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Laurence Berthon-Nigond, Amaury Paquet, Georges Saint-Louis, Philippe Guilbaud. How phase modifiers disrupt third-phase formation in solvent extraction solutions. *Solvent Extraction and Ion Exchange*, 2021, 39 (2), pp.204-232. 10.1080/07366299.2020.1831782 . cea-04722325

**HAL Id: cea-04722325**

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Submitted on 4 Oct 2024

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# How phase modifiers disrupt third-phase formation in solvent extraction solutions

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## KEYWORDS.

Liquid-liquid extraction, third phase formation, modifier, lanthanide, TODGA, 1-octanol, DMDOHEMA, molecular dynamic simulation, FTIR, ESI-MS, SWAXS

## ABSTRACT

The structure of complex organic solutions based of N,N,N',N'-tetraoctyldiglycolamide (TODGA) used in actinides separation processes was characterized after water and neodymium extraction. The organic phases were characterized using FTIR spectroscopy, ESI-MS spectrometry, Small and Wide Angle X-ray Scattering (SWAXS) and molecular dynamic simulations. The role of the “phase modifier” like 1-octanol (used in the innovative SANEX process) or the “co-extractant” like DMDOHEMA (used, for example, in the EURO-GANEX process) added in the organic phase to avoid a third phase formation was investigated at molecular and supramolecular scale. Without metallic cation, in 0.2 mol.L<sup>-1</sup> TODGA solution in *n*-heptane, TODGA molecules are organized in monomers and small aggregates containing mainly two or three TODGA molecules. After Nd(NO<sub>3</sub>)<sub>3</sub> extraction, complexes or aggregates are formed where each neodymium cation is surrounded in average by 2 to 4 TODGA, 3 nitrate ions and 1 to 2 water molecules. Polymetallic species (aggregates) may also be formed. Adding 5% vol 1-octanol or 0.5 mol.L<sup>-1</sup> DMDOHEMA to 0.2 mol.L<sup>-1</sup> TODGA solution in *n*-heptane leads to the formation of mixed aggregates containing TODGA and octanol molecules or

TODGA and DMDOHEMA molecules. These molecules both interact directly with the extracted metallic cation in the organic phase, modifying the structure of the neodymium species, and improving their solubility in this organic phase. At least, one TODGA molecule remains in the cation first coordination sphere in both cases and preserves its significant role in the complexation/selectivity of the cations. But both 1-octanol and DMDOHEMA have a role in the speciation of the cations in the organic phase: 1-octanol replaces water molecule in the first coordination sphere of Nd, it acts as a co-surfactant; DMDOHEMA drives the organization, DMDOHEMA molecules replace partially TODGA in the first coordination sphere of Nd.

## 1. INTRODUCTION

Partitioning of the minor actinides such as americium and curium and their transmutation is an efficient way to reduce the radiotoxicity of radioactive waste, which is generated during the reprocessing of nuclear spent fuel. A lot of research has been done to design and synthesize efficient extractants to separate trivalent actinides. In the framework of European projects, several processes have been developed<sup>1, 2</sup> using malonamide extractants. In these processes, trivalent actinides are coextracted with trivalent lanthanides in the first step, and the An(III)/Ln(III) separation is carried out in a second step using aqueous complexing agents. The distribution ratio for these extractants requires the use of high concentration of malonamide ligands (0.5 to 0.7 mol.L<sup>-1</sup>). Therefore, a new class of diamide extractants, the diglycolamides (DGA) ligands with an ether bridge between the two carbonyl groups were developed by Sasaki et al.<sup>3-6</sup> for the recovery of actinides from nuclear waste. Due to their tridentate character, these ligands present higher affinity to trivalent actinides and trivalent lanthanides than malonamides.<sup>5, 7</sup>

Among the diglycolamides, the N,N,N',N'-tetraoctyl diglycolamide (TODGA) was, more than 15 years ago, identified as a promising extractant.<sup>8-10</sup> It has been evaluated extensively for actinides partitioning and tested even with genuine nuclear waste solution.<sup>6</sup> The chemistry of diglycolamide has been reviewed by Ansari et al.<sup>6</sup> One drawback of this extractant family is its limited loading capacity without third phase formation in alkane, *i.e.* the maximum concentration of metal ions or acid that can be loaded in the organic phase. Typically, a third phase (*i.e.* the splitting of the organic phase into two phases) is observed when 0.2 mol.L<sup>-1</sup> TODGA in *n*-dodecane is contacted with 4 mol.L<sup>-1</sup> HNO<sub>3</sub> or, when 0.2 mol.L<sup>-1</sup> TODGA in TPH is contacted with 0.1 mol.L<sup>-1</sup> Nd(NO<sub>3</sub>)<sub>3</sub> in 5 mol.L<sup>-1</sup> nitric acid.<sup>9, 11-15</sup> Although the maximum solute concentration in the organic phase, or the limiting organic concentration (LOC),

increases with the TODGA concentration and the temperature, phase modifiers are usually introduced into the solvent composition to use this molecule in actual solvent extraction processes. In a recent review, Whittaker et al. present the current state of knowledge regarding the application of DGA extractants in minor actinides separation processes, focusing specially on the use of modifiers.<sup>16</sup>

A series of N,N-dialkyl monoamides with varying alkyl group and chain length were evaluated as phase modifier. For example, the addition of 0.5M N,N dihexyl octanamide (DHOA) as phase modifier to 0.1 mol.L<sup>-1</sup> TODGA in n-dodecane increases the LOC value for Nd from 0.008 to 0.033 mol.L<sup>-1</sup> at 3 mol.L<sup>-1</sup> HNO<sub>3</sub>.<sup>10, 11, 14, 17, 18</sup> The addition of TBP to a TODGA solution prevent the third phase formation too: a process using a solvent composed of 0.2 mol.L<sup>-1</sup> TODGA + 0.5 mol.L<sup>-1</sup> TBP in alkane has been developed for the separation of actinides (III) and lanthanides (III) or for a group actinides extraction (GANEX) process to separate all actinides from fission products.<sup>9, 19-23</sup> Another possibility to suppress the third phase consist in replacing *n*-dodecane by pure 1-octanol<sup>11</sup> or adding 5% of 1-octanol in the organic phase<sup>12</sup>. Thus, in the innovative-SANEX process developed in the frame of several European project, the solvent consists of 0.2 mol.L<sup>-1</sup> TODGA + 5% vol 1-octanol in TPH.<sup>12, 24-27</sup> Finally, DMDOHEMA which is used as the extractant for the DIAMEX – SANEX process<sup>28</sup> was also tested to increase the loading capacity of the TODGA-based process. Thus, the combination of 0.2 mol.L<sup>-1</sup> TODGA and 0.5 mol.L<sup>-1</sup> DMDOHEMA in kerosene was selected as the most suitable organic phase composition for the second cycle of the EURO-GANEX process.<sup>29-32</sup>

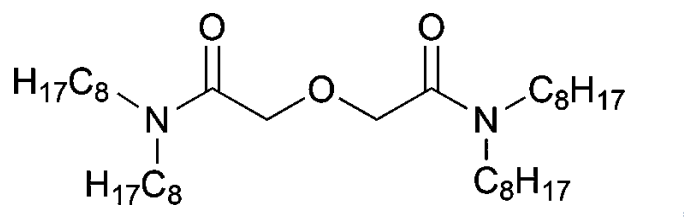


Figure 1 : schematic representation of the TODGA molecule

It is important to note that for all these processes, the concentration of the ‘phase modifier’ or ‘co-extractant’ in the organic phase is significant (for example 5% of 1-octanol in dodecane solution represents  $0.32 \text{ mol.L}^{-1}$ ), a higher concentration than the TODGA concentration and that this could induce changes in the speciation at both molecular and supramolecular scales.

