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Understanding the synergistic effect on lanthanides(III) solvent extraction by systems combining a malonamide and a dialkyl phosphoric acid

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A B S T R A C T

To separate minor actinides from lanthanides for used nuclear fuel reprocessing, solvent extraction processes combining neutral and acidic extractants are considered. Mixed systems present singular extraction properties where synergistic effects can be observed but information on chemical equilibria is lacking to properly model such behavior. Speciation of Eu(III) and Nd(III) complexes formed in an organic phase combining *N,N'*-dimethyl-*N,N'*-dioctylhexylethoxy malonamide (DMDOHEMA) and di(2-ethylhexyl)phosphoric acid (HDEHP) was investigated through electrospray ionization mass spectrometry (ESI-MS), time-resolved laser-induced fluorescence spectroscopy (TRLIFS), UV-Visible, nuclear magnetic resonance (NMR), extended X-ray absorption fine structure (EXAFS) and density functional theory (DFT) calculations. A method consists of adding one of the ligands to a solution containing Ln(III) complexes formed with the other ligand while following changes by each technique was used. In both cases, significant modifications in the metal coordination sphere were observed due to formation of mixed complexes containing both ligands: addition of DMDOHEMA to a Ln-HDEHP solution led to the formation of Ln(DEHP)₃(HDEHP)₂(DMDOHEMA) complexes while addition of HDEHP to a Ln-DMDOHEMA solution gave Ln(NO₃)_{3-n}(DEHP)_n(HDEHP)_m(DMDOHEMA)_{x'} (0 ≤ n ≤ 3; n + m ≥ 1 and 1 ≤ x' ≤ 3) complexes.

Keywords:

Solvent extraction

Synergism

Malonamides

Dialkyl phosphoric acid

HDEHP

Lanthanides

Mixed complexes

1. Introduction

Hydrometallurgical processes such as solvent extraction are commonly used in the chemical treatment of used nuclear fuel (Rydberg and Musikas, 2004). Solvent extraction consists of contacting a water-immiscible organic phase containing amphiphilic 'extractant' molecules with an aqueous phase in which metal ions are dissolved. The targeted solute is selectively extracted in the organic phase due to specific properties of the extractant molecule, and separated from other aqueous solutes. Often, a single extractant is not efficient enough and a mixture of

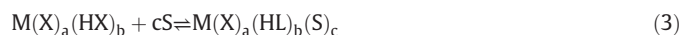
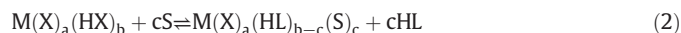
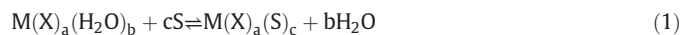
two extractants has to be used. It has been observed that certain combinations of two extractants give, under well-defined experimental conditions, an enhanced extraction compared to what is obtained using the extractants separately. This phenomenon is known as synergism or synergic extraction (Irving and Edgington, 1960; Irving and Edgington, 1961a; Irving and Edgington, 1961b; Irving and Edgington, 1961c; Choppin, 1981; Rublev, 1983; Ramakrishna and Patil, 1984; Marcus and Kertes, 1969; Kertes, 1971; Mathur, 1983). Synergism occurs in systems often involving an acidic extractant (HX) and a neutral extractant (S). Understanding and controlling synergic interactions of combined extractants is critical in order to develop efficient separation systems. The primary cause for synergism is generally accepted to be an increase in hydrophobic character of the extracted metal complex in the presence of the mixture of extractants. It has been established that mixed complexes are formed where both extractants are coordinated to the metal ion (Lumetta et al., 2010; Slavetskii et al., 1989; Johnson, 2014). Synergism may have several origins and different mechanisms have been proposed: (i) the second ligand (S) displaces any residual coordinated water molecule from the metal ion complex formed with the first ligand (HX) thus making it more lipophilic (Eq. (1)) (Irving and Edgington, 1960; Kandil et al., 1975); (ii) the second ligand (S) displaces

Abbreviations: DFT, density functional theory; DIAMEX-SANEX, diamide extraction – selective actinide extraction; DMDOHEMA, *N,N'*-dimethyl-*N,N'*-dioctylhexylethoxymalonamide; ESI-MS, electrospray ionization mass spectrometry; EXAFS, extended X-ray absorption fine structure; EXAm, extraction of americium; GANEX, group actinide extraction; HDEHP, di(2-ethylhexyl)phosphoric acid; HDHP, dihexylphosphoric acid; HDMP, dimethylphosphoric acid; NMR, nuclear magnetic resonance; PUREX, plutonium uranium extraction; SWAXS, small and wide angle X rays scattering; TMMA, *N,N,N',N'*-tetramethyl malonamide; TPH, hydrogenated tetrapropylene; TRLIFS, time-resolved laser-induced fluorescence spectroscopy; XAS, X-ray absorption structure.

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the molecule of the first ligand (HX) in the metal coordination sphere (Eq. (2)) (Liem and Dyrssen, 1966); (iii) addition of the second ligand (S) leads to an expansion of the coordination sphere of the metal ion (Eq. (3)) (Kandil et al., 1975; Bhatti, 1980). Fundamental chemistry underlying mixed solvents combining acidic extractants with neutral extractants is complex and not well understood yet.



In this study, a system combining an acidic extractant: HDEHP (di(2-ethylhexyl)phosphoric acid, abbreviated HL) with a neutral extractant: DMDOHEMA (*N,N'*-dimethyl-*N,N'*-dioctylhexylethoxymalonamide, abbreviated D), both dissolved in an aliphatic diluent (Fig. 1), was studied. This system was chosen for its application in nuclear fuel reprocessing where it is used to extract actinides and lanthanides from aqueous solutions (Baron et al., 2001; Madic et al., 2002; Miguiditchian et al., 2007; Poinssot et al., 2012; Montuir et al., 2012; Pacary et al., 2012; Rostaing et al., 2012). In an effort to further decrease radiotoxicity of the nuclear liquid waste, several hydrometallurgical processes have been developed by the French 'commissariat à l'énergie atomique et aux énergies alternatives' (CEA) (Poinssot et al., 2012; Warin, 2007). Following the PUREX (plutonium uranium extraction) process in the recycling scheme, the DIAMEX-SANEX (diamide extraction – selective actinide extraction) process was developed to recover minor actinides americium and curium. A modification of the DIAMEX-SANEX process, called the EXAm (americium extraction) process, was designed to solely recover americium from PUREX raffinates (Montuir et al., 2012; Pacary et al., 2012; Rostaing et al., 2012; Vanel et al., 2012; Muller et al., 2011). The GANEX (group actinide extraction) process was developed for an homogenous recycling of actinides following dissolution of the spent fuel. The second cycle of the GANEX process is based on an adaptation of the DIAMEX-SANEX process to separate transuranic elements (Miguiditchian et al., 2007; Miguiditchian et al., 2009). The DIAMEX-SANEX, the EXAm and the second cycle of the GANEX process utilize an organic phase which combines DMDOHEMA and HDEHP, usually with concentrations of about 0.6 M and 0.3 M respectively in TPH. Under highly acidic aqueous conditions ($[HNO_3] > 3 \text{ mol L}^{-1}$), both actinides(III) and lanthanides(III) are extracted into the organic phase. The An(III) ions can then be selectively recovered by back-extraction into the aqueous phase employing an actinide selective complexing agent at lower acidity ($pH \approx 3$) while the Ln(III) ions remain in the organic phase (Madic et al., 2002; Muller et al., 2011; Baron et al., 2001). The DMDOHEMA extracts An(III) and Ln(III) with a solvation number between 2 and 4 depending on multiple parameters such as temperature, acidity and metal ion concentration (Ellis et al., 2013; Ellis et al., 2014; Charbonnel et al., n.d.; Gannaz et al., 2006; Gannaz et al., 2007;

