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IN BINARY MIXTURES OF EXTRACTANTS**

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# DETERMINATION OF SEPARATION FACTORS OF Tb AND Yb IN BINARY MIXTURES OF EXTRACTANTS

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## ABSTRACT

The values obtained for the separation factors of Tb and Yb, in nitric medium, using binary mixtures of HDEHP (di-(2-ethylhexyl) phosphoric acid), HTTA (thenoyltrifluoroacetone), TBP (tributylphosphate) and TOPO (tri-n-octylphosphine oxide) were calculated.

It was observed, from the results obtained, that the separation factor between Tb and Yb is not improved by the presence of the second extractor, not even when the synergistic effect occurs.

## DETERMINAÇÃO DOS FATORES DE SEPARAÇÃO DE Tb E Yb EM MISTURAS BINÁRIAS DE EXTRATORES

## RESUMO

Foram calculados os fatores de separação dos elementos térbio e itérbio, em meio nítrico, usando misturas binárias de HDEHP (ácido di-(2-etilhexil) fosfórico, HTTA (tenoitrifluoroacetona), TBP (fosfato de tri-n-butila) e TOPO (óxido de tri-n-octilfosfina).

Observou-se, a partir dos resultados obtidos, que o fator de separação entre térbio e itérbio não é melhorado pela presença do segundo extrator, nem mesmo quando ocorre o efeito sinérgico.

## INTRODUCTION

The purpose of the present paper was to improve the separation between the lanthanides by means of the synergistic effect observed when binary mixtures of extractants are used. After the determination of the separation factors by means of liquid-liquid extraction, it was intended to apply the extraction chromatographic technique. The extractants mixture giving the best results in the previous experiments would be used as the stationary phase.

Although a large number of references concerning the occurrence of the synergistic effect is available in the literature, there are just a few examples of its application in extraction chromatography<sup>(1,2,6,7,8)</sup>.

Aly and El Haggan<sup>(1)</sup> studied the separation of Eu from Sm by applying the synergistic effect of HTTA and DBDECP (N, N dibutyl diethyl carbamyl phosphonate) mixture by means of extraction chromatography. HTTA, DBDECP and their mixture were adsorbed in hydrophobic celite and acetic-sodium acetate buffer was used as eluent. The authors<sup>(1)</sup> concluded that the HTTA-DBDECP mixture improves the separation between the lanthanides.

Aly and Raieh<sup>(2)</sup> investigated the chromatographic behaviour of the same system for the separation of Eu, Sm, Cf and Cm and established the best conditions for their separation.

More recently, Korothin<sup>(7)</sup> applied the synergistic effect of the HTTA/TBP mixture for the extraction chromatography of Am and Eu, obtaining good results. In a subsequent work<sup>(8)</sup>, the separation of several elements was studied by using the same system and the same technique.

Kopkar and Mathur<sup>(6)</sup>, studying the synergistic extraction of trivalent actinides, determined the separation factors for Am(III) and Cm(IV) ( $\alpha \frac{A_m}{C_m}$ ), using HTTA and synergistic mixtures HTTA/TOPO and HTTA/DOSO (di-n-octylsulphoxide). They verified that  $\alpha \frac{A_m}{C_m}$  is higher for HTTA than for the mixtures.

The extraction behaviour of La and Yb, in nitric medium, when binary mixtures of HDEHP, HTTA, TOPO and TBP, in cyclohexane are used as extractants, was reported in previous papers<sup>(3-4)</sup>. Based upon the results obtained, the present work was carried out in order to establish the separation factors for Tb and Yb for the six binary mixtures studied in the mentioned paper. The main purpose was to separate the lanthanide elements and to apply the extraction chromatography technique using as stationary phase the extractant mixture which would present the higher separation factor.

The elements Tb and Yb were chosen because they are sufficiently close ( $Z = 65$  and  $70$ , respectively) within the group of lanthanides and the gamma-ray spectra of the respective tracers,  $^{160}\text{Tb}$  and  $^{169}\text{Yb}$  present peaks in distinct energies; thus it is possible to measure each activity, simultaneously, in the phases and to calculate the separation factor in the same experimental conditions.

## EXPERIMENTAL

### Equipment

A 4096 channel analyser coupled to a Ge-Li detector, with a resolution of 2.45 keV (FWHM) for the 1332 KeV photopeak of  $^{60}\text{Co}$  was used.

