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DI-(2-ETHYLHEXYL) PHOSPHORIC ACID IN AMSCO

by

Tom Kyriacou Ioannou

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NOMENCLATURE

L,M,N - trivalent lanthanide cations (Sm,Nd,Ce)

(HG)$_2$ - dimeric molecule of di-(2-ethylhexyl) phosphoric acid.

$K_M$ - thermodynamic equilibrium constant for the extraction of M.

$H^+$ - equilibrium hydrogen ion concentration in the aqueous phase (moles/l.).

$x_M^*$ - molarity of lanthanide ion M in the equilibrated aqueous phase for a single-component system.

$y_M^*$ - molarity of lanthanide ion M in the equilibrated organic phase for a single-component system.

$X_{T}(M,N)$ - total molarity of lanthanides in the equilibrated aqueous phase for a binary system M,N.

$Y_{T}(M,N)$ - total molarity of lanthanides in the equilibrated organic phase for a binary system M,N.

$x_M(M,N)$ - equilibrium molarity in the aqueous phase of species M for a binary system M,N.

$y_M(M,N)$ - equilibrium molarity in the organic phase of species M for a binary system M,N.

$N_{M,A}(M,N)$ - mole fraction of species M in the equilibrated aqueous phase for a binary system M,N.

$= \frac{x_M(M,N)}{X_{T}(M,N)}$. 
\(X_T^{(L,M,N)}\) - total molarity of lanthanides in the equili-brated aqueous phase for a ternary system \(L,M,N\).

\(Y_T^{(L,M,N)}\) - total molarity of lanthanides in the equili-brated organic phase for a ternary system \(L,M,N\).

\(x_M^{(L,M,N)}\) - equilibrium molarity in the aqueous phase of species \(M\) for a ternary system \(L,M,N\).

\(y_M^{(L,M,N)}\) - equilibrium molarity in the organic phase of species \(M\) for a ternary system \(L,M,N\).

\(N_{M,A}^{(L,M,N)}\) - mole fraction of species \(M\) in the equilibrated aqueous phase for a ternary system \(L,M,N\)

\[= \frac{x_M^{(L,M,N)}}{X_T^{(L,M,N)}}.\]

\(\beta_{M,N}\) - concentration separation factor of species \(M\) with respect to \(N\).

\(\bar{Y}_M\) - organic molarity of lanthanide \(M\) assuming ideal behavior (no interaction) in a multi-component extraction system - partial extractability.

\(\bar{Y}_T\) - total organic molarity assuming ideal behavior analogous to Raoult's Law for ideal solutions.

\(\Delta Y_M\) - deviation from ideality of the organic concentration of lanthanide \(M\).

\[= Y_M - \bar{Y}_M\]
\[ \Delta Y_T \] - deviation from ideality of the total organic molarity.

\[ = \Delta y_L + \Delta y_M + \ldots \text{ etc.} \]
INTRODUCTION

The rare earth elements, commonly known as lanthanides, with atomic numbers 57 to 71 are relatively abundant in nature and are found in scarce minerals. They make up about one-sixth of all naturally occurring elements, yet the entire group occupies only one position on the periodic chart. This group of elements, of which samarium, neodymium and cerium are members, have nearly identical chemical properties in aqueous solutions. Consequently, they present a great challenge in attempting to separate rare earth mixtures into individual components. Even though the lanthanides are not very radioactive in nature, they are often found in the same minerals with radioactive thorium or uranium. Since they are also formed as nuclear fission products, they have important relationships with nuclear science and technology. Scientific curiosity and the fact that research has developed a number of commercial uses for them, beneficial to mankind, are also good reasons for studying the lanthanides.

The ion-exchange technique was developed (39) as a method of separation which can produce purified lanthanides of at least 99.99%. Today, ion-exchange is still the most common industrial method of separating the rare earths. However, since the process requires long residence times and a high capital investment for the processing of solutions, there is a possibility that more economical processing methods can be
Solvent extraction offers some economic advantages and can easily be adapted as a continuous process. Therefore, it has become an attractive possibility for the separation and purification of the lanthanides on an industrial scale. The separation of cerium (IV) from mixtures of fission products or from mixtures of rare earth elements can readily be accomplished by liquid-liquid extraction as well as by other means.

Until recently, fundamental solvent extraction chemistry studies were usually carried out at tracer concentrations. Often, however, the actual chemistry of the reactions involved in solvent extraction at macro-concentrations is extremely complex due to many unknown factors. This makes it very difficult to optimize a specific process with respect to solvent selectivity and other operating conditions without obtaining an extensive amount of equilibrium data in the laboratory. Therefore, if the multi-component equilibrium data can be correlated reliably, the desired operating conditions for a multi-stage extractor can be selected as a function of the various process variables.

In this study, the acidic organophosphorous compound, di-(2-ethylhexyl) phosphoric acid (hereafter abbreviated D2EHPA), was used as the solvent and Amsco Odorless Mineral Spirits as the diluent. D2EHPA is a promising solvent for the separation of the lanthanides. This can be attributed to its
insolubility in water, rapid phase separation from the aqueous phase, and its ability to achieve high separation factors.

The research herein was concerned with the correlation of data for a ternary salt system. It was anticipated that a successful correlation in terms of individual components could be extrapolated to a multi-component system. Specifically, it was intended to:

1. Obtain equilibrium data for the single-component system CeCl$_3$-HCl-H$_2$O-1 M D2EHPA-Amsco.
2. Develop a model to predict the organic phase concentration upon specification of the aqueous phase for the above system.
3. Obtain equilibrium data for the binary system SmCl$_3$-NdCl$_3$-HCl-H$_2$O-1 M D2EHPA-Amsco as a function of acidity and mole fraction of samarium in the aqueous phase. It was also intended to study the interaction effects, which are strongly evident, in terms of single-component data and correlate them.
4. Obtain equilibrium data for the ternary system, SmCl$_3$-NdCl$_3$-CeCl$_3$-HCl-H$_2$O-1 M D2EHPA-Amsco, and study the separation factor variation, if any, as a function of acidity, mole fraction of one element, and molar ratio of the other two in the aqueous phase. Furthermore, the interaction effect in terms of single-component data would be investigated and correlated.
5. Develop a model to predict the organic phase concentration upon specification of the aqueous phase in the ternary system.
LITERATURE REVIEW

Separation and purification of the rare earth elements can be attained by liquid-liquid solvent extraction. Solvents which are commonly utilized for this purpose are the organophosphorous compounds which can be categorized as either neutral or acidic. Since the neutral organophosphorous compounds, such as tri-n-butyl phosphate (TBP), are not part of this study, a detailed discussion will not be undertaken. Healy and McKay (15) postulated that the extraction of rare earths with TBP gives a non-conducting complex which is due to the extraction of neutral species into the organic phase.

In 1953, Scadden and Ballou (33) reported the first study of lanthanide extraction with acidic organophosphorous compounds. Using a mixture of dibutyl and monobutyl phosphoric acids as the extractant, they studied the separation of a niobium-zirconium mixture. In addition, the fractionation of a complex mixture of fission products which consisted of trivalent cerium, lanthanum, yttrium and holmium, was also studied. These investigators demonstrated that the acidic organophosphorous compounds are effective agents for the separation of heavy and light lanthanides. This conclusion was deduced from their findings that a 0.6 M phosphoric acid mixture extracted more than 95% of the holmium and yttrium and less than 5% of the lanthanum and Ce(III).
An intensive study of the acidic organophosphorous compounds as extractants was undertaken by Peppard et al. of the Argonne National Laboratory in 1956. They determined some of the chemical properties of these compounds and the mechanisms by which the lanthanides and actinides are extracted with these solvents. All their work was performed at tracer concentrations. It is essential to note, however, that the mechanisms change at macro-concentrations of rare earth solutions.

In 1957, Peppard et al. (26) reported on the extraction on trivalent lanthanides and yttrium by D2EHPA using toluene as the diluent. This solvent was chosen because its solubility in aqueous phases is negligible and it gives a high degree of separation. They demonstrated by means of tracer techniques that, as the atomic number of the lanthanides increases, the extractability also increases. These findings are true for the extraction of lanthanides from aqueous chloride, nitrate and sulfate media. In later studies, Peppard et al. (25), employing radiometric techniques, determined that the distribution ratio was inversely third-power dependent on the acidity of the aqueous phase. At low acidities, the extraction of the lanthanides was very high and saturation of the solvent occurred when the mole ratio of cations to active solvent in the organic phase was 1 to 6. At this point an amorphous third phase solid was noted.
In further studies, Peppard et al. (24), using a cryoscopic method, determined the state of aggregation of D2EHPA. It was found to be dimeric in benzene and naphthalene and very strongly hydrogen bonded. On the basis of all their findings at tracer concentrations, they proposed the following ion-exchange mechanism for the extraction of trivalent rare earths by D2EHPA:

\[ M^{+3} + 3(\text{HG})_2 \rightarrow M(\text{HG}_2)_3 + 3H^+ \]  

where \((\text{HG})_2\) represents the dimeric solvent and \(M(\text{HG}_2)_3\) the metal complex in the organic phase. Equation 1 is valid (25, 26) at tracer concentrations of trivalent lanthanides and actinides in aqueous chloride, nitrate, sulfate and perchlorate solutions at low acidities. It represents the extraction of these metal ions by monoacidic organophosphorous solvents which dimerize in the diluent.

Baes, Zingaro and Coleman (4), in an investigation on the extraction of uranium with D2EHPA, showed that D2EHPA was dimeric in hexane from 0.01 M to 1.0 M D2EHPA. At higher solvent concentrations, however, higher aggregates occur. They proposed the following mechanism for the extraction of uranyl ions for low organic loadings:

\[ \text{UO}_2^{+2} + 2(\text{HG})_2 \rightarrow \text{UO}_2(\text{HG}_2)_2 + 2H^+. \]
In the same study they found that no water of hydration was associated with either the free D2EHPA or the uranium-D2EHPA complexes. Furthermore, they reported that as the ratio of metal to solvent concentration in the organic phase exceeded 0.45, there was a noticeable increase of the viscosity, and the formation of chain polymers occurred with the following mechanism:

\[ \text{HG}_2\text{(UO}_2\text{)G}_2\text{H} + \text{HG}_2\text{(UO}_2\text{)G}_2\text{H} \to \text{HG}_2\text{(UO}_2\text{)G}_2\text{H} + \text{HG}_2\text{(UO}_2\text{)G}_2\text{H}. \] (3)

In later studies, Baes and Baker (3) showed that when the diluent was n-octane, the D2EHPA existed as both dimeric and trimeric in equilibrium with each other,

\[ 3\text{(HG)}_2 \rightleftharpoons 2\text{(HG)}_3. \] (4)

The equilibrium constant for the above mechanism was reported as 10 mole\(^{-1}\).

In 1967, Rigg and Garner (29) studied the extraction of vanadium with D2EHPA (in kerosene). They showed that the distribution ratio of vanadium decreased at very high solvent loadings. Their results suggested that the extracted complex, under the conditions studied, involved D2EHPA monomers rather than dimers. These workers found no evidence of either chloro or hydroxy-group participation in the extracted complex, and that the ionic strength variation appeared to have no significant effect on the reaction. However, Peppard et al. (23, 24),
in a study of the extraction of tracer level tetravalent thorium from aqueous chloride, nitrate and perchlorate media with D2EHPA, found that the organic phase extracted the nitrate anion. They found that the nitrate to thorium ratio in the organic phase was approximately 1.0 at saturation of the organic phase.

Sato (30, 31, 32) investigated the extraction of U(IV) by D2EHPA (in kerosene) from acidic aqueous sulfate, nitrate and chloride solutions. He found that nitric acid is extracted into the organic phase as:

\[ \text{HNO}_3 + (\text{HG})_2 \rightleftharpoons \text{HNO}_3 \cdot (\text{HG})_2. \] (5)

Upon studying the sulfate system, Sato reported that at low \( \text{H}_2\text{SO}_4 \) concentrations and high uranium concentrations, a polymeric uranium-D2EHPA complex was formed. These complexes were also formed in hydrochloric acid media. He found that in the chloride system, however, the distribution ratio decreases as the total chloride in the aqueous phase increases. This effect is due to the presence of \( \text{UO}_2\text{Cl}^+ \) chlorocomplexes. It was also reported that the extraction from nitrate and chloride media is more complex than from sulfate solutions.

In 1963, Pierce and Peck (28) investigated the extraction of the lanthanides by D2EHPA (in toluene) from acidic perchlorate solutions at tracer concentrations. These investigators calculated the expected degree of separation when two rare earths were extracted simultaneously by using the ratio
of the distribution coefficients. The average value for the nearest neighbors was found to be 2.40.

Shaw and Bauer (34) reported on the extraction of trivalent cerium by D2EHPA (in xylene) from acidic aqueous nitrate solutions. They found that the extraction of trivalent cerium decreases as the acidity increases. It reaches a minimum value at an acid concentration of 5 M and it increases again at higher acid concentrations. This phenomenon indicated a reaction mechanism change but no explanations were given. They stated that at low acid concentrations, the extraction exhibits characteristics of ion-exchange phenomena. At high acidities, the neutral rare earth nitrate molecule may be extracted in the form of a complex of the type $M(\text{NO}_3)_3 \cdot 3\text{EHPA}$. These workers reported that partition between light and heavy lanthanides is generally best at low aqueous acidities. Similarly, the partition between Ce(IV) from trivalent members is best at low acid concentrations.

Cerium studies were also performed in 1965 by Alian and Moustapha (2). They investigated the extraction of cerium (III) with tri-n-octyl phosphine oxide (TOPO) in toluene from acidic aqueous nitrate media. The variables were nitric acid and lithium nitrate concentrations in the aqueous phase. These workers found that trivalent cerium, extracted with the above neutral organophosphorous compound, forms a trisolvate complex $\text{Ce(NO}_3)_3 \cdot 3\text{TOPO}$. They reported that the cerium partition
coefficient increases initially as lithium nitrate concentration increases; it reaches a maximum and then decreases continuously. They also reported that in the extraction of cerium (III) with 0.1 M TOPO, the distribution ratio of cerium (III) as a function of acidity increases slightly at very low acid concentrations; it reaches a maximum and then decreases continuously. When the nitric acid concentration is raised above 10 M, the distribution coefficient increases again.

In 1967, Tedesco, Rami and Gonzalez Quintana (40) studied the extraction of tetravalent cerium at tracer levels from aqueous sulfate solutions by D2EHPA dissolved in kerosene. They found that the partition coefficient of Ce(IV) increases with sulfate concentration up to about 0.8 M and then decreases continuously. The maximum occurred at a pH of \( \sim 1.3 \) for tracer level cerium. The inflection of the curve was explained by assuming a change in the composition of the aqueous phase. At low sulfate level, an increase in the anion produces an increase in the proportion of the more soluble species with a corresponding increase of the extraction. At higher anion concentrations, the complexing of Ce(IV), \([\text{Ce(SO}_4^2])^+\), is high enough to counteract the effect and the extraction is lowered. These workers also reported that sulfate was not found in the organic phase in either equilibrium or saturation tests. Furthermore, they found that the mole ratio of D2EHPA to cerium in the saturated organic phase decreased as the pH increased.
until it reached a constant value of 2.0. These results were explained by assuming that hydrolyzed forms of the Ce$^{4+}$ ion formed in increasing amounts as the pH was increased.

