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INTERACTION EFFECT BETWEEN THENOYLTRIFLUOROACETONE AND TRI-n-OCTYLPHOSHINE OXIDE IN THE SYNERGISTIC EXTRACTION OF TRIVALENT LANTHANIDES. DETERMINATION OF THE COMPOSITION OF THE EXTRACTED SPECIES[*]

OF THE EXTRACTED SPECIES[*]

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The distribution constant $K_{D(HTTA)}$ of thenoyltrifluoroacetone between 10^{-3} M HNO_3 and cyclohexane was determined by means of spectrophotometric measurements of HTTA concentration in the aqueous phase. The distribution ratio, D′, of HTTA, when tri-n-octylphosphine (TOPO) is present, and the equilibrium constant, β'_n, of the reaction between HTTA and TOPO in the organic phase were also determined. By means of the known $K_{D(HTTA)}$ and D′ values, the equilibrium constant of the HTTA-TOPO interaction was calculated. Making use of $K_{D(HTTA)}$ and β'_n values and of the slope analysis method, the composition of the extracted lanthanide complexes was established. By considering the interaction reaction between the extractants, the species $Ln(TTA)_3 \cdot TOPO$ and $Ln(TTA)_3 \cdot 2(TOPO)$, for Ln = La and Yb, were identified in the organic phase. The equilibrium constants of the reactions that give rise to the species were also calculated.

Introduction

The extraordinary interest caused by the synergistic effect, after its first observation by CUNNINGHAM et al.[1] for lanthanide extraction, attests to the importance of this effect.

Two papers[2,3] published recently present a review concerning the synergistic extraction of some metallic ions by means of mixtures of extractants. Attention must

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be drawn to the fact that the interaction between a chelating agent and a neutral ligand may or may not be of importance in the study of the composition of the synergistic extracted species. While some researchers[4-7] do not take this interaction into account, other authors do.[8,13] KHOPKAR and MATHUR,[12,13] for instance, by taking into account the interaction between the extractors, established the composition of synergistic species produced when trivalent actinides were extracted by binary mixtures of HTTA and several neutral oxo-donors in xylene.

Within this same field of investigation, the interaction between HTTA and TOPO in cyclohexane was studied in the present paper. The mixture HTTA–TOPO was chosen since a very pronounced synergistic effect was observed for lanthanide extraction as reported in a previous paper.[14]

Theoretical considerations

HTTA distribution constant and HTTA · n · TOPO equilibrium constant

The HTTA distribution constant is defined as:

$$K_{D(HTTA)} = \frac{[HTTA]_o}{[HTTA]_a} \tag{1}$$

where the lower indexes "o" and "a" mean species in organic and aqueous phase, respectively.

The interaction between HTTA and TOPO (indicated by S) is expressed by the following equation:

$$HTTA_o + n\,S_o \overset{\beta'_n}{\rightleftharpoons} (HTTA \cdot n\,S)_o \tag{2}$$

in which the equilibrium constant (β'_n) is:

$$\beta'_n = \frac{[HTTA \cdot nS]_o}{[HTTA]_o\,[S]_o^n}\,. \tag{3}$$

For the HTTA–S mixture, the HTTA distribution ratio (D') is given by:

$$D' = \frac{[HTTA]_o + [HTTA \cdot nS]_o}{[HTTA]_a}\,. \tag{4}$$

From Eqs (1) and (3), Eq. (4) can be rewritten as:

$$D' = K_{D(HTTA)} (1 + \beta'_n [S]_o^n) \tag{5}$$

Assuming n = 1 in Eq. (2) and combining Eq. (1), (3) and (4), the free oxo-donor concentration $[S]_o$ can be calculated as:

$$[S]_o = C_S - (D' - K_{D(HTTA)}) \cdot \frac{C_{HTTA}}{D' + 1} \tag{6}$$

where C_S and C_{HTTA} are the initial concentrations of S and HTTA, respectively.

According to Eq. (5), a straight line must be obtained for D′ as a function of $[S]_o$ (equilibrium concentration of free neutral oxo-donor in the organic phase), if n = 1. The intercept of the straight line is the $K_{D(HTTA)}$ value and the slope is the $K_{D(HTTA)} \cdot \beta'_n$ product.

