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# Solvent extraction of lanthanum(III), europium(III) and lutetium(III) by bis(4-acyl-5-hydroxypyrazoles) derivatives

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## Abstract

The liquid–liquid extraction of some trivalent rare earths Ln(III) (Ln: La, Eu, Lu), performed from 0.1 M NaNO<sub>3</sub> aqueous solutions by two bis(4-acyl-5-hydroxypyrazoles), 1,12-bis(1'-phenyl-3'-methyl-5'-hydroxy-4'-pyrazolyl)-dodecane-1,12-dione (HL-10-LH) and 1,6-bis(1'-phenyl-3'-methyl-5'-hydroxy-4'-pyrazolyl)-hexane-1,6-dione (HL-4-LH), in chloroform, has been studied. The processes of extraction have been determined by the slope analysis method and by analyzing a function that allows the simultaneous treatment of all the experimental points obtained in different conditions. With HL-10-LH, the stoichiometries of the extracted species differ for the three lanthanides. The ligands are biscoordinated and tetracoordinated in the extracted complexes of lanthanum and europium, La<sub>2</sub>(L-10-L)<sub>2</sub>(L-10-LH)<sub>2</sub> and Eu<sub>n</sub>(L-10-L)<sub>n</sub>(L-10-LH)<sub>n</sub> (*n* = 1, 2). They are exclusively biscoordinated in the complex of lutetium, Lu(L-10-LH)<sub>3</sub>. The complex of europium extracted by HL-4-LH at weak extraction yields, Eu(L-4-L)(L-4-LH), and the corresponding extraction constant are comparable to the ones obtained for HL-10-LH, whereas polynuclear species are extracted at high extraction yields. The extraction efficiency with HL-10-LH increases with the ascending atomic number of Ln (La < Eu < Lu). A comparison between HL-10-LH and HPMBP (1-phenyl-3-methyl-4-benzoyl-5-hydroxy-pyrazole) for the same concentration of complexation sites shows that the extraction by HL-10-LH is more effective. Moreover, a better selectivity of extraction was obtained with HL-10-LH.

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**Keywords:** Solvent extraction; Bis(4-acyl-5-hydroxy-pyrazoles); Lanthanides; Separation

## 1. Introduction

During the last decade, the research of new processes for the treatment of nuclear waste has created a renewed interest in the extraction of the 4f elements [1]. Moreover, since currently thousand operations of extraction are necessary to isolate each element of the lanthanides series from the natural mixture, the improvement of the intra-group separation of lanthanides is also a relevant objective [2–8]. It is within this scope that some extractants, able to extract totally or separately the trivalent elements 4f, have been tested.

The bis(4-acyl-5-hydroxypyrazoles) HL-*n*-LH, represented in Fig. 1 by H)–(H, are acidic multidentate and bis-chelating ligands in which two units 1-phenyl-3-methyl-4-acyl-5-hydroxy-pyrazoles are bound by a polymethylene chain of

variable length. Each molecule has four oxygen atoms and two acidic sites of complexation (c.f. Scheme 1). This particular structure enables them to form a variety of complexes; in the case of a trivalent cation, the three possible modes of coordination by cation exchange and chelation are represented in Fig. 1 in a hypothetical complex. It is also to be noted that the protonated “–LH” groups may act as neutral O-donor ligands.

Dong et al. [9] were the first to use HL-*n*-LH of different polymethylene chain length in the extraction of UO<sub>2</sub><sup>2+</sup> in chloroform: they demonstrated a higher efficiency of extraction by HL-*n*-LH than by their parent compounds 4-acyl-5-hydroxypyrazoles (HL) which was later confirmed and explained by a higher lipophilicity of the former ones [10,11]. The extraction of transition metals (Cu<sup>2+</sup>, Zn<sup>2+</sup>, Co<sup>2+</sup> and In<sup>3+</sup>) by these ligands were explored by our group [12]. Miyazaki et al. [13] studied the effect of the polymethylene chain length (*n* = 0–8, 10, 20) on the extraction of copper(II) by HL-*n*-LH. They found that the extracted species vary with “*n*”: Cu(L-*n*-L) for *n* = 8, 10, 20 and Cu(L-*n*-LH)<sub>2</sub> or Cu<sub>2</sub>(L-*n*-L)<sub>2</sub> for *n* = 1–7. Due to

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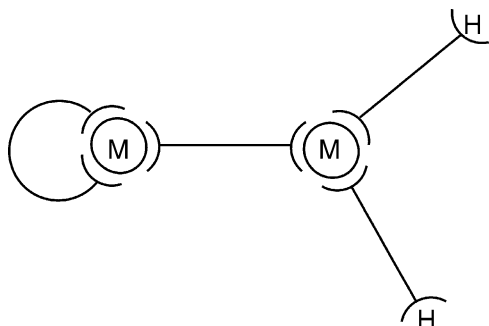


Fig. 1. Hypothetical complex of a trivalent cation with a bis(4-acyl-5-hydroxypyrazole).

steric requirements of the Cu<sup>2+</sup> cation that forms square-planar coordination complexes, the bis(acyl-hydroxypyrazoles) with short polymethylene chains ( $n \leq 7$ ) are not able to fold onto it to give tetracoordinated 1:1 complexes like Cu(L-8-L) [14]. Therefore, they act as biscoordinating ligands in 1:2 complexes or as bridging tetracoordinating ligands in 2:2 complexes. The bis(acyl-hydroxypyrazoles) HL-*n*-LH ( $n=0, 1-8, 10, 20, 22$ ) have been used for the liquid–liquid extraction of Am<sup>3+</sup> [10], Th<sup>4+</sup> [10,15], Cu<sup>2+</sup> [13,16], Ni<sup>2+</sup> [17], Zn<sup>2+</sup> [17,18], Hg<sup>2+</sup> [19], UO<sub>2</sub><sup>2+</sup> [9,10,15,19–22], VO<sub>2</sub><sup>2+</sup> [21,22], Be<sup>2+</sup> [23], Sc<sup>3+</sup> [23], Y<sup>3+</sup> [23], In<sup>3+</sup> [24], La<sup>3+</sup> [25,26] or lanthanides(III) [10,27–31]. Takeishi et al. [11] postulated a procedure for the successive separation of the actinides in nitric acid medium using HL-8-LH.

The complexation of trivalent lanthanides by HL-*n*-LH ( $n=4,5,7,8$ ) has also been studied [32] in homogeneous water–acetonitrile(60–40%) medium (NaClO<sub>4</sub>, I = 1 M). The stoichiometry of the major complexes depend upon the length of the polymethylene chain: the folding of the ligand upon the metallic centre was not observed for the bis(acyl-hydroxypyrazoles) with  $n=4$  or 5 that give Ln(L-*n*-L)Ln<sup>4+</sup> complexes, but it was for  $n=7$  or 8, giving Ln(L-*n*-L)<sup>+</sup> species. HL-*n*-LH are equal or better complexants than their parent compounds.

