with the cations in oxidation state III, the most common one for all the elements of the lanthanide series and for the trans-uranium elements of the actinide series.

Liquid-liquid extraction is one of the most important techniques for the quantitative separation of lanthanide or actinide elements which are similar in properties. Until recently, fundamental solvent extraction chemistry studies were usually carried out at tracer concentrations for the lanthanide elements. The actual chemistry of the reactions involved in solvent extraction at macro-concentration is extremely complicated due to many unknown factors.

Due to the lack of precise information, the solvent extraction of the lanthanides and actinides from an aqueous salt solution to organophosphorus compounds has been somewhat difficult to thermodynamically analyze for a number of reasons. First, during the extraction, a considerable amount of hydrogen ions are liberated into the aqueous phase when the acidic organophosphorus compound is the extractant. Therefore, for the extraction of a single component lanthanide or actinide salt, the final equilibrated aqueous

phase will form a binary electrolyte solution which contains the remaining lanthanide or actinide ions, the hydrogen ions, and the ligands. Second, there is considerable difficulty in determining the neutral organophosphorus compound concentration such as tri-n-butyl phosphate (TBP) in the coextraction of nitric acid and water into the organic phase. Third, at relative high concentrations, the lanthanide and actinide ions form a series of complexes with a ligand; M^{+3} , MB^{+2} , MB^{+1} , and MB in the aqueous phase, where B represent a ligand. This make the system more complicated. Fourth, until recently, the extraction mechanism of lanthanides at higher concentration was not well defined.

The objectives of this investigation are:

- (1) To review the progress achieved in the field of liquid-liquid extraction of lanthanides and actinides from aqueous salt solution by organophosphorus compounds such as di-(2-ethylhexyl) phosphoric acid (HDEHP) and TBP.
- (2) To develop thermodynamic models for single, binary, and multicomponent systems and to quantitatively describe and predict the equilibrium relationships for liquid-liquid extraction of lanthanide and actinide nitrates by organophosphorus compounds (TBP and HDEHP);
- (3) To make optimal use of the published data in literatures for relating the lanthanide and actinide nitrates complex formation in the aqueous phase to the liquid-liquid

extraction equilibria;

(4) To experimentally study the liquid-liquid extraction of lanthanum and neodymium from its nitrate solutions by HDEHP and to use the equilibrium data to determine the complex formation constants and the distribution coefficients at different ionic strengths;

(5) To experimentally study the liquid-liquid extraction of lanthanum and neodymium from their nitrate solution by HDEHP and to use the equilibrium data to determine the separation factors and the complex formation constants in the binary component system;

(6) To experimentally study the liquid-liquid extraction of lanthanum and neodymium from their chloride-nitrate solution by HDEHP and to use the equilibrium data to determine the separation factors and the complex formation constants in the binary component system;

(7) To experimentally study the liquid-liquid extraction of lanthanum, neodymium and samarium from their nitrate solution by HDEHP and to use the equilibrium data to determine the separation factors relative to each other and the complex formation constants in the ternary component system and

(8) To use the experimental data for testing the consistency between the predicted values and the experimental results.

LITERATURE REVIEW

Liquid-liquid Extraction of Lanthanides
by Organophosphorus Compounds

The organophosphorus solvents were characterized as either acidic or neutral compounds by Blake, et al. (12). They pointed out that the acidic organophosphorus compounds were usually extracted by a cation exchange between the extractable metal ion and the hydrogen ion of the acidic solvent. The neutral organophosphorus compounds extract a neutral specie from the aqueous phase and will be expected to be more efficient in concentrated aqueous solutions of rare earth where a large fraction of the total rare earth present would be in the extractable neutral form. It also follows that the acidic organophosphorus compounds will be the best for dilute aqueous solutions since the ionic specie is being extracted. A frequent solvent used in extraction application is the neutral organophosphorus compound tri-n-butyl phosphate (TBP). Acidic organophosphorus compound are also being studied as possible extractants. A very promising extractant of this type is di-(2-ethylhexyl)phosphoric acid (HDEHP).

Scadden and Ballou (92) reported for the first time the application of a mixture of di-butyl and mono-butyl phosphoric acid as the extractant in the separation of

zirconium and niobium. They also found that the yttrium group can be separated from the other rare earths with 0.6 M di-n-butyl phosphoric acid in di-n-butyl ether.

Peppard, et al. (82) employed tracer technique to demonstrate that the extractibility of lanthanides from aqueous chlorides, nitrates and sulfates by HDEHP in toluene increased as the atomic number increased. They also found that the extractability of HDEHP for the lanthanides was inversely third power dependent on the aqueous acidity and directly third power dependent on the solvent concentration. The extraction of the lanthanides into HDEHP and diluent from an aqueous phase may be expressed, to a closed approximation, by the following equation:

where (HG) represents a monomeric HDEHP molecule and subscripts A and O denote the aqueous and organic phases respectively.

By using the freezing point depression technique and infrared spectroscopy, Peppard, et al. (79) later showed that the monoacidic organophosphoric acid was strongly dimerized in benzene and naphthalene. Peppard, et al. (80) then studied the extraction of lanthanides and actinides from perchlorate solution by compounds of the type $(RO)_2PO(RO)_2$ and $(RO)_2PO(RO)_2$

in toluene, where R was 2-ethylhexyl and para(1,1,3,3-tetramethylbutyl)phenyl. Based on the above information, they revised their extraction mechanism given by Equation 1, and proposed the following mechanism for the extraction of trivalent lanthanides and actinides:

where (HG)₂ represents a dimeric extractant molecule.

Equation 2 was shown to be valid by Peppard, et al. (80) for the extraction by monoacidic organophosphorus extractants (in dimerizing) of trivalent lanthanides and actinides from aqueous chloride, nitrate, sulfate and perchlorate solutions at conditions far removed from the extractant saturation.

Kosinski and Bostian (55) reported on the the extraction of lanthanum by HDEHP from aqueous nitrate solutions over a wide range of concentration. On the basis of material balance data and infrared analysis of the organic phase, they proposed three extraction reactions which occurs simultaneously:

In each reaction, the lanthanum ion replaces hydrogen ion and interacts with the P=O structure of HDEHP.

In a series of articles (47, 48, 93) Hesford and McKay, Hesford et al., and Scargill et al. showed that all of the lanthanides appeared to form a trisolvated complex $\text{M}(\text{NO}_3)_3 \cdot 3\text{TBP}$ in the organic phase (where M represent any particular rare earth). Trace methods were used and the solvent was one to five percent TBP in kerosene. The general reaction

was assumed.

Bostian and Smutz (13) investigated the mechanism of extraction by TBP in neodymium nitrate solutions up to saturation. Infrared studies indicate that the complexing occurs at the P=O bond of the TBP. It was concluded that the complexing reaction was:

These results, together with similar results for dilute solutions (47,48,93) indicate that the complex $\text{M}(\text{NO}_3)_3 \cdot 3\text{HDEHP}$ was the complex formed over the full range of concentration.

Smutz and Lenz (105) made a comparison of monomeric and dimeric HDEHP as lanthanide extractants. They prepared the monomeric HDEHP by diluting pure HDEHP with n-decylalcohol and dimeric HDEHP by diluting pure HDEHP with Amsco 125-82. They found that dimeric HDEHP extracts approximately 40 times as much Sm as the monomeric HDEHP for a given equilibrium aqueous phase. Thus, dimeric HDEHP is seen as a much more efficient extractant than monomeric HDEHP under the experimental conditions used. Peppard (78) and Base (6) proposed that the monomer forms only in polar solvents such as high molecular weight carboxylic acids. The dimer predominates in nonpolar solvents such as hydrocarbon diluents.

Extensive studies concerning the separation of two or more rare earths using HDEHP by liquid-liquid extraction from aqueous nitrate and chloride solutions can be found in the works of Smutz, et al. (102, 103, 104, 106, 107, 109). The additional information on extraction by organophosphorus acids can be found in the works of Peppard (78) and Eyring (29).

Harada, et al. (44, 45) studied the polymerization of iron and rare earths and HDEHP. They reported that in the extraction of rare earths by HDEHP, the extraction mechanism can be represented by Equation 2. When an additional metal ions are added into the organic phase, it will result in an irreversible polymerization reaction which can be represented by:

The polymer $(MG) \overset{+}{|} \overset{O}{\underset{3}{\text{O}}}$ cannot be dissolved by dilute acid at room temperature. They also defined the limiting conditions for the formation of iron and rare earth polymers during their extraction with HDEHP.

Fidelis (30) studied the temperature effect on the extraction of lanthanides in the HDEHP-nitric acid system. She found a decrease in the distribution coefficient with an increase of temperature between 10° C to 50° C in the case of each lanthanide. The plots of log{distribution coefficient} against 1/T were found to be straight lines for the range of temperature investigated. An equation relate to the enthalpy and the temperature was given.

Liquid-Liquid Extraction of Actinides by Organophosphorus Compounds

Liquid-liquid extraction processes of inorganic salts have been rapidly developed in recent years. Many solvents have been tried. Great interest has been shown in tri-n-butyl phosphate (TBP) for the extraction of actinide elements. Many inorganic nitrates dissolve freely in TBP and form complexes with the solvent. Healy and McKay (46) determined the number of TBP molecules attached to the inorganic nitrate by partition experiments between TBP and water. The aqueous phase was kept constant in composition and TBP was diluted by an inert diluent, e.g., benzene or kerosene. The partition of a trace of the inorganic nitrate was then measured by a series of dilutions. A plot of $\log(\text{distribution coefficient})$ vs. $\log(\text{TBP})$, showed that it follows the square law for uranyl nitrate and cubic law for americium (III) nitrate. The following formulas have been determined for the different complexes:

(9)

Healy and McKay (46) also proposed that M exists in TBP as a complex with the formula $M(NO_3)_p \cdot qTBP$. The solvent extraction mechanism then can be represented by:

with the equilibrium constant as follows:

$$K_e = \frac{|M(NO_3)_p \cdot qTBP|_O}{|M^{+p}|_A |NO_3^-|_A^p |TBP|_O^q} \quad (11)$$

The subscripts A and O denote the aqueous and organic phase respectively.

Sato (90, 91) used TBP to extract uranyl nitrate from nitric acid solutions and found that the extraction efficiency is increased by the presence of the common nitrate ion and the distribution coefficient reaches maximum at about 6 M nitric acid concentration. He also concluded that the extraction of nitric acid decreases linearly with increasing uranyl nitrate extraction.

Lietzke and Stoughton (62) studied the solvent extraction of uranyl nitrate and nitric acid by TBP. They developed a mathematical model to describe the solvent

extraction equilibria over wide range of concentration of the material being extracted, salting agent, and extractant. In their model, the Debye-Huckel term of low and a linear term of high ionic concentration corrections (i.e., activity coefficient changes) in the aqueous phase are used. The model has been successfully applied to the extraction of uranyl nitrate by TBP dissolved in an inert diluent. They also suggested that with precise and consistent data the method is capable of evaluating all the equilibrium parameters involved in relatively complex extraction systems.

Hahn and Vander Wall (43) examined the interactions between the TBP and its principal decomposition product dibutyl phosphoric acid (DBP), uranyl nitrate, and nitric acid which are of considerable interest in the reprocessing of nuclear fuels. The phosphoryl complexes not only affect the extraction behavior of uranium, but also forms an interphase precipitate and pose a serious problem. They found that the stripping of uranium(IV) from TBP-Amsco solutions into dilute nitric acid is hindered by the presence of dibutyl phosphoric acid because of an undesirable complex $(\text{UO}_2(\text{NO}_3)_2 \cdot \text{DBP} \cdot \text{TBP})_x$ which is formed. Comparison of experimental and calculated data favors a value of $x = 2$ in the above empirical formula. The formation constant for this complex is 12.5.

Shevchenko and Fedorov (99) studied the temperature effect on the extraction of uranyl, plutonium nitrates and some fission products by TBP. They found that uranyl nitrate distribution coefficient decreases with a rise in temperature, and the reaction

is exothermic. A linear relation of $\log K_d$ vs. $1/T$ make it possible to conclude that the above reaction obeys the Van't Hoff's equation.

Base, et al. (7, 8) separated U(IV) and Fe(III) from perchlorate solution by HDEHP in n-hexane and n-octane. They showed that when the diluent was n-octane, the HDEHP existed as both dimeric and trimeric in equilibrium with each other.

The equilibrium constant for the above mechanism was reported as 10 mole^{-1} . They also reported the distribution of uranium(IV) between acidic aqueous perchlorate solutions and solutions of di-(2-ethylhexyl) phosphoric acid in n-hexane. They also found that at low uranium concentration levels, the distribution coefficient is directly proportional to the

square of the equilibrated organic concentration and inversely second-power of the aqueous acidity. They proposed that the extraction mechanism is

where the subscripts A and O denote the aqueous and organic phases respectively.

Sato (87, 88, 89) also studied the extraction of U(VI) by HDEHP in kerosene from acidic sulfate, nitrate, and chloride systems. He found that the extraction from nitrate and chloride media was more complex than from sulfate solutions. He also concluded that nitric acid is extracted into the organic phase as:

The above mechanism is somewhat doubtful, however, since HDEHP does not behave as a neutral extractant, and also the experimental concentrations of nitric acid in the solutions studied by Sato were low enough to allow complete dissociation to the acid.

Ul'yanov, et al. (114) studied the extraction of uranium (VI) from aqueous perchlorate solutions of HDEHP in n-octane.

It was shown that at the low HDEHP concentration region ($\ll 10^{-4}$ M), the reaction is

where HG is the monomer of HDEHP and the subscripts A and O denote the aqueous and organic phase respectively. When the HDEHP concentration in n-octane $\gg 10^{-4}$ M, the dimer is practically the only form present in the organic phase.

Nemodruk (71) studied the dependence of distribution coefficient of uranium (VI) on the perchloric acid concentration in the case of its extraction with 0.0176 M solution of HDEHP in carbon tetrachloride. He found that with increasing perchloric acid concentration the distribution coefficient of uranium (VI) decrease sharply, reaching a minimum at 4 M, and as the concentration of perchloric acid further increased, it rises again. He explained that uranium (VI) is extracted from solutions with perchloric acid concentration below 4 M according to the ion exchange mechanism with the participation of the UO^{+2}_2 ion in the formation of an extractable complex. At high perchloric acid concentration, the quadruply charged ion UO^{+4} , which forms stronger complexes with HDEHP and becomes the extractable complex. Increasing the perchloric acid

concentration shifts the equilibrium

in the direction of the UO_2^{+4} formation. Therefore, the distribution coefficient of U(VI) again increases above 4 M perchloric acid concentration.

Rozen, et al. (85) studied the reaction mechanism of uranyl nitrate with HDEHP in acid media by the extraction method. They found that the extraction constant is 1200 and the purely solvated complex $\text{UO}_2(\text{NO}_3)_2 \cdot 2(\text{HG})$ is hardly formed. A model equation was obtained to calculate the distribution coefficient of uranium (VI) over all ranges of acidity in the extraction by HDEHP. They concluded that by neglecting the activity coefficients in the analysis of extraction equilibria at an acidity higher than 2 M will result in the discovery of compounds which do not exist and to miss those that are actually formed. They also reported that at low acidities the extraction mechanism was found to be:

At higher acidities, considerable amounts of $\text{UO}_2^{+2} (\text{HG})_2$ were found in the organic phase. This was explained by the

following organic phase reaction;

Lanthanide Complexes in Aqueous Solution

The sequence of stabilities of lanthanide complexes as a function of atomic number have been of interest for a number of years. Attempts to correlate this sequence with various properties of the lanthanide ions have been less than successful. A major reason for this difficulty has been the lack of complete thermodynamic data. Due to its +3 charge the lanthanide ion forms stable complexes with many common anions such as chloride, nitrate, and sulfate. The degree of formation (or complexation) is described by inorganic stability constant of the complex which is analogous to an acid dissociation constant.

Choppin and Strazik (16) have determined that lanthanide nitrate complexes are outer-sphere in nature. This means that there is a monolayer of water molecules between the nitrate and lanthanide ions. This layer of water acts as a dielectric and reduces the strength of the ionic bond which forms the complex. Therefore, it is assumed that the neutral species $\text{M}(\text{NO}_3)_3$ is present only at lanthanide concentration

approaching the solubility limit. In this work, the presence of the neutral species $M(NO_3)_3$ was neglected since all of the solutions studied were below the solubility limit.

Connick and Mayer (21) measured the activity coefficients and association constants of cerous salts by using the ion exchange method. The exchange equilibrium of +3 and +1 positive ions between a resin and an aqueous phase was proposed as:

where the subscripts A and R represent the aqueous and resin phases respectively. The stability constants for $CeCl^{+2}$ and $CeNO_3^{+2}$ were reported.

Fomin, et al. (32) determined the stability constants of $Ce(NO_3)_{3-x}$ ions by extraction with tri-n-butyl phosphate. Stability constants of the nitrate complex ions of cerium $Ce(NO_3)^{+2}$ and $Ce(NO_3)_2^{+1}$ were calculated and found to be 11 ± 2.5 and 32 ± 7 respectively. They also found that the equilibrium constants of the reaction

equals one.

Krumholz (58) used the spectrophotometric method to determine the stability constants of neodymium from nitrate ion concentrations of 0.06 to 2.0 M. The degree of formation of neodymium $\text{Nd}(\text{NO}_3)_{3-x}$ ions were also given in detail.

Kriss and Sheka (56) studied the complex formation of the system of $\text{M}(\text{NO}_3)_3 - \text{HNO}_3$ for a series of lanthanides by means of the ion exchange method. It was found that cationic forms of the lanthanide complexes predominate at nitric acid concentration of 1-1.5 M; electrically neutral complexes predominate in the solution in a concentration range between 3-4 M; and at nitric acid concentration up to 7 M the elements of the yttrium group remain in the form of electrically neutral complexes. The formation constants for the complexes of La^{+3} and Yb^{+3} with nitric acid were also determined.

Peppard, et al. (81) used the distribution method to determine the stability constants for the chloride and nitrate single ligand complexes of the same lanthanides and actinides. In general, they also found that nitrate ions form a stronger complex with the lanthanide ions than the chloride ion.

Choppin and Unrein (17) determined the stability constants for some halide complexes of the lanthanide elements at ionic strengths of 1 M by liquid cation exchange extraction method. The enthalpy and entropy values indicate

that these complexes are ionic and possibly of outer-sphere type. Formation constants of some europium (III) complexes were reported by Barnes (5) from measurements on spectra assigned to ligand-to-metal charge transfer. Sekine (96) measured the stability constants for the complex formation of La(IV), Eu(IV), Lu(IV), and Am(IV) with oxalate, sulphate, chloride and thiocyanate ions. He found that the stability of the complexes with different ligand decrease in the order of oxalate > sulphate > thiocyanate > chloride. By extraction method, Smelov and Vereshchagin (101) investigated the complex formation of cerium (IV) with nitrate ions. The stability constants of the complex ions were given. The equilibrium constants for the reaction of cerium (IV) with the tri-n-butyl phosphate phase was also calculated.

Goto and Smutz (39) determined the stability constants for the formation of LaCl^{+2} , PrCl^{+2} , NdCl^{+2} and SmCl^{+2} potentiometrically at an ionic strength of 1.0 M and at 25° C in a NaClO_4 medium. The values were 1.60 ± 0.03 , 1.58 ± 0.05 , 1.62 ± 0.04 , and 1.62 ± 0.06 for La, Pr, Nd, and Sm respectively. From a statistical point of view it was shown that there is no difference among the values obtained.

Choppin and Strazik (16) also measured the stability constants for the mononitrate complexes of Ce(III), Pm(III), Eu(IV), Tb(IV), Tm(IV) and Am(III) by solvent extraction method. Sekine (94, 95, 97) studied trivalent actinide and

lanthanide complexes for chloride, sulfate and oxalate ions.

He reported the values of k_1 and k_2 in details.

Coward and Kiser (22) studied the NdNO_3^{+2} association by spectrophotometric method. The results indicate that NdNO_3^{+2} is the only important absorbing species (at 579 m μ) other than Nd^{+3} and that the NdNO_3^{+2} is formed with an association constant of 0.77 at an ionic strength of 4.2 M.

