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SEPARATION OF THE HEAVIER RARE EARTHS

BY FRACTIONAL SOLVENT EXTRACTION

by

Norman Earl Thomas

M. S. Thesis, February 1970

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244

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SEPARATION OF THE HEAVIER RARE EARTHS
BY FRACTIONAL SOLVENT EXTRACTION

by

Norman Earl Thomas

A Thesis Submitted to the
Graduate Faculty in Partial Fulfillment of
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TABLE OF CONTENTS

	Page
NOMENCLATURE	iii
ABSTRACT	v
INTRODUCTION	1
LITERATURE REVIEW	3
EXPERIMENTAL	5
RESULTS AND DISCUSSION	9
CORRELATION OF TOTAL DISTRIBUTION COEFFICIENTS FOR YbCl ₃ -TmCl ₃ -HCl-H ₂ O-1M D2EHPA-Amsco	30
VERIFICATION OF TOTAL DISTRIBUTION COEFFICIENT MODEL	43
CONCLUSIONS	57
LITERATURE CITED	60
ACKNOWLEDGMENTS	63

NOMENCLATURE

RE	trivalent lanthanide: Tm, Yb.
() _A	species in the aqueous phase.
() _O	species in the organic phase.
X _T	total concentration of rare earth in the aqueous phase at equilibrium, moles/liter.
X _{RE}	concentration of species RE in the aqueous phase at equilibrium, moles/liter.
Y _T	total concentration of rare earth in the organic phase at equilibrium, moles/liter.
Y _{RE}	concentration of species RE in the organic phase at equilibrium, moles/liter.
N _{RE}	mole fraction of species RE on a solvent free basis.
(H ⁺) _A	hydrogen ion concentration in aqueous phase at equilibrium, moles/liter.
E _A ^O	total distribution coefficient, defined as the total concentration of rare earth in the organic phase divided by the total concentration of rare earth in the aqueous phase at equilibrium.
(E _A ^O) _{RE}	distribution coefficient for species, RE, defined as the concentration of species RE in the organic phase divided by the concentration of species RE in the aqueous phase at equilibrium.

$\beta_{Yb, Tm}$	separation factor of Yb with respect to Tm $= \frac{(E_A^O)_{Yb}}{(E_A^O)_{Tm}}$, when both Yb and Tm are present together.
$(HG)_2$	dimeric molecule of di-(2-ethylhexyl) phosphoric acid.
K	equilibrium constant for the ion-exchange extraction mechanism.
η	composition variable defined by Equation 14.
A	the organic concentration of thulium at a fixed but arbitrary value of X_T on a pure Tm distribution plot.
B	the difference at a fixed but arbitrary value of X_T between the organic concentrations of Yb and Tm on their respective pure distribution plot.
H	flow rate of aqueous scrub solvent, liters/unit time.
L	flow rate of organic solvent, liters/unit time.
F	flow rate of aqueous feed solution, liters/unit time.
$\bar{H}$	flow rate of aqueous, extract-side streams, liters/unit time. $= H + F$.
n	arbitrary ideal stage in an extraction cascade.
S_n	organic solvent stream leaving stage n.
R_n	aqueous solvent stream leaving stage n.

ABSTRACT

Equilibrium data were obtained for the systems TmCl_3 -5M $\text{HCl-H}_2\text{O}$ -1M D2EHPA (in Amsco Odorless Mineral Spirits) and YbCl_3 - TmCl_3 -5M $\text{HCl-H}_2\text{O}$ -1M D2EHPA-Amsco. The separation factor for YbCl_3 with respect to TmCl_3 was found to be essentially constant with an arithmetic average value of 3.22.

An empirical correlation was developed for predicting the total distribution coefficients for the binary lanthanide system YbCl_3 - TmCl_3 -5M $\text{HCl-H}_2\text{O}$ -1M D2EHPA-Amsco.

A digital computer program was written, using the experimental distribution function and the experimental value of the separation factor, to predict the operating conditions necessary for the fractional extraction of a 90 percent YbCl_3 -10 percent TmCl_3 -5M HCl feed into a 98 percent YbCl_3 extract product at 90 percent YbCl_3 recovery. A comparison of the results predicted by the computer technique and the results obtained experimentally by a laboratory simulation of the extraction process indicated that the technique was valid.

INTRODUCTION

The lanthanide elements were originally known as the Rare Earth elements for their occurrence in oxide (or in old usage, earth) mixtures. Separation of these mixtures into the individual components is extraordinarily laborious because of their chemical similarity.

Prior to the development of ion-exchange techniques (24), the only separation techniques used were fractional crystallization and fractional precipitation. These methods were slow and tedious, but, in most cases, separations were possible. All such procedures have now been replaced by ion exchange processes. However, the rather low throughput and relatively high production costs made the development of a more economical method of separation desirable.

Solvent extraction has become an important technique for separation and purification of multicomponent systems. In many cases it is more economical than other methods and can easily be adapted to continuous operation.

In this study di-(2-ethylhexyl) phosphoric acid (hereafter abbreviated D2EHPA), was used as the solvent. D2EHPA was found to be an excellent solvent for separating the heavier lanthanides. It gave high separation factors, was almost immiscible in water, and could be readily separated from the aqueous phase when diluted with Amsco Odorless Mineral Spirits.

The purpose of this work was fourfold:

1. to obtain equilibrium data for the system TmCl_3 - HCl - H_2O -D2EHPA-Amsco,
2. to obtain equilibrium data for the binary lanthanide system YbCl_3 - TmCl_3 - HCl - H_2O -D2EHPA-Amsco,
3. to develop a model for the total distribution coefficient in the YbCl_3 - TmCl_3 system,
4. to use the model to predict the operating conditions necessary to perform a desired separation of Yb and Tm, assuming ideal stage behavior.

LITERATURE REVIEW

The organophosphates, both the neutral and acidic compounds, have been the solvents used predominantly in extraction of the rare earths. The solvent tri-n-butyl phosphate (TBP) is probably the best known of the organophosphorus extractants. However, the acidic solvent di-(2-ethylhexyl) phosphoric acid has been shown to be a very promising extractant.

Scadden and Ballou (18) began studying acidic organophosphorus compounds as extractants in 1953. They observed that dibutyl phosphoric acid in di-n-butyl ether effected a significant separation between the light and heavy rare earths.

Peppard et al. (15) of Argonne National Laboratory, in 1957, used tracer concentrations of lanthanides to obtain distribution ratios and to find acid and solvent dependencies of the distribution ratio. A direct third-power dependence on the concentration of free solvent, D2EHPA, in a toluene diluent, and an inverse third-power dependence on the aqueous acidity were determined.

In 1963, Pierce and Peck (17) studied the extraction of tracer quantities of rare earths using D2EHPA in toluene and perchloric acid in water as solvents. Separation factors for each rare earth relative to each of the others were reported.

The equilibrium data reported heretofore have been measured for tracer concentrations of rare earths in D2EHPA. In 1965, the first data at concentrations suitable for operating a commercial extractor were reported for this solvent. Goto and Smutz (6) reported equilibrium data for the system Pr-Nd-HCl-D2EHPA with HCl as a parameter.