In the present work, the extraction in chloroform of three lanthanides (La<sup>3+</sup>, Eu<sup>3+</sup> and Lu<sup>3+</sup>) of different ionic radii, from nitrate medium, by two HL-*n*-LH ( $n=4$  and 10), representative of bis(4-acyl-5-hydroxypyrazoles) with short and long chain, respectively, is studied. Since HL-10-LH has been already used in the micellar extraction of europium [33], and moreover, since

studies of lanthanide extraction by silicas doped with HL-10-LH are currently carried on in our team, a detailed study is carried out with this extractant, which will allow a comparison between these three techniques of extraction: a basic question would be to see how low the pH can be to obtain significant metal extraction yields. The selectivity of extraction by HL-10-LH is determined by operating a simultaneous extraction of the three lanthanides ions, and then compared to the extraction by HPMBP.

## 2. Experimental

### 2.1. Reagents

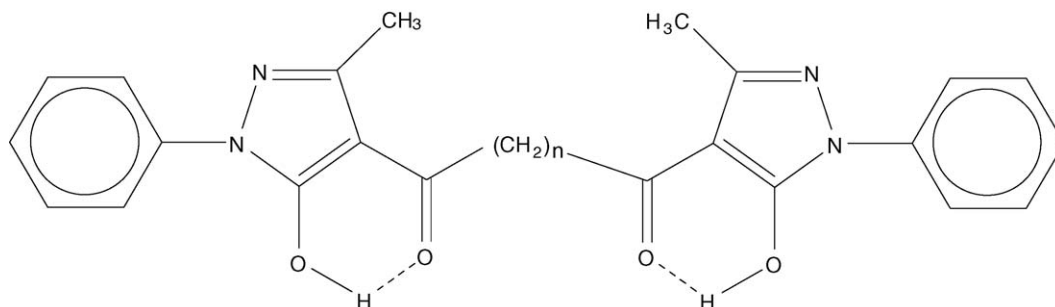
The water used was deionized and obtained from a MilliQ RG, Millipore apparatus. Inorganic chemicals were purchased from Prolabo and Merck and were of analytical grade. Organic chemicals for the syntheses were Aldrich and Fluka products. The bis-acylpyrazolones: 1,12-bis[1'-phenyl-3'-methyl-5'-hydroxy-4'-pyrazolyl]-dodecane-1,12-dione (HL-10-LH) and 1,6-bis[1'-phenyl-3'-methyl-5'-hydroxy-4'-pyrazolyl]-hexane-1,6-dione (HL-4-LH) were prepared by Jensen's method [34] and recrystallized three times in a chloroform–ethanol mixture. Their purity was checked by <sup>1</sup>H NMR. The chloroform used for the extractions was purchased from Prolabo (99%, “Normapur” quality). Lanthanide stock solutions (1000 ppm,  $\approx 6.5 \times 10^{-3}$  M) were prepared from the corresponding lanthanide oxide by reaction with nitric acid ( $\approx 1$  M) and dilution with water.

### 2.2. Extraction and analytical procedures

(The index “org” refers to the organic phase, “aq” to the aqueous phase, “i” denotes initial concentration before contacting the phases and “t” denotes total concentration).

The solutions of the extractants, HL-10-LH and HL-4-LH, were prepared by dissolving a weighed sample in chloroform pre-equilibrated with water. The aqueous phases were prepared using NaNO<sub>3</sub> to control the ionic strength and diluted HNO<sub>3</sub> to adjust the acidity.

The distribution curves log *D* versus pH were drawn from measurements using batch technique in thermostated ( $25.0 \pm 0.2$  °C) vessels equipped with a magnetic agitator and combined glass electrode connected to a “PHN78 Tacussel” pH-



Scheme 1. The extractants (enol form).  $n=10$ , HL-10-LH;  $n=4$ , HL-4-LH.

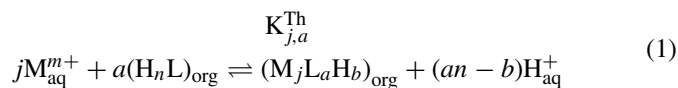
meter that reads the pH to 0.01. For the first experimental point, a volume of the organic phase was contacted with an equal volume of the aqueous phase under stirring (700–800 rpm), for 30 min, which is long enough to reach the thermodynamic equilibrium. The equilibrium pH was measured. The phases were separated by gravity. Then, an aliquot of both phases was withdrawn for the determination of metal concentrations and log  $D$  calculation (see below), hence the first point ( $\log D$ ,  $\text{pH}_{\text{eq}})_1$ . The pH was then increased by the addition of an aliquot of  $\text{Na}^+(\text{OH}^-, \text{NO}_3^-)$  0.1 M solution. An equal volume of the organic solution was then added to the system. The extraction sequence was then repeated to obtain the second experimental point ( $\log D$ ,  $\text{pH}_{\text{eq}})_2$ . Measurements at increasing pH's were thus performed.

In the above described experiments, only one organic phase and one aqueous phase, whose pH is modified after each sampling, are opposed to determine a whole log  $D$  versus pH curve; thus, the overall duration of contact between those phases may be as high as 6–7 h. Then some scattered experimental points were also obtained in test-tubes, without varying the pH, such that the contact time between the phases never exceeds 30 min. The data obtained by both experimental methods were similar.

In order to determine the concentration of the metal ions, the withdrawn aliquots of aqueous phase were diluted with water for analysis by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) using a Jobin Yvon – JY138 ultratrace apparatus. The metal in aliquots of organic phase was quantitatively stripped by  $\text{HNO}_3$  1 M, the aqueous phase obtained was also diluted and analyzed by ICP-AES. Points with a mass balance inferior to 95% were rejected.

### 3. Treatment of the data

Let us consider the extraction of a metal cation  $\text{M}^{m+}$  by an acidic extractant  $\text{H}_n\text{L}$  as the single extracted species  $(\text{M}_j\text{L}_a\text{H}_b)_{\text{org}}$ . At equilibrium, the species present in the aqueous phase are  $\text{M}^{m+}$  and  $\text{MX}_n^{(m-n)+}$ , where  $\text{X}$  = inorganic anion, and the species present in the organic phase are  $\text{H}_n\text{L}$  and  $(\text{M}_j\text{L}_a\text{H}_b)$ . The extraction equilibrium is written as:



The neutrality of the extracted complex implies  $an - b = mj$ .

