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ABSTRACT

In this paper the behaviour of Yb and La in extraction systems, using as extractant binary mixtures of thenoyltrifluoroacetone (HTTA), di-(2-ethyl hexyl) phosphoric acid (HDEHP) and tributylphosphate (TBP) is studied, by means of the radioactive tracers ^{140}La and ^{169}Yb . Different concentrations of nitric acid and NaNO_3 as salting out were used as aqueous phase.

Distribution coefficients obtained for the two elements, using a mixture of HTTA-TBP were found to be much higher than those obtained with each of the extractants, showing synergistic effect.

A small synergistic effect was seen to exist for La, but an antagonistic effect was observed for Yb, when a mixture of HTTA plus HDEHP was used in both cases. An antagonistic effect was also found for Yb by using a mixture of HDEHP plus TBP, whereas the extraction of La was found to be independent in the TBP concentration when this mixture was used.

INTRODUCTION

Cunningham and co-workers⁽³⁾ were the first to observe the phenomenon which occurs in the extraction of metallic species by mixtures of extracting agents. They observed that the distribution ratio of the ions Pr^{+3} and Nd^{+3} obtained with mixture of HTTA and TBP, was much greater than that obtained with each of the extracting agents used separately, in the same conditions. This phenomenon was named synergism or synergistic effect by Brown and co-workers⁽²⁾.

Blake et al⁽¹⁾, studying this phenomenon, observed a large enhancement in the extraction of uranium (VI) by means of a mixture of dialkylphosphoric acid $(\text{RO})_2\text{PO}(\text{OH})$ and neutral reagent $(\text{RO})_3\text{PO}$.

Irving and Edgington⁽¹⁰⁾, investigating analogous systems in which the dialkylphosphoric acid is replaced by HTTA, found strong synergistic effects in uranium (VI) extraction.

Healy⁽⁶⁾ showed that synergism is a general effect, occurring in the extraction of alkaline earths, trivalent lanthanides, trivalent actinides and thorium (IV).

A review of the papers concerned with the synergistic effect in the extraction of lanthanides showed that several researchers observed this effect in the extraction of these elements^(4,7,9,11,13,15,18).

Irving and Edgington⁽¹¹⁾ observed synergistic effect in the extraction of Pu^{+3} , Am^{+3} and Eu^{+3} by mixtures of HTTA-TBP and HTTA-TBPO (tri-n-butyl phosphine oxide), in cyclohexane.

^(*) Paper presented at the "XXIII Brazilian Congress of Chemistry", held in Blumenau, S. C., Brasil, from 10 to 16 October 1982. Work partly supported by the "Comissão Nacional de Energia Nuclear".

Zangen⁽¹⁸⁾ studied the synergistic extraction of trivalent lanthanides and actinides, alkaline earths and thorium from hydrochloric solutions, using a combination of a mono acidic phosphate or phosphonate ester (the chelating agent) with a neutral organophosphorus compound (the synergist) at different concentrations, in cyclohexane.

Farbu and coworkers⁽⁴⁾ studied the synergistic extraction of trivalent lanthanides from perchloric medium, by mixtures of HTTA and TBP, in carbon tetrachloride. The results obtained showed a large synergistic effect.

Hirashima and co-workers⁽⁹⁾ studied the effect of some reagents together with HDEHP for the extraction of the lanthanides in hydrochloric medium. The reagents investigated were TBP, HTTA, AA (acetylacetone) and TOA (tri-n-octylamine). They observed that the addition of both TBP and AA or TOA gives rise to an antagonistic effect whereas the addition of HTTA leads to a synergistic effect.

Mathur and co-workers⁽¹⁵⁾ studied the synergistic extraction of Eu(III) with mixtures of HTTA and some neutral oxodons, like TBP, in benzene. They confirmed the occurrence of the synergistic effect in all the mixtures studied.

Kandil and Farah⁽¹³⁾ presented some results for the extraction of Tb^{+3} and Eu^{+3} with HDEHP using seven different solvents. They observed antagonistic effects for the extraction of these elements with mixtures of HDEHP plus TBP and HDEHP plus TOPO (tri-n-octylphosphine oxide).

According to Marcus and Kertes⁽¹⁴⁾, the synergism is essentially an organic-phase reaction, due to at least one of two fundamental factors:

1. the extractive power of the extracting agent increases if another extractant is added to the solution,
2. the composition of the metal-bearing species in the organic phase, when using a mixture of extracting agents, is not the same as in the case of a one extractant system. There is an enhancement in the organic character of the complex formed between the metal and the extracting agents, giving, as a consequence, a major extraction.

However, the diversity of systems in which the synergism has been observed indicates that the mechanism cannot be the same in all cases. According to Marcus and Kertes⁽¹⁴⁾, there are four different types of synergistic combinations:

- chelating agent plus a neutral ligand. For instance: HTTA + TBP.
- alkylphosphoric acid plus a neutral ligand. For instance: HDEHP + TBP.
- combination of two neutral ligands. For instance: TBP + TOPO.
- combination of two acid ligands. For instance: HTTA plus AA or HTTA plus HDEHP.

The purpose of the present work is to study the extraction behaviour of the ions La^{+3} and Yb^{+3} by using mixtures of HTTA plus TBP, HTTA plus HDEHP and TBP plus HDEHP, in cyclohexane and by using ^{140}La and ^{169}Yb as radioactive tracers.

The elements La and Yb respectively, the lightest and one of the heaviest of the lanthanides, were chosen to point out any possible difference in the behaviour of all the elements of the group.

An attempt is also made in order to establish which mixtures of extracting agents exhibit the highest synergistic effect in the extraction of lanthanides and which are the best experimental conditions for the occurrence of this effect.

Having in mind all the results obtained experimentally, it is intended, afterwards, to verify the feasibility of using these mixtures for the individual separation of the lanthanides.

EXPERIMENTAL

Equipments used:

- Nuclear Chicago single-channel analyser, model 8775, coupled to a well-type 5.1 x 4.4 cm NaI(Tl) scintillation detector.
- Mechanical stirrer thermostated at 25°C.
- Cylindrical separatory funnels, 20 ml capacity.

Reagents

Besides the usual chemical reagents, the following were also used:

- TBP of commercial use, purified as described by Rolt⁽¹⁷⁾.
- HDEHP of Consolidated Midland Corporation used without previous purification.
- HTTA of Aldrich Chemical Co Inc., used without previous purification.

The HTTA was left under vacuum in the presence of P₂O₅ during 24 hours.

- HNO₃ p.a. Carlo Erba.
- Sodium Nitrate p.a. Baker & Adamson.
- Cyclohexane BDH Laboratory Reagents, used as diluent.
- Radioactive Tracers - ¹⁶⁹Yb and ¹⁴⁰La were obtained by irradiation of 2 mg of the respective oxides in thermal neutron flux of 10¹² n.cm⁻².s⁻¹ during 8 hours. After the irradiation the oxides were dissolved with 10 ml of HNO₃ 10⁻²M.