Meridiano, 2009). It is also known to form reversed aggregates from 4 up to 10 molecules in alkanes depending on the experimental conditions (Ellis et al., 2013; Ellis et al., 2014; Bosland, 2006; Meridiano et al., 2009; Guilbaud & Zemb, 2012; Gannaz, 2006; Guilbaud & Zemb, 2015). The main features of HDEHP are formation of hydrogen-bonded dimers in alkanes (Kolarik, 2010; Buch et al., 2002) and extraction of An(III) and Ln(III) by three dimers at low acidity: $M(L.HL)_3$ (Lumetta et al., 2010; Peppard et al., 1957; Kandil & Farah, 1980; Jensen et al., 2001; Leclerc et al., 2008; Grimes et al., 2012a; Grimes et al., 2012b; Zalupski & Nash, 2008; Marie et al., 2012).

Literature concerning the behavior of these two extractants used jointly is quite limited (Antonio et al., 2008; Berthon et al., 2010). In a previous study, D-HL organic solutions were investigated after lanthanide extraction (Muller et al., 2016). Synergistic and antagonistic effects were observed depending on experimental conditions (acid or metal concentration). The change in extracting properties of this system was explained by the presence of several competitive equilibria: formation of a D-HL adduct resulting in an antagonistic effect and formation of M-D-HL ternary complexes responsible for the synergistic extraction. Knowing the mixed metal ion species coordination structure would help define their extracting properties and better understand the synergistic effect observed on extraction. In the present paper, focus is placed on the characterization of Eu(III) and Nd(III) coordination sphere in the presence of both extractants in the organic phase. To characterize these metal ion species, structural changes induced by the variation of the ratio of extractants were investigated using several spectrometric techniques combined with theoretical calculations.

2. Experimental

The two reagents HDEHP ($\geq 97\%$) and DMDOHEMA ($\geq 99\%$) were purchased from Sigma-Aldrich and Pharmasynthese (Lisses, France) while hydrogenated tetrapropylene (TPH) was supplied by Novasep SAS and used as received. Europium nitrate ($\geq 99.9\%$) and neodymium nitrate ($\geq 99.9\%$) were purchased from Alfa Aesar and Fluka.

Spectrometry techniques used in this study, UV-Visible, electrospray ionization mass spectrometry (ESI-MS), time-resolved laser-induced fluorescence spectroscopy (TRLIFS), and nuclear magnetic resonance, were described in a previous publication (Muller et al., 2016).

For each technique, the initial organic solution of 0.6 M DMDOHEMA or 0.3 M HDEHP in TPH was prepared by weight and contacted to an equal volume of 0.01–0.04 M $Ln(NO_3)_3$ in 0.05 M HNO_3 as the aqueous phase. Phases were shaken together on a vortex for 15 min (2000 rpm) and centrifuged for 5 min (4000 rpm) at room temperature (23 °C). The organic phase was separated and analyzed. For UV-Vis and TRLIFS techniques, small aliquots of the other ligand were directly added to the quartz cuvette containing the initial organic solution and shaken on a vortex for 2 min. For NMR and ESI-MS studies, the organic solution was kept in a glass vial. After a small aliquot of pure ligand was added,

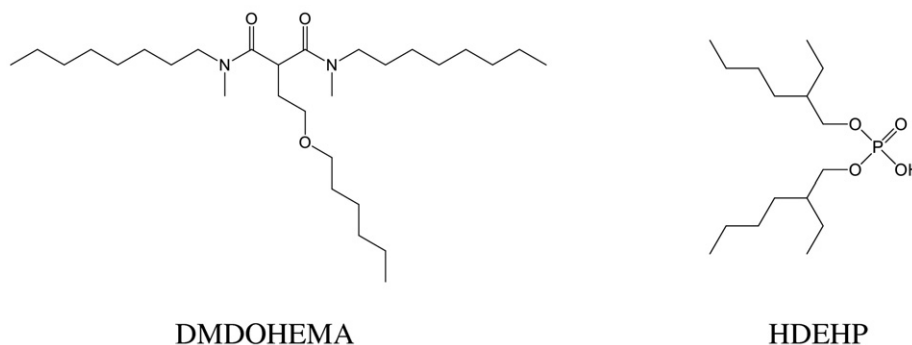


Fig. 1. Semi-developed formula of DMDOHEMA and HDEHP molecules.

the vial was shaken on a vortex for 2 min and a sufficiently large volume of solution was taken for analysis. This was repeated for each addition of pure ligand until no further spectral changes were observed. All quantities were measured by weight.

2.1. X-ray absorption structure (XAS) data collection and analysis

The Eu(III) L_3 -edge spectra were collected in fluorescence mode at beamline 12-BM-B (Beno et al., 2001) (Advanced Photon Source (APS), Argonne National Laboratory), with multielement Ge detector (Canberra). Incident X-ray energy was calibrated using the inflection point energy of the K-edge of Fe foil (7.112 keV) being close to the L_3 -edge energy of Eu (6.977 keV). Micro X-cells (SPEX 3577) fitted with Kapton® film windows (7.5 μm gauge, Chemplex Industries, No. 440) were used for data acquisition. Three one-hour scans to $k_{\text{max}} = 11 \text{ \AA}^{-1}$ were averaged. All $k^3\chi(k)$ EXAFS analysis was performed in identical fashion using EXAFSPAK (For documentation and availability, see <http://www-srsl.slac.stanford.edu/exafspak.html>). Curve-fitting was performed using theoretical phase and amplitude functions calculated with FEFF8.01 (Rehr and Albers, 2000) and a fixed scale factor ($S_0^2 = 0.9$). Errors in coordination numbers calculated for EXAFS are typically at least ± 1 , regardless of the statistical error computed from FEFF (the program used in solving the EXAFS equation). Therefore, EXAFS errors that were computed below 1 are all quoted as 1. In this sense, the quotation of coordination numbers to one decimal place is statistically valid based on the fitting, but in practice the reliability of EXAFS in calculating physical coordination numbers is at least ± 1 so this is used as the error. All other errors are quoted directly from the solution to the fitting of the EXAFS data, corresponding to the last significant figure of the quoted value.

2.2. Theoretical calculations

Geometries of metal complexes were optimized at the density functional theory (DFT) level with the Gaussian 09 software (Frisch et al., 2009). Becke's hybrid functional (B3LYP) was employed. Optimized geometries were characterized by harmonic frequency analysis as local minima. Calculations were done in the presence of a continuum solvent model corresponding to *n*-dodecane. For lanthanides, the 4f-in-core relativistic effective core potential (RECP) and the corresponding basis set suggested by Dolg et al. were used (Dolg et al., 1989). A 6-31 + G(d,p) basis set was employed for other atoms. To reduce computational time, alkyl chains were replaced by methyl groups: dimethylphosphoric acid (HDMP) to represent HDEHP and *N,N,N',N'*-tetramethyl malonamide (TMMA) to model DMDOHEMA (Fig. 2).