The thermodynamic constant  $K_{j,a}^{\text{Th}}$  is given by

$$K_{j,a}^{\text{Th}} = \frac{|\text{M}_j\text{L}_a\text{H}_b|_{\text{org}} |\text{H}^+|_{\text{aq}}^{jm}}{|\text{M}^{m+}|_{\text{aq}}^j |\text{H}_n\text{L}|_{\text{org}}^a} = \frac{[\text{M}_j\text{L}_a\text{H}_b]_{\text{org}} [\text{H}^+]_{\text{aq}}^{jm}}{[\text{M}^{m+}]_{\text{aq}}^j [\text{H}_n\text{L}]_{\text{org}}^a} \times \frac{\gamma_{\text{M}_j\text{L}_a\text{H}_b, \text{org}} \gamma_{\text{H}^+, \text{aq}}^{jm}}{\gamma_{\text{M}^{m+}, \text{aq}}^j \gamma_{\text{H}_n\text{L}, \text{org}}^a} \quad (2)$$

where “|” symbolizes activity, “[ ]” concentration and “ $\gamma$ ” activity coefficient. When the ionic strength is kept constant in the aqueous phase and when organic solutions are diluted, the ratio of the activity coefficients will be constant, which generates a

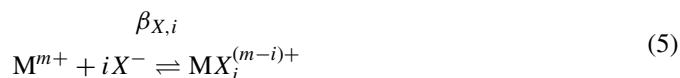
conditional constant:

$$K_{j,a}^* = \frac{[\text{M}_j\text{L}_a\text{H}_b]_{\text{org}} [\text{H}^+]_{\text{aq}}^{jm}}{[\text{M}^{m+}]_{\text{aq}}^j [\text{H}_n\text{L}]_{\text{org}}^a} \quad (3)$$

The distribution ratio  $D$  of the metal ion can be expressed as follows:

$$D = \frac{[\text{M}]_{\text{org}, \text{t}}}{[\text{M}]_{\text{aq}, \text{t}}} = \frac{j[\text{M}_j\text{L}_a\text{H}_b]_{\text{org}}}{[\text{M}^{m+}]_{\text{aq}} (1 + \sum_i \beta_{X,i} [\text{X}^-]_{\text{aq}}^i)} \quad (4)$$

$[\text{M}]_{\text{org}, \text{t}}$  and  $[\text{M}]_{\text{aq}, \text{t}}$  (“t” for “total”) are the analytical concentrations of  $\text{M}$  in both phases.  $\beta_{X,i}$  is the complexation constant of  $\text{M}^{m+}$  by  $\text{X}^-$  in the aqueous phase:



At constant ionic strength  $C = (1 + \sum_i \beta_{X,i} [\text{X}^-]_{\text{aq}}^i)$  remains constant. The expression of the distribution ratio becomes:

$$D = j[\text{M}_j\text{L}_a\text{H}_b]_{\text{org}} [\text{M}^{m+}]_{\text{aq}}^{-1} C^{-1} = jK_{j,a}^* [\text{M}^{m+}]_{\text{aq}}^{j-1} [\text{H}_n\text{L}]_{\text{org}}^a [\text{H}^+]_{\text{aq}}^{-jm} C^{-1} \quad (6)$$

Then

$$\log D = (j - 1) \log [\text{M}^{m+}]_{\text{aq}} + a \log [\text{H}_n\text{L}]_{\text{org}} + (jm) \text{pH} + \log j + \log K_{j,a}^* - \log C \quad (7)$$

Let us define  $\log K_{j,a} = \log K_{j,a}^* - \log C$ ; this term is constant at constant ionic strength and will be considered as the logarithm of the conditional extraction constant.

The slope analysis method often allows the determination of the stoichiometry of the extracted complex. Two cases must be considered:

- (1)  $j = 1$ , mononuclear complex: by plotting  $\log D$  against one of the parameters ( $\log [\text{H}_n\text{L}]_{\text{org}}$ , pH) while maintaining the other one constant, the stoichiometric coefficients  $a$  and  $m$  could be determined from the integer slopes of the lines obtained.
- (2)  $j > 1$ , polynuclear complex: by plotting  $\log(D/j[\text{M}^{m+}]_{\text{aq}}^{j-1})$  against the same parameters, lines of slopes  $a$  and  $jm$  would be obtained respectively for  $\log [\text{H}_n\text{L}]_{\text{org}}$  and for pH.

Since  $j$  is unknown, several values have to be tested, until integer slopes and auto coherent results are obtained.

When a dinuclear complex is extracted, the shape of the experimental curves  $\log D$  versus pH can be easily deduced from the theoretical work of Khol'kin et al. [35]. These authors showed that when two metal ions  $\text{M}^{m+}$  and  $\text{N}^{n+}$  of identical initial aqueous concentrations are co-extracted as a single complex  $(\text{MNL}_{m+n}(\text{HL})_s)_{\text{org}}$ , by the same acidic extractant HL, the curve  $\log D$  versus pH is linear with a slope equal to  $(m + n)$  for low extractions, whereas the slope is  $(m + n)/2$  for high extractions and a break of slope is observed for  $D \cong 1$ . These results can obviously apply if only one ion  $\text{M}^{m+}$  is extracted in the form of

a binuclear complex: the slope of the experimental curve  $\log D$  versus pH would vary from  $2m$  to  $m$  with increasing pH.

The method preferentially used in this work consists in considering a single function  $A_{j,a}$  versus pH calculated from all the experimental data with the assumption that  $M_jL_aH_b$  is the only extracted species.  $A_{j,a}$  is defined by

$$A_{j,a} = \log \left( \frac{D}{j[M^{m+}]_{\text{aq}}^{(j-1)}} \right) - a \log [H_nL]_{\text{org}} \quad (8)$$

From (7), it follows that, if  $M_jL_aH_b$  is indeed extracted,

$$A_{j,a} = \log K_{j,a} + (jm)\text{pH} \quad (9)$$

and the plot of  $A_{j,a}$  versus pH is a straight line of slope  $mj$ . Note that the difference between the extractant concentration at equilibrium  $[H_nL]_{\text{org}}$  and its initial (subscriber “i”) concentration before contacting the phases must be taken into account:

$$\begin{aligned} [H_nL]_{\text{org}} &= [H_nL]_{i,\text{org}} - a[M_jL_aH_b]_{\text{org}} - [H_nL]_{t,\text{aq}} \\ &= [H_nL]_{i,\text{org}} - \left( \frac{a}{j} \right) [M]_{t,\text{org}} - [H_nL]_{t,\text{aq}} \end{aligned}$$

With this method, all the extraction data, obtained for different values of  $[H_nL]_{i,\text{org}}$  or  $[M^{m+}]_{i,\text{aq}}$ , are gathered in a single graph for a given hypothesis, which allows an accurate choice between the possible extraction processes.