Recently, Navratil and Dubinin (20) studied the extraction of Ce(IV) with dibutyl phosphoric acid (HDBP) in carbon tetrachloride. The aqueous solutions consisted of nitric, perchloric and hydrochloric acids in the presence of NaBrO$_3$ for the oxidation of cerium. They found that cerium is oxidized to its tetravalent state only in nitric acid medium at NaBrO$_3$ concentrations of $\geq 0.06$ M. Furthermore, in the HCl medium with chloride concentration $\geq 0.1$ M, the tetravalent cerium was reduced. In addition, they reported that the distribution of Ce(IV) in nitric acid medium was five orders of magnitude higher than in the other media. They reported that the extraction mechanism for tetravalent cerium is of the solvation type (independent of acidity) and may be described by the scheme:

$$\text{Ce}^{4+} + 4\text{NO}_3^- + 4 \text{HDBP} \xrightarrow{\text{HDBP}} [\text{Ce(NO}_3)_4 \text{HDBP})_4] . \quad (6)$$

At moderate concentrations of HCl and HClO$_4$, the extraction of trivalent cerium is controlled first by the ion-exchange mechanism,

$$\text{Ce}^{3+} + 3\text{HDBP} \xrightarrow{\text{HDBP}} \text{Ce(DBP)}_3 + 3\text{H}^+ \quad (7)$$

and at a certain limiting concentration of mineral acid, by
the solvation mechanism

\[ \text{Ce}^{+3} + 3X^- + 3\text{HDBP} \rightarrow [\text{CeX}_3(\text{HDBP})_3] \quad (8) \]

where \( X^- \) is the anion.

Fidelis (7) investigated the effect of temperature on the extraction of lanthanides by HEH\(\Phi\)P (in n-heptane) from aqueous nitrate solutions. This worker's conclusions were stated as follows:

1. The extraction coefficients of all lanthanides decrease with increase in temperature.
2. The effect of temperature on the separation coefficients depends on \( Z \);
   a. the separation coefficients of lanthanides of atomic number \( Z < 61 \) increase with increase in temperature
   b. the separation coefficients of lanthanides of atomic number \( Z > 61 \) diminish with increase in temperature.
3. The effect of temperature on the coefficient \( \beta \) is generally greater, the greater the value of the coefficient \( \beta \).

In an effort to understand better the mechanism of lanthanide extraction by D2EHPA at macro-concentrations, Kosinski and Bostian (17) studied the displacement of water molecules from the D2EHPA as lanthanum was extracted from aqueous nitrate media at macro-concentrations. By material
balance data and i.r. analysis of the organic phase, these workers confirmed the displacement of water as the lanthanum concentration in the organic phase increased. They calculated the stoichiometry of water in the mechanisms and proposed three reactions which probably occur simultaneously:

\[
\begin{align*}
\text{La}^{3+} + 3(HG)_2 \cdot H_2O & \rightarrow \text{La}(HG)_2)_3 + 3H_2O + 3H^+ \\
\text{LaNO}_3^{2+} + 2(HG)_2 \cdot H_2O & \rightarrow \text{La(NO}_3)_2(HG)_2)_2 + 2H_2O + 2H^+ \\
\text{La(NO}_3)_2^{+1} + (HG)_2H_2O & \rightarrow \text{La(NO}_3)_2HG_2 + H_2O + H^+ .
\end{align*}
\]

In each reaction, the lanthanum ion replaces hydrogen ions and interacts with the P=O structure of D2EHPA.

Equilibrium data for the extraction of the lanthanides by D2EHPA from acidic aqueous solutions were reported by many investigators only at tracer concentrations. Recently, however, equilibrium data at macro-concentrations were made available. In 1965, Goto and Smutz (11) reported on the separation of Nd with respect to Pr for 1 M D2EHPA (in Amsco 125-82) from perchlorate, nitrate, chloride, and chloride-nitrate solutions. The separation factor was expressed by an equation comprised of two parts: (1) the separation ability of the solvent itself (the ratio of equilibrium constants), and (2) an aqueous ligand-dependent term. Goto and Smutz (10) proposed a technique for predicting the composition of one phase upon specification
of the other for PrCl$_3$-NdCl$_3$ mixtures. Due to the chemical similarity of Pr and Nd, they assumed that the total rare earth concentration in the organic phase was linearly dependent on the mole fraction of either species in the aqueous phase. Goto and Smutz (12), using a potentiometric method, also measured the stability constants for LaCl$^{+2}$, PrCl$^{+2}$, NdCl$^{+2}$, SmCl$^{+2}$. The results showed a stability constant of approximately 1.60 for all species.

In a later paper, Goto (9) measured the distribution coefficients of Y, Er and Ho and the separation factors of some lanthanides with respect to Y at macro-concentrations. The extractions were from aqueous chloride solutions using the extractant D2EHPA in n-heptane. He found that the separation factors of Y with respect to Er is between 1.1 and 1.2 and is almost independent of acid and lanthanide concentrations unless the ratio of Er to Y is extremely small. Since there was no variation of $\beta$ with acidity it might mean that the stability constants of YCl$^{+2}$ and ErCl$^{+2}$ are almost the same. Since the separation factor increased slightly at small ratios of Er to Y, Goto suggests that the activity coefficient of Er in either the organic or the aqueous phase, in the presence of a comparable amount of Y, differs from that at an extremely small ratio of Er. He also found that the extractability of Ho is about half that of Y. Goto reported that the separation factor of Er with respect to Ho, therefore, was between 2.1 and 2.4. In
the same study he also reported that in the three salt system, the separation factor of the pairs remains the same as in the two salt system.

The author (16) also obtained equilibrium data for Sm and Nd in hydrochloric acid. A non-linear correlation technique was employed in order to obtain an empirical model for each of the individual elements. The model predicts the organic concentration upon specification of the aqueous concentration and acidity. The correlation was extended to predict the equilibrium of the binary system SmCl₃-NdCl₃ over a limited range of concentrations and acidities.

Other contributors to macro-concentration equilibrium data are Battista, Mize and Smutz (6), Lenz and Smutz (18), Owens and Smutz (22) and Nair and Smutz (19).

Some chemical and physical properties of the rare earth elements were determined by Spedding et al. (35, 36, 37, 38). The heats of dilution of the rare earth chlorides were measured as well as heat capacities, viscosities and apparent molal volumes. A coordination number of nine was suggested for both trivalent lanthanum and neodymium due to the similarity of their hydrated ion structures.
DEVELOPMENT OF FUNDAMENTAL SEPARATION
FACTOR RELATIONSHIPS

Binary Systems

In a lanthanide extraction system consisting of two rare earth elements, it is possible to predict all the organic phase rare earth concentrations if the aqueous phase rare earth concentrations, acidity and separation factor are specified. The mole fraction of each element in the organic phase may be expressed as a function of the molar ratio of the elements in the aqueous phase and the separation factor between them. If two elements (M,N) are extracted simultaneously, the separation factor is defined as:

\[ \beta_{M,N} = \frac{Y_M}{X_M} \cdot \frac{X_N}{Y_N} \]  \hspace{1cm} (12)

where \( Y_M, Y_N \) are the molarities of the respective elements in the organic phase and \( X_M, X_N \) are their molarities in the aqueous phase at equilibrium. Since the total molarity, \( Y_T \), of the two species in the organic phase is

\[ Y_T = Y_M + Y_N \]  \hspace{1cm} (13)

substituting \( Y_N \) from Equation 13 in Equation 12 we obtain

\[ \beta_{M,N} = \left( \frac{X_N}{X_M} \right) \cdot \frac{Y_M}{Y_T-Y_M} \]  \hspace{1cm} (14)
Rearranging Equation 14 and solving for mole fraction of \( M \) (or \( N_j^{(M,N)} \)) in the organic phase, we have

\[
N_{\text{M}}(M,N) = \frac{Y_M}{Y_T} = \frac{1}{1 + \frac{1}{\beta_{M,N}} \left( \frac{x_N}{x_M} \right)}.
\]  

(15)

Similarly, the mole fraction of \( N \) is

\[
N_{\text{N}}(M,N) = \frac{Y_N}{Y_T} = \frac{1}{1 + \beta_{M,N} \left( \frac{x_M}{x_N} \right)}.
\]  

(16)

Ternary Systems

In a ternary extraction system containing three lanthanides \( (L,M,N) \), where the extractability of \( L > M > N \), a general expression may be derived to predict the mole fraction of each element in the organic phase. The mole fraction of each element may be expressed as a function of the separation factors of two of the three pairs and the molar ratios of species in the aqueous phase at equilibrium. From the definition of the separation factor of any pair of the three elements extracted simultaneously we have

\[
\beta_{L,M} = \frac{Y_L}{X_L} \cdot \frac{x_M}{y_M}.
\]  

(17)
Since the total molarity, $Y_T$, of rare earths in the organic phase is

$$Y_T = Y_L + Y_M + Y_N$$  \hspace{1cm} (18)

substituting $y_M$ from Equation 18 into Equation 17, gives

$$\beta_{L,M} = \left(\frac{x_M}{x_L}\right) \left[ \frac{1}{\frac{Y_T}{Y_L} - 1 - \frac{Y_N}{Y_L}} \right]$$  \hspace{1cm} (19)

Solving for the mole fraction of L ($y_L/Y_T$ or $N_L(L,M,N)$ in the organic phase gives

$$N_L(L,M,N) = \frac{Y_L}{Y_T} = \frac{1}{1 + \frac{1}{\beta_{L,M}} \left(\frac{x_M}{x_L}\right) + \frac{x_N}{Y_L}}$$ \hspace{1cm} (20)

Also from the definition of the separation factor between L and N one obtains

$$\beta_{L,N} = \frac{y_L}{x_L} \cdot \frac{x_N}{y_N}$$ \hspace{1cm} (21)

Solving for $y_N/y_L$ in Equation 21 and substituting in Equation 20, the following relation is obtained:

$$N_L(L,M,N) = \frac{Y_L}{Y_T} = \frac{1}{1 + \frac{1}{\beta_{L,M}} \left(\frac{x_M}{x_L}\right) + \frac{1}{\beta_{L,N}} \left(\frac{x_N}{x_L}\right)}$$ \hspace{1cm} (22)
By similar manipulations the mole fractions of M and N in the organic phase are as follows:

\[
N_M(L,M,N) = \frac{Y_M}{Y_T} = \frac{1}{1 + \beta_{L,M} \left( \frac{x_L}{x_M} \right) + \beta_{M,N} \left( \frac{x_N}{x_M} \right)},
\]

(23)

\[
N_N(L,M,N) = \frac{Y_N}{Y_T} = \frac{1}{1 + \beta_{L,N} \left( \frac{x_L}{x_N} \right) + \beta_{M,N} \left( \frac{x_M}{x_N} \right)}.
\]

(24)

Equations 22, 23 and 24 are general and can be applied for any ternary system (L,M,N).
EXPERIMENTAL PROCEDURES

Materials

The rare earth oxides utilized throughout this study were provided by the Rare Earth Separation Group of the Ames Laboratory of the Atomic Energy Commission. As determined by emission spectroscopy, the oxides were of greater than 99.9% purity with respect to other lanthanides. The cerium oxide was formed from cerium perchlorate burned at a low temperature of \( \approx 250^\circ C \). This low-fired cerium oxide is necessary in order to facilitate the reaction with hydrochloric acid which reacts slowly with high-fired cerium. All acids and other chemicals used in this work were of reagent grade purity.

The extractant D2EHPA was supplied by the Union Carbide Corporation and was 98.8% monoacidic. The hydrocarbon diluent (Amsco Odorless Mineral Spirits), supplied by the American Mineral Spirits Company, was added to an appropriate amount of D2EHPA in order to form a 1 M D2EHPA solution on a monomer basis.

Preparation of Rare Earth Chloride Stock Solutions

The trivalent rare earth oxides were reacted with 50% excess HCl from the stoichiometric amount. The reaction

\[
\text{RE}_2\text{O}_3 + 6\text{HCl} \xrightarrow{\text{tit}} 2\text{RECl}_3 + 3\text{H}_2\text{O}
\]

(25)
was allowed to continue until the solution was clear. The excess acid was then evaporated by heating on a hot plate until the RECl$_3$ salt precipitated. The salt was dissolved in distilled water and diluted to the required volume. Hydrolysis of the rare earths was evident at this point due to the acid-deficient medium. The solution was titrated with dilute HCl to the equivalence point (the point at which the RE:Cl ratio is 1:3) which made the solution clear. A slight excess of HCl was added in order to assure the absence of hydrolytic products.

The cerium oxide was treated differently due to its high oxidation potential. The low-fired tetravalent cerium was reacted with an excess of HCl:

$$2\text{CeO}_2 + 8\text{HCl} \rightarrow 2\text{CeCl}_3 + 4\text{H}_2\text{O} + \text{Cl}_2 \uparrow.$$  \hspace{1cm} (26)

The above reaction, however, was very slow and it was allowed to continue for twenty-four hours at 90°C. This low temperature was necessary in order to prevent the oxidation of CeCl$_3$. After the reaction was completed and most of the cerium was in solution, there was some undissolved fine material suspended in the solution. This was probably some high temperature cerium which reacts extremely slowly with HCl. The solution was then filtered several times with a very fine filter paper. When the solution was very clear and colorless, an aliquot was titrated with 0.5 N NaOH to find the equivalence point. This was determined from the break-point of a plot of pH versus ml
NaOH added. The pH at the equivalence point was \( \approx 2.5 \). The CeCl\(_3\) stock solution was adjusted to a slightly lower pH. A slight excess of acid is essential in order to maintain the trivalent state of cerium and prevent hydrolysis. There is a tendency for cerium to oxidize to its tetravalent state if the solution is acid-deficient. This can be attributed to the fact that cerium hydrolyzes in an acid-deficient medium and that hydrolyzed cerium seeks its tetravalent state. A slight amount of tetravalent cerium causes the solution to change color from colorless to brown. If this occurs, a slight amount of hydrogen peroxide reduces the cerium, but the excess hydrogen peroxide must be boiled off.

CeCl\(_3\) Equilibrium Studies

The initial solutions were prepared by diluting an appropriate amount of RECl\(_3\) stock solution and HCl in volumetric flasks. The initial solutions were then contacted with equal volumes of 1 M D2EHPA in separatory funnels. They were then shaken for fifteen minutes on a separatory funnel shaker and allowed to stand for at least one hour. The equilibration was repeated four times and the last time the solutions were allowed to stand for at least twelve hours undisturbed before the phases were separated.

