**Mechanism for Solvent Extraction of Lanthanides from Chloride
Media by Basic Extractants**

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Abstract

The solvent extraction of lanthanides from chloride media to an organic phase containing an anion exchanger in the chloride form is known to show low extraction percentages and small separation factors. The coordination chemistry of the lanthanides in combination with this kind of extractants is poorly understood. Previous work has mainly used solvent extraction based techniques (slope analysis, fittings of the extraction curves) to derive the extraction mechanism of lanthanides from chloride media. In this paper, EXAFS spectra, luminescence lifetimes, excitation and emission spectra and organic phase loadings of lanthanides in dry, water-saturated and diluted Aliquat 336 chloride or Cyphos IL 101 have been measured. The data show the formation of the hydrated lanthanide ion $[\text{Ln}(\text{H}_2\text{O})_{8-9}]^{3+}$ in undiluted and diluted Aliquat 336 and the complex $[\text{LnCl}_6]^{3-}$ in dry Aliquat 336. The presence of the same species $[\text{Ln}(\text{H}_2\text{O})_{8-9}]^{3+}$ in the aqueous and in the organic phase explains the small separation factors and the poor selectivities for the separation of mixtures of lanthanides. Changes in separation factors with increasing chloride concentrations can be explained by changes in stability of the lanthanide chloro complexes in the aqueous phase, in combination with the extraction of the hydrated lanthanide ion to the organic phase. Finally, it is shown that the organic phase can be loaded with $107 \text{ g} \cdot \text{L}^{-1}$ of Nd(III) under the optimal conditions.

Keywords: Aliquat 336, basic extractants, extraction mechanism, lanthanides, solvent extraction, speciation.

Introduction

Solvent extraction is currently the most common technique used for the separation and purification of metals on an industrial scale [1, 2]. In solvent extraction, a metal-containing aqueous phase is contacted with a water immiscible organic phase containing an extractant, a diluent and sometimes a modifier. The extractant is a molecule which reacts with the metal initially present in the aqueous phase, forming a hydrophobic species, soluble in the organic phase. The diluent is generally an aromatic or aliphatic hydrocarbon, preferentially with a low solubility in the aqueous phase. A modifier is sometimes added to change the physical properties of the organic phase (e.g. to avoid emulsification or gel formation, to increase metal loadings, *etc.*). The metals distribute between the aqueous and the organic phase, based on their differences in affinity for the metal-coordinating molecules in the aqueous and/or the organic phase and the solubilities of these species in both phases.

Due to the very similar chemical properties of the lanthanides [3], their separation on industrial scale is a major challenge in extractive metallurgy [4, 5]. The extractants used for the separation of rare earths can be divided into three main groups: (a) cation exchangers or acidic extractants (e.g. dialkyl phosphoric acids or carboxylic acids) [6–9], (b) molecule exchangers or neutral extractants (e.g. phosphine oxides, amides) [9–11], and (c) anion exchangers or basic extractants (e.g. protonated amines or quaternary ammonium salts) [9, 12–15]. The extraction mechanism of metals by anion exchangers is generally proposed as the exchange of a negatively charged metal complex initially present in the aqueous phase by anions initially present in the organic phase. For instance, the mechanism for solvent extraction of lanthanides from a nitrate-containing aqueous phase to a nitrate-containing organic phase is commonly written as [14–16]:

where Q is a cation (quaternary ammonium or phosphonium cation, or a protonated primary, secondary or tertiary amine). The horizontal bars indicate that the species is present in the organic phase.

Unfortunately, and in contrast to many transition metals, the extraction and separation of lanthanides from chloride media by anion exchangers is very challenging because the extraction percentages are low and the separation factors for adjacent lanthanide ions are small [9, 17–20]. This is unfortunate, because separation schemes for lanthanides based on HCl are cheaper than those based on HNO₃, and also cause less issues with waste water treatment. The low affinity of lanthanides for chloride anions in aqueous solutions might be one of the reasons for the low extraction percentages [21–23]. However, it does not clarify the small separation factors.

In this paper, an explanation is given for the small and changing separation factors obtained for the extraction of lanthanides from chloride media by the basic extractants Aliquat 336 (trioctyl/decylmethylammonium chloride, [A336][Cl]) and trihexyl(tetradecyl)phosphonium chloride (Cyphos IL 101, [C101][Cl]) (Figure 1). The speciation of the lanthanides in the organic phase and the mechanism of extraction is investigated by FTIR spectroscopy, luminescence spectroscopy, luminescence lifetime measurements and EXAFS spectroscopy.

Figure 1. Left: trihexyl(tetradecyl)phosphonium chloride (Cyphos IL 101, [C101][Cl]). Right: tricaprylmethylammonium chloride, the main component of Aliquat 336 ([A336][Cl]).

Experimental details

Chemicals

Aliquat 336, ([A336][Cl], mixture of methyl tri(octyl/decyl) ammonium chloride, 88-90 molar %) and deuterated water (D₂O, 99 molar%) were obtained from Sigma–Aldrich (Diegem, Belgium). Trihexyl(tetradecylphosphonium) chloride (Cyphos IL 101, [C101][Cl], (97 molar %) was obtained from Cytec Industries (Woodland Park, US). Eu₂O₃ (99.995 wt%) was obtained from Inframat Advanced Materials (Manchester, USA). LiCl (99.9 wt%), HCl (~37 wt%), ethyl acetate (> 99.5 wt%), heptane (> 99.5 wt%) and toluene (> 99.5 wt%) were obtained from VWR (Haasrode, Belgium). NdCl₃·6H₂O (99.9 wt%), DyCl₃·6H₂O (99.9 wt%) and LuCl₃·6H₂O (99.9 wt%) were obtained from Strem Chemicals (Kehl, Germany). Gallium and praseodymium standards (1000 mg·L⁻¹) were purchased from Merck (Overijse, Belgium). The silicone solution SERVA for siliconizing the quartz glass sample carriers for TXRF measurements was obtained from SERVA Electrophoresis GmbH (Heidelberg, Germany).