At the molecular scale, different stoichiometries from 1:2 to 1:4 metal(III):TODGA complexes are reported in the literature. Most of these stoichiometries are derived from solvent extraction slope analysis data. Some authors propose the 1:2 stoichiometry for metal(III):TODGA complex in polar diluents<sup>33-35</sup> and a 1:3 (or 1:4) stoichiometry in non-polar diluents.<sup>11, 12, 34-40</sup> The metal(III) : TODGA complexes were characterized by spectroscopy techniques and DFT calculation.<sup>41</sup> TRIFS studies on Eu(III)-TODGA-diluent-HNO<sub>3</sub> revealed that the inner coordination sphere of Eu was completely dehydrated whatever the diluent used: dodecane, toluene, octanol or even in presence of  $0.5 \text{ mol.L}^{-1}$  DHOA.<sup>40, 42, 43</sup> EXAFS measurements of TODGA in isododecanol-alkane after lanthanides extraction suggest the presence of  $[\text{Ln}(\text{DGA})_3]^{3+}$  in which the DGA molecules would be tridentate.<sup>39, 44</sup> IR spectroscopy confirm that the carbonyl group of the amide function coordinate with lanthanides<sup>34, 38</sup> whereas the coordination of the ether function is less clear. ESI-MS analyses of organic solution after europium extraction reveal the presence of  $[\text{Eu}(\text{TODGA})_4]^{3+}$  indicating the presence of 4

TODGA molecules around the metal ions which is consistent with some of the slope analysis results.<sup>38</sup>

On the other hand, it is now well known that the third phase formation is correlated to the interaction between aggregates of extractant molecules in the organic phase.<sup>45-49</sup> The aggregation of TODGA in organic solution were investigated by vapor pressure osmometry, small angle X ray, small angle neutrons scattering and dynamic light scattering analyses<sup>15, 33, 50-53</sup>. TODGA in aliphatic diluent solutions after contact with aqueous phases (nitric acid with and without neodymium salts) are composed of polydisperse mixture containing monomers, dimers and small reverse “micelles” of TODGA tetramers. They respective proportions depend on the TODGA concentration, the nature and concentration of extracted solutes as well as the nature of the diluent.<sup>15, 33, 50-53</sup> Some study of the aggregation of TODGA in *n*-dodecane with 0.5 mol.L<sup>-1</sup> DHOA or 5% of 1-octanol revealed that the size of the aggregate is bigger in presence of 1-octanol than in presence of DHOA.<sup>53</sup> When *n*-dodecane is replaced by pure 1-octanol, no TODGA aggregate are observed in solution.<sup>33</sup>

Some authors assume that the high affinity of TODGA for M(III) cations could be due to the organization of the species in solution, and especially in alkane diluents where the aggregates formed could provide a preorganized cavity to encapsulate species involving trivalent metallic cations.<sup>6</sup> They also suggest that when alkane is replaced by 1-octanol, the interactions of TODGA with 1-octanol inhibit the formation of preorganized reverse micelles and then the extraction of trivalent cation.

Some molecular dynamic simulation were performed for TODGA solution in dodecane containing water, nitric acid or lanthanide nitrate<sup>41, 54, 55</sup> but none of these studies took into account concentration effects on the speciation.

All these experimental and theoretical investigations have significantly contributed to increase the knowledge of the TODGA organic solutions. However, the role of the phase modifier or the co-extractant was not investigated at the molecular scale and remains to be better understood. In this paper, we applied the method coupling experimental and theoretical characterization already used for the description of organic solutions in several solvent extraction systems.<sup>56-59</sup> The composition of the organic phase is determined experimentally and used to build molecular dynamics simulation boxes with the same composition as the experimental solutions. The representativeness of the simulation is then checked by comparing experimental data (densities and both small and wide angle X-ray scattered intensities) with the calculated one.

This paper aims to provide a better understanding of the role of the phase modifier or co-extractant on the molecular and supramolecular organization of the organic solution (after water and neodymium extraction). Organic phases containing either TODGA 0.2 mol.L<sup>-1</sup> in *n*-heptane, TODGA 0.2 mol.L<sup>-1</sup> in *n*-heptane + 5% v<sub>01</sub> of 1-octanol (corresponding to 0.32 mol.L<sup>-1</sup>) (used in the innovative SANEX process) or TODGA 0.2 mol.L<sup>-1</sup> in *n*-heptane + 0.5 mol.L<sup>-1</sup> DMDOHEMA (used, for example, in the EURO-GANEX process) were chosen and investigated after water and neodymium nitrate extraction.

## 2. EXPERIMENTAL SECTION

### Materials

TODGA and DMDOHEMA were synthesized by Pharmasynthese company (purity by GC-FID > 99%). 1-octanol and *n*-heptane was used without further purification (Sigma-Aldrich, anhydrous > 99%). The organic phases were prepared by dissolving weighed amounts of reagent.



Aqueous neodymium nitrate solutions were prepared by dissolution of hexahydrated neodymium (III) nitrate obtained from Prolabo (purity > 99%) into a solution of 3 mol·L<sup>-1</sup> lithium nitrate (at reagent grade-Prolabo) 0.01 mol·L<sup>-1</sup> nitric acid with deionized water produced by the milli-Q Plus apparatus (Millipore).

## **Solvent Extraction**

### **Water extraction:**

Organic solutions were contacted with deionized water with a  $V_{\text{org}}/V_{\text{aq}}$  volume ratio of 1. Extraction were performed at room temperature (25°C) with 30 min stirring. Aqueous and organic phases were separated after 5 minutes centrifugation.

### **Neodymium nitrate extraction:**

Extractions were conducted by contacting suitable volumes of an aqueous phase with an organic phase to reach the targeted Nd(III) concentration in the organic phase (see Table 1). Extraction were performed at room temperature (25°C) with 30 min stirring then aqueous and organic phases were separated after centrifugation for 5 minutes. The experimental conditions ( $V_{\text{org}}/V_{\text{aq}}$ , and compositions of the initial aqueous and organic phases are reported in Table 1).

**Table 1:** Composition of the initial aqueous and organic solutions.  $V_{org}/V_{aq}$  represent the ratio between organic to aqueous solution for the neodymium extraction.

	<b>Initial aqueous phase</b>	<b>Initial organic phase</b>	<b><math>V_{org}/V_{aq}</math></b>
<b>TODGA 0.2M Nd 0.019M</b>	Nd(NO <sub>3</sub> ) <sub>3</sub> 0.02M LiNO <sub>3</sub> 3M HNO <sub>3</sub> 10 <sup>-2</sup> M	TODGA 0.2M in <i>n</i> -heptane	1/1
<b>TODGA 0.2M Nd 0.059M</b>	Nd(NO <sub>3</sub> ) <sub>3</sub> 0.05M LiNO <sub>3</sub> 3M HNO <sub>3</sub> 10 <sup>-2</sup> M		1/1.28
<b>TODGA 0.2M Octanol 0.32M Nd 0.063M</b>	Nd(NO <sub>3</sub> ) <sub>3</sub> 0.05M LiNO <sub>3</sub> 3M HNO <sub>3</sub> 10 <sup>-2</sup> M	TODGA 0.2M Octanol 0.32M in <i>n</i> -heptane	1/1.28
<b>TODGA 0.2M Octanol 0.32M Nd 0.079M</b>			1/2
<b>TODGA 0.2M DMDOHEMA 0.5M Nd 0.059M</b>	Nd(NO <sub>3</sub> ) <sub>3</sub> 0.05M LiNO <sub>3</sub> 3M HNO <sub>3</sub> 10 <sup>-2</sup> M	TODGA 0.2M DMDOHEMA 0.5M in <i>n</i> -heptane	1/1.28
<b>TODGA 0.2M DMDOHEMA 0.5M Nd 0.093M</b>			1/2

## Titration

### Water concentration :

To determine the equilibrium concentration of water in each organic phase, Karl Fischer titrations were performed on a Metrohm 831 KF coulometer with a range of detection between 10 µg and 10 mg of water. The reliability of the method was checked by the measurement of water content in a standard sample (Hydranal – Water standard 1.0 from Riedel de Haëns). The titrations were performed at least in triplicate to provide an estimated uncertainty of less than ± 5 %.