The water used throughout the experiments was distilled after being deionized.

Experimental Procedure

The aqueous phases were prepared by keeping constant the concentrations of the metallic ions (10⁻⁴M) and of the salting out agent (NaNO₃ 1M).

The pH the aqueous phase was varied by adding HNO₃ or NaOH. The organic phase were prepared by dissolving convenient amounts of the extracting agents with cyclohexane in order to obtain the desired concentration.

Prior to the metal extraction experiments the organic phase were shaken with a solution having the same pH and the same salting out agent concentration as that of the aqueous phases in order to establish the equilibrium between the two phases.

With 5 minutes of contacting time the equilibrium of extraction was achieved. To get more assurance a contacting time of 10 minutes was chosen for the following experiments.

A O/A ratio of one was used in all experiments (5 ml volume). After the mixing and the settling of the two phases the activities of 1 ml aliquots of the organic and aqueous phases were measured. Considering that no loss occurs during the extraction, it can be assumed that.

$$C = 5 (C_A + C_O)$$

where,

C = count rate of the radioactive tracer used in the experiment

C_A = count rate of 1 ml of the aqueous phase after equilibrium

C_O = count rate of 1 ml of the organic phase after equilibrium

The distribution ratio (D) of the metal ions is given by the equation.

$$D = \frac{C_O}{C_A}$$

since the two phases volumes are the same

Determination of the Synergistic Factor⁽¹⁶⁾

The evaluation of the synergistic effect was studied by means of a synergistic factor. This synergistic factor, F , is given by:

$$F = \frac{D_{1,2}}{D_1 + D_2}$$

where,

D_1 = distribution ratio obtained with the extracting agent 1.

D_2 = distribution ratio obtained with the extracting agent 2.

$D_{1,2}$ = distribution ratio obtained with a mixture of the extracting agents 1 and 2.

The magnitude of F represents synergism or antagonism:

where,

$F > 1$ —————> a synergistic effect exists or

$F < 1$ —————> a antagonistic effect exists

A) EXTRACTION WITH ONE EXTRACTANT

In order to evaluate the antagonism or the synergism, a comparison between the distribution data obtained with each extractant separately and with the mixtures was made.

- Extraction with TBP – Figure 1 shows the extraction curves obtained for La and Yb by using TBP 1M. The pH varied from 1 to 4.
- Extraction with HDEHP – As HDEHP is a good extractant for lanthanides, several extractions were carried out by using a concentration range from $2.6 \times 10^{-3} \text{ M}$ to $5.0 \times 10^{-2} \text{ M}$. In Figure 2 the extraction curves obtained with HDEHP $1 \times 10^{-2} \text{ M}$ and $5 \times 10^{-2} \text{ M}$ are reported.
- Extraction with HTTA – The best experimental conditions for La and Yb extraction were obtained with HTTA 0.1M. The corresponding extraction curves are presented in Figure 3.

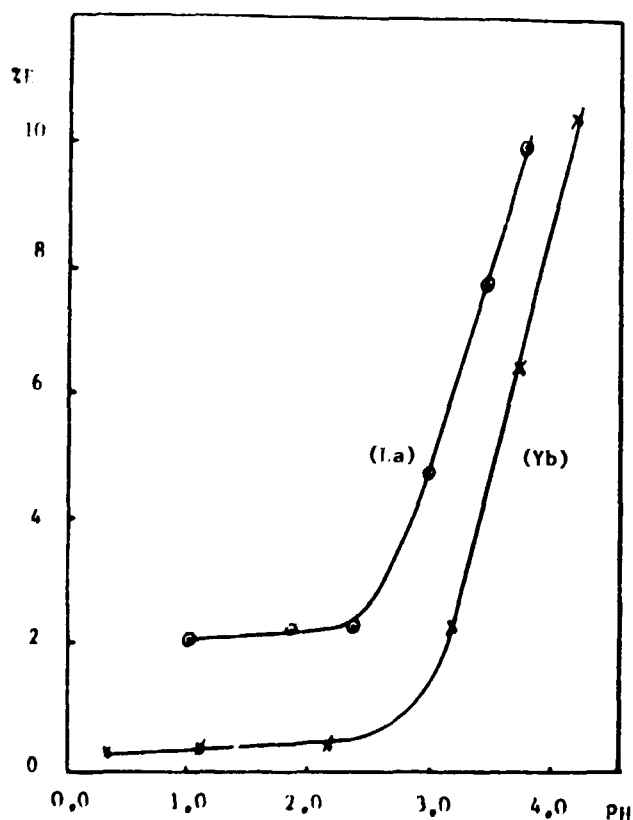


Figure 1 -- Extraction Curve of the Elements La and Yb, in HNO_3 Medium, by Using 1M TBP in Cyclohexane. $[\text{La}] = [\text{Yb}] = 1 \times 10^{-4} \text{ M}$, $[\text{NaNO}_3] = 1 \text{ M}$.

B) EXTRACTION USING A MIXTURE OF EXTRACTING AGENTS

Two series of experiments were carried out:

- a) experiments in which the final concentration of the extracting agents was kept constant and
- b) experiments in which the concentration of one extracting agent was kept constant and the concentration of the other was changed.

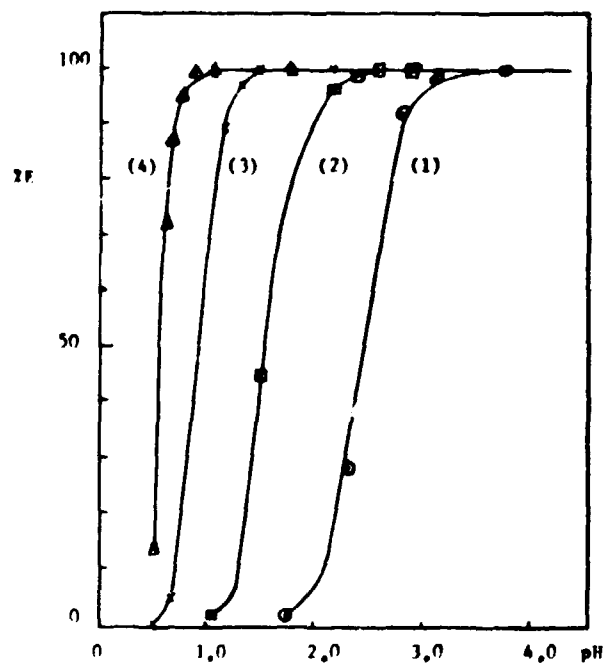


Figure 2 - Extraction Curve of the Elements La and Yb, in HNO₃ Medium, by Using HDEHP in Cyclohexane. [La] = [Yb] = 1 x 10⁻⁶ M, [NaNO₃] = 1M.

