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Solid-Liquid Extraction of Lanthanum(III), Europium(III), and Lutetium(III) by Acyl-Hydroxypyrazoles Entrapped in Mesostructured Silica

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Abstract: The solid-liquid extraction of lanthanum(III), europium(III), and lutetium(III) by mesostructured silicas doped with 1-phenyl-3-methyl-4-stearoyl-5-pyrazolone (HPMSP, bearing one chelating site) or with 1,12-bis(1′-phenyl-3′-methyl-5′-hydroxy-4′-pyrazolyl)-dodecane-1,12-dione (HL-10-LH, bearing two chelating sites) has been studied and compared to the analogous solvent and micellar extractions in terms of the stoichiometry of the extracted complex and of the extraction efficiency. The solid-liquid extraction order in the lanthanoid series is La < Eu < Lu; it is the usual liquid-liquid extraction order obtained with acidic extractants. A theoretical model is used to determine the stoichiometries of the extracted complexes and the extraction yield is measured as a function of the pH, of the extractant/metal ratio (S/M) and of the volume ratio of the two phases (ϕ). For HPMSP, the extracted complexes involve three ligand molecules for one metal. For HL-10-LH, the complex stoichiometries are found to be either Ln(L-10-L)(L-10-LH) (Ln = La, Eu) or $Lu_2(L\text{-}10\text{-}L)_3$ for S/M = 25, or $Eu_2(L\text{-}10\text{-}L)_3$ for S/M = 5. For the first time, the synergistic solid-liquid extraction is studied after a successful attempt at simultaneously immobilizing both extractants HL-10-LH and 2,4,6-tri(2-pyridyl)-1,3,5-triazine, "TPTZ", into silica; the complex extracted in this case differs from the one obtained in solvent extraction.

Keywords: Solid-liquid extraction, doped silica, acyl-hydroxypyrazoles, lanthanoids, complex stoichiometry

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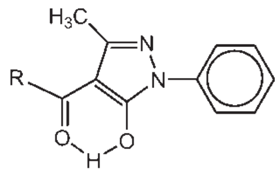
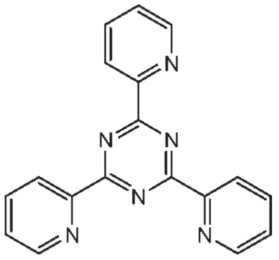
INTRODUCTION

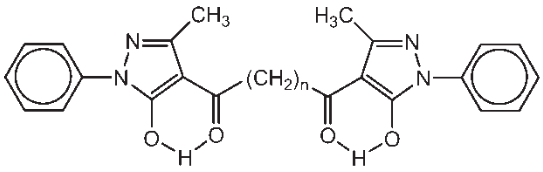
4-acyl-5-hydroxypyrazole derivatives, HL, belong to the family of β-diketones which are cation exchangers and chelating agents of metal ions used in liquid-liquid extraction. Compared with the currently used lipophilic substituted acetylacetones (typically $pK_a = 6.25$), their higher acidity pK_a (2.6–4.0) allows extractions at lower pH's. Particularly, they form stable extractable complexes, in acidic solutions, with lanthanoids ions (1–3) and actinoids ions (4, 5). α,ω-bis(5-hydroxy-pyrazol-4-oyl) alcanes, HL-n-LH, are better extractants than the corresponding 4-acyl-5-hydroxypyrazoles in solvent extraction. They give rise to a multitude of coexisting complexes, especially polynuclear ones (6). They are efficient extractants for lanthanoid ions (7, 8).



HL
R = $C_{17}H_{35}$, HPMSP = L
R = Ph, HPMBP



TPTZ = B



HL-n-LH
n = 10, HL-10-LH = L_2

The liquid-liquid extraction is the most used method at the industrial scale. However, research is developed to promote the solid-liquid extraction method. The latter could replace the former insofar as it brings some advantages over the standard solvent extraction:

i) saving of time and solvent
ii) high preconcentration factors even in the presence of great volumes of samples
iii) on-line coupling with a chromatographic separation
iv) prevention of the third phase problems often encountered in liquid-liquid extraction.