In the present work, from the data upon the distribution and deprotonation of the bis(4-acyl-5-hydroxypyrazoles) reported in [13,16], it may be stated that the acidity constants of HL-10-LH are similar to that of HL-8-LH and its distribution constant slightly superior, i.e.  $\text{p}K_{a1} \approx 4.6$ ;  $\text{p}K_{a2} \approx 5.2$  and  $\log K_d \geq 6.9$ . It implies that, in the pH range of the present study,  $([HL-10-LH]_{\text{org}}/[L-10-LH^-]_{\text{aq}}) \geq 10^{11}$ ,  $([HL-10-LH]_{\text{org}}/[L-10-L^{2-}]_{\text{aq}}) \geq 10^{6.7}$  (values calculated at  $\text{pH} = 5$ ), and  $([HL-10-LH]_{\text{org}}/[HL-10-LH]_{\text{aq}}) \geq 10^{6.9}$ . Therefore  $[H_nL]_{t,\text{aq}}$  may be neglected in the mass balance of  $H_nL$ . Moreover, aggregation of HL- $n$ -LH was never observed, either in aqueous phase or in organic phase.

## 4. Results

### 4.1. Extraction of lanthanum(III) by HL-10-LH

The experimental plots of  $\log D$  versus pH are shown in Fig. 2. They are linear with slopes 3 for  $\log D > 0$ . For  $\log D < 0$ , the value of the slope is obviously higher. Taking into account the study of Khol'kin, that suggests the extraction of a binuclear species in this case, several extraction processes were tested corresponding to the extraction of  $\text{La}_2(\text{L-10-L})_3$ ,  $\text{La}_2(\text{L-10-L})_2(\text{L-10-LH})_2$  or  $\text{La}_2(\text{L-10-L})(\text{L-10-LH})_4$ . The corresponding  $A_{xy}$  functions were calculated and plotted versus pH (Figs. 3–5). Compared with the theoretical value of 6.0,  $A_{25}$  versus pH shows a slope close to 7 and the corresponding process must be rejected. Both  $A_{24}$  versus pH and  $A_{23}$  versus pH show acceptable slopes 6.2 and 6.1, respectively, though the correlation coefficient of the latter line is lower than that of the former. The corresponding extraction constants have been determined by averaging

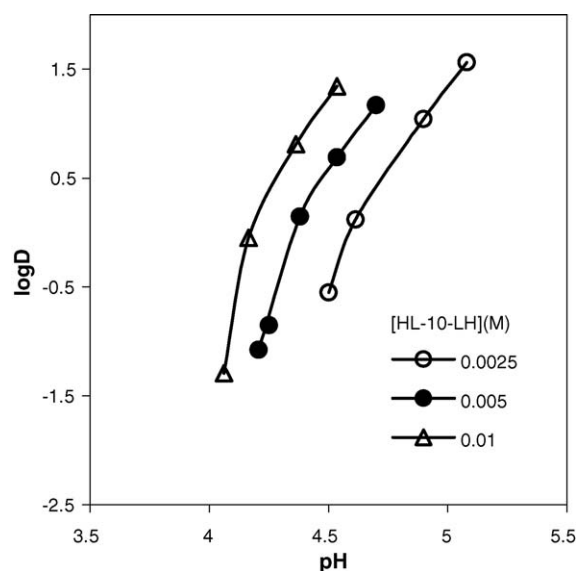


Fig. 2. Extraction of  $\text{La}^{3+}$  from nitrate medium in chloroform at 25 °C.  $[(\text{Na,H})\text{NO}_3] = 0.1 \text{ M}$ ;  $[\text{La}^{3+}]_{i,\text{aq}} = 2 \times 10^{-4} \text{ M}$  (The drawn curves are guides for the eye).

the values calculated for every experimental point:  $\log K_{24}^{\text{La}} = -12.9 \pm 0.2$  and  $\log K_{24}^{\text{La}} = -15.4 \pm 0.5$ . The uncertainty upon this last constant is quite high compared with the experimental uncertainty upon each  $\log K$  value ( $\approx \pm 0.14$ , due to the uncertainty upon the metal determination) and with that observed in comparable cases: see below  $\log K_{13}^{\text{Lu}} = \pm 0.1$ . Therefore, the other process corresponding to the major extracted species  $\text{La}_2(\text{L-10-L})_2(\text{L-10-LH})_2$  must be taken into consideration. The corresponding extraction equilibrium is written:

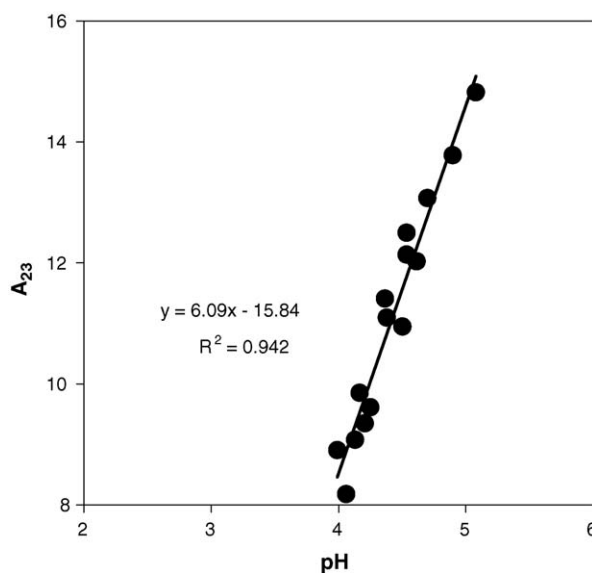
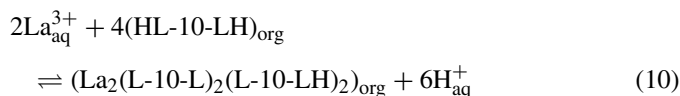


Fig. 3. Extraction of  $\text{La}^{3+}$  by HL-10-LH in the conditions of the Fig. 2: A  $v$ . pH calculated with the assumption that  $\text{La}_2(\text{L-10-L})_3$  is the only extracted complex. (The drawn line is linear regression).

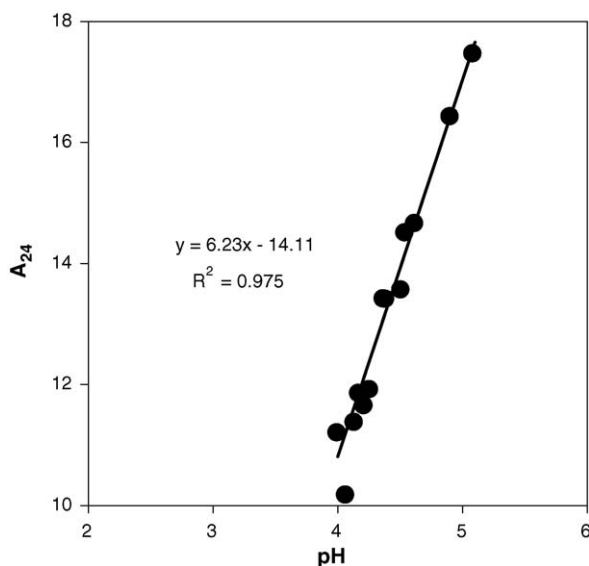


Fig. 4. Extraction of  $\text{La}^{3+}$  by HL-10-LH in the conditions of the Fig. 2: A vs. pH calculated with the assumption that  $\text{La}_2(\text{L-10-L})_2(\text{L-10-LH})_2$  is the only extracted complex. (The drawn line is linear regression).