Separation factors for the SmCl_3 - NdCl_3 -HCl-D2EHPA system were reported by Battista, Mize, and Smutz (3) to be higher than those for the $\text{Sm}(\text{NO}_3)_3$ - $\text{Nd}(\text{NO}_3)_3$ - HNO_3 -D2EHPA system.

Other contributors to equilibrium data for concentrations greater than tracer-level were Nair and Smutz (11) who obtained data for La, Pr, Nd, and Sm for the D2EHPA-HCl system, Lenz (9), Owens (12), Ioannou (8), and Goto (5). Owens extended the study of macro equilibrium data for the above system to the lanthanides (Gd, Dy, Er, and Yb). Ioannou reported more complete data for the single component systems of Nd and Sm in D2EHPA-Amsco and for Nd-Sm mixtures. In addition, Ioannou presented models for predicting equilibrium data for the Sm-Nd mixtures. Goto obtained data for YCl_3 , ErCl_3 , and HoCl_3 for D2EHPA in n-heptane and showed that the separation factor for the Er-Y pair was essentially the same in a multi-salt system as in a two salt system.

EXPERIMENTAL

The lanthanide oxides used in this study were obtained as the oxides from the Rare-Earth Separations Group of the Ames Laboratory of the Atomic Energy Commission. The purity of the oxides was greater than 99.9 percent with respect to the presence of other rare-earth oxides as determined by emission spectroscopy.

The D2EHPA was obtained from Union Carbide Corporation and was then mixed with Amsco Odorless Mineral Spirits (hydrocarbon diluent) obtained from American Mineral Spirits Company to form a 1M solution of D2EHPA on a monomeric basis (hereafter designated 1M D2EHPA). Titration with sodium hydroxide indicated that the undiluted D2EHPA was 98.8 percent monoacidic. The hydrochloric acid was reagent grade material.

The rare earth oxides were reacted with excess HCl according to the reaction:

Excess chloride was removed by boiling the solution until the pH was about 3.5. In this pH range hydrolysis of the rare earths was evident, therefore HCl was added until the pH was about 1.0 after the solution had been heated below the boiling point for several hours. This assured the removal of any hydrolysis products.

Primary stock solutions of YbCl_3 and TmCl_3 of known concentrations of rare earth chloride were used in the preparation of the feed solutions. The correct amounts of the primary stock solutions and of HCl were measured volumetrically into a volumetric flask, and distilled water was added to give the desired initial rare earth chloride concentration and acidity.

A known volume of aqueous feed solution was equilibrated with an equal volume of the organic solvent (1M D2EHPA) in a separatory funnel by shaking the two phases vigorously for three minutes, allowing the phases to separate for at least one hour, and then shaking vigorously for an additional two minutes. The separatory funnel was then allowed to remain undisturbed for at least 12 hours before the two phases were separated and the analysis begun.

After removal from the separatory funnel, the organic phase was often cloudy, probably due to entrained aqueous material. To remove the cloudiness, the organic phase was centrifuged for at least 15 minutes in a clinical centrifuge. After centrifuging the organic phase was quite clear, though not colorless.

When TmCl_3 was the only solute, a portion of the organic phase was measured volumetrically into a separatory funnel where it was contacted four times with double volumes of approximately 8M HCl . This removed the Tm quantitatively

from the organic phase.

When YbCl_3 or a mixture of YbCl_3 and TmCl_3 were the organic solutes, a portion of the organic phase was measured into a separatory funnel where it was contacted four times with 8M HCl and with an acid to organic solvent volume ratio of 12.5:1. This removed the YbCl_3 completely into the aqueous phase.

The aqueous strip solution was recovered in a volumetric flask, diluted, and filtered to remove any excess organic present. A known sample of this solution was analyzed for lanthanide content, and the concentration of rare earth in the organic phase was calculated.

The total lanthanide concentration of the initial phase, the equilibrated aqueous phase, and the organic back-extract were determined by titrating with standardized EDTA. Arsenazo was the indicator and pyridine was used as the buffer, as described by Fritz et al. (4). All equilibrium data were obtained at a temperature of $25 \pm 1^\circ\text{C}$.

The titration of the organic strip solution was very slow and the color change was not distinct. This effect was probably caused by the presence of organic and inorganic phosphates complexed with the indicator. The difficulty was resolved by acidifying the solution to a pH of 2 by adding several drops of concentrated HCl. The HCl dissolved the sparingly soluble complexes and the titration was con-

tinued, after readjusting the pH. This procedure gave a sharper end-point.

The acidity of the initial and final aqueous solutions was measured using Dowex 50 x 8 cation exchange resin as outlined by Adams and Campbell (1). The resin exchanged three hydrogen ions for one rare earth ion; then the total hydrogen ion present was titrated using standardized sodium hydroxide with phenolphthalein as indicator.

The binary system $\text{YbCl}_3\text{-TmCl}_3\text{-HCl-H}_2\text{O-1M D2EHPA-Amsco}$ was also studied and the total equilibrium data were determined employing the same methods as described for the single-component systems. In addition, the compositions of all phases were required. The relative amounts of YbCl_3 and TmCl_3 in all phases were determined spectrophotometrically following the method given by Banks and Klingman (2).

Aliquots of the equilibrated aqueous and back-extract solutions were utilized to precipitate the lanthanide with saturated oxalic acid. The oxalates were then ignited to the oxides in an 800°C oven and weighed samples of the oxide mixtures were dissolved in perchloric acid to form a 1M perchlorate solution. The relative amounts of YbCl_3 and TmCl_3 were determined using a Beckman DU-2 spectrophotometer. The absorbance of YbCl_3 was read at a wavelength of 974.0 m μ and a slit width of 0.02 mm. The absorbance of TmCl_3 was read at a wavelength of 683.0 m μ and a slit width of 0.02 mm.

RESULTS AND DISCUSSION

Equilibrium Data for the System
 TmCl_3 -5M HCl-H₂O-1M D2EHPA-Amsco

The experimental equilibrium data for the system TmCl_3 -5M HCl-H₂O-1M D2EHPA in Amsco are presented graphically in Figure 1 where the concentration of thulium chloride in the organic phase as a function of the aqueous thulium chloride concentration is shown. The concentration of HCl in the aqueous phase must be associated with each point. The equilibrium data used in plotting Figure 1 are given in Table 1. The initial feed concentrations of thulium chloride and HCl which were equilibrated with 1M D2EHPA in Amsco, the equilibrium concentrations of thulium in the aqueous and organic phases, and the equilibrium acidity in the aqueous phase are also given.

The shape and position of the equilibrium curve in Figure 1 agreed with the shape of similar curves reported by Owens (12) for the YbCl_3 and ErCl_3 systems. More specifically, TmCl_3 was found to be more extractable than ErCl_3 but less extractable than YbCl_3 at 5M HCl. The organic solute concentration increased very rapidly at low aqueous concentrations and then increased steadily as the aqueous concentration was further increased to saturation.