3. Results

To understand the role of each extractant in metal ion complexes, various spectrometric methods were used to probe the coordination sphere of the metal ion complexed by one extractant and the changes induced by addition of the other extractant to the solution.

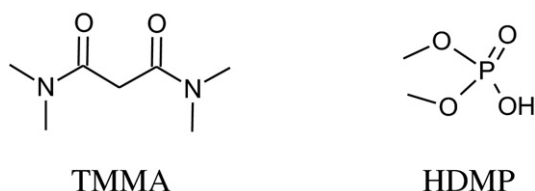


Fig. 2. Semi-developed formula of TMMA and HDMP molecules.

3.1. Addition of DMDOHEMA to HDEHP-Metal ion solution

The effect of adding DMDOHEMA to an HDEHP organic phase after metal extraction was investigated. Analyses were performed on HDEHP organic solutions after extraction of Nd(III) or Eu(III) from a low acidic aqueous phase (0.05 M HNO_3) to form known $\text{M}(\text{L})_3(\text{HL})_3$ complexes. Increasing amounts of malonamide ligand were then added to the organic phase.

3.1.1. ESI-MS

The Nd(III)-HL solutions were first analyzed by ESI-MS after each addition of malonamide. The ESI-MS gives information on the stoichiometry of metal-ligand species in the gas phase and has been used to characterize similar systems before (Ellis et al., 2014; Leclerc et al., 2008; Marie et al., 2012; Antonio et al., 2008; Berthon et al., 2010). Stability studies (skimmer voltage and MS/MS spectra) of ions give information about possible existence and stable complexes in solution. Spectrum of the initial organic phase displays expected $\text{Nd}(\text{L})_2(\text{HL})_y^+$ ions ($y = 2$ to 4) which correspond to ionization of $\text{Nd}(\text{L})_3(\text{HL})_3$ complexes in the gas phase. These species are no longer observed after addition of DMDOHEMA to the organic solution, replaced by mixed ions containing both ligands (Fig. 3, all ions detected are listed in Table A-1 in Appendix). Increase of skimmer voltage confirmed stability of the mixed ions and suggests that they are possible species in solution. Fragmentation spectra of mixed Nd(III) species are similar to those obtained in the previous study (Muller et al., 2016): for high stoichiometry species ($[\text{NdD}_2\text{L}_2]^+$, $[\text{NdD}(\text{HL})\text{L}_2]^+$ $[\text{NdD}_3\text{L}]^+$) departure of a ligand molecule (DMDOHEMA or HDEHP) is observed until $[\text{NdDL}_2]^+$ or $[\text{NdD}_2\text{L}]^{2+}$ ions are obtained. A loss of alkyl chain of either DMDOHEMA or HDEHP is observed after fragmentation of $[\text{NdDL}_2]^+$ or $[\text{NdD}_2\text{L}]^{2+}$. This indicates that DMDOHEMA molecules are present in the metal coordination sphere together with HDEHP and give mixed species more stable than M-HL complexes.

3.1.2. UV-Visible

The Nd(III)-HL organic solution was analyzed by UV-Visible spectrophotometry as well. Changes in the spectra after addition of DMDOHEMA to the Nd-HL solution (Fig. 4) indicate changes in the metal ion coordination environment. Several isosbestic points are observed (at 572, 603, 734, 762 and 786 nm), indicating that two Nd-containing species are present in solution. Knowing that the initial species is the $\text{Nd}(\text{L})_3(\text{HL})_3$ complex and that mixed species were observed by ESI-MS, the second species could be a mixed complex involving both ligands.

3.1.3. TRLIFS

To investigate further the direct environment around the metal ions, TRLIFS was used. Fluorescence emission spectra of Eu(III) species after addition of pure diamide to the Eu(III)-HL initial organic solution display an isosbestic point around 612 nm (Fig. A-1 in Appendix). This is consistent with UV-Vis results and indicates formation of one new species. The calculated relative intensity of the two transition bands ($^5\text{D}_0 \rightarrow ^7\text{F}_2$ observed around 616 nm and $^5\text{D}_0 \rightarrow ^7\text{F}_1$ observed at 592 nm) $I_{616\text{nm}}/I_{592\text{nm}}$ increases from 1.4 to 1.7 for 0.01 M of DMDOHEMA added and up to 2.0 for 1 M added (Table A-2 in Appendix). Such an increase indicates modification in the coordination sphere of the metal ion, even with a small amount of malonamide added ($[\text{D}]/[\text{HL}] = 1/30$). A variation in Eu(III) lifetime depending on the concentration of added diamide is observed as well (Table A-2 in Appendix and Fig. 5). The slight increase for the first additions cannot be attributed to departure of water molecules due to the non-negligible error on the measure ($\pm 5\%$ on lifetime). But the subsequent fluorescence lifetime tendency to decrease, in both HNO_3 and DNO_3 media, indicates that an inhibitory molecule is entering Eu(III) first coordination sphere. The DMDOHEMA molecule is a plausible inhibitory molecule and can

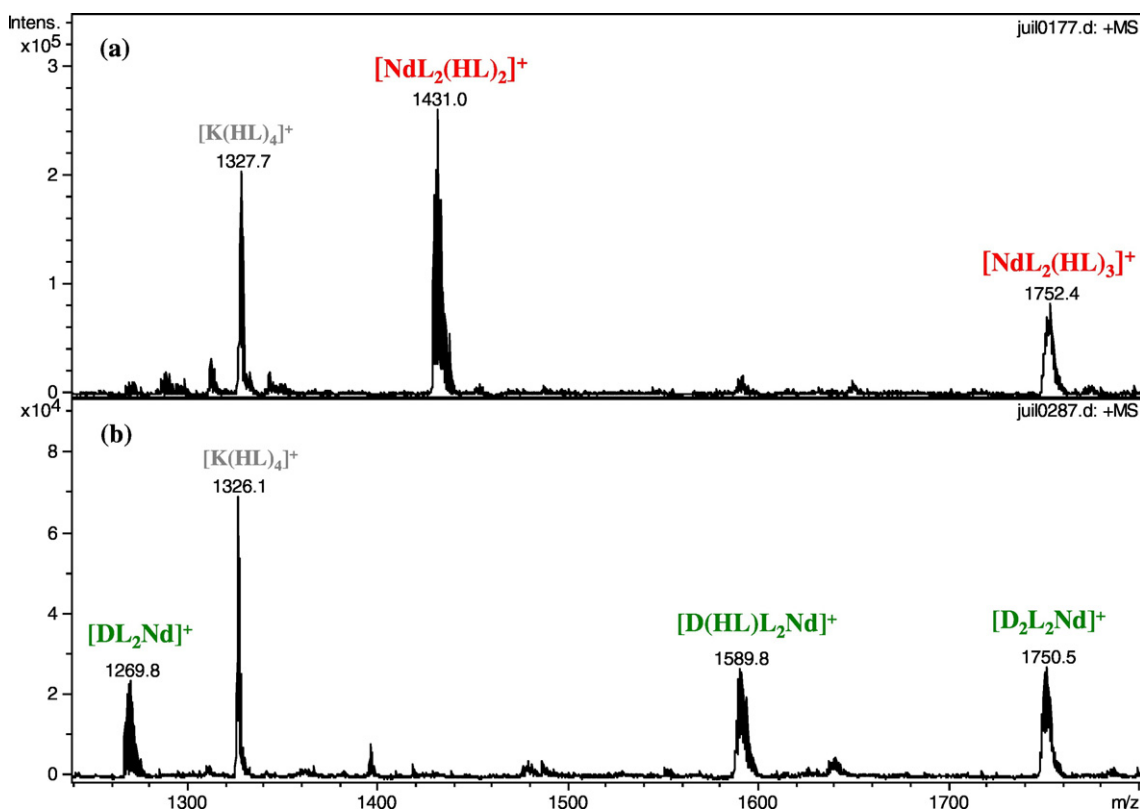


Fig. 3. (a) ESI-MS spectra of an HDEHP organic phase after Nd(III) extraction and (b) addition of 0.02 M DMDOHEMA. The concentrations of Nd(III) and HDEHP were 0.015 M and 0.3 M in TPH. Skimmer 1 of 70 V. The species observed at $m/z = 1326-1327$ is assigned to a parasite ion $[K(HL)_4]^+$ formed during the ionization process.

bond Eu(III) upon its addition to the organic phase thus forming mixed species as suggested previously.