#### 4.2. Extraction of europium(III) by HL-10-LH

Some extraction data are reported in Fig. 6. They cannot be treated by the slope analysis method. Therefore, to determine the major extracted complex, several assumptions were made and the  $A_{xy}$  functions were calculated accordingly: the species  $\text{Eu}(\text{L-10-L})(\text{L-10-LH})$ ,  $\text{Eu}(\text{L-10-LH})_3$ ,  $\text{Eu}_2(\text{L-10-L})_3$ ,  $\text{Eu}_2(\text{L-10-L})_2(\text{L-10-LH})_2$ ,  $\text{Eu}_2(\text{L-10-L})(\text{L-10-LH})_4$ ,  $\text{Eu}_3(\text{L-10-L})_4(\text{L-10-LH})$ ,  $\text{Eu}_3(\text{L-10-L})_3(\text{L-10-LH})_3$  and  $\text{Eu}_3(\text{L-10-L})_2(\text{L-10-LH})_5$  were considered. Two assumptions only are acceptable:  $\text{Eu}(\text{L-10-L})(\text{L-10-LH})$ , since  $A_{12}$  versus pH has a 3.35 slope for a theoretical slope of 3 (Fig. 7), and  $\text{Eu}_2(\text{L-10-L})_2(\text{L-10-LH})_2$ , since  $A_{24}$  versus pH has a 5.99 slope for a theoretical slope of

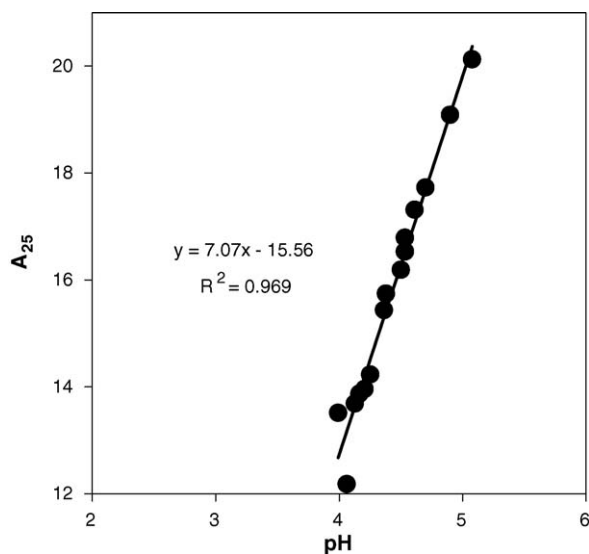


Fig. 5. Extraction of  $\text{La}^{3+}$  by HL-10-LH in the conditions of the Fig. 2: A vs. pH calculated with the assumption that  $\text{La}_2(\text{L-10-L})(\text{L-10-LH})_4$  is the only extracted complex (The drawn line is linear regression).

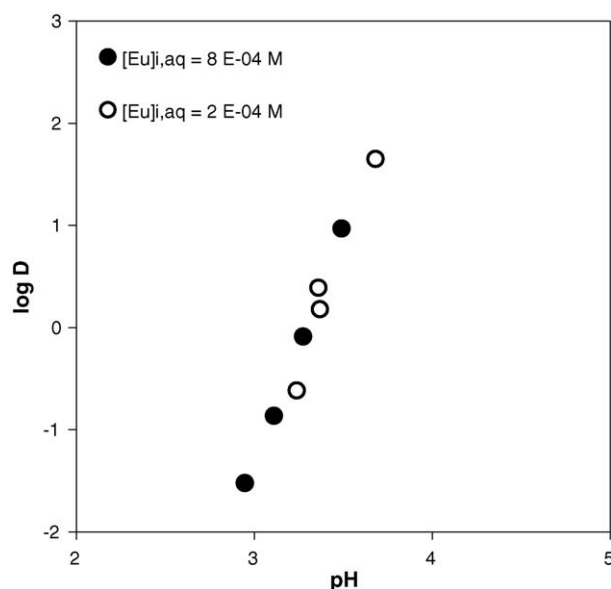


Fig. 6. Extraction of  $\text{Eu}^{3+}$  from nitrate medium 0.1 M by HL-10-LH 0.01 M in chloroform at 25 °C.

6 (Fig. 8), with the same correlation coefficient. The extraction equilibrium could be either (11) or (12):

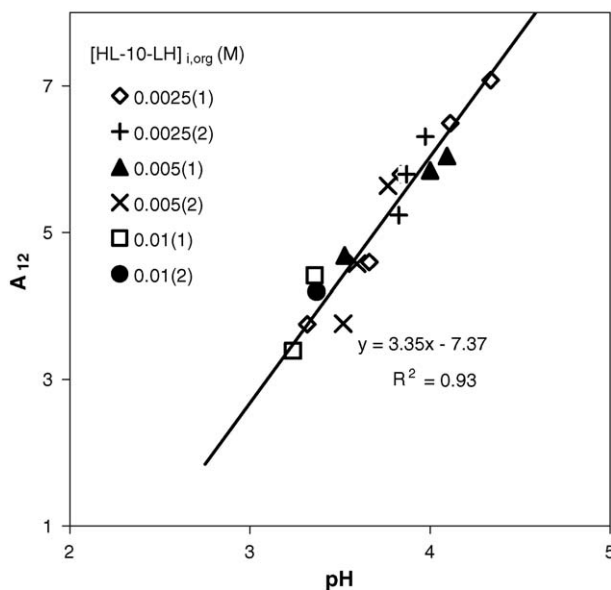
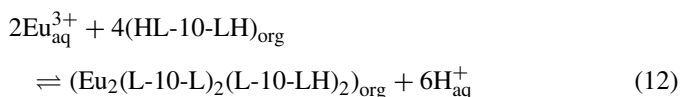
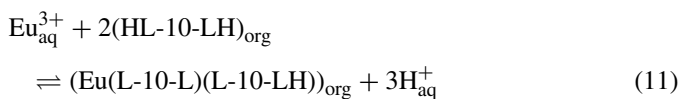


Fig. 7. Extraction of  $\text{Eu}^{3+}$  from nitrate medium 0.1 M by HL-10-LH in chloroform at 25 °C.  $[\text{Eu}^{3+}]_{\text{i,aq}} = 2 \times 10^{-4}$  M. A vs. pH calculated with the assumption that  $\text{Eu}(\text{L-10-L})(\text{L-10-LH})$  is the only extracted complex. (The drawn line is linear regression).