The phases were clear when they were separated, however, the organic phase was centrifuged for ten minutes in order to
remove any entrained aqueous material. A volumetric sample of
the organic phase was then measured into a separatory funnel
and contacted four times with an equal volume of 6 N HCl in
order to remove the rare earths quantitatively. After four
back-extractions, the collected strip was filtered into a
volumetric flask in order to remove any solvent present and
was finally diluted to volume. A volumetric sample of this
solution was analyzed for cerium after the excess acid had
been evaporated. The concentration of cerium in the organic
phase was then calculated.

The cerium concentrations of the initial solutions, the
equilibrated aqueous phases, and the organic back-extracts
were determined titrimetrically with standardized EDTA.
Arsenazo was the indicator and pyridine was the buffer as
described by Fritz et al. (8). A slight amount of ascorbic
acid was added to the solution in order to maintain the tri-
valent state of cerium. In almost all the samples, a titration
with and without ascorbic acid gave the same results. This
showed the absence of tetravalent cerium.

The EDTA was standardized against a solution of rare earth
chloride of known concentration. The concentration of the
lanthanide solution was determined gravimetrically by precipi-
tating an aliquot of the rare earth chlorides as oxalates,
burning the oxalates to the oxides at 800°C and weighing the
oxide on an analytical balance.
The color change of the organic strip titration was not very distinct. It is believed that the anomaly is attributed to the formation of organic and inorganic phosphate complexes with the indicator and EDTA. In order to resolve this difficulty, the solution was acidified before the end-point with several drops of concentrated HCl to pH of 2. The HCl dissolved the soluble complexes and the titration was continued after readjusting the pH. This resulted in a sharper end-point.

The method used for the determination of the hydrogen ion concentration is one employing the cation exchange resin Dowex 50 X 8 as described by Adams and Campbell (1). For every lanthanide ion attached to the resin, three hydrogen ions are released to the aqueous phase. The total acidity (free acid and hydrogen ion released by the resin) was determined by titration with standard NaOH using phenolphthalein as the indicator.

Binary System Equilibrium Studies

The binary system SmCl₃-NdCl₃-HCl-H₂O-1 M D2EHPA-Amsco was studied at different conditions than in previous work (16). The same techniques as in the single-component system were utilized in order to obtain the total lanthanide concentrations. In this system, the composition of each phase containing both Sm and Nd was also determined in order to calculate the
separation factors. The concentration of each species was obtained spectrophotometrically as described by Banks and Klingman (5) with some modifications. Aliquots of the organic strips and equilibrated aqueous phases were pipetted into 30 ml beakers. The solution was evaporated on a hot plate at 110°C, being careful to avoid bumping, until the salt was formed. An appropriate amount of perchloric acid was added in order to form the rare earth perchlorates and make a 1 M solution. After the reaction was completed, the heating was continued at 250°C for a few minutes in fuming perchloric acid. The solutions were left under a heating lamp until there was no chloride present as determined by silver nitrate tests. The samples were diluted in a volumetric flask and the absorbance of each species was read on a DU-2 spectrophotometer. The absorbance of Sm was read at a wavelength of 401.5 μm and a slit width of 0.02 mm. The absorbance of Nd was read at a wavelength of 575.5 μm and a slit width of 0.02 mm. The molarity of each species was calculated with respect to standard Nd(ClO₄)₃ and Sm(ClO₄)₃ solutions using a direct relationship of absorbance to concentration. This is possible since there is no interference between Sm and Nd.

Ternary System Equilibrium Studies

The ternary system SmCl₃-NdCl₃-CeCl₃-HCl-H₂O-1 M D2EHPA-Amsco was investigated and separation factors were obtained. The total rare earth concentrations in each phase were determined as in the above discussion. The relative amounts of Sm
and Nd were obtained spectrophotometrically as described above but in the presence of cerium. Even though there was no evidence of tetravalent cerium in the solutions, a drop of 0.05% hydrogen peroxide was added to assure the trivalent state of cerium and the excess peroxide was evaporated by boiling. The cerium content in each phase was determined by an oxidation-reduction technique. A volumetric sample of RECl₃ mixture, ~0.1 M, containing Sm, Nd and Ce was placed in a 600 ml beaker and reacted with 10 ml of concentrated H₂SO₄ as follows:

\[
2\text{CeCl}_3 + 3\text{H}_2\text{SO}_4 \xrightarrow{\Delta} \text{Ce}_2(\text{SO}_4)_3 + 6\text{HCl} \quad (27)
\]

In order to remove all of the hydrochloric acid, the solution was evaporated on a hot plate until fumes of sulfur trioxide were evolved (a thick white fume). The solution was then cooled and diluted to about 400 ml with distilled water. In order to oxidize the trivalent cerium in its sulfate form, an excess amount of K₂S₂O₈ was added to the solution and about 0.05 grams of AgNO₃ was used as a catalyst. The solution was then boiled vigorously for about forty-five minutes in order to decompose the excess K₂S₂O₈. At this point the solution was orange which is the characteristic color of ceric sulfate. The wall of the beaker was rinsed with distilled water and the solution boiled for an additional twenty minutes. After the solution was cooled, the tetravalent cerium in solution was reduced with a known excess amount of standardized iron (II)
sulfate. The excess iron (II) was back-titrated with standardized ceric sulfate solution using one ml of 0.001 M ferroin as the indicator. The molarity of CeCl₃ was then calculated.

The ceric sulfate was standardized with arsenic (III) oxide using a drop of osmic acid solution as a catalyst and ferroin as the indicator. The iron (II) sulfate was standardized against the above ceric sulfate solution.
DISCUSSION OF RESULTS

Equilibrium for the System
CeCl₃-HCl-H₂O-1 M D2EHPA-Amsco

Equilibrium data for the above system were obtained at aqueous metal concentrations ranging from 0.1 M to 1.5 M and aqueous acidities ranging from 0.3 M to 0.7 M. The data are presented in Table 1 and also plotted in Figure 1. It is essential to note that the constant acidity parameter should not be regarded as the true acidity for each point since it varies slightly.

The shape of these equilibrium curves and the pronounced displacement with respect to aqueous acidity suggests that trivalent cerium is extracted in the same manner as the other lower rare earths (10, 16, 18, 19) when D2EHPA is the extractant and chloride the anion. The maxima of the curves, within the range of the data, occur at an aqueous concentration of approximately 0.4 mole/liter as compared to Nd and Sm of \( \approx 0.45 \) M and \( \approx 0.5 \) M (16) respectively. As expected, the extractability of Ce(III) increases as the acidity of the aqueous phase decreases for any fixed aqueous metal concentration.

Even though Equation 1 represents the mechanism of extraction for the rare earth salts at tracer concentrations and low acidities, it should be noted that the reaction
Table 1. Equilibrium data for the system CeCl$_3$-HCl-H$_2$O-1 M D2EHPA-Amsco

<table>
<thead>
<tr>
<th>Aqueous concentration (moles/l.)</th>
<th>Final acidity (moles/l.)</th>
<th>Organic concentration (moles/l.)</th>
</tr>
</thead>
<tbody>
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<td>0.0676</td>
</tr>
<tr>
<td>0.1985</td>
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<td>0.302</td>
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Table 1 (Continued)

<table>
<thead>
<tr>
<th>Aqueous concentration (moles/1.)</th>
<th>Final acidity (moles/1.)</th>
<th>Organic concentration (moles/1.)</th>
</tr>
</thead>
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<td>0.5768</td>
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<td>0.0370</td>
</tr>
</tbody>
</table>

becomes more complex at macro-concentrations and cannot be used to predict the equilibrium data in this study. Several explanations for the changing chemistry offered by Lenz and Smutz (18) are: (1) as the ionic strength increases, HCl activity also increases, (2) as the organic rare earth concentration increases, the free extractant concentration decreases, and (3) strong complexing between the lanthanide and chloride in the aqueous phase exists. Owens (21) also demonstrated that if the HCl activity is the parameter rather than acid concentration, the equilibrium curves may not exhibit a relative maximum.
Figure 1. Equilibrium data for the system CeCl$_3$-HCl-H$_2$O-1 M D2EHPA-Amsco
If one makes the gross assumption that the ratio of activity coefficients is almost unity in Equation 1, then the equilibrium constant for the single-component reaction can be written in terms of concentrations as:

\[ K_M = \frac{[M(HG_2)]_0^3[H]^3_A}{[(HG)_2]^3[M^+]_A}. \]  

(28)

For simplicity, let the organic concentration of the metal be equal to \( y_M^* \) and the aqueous concentration be equal to \( x_M^* \).

Expressing the above relation in terms of logarithms, the following is obtained:

\[ \ln y_M^* = \ln K_M [(HG)_2]^3 x_M^* - 3 \ln H^+ . \]  

(29)

This acid dependency relation is plotted in Figure 2 with \( x_M^* \) as a parameter. Assuming that the free solvent concentration \((HG)_2\) is almost constant, the equation shows a straight line relationship for any constant \( x_M^* \) with a slope of -3.0. However, from Figure 2, it is noted that the curves are not linear and that the slope varies continuously. In fact, the slope is -3.0 at high acidities of \( \sim 0.7 \text{ M} \), it changes to -2.0 at an acidity of \( \sim 0.55 \text{ M} \) and finally to -1.0 at a low acidity of \( \sim 0.3 \text{ M} \).

The slope variation is expected to continue as the acidity is increased until the extraction reaches a minimum and the slope becomes zero. At still higher acidities, it is
Figure 2. Acid dependency curves for the system CeCl$_3$-HCl-$\text{H}_2\text{O}$-1 M D2EHPA-Amsco
anticipated that the slope will become positive and the extraction will increase again. This phenomenon was reported by Harada and Smutz (13) in a study of the extraction of yttrium with D2EHPA. The acid dependency curves suggest that a more complex mechanism of extraction is taking place rather than the simple ion-exchange reaction of Equation 1.

Even though the chemistry of the system is not well understood, it is interesting to note that for any constant $x^*_M$, the acid dependency curves of Figure 2 are almost parallel. This phenomenon suggests that in the range of the data, the "effective" chemistry taking place is the same, as the acidity varies, for any constant aqueous concentration. This is true for Ce and the other lower lanthanides.

At lower acidities, the extraction is higher, but the slope is farthest from -3.0. Silver nitrate tests showed very little chloride present in the organic phase, therefore, the mechanism change cannot be explained in terms of chloro-complexes that might have been extracted as it is the case for the higher rare earths at higher acidities. It is believed, however, that at the low acidities studied, cerium hydroxo-complexes such as $[\text{Ce(OH)}_2]^+$ and $[\text{Ce(OH)}]^+$ become more appreciable. Assuming that an effective chemical reaction is taking place, of the same form as Equation 1 but with a variable stoichiometry, the reaction can be written as:
\[ M(OH)_n^{+(3-n)} + (3-n)H_2G_2 \rightarrow M(OH)_n(HG_2)^{(3-n)} + (3-n)H^+ \]  (30)

where \( n \) is an integer and varies from 0 to 2. The acid dependency relation for the above mechanism is

\[ \ln y_M^* = (\ln K_M)[H_2G_2]^{(3-n)} x_M^* - (3-n) \ln H^+ \]  (31)

For any constant \( x_M^* \) at the lower acidities, \( n \) approaches 2 and the slope approaches -1.0 where at the higher acidities, \( n \) is zero and the slope approaches -3.0. It should be noted that the free solvent concentration also varies slightly and it is a function of the organic concentration. In fact, \([H_2G_2]\) at equilibrium is \( C_I = 2(3-n)y_M^* \) where \( C_I \) is the initial D2EHPA concentration on a monomer basis.

From the equilibrium curves in Figure 1 it is noted that as \( x_M^* \) increases for any \( H^+ \) parameter, the extraction reaches a maximum and then decreases. This is probably due to the variation of the ionic strength of the solution and also due to the intermolecular interaction effects of the metal ions in both phases. From the yttrium equilibrium data reported by Harada and Smutz (13), it is observed that when the log of the distribution coefficient is plotted against log \( x_M^* \), a constant value of the distribution coefficient is maintained for all organic concentrations < 0.015 M. This constancy suggests that at low concentrations there are no interaction effects between the intermolecular forces of Y in either of the two
phases. However, at organic concentrations of > 0.015 M, the distribution coefficient decreases as $x_M^*$ increases. This indicates an interaction effect in the organic phase, greater than that in the aqueous phase, due to the intermolecular forces of Y. As a result, the extractability decreases. At aqueous concentrations of Y greater than one tenth of the saturation concentration of $YCl_3 \cdot 6H_2O$ at a specific acidity, the distribution coefficient was observed to increase slightly once again. This shows that the interaction effect in the aqueous phase between metal ions becomes more pronounced. However, the interaction in the organic phase is still high.

Even though data in the very low concentration region are not available for CeCl$_3$, NdCl$_3$, or SmCl$_3$, it is reasonable to assume that the interaction effects mentioned above are also present in the extraction of each pure element of Ce, Nd and Sm. If there was no interaction, the equilibrium curves would be straight lines and thus no maximum would be observed. The interaction effect is probably greater in the organic phase due to the fact that the hydration number of the metal in the organic phase is much smaller than that in the aqueous phase. In other words, the hypothetical solubility of $M(HG_2)_{3}$ compound in the organic phase is less than the solubility of $MCl_3$ in the aqueous phase.

All the effects and deviations mentioned above probably change the activity coefficient of each ion present when a
change in the system's variables occurs. Since it is not possible at this time to measure the activity of each ion present, it is necessary to measure concentrations. The data can then be correlated in order to predict the equilibrium of the system.

Development of Model for Predicting CeCl$_3$ Equilibrium Data

In a solvent extraction system containing one lanthanide, the organic concentration, $y_m^*$, of the metal ion is a function of the aqueous concentration, $x_m^*$, and the aqueous hydrogen ion concentration $H^+$. In mathematical terms this can be stated as follows:

$$ y_m^* = f(x_m^*, H^+) $$

(32)

where $x_m^*$ and $H^+$ are the independent variables and $y_m^*$ the dependent variable. It is desired to obtain a mathematical model with two independent variables that can be used to correlate the equilibrium data for CeCl$_3$ in Table 1. Since the form of the model was proposed for Sm and Nd in previous work (16) it will also be utilized to correlate the cerium data. The model is as follows:

$$ y_{Ce}^* = a_2 x^2 e^{-a_4 + a_5 H + a_6 H^2} $$

(33)
where \((a_1, \ldots, a_6)\) is a vector of arbitrary constants to be evaluated empirically. Since the above model is non-linear in the parameters, a non-linear correlation technique is required to fit the experimental data. The Hartley modified Gauss-Newton method (14) was selected and will be used throughout this study to fit the data in the least squares sense. A summary of the technique was given in previous work (16).