In this work, the HTTA, S and HTTA · S hydrated species were disregarded as well as the contribution of the concentration variation in the activity coefficients.

Slope analysis method

Calculation of the equilibrium constants. The following reaction occurs when a trivalent lanthanide ion (Ln^{+3}) is extracted by HTTA:

$$Ln_a^{+3} + 3\,HTTA_o \overset{K_{ex}}{\rightleftharpoons} (Ln(TTA)_3)_o + 3H_a^+ \tag{7}$$

for which the extraction constant is given by:

$$K_{ex} = \frac{[Ln(TTA)_3]_o\ [H^+]_a^3}{[Ln^{+3}]_a\ [HTTA]_o^3}\ . \tag{8}$$

The distribution ratio (D) of the lanthanide, when HTTA is only extractor in the system, is:

$$D = \frac{[Ln(TTA)_3]_o}{[Ln^{+3}]_a} \tag{9}$$

where the concentration of lanthanide complexes with HTTA in the aqueous phase was considered as negligible.

From Eqs (8) and (9) the following equation can be derived:

$$D = K_{ex} \frac{[HTTA]_o^3}{[H^+]_a^3} \tag{10}$$

According to Eq. (10), a straight line should be found for log D as a function of log [HTTA], if the pH of the aqueous phase is kept constant. The slope of the straight line gives the number of HTTA molecules that react with one lanthanide ion.

The following synergistic reaction takes place when the extraction of a lanthanide ion in a HTTA–S mixture occurs:

$$Ln^{+3} + 3HTTA_o + y\,S_o \overset{K_{syn,y}}{\rightleftharpoons} (Ln(TTA)_3 \cdot yS)_o + 3H_a^+ \tag{11}$$

whose equilibrium constant ($K_{syn,y}$) is:

$$K_{syn,y} = \frac{[Ln(TTA)_3 \cdot yS]_o}{[Ln^{+3}]_a} \cdot \frac{[H^+]_a^3}{[HTTA]_o^3\,[S]_o^y} \tag{12}$$

The distribution ratio of the lanthanide in synergistic extraction can be expressed by:

$$D_{syn,y} = K_{syn,y} \frac{[HTTA]_o^3\,[S]_o^y}{[H^+]_a^3} \tag{13}$$

Assuming that $Ln(TTA)_3 \cdot S$ and $Ln(TTA)_3 \cdot 2S$ are the only synergistic species formed in the organic phase, the overall distribution ratio (D_T) of Ln is given by:

$$D_T = D + D_{syn,1} + D_{syn,2}\,. \tag{14}$$

By introducing the value of $D_{syn,y}$ of Eq. (13) in Eq. (14), for y = 1 and 2, the following equation is obtained:

$$\frac{D_T - D}{[S]_o} = K_{syn,1} \frac{[HTTA]_o^3}{[H^+]_a^3} + K_{syn,2} \frac{[HTTA]_o^3\,[S]_o}{[H^+]_a^3}\,. \tag{15}$$

According to Eq. (15), if $Ln(TTA)_3 \cdot S$ and $Ln(TTA)_3 \cdot 2S$ are the only synergistic species in the organic phase and $[H^+]_a$ and $[HTTA]_o$ are invariable, a straight line should be obtained when $(D_T - D)/[S]_o$ is plotted as a function of $[S]_o$. The slope (m) and intercept (c) of this straight line are:

$$m = K_{syn,2} \frac{[HTTA]_o^3}{[H^+]_a^3}, \tag{16}$$

$$c = K_{syn,1} \frac{[HTTA]_o^3}{[H^+]_a^3} . \tag{17}$$

From these equations, $K_{syn,1}$ and $K_{syn,2}$ may be calculated

Calculation of the equilibrium constants β_1, β_2 and K_2. In the organic phase the following reactions occur:

$$(Ln(TTA)_3)_o + S_o \xrightleftharpoons{\beta_1} (Ln(TTA)_3 \cdot S)_o, \tag{18}$$

$$(Ln(TTA)_3)_o + 2S_o \xrightleftharpoons{\beta_2} (Ln(TTA)_3 \cdot 2S)_o, \tag{19}$$

$$(Ln(TTA)_3 \cdot S)_o + S_o \xrightleftharpoons{K_2} (Ln(TTA)_3 \cdot 2S)_o. \tag{20}$$