La { (1) 1 x 10⁻² M HDEHP
(2) 5 x 10⁻² M HDEHP
Yb { (3) 1 x 10⁻² M HDEHP
(4) 5 x 10⁻² M HDEHP

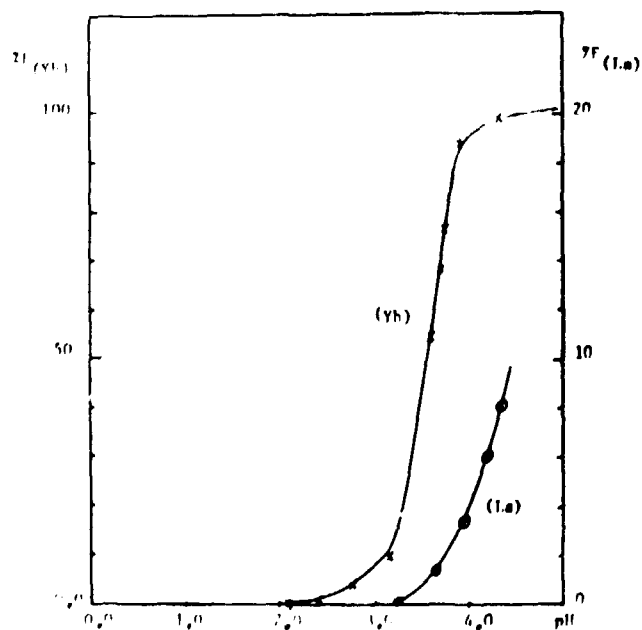


Figure 3 - Extraction Curve of the Elements La and Yb, in HNO₃ Medium, by using 0.1M HTTA in Cyclohexane. [La] = [Yb] = 1 x 10⁻⁶ M, [NaNO₃] = 1M.

B.1) Extractions with HDEHP and HTTA mixtures

a) constant final concentration

For the extraction of both La and Yb the final concentration of both extractants combined was:

$$[\text{HDEHP}] + [\text{HTTA}] = 1 \times 10^{-2} \text{ M}$$

For La a pH of 2.5 was used in the aqueous phase, whereas for Yb (which is more easily extracted with HDEHP) a pH of 1.0 was chosen for the aqueous phase. Figures 4 and 5 show the variation of log D versus the concentration of the two extractants for La and Yb, respectively.

b) variable final concentration

Two different concentrations were chosen for HDEHP and the HTTA concentration was varied. For La, the following experimental conditions were used:

$$[\text{HDEHP}] = 2 \times 10^{-2} \text{ M}$$

$$[\text{HDEHP}] = 4 \times 10^{-3} \text{ M}$$

$$[\text{HTTA}] \text{ from } 1 \times 10^{-4} \text{ M to } 1 \times 10^{-1} \text{ M}$$

$$\text{pH (aqueous phase)} = 2.5$$

In a same way, to study the behaviour of Yb, the following conditions were used:

$$[\text{HDEHP}] = 8 \times 10^{-3} \text{ M}$$

$$[\text{HDEHP}] = 2 \times 10^{-3} \text{ M}$$

$$[\text{HTTA}] \text{ from } 1 \times 10^{-4} \text{ M to } 1 \times 10^{-1} \text{ M}$$

$$\text{pH (aqueous phase)} = 1.0$$

The results obtained are summarized in Tables I and II.

B.2) Extractions with HDEHP and TBP mixtures

a) constant final concentration

In order to study the behaviour of La, the following conditions were used:

$$[\text{HDEHP}] + [\text{TBP}] = 1 \times 10^{-2} \text{ M}$$

and pH = 2.5 for the aqueous phase.

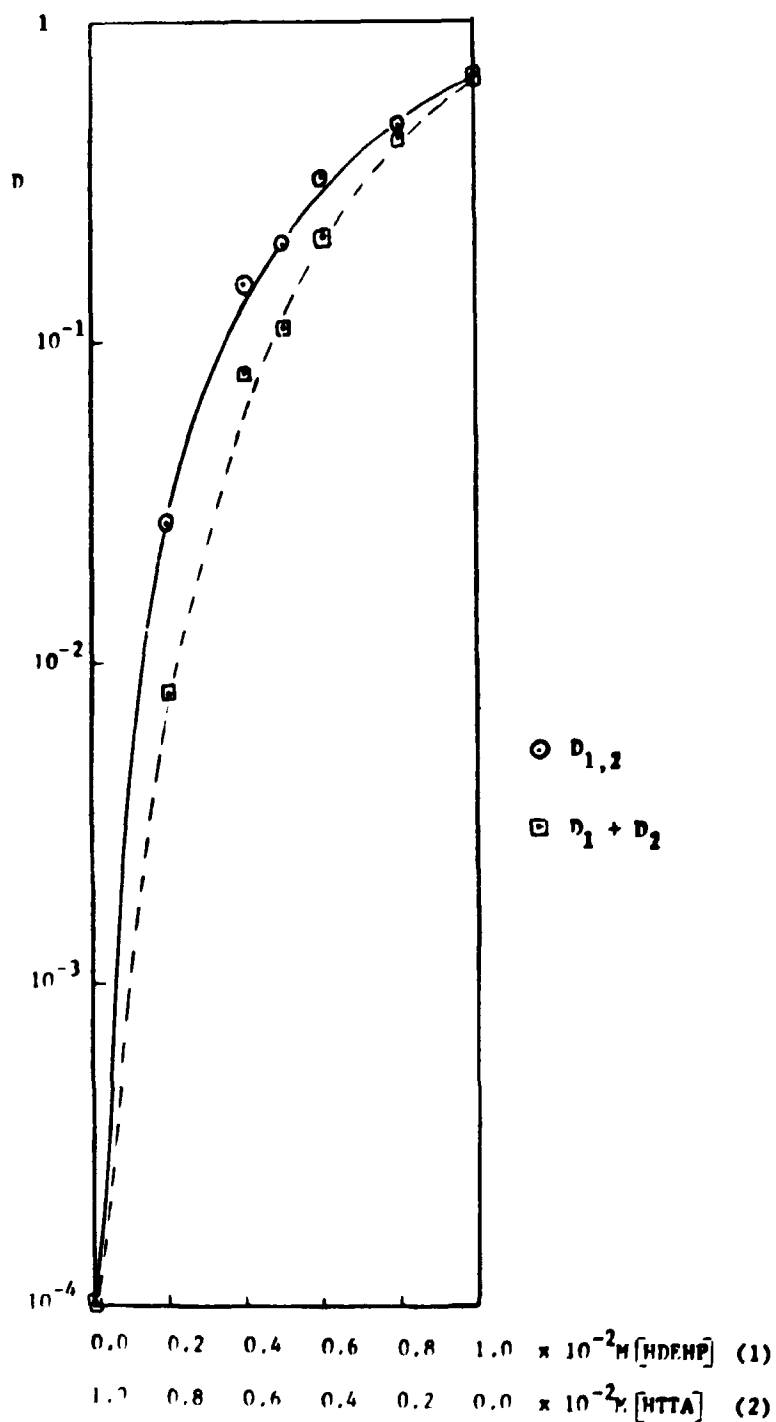


Figure 4 - Variation of the Distribution Ratio of La Versus the concentration of the Extracting agents. (pH of the Aqueous Phase = 2.50, $[La] = 1 \times 10^{-4} M$, $[NaNO_3] = 1M$).