Mikhailichenko and Kurdin (66) determined the stability constants for NdNO_3^{+2} and GdNO_3^{+2} by an extraction method. The values of the stability constants are 1.75 ± 0.2 , and 1.07 ± 0.2 for NdNO_3^{+2} and GdNO_3^{+2} respectively at an ionic strength equal to 1 M. These values were larger than the values obtained by Krumholz (58).

Khopkar and Narayanankutty (53) studied the effect of ionic media on the stability constants for chloride, nitrate, and thiocyanate complexes of americium (IV) and europium (IV). For chloride complexes, they found that the first stability constant k_1 increased regularly with decreasing hydration of the cation medium. The effect of cation medium on the stabilities of nitrate and thiocyanate complexes has been found to be much smaller.

By using the extraction method, Choppin, et al. (18) studied the effect of changes in ionic medium on stability constants of $\text{Eu}(\text{NO}_3)_3^{+2}$. They found that the stability constants k_1 for this complexes with different ionic media

decreased in the order of $\text{NaNO}_3 > \text{HNO}_3 > \text{LiNO}_3$. The values of enthalpy, entropy, and free energy at 25° C for $\text{Eu}(\text{NO}_3)_3^{+2}$ were also reported by them.

Kriss and Sheka (57) also determined the stability constants for the binary system of ytterbium and neodymium nitrates in 1 M solution of TBP in carbon tetrachloride. The stability constants for ytterbium and neodymium in binary system were given.

Ryabchikov and Terentyeva (86) and Moller (67) have thoroughly reviewed the coordination chemistry and the complex stability constants of rare earth metal ions.

A more recent collection of the metal complex stability constants are included in the contributions of Choppin (15) and Martell and Sillen (64).

Actinide Complexes in Aqueous Solution

Ahrland (1) used the potentiometric method to study the hydrolysis of the six-valent uranium in aqueous solutions. He found that uranyl ion UO_2^{+2} is the only existing complex of six-valent uranium in aqueous solution from pH = 0.1 to pH = 2. Over the pH ranges, the hydrolysis complexes are gradually formed. UO_2^{+2} may therefore be regarded as a complex forming central group. The hydrolysis becomes appreciable at pH = 3.0. The first dissociation constant was determined

at an ionic strength of one. Later, Ahrland (2, 3) studied the complex formation of uranyl sulfate, chloride, bromide, and nitrate by potentiometric method. The potentiometric investigation was carried out according to the method of ligand displacement proposed by Fronaeus (37). The complex formation constants were determined for the complexes of uranyl sulfate, chloride, bromide, and nitrate at an ionic strength of one.

Day and Powers (26) extracted uranyl ion from aqueous solutions of sodium perchlorate, chloride, nitrate, sulfate and fluoride with benzene solutions of 2-thenoyltrifluoroacetone. The stability constants for uranyl complexes with the anions of perchlorate, chloride, nitrate, sulfate and fluoride were determined at an ionic strength of 2 M and at 10°, 25°, and 40° C.

Grenthe and Noren (40) used Fronaeus's method (38) to study the nitrate and chloride complexes of Pu^{4+} in an acid perchlorate medium of an ionic strength 4 M at 20° C. The stability constants for plutonium nitrate and chloride complexes were reported.

McKay and Woodhead (65) used the spectrophotometric method to study the nitrate complexes of uranium (IV). The stability constants for the nitrate complex formation of uranium (IV) have been determined. Those for nitrate complex formation vary considerably with total salt concentration in

the range of 1 - 4 M.

Using a liquid-liquid extraction method Lucas (63) determined the stability constant of the neutral species $\text{Pu}(\text{SO})_4$ corresponding to the equilibrium:

The stability constant is 3.8 ± 0.7 at an ionic strength of 1.0 M at $23 \pm 0.5^\circ \text{C}$.

Ermolaev and Krot (28) studied complex formation of U(IV) with nitrate ion spectrophotometrically and by ion exchange methods. It was observed that depending on the nitrate ion concentration, complex ions right up to $\text{U}(\text{NO})_6^{3-2}$ are formed successively in nitric acid solutions. The stability constant of the uranium nitrate complexes $\text{U}(\text{NO})_{3-i}^{4-i}$ ($i = 1, 2, 3$, and 4) were determined spectrophotometrically and confirmed by ion exchange method.

Laxminarayanan, et al. (59) used liquid-liquid extraction method to determine the stability constants for nitrate complexes of plutonium (IV) by using tri-n-butyl phosphate (TBP) as the solvent. The stability constants for sulfate ions with plutonium (IV) had also been determined in nitrate media.

Moskvin (68) conducted further investigation of complex formation of the actinide elements with anions of a number of

acids in aqueous solutions by using solubility, ion exchange, liquid-liquid extraction, potentiometry and other methods. He also summarized the data on the composition and stability constants of the actinides formed under the experimental conditions. Moskvina (69) measured the complex formation constant of Pu (IV) in sulfate solutions by spectrophotometric method. The existence of the complexes with M : ligand ratios of 1 : 1 and 1 : 2 was confirmed. Moskvina (70) also used the liquid-liquid extraction method to study the complex formation of neptunium (IV) in nitrate solutions. The equilibrium constant for complex formation by Pu (IV) nitrate with tri-n-butyl phosphate was determined. The step formation constants of the nitrate-complexes of Np (IV) with M : ligand ratios from 1 to 4 at ionic strengths of 2 and 4 were calculated.

Liquid-Liquid Extraction of Nitric Acid by Tri-n-butyl Phosphate

The partition of nitric acid between water and TBP in kerosene have been studied by Healy and McKay (46) and Alcock, et al. (4). They found a strong saturation effect when the composition HNO_3 .TBP had been reached, especially at low TBP concentrations. There is strong evidence that most or all of the nitric acid dissolves in the organic phase in the form of

a 1 : 1 compound, $\text{HNO}_3 \cdot \text{TBP}$. At low TBP concentration the experimental data fit very well a theoretical curve based on the relation of

and

$$\frac{[\text{HNO}_3 \cdot \text{TBP}]_O}{[\text{HNO}_3]_A [\text{TBP}]_O} = \text{Equilibrium Constant} = K_e \quad (24)$$

where subscripts A and O represent the aqueous and organic phases respectively. At high acidities, a third phase can be formed in TBP-kerosene-water-nitric acid system because of the probable formation of the compound $(\text{C}_4\text{H}_9\text{O})_3\text{P}-\text{O} \rightarrow \text{HONO}_2$. The equilibrium constant based on the experimental data, is equal to 0.16. Later, Fomin and Maiorova (31) studied the distribution of nitric acid between the aqueous phase and 1 M TBP solutions in benzene. The reaction constant for the reaction

and

$$\frac{[\text{HNO}_3 \cdot \text{TBP}]_0}{[\text{HNO}_3]_A [\text{TBP}]_0} = \text{Equilibrium Constant} = K_e \quad (26)$$

is equal to 0.22 ± 0.02 while the nitric acid concentration in the initial solution used varied up to 4 M.

Sheka and Kriss (98) studied the reaction between nitric acid and TBP by means of physicochemical analytical method using the dielectric constant as the measured property. They found that the compound $\text{HNO}_3 \cdot \text{TBP}$ predominates at nitric acid concentration up to 4 M and $3\text{HNO}_3 \cdot \text{TBP}$ is the major compound up to 9 M nitric acid concentration in the system of nitric acid-TBP-carbon tetrachloride. Shuler (100) studied the nitric acid in TBP solutions by partition and spectroscopic methods. His results indicated the formation $\text{H}_2\text{O} \cdot \text{TBP}$, $\text{HNO}_3 \cdot \text{H}_2\text{O} \cdot \text{TBP}$, $2\text{HNO}_3 \cdot \text{H}_2\text{O} \cdot \text{TBP}$, $3\text{HNO}_3 \cdot \text{H}_2\text{O} \cdot \text{TBP}$, and $4\text{HNO}_3 \cdot \text{H}_2\text{O} \cdot \text{TBP}$ in solutions of TBP and nitric acid. This is considerably more complex than at first supposed. Davis (23, 24) made a series of studies on the thermodynamic of extraction of nitric acid by TBP. An empirical equation was given to correlate the distribution coefficient of nitric acid between TBP-Amsco 125-82 solutions and aqueous solutions up to 5 M in aqueous phase. He found that TBP in Amsco 125-82 shows nearly ideal solution volume additivity. An equation for the molal volume

of solution containing TBP, Amsco 125-82, nitric acid and water is also given at 25° C.

By using the smoothed equilibrium data as well as the Gibbs-Duhem equation, Davis, et al. (25) obtained the rational activity and activity coefficient (based on pure anhydrous TBP as the standard state) of TBP in equilibrium with water-nitric acid for aqueous nitric acid concentration ranging from 0 to 15 M.

BASIC THEORY

The Theory of Mononuclear Complexes Equilibria

It is well-known that hydrogen and acetate ions in a dilute solution of acetic acid are generally associated as the uncharged molecules HAc. The phenomena of ionic association is widespread. It occurs in all solutions of weak electrolytes, and in so called 'strong' electrolytes, which were previously considered to be completely dissociated. Therefore, we can define a complex as a specie formed by association of two or more simpler species each capable of independent existence. The formation of a complex is not restricted to association between two opposite charged ions. A proton, a metal cation or another positively charged species may react with an electron donor, whether it is negatively charged, electrically neutral, or even positively charged.

If a solution contains two species A and B, they may react to form one or more complexes of the form $A B_{\frac{a}{b}}$, where $a \geq 1$, $b \geq 0$. It has been found that the only mononuclear complexes, for which $a = 1$ and $b = n$, are formed in a large number of systems, especially in dilute solutions. For the mononuclear complexes, the ion or molecule A is defined as the central group of the complex AB_n , and B is usually called the ligand. Most mononuclear complexes formed in aqueous

solution can be represented by one of the following two main types: (1) Bronsted acid, in which hydrogen ions act as ligands and are associated with a central group, and (2) metal complexes, which usually consist of one or more neutral or anionic ligands coordinated to a central metal ion. The present investigations study the complexity of the lanthanide and actinide ions with the nitrate ion, which is the case for mononuclear metal complexes.

Equilibrium constants for the formation of complexes in solution at a given temperature are usually reported either as activity quotients, which should be independent of the ionic medium, or as concentration quotients, which are valid only in a solution of a particular composition. The constants represented by concentration quotients are usually referred to as stoichiometric stability constants. If concentration quotients are determined in the presence of a large amount of excess background salt, it may be assumed that the activity coefficients are independent of the concentrations of the reacting species and only depend on the nature and concentration of the bulk electrolyte.

When a mononuclear species AB_n are formed in a solution, the activity of the species can be related to the activity of B and A by the law of mass action. The formation equilibrium constant or stability constant of the reaction

is given by:

$$T_{kn} = \frac{|AB|_n}{|A| |B|^n} \quad (28)$$

Here $| |$ denotes the activities of the species and T_{kn} is called thermodynamic over-all stability constant. The term 'thermodynamic' denotes the activity quotient. When the preceding complex AB_{n-1} exists, the formation stability constant for the single-step reaction

is given by

$$T_{sn} = \frac{|AB|_n}{|AB|_{n-1} |B|} \quad (30)$$

T_{sn} is defined as the thermodynamic stepwise stability constant. According to the definitions of over-all and stepwise stability constants, the relation between them can be expressed by:

$$T_{kn} = T_{s1} T_{s2} T_{s3} \dots = \prod_{n=1}^n T_{sn} \quad (31)$$

In general, different concentration scales of molar (M), molal (m) and mole fraction (x) are used. The numerical values of the stability constants of a given complex depend on both the experimental conditions and the units in which the activity terms are expressed. In this work, the molar concentration scale (moles solute per liter of solution) was used.

The activity of a component i is defined by

$$\bar{a}_i = \frac{f_i}{f_i^o} \quad (32)$$

where f_i^o is the fugacity of component i in its standard (or reference) state, denoted by the superscript o . The activity coefficient is defined by the departure of a solution from ideal behavior. Therefore, the activity coefficient γ is the ratio of activity to a numerical expression of composition and can be represented by:

$$r_i = \frac{\bar{a}_i}{x_i} = \frac{f_i^o}{x_i f_{ii}} \quad (33)$$

or

$$f_i = x_i r_i f_{ii}^o \quad (34)$$

where x_i represents the mole fraction. Both activity and activity coefficient will always be positive quantities whose values will depend on the standard state specified. For a component in the liquid phase, the independent variables which determine the standard state are the temperature, a fixed composition and a specified pressure. At constant temperature and pressure the unsymmetrical for normalization of activity is often used. The standard state convention in a solution is

$$r_1 \rightarrow 1 \text{ as } x_1 \rightarrow 1 \text{ for solvent} \quad (35)$$

$$r_2 \rightarrow 1 \text{ as } x_2 \rightarrow 0 \text{ for solute.} \quad (36)$$

It is often possible to control the activity coefficient in an aqueous solution by using a constant ionic medium,

i.e., measurements are made in the presence of a large amount of excess background salts. It can be assumed that the activity coefficients are independent on the concentration of the reacting species and depend only on the nature and concentration of the bulk electrolyte. The concept of ionic strength was introduced in 1912 by Lewis and Randall (60) who stated that 'in dilute solutions, the activity coefficient of a given strong electrolyte is the same in all solutions of the same ionic strength'. Debye and Huckel (27) in 1923 derived a theoretical relationship between the activity coefficient and the ionic strength. Since then many workers have attempted to keep activity coefficients constant by using solutions of constant ionic strength.

Debye and Huckel (27) proposed that the electrolyte's departure from the ideal solution behavior can be partially explained by electrostatic forces between the ions. They also developed the following relationship for the activity coefficient γ , of an electrolyte in solution:

$$\log \gamma_{\pm} = \frac{-A |Z_1 Z_2| I^{1/2}}{1 + BaI^{1/2}} \quad (37)$$

where A, B = Debye-Huckel constants

Z_1, Z_2 = ionic charge of the cation and anion respectively

a = distance of the closest approach to the reference ion
 I = ionic strength.

The ionic strength I for multicomponent electrolyte solution is defined as:

$$I = \frac{1}{2} \sum_{i=1}^n M_i Z_i^2 \quad (38)$$

where M_i and Z_i are the molarity and the charge of a particular ionic species in solution respectively. It is very clear that at very low values of I , i.e., in very dilute solutions, the term (BaI) will ultimately become negligible compared to one, and Equation 37 approach the form:

$$\log r_{\pm} = -A |Z_1 Z_2| I^{1/2} \quad (39)$$

This is the Debye-Huckel limiting law. Examination of this law shows that $\log r_{\pm}$ becomes linear with the square root of the concentration at high dilutions. In Equation 37, the numerator of the right hand side, $-A |Z_1 Z_2| I^{1/2}$ gives the effect of long range electrostatic forces, while the denominator $(1 + BaI^{1/2})$ shows how these are modified by the short range interactions between ions. Debye and Huckel take the ions to be nondeformable spheres of equal radii. In

an actual solution, there will be the short range interactions between ions and solvent molecules to be considered as well as other types of short range interactions between ions, which can not be represented by the rigid sphere's model. Guggenheim (41) in 1957 extended the Equation 37 to include these interactions by adding a linear term in the concentration, thus:

$$\log r_{\pm} = \frac{-A \left| \frac{Z_1 Z_2}{1} \right| I^{1/2}}{1 + BaI} + bI \quad (40)$$

where b is an empirical constant characterizing the change in the dielectric constant of the medium near an ion.

A more simple form of Equation 37 is proposed by Gunelberg (42)

$$\log r_{\pm} = \frac{-A \left| \frac{Z_1 Z_2}{1} \right| I^{1/2}}{1 + I} \quad (41)$$

Although this equation has no adjustable parameters, it still gives fairly good result in a number of electrolytes up to $I = 0.1$ M. It can also be improved by adding a linear term in the concentration:

$$\log r_{\pm} = \frac{-A \left| \frac{Z_1 Z_2}{1} \right| I^{1/2}}{1 + I^{1/2}} + b I \quad (42)$$

similar to Guggenheim's (41), where b is an adjustable parameter.

If we keep the activity coefficient $r_{\pm}$ of each species constant throughout a series of measurements, e.g., by the use of a suitable ionic medium, the stoichiometric over-all stability constant can be obtained by using corresponding concentration quotients to the reaction in Equation 27 as:

$$K_n = \frac{(AB)_n}{(A)(B)} = T \frac{r_A^n r_B^n}{r_{AB}^n} \quad (43)$$

where the parentheses indicate equilibrated concentrations. The activity coefficients must be expressed in the same concentration scale as the stability constants. If the activity coefficients of all species are effectively held constant throughout the investigation, the stoichiometric stability constants can be determined by concentration

quotients of the corresponding species. Any comparison of stoichiometric stability constants must be at the same temperature and ionic medium. The thermodynamic stability constants are commonly obtained by extrapolating stoichiometric constants, determined at a number of ionic strengths, to infinite dilution.

For weak complexing anions such as those used in the present work, it is generally assumed that the metal species present in the aqueous phase are A , AB , AB_2 , ..., AB_m (39, 47, 81). Consider that mononuclear complex formation reaction system can be represented by the following equilibria:

The total concentration of ligand B and the central group A are represented by:

$$(B)_T = (B) + (AB) + 2(AB_2) + \dots + n(AB_n) + \dots + m(AB_m) \tag{45}$$

and

$$(A)_T = (A) + (AB) + (AB)_2 + \dots + (AB)_n + \dots + (AB)_m. \quad (46)$$

From the definition of a stoichiometric over-all stability constant, Equation 43 can be written as:

$$(AB)_n = k_n (A) (B)_n. \quad (47)$$

According to this definition, Equations 45 and 46 can be expressed as:

$$(B)_T = (B) + (A) \sum_{n=1}^m k_n (B)_n \quad (48)$$

and

$$(A)_T = (A) \left(1 + \sum_{n=1}^m k_n (B)_n \right). \quad (49)$$

The terms (A) and (B) are the corresponding free concentrations. In a homogeneous system, values of (A) and (B) are usually known from the compositions of the initial solutions.

In 1915, Bjerrum (as cited by 84) introduced the use of a variable by defining the degree of formation of a complex AB_i in the system of Equation 44 with $n = i$ as follows:

$$a_i = \frac{(AB)_i}{(A)_T + (AB) + (AB)_2 + \dots + (AB)_i + \dots + (AB)_m} \quad (50)$$

By making use of Equation 47, Equation 50 becomes

$$a_i = \frac{k_i (B)^i}{1 + \sum_{n=1}^m k_n (B)^n} \quad (51)$$

Another variable which was also introduced by Bjerrum in 1915 was the number of ligands bound to each central group. It is represented by the formula

$$\bar{n} = \frac{(B)_T - (B) + (AB) + 2(AB)_2 + \dots + n(AB)_n}{(A)_T + (AB) + (AB)_2 + \dots + (AB)_n} \quad (52)$$

or

$$\bar{n} = \frac{k_1 (B) + 2k_2 (B)^2 + \dots + nk_n (B)^n}{1 + k_1 (B) + k_2 (B)^2 + \dots + k_n (B)^n} \quad (53)$$

By rearranging Equation 53 gives:

$$\frac{\bar{n}}{1-\bar{n}} = k_1 (B) + \frac{2-\bar{n}}{1-\bar{n}} k_2 (B)^2 + \dots + \frac{n-\bar{n}}{1-\bar{n}} k_n (B)^n. \quad (54)$$

If the free ligand concentration, (B) is measurable, the value of $\bar{n}$ can be determined. Consequently, the stability constants, k in Equation 54 can then be determined. In an attempt to obtain k_1 , Equation 54 can be reduced to

$$\frac{\bar{n}}{1-\bar{n}} = k_1 (B) \quad (55)$$

or

$$k_1 = \frac{\bar{n}}{1-\bar{n}} \frac{1}{(B)}. \quad (56)$$

When $1 - \bar{n}$ differs appreciably from zero, (B) is sufficiently small, and $k_2, k_3 \dots$ have approximately the same or less magnitude as k_1 . Because the terms involving $k_2, k_3, \dots$ will be negligible under these conditions, Equation 56 gives directly the values of k_1 . According to Equation 56, there are two different ways to obtain k_1 for various concentrations of (A) in this equation.

One method would be to vary the total concentration of metal added to the system. The other would be to vary the amount of ligands.