According to MATHUR et al.[15] the following equations are used for the calculation of equilibrium constants (β_1, β_2 and K_2):

$$\beta_1 = \frac{c}{D}, \tag{21}$$

$$\beta_2 = \frac{m}{D}, \tag{22}$$

$$K_2 = \frac{\beta_2}{\beta_1}. \tag{23}$$

Correction introduced for the HTTA–TOPO interaction. Based on a paper by KHOPKAR and MATHUR,[12] the correction for HTTA–TOPO interaction was applied in order to calculate [TOPO] free as well as the normalized or corrected log D values (log D*). The calculation of log D* values was made by taking into account the slopes (x) of the straight lines obtained when log D was plotted versus free $[\mathrm{TOPO}]_o$ at a fixed concentration of HTTA; then the following empirical equation was applied for the correction of log D values:

$$\log D_{II} = \log D_I - x\left\{\log\,[\mathrm{TOPO}]_I - \log\,[\mathrm{TOPO}]_{II}\right\} \tag{24}$$

where indexes (I) and (II) are related to two experimental concentrations of TOPO.

The value determined for x was used by KHOPKAR and MATHUR[12] for the correction of log D_T, taking into account the variation of the free TOPO concentration in the organic phase, according to the following equation:

$$\log D^* = \log D_T - x\left\{\log\,[\mathrm{TOPO}]_I - \log\,[\mathrm{TOPO}]_{II}\right\} \tag{25}$$

where D* is the corrected lanthanide distribution ratio.

Experimental

Equipment

Nuclear Chicago single channel analyzer, model 8775, coupled to a well-type 5.1 cm × 4.4 cm NaI(Tl) scintillation detector, for radioactivity measurements. Spectrophotometer Beckman Model DB with quartz cells of 10 mm.

Reagents

HTTA of analytical grade from Aldrich Chemical Co. Inc. was left under vacuum in the presence of P_2O_5 for 24 hours before use. TOPO of analytical grade from Polysciences, Inc., was used without any previous purification. Cyclohexane BDH of laboratory grade was used as diluent. All other reagents were of analytical grade.

Radioactive tracers

^{169}Yb and ^{140}La were obtained by irradiation of 2 mg of La_2O_3 and of Yb_2O_3 in the IEA-R1 reactor at a 10^{12} n · cm^{-2} · s^{-1} thermal neutron flux for about 8 hours. After irradiation, the oxides were dissolved with nitric acid with heating. The residue was redissolved in 10 ml of 10^{-2}M HNO_3.

Procedure

(1) *Determination of the HTTA distribution constant ($K_{D(HTTA)}$).* HTTA solutions with concentrations ranging from $5.0 \cdot 10^{-3}$ to 0.10M in cyclohexane were prepared and equilibrated with $1.0 \cdot 10^{-3}$M HNO_3 in a thermostated mechanical stirrer for five hours at 25 °C.

After separation of the phases, an aliquot was pipetted from each aqueous phase. The aliquots were diluted with water to a suitable volume and the absorbance was measured at 292 nm, using $1.0 \cdot 10^{-3}$M HNO_3 as reference solution.

From the known molar absorptivity at 292 nm ($7880\ l \cdot mol^{-1} \cdot cm^{-1}$)[16,17] the HTTA concentration in each aqueous phase was calculated and then the $K_{D(HTTA)}$ value was determined by using equation (1).

(2) *Determination of the formation constant (β'_n) of the HTTA · n · TOPO species.* Organic phases with a fixed HTTA concentration (0.020M) and variable TOPO concentrations (0.0005 to 0.250M) were prepared. The experimental procudure was the same as described in item 1. The HTTA concentration in the aqueous phase was measured and D' was calculated by using Eq. (4).