In 5M HCl, it was found that the maximum allowable aqueous concentration of TmCl_3 was 1.537 moles/liter before

Figure 1. Equilibrium data for the system TmCl_3 -5M HCl-
 H_2O -1M D2EHPA in Amsco at 25° C

Table 1. Equilibrium data for the system $\text{TmCl}_3\text{-HCl-H}_2\text{O-1M D2EHPA}$ in Amsco at approximately 5.0M HCl and 25°C

Species	Initial aqueous phase concentration moles/liter	Equilibrium aqueous phase concentration moles/liter	Equilibrium organic phase concentration moles/liter	Predicted organic phase concentration moles/liter
TmCl_3	0.139	0.072	0.070	0.076
HCl	4.74	4.92		
TmCl_3	0.343	0.246	0.095	0.094
HCl	4.62	4.92		
TmCl_3	0.599	0.490	0.109	0.106
HCl	4.32	4.77		
TmCl_3	0.854	0.741	0.113	0.113
HCl	4.27	4.72		
TmCl_3	1.121	0.986	0.120	0.119
HCl	4.68	4.92		

Table 1. (Continued)

Species	Initial aqueous phase concentration moles/liter	Equilibrium aqueous phase concentration moles/liter	Equilibrium organic phase concentration moles/liter	Predicted organic phase concentration moles/liter
TmCl ₃	1.358	1.234	0.125	0.123
HCl	4.68	4.95		
TmCl ₃	1.615	1.484	0.135	0.127
HCl	4.68	4.93		
TmCl ₃	1.674	1.537	0.137	0.128
HCl	4.51	4.77		

white $\text{TmCl}_3 \cdot 6 \text{H}_2\text{O}$ crystals were formed. In addition, for systems with higher HCl concentration, the solubility of TmCl_3 was reduced further because the solutions more readily became saturated with chloride ions which forced the TmCl_3 to crystallize out as a solid phase. This suggests that an unwanted third phase could be formed in an extractor not only by insoluble polymer formation at high thulium concentrations in the organic phase (13, 15) but also by crystal formation at high TmCl_3 aqueous concentrations which exceed the solubility limit for a particular acidity in the aqueous phase.

Single Component Equilibrium Equations

The equilibrium distributions for the single component lanthanide systems, TmCl_3 -5M HCl- H_2O -1M D2EHPA-Amsco and YbCl_3 -5M HCl- H_2O -1M D2EHPA-Amsco, were represented in the form:

$$Y_{\text{RE}} = K_{\text{RE}}(X_{\text{RE}})^N ,$$

which, on taking logarithms, gives:

$$\log Y_{\text{RE}} = \log K_{\text{RE}} + N \log X_{\text{RE}} ,$$

where RE = Tm or Yb, K is a constant, and $N < 1.0$.

Thus, N is the slope of the straight line obtained from a log-log plot of Y_{RE} against X_{RE} . Figure 2 is such a plot. For straight lines through the Yb-5M HCl data

Figure 2. Dependency of extractability on aqueous RECl_3 concentration for the systems YbCl_3 -5M HCl- H_2O -1M D2EHPA and TmCl_3 -5M HCl- H_2O -1M D2EHPA in Amsco at 25° C

reported by Owens (12) and the TmCl_3 -5M HCl data of this work, the slopes were both 0.168. At $X_{\text{RE}} = 1.00$, $Y_{\text{RE}} = K_{\text{RE}}$. Thus, the constants are $K_{\text{Tm}} = 0.120$ and $K_{\text{Yb}} = 0.155$, and the experiment equations are:

$$Y_{\text{Yb}} = 0.155 (X_{\text{Yb}})_A^{0.168}, \quad (\text{H}^+)_A = 5.0\text{M} \quad (1)$$

$$Y_{\text{Tm}} = 0.120 (X_{\text{Tm}})_A^{0.168}, \quad (\text{H}^+)_A = 5.0\text{M} \quad (2)$$

These equations can be used to predict the distribution data in the range $(X_{\text{T}})_A = 0.1$ to 1.54 moles/liter with an accuracy of ± 6 percent. Predictions using these equations are given in Table 1.

Previous data by Harada (7) showed that below $X_{\text{Yb}} = 0.01$ the simple ion exchange reaction was the predominate extraction mechanism. Therefore, in this range, $(Y_{\text{T}})_0 = C(X_{\text{T}})_A^{1.00}$ where C is a constant. Between $(X_{\text{T}})_A = 0.01$ and 0.1 was a transition regime where the exponent on $(X_{\text{T}})_A$ varied rapidly from 1.00 to 0.168 , respectively. The upper limit on $(X_{\text{T}})_A$, 1.54M , was the solubility limit of TmCl_3 in 5M HCl .

Binary Equilibrium Data for the System YbCl_3 - TmCl_3 -5M HCl- H_2O -1M D2EHPA in Amsco

Table 2 gives the equilibrium data for the YbCl_3 - TmCl_3 -5M HCl- H_2O -1M D2EHPA-Amsco system over the range of YbCl_3 final aqueous molar ratios from $(N_{\text{Yb}})_A = 0.0$ to 1.00

Table 2. Equilibrium data for the system $\text{YbCl}_3\text{-TmCl}_3\text{-HCl-H}_2\text{O}$ -1M D2EHPA in Amsco at approximately 5.0M HCl and 25° C

Species	Initial aqueous phase concentration moles/liter	Equilibrium aqueous phase concentration moles/liter	Equilibrium organic phase concentration moles/liter
RECl_3	0.357	0.245	0.112
YbCl_3	0.205	0.120	0.084
TmCl_3	0.152	0.125	0.028
HCl	4.62	4.89	
RECl_3	0.360	0.243	0.117
YbCl_3	0.286	0.179	0.106
TmCl_3	0.074	0.064	0.011
HCl	4.59	4.92	
RECl_3	0.365	0.244	0.121
YbCl_3	0.336	0.218	0.116
TmCl_3	0.029	0.026	0.005
HCl	4.58	4.99	
RECl_3	1.561	1.426	0.135
YbCl_3	0.166	0.134	0.032
TmCl_3	1.395	1.292	0.103
HCl	4.97	5.24	

Initial organic concentration moles/liter	Initial aqueous phase molar ratio moles/moles	Equilibrium aqueous phase molar ratio moles/moles	Equilibrium organic phase molar ratio moles/moles
0.00	1.0000	1.0000	1.0000
	0.5748	0.4884	0.7554
	0.4252	0.5116	0.2446
0.00	1.0000	1.0000	1.0000
	0.7946	0.7381	0.9051
	0.2054	0.2619	0.0949
0.00	1.0000	1.0000	1.0000
	0.9213	0.8948	0.9628
	0.0787	0.1052	0.0372
0.00	1.0000	1.0000	1.0000
	0.1063	0.0939	0.2371
	0.8937	0.9061	0.7629

Table 2. (Continued)