Samples

A 50 mL sample of [A336][Cl] was dried by stirring for 12 h at 50 °C at a Schlenk line. Europium(III) chloride (EuCl_3) was prepared by dissolving Eu_2O_3 in a small excess of HCl. Water and the remaining acid was removed by evaporation on a rotary evaporator. The EuCl_3 product was further dried for 48 h at 80 °C on a Schlenk line. Afterwards, the dried Eu(III) salt was dissolved in different amounts of dry, water (H_2O) and deuterium (D_2O) saturated [A336][Cl] by stirring overnight at 22 ± 1 °C. The remaining water content in the organic phase after Eu(III) dissolution was measured by coulometric Karl Fischer titration (Mettler-Toledo, model DL39). The europium concentrations in [A336][Cl] were quantified by total reflection X-ray fluorescence (TXRF) (Bruker, S2 Picofox) [24, 25].

Spectroscopic techniques

Infrared spectra were recorded using a Bruker Vertex 70 Fourier transform infrared (FTIR) spectrometer with an attenuated total reflectance module (Platinum ATR) with a resolution of 4 cm^{-1} and a total of 32 scans. The concentrations of the lanthanides in the organic phase were determined with a benchtop total reflection X-ray fluorescence (TXRF) spectrometer (Picofox S2, Bruker) [24, 25]. A $1000\text{ mg}\cdot\text{L}^{-1}$ praseodymium standard was added and the mixture was diluted with ethanol to obtain one homogeneous phase. The quartz sample carriers were first treated with 20 μL of silicone solution in isopropanol to make the quartz surface hydrophobic. Afterwards, the sample carriers were dried for 5 minutes in a hot air oven at 60 °C, followed by the addition of 5 μL of the ethanol solution and another drying step of 20 minutes at 60 °C. The samples were measured for 200 seconds on the spectrometer operating at 50 kV and 750 μA . The steady-state photoluminescence measurements were recorded on an Edinburgh Instruments FS900, with a 450 W xenon lamp as light source and a red-sensitive

photomultiplier tube (Hamamatsu 928P). The excitation spectra were measured between 240 and 580 nm, and the emission spectra between 500 and 850 nm. The emitted light was collected at an angle of 90° with respect to the excitation light beam. The spectra were corrected in real time for fluctuations of the lamp intensity and for the optical system of the excitation monochromator via a reference silicon diode. All spectra were also corrected for the optical system of the emission monochromator and for the response of the photomultiplier. For measurement of the excitation spectra, the emission was monitored at 611.3 nm, whereas for the emission spectra the wavelength of the maximum in the excitation spectrum was used for excitation of the Eu(III) ions. The emission decay curves were measured on an Edinburgh Instruments FS-920P spectrofluorimeter, with a 50 W microsecond flashlamp (2 μ s FWHM, repetition rate: 50 Hz), and a red-sensitive photomultiplier (Hamamatsu R2658P).

Extended X-ray Absorption Fine Structure (EXAFS) spectra of the Lu L_{III} edge (9245 eV), the Nd L_{III} edge (6211 eV) and the Dy L_{III} edge (7795 eV) were measured at the Dutch-Belgian Beamline (DUBBLE, BM26A) of the European Synchrotron Radiation Facility (ESRF) in Grenoble (France). The energy of the X-ray beam was tuned by a double-crystal monochromator operating in fixed-exit mode using a Si(111) crystal pair. The measurements were done in transmission mode using Ar/He gas filled ionization chambers at ambient pressure. A brass sample holder with Kapton® windows and a flexible polymeric spacer (VITON®) with thicknesses ranging between 0.5 and 2.0 mm were used as a sample holder. Standard procedures were used for pre-edge subtraction and data normalization in order to isolate the EXAFS function (χ). The EXAFS oscillations, isolated by a smoothing spline using the program VIPER [30], were k^3 -weighted and Fourier transformed using a Gaussian rounded ends window function. The data were fitted in $R + \Delta$ (Å) space using the *ab initio* code FEFF 7.0 [31], which was used to calculate the theoretical phase and amplitude

functions that were subsequently used in the non-linear least-squares refinement of the experimental data. Estimated errors on the different parameters are shown between parentheses and calculated by VIPER. An octahedral hexachloride lanthanide complex was used as model for modelling the lanthanide complexes in the dry extractant and a single lanthanide-oxygen path was used to model the EXAFS functions of the lanthanide aquo complexes. The amplitude reduction factor S_0 was fixed at 1.1 for all samples. $[\text{LuCl}_6][\text{C101}]_3$ was prepared by dissolving 100 mg of $\text{LuCl}_3 \cdot 6\text{H}_2\text{O}$ in 5 mL Aliquat 336 and drying the sample at the Schlenk line at 60 degrees for 2 days. The EXAFS samples of Nd(III), Dy(III) and Lu(III) were prepared by extraction of $0.05 \text{ mol} \cdot \text{L}^{-1}$ Ln(III) to water saturated $[\text{A336}][\text{Cl}]$ from an aqueous phase containing $11 \text{ mol} \cdot \text{L}^{-1}$ LiCl.

Sample preparations and extractions

The speciation of Eu(III) in the extraction to undiluted $[\text{A336}][\text{Cl}]$, undiluted $[\text{C101}][\text{Cl}]$ or $[\text{A336}][\text{Cl}]$ diluted in toluene, heptane or ethyl acetate was studied as well. The aqueous feed solution contained $50 \text{ g} \cdot \text{L}^{-1}$ Eu(III) ($0.20 \text{ mol} \cdot \text{L}^{-1}$) and $8.5 \text{ mol} \cdot \text{L}^{-1}$ LiCl before the extraction and an O:A volume ratio of 0.45 was used to increase the metal concentration in the organic phase. Concentrations of 10 v% ($\pm 0.16 \text{ mol} \cdot \text{L}^{-1}$) $[\text{A336}][\text{Cl}]$ in toluene, heptane and ethyl acetate were used. Concentration of 1 and 90 v% of $[\text{A336}][\text{Cl}]$ in toluene were used to study the speciation of the Eu(III) ion as a function of the extractant concentration ($[\text{A336}][\text{Cl}]$) in toluene. All extractions were done by shaking the samples at 2000 rpm and $70.0 \pm 0.1 \text{ }^\circ\text{C}$ for 2 h in TMS-300 Thermoshakers (Allsheng).