### Nd concentration

Neodymium concentration were determined by ICP-AES. Analyses were performed with a JobinYvon 2000S ICP-AES. After extraction in the organic phase, metallic cations were stripped by 0.01mol.L<sup>-1</sup> HNO<sub>3</sub> aqueous phase (1/100 organic/aqueous phase volume ratio) and

then diluted 0.3M HNO<sub>3</sub> before ICP-AES analysis. Reference solutions of neodymium (III) nitrate in the range 1-50 mg·L<sup>-1</sup> were used for calibration.

### **Density measurement**

Density measurements of the organic solutions were performed at 25°C using an Anton Paar Stabinger viscosimeter SVM 300.

### **FT-IR spectroscopy.**

Infrared measurements were performed using a Bruker Vertex 70 FTIR spectrometer equipped with an ATR (attenuated total reflectance) cell. All spectra were collected between 650 and 4000 cm<sup>-1</sup> using 32 scans and a resolution of 2 cm<sup>-1</sup>.

### **ESI-MS mass spectrometry.**

The mass spectrometry measurements were recorded in positive ionization mode using a Bruker Daltonics micrOTOF-Q II quadrupole time-of-flight mass spectrometer equipped with an electrospray interface. A syringe infusion pump, Cole Palmer, delivered the sample at a rate of 180 μL·h<sup>-1</sup> to the electrospray source. The QTOF was mass calibrated daily using an Agilent (G1969-85000) ESI Low concentration tuning solution. The capillary voltage was set to -4500 V with an end-plate offset voltage of -500 V. Nitrogen was employed as the drying and nebulizing gas. The drying gas flow rate was set to 4.0 L·min<sup>-1</sup>, the nebulizing gas pressure was set to 0.4 bar, and the source temperature was set to 180 °C. Spectra were recorded over a mass range of m/z 40–3000. Tandem mass spectra were obtained from collision-induced dissociation (CID) with nitrogen. All samples were diluted by a factor of 1000 to 10000 in an acetonitrile/water (50/50) mixture prior to any injection into the ESI-MS. Species were identified by comparison with an isotopic pattern calculated using the DataAnalysis 4.0 software.

## Small and wide angle X-ray scattering

Small and wide-angle X-ray scattering (SWAXS) experiments were carried out on a bench built by Xenocs and using Mo radiation ( $\lambda = 0.71 \text{ \AA}$ ). Collimation was applied using a 12: $\infty$  multilayer Xenocs mirror (for Mo radiation) coupled to two sets of Forvis scatterless slits providing a  $0.8 \text{ mm} \times 0.8 \text{ mm}$  X-ray beam at the sample position. 2mm diameter quartz capillaries containing the samples were used. A large on-line 2D scanner detector (MAR Research 345) located at 750 mm from the sample stage was used to record the scattered beam. A large  $q$ -range ( $2 \times 10^{-1}$  to  $30 \text{ nm}^{-1}$ ) with  $q$  defined as  $q = [(4\pi)/\lambda]\sin(\theta/2)$  was covered thanks to an off-centre detection ( $\theta$  being the scattering angle). Data pre-analysis was performed using FIT2D software to transform isotropic 2D scattering in 1D scattering curves. Absolute intensities in  $\text{cm}^{-1}$  were obtained using either a 2.36 mm thick high-density polyethylene sample (from Goodfellow®) as a calibration standard or water for which the level of scattering at low  $q$  proportional to its compressibility is known at 293K and 1 atm ( $1.64 \cdot 10^{-2} \text{ cm}^{-1}$ ).

## Molecular dynamic simulations

Molecular dynamic (MD) simulations have been performed using the AMBER 14 software with the parm99 force field<sup>60</sup> and taking explicitly into account all atoms polarization effects. Water molecules were described using the POL3 model<sup>61</sup>. The polarizable models for  $\text{Nd}^{3+}$ ,  $\text{NO}_3^-$  and *n*-heptane are described in previously published studies<sup>62</sup>. Atomic partial charges on TODGA, DMDOHEMA and 1-octanol were calculated using the restricted electrostatic potential (RESP) procedure<sup>63, 64</sup>. The MD simulation boxes compositions were defined based on the corresponding experimental analyses of the organic phases, for which all compounds concentrations have been determined (see Table 1 and Table 4). Initial MD simulation boxes were built using a random distribution of the corresponding molecules. These systems were then equilibrated at 300 K and 1 atm during at last 2ns. After checking the equilibration by

assessing the stability of classical parameters such as the volume, density and kinetic energy of the simulated box, production runs were subsequently collected during 5 to 10 ns. The equation of motion was numerically integrated using a 1 fs time step, and simulations were carried out in the NPT ensemble, using a 15 Å truncation cut-off, applying periodic boundary conditions to the simulations boxes and particle mesh Ewald for the long-range interactions calculation. SWAXS intensities were computed taking into account the whole MD trajectories using the nMoldyn software.<sup>65</sup> The trajectories were then analyzed computing radial distribution functions in order to determine the aggregation cut-off distances and the corresponding aggregates populations were counted using the CPPTRAJ AmberTools module<sup>66</sup>. These sets of parameters have already provided results in good agreement with experimental data.<sup>58, 67</sup>

### 3. RESULTS

#### Water extraction

Organic phases containing either TODGA 0.2 mol.L<sup>-1</sup> alone, TODGA 0.2 mol.L<sup>-1</sup> + 5% vol (0.32 mol.L<sup>-1</sup>) 1-octanol, or TODGA 0.2 mol.L<sup>-1</sup> + DMDOHEMA 0.5 mol.L<sup>-1</sup> in *n*-heptane have been contacted with pure water in order to assess the speciation and extractants organization in these solutions. After equilibration, the amount of water in the organic phase has been determined. The composition of the resulting experimental organic phase is reported in *Table 2*(left). The presence of 0.32 mol.L<sup>-1</sup> 1-octanol in the organic phase leads to a slight increase in the water concentration (0.08 vs. 0.06). The presence of 0.5 mol.L<sup>-1</sup> DMDOHEMA leads to a significant increase in the water concentration. It is well known that DMDOHEMA in alkane extract significant quantity of water: 0.15 mol.L<sup>-1</sup> of water is extracted by 0.5M DMDOHEMA in *n*-heptane.<sup>68</sup> The quantity of water extracted by 0.2 mol.L<sup>-1</sup> TODGA + 0.5 mol.L<sup>-1</sup> DMDOHEMA solution is a slightly higher than the addition of the concentration extracted by the solutions of the single extractant (0.25 vs. 0.21 mol.L<sup>-1</sup>). It is likely that this

slight increase in the concentration of water is due to a higher organization of the species in the organic phase as previous studies showed that the water extraction in the organic phase is correlated to the aggregation of the solution.<sup>68</sup>

**Table 2:** Composition of the experimental solutions (left) and corresponding number of molecules in the MD simulation (right) (T is TODGA and D is DMDOHEMA).