Species	Initial aqueous phase concentration moles/liter	Equilibrium aqueous phase concentration moles/liter	Equilibrium organic phase concentration moles/liter
RECl ₃	0.138	0.177	0.095
YbCl ₃	0.000	0.013	0.019
TmCl ₃	0.138	0.164	0.076
HCl	4.95	4.83	
RECl ₃	0.343	0.246	0.095
YbCl ₃	0.000	0.000	0.000
TmCl ₃	0.343	0.246	0.095
HCl	4.62	4.92	

Initial organic concentration moles/liter	Initial aqueous phase molar ratio moles/moles	Equilibrium aqueous phase molar ratio moles/moles	Equilibrium organic phase molar ratio moles/moles
0.135	1.0000	1.0000	1.0000
0.032	0.0000	0.0733	0.1994
0.103	1.0000	0.9267	0.8005
0.00	1.0000	1.00	1.00
	0.0000	0.00	0.00
	1.0000	1.00	1.00

when the total concentration of rare earth chloride was 0.244 moles/liter. The initial aqueous feed concentrations and molar ratios of YbCl_3 , TmCl_3 , RECl_3 (i.e., total rare earth chloride), and HCl which were equilibrated with 1M D2EHPA in Amsco, and the equilibrium concentrations and molar ratios of these species in the aqueous and organic phases were given. When the initial organic concentrations were not zero, equilibrium was reached by back-extraction (i.e., scrubbing).

Figure 3 gives the equilibrium data in graphical form and indicates the total concentration of rare earth chloride (i.e., YbCl_3 - TmCl_3) in the organic phase as the ytterbium final aqueous molar ratio was varied. Figure 4 presents the same data but shows the total YbCl_3 - TmCl_3 concentration in the organic phase as the equilibrium organic molar ratio of Yb, $(N_{\text{Yb}})_0$, was varied. For both graphs, the aqueous concentration of HCl and rare earth chloride must be associated with each point.

The curves in Figures 3 and 4, at 5M HCl and 0.24M RECl_3 , agree with the shape of similar curves reported by Ioannou (8) for the SmCl_3 - NdCl_3 system. More specifically, the variation of the total organic concentration of RECl_3 with respect to the YbCl_3 aqueous molar ratio was found to be slightly greater than a linear variation, and the variation of the total organic concentration of RECl_3 with

Figure 3. Equilibrium data for the system $YbCl_3$ - $TmCl_3$ -5M HCl - H_2O -1M D2EHPA in Amsco at $25^\circ C$

Figure 4. Equilibrium data for the system YbCl₃-TmCl₃-5M HCl-H₂O-1M D2EHPA in Amsco at 25° C

respect to the Yb organic molar ratio was found to be slightly less than a linear variation.

The difference in variations for these two cases can be attributed to the selectivity of the D2EHPA solvent for Yb with respect to Tm. This selectivity caused all the Yb organic molar ratios to be greater than the corresponding equilibrium aqueous molar ratios and, concomitantly, caused Figures 3 and 4 to differ.

Separation Factor: $\beta_{Yb,Tm}$

In conjunction with the above experiments, a separation factor (or selectivity) study was carried out. The separation factor of Yb with respect to Tm is defined mathematically as,

$$\beta_{Yb,Tm} = \frac{(E_A^O)_{Yb}}{(E_A^O)_{Tm}} = \frac{(Y/X)_{Yb}}{(Y/X)_{Tm}}$$

when both Yb and Tm are present together. Figure 5 shows the separation factor, $\beta_{Yb,Tm}$, obtained using 1M D2EHPA as the solvent and a 5M HCl solution as the aqueous phase. The aqueous molar ratio of $YbCl_3$ varied from 0.1 to 0.9.

The arithmetic average separation factor found when equilibrium was reached by forward-extraction (i.e., contacting an aqueous feed with pure organic solvent) was 3.22. In addition, when equilibrium was reached by back-extraction (i.e., scrubbing an organic feed with an aqueous

Figure 5. Separation factors, $B_{\text{Yb,Tm}}$, for the system YbCl_3 - TmCl_3 -5M HCl - H_2O -1M D2EHPA in Amsco at 25°C

solution of TmCl_3 -5M HCl), the separation factor was 3.15. However, in both the above cases, the separation factor agreed with the value of 3.09 reported by Pierce and Peck (17) for tracer level concentrations of Tm and Yb in an aqueous perchlorate system.

Binary Equilibrium Equations

The smooth curves in Figures 3 and 4 were represented in the form:

$$\begin{aligned} (Y_T)_O &= A + B (N_{Yb})^b, & (X_T)_A &= \text{constant, or} \\ & & (H^+)_A &= \text{constant} \\ (Y_T)_O - A &= B(N_{Yb})^b \end{aligned}$$

which, on taking logarithms, gives:

$$\log (Y_T - A) = \log B + b \log (N_{Yb}),$$

where A is the organic concentration of thulium, Y_{Tm} , at a fixed but arbitrary value of $(X_T)_A$ on a pure TmCl_3 distribution plot and where the constant B is the difference at $(X_T)_A$ between the organic concentrations of YbCl_3 and TmCl_3 on their respective pure distribution plot as shown in Figure 6. Thus, b is the slope of a log-log plot of the difference $(Y_T - Y_{Tm})_O$ against N_{Yb} . Figure 7 is a log-log plot of $(Y_T - Y_{Tm})_O$ against $(N_{Yb})_A$, with a slope of 0.699, and Figure 8 is a log-log plot of $(Y_T - Y_{Tm})_O$ against $(N_{Yb})_O$, with a slope of 1.78. The linear log-log relation

Figure 6. Equilibrium data for the systems YbCl_3 -5M HCl - H_2O -1M D2EHPA and TmCl_3 -5M HCl - H_2O -1M D2EHPA in Amsco at 25° C

Figure 7. Dependency of total organic concentration of RECl₃ on aqueous molar ratio of Yb: (H⁺)_A = 5.0M, (X_T)_A = 0.24M, 25° C

Figure 8. Dependency of total organic concentration of $RECl_3$ on organic molar ratio of Yb: $(H^+)_{\text{A}} = 5.0M$, $(X_{\text{T}})_{\text{A}} = 0.24 M$, $25^\circ C$

was obeyed very well. Thus, the experiment equations for the dependency of extractability on molar ratio are:

$$\begin{aligned} (Y_T)_O &= 0.095 + 0.028 (N_{Yb})_A^{0.699}, & (X_T)_A &= 0.24M, & (3) \\ & & (H^+)_A &= 5.0M \end{aligned}$$

and

$$\begin{aligned} (Y_T)_O &= 0.095 + 0.028 (N_{Yb})_O^{1.78}, & (Y_F)_A &= 0.24M, & (4) \\ & & (H^+)_A &= 5.0M \end{aligned}$$