D_1 - Distribution Ratio of La Obtained by Using HDEHP (1) as extracting Agent.

D_2 - Distribution Ratio of La Obtained by Using HTTA (2) as Extracting Agent.

$D_{1,2}$ - Distribution Ratio of La Obtained by using a Mixture of the two Extracting Agents.

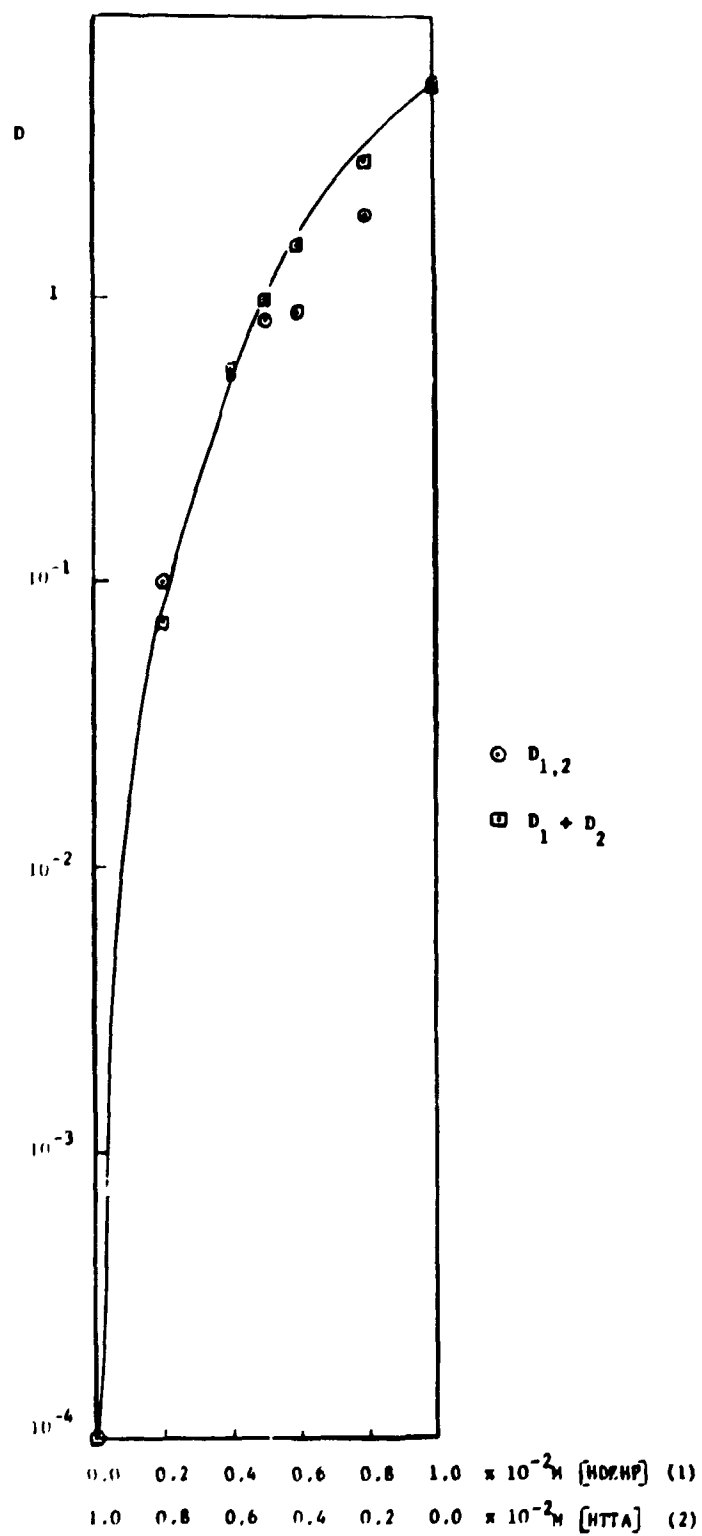


Figure 5 - Variation of the Distribution Ratio of Yb Versus the Concentration of the Extracting Agents. (pH of the Aqueous Phase = 1.0, [Yb] = $1 \times 10^{-4} M$, [NaNO₃] = 1M).

Table I

Distribution Ratio of La as a Function of the Concentration of HTTA,
for two Fixed Concentrations of HDEHP in the Organic Phase.
pH of the Aqueous Phase = 2.45

[HTTA], M	[HDEHP]					
	4 x 10 ⁻³ M			2 x 10 ⁻² M		
	D _{1,2}	D ₁ + D ₂	F	D _{1,2}	D ₁ + D ₂	F
—	0.06	0.06	1.0	2.1	2.1	1.0
1 x 10 ⁻⁴	0.06	0.06	1.0	2.3	2.1	1.1
5 x 10 ⁻⁴	0.06	0.06	1.0	2.4	2.1	1.1
1 x 10 ⁻³	0.06	0.06	1.0	2.4	2.1	1.1
5 x 10 ⁻³	0.11	0.06	1.8	2.9	2.1	1.4
1 x 10 ⁻²	0.20	0.06	3.3	3.8	2.1	1.8
5 x 10 ⁻²	0.60	0.06	10	9.2	2.1	4.4
1 x 10 ⁻¹	1.1	0.06	18	17.4	2.1	8.3

Table II

Distribution Ratio of Yb as a Function of the Concentration of HTTA, for
two Fixed Concentrations of HDEHP in the Organic Phase.
pH of the Aqueous Phase = 1.00

[HTTA] M	[HDEHP]					
	4 x 10 ⁻³ M			2 x 10 ⁻² M		
	D _{1,2}	D ₁ + D ₂	F	D _{1,2}	D ₁ + D ₂	F
—	4.3	4.3	1.0	1.7	1.7	1.0
1 x 10 ⁻⁴	4.6	4.3	1.1	1.8	1.7	1.1
5 x 10 ⁻⁴	4.5	4.3	1.0	2.1	1.7	1.2
1 x 10 ⁻³	4.9	4.3	1.1	1.5	1.7	0.9
5 x 10 ⁻³	4.8	4.3	1.1	1.7	1.7	1.0
1 x 10 ⁻²	5.1	4.3	1.2	1.4	1.7	0.8
5 x 10 ⁻²	5.0	4.3	1.2	2.0	1.7	1.2
2 x 10 ⁻¹	4.2	4.3	1.0	2.0	1.7	1.2

The curves obtained in these experiments are depicted in Figure 6.