Since the non-linear method of estimation involves an iterative process, a good initial estimate of the parameters is essential in order to activate the iteration procedure and assure convergence. The computer routine for the modified Gauss-Newton technique was programmed for the IBM 360 computer and was utilized to obtain the parameter vector \((a_1, \ldots, a_6)\) which minimizes the sum of squares of the residuals. The initial "guess" of the parameter vector used for the CeCl₃ data is \((0.0206, 0.262, -0.588, -0.954, -2.726, 1.981)\). The model and the parameter vector obtained after convergence are

\[
y_{Ce}^* = a_1 x^2 e^{a_3 x} (a_4 + a_5 H + a_6 H^2)
\]

where \((a_1, \ldots, a_6) = (0.01656, 0.3588, -0.8581, -0.7032, -5.389, 4.927)\). Equation 34 predicts best in the ranges \(0.15 \leq x \leq 1.4\) and \(0.3 \leq H \leq 0.7\) with an average error (residual divided by experimental) of less than 3%. This model was used to calculate \(y_{Ce}^*\) for different constant acidity parameters \(H^+\) and
the results were plotted in Figure 1 as a comparison with the experimental data.

For simplicity, the models obtained in previous work (16) for predicting the equilibria of NdCl₃ and SmCl₃ are presented here in Equations 35 and 36.

\[ y_{Nd}^* = b_2 x_1^* e^{b_3 x_1^* (b_4 + b_5 H + b_6 H^2)} \]  
where \((b_1, \ldots, b_6) = (0.02048, 0.2577, -0.5758, -0.9282, -2.9195, 0.5755)\).

\[ y_{Sm}^* = c_2 x_1^* e^{c_3 x_1^* (c_4 + c_5 H + c_6 H^2)} \]  
where \((c_1, \ldots, c_6) = (0.08674, 0.2448, -0.4742, -0.9287, 0.3133, -1.4158)\).

Equilibrium for the Binary System SmCl₃-NdCl₃-HCl-H₂O-1 M D2EHPA-Amsco

Equilibrium data for the above binary solute system were obtained for the purpose of studying the interaction effects when two different metal ions are extracted simultaneously. The total aqueous lanthanide concentration, \(X_T(M,N)\), was kept constant and the mole fraction of samarium in the aqueous phase \(x_{Sm}/X_T\) or \(N_{Sm,A}(M,N)\) was varied from 0.1 to 0.9. The aqueous acidity was also varied from 0.35 M to 0.9 M. For brevity, the symbols \((M,N)\), indicating a binary mixture, will be omitted
unless it is necessary for clarity. Also \( x_{Sm} / x_T \) and \( N_{Sm,A} \) will be used interchangeably.

Equilibrium data and separation factors for the systems where \( x_T \) is approximately 0.64 M and 0.11 M are given in Tables 2 and 3 respectively. In order to obtain a constant acid concentration parameter \( H^+ \), the total organic concentration, \( Y_T \), of Tables 2 and 3 was plotted against \( H^+ \) at a constant \( N_{Sm,A} \) and shown in Figures 3 and 4 respectively. The values of \( Y_T \), which correspond to a constant acidity at different mole fractions of Sm in the aqueous phase, were read from the above graphs and plotted in Figure 5 and 6 with the acidity as a parameter. The end-points in Figures 5 and 6 were obtained from single-component data. If one assumes that, under the specific conditions of the system, all of the rare earths in the aqueous phase are pure Nd (\( N_{Sm,A} = 0 \)) then Equation 35 is used to calculate \( y_{Nd}^* \). Likewise, if all of the lanthanides are pure Sm (\( N_{Sm,A} = 1 \)), Equation 36 gives \( y_{Sm}^* \).

It should be noted that in Figure 5, the \( H^+ = 0.4 \) M straight line is probably in great error. This is due to the fact that the pure Sm point, as predicted by Equation 36, is well above the experimental range. The concentration predicted is probably hypothetical since at this concentration gel formation occurs.

In Figures 5 and 6, a straight line is drawn between the pure Nd and pure Sm organic concentrations for each acidity. This line predicts the total organic concentration as a
Table 2. Equilibrium data and separation factors for the system SmCl₃-NdCl₃-HCl-H₂O-1 M D2EHPA-Amsco at ~ 0.64 M total aqueous concentration

<table>
<thead>
<tr>
<th>Aqueous phase concentrations (mole/l.)</th>
<th>Mole fraction</th>
<th>Organic phase concentrations (moles/l.)</th>
<th>Separation factors (βₘ₉,Ν₉)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>Total RE</td>
<td>Sm</td>
<td>Nd</td>
</tr>
<tr>
<td>-----</td>
<td>----------</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
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<td>0.6378</td>
<td>0.08118</td>
<td>0.5568</td>
</tr>
<tr>
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<td>0.6358</td>
<td>0.1897</td>
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<td>0.6308</td>
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</table>

*Gel formation
Table 3. Equilibrium data and separation factors for the system SmCl$_3$-NdCl$_3$-HCl-H$_2$O-1 M D2EHPA-Amsco at ~0.11 M total aqueous concentration

<table>
<thead>
<tr>
<th>Aqueous phase concentrations (mole/l.)</th>
<th>Mole fraction $x_{Sm}/x_T$</th>
<th>Organic phase concentrations (mole/l.)</th>
<th>Separation factors $\beta_{Sm,Nd}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>Total RE</td>
<td>Sm</td>
<td>Nd</td>
</tr>
<tr>
<td>-----</td>
<td>----------</td>
<td>----</td>
<td>----</td>
</tr>
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<td>0.1080</td>
<td>0.01118</td>
<td>0.09371</td>
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<td>0.394</td>
<td>0.1079</td>
<td>0.05717</td>
<td>0.05076</td>
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<td>0.009544</td>
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<td>0.1098</td>
<td>0.01783</td>
<td>0.09205</td>
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</tr>
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</tr>
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<td>0.06566</td>
<td>0.04946</td>
</tr>
<tr>
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<td>0.844</td>
<td>0.1115</td>
<td>0.03497</td>
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</tr>
<tr>
<td>0.813</td>
<td>0.1091</td>
<td>0.07839</td>
<td>0.03078</td>
</tr>
</tbody>
</table>
Figure 3. Acid dependency curves for the system SmCl$_3$-NdCl$_3$-HCl-H$_2$O-1 M D2EHPA-Amsco at $X_T \sim 0.64$ M
Figure 4. Acid dependency curves for the system SmCl$_3$-NdCl$_3$-HCl-H$_2$O-1 M D2EHPA-Amsco at $X_T \sim 0.11$ M.
Figure 5. Total lanthanide concentration in the organic phase for the system SmCl$_3$-NdCl$_3$-HCl-H$_2$O-1 M D2EHPA-Amsco at $X_T \sim 0.64$ M
Figure 6. Total lanthanide concentration in the organic phase for the system SmCl$_3$-NdCl$_3$-HCl-H$_2$O-1 M D2EHPA-Amsco at $X_T \sim 0.11$ M
function of \( N_{\text{Sm}}/N_{\text{Nd}} \) and \( H^+ \) if interaction effects between Sm and Nd were absent. In other words, ideal behavior is followed. The straight line behavior for a mixture of two elements, extracted simultaneously, is obtained by making several simplifying assumptions analogous to Raoult's Law for ideal solutions. Suppose that the system variables \((X_T, N_{\text{Sm}}, N_{\text{Nd}}, H)\) are specified, then, one may assume that the Sm and Nd in the aqueous phase could be separated into two individual compartments, each occupying a volume proportional to its mole fraction. Further, the content of each compartment may be equilibrated with a corresponding equal volume of D2EHPA. After equilibrium has been attained and phases separated, the concentration of each pure element in the organic phase, \( y_{\text{Sm}}^* \) and \( y_{\text{Nd}}^* \), may be obtained by measuring the concentration in each of the hypothetical compartments. However, if the content of each compartment in the organic phase is allowed to mix before the concentration of each element is measured, then the mixture concentration would differ from that of \( y_{\text{Sm}}^* \) and \( y_{\text{Nd}}^* \) since they are contained in a greater volume. In fact, the concentration of each species in the organic phase would be its concentration in the pure state multiplied by its mole fraction in the aqueous phase. The concentration of each element in the organic phase extracted as described above may be expressed as:
It would be convenient at this time to define the new terms \( \bar{y}_{Sm} \) and \( \bar{y}_{Nd} \) as the "partial extractabilities" of each species. It should be emphasized again that the partial extractabilities are obtained only when the elements are extracted without interfering with each other. Nevertheless, there is an inherent constant interaction effect between like ions in the extraction of the pure components, as mentioned in the Equilibrium of CeCl\(_3\)-HCl-H\(_2\)O-1 M D2EHPA-Amsco section.

Therefore, the total organic concentration, if no interaction exists between Sm and Nd, would be the sum of the partial extractabilities,

\[
\bar{y}_T = y_{Sm}^* \frac{x_{Sm}}{X_T} + y_{Nd}^* \frac{x_{Nd}}{X_T},
\]

where \( \bar{y}_T \) is the total organic concentration if interaction is absent. The above equation indicates a straight line relationship between \( y_{Nd}^* \) and \( y_{Sm}^* \) as shown in Figures 5 and 6. This straight line relationship is derived by making the assumption that in the extraction process, the intermolecular forces of
attraction in the binary system are the same as in the single-component system for both phases. In other words, there are no interaction or synergistic effects present in the binary system. From the actual data in Figures 5 and 6, however, it is noted that the experimental $Y_T$ deviates from linearity. The difference between the experimental value and the corresponding value on the straight line, $\Delta Y_T$, is a measure of the total interaction effect. Once $\Delta Y_T$ is known under the conditions of the system, then the total organic concentration may be calculated as follows:

$$Y_T = y_{Sm}^* \frac{x_{Sm}}{x_T} + y_{Nd}^* \frac{x_{Nd}}{x_T} + \Delta Y_T.$$  \hspace{1cm} (40)

The data obtained at a total aqueous concentration, $x_T$, of approximately 0.64 M represents the concentration at which extraction is near a maximum for any one acidity. This is observed from the CeCl$_3$ equilibrium data curves in Figure 1 and also in previous work (16) for the equilibrium data of NdCl$_3$ and SmCl$_3$. At the above $x_T$, where extraction is a maximum, it is expected that the interaction effects, $\Delta Y_T$, will also be a maximum for any $x_{Sm}/x_T$ and any acidity $H^+$. A comparison between the total interaction effects in Figures 5 and 6 indicates that the above expectation is true. From either Figure 5 or 6, it is also observed that at any constant $x_{Sm}/x_T$, the deviation from linearity becomes less as the acidity
increases. From the above observations, it seems that the total interaction effect is a direct function of the total extraction and that as the extraction decreases, linearity is approached.

It is noted from Figures 5 and 6 that $\Delta Y_T$ is positive for most of the $X_{Sm}/X_T$ range but becomes slightly negative at high mole fractions of Sm in the aqueous phase. Even though the data are subject to analytical errors, possible explanations for this discrepancy are as follows: (1) At high mole fractions of Sm in the aqueous phase, the mole fraction of Sm in the organic phase approaches 1 since $\beta_{Sm,Nd} \sim 8.8$; thus, intermolecular interaction is greater in the organic (2). The hydration number in the organic phase probably changes as the extraction changes, thus increasing the interaction in the organic phase.

From Tables 2 and 3, it is seen that the separation factor, $\beta_{Sm,Nd}$ variation for all conditions studied is not significant enough to draw any conclusions. The fact that the separation factor for the Sm-Nd system remains approximately constant for all conditions studied, was observed in previous work (16). Therefore, an arithmetic average of $\beta_{Sm,Nd}$ should be utilized for predicting equilibrium data. The average $\beta_{Sm,Nd}$ for $X_T \sim 0.64$ M is 8.79 and for $X_T \sim 0.11$ is 7.99. This is close to the value reported by Pierce and Peck (28) when Sm and Nd were extracted with D2EHPA from aqueous perchlorate solutions.
In order to understand better the total interaction effect, $\Delta Y_T$, it is essential to study the behavior of each individual component in the organic phase, $y_{\text{Sm}}$ and $y_{\text{Nd}}$.

The organic concentrations of the individual components $y_{\text{Sm}}$ and $y_{\text{Nd}}$ were calculated employing Equations 15 and 16 respectively. The variable $x_{\text{Nd}}/x_{\text{Sm}}$ in the aqueous phase was specified while the corresponding $Y_T$ for each acidity was read from Figures 5 and 6. The arithmetic average of $\beta_{\text{Sm},\text{Nd}}$ given above was utilized for each of the two total aqueous concentrations. The individual organic concentrations calculated for $H^+ = 0.5\,\text{M}$ and $X_T \approx 0.64\,\text{M}$ as well as the corresponding $Y_T$ are plotted in Figure 7. It is noted from Figure 7 that the total interaction effect $\Delta Y_T$ is equal to the summation of the individual interaction effects $\Delta y_{\text{Sm}}$ and $\Delta y_{\text{Nd}}$. Each interaction effect is the deviation of the concentration of each element in the organic phase from the partial extractability (ideal behavior) as defined in Equations 37 and 38. Therefore,

$$\Delta y_{\text{Sm}} = y_{\text{Sm}} - \bar{y}_{\text{Sm}} = y_{\text{Sm}} - y_{\text{Sm}}(x_{\text{Sm}}/X_T) \tag{41}$$

$$\Delta y_{\text{Nd}} = y_{\text{Nd}} - \bar{y}_{\text{Nd}} = y_{\text{Nd}} - y_{\text{Nd}}(x_{\text{Nd}}/X_T) \tag{42}$$

The above interaction effects are important for predicting equilibrium data and they will be correlated as a function of $x_{\text{Sm}}/X_T$ and aqueous acidity. A reliable correlation for predicting $\Delta y_{\text{Sm}}$ and $\Delta y_{\text{Nd}}$ can be employed to calculate the total
Figure 7. Organic concentrations for the system SmCl₃-NdCl₃-HCl-H₂O-1 M D2EHPA-Amsco at H⁺ = 0.5 M and Xₜ = 0.64 M
Table 4. Sm-Nd interaction effects for the system SmCl₃-NdCl₃-HCl-H₂O-1 M D2EHPA-
Amsco at ~ 0.64 M total aqueous concentration

<table>
<thead>
<tr>
<th>Acidity (moles/1.)</th>
<th>Mole fraction (moles/1.)</th>
<th>Experimental</th>
<th>Predicted</th>
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<td></td>
<td>x Sm/x T</td>
<td>Y T</td>
<td>Δy Sm</td>
</tr>
<tr>
<td>HCl</td>
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<td></td>
<td></td>
</tr>
<tr>
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<td>0</td>
<td>0.0597</td>
<td>---</td>
</tr>
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Table 5. Sm-Nd interaction effects for the system SmCl$_3$-NdCl$_3$-HCl-H$_2$O-1 M D2EHPA-Amsco at ~ 0.11 M total aqueous concentration

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<th>Mole fraction</th>
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Table 5 (Continued)

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<th>Deviations from ideality</th>
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<th>Predicted</th>
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<td>$\Delta y_{Nd}$</td>
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organic concentration $Y_T$.

\[
Y_T = Y_Sm \left( \frac{x_{Sm}}{X_T} \right) + \Delta Y_{Sm} + Y_{Nd} \left( \frac{x_{Nd}}{X_T} \right) + \Delta Y_{Nd}.
\]  

Using Equations 41 and 42, $\Delta Y_{Sm}$ and $\Delta Y_{Nd}$ were calculated as a function of $x_{Sm}/X_T$ and $H^+$. The results are presented in Tables 4 and 5 for $X_T \approx 0.64$ M and 0.11 M respectively. The predicted values are also shown in Tables 4 and 5 for comparison.