The extraction of NdCl_3 to water saturated $[\text{C101}][\text{Cl}]$ from aqueous solutions containing 7 to $11 \text{ mol} \cdot \text{L}^{-1}$ of LiCl was studied by mixing different volumes of an $11 \text{ mol} \cdot \text{L}^{-1}$ LiCl solution, with water and with an $11 \text{ mol} \cdot \text{L}^{-1}$ LiCl solution containing $44 \text{ g} \cdot \text{L}^{-1}$ Nd(III). The final Nd(III) concentration in the feed solution after mixing the three solutions was always $22 \text{ g} \cdot \text{L}^{-1}$ (0.15

mol·L⁻¹). An organic-to-aqueous phase ratio (O:A volume ratio) of 1 was used. Water saturation of the extractants was done at 22 ± 1 °C. The LiCl concentration in the aqueous phase for the extraction of 22 g·L⁻¹ Nd(III) (0.15 mol·L⁻¹) to [C101][Cl] diluted in toluene was 11 mol·L⁻¹. The extractant-to-toluene ratio in the solvent was varied but the O:A ratio was kept constant at 1. The Nd(III) loading into water-saturated [C101][Cl] was studied by varying the O:A ratio between 1 and 0.27, with the aqueous phase containing 44 g·L⁻¹ Nd (0.30 mol·L⁻¹) and 11 mol·L⁻¹ of LiCl. In this case, the volume of the aqueous phase was always 1 mL. Phase separation was accelerated by centrifugation (Heraeus Megafuge 1.0). The Nd(III) concentrations in the aqueous and organic phase were quantitatively measured by TXRF with an internal praseodymium standard of 1000 mg·L⁻¹. The organic phase was diluted with ethanol and the aqueous phase with water.

The magnitude of lanthanide extraction is described by the *distribution ratio* (D), defined as the ratio between the lanthanide concentration in respectively the organic and the aqueous phase at equilibrium (equation 2), and the *extraction percentage* (% E) defined as the amount of lanthanide extracted over the total amount of lanthanides in the extraction system (equation 3):

$$D = \frac{[Ln]_{org}}{[Ln]_{aq}} \quad (2)$$

$$\%E = \frac{\text{Amount of Ln in the organic phase}}{\text{Amount of Ln in the aqueous and organic phase}} \times 100 \quad (3)$$

The separation between 2 lanthanides is quantified by the separation factor $\alpha_{Ln1/Ln2}$:

$$\alpha_{Ln1/Ln2} = \frac{D_{Ln1}}{D_{Ln2}} \quad (4)$$

The physical and chemical properties of the extractants are studied elsewhere [26–29].

Results and discussion

Speciation

The distribution of lanthanides between the chloride-containing aqueous phase and the extractant-containing organic phase depends on the interaction of the lanthanides with the anions or molecules in the aqueous and organic phase respectively. The stability constants of lanthanides with chloride anions are low, especially when comparing to those reported for transition metals [21, 23, 32]. Consequently, the aqueous phase contains only the following species: $[\text{Ln}(\text{H}_2\text{O})_x]^{3+}$, $[\text{LnCl}(\text{H}_2\text{O})_y]^{2+}$ and at very high chloride concentrations possibly $[\text{LnCl}_2(\text{H}_2\text{O})_z]^+$. The positively charged lanthanide complexes are strongly hydrated by water molecules in their first coordination sphere. In addition, also a second hydration shell and a structure-breaking hydration shell are present around the positively charged lanthanide complex. This results in high lanthanide hydration energies in comparison to species with a lower charge density (e.g. metal chloro complexes with lower charges). This kind of phenomena is generally described in terms of the Hofmeister series [33, 34], where cations and anions are ordered as a function of their charge density and hydration energy. As a result, species with a weak hydration (low charge density), preferentially distribute towards the organic phase compared to species with a strong hydration (high charge density), such as lanthanides in a chloride-containing aqueous phase.

The reported distribution ratios for lanthanides at trace concentrations are very low. For instance, distribution ratios between 1 and 10 were obtained for the extraction of $0.1 \text{ mmol}\cdot\text{L}^{-1}$ of lanthanides at LiCl concentrations of $12 \text{ mol}\cdot\text{L}^{-1}$ with $0.22 \text{ mol}\cdot\text{L}^{-1}$ Adogen 464 (methyl tri(octyl/decyl) ammonium chloride) dissolved in o-xylene phase [18]. The speciation in solutions with such a low lanthanide concentrations is difficult to study. Therefore, to find the most stable lanthanide species in an organic phase containing a quaternary ammonium salt, we decided to study first the speciation of Eu(III) in the quaternary compound $[\text{A336}][\text{Cl}]$ by

addition of the Eu(III) chloride rather than by solvent extraction. Quaternary ammonium compounds are generally better in extracting metals than primary, secondary and tertiary amines because of their higher hydrophobicity. The speciation of lanthanides in undiluted water-saturated [A336][Cl] was studied because in solvent extraction, undiluted extractants were used to maximize the distribution ratios and metal concentrations in the organic phase. The water content in undiluted Eu(III)-containing [A336][Cl] was selected in such a way that they were very similar to the ones obtained in extractions. Therefore, [A336][Cl] was first presaturated with water before the Eu(III) salt was added. Eu(III) was also dissolved in dry [A336][Cl] where the chlorides are the only possible ligands for Eu(III). The different samples, their abbreviations (water-saturated = **W** and dry IL = **D**) and their composition can be found in Table 1.