For Yb, the final concentration of the extracting agent was $8 \times 10^{-3} \text{ M}$ and the pH of the aqueous phase was 1.0. Figure 7 shows the curves obtained in these experiments.

b) variable final concentration

Two different concentrations were chosen for HDEHP and the TBP concentration was varied. For La the following experimental conditions were used:

$$[\text{HDEHP}] = 5 \times 10^{-3} \text{ M}$$

$$[\text{HDEHP}] = 2 \times 10^{-2} \text{ M}$$

$$[\text{TBP}] \text{ from } 5 \times 10^{-4} \text{ M to } 1.83 \text{ M}$$

$$\text{pH (aqueous phase)} = 2.5$$

The results obtained are summarized in Table III.

The experimental conditions used for the study of Yb are:

$$[\text{HDEHP}] = 6 \times 10^{-3} \text{ M}$$

$$[\text{HDEHP}] = 1 \times 10^{-2} \text{ M}$$

$$[\text{TBP}] \text{ from } 1 \times 10^{-4} \text{ M to } 1.83 \text{ M}$$

$$\text{pH (aqueous phase)} = 1.0$$

The results obtained in the two series of experiments with Yb summarized in Table IV.

B.3) Extraction with Mixtures of TBP and HTTA

a) constant final concentration

Two experiments concerning La and Yb were carried out by using the same conditions, i.e., final concentration of the extracting agent equal to 0.1M and pH of the aqueous phase equal to 3.5. The curves obtained for the extraction of La and Yb are reported in Figure 8 and 9, respectively.

b) variable final concentration

Two different concentrations were chosen for HTTA and the TBP concentration was varied. For the study of La, the following experimental conditions were used:

$$[\text{HTTA}] = 1 \times 10^{-1} \text{ M}$$

$$[\text{HTTA}] = 2 \times 10^{-1} \text{ M}$$

$$[\text{TBP}] \text{ from } 1 \times 10^{-3} \text{ M to } 1.83 \text{ M}$$

$$\text{pH (aqueous phase)} = 3.5$$

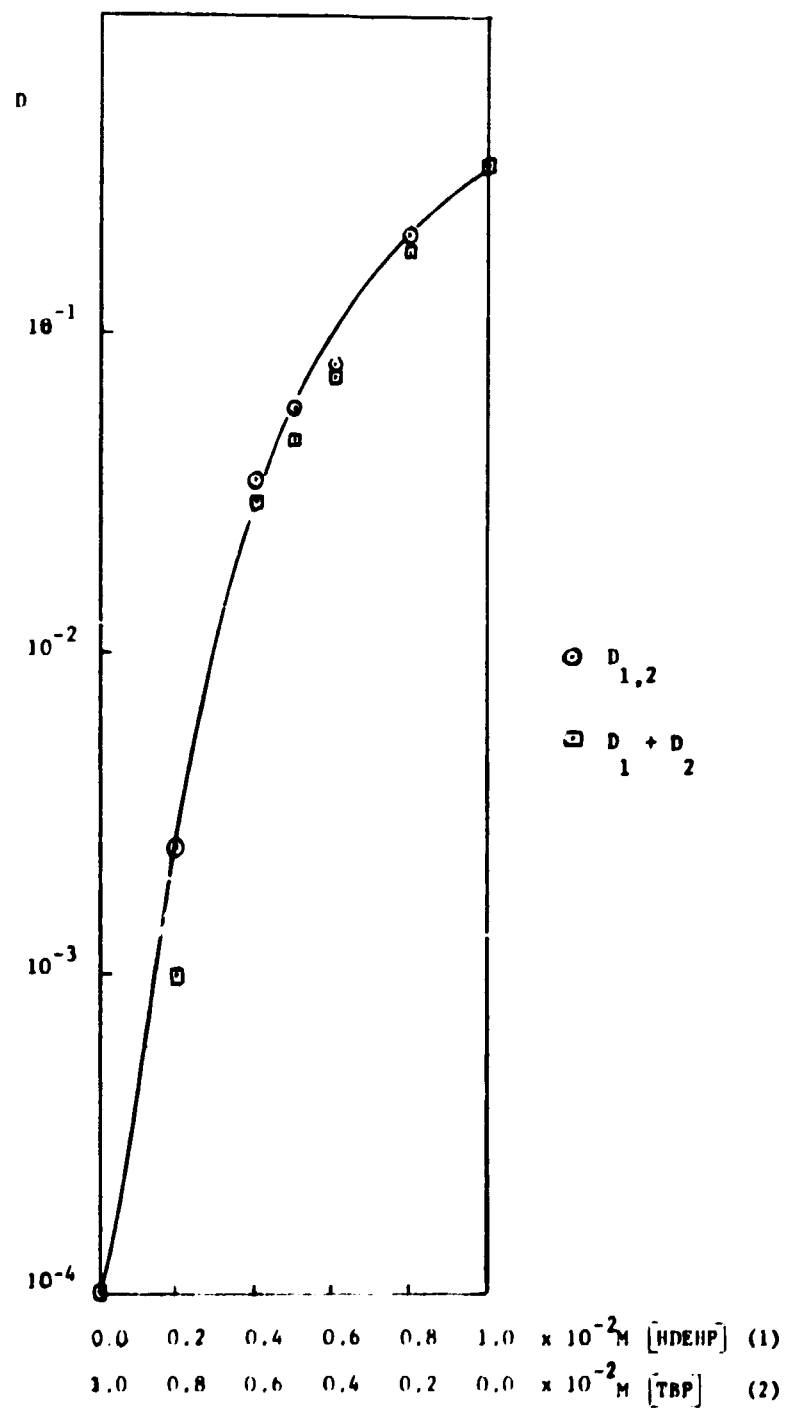


Figure 6 - Variation of the Distribution Ratio of La Versus the Concentration of the Extracting Agents. (pH of the Aqueous Phase = 2.50, [La] = 1×10^{-4} M, [NaNO₃] = 1M).