Concentration (mol.L <sup>-1</sup> )		$\rho_{\text{exp}}$ (g/cm <sup>3</sup> )	$\rho_{\text{calc}}$ (g/cm <sup>3</sup> )	Number of molecules in the simulation					
ligands	H <sub>2</sub> O			heptane	T	D	octanol	H <sub>2</sub> O	
TODGA	0.2	0.06	0.717	0.712	3000	106	0	0	30
TODGA	0.2 + 5% octanol	0.08	0.722	0.715	2750	94	0	144	41
TODGA	0.2 + DMDOHEMA 0.5	0.25	0.781	0.782	2000	100	245	0	122

The presence of interactions between species has first been checked by ESI-MS analysis. As reported in the literature, the structural organization of surfactants in the gas phase is considered to depend on the nature and composition of the starting solution<sup>69</sup>. Previous analysis of organic phases by ESI-MS shown consistency between the species identified in the mass spectra and the adducts or complexes existing in the solution<sup>28, 59, 70-74</sup>. The Figure 2 reports the ESI-MS spectra in positive ionization mode corresponding to organic solutions after contact with water. The assignment of the main species is presented in Table 3. The analysis of the solution of TODGA 0.2 mol.L<sup>-1</sup> in *n*-heptane indicate the presence of ions containing 1 to 5 TODGA molecules, which would be consistent with the possible presence of aggregate containing up to 5 TODGA molecules in the organic phase. For organic solution containing 0.32 mol.L<sup>-1</sup> of 1-octanol, no species containing 1-octanol molecules are observed in the gaz phase. It is worth noting that the interaction between 1-octanol and other species are very low and that 1-octanol molecules are volatile. This does not mean therefore that 1-octanol molecules are excluded from the aggregates in the solution. Moreover, ions containing several TODGA molecules are less abundant suggesting a decrease of the interaction between TODGA molecules. For solution containing 0.2 mol.L<sup>-1</sup> TODGA + 0.5 mol.L<sup>-1</sup> DMDOHEMA ; DMDOHEMA and TODGA

species containing 1 to 2 molecules are formed as well as mixed species involving the two ligands. Even if these information's are only qualitative, this shows that the speciation in the organic phase (adducts or aggregates distribution) depends strongly on the composition of the solutions.

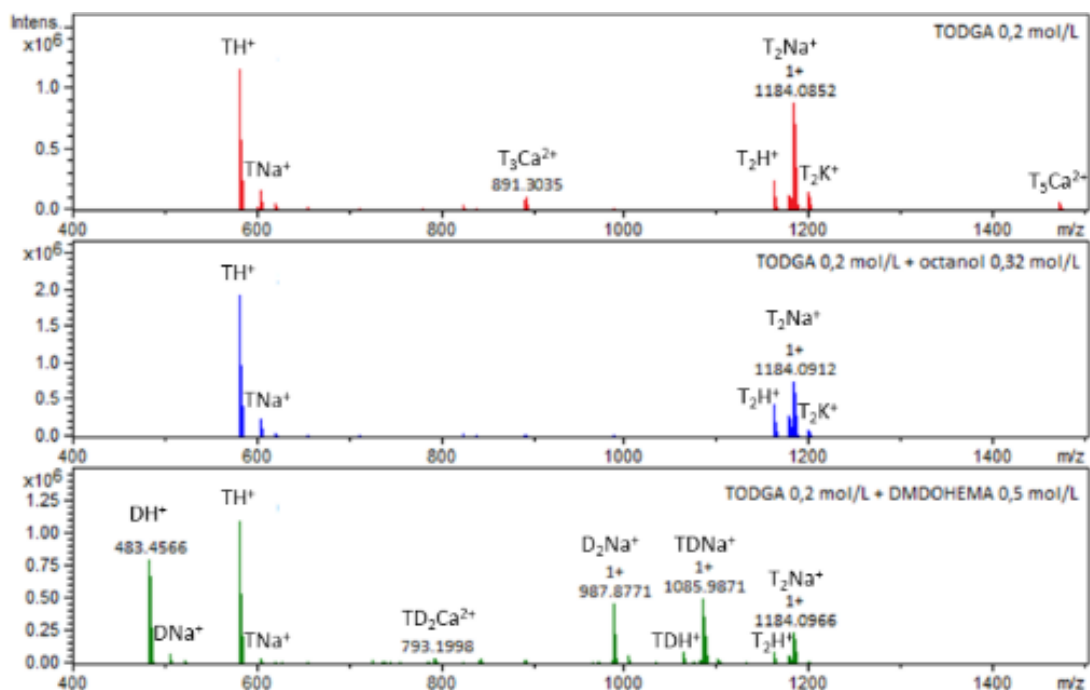


Figure 2: ESI-MS spectra of the organic phases after contact with pure water. TODGA 0.2M (top), TODGA 0.2M + 5%<sub>vol</sub> 1-octanol (center) and TODGA 0.2M + DMDOHEMA 0.5M (bottom). Dilution x10000 in CH<sub>3</sub>CN/water (50%/50%).

Table 3: m/z ratios and assignments of the main ions detected by ESI-MS for solutions of TODGA 0.2M in n-heptane, TODGA 0.2M + 5%vol 1-octanol in n-heptane, and TODGA 0.2M + DMDOHEMA 0.5M in n-heptane (T = TODGA and D = DMDOHEMA).

m/z			Assignment
TODGA	TODGA Octanol	TODGA DMDOHEMA	
/	/	483.4	DH <sup>+</sup>
/	/	505.4	DNa <sup>+</sup>
/	/	521.4	DK <sup>+</sup>
581.6	581.6	581.6	TH <sup>+</sup>
603.5	603.5	603.5	TNa <sup>+</sup>
619.5	619.5	619.5	TK <sup>+</sup>
/	/	792.7	TD <sub>2</sub> Ca <sup>2+</sup>
890.8	/	/	T <sub>3</sub> Ca <sup>2+</sup>
/	/	987.9	D <sub>2</sub> Na <sup>+</sup>
/	/	1003.8	D <sub>2</sub> K <sup>+</sup>
/	/	1064.4	TDH <sup>+</sup>
/	/	1085.4	TDNa <sup>+</sup>
1162.1	1162.1	1162.1	T <sub>2</sub> H <sup>+</sup>
1181	/	/	T <sub>4</sub> Ca <sup>2+</sup>
1184.1	1184.1	1184.1	T <sub>2</sub> Na <sup>+</sup>
1200.1	1200.1	/	T <sub>2</sub> K <sup>+</sup>
1471.3	/	/	T <sub>5</sub> Ca <sup>2+</sup>

To obtain a comprehensive analysis of the organization of such organic solutions, Small and Wide Angle X-ray Scattering (SWAXS) measurements have been performed (see Figure 3 left). In all cases a “solvent pic” corresponding to the carbon-carbon correlation distance in aliphatic chains is observed at  $1.42 \text{ \AA}^{-1}$ . The intensity upturns followed by a plateau at low scattering angles suggest heterogeneities in X-ray scattering length density within the bulk phase and that is usually attributed to the formation of inverse aggregates in these systems. Moreover, at high concentration of extractants (TODGA + DMDOHEMA) a slight excess of scattering is visible around  $0,2-0,3 \text{ \AA}^{-1}$  and could correspond to a broad scattering peak, the sign of characteristic distance of correlation between aggregates. Molecular dynamic (MD) simulations have also been performed for theoretical solution with exactly the same composition than the experimental ones (Table 2 and Figure 4): MD simulations boxes were built with molecule amounts calculated from the experimentally obtained composition and molecules initially randomly distributed. The acceptability of the structure obtained with the MD simulations is



checked by comparing experimental data like the solution density and the SWAXS signal with the calculated ones (Table 2 and Figure 3). Then a comprehensive analysis of the MD simulated organic phase allows us to characterize the structure in the solutions both at the molecular and supramolecular scales.