### Materials and Reagents

The radioactive tracers  $^{160}\text{Tb}$  and  $^{169}\text{Yb}$  were obtained by irradiating 2mg of their respective oxides (spectrographic grade) in the IEA-R1 reactor in a  $10^{12} \text{ ncm}^{-2} \text{ s}^{-1}$  thermal neutron flux for about 8 hours. After irradiation, the oxides were dissolved in 2M  $\text{HNO}_3$ ; the excess of the acid was eliminated by evaporation and the residue was redissolved in 10 mL of  $10^{-2} \text{ M HNO}_3$ .

Tri-n-butylphosphate (TBP), of commercial grade, was purified according to the procedure described by Rolf<sup>(9)</sup>.

Di(2-ethylhexyl) phosphoric acid (HDEHP), from Consolidated Midland Corporation, was used without any previous purification.

Thenoyltrifluoroacetone (HTTA), from Aldrich Chemical Co. Inc., was left under vacuum in the

presence of  $P_2O_5$  during 24 hours, before use.

Tri-n-octylphosphine oxide (TOPO), from Polysciences Inc., was also used without any previous purification.

Cyclohexane, from BDH Laboratory Reagents.

All the other reagents were of analytical grade.

### Procedure

The concentration of the metallic ions and respective radioactive tracer was kept constant in the aqueous phase as well as the ionic strength (1.0M  $NaNO_3$ ).

The organic phases were prepared by dissolving, separately, each extractant in cyclohexane, the concentration being two times higher than that desired in the final mixture. By adding suitable volumes of those solutions, the binary mixtures used were obtained.

Each mixture was pre-equilibrated with a 1.0M  $NaNO_3$  solutions with the same pH as that of the aqueous solution to be used in the experiment. This operation avoids any variation of volume during the extraction experiment. An aliquot of 5mL of each organic and aqueous phases was pipetted and shaken during 30 min. using a mechanical stirrer thermostated at 25°C.

After the separation of the phases, the pH of the aqueous solution was measured and 2 mL of each phase were transferred to counting tubes.

The gamma-ray spectra were obtained and the areas of the peaks in 870 and 177 keV of  $^{160}Tb$  and  $^{169}Yb$ , respectively, were calculated by the equation:

$$D_M = \frac{A_{M_o}}{A_{M_a}}$$

Where:

$A_{M_o}$  = area of the peak of  $M^*$  present in 2 mL of the organic phase;

$A_{M_a}$  = area of the peak of  $M^*$  present in 2 mL of the aqueous phase;

$M^*$  = being the radioactive tracer of M.

Determination of the separation factor ( $\alpha \frac{Y_b}{T_b}$ )

The separation factor was calculated by using the following equation:

$$\alpha \frac{Y_b}{T_b} = \frac{D_{Yb}}{D_{Tb}}$$

## RESULTS

### HDEHP - HTTA mixture

According to Table I, it can be observed that the presence of HTTA in the mixture does not improve the separation factor obtained with HDEHP alone.

Table I

Separation factors obtained with the HDEHP-HTTA mixture, for Tb and Yb

$$\text{pH} = 1.10, [\text{HDEHP}] = 6.0 \times 10^{-3} \text{ M}$$

Experiment	[HTTA] (M)	D		Yb $\alpha$ Tb
		Tb	Yb	
1	—	0.031	5.92	191
2	$6.0 \times 10^{-5}$	0.030	6.44	215
3	$6.0 \times 10^{-4}$	0.026	6.70	258
4	$6.0 \times 10^{-3}$	0.025	6.26	250
5	$6.0 \times 10^{-2}$	0.024	4.46	186
6	$2.0 \times 10^{-1}$	0.032	3.43	107
7 (*)	$2.0 \times 10^{-1}$	0.000	0.00	—

(\*) Without HDEHP

**HDEHP - TBP mixture**

The results presented in Table II show that the behaviour of TBP is similar to that of HTTA in the mixtures with HDEHP. While TBP concentration does not exceed  $5.0 \times 10^{-3}$  M, no alteration is observed in the separation factor, whereas, above this concentration a decrease appears.

Table II

Separation factors obtained with the HDEHP - TBP mixture, for Tb and Yb

$$\text{pH} = 1.05, [\text{HDEHP}] = 5.0 \times 10^{-3} \text{ M}$$

Experiment	TBP	D		Yb $\alpha$ Tb
		Tb	Yb	
1	—	0.007	2.10	299
2	$5.0 \times 10^{-5}$	0.007	2.25	321
3	$5.0 \times 10^{-4}$	0.006	1.78	297
4	$5.0 \times 10^{-3}$	0.008	1.93	241
5	$5.0 \times 10^{-2}$	0.007	0.94	134
6	$5.0 \times 10^{-1}$	0.011	0.030	2.6

**HDEHP - TOPO mixture**

When mixed with HDEHP, TOPO presents a behaviour different of that observed for HTTA-HDEHP or TBP-HDEHP mixtures. According to Table III, the distribution ratio of Tb increases with the TOPO concentration in the mixture, whereas the distribution ratio of Yb is almost constant. Therefore, the separation factor decreases when the TOPO concentration in the mixture increases.