Models for Predicting $\Delta Y_{Sm}$ and $\Delta Y_{Nd}$ for the System SmCl$_3$-NdCl$_3$-HCl-H$_2$O-1 M D2EHPA-Amsco

The individual component interaction effects $\Delta Y_{Sm}$ and $\Delta Y_{Nd}$, which were presented in Tables 4 and 5, are shown in Figures 8 and 9 as a function of $x_{Sm}/X_T$ and acidity. In order to correlate the data in Figure 8 for $X_T \approx 0.64$ M as a function of $N_{Sm,A}$ and $H^+$, the following two empirical models are proposed:

\[
\Delta Y_{Sm} = a_1 N_{Sm,A} (1 - N_{Sm,A}) a_3 (a_4 - N_{Sm,A}) e^{a_5 H^+} \quad (44)
\]

\[
\Delta Y_{Nd} = b_1 N_{Sm,A} (1 - N_{Sm,A}) b_3 b_4 e^{b_5 H^+} \quad (45)
\]

where $(a_1, \ldots, a_5)$ and $(b_1, \ldots, b_4)$ are arbitrary constants to be evaluated empirically. Since the above models are non-linear in the parameters, the Gauss-Newton (14) analogy will be
Figure 8. Sm and Nd deviations from ideality for the system SmCl₃-NdCl₃-HCl-H₂O-1 M D2EHPA-Amsco at Xₜ ~ 0.64 M
Figure 9. Sm and Nd deviations from ideality for the system SmCl$_3$-NdCl$_3$-HCl-H$_2$O-1 M D2EHPA-Amsco at $X_T \sim 0.11$ M
utilized to fit the experimental data. The parameter vectors of Equations 44 and 45 converged to

\[(a_1, \ldots, a_5) = (2.2023, 0.7422, 0.4096, 0.9008, -4.002) \] (44a)

and

\[(b_1, \ldots, b_4) = (-0.4239, 0.5075, 1.1582, -3.8522) \] (45a)

respectively. Equation 44 predicts the data best in the ranges \(0.1 \leq N_{Sm,A} \leq 0.9\) and \(0.5 \leq H^+ \leq 0.8\) with an average error of less than 7%. Equation 45 predicts best in the ranges \(0.05 \leq N_{Sm,A} \leq 0.9\) and \(0.4 \leq H^+ \leq 0.8\) with an average error of less than 4%.

The data in Figure 9 for \(X_T \sim 0.11\) M are correlated non-linearly as previously described. The mathematical models and parameter vectors are:

\[\Delta y_{Sm} = C_1 N_{Sm,A} (1 - N_{Sm,A}) C_2 e^{C_3 H^+} \] (46)

where \((C_1, \ldots, C_4) = (0.5612, 0.6775, 1.2931, -3.4724),\)

\[\Delta y_{Nd} = d_1 N_{Sm,A} (1 - N_{Sm,A}) d_2 e^{d_3 H^+} \] (47)

where \((d_1, \ldots, d_4) = (-0.3099, 0.5959, 1.2315, -3.3533).\)

Equation 46 predicts the data best in the ranges \(0.05 \leq N_{Sm,A} \leq 0.9\) and \(0.4 \leq H^+ \leq 0.7\) with an average error of less than 3%.
Equation 47 predicts best in the ranges, \(0.1 \leq N_{Sm,A} \leq 0.9\) and \(0.4 \leq H^+ \leq 0.7\) with an average error of less than 3.5%.

Since the individual interaction effects described by Equations 44, 45, 46 and 47 are a function of the aqueous phase variables only, they can be substituted directly into Equation 43 in order to calculate the total organic concentration \(Y_T\).

**Equilibrium for the Ternary System**

\[\text{SmCl}_3-\text{NdCl}_3-\text{CeCl}_3-\text{HCl}-\text{H}_2\text{O}-1 \text{ M D2EHPA-Amsco}\]

Equilibrium data for the above ternary system were obtained in order to measure the interaction effect of each component and study the separation factor variation, if any, under different conditions of the equilibrated aqueous phase. The total lanthanide concentration in the equilibrated aqueous phase, \(X_T(Sm,Nd,Ce)\), was kept constant at approximately 0.64 M while the acidity was varied from 0.4 M to 0.8 M. The mole fraction of cerium in the equilibrated aqueous phase was also varied from 0.1 to 0.9 while the mole fraction of Sm on a cerium-free basis, \(X_{Sm}^{\text{Sm}}/(X_{Sm} + X_{Nd})\), was varied from 0.1 to 0.9.

The equilibrium data, and separation factors under the conditions at which \(X_{Sm}^{\text{Sm}}/(X_{Sm} + X_{Nd}) = 0.1, 0.5\) and 0.9 are presented in Tables 6, 7 and 8 respectively. In order to adjust the data to a constant acid concentration parameter, the total organic concentration, \(Y_T(Sm,Nd,Ce)\) was plotted against \(H^+\) at a constant parameter, \(N_{Ce,A}\). The data from
Table 6. Equilibrium data and separation factors for the system SmCl₃-NdCl₃-CeCl₃-HCl-H₂O-1 M D2EHPA-Amsco at $X_T \approx 0.64$ M and $x_{Sm}/(x_{Sm} + x_{Nd}) \approx 0.1$

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<th>Total RE</th>
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Separation factors

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Table 7. Equilibrium data and separation factors for the system SmCl$_3$-NdCl$_3$-CeCl$_3$-HCl-H$_2$O-1 M D2EHPA-Amsco at $x_T \sim 0.64$ M and $x_{Sm}/(x_{Sm} + x_{Nd}) \sim 0.5$

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<tr>
<th>No.</th>
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<th>Sm</th>
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<th>Ce</th>
<th>Total RE</th>
<th>Sm</th>
<th>Nd</th>
<th>Ce</th>
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<td>1</td>
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<td>0.1565</td>
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Separation factors

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<th>$\beta_{Nd,Ce}$</th>
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Table 8. Equilibrium data and separation factors for the system SmCl$_3$-NdCl$_3$-CeCl$_3$-HCl-H$_2$O-1 M D2EHPA-Amsco at $X_T \sim 0.64$ M and $x_{Sm}^S/(x_{Sm}^S + x_{Nd}^S) \sim 0.9$

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<tr>
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<th>Sm</th>
<th>Nd</th>
<th>Ce</th>
<th>Total RE</th>
<th>Sm</th>
<th>Nd</th>
<th>Ce</th>
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Separation factors

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<th>$\beta_{Sm, Nd}$</th>
<th>$\beta_{Nd, Ce}$</th>
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<td>8.52</td>
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Tables 6, 7 and 8 are given in Figures 10, 11 and 12 respectively. The values of $Y_T(Sm,Nd,Ce)$ corresponding to different mole fractions of cerium in the aqueous phase were read from the above graphs and plotted in Figures 13, 14 and 15 respectively, with the acid concentration as a parameter. The end-points in Figures 13, 14 and 15 at 0.0% cerium ($N_{Ce,A} = 0$) were determined using the Sm-Nd mixture data. From the ternary system, if the mole fraction of Sm in the aqueous phase is specified on a cerium-free basis, $x_{Sm}/(x_{Sm} + x_{Nd})$, then the values of $Y_T(Sm,Nd)$ can be read from Figure 5 at each acidity and plotted in Figures 13, 14 and 15. The above values can also be calculated directly employing Equation 43. However, one must realize that in this relation instead of substituting the mole fraction of Sm, $x_{Sm}/X_T$, of the ternary system, one substitutes the mole fraction of Sm on a cerium-free basis, $x_{Sm}/(x_{Sm} + x_{Nd})$. The end-points of Figures 13, 14 and 15 at 100% cerium ($N_{Ce,A} = 1$) were calculated using Equation 34. This equation can be used, assuming that under the conditions of the system all of the rare earths, $X_T(Sm,Nd,Ce)$, are pure cerium.

The individual component interaction effects $\Delta Y_{Sm}$, $\Delta Y_{Nd}$ and $\Delta Y_{Ce}$ of the ternary system may be obtained in an analogous manner as explained in the section entitled Equilibrium of SmCl$_3$-NdCl$_3$-HCl-H$_2$O-1 M D2EHPA-Amsco. The partial extractabilities in the ternary system are defined as:
Figure 10. Acid dependency curves for the system $\text{SmCl}_3$-$\text{NdCl}_3$-$\text{CeCl}_3$-$\text{HCl}$-$\text{H}_2\text{O}$-1 M D2EHPA-Amsco at $X_T \sim 0.64$ M and $x_{\text{Sm}}/(x_{\text{Sm}} + x_{\text{Nd}}) \sim 0.1$
Figure 11. Acid dependency curves for the system SmCl$_3$-NdCl$_3$-CeCl$_3$-HCl-H$_2$O-1 M D2EHPA-Amsco at $X_T$ $\approx$ 0.64 M and $x_{Sm}/(x_{Sm} + x_{Nd})$ $\approx$ 0.5
Figure 12. Acid dependency curves for the system SmCl$_3$-NdCl$_3$-CeCl$_3$-HCl-H$_2$O-1 M D2EHPA-Amsco at $X_T$ ~ 0.64 and $x_{Sm}/(x_{Sm} + x_{Nd})$ ~ 0.9.
Figure 13. Total concentration in the organic phase for the system SmCl$_3$-NdCl$_3$-CeCl$_3$-HCl-H$_2$O-1 M D2EHPA-Amsco at $X_T \sim 0.64$ M and $x_{Sm}/(x_{Sm} + x_{Nd}) \sim 0.1$. 
Figure 14. Total concentration in the organic phase for the system $\text{SmCl}_3 - \text{NdCl}_3 - \text{CeCl}_3 - \text{HCl} - \text{H}_2\text{O}$-1 M D2EHPA-Amsco at $X_T \sim 0.64$ M and $x_{\text{Sm}} / (x_{\text{Sm}} + x_{\text{Nd}}) \sim 0.5$
Figure 15. Total concentration in the organic phase for the system SmCl$_3$-NdCl$_3$-CeCl$_3$-HCl-H$_2$O-1 M D2EHPA-Amsco at $X_T \sim 0.64$ M and $x_{\text{Sm}}/(x_{\text{Sm}} + x_{\text{Nd}}) \sim 0.9$.
The above straight lines are plotted in Figure 16 for the conditions where \( H^+ = 0.5 \text{ M} \) and \( x_{\text{Sm}}/(x_{\text{Sm}} + x_{\text{Nd}}) = 0.5 \). These lines represent the extraction of each component under the assumption that the metal ions do not interact during the extraction process. In other words, it is assumed that ideal behavior analogous to Raoult's law occurs. Under the above assumptions, therefore, the total organic concentration in the ternary system may be predicted by the summation of the partial extractabilities,

\[
\overline{Y}_{\text{Sm}} = Y_{\text{Sm}}^* \frac{x_{\text{Sm}}}{x_T} \tag{48a}
\]

\[
\overline{Y}_{\text{Nd}} = Y_{\text{Nd}}^* \frac{x_{\text{Nd}}}{x_T} \tag{48b}
\]

\[
\overline{Y}_{\text{Ce}} = Y_{\text{Ce}}^* \frac{x_{\text{Ce}}}{x_T} \tag{48c}
\]

It should be noted that the right hand side of Equation 49 is a function of the equilibrium aqueous phase variables only. This is true since the pure component organic concentrations \( Y_{\text{Ce}}^* \), \( Y_{\text{Nd}}^* \) and \( Y_{\text{Sm}}^* \) are a function of the total aqueous concentration and aqueous acidity as shown in Equations 34, 35 and 36 respectively.
Figure 16. Organic concentrations for the system SmCl₃-
NdCl₃-CeCl₃-HCl-H₂O-1 M D2EHPA-Amsco at
H⁺ = 0.5 M, Xₜ ≈ 0.64 M and Xₜ/Xₚ ≈ 0.5
From Figure 16, it is observed that the experimental data for the total organic concentration deviate from the linear relation of Equation 49. This is expected since during the extraction process there is a definite interaction between the different metal ions in both phases and also between like ions. These interactions work synergistically and increase the total organic concentration from that of Equation 49 by a $\Delta Y_T$. As previously discussed, the total interaction effect is the summation of all the individual component interaction effects,

$$\Delta Y_T = \Delta Y_{Sm} + \Delta Y_{Nd} + \Delta Y_{Ce} . \tag{50}$$

The addition of Equations 49 and 50 gives the $Y_T$ as measured experimentally. The above interaction effects need to be determined and correlated as a function of $x_{Ce}/x_T$, $H^+$ and $x_{Sm}/(x_{Sm} + x_{Nd})$. Each individual term may be obtained by subtracting the partial extractability $y_M$ from the corresponding experimental concentration at each condition studied.

$$\Delta Y_{Sm} = Y_{Sm} - \bar{y}_{Sm} = y_{Sm} - y^*_{Sm}(x_{Sm}/x_T) \tag{51a}$$

$$\Delta Y_{Nd} = Y_{Nd} - \bar{y}_{Nd} = y_{Nd} - y^*_{Nd}(x_{Nd}/x_T) \tag{51b}$$

$$\Delta Y_{Ce} = Y_{Ce} - \bar{y}_{Ce} = y_{Ce} - y^*_{Ce}(x_{Ce}/x_T) \tag{51c}$$

Before this is done, however, we need to discuss the separation factor variation.
It is noted from Tables 6, 7 and 8 that the separation factor of any pair of elements in the Sm-Nd-Ce system remains approximately constant under all conditions studied. As discussed previously, the separation factor remained constant in the Sm-Nd binary system for all conditions studied. Another observation to be made from the separation factor studies is that $\beta$ for each pair in the ternary system is almost the same as in the binary system. The average $\beta_{\text{Sm, Nd}}$ in Tables 6, 7 and 8 for the ternary system is $\approx 8.96$ while that of the binary system in Tables 2 and 3 is $\approx 8.40$. In order to verify that $\beta_{\text{Sm, Ce}}$ and $\beta_{\text{Nd, Ce}}$ in the ternary system are also the same as in the corresponding binary systems, several equilibrium data points were obtained for the Sm-Ce and Nd-Ce systems. The equilibrium data and separation factors are presented in Table 9. It is noted from Tables 6, 7 and 8 that the average $\beta_{\text{Sm, Ce}}$ and $\beta_{\text{Nd, Ce}}$ in the ternary system are 19.08 and 2.23 respectively. From Table 9 for the binary systems, $\beta_{\text{Sm, Ce}} = 18.9$ and $\beta_{\text{Nd, Ce}} = 2.01$. The values are all very close, well within the experimental error, and one may conclude that the separation factor in a binary system remains the same for the corresponding pairs in the ternary system.