All results are consistent: when DMDOHEMA is added to the lanthanide-HDEHP solution, a molecule of malonamide enters the metal ion coordination sphere in the $Ln(L)_3(HL)_3$ complex. Two possibilities have to be considered: 1/HDEHP molecules leave the coordination sphere to make enough room for DMDOHEMA to bond the metal ion; or 2/ DMDOHEMA adds to the inner-sphere without displacing HDEHP (6 molecules of HDEHP would occupy 6 coordination sites, leaving enough room in the inner sphere to add one more ligand molecule).

3.1.4. NMR

To quantify the number of HDEHP molecules involved in metal species, ^{31}P nuclear magnetic resonance spectrometry (NMR) was used.

Previous studies by Marie et al. (Marie et al., 2012) on Eu-HDEHP complexes showed that the rate of ligand exchange in the $Eu(L)_3(HL)_3$ complex is slow (as measured at the NMR time scale). Two peaks can be observed and assigned to free or complexed HDEHP molecules. Estimation of the number of phosphorus ligands involved in complexes is possible through integration of those peaks. Spectra obtained after addition of pure malonamide to the Eu-HDEHP complex can be found in Supporting Information (Fig. A-2). The initial Eu-HDEHP spectrum (no malonamide) shows two peaks at 0 ppm and -126 ppm which confirms that free and bonded HDEHP are in a slow exchange mode. The free HDEHP signal increases in intensity when increasing the concentration of malonamide. This indicates that one or several HDEHP molecules come off the Eu-HDEHP complex leaving enough space for DMDOHEMA molecules to form Eu-DMDOHEMA-HDEHP complexes. The HDEHP

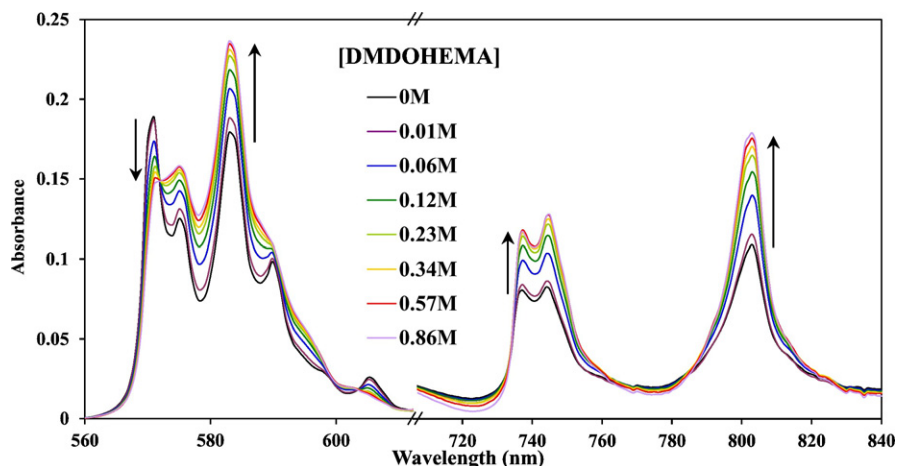


Fig. 4. UV-Visible spectra of Nd(III)-HDEHP solution with progressive addition of pure DMDOHEMA. The concentrations of Nd(III) and HDEHP were 0.015 M and 0.3 M in TPH.

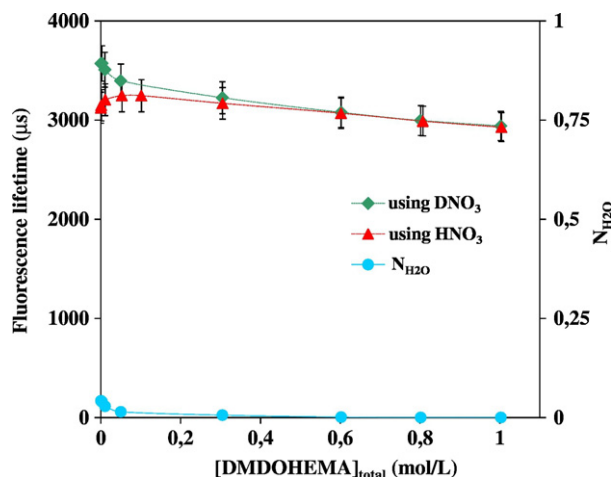


Fig. 5. Fluorescence lifetime of europium after extraction by HDEHP from a 0.05 M HNO₃ or DNO₃ aqueous phase and addition of DMDOHEMA. The concentrations of Eu(III) and HDEHP were 0.01 M and 0.3 M in TPH.

release mechanism is slow at the NMR time scale. The fact that the bonded HDEHP peak is not split into two peaks means that complexes involving different HDEHP sites are in a fast exchange mode in solution. As previously observed (Muller et al., 2016), this peak is assigned to both Eu-HDEHP and Eu-HDEHP-DMDOHEMA ³¹P sites and a fast chemical exchange involving malonamide molecules and Eu-HDEHP complexes would be most likely occurring.

The number of HDEHP molecules involved in metal ion complexes was calculated for each addition (Table 1); it decreases from 6.0 ± 0.6 with no malonamide, which is consistent with the literature data (Lumetta et al., 2010; Peppard et al., 1957; Kandil & Farah, 1980; Jensen et al., 2001; Leclerc et al., 2008; Grimes et al., 2012a; Grimes et al., 2012b; Zalupski & Nash, 2008; Marie et al., 2012; Antonio et al., 2008), down to 4.9 ± 0.5 for a 0.6 M DMDOHEMA concentration. Assuming that the mixed complex is the only metal ion species present after the last addition, five HDEHP ligands are involved in this complex and one HDEHP molecule left the metal ion environment.

The concentrations of Eu(III) and HDEHP were 0.04 M and 0.3 M in deuterated *n*-dodecane.

3.1.5. EXAFS

The Eu(III) L₃-edge EXAFS data were collected from the series by adding DMDOHEMA to the 0.3 M HDEHP-Eu(III) organic phase. The phase shift corrected FT data are shown in Fig. 6. The data were fitted with a 2-shell O,P model to account for the peaks at $r = 2.3$ and 3.8 Å, respectively, yielding good fits in all cases (Fig. A-3 in Appendix). The coordination number of P is indicative of the number of HDEHP molecules coordinating to the inner-sphere and this ranges between 6.8 and 5.7 (Table 2). Coordination numbers determined using EXAFS have an error of at about 10%, that is around ± 1 so that, unless there is a systematic change in coordination number that correlates with a systematic change in bond length, one cannot confidently draw conclusions. Although The EXAFS is not precise enough to detect the displacement of one HDEHP from the inner-sphere, a decrease in the coordination number of P is observed upon the addition of

Table 1

Number of HDEHP molecules bonded to Eu(III) as a function of pure DMDOHEMA concentration added to the Eu-HDEHP organic solution.