Table 1. Sample names and compositions of the different samples

Sample names	[H ₂ O] (wt%)	(g·L ⁻¹)	[Eu(III)] (mol·L ⁻¹)
W0	Water-saturated ^a	0	0
W1	Water-saturated ^a	1.8	0.01
W2	Water-saturated ^a	16.9	0.11
W3	Water-saturated ^a	73.8	0.49
D0	n.a. ^b	0	0
D1	0.11	1.6	0.01
D2	0.12	15.4	0.10
D3	0.09	82.4	0.54

^a[A336] was saturated with water before the addition of the EuCl₃ salt, ^bnot available.

The FTIR spectra of dry (**D0**), water-saturated (**W0**) and Eu(III)-containing dry (**D3**) and water-saturated (**W3**) [A336][Cl] are shown in Figure 2. The main vibrational bands of the cation are visible at 2956 to 2853 cm⁻¹ (C–H stretching), 1464 cm⁻¹ (N–CH₂ stretching), 1377 cm⁻¹ (CH₂ wagging) and 722 cm⁻¹ (CH₂ rocking) [35]. No significant differences were

observed in the position and intensities of the peaks in the spectra of the different samples, except for the presence of strong water peaks in water-saturated [A336][Cl] around 1631 cm^{-1} and in the region between 3000 and 3500 cm^{-1} .

Figure 2. FTIR spectra of dry (**D0**), water-saturated (**W0**) and Eu(III)-containing dry (**D3**) and water-saturated (**W3**) [A336][Cl].

The speciation of Eu(III) in dry [A336][Cl] was studied by measuring the excitation and emission spectra of the different samples (**D1**, **D2** and **D3**). A chloro europate(III) complex is expected, as the sole ligands present in dry [A336][Cl] are chlorides. The presence of the $[\text{LnCl}_6]^{3-}$ complexes in quaternary phosphonium or imidazolium salts has already been reported in the literature [36–38]. The excitation spectra of the dry [A336][Cl] samples containing the Eu(III) ion have a broad excitation band arising from the singlet ground state of the [A336] cation and sharp peaks which can be attributed to the $^7\text{F}_0$ electronic level of the Eu(III) ion (Figure 3). The different peaks in the excitation spectra only change in absolute intensity and not in relative intensity when the Eu(III) concentration is increased. Also the

relative intensities of the peaks found in the emission spectra are invariable as a function of the Eu(III) concentration (Figure 4). The low intensity of the hypersensitive $^5D_0 \rightarrow ^7F_2$ transition in the emission spectra suggests a high symmetry with an inversion center around the central Eu(III) ion [39]. Based on the general coordination geometry of lanthanides, a seven, eight or nine coordinated Eu(III) cation can be excluded and an octahedral $[EuCl_6]^{3-}$ structure is the most probable complex present in dry $[A336][Cl]$. Another remarkable point is that the $^5D_0 \rightarrow ^7F_2$ transition shows a splitting pattern with a higher resolution than expected for liquid samples, as a consequence of the well-defined symmetry around the emitting Eu(III) ion. The presence of the $^5D_1 \rightarrow ^7F_{0-3}$ emission bands is another piece of evidence that chloride ions and not water molecules coordinate the Eu(III) center in dry $[A336][Cl]$ [39]. Water molecules efficiently promote the radiationless decay of the 5D_1 level to the 5D_0 level, and for Eu(III) complexes with coordinated water molecules in general no emission from the 5D_1 level is observed.

Figure 3. Excitation spectra of dry, Eu(III)-containing $[A336][Cl]$ ($\lambda_{em} = 611.3$ nm).

Figure 4. Emission spectra of dry, Eu(III)-containing [A336][Cl] (λ_{ex} : **D1** = 325.0 nm; **D2** and **D3** = 465.0 nm).

The presence of the $[\text{LnCl}_6]^{3-}$ complex in dry [A336][Cl] was confirmed by EXAFS measurements. Lutetium was selected as the lanthanide probe because of its higher L_{III} -edge energy. This is, in general, associated with a better signal-to-noise ratio and EXAFS oscillations observable in a larger k -range in comparison to the L_{III} -edge of for instance Eu(III). Therefore, measurements on Lu(III) result in better data quality than those of lighter lanthanides. The octahedral $[\text{LuCl}_6]^{3-}$ complex was used as model for fitting. A good fit to the experimental data was obtained using the Lu-Cl single scattering (SS) and Lu-Cl₁-Lu-Cl₂ multiple scattering (MS) paths (Figure 5 and 6, Table 2). The amplitude reduction factor S_0 was set to 1.1 to obtain a coordination number of 6.

Figure 5. k^3 -Weighted EXAFS function $\chi(k)$ (black) and model (red) of the $[\text{LuCl}_6]^{3-}$ complex in dry $[\text{A336}][\text{Cl}]$.

Figure 6. Fourier transform (black) and model (red) of the EXAFS function of the $[\text{LuCl}_6]^{3-}$ complex in dry $[\text{A336}][\text{Cl}]$.

Table 2. EXAFS fitting results of the $[\text{LuCl}_6]^{3-}$ complex in dry $[\text{A336}][\text{Cl}]$.

Scattering path	N	r (Å)	σ^2 (Å ²)
Lu-Cl ₁ (SS)	6.1(2)	2.611(3)	0.009(1)
Lu-Cl ₁ -Lu-Cl ₂ (MS)	6.1(2)	5.222(3)	0.016(2)

The data were Fourier transformed between $k = 3.5$ and 11.65 Å^{-1} with a Gaussian rounded ends window function and the model was fitted to the data between $R = 0$ and 5.33 Å . N = coordination number, r = bond length and σ^2 = Debye-Waller factor.