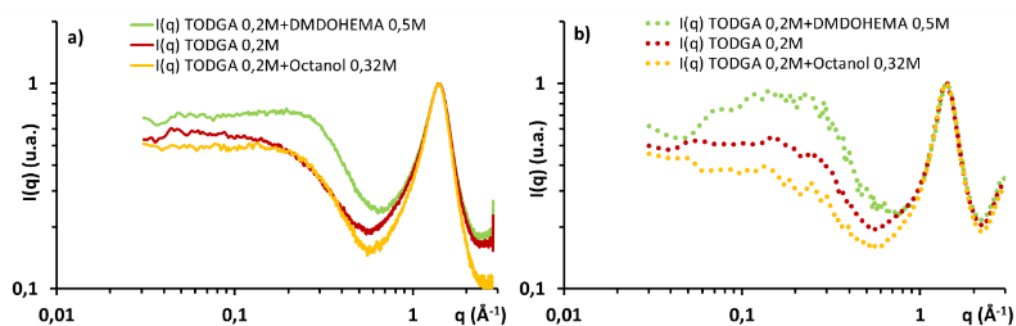


Figure 3: Experimental (a) and calculated (b) SWAXS signals for the the organic phases after contact with pure water.

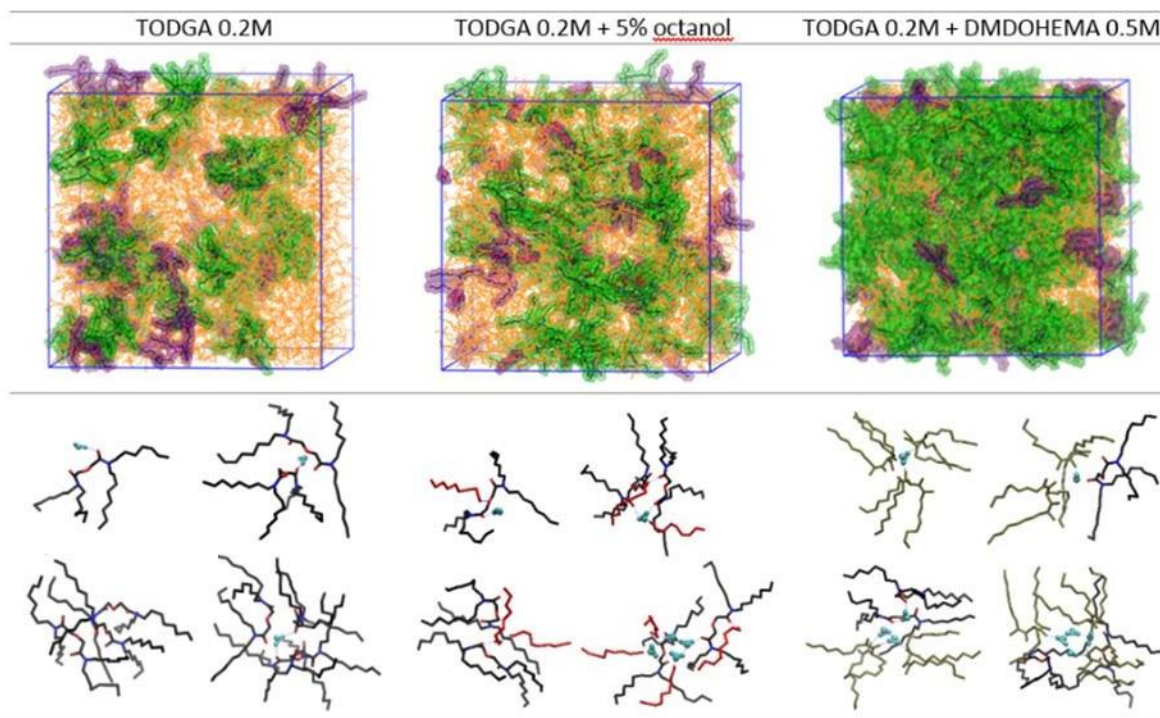


Figure 4: Snapshots of the MD simulation boxes (top) and corresponding typical aggregates (bottom) after extraction of water. Top: Diluent molecules are in orange, extractant monomers are highlighted in purple, and aggregates are highlighted in green. Bottom: representative structures of predominant aggregates observed in the simulation boxes. TODGA molecule are in black, 1-octanol in red and DMDOHEMA in green.

In the organic phase containing TODGA only, 26% of the TODGA molecules are monomers. The 74% remaining form small labile aggregates containing mainly 2 to 3 TODGA molecules with a very low amount of water molecules in these aggregates. Adding 5% vol 1-octanol (0.32 mol.L<sup>-1</sup>) leads to (i) a small increase of the amount of water in the organic phase ([H<sub>2</sub>O] ranges from 0.06 to 0.085 mol.L<sup>-1</sup>), (ii) a decrease of the aggregation state of the solution (40% of the TODGA molecules are monomers) and (iii) the formation of mixed aggregates that contain 1 to 3 TODGA and 1 to 4 octanol molecules. These mixed aggregates solvate more water than the aggregates formed with TODGA only. These results are consistent with the ESI-MS results indicating a decrease of the abundance of ions containing several TODGA molecules in presence of 1-octanol.

In the organic phases containing 0.2 mol.L<sup>-1</sup> TODGA and 0.5 mol.L<sup>-1</sup> DMDOHEMA, the DMDOHEMA extractants drive the organization: each aggregate contains at least one DMDOHEMA, and none of the aggregates is formed with only TODGA whereas some aggregates containing only DMDOHEMA are observed. The amount of water in these TODGA+DMDOHEMA organic phase is much higher ([H<sub>2</sub>O] = 0.25 mol.L<sup>-1</sup>) than in the solution that contain TODGA only, this results in the presence of water molecules in most of the aggregates. These observations are in good agreement with the ESI-MS results.

### **Neodymium nitrate extraction**

Organic phases (TODGA 0.2 mol.L<sup>-1</sup> alone, TODGA 0.2 mol.L<sup>-1</sup> + 5% vol. (i.e. 0.32 mol.L<sup>-1</sup>) 1-octanol, or TODGA 0.2 mol.L<sup>-1</sup> + DMDOHEMA 0.5 mol.L<sup>-1</sup> in *n*-heptane) have been contacted with aqueous phases containing different concentration of neodymium nitrate in order to assess the influence of the neodymium salt loading on the structure of the complexes and aggregates formed in the organic phases. Each organic phase has been characterized using FTIR spectroscopy, ESI-MS spectrometry, Small and Wide Angle X-ray Scattering (SWAXS) and

molecular dynamic simulations. The compositions of the studied organic phases are reported in Table 4. In order to compare the different solutions, the initial  $\text{Nd}(\text{NO}_3)_3$  aqueous concentrations (before extraction) have been chosen in order to obtain a comparable  $\text{Nd}(\text{NO}_3)_3$  concentration after extraction in the organic phase (around  $0.06 \text{ mol.L}^{-1}$ ). This concentration corresponds to the maximum neodymium concentration in the organic phase before third phase formation for the  $0.2 \text{ mol.L}^{-1}$  TODGA solution in *n*-heptane. In presence of 5%  $\text{vol}$  of 1-octanol, or  $0.5 \text{ mol.L}^{-1}$  DMDOHEMA, this value is increased. As indicated in Table 4, the coextracted water concentration in the organic phase increases with the neodymium extraction, about 1 to 2 water molecules per neodymium molecule which is consistent with literature data.<sup>28</sup>

**Table 4: Composition of the studied experimental solutions (left) and corresponding number of molecules in the MD simulation (right) (T is TODGA and D is DMDOHEMA). Values in bracket correspond to the extracted water concentration when organic phases are contacted with water only.**