Thus, 4-acyl-5-hydroxypyrazoles derivatives have already constituted the subject of some studies of solid-liquid extraction of metal cations. Todorova, Ivanova, and co-workers (9, 10) have grafted HPMBP (1-phenyl-3-methyl-4-benzoyl-5-hydroxy-pyrazole) and its derivatives on a styrene-divinylbenzene copolymer. Then, they have highlighted the ability of the solids to extract noble metals from NaCl medium at pH 6–8. Gao and co-workers (11) have studied the extraction and the elution of thorium and scandium on a paraffin grafted with HPMBP. They have determined the stoichiometry of the extracted complexes by the "slope analysis" method: $Th(PMBP)_4$ and $Sc(PMBP)_3$. Tong and co-workers (12–14) have studied the preconcentration of various metals by a commercial silica gel impregnated with HPMSP (1-phenyl-3-methyl-4-stearoyl-5-hydroxy-pyrazole). They have shown that cadmium, copper, lead, manganese, zinc, and iron are quantitatively retained in batch and in column at $pH > 6$. Indium is retained at $pH > 2.8$, and eluted with HCl 1 M. Copper, cobalt, and nickel are quantitatively retained in acetate medium at $pH > 4$, the copper capacity being $43\ \mu mol \cdot g^{-1}$. The study in dynamic mode was reproduced ten times without any reduction in the extraction capacity. Anzai et al. (15) have demonstrated the quantitative adsorption of copper(II) ion, in a pH range of 2.5 to 11.0, on a porous resin loaded with HPMBP. They have found a maximum sorption capacity of $53\ \mu mol \cdot g^{-1}$. Sato et al. (16) have loaded HPMSP on a silica gel and have studied the retention of iron(III) on the adsorbent from an aqueous solution of $pH > 2$ in a batch experiment. The recovery of a $8\ mg \cdot L^{-1}$ sample solution was about 100%. In a column experiment, iron(III) was quantitatively retained when the flow rate was lower than $8\ mL \cdot min^{-1}$.

Our team (17) has prepared polybutadiene gels loaded with 4-acyl-5-hydroxypyrazoles (HL) to study the extraction of copper ion from perchlorate medium: evidence was given of the extraction of CuL_2. The diffusion of CuL_2 into the gels was the rate controlling factor of the extractions. Later, we have studied the sorption of copper by a mesostructured silica doped with HPMSP at 0.43 mmol of ligand per g (18). The capacity of this material to extract copper was $0.2\ mmol \cdot g^{-1}$ in a 0.1 M $NaNO_3$ medium at pH 2.3. In another article (19), we have shown that these mesostructured silicas doped with HPMSP and HL-10-LH are efficient sorbents for the removal of copper and europium from aqueous nitric solutions. Europium 2×10^{-4} M was recovered at 100% in 10 minutes. In these studies, ligand entrapment has been chosen because it presents some advantages compared to the other methods of immobilization: a strong immobilization of the ligand compared to impregnation (20) and the elimination of the delicate reagent derivatization step compared to grafting.

In this work, the solid-liquid extraction of La, Eu, and Lu, representatives of the lanthanoid series, with silica doped by HPMSP or HL-10-LH is studied. Thus a comparison between the bis-compound HL-10-LH and the parent compound HPMSP can be made. The major point of interest is the determination of the stoichiometry of the complexes formed in the silicic matrix. The influences of the ratios S/M, number of chelating sites over the initial number of metal ions, and ϕ, ratio of the phase volumes, on the extraction are investigated. A silica doped by the mixture of HL-10-LH and TPTZ (TPTZ = B: 2,4,6-tri(2-pyridyl)-1,3,5-triazine) is synthesized with the hope of reproducing inside the silica the synergistic effect observed in liquid-liquid extraction (21).

A comparison between the solid-liquid and the liquid-liquid extraction is done since the liquid-liquid extraction of the same three lanthanoids ions has already been studied in the same conditions using the same extractants (22). The solid-liquid extraction of europium with a silica doped by HL-10-LH is compared to the micellar extraction of europium by HL-10-LH solubilized in micelles of cetyltrimethylammonium bromide CTAB (23).

EXPERIMENTAL

Chemicals

HL-10-LH was prepared using Jensen's method (24) from 1-phenyl-3-methyl-pyrazol-5-one (Fluka, "purum" quality) and dodecanedioyl dichloride. The latter was synthesized from dodecanedioic acid (Aldrich, 99%) and thionyl chloride (Fluka, 99%, "puriss" quality). HL-10-LH was recrystallized from a chloroform-ethanol (3:2) mixture. HPMSP was prepared according to the same method from 1-phenyl-3-methyl-5-pyrazolone and stearoyl chloride (Aldrich, 99%). It was recrystallized from a toluene-ethanol (1/9) solution. TPTZ was an Aldrich product (98%). The syntheses of the doped silicas were performed in basic media according to a sol-gel process, beginning with the solubilization of the extractant(s) in a micellar phase followed by the precipitation of silica around micelles, after hydrolysis and polymerization of the silica precursor, tetraethoxysilane (see synthesis scheme below). These syntheses, the materials and the determination of the quantity of immobilized ligand are extensively described in a previous paper (18). In short, lamellar structures with *ca.* 36 Å interplane d_{001} distances are obtained; the silica frames, obtained after calcination, are lamellar porous materials with specific surface areas S_{BET} close to $1000\,m^2 \cdot g^{-1}$ and pore volumes close to $1\,cm^3 \cdot g^{-1}$. Lanthanoid stock solutions (1000 ppm, $\approx 6.5 \times 10^{-3}$ M) were prepared from the corresponding lanthanoid oxide by reaction with nitric acid HNO_3 1 M and dilution with water. Water used was deionized and obtained from a MilliQ RG, Millipore apparatus. The pH of the solutions was adjusted with drops of diluted HNO_3 or NaOH (Merck Titrisol) and their ionic strength was kept equal to 0.1 by addition of sodium nitrate (Prolabo, 99.5%).