The organic concentration of each component, $Y_{\text{Sm}}$, $Y_{\text{Nd}}$ and $Y_{\text{Ce}}$ were calculated through Equations 22, 23 and 24, using an average separation factor. All the aqueous phase variables were specified and the corresponding $Y_T(\text{Sm, Nd, Ce})$ for each
Table 9. Equilibrium data and separation factors for the systems (SmCl$_3$-CeCl$_3$ and NdCl$_3$-CeCl$_3$) - HCl-H$_2$O-1 M D2EHPA-Amsco at ~ 0.64 M total aqueous concentration

<table>
<thead>
<tr>
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<th>HCl (moles/l.)</th>
<th>Total RE (moles/l.)</th>
<th>Sm (moles/l.)</th>
<th>Nd (moles/l.)</th>
<th>Ce (moles/l.)</th>
<th>Sm (moles/l.)</th>
<th>Nd (moles/l.)</th>
<th>Ce (moles/l.)</th>
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<tr>
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Separation factors

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<th>$\beta_{Nd,Ce}$</th>
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acidity was read from Figures 13, 14 and 15. The average separation factors utilized in the expressions are $\beta_{\text{Sm,Ce}} = 19.50$, $\beta_{\text{Sm,Nd}} = 9.06$, and $\beta_{\text{Nd,Ce}} = 2.16$. These values are near the ones published by Pierce and Peck (28). The composition of the organic phase in the ternary system under the conditions that $H^+ = 0.5$ M and $x_{\text{Sm}}/(x_{\text{Sm}} + x_{\text{Nd}}) = 0.5$ for various $x_{\text{Ce}}/X_T$ are plotted in Figure 16. The above Figure shows the individual interaction effects clearly. Since the interaction effects defined by Equations 51a, b and c are important in predicting equilibrium data, they will be correlated as a function of $x_{\text{Ce}}/X_T$, $x_{\text{Sm}}/(x_{\text{Sm}} + x_{\text{Nd}})$ and $H^+$. The calculated values are tabulated as a function of $H^+$ and $x_{\text{Ce}}/X_T$ in Tables 10, 11 and 12 for the conditions $x_{\text{Sm}}/(x_{\text{Sm}} + x_{\text{Nd}}) = 0.1, 0.5$ and 0.9, respectively. The predicted values are also shown in these tables for comparison. Once a correlation is available to predict $\Delta y_{\text{Sm}}, \Delta y_{\text{Nd}}$ and $\Delta y_{\text{Ce}}$ in terms of the equilibrium aqueous phase variables, then the organic concentration may be calculated as follows:

$$Y_T = Y_{\text{Sm}}^* \left(\frac{x_{\text{Sm}}}{X_T}\right) + \Delta y_{\text{Sm}} + Y_{\text{Nd}}^* \left(\frac{x_{\text{Nd}}}{X_T}\right) + \Delta y_{\text{Nd}} + Y_{\text{Ce}}^* \left(\frac{x_{\text{Ce}}}{X_T}\right) + \Delta y_{\text{Ce}}.$$ (52)
Table 10. Sm-Nd-Ce interaction effects for the system SmCl$_3$-NdCl$_3$-CeCl$_3$-HCl-H$_2$O-1 M D2EHPA-Amsco at $X_T$ ~ 0.64 M and $x_{Sm}/(x_{Sm} + x_{Nd})$ ~ 0.1

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Table 11. Sm-Nd-Ce interaction effects for the system SmCl$_3$-NdCl$_3$-CeCl$_3$-HCl-H$_2$O-1 M D2EHPA-Amsco at $X_T \sim 0.64$ M and $x_{Sm}/(x_{Sm}+x_{Nd}) \sim 0.5$

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Table 12. Sm-Nd-Ce interaction effects for the system SmCl₃-NdCl₃-CeCl₃-HCl-H₂O-1 M D2EHPA-Amsco at Xₜ ~ 0.64 M and x₅₉/ₙ₉ ~ 0.9

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<th>Predicted</th>
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</thead>
<tbody>
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<td>ΔY₅₉</td>
<td>ΔYₙ₉</td>
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<td>0.05049 -0.00124 -0.02583</td>
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<td>0.02226 -0.00013 -0.00706</td>
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<tr>
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<td>Mole fraction</td>
<td>Org. conc. (moles/l.)</td>
<td>Aqueous</td>
<td>Deviations from ideality</td>
</tr>
<tr>
<td>----------------</td>
<td>----------------</td>
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<td>---------</td>
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<td></td>
<td>Experimental</td>
</tr>
<tr>
<td></td>
<td>$x_{Ce}/x_T$</td>
<td>Total RE</td>
<td>$\Delta Y_{Sm}$</td>
<td>$\Delta Y_{Nd}$</td>
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<td>-0.000101</td>
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<tr>
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<td>0.0283</td>
<td>0.01121</td>
<td>-0.000013</td>
</tr>
</tbody>
</table>
Models for Predicting Individual Interaction Effects for the System SmCl₃-NdCl₃-CeCl₃-HCl-H₂O-1 M D2EHPA-Amsco

The interaction effects presented in Tables 10, 11 and 12 for the above ternary system are plotted in Figures 17, 18 and 19, respectively. It is observed from these graphs that $\Delta y_{\text{Ce}}$ and $\Delta y_{\text{Nd}}$ are of the same form for all $x_{\text{Sm}}/(x_{\text{Sm}} + x_{\text{Nd}})$ values and mostly negative. However, $\Delta y_{\text{Sm}}$ seems to possess a positive displacement of maxima to a higher value of $x_{\text{Ce}}/x_{\text{T}}$ as $x_{\text{Sm}}/(x_{\text{Sm}} + x_{\text{Nd}})$ is increased. The reason why this happens is not well understood, however, it is believed to be dependent on the separation factors of each pair, the pure component equilibrium data, the mole fraction of each component in the aqueous phase and the total extractability, $Y_{\text{T}}$. All the reasons mentioned above have an effect on the intermolecular interaction of all ions and thus change the deviation from ideality.

Since the empirical models required to correlate all the interaction effects are non-linear in the parameters, the Gauss-Newton (14) technique was utilized to estimate the parameter vectors. Since the procedure was explained for the binary system, the model and the results will be presented without explanation. The empirical models and parameter vectors for the data in Figure 17 for $x_{\text{Sm}}/(x_{\text{Sm}} + x_{\text{Nd}}) = 0.1$ are:

$$\Delta y_{\text{Sm}} = a_1 (N_{\text{Ce}} + a_2) (1-N_{\text{Ce}})^{a_3} e^{a_4 H^+}$$

(53a)
Figure 17. Sm, Nd and Ce deviations from ideality for the system SmCl$_3$-NdCl$_3$-CeCl$_3$-HCl-H$_2$O-1 M D2EHPA-Amsco at $X_T \sim 0.64$ M and $X_{Sm}/(X_{Sm} + X_{Nd}) \sim 0.1$.
Figure 18. Sm, Nd and Ce deviations from ideality for the system SmCl₂-NdCl₂-CeCl₂-HCl-H₂O-1 M D2EHPA-Amsco at \( X_T \sim 0.64 \) M and \( x_{Sm}/(x_{Sm} + x_{Nd}) \sim 0.5 \).
Figure 19. Sm, Nd and Ce deviations from ideality for the system SmCl$_3$-NdCl$_3$-CeCl$_3$-HCl-H$_2$O-1 M D2EHPA-Amsco at $X_T \sim 0.64$ M and $x_{Sm}/(x_{Sm} + x_{Nd}) \sim 0.9$. 
where \((a_1, \ldots, a_4) = (0.09574, 1.3466, 0.8669, -3.313)\),

\[
\Delta y_{Nd} = b_1 (1-N_{Ce})^b_2 (b_3 - N_{Ce}) e^{b_4 H^+}
\]  
(53b)

where \((b_1, \ldots, b_4) = (-0.2024, 0.6816, 0.6191, -4.1348)\),

\[
\Delta y_{Ce} = C_1 N_{Ce}^C_2 (1-N_{Ce}) e^{C_3 C_4 H^+}
\]  
(53c)

where \((C_1, \ldots, C_4) = (-0.8377, 1.234, 0.9534, -7.086)\).

Equation 53a predicts best with an average error of less than 2.8% in the ranges \(0.1 \leq N_{Ce} \leq 0.9\) and \(0.4 \leq H^+ \leq 0.7\).

Equations 53b and 53c predict best with an average error of less than 2.8% and 3.5% respectively in most of the ranges of the experimental data except at extreme values. The data in Figure 18 for \(x_{Sm}/(x_{Sm} + x_{Nd}) = 0.5\) are predicted by the models

\[
\Delta y_{Sm} = d_1 H^+(N_{Ce} + d_2) (1-N_{Ce}) e^{d_3 H^+}
\]  
\(\)  
(54a)

where \((d_1, \ldots, d_4) = (0.7362, 0.4054, 1.2928, -3.2453)\),

\[
\Delta y_{Nd} = g_1 (1-N_{Ce}) e^{g_2 g_3 H^+}
\]  
(54b)

where \((g_1, \ldots, g_3) = (-0.1356, 1.5785, -3.8826)\),
\[ \Delta Y_{Ce} = h_1 N_{Ce} (1-N_{Ce}) e^{h_3 N_{Ce}^2} e^{h_4 N_{Ce}^3} \]  \hspace{1cm} (54c)

where \((h_1, \ldots, h_4) = (-0.7586, 1.2834, 0.6870, -5.7577)\).

Equation 54a predicts best in the ranges \(0.05 \leq N_{Ce} \leq 0.9\) and \(0.4 \leq H^+ \leq 0.8\) with an average error of less than 3.5%.

Equation 54b predicts best in the ranges \(0.1 \leq N_{Ce} \leq 0.9\) and \(0.4 \leq H^+ \leq 0.7\) with an average error of less than 3.2%.

Equation 54c predicts the data with an average error of less than 3% in most of the range except at extreme values. The data in Figure 19 for \(x_{Sm}/(x_{Sm} + x_{Nd}) = 0.9\) are predicted by the models,

\[ \Delta y_{Sm} = k_1 N_{Ce} (1-N_{Ce}) e^{k_2 N_{Ce}^2} e^{k_3 N_{Ce}^3} e^{k_4 N_{Ce}^4} \]  \hspace{1cm} (55a)

where \((k_1, \ldots, k_4) = (0.9567, 0.006978, 0.9620, -3.0384)\).

\[ \Delta y_{Nd} = p_1 (1-N_{Ce}) e^{p_2 N_{Ce}^2} e^{p_3 N_{Ce}^3} \]  \hspace{1cm} (55b)

where \((p_1, \ldots, p_3) = (-0.02864, 1.3877, -3.6660)\),

\[ \Delta y_{Ce} = m_1 N_{Ce} (1-N_{Ce}) e^{m_2 N_{Ce}^2} e^{m_3 N_{Ce}^3} e^{m_4 N_{Ce}^4} \]  \hspace{1cm} (55c)

where \((m_1, \ldots, m_4) = (-0.6074, 1.2247, 0.4916, -5.3225)\).
The average error of Equation 55a is less than 2.2% for
0.1 ≤ N_{Ce} ≤ 0.9 and 0.4 ≤ H^+ ≤ 0.8. The average error of
Equations 55b and 55c is less than 2.8% and 3% respectively,
in most of the range except at extreme conditions. The calcu­
lated Δy_{Sm}, Δy_{Nd} and Δy_{Ce} for the conditions where x_{Sm}/(x_{Sm} + 
x_{Nd}) = 0.1, 0.5 and 0.9 are presented in Tables 10, 11 and 12
respectively for comparison with the experimental data.

A summary of all the mathematical models available for
predicting the organic phase are presented in Table 13. From
here on, a Roman numeral will be assigned to each model and the
reference will be made with respect to the models in Table 13.
Table 13. Empirical models

<table>
<thead>
<tr>
<th>No.</th>
<th>Model followed by parameter vector</th>
<th>Data predicted</th>
<th>Avg. error less than</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>$y_{Ce} = a_1 x^2 + a_2 x e^{3H}$</td>
<td>Single-component, CeCl$_3$</td>
<td>3%</td>
</tr>
<tr>
<td></td>
<td>$(a_1, \ldots, a_6) = (0.01656, 0.3588, -0.8581, -0.7032, -5.3893, 4.927)$</td>
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<td></td>
</tr>
<tr>
<td>II</td>
<td>$y_{Nd} = b_1 x^2 + b_2 x e^{3H}$</td>
<td>Single-component, NdCl$_3$</td>
<td>6%</td>
</tr>
<tr>
<td></td>
<td>$(b_1, \ldots, b_6) = (0.02048, 0.2577, -0.5758, -0.9282, -2.9195, 0.5755)$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>$y_{Sm} = c_1 x^2 + c_2 x e^{3H}$</td>
<td>Single-component, SmCl$_3$</td>
<td>5%</td>
</tr>
<tr>
<td></td>
<td>$(c_1, \ldots, c_6) = (0.08674, 0.2448, -0.4742, -0.9287, 0.3133, -1.4158)$</td>
<td></td>
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<tr>
<td>IV</td>
<td>$\Delta y_{Sm} = a_1 N_{Sm} x_{Sm}^2 (1-N_{Sm}) x_{Sm}^3 (a_4-N_{Sm}) x_{Sm}^{a_5} e^{a_6 H^+}$</td>
<td>Interaction effect of Sm in binary system at $X_T(Sm,Nd) \sim 0.64$ M</td>
<td>7%</td>
</tr>
<tr>
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<td>$(a_1, \ldots, a_5) = (2.2023, 0.7422, 0.4096, 0.9008, -4.002)$</td>
<td></td>
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</tr>
<tr>
<td>No.</td>
<td>Model followed by parameter vector</td>
<td>Data predicted</td>
<td>Avg. error less than</td>
</tr>
<tr>
<td>-----</td>
<td>-----------------------------------</td>
<td>----------------</td>
<td>---------------------</td>
</tr>
<tr>
<td>V</td>
<td>$\Delta y_{\text{Nd}} = b_1 N_{\text{Sm}}^2 (1 - N_{\text{Sm}}) e^{b_3 N_{\text{Sm}} b_4 H^+}$</td>
<td>Interaction effect of Nd in binary system at $X_T(\text{Sm,Nd}) \sim 0.64$ M</td>
<td>4%</td>
</tr>
<tr>
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<td>$(b_1, \ldots, b_4) = (-0.4239, 0.5075, 1.1582, -3.8522)$</td>
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<tr>
<td>VI</td>
<td>$\Delta y_{\text{Sm}} = c_1 N_{\text{Sm}}^2 (1 - N_{\text{Sm}}) e^{c_3 N_{\text{Sm}} c_4 H^+}$</td>
<td>Interaction effect of Sm in binary system at $X_T(\text{Sm,Nd}) \sim 0.11$ M</td>
<td>3%</td>
</tr>
<tr>
<td></td>
<td>$(c_1, \ldots, c_4) = (0.5612, 0.6775, 1.2931, -3.4724)$</td>
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<tr>
<td>VII</td>
<td>$\Delta y_{\text{Nd}} = d_1 N_{\text{Sm}}^2 (1 - N_{\text{Sm}}) e^{d_3 N_{\text{Sm}} d_4 H^+}$</td>
<td>Interaction effect of Nd in binary system at $X_T(\text{Sm,Nd}) \sim 0.11$ M</td>
<td>3.5%</td>
</tr>
<tr>
<td></td>
<td>$(d_1, \ldots, d_4) = (-0.3099, 0.5959, 1.2315, -3.3533)$</td>
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<tr>
<td>VIII</td>
<td>$\Delta y_{\text{Sm}} = a_1 (N_{\text{Ce}} + a_2) (1 - N_{\text{Ce}}) e^{a_3 N_{\text{Ce}} a_4 H^+}$</td>
<td>Interaction effect of Sm in ternary system for $x_{\text{Sm}}/(x_{\text{Sm}} + x_{\text{Nd}}) = 0.1$ and $X_T(\text{Sm,Nd,Ce}) \sim 0.64$ M</td>
<td>2.8%</td>
</tr>
<tr>
<td></td>
<td>$(a_1, \ldots, a_4) = (0.09574, 1.3466, 0.8669, -3.313)$</td>
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Table 13 (Continued)