	Experiments			Simulations						
	Concentration (mol/L)		$\rho_{\text{exp}}$ ( $\text{g/cm}^3$ )	$\rho_{\text{calc}}$ ( $\text{g/cm}^3$ )	Number of molecules					
	$\text{Nd}(\text{NO}_3)_3$	$\text{H}_2\text{O}$			heptane	T	D	Oct	$\text{Nd}(\text{NO}_3)_3$	$\text{H}_2\text{O}$
<b>TODGA 0.2M</b>	0.019	0.08 (0.06)	0.720	0.714	2750	93	0	0	9	38
	0.059	0.15 (0.06)	0.731	0.728	2500	86	0	0	25	64
<b>TODGA 0.2M</b>	0.063	0.21 (0.08)	0.739	0.733	2750	94	0	144	31	41
<b>+ 5%<math>\text{vol}</math> Octanol</b>	0.079	0.21 (0.08)	0.744	0.738	2750	94	0	144	39	41
<b>TODGA 0.2M</b>	0.059	0.38 (0.25)	0.798	0.798	2000	99	245	0	29	185
<b>+ DMDOHEMA 0.5M</b>	0.093	0.41 (0.25)	0.809	0.807	2200	109	270	0	50	220

## Infrared and UV-visible spectroscopies

Infrared spectra of the organic phases before and after extraction of neodymium nitrate are reported in Figure 5. The first relevant vibration band to look at is the one corresponding to the amide C=O organic function. For the three solutions (organic phases containing TODGA only, TODGA + 5%  $\text{vol}$  1-octanol, or TODGA + DMDOHEMA), the absorbance of the free C=O vibration band at  $1652 \text{ cm}^{-1}$  decreases after nitrate neodymium extraction in the organic phase

and a vibration band corresponding to a bonded C=O bond appears at 1616  $\text{cm}^{-1}$ . The location of this bonded C=O vibration band is the same for the three organic phases indicating that the interaction between the amide function and the Nd(III) cation is similar in all cases as previously observed by Sasaki et al.<sup>34, 38</sup>.

For the two first solutions (TODGA only, and TODGA + 5% v/v 1-octanol), the ether C-O-C vibration band is only slightly moved (from 1126 to 1122  $\text{cm}^{-1}$ ) after Nd(NO<sub>3</sub>)<sub>3</sub> extraction indicating a very small interaction between Nd<sup>3+</sup> and the ether function of the TODGA extractant, in agreement with Sasaki's results.<sup>34</sup> For the last organic phase (TODGA 0.2 mol.L<sup>-1</sup> + DMDOHEMA 0.5 mol.L<sup>-1</sup>), the C-O-C vibration band is located at 1114  $\text{cm}^{-1}$  and is not moved upon neodymium nitrate extraction. In this last case, this vibration band is mainly due to the DMDOHEMA that is at a concentration more than twice higher than the TODGA concentration. This is in agreement with previous studies on DMDOHEMA alone that show that the ether bond does not bind the lanthanide cations.

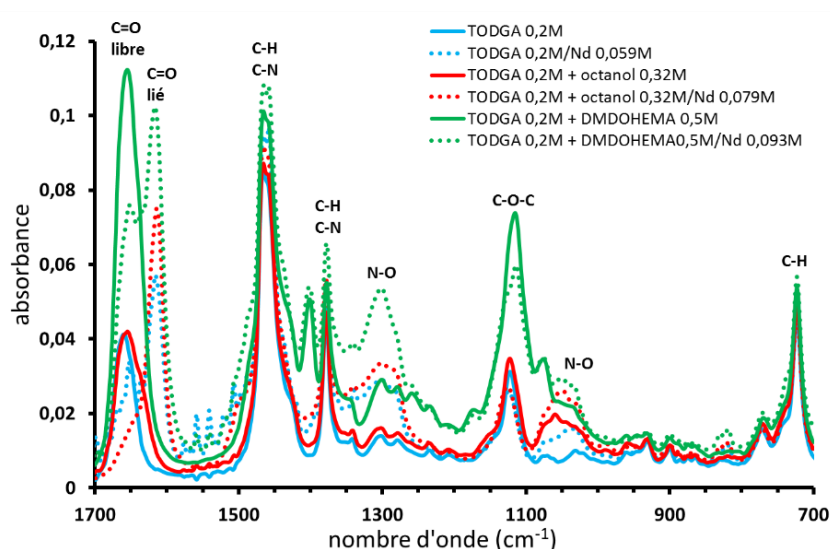


Figure 5 : infrared spectra of the TODGA solutions before and after extraction of neodymium nitrate. blue: TODGA 0.2M in n-heptane, red: TODGA 0.2M + 5% 1-octanol in heptane and green: TODGA 0.2M + DMDOHEMA 0.5M in n-heptane. Plain lines: solutions before neodymium extraction – dashed lines: solutions after neodymium extraction.

UV-visible spectroscopy was used to explore the neodymium environment after extraction for each solution (Figure 6). A change in the coordination sphere of the cation should induce a change in the absorption band <sup>75-77</sup>. The similarity of the spectra obtained after extraction of about 0.06 mol.L<sup>-1</sup> Nd for each of these 3 solutions with or without 1-octanol or DMDOHEMA (Figure 6) shows that the immediate surrounding of the neodymium cations does not drastically change. It is possible that 1-octanol molecules or DMDOHEMA molecule replace water or TODGA molecule around the metallic cation without changing the strength of the interactions.

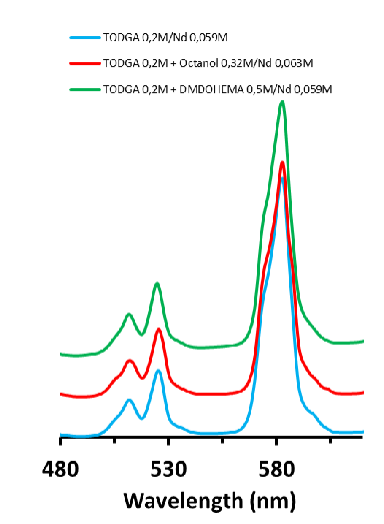


Figure 6 : UV-visible spectra of the TODGA solutions after extraction of about 0.06 M neodymium nitrate. blue: TODGA 0.2 mol/L in n-heptane, red: TODGA 0.2 mol/L + 5% 1-octanol in n-heptane and green: TODGA 0.2 mol/L + DMDOHEMA 0.5 mol/L in n-heptane.

## ESI-MS analysis

The Figure 7 reports the ESI-MS spectra in positive ionization mode corresponding to the organic solutions after neodymium extraction. The assignment of the main species is presented in Table 5. After extraction of Nd(NO<sub>3</sub>)<sub>3</sub> in the 0.2 mol.L<sup>-1</sup> TODGA organic phase, ions containing Nd<sup>3+</sup> surrounded by 3 to 5 TODGA are observed on ESI-MS spectra (Figure 7a). In the organic phases with 5% v<sub>o1</sub> 1-octanol, the number of TODGA surrounding the Nd<sup>3+</sup> cations decreases: 2 to 4 TODGA only, with a very low intensity for the species with 4 TODGA (Figure 7b). As for experiments without metallic cation, 1-octanol molecules are not observed on these

spectra but the decrease number of TODGA extractants around  $\text{Nd}^{3+}$  suggests that some 1-octanol molecules may have replaced some TODGA around the cation in the solution. For the TODGA-DMDOHEMA organic phase (Figure 7c), Nd(III) is located in mixed aggregates (*i.e.* containing both TODGA and DMDOHEMA extractants), or in complexes or aggregates containing either TODGA or DMDOHEMA. All these species intensities are very low on the ESI-MS spectra due to the high polydispersity of the species observed.