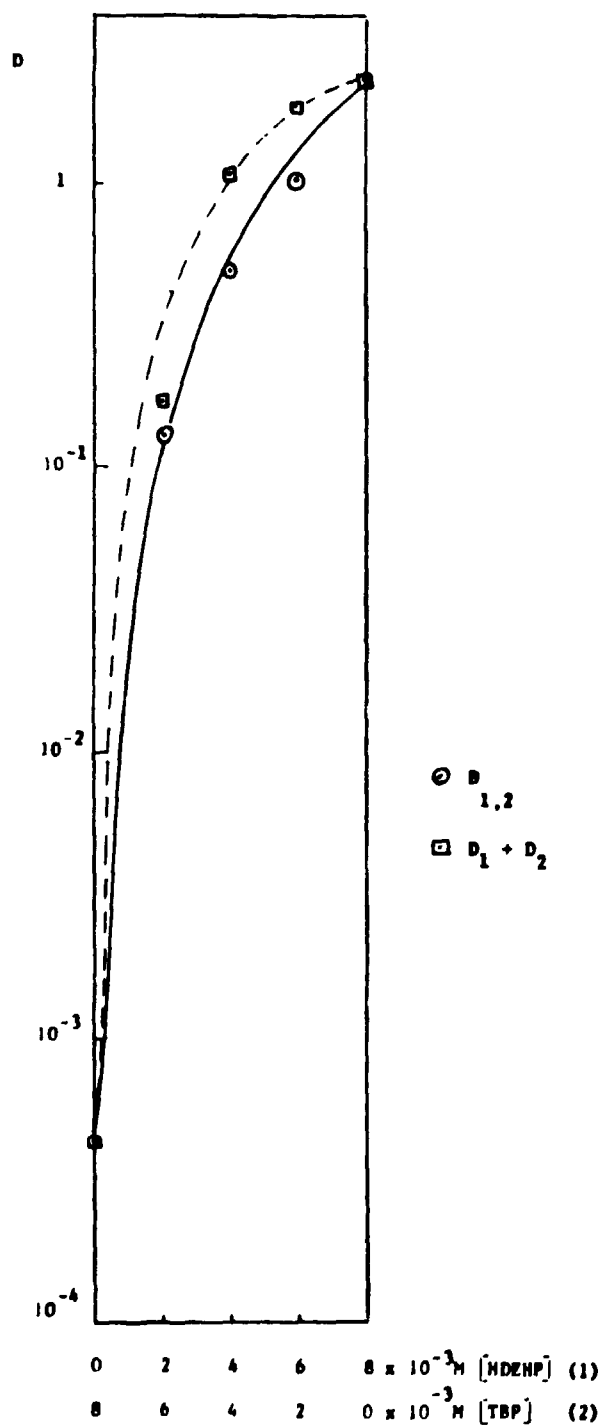


Figure 7 - Variation of the Distribution Ratio of Yb Versus the Concentration of the Extracting Agents. (pH of the Aqueous Phase = 1.00, [Yb] = 1×10^{-4} M, [NaNO₂] = 1M).

Table III

Distribution Ratio of La as a Function of the Concentration of TBP, for
two Fixed Concentrations of HDEHP in the Organic Phase.
pH of the Aqueous Phase = 2.45

[TBP] M	[HDEHP]					
	5×10^{-2} M			2×10^{-2} M		
	$D_{1,2}$	$D_1 + D_2$	F	$D_{1,2}$	$D_1 + D_2$	F
2×10^{-4}	—	—	—	1.84	1.9	1.00
5×10^{-4}	0.055	0.06	1.0	—	—	—
2×10^{-3}	—	—	—	1.90	1.9	1.00
5×10^{-3}	0.061	0.06	1.0	—	—	—
2×10^{-2}	—	—	—	2.00	1.9	1.05
2.5×10^{-2}	0.061	0.06	1.0	—	—	—
5×10^{-2}	0.083	0.06	1.4	—	—	—
1×10^{-1}	0.098	0.06	1.6	2.20	1.9	1.15
2×10^{-1}	—	—	—	2.20	1.9	1.15
2.5×10^{-1}	0.107	0.06	1.8	—	—	—
5×10^{-1}	0.105	0.06	1.7	—	—	—
1.0	—	—	—	2.10	1.9	1.10
1.8	—	—	—	2.30	1.9	1.20
—	0.06	0.06	—	1.90	1.9	1.00

Table IV

Distribution Ratio of Yb as a Function of the Concentration of TBP, for
two Fixed Concentrations of HDEHP in the Organic Phase.
pH of the Aqueous Phase = 1.05

[TBP] M	[HDEHP]					
	6×10^{-3} M			1×10^{-2} M		
	$D_{1,2}$	$D_1 + D_2$	F	$D_{1,2}$	$D_1 + D_2$	F
—	0.4	0.4	1.0	1.8	1.8	1.0
1×10^{-4}	0.6	0.4	1.5	4.0	1.8	2.2
5×10^{-4}	—	—	—	3.5	1.8	1.9
1×10^{-3}	0.6	0.4	1.5	3.4	1.8	1.9
1×10^{-2}	0.6	0.4	1.5	2.8	1.8	1.5
5×10^{-2}	0.4	0.4	1.0	2.0	1.8	1.1
1×10^{-1}	0.2	0.4	0.50	0.9	1.8	0.5
5×10^{-1}	0.03	0.4	0.075	0.07	1.8	0.04
1.0	0.02	0.4	0.05	0.04	1.8	0.02
1.8	0.03	0.4	0.075	0.04	1.8	0.02