By means of the known D' and $K_{D(HTTA)}$ values introduced in Eq. (6), the free TOPO concentration in the organic phase was calculated.

(3) *Determination of the $Ln(TTA)_x \cdot y(TOPO)$ complexes composition.* The slope analysis method was applied by using three sets of experiments where two variables were kept constant in each run. The preparation of aqueous phases and the procedure for D values calculation were the same for all sets. The aqueous phases were prepared by means of lanthanide nitrate solutions and the corresponding radioactive tracers. The final concentration of lanthanides varied from 10^{-4} to 10^{-5}M and the ionic strength was kept constant (1M $NaNO_3$).

For the extraction operation, 5 ml of each phase was shaken for 15 minutes in a mechanical stirrer thermostated at 25 °C. After phase separation, 1 ml aliquots were pipetted and the respective activities were measured for the calculation of D values.

The composition of the complexes was established from the slopes of the straight lines obtained by plotting log D versus the logarithm of the variable concentrations (HTTA, H or TOPO).

Results

The $K_{D(HTTA)}$ values are presented in Table 1. The mean value is 5.0±0.08.

Fig. 1 shows the dependence of the distribution ratio, D', of HTTA on the free TOPO concentration. A straight line may be observed up to 0.15M TOPO concentration, indicating that n = 1 in the Eq. (2) when TOPO varied from $5 \cdot 10^{-4}$ to 0.15M.

Table 1
Distribution constant ($K_{D(HTTA)}$) of HTTA in the system cyclohexane and $1.0 \cdot 10^{-3}$M HNO_3

C_{HTTA}, M × 10^3	$[HTTA]_a$, M × 10^3	$K_{D(HTTA)}$
5.0	0.81	5.17
7.5	1.24	5.05
10.0	1.67	4.99
20.0	3.38	4.92
70.0	11.68	4.99
100.0	16.75	4.97
		Mean 5.01±0.08

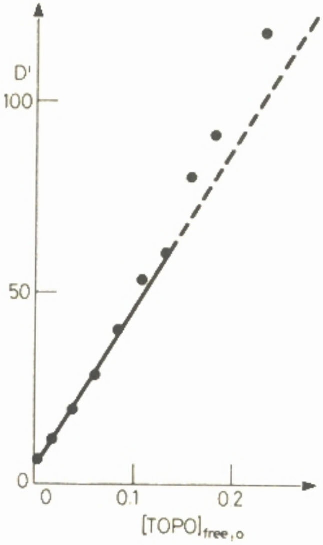

Fig. 1. Variation of the HTTA distribution ratio as a function of free TOPO concentration in the organic phase, C_{HTTA} = 0.020M, $[HNO_3]$ = $1.0 \cdot 10^{-3}$M

The method of least squares was applied to D′ values concerning TOPO concentrations up to 0.15M. The parameters of the straight line obtained are: intercept: 4±1 ($K_{D(HTTA)}$), slope: 433±13 ($\beta'_n \cdot K_{D(HTTA)}$).

The value $K_{D(HTTA)} = 5.0$ was assumed, as it is consistent with two methods of calculation. The value $\beta' = 87$ was obtained for the equilibrium constant of HTTA–TOPO interaction, disregarding the associated error.

For the composition of $Ln(TTA)_x \cdot y(TOPO)$ species, the following results were obtained:

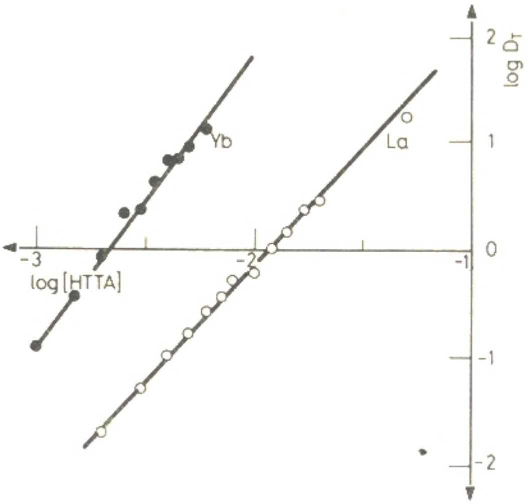

Fig. 2. Variation of the logarithm of La and Yb distribution ratios as a function of the logarithm of HTTA concentration, when TOPO concentration and pH are constant; $[La] = 9.0 \cdot 10^{-5}M$, $[Yb] = 1.0 \cdot 10^{-5}M$, $[TOPO] = 3.0 \cdot 10^{-4}M$, $[NaNO_3] = 1.0M$, pH (La) 2.90, pH (Yb) 2.80