Table 5: m/z ratios and assignments of the main ions detected by ESI-MS for solutions of TODGA 0.2M in n-heptane, TODGA 0.2M in n-heptane + 5% 1-octanol, and TODGA 0.2M + DMDOHEMA 0.5M in n-heptane after neodymium nitrate extraction. T = TODGA and D = DMDOHEMA. Ions containing  $\text{Nd}^{3+}$  are in bold and \* indicates that the abundance of the species are very low.

m/z			Assignments
TODGA	TODGA Octanol	TODGA DMDOHEMA	
/	/	483.4	DH <sup>+</sup>
/	/	502.4	D <sub>2</sub> Ca <sup>2+</sup>
/	/	505.4	DNa <sup>+</sup>
/	/	<b>529.7*</b>	<b>D<sub>3</sub>Nd<sup>3+</sup></b>
581.6	581.6	581.6	TH <sup>+</sup>
600.5	/	/	T <sub>2</sub> Ca <sup>2+</sup>
603.5	603.5	603.5	TNa <sup>+</sup>
<b>627.8</b>	<b>627.8</b>	/	<b>T<sub>3</sub>Nd<sup>3+</sup></b>
/	/	<b>691.6*</b>	<b>D<sub>4</sub>Nd<sup>3+</sup></b>
/	/	<b>723.8*</b>	<b>D<sub>3</sub>TNd<sup>3+</sup></b>
/	/	743.7	D <sub>3</sub> Ca <sup>2+</sup>
/	/	792.7	D <sub>2</sub> TCa <sup>2+</sup>
<b>821.3</b>	<b>821.3</b>	/	<b>T<sub>4</sub>Nd<sup>3+</sup></b>
/	/	<b>825.6*</b>	<b>D<sub>3</sub>Nd(NO<sub>3</sub>)<sup>2+</sup></b>
/	/	<b>851.3*</b>	<b>D<sub>5</sub>Nd<sup>3+</sup></b>
/	/	<b>885.6*</b>	<b>D<sub>4</sub>TNd<sup>3+</sup></b>
890.8	890.8	890.8	T <sub>3</sub> Ca <sup>2+</sup>
/	/	<b>917.8*</b>	<b>D<sub>3</sub>T<sub>2</sub>Nd<sup>3+</sup></b>
/	/	<b>923.7*</b>	<b>DT<sub>2</sub>Nd(NO<sub>3</sub>)<sup>2+</sup></b>
<b>972.8</b>	<b>972.8</b>	<b>972.8*</b>	<b>T<sub>3</sub>Nd(NO<sub>3</sub>)<sup>2+</sup></b>
/	/	987.9	D <sub>2</sub> Na <sup>+</sup>
/	/	<b>1012.2*</b>	<b>D<sub>6</sub>Nd<sup>3+</sup></b>
<b>1015.9</b>	/	/	<b>T<sub>5</sub>Nd<sup>3+</sup></b>
/	/	<b>1046.9*</b>	<b>D<sub>5</sub>TNd<sup>3+</sup></b>
/	/	<b>1066.8*</b>	<b>D<sub>4</sub>Nd(NO<sub>3</sub>)<sup>2+</sup></b>
/	/	1085.4	DTNa <sup>+</sup>
1162.1	/	/	T <sub>2</sub> H <sup>+</sup>
/	/	<b>1173.0*</b>	<b>D<sub>7</sub>Nd<sup>3+</sup></b>
1184.1	1184.1	1184.1	T <sub>2</sub> Na <sup>+</sup>
/	/	<b>1207*</b>	<b>D<sub>6</sub>TNd<sup>3+</sup></b>
/	/	<b>1230.7*</b>	<b>D<sub>2</sub>Nd(NO<sub>3</sub>)<sub>2</sub><sup>+</sup></b>
<b>1263.1</b>	<b>1263.1</b>	<b>1263.1*</b>	<b>T<sub>4</sub>Nd(NO<sub>3</sub>)<sup>2+</sup></b>
/	/	<b>1308.1*</b>	<b>D<sub>5</sub>Nd(NO<sub>3</sub>)<sup>2+</sup></b>
/	<b>1428.0</b>	/	<b>T<sub>2</sub>Nd(NO<sub>3</sub>)<sub>2</sub><sup>+</sup></b>

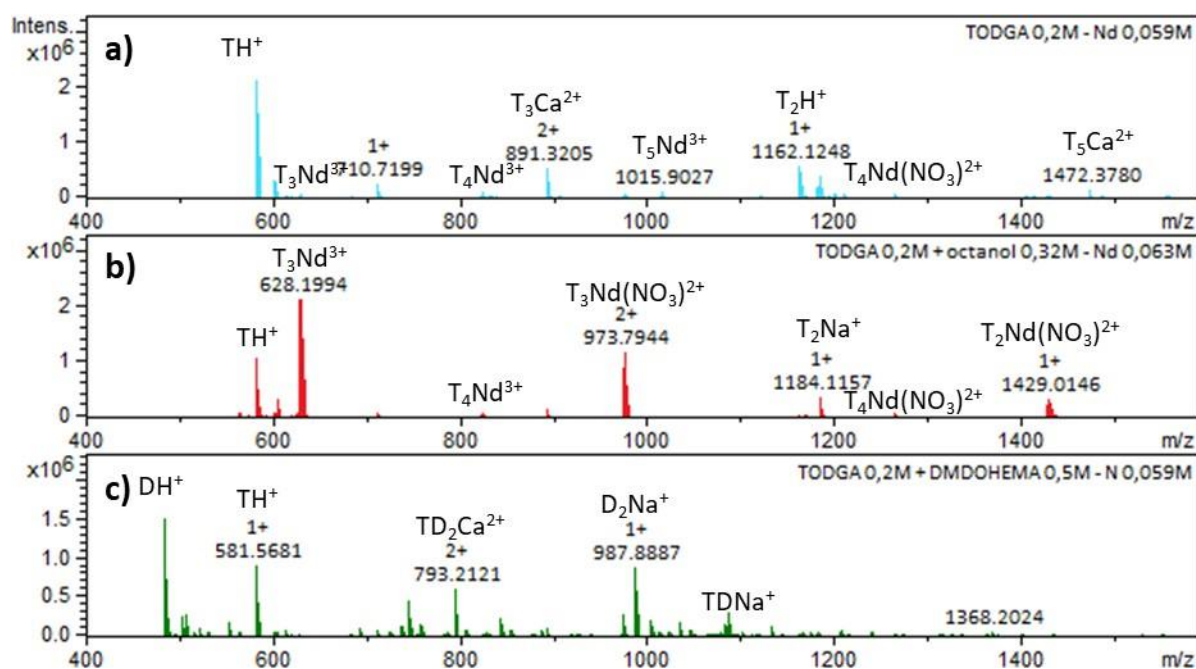


Figure 7 : ESI-MS spectra of the solutions: TODGA 0.2 mol.L<sup>-1</sup> (a), TODGA 0.2 mol.L<sup>-1</sup> + 5%<sub>vol</sub> 1-octanol (b) and TODGA 0.2 mol.L<sup>-1</sup> + DMDOHEMA 0.5 mol.L<sup>-1</sup> (c) in n-heptane after extraction of about 0.06 mol.L<sup>-1</sup> neodymium nitrate. Dilution 10000 in CH<sub>3</sub>CN/water 50%/50%.

### Small and Wide Angle X-ray Scattering

The experimental SWAXS intensities of the organic phases loaded with Nd(NO<sub>3</sub>)<sub>3</sub> are reported on Figure 8. In all cases the “solvent pic” corresponding to the carbon-carbon correlation distance is still observed at 1.42 Å<sup>-1</sup>. On the other hand, the shape and the intensities of the SAXS signal differ upon the composition of the organic phase and the intensities are larger than 1 cm<sup>-1</sup>.

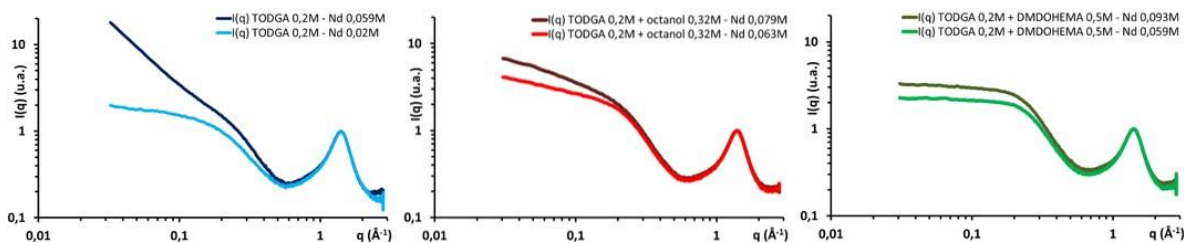


Figure 8 : Experimental SWAXS Intensities of the organic phases: TODGA 0.2M (blue), TODGA 0.2M + 5% octanol (red) and TODGA 0.2M + DMDOHEMA 0.5M (green) in n-heptane after extraction of neodymium nitrate.