Table III

Separation factors obtained with the HDEHP - TOPO mixture, for Tb and Yb.

$$\text{pH} = 1.05, [\text{HDEHP}] = 5.0 \times 10^{-3} \text{ M}$$

Experiment	[TOPO] (M)	D		Yb $\alpha$ Tb
		Tb	Yb	
1	—	0.01	2.28	228
2	$5.0 \times 10^{-5}$	0.01	2.16	216
3	$5.0 \times 10^{-4}$	0.02	2.62	131
4	$5.0 \times 10^{-3}$	0.19	2.47	13
5(*)	$5.0 \times 10^{-3}$	0.05	0.06	1.2

(\*) Without HDEHP

#### HTTA - TBP mixture

According to Table IV, the presence of TBP has the effect of decreasing the separation factor of the two elements.

Table IV

Separation factors obtained with the HTTA-TBP mixture, for the elements Tb and Yb.

$$\text{pH} = 3.50 [\text{HTTA}] = 5.0 \times 10^{-3} \text{ M}$$

Experiment	[TBP] (M)	D		Yb $\alpha$ Tb
		Tb	Yb	
1	—	0.015	0.33	22
2	$5 \times 10^{-5}$	0.056	0.59	10.5
3	$1 \times 10^{-4}$	0.75	1.68	2.2
4	$5 \times 10^{-3}$	37.1	35.0	0.94
5	$4 \times 10^{-1}$	570	250	0.44
6	$5 \times 10^{-1}$	389	268	0.69
7	1.83	273	45.9	0.17

#### HTTA - TOPO mixture

From the results presented in Table V, it can be observed that the synergistic effect, due to the addition of TOPO to HTTA, increases with the TOPO concentration in the mixtures, and the separation factor decreases.

Table V

Separation factors obtained with the mixture HTTA - TOPO, for Tb and Yb

$$\text{pH} = 3.50, [\text{HTTA}] = 2.0 \times 10^{-3} \text{ M}$$

Experiment	TOPO (M)	D		Yb $\alpha$ Tb
		Tb	Yb	
1	—	0.000	0.007	—
2	$2.0 \times 10^{-6}$	0.002	0.02	10
3	$2.0 \times 10^{-5}$	0.02	0.15	7.5
4	$2.0 \times 10^{-4}$	0.60	0.69	1.1
5	$2.0 \times 10^{-3}$	93.8	72.8	0.8
6	$2.0 \times 10^{-2}$	> 93.8	> 72.8	—
7 <sup>(*)</sup>	$2.0 \times 10^{-3}$	0.011	0.02	0.55
8 <sup>(*)</sup>	$2.0 \times 10^{-2}$	2.95	1.26	2.3

(\*) Without HTTA

According to the results presented in Table VI, the presence of TBP, in concentrations ranging from  $2.0 \times 10^{-5}$  to 1.33M, does not affect the value of the separation factor obtained when TOPO is the only extractant.

Table VI

Separation factors obtained with the mixture TBP-TOPO, for Tb and Yb

$$\text{pH} = 1.05, [\text{TOPO}] = 2.0 \times 10^{-2} \text{ M}$$

Experiment	TBP M	D		Tb $\alpha$ Yb
		La	Yb	
1	—	0.79	0.21	3.8
2	$2.0 \times 10^{-5}$	0.79	0.23	3.4
3	$2.0 \times 10^{-4}$	0.83	0.21	3.9
4	$2.0 \times 10^{-3}$	0.94	0.26	3.6
5	$2.0 \times 10^{-2}$	0.73	0.20	3.6
6	$2.0 \times 10^{-1}$	0.53	0.16	3.5
7	1.33	0.63	0.17	3.7

## CONCLUSION

From results presented, it is concluded that the application of the extraction chromatography technique is purposeless for the lanthanides separation by means of the extractants mixtures described, inasmuch as the separation factor  $\alpha \frac{Yb}{Tb}$  is lower for the mixtures than for each of the extractors used separately.

The same conclusion was reached at by Genov and Georgiev<sup>(5)</sup> when they tried to improve the separation between Pr and Yb by using extractions with the HTTA-TBP mixture instead of HTTA alone. According to them,  $\alpha_{Pr}^{Yb} = 1,5 \times 10^2$  when HTTA is used as extractant and decreases to approximately 3 when the HTTA-TBP mixture is used.

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