The excitation spectra of Eu(III) dissolved in water-saturated $[\text{A336}][\text{Cl}]$ (**W1**, **W2** and **W3**) also show the broad excitation band arising from the singlet ground state of the $[\text{A336}]^+$ cation and sharp peaks which can be attributed to transitions from the $^7\text{F}_0$ ground state to excited electronic levels of the Eu(III) ion (Figure 7). Also here, the different peaks in the excitation spectra only change in absolute intensity and not in relative intensity when increasing the Eu(III) concentration in $[\text{A336}][\text{Cl}]$, suggesting that the speciation of the Eu(III) ion is invariable as a function of the Eu(III) concentration. However, the spectra show different splitting patterns in the Eu(III) excitation bands compared to dry, Eu(III)-containing $[\text{A336}][\text{Cl}]$ (**D1**, **D2** and **D3**), indicating a different coordination around the Eu(III) ion.

The most interesting observation in the emission spectra of Eu(III) in water-saturated $[\text{A336}][\text{Cl}]$ is the relative intensity of the $^5\text{D}_0 \rightarrow ^7\text{F}_3$ band in comparison to the $^5\text{D}_0 \rightarrow ^7\text{F}_{1,2,4}$ bands (Figure 8). The hypersensitive $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition is less intense than the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ magnetic dipole transition and the $^5\text{D}_0 \rightarrow ^7\text{F}_4$ transition. The peak intensity ratio R_{21} between the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ and $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition is 0.70 for sample **W2** and 0.79 for sample **W3**. The observation made in the emission spectra suggest that the most stable Eu(III) species present in water-saturated $[\text{A336}][\text{Cl}]$ contains mainly coordinated water ligands. However, the

spectra do not provide sufficient proof to exclude the presence of a small number of coordinating chloride anions.

Figure 7. Excitation spectra of Eu(III)-containing water-saturated [A336][Cl] ($\lambda_{em} = 592.0$ nm).

Figure 8. Emission spectra of Eu(III)-containing water-saturated [A336][Cl] ($\lambda_{ex} = 394.0$ nm).

The linearized emission decay curves of the 5D_0 level of the Eu(III) ion were measured and analyzed to determine the number of coordinated water ligands. All curves could be fitted by monoexponential functions, which indicates that only one species is present in the organic phase. Lifetime values of Eu(III) in water-saturated [A336][Cl] were 0.13 for **W1** and 0.12 ms for **W2** and **W3**. In case of dry [A336][Cl], the lifetimes were 1.14, 1.83 and 2.42 ms for samples **D1**, **D2** and **D3**, respectively. The lifetime increase with increasing Eu(III) concentration was also observed for the [A336][Cl] samples presaturated with deuterated water, where the lifetime increased from 0.43 ms (**W1-deuterated**) to 0.70 ms (**W3-deuterated**). The increase in lifetime can be attributed to the non-negligible water (H₂O) concentrations in the organic phase after drying (± 0.1 wt%). This might lead to the coordination of a small amount of water to some of the Eu(III) cations, especially when the Eu(III) concentration is low, resulting in smaller lifetimes. The differences in lifetimes between the samples in dry and water-saturated [A336][Cl] also suggest different complexes. The lifetime in the dry samples is about 20 times longer than the lifetimes for the water-saturated [A336][Cl] (e.g. $\tau_{A3} = 2.42$ ms and $\tau_{W3} = 0.12$ ms). The number of water molecules (q) coordinated to the Eu(III) ion were calculated via the Sudnick-Horrocks equation [40]:

$$q_{HS} = 1.05 \left[\frac{1}{\tau_{H_2O}} - \frac{1}{\tau_{D_2O}} \right] \quad (5)$$

where τ_w is the emission lifetime of the Eu(III) ion in case of H₂O and τ_D is the emission lifetime of the Eu(III) ion when H₂O is replaced by D₂O [41]. The number of coordinating water molecules was found to be 7.5 (**W1**), 7.9 (**W2**) and 8 (**W3**). The error on these q values is estimated to be ± 0.5 (water molecules), according to the theory of Sudnick and Horrocks.

Furthermore, the Sudnick-Horrocks formula is an experimentally determined equation, which might result in a slight underestimation of q in our samples. The coordination number of europium in aquo complexes is generally between 8 and 9. Therefore, these calculated q values most likely indicate the presence of an Eu(III) aquo complex in the water-saturated extractants. However, the low values of q might also indicate that the coordination sphere of Eu(III) is not fully saturated with water molecules alone, and consequently also one chloride ligand could be coordinated to the Eu(III) center. This is unlikely, but cannot be fully excluded based on the combination of the luminescence spectra and emission lifetime measurements.

The presence of a lanthanide aquo complex, extracted in the organic phase was confirmed by EXAFS spectroscopy. X-ray absorption spectra were recorded of Nd(III), Dy(III) and Lu(III) extracted from an 8 mol·L⁻¹ LiCl solution to [A336][Cl]. In all three cases, the Fourier transform contained one broad peak. A good fit of the Fourier transform was obtained by fitting only the Ln-O single scattering path with Ln(H₂O) as model. Any fit including a chlorine atom at a distance slightly longer than the Ln-O bond distance resulted in unreasonable parameters. The amplitude reduction factor S_0 was set to 1.1, in accordance to the results obtained for [LuCl₆]³⁻. Coordination numbers of 7.7 for Lu(III), 8.5 for Dy(III) and 8.9 for Nd(III) were obtained, indicating the presence of [Ln(H₂O)₈]³⁺ or [Ln(H₂O)₉]³⁺ complexes in the organic phase. The bond distances and coordination numbers, summarized in Figures 9 and 10 and in Table 3, are in agreement with EXAFS data and crystal structures of hydrated lanthanide complexes [42], and with the results and conclusions obtained from the luminescence lifetime measurements. Since it was not possible to obtain a good fit including a chlorine atom at a distance slightly longer than the Ln-O distance, one can conclude that the

lanthanide species present in the organic phase most likely does not contain any coordinated chlorine atom in its first coordination shell.

Figure 9. k^3 -weighted EXAFS function $\chi(k)$ (black) and model (red) of the $[\text{Ln}(\text{H}_2\text{O})_{8-9}]^{3+}$ complex in water saturated [A336][Cl].

Figure 10. Fourier transform (black) and model (red) of the EXAFS function $\chi(k)$ of $[Ln(H_2O)_{8-9}]^{3+}$ in water saturated [A336][Cl].