CORRELATION OF TOTAL DISTRIBUTION COEFFICIENTS

FOR $\text{YbCl}_3\text{-TmCl}_3\text{-HCl-H}_2\text{O-1M D2EHPA-Amsco}$

Owens (12) and Peterson (16) found that the total distribution coefficient, E_A^O , for a binary lanthanide mixture, thulium chloride-ytterbium chloride- $\text{H}_2\text{O-HCl-1M D2EHPA}$ in Amsco, was a function of the following parameters at equilibrium: total concentration of rare earth chloride in the aqueous phase, $(X_T)_A$, molar ratio (i.e., mole fraction on a solvent free basis) of ytterbium in the aqueous phase, $(N_{Yb})_A$, and acidity of the aqueous phase, $(H^+)_A$. In mathematical form this may be stated:

$$E_A^O = f((X_T)_A, (N_{Yb})_A, (H^+)_A) = \frac{(Y_T)_O}{(X_T)_A} .$$

In differential form, the expression is,

$$\begin{aligned} dE_A^O &= \left[\frac{\partial E_A^O}{\partial (X_T)_A} \right]_{(N_{Yb})_A, (H^+)_A} d(X_T)_A + \left[\frac{\partial E_A^O}{\partial (N_{Yb})_A} \right]_{(X_T)_A, (N_{Yb})_A} d(N_{Yb})_A \\ &+ \left[\frac{\partial E_A^O}{\partial (H^+)_A} \right]_{(X_T)_A, (N_{Yb})_A} d(H^+)_A . \end{aligned}$$

A study of the variations of E_A^O with $(X_T)_A$, $(N_{Yb})_A$, and $(H^+)_A$ made it possible to develop an experimental model for E_A^O in the system $\text{YbCl}_3\text{-TmCl}_3\text{-HCl-H}_2\text{O-D2EHPA-Amsco}$.

Interpretation of Partial Derivatives of E_A^O

The partial derivative,

$$\left[\frac{\partial E_A^O}{\partial (X_T)_A} \right]_{(N_{Yb})_A, (H^+)_A},$$

is the change of the total distribution, E_A^O , with total $RECl_3$ concentration in the aqueous phase at constant molar ratio of $YbCl_3$ in the aqueous phase and at constant acidity of the aqueous phase. For this experimental model of the extraction process, it was assumed that the dependence of E_A^O on $(X_T)_A$ would be the same for intermediate values of $(N_{Yb})_A$ as for the boundary values of zero and unity.

The partial derivative,

$$\left[\frac{\partial E_A^O}{\partial (N_{Yb})_A} \right]_{(X_T)_A, (H^+)_A},$$

is the change of E_A^O with molar ratio of ytterbium in the aqueous phase at constant total $RECl_3$ aqueous concentration and at constant acidity of the aqueous phase. For this model, the dependence of E_A^O on $(N_{Yb})_A$ was assumed to be the same for different fixed but arbitrary values of $(X_T)_A$.

The partial derivative,

$$\left[\frac{\partial E_A^O}{\partial (H^+)_A} \right]_{(X_T)_A, (N_{Yb})_A},$$

is the change of E_A^0 with the final acidity of the aqueous phase when $(X_T)_A$ and $(N_{Yb})_A$ are constant. The extraction of lanthanide ions by D2EHPA at tracer levels was reported by Peppard et al. (14) to be a simple ion exchange reaction:

The equilibrium constant for the extraction reaction is:

$$K = \frac{[RE(HG_2)_3][H^+]^3}{[RE^{+3}][(HG)_2]^3} ,$$

where $[HG]$ = concentration of D2EHPA monomer, $\begin{matrix} RO \\ RO \\ HO \end{matrix} \begin{matrix} \diagup \\ \diagdown \end{matrix} P = O$.

$$\text{Since } E_A^0 = \frac{[RE(HG_2)_3]_O}{[RE^{+3}]_A} , \text{ then } K = E_A^0 \frac{[H^+]^3}{[(HG)_2]^3} .$$

When the activity coefficients are assumed to be unity,

$$E_A^0 = \frac{(Y_T)_O}{(X_T)_A} = K[(HG)_2]^3 [H^+]^{-3} .$$

But this inverse third power dependence of E_A^0 on $(H^+)_A$ is not followed at high $RECl_3$ concentrations (7, 8). Thus, other correlations of E_A^0 to $(H^+)_A$ were considered.

Because of the high extractability of the heavier rare earth chlorides by D2EHPA, it was necessary to have high acidities (5M to 8M) in the aqueous phase to avoid formation of an insoluble polymer (15) in the organic phase. However, in the region of 8M HCl, it has been shown (7, 10) that the

distribution coefficients for the heavier rare earths-HCl-H₂O-D2EHPA-Amsco systems exhibit minimum values with respect to the acidity, and that the variation of E_A^0 with $(H^+)_A$ is small in this region. Thus, for this extraction process in this work which operated in the region of 5M HCl, the acid dependence of the distribution coefficient was neglected (i.e.,

$$\left[\frac{\partial E_A^0}{\partial (H^+)_A} \right]_{(X_T)_A, (N_{Yb})_A} = 0),$$

and the acidity assumed to be constant at 5M HCl.

Although these assumptions appear quite reasonable, they can only be justified by the comparison of predicted values with observed experimental results to be shown in the "Verification of Model" section.

Development of Model for the Total Distribution Function

In general, the total distribution function has been described as:

$$E_A^0 = f[(X_T)_A, (N_{Yb})_A, (H^+)_A] = \frac{(Y_T)_0}{(X_T)_A}, \quad (5)$$

or, in differential form,

$$\begin{aligned}
dE_A^O &= \left[\frac{\partial E_A^O}{\partial (X_T)_A} \right]_{(N_{Yb})_A, (H^+)_A} d(X_T)_A + \left[\frac{\partial E_A^O}{\partial (N_{Yb})_A} \right]_{(X_T)_A, (H^+)_A} d(N_{Yb})_A \\
&+ \left[\frac{\partial E_A^O}{\partial (H^+)_A} \right]_{(X_T)_A, (N_{Yb})_A} d(H^+)_A .
\end{aligned} \tag{6}$$

However, for reasons stated previously,

$$\left[\frac{\partial E_A^O}{\partial (H^+)_A} \right]_{(X_T)_A, (N_{Yb})_A} = 0 .$$

Thus, the differential equation becomes:

$$dE_A^O = \left[\frac{\partial E_A^O}{\partial (X_T)_A} \right]_{(N_{Yb})_A, (H^+)_A} d(X_T)_A + \left[\frac{\partial E_A^O}{\partial (N_{Yb})_A} \right]_{(X_T)_A, (H^+)_A} d(N_{Yb})_A . \tag{7}$$

The equilibrium distributions of $TmCl_3$ and $YbCl_3$, at constant aqueous molar ratios of $YbCl_3$ and at a constant aqueous acidity of 5M HCl, have been shown to conform to the respective experimental equations:

$$Y_{Yb} = 0.155 (X_{Yb})^{0.168}, \quad (N_{Yb})_A = 1.00, \quad (H^+)_A = 5.0M \tag{1}$$

$$Y_{Tm} = 0.120 (X_{Tm})^{0.168}, \quad (N_{Yb})_A = 0.00, \quad (H^+)_A = 5.0M \tag{2}$$

and in general,

$$(Y_T)_O = k(X_T)_A^{0.168}, \quad (N_{Yb})_A = \text{constant}, \quad (H^+)_A = 5.0M, \quad (8)$$

where k is a constant. Thus,

$$E_A^O = \frac{(Y_T)_O}{(X_T)_A} = \frac{k(X_T)_A^{0.168}}{(X_T)_A} = k(X_T)_A^{-0.832}, \quad (N_{Yb})_A = \text{constant}, \quad (H^+)_A = 5.0M \quad (9)$$