<table>
<thead>
<tr>
<th>No.</th>
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<th>Data predicted</th>
<th>Avg. error less than</th>
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<tr>
<td>IX</td>
<td>$\Delta y_{Nd} = b_1(l-N_{Ce})^b_2(l-N_{Ce})^b_4H^+$</td>
<td>Interaction effect of Nd in ternary system for $x_{Sm}/(x_{Sm} + x_{Nd}) = 0.1$ and $X_T(Sm,Nd,Ce) \approx 0.64$</td>
<td>2.8%</td>
</tr>
<tr>
<td></td>
<td>$(b_1,...,b_4) = (-0.2024, 0.6816,$ $0.6191, -4.1348)$</td>
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<td></td>
</tr>
<tr>
<td>X</td>
<td>$\Delta y_{Ce} = c_1N_{Ce}^c_2(l-N_{Ce})^c_3e_4H^+$</td>
<td>Interaction effect of Ce in ternary system for $x_{Sm}/(x_{Sm} + x_{Nd}) = 0.1$ and $X_T(Sm,Nd,Ce) \approx 0.64$</td>
<td>3.5%</td>
</tr>
<tr>
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<td>$(c_1,...,c_4) = (-0.8377, 1.234,$ $0.9534, -7.086)$</td>
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<tr>
<td>XI</td>
<td>$\Delta y_{Sm} = d_1H^+(N_{Ce} + d_2)(l-N_{Ce})^d_3H^+d_4H^+$</td>
<td>Interaction effect of Sm in ternary system for $x_{Sm}/(x_{Sm} + x_{Nd}) = 0.5$ and $X_T(Sm,Nd,Ce) = 0.64$ M</td>
<td>3.5%</td>
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<tr>
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<td>$(d_1,...,d_4) = (0.7362, 0.4054,$ $1.2928, -3.2453)$</td>
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<td>XII</td>
<td>$\Delta y_{Nd} = g_1(l-N_{Ce})^g_2g_3H^+$</td>
<td>Interaction effect of Nd in the ternary system for $x_{Sm}/(x_{Sm} + x_{Nd}) = 0.5$ and $X_T(Sm,Nd,Ce) \approx 0.64$ M</td>
<td>3.2%</td>
</tr>
<tr>
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<td>$(g_1,...,g_3) = (-0.1356, 1.5785,$ $-3.8826)$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>No.</td>
<td>Model followed by parameter vector</td>
<td>Data predicted</td>
<td>Avg. error less than</td>
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<td>-----------------------------------</td>
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<td>---------------------</td>
</tr>
<tr>
<td>XIII</td>
<td>( \Delta y_{Ce} = h_1 N_{Ce} (1-N_{Ce}) e e_4 H^+ )</td>
<td>Interaction effect of Ce in ternary system for ( x_{Sm}/(x_{Sm} + x_{Nd}) = 0.5 ) and ( X_T(Sm,Nd,Ce) \sim 0.64 \text{ M} )</td>
<td>3.0%</td>
</tr>
<tr>
<td>(h_1,...,h_4) = (-0.7586, 1.2834, 0.6870, -5.7577)</td>
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<tr>
<td>XIV</td>
<td>( \Delta y_{Sm} = k_1 H^+(N_{Ce} + k_2) (1-N_{Ce}) k_3 H^+ e k_4 H^+ )</td>
<td>Interaction effect of Sm in ternary system for ( x_{Sm}/(x_{Sm} + x_{Nd}) = 0.9 ) and ( X_T(Sm,Nd,Ce) \sim 0.64 \text{ M} )</td>
<td>2.2%</td>
</tr>
<tr>
<td>(k_1,...,k_4) = (0.9567, 0.006978, 0.9620, -3.0384)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XV</td>
<td>( \Delta y_{Nd} = p_1 (1-N_{Ce}) e p_3 H^+ )</td>
<td>Interaction effect of Nd in ternary system for ( x_{Sm}/(x_{Sm} + x_{Nd}) = 0.9 ) and ( X_T(Sm,Nd,Ce) \sim 0.64 \text{ M} )</td>
<td>2.8%</td>
</tr>
<tr>
<td>(p_1,...,p_3) = (-0.02864, 1.3877, -3.666)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XVI</td>
<td>( \Delta y_{Ce} = m_1 N_{Ce} (1-N_{Ce}) e m_3 e m_4 H^+ )</td>
<td>Interaction effect of Ce in ternary system for ( x_{Sm}/(x_{Sm} + x_{Nd}) = 0.9 ) and ( X_T(Sm,Nd,Ce) \sim 0.64 \text{ M} )</td>
<td>3.0%</td>
</tr>
<tr>
<td>(m_1,...,m_4) = (-0.6074, 1.2247, 0.4916, -5.3225)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
METHODS OF CALCULATION

Prediction of the Organic Phase for the System
SmCl₃-NdCl₃-HCl-H₂O-1 M D2EHPA

A procedure for calculating the organic concentrations upon specification of the aqueous phase for the above binary system in terms of single-component data will be presented.

Example 1:

Given the aqueous conditions for the binary system

\[ H^+ = 0.6 \, M \]
\[ X_T = 0.64 \, M \]

\[ N_{Sm} = x_{Sm}/X_T = 0.50 \]
\[ N_{Nd} = x_{Nd}/X_T = 0.50 \]

Calculate the organic concentrations.

a. Calculate \( y_{Nd}^{*} \) and \( y_{Sm}^{*} \) from Models II and III respectively assuming that all of the rare earths in the aqueous phase \( X_T(\text{Sm}, Nd) \) are one element only.

\[ y_{Nd}^{*} = 0.0447 \, M \]
\[ y_{Sm}^{*} = 0.1087 \, M \]

b. Calculate the interaction effects \( \Delta y_{Sm} \) and \( \Delta y_{Nd} \) at

\[ X_T \approx 0.64 \, M \] for the binary system using Models IV and V respectively.

\[ \Delta y_{Sm} = 0.02418 \, M \]
\[ \Delta y_{Nd} = -0.01325 \, M \]

c. Utilizing Equation 43, one may calculate the total organic molarity,
\[ Y_T = Y_{Sm} \left( \frac{x_{Sm}}{x_T} \right) + Y_{Nd} \left( \frac{x_{Nd}}{x_T} \right) + \Delta Y_{Sm} + \Delta Y_{Nd} \]

\[ = 0.1087(0.5) + 0.0447(0.5) + 0.02418 - 0.01325 \]

\[ Y_T = 0.08763 \text{ M} \]

The experimental value is 0.0873 M.

d. The composition of the organic phase may be calculated employing Equations 15 and 16. An average \( \beta_{Sm, Nd} = 8.8 \) may be used in the expression and the \( Y_T \) calculated above.

\[ Y_{Sm} = \frac{Y_T}{1 + \frac{1}{\beta_{Sm, Nd}} \left( \frac{x_{Nd}}{x_{Sm}} \right)} \]

\[ Y_{Sm} = \frac{0.08763}{1 + \frac{1}{8.8} (0.5)} \]

\[ Y_{Sm} = 0.07869 \text{ M} \]

The experimental value is 0.07838 M.

\[ Y_{Nd} = \frac{0.08763}{1 + 8.8 \left( \frac{0.5}{0.5} \right)} \]

\[ Y_{Nd} = 0.008942 \text{ M} \]

The experimental value is 0.00892 M.

Example 2:

Given:

\[ H^+ = 0.6 \text{ M} \]

\[ x_T = 0.11 \text{ M} \]

\[ N_{Sm} = 0.5 \]

\[ N_{Nd} = 0.5 \]
Calculate the organic concentrations

a. From Models II and III

\[ Y_{Sm}^* = 0.0908 \text{ M} \]
\[ Y_{Nd}^* = 0.0385 \text{ M} \]

b. Calculate the interaction effects \( \Delta y_{Sm} \) and \( \Delta y_{Nd} \) at \( X_T = 0.11 \text{ M} \) for the binary system using Models VI and VII respectively,

\[ \Delta y_{Sm} = 0.01783 \text{ M} \]
\[ \Delta y_{Nd} = -0.01168 \text{ M} \]

c. From Equation 43, the total organic concentration is

\[ Y_T = 0.0385(0.5) + 0.0908(0.5) + 0.01783 -0.01168 \]
\[ Y_T = 0.0708 \text{ M} \]

The experimental value is 0.0710 M.

d. The composition of the organic phase from Equations 15 and 16 using an average \( \beta_{Sm,Nd} = 8.0 \) is

\[ Y_{Sm} = 0.06293 \text{ M} \] compared to the ideal value of 0.0454 M
\[ Y_{Nd} = 0.00787 \text{ M} \] compared to the ideal value of 0.01925 M

The experimental values are 0.06309 M and 0.00791 M respectively.

Prediction of the Organic Phase for the System
SmCl₃-NdCl₃-CeCl₃-HCl-H₂O-1 M D2EHPA-Amsco

At this point, a stepwise calculation procedure will be presented for predicting the organic phase upon specification of the aqueous phase for the above system.
Example 1:

Given the equilibrium conditions in the aqueous phase for the above ternary system,

\[ H^+ = 0.4 \text{ M} \]
\[ x_T = 0.64 \text{ M} \]
\[ N_{\text{Ce}} = \frac{x_{\text{Ce}}}{x_T} = 0.1 \]
\[ N_{\text{Nd}} = \frac{x_{\text{Nd}}}{x_T} = 0.81 \]
\[ N_{\text{Sm}} = \frac{x_{\text{Sm}}}{x_T} = 0.09; \frac{x_{\text{Sm}}}{x_{\text{Sm}} + x_{\text{Nd}}} = 0.1 \]

we need to calculate

- \( Y_T \) = total organic molarity
- \( Y_{\text{Sm}} \) = samarium organic molarity
- \( Y_{\text{Nd}} \) = neodymium organic molarity
- \( Y_{\text{Ce}} \) = cerium organic molarity

a. Calculate \( Y_{\text{Ce}}^* \), \( Y_{\text{Nd}}^* \) and \( Y_{\text{Sm}}^* \) using Models I, II and III respectively. \( H \) is the aqueous acidity, \( H^+ \), and \( x \) is the total aqueous molarity, \( x_T \), assuming all the rare earths in the aqueous phase is one element only.

\[ Y_{\text{Ce}}^* = 0.0246 \text{ M} \]
\[ Y_{\text{Nd}}^* = 0.0446 \text{ M} \]
\[ Y_{\text{Sm}}^* = 0.1087 \text{ M} \]

b. Calculate the total interaction effect, \( \Delta Y_T \), for the conditions where \( \frac{x_{\text{Sm}}}{x_{\text{Sm}} + x_{\text{Nd}}} = 0.1 \) and \( x_T \sim 0.64 \text{ M} \) by adding \( \Delta Y_{\text{Sm}}, \Delta Y_{\text{Nd}} \) and \( \Delta Y_{\text{Ce}} \) which can be predicted by Models VIII, IX and X respectively,
\[ \Delta Y_{Sm} = 0.01732 \text{ M} \]
\[ \Delta Y_{Nd} = -0.008179 \]
\[ \Delta Y_{Ce} = -0.000629 \]
\[ \Delta Y_T = \Delta Y_{Sm} + \Delta Y_{Nd} + \Delta Y_{Ce} = 0.008512 \text{ M} \]

c. Using Equation 52, calculate the total organic concentration,
\[
Y_T = Y_{Sm} \left( \frac{x_{Sm}}{x_T} \right) + Y_{Nd} \left( \frac{x_{Nd}}{x_T} \right) + Y_{Ce} \left( \frac{x_{Ce}}{x_T} \right) + \Delta Y_T,
\]
\[ Y_T = 0.1087(0.09) + 0.0446(0.81) + 0.0246(0.1) + 0.008512 \]
\[ Y_T = 0.05688 \text{ M} \]

The experimental value for \( Y_T \) is 0.0574 M.

d. Calculate \( Y_{Sm}, Y_{Nd} \) and \( Y_{Ce} \) employing Equations 22, 23 and 24 respectively. In these relations an average separation factor for each pair should be used \( \beta_{Sm,Ce} = 19.5, \)
\( \beta_{Sm,Nd} = 9.06, \beta_{Nd,Ce} = 2.16 \) and the \( Y_T \) calculated in step c,
\[
Y_{Sm} = \frac{Y_T}{1 + \frac{1}{\beta_{Sm,Nd}} \left( \frac{x_{Nd}}{x_{Sm}} \right) + \frac{1}{\beta_{Sm,Ce}} \left( \frac{x_{Ce}}{x_{Sm}} \right)}
\]
\[ = \frac{0.05688}{1 + \frac{1}{9.06} \left( \frac{0.81}{0.09} \right) + \frac{1}{19.5} \left( \frac{0.1}{0.09} \right)} \]
\[ Y_{Sm} = 0.02774 \text{ M}. \]
The experimental value is 0.02795 M.

\[ Y_{\text{Nd}} = \frac{Y_T}{1 + \beta_{\text{Sm,Nd}} \frac{x_{\text{Sm}}}{x_{\text{Nd}}} + \frac{1}{\beta_{\text{Nd, Ce}}} \frac{x_{\text{Ce}}}{x_{\text{Nd}}}} \]

\[ = \frac{0.05688}{1 + 9.06 \left( \frac{0.09}{0.81} \right) + \frac{1}{2.16} \left( \frac{0.1}{0.81} \right)} \]

\[ Y_{\text{Nd}} = 0.02756 \text{ M.} \]

The experimental value is 0.02781 M.

\[ Y_{\text{Ce}} = \frac{Y_T}{1 + \beta_{\text{Sm, Ce}} \frac{x_{\text{Sm}}}{x_{\text{Ce}}} + \beta_{\text{Nd, Ce}} \frac{x_{\text{Nd}}}{x_{\text{Ce}}}} \]

\[ = \frac{0.05688}{1 + 19.5 \left( \frac{0.09}{0.1} \right) + 2.16 \left( \frac{0.81}{0.1} \right)} \]

\[ Y_{\text{Ce}} = 0.001578 \text{ M.} \]

The experimental value is 0.001592 M.