Techniques

The solid-liquid extraction experiments were carried out in thermostated polypropylene tubes (25 ± 0.2°C). In a typical experiment, 10 mL of an aqueous phase were contacted with 0.1 g of doped silica under stirring (700–800 rpm) during 60 min, which is long enough to reach equilibrium. The ionic strength of the aqueous solution was kept constant $[(Na,H)NO_3] = 0.1\ M$ and its pH was close to 2. The solid was then separated from the aqueous solution by centrifugation for 5 min at 12500 rpm. In order to determine the concentration of the lanthanoid ion remaining in the aqueous phase after extraction, 1 ml of the aqueous solution was withdrawn and diluted for analysis by ICP-AES (Inductively Coupled Plasma - Atomic Emission Spectrometry) using a Jobin Yvon JY138 ultratrace apparatus. The quantity of the metal ion extracted in the solid phase was determined by the difference between the initial quantity and the quantity of metal remaining in the aqueous solution. After separation of the two phases, the pH of the aqueous solution was measured and constitutes the equilibrium pH.

METHOD OF DETERMINATION OF THE EXTRACTED COMPLEX STOICHIOMETRY

In order to determine the most likely stoichiometry of the extracted complex in the solid phase, let us consider the following general extraction equilibrium:

$$\mathrm{iM_{aq}^{m+} + j(H_nL)_s + kB_s \rightleftharpoons (M_iL_jH_\ell B_k)_s + imH_{aq}^{+}} \tag{1}$$

where H_nL is the acidic extractant, B the synergistic agent (when it exists), and M^{m+} the metal ion; "s" and "aq" denote species in the solid phase and the aqueous phase respectively.

The conditional extraction constant, a function of concentrations, can be expressed as follows:

$$\mathrm{K_{ijk}^{*} = \frac{[M_iL_jH_\ell B_k]_s[H^+]_{aq}^{im}}{[M^{m+}]_{aq}^{i}[H_nL]_s^{j}[B]_s^{k}}} \tag{2}$$

$[M^{m+}]_{aq}$ is related to the measurable metal concentration $[M]_{aq,total}$ by the following equation:

$$\mathrm{[M]_{aq,total} = [M^{m+}]_{aq}\left(1 + \sum\nolimits_a \beta_{X,a}[X^-]_{aq}^{a}\right)} \tag{3}$$

where $\beta_{X,a}$ is the ath complexation constant of M^{m+} by the inorganic aqueous anion X^-. In this work, the ionic strength is kept constant, $[X^-]_{aq} = 0.1$ M. Thus, $C = (1 + \sum_a \beta_{X,a}[X^-]^a_{aq})$ is a constant. K^*_{ijk} becomes:

$$K^*_{ijk} = \frac{[M_iL_jH_\ell B_k]_s[H^+]^{im}_{aq}C^i}{[M^{m+}]^i_{aq,t}[H_nL]^j_s[B]^k_s} \tag{4}$$

By considering that $(M_iL_jH_\ell B_k)_s$ is the only extracted species, the metal distribution ratio is written:

$$\begin{aligned} D &= \frac{[M]_{s,total}}{[M]_{aq,total}} = \frac{i[M_iL_jH_\ell B_k]_s}{[M]_{aq,t}} \\ &= iK^*_{ijk}[M]^{i-1}_{aq,t}[H_nL]^j_s[B]^k_s[H^+]^{-im}_{aq}C^{-i} \end{aligned} \tag{5}$$

$$\begin{aligned} \log D &= (i-1)\log[M]_{aq,t} + j\log[H_nL]_s + k\log[B]_s \\ &\quad + (im)\,pH + \log i + \log K^*_{ijk} - i\log C \end{aligned} \tag{6}$$

with $\log K^*_{ijk} - i\log C = \log K_{ijk}$, constitutes the logarithm of the conditional apparent extraction constant.

By rearranging equation (6), a function "A_{ijk}" can be defined as follows:

$$A_{ijk} = \log(D/i[M]^{(i-1)}_{aq,t}) - j\log[H_nL]_s - k\log[B]_s \tag{7}$$

It follows:

$$A_{ijk} = \log K_{ijk} + (im)\,pH \tag{8}$$

To determine the stoichiometry of the extracted complex, several hypotheses have to be tested. For every hypothesis, the value of log K_{ijk} is calculated for each experimental point. If log K_{ijk} values show a dependency upon any parameter, the corresponding stoichiometry is rejected. Moreover, for every other hypothesis, the plot of A_{ijk} versus pH is drawn. The hypothesis corresponding to the actual complex will lead to a straight line of slope "im." The value of the experimental slope may allow a choice between the possible stoichiometries.