Therefore,

$$\left[\frac{\partial E_A^O}{\partial (X_T)_A} \right]_{(N_{Yb})_A, (H^+)_A} = -0.832 k(X_T)_A^{-1.832}. \quad (10)$$

But by Equation 9, $k = E_A^O (X_T)_A^{0.832}$. Eliminating k from Equation 10,

$$\left[\frac{\partial E_A^O}{\partial (X_T)_A} \right]_{(N_{Yb})_A, (H^+)_A} = -0.832 \frac{E_A^O}{(X_T)_A}. \quad (11)$$

The variation of $(Y_T)_O$ with the equilibrium molar ratio of Yb in the aqueous phase, when the total aqueous concentration was constant and when the aqueous acidity was constant, was shown to conform to the experimental equation:

$$(Y_T)_O = 0.095 + 0.028 (N_{Yb})_A^{0.699}, \quad (X_T)_A = 0.24M \quad (3) \\ , \quad (H^+)_A = 5.0M$$

and in general,

$$(Y_T)_O = A + B (N_{Yb})_A^{0.699}, \quad (X_T)_A = \text{constant}, \quad (12)$$

$$(H^+)_A = \text{constant}$$

where the constants A and B were previously defined. The equilibrium distribution coefficient for pure Tm is:

$$(E_A^O)_{Tm} = \frac{(Y_{Tm})_O}{(X_{Tm})_A}.$$

It follows that: $A = (E_A^O)_{Tm} \cdot (X_T)_A$ and that Equation 12 becomes:

$$(Y_T)_O = (E_A^O)_{Tm} \cdot (X_T)_A + B(N_{Yb})_A^{0.699}, \quad (X_T)_A = \text{constant},$$

$$, (H^+)_A = \text{constant} \quad (13)$$

To simplify the mathematical expression (Equation 13) and to facilitate the solution of the differential equation (Equation 7), a new variable, η , was defined as:

$$\eta = (N_{Yb})_A^{0.699} + (E_A^O)_{Tm} \frac{(X_T)_A}{B}, \quad (14)$$

where $(X_T)_A$ and concomitantly $(E_A^O)_{Tm}$ are fixed.

Thus, from Equations 13 and 14:

$$(Y_T)_O = B \left[\eta - (E_A^O)_{Tm} \cdot \frac{(X_T)_A}{B} \right] + (E_A^O)_{Tm} \cdot (X_T)_A$$

$$= B\eta - (E_A^O)_{Tm} \cdot (X_T)_A + (E_A^O)_{Tm} \cdot (X_T)_A$$

Thus, $(Y_T)_O = B\eta$ and

$$E_A^O = \frac{(Y_T)_O}{(X_T)_A} = \frac{B\eta}{(X_T)_A}, \quad \begin{array}{l} (X_T)_A = \text{constant} \\ (H^+)_A = \text{constant} \end{array} \quad (15)$$

Therefore,

$$\left[\frac{\partial E_A^O}{\partial \eta} \right]_{(X_T)_A, (H^+)_A} = \frac{B}{(X_T)_A} = -\frac{E_A^O}{\eta}.$$

Recasting the last term of Equation 7 in terms of $\eta = \eta[(N_{Yb})_A]$,

$$\left[\frac{\partial E_A^O}{\partial (N_{Yb})_A} \right]_{(X_T)_A, (H^+)_A} = \left[\frac{\partial E_A^O}{\partial \eta} \cdot \frac{\partial \eta}{\partial (N_{Yb})_A} \right]_{(X_T)_A, (H^+)_A}$$

and

$$d(N_{Yb})_A = \left[\frac{\partial (N_{Yb})_A}{\partial \eta} \right]_{(X_T)_A, (H^+)_A} d\eta + \left[\frac{\partial (N_{Yb})_A}{\partial (X_T)_A} \right]_{\eta, (H^+)_A} d(X_T)_A.$$

Since in Equation 14, $(H^+)_A$ and $(X_T)_A$ are fixed,

$$d(N_{Yb})_A = \left[\frac{\partial (N_{Yb})_A}{\partial \eta} \right]_{(X_T)_A, (H^+)_A} d\eta.$$

Thus,

$$\begin{aligned} \left[\frac{\partial E_A^O}{\partial (N_{Yb})_A} \right]_{(X_T)_A, (H^+)_A} d(N_{Yb})_A &= \left[\frac{\partial E_A^O}{\partial \eta} \cdot \frac{\partial \eta}{\partial (N_{Yb})_A} \right] \cdot \left[\frac{\partial (N_{Yb})_A}{\partial \eta} \right] d\eta \\ &= \left[\frac{\partial E_A^O}{\partial \eta} \right]_{(X_T)_A, (H^+)_A} d\eta \end{aligned}$$

and the differential equation (Equation 6) becomes:

$$dE_A^0 = \left[\frac{\partial E_A^0}{\partial (X_T)_A} \right]_{(N_{Yb})_A, (H^+)_A} d(X_T)_A + \left[\frac{\partial E_A^0}{\partial \eta} \right]_{(X_T)_A, (H^+)_A} d\eta$$

Substituting for the partial derivatives,

$$dE_A^0 = -0.832 \frac{E_A^0}{(X_T)_A} d(X_T)_A + \frac{E_A^0}{\eta} d\eta$$

$$\frac{dE_A^0}{E_A^0} = -0.832 \frac{d(X_T)_A}{(X_T)_A} + \frac{d\eta}{\eta}$$

$$\begin{aligned} d \ln E_A^0 &= -0.832 d \ln (X_T)_A + d \ln \eta \\ &= d \ln (X_T)_A^{-0.832} + d \ln \eta \\ &= d [\ln (X_T)_A^{-0.832} + \ln \eta] = d \ln \eta (X_T)_A^{-0.832} \end{aligned}$$

Integrating,

$$\int d \ln E_A^0 = \int d \ln \eta (X_T)_A^{-0.832} + \ln R^*$$

where $\ln R^*$ is a constant of integration. Thus,

$$\begin{aligned} \ln E_A^0 &= \ln \eta (X_T)_A^{-0.832} + \ln R^* \\ &= \ln (R^* \eta (X_T)_A^{-0.832}) \end{aligned}$$

Removing the logarithms,

$$E_A^0 = R^* \eta (x_T)_A^{-0.832} = \frac{R^* \eta}{(x_T)_A^{0.832}} \quad (16)$$