Table 3. EXAFS fitting results of $[Ln(H_2O)_{8-9}]^{3+}$ in [A336][Cl].

Scattering path	N	r (Å)	σ^2 (Å ²)
Nd-O (SS)	8.9(13)	2.490(19)	0.010(2)
Dy-O (SS)	8.5(2)	2.398(4)	0.010(1)
Lu-O (SS)	7.7(4)	2.336(5)	0.009(6)

N = coordination number, r = bond length and σ^2 = Debye-Waller factor.

411 The speciation of the Eu(III) complexes extracted into [A336][Cl], [C101][Cl] and
 412 [A336][Cl] diluted in the apolar aliphatic solvent heptane, in the apolar aromatic solvent
 413 toluene and in the polar solvent ethyl acetate was studied as well. The excitation and emission
 414 spectra of Eu(III) in the different solvents are shown in Figures 11 and 12. The peak
 415 intensities and multiplicity of the excitation and emission spectra of Eu(III) in undiluted and
 416 diluted [A336][Cl] are very similar, indicating that the coordination environment around the
 417 Eu(III) cation is independent of the tested diluents. In addition, the spectra are also very
 418 similar to those obtained for samples **W1**, **W2** and **W3**. The excitation and emission spectra
 419 of Eu(III) extracted into [C101][Cl] are slightly different from those obtained for [A336][Cl].
 420 The peak intensity corresponding to the $^5D_0 \rightarrow ^7F_2$ transition is more intense in case of Eu(III)
 421 extracted into [C101][Cl] compared to that of Eu(III) extracted into [A336][Cl]. This might be
 422 due to the coordination of phosphine oxides impurities in [C101][Cl] (± 3 wt%), resulting in a
 423 less symmetrical structure around the Eu(III) ion and a higher intensity of the $^5D_0 \rightarrow ^7F_2$
 424 transition [39]. Notice that the emission spectrum of Eu(III) in water at low chloride
 425 concentrations, known to contain $[Eu(H_2O)_9]^{3+}$ in a D_{3h} symmetry, is different from the
 426 spectrum of Eu(III) dissolved in water-saturated [A336][Cl] those Eu^{3+} spectra obtained after
 427 extraction in the organic solvents. The higher intensity of the $^5D_0 \rightarrow ^7F_2$ transition for Eu(III)
 428 extracted and the presence of a peak representing the $^5D_0 \rightarrow ^7F_0$ suggest a decrease in
 429 symmetry around the Eu(III) ion. This might be due to either a decrease in the number of
 430 water molecules coordinating the lanthanide ion from 9 in the high water content containing
 431 aqueous phase to for instance 8 in a hydrophobic organic phase, or a different geometry of the
 432 $[Ln(H_2O)_9]^{3+}$ species in the aqueous and organic phase, or the coordination of one chloride
 433 ion.

Figure 11. Excitation spectra of solutions containing $50 \text{ g}\cdot\text{L}^{-1}$ Eu(III) ($0.35 \text{ mol}\cdot\text{L}^{-1}$) in water and of the Eu(III) complexes extracted from $8.5 \text{ mol}\cdot\text{L}^{-1}$ LiCl to 10 v% of $[\text{A336}][\text{Cl}]$, $[\text{C101}][\text{Cl}]$ and $[\text{A336}][\text{Cl}]$ in ethyl acetate, toluene and heptane ($\lambda_{\text{em}} = 592.0 \text{ nm}$).

Figure 12. Emission spectra of solutions containing $50 \text{ g}\cdot\text{L}^{-1}$ Eu(III) ($0.35 \text{ mol}\cdot\text{L}^{-1}$) in water and of the Eu(III) complexes extracted from $8.5 \text{ mol}\cdot\text{L}^{-1}$ LiCl to 10 v% of $[\text{A336}][\text{Cl}]$, $[\text{C101}][\text{Cl}]$ and $[\text{A336}][\text{Cl}]$ in ethyl acetate, toluene and heptane ($\lambda_{\text{ex}} = 394.0 \text{ nm}$).

The water content of the organic phase is of crucial importance for the speciation of the lanthanide ions in the organic phase as it was demonstrated that the lanthanides are coordinated with six chlorides in a water free organic phase and with 8 or 9 water molecules in case of an organic phase saturated with water. The water content of the organic phase is low when low concentrations of quaternary compounds are used. Nevertheless, the Eu(III) excitation and emission spectra of 1 v% of [A336][Cl] in toluene are similar to those obtained at 10 and 90 v% [A336][Cl] in toluene and also to water saturated [A336][Cl] (Figure 13 and 14). This demonstrates that there is no change in speciation as a function of the concentration of quaternary ammonium extractant in the organic phase, varying between 1 and 90 v% of [A336][Cl] in toluene.

Figure 13. Excitation spectra of Eu(III) complexes extracted from $8.5 \text{ mol} \cdot \text{L}^{-1}$ LiCl to different volume percentages (v%) of [A336][Cl] in toluene or to water saturated [A336][Cl] ($\lambda_{em} = 592.0 \text{ nm}$).

Figure 14. Emission spectra of Eu(III) complexes extracted from $8.5 \text{ mol} \cdot \text{L}^{-1} \text{ LiCl}$ to different volume percentages (v%) of [A336][Cl] in toluene or to water saturated [A336][Cl] ($\lambda_{\text{ex}} = 394.0 \text{ nm}$).

Extraction mechanism

Based on the data obtained from luminescence spectroscopy, lifetime measurements and EXAFS spectroscopy and on what is known about the speciation of lanthanides in aqueous media [21, 23, 32], we conclude that the equilibria involved in the extraction of lanthanides from chloride media to basic extractants in the organic phase can be written as:

Equation (6) represents the decomplexation of chloride ions to the lanthanide ion in an aqueous phase containing chloride anions which might be in the first or second coordination

sphere [40]. Equation (7) represents the distribution of the lanthanide aquo complex between the aqueous to the organic phase containing the basic extractant.