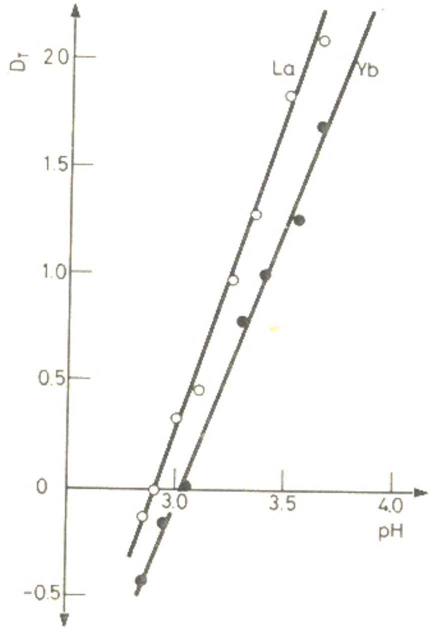

Fig. 3. Variation of the logarithm of La and Yb distribution ratios as a function of the pH, for a fixed concentration of HTTA and TOPO $[La] = 5.0 \cdot 10^{-5}M$, $[Yb] = 2.0 \cdot 10^{-5}M$, $[HTTA]_{La} = 4.0 \cdot 10^{-2}M$, $[HTTA]_{Yb} = 6.0 \cdot 10^{-3}M$, $[TOPO]_{La} = 6.0 \cdot 10^{-5}M$, $[TOPO]_{Yb} = 3.0 \cdot 10^{-5}M$, $[NaNO_3] = 1.0M$

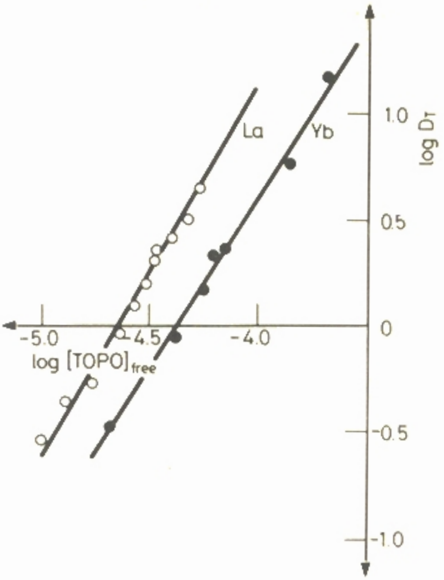

Fig. 4. Variation of the logarithm of La and Yb distribution ratios as a function of the logarithm of free TOPO concentration, when HTTA concentration and pH are constant; $[La] = 8.0 \cdot 10^{-5}M$, $[Yb] = 1.0 \cdot 10^{-5}M$, $[HTTA]_{La} = 4.0 \cdot 10^{-2}M$, $[HTTA]_{Yb} = 6.0 \cdot 10^{-3}M$, pH (La) 2.90, pH (Yb) 2.75, $[NaNO_3] = 1.0M$

(a) *Variation of log D_T as a function of log [HTTA].* Fig. 2 shows the straight lines obtained. By using the least squares method, the following equations were established: for La: $y = 2.1x + 4.1$ (correlation coefficient = 0.998), for Yb: $y = 2.7x + 7.2$ (correlation coefficient = 0.994).

(b) *Variation of log D_T as a function of pH.* The results obtained are presented in Fig. 3. The slopes of the straight lines give the number of hydrogen atoms which take part in complex formation: for La: $y = 2.9x - 8.4$ (correlation coefficient = 0.996), for Yb: $y = 2.6x - 7.9$ (correlation coefficient = 0.996).