An error inferior or equal to 15% is tolerated between the theoretical and the experimental value of the slope. The calculation of this value is influenced by a great number of experimental parameters (logK_{ijk}, logD, pH and $[H_nL]_s$) whose determination is error prone. The most likely stoichiometry is deduced in each case not only from the lowest standard deviation on the value of log K_{ijk} but also from the consistency between the experimental and the theoretical slope of A_{ijk} versus pH.

In the present article, the experimental results are presented as extraction percentage (Y%) versus pH curves:

$$Y(\%) = \frac{n_{Ln_S}}{n_{Ln_{aq}} + n_{Ln_S}} \times 100 \tag{9}$$

where $n_{Ln,s}$ and $n_{Ln,aq}$ are the number of Ln in the solid phase, and the number of Ln in the aqueous phase at equilibrium respectively. To confirm the choice of the extracted complex stoichiometry, a calculation of "theoretical" values of Y at every pH is carried out, taking into account the initial values of the reactant concentrations, their mass-balances and the value of K_{ijk} determined from equation (8). This calculation method is well-described in a previous paper (25). The theoretical curves obtained will be reported in the figures corresponding to the experimental measurements.

For every experimental system, the three following criteria must match for the selected stoichiometry: better ΔlogK, better adequacy between the theoretical and the experimental slope value and better fit for Y versus pH curves. It is the case for all the systems studied below.

RESULTS AND DISCUSSION

Solid-Liquid Extraction of La(III), Eu(III), and Lu(III) by Two Silicas Doped with HPMSP or HL-10-LH

The extraction yield of Ln(III) (Ln: La, Eu, and Lu) by silicas doped with HPMSP or HL-10-LH has been determined at different pH values. Two silicas, containing the same number of chelating sites "S," have been synthesized: Si@L(0.38) contains 0.38 mol/kg of HPMSP = L (i.e. 0.38 mol/kg of "S") and Si@L_2(0.38) contains 0.19 mol/kg of HL-10-LH = L_2 (i.e. 0.38 mol/kg of "S", also).

According to Equation (6), the parameters that influence the extraction are metal and ligand concentrations. The latter represent quantities related to a volume of aqueous or organic phase. Therefore, the following two ratios were considered:

$$\frac{S}{M} = \frac{\text{number of chelating sites}}{\text{initial number of Ln in solution}} \tag{10}$$

and

$$\phi = \frac{\text{Volume of the aqueous phase}}{\text{Pore volume of the solid phase}} \tag{11}$$

Indeed, Guiguemde et al. (26) have shown, in the solvent extraction of copper(II) by HL-n-LH, that the nature of the extracted species depends on the S/M ratio. Hebrant et al. (23, 27) have already shown the dependence

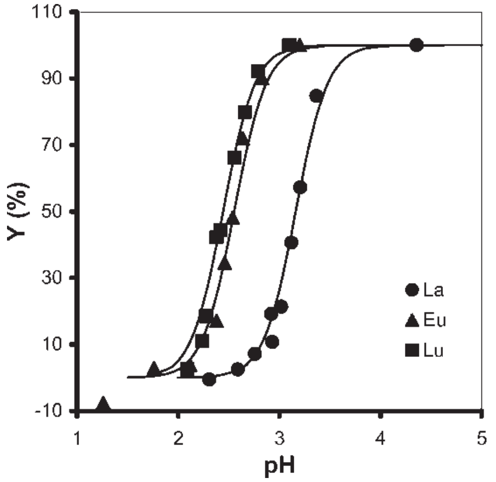


Figure 1. Extraction yield of La(III), Eu(III) and Lu(III) versus pH. Silica = Si@L(0.38). T = 25°C. $[Ln^{3+}]_{0,aq} = 1.6 \times 10^{-4}$ M. $[(Na,H)NO_3] = 0.1$ M. [S]/[M] = 25. $\phi = 210$. (The drawn curves are theoretical fits obtained for log K_{13} (La) = −6.2, log K_{13} (Eu) = −4.5, log K_{13} (Lu) = −4.1).

of the micellar extraction on these ratios. We have demonstrated in a previous work (25) that the solid-liquid extraction of europium(III) by silica loaded with 4-acylhydroxypyrazoles varies with the S/M ratio.

The curves Y versus pH relative to the solid-liquid extraction of La(III), Eu(III) and Lu(III) from a nitrate medium 0.1 M by the two silicas Si@L(0.38) and Si@L_2(0.38) are plotted on Figs. 1 and 2 respectively. They are determined for S/M = 25 and $\phi = 210$. These values were chosen such as "S" is always much greater than "M" and thus the saturation of the chelating sites in the solid by the metal is far from reached. No leaching of the extractant is observed in the aqueous phase during the extraction. Moreover, several tests of Ln(III) extraction on the un-doped material underwent at pH ≤ 6 show no metal adsorption. On the other hand, the extraction yield reaches 100% for doped silicas. These observations prove that the extractions are due to the presence of the extractant doped in the silicic matrix.