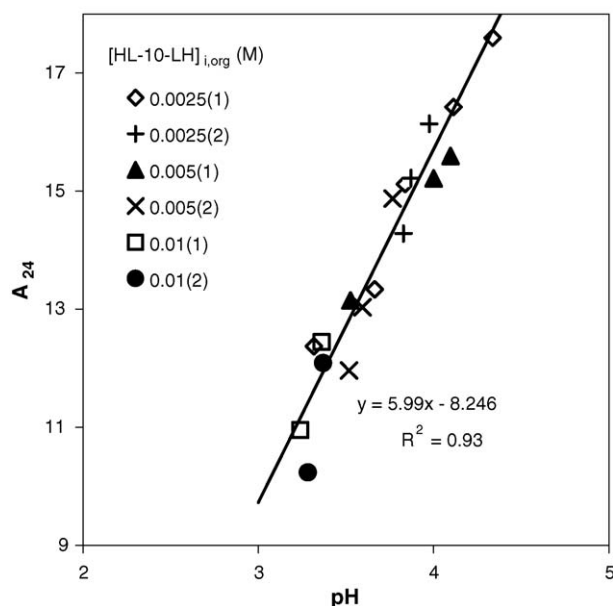


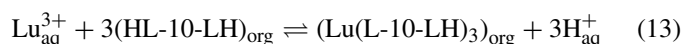
Fig. 8. Extraction of  $Eu^{3+}$  by HL-10-LH in the conditions of Fig. 7. A vs. pH calculated with the assumption that  $Eu_2(L-10-L)_2(L-10-LH)_2$  is the only extracted complex. (The drawn line is linear regression).

The corresponding extraction constants would be respectively:  $\log K_{12}^{Eu} = -6.1 \pm 0.3$  and  $\log K_{24}^{Eu} = -8.3 \pm 0.5$

Since Eq. (7) shows that  $\log D$  is independent from  $[M^{m+}]_{aq}$  if a mononuclear complex ( $j=1$ ) is extracted and since, at a given pH, it increases with  $[M^{m+}]_{aq}$  if a di- or polynuclear complex is extracted, the initial concentration of  $Eu^{3+}$  has been quadrupled to choose between these stoichiometries. The results are plotted in Fig. 6. For both initial  $Eu^{3+}$  concentrations, the observed curves disagree with the extraction of a monomeric species (lines of slope 3) and with the one of a binuclear complex (curves such as those in Fig. 2). Moreover though the  $pH_{1/2}$  decreases with increasing values of  $[Eu^{3+}]_{i,org}$ , the effect is weaker than expected in the case of a binuclear complex where  $\Delta pH_{1/2}$  would be 0.08. Therefore, the choice is impossible. Most probably a mixture of both species is extracted.

#### 4.3. Extraction of lutetium(III) by HL-10-LH

The curves  $\log D$  versus pH at different concentrations of HL-10-LH are shown in Fig. 9. From the same data, the curves of Fig. 10 have been drawn. In every case, the slopes of the lines are close to 3, therefore the mononuclear  $Lu(L-10-LH)_3$  species is extracted, according to the equilibrium:



$K_{13}^{Lu}$  was calculated for every experimental point:  $\log K_{13}^{Lu} = -2.4 \pm 0.1$ . From this value of the extraction constant, the theoretical values of  $\log D$  versus pH were calculated. They are drawn in Fig. 9. A good fit with the experimental points is obtained.

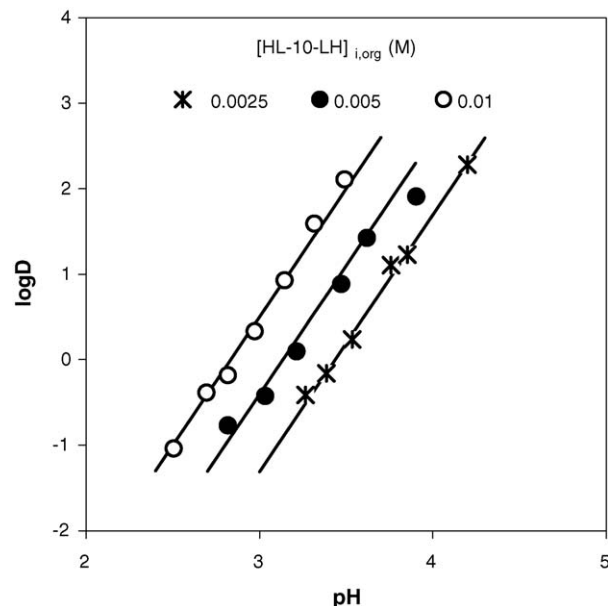


Fig. 9. Extraction of  $Lu^{3+}$  from nitrate medium by HL-10-LH in chloroform at 25 °C.  $[(Na,H)NO_3] = 0.1$  M;  $[Lu^{3+}]_{i,org} = 2 \times 10^{-4}$  M. (The drawn lines are the theoretical fits obtained for  $\log K_{13} = -2.4$ ).

#### 4.4. Simultaneous extraction of the three lanthanides by HL-10-LH

The three lanthanide cations were extracted simultaneously ( $La^{3+}$ ,  $Eu^{3+}$  and  $Lu^{3+}$ ) under the same conditions as above, with the aim of checking the extraction order and selectivity. The results are reported in Fig. 11. The extraction percentages of the three lanthanides are the same as those obtained when each cation is alone in the aqueous phase.

At low pH where neither lutetium nor europium are quantitatively extracted, the observed order of extraction observed is

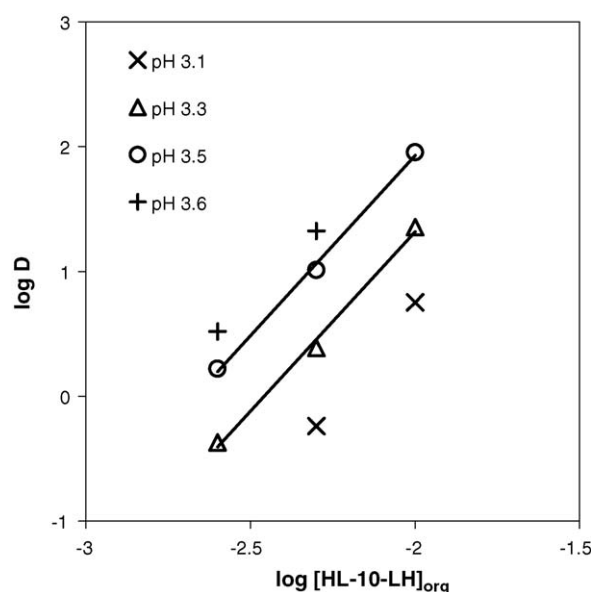


Fig. 10. Extraction of  $Lu^{3+}$  by HL-10-LH in the same conditions as in Fig. 9 (The drawn lines are linear regressions).