(c) *Variation of log D_T as a function of log $[TOPO]_{free}$ in the organic phase.* The HTTA concentration was chosen in such a way that the HTTA–TOPO interaction may be disregarded.

Equations (5) and (6) were used for the $[TOPO]_{free}$ calculation in the organic phase. Fig. 4 shows the straight lines determined: for La: $y = 1.65x + 7.7$ (correlation coefficient = 0.992), for Yb: $y = 1.60x + 7.0$ (correlation coefficient = 0.995).

In accordance with Eq. (13), the slope of the straight line gives the number of TOPO molecules in the complex produced.

(d) *Log D* calculation.* The results obtained for La and Yb were used for the correction of log D_T, when the variable was the HTTA concentration. Taking into

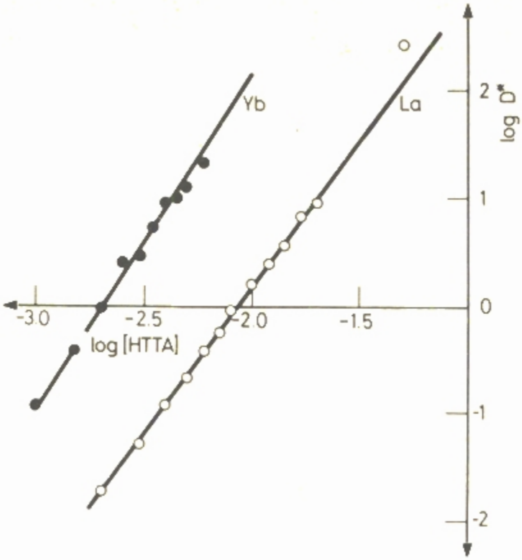

Fig. 5. Variation of the logarithm of La and Yb corrected distribution ratios as a function of the logarithm of HTTA concentration; $[La] = 9.0 \cdot 10^{-5}$ M, $[Yb] = 1.0 \cdot 10^{-5}$ M, $[TOPO] = 3.0 \cdot 10^{-4}$ M, pH (La) 2.90, pH (Yb) 2.80, $[NaNO_3] = 1.0$M

account the HTTA–TOPO interaction, the free TOPO concentration in the organic phase was calculated. In order to calculate log D*, log D_T was normalized with regard to the higher experimental concentration of free TOPO, in accordance with Eq. (19). The results obtained for La and Yb are shown in Fig. 5. The equations of log D* as a function of log [HTTA], indicated by y and x, respectively, are: for La: $y = 2.9x + 6.0$ (correlation coefficient = 0.997), for Yb: $y = 2.9x + 7.9$ (correlation coefficient = 0.996)

(e) *Determination of y for the $Ln(TTA)_3 \cdot y$ TOPO complex.* By using the results of item (c) and Eqs (5) and (6), the $(D_T-D)/[TOPO]_{free}$ ratios were calculated. By applying the least squares method to the $(D_T-D)/[TOPO]_{free}$ values as a function of $[TOPO]_{free}$, straight lines were obtained (Fig. 6). The corresponding parameters are:

	Intercept (c)	Slope (m)	Correlation coefficient
For La	$(1.3\pm0.3) \cdot 10^4$	$(1.36\pm0.09) \cdot 10^9$	0.987
For Yb	$(9.0\pm1.2) \cdot 10^3$	$(2.8\ \pm0.1) \cdot 10^8$	0.993

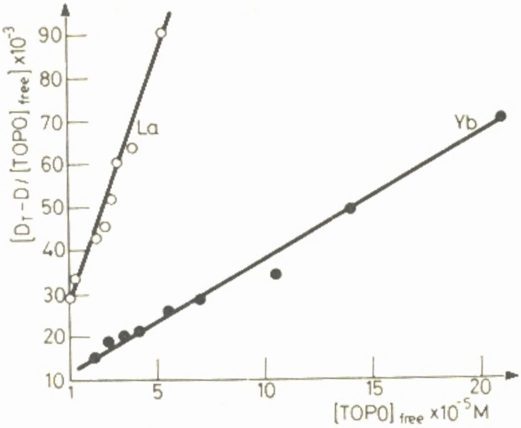

Fig. 6. Variation of the ratio $(D_T - D)/[TOPO]_{free}$ as a function of the free TOPO concentration, according to the experiments with La and Yb; $[La] = 9.0 \cdot 10^{-5}M$, $[Yb] = 1.0 \cdot 10^{-5}M$, $[HTTA]_{La} = 4.0 \cdot 10^{-2}M$, $[HTTA]_{Yb} = 6.0 \cdot 10^{-3}M$, pH (La) 2.90, pH (Yb) 2.75, $[NaNO_3] = 1.0M$