[DMDOHEMA] (mol L ⁻¹)	Number of HDEHP molecules bonded to Eu(III)
0.0	6.0 ± 0.6
0.1	5.8 ± 0.6
0.3	5.7 ± 0.6
0.6	4.9 ± 0.5

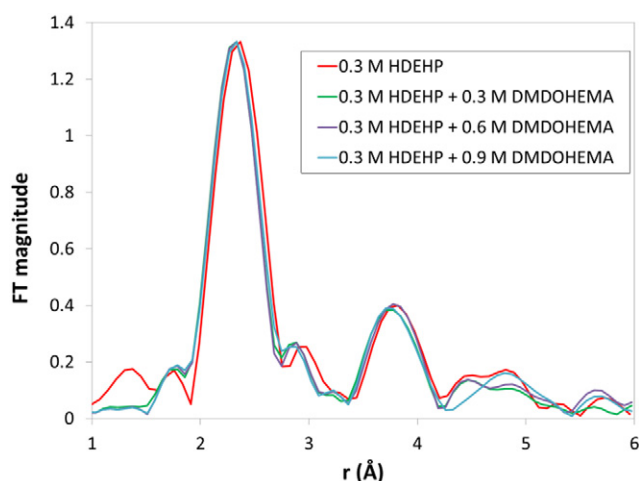


Fig. 6. Fourier transforms of EXAFS data for europium species after extraction by HDEHP from a 0.05 M HNO₃ aqueous phase and progressive addition of pure DMDOHEMA. The concentrations of Eu(III) and HDEHP were 0.01 M and 0.3 M in dodecane.

malonamides with a decrease of the Eu—P bond distance from 3.849 to 3.818 Å (bond lengths calculated from EXAFS are generally accurate up to 0.003 Å).

Focusing now on the inner-sphere oxygen, the EXAFS data fitting shows a systematic increase in coordination number of oxygen in the inner-sphere from 5.7 to 6.6 that correlates with a lengthening of the Eu—O bond distance from 2.290 to 2.307 Å. This confirms that addition of DMDOHEMA is impacting the inner-coordination sphere, but the mechanism is not clear. It could be that DMDOHEMA displaces HDEHP from the inner-sphere, but the extent of displacement is insufficient to show a systematic decrease in the phosphorus coordination number. According to the NMR results above, the change in phosphorus coordination number in this concentration range would only be expected to be about -1, which is within the margin of error. Alternatively, the increase in oxygen coordination number and bond length, along with the apparently constant phosphorus coordination number and bond length, might suggest that DMDOHEMA adds to the inner coordination sphere without displacing HDEHP.

3.1.6. DFT calculations

Geometries of the proposed species (ML₃(HL)₃; ML₃(HL)₃D and ML₃(HL)₂D) were optimized from DFT calculations for Nd(III) and Eu(III). The HDEHP and DMDOHEMA molecules were modeled using short alkyl chains ligands HDMP (dimethylphosphoric acid) and TMMA (*N,N,N',N'*-tetramethylmalonamide). For Ln(III)-HDMP species, it is assumed that the metal ion is coordinated to three HDMP and three DMP⁻ ligands, as obtained from experimental data. Two

Table 2

Summarized metrics with a two-shell O, P model fit EXAFS data for europium species after extraction by HDEHP from a 0.05 M HNO₃ aqueous phase and addition of pure DMDOHEMA.

	DMDOHEMA (mol L ⁻¹)			
	0	0.3	0.6	0.9
CN ^a (O)	5.7(10)	6.0(10)	6.2(10)	6.6(10)
CN ^a (P)	6.8(10)	5.8(10)	5.7(10)	5.8(10)
r ^b (Eu—O) (Å)	2.290(4)	2.295(4)	2.295(3)	2.307(3)
r ^b (Eu—P) (Å)	3.849(13)	3.805(8)	3.816(6)	3.818(6)
σ ^{2c} (O) (Å ²)	0.0045(5)	0.0057(6)	0.0056(4)	0.0067(4)
σ ^{2c} (P) (Å ²)	0.013(2)	0.011(1)	0.010(1)	0.011(2)

The concentrations of Eu(III) and HDEHP were 0.01 M and 0.3 M in dodecane. Error is given in brackets corresponding to the last significant figure.

^a CN is the coordination number.

^b r is bond length in angstroms (1 Angstrom = 10⁻¹⁰ m).

^c σ² is the Debye – Waller factor.

Table 3

Average Ln-O and Ln-P distances (Å) in Nd(III) and Eu(III) complexes with HDMP and TMMA calculated using B3LYP density functional.

Complex	CN(O) ^a	Number of ligands ^b	r(Nd—O) (Å)	r(Nd—P) (Å)	r(Eu—O) (Å)	r(Eu—P) (Å)
M(L) ₃ (LH) ₃	6	6 L _{mono}	2.383	3.821	2.333	3.774
M(L) ₂ (LH) ₃	7	5 L _{mono}	2.412	3.868	2.366	3.801
M(L) ₃ (LH) ₃ D	7	1 L _{bid}	2.566	3.113	2.523	3.072
		6 L _{mono}	2.429	3.884	2.384	3.802
M(L) ₃ (LH) ₃ D	8	1 D _{mono}	2.494	–	2.451	–
		6 L _{mono}	2.460	3.879	2.414	3.837
M(L) ₂ (LH) ₃ D	6	1 D _{bid}	2.574	–	2.539	–
		5 L _{mono}	2.375	3.815	–	–
M(L) ₂ (LH) ₃ D	7	1 D _{mono}	2.393	–	–	–
		5 L _{mono}	2.399 2.536	3.860	2.360	3.793
		1 D _{bid}			2.475	

L and D stand for DMP and TMMA, respectively.

^a CN(O) is the oxygen coordination number.^b L_{mono} and D_{mono} refer to monodentate ligands, L_{bid} and D_{bid} refer to bidentate ligands.

geometries were optimized: one with six monodentate HDMP/DMP[−] ligands and one with five monodentate and a single bidentate ligand. Two stable structures with no imaginary frequencies were obtained. Optimized distances are collected in Table 3. Calculated distances with Eu(III) are in very good agreement with EXAFS distances for the structures with six monodentate ligands (Table 2). A very good agreement is also found with EXAFS distances reported for Nd(III)-HDHP (dihexylphosphoric acid) (Gannaz et al., 2006). The average EXAFS-determined Nd—O and Nd—P distances were 2.39 Å and 3.94 Å, respectively, whereas calculated distances are 2.38 Å and 3.82 Å for the structure with six monodentate ligands. According to the calculations, the presence of a bidentate DMP[−] ligand induces an increase and a significant splitting of M—O and M—P distances. This splitting is not observed on EXAFS spectra. These results are consistent with the predominant formation of a MO₆ coordination with six monodentate ligands, as reported from the EXAFS analysis (Gannaz et al., 2006). The optimized molecular structure is shown in Fig. 7a.