The extraction constants and "A" functions were calculated using equations (5)–(8), after substitution of any species "P" in the aqueous phase and any species "Q" in the solid phase respectively by:

$$[P]_{aq} = \frac{n_{P,aq}}{V_{aq}} \tag{12}$$

$$[Q]_s = \frac{n_{Q,s}}{m} \tag{13}$$

where $n_{P,aq}$ and $n_{Q,s}$ are the numbers of moles of "P" and "Q" in the aqueous phase and the solid phase respectively; V_{aq} is the volume of the aqueous phase

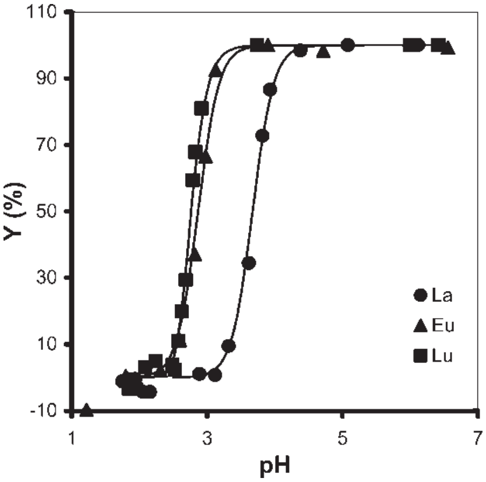


Figure 2. Extraction yield of La(III), Eu(III) and Lu(III) versus pH. Silica = Si@L_2(0.38). T = 25°C. $[Ln^{3+}]_{0,aq} = 1.6 \times 10^{-4}$ M. $[(Na,H)NO_3] = 0.1$ M. S/M = 25. $\phi = 210$. (The drawn curves are theoretical fits obtained for log K_{12} (La) = −7.6, log K_{12} (Eu) = −5.1, log K_{23} (Lu) = −8.6).

(L) and m is the mass of the solid phase (g). K_{ijk} an A_{ijk} were calculated from the experimental points determined with enough precision ($5\% < Y < 95\%$). The results are gathered in Table 1.

With the silica doped by HPMSP, the most likely extracted species for the three lanthanoids is $Ln(PMSP)_3$, its formation follows equilibrium (14):

$$Ln^{3+}_{aq} + 3(HPMSP)_s \rightleftharpoons (Ln(PMSP)_3)_s + 3H^+_{aq};\ K^L_{13}(Ln) \qquad (14)$$

This stoichiometry was found by Freiser in solvent extraction of trivalent lanthanoid ions (La, Pr, Eu and Yb) with several 1-phenyl-3-methyl-4-acyl-5-pyrazolone in chloroform (28, 29). Hebrant et al. (23) have proposed also the extraction of $Eu(PMLP)_3$ in the micellar extraction of europium by HPMLP (1-phenyl-3-methyl-4-lauroyl-5-pyrazolone) in micelles of cetyltrimethylammonium bromide.

In the case of the extraction by the silica doped with HL-10-LH, the most likely extracted species are Ln(L-10-L)(L-10-LH) for lanthanum and europium, and $Lu_2(L\text{-}10\text{-}L)_3$ for lutetium. Thus the extraction equilibriums are:

$$Ln^{3+}_{aq} + 2(HL10LH)_s \rightleftharpoons (Ln(L10L)(L10LH))_s + 3H^+_{aq};\ K^{L2}_{12}(La, Eu) \qquad (15)$$

$$2Lu^{3+}_{aq} + 3(HL10LH)_s \rightleftharpoons (Lu_2(L10L)_3)_s + 6H^+_{aq};\ K^{L2}_{23}(Lu) \qquad (16)$$

Many authors have proposed the extraction of La(L-n-L)(L-n-LH) (30–34) and Eu(L-n-L)(L-n-LH) (4, 8, 33) in solvent extraction. We have already demonstrated the formation of Eu(L-10-L)(L-10-LH) in a chloroform phase

Table 1. Extraction constants calculated for different stoichiometries of extracted complex and corresponding slopes of A_{ijk} versus pH. $S/M = 25$. $\phi = 210$. $T = 25°C$. $[(Na,H)NO_3] = 0.1$ M