Rearranging the expression for η ,

$$\eta = (N_{Yb})_A^{0.699} + (E_A^0)_{Tm} \cdot \frac{(x_T)_A}{B};$$

but by Equation 14:

$$\frac{(x_T)_A}{B} = \frac{\eta}{E_A^0}.$$

Thus,

$$\eta = (N_{Yb})_A^{0.699} + (E_A^0)_{Tm} \frac{\eta}{E_A^0},$$

or

$$\eta \left[1 - \frac{(E_A^0)_{Tm}}{E_A^0} \right] = (N_{Yb})_A^{0.699},$$

and

$$\eta = \frac{(N_{Yb})_A^{0.699}}{\left[1 - \frac{(E_A^0)_{Tm}}{E_A^0} \right]} = (N_{Yb})_A^{0.699} \frac{E_A^0}{E_A^0 - (E_A^0)_{Tm}}$$

Recasting E_A^0 (Equation 16) in terms of $(N_{Yb})_A$:

$$E_A^0 = \frac{R^*}{(x_T)_A^{0.832}} \left[(N_{Yb})_A^{0.699} \frac{E_A^0}{E_A^0 - (E_A^0)_{Tm}} \right].$$

Rearranging terms,

$$E_A^O \left[\frac{E_A^O - (E_A^O)_{Tm}}{E_A^O} \right] = E_A^O - (E_A^O)_{Tm} = \frac{R^* (N_{Yb})_A^{0.699}}{(X_T)_A^{0.832}} .$$

Therefore,

$$E_A^O = (E_A^O)_{Tm} + \frac{R^* (N_{Yb})_A^{0.699}}{(X_T)_A^{0.832}} . \quad (17)$$

From Equation 2, it follows that:

$$\begin{aligned} (E_A^O)_{Tm} &= \frac{Y_{Tm}}{X_{Tm}} = \left[\frac{(Y_T)_O}{(X_T)_A} \right]_{N_{Yb} = 0.0} = \frac{0.120 (X_T)_A^{0.168}}{(X_T)_A} \\ &= \frac{0.120}{(X_T)_A^{0.832}} , \quad N_{Yb} = 0.0 . \end{aligned} \quad (18)$$

Combining Equations 17 and 18,

$$E_A^O = \frac{0.120 + R^* (N_{Yb})_A^{0.699}}{(X_T)_A^{0.832}} . \quad (19)$$

Determination of the constant R^*

$$R^* = \frac{E_A^O (X_T)_A^{0.832} - 0.120}{(N_{Yb})_A^{0.699}}$$

Using the boundary condition (Equation 1),

$$(Y_T)_O = 0.155 (X_T)_A^{0.168} , \quad N_{Yb} = 1.00 , \quad \text{or}$$

$$E_A^O = \frac{(Y_T)_O}{(X_T)_A} = \frac{0.155 (X_T)_A^{0.168}}{(X_T)_A} = \frac{0.155}{(X_T)_A^{0.832}} .$$

Thus,

$$R^* = \frac{0.155 - 0.120}{1.00} = 0.035$$

and Equation 19 becomes:

$$E_A^O = \frac{0.120 + 0.035 (N_{Yb})_A^{0.699}}{(X_T)_A^{0.832}} \quad (20)$$

The region of applicability of this model was the same as that for the experimental Equations 1, 2, 3, and 4:

$$(H^+)_A = 5M$$

$$0.1 \leq (X_T)_A \leq 1.54$$

$$0.0 \leq (N_{Yb})_A \leq 1.00$$

In stage-by-stage calculations for an extractor, it was convenient to have E_A^O expressed in terms of the total organic concentration and the organic molar ratio of Yb. A similar development to the one above, using Equation 4, gave:

$$(E_A^O)^{0.168} = \frac{0.120 + 0.035 (N_{Yb})_O^{1.78}}{(Y_T)_O^{0.832}} \quad (21)$$

where

$$(H^+)_{\text{A}} = 5M$$

$$0.08 \leq (Y_{\text{T}})_{\text{O}} \leq 0.176$$

$$0.00 \leq (N_{\text{Yb}})_{\text{O}} \leq 1.00$$

The upper limit on $(Y_{\text{T}})_{\text{O}}$, 0.176, is the solubility limit of the solvent.

VERIFICATION OF
TOTAL DISTRIBUTION COEFFICIENT MODEL

To test the precision of the total distribution coefficient model by comparison of predicted results with experimental results and to design an extraction process for the fractional extraction of a 90 percent YbCl_3 -10 percent TmCl_3 -5N HCl feed into a 98 percent YbCl_3 extract product at 90 percent YbCl_3 recovery, a computer simulation and a laboratory simulation of the process were carried out.

A modification of the computer program developed by Sebenik (23) for the system $\text{La}(\text{NO}_3)_3$ - $\text{Pr}(\text{NO}_3)_3$ - $\text{Nd}(\text{NO}_3)_3$ - $\text{Sm}(\text{NO}_3)_3$ - HNO_3 - H_2O -TBP (Tri-n-butyl phosphate) was used to simulate the extraction of the TmCl_3 - YbCl_3 - H_2O -HCl-D2EHFA system. Briefly, Sebenik's technique is a stage-by-stage calculation of all stream compositions for a fractional extraction cascade. It used a trial-and-error calculation starting with the flow rates of the two solvents, the number of ideal stages, the composition and flow rate of the feed, and an assumed total rare earth concentration for either the extract or the raffinate stream.

Mismatches at the feed stage are defined as the positive difference between the aqueous concentration of a component calculated from the scrub-side and that calculated from the extract-side of the cascade. A systematic reduction by a constant step is made in the

assumed end-stream concentration for the component most mismatched at the feed stage, and this mismatch is recalculated in a repetitive fashion until the difference of the mismatch changes sign.

When the difference is still greater than a predefined tolerance, the step size is reduced, and the originally assumed concentration is again decremented. This reduction in step size is continued until the difference is within tolerance. The equilibrium data are stored directly in the computer memory in tabular form, and the equilibrium distribution coefficients calculated empirically from the data.

In modifying Sebenik's digital computer program, the mathematical correlations for the total distribution coefficient, Equations 20 and 21 were used, rather than direct data input, for the system YbCl_3 - TmCl_3 -5M HCl - H_2O -1M D2EHPA.

The predicted results of the computer simulation of the process are shown in Figure 9 in a fashion analogous to the McCabe-Thiele method of distillation calculations. The predicted multicomponent equilibrium data lie inside the equilibrium curves for the pure components, YbCl_3 and TmCl_3 .

Under the same conditions (see Figure 10) as the computer simulation, a laboratory simulation of the process was carried out using a simulated column technique. A

Figure 9. Stages for fractional extraction of 90 percent YbCl_3 -10 percent TmCl_3 -5M HCl feed

Figure 10. Operating conditions for eight stage, simulated extractor: $H = 25.4$ ml, $L = 200.0$ ml, $F = 30.7$ ml

simulated column experiment is a batchwise approximation to a continuous, steady-state, extraction process. The error in the approximation may be made arbitrarily small by increasing the number of cycles the experiment is run. The mechanics and mathematical derivations involved are well accepted and have been discussed extensively by Scheibel (19, 20, 21, 22).

In carrying out equilibrations, both phases were equilibrated in 500-ml separatory funnels, shaken for five minutes, and allowed to stand for 30 minutes. The temperature was $25^{\circ} \pm 1^{\circ}$ C. The simulated column cycles were continued until the total rare earth concentration of the extract and the raffinate reached steady-state. Figure 11 showed that steady-state was achieved in 15 cycles, neglecting minor fluctuations in the data.