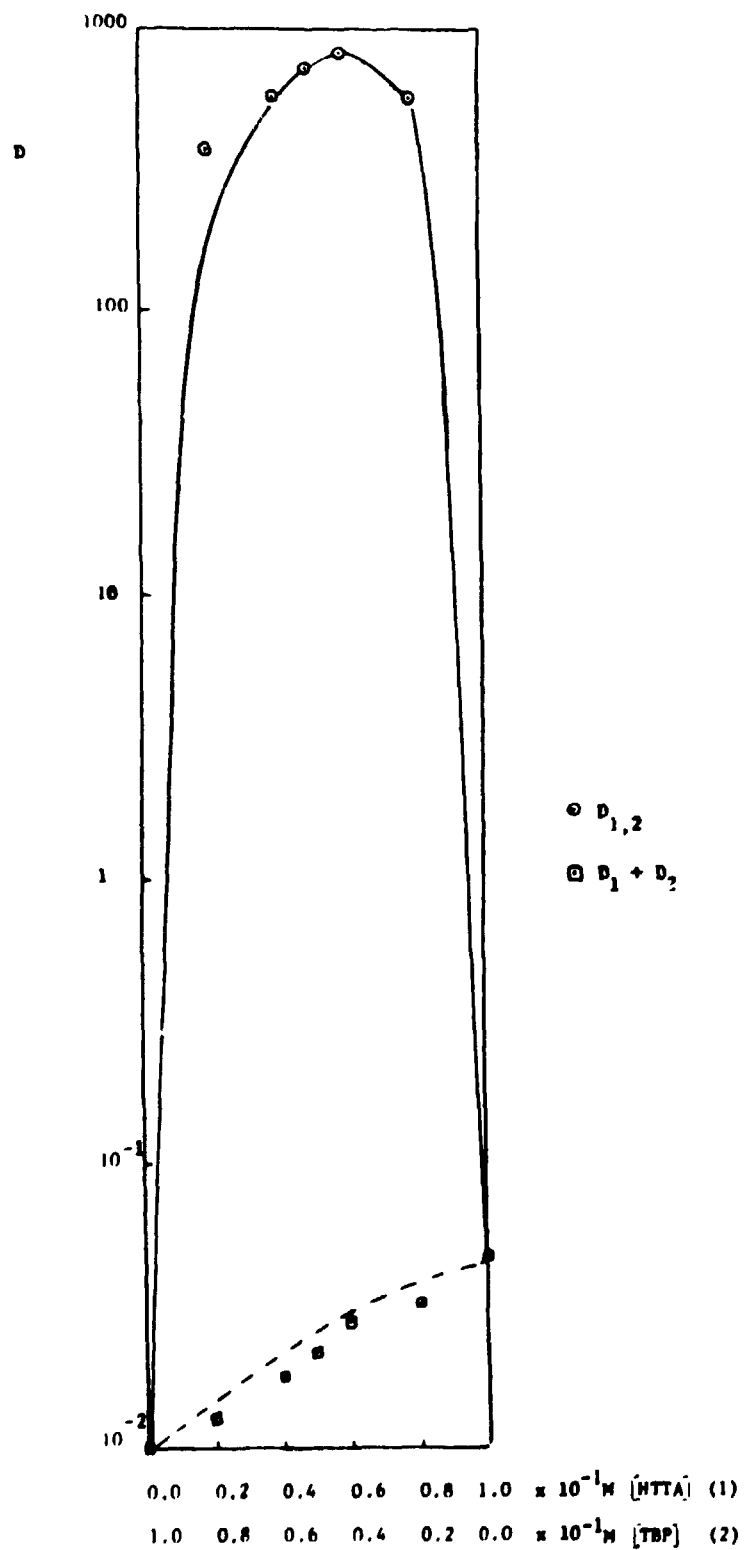


Figure 8 - Variation of the Distribution Ratio of La Versus the Concentration of the Extracting Agents. (pH of the Aqueous Phase = 3.4, $[La] = 1 \times 10^{-4} M$, $[NaNO_3] = 1M$).

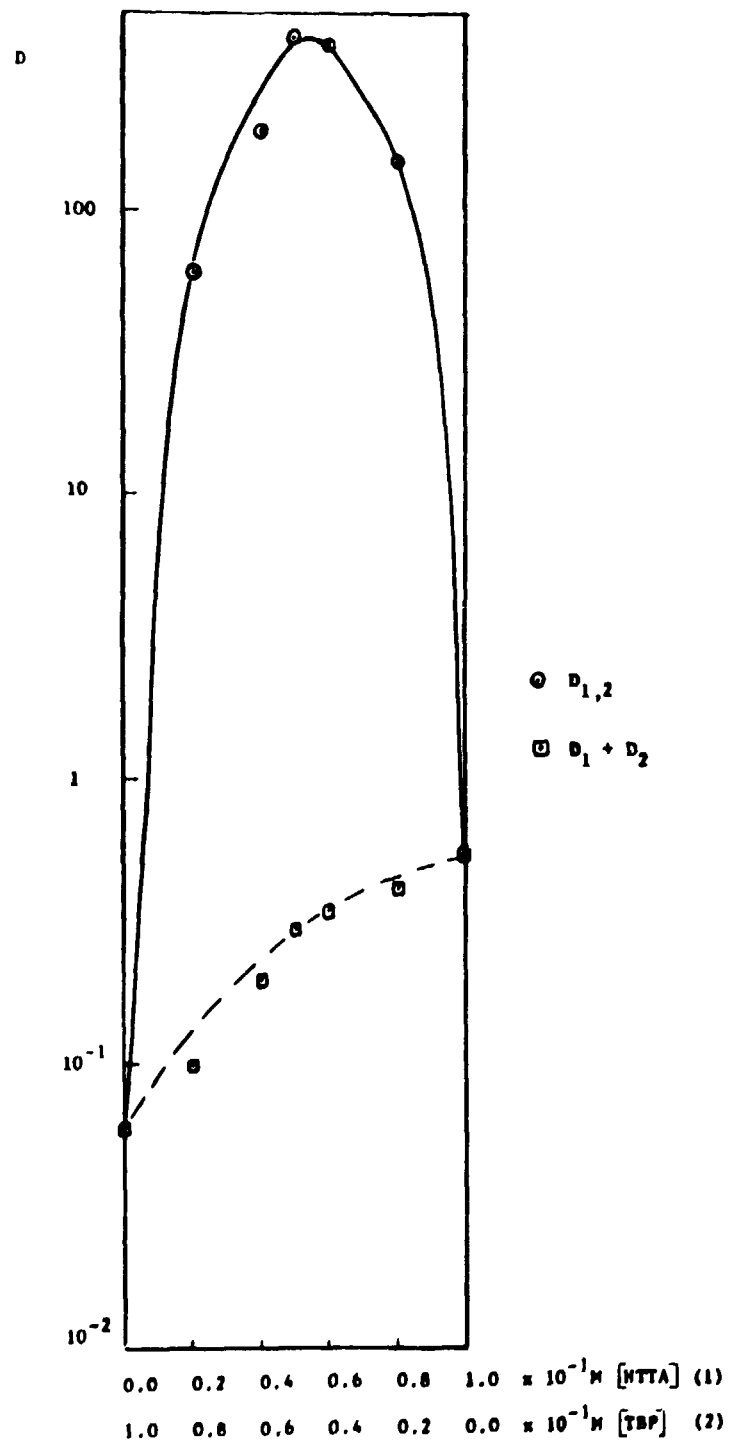


Figure 9 -- Variation of the Distribution Ratio of Yb Versus the Concentration of the Extracting Agents.
 (pH of the Aqueous Phase = 3.4, [Yb] = 1×10^{-4} M, [NaNO₃] = 1M).

The experimental conditions used for the study of Yb are:

$$[\text{HTTA}] = 1 \times 10^{-2} \text{ M}$$

$$[\text{HTTA}] = 4 \times 10^{-2} \text{ M}$$

$$[\text{TBP}] \text{ from } 1 \times 10^{-4} \text{ M to } 1.2 \text{ M}$$

$$\text{pH (aqueous phase)} = 3.5$$

The results obtained for La and Yb, are summarized in Tables V and VI, respectively.