The other method to calculate the stability constant is by making use of the definition of the distribution coefficient

$$K_d = \frac{(A)_O^T}{(A)_A^T} \quad (57)$$

where

$$(A)_O^T = (AB)_n^T \quad (58)$$

$$(A)_A^T = (A)_A^T + (AB)_A^T + \dots + (AB)_n^T \quad (59)$$

and the subscripts A and O denote the aqueous and organic phases respectively. When no complexing ligands are present, i.e., $(B) = 0$, the distribution coefficient is given by

$$K_d^0 = \frac{(A)_O^T}{(A)_A^T} \quad (60)$$

Dividing Equation 60 by Equation 57 gives

$$\frac{K_d^0}{K_d} = \frac{(A)_A + (AB)_A + (AB)_2^2 A + \dots + (AB)_n^n A}{(A)_A} \quad (61)$$

Substituting Equation 47 into Equation 61 for $(AB)_n$ gives

$$\frac{K_d^0}{K_d} = 1 + k_1 (B) + k_2 (B)^2 + \dots + k_n (B)^n \quad (62)$$

If only the first complex is presented, a plot of $1 / K_d$ vs. (B) gives a straight line whose slope is equal to k_1 / K_d^0 and the intercept is equal to $1 / K_d^0$. This is how the stability constant can be determined from the distribution data.

DEVELOPMENT OF THERMODYNAMIC LIQUID-LIQUID EXTRACTION MODELS

The development of suitable thermodynamic models to describe the liquid-liquid extraction of lanthanides and actinides from aqueous acidic solutions by organophosphorus compounds have been studied by several investigators (49, 50, 51, 52, 72, 73, 74, 75, 76, 111, 112, 113)

Based on Peppard's, et al. (80) extraction mechanism for the extraction of rare earth metals by HDEHP from aqueous acidic chloride media, Ioannou et al. (50, 51, 52) developed an empirical equation to predict the organic phase concentration upon specification of the aqueous phase for single component system of Sm and Nd. Based on the data for single component systems, the model was extended to predict equilibrium data for binary and ternary systems. The mathematical models expressed the lanthanide organic concentration as a function of the aqueous metal concentration and acidity. The models for Sm, Nd and Ce predict the experimental data with an average error of less than 5%, 6%, and 3% respectively, within the concentration ranges studied.

O'Brien (75) and O'Brien and Bautista (76) developed a thermodynamic model to predict the distribution coefficient for the single component system of neodymium nitrate-nitric acid-water-HDEHP-Amsco. This was based on Kosinski and

Bostian's (55) extraction mechanism as well as the formation of lanthanide anion complexes in the aqueous phase. The developed thermodynamic model is a function of the hydrogen ion activity in the aqueous phase, the nitrate ion activity in the aqueous phase, the activity of the HDEHP dimer in the organic phase, and the stability constants for the formation of the lanthanide-nitrate complexes.

Nevarez (72) and Nevarez and Bautista (73) derived a predictive thermodynamic equilibrium model for the liquid-liquid extraction of cobalt (II) in cobalt chloride-hydrochloric acid-water-TBP system. The ratio of the activity coefficients was assumed to vary slightly with concentrations. Therefore, the quotient of activity coefficients could be represented by a constant. With this assumption, Nevarez, et al. (74) modified O'Brien's model (75, 76) and a more simple form was obtained. This model gave almost the same results as O'Brien's model. By using the same modeling technique, Hoh and Bautista (49) developed a chemically based model for copper-LIX65N and copper-KELEX 100 systems. The model gave very good results using the published data of Spink and Okuhara (110). The correlation coefficient R^2 between the predicted and experimental data is 0.99 for both systems.

Thomas and Burkhart (111) developed empirical equations to predict the single component equilibrium data for Tm, Yb, and Lu. The correlations fit the equilibrium data quite

well. Later, Thomas, et al. (113) and Thomas and Burkhart (112) developed another empirical correlations for predicting total distribution coefficients for the Yb-Tm, Lu-Yb, and Lu-Tm mixtures. Good agreement between the experimental and predicted data were obtained.

Forrest and Hughes (33) summarized the existing models for the liquid-liquid extraction of metals. They divided the models into three main categories: (1) chemically based models which seek to model the data on the basis of the known chemistry of the extraction, (2) semi-empirical models using analogies between gas adsorption and vapor-liquid equilibria and (3) totally empirical models which use generalized mathematical expressions such as polynomials. Forrest and Hughes (34) also showed that for the copper-LIX64N system, a polynomial gives the best fit. A modified chemical model is however only slightly worse. For the chromate-Aliquat 336 system the chemical model is better than the polynomial.

Bauer and Chapman (11) made a statistical modeling procedures to correlate experimental data for the extraction of copper from acid sulfate solutions by KELEX 100 in xylene. They relate the equilibrium constant as a function of temperature, ionic strength and the mole fractions of sulfuric acid and copper chelate in the organic and aqueous phases respectively. This correlation, which omits the organic phase activity coefficient terms, fits their data

with a standard error of ± 10 percent.

The thermodynamic models developed in this work describe the liquid-liquid extraction of lanthanides and actinides from aqueous acidic solution by organophosphorous compounds. These models were based on the earlier works of O'Brien (75, 76), Nevarez (72), Nevarez and Bautista (73) and Nevarez, et al. (74). This thermodynamic model approach has been extended to other single component systems and for the first time to binary and ternary systems. The models would predict the distribution coefficients and separation factors for lanthanides and actinides at different experimental conditions.

Lanthanide Nitrate Complexes for Single, Binary and Multicomponent Systems

The case of neodymium nitrate complexes

The extraction mechanism for neodymium nitrate by HDEHP was proposed by Peppard, et al. (80) as:

Here (HG)₂ represents the dimeric extractant molecule.

The equilibrium constant K_e can be represented by:

$$K_e = \frac{[Nd(HG)_2]_O [H^+]_A^{+3}}{[Nd]_A [(HG)_2]_O} \quad (63)$$

where the $| |$ represent the activities and the subscripts A and O denote the aqueous and organic phases respectively. By using the relation between the activity and activity coefficient, Equation 63 can be written as:

$$K_e = \frac{(Nd(HG)_2)_O (H^+)_A^3}{(Nd)_A ((HG)_2)_O} \frac{r_{Nd(HG)_2}^3}{r_{H^+}^3} \quad (64)$$

The total neodymium ion concentration in the organic phase can be written as :

$$(Nd)_O^T = K_e \frac{(Nd)_A^3 ((HG)_2)_O^3}{(H^+)_A^3} \frac{r_{(HG)_2}^3}{r_{H^+}^3} \frac{r_{Nd^{+3}}}{r_{Nd(HG)_2}^3} \quad (65)$$

For weak complexing anions such as in the present work, it is generally assumed that the metal species present in

aqueous phase are M^{+3} , MB^{+2} , MB^{+1} and MB (39, 47, 81). The formation of the neodymium nitrate inorganic complexes in the aqueous solutions are given by the following reactions:

The stoichiometric over-all stability constants k_1 , k_2 , and k_3 were previously defined and can be represented by the following equations:

$$k_1 = \frac{(NdNO_3^{+2})}{(Nd^{+3})(NO_3^-)} \quad (69)$$

$$k_2 = \frac{(Nd(NO_3)_2^{+1})}{(Nd^{+3})(NO_3^-)^2} \quad (70)$$

$$k_3 = 0 \quad (71)$$

where the parentheses refer to the concentrations of the species. The total neodymium ion concentration in the aqueous phase is given by:

$$(\text{Nd})_A^T = (\text{Nd}^{+3}) + (\text{NdNO}_3^{+2}) + (\text{Nd}(\text{NO}_3)_2^{+1}). \quad (72)$$

Substitution of Equation 69 and 70 into Equation 72 gives:

$$\begin{aligned} (\text{Nd})_A^T &= (\text{Nd}^{+3}) (1 + k_1 (\text{NO}_3)^{-1} + k_2 (\text{NO}_3)^{-2}) \\ &= (\text{Nd}^{+3}) (1 + \sum_{i=1}^n k_i (\text{NO}_3)^{-i}). \end{aligned} \quad (73)$$

The distribution coefficient K_d is defined for a single component system by the ratio of the total concentration of the neodymium species in the organic phase to the total concentration of the neodymium species in the aqueous phase:

$$K_d = \frac{(\text{Nd})_C^T}{(\text{Nd})_A^T}. \quad (74)$$

Substitution of Equations 65 and 73 into Equation 74 yields:

$$K_d = \frac{((HG)_2)^3}{(H)_A^3} \cdot \frac{1}{1 + \sum_{i=1}^n k_i (NO)_3^{-i}} \cdot K_e \cdot \frac{r_{(HG)_2}^3 r_{Nd^{+3}}}{r_{Nd(HG)_2}^3 r_{H^+}^3} \quad (75)$$

From Equation 51, the degree of formation can be written as:

$$\alpha_o = \frac{1}{1 + \sum_{i=1}^n k_i (NO)_3^{-i}} \quad (76)$$

At this point, the assumption is made that the ratio of the activity coefficients of the molecules obtained in Equation 75 varies slightly with concentration. Should this assumption hold, then the quotient of activity coefficients in Equation 75 can be represented as a constant value given by:

$$K_r = \frac{r_{Nd(HG)_2}^3 r_{H^+}^3}{r_{(HG)_2}^3 r_{Nd^{+3}}^3} \quad (77)$$

Combining this activity coefficient ratio constant with the

liquid-liquid extraction equilibrium constant, that is

$$K_1 = \frac{K_e}{K_r} \quad (78)$$

gives a value for an effective equilibrium constant K_1 for the extraction equilibria. Substitution of Equations 76, 77 and 78 into Equation 75 gives:

$$K_d = K_1 a_o \frac{((HG)_2)^3}{(H)_A^3} \quad (79)$$

Defining

$$\frac{((HG)_2)^3}{(H)_A^3} = \phi \quad (80)$$

then, Equation 79 becomes

$$K_d = K_1 a_o \phi \quad (81)$$

By definition, the separation factor for a binary

component system of two different lanthanides, M and N, can be written as:

$$S_{M-N} = \frac{\frac{(K)}{d_M} \frac{K a \phi^3}{1M oM M}}{\frac{(K)}{d_N} \frac{K a \phi^3}{1N oN N}} \quad (82)$$

Since a binary system has the same organic and aqueous phases, it can be written:

$$\phi_M = \phi_N \quad (83)$$

By defining

$$\frac{\frac{K}{1M}}{\frac{K}{1N}} = K_{M-N} \quad (84)$$

then, Equation 82 can be written as:

$$S_{M-N} = K_{M-N} \frac{\frac{a}{oM}}{\frac{a}{oN}} \quad (85)$$

From this equation, it can be seen that the separation factor for two metallic species in a binary component system is only dependent on the degrees of formation of the two components.

in the aqueous phase. The usefulness of this approach is that it simplifies the analysis of a liquid-liquid extraction system containing two or more lanthanides.

The case of cerium nitrate complexes

Hesford and McKay (47), Hesford, et al. (48), Scargill, et al. (93) and Bostian and Smutz (13) related the extraction mechanism of trivalent cerium by tri-n-butyl phosphate. These investigators proposed the following extraction mechanism:

The liquid-liquid extraction equilibrium constant can be represented by:

$$K_e = \frac{|\text{Ce}(\text{NO}_3)_3 \cdot 3\text{TBP}|_O}{|\text{Ce}^{+3}|_A |\text{NO}_3^-|_{3O}^3 |\text{TBP}|_O^3} \quad (87)$$

where $| |$ refer to the activities of each species.

The complex formation of inorganic trivalent cerium nitrates in aqueous phase can be represented by the following complexing reactions:

The stoichiometric over-all stability constants can be represented by the following equations:

$$k_1 = \frac{(\text{CeNO}_3^{+2})}{(\text{Ce}^{+3})(\text{NO}_3^-)} \quad (91)$$

$$k_2 = \frac{(\text{Ce}(\text{NO}_3)_2^{+1})}{(\text{Ce}^{+3})(\text{NO}_3^-)^2} \quad (92)$$

$$k_3 = 0 \quad (93)$$

where the parentheses represent the concentration of the species in the reaction (88) to (90). Following the same procedures as used in the neodymium nitrate complexes, the following model equation can be derived:

$$K_d = K_a \frac{(\text{NO}_3)_A^3 (\text{TBP})_O^3}{(\text{HNO}_3)_A^3 (\text{H}_2\text{O})_A^3} \quad (94)$$

where a_o is the degree of formation, K_1 is the effective equilibrium constant for the extraction mechanism given by Equation 86.

Healy and McKay (46) reported that nitric acid will dissolve in TBP forming the complex $(\text{HNO}_3)_3 \cdot \text{TBP}$. Alcock, et al. (4) and Fomin and Maiorova (31) proposed that the reaction between nitric acid and TBP is given by the equation

and the equilibrium constant by the equation

$$K_e = \frac{(\text{HNO}_3)_3 \cdot \text{TBP}_O}{(\text{H})_A (\text{NO}_3)_A^3 (\text{TBP})_O} \quad (96)$$

Fomin and Maiorova (31) reported that the equilibrium constant of the reaction represented by Equation 95 and 96 is equal to 0.22 ± 0.02 when the initial nitric acid concentration does not exceed 4 M. Since it was difficult to determine the free TBP concentration, it was desirable to

determine the concentration of $\text{HNO}_3 \cdot \text{TBP}$ by estimating the concentration of nitric acid in the organic phase. Equation 96 can be rewritten as:

$$(\text{TBP})_0 = \frac{(\text{HNO}_3 \cdot \text{TBP})_0}{1 + \frac{(\text{H}^+)_A (\text{NO}_3^-)_A K_e}{(\text{HNO}_3)_A}} \quad (97)$$

Substitution of Equation 97 into Equation 94 gives:

$$K_d = \frac{K_a (\text{HNO}_3 \cdot \text{TBP})_0}{(\text{HNO}_3)_0 + \frac{(\text{H}^+)_A (\text{NO}_3^-)_A K_e}{(\text{HNO}_3)_A}} \quad (98)$$

Since K_e is a constant, it can be defined as:

$$K'_e = \frac{K_e}{(\text{HNO}_3)_A} \quad (99)$$

and the model given by Equation 98 becomes

$$K_d = K' a_{10} \frac{(HNO_3 \cdot TBP)^3}{(H^+)^3} \quad (100)$$

For the binary system, the separation factor for two different lanthanides, M and N, can be shown as:

$$S_{M-N} = K' \frac{a_{OM}}{a_{ON}} \quad (101)$$

where

$$K'_{M-N} = \frac{K'_{1M}}{K'_{1N}} \quad (102)$$

a_{OM} and a_{ON} are the degrees of formation for the species M and N respectively in the aqueous phase of a binary system.

Comparison of Equations 100 with 79 show that the model equations obtained for the single component systems are of the same type. The distribution coefficients in each case are directly third power dependent on the solvent concentration and on the degree of formation and inversely third power dependent on the hydrogen ion concentration in the aqueous phase. The conclusion from Equations 85 and 101 is

that the model equations for binary component systems are the same regardless of the extraction mechanisms or the organic solvents used. The separation factor is dependent on the degree of formation of each species in the aqueous phase for a binary component system.

Actinide Nitrate Complexes for Single, Binary and Multicomponent Systems

The case of plutonium (IV) and neptunium (IV) nitrate complexes

Healy and McKay (46) reported that tetravalent actinide nitrates dissolve in tri-n-butyl phosphate to form the complexes of $M(NO_3)_4 \cdot 2TBP$, where M represent the plutonium (IV) and neptunium (IV) ionic species. They also proposed that the extraction of plutonium (IV) and neptunium (IV) into TBP can be represented by the reaction

and the equilibrium constant by

$$K = \frac{|M(NO)_3| \cdot 2TBP|_0}{|M|^{+4} |NO|^{-4} |TBP|^2} \quad (104)$$

where the $| |$ denote the activities of each species.

Fomin and Maiorova (31), Moskvina (70) and Laxminarayanan, et al. (59) proposed the following complex formation reactions:

Similarly, the stoichiometric over-all stability constants can be represented by:

$$K_1 = \frac{(MNO)^{+3}}{(M)^{+4} (NO)^{-3}} \quad (109)$$

$$k_2 = \frac{(M(NO)_3)_2^{+2}}{(M)_3^{+4} (NO)_3^{-2}} \quad (110)$$

$$k_3 = \frac{(M(NO)_3)_3^{+1}}{(M)_3^{+4} (NO)_3^{-3}} \quad (111)$$

$$k_4 = \frac{(M(NO)_3)_4}{(M)_3^{+4} (NO)_3^{-4}} \quad (112)$$

The parentheses represent the concentration for each species. By making use of the same modeling technique as in the previous cases, the following model equation for plutonium (IV) and neptunium (IV) nitrate complexes can be derived.

$$K_d = K_a \frac{(NO)_3^{-4} (TBP)_2}{(M)_3^{+4} (NO)_3^{-4}} \quad (113)$$

where K_d is the effective equilibrium constant and a_1 is the degree of formation. Substitution of Equations 97 and 99 into Equation 113 gives:

$$K_d = K' a_{\text{HNO}_3} a_{\text{TBP}}^2 \frac{a_{(\text{NO}_3)_2\text{A}}}{a_{(\text{H})^+}^2} \quad (114)$$

For a binary system, the separation factor for two different actinides, M and N, in the liquid-liquid extraction binary component system is given by

$$S_{\text{M-N}} = K \frac{a_{\text{OM}}}{a_{\text{ON}}} \quad (115)$$

or

$$S_{\text{M-N}} = K' \frac{a_{\text{OM}}}{a_{\text{ON}}} \quad (116)$$

and $K_{\text{M-N}}$ and $K'_{\text{M-N}}$ were defined by Equations 84 and 102 respectively.

Table 1 is the comparison of the model equations for lanthanide and actinide nitrates. It shows that for binary component system, no matter what organic solvents are used, the thermodynamic model equation is the same for all cases. For a single component system the thermodynamic model equation is dependent on the free organic concentration, the ligand concentration, the hydrogen ion concentration and

Table 1. Comparison of the thermodynamic model equations for lanthanide and actinide nitrates

Inorganic complex	Organic solvent	Predictive K equation	Predictive S equation
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		$K_d = K_d^0 \frac{a_{(HG)}^3}{a_{H^+}^3 + a_A}$	$S_{M-N} = K_{M-N} \frac{a_{OM}}{a_{ON}}$
	HDEHP		

Lanthanide nitrate complexes		$K_d = K_d^0 \frac{a_{(NO_3^-)}^3}{a_A^3}$	$S_{M-N} = K_{M-N} \frac{a_{OM}}{a_{ON}}$
	TBP	$K_d = K_d^0 \frac{a_{(HNO_3 \cdot TBP)}^3}{a_{H^+}^3 + a_A}$	$S_{M-N} = K'_{M-N} \frac{a_{OM}}{a_{ON}}$

Table 1 Continued

Inorganic complex	Organic solvent	Predictive K equation	Predictive S equation
		d	M-N

Actinide nitrate
complexes

TBP

$$K_d = K_a \frac{(\text{NO}_3)_3 \text{A}^{-4}}{(\text{TBP})^2} \quad S_{M-N} = K' \frac{a_{\text{OM}}}{a_{\text{ON}}}$$

the degree of formation. In other words, the predictive thermodynamic model equation for a single component system is dependent on the extraction mechanism. Therefore, for the following extraction mechanism

the predictive K_d equation can be written as

$$K_d = K_1 a_1 (NO_3^-)_3^p (TBP)_O^q \quad (118)$$

or

$$K_d = K_1' a_1 (HNO_3)_3^p (TBP)_O^q \frac{(NO_3^-)_3^{p-q}}{(H)_A^q} \quad (119)$$

Similarly the predictive K_d equation for the extraction mechanism

is

$$K_d = K_1 a_1 \phi^p \quad (121)$$

EXPERIMENTAL PROCEDURES

Materials

The rare earth oxides utilized in this work have a purity greater than 99.9% with respect to other lanthanides, and were supplied by the Rare Earth Separation Group of the Ames Laboratory.