A complete compilation of the experimental conditions and the experimental-predicted comparisons are given in Figures 12 to 16 and Table 3. In all stages except for the first, the experimental and predicted results agree quite well. For the first stage, the extract concentration was significantly less than that predicted by the model for 5M HCl equilibrium data. This was because the aqueous acidity was much greater than 5M (i.e., 6.02); the increased acidity reduced the extractability of the rare earths.

Figure 11. Approach to steady state for the extract and for the raffinate, laboratory simulation of continuous fractional extraction

Figure 12. Comparison of stagewise total rare earth chloride concentrations in the organic phase

Figure 13. Comparison of stagewise total rare earth chloride concentrations in the aqueous phase

Figure 14. Comparison of stagewise individual rare earth chloride concentrations in the organic phase

Figure 15. Comparison of stagewise individual rare earth chloride concentrations in the aqueous phase

Figure 16. Acidity variation in extraction process

Page 54

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Table 3. Comparison of experimental and predicted stagewise molarities for simulated cascade

Stream	Total RECl ₃ concentration moles/liter		Ytterbium concentration moles/liter		Thulium concentration moles/liter		HCl concentration moles/liter	
	Exp.	Pred.	Exp.	Pred.	Exp.	Pred.	Exp.	Pred.
R ₁	0.078	0.080	0.043	0.043	0.0362	0.0373	6.09	6.29
R ₂	0.340	0.412	0.243	0.304	0.0937	0.1082	5.47	5.30
R ₃	0.518	0.535	0.439	0.452	0.0812	0.0826	5.05	4.93
R ₄	0.556	0.564	0.512	0.501	0.0583	0.0631	4.87	4.84
R ₅	0.265	0.304	0.240	0.277	0.0239	0.0271	4.82	4.58
R ₆	0.193	0.200	0.178	0.185	0.0173	0.0151	4.95	4.90
R ₇	0.142	0.135	0.133	0.126	0.0096	0.0087	5.06	5.09
R ₈	0.090	0.077	0.088	0.073	0.0054	0.0042	5.20	5.27
R ₉	0.000	0.000	0.000	0.000	0.0000	0.0000	5.45	5.50
S ₀	0.000	0.000	0.000	0.000	0.0000	0.0000	0.00	0.00
S ₁	0.073	0.093	0.060	0.073	0.0172	0.0199	0.00	0.00
S ₂	0.121	0.128	0.108	0.115	0.0140	0.0127	0.00	0.00
S ₃	0.135	0.136	0.127	0.129	0.0083	0.0073	0.00	0.00

Table 3. (Continued)

Stream	Total RECl ₃ concentration moles/liter		Ytterbium concentration moles/liter		Thulium concentration moles/liter		HCl concentration moles/liter	
	Exp.	Pred.	Exp.	Pred.	Exp.	Pred.	Exp.	Pred.
S ₄	0.137	0.138	0.132	0.133	0.0057	0.0052	0.00	0.00
S ₅	0.127	0.125	0.124	0.122	0.0052	0.0037	0.00	0.00
S ₆	0.120	0.117	0.119	0.114	0.0033	0.0029	0.00	0.00
S ₇	0.114	0.110	0.113	0.107	0.0029	0.0023	0.00	0.00
S ₈	0.101	0.100	0.099	0.098	0.0023	0.0018	0.00	0.00
F	0.802	0.796	0.725	0.717	0.0775	0.0796	5.03	5.00

CONCLUSIONS

1. The shape of the thulium chloride equilibrium curve at 5M HCl agreed with the shape of similar curves reported by Owens (12) for the YbCl_3 and ErCl_3 systems. Tm was found to be more extractable than Er but less extractable than Yb at 5M HCl.
2. As reported by Owens (12), stripping the Yb-containing organic phase four times with double volumes of 8M HCl would not remove all of the Yb from the organic phase. However, under the above conditions, Tm was removed quantitatively.
3. The back-extraction technique (four back-extractions with 8M HCl and with an acid to organic solvent volume ratio of 12.5:1) developed by Harada while at the Ames Laboratory of the U.S. Atomic Energy Commission has been found to remove the Yb quantitatively from the organic phase. The fact that the organic concentration of Yb can now be determined experimentally, rather than by difference, is a significant advance in studies of this type.
4. The total distribution coefficient, E_A^0 , for the binary lanthanide mixture, thulium chloride-ytterbium chloride-HCl-H₂O-1M D2EHPA in Amsco, was a function of the following parameters at equilibrium: the total concentration of rare earth chloride in the aqueous phase,

$(X_T)_A$, the molar ratio (i.e., mole fraction on a solvent free basis) of ytterbium in the aqueous phase, $(N_{Yb})_A$, and the acidity of the aqueous phase, $(H^+)_A$, or in mathematical form:

$$E_A^0 = f[(X_T)_A, (N_{Yb})_A, (H^+)_A] = \frac{(Y_T)_O}{(X_T)_A} .$$

The equilibrium data at 5M HCl conformed to the experimental equation:

$$E_A^0 = \frac{0.120 + 0.035 (N_{Yb})_A^{0.699}}{(X_T)_A^{0.832}} , (H^+)_A = 5.0M .$$

$$0.1 \leq (X_T)_A \leq 1.54$$

$$0.0 \leq (N_{Yb})_A \leq 1.00$$

The average error (difference between experimental and predicted divided by experimental) of this equation was less than 6 percent.

5. It was possible to write a digital computer program, using the experimental distribution function and the experimental value of the separation factor, to predict the operating conditions necessary for the fractional extraction of a 90 percent $YbCl_3$ -10 percent $TmCl_3$ -5M HCl feed into a 98 percent $YbCl_3$ extract product at 90 percent $YbCl_3$ recovery, with 1M D2EHPA in Amsco and 5M HCl in H_2O as solvents. A comparison of the results predicted by the computer technique and the results

obtained experimentally by a laboratory simulation of the extraction process indicated that the technique was valid.

6. The separation factor of Yb with respect to Tm, $\beta_{Yb,Tm}$, was found to be essentially constant and to have an arithmetic average value of 3.22.
7. The assumption made that the aqueous phase acidity, $(H^+)_{A}$, was constant at 5.0 moles/liter was valid for this extraction process as shown in Figure 16.
8. Although not demonstrated, for the $TmCl_3$ - $YbCl_3$ system, it would be possible to predict accurately the operating conditions necessary to produce a high purity Tm raffinate product and to separate feeds with higher total $RECl_3$ concentrations and with different compositions than considered in this study. Models for the multi-component equilibrium data of other binary heavier rare earth systems, such as Er-Lu, can be developed using the procedures of this study.
9. The solvent extraction process described was operated with what appeared to be the highest possible total rare earth concentration in the organic phase without the formation of an unwanted insoluble polymer (13, 15). Thus, in an actual industrial process, the total $RECl_3$ organic concentration would probably be reduced to allow for fluctuations from the steady state concentration.

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