			log K_{ijk}				A vs. pH exp. Slope		
Ligand	Silica	Tested stoichiometry	La	Eu	Lu	A vs. pH th. Slope	La	Eu	Lu
HPMSP	Si@L(0.38)	$Ln(PMSP)_3$	−6.2 ± 0.1	−4.46 ± 0.17	−4.09 ± 0.16	3	3.3	3.4	3.4
		$Ln(PMSP)_3HPMSP$	−5.7 ± 0.2	−4.04 ± 0.21	−3.60 ± 0.2	3	3.7	3.5	3.6
		$Ln(PMSP)_2NO_3$	−1.1 ± 0.5	−1.4 ± 0.4	−1.1 ± 0.3	2	3.3	3.3	3.3
HL-10-LH	$Si@L_2(0.38)$	Ln(L-10-LH)(L-10-L)	−7.6 ± 0.1	−5.09 ± 0.21	−4.9 ± 0.3	3	3.1	3.4	5.0
		$Ln(L\text{-}10\text{-}LH)_3$	−6.4 ± 0.2	−4.27 ± 0.27	−4.1 ± 0.3	3	3.4	3.6	5.5
		$Ln_2(L\text{-}10\text{-}L)_3$	−14.0 ± 0.5	−8.8 ± 0.6	−8.6 ± 0.1	6	4.5	4.4	6.9
		$Ln_2(L\text{-}10\text{-}L)_2(L\text{-}10\text{-}LH)_2$	−13.2 ± 0.4	−8.0 ± 0.6	−7.9 ± 0.2	6	4.6	4.5	7.3
		$Ln_2(L\text{-}10\text{-}L)(L\text{-}10\text{-}LH)_4$	−12.4 ± 0.4	−7.2 ± 0.5	−7.1 ± 0.2	6	4.9	4.8	7.8

th. = theoretical, exp. = experimental.

by solvent extraction for the same S/M value (22). In this work, $Lu_2(L\text{-}10\text{-}L)_3$ was an unexpected stoichiometry, especially because the most frequently extracted species found in solvent extraction is Lu(L-n-L)(L-n-LH) (8, 33, 35); however, $Lu_2(L\text{-}n\text{-}L)_3$ was synthesized and characterized in the solid state for $n \leq 4$ (36, 37).

Influence of the Ratio S/M on the Solid-Liquid Extraction

To study the influence of S/M, extraction experiments were carried out and Y versus pH curves are plotted on Figs. 3 and 4. They correspond to the extraction of europium with Si@L(0.38) and Si@L_2(0.38) for S/M = 5 and 25 keeping $\phi = 210$. The variation of S/M was done by changing the initial europium concentration from 1.6×10^{-4} M (S/M = 25) to 8.1×10^{-4} M (S/M = 5).

In the case of europium extraction by Si@L(0.38), no effect of the S/M ratio is observed. However, in the case of europium extraction by Si@L_2(0.38), a shift of the extraction towards low pH's is noticed when S/M decreases. To explain these observations, the stoichiometry of the extracted complex was determined in each case, for S/M = 5, according to the method described above. The most likely stoichiometries are $Eu(PMSP)_3$ for the extraction by Si@L(0.38) and $Eu_2(L\text{-}10\text{-}L)_3$ for the extraction by Si@L_2(0.38). Thus, the effect observed in the latter case is likely due to the

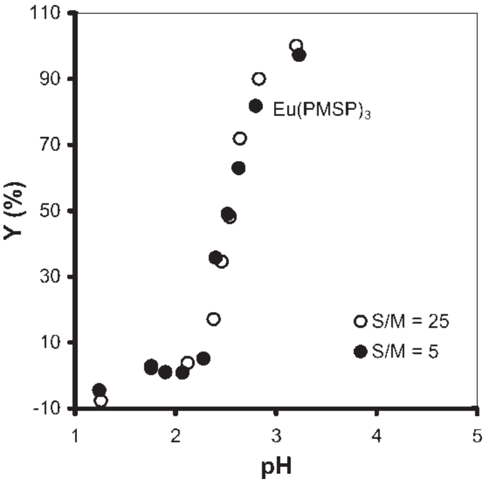


Figure 3. Effect of the ratio (Number of chelating site)/(Initial number of metal) (S/M) on the extraction of europium by Si@L(0.38) from a nitrate medium $[(Na,H)NO_3] = 0.1$ M. T = 25°C. $\phi = 210$. $[Eu^{3+}]_{0,aq} = 1.6 \times 10^{-4}$ M (S/M = 25), 8.1×10^{-4} M (S/M = 5).

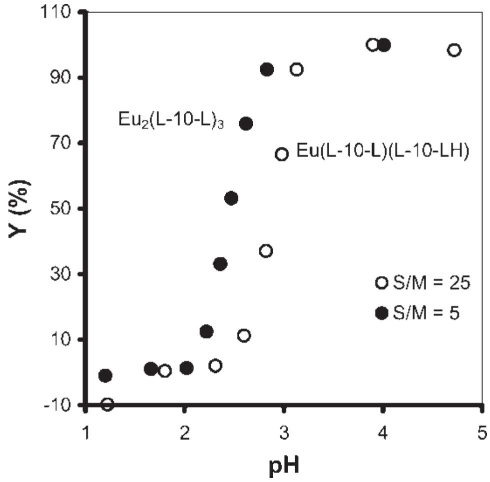


Figure 4. Effect of the ratio (Number of chelating site)/(Initial number of metal) (S/M) on the extraction of europium by Si@L_2(0.38) from a nitrate medium $[(Na,H)NO_3] = 0.1$ M. T = 25°C. $\phi = 210$. $[Eu^{3+}]_{0,aq} = 1.6 \times 10^{-4}$ M (S/M = 25), 8.1×10^{-4} M (S/M = 5).

change of the extracted species from Eu(L-10-L)(L-10-LH) to Eu_2(L-10-L)$_3$ when S/M decreases. In fact when S/M decreases, the metal initial concentration in aqueous phase increases, which favours the formation of the dinuclear species (26).