The HDEHP was obtained from Union Carbide Corporation. It is monoacidic and had a purity of 98.8%. One molar solution of dimeric HDEHP was prepared by diluting pure HDEHP with Amsco 125-82 (a high molecular weight hydrocarbon diluent), obtained from the American Mineral Spirits Co. The HDEHP concentration was based on monomer basis, thus dimeric HDEHP was 0.5 M on a dimer basis.

Sodium nitrate (A. R. grade) was dried in an oven at 105° C for at least 2 hours and was used to adjusting the ionic strength. All other materials were A. R. grade and were used without further purification.

Preparation of the Rare Earth Stock Solutions

The rare earth nitrate solutions were prepared by reacting the particular rare earth oxides with an excess amount of concentrated reagent grade nitric acid. The excess acid is removed by boiling down the solution on a hot plate

and subsequent dilution with distilled water. In order to overcome the hydrolysis of the highly charged lanthanide ions, the stock solutions were titrated with nitric acid. The titration can be followed with a pH meter, and the end point is determined by the point of discontinuity in a plot of pH vs. milliliters of acid added. At this pH the ratio of lanthanide to anion is 1 : 3. It has been determined that the end point of lanthanide nitrate solutions occurs at pH = 3. Thus all stock solutions were adjusted to this value in order to overcome the hydrolysis effect. The concentrations of these stock solutions were determined by oxalate precipitation method. The precipitates were converted to their oxides by drying and burning the oxalates to the oxides and weighing the oxides after cooling in a desiccator.

The rare earth chloride stock solution was prepared in the same way as the rare earth nitrate stock solution. The same method was used to determine the concentration of the rare earth chloride stock solution.

Equilibrium Studies

The initial aqueous solutions were prepared by diluting an appropriate amount of rare earth nitrate and chloride stock solutions with distilled water and nitric acid in volumetric flasks. Equal volumes of initial aqueous

solutions and 1 M HDEHP were introduced in a separatory funnel and then shaken vigorously twice for half an hour using a shaking machine. A settling time of 30 minutes was allowed between shakings and then allowed to stand for at least twelve hours before the phases were separated. A volumetric sample of the organic phase was then contacted four times with 6 M nitric acid in order to remove the extracted species. This solution was evaporated to remove the excess acid before dilution with distilled water. The lanthanide concentration in the organic phase was analyzed by titration with standardized EDTA solution. Arsenazo was the indicator and pyridine was the buffer used following the procedures described by Fritz, et al. (36). EDTA titration was also used to analyze the lanthanide concentration in the aqueous phase. All equilibrium studies were done at room temperature $24^{\circ} \pm 1^{\circ} \text{C}$.

The hydrogen ion concentration of the equilibrated aqueous phase was determined using a Beckman pH and saturated calomel electrodes. The electrode potential was measured using an Orion 801 digital pH/mv meter. It also should be mentioned that the pH electrode was calibrated before and during use with buffer solution of 4.01 and 2.27 pH values.

The total nitrate concentration in the organic phase was measured by using the nitrate ion electrode. A volumetric sample of an organic phase is contacted several times with a

strong acid. The acid must have a very small selective constant in order to minimize the interference effect to the nitrate ion electrode. Sulfuric acid with a selective constant $k = 3 \times 10^{-5}$ was chosen for this purpose. Equal volumes of 3×10^{-5} M sulfuric acid were contacted three times with the organic equilibrated phase. The total nitrate ion concentration was then analyzed by the nitrate ion electrode. Suitable standards were prepared containing sulfuric acid as the background to determine the exact amount of nitrate ion concentration in the sample. The equilibrated concentration of the HDEHP dimers can be estimated from the equation:

$$(\text{HG})_2^{\text{E}} = (\text{HG})_2^{\text{I}} - 3(\text{M})_0^{\text{T}} + (\text{NO}_3^-)_0^{\text{T}} \quad (122)$$

The chloride and nitrate ion concentrations in the solutions of lanthanum chloride and neodymium nitrate were difficult to determine accurately because of their mutual interference relative to each other. The selective constant of the chloride ion relative to the nitrate ion is $k = 4 \times 10^{-4}$ and the nitrate ion relative to the chloride ion is $k^x = 4.2$. The procedure reported by Lieth (61) for nitrate in fertilizer was used as an interference free procedure for nitrate in the lanthanum and neodymium solutions. An aliquot containing less than 90 mg of nitrate was placed in a 250 ml Erlenmeyer flask and enough water added to bring the volume

to about 23 ml. Twenty-five milliliters of 0.2 N ferrous sulfate solution in 4.5 N sulfuric acid containing 0.5 N sodium chloride is then pipetted into the flask, followed by 20 ml of concentrated sulfuric acid. The solution is brought to a rapid boil, boiled for four minutes and then removed and cooled rapidly to room temperature. Fifty milliliters of water is added, then 1.0 ml of 0.0025 N ferron indicator solution and the remaining ferrous ion titrated with 0.1 N potassium dichromate solution to a clear light green end-point. The difference between a blank value for the ferrous sulfate and the sample solution gave the amount of ferrous iron oxidized by nitrate. The amount of nitrate was then calculated from this value. The determination of chloride ion concentration in the sample solution followed the titration portion of the technique reported by Cheng (14). One half milliliter or smaller aliquot of the sample solution was taken and placed in a 250 ml beaker containing 20 ml of water. Two ml of 0.5 N potassium hydroxide solution was added and 100 ml of ethanol. The apparent pH was adjusted to 3.6 with 0.5 and 0.05 N nitric acid, ten drops of 5% diphenyl carbizone in ethanol added and the solution titrated with standardized 0.01 N mercuric nitrate solution to a violet colored end-point. Milligrams of chloride per milliliter of sample was calculated from the volume of titrant used.

Separation Factor Studies

The binary system lanthanum nitrate-neodymium nitrate-water-nitric acid-HDEHP-Amsco and the ternary system lanthanum nitrate-neodymium nitrate-samarium nitrate-nitric acid-water-HDEHP-Amsco were also studied. The same technique as in the single component system were utilized in order to obtain the total lanthanide concentrations in the equilibrated aqueous and organic phases. The composition of each phase containing neodymium, lanthanum and samarium were also determined in order to calculate the separation factors relative to each other. The relative amount of each species were obtained by flame spectroscopy as described by Knisely, et al. (54).

Ion Selective Electrode Measurements

The Orion nitrate ion-selective electrode and the Orion double junction reference electrode were used in this work. The nitrate electrode provides rapid, accurate analysis over a concentration range of 10^{-1} M to 10^{-5} M. Once the electrode is calibrated in standard solutions of known activities or concentrations, it responds directly to sample nitrate ion activity or concentration. The double junction reference electrode gave a stable reference of the voltage regardless of the sample concentration. The Orion 801 digital pH/mv meter which covers a range of +1000 mv to -1000

mv with a precision of 0.1 mv, was used to measure the electrical potentials between the electrodes. Figures 1 and 2 show the details of the nitrate ion selective electrode as well as the electrode system.

The standardization of the electrode system with a suitable electrolyte should be done before using an ion-selective electrode. As suggested by Bates and Alfenaar (9), the sodium nitrate solution was used as the standard solution and the chloride convention which was proposed by Bates and Guggenheim (10) was used to determine the nitrate ion activities in the sodium nitrate solution. One or two sets of the standard sodium solutions were prepared to bracket the expected sample nitrate concentration range. No two standards should be more than one decade apart in nitrate level. Beginning with the most dilute standard, the meter millivolt reading of the standards is recorded and plotted against the nitrate ion activities on a semi-logarithmic graph paper. The electrode was found to exhibit a good Nernstian response to nitrate ion standard solutions within the concentration range studied. Figures 3, 4 and Table 2 show the results of the nitrate electrode calibration. The constant term E in the Nernst equation:

$$E = \text{Constant} + \frac{2.3 RT}{ZF} \log \bar{a} \quad (123)$$

Figure 1. Comparison between the conventional glass pH electrode and the liquid membrane electrode.

Figure 2. General ion selective electrode system.

Figure 3. Nitrate ion electrode calibration data -- ionic activity.

Figure 4. Nitrate ion electrode calibration data -- ionic concentration.

Table 2. Nitrate electrode calibration data by using sodium nitrate as the calibrating salt

(NO_3^-) 3	$ \text{NO}_3^- $ 3	E (mv) 1	E (mv) 2	E_a
0.1	0.075	-10.9	-11.2	-77.49
0.02	0.0174	+26.9	+28.7	-77.25
0.01	0.0094	+43.3	+43.1	-77.80
0.002	0.0019	+81.4	+83.9	-76.90
0.0012	0.00097	+101.3	+101.9	-77.08

can be calculated over the entire experimental concentration range. Here E is the potential, in millivolts, RT/F is the Nernst factor which depends on the temperature, $\bar{a}$ is the activity of the ion to which the membrane is permeable, and z is its charge. The constant term in this equation is dependent on what reference electrode is used, on the choice of ion activity in the inner solution and also on the liquid-liquid junction potential at the salt bridge connection. The constant term is very sensitive to change in the reference electrode and should be calibrated before and after the measurements.

When other ions are presented in a sample solution, interference will cause uncertain determination of the particular ion being studied. To overcome this difficulty, the following empirical equation is useful:

$$E = \text{Constant} + \frac{2.3 RT}{Z_A F} \log \left(\bar{a} + \sum_i k_{xi} b_i^{\frac{Z_B}{Z_A}} \right). \quad (124)$$

Here $\bar{a}$ and b represent the activities of the sought-for ion and the interfering ion respectively. Raised to a power equal to the charged ratio, the activity of each interfering ion in the sample is multiplied by a weighting factor, the selective constant k_x . This equation has been tested with a wide variety of electrodes and a large number of interfering ions by Coetzee and Freiser (19, 20) and Freiser (35). Their experimental results are in agreement at low concentrations of interfering ions.

One more problem is the liquid junction potential of the reference electrode. This junction potential is caused by the slight separation of ionic charges that results from the tendencies of the various ions to diffuse at an unequal rate across the solution boundary. This effect can be overcome by using a suitable reference electrode with a solution of approximately the same ionic strength and having similar

values for the ionic mobilities as that for the samples to be used. This is capable of reducing the ionic diffusion and, hence, the liquid junction potential. In this work, a double junction reference electrode is used to minimize the junction potential problem.

Simple Linear Regression Analysis

Statistical methods applicable to scientific research have been discussed in detail by Ostle and Mensing (77). The statistical method used in this investigation was mainly the simple linear regression analysis technique. To deal with this problem mathematically, one needs to introduce some criterion which judges how well a regression equation fits the set of data. The least square criterion is used to minimize the sum of the squares of the vertical distances between the data points and the appropriate line. The line which minimizes this sum is called the least square regression line which represents the best fit. In order to seek a correlation that reflects the goodness of the fit, the correlation coefficient is defined as

$$R^2 = \frac{\text{Sum of squares due to regression}}{\text{Total (corrected) sum of squares}} \quad (125)$$

with the limit $0 \leq R^2 \leq 1$. If the data fit the regression line very well, R^2 will approach 1. Similarly, if the regression line is a poor fit, the data points will be widely scattered about the regression line and R^2 will approach 0, reflecting very poor correlation.

DISCUSSION OF RESULTS

Application of Published Data to the Thermodynamic
Liquid-Liquid Extraction Models

The system neptunium nitrate-nitric acid-water-TBP-benzene

Moskvin (70) studied the complex formation of neptunium nitrate by using the liquid-liquid extraction method at ionic strength $I = 2$ M. The stoichiometric stability constants of nitrate-complexes of Np (IV) were reported as $k = 6.8$, $k = 20.6$, $k = 35.3$ and $k = 34.3$ and the equilibrium data are given in Table 3. From these equilibrium data the degree of formation can be calculated according to Equation 76.

$$a_o = \frac{1}{1 + \sum_i k_i (\text{NO}_3)_3} \quad (76)$$

When the degrees of formation and the equilibrium data are available, the effective equilibrium constant K_1 in each set of data can be calculated by the model Equation 113

$$K_d = K_1 a_o^{-4} (\text{NO}_3)_3^{-2} (\text{TBP})_0 \quad (113)$$

or

$$K_1 = \frac{K_d}{a_3(\text{NO}_3^-) a_0(\text{TBP})} \quad (126)$$

Figure 5 is the plot of the degree of formation a_0 vs. the nitrate ion concentrations at ionic strength $I = 2$ M. The plot shows the degree of formation decreases sharply as the

"Table 3. Equilibrium data for the system neptunium nitrate-nitric acid-water-TBP-benzene¹

(NO ₃ ⁻), M 3 A	k _d	stability constants
0.0	0.00503	
0.1	0.00775	k = 6.8
0.2	0.06845	1
0.4	0.354	
0.6	0.776	k = 20.6
0.8	1.10	2
1.0	1.40	
1.2	1.62	k = 35.3
1.4	1.67	3
1.6	1.82	
1.8	1.91	k = 34.3
2.0	2.23	4

¹Experimental conditions:

Ionic Strength $I = 2.0$ M

(TBP) = 1.0 M

$T = 25^\circ \pm 1^\circ$ C.

Equilibrium data were reported by Moskvina (70).

Figure 5. Degree of formation α_0 for neptunium nitrate
in aqueous phase.

nitrate ion concentration increases from 0 to 0.6 M. The value of effective equilibrium constant K was found by linear regression analysis of the available data and is equal to 126.34 ± 2.43 . Table 4 shows the results of the calculated degrees of formation and the effective equilibrium constants. Using the value of the effective equilibrium constant, the model Equation 113 can now be written as:

$$K = 126.3357 a_o \frac{(\text{NO}_3^-)^4}{3 A} \frac{(\text{TBP})^2}{O} \quad (127)$$

The distribution coefficients can be calculated at different nitrate ion and TBP concentrations using this model equation. Table 4 also shows the comparison between the calculated K_d

Table 4. The calculated degree of formation and the effective equilibrium constant for the system neptunium nitrate-nitric acid-water-TBP-benzene

(NO_3^-) , M 3 A	a_o	K 1	K (data) ¹ d	K (model) d
0.1	0.5196	149.160	0.0078	0.0063
0.2	0.2840	150.530	0.0685	0.0568
0.4	0.0985	140.400	0.3540	0.3184
0.6	0.0407	147.093	0.7760	0.6671
0.8	0.0193	138.968	1.1000	1.0005
1.0	0.0102	137.199	1.4000	1.2880
1.2	0.0059	133.552	1.6200	1.5325
1.4	0.0036	121.514	1.6700	1.7359
1.6	0.0023	120.524	1.8200	1.9077
1.8	0.0016	117.523	1.9100	2.0529
2.0	0.0011	129.368	2.2300	2.1780

¹Data were reported by Moskvina (70).

values obtained by Equation 127 and the experimental K_d data reported by Moskvina (70). Figure 6 is the plot for K_d (model) vs. K_d (data) with a correlation coefficient $R^2 = 0.996$. It shows that the model equation 126 gives good predictive distribution coefficients within the experimental conditions and at ionic strength $I = 2$ M.

The system plutonium nitrate-nitric acid-water-TBP-toluene

Laxminarayanan, et al. (59) determined the stability constants for nitrate complexes of plutonium by a solvent extraction method using TBP as the solvent and toluene as the diluent. Table 5 shows the stability constants for plutonium nitrate complexes at different ionic strengths. Table 6 gives the equilibrium data for this system which was reported by Laxminarayanan, et al. (59). They did not report the

Table 5. Stability constants for plutonium nitrate complexes¹

Ionic strength $I, (M)$	Stability Constants			
	k_1	k_2	k_3	k_4
1.02	5.3	9.2	4.0	---
1.90	4.0	7.5	4.0	1.2
4.70	4.6	14.8	10.8	2.0

¹Data were reported by Laxminarayanan, et al. (59).

Figure 6. The comparison between the K_d (model) and the K_d (data) obtained experimentally by Moskvina (70) for the system $\text{Np}(\text{NO}_3)_3 - \text{HNO}_3 - \text{H}_2\text{O} - \text{TBP} - \text{Benzene}$.

equilibrium hydrogen ion concentration in the aqueous phase. However, the hydrogen ion concentrations in the sample solutions were reported in detail. It can be assumed that the changes of the hydrogen ion concentrations before and after the equilibration varied very slightly since the neutral organophosphorus compound only extract the neutral species from the aqueous phase. No hydrogen ion is liberated

Table 6. Equilibrium data for the system plutonium nitrate-nitric acid-water-TBP-toluene¹

(NO ⁻) 3 A M	K d	(HNO ₃ . TBP) 3 M	I M	(H ⁺) M
0.22	0.13	0.049	1.02	1.02
0.42	0.49	0.070	1.02	1.02
0.62	1.04	0.089	1.02	1.02
0.82	1.65	0.104	1.02	1.02
1.02	2.19	0.128	1.02	1.02
0.26	0.46	0.049	1.90	0.6
0.51	1.68	0.070	1.90	0.6
0.61	2.25	0.075	1.90	0.6
0.75	2.43	0.078	1.90	0.6
0.91	3.17	0.087	1.90	0.6
1.16	4.55	0.105	1.90	0.6
1.40	5.66	0.127	1.90	0.6
1.70	5.20	0.129	1.90	0.6
1.90	7.34	0.131	1.90	0.6
0.30	8.12	0.123	4.70	0.7
0.50	20.61	0.139	4.70	0.7
0.72	24.60	0.139	4.70	0.7
0.92	33.86	0.172	4.70	0.7
1.12	44.18	0.184	4.70	0.7
1.32	53.70	0.214	4.70	0.7
1.52	69.52	0.239	4.70	0.7

¹Equilibrium data were reported by Laxminarayanan, et al. (59).

from the organic phase to the aqueous phase. Should this assumption hold, their equilibrium data can be used to test the consistency of the developed thermodynamic model.

The degree of formation can be calculated by using Equation 51 and the equilibrium data as well as the stability constants of the plutonium nitrate complexes. The effective equilibrium constants K'_1 can then be calculated according to the model given by Equation 114.

$$K'_d = K'_1 a_{\text{HNO}_3} a_{\text{TBP}} \frac{(\text{NO}_3^-)_A^2}{(\text{H}^+)_A^2} \quad (114)$$

The calculated degrees of formation and the effective equilibrium constants are presented in Table 7. Figure 7 gives the plot of degree of formation vs. the nitrate ion concentrations at ionic strength $I = 1.02$. The dotted lines represent the extrapolation to the regions of low nitrate ion concentration. Table 7 shows that the fluctuation of K'_1 values was not so large within each ionic strength range and no particular trend could be observed in each case. These are good indications that support the assumption of a constant activity ratio.

A linear regression analysis technique can be applied to estimate the effective equilibrium constant K'_1 in the model

Equation 114. The calculated effective equilibrium constants were 2891.0, 2659.08 and 889898.65 at ionic strengths of 1.01, 1.9 and 4.7 M respectively. From the regressed value K'_1 ($K'_1 = K_1 / K_e$), the model was solved for the predicted distribution coefficients at each specific ionic strength using Laxminarayanan's, et al. (59) data given in Table 6. The results are shown in Table 8 and Figure 8. Good results were obtained by using the predictive thermodynamic model equation at constant ionic strength.

Table 7. The calculated degree of formation and the effective equilibrium constant for the system plutonium nitrate-nitric acid-water-TBP-toluene

(NO ₃) ₃ A, M	K' ₁	a ₀	a ₁	a ₂	a ₃	a ₄	I M
0.22	3088.77	0.3768	0.4394	0.1678	0.0161	0.0000	1.02
0.42	3034.64	0.1944	0.4326	0.6154	0.0576	0.0000	1.02
0.62	3118.58	0.1139	0.3744	0.4030	0.1086	0.0000	1.02
0.82	3242.65	0.0728	0.3164	0.4503	0.1605	0.0000	1.02
1.02	2703.08	0.0494	0.2673	0.4733	0.2099	0.0000	1.02
0.26	2675.99	0.3813	0.3966	0.1933	0.0268	0.0021	1.90
0.51	2658.64	0.1785	0.3641	0.3490	0.0947	0.0145	1.90
0.61	2826.92	0.1369	0.3340	0.3820	0.1243	0.0228	1.90
0.75	2629.31	0.0972	0.2917	0.4102	0.1641	0.0370	1.90
0.91	2674.25	0.0681	0.2478	0.4229	0.2052	0.0560	1.90
1.16	2666.29	0.0414	0.1922	0.4179	0.2586	0.0899	1.90
1.70	2302.39	0.0169	0.1150	0.3644	0.3322	0.1694	1.90
1.90	3358.90	0.0127	0.0965	0.3438	0.3484	0.1986	1.90
0.30	529545.60	0.2488	0.3433	0.3314	0.0725	0.0040	4.70
0.50	798810.40	0.1180	0.2714	0.4366	0.1593	0.0148	4.70
0.72	898068.80	0.0604	0.2001	0.4635	0.2435	0.0325	4.70
0.92	824479.80	0.0362	0.1533	0.4538	0.3047	0.0519	4.70
1.12	988997.60	0.0232	0.1197	0.4314	0.3526	0.0731	4.70
1.32	948022.00	0.0157	0.0952	0.4044	0.3895	0.0952	4.70
1.52	1056470.00	0.0110	0.0770	0.3766	0.4178	0.1176	4.70

Figure 7. Degree of formation α_i for plutonium nitrate in the aqueous phase at ionic strength $I = 1.02 \text{ M}$.