Example 2:

Specifying,

\[ H^+ = 0.616 \text{ M} \]

\[ X_T = 0.6198 \text{ M} \]

\[ N_{\text{Ce}} = \frac{x_{\text{Ce}}}{X_T} = 0.1097 \]

\[ N_{\text{Nd}} = \frac{x_{\text{Nd}}}{X_T} = 0.4321 \]

\[ N_{\text{Sm}} = \frac{x_{\text{Sm}}}{X_T} = 0.4582; \ x_{\text{Sm}}/(x_{\text{Sm}} + x_{\text{Nd}}) = 0.5147, \]
we need to calculate the organic phase concentrations

a. As explained in Example 1

\[ y^*_{Ce} = 0.02326 \text{ M} \]
\[ y^*_{Nd} = 0.04271 \text{ M} \]
\[ y^*_{Sm} = 0.1066 \text{ M} \]

b. Since \( \frac{x_{Sm}}{x_{Sm} + x_{Nd}} \approx 0.5 \) use Models XI, XII and XIII to calculate \( \Delta y^*_{Sm} \), \( \Delta y^*_{Nd} \) and \( \Delta y^*_{Ce} \) respectively

\[ \Delta y^*_{Sm} = 0.02885 \text{ M} \]
\[ \Delta y^*_{Nd} = -0.010325 \text{ M} \]
\[ \Delta y^*_{Ce} = -0.001184 \text{ M} \]
\[ \Delta y^*_{T} = 0.01734 \text{ M} \]

c. From Equation 52, the total organic molarity is

\[ y^*_{T} = 0.08708 \text{ M} \]

The experimental value of \( y^*_{T} \) is 0.08629 M.

d. The composition of the organic phase may be obtained as described in Example 1

\[ y_{Sm} = 0.07800 \text{ M} \]

The experimental value is 0.07744 M,

\[ y_{Nd} = 0.00812 \text{ M} \]

The experimental value is 0.00799 M

\[ y_{Ce} = 0.00086 \text{ M} \]

The experimental value is 0.000857 M.

If one specifies a condition where \( \frac{x_{Sm}}{x_{Sm} + x_{Nd}} \) is not exactly 0.1, 0.5 or 0.9, it is necessary to calculate the interaction effects and total organic molarity using the
relations in Table 13 for \( \frac{x_{\text{Sm}}}{x_{\text{Sm}} + x_{\text{Nd}}} = 0.1, 0.5 \) and 0.9. Once this is done, an interpolation procedure gives the results at the desired condition of \( \frac{x_{\text{Sm}}}{x_{\text{Sm}} + x_{\text{Nd}}} \).

All the ternary system studies were performed at a total aqueous concentration \( X_T(\text{Sm, Nd, Ce}) = 0.64 \text{ M} \). This concentration was chosen because the extraction is maximum there for any one acidity and thus the interaction effects are larger. However, if one wishes to perform a calculation at a different \( X_T \), it would be possible to extrapolate from the \( X_T = 0.64 \text{ M} \) data. This is possible since there exists a characteristic parallelism at different total aqueous concentrations which is derived from the single-component data and carried through the binary and ternary systems. This parallelism is shown in Figure 20 for the conditions where \( H^+ = 0.6 \text{ M} \), \( \frac{x_{\text{Sm}}}{x_{\text{Sm}} + x_{\text{Nd}}} = 0.5 \) and at two different \( X_T \) (0.11 M and 0.64 M).

The single-component data may be calculated for any acidity and any total aqueous concentration using Models I, II, and III. The pure component data allows one to know the end-points on the binary system. Knowing the mole fraction of Sm on a cerium-free basis and the acidity, the total organic concentration, \( Y_T(\text{Sm, Nd}) X_T = 0.64 \text{ M} \), may be calculated through Equation 43 and Models IV and V. Once \( Y_T(\text{Sm, Nd}) X_T = 0.64 \) is known then \( Y_T(\text{Sm, Nd}) X_T = 0.11 \) may be calculated from the following relation:
Figure 20. Comparison of organic molarities for the systems (SmCl₃,NdCl₃,CeCl₃, SmCl₃-NdCl₃,SmCl₃-NdCl₃-CeCl₃)-HCl-H₂O-1 M D2EHPA-Amsco at H⁺ = 0.6 M.
Knowing $y_T$ at the two different concentrations, therefore, we also know the left end-points on the ternary system. The right end-points for $y^*_{Ce}$ may be obtained from Model I. Again the total organic concentration, $y_T^{(Sm,Nd,Ce)} x_T = 0.64$ for the ternary system at $x_T = 0.64$ and $x_{Sm}/(x_{Sm} + x_{Nd}) = 0.5$ may be calculated from Equation 52 and Models XI, XII and XIII at the specified $N_{CC}$ and $H^+$. After calculating $y_T^{(Sm,Nd,Ce)} x_T = 0.64$ and knowing the end-points, we can calculate $y_T^{(Sm,Nd,Ce)} x_T = 0.11$ using the following relation:

\[
\frac{y_{Sm}^* x_T = 0.64 - y_{Nd}^* x_T = 0.64}{y_{Sm}^* x_T = 0.11 - y_{Nd}^* x_T = 0.11} = 0.64
\]

\[
\frac{y_T^{(Sm,Nd)} x_T = 0.64 - y_{Nd}^* x_T = 0.64}{y_T^{(Sm,Nd)} x_T = 0.11 - y_{Nd}^* x_T = 0.11} = 0.64
\]

(56)

\[
\frac{y_T^{(Sm,Nd,Ce)} x_T = 0.64 - y_{Ce}^* x_T = 0.64}{y_T^{(Sm,Nd,Ce)} x_T = 0.11 - y_{Ce}^* x_T = 0.11} = 0.64
\]

(57)
In order to test the above technique for calculating the organic concentrations for the ternary system at an \( X_T = 0.10 \) M, two data points were studied and the equilibrium data presented in Table 14.

Example 3.

Given:
\[
\begin{align*}
H^+ & = 0.578 \text{ M} \\
X_T & = 0.1004 \text{ M} \\
N_{Ce} & = 0.0807 \\
N_{Nd} & = 0.4138 \\
N_{Sm} & = 0.506; \frac{x_{Sm}}{(x_{Sm} + x_{Nd})} = 0.55,
\end{align*}
\]

calculate organic concentrations.

a. Calculate the pure component data for the above acidity at \( X_T = 0.11 \text{ M} \) and \( 0.64 \text{ M} \) using Models I, II and III

\[
\begin{align*}
x_T & = 0.10 & x_T & = 0.64 \\
y_{Ce}^* & = 0.0224 \text{ M} & y_{Ce}^* & = 0.0265 \text{ M} \\
y_{Nd}^* & = 0.0408 \text{ M} & y_{Nd}^* & = 0.0476 \text{ M} \\
y_{Sm}^* & = 0.0933 \text{ M} & y_{Sm}^* & = 0.1119 \text{ M}
\end{align*}
\]

b. Calculate \( Y_T(Sm,Nd) \) \( X_T = 0.64 \) using Equation 43 and Models IV and V

\[
\begin{align*}
\Delta y_{Sm} & = 0.02269 \text{ M} \\
\Delta y_{Nd} & = -0.01333 \text{ M} \\
Y_T(Sm,Nd)_{0.64} & = (0.119)(0.55) + 0.0476(0.45) + 0.02269 - 0.01333 \\
Y_T(Sm,Nd)_{0.64} & = 0.09232 \text{ M}
\end{align*}
\]
Table 14. Equilibrium data and separation factors for the system SmCl₃-NdCl₃-
CeCl₃-HCl-H₂O-1 M D2EHPA-Amsco at ~ 0.10 M total aqueous concentration

<table>
<thead>
<tr>
<th>No.</th>
<th>HCl</th>
<th>Total RE</th>
<th>Sm</th>
<th>Nd</th>
<th>Ce</th>
<th>Total RE</th>
<th>Sm</th>
<th>Nd</th>
<th>Ce</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.551</td>
<td>0.1082</td>
<td>0.00985</td>
<td>0.04801</td>
<td>0.05034</td>
<td>0.04247</td>
<td>0.02255</td>
<td>0.01378</td>
<td>0.006167</td>
</tr>
<tr>
<td>2</td>
<td>0.578</td>
<td>0.1004</td>
<td>0.05079</td>
<td>0.04155</td>
<td>0.008104</td>
<td>0.07423</td>
<td>0.06124</td>
<td>0.007671</td>
<td>0.0005324</td>
</tr>
</tbody>
</table>

Separation factors

<table>
<thead>
<tr>
<th>No.</th>
<th>$\beta_{\text{Sm,Ce}}$</th>
<th>$\beta_{\text{Sm,Nd}}$</th>
<th>$\beta_{\text{Nd,Ce}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>18.68</td>
<td>7.98</td>
<td>2.34</td>
</tr>
<tr>
<td>2</td>
<td>18.36</td>
<td>6.53</td>
<td>2.81</td>
</tr>
</tbody>
</table>
c. Calculate $y_{T(Sm,Nd)}^{0.10}$ using Equation 56

$$y_{T(Sm,Nd)}^{0.10} = 0.0408 + (0.09232 - 0.0476) \frac{(0.0933 - 0.0408)}{(0.1119 - 0.0476)}$$

$$y_{T(Sm,Nd)}^{0.10} = 0.07731 \text{ M}$$

d. Calculate $y_{T(Sm,Nd,Ce)}^{0.64}$ using Equation 52 and Models XI, XII and XIII

$$\Delta y_{Sm} = 0.02991 \text{ M}$$

$$\Delta y_{Nd} = -0.01418 \text{ M}$$

$$\Delta y_{Ce} = -0.001078 \text{ M}$$

$$\Delta y_T = 0.01465$$

$$y_{T(Sm,Nd,Ce)}^{0.64} = 0.1119(0.506) + 0.0476(0.4138) + 0.0265(0.0807) + 0.01465$$

$$y_{T(Sm,Nd,Ce)}^{0.64} = 0.09309 \text{ M}$$

e. Calculate $y_{T(Sm,Nd,Ce)}^{0.10}$

$$y_{T(Sm,Nd,Ce)}^{0.10}$$ using Equation 57 is

$$y_{T(Sm,Nd,Ce)}^{0.10} = 0.0224 + (0.09309 - 0.0265) \frac{(0.07731 - 0.0224)}{(0.09232 - 0.0265)}$$

$$y_{T(Sm,Nd,Ce)}^{0.10} = 0.0779 \text{ M}$$

The experimental value is 0.0742.

The calculated value is expected to be slightly higher since the results were calculated using the models at $x_{Sm} / (x_{Sm} + x_{Nd}) = 0.5$. In order to obtain a more accurate answer, it is necessary to calculate $y_T$ for $x_{Sm} / (x_{Sm} + x_{Nd}) = 0.1, 0.5$ and 0.9 and interpolate to 0.55.

f. Calculate the organic composition using Equations 22, 23 and 24. The $b$s obtained in Table 14 will be utilized here.
$Y_{\text{Sm}} = 0.0687 \text{ M}$

The experimental value is 0.06124 M

$Y_{\text{Nd}} = 0.0086 \text{ M}$

The experimental value is 0.00767 M.

$Y_{\text{Ce}} = 0.0006 \text{ M}$

The experimental value is 0.0005324 M.

It should be noted that if more accurate results are required for different $X_T$, more equilibrium data should be taken at each concentration and correlated.
CONCLUSIONS

1. The equilibrium curves for the extraction of trivalent cerium by D2EHPA from acidic aqueous chloride solutions are similar in shape to the other lower lanthanides.

2. The equilibrium data for CeCl$_3$ may be predicted by using an empirical model of two independent variables (acidity and aqueous lanthanide molarity).

3. In the binary system, SmCl$_3$-NdCl$_3$-HCl-H$_2$O-l M D2EHPA-Amsco, the total organic concentration may be predicted by the sum of a series of linear terms analogous to Raoult's Law for ideal solutions and terms including the interaction effects (deviation from ideality). The deviation is due to intermolecular interactions between like and unlike ions in both phases and may be predicted with an average error of less than 3.4%. Furthermore, the total interaction effect, $\Delta Y_T$, is equal to the sum of the individual interaction effects, $\Delta Y_{Sm}$ and $\Delta Y_{Nd}$.

4. The separation factor, $\beta_{Sm,Nd}$, for the binary system is essentially constant for all conditions studied at different acidities, different total aqueous concentrations and different mole fractions of Sm in the aqueous phase. The arithmetic average of $\beta_{Sm,Nd}$ ~ 8.4.

5. In the ternary system SmCl$_3$-NdCl$_3$-CeCl$_3$-HCl-H$_2$O-l M D2EHPA-Amsco, the total organic concentration, $\Delta Y_T$, is a function of the aqueous acidity, the total lanthanide aqueous concentration, the mole fraction of Ce in the aqueous phase and
the ratio of Sm:Nd in the aqueous phase. At three different Sm:Nd ratios, $Y_T$ may be predicted by the sum of a linear term composed of three partial extractabilities due to ideal behavior and a nonlinear term which is a measure of the interaction effect (deviation from ideality).

6. In the ternary system, the separation factor of each combination pair of elements remains essentially constant for all experimental conditions studied. The arithmetic average of the separation factors are $\beta_{\text{Sm},\text{Ce}} \sim 19.5$, $\beta_{\text{Sm},\text{Nd}} \sim 9.06$ and $\beta_{\text{Nd},\text{Ce}} \sim 2.16$.

7. The separation factor of each pair of elements, in a system where three elements are extracted simultaneously, remains the same as in the case where each pair is extracted together, for all conditions studied.

8. The magnitude of the total interaction effect, $\Delta Y_T$, for either the binary or the ternary system is directly proportional to the total extraction. As the extraction decreases, the total organic molarity approaches linearity when plotted against the mole fraction of any element in the aqueous phase.
BIBLIOGRAPHY


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