Influence of the Volume Ratio of the Two Phases (ϕ) on the Solid-Liquid Extraction

To determine the influence of (ϕ), the extraction of europium by Si@L_2(0.38) was then studied from a nitrate medium 0.1 M for S/M = 5 and $\phi = 100$ and compared to the same data with $\phi = 210$ (Fig. 5). A moderate increase of the extraction yield was observed in the former case. The most likely extracted complex for S/M = 5 and $\phi = 100$ was also found to be Eu_2(L-10-L)$_3$. Since the europium concentration for $\phi = 100$ is 2.1 times that of its concentration for $\phi = 210$, the observed increase of Y is due to this increase of $[Eu]_{aq,t}$ according to equation (6).

Synergistic Solid-Liquid Extraction

A frequent case in solvent extraction with cation exchangers is the simultaneous utilization of an anion exchanger or an electron donor extractant in order to heighten the extraction and to shift it to lower pH's. It is what we

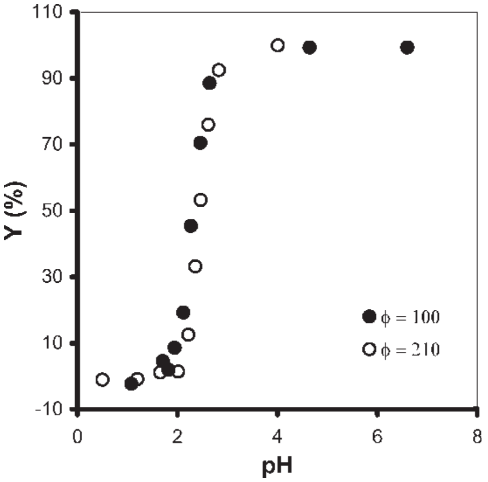


Figure 5. Effect of the volume ratio of the two phases (ϕ) on the europium extraction by Si@L_2(0.38) from a nitrate medium [(Na,H)NO_3] = 0.1 M. S/M = 5. $[Eu^{3+}]_{0,aq} = 17 \times 10^{-4}$ M ($\phi = 100$), 8.1×10^{-4} M ($\phi = 210$).

have tried to do in solid-liquid extraction by synthesizing for the first time a silica containing two extractants: an acidic extractant HL-10-LH and a neutral electrons donor extractant TPTZ (B). TPTZ has already been used as a synergistic agent by Vitorge (38) in the solvent extraction of Ln (III) with α-bromo decanoic acid in decanol and by our group (21) to extract Ln(III) with HL-10-LH in chloroform. With this solid, the extraction of europium for S/M = 25 and $\phi = 210$ was studied. The obtained results are represented in Fig. 6. Several stoichiometries were tested according to the procedure described previously in order to fit a theoretical model to the experimental points: Eu(L-10-LH)$_3$B; Eu(L-10-L)(L-10-LH)B; Eu(L-10-L)B,NO_3; Eu(L-10-LH)$_2$B,NO_3; Eu$_2$(L-10-L)$_3$B$_2$; Eu$_2$(L-10-L)$_2$(L-10-LH)$_2$B$_2$; Eu$_2$(L-10-L)(L-10-LH)$_4$B$_2$; Eu$_2$(L-10-L)$_2$B$_2$,(NO_3)$_2$ and Eu$_2$(L-10-L)(L-10-LH)$_2$B$_2$,(NO_3)$_2$.

The most likely stoichiometry is obtained for Eu(L-10-LH)$_3$B. The extraction equilibrium is:

$$\mathrm{Eu^{3+}_{aq} + 3(HL10LH)_s + B_s \rightleftharpoons Eu(L10LH)_3B_s + 3H^+_{aq};\ K^{L2,B}_{131}(Eu)} \quad (17)$$

A first observation is the shifting of the synergistic solid-liquid extraction to lower pH values, in comparison with the extraction with HL-10-LH alone: $\Delta pH_{1/2} = 0.17$ ($pH_{1/2}$ corresponds to Y = 50%). This implies the presence of a synergistic effect, but of a lesser magnitude than in liquid-liquid extraction ($\Delta pH_{1/2} = 1.28$). The presence of TPTZ modifies the stoichiometry of the extracted complex by the silica doped with HL-10-LH alone: Eu(L-10-LH)$_3$TPTZ in comparison with Eu(L-10-L)(L-10-LH), as well as the