Table 8. Model predictions for the system plutonium nitrate-nitric acid-water-TBP-toluene

(NO ⁻) ₃ A, M	I, M	K (data) ¹ d	K (model) d
0.22	1.02	0.130	0.116
0.42	1.02	0.490	0.463
0.62	1.02	1.040	0.954
0.82	1.02	1.650	1.474
1.02	1.02	2.190	2.341
0.26	1.90	0.460	0.452
0.51	1.90	1.680	1.675
0.61	1.90	2.250	2.127
0.75	1.90	2.430	2.450
0.91	1.90	3.170	3.164
1.16	1.90	4.550	4.547
1.40	1.90	5.660	5.328
1.70	1.90	5.200	6.009
1.90	1.90	7.340	5.823
0.30	4.70	8.120	17.790
0.50	4.70	20.610	24.700
0.72	4.70	24.600	26.700
0.92	4.70	23.860	35.590
1.12	4.70	44.196	44.690
1.32	4.70	53.706	53.400
1.52	4.70	69.526	62.290

¹Data were reported by Laxminarayanan, et al. (59).

The system cerium nitrate-nitric acid-water-TBP-benzene

Using the extraction method, Fomin, et al. (32) calculated the stability constants for cerium nitrate complexes. These stability constants were found to be 11 ± 2.5 and 32 ± 7 for $k_1(\text{CeNO}^{+2})$ and $k_2(\text{Ce}(\text{NO})^{+1})$ respectively at ionic strength of 2.0 M. Table 9 shows the equilibrium data for this system obtained by Fomin, et al. (32). The degree of formation was calculated using Equation 76. The

Figure 8. The comparison between the K_d (model) and the K_d (data) obtained experimentally by Laxminarayanan et al. (59) for the system $\text{Pu}(\text{NO}_3)_4 - \text{HNO}_3 - \text{H}_2\text{O} - \text{TBP} - \text{Toluene}$.

Table 9. The equilibrium data for the system cerium nitrate-nitric acid-water-TBP-toluene¹

(NO ₃ ⁻), M	(H ⁺), M	(TBP), M	K _d
0.29	2.03	1.00	0.004
0.50	2.00	0.98	0.007
0.75	2.00	0.975	0.015
1.00	2.00	0.969	0.020
1.25	2.01	0.945	0.026
1.50	1.99	0.935	0.031
1.75	2.00	0.905	0.036
2.00	2.00	0.875	0.034

¹Data were reported by Fomin, et al. (32).

effective equilibrium constants were estimated for this system using the model given by Equation 94.

$$K_d = K_a \frac{(NO_3^-)^3}{(H^+)^3} \frac{(TBP)^3}{(C)^3} \quad (94)$$

The calculated effective equilibrium constants and the degrees of formation are shown in Table 10. The average value of the regressed K's is equal to 1.0285 ± 0.019.

The predictive model equation for this system can be represented by:

$$K_d = 1.0285 a \frac{(NO_3^-)^3}{(H^+)^3} \frac{(TBP)^3}{(C)^3} \quad (128)$$

Table 10 also presents the comparison between K (data) and K_d

Table 10. The calculated degree of formation and effective equilibrium constant for the system cerium nitrate-nitric acid-water-TBP-benzene

(NO ⁻) _{3 A} , M	K ₁	a _o	K (data) _d ¹	K (model) _d
0.29	1.1285	0.1453	0.0040	0.0036
0.50	0.8627	0.0689	0.0070	0.0087
0.75	1.0453	0.0367	0.0150	0.0144
1.00	0.9671	0.0227	0.0200	0.0211
1.25	1.0213	0.0154	0.0260	0.0257
1.50	1.0220	0.0112	0.0310	0.0308
1.75	1.0895	0.0085	0.0360	0.0339
2.00	0.9745	0.0066	0.0340	0.0355

¹Data were reported by Fomin, et al. (32).

K (model)_d. Figure 9 illustrates these comparisons. It shows good agreement between K (data)_d and K (model)_d at constant ionic strength.

It was shown by several investigators (4, 31, 46) that a corresponding reaction

also takes place during the extraction reaction. The equilibrium constant for this reaction can be represented by:

$$K_e = \frac{(\text{HNO}_3|\text{TBP})_O}{(\text{H}^+)_A (\text{NO}_3^-)_{3A} (\text{TBP})_O} \quad (26)$$

Figure 9. The comparison between the K_d (model) and the K_d (data) obtained experimentally by Pomin et al. (32) for the system $\text{Ce}(\text{NO}_3)_3 - \text{HNO}_3 - \text{H}_2\text{O} - \text{TBP} - \text{Benzene}$.

Fomin, et al. (31) reported that the equilibrium constants remain constant when the nitric acid concentration in the initial solution used is about 4 M. Table 11 shows the comparison between the concentrations of (TBP) and (HNO₃.TBP).

The effective equilibrium constant K', the regressed value K' and the predicted distribution coefficients were determined using the model given in Equation 101.

$$K_d = K'_d \frac{(HNO_3.TBP)_0^3}{(H^+)_A^3} \quad (101)$$

Table 12 shows these results and Figure 10 shows the comparison between the predicted and the experimental

Table 11. The comparison between (TBP) and (HNO₃.TBP) for the system cerium nitrate-nitric acid-water-TBP-benzene

(NO ₃ ⁻), M 3 A	(H ⁺), M	(TBP), M 0	(HNO ₃ .TBP), M 3 0
0.29	2.03	1.000	0.1295
0.50	2.00	0.980	0.2156
0.75	2.00	0.975	0.3216
1.00	2.00	0.969	0.4262
1.25	2.01	0.945	0.5222
1.50	1.99	0.930	0.6107
1.75	2.00	0.900	0.6930
2.00	2.00	0.870	0.7656

Table 12. Model predictions for the system cerium nitrate-nitric acid-water-TBP-benzene using $(\text{HNO}_3/\text{TBP})$ as the organic concentration ³

(NO_3^-) , M	K^1	K (data) ¹	K (model)
³ A	1	d	d
0.29	105.26	0.0040	0.0036
0.50	81.4	0.0070	0.0082
0.75	98.33	0.0150	0.0150
1.00	91.32	0.0200	0.0210
1.25	95.34	0.0260	0.0260
1.50	96.04	0.0310	0.0310
1.75	103.15	0.0360	0.0335
2.00	91.84	0.0340	0.0355

¹Data were reported by Fomin, et al. (32).

results. Comparison of Figures 9 and 10 show no significant difference in the correlation. Therefore, when either the concentration of (TBP) or $(\text{HNO}_3/\text{TBP})$ is available, the distribution coefficients can be predicted by using the model given by Equation 95 or 101 respectively. The developed model equations gives good results at constant ionic strength.

Comparison of the results obtained from the three different single component systems in this work and the other results (72, 73, 74, 75, 76) indicate that better predictive distribution coefficients are obtained at constant ionic strength. The activity coefficients at constant ionic strength are assumed to be independent of the concentrations of the reacting species and dependent only on the nature and concentration of the bulk electrolyte. Therefore, the

Figure 10. The comparison between the K_d (model) and the K_d (data) obtained experimentally for the system $\text{Ce}(\text{NO}_3)_3 - \text{HNO}_3 - \text{H}_2\text{O} - \text{TBP} - \text{Benzene}$ by using $(\text{HNO}_3 \cdot \text{TBP})_O$ as the organic concentration.

quotient of activity coefficients is a constant. This gives a good representative effective equilibrium constant for each of the cases examined. The effective equilibrium constant is defined by the equation

$$K_1 = \frac{K_e}{K_r} \quad (78)$$

where K_r is the activity coefficient ratio. From this relation it can be concluded that the effective equilibrium constant is still a constant at the condition of constant ionic strength. In other words, if the quotient of activity coefficients is not constant, the effective equilibrium constant also varies with the changing K_r . In this case K_1 is no longer a constant. As a result, this will give an inaccurate predictive distribution coefficients when using the model equations given in Table 1.

The system neodymium nitrate-ytterbium nitrate-nitric acid-water-TBP-carbon tetrachloride

The very limited data available in the literature indicates the need for further study of the nitrate complexes of lanthanides, especially for a binary component system. The only useful data set found was the work done by Kriss and Sheka (57). By using an extraction method, the first

and second stability constants for the species of MNO_3^{+2} and $M(NO_3)_2^{+1}$ respectively, were determined for neodymium and ytterbium in a binary component system. The stability constants they obtained were $k_1 = 3.3$ and $k_2 = 4.6$ for neodymium nitrate complexes and $k_1 = 3.7$ and $k_2 = 6.1$ for ytterbium nitrate complexes. These experiments were done at constant ionic strength $I = 3.0$ M. Table 13 shows the equilibrium data for this system which was reported by Kriss and Sheka (57).

The degrees of formation for neodymium and ytterbium nitrate complexes were calculated using Equation 76

$$\alpha_o = \frac{1}{1 + \sum_i k_i (NO_3)_3} \quad (76)$$

Table 13. Extraction of nitric acid, neodymium and ytterbium in the presence of perchloric acid with 1 M TBP in carbon tetrachloride¹

Initial Acid Cconc. M		(NO ₃ ⁻) 3 A M	(HNO ₃ . TBP) 3 M	K _d		S Nd-Yb
HNO ₃	HClO ₄			Nd	Yb	
0.6	2.4	0.425	0.195	0.0131	0.0070	1.871
1.2	1.8	0.923	0.370	0.0200	0.0109	1.834
1.8	1.2	1.467	0.377	0.0235	0.0090	2.610
2.4	1.6	2.021	0.421	0.0234	0.0074	3.162
3.0	0.0	2.540	0.508	0.0223	0.0073	3.054

¹Data were reported by Kriss and Sheka (57).

Table 14 gives these results as well as the constant $K_{\text{Nd-Yb}}$ which were calculated using the binary model Equation 85 together with the equilibrium data given in Table 13. The regression value of $K_{\text{Nd-La}}$ (the ratio of the effective equilibrium constant for neodymium to ytterbium) is equal to 2.0569 ± 0.1936 . The correlation coefficient R^2 between the experimental and predicted data is equal to 0.966.

Table 15 and Figure 11 show the relations between the predicted separation factors from the model Equation 85 and those obtained experimentally by Kriss and Sheka (57). Because there are only five data points in their experimental results, it is difficult to draw any conclusions for the apparent agreement between the predicted and experimental values.

Based on the above model applications, the modeling procedures can be summarized as follows:

- (1) Calculate from Equation 62 the stability constants by linear regression analysis of the reciprocal of the distribution coefficients and the ligand concentrations.
- (2) Calculate the degrees of formation from Equation 51 or 76 using the equilibrium data and the calculated stability constants.
- (3) Calculate by linear regression analysis technique the effective equilibrium constant using the equilibrium data and the calculated degrees of formation.

(4) The predictive distribution coefficients (or separation factors) can be calculated using the equilibrium data, the regression value of effective equilibrium constant as well as the suitable model equation.

Table 14. Calculated degrees of formation and the ratio of the effective equilibrium constant for Nd and Yb for the system neodymium nitrate-ytterbium nitrate-water-TBP-carbon tetrachloride

(NO ⁻) ₃ A, M	(a) _{o Nd}	(a) _{o Yb}	(a) _{o Nd} / (a) _{o Yb}	K ¹ _{Nd-Yb}
0.425	0.3093	0.2722	1.1370	1.6456
0.923	0.1256	0.1040	1.2076	1.5195
1.467	0.0635	0.0511	1.2432	2.099
2.540	0.0256	0.0200	1.2800	2.3895
2.021	0.0378	0.0299	1.2642	2.4996

¹K_{Nd-Yb} = the ratio of the effective equilibrium constant for Nd and Yb.

Table 15. Model predictions for the system neodymium nitrate-ytterbium nitrate-water-TBP-carbon tetrachloride

(NO ⁻) ₃ A, M	S _{Nd-Yb} (data) ¹	S _{Nd-Yb} (model)
0.425	1.871	2.3386
0.932	1.834	2.4839
1.467	2.614	2.5571
2.021	3.162	2.6328
2.541	3.054	2.6003

¹Data were reported by Kriss and Sheka (57).

Figure 11. The comparison between the $S_{\text{Nd-Yb}}$ (model) and the $S_{\text{Nd-Yb}}$ (data) obtained experimentally by Kriss and Sheka (57) for the neodymium nitrate-ytterbium nitrate-water-TBP-carbon tetrachloride.

HDEHP Solvent Extraction Analysis

The system lanthanum nitrate-sodium nitrate-nitric acid-water-HDEHP-Amsco

Equilibrium study on this system was performed as described in the Procedures section. Table 16 shows the equilibrium data for this system at different ionic strengths. The ionic strength was maintained constant by adding proper amount of sodium nitrate into the tested solutions.

The analysis of nitrate ion concentration in the equilibrium aqueous phase was measured using a nitrate ion selective electrode as described in the Procedures section. Table 17 and Figure 12 show the nitrate standards and calibration curve for the nitrate ion-selective electrode respectively. Table 18 shows the nitrate ion concentration in the equilibrated aqueous phase at ionic strength $I = 3.26$ M.

The nitrate ion concentration in the equilibrated organic phase can also be determined as outlined in the Procedures section. Volumetric samples of the equilibrated organic phase were first back-extracted three times with 3 M sulfuric acid, diluted and then the nitrate ion concentration was measured by using the nitrate ion-selective electrode. The details of this technique will be elaborated on the

Table 16. Equilibrium data for the system lanthanum nitrate-sodium nitrate-nitric acid-water-HDEHP-Amsco

(NC-) 3 A	(La) A	(La) O	((HG)) 2 O	(H+) A	K d	I M
0.1175	0.0217	0.0696	0.2911	0.1684	3.2028	1.0
0.1200	0.0126	0.0630	0.3109	0.1645	5.0000	1.0
0.1225	0.0069	0.0574	0.3279	0.1333	8.2750	1.0
0.1750	0.0028	0.0476	0.3572	0.1127	16.8127	1.0
0.1950	0.0015	0.0376	0.3872	0.0914	25.5700	1.0
0.2150	0.0008	0.0262	0.4214	0.0905	31.1900	1.0
0.2000	0.0397	0.0738	0.2786	0.1550	1.9070	1.5
0.2350	0.0290	0.0710	0.2870	0.1400	2.4550	1.5
0.2450	0.0237	0.0690	0.2930	0.1350	2.8900	1.5
0.2750	0.0139	0.0624	0.3128	0.1199	4.5020	1.5
0.2900	0.0085	0.0524	0.3380	0.1164	6.3450	1.5
0.3050	0.0034	0.0497	0.3509	0.0897	14.2310	1.5
0.3650	0.0008	0.0281	0.4157	0.0749	33.4520	1.5
0.2950	0.1109	0.0857	0.2429	0.1442	0.7727	2.5
0.3175	0.0907	0.0807	0.2580	0.1400	0.8894	2.5
0.3600	0.0662	0.0756	0.2731	0.1346	1.1420	2.5
0.3850	0.0517	0.0693	0.2920	0.1306	1.3410	2.5
0.4050	0.0328	0.0693	0.2920	0.1156	2.1134	2.5
0.4450	0.0159	0.0567	0.3298	0.1050	3.5800	2.5
0.4700	0.0051	0.0516	0.3452	0.0751	10.2530	2.5
0.4850	0.0008	0.0249	0.4250	0.0641	29.7600	2.5
0.3090	0.1615	0.0907	0.2360	0.2009	0.5618	3.26
0.3375	0.1418	0.0819	0.2612	0.1995	0.5782	3.26
0.3610	0.1197	0.0850	0.2504	0.1914	0.7101	3.26
0.3950	0.1008	0.0788	0.2689	0.1888	0.7816	3.26
0.4225	0.0756	0.0724	0.2875	0.1782	0.9574	3.26
0.4475	0.0540	0.0736	0.2836	0.1592	1.3622	3.26
0.4725	0.0315	0.0693	0.2957	0.1400	2.2000	3.26
0.5000	0.0173	0.0567	0.3336	0.1309	3.2780	3.26
0.5400	0.0514	0.0448	0.3706	0.1011	8.7150	3.26
0.5950	0.0008	0.0243	0.4312	0.0764	30.8600	3.26
0.4450	0.2120	0.0967	0.2099	0.1761	0.4560	4.0
0.5350	0.1693	0.0913	0.2261	0.1686	0.5570	4.0
0.6050	0.1418	0.0850	0.2450	0.1650	0.5994	4.0
0.6750	0.1182	0.0866	0.2402	0.1570	0.8156	4.0
0.6900	0.0958	0.0838	0.2485	0.1559	0.8749	4.0
0.7550	0.0706	0.0743	0.2770	0.1495	1.0388	4.0
0.7900	0.0548	0.0725	0.2825	0.1380	1.3221	4.0
0.8300	0.0365	0.0659	0.3024	0.1300	1.8016	4.0

Table 17. Nitrate electrode data for nitrate standards

Standard No.	(NO ⁻), M 3	mv
1	0.1	-1.9
2	0.05	-9.6
3	0.01	41.1
4	0.008	46.2
5	0.004	62.2
6	0.002	77.1
7	0.001	94.7
8	0.0005	110.7

Table 18. Nitrate ion concentrations in the equilibrated aqueous phase for the system lanthanum nitrate-sodium nitrate-nitric acid-water-HDEHP-Amsco at I=3.26 M

Sample No.	EMF mv	DF ¹	Nitrate Ion Conc. ²	Nitrate Ion Conc. in Aq.
1	50.9	50	0.0062	0.3090
2	48.9	50	0.0068	0.3375
3	47.7	50	0.0072	0.3610
4	45.8	50	0.0079	0.3950
5	44.1	50	0.0085	0.4225
6	42.9	50	0.0090	0.4475
7	41.7	50	0.0095	0.4725
8	40.5	50	0.0100	0.5000
9	38.9	50	0.0108	0.5400
10	36.4	50	0.0119	0.5950

¹DF = Dilution factor.²Read from Figure 12.

Figure 12. Calibration curve for the nitrate ion-selective electrode.

experiments at $I = 3.26$ M. The standards were prepared with different nitrate ion concentration and a constant background concentration of sulfuric acid (0.3 M). The percentage of the interference of the sulfate ion for the nitrate electrode was calculated by Equation 124 and was found to be negligible. These results are shown in Table 19. Figure 13 and Table 20 show that only a small amount of nitrate ion remain in the equilibrated organic phase. Therefore, the nitrate ion content in the equilibrated organic phase can be neglected without introducing significant errors within the concentration ranges studied.

The possibility of the coextraction of sodium ion together with the lanthanides into the organic phase was also examined. If a significant amount of sodium ions are being coextracted, then the equilibrated organic dimer concentration can not be calculated by Equation 122. In order to check this possibility, another run for the system sodium nitrate-nitric acid-water-HDEHP-Amsco was performed by following the same equilibrium procedures as described in the Procedures section. Table 21 shows the sodium ion concentrations in the aqueous phase before and after the equilibration. From these results, we concluded that there is only a very small amount of sodium ions being extracted into the organic phase at the experimental conditions. Therefore, Equation 122 is still valid in calculating the

Table 19. Nitrate electrode data for nitrate-sulfate standards

Standard	(NO ⁻), M 3	(SO ⁻²) 4	EMF mv	Percent Interference ¹
1	0.104	0.3	-39.6	0.016
2	0.0415	0.3	-8.9	0.039
3	0.0115	0.3	30.39	0.16
4	0.008	0.3	35.8	0.21
5	0.004	0.3	53.8	0.41
6	0.002	0.3	70.3	0.82
7	0.001	0.3	80.6	1.6
8	0.0005	0.3	99.6	3.2
9	0.00015	0.3	126.2	10.6

¹Calculated by using Equation 124.