Geometries corresponding to the formation of mixed species with TMMA in the lanthanide inner coordination sphere were further optimized. Two different coordination environments were considered and several structures were obtained (Table 3). The first coordination environment corresponds to the addition of a TMMA ligand and results in seven monodentate molecules in the coordination sphere (Fig. 7b as an example). In the second coordination environment, one diamide coordinates the metal ion and repels one HDMP molecule to the outer coordination sphere; this results in six molecules in the inner coordination sphere (Fig. 7c as an example). In the optimized structures, HDMP are monodentate while diamide are either mono- or bidentate. The number of oxygen coordinated to the lanthanide cation varies from 6 to 8. As can be seen in Table 3, a change in first-shell coordination number is systematically associated with a significant change of M—O and M—P

distances. To discriminate between the two coordination environments, we turn to EXAFS results. No significant changes are observed on EXAFS spectra upon TMMA addition and the fitted M—O distances remain very similar. The only mechanism that can be consistent with EXAFS and calculated distances corresponds to the replacement of one HL ligand by a monodentate diamide with HDMP and HDMP-TMMA species being both MO₆. This is consistent with NMR results, which points to the replacement of one HDEHP molecule upon DMDOHEMA addition.

We further computed energy variation associated with both mechanisms. The first mechanism is represented by Eq. (4):



In the second mechanism, a HDMP ligand is expelled to the outer coordination sphere as described in Eq. (5):



Enthalpy and free energy variation were calculated at the DFT level for both reactions (Table 4). Such energy values determined using quantum chemical methods are only qualitative. In the calculations, the malonamide is considered as monodentate. Solvent effects beyond the inner shell are only described using a dielectric continuum model and configurational entropy is not determined from such calculations. However, they are useful to probe the steric hindrance in the lanthanide inner coordination sphere and get the driving force for the mixed species formation. According to results listed in Table 4, enthalpy variation is negative for both ions and both reactions by a few tenths of kJ mol^{−1}. It is more negative for the first reaction corresponding to the addition of a diamide in the coordination sphere and inducing an increase of the coordination number. This indicates that the coordination sphere of the

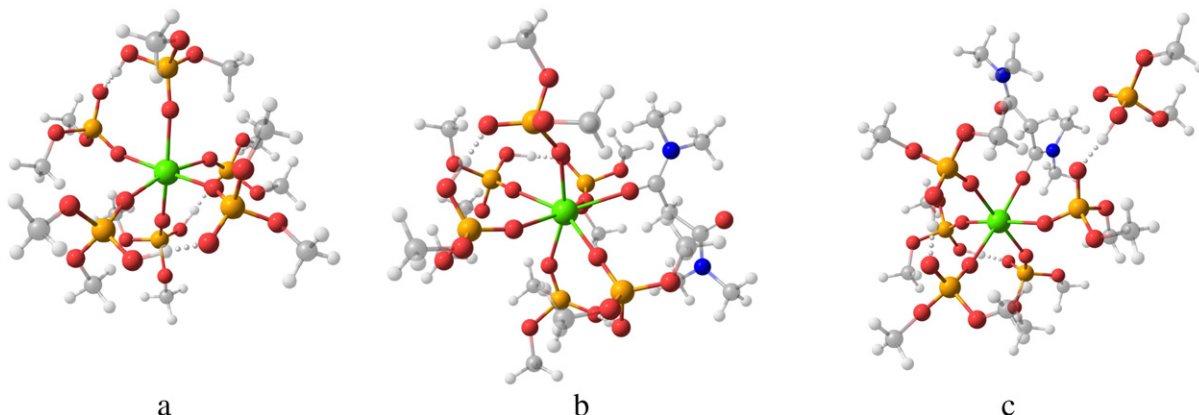


Fig. 7. Optimized structure of Nd(L)₃(HL)₃ (a) Nd(L)₃(HL)₃D_{mono} (b) Nd(L)₃(HL)₂D_{mono}...HL (c).

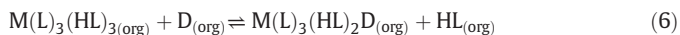
Table 4

Calculated enthalpy and free energy differences at the DFT level corresponding to Eqs. (4) and (5).

	Enthalpy and free energy (kJ mol ⁻¹)	Nd		Eu	
		H	G	H	G
Eq. (4)	M(L) ₃ (HL) ₃ + D → M(L) ₃ (HL) ₃ D	-22	+42	-15	+54
Eq. (5)	M(L) ₃ (HL) ₃ + D → M(L) ₃ (HL) ₂ D...HL	-14	+31		

metal ion is not saturated and could accommodate an additional ligand. Free energy variations become positive because of strong loss of entropy following the metal-diamide bonding. The entropy loss is lower for the second reaction because of departure of one HDMP ligand from the inner sphere. As expected, there is a strong entropy gain in the second reaction due to the release of one ligand from the coordination sphere. Consequently, free energy variations become more favorable for the second reaction, even though free energy variations are positive for both reactions at this level of calculations that does not include configurational entropy. These results indicate that preference for the replacement of a HDMP ligand by a diamide rather than its addition is controlled by entropic effects.

Considering results obtained from various techniques, it appears that addition of malonamide to Ln-HDEHP complexes leads to formation of a new species. The DMDOHEMA seems to take the place of one HDEHP molecule in Ln-HDEHP complexes, forcing their decomplexation and forming mixed complexes. A neutral HDEHP molecule is more likely to leave the complex than a deprotonated one as free charged species are not encountered in alkanes. The corresponding equilibrium can be written as follows:



$$\text{with } K'_{1,5} = \frac{[M(L)_3(HL)_2D]_{(org)}[HL]_{(org)}}{[M(L)_3(HL)_3]_{(org)}[D]_{(org)}}$$

where HL is the monomeric HDEHP molecule, and D the DMDOHEMA molecule.

3.1.7. Formation constant calculation

Due to the presence of isosbestic points, UV-Visible spectroscopy data for Nd-HDEHP-DMDOHEMA solutions were analyzed considering two species: a single initial complex Nd(L)₃(HL)₃ and a single final mixed complex Nd(L)₃(HL)₂(D). Initial and final spectra were assigned to these two species and intermediate spectra are calculated through a combination of these two spectra according to the following equation:

$$A_\lambda = x_1 \cdot A_{1,\lambda} + x_2 \cdot A_{2,\lambda} \quad (7)$$

where A_λ represents the total absorbance at wavelength λ, x₁ and x₂ the mole fractions of species 1 and 2 in solution and A_{1,λ} and A_{2,λ} the absorbance of species 1 and 2 at wavelength λ. Mole fractions were calculated by optimization of the errors between calculated and experimental spectra. The concentration of each complex was calculated and the formation constant determined to be: log K'_{1,5} = 0.7 ± 0.1. Evolution of the proportion of each complex in solution can be seen Fig. A-4.

3.2. Addition of HDEHP to DMDOHEMA-Metal ion solution

The influence of HDEHP on Ln-DMDOHEMA complexes was investigated the same way the influence of DMDOHEMA on Ln-HDEHP complexes was studied. After extraction of Nd(III) or Eu(III) by DMDOHEMA from a 0.05 M HNO₃ aqueous phase, aliquots of pure HDEHP were added to the organic solution and analyzed by various analytical techniques.