All results strongly suggest the formation of $[\text{Ln}(\text{H}_2\text{O})_{8-9}]^{3+}$ in the organic phase obtained after extraction, with only water as a coordinating ligand and no coordinating chloride ions, in contrast to the coordination of lanthanides in the aqueous phase where both inner-sphere and outer-sphere complexes with a chloride anions can be found [32, 43]. However, the experimental proof is not sufficient to make an absolute statement on this matter. The emission spectra of Eu(III) in water and in the organic phase were different, suggesting a different coordination chemistry or symmetry/geometry of the lanthanide complex.

Furthermore, the fact that the incorporation of a Ln-Cl scattering path in the fit of the EXAFS data did not give good results does not necessarily mean that no coordinating chloride ligand is present since it may simply be difficult or even impossible to distinguish one chloride in the proximity of 8 oxygen atoms in the same coordination shell with EXAFS.

The results and conclusions obtained are significantly different from the extracted complex proposed by other groups based on solvent extraction experiments with quaternary ammonium compounds. Sohsas *et al.* reported the presence of $[\text{LnCl}_4]^-$, $[\text{LnCl}_5]^{2-}$ and $[\text{LnCl}_6]^{3-}$ in the organic phase depending on the extractant (Adogen 464) concentration [18], whereas Mikhailichenko *et al.* reported the presence of only $[\text{LnCl}_5]^{2-}$ for the extraction of lanthanides with trialkyl benzyl ammonium chloride [19]. Khopkar *et al.* proposed, based on the absorption spectra of Nd(III), a lanthanide hexachloride complex $[\text{LnCl}_6]^{3-}$ in case of quaternary ammonium salts and a tetrachloro complex $[\text{LnCl}_4]^-$ or a pentachloro complex $[\text{LnCl}_5]^{2-}$ in case of tertiary amines [20].

The high concentration of water in the aqueous phase and the low concentration in the organic phase inevitably lead to a low affinity of the hydrated lanthanide species for the organic phase and a high stability of the $[\text{Ln}(\text{H}_2\text{O})_{8-9}]^{3+}$ in the aqueous phase [44]. Therefore, a high

concentration of salting-out agent is required to decrease the free water content in the aqueous phase and to induce lanthanide extraction to the organic phase. Sohsah *et al.* reported that the separation factors increase as a function of the chloride concentration in the aqueous phase [18]. The distribution ratios of the heavy lanthanides significantly increase with increasing chloride concentrations. However, the distribution ratios of the light lanthanides are stable or even decrease upon the addition of chloride ions (e.g. for La). This is not surprising if one looks to equation (8), which is a combination of equation (6) and (7) and taking into account that the stability constants of lanthanides with chloride ions are decreasing from the light to the heavy lanthanides [21–23]. Therefore, equation (8) is shifted relatively more to the left in case of La(III) than in case of Lu(III) when the chloride concentration is increased, resulting in an increase in the separation factors:

The effect of adding metal complexing anions in the aqueous phase, inducing decreasing metal distribution ratios or decreasing extraction percentages is widely known for acidic extractants. For instance, metals forming strong chloro complexes such as Pd(II), Hg(II) and In(III), can be quantitatively extracted from 1 mol·L⁻¹ NaNO₃ by the acidic extractant versatic acid at a pH of 3, but no extraction occurs at this pH from 1 mol·L⁻¹ NaCl [45]. This kind of effect can be used to obtain a good separation between metals having very close pH depending extraction curves at low ionic strengths. A similar extraction behavior and complexing anion effect is observed for this kind of systems.

Extractions

The extraction and loading of Nd(III) into water saturated [C101][Cl] was studied because Nd(III) is often used as a model lanthanide ion in solvent extraction studies and because of its important application in NdFeB magnets. In addition, many papers have been published recently discussing the recycling of rare earths from NdFeB permanent magnets via hydrometallurgical flow sheets [46, 47]. In our extraction experiments, [C101][Cl] was selected as the extractant because it shows higher extraction percentages than [A336][Cl] under the same conditions (*vide infra*). First, the extraction of a feed solution containing 22 g·L⁻¹ Nd(III) (0.15 mol·L⁻¹) to [C101][Cl] was studied as a function of the LiCl concentration. The extraction percentages and distribution ratios of Nd(III) increased with increasing LiCl concentration (Figure 15, Table 4). The extraction percentages were higher than 90% at LiCl concentrations above 10 mol·L⁻¹. The Nd(III) concentration in the organic phase at these conditions is approximately 20 g·L⁻¹ (0.15 mol·L⁻¹). The Nd(III) extraction at LiCl concentrations above 11 mol·L⁻¹ was not studied because of the solubility limit of NdCl₃ at such high chloride concentrations. No corrections in the distribution ratios and the percentage extractions were done for volume changes. Volume changes were minimized by presaturating the organic phase with water. However, a fresh contact of the water saturated extractant with an aqueous phase with high ionic strength, might pull water out of the organic phase.

Figure 15. Extraction percentage (%E) and distribution ratio (D) of $22 \text{ g}\cdot\text{L}^{-1}$ Nd(III) ($0.15 \text{ mol}\cdot\text{L}^{-1}$) to water-saturated [C101][Cl].

Table 4. Extraction percentage (%E) and distribution ratio (D) of $22 \text{ g}\cdot\text{L}^{-1}$ Nd(III) ($0.15 \text{ mol}\cdot\text{L}^{-1}$) to water-saturated [C101][Cl].