Table 20. Nitrate electrode data for organic samples back-extracted at I = 3.26 M

Sample No.	EMF mv	DF ¹	Nitrate Ion Conc. ²	Nitrate Ion Conc. in Org.
1	100.4	20	0.00041	0.0082
2	106.5	20	0.00036	0.0072
3	115.1	20	0.00027	0.0054
4	115.4	20	0.000265	0.0053
5	116.2	20	0.00023	0.0046
6	116.9	20	0.00022	0.0044
7	118.7	20	0.00019	0.0038
8	119.1	20	0.000185	0.0037
9	119.8	20	0.00018	0.0036
10	130.2	20	0.000100	0.0020

¹DF = Dilution factor.²Read from Figure 13.

Figure 13. Nitrate-sulfate calibration curve for nitrate-ion selective electrode.

Table 21. The extraction of sodium nitrate using HDEHP as the organic solvent

Sample No.	(Na), M Before Equilibrium	(Na), M After Equilibrium
1	2.96	2.96
2	2.48	2.48
3	1.98	1.98
4	1.50	1.46
5	1.00	1.00
6	0.50	0.48

equilibrated organic dimer concentrations. The calculated equilibrated organic dimer concentrations are presented in Table 16.

A linear regression analysis of the equilibrated nitrate ion concentrations and the reciprocal of the distribution coefficients gave the following equation.

$$\frac{K_d^0}{K_d} = 1 + k_1 (\text{NO}_3^-) + k_2 (\text{NO}_3^-)^2 \quad (129)$$

Table 22 shows the calculated stability constants for the system lanthanum nitrate-HDEHP as a function of ionic strength at the experimental conditions. It shows that the stability constant decreases as the ionic strength increases. Figure 14 shows this relationship.

Table 22. Calculated stability constants for the system lanthanum nitrate-sodium nitrate-nitric acid-water-HDEHP-Amsco

Ionic Strength I, M	K^o_d	<u>Stability Constant</u>	
		k_1	k_2
1.0	2.148	4.613	54.890
1.5	0.828	2.849	20.250
2.5	0.310	2.046	10.080
3.26	0.253	1.770	7.780
4.0	0.255	1.016	2.898

By using an ion exchange method, Kriss and Sheka (56) reported that $k_1 = 1.8$ and $k_2 = 2.7$ for lanthanum nitrate complexes at ionic strength $I = 3.26$ M. Perchloric acid was used as an ionic medium. Comparison of their data and the values obtained in this work showed that there is not much difference for the first stability constant. The value obtained in this work for the second stability constant is almost three times bigger than their value. Peppard, et al. (81) using the extraction method and reported that the first stability constant for lanthanum nitrate at ionic strength $I = 1.0$ M is equal to 1.3 ± 0.3 . Nitric acid and sodium perchlorate were used as the ionic media. This value is smaller than the data obtained in this work. They did not report a value for the second stability constant. According to Cower and Kiser's (22) result, the neodymium mononitrate complex is the only important absorbing specie other than the

Figure 14. Stability constant as a function of ionic strength for the system $\text{La}(\text{NO}_3)_3 - \text{NaNO}_3 - \text{HNO}_3 - \text{H}_2\text{O} - \text{HDEHP} - \text{Amsco}$.

free neodymium ion. Therefore, the second stability constant is not so important as the first stability constant in an inorganic solution. It was shown in the Theoretical section that any comparison of stoichiometric stability constants must be at the same temperature, ionic medium and the experimental method. Since the two sets of data are not at exactly the same experimental conditions, it is not possible to compare their stability constant values.

Linear regression analysis of the stability constants and the ionic strengths for the system lanthanum nitrate-HDEHP yield the following results:

$$k_1 = 11.953 - 10.792 I + 3.886 I^2 - 0.468 I^3 \quad (130)$$

$$k_2 = 194.961 - 206.539 I + 74.028 I^2 - 8.609 I^3 \quad (131)$$

where I is the ionic strength. The correlation coefficients R^2 for k_1 and k_2 are 0.999 and 0.986 respectively.

The degrees of formation and the effective equilibrium constant were calculated from the stability constants and the equilibrium data using Equations 76 and 81 respectively. Table 23 shows these results. By using linear regression analysis, the regressed value of the effective equilibrium constant at different ionic strengths were obtained and are

Table 23. Calculated degree of formation and effective equilibrium constant for the system lanthanum nitrate-sodium nitrate-nitric acid-water-HDEHP-Amsco

I, M	a _o	K ₁	Regressed K ₁	R ²
1.0	0.436	1.423	1.412	0.991
	0.428	1.732		
	0.420	1.325		
	0.287	1.838		
	0.251	1.338		
	0.221	1.396		
1.5	0.420	0.783	0.919	0.999
	0.358	0.796		
	0.343	0.825		
	0.301	0.842		
	0.283	0.916		
	0.266	0.894		
2.5	0.211	0.928	0.439	0.999
	0.407	0.398		
	0.379	0.375		
	0.332	0.412		
	0.308	0.390		
	0.291	0.451		
3.26	0.259	0.446	0.813	0.999
	0.242	0.437		
	0.232	0.440		
	0.437	0.794		
	0.403	0.640		
	0.377	0.841		
4.0	0.343	0.788	0.575	0.994
	0.319	0.715		
	0.299	0.807		
	0.280	0.834		
	0.261	0.759		
	0.237	0.747		
	0.208	0.825	0.575	0.994
	0.497	0.542		
	0.424	0.544		
	0.376	0.481		
	0.375	0.680		
	0.327	0.661		
	0.295	0.554		
	0.279	0.553		
	0.262	0.585		

also presented in Table 23. The predicted distribution coefficients were then calculated using the model Equation 81. Table 24 and Figure 15 show the comparison between the predicted distribution coefficients and the experimental data. It can be seen in Figure 15 that better agreement between the experimental and predicted data were obtained at lower ionic strengths than at higher ionic strengths. This is so because for dilute solutions, the activity coefficients are not significant and therefore can be neglected. This result in a constant quotient of activity coefficients for each ionic species present in the solutions. Excellent agreement between the experimental and the predicted data were still obtained at the experimental conditions. Figure 16 shows the relations between the distribution coefficient and the hydrogen ion concentration. It shows that the hydrogen ion concentration decreases as the distribution coefficient increases. The solid line indicates the regressed value for experimental data and the dotted line show the regressed line for the predicted values. The predicted and experimental distribution coefficients as a function of hydrogen ion concentration in the equilibrated aqueous phase are shown to be in close agreement. It is inadequate to express the distribution coefficient as a function of hydrogen ion concentration in the equilibrated aqueous phase because the correlation coefficient obtained

Table 24. Model predictions for the system lanthanum
nitrate-sodium nitrate-nitric acid-water-HDEHP-
Amsco

K (data) d	K (model) d	Ionic Strength M	R ²
3.203	3.179	1.0	0.991
5.000	4.076		
8.275	8.819		
16.813	12.917		
25.570	26.987		
31.190	31.543		
1.907	2.239	1.5	0.999
2.455	2.836		
2.891	3.220		
4.502	4.916		
6.345	6.367		
14.231	14.640		
33.452	33.119	2.5	0.999
0.773	0.854		
0.889	1.040		
1.142	1.218		
1.341	1.512		
2.113	2.056		
3.580	3.527	3.26	0.999
10.253	10.304		
29.760	29.730		
0.562	0.576		
0.578	0.736		
0.710	0.686		
0.782	0.806	4.0	0.994
0.957	1.088		
1.362	1.371		
2.200	2.144		
3.278	3.513		
8.715	9.479		
30.860	30.591	4.0	0.994
0.456	0.484		
0.557	0.589		
0.599	0.709		
0.816	0.670		
0.875	0.761		
1.039	1.077	4.0	0.994
1.322	1.376		
1.802	1.772

Figure 15. Comparison between K_d (data) and K_d (model) for the
 system $\text{La}(\text{NO}_3)_3 - \text{NaNO}_3 - \text{HNO}_3 - \text{H}_2\text{O} - \text{HDEHP} - \text{Amsco}$

Figure 16. The relations between the hydrogen ion concentration and the distribution coefficient.

for the experimental and predicted data were 0.763 and 0.770 respectively. Equations 132 and 133 show this relations for the experimental and predicted data respectively.

$$K_d(\text{data}) = 100.74 - 1.44 \times 10^3 (H) + 6.54 \times 10^3 (H)^2 - 9.15 \times 10^3 (H)^3 \quad (132)$$

$$K_d(\text{model}) = 100.64 - 1.43 \times 10^3 (H) + 6.47 \times 10^3 (H)^2 - 8.90 \times 10^3 (H)^3. \quad (133)$$

Figure 17 shows the metal ion concentration in the organic phase as a function of distribution coefficient. The metal ion concentration in the organic phase decreases as the distribution coefficient increases. The linear regression analysis to correlate the distribution coefficient as a function of the metal ion concentration in the equilibrated organic phase for the experimental and predicted data respectively are as follows:

$$K_d(\text{data}) = 64.778 - 1.51 \times 10^3 (La) + 8.33 \times 10^3 (La)^2 + 5.42 \times 10^3 (La)^3 \quad (134)$$

$$K_d(\text{model}) = 66.126 - 1.59 \times 10^3 (La) + 9.86 \times 10^3 (La)^2 + 2.91 \times 10^3 (La)^3. \quad (135)$$

Where (La) is the lanthanum ion concentration in the equili-

Figure 17. The relations between the metal ion concentration in the organic phase and the distribution coefficient.

brated organic phase. The correlation coefficients R^2 for the experimental and predicted data are 0.954 and 0.955 respectively.

The system neodymium nitrate-sodium nitrate-nitric acid-water-HDEHP-Amsco

Analysis of equilibrium HDEHP extraction data on this system was performed as described in the Procedures section. The equilibrium metal concentrations in the aqueous and organic phase, the equilibrium acid and nitrate ion concentrations of the aqueous phase, along with the calculated distribution coefficients as well as the equilibrium HDEHP dimer concentrations are presented in Table 25. The analysis of organic phase for the estimation of the equilibrium HDEHP dimer concentration was the same as the lanthanum nitrate system.

The equilibrium nitrate ion concentrations and the experimental distribution coefficients were used in Equation 129 to calculate the stability constants for this system. The calculated stability constants are shown in Table 26. The stability constants decreased as the ionic strength increased.

Linear regression analysis of the stability constants as a function of ionic strength for the system neodymium nitrate-HDEHP yielded the following results:

$$k_1 = 5.712 - 1.906 I + 0.109 I^2 + 0.0151 I^3 \quad (136)$$

$$k_2 = 95.618 - 70.549 I + 18.066 I^2 - 1.541 I^3. \quad (137)$$

The correlation coefficients for both cases are 0.999.

Table 25. Equilibrium data for the system neodymium nitrate-sodium nitrate-nitric acid-water-HDEHP-Amsco

(NO ⁻) 3 A	(Nd) A	(Nd) O	((HG)) 2 O	(H ⁺) A	K d	I M
0.1510	0.0038	0.0718	0.2847	0.1457	19.0000	1.0
0.1565	0.0032	0.0692	0.2924	0.1455	21.5200	1.0
0.1760	0.0022	0.0608	0.3176	0.1420	26.7800	1.0
0.1925	0.0015	0.0490	0.3532	0.1359	33.3200	1.0
0.2050	0.0008	0.0370	0.3891	0.1345	43.2500	1.0
0.2300	0.0003	0.0249	0.4253	0.1180	77.7500	1.0
0.2200	0.0708	0.0804	0.2590	0.3051	1.1340	2.0
0.2810	0.0457	0.0804	0.2589	0.2599	1.7600	2.0
0.3300	0.0161	0.0835	0.2495	0.2090	2.4140	2.0
0.3650	0.0100	0.0618	0.3147	0.1832	6.1199	2.0
0.3800	0.0066	0.0564	0.3308	0.1680	8.5230	2.0
0.3590	0.0042	0.0462	0.3615	0.1655	10.8600	2.0
0.3800	0.0901	0.1036	0.1889	0.2138	1.1500	3.0
0.4800	0.0674	0.1070	0.1781	0.1710	1.5920	3.0
0.5400	0.0492	0.1023	0.1940	0.1607	2.0760	3.0
0.5700	0.0328	0.0921	0.2236	0.1570	2.8110	3.0
0.6100	0.0177	0.0779	0.2662	0.1510	4.4150	3.0
0.6700	0.0079	0.0667	0.2999	0.1355	8.4630	3.0
0.4300	0.1748	0.1270	0.1190	0.2420	0.7305	4.0
0.4850	0.1355	0.1166	0.1502	0.2420	0.8598	4.0
0.5200	0.1103	0.1160	0.1520	0.2382	1.0571	4.0
0.5450	0.0914	0.1103	0.1691	0.2333	1.2070	4.0
0.5900	0.0790	0.0975	0.2075	0.2330	1.2342	4.0
0.6450	0.0536	0.0976	0.2072	0.2233	1.8210	4.0
0.6200	0.2269	0.1210	0.1316	0.2309	0.5400	5.0
0.7200	0.1765	0.1230	0.1310	0.2078	0.7140	5.0
0.8200	0.1386	0.1130	0.1611	0.2051	0.8180	5.0
0.9250	0.1134	0.1135	0.1595	0.2015	1.0000	5.0
0.9400	0.0654	0.1050	0.1850	0.2005	1.1330	5.0
0.9750	0.0756	0.1040	0.1880	0.1969	1.4170	5.0

Table 26. Calculated stability constants for the system
neodymium nitrate-sodium nitrate-nitric acid-
water-HDEHP-Amsco

Ionic Strength I, M	K _o d	<u>stability constant</u>	
		k 1	k 2
1.0	8.040	3.935	41.61
2.0	0.528	2.445	14.386
3.0	0.527	1.409	5.502
4.0	0.341	1.266	4.845
5.0	0.279	0.806	1.89

Figure 18 shows the stability constants as a function of ionic strength for this system.

The degree of formation and the effective equilibrium constant are calculated using Equations 76 and 81 respectively from the stability constants and the equilibrium data. Table 27 shows these results in detail.

The predicted distribution coefficients were calculated from Equation 81 using the regressed effective equilibrium constants and the equilibrium data. Table 28 and Figure 19 show the good agreement between the experimental and predicted distribution coefficients. The correlation coefficients R^2 are also given in detail at the different experimental conditions. Better agreements between the predicted and the experimental distribution coefficients were obtained at lower ionic strengths than at higher ones. For dilute solutions, the quotient of activity coefficients is

Figure 18. Stability constant as a function of ionic strength for the system $\text{Nd}(\text{NO}_3)_3$ - NaNO_3 - HNO_3 - H_2O - HDEHP-Amsco.

Table 27. Calculated degree of formation and effective equilibrium constant for the system neodymium nitrate-sodium nitrate-nitric acid-water-HDEHP-Amsco

Ionic Strength I, M	α_o	K_1	Regressed K_1	R^2
1.0	0.627	4.060	3.305	0.992
	0.619	4.284		
	0.591	4.051		
	0.569	3.608		
	0.554	3.227		
	0.525	3.164		
2.0	0.650	2.854	2.132	0.996
	0.593	3.004		
	0.554	2.564		
	0.528	2.285		
	0.518	2.161		
	0.509	2.049		
3.0	0.651	2.560	1.554	0.991
	0.597	2.362		
	0.568	2.078		
	0.555	1.755		
	0.538	1.498		
	0.514	1.517		
4.0	0.648	9.487	4.175	0.923
	0.620	5.804		
	0.603	6.746		
	0.592	5.356		
	0.575	3.052		
	0.551	4.140		
5.0	0.667	4.374	2.953	0.973
	0.633	4.504		
	0.602	2.809		
	0.573	3.520		
	0.569	2.535		
	0.560	2.907		

Table 28. Model predictions for the system neodymium
nitrate-sodium nitrate-nitric acid-water-HDEHP-
Amsco

K (data) d	K (model) d	Ionic Strength I, M	R ²
19.00	19.07	1.0	0.992
21.52	20.77		
26.78	25.31		
32.32	33.17		
43.25	40.92		
77.75	76.89		
1.13	1.22	2.0	0.996
1.76	1.56		
2.41	2.25		
6.12	5.94		
8.52	8.47		
10.86	11.05		
1.15	0.99	3.0	0.991
1.59	1.30		
2.08	1.78		
2.81	2.74		
4.42	4.78		
8.46	8.40		
0.74	0.41	4.0	0.923
0.86	0.72		
1.06	0.73		
1.21	1.01		
1.23	1.71		
1.82	1.73		
0.54	0.47	5.0	0.973
0.71	0.56		
0.82	0.93		
1.00	0.84		
1.11	1.30		
1.42	1.37

Figure 19. Comparison between K_d (data) and K_d (model) for the system $\text{Nd}(\text{NO}_3)_3 - \text{NaNO}_3 - \text{HNO}_3 - \text{H}_2\text{O} - \text{HDEHP} - \text{Amsco}$.

nearly constant for the ionic species present in the solution.

Cower and Kiser (22) measured the first stability constant of the neodymium nitrate complex using spectrophotometric method with sodium perchlorate as the ionic medium. They reported that $k = 0.77$ at an ionic strength $I = 4.2$ M. From Equation 136, the first stability constant can be calculated at ionic strength of 4.2 M and is equal to 0.749. This is in good agreement with Cower and Kiser's (22) value. At ionic strength $I = 1.0$ M, Mikhailichenko and Kurdin (66) determined the first stability constant to be 1.75 ± 0.2 by extraction of trace amount of radioactive Nd^{147} in HDEHP using perchloric acid, sodium perchlorate, nitric acid and sodium nitrate as the ionic media. This value is lower than was obtained in this work. The stability constants obtained in this work are also larger than Krumholz's (58) data obtained by spectrophotometric method using sodium nitrate as the ionic medium.

At higher ionic strength (up to $I = 4.0$ M) the stability constants obtained in this work with lanthanum-HDEHP and neodymium-HDEHP systems are in good agreement with the results of other investigators (22, 56). But at ionic strength below to 1.0 M, the stability constant values obtained in this work are larger than those reported by other investigators (58, 66, 81). The explanation for this are as follows: (1) At lower ionic strength the titration errors

are relatively higher for the low metal ion concentration in the equilibrated organic and aqueous phases. This can be seen by examining the data presented in Tables 16 and 25 for lanthanum and neodymium nitrate systems respectively. A difference of one drop of titrating solution could cause a large differences in the concentration and therefore in the distribution coefficients. (2) The difference in the reported stability constants by the various investigators (56, 66, 81) and this work is due to the dependence of stability constant to temperature, ionic medium and the experimental method. Choppin, et al. (18) found that the first stability constant for lanthanides decreases in the order of sodium nitrate > nitric acid > lithium nitrate as the ionic media. Therefore, when sodium nitrate is used, higher stability constant is to be expected. (3) Smutz and Lenz (104) reported that Sm and Nd are extracted by HDEHP from acidic nitrate and perchlorate media according to the following two reaction mechanisms:

where A^{-} is either perchloric or nitrate ion and Y is some as yet undetermined extractant entity having the solvation

number, b. The presence of additional complexes in the organic phase can cause variations in the distributions coefficients. Previous investigators (56, 66, 81) neglected the second reaction mechanism given by Equation 138 at lower ionic strength. Smutz and Lenz (104) also indicated that when the equilibrated samarium concentration in the organic phase is larger than 0.125 M, the equilibrated perchlorate ion concentration in the organic phase increased as the extracted samarium concentration increased linearly with a constant slope of 2.95. They also reported that the separation factors between samarium and neodymium decreased as the initial perchloric acid in the aqueous phase increased. In other words, the distribution coefficients also varied as the perchloric acid concentration in the aqueous phase varied. (4) Smutz, et al. (108) in their study of the effect of diluent upon the equilibrium of the neodymium chloride-HDEHP system concluded that the organic phase metal concentration is highest when the diluent is Amsco 125-82 and decreases in the order of cyclohexane > carbon tetrachloride > toluene > benzene. In this work, Amsco 125-82 was used as the diluent. Some of the previous investigators (56, 66, 81) used the diluents other than Amsco (125-82). The higher distribution coefficients obtained in this work resulted in higher stability constants. The four reasons given above could explain the inconsistency among the

reported stability constants at lower ionic strengths.