3.2.1. ESI-MS

Species including both extractant molecules are observed on ESI-MS spectra performed after addition of HDEHP aliquots to a Nd-DMDOHEMA organic solution (Fig. 8). Initially, the most intense peak is identified as the [D₂Nd(NO₃)₂]⁺ ion, probably coming from the Nd(NO₃)₃(DMDOHEMA)₂ complex in solution (Ellis et al., 2014; Charbonnel et al., n.d.; Gannaz et al., 2007; Muller et al., 2016). Addition of HDEHP gives rise to [D₂LNd(NO₃)₂]⁺, then [D₂L₂Nd]⁺ and [D₂L₂(HL)Nd]⁺ ions. The successive formation of these ions in the gas phase suggests that nitrates coordinated to the metal ion are being replaced by deprotonated HDEHP molecules. The three nitrates of Nd(NO₃)₃(DMDOHEMA)₂ could be replaced by 3 DEHP⁻ to form Nd(DEHP)₃(DMDOHEMA)₂ in solution. Another initial ion, [D₃Nd(NO₃)₂]⁺, may be obtained by ionization of Nd(NO₃)₃(DMDOHEMA)₃ species. Indeed, it is well known that several Ln-DMDOHEMA complexes can be formed in solution (Ellis et al., 2014; Charbonnel et al., n.d.; Gannaz et al., 2007; Muller et al., 2016). Consequently, the [D₂L₂(HL)Nd]⁺ ion could also come from the [D₃Nd(NO₃)₂]⁺ ion where one DMDOHEMA molecule is replaced by one protonated HDEHP and nitrate ions are replaced by deprotonated HDEHP molecules.

3.2.2. UV-Visible spectroscopy

Changes in the metal coordination sphere were identified after addition of HDEHP to Nd/Eu-DMDOHEMA solutions: UV-Visible spectra of Nd loaded organic phases show a decrease of intensity of characteristic peaks at 580, 740 and 800 nm as well as some changes in their shape and shift (Fig. A-5 in Appendix) indicating formation of new species.

3.2.3. TRLIFS

The fluorescence emission spectra of Eu(III) species were recorded (Fig. A-6 in Appendix) and their lifetime and hydration number were calculated (Fig. 9). Addition of HDEHP to the Eu-DMDOHEMA solution leads to a decrease in intensity of the 616 nm hypersensitive band (⁵D₀ → ⁷F₂ transition) while broadening with appearance of two or more indistinct bands. The relative intensity of the two transition peaks (I_{616nm}/I_{592nm}) decreases from 6 down to 3 (Fig. A-7 in Appendix) and europium species lifetime increases from 500 μs to about 2 ms, consistent with a decrease of europium hydration number from 1.2 (with no HDEHP) down to 0. These observations reflect a change in the environment of Eu(III) and can be interpreted by formation of new dehydrated species in solution. Experiments performed with an initial deuterated aqueous phase show an increase in Eu(III) lifetime although no H₂O molecule is present. Another inhibitory molecule leaving the metal ion coordination sphere is DMDOHEMA. This is consistent with the slight decrease of europium lifetime when DMDOHEMA enters the coordination sphere of Eu-HDEHP complexes (Fig. 5).

In the organic phase, multiple Ln-DMDOHEMA species in which the metal ion is surrounded by several molecules of DMDOHEMA, water and nitrates co-exist (Ellis et al., 2013; Ellis et al., 2014). Addition of HDEHP to a Ln-DMDOHEMA solution leads to new species in which HDEHP replaces water molecules and eventually nitrate ions in the Ln-DMDOHEMA complex, forcing departure of inhibitory diamide molecules. Geometry of these complexes was not optimized due to the possibility of multiple species.

4. Discussion

Solvent extraction of lanthanide(III) by a mixture of DMDOHEMA and HDEHP in TPH differs from the extraction by either of the ligands alone: a synergistic effect is observed on the distribution ratios (Muller et al., 2016). Use of the 'addition method' to characterize the organic phase by various and complementary analytical techniques showed existence of mixed metal species more stable than the one-ligand-species.

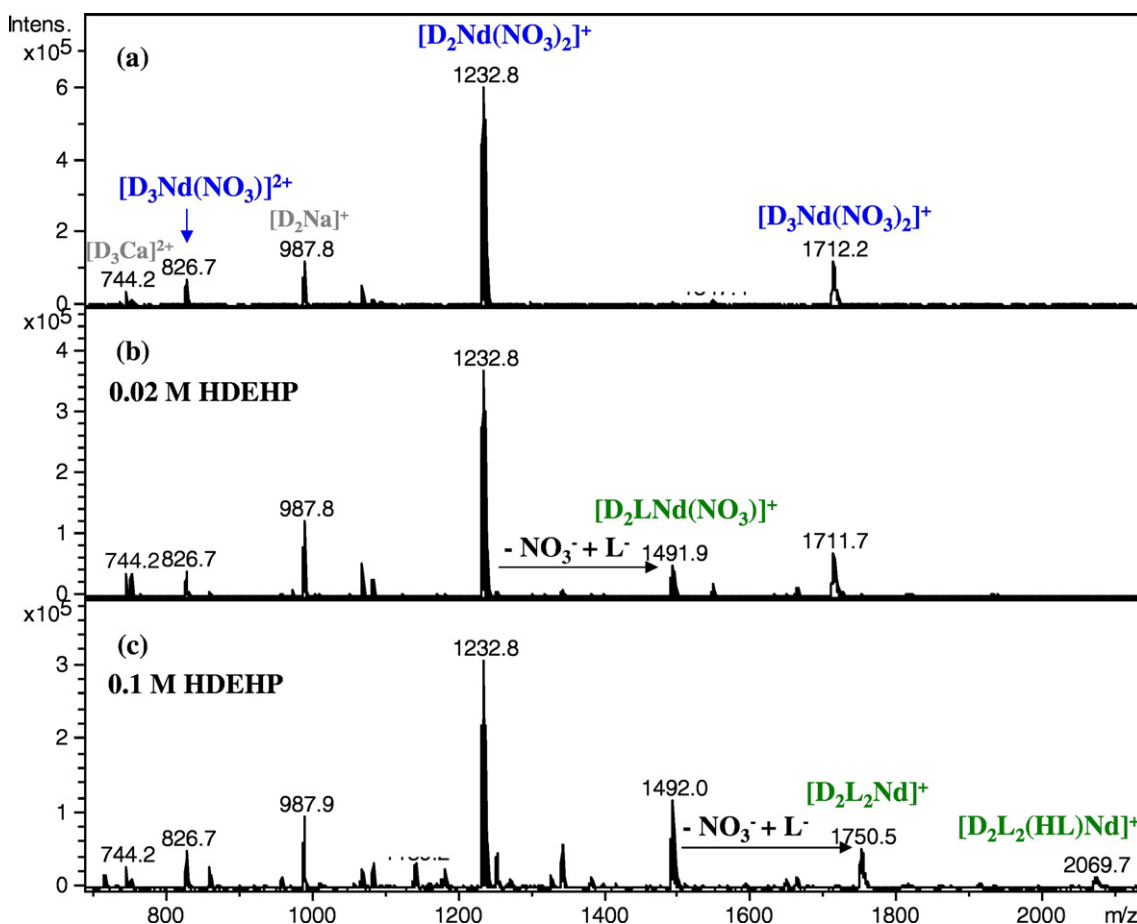


Fig. 8. ESI-MS spectra of DMOHEMA organic phases after Nd(III) extraction (a) and addition of 0.02 M (b) or 0.1 M (c) of HDEHP. The concentrations of Nd(III) and DMOHEMA were 0.01 M and 0.3 M in TPH, then diluted to 1/100 in EtOH. Skimmer 1 of 40 V. D = DMOHEMA, HL = HDEHP. $[D_3Ca]^{2+}$ and $[D_2Na]^+$ are parasite ions formed during the ionization process.