Table 2
Equilibrium constants of the $Ln(TTA)_3 \cdot (TOPO)$ and $Ln(TTA)_3 \cdot 2(TOPO)$ complexes

Element	log $K_{syn,1}$	log $K_{syn,2}$	log β_1	log β_2	log K_2
La	−0.3±0.2	4.67±0.07	6.5±0.2	11.6 ±0.1	5.0±0.2
Yb	2.4±0.1	6.88±0.04	6.3±0.1	10.82±0.04	4.5±0.1

(f) *Determination of the equilibrium constants.* By using Eqs (23), (24) and (25) the equilibrium constants β_1, β_2 and K_2 were determined. Table 2 presents these results.

Discussion

Rigorously, the HTTA distribution constant must be defined as:

$$K_{D(HTTA)} = \frac{[HTTA_{enol}]_o + [HTTA \cdot H_2O]_o}{[HTTA_{enol}]_a + [HTTA \cdot H_2O]_a}$$

taking also into account the HTTA keto-hydrated form. When TOURNIER and DAVIS[8] studied the kerosene HTTA/TBP/dilute HNO_3 system, the enolic form of

HTTA in the aqueous phase was disregarded because kerosene was used as diluent. Later on, COX and DAVIS[9] did not take into account the concentration of the keto-hydrated form of HTTA in the organic phase when the water solubility in the diluent was low. The same approach was used in the present paper, as the solubility of water in cyclohexane is low (0.04 g/l).[18]

The value obtained for $K_{D(HTTA)}$ (5.0 or 4±1) is acceptable, if the experimental error is taken into account. This value agrees also with $K_{D(HTTA)} = 5.5$ determined by TOURNIER and DAVIS[8] when the same system was studied, although the pH of the aqueous phase was different.

The linearity for the variation of D′ as a function of the free TOPO concentration in the organic phase was observed up to 0.15M $[TOPO]_{free}$ (Fig. 1). The behaviour of the system changes when TOPO concentration is higher than 0.15M. A gradual transformation of the enolic form of HTTA into the keto-hydrated form and its interaction with TOPO is a possible explanation for this behaviour.

When La and Yb distributions were studied as function of the HTTA concentration (Fig. 2), the slopes of the straight lines were lower than the expected values, 2.1 and 2.7 for La and Yb, respectively. This disagreement was assumed as resulting from the HTTA–TOPO interaction.

Moreover, the slopes of the straight lines obtained, 1.65 for La and 1.60 for Yb (Fig. 4), when the variation of the distribution ratio was studied as a function of the free TOPO concentration, did not allow to establish the y value for the $Ln(TTA)_x \cdot y(TOPO)$ complex.

The expected value, x = 3, was obtained only when the variation of the corrected log D* was studied as a function of log [HTTA] (Fig. 5). The experimental values for the slopes of the straight lines, 2.9 for both lanthanides, were considered good enough to assume x = 3.

In the determination of y values, straight lines were obtained for both elements, when the $(D_T - D)/[TOPO]_{free}$ ratio was studied as a function of $[TOPO]_{free}$ (Fig. 6). The results proved the validity of the initial supposition that $Ln(TTA)_3 \cdot TOPO$ and $Ln(TTA)_3 \cdot 2\ TOPO$ are the synergistic species present in the organic phase.

These results permit to conclude that the interaction between the extractants must also be considered in studies of the composition of synergistic species extracted.

Table 2 presents the values obtained for $K_{syn,1}$, $K_{syn,2}$, β_1, β_2 and K_2 for La and Yb in the present work.

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