In addition, the stability constants obtained in this work for the complexes of lanthanum nitrate are larger than neodymium nitrate and this is in agreement with Kriss and Sheka's (56) results where the stability constants of nitrate anionic complexes of rare earth elements falls with an increase in the atomic number of the lanthanides in the order $\text{La} > \text{Pr} > \text{Nd} > \text{Sm} > \text{Dy} > \text{Yb}$.

The system lanthanum nitrate-neodymium nitrate-nitric acid-water-HDEHP-Amsco

Equilibrium study for the above binary metal system was performed as described in the Procedures section. The total aqueous lanthanide concentrations were kept constant at each range of ionic strength. The mole fractions of lanthanum in the aqueous phase were varied from 0.16 to 0.86. The total rare earth concentrations in each phase and the relative amount of lanthanum and neodymium were obtained as described in the Procedures section. The nitrate ion concentration in the equilibrated aqueous phase was measured by nitrate ion-selective electrode as described in the Procedures section. Table 29 presents the equilibrium data for this binary system. The equilibrated nitrate ion concentrations are given in Table 31. It can be seen in Table 29 that the

Table 29. Equilibrium data for the system lanthanum nitrate-neodymium nitrate
-nitric acid-water-HDEHP-Amsco

No	I, M	T			T			(K)		S
		(RE) A	(La) A	(Nd) A	(RE) O	(La) O	(Nd) O	d La	d Nd	
1		0.1796	0.0405	0.1391	0.1230	0.0078	0.1151	0.1934	0.8273	4.2772
2		0.1859	0.0856	0.1003	0.1166	0.0174	0.0992	0.2030	0.9895	4.8753
3	1.8	0.1891	0.1216	0.0675	0.1134	0.0321	0.0813	0.2643	1.2034	4.5540
4		0.1922	0.1547	0.0375	0.1104	0.0513	0.0591	0.3312	1.5765	4.7602
5		0.1954	0.1782	0.0173	0.1071	0.0758	0.0313	0.4254	1.8156	4.2618
6		0.2710	0.0591	0.2119	0.1323	0.0106	0.1217	0.1797	0.5743	3.1955
7		0.2836	0.1246	0.1590	0.1260	0.0210	0.1050	0.1688	0.6603	3.9122
8	2.4	0.2962	0.1855	0.1107	0.1071	0.0323	0.0748	0.1741	0.6755	3.8795
9		0.3024	0.2362	0.0662	0.1009	0.0447	0.0562	0.1893	0.8488	4.4844
10		0.3088	0.2758	0.0330	0.1008	0.0709	0.0299	0.2570	0.9069	3.5292
11		0.3718	0.0834	0.2884	0.1198	0.0073	0.1125	0.0880	0.3899	4.4304
12		0.3782	0.1599	0.2183	0.1134	0.0166	0.0968	0.1040	0.4433	4.2644
13	3.0	0.3844	0.2296	0.1548	0.1135	0.0342	0.0793	0.1489	0.5123	3.4397
14		0.3970	0.3031	0.0939	0.1072	0.0506	0.0566	0.1670	0.6024	3.6070
15		0.4096	0.3658	0.0438	0.0919	0.0630	0.0289	0.1723	0.6598	3.8305
16		0.4853	0.1070	0.3783	0.1195	0.0089	0.1106	0.0838	0.2925	3.4919
17		0.4916	0.2025	0.2892	0.1133	0.0151	0.0982	0.0746	0.3396	4.5514
18	3.6	0.4979	0.2900	0.2080	0.1070	0.0273	0.0797	0.0943	0.3830	4.0612
19		0.5105	0.3782	0.1333	0.0944	0.0358	0.0586	0.0946	0.4434	4.6893
20		0.5231	0.4608	0.0623	0.1208	0.0699	0.0329	0.1519	0.5287	3.4816
21		0.5816	0.1177	0.4648	0.1233	0.0077	0.1156	0.0650	0.2467	3.7959
22		0.5924	0.2375	0.3549	0.1171	0.0176	0.0995	0.0743	0.2830	3.7736
23	4.2	0.5987	0.3468	0.2519	0.1111	0.0252	0.0859	0.0727	0.3409	4.6868
24		0.5987	0.4413	0.1574	0.1113	0.0444	0.0669	0.1007	0.4248	4.2200
25		0.6050	0.5369	0.0681	0.1053	0.0665	0.0388	0.1238	0.5699	4.6015

separation factor is approximately a constant and is independent of the lanthanide concentration with an arithmetical average value of 4.016. The separation factor is also independent of the ratio of the two rare earths. Figure 20 shows the relation between the average separation factor and the total rare earth concentration in the aqueous phase. It indicates that the separation factor increases slightly as the total rare earth concentration in the aqueous phase increases from 0.4 to 0.7 M. The data obtained at 0.3 M might have some analytical errors. An extrapolation of the trend of this plot gives an average separation factor of 3.68 at 0.3 M rare earth concentration. This is confirmed by Smutz and Goto's (102) results who found that the separation factors increased very slightly as the lanthanide concentration increases.

From the available equilibrium data, the stability constants for lanthanum and neodymium nitrate complexes in their binary system were calculated individually by Equation 128. Table 30 shows these results. It indicates that the stability constant decreases as the ionic strength increases and have the same trend as the single component system.

Linear regression analysis of stability constants for lanthanum and neodymium nitrate complexes in their binary system and ionic strengths yield the following results:

Figure 20. The relation between the separation factor and total rare earth concentration in aqueous phase.

Table 30. Calculated stability constants for the system
lanthanum nitrate-neodymium nitrate-nitric acid-
water-HDEHP-Amsco

Ionic Strength I, M	k ₁		k ₂	
	La	Nd	La	Nd
1.8	8.055	8.450	16.454	18.039
2.4	8.613	8.701	18.522	18.924
3.0	7.796	7.532	15.214	14.227
3.6	3.546	3.685	3.141	3.375
4.2	3.149	3.221	2.498	2.602

for lanthanum nitrate complexes:

$$k_1 = -42.158 + 55.870 I - 19.212 I^2 + 2.017 I^3 \quad (139)$$

$$k_2 = -141.75 + 176.80 I - 61.117 I^2 + 6.484 I^3 \quad (140)$$

the correlation coefficients R^2 for k_1 and k_2 are 0.994
and 0.991 respectively,

for neodymium nitrate complexes:

$$k_1 = -35.921 + 50.074 I - 17.492 I^2 + 1.853 I^3 \quad (141)$$

$$k_2 = -121.86 + 159.28 I - 56.257 I^2 + 6.024 I^3 \quad (142)$$

the correlation coefficients R^2 for k_1 and k_2 are 0.997
and 0.998 respectively.

Table 31. The calculated degrees of formation for La and Nd in the system lanthanum nitrate-neodymium nitrate-nitric acid-water-HDEHP-Amsco

No	(NO ⁻) ₃ A, M	(a) o La	(a) o Nd	(a) o Nd ----- (a) o La	I, M
1	0.2080	0.2952	0.2826	0.9574	1.8
2	0.2125	0.2895	0.2770	0.9569	1.8
3	0.2175	0.2833	0.2709	0.9564	1.8
4	0.2240	0.2755	0.2633	0.9558	1.8
5	0.2350	0.2630	0.2511	0.9547	1.8
6	0.2300	0.2525	0.2499	0.9896	2.4
7	0.2310	0.2514	0.2488	0.9896	2.4
8	0.2340	0.2482	0.2456	0.9895	2.4
9	0.2365	0.2455	0.2429	0.9895	2.4
10	0.2375	0.2445	0.2419	0.9895	2.4
11	0.2475	0.2590	0.2677	1.0337	3.0
12	0.2500	0.2564	0.2651	1.0338	3.0
13	0.2515	0.2549	0.2636	1.0340	3.0
14	0.2540	0.2524	0.2610	1.0341	3.0
15	0.2650	0.2504	0.2590	1.0343	3.0
16	0.5600	0.2518	0.2426	0.9633	3.6
17	0.5625	0.2507	0.2415	0.9632	3.6
18	0.5700	0.2474	0.2383	0.9630	3.6
19	0.5725	0.2463	0.2372	0.9629	3.6
20	0.5750	0.2453	0.2361	0.9629	3.6
21	0.5800	0.2727	0.2671	0.9795	4.2
22	0.5850	0.2705	0.2649	0.9794	4.2
23	0.5900	0.2683	0.2627	0.9793	4.2
24	0.6000	0.2639	0.2584	0.9792	4.2
25	0.6200	0.2556	0.2502	0.9788	4.2

Table 31 shows the degree of formation for these two rare earths which were calculated as described in the Theoretical section. The ratio of the degree of formation of

neodymium to lanthanum is also presented in Table 31. The ratios of effective equilibrium constant for neodymium-lanthanum, K_{Nd-La} , were calculated by the model Equation 85 using the degrees of formation as well as the equilibrium data for this binary component system. Linear regression analysis was applied to estimate the regressed value of K_{Nd-La} at each ionic strength studied. The predicted separation factors were then calculated by making use of the regressed value of K_{Nd-La} along with the calculated ratio of the degree of formation which are presented in Table 31. Table 32 shows the excellent agreement between the experimental data and the calculated separation factors using the model Equation 85. The calculated K_{Nd-La} data and the regressed K_{Nd-La} values together with the correlation coefficient R^2 are also presented in this table.

The system lanthanum chloride-neodymium nitrate-nitric acid-water-HDEHP-Amsco

The binary lanthanide system with different ligands (chloride-nitrate) was studied following the same experimental methods described in the Procedures section. Table 33 presents the feed conditions for this system. Table 34 shows the equilibrium data, the distribution coefficients, and the separation factors for lanthanum chloride and neodymium nitrate. The results indicate that the separation

Table 32. Model prediction for the system lanthanum nitrate-neodymium nitrate-nitric acid-water-HDEHP-Amsco

No	I, M	K Nd-La	K Nd-La (regressed)	R ²	S ¹ data	S ¹ Nd-La model
1	1.8	4.4675			4.2770	4.5524
2	1.8	5.0948			4.8750	4.5500
3	1.8	4.7615	4.7549	0.9971	4.5540	4.5476
4	1.8	4.9803			4.7600	4.5448
5	1.8	4.4705			4.2680	4.5395
6	2.4	3.2290			3.1950	3.8000
7	2.4	3.9533			3.9122	3.8000
8	2.4	3.9205	3.8400	0.9873	3.8795	3.8000
9	2.4	4.5316			4.4840	3.8000
10	2.4	3.5668			3.5290	3.8000
11	3.0	4.2861			4.4300	3.9131
12	3.0	4.1248			4.2640	3.9135
13	3.0	3.3267	3.7855	0.9907	3.4400	3.9142
14	3.0	3.4880			3.6070	3.9146
15	3.0	3.7036			3.8300	3.9154
16	3.6	3.6250			3.4920	4.0560
17	3.6	4.2747			4.5510	4.0560
18	3.6	4.2170	4.2105	0.9848	4.0610	4.0547
19	3.6	4.8695			4.6890	4.0543
20	3.6	3.6163			3.4820	4.0543
21	4.2	3.8755			3.7960	4.2167
22	4.2	3.8533			3.7740	4.2162
23	4.2	4.7859	4.3049	0.9917	4.6870	4.2158
24	4.2	4.3098			4.2200	4.2154
25	4.2	4.7010			4.6010	4.2136

¹S = separation factor for Nd and La.
Nd-La

Table 33. Feed conditions for the system lanthanum chloride-neodymium nitrate-nitric acid-water-HDEHP-Amsco

No	Feed Ratio	(LaCl) 3	(Nd(NO)) 3 3	I
	La : Nd	M	M	M
1	1:6	0.441	0.448	2.64
2	2:5	0.441	0.448	2.64
3	3:4	0.441	0.448	2.64
4	4:3	0.441	0.448	2.64
5	5:2	0.441	0.448	2.64
6	6:1	0.441	0.448	2.64
7	1:6	0.557	0.560	3.36
8	2:5	0.557	0.560	3.36
9	3:4	0.557	0.560	3.36
10	4:3	0.557	0.560	3.36
11	5:2	0.557	0.560	3.36
12	6:1	0.557	0.560	3.36
13	1:1	0.338	0.340	2.04
14	1:1	0.376	0.380	2.28
15	1:1	0.426	0.430	2.58
16	1:1	0.476	0.474	2.82
17	1:1	0.536	0.538	3.24

factors are independent of the lanthanide concentration but dependent on the initial feed ratios of lanthanum chloride and neodymium nitrate. When the feed solutions have equal amount of the two salts, the separation factors are nearly a constant and is equal to 4.16. This result was also obtained by Smutz and Goto (102). This could be explained by the fact that the equal amount of feed ratios of La and Nd in the tested solutions have approximately the same equilibrated chloride and nitrate ion concentration. This gives an

Table 34. Equilibrium data for the system lanthanum chloride
neodymium nitrate-nitric acid-water-HDEHP-Amsco

No.	(La) A	(Nd) A	(La) O	(Nd) O	(K) d La	(K) d Nd	S Nd-La
1	0.0760	0.2702	0.0110	0.0911	0.1451	0.3371	2.3231
2	0.1420	0.2071	0.0198	0.0788	0.1395	0.3805	2.7283
3	0.2034	0.1483	0.0267	0.0680	0.1312	0.4587	3.4958
4	0.2551	0.1020	0.0337	0.0569	0.1321	0.5580	4.2252
5	0.3020	0.0579	0.0452	0.0426	0.1497	0.7348	4.9058
6	0.3447	0.0246	0.0575	0.0261	0.1666	1.0607	6.3649
7	0.0997	0.3589	0.0100	0.0967	0.1011	0.2695	2.6642
8	0.1835	0.2765	0.0209	0.0845	0.1137	0.3058	2.6894
9	0.2539	0.2020	0.0290	0.0711	0.1117	0.3520	3.1500
10	0.3533	0.1341	0.0359	0.0600	0.1073	0.4472	4.1728
11	0.3912	0.0809	0.0481	0.0452	0.1229	0.5588	4.5463
12	0.4507	0.0336	0.0555	0.0256	0.1231	0.7652	6.1398
13	0.1752	0.0764	0.0316	0.0605	0.1800	0.7911	4.3927
14	0.1930	0.0951	0.0300	0.0606	0.1558	0.6377	4.0943
15	0.2227	0.1128	0.0306	0.0641	0.1371	0.5684	4.1398
16	0.2568	0.1206	0.0525	0.0629	0.1265	0.5470	4.1233
17	0.2963	0.1379	0.0370	0.0685	0.1247	0.4969	3.9839

approximately constant ratio of degrees of formation between these two salts. Therefore, according to Equation 85, constant separation factors were obtained. This could be seen in Table 36. The first two set of samples have different La and Nd feed ratios and resulted in different separation factors varying from 2.32 to 6.36. This is due to the large difference in chloride and nitrate ion concentrations in the feed solution and resulted in a bigger difference between the equilibrated chloride and nitrate ion concentrations in the equilibrated aqueous phase. As a result, the ratios of the degree of formation for these two lanthanides varied from 0.1 to 2.3. According to Equation

Table 35. Extrapolated stability constants for the system lanthanum chloride-neodymium nitrate-nitric acid-water-HDEHP-Amsco

I, M	k ₁		k ₂	
	La	Nd	La	Nd
2.04	3.78	12.21	3.00	0.63
2.28	3.08	8.93	2.42	0.95
2.58	2.33	7.55	1.90	1.30
2.64	2.19	7.21	1.74	1.36
2.82	1.72	6.44	1.40	1.60
3.24	0.78	4.07	0.68	2.00
3.36	0.33	3.89	0.26	2.23

85, the separation factors can not be a constant. Table 35 presents the stability constants of lanthanum and neodymium in their chloride-nitrate binary system. These constants were calculated by using linear regression analysis technique as before. The last set of data in Table 33 is not at the condition of constant ionic strength and the stability constant can not be calculated. However, based on the first two sets of data, the stability constants in the third set can be linearly estimated by extrapolation. These extrapolated values are presented in Table 35. Table 36 shows the equilibrium chloride and nitrate ion concentrations and the calculated degree of formation. Table 37 gives the comparison of the separation factors obtained experimentally

Table 36. The calculated degrees of formation for La and Nd in the system lanthanum chloride-neodymium nitrate-nitric acid-water-HDEHP-Amsco

No.	(NO ₃ ⁻)	(Cl ⁻)	(a)	(a)	(a)
	3 A	A	o Nd	o La	o Nd
	M	M			
1	1.1420	0.1780	0.0909	0.6916	0.1341
2	0.9480	0.3724	0.1105	0.4857	0.2275
3	0.7484	0.5670	0.1398	0.3566	0.3920
4	0.5677	0.7650	0.1809	0.2736	0.6611
5	0.3762	0.9450	0.2585	0.2160	1.1953
6	0.1919	1.1311	0.4110	0.1751	2.3477
7	1.3299	0.2370	0.0992	0.9147	0.1085
8	1.1968	0.4767	0.1134	0.8217	0.1380
9	0.9581	0.7137	0.1481	0.7309	0.2026
10	0.6516	0.9535	0.2236	0.6449	0.3466
11	0.4371	1.1871	0.3202	0.5692	0.5626
12	0.2129	1.4274	0.5184	0.5006	1.0356
13	0.5030	0.4960	0.1370	0.2768	0.4949
14	0.5770	0.5470	0.1546	0.2934	0.5270
15	0.6320	0.6300	0.1590	0.3104	0.5122
16	0.6870	0.7090	0.1618	0.3421	0.4731
17	0.7670	0.7940	0.1887	0.4466	0.4265

and the predicted values calculated by the model Equation

85. It shows that the predictive model only works when the feed have equal amount of the two initial salts. This could be explained by two-suffix Margules equations (83)

$$\ln r_1 = \frac{A}{RT} x_2^2 \quad (143)$$

$$\ln r_2 = \frac{A}{RT} x_1^2 \quad (144)$$

Table 37. Model prediction for the system lanthanum chloride neodymium nitrate-nitric acid-water-HDEHP-Amsco

No.	K Nd-La	K Nd-La (Regressed)	R ²	S ¹ Nd-La	
				data	model
1	18.1588			2.3866	0.4913
2	12.7407			2.8979	0.8506
3	9.9387	3.7380	0.8160	3.8963	1.4656
4	7.3036			4.8284	2.4716
5	4.6015			5.5000	4.4677
6	2.9297			6.8779	8.7773
7	25.5320			2.7704	0.8833
8	20.6998			2.8752	1.1235
9	17.0630	8.1410	0.8610	3.4567	1.6494
10	13.7983			4.7831	2.8218
11	9.0290			5.0795	4.5804
12	6.4903			6.7214	8.4312
13	4.6355			4.3930	4.1988
14	4.4983			4.0950	4.4712
15	4.1584	8.4842	0.9960	4.1400	4.3456
16	3.8733			4.1230	4.0139
17	3.6799			3.9840	3.6185

¹S = separation factor for Nd and La.
Nd-La

which shows that the activity coefficients for molecules in a binary mixture are a function of compositions at constant temperature and pressure. A is an empirical constant with the units of energy and x_1 and x_2 are the mole fractions of solutes 1 and 2 respectively. Therefore, when $x_1 = x_2$, Equations 143 and 144 give $r_1 = r_2$. This is in agreement with the assumption made in developing the model equations. In other words, if $x_1 \neq x_2$, Equations 143 and 144 will result in significant difference between r_1 and r_2 due to increasing significance of the interaction effects of the

molecules. Therefore, the chemically based predictive model equations are applicable to mixture of molecules which are similar in size, shape and chemical and physical properties. If the mixture of molecules have a significant differences the model only give satisfactory results when equal mole fractions of the solutes are present in the mixture.