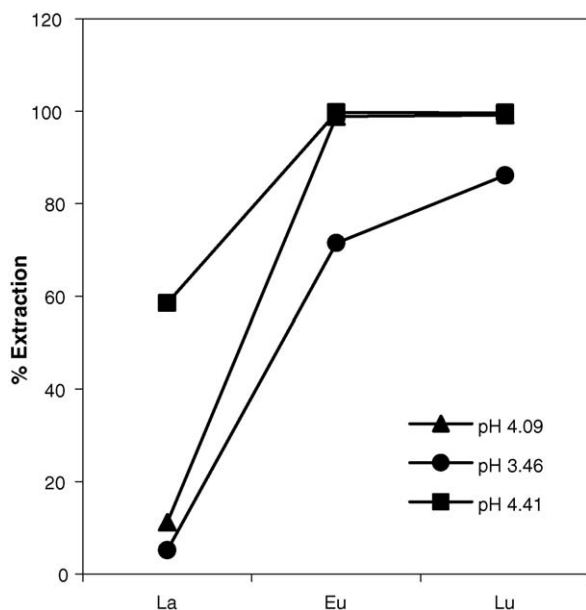
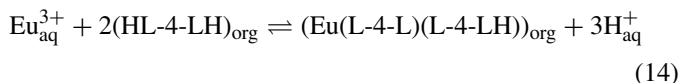


Fig. 11. Simultaneous extraction of  $\text{La}^{3+}$ ,  $\text{Eu}^{3+}$  and  $\text{Lu}^{3+}$  from nitrate medium by HL-10-LH in chloroform at 25 °C.  $[(\text{Na,H})\text{NO}_3] = 0.1 \text{ M}$ ;  $[\text{HL-10-LH}]_{i,\text{org}} = 5 \times 10^{-3} \text{ M}$ ;  $[\text{Ln}^{3+}]_{i,\text{aq}} = 2 \times 10^{-4} \text{ M}$ . (The drawn lines are guides for the eye).

$\text{La} < \text{Eu} < \text{Lu}$ : it is the most usual order of extraction observed with acidic extractants. A good separation between lanthanum and europium, and between lanthanum and lutetium is obtained, contrary to europium and lutetium.

#### 4.5. Influence of the alkyl chain length: extraction of Eu by HL-4-LH

To study the influence of the alkyl chain length on the extraction, the extraction of europium by HL-4-LH has been undertaken under the same experimental conditions as by HL-10-LH. The experimental data have been treated in the same manner, i.e. by calculating different  $A_{xy}$  functions with the assumption that only one complex is extracted with a given (metal:ligand) stoichiometric ratio. The ratios (1:2), (1:3), (2:3), (2:4), (2:5), (3:6) and (3:7) were tested. Only  $A_{12}$ ,  $A_{24}$  and  $A_{36}$  give acceptable results, taking into account a change of extraction process at a pH close to 3.4 (Figs. 12–14). The slope of the curve  $A_{12}$  versus pH, calculated for the points of low extraction, is 3.19 for a theoretical slope of 3, which implies the extraction of  $\text{Eu}(\text{L-4-L})(\text{L-4-LH})$ , according to the equilibrium:



The corresponding extraction constant has been calculated:  $\log K_{12}^{\text{Eu}}(\text{HL-4-LH}) = -6.2 \pm 0.1$ .

At higher pH's, the curve  $A_{24}$  versus pH shows an experimental slope value of 6.21 compared with a theoretical value of 6 (Fig. 13). This would agree with the extraction of  $\text{Eu}_2(\text{L-4-L})_2(\text{L-4-LH})_2$  with an extraction constant such as  $\log K_{24}^{\text{Eu}}(\text{HL-4-LH}) = -6.0 \pm 0.7$ . In the same pH range, the curve  $A_{36}$  versus pH shows an experimental slope of 9.11

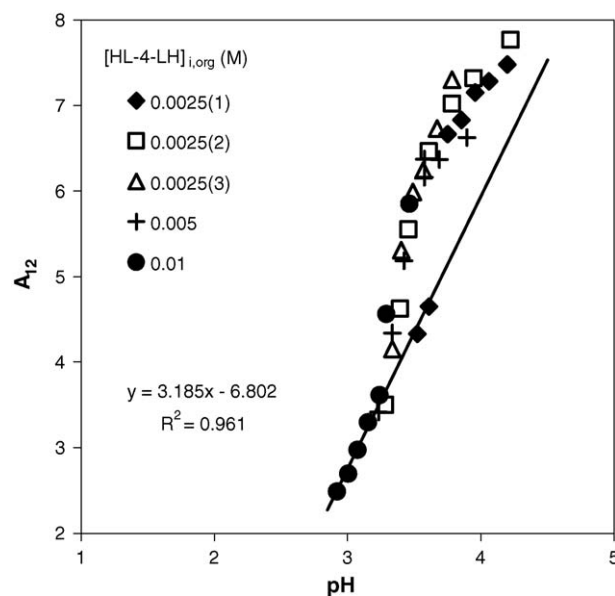


Fig. 12. Extraction of  $\text{Eu}^{3+}$  from nitrate medium 0.1 M by HL-4-LH in chloroform at 25 °C.  $[\text{Eu}^{3+}]_{i,\text{aq}} = 2 \times 10^{-4} \text{ M}$ . A vs. pH calculated with the assumption that  $\text{Eu}(\text{L-4-L})(\text{L-4-LH})$  is the only extracted species. (The drawn line is the linear regression for points of low extraction).

compared with a theoretical value of 9 (Fig. 14). This would correspond to the extraction of  $\text{Eu}_3(\text{L-4-L})_3(\text{L-4-LH})_3$  with  $\log K_{36}^{\text{Eu}}(\text{HL-4-LH}) = -7.1 \pm 0.9$ . However, in both cases the correlation coefficients of the fitting curves are low (resp. 0.852 and 0.858 for  $A_{24}$  and  $A_{36}$ ) and the uncertainties upon the values of the constants are high (resp.  $\pm 0.7$  and  $\pm 0.9$ ); these values are close to one another, therefore the co-extraction of both species is probable.

In the experimental conditions of the Fig. 6 ( $[\text{Eu}^{3+}]_{i,\text{aq}} = 2 \times 10^{-4} \text{ M}$ ,  $[\text{HL-}n\text{-LH}]_{i,\text{org}} = 10^{-2} \text{ M}$ ), the pH's

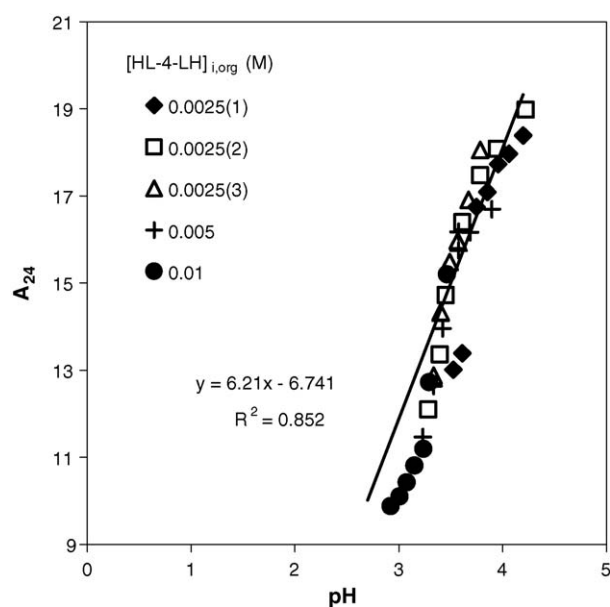


Fig. 13. Extraction of  $\text{Eu}^{3+}$  in the same conditions of Fig. 12. A vs. pH calculated with the assumption that  $\text{Eu}_2(\text{L-4-L})_2(\text{L-4-LH})_2$  is the only extracted species. (The drawn line is the linear regression for points of high extraction).