The HDEHP is a cation exchanger extractant. Metal ions are extracted from the aqueous phase through exchange of three protons to give $M(L)_3(HL)_3$ complexes in the organic phase and no water nor nitrates are transferred. Addition of diamide to that organic solution causes departure of a dialkylphosphoric acid molecule from the metal coordination sphere to form a non-hydrated mixed complex described by the equilibrium in Eq. (6).

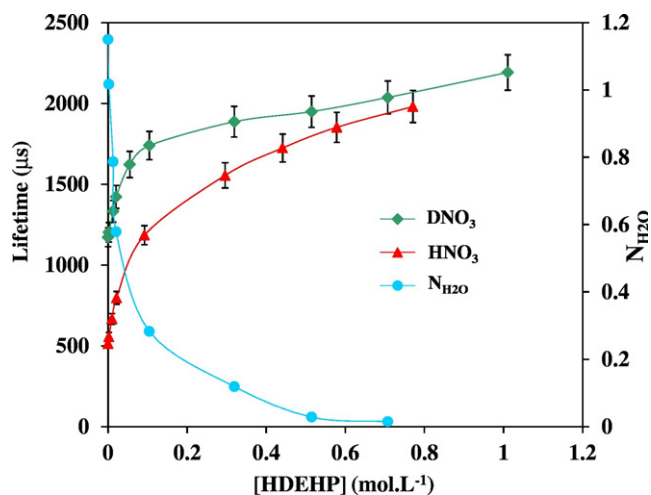
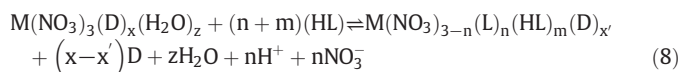


Fig. 9. Fluorescence lifetime of europium after extraction by DMOHEMA from a 0.05 M HNO_3/H_2O or DNO_3/D_2O aqueous phase, and addition of HDEHP. The concentrations of Eu(III) and DMOHEMA were 0.01 M and 0.6 M in TPH.

Addition of a monodentate malonamide to replace HDEHP molecule stabilizes the initial complex making it more extractible without increasing the coordination number.

When starting from a metal-loaded DMOHEMA organic solution, nitrate and water molecules are present in initial Ln-malonamide species. Diamide metal complexes are in the heart of aggregates slightly larger (Ellis et al., 2013; Ellis et al., 2014) than the complex. Aggregation makes it difficult to have an accurate representation of the extracted metal complexes. The stoichiometry considered here is $M(NO_3)_3(D)_x(H_2O)_z$ ($2 \leq x \leq 4$ and $1 \leq z \leq 2$). Addition of HDEHP to such a solution leads to formation of new mixed species by departure of water, diamide molecules and possibly nitrates replaced by HDEHP. The following equilibrium is suggested:



with $2 \leq x \leq 4$; $1 \leq z \leq 2$; $0 \leq n \leq 3$; $n+m \geq 1$ and $1 \leq x' \leq 3$.

This complex is thought to be more stable than DMOHEMA metal complexes due to addition of DEHP⁻ species to replace nitrate group and departure of water making it more lipophilic, thus more easily extractible.

For both systems described by Eqs. (6) and (8) synergism may be due to the formation of stronger mixed species formed by displacement of molecules due to the addition of a second ligand to complexes formed with the other ligand (DMDOHEMA is displacing HDEHP molecule or (H)DEHP is displacing nitrate, any residual coordinated water and DMOHEMA ligand). The noticeable difference between the two

experimental procedures is that an extraction starting with DMDOHEMA involves the co-extraction of nitrates with the cation, which is not the case when HDEHP is used first.

In real liquid-liquid extraction systems, like the DIAMEX-SANEX, GANEX or EXAM processes, An(III) and Ln(III) are extracted to the organic phase under high aqueous nitric acid concentrations, whereas separation of An(III) and Ln(III) is accomplished by contacting the loaded organic phase with a buffer aqueous phase maintained at pH 3 and containing a complexing agent (Muller et al., 2016). Thus, in the extraction conditions in which the nitrate concentration in aqueous phase is high ($>3 \text{ mol L}^{-1}$), the $\text{Ln}(\text{NO}_3)_{3-n}(\text{L})_n(\text{HL})_m(\text{D})_x$ quaternary species is favored. This is consistent with studies from Tkac and coworkers (Tkac et al., 2012) on the Ln- NO_3 -CMPO-HDEHP system where they observe that nitrates participate in the coordination sphere of the metal ion. Under low acidity conditions in aqueous phase, in which the nitrate concentration is negligible, the $\text{Ln}(\text{L})_3(\text{HL})_2(\text{D})$ species would be rather formed.

5. Conclusion

The HDEHP ligand is well known to form $\text{Ln}(\text{DEHP})_3(\text{HDEHP})_3$ organic complexes while DMDOHEMA is known to form $\text{Ln}(\text{NO}_3)_3(\text{DMDOHEMA})_x(\text{H}_2\text{O})_y$ species. The coordination environment of lanthanide complexes obtained after addition of DMDOHEMA to Ln-HDEHP complexes or addition of HDEHP to Ln-DMDOHEMA species was characterized by several spectroscopic techniques as well as theoretical calculations. Synergic extraction observed in some experimental conditions arises from the formation of mixed complexes containing both extractants, completely dehydrated under all investigated experimental conditions and stronger than M-HDEHP and M-DMDOHEMA complexes. These adducts are more hydrophobic and thus better extracted than the complexes of metal ions with single extractants. Depending on initial conditions, two different mechanisms are proposed for the formation of mixed complexes which are responsible for the synergistic effect.

In the absence of nitrate, addition of DMDOHEMA to Ln-HDEHP leads to Ln-HDEHP-DMDOHEMA ternary complexes. A ligand displacement reaction occurs without increasing the coordination number: a monodentate malonamide replaces a HDEHP molecule in the metal ion environment.

The addition of HDEHP to Ln- NO_3 -DMDOHEMA species leads to significant changes in the metal environment: quaternary complexes containing both extractants and nitrates are probably formed. The HDEHP ligand enters the lanthanide coordination sphere while displacing water molecules, DMDOHEMA and possibly nitrates.

Organic solutions based on malonamide and/or dialkylphosphoric acid are generally not molecular solutions but rather solution of structured extractant aggregates (Ellis et al., 2013; Ellis et al., 2014; Meridiano et al., 2009; Guilbaud & Zemb, 2015; Antonio et al., 2008; Ferru et al., 2014; Dejugnat et al., 2014a; Dejugnat et al., 2014b). Metal ion complexes are in the polar core of reverse-micelle-type aggregates. To further understand this synergistic system behavior, its characterization on a supramolecular scale would be helpful. Taking aggregates of extractant into consideration might give a better representation of the organic phase. Combining small and wide angle X rays scattering (SWAXS) experiments with theoretical calculation (Molecular dynamic simulations) will allow one to provide information about the speciation of such phases at both molecular and supramolecular scales (Ellis et al., 2014; Ferru et al., 2014; Rodrigues et al., 2014; Pecheur et al., 2016).

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.hydrmet.2017.02.012>.

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