Table V

Distribution Ratio of La as a Function of the Concentration of TBP, for two Fixed Concentrations of HTTA in the Organic Phase. pH of the aqueous Phase = 3.40

[TBP] M	[HDEHP]					
	$1 \times 10^{-1} \text{ M}$			$1.6 \times 10^{-1} \text{ M}$		
	$D_{1,2}$	$D_1 + D_2$	F	$D_{1,2}$	$D_1 + D_2$	F
—	0.03	0.03	1.0	1.0	1.0	1.0
1×10^{-3}	15	0.03	500	—	—	—
2×10^{-3}	—	—	—	28	1.0	28
1×10^{-2}	340	0.03	11333	—	—	—
2×10^{-2}	—	—	—	453	1.0	453
5×10^{-2}	1485	0.03	49500	—	—	—
1×10^{-1}	2574	0.03	85800	—	—	—
2×10^{-1}	—	—	—	617	1.0	617
5×10^{-1}	2305	0.03	76833	—	—	—
8×10^{-1}	—	—	—	961	1.0	961
1.0	1935	0.10	19350	—	—	—
1.6	—	—	—	1008	1.2	840
1.8	1800	0.20	9000	651	1.2	542

Table VI

Distribution Ratio of Yb as a Function the Concentration of TBP, for two Fixed Concentrations of HTTA in the Organic Phase. pH of the aqueous Phase = 3.40

[TBP] M	[HTTA]					
	$1 \times 10^{-2} \text{ M}$			$4.0 \times 10^{-2} \text{ M}$		
	$D_{1,2}$	$D_1 + D_2$	F	$D_{1,2}$	$D_1 + D_2$	F
—	0.2	0.2	1.0	0.5	0.5	1.0
1×10^{-4}	1.2	0.2	6	—	—	—
4×10^{-4}	—	—	—	22	0.5	44
1×10^{-3}	4.7	0.2	23	—	—	—
4×10^{-3}	—	—	—	67	0.5	134
1×10^{-2}	103	0.2	515	—	—	—
2×10^{-2}	346	0.2	1730	—	—	—
4×10^{-2}	—	—	—	1545	0.5	3090
5×10^{-2}	394	0.2	1970	—	—	—
2×10^{-1}	—	—	—	2067	0.5	4134
4×10^{-1}	345	0.2	1725	2345	0.5	4690
8×10^{-1}	—	—	—	2837	0.5	5674
1.0	146	0.2	730	—	—	—
1.2	—	—	—	1048	0.5	2096

DISCUSSION

According to the results summarized in Figure 1, 2 and 3 it can be seen that HDEHP is the most efficient of the three extractants studied, under the experimental conditions already described.

From a point of view of the study of the synergistic effect, it is possible to establish (Figure 2) that the concentration of HDEHP used to extract La cannot exceed 1×10^{-2} M, when the pH of the aqueous phase is 2.5. In the same conditions the pH of the aqueous phase cannot exceed 1.0 for the extraction of Yb.

From Figures 1 and 3 it can be concluded that it is more convenient to work with a fixed concentration of HTTA and change the concentration of the other extracting agent i.e., TBP. The HTTA concentration in the mixture cannot exceed 0.1M in order to avoid a complete extraction of La with HTTA alone. According to Figure 3, the extractions of La and Yb are of about 1% and 40%, respectively, when a HTTA concentration of 0.1M and a pH of 3.5 for the aqueous phase are used. For this reason, the HTTA concentration was kept constant and that of TBP was changed.

Change in the TBP concentration in the mixtures with HTTA or HDEHP have very little or no influence on the lanthanides extraction when the action of the extracting agents is considered separately.

Evidence of the Synergistic Effect

The mixtures of HTTA and HDEHP, according to Figures 4 and 5 and Tables I and II, do not present a pronounced synergistic effect in the extraction of the two lanthanides. An enhancement is observed in the extraction of La (Table I) when the HTTA concentration is increased and the HDEHP concentration is kept constant and equal to 2×10^{-2} M. The same effect was not observed for the Yb (see Table II).

Hirashima⁽⁹⁾ also observed the same trend in the synergistic effect in the extraction of the lanthanides with the mixture HTTA plus HDEHP. This effect decreases as the atomic number of these elements increases and, still according with Hirashima⁽⁹⁾, this behaviour is dependent on the ionic radius of the lanthanides.

The HDEHP plus TBP mixture (see Table III and Figure 6) presents the same effect on the extraction of La as the solution of HDEHP. On the extraction of Yb, on the other hand, an antagonistic effect is observed as the TBP concentration is increased (see Table IV). This effect is clearly seen in Figure 7, that depicts the variation of the distribution ratio of Yb versus the concentration of both extracting agents. For these experiments the summation of the two concentrations in the mixture was kept constant. This antagonistic effect was explained by Ferraro and Peppard⁽⁵⁾ assuming a direct interaction between HDEHP and TBP molecules, with consequent formation of an association product which removes these reagents from the extraction system. The effect increases as the concentration of TBP in the mixture also increases. It is interesting to remark that in the present work the antagonistic effect was observed only in the extraction of Yb.

A pronounced synergistic effect is observed in the La and Yb extraction with mixtures of HTTA plus TBP (see Tables V and VI and Figures 8 and 9). This effect is very evident because both HTTA and TBP, when used separately, are not good extractants for the lanthanides, as it can be seen in Figures 1 and 3. It is interesting to observe that HTTA is a good extractant for the heavy lanthanides (Yb), but is quite ineffective for the light ones (La). Despite the fact that the distribution ratio is high for the two lanthanides, when a mixture of HTTA plus TBP is used, an inversion seems to occur, i.e., the La extraction is favoured with regard to that of Yb. This behaviour was already discussed by Healy⁽⁸⁾ who established, as a general rule, that the HTTA alone forms more stable complexes $(Ln(TTA)_3)$ with heavy lanthanides than with light ones, but the synergist (the weak donor, TBP, in this case) forms a more stable complex

(Ln(TTA)₃(TBP)₂) with the light lanthanides than with the heavy ones, whereas the mixture of the extraction agents is used (HTTA + TBP).

Comparing the effect of the mixtures HTTA plus TBP and HDEHP plus TBP in the lanthanides extraction, Baes⁽¹⁾ attributed the differences observed in their behaviour to two major factors:

1. the complexes formed between M(A₂H)₂ and TBP are much less stable than those formed between M(TTA)_Z and TBP, where A₂H is a dimer of HDEHP and Z is the metal charge;
2. the interaction between the HDEHP and TBP is much stronger than that between HTTA and TBP, because the hydrogen bond between two phosphoryl oxygens (HDEHP and TBP) is stronger than that between a phosphoryl group (from TBP) and a carboxylic group (from HTTA).

RESUMO

Estudou-se o comportamento do Yb e do La em sistemas de extração onde o agente extrator foi constituído por misturas de tetratrilfluoroacetona (HTTA), ácido di-(2-etilhexil) fosfórico (HDEHP) e tributilfosfato (TBP), dois a dois.

O comportamento dos elementos citados foi acompanhado por meio dos traçadores radioativos ¹⁴⁰La e ¹⁶⁹Yb. A fase aquosa usada em todas as extrações continha HNO₃ em várias concentrações e NaNO₃ como agente salino.

Observou-se que usando a mistura (HTTA-TBP) os elementos citados apresentaram uma razão de distribuição bem maior que a obtida com cada um dos dois agentes extratores usados isoladamente, mostrando assim a existência de um efeito sinérgico.

Usando a mistura (HTTA-HDEHP) observou-se um pequeno efeito sinérgico para o La e um efeito antagônico para o Yb. Observou-se também, um efeito antagônico para o Yb, enquanto a extração do La independe da concentração de TBP, quando foi usada a mistura HDEHP-TBP.

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