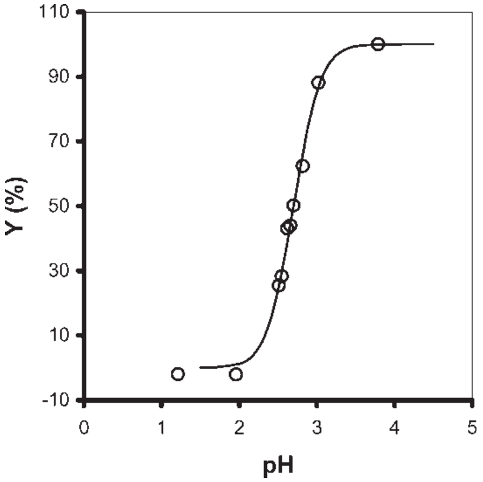


Figure 6. Extraction yield of Eu(III) versus pH with Si@L_2B(0.38 L;0.2 B) at 25 °C from a nitrate medium 0.1 M. $[Eu^{3+}]_{0,aq} = 1.41 \times 10^{-4}$ M. $S/M = 25$. $\phi = 210$. (The drawn line is the theoretical fit calculated for $\log K_{131} = -3.04$).

stoichiometry of the complex formed in the synergistic extraction in chloroform Eu(L-10-L)(L-10-LH)TPTZ (21).

COMPARISONS AND CONCLUSION

The $pH_{1/2}$ values ($Y = 50\%$) of various systems of liquid-liquid and solid-liquid extractions are gathered in Table 2. The solid-liquid extraction order by acidic extractants is the usual order obtained in liquid-liquid extraction: La < Eu < Lu.

For $S/M = 25$, the silica doped by HPMSP allows extractions at a lower pH than the silica doped with HL-10-LH for the three lanthanoids ions (Table 2),

Table 2. $pH_{1/2}$ values of Ln(III) with various liquid-liquid and solid-liquid extraction systems at 25°C. $[(Na,H)NO_3] = 0.1$ M. $S/M = 25$

	Liquid-liquid extraction			Solid-liquid extraction		
	HPMDP[a]	HL10LH	HL10LH/TPTZ	HPMSP	HL10LH	HL10LH/TPTZ
La	6.72	4.58	3.22	3.13	3.7	—
Eu	5.72	3.77	2.49	2.56	2.87	2.7
Lu	—	3.43	2.74	2.45	2.76	—

[a] $[ClO_4^-] = 0.1$ M, (29).

which is not the case of solvent extraction where bis-acylpyrazolones are better extractants than their parent compounds. This observation was explained in solvent extraction by the better lipophilicity of the former ones (4, 39). In solid-liquid extraction, the ligand lipophilicity is not the crucial factor because the ligand is immobilized on the silicic matrix contrary to the solvent extraction where the complex is distributed between the two phases.

For $S/M = 5$, on the contrary, HL-10-LH induces a better solid-liquid extraction of europium than entrapped HPMSP ($\Delta pH_{1/2} = 0.1$). Thus, we regain the better efficiency of the bis-compound already obtained in micellar extraction of europium for $S/M = 5$.

At low pH, the solid-liquid extraction of the three lanthanoids cations (La^{3+}, Eu^{3+} and Lu^{3+}) is more efficient than the liquid-liquid one for a given lanthanoid. This is observed for pyrazolones (HPMSP, HPMDP: 1-phenyl-3-methyl-4-decanoyl-5-hydroxy-pyrazole) and for the bispyrazolone (HL-10-LH). Efficient extractions at low pH are important for the industrial effluents reprocessing performed in acid medium: waste resulting from nuclear fuel or from acidic percolation of ores.

The magnitude of the synergistic effect obtained with TPTZ in the solid-liquid extraction of europium with HL-10-LH is lesser than that obtained in liquid-liquid extraction. This observation illustrates a great difference in solvation and chemical environment between the solid-liquid and the liquid-liquid systems. It is noticeable that the $pH_{1/2}$ of the non-synergistic solid-liquid and liquid-liquid extractions of europium by HL-10-LH are outspread while the $pH_{1/2}$ of the synergistic extractions are close. In the case of the extractions without synergy, the complex extracted in the organic phase is hydrated, with likely three water molecules in its first coordination sphere, which limits its lipophilicity and hence limits its extraction. In the solid-liquid system, the complexation and the immobilization of europium could take place at the micelle-silica interface, allowing an efficient extraction of the hydrated complex. Thus, while in liquid-liquid extraction the high synergistic effect is due to the increase of lipophilicity of the extracted complex by replacement of three water molecules by one TPTZ molecule, and also to the increase of the stability of the extracted complex by TPTZ coordination, in solid-liquid extraction the low synergistic effect could be due to the latter only.

This work enabled us to compare the solid-liquid extraction of lanthanum, europium, and lutetium with their liquid-liquid extraction by HPMSP and HL-10-LH, and to compare the solid-liquid extraction with the micellar extraction of europium by HL-10-LH. This comparison was possible after the determination of the stoichiometries of the extracted complexes inside the silicic matrix. The two phases' volume ratio does not affect the solid-liquid extraction processes. However, the extractant/metal ratio S/M is able to induce a change in the extracted species as well as a displacement of the extraction with pH variation. For the first time, the concept of synergistic extraction was introduced in solid-liquid extraction.

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