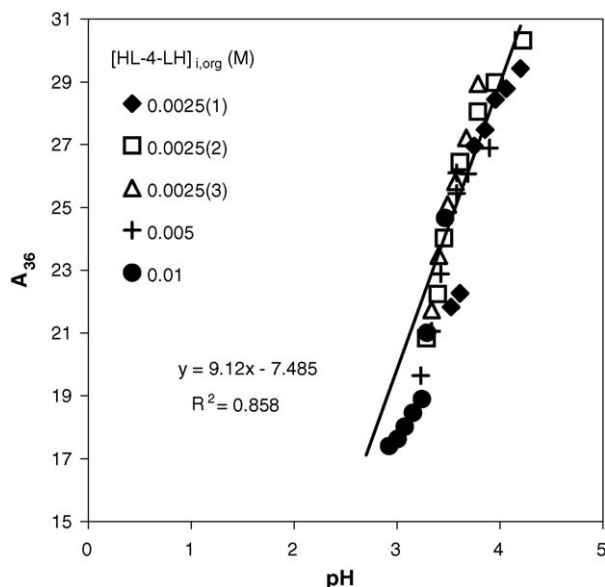


Fig. 14. Extraction of  $\text{Eu}^{3+}$  in the same conditions of Fig. 12. A vs. pH calculated with the assumption that  $\text{Eu}_3(\text{L-4-L})_3(\text{L-4-LH})_3$  is the only extracted species (The drawn line is the linear regression for points of high extraction).

of half extraction, “ $\text{pH}_{1/2}$ ”, corresponding to  $[\text{M}]_{\text{aq,t}} = [\text{M}]_{\text{org,t}}$ , is 3.23 for HL-4-LH and 3.34 for HL-10-LH, which means that the extraction efficiency of HL-4-LH is slightly better than HL-10-LH’s.

## 5. Comments

With the aim of comparing the extraction of the studied lanthanides by the bis(4-acyl-5-hydroxypyrazoles) and by their parent compounds 4-acyl-5-hydroxypyrazoles, some values of  $\text{pH}_{1/2}$  were gathered in Table 1.

For a given lanthanide ion, HL-10-LH is a better extractant than HPMBP, not only for the same concentration in extractant, but also for the same concentration in complexation sites. The formation constants of  $\text{Ln}(\text{PMBP})_2^{+}$  and of  $\text{Ln}(\text{L-}n\text{-L})^{+}$  ( $n = 7$  and 8) from the aqua lanthanide ions and the deprotonated ligands, in mixed homogeneous water–acetonitrile medium, are known [32]. It is shown that the stabilities of those complexes are similar. Thus, the efficiency of HL-10-LH is probably due to the greater lipophilicity of the bis(acylpyrazolonates). The structures of the solids  $[\text{Ln}_2(\text{L-3-L})_3(\text{DMF})_4] \cdot \text{DMF}$  ( $\text{Ln}$ : Tb [37], Sm [38], Dy [39]), where two molecules of DMF are coordinated upon each Ln, indicate that the complexes extracted by HL-10-

LH must contain water molecules in the first coordination sphere of the metal, like those extracted by HPMBP. However, the long polymethylene chain might prevent the formation of a H-bonded cluster of numerous H-bonded water molecules around the metal “coordination iceberg”, which would contribute to a much better lipophilicity of the former ones than the latter ones.

For both HPMBP and HL-10-LH, the extraction efficiency increases with the atomic number:  $\text{La} < \text{Eu} < \text{Lu}$ . From the difference between the values of  $\text{pH}_{1/2}$  of the three lanthanides, we can see that HL-10-LH is more selective than HPMBP. A good separation between the three lanthanides is obtained, which is interesting for the applications in waste treatment.

The present work allows a quantitative comparison with the micellar extraction–ultrafiltration of europium by the same extractants [33]. Defining  $S/M$  as the ratio of the total number of chelating sites “LH” on the total number of metallic centers in the systems, and considering a  $2 \times 10^{-4}$  M aqueous solution, the  $\text{pH}_{1/2}$ ’s are 1.36, 1.96 for a micellar extraction with HL-10-LH and with HL-4-LH respectively, both of them with  $S/M = 5$ ; for the above liquid–liquid extraction the  $\text{pH}_{1/2}$ ’s are 3.34, 3.23, with HL-10-LH and with HL-4-LH respectively, in the presence of a large excess of ligand:  $S/M = 100$ . The micellar extraction is obviously much more efficient. It is noticeable that for low extraction yields,  $\text{Eu}(\text{L-4-L})(\text{L-4-LH})$  is extracted in the chloroformic phase as well as in the micellar phase, while for HL-10-LH, the stoichiometries of the europium complexes are different: the metal to ligand ratio is 1:2 for the liquid–liquid extraction and 2:3 for the micellar extraction. This unique extraction of  $\text{Ln}_2(\text{L-3-L})_3$  in micelles was attributed to a confinement effect.

## 6. Conclusion

The study of the extraction of representatives of light, medium and heavy lanthanides by polymethylene-bis(acylpyrazolonates) shows that those extractants are more efficient and more selective than their parent compound HPMBP. However, they are much less efficient in liquid–liquid systems than in the micellar extraction. This work is currently pursued thanks to the study of synergistic extraction in liquid–liquid, water–micelles and liquid–solid systems.

## Acknowledgement

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Table 1

Values of  $\text{pH}_{1/2}$  corresponding to the extraction of La(III), Eu(III) and Lu(III) in chloroform by HPMBP and HL-10-LH, respectively

Ligand	La (Z = 57)	Eu (Z = 63)	Lu (Z = 71)	Medium	Reference
HPMBP 0.01 M	4.42	3.78	3.44	$\text{NaClO}_4$	[36]
HPMBP 0.01 M	4.40	3.80	–	$\text{NaNO}_3$	#
HL-10-LH 0.01 M	4.17	3.34	2.84	$\text{NaNO}_3$	#
HL-10-LH 0.005 M	4.31	3.61	3.16	$\text{NaNO}_3$	#

# our work,  $I = 0.1$ ,  $[\text{Ln(III)}]_{\text{aq}} = 2 \times 10^{-4}$  M.

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