LiCl concentration (mol L^{-1})	%E (%)	Distribution ratio
7	53.4	1.1
7.5	61.0	1.5
8	71.2	2.4
8.5	77.2	3.3
9	82.5	4.7
9.5	87.2	6.8
10	89.9	8.9
10.5	92.3	12.1
11	94.3	16.6

Loading studies of [C101][Cl] also confirmed that the species present in the organic phase was not $[\text{LnCl}_5(\text{H}_2\text{O})_x]^{2-}$ or $[\text{LnCl}_6]^{3-}$ as it was possible to load more lanthanide in the organic phase than an extractant/lanthanide molar ratio of 2:1. By decreasing the O:A phase ratio under equal conditions ($\text{Nd}_{\text{aq,initial}} = 44 \text{ g}\cdot\text{L}^{-1}$ ($0.30 \text{ mol}\cdot\text{L}^{-1}$), LiCl concentration = $11 \text{ mol}\cdot\text{L}^{-1}$),

the extraction percentage decreased, but the metal loading in the organic phase increased (Figure 16, Table 5). At a phase ratio of 0.27, the organic phase contained $107 \text{ g}\cdot\text{L}^{-1}$ of Nd ($0.74 \text{ mol}\cdot\text{L}^{-1}$). This corresponds to an extractant/Nd ratio in the organic phase of about 1.3, assuming no volume changes by contacting the water-saturated organic phase with an aqueous phase of high ionic strength or by uptake of a significant volume of Nd. Notice that the concentration of Nd(III) in the organic phase is very high.

Figure 16. Nd(III) concentration in the organic phase and extraction percentage (%E) as a function of the O:A ratio from an aqueous phase containing $11 \text{ mol}\cdot\text{L}^{-1}$ LiCl and an initial Nd(III) concentration of $44 \text{ g}\cdot\text{L}^{-1}$ ($0.30 \text{ mol}\cdot\text{L}^{-1}$).

Table 5. *Nd(III) concentration in the organic phase and extraction percentage (%E) as a function of the O:A ratio from an aqueous phase containing 11 mol·L⁻¹ LiCl and an initial Nd(III) concentration of 44 g·L⁻¹ (0.30 mol·L⁻¹).*

<i>O:A ratio</i>	Nd(II) concentration (gram·L ⁻¹)	Nd(II) concentration (mol·L ⁻¹)	%E
0.77	12.7	0.08	77.1
0.72	17.0	0.11	71.8
0.66	20.4	0.13	68.9
0.60	26.8	0.18	62.5
0.55	30.3	0.20	61.1
0.49	46.0	0.30	47.3
0.44	54.5	0.36	44.2
0.38	73.2	0.48	34.9
0.33	79.2	0.52	39.2
0.28	107.3	0.71	32.2

The effect of diluting [C101][Cl] with toluene on the extraction of 22 g·L⁻¹ Nd(III) (0.30 mol·L⁻¹) from a solution containing 11 mol·L⁻¹ LiCl was also tested (Figure 17, Table 6). An increase in the extractant concentration resulted in an increase in the extraction percentages. The same %E was obtained at lower extractant concentrations in comparison to water-saturated [C101][Cl]. This means that the %E can be increased in comparison to undiluted [C101][Cl] by adding small amounts of a hydrophobic diluent such as toluene. For the same reason, the extraction for the extraction percentage of Nd(III) to [A336][Cl] is lower than the extraction percentage for the extraction of Nd(III) to [C101][Cl]. The extractant concentration of [A336][Cl] in water-saturated [A336][Cl] is higher because of its lower molecular mass in comparison to water-saturated [C101][Cl]. However, the fact that the water content is higher results in a less hydrophobic phase and lower extraction percentages.

Figure 17. Extraction percentage (%E) of Nd(III) to [C101][Cl] diluted in toluene (black), water-saturated [C101][Cl] (red) and water-saturated [A336][Cl] (blue). O:A ratio = 1, $Nd_{in} = 22 \text{ g}\cdot\text{L}^{-1}$ ($0.30 \text{ mol}\cdot\text{L}^{-1}$).

Table 6. Extraction percentage (%E) of Nd(III) to [C101][Cl] diluted in toluene, water-saturated [C101][Cl] and water-saturated [A336][Cl]. O:A ratio = 1, $Nd_{in} = 22 \text{ g}\cdot\text{L}^{-1}$ ($0.30 \text{ mol}\cdot\text{L}^{-1}$).

Extractant concentration (mol L^{-1})	%E (%) to water-saturated [C101][Cl]	%E (%) to toluene diluted [C101][Cl]	%E (%) to water-saturated [A336][Cl]
0	0		
0.16	12.2		
0.33	33.5		
0.51	51.4		
0.67	67.1		
0.84	80.0		
1.01	89.5		
1.18	93.8		
1.35	97.5		
1.58		94.3	
1.76			64.4

Conclusions

The extraction mechanism of lanthanides from chloride media to basic extractants was investigated by luminescence spectroscopy, luminescence life time measurements and EXAFS spectroscopy. The lanthanides distributed between the organic and the aqueous phase as a hydrated $[\text{Ln}(\text{H}_2\text{O})_{8-9}]^{3+}$ complex upon the addition of high concentrations of chloride ions to the aqueous phase. The lanthanide complex presented in the organic phase had a lower symmetry than the tricapped trigonal structure of $[\text{Ln}(\text{H}_2\text{O})_9]^{3+}$ in the aqueous phase. This might be due to a decrease in coordinated water ligands from 9 in the aqueous phase to 8 in the organic phase, by a change in the coordination geometry of the $[\text{Ln}(\text{H}_2\text{O})_9]^{3+}$ species in the

organic phase in comparison to the coordination geometry in the aqueous phase or maybe because of the coordination of one chloride ion. However, the assumption that one chloride ion is coordinating to the lanthanide ion in the organic phase was not supported by the EXAFS measurements or by the combination of lifetime and luminescence measurements. On the other hand, no information was obtained for the lanthanides lighter than Nd(III), so the presence of a coordinating chloride anion to for instance lanthanum cannot be completely excluded. These new insights explain the high chloride concentrations required for lanthanide extraction from chloride media and the small but changing separation factors obtained for lanthanide extraction for chloride media to basic extractants. In addition, the data demonstrate that the species in the aqueous phase is different from what has been reported in the literature, based on solvent extraction techniques. These new insights in the extraction of lanthanides from chloride media to basic extractants opens new opportunities for improving lanthanide separations in this kind of systems by the addition of, for instance, acidic complexing agents in the aqueous phase.

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