The system lanthanum nitrate-neodymium nitrate-samarium nitrate-nitric acid-water-HDEHP-Amsco

The above ternary system was investigated as described in the Procedures section. Table 38 shows the initial feed conditions for this system. The total rare earth concentrations in each set of data were kept constant. The amount of neodymium nitrate in each samples were kept constant and the relative amount of lanthanum and samarium were varied in the tested solutions. The total rare earth concentrations in each phase and the relative amount of La, Nd and Sm were obtained as described in the Procedures section. Table 39 presents the equilibrium data for this system. It indicates that the separation factors are independent of the total rare earth concentrations and the initial feed ratios of the three lanthanides. An arithmetical average values of 3.29, 21.96 and 6.9 were obtained for the separation factors of Nd-La, Sm-La and

Table 38. Feed conditions for the system lanthanum nitrate
neodymium nitrate-samarium nitrate-nitric acid-
water-HDEHP-Amsco

No	Feed Ratio	(La(NO ₃) ₃) M	(Nd(NO ₃) ₃) M	(Sm(NO ₃) ₃) M
1	5:15:30	0.3307	0.3409	0.3409
2	10:15:25	0.3307	0.3409	0.3409
3	15:15:20	0.3307	0.3409	0.3409
4	20:15:15	0.3307	0.3409	0.3409
5	25:15:10	0.3307	0.3409	0.3409
6	30:15:5	0.3307	0.3409	0.3409
7	5:15:30	0.3842	0.3896	0.3896
8	10:15:25	0.3842	0.3896	0.3896
9	15:15:20	0.3842	0.3896	0.3896
10	20:15:15	0.3842	0.3896	0.3896
11	25:15:10	0.3842	0.3896	0.3896
12	30:15:5	0.3842	0.3896	0.3896
13	5:15:30	0.4419	0.4383	0.4419
14	10:15:25	0.4419	0.4383	0.4419
15	15:15:20	0.4419	0.4383	0.4419
16	20:15:15	0.4419	0.4383	0.4419
17	25:15:10	0.4419	0.4383	0.4419
18	30:15:5	0.4419	0.4383	0.4419
19	5:15:30	0.5546	0.5465	0.5411
20	10:15:25	0.5546	0.5465	0.5411
21	15:15:20	0.5546	0.5465	0.5411
22	20:15:15	0.5546	0.5465	0.5411
23	25:15:10	0.5546	0.5465	0.5411
24	30:15:5	0.5546	0.5465	0.5411

Table 39. Equilibrium data for the system lanthanum nitrate-neodymium nitrate-samarium nitrate-nitric acid-water-HDEHP-Amsco

No	(La) A	(Nd) A	(Sm) A	(La) O	(Nd) O	(Sm) O
1	0.0300	0.0756	0.1134	0.0013	0.0100	0.1050
2	0.0592	0.0728	0.0898	0.0028	0.0119	0.1044
3	0.0902	0.0724	0.0632	0.0063	0.0141	0.0905
4	0.1203	0.0715	0.0382	0.0083	0.0187	0.0757
5	0.1500	0.0617	0.0241	0.0136	0.0264	0.0628
6	0.1683	0.0593	0.0106	0.0275	0.0306	0.0352
7	0.0328	0.0911	0.1439	0.0016	0.0112	0.1117
8	0.0714	0.0875	0.1117	0.0031	0.0108	0.1051
9	0.1064	0.0863	0.0806	0.0057	0.0123	0.0983
10	0.1398	0.0851	0.0538	0.0102	0.0137	0.0882
11	0.1753	0.0793	0.0295	0.0173	0.0210	0.0672
12	0.2058	0.0702	0.0135	0.0274	0.0269	0.0430
13	0.0408	0.1070	0.1715	0.0014	0.0110	0.1174
14	0.0855	0.1035	0.1398	0.0028	0.0121	0.1055
15	0.1298	0.0985	0.1016	0.0062	0.0170	0.0946
16	0.1717	0.0953	0.0685	0.0095	0.0187	0.0854
17	0.2082	0.0921	0.0392	0.0201	0.0230	0.0696
18	0.2494	0.0852	0.0171	0.0298	0.0313	0.0413
19	0.0535	0.1339	0.2333	0.0012	0.0111	0.1163
20	0.1112	0.1301	0.1862	0.0031	0.0118	0.1096
21	0.1630	0.1307	0.1392	0.0059	0.0130	0.1028
22	0.2141	0.1290	0.0978	0.0089	0.0188	0.0886
23	0.2759	0.1060	0.0609	0.0144	0.0322	0.0670
24	0.3202	0.1104	0.0227	0.0282	0.0370	0.0457

I, M	(K) d La	(K) d Nd	(K) d Sm	S Nd-La	S Sm-La	S Sm-Nd
2.01	0.0448	0.1329	0.9258	2.9658	20.6676	6.9685
2.01	0.0476	0.1638	1.1617	3.4385	24.3816	7.0908
2.01	0.0699	0.1951	1.4305	2.7897	20.4530	7.3316
2.01	0.0694	0.2620	1.9825	3.7780	28.5925	7.5682
2.01	0.0906	0.4282	2.6101	4.7235	28.7935	6.0958
2.01	0.1634	0.5169	3.3323	3.1639	20.3974	6.4469
2.28	0.0489	0.1230	0.7762	2.5155	15.8754	6.3111
2.28	0.0440	0.1231	0.9410	2.7948	21.3634	7.6441
2.28	0.0532	0.1427	1.2199	2.6850	22.9500	8.5476
2.28	0.0732	0.1614	1.6386	2.2053	22.3894	10.1527
2.28	0.0988	0.2644	2.2760	2.6763	23.0365	8.6075
2.28	0.1334	0.3835	3.1787	2.8755	23.8344	8.2887
2.70	0.0338	0.1027	0.6847	3.0408	20.2742	6.6674
2.70	0.0330	0.1167	0.7549	3.5398	22.8906	6.4667
2.70	0.0478	0.1726	0.9307	3.6149	19.4889	5.3913
2.70	0.0554	0.1961	1.2464	3.5437	22.5188	6.3545
2.70	0.0967	0.2501	1.7749	2.5875	18.3602	7.0975
2.70	0.1197	0.3647	2.4131	3.0698	20.1606	6.5673
3.30	0.0219	0.0826	0.4983	3.7718	22.7439	6.0301
3.30	0.0277	0.0904	0.5885	3.2624	21.2336	6.5086
3.30	0.0360	0.0994	0.7387	2.7613	20.5302	7.4302
3.30	0.0416	0.1453	0.9062	3.4968	21.8052	6.2375
3.30	0.0516	0.3033	1.1002	5.8823	21.3361	3.6272
3.30	0.0880	0.3353	2.0172	3.8092	22.9189	6.0167

Sm-Nd respectively. By using the modeling techniques which were summarized in the Applications section, Tables 40, 41, 42, 43 and 44 were obtained. Table 40 shows the calculated stability constants for individual lanthanides in their ternary component system. Table 41 gives the degrees of formation for each lanthanides in this system. The equilibrium nitrate ion concentrations are also presented in this table. Tables 42, 43 and 44 are the comparisons between the separation factors obtained experimentally and the values calculated by the model Equation 85 for Nd-La, Sm-La and Sm-Nd binaries respectively. The agreement between the experimental and predicted data are not as good as the binary system discussed previously. In the binary component, there is only one interaction effect that was neglected, i.e., the interaction between lanthanum and neodymium. In a ternary component system, there are four interaction effects which were ignored, i.e., the interactions between Nd-La, Sm-La, Sm-Nd and Sm-Nd-La. The results, therefore were not as good as the binary model.

Examination of the correlation coefficients R^2 between the experimental and predicted data for single, binary and ternary system gave an arithmetical average values of 0.992, 0.990 and 0.977 respectively. The single component system appear to give the best predicted results. The binary gives the better results than the ternary systems.

Table 40. Calculated stability constants for the system
lanthanum nitrate-neodymium nitrate-samarium
nitrate-nitric acid-water-HDEHP-Amsco

I, M	k ₁			k ₂		
	La	Nd	Sm	La	Nd	Sm
2.04	1.95	2.14	2.08	0.95	1.15	1.08
2.33	2.01	2.02	2.10	1.01	1.02	1.10
2.67	1.59	1.58	1.57	0.63	0.64	0.62
3.30	1.55	1.54	1.51	0.60	0.60	0.57

Table 41. Calculated degrees of formation for the system
lanthanum nitrate-neodymium nitrate-samarium
nitrate-nitric acid-water-HDEHP-Amsco

No	(NO ⁻)	(a)	(a)	(a)
	3 A	o La	o Nd	o Sm
1	0.9890	0.2595	0.2360	0.2428
2	0.9870	0.2601	0.2365	0.2433
3	0.9820	0.2614	0.2378	0.2445
4	0.9790	0.2621	0.2385	0.2453
5	0.9770	0.2627	0.2390	0.2458
6	0.9730	0.2637	0.2400	0.2468
7	1.1270	0.2198	0.2189	0.2100
8	1.1320	0.2187	0.2179	0.2090
9	1.1160	0.2221	0.2212	0.2123
10	1.1290	0.2193	0.2185	0.2096
11	1.1190	0.2214	0.2206	0.2116
12	1.1200	0.2212	0.2203	0.2114
13	1.1910	0.2646	0.2635	0.2670
14	1.1870	0.2655	0.2644	0.2679
15	1.2020	0.2622	0.2612	0.2647
16	1.2150	0.2595	0.2585	0.2619
17	1.2300	0.2564	0.2553	0.2588
18	1.2480	0.2527	0.2517	0.2551
19	1.4320	0.2252	0.2253	0.2314
20	1.4380	0.2242	0.2243	0.2304
21	1.4770	0.2179	0.2181	0.2240
22	1.4870	0.2163	0.2165	0.2224
23	1.5060	0.2134	0.2136	0.2194
24	1.5490	0.2070	0.2071	0.2129

Table 42. Model prediction for Nd-La in the system
lanthanum nitrate-neodymium nitrate-samarium
nitrate-water-HDEHP-Amsco

No	S ¹ Nd-La data	model	K Nd-La (regressed)	R ²
1	2.9660	3.4451	3.8266	0.9670
2	3.4380	3.4807		
3	2.7800	3.4814		
4	3.7780	3.4818		
5	4.7230	3.4822		
6	3.1640	3.4830		
7	2.5160	2.6254	2.6357	0.9931
8	2.7950	2.6254		
9	2.6850	2.6254		
10	2.2050	2.6254		
11	2.6763	2.6254		
12	2.8750	2.6254		
13	3.0408	3.2323	3.2460	0.9872
14	3.5398	3.2323		
15	3.6149	3.2336		
16	3.5347	3.2336		
17	2.5875	3.2320		
18	3.0698	3.2330		
19	3.7718	3.8312	3.8312	0.9382
20	3.2624	3.8313		
21	2.7631	3.8313		
22	3.4968	3.8313		
23	5.8823	3.8274		
24	3.8092	3.8312		

¹S = separation factor for Nd and La.
Nd-La

Table 43. Model prediction for Sm-La in the system
lanthanum nitrate-neodymium nitrate-samarium
nitrate-water-HDEHP-Amsco

No	S ¹ Sm-La		K Sm-La (regressed)	R ²
	data	model		
<hr/>				
1	20.6670	22.5421		
2	24.3820	22.5421		
3	20.4530	22.5469	24.1015	0.981
4	20.5930	22.5493		
5	28.7940	22.5516		
6	20.3970	22.5542		
<hr/>				
7	15.8760	21.3160		
8	21.3630	22.0788		
9	22.9500	22.1100	22.3041	0.9850
10	22.3890	21.3138		
11	23.0370	21.3182		
12	23.8340	21.3182		
<hr/>				
13	20.2742	20.6156		
14	22.8906	20.6156		
15	19.4889	20.6156	20.4317	0.9440
16	22.5188	20.6156		
17	18.3602	20.6156		
18	20.1606	20.6156		
<hr/>				
19	22.7439	21.7508		
20	21.2336	21.7550		
21	20.5302	21.7613	21.1686	0.9985
22	21.8052	21.7656		
23	21.3361	21.7635		
24	22.9189	21.7719		
<hr/>				

¹S = separation factor for Sm and La.
Sm-La

Table 44. Model prediction for Sm-Nd in the system
lanthanum nitrate-neodymium nitrate-samarium
nitrate-water-HDEHP-Amsco

No	S ¹ Sm-Nd data	model	K Sm-Nd (regressed)	R ²
1	6.3110	8.1635		
2	7.6440	8.4324		
3	8.5480	8.4409	8.5090	0.9800
4	10.1530	8.1635		
5	8.6080	8.1652		
6	8.2890	8.1652		
7	6.9690	6.9177		
8	7.0910	6.9177		
9	7.3310	6.9170	6.7267	0.9950
10	7.5680	6.9170		
11	6.0960	6.9164		
12	6.4470	6.9164		
13	6.6674	6.4231		
14	6.4667	6.4231		
15	5.3913	6.4244	6.3394	0.9936
16	6.3545	6.4231		
17	7.0975	6.4263		
18	6.5673	6.4250		
19	6.0301	5.9735		
20	6.5086	5.9741		
21	7.4302	5.9735	5.8159	0.9640
22	6.2357	5.9746		
23	3.6272	5.9741		
24	6.0167	5.9787		

¹S = separation factor for Sm and Nd.
Sm-Nd

CONCLUSIONS AND RECOMMENDATIONS

1. Chemically based thermodynamic models to predict the distribution coefficients and the separation factors for the liquid-liquid extraction of lanthanides-organophosphorus compounds and actinides-organophosphorus compounds have been developed by assuming that the quotient of the activity coefficients of each species varies slightly with its concentrations, by using the aqueous lanthanide or actinide complexes stoichiometric stability constants expressed as its degrees of formation, by making use of the extraction mechanism and the equilibrium constant for the extraction reaction. The details of the model equations are shown in Table 1.

2. For a single component system, the thermodynamic model equations which predicts the distribution coefficients, is dependent on the free organic concentration, the equilibrated ligand and hydrogen ion concentrations, the degree of formation, and on the extraction mechanism. Equations 118, 119 and 121 are the generalized model equations for the extraction mechanisms given by Equations 117 and 120.

3. For a binary component system, the thermodynamic model equation which predicts the separation factors is the same for all cases. This model equation is dependent on the

degrees of formation of each species in their binary system and can also be used in a ternary component system to predict the separation factors for the solutes relative to each other. Equation 115 and 116 are the developed model equations for a binary and ternary systems.

4. The procedures for the development of a model equations for application to the liquid-liquid extraction system can be summarized as follows: (1) Calculate the stability constants by Equation 62. (2) Calculate the degree of formation by Equation 51. (3) Estimate the effective equilibrium constant by a linear regression technique. (4) The predicted distribution coefficients or separation factors can be obtained by using the equilibrium data as well as the suitable thermodynamic model equation.

5. When using the developed model equations in this work, the following informations should be available: (1) the stability constants, (2) the equilibrated ligand and hydrogen ion concentrations in the aqueous phase, (3) the equilibrated organic concentration and (4) the distribution coefficients and the separation factors for single and binary systems respectively.

6. The single component system gives the best predicted data in all cases. The binary predictive model equation gives slightly better results than the ternary predictive model. The slight decrease in agreement is due to the

interaction effects between the molecules which are not taken into account in the binary and ternary predictive model equations. There are four interaction terms in the ternary system compared to one in the binary system.

7. The binary predictive thermodynamic model equation is better for molecules that have similar chemical and physical properties. When the molecules have very similar properties, the separation factors for these systems remain nearly constant and are independent of the total rare earth concentrations and the initial feed ratios of the solutes.

8. For a mixed ligand (chloride-nitrate) system, the binary model equation can be applied only when equal mole fractions of solutes are presented in the initial feed solutions. The separation factors for this mixed ligand system are independent of the total rare earth concentrations but dependent on the mole fractions of the initial feed solutions.

9. The developed thermodynamic model equations can be used with a few data points to predict extraction trends which would otherwise be difficult to determine experimentally.

10. This model development methods can readily be extended to the other liquid-liquid extraction systems, for example, Cu^{+2} -LIX65N, Cu^{+2} -KELEX100 and Cu^{+2} - Fe^{+3} -LIX or KELEX systems. The predictive model equations for distribution coefficients and separation factors can be

formulated with ease. The use of other specific ion electrodes presently available can be applied to study the copper extraction from sulfate, chloride, and ammonia aqueous phases.

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APPENDIX: DEVELOPMENT OF THE PREDICTIVE THERMODYNAMIC
MODEL EQUATION FOR MORE THAN ONE EXTRACTABLE SPECIE

Kosinski and Bostian (55) reported that there are three extractable species of lanthanide nitrates present in the organic phase and their extraction mechanisms can be represented by:

The equilibrium constants for Equations 2, 145 and 146 respectively can be written as:

$$K_{e1} = \frac{(M(HG)_2^+)(H^+)^3}{(M^{+3})(HG)_2^3} \cdot K_{r1} \quad (147)$$

$$K_{e2} = \frac{(M(NO)_3)(HG)_2^2(H)^{+2}}{(MNO)_3^2((HG)_2)} \cdot K_{r2} \quad (148)$$

$$K_{e3} = \frac{(M(NO)_3)(HG)_2^2(H)^{+1}}{(M(NO)_3^2)((HG)_2)} \cdot K_{r3} \quad (149)$$

where K_{r1} , K_{r2} and K_{r3} are the quotients of the activity coefficients for Equations 2, 145 and 146 respectively and have the same form as Equation 77. The total metal ion concentrations in the organic phase can be written as:

$$(M)_O^T = (M(HG)_2)_3 + (MNO)_3^2(HG)_2 + (M(NO)_3)_2^2(HG)_2 \quad (150)$$

Substitution of Equations 147, 148 and 149 into Equation 150 yields

$$(M)_O^T = \frac{K_{e1} (M)_3^3 ((HG)_2)^3}{K_{r1} (H)^{+3}} + \frac{K_{e2} (MNO)_3^2 ((HG)_2)^2}{K_{r2} (H)^{+2}}$$

$$+ \frac{K_{e3} (M(NO)_3^+)^2 ((HG)_2)}{K_{r3} (H)} \quad (151)$$

For the inorganic complex formation, Equations 69 and 70 give

$$(MNO_3^{+2}) = k_1 (M^+)^3 (NO_3^-)^2 \quad (152)$$

$$(M(NO)_3^+)^2 = k_2 (M^+)^3 (NO_3^-)^2 \quad (153)$$

Defining the effective equilibrium constant as

$$K_i = \frac{K_{ei}}{K_{ri}} \quad (154)$$

and

$$\phi = \frac{((HG)_2)^2}{(H)} \quad (80)$$

Equation 151 can be rewritten as:

$$(M)_0^T = (M^+)^3 [K_1 \phi + K_2 k_1 (NO_3^-)^2 \phi + K_3 k_2 (NO_3^-)^2 \phi] \quad (155)$$

The total metal ion concentrations in the aqueous phase can

be represented by Equation 156

$$(M)_A^T = (M)_A^{+3} [1 + \sum_i k_i (NO_3^-)^i] \quad (156)$$

Substituting Equations 155 and 156 into Equation 74 gives

$$K_d = \frac{(M)_O^T}{(M)_A^T} = \frac{K_1 O_3 + K_2 k_1 (NO_3^-)_O^2 + K_3 k_2 (NO_3^-)_O^3}{1 + \sum_i k_i (NO_3^-)_A^i} \quad (157)$$

Making use of the definition of the degree of formation given in Equations 51 and 76

$$a_i = \frac{k_i (NO_3^-)_i^i}{1 + \sum_i k_i (NO_3^-)_i^i}, \quad i = 1, 2, 3, \dots \quad (51)$$

$$a_o = \frac{1}{1 + \sum_i k_i (NO_3^-)_i^i} \quad (76)$$

into Equation 157 yields

$$K_d = K_1 a_{1o}^3 + K_2 a_{21}^2 + K_3 a_{32}^2 \quad (158)$$

Equation 158 is the predictive thermodynamic model equation

for the case of three extractable species in the organic phase.

The following equation can be obtained for the separation factor between metals M and N.

$$S_{M-N} = \frac{(K_d)_M \left((K a \phi)_{10}^3 + (K a \phi)_{21}^2 + (K a \phi)_{32} \right)_M}{(K_d)_N \left((K a \phi)_{10}^3 + (K a \phi)_{21}^2 + (K a \phi)_{32} \right)_N} \quad (159)$$