For the TODGA 0.2 mol.L<sup>-1</sup> organic phases (blue curves on Figure 8) and at low (0.02 mol.L<sup>-1</sup>) Nd(NO<sub>3</sub>)<sub>3</sub> concentration, the scattering intensity upturn is more pronounced than those previously observed without salts, while a more significant signal and close to a q<sup>-1</sup> decay is observed at 0.06 mol.L<sup>-1</sup> Nd(NO<sub>3</sub>)<sub>3</sub>. It is worth noting that the latest solution is very close to the cation saturation (*i.e.* just before demixion of the organic phase). The shape of these SAXS intensities suggest the formation of small aggregates at low neodymium concentration and the formation of large (or elongated) aggregates at higher neodymium concentration.

Adding 5% v<sub>01</sub> 1-octanol results in SAXS intensities upturn less pronounced and much less dependant on Nd(NO<sub>3</sub>)<sub>3</sub> concentration in the organic phase with a slightly higher intensity for the highest Nd(NO<sub>3</sub>)<sub>3</sub> concentration. No plateau is observed in this q-range suggesting either inverse aggregates with size polydispersity or slightly elongated clusters and whatever neodymium concentration. However, the level of the scattering intensities is still much higher than the previously observed without salt meaning that these aggregates contains Nd salts.

For the organic phases with TODGA 0.2 mol.L<sup>-1</sup> + DMDOHEMA 0.5 mol.L<sup>-1</sup>, the SAXS profiles show again a plateau below 0.1 Å<sup>-1</sup> that suggests the formation of smaller and finite sized aggregates similar to those observed in DMDOHEMA organic phases without TODGA.<sup>72</sup>



## **Molecular dynamic simulation**

Molecular dynamic simulations have been performed for the six organic phases containing neodymium nitrate with composition of the solutions issuing from the experimental analysis (as reported in Table 4). Snapshots of the MD simulation boxes as well as the corresponding SWAXS intensity are reported on Figure 9. It should be notice that the calculated SWAXS intensities for the solutions are slightly lower than the experimental ones especially for the solution of TODGA 0.2 mol.L<sup>-1</sup> in *n*-heptane. The low calculated intensities for the less concentrated solution (0.019 mol.L<sup>-1</sup> of Nd) could be due to the very small number of molecules of neodymium in the simulation box (only 9 molecules). However, the calculated profiles are in relatively good agreement with the experimental one giving support to the MD simulation results.

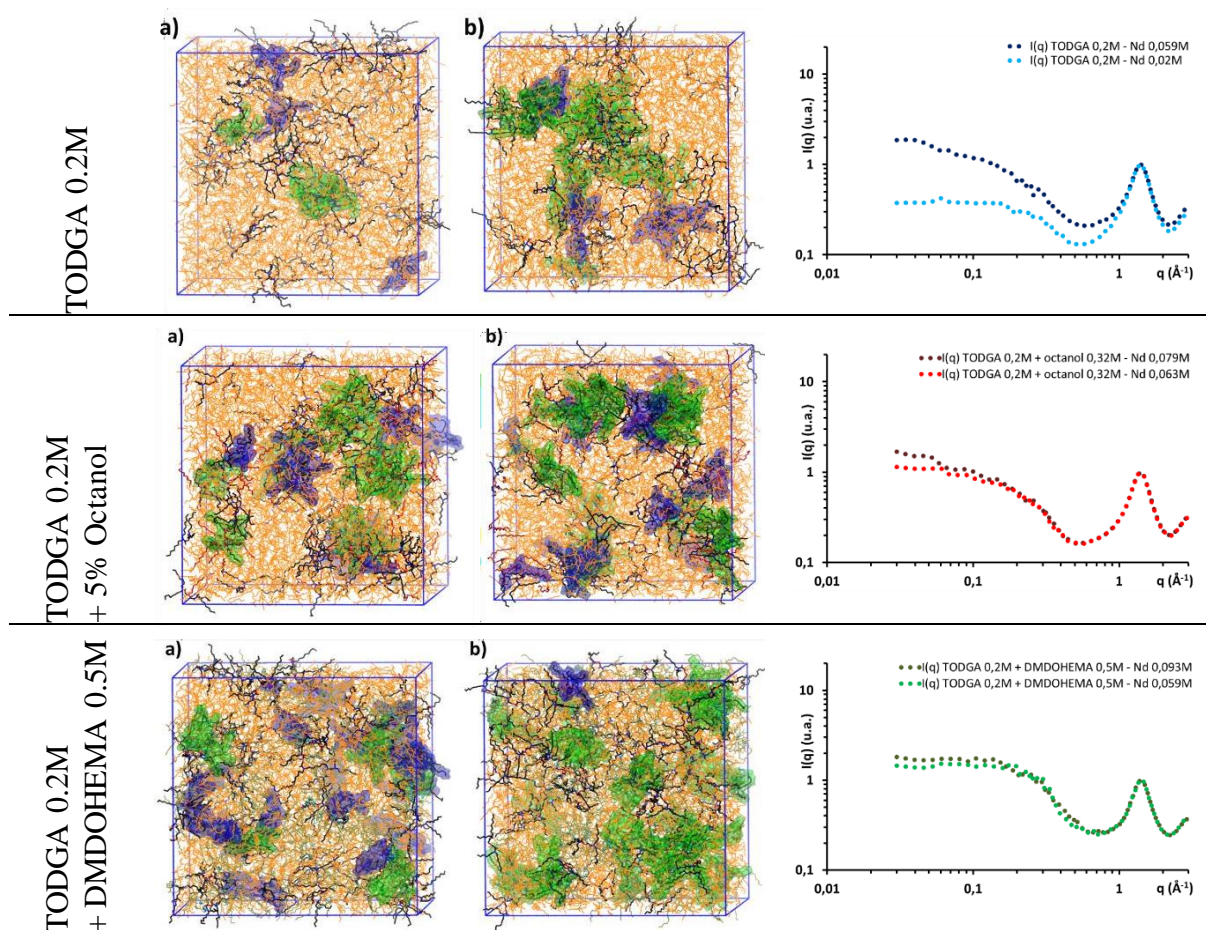


Figure 9 : MD boxes simulation snapshots for: a) low and b) high neodymium nitrate concentrations and corresponding calculated SWAXS intensities in TODGA 0.2M (first line), TODGA 0.2M + 5% octanol (second line) and TODGA 0.2M + DMDOHEMA 0.5M (last line) in *n*-heptane after extraction of neodymium nitrate. Heptane: orange, carbon atoms: black, nitrogen atoms: blue and oxygen atoms: red. The monometallic complexes or aggregates are highlighted in blue and the polymetallic aggregates are highlighted in green.

### TODGA 0.2M in *n*-heptane

The molecular dynamics simulations trajectories analysis shows that; when TODGA is used as the extractant, without any phase modifier or co-extractant, mainly polymetallic species are formed. Even at low neodymium concentration in the organic phase ( $[\text{Nd}]_{\text{org}} = 0.019 \text{ mol.L}^{-1}$ ), only 44% neodymium are involved in monometallic complexes. The proportion of monometallic complexes decrease to 14% when the neodymium concentration is increase to  $0.059 \text{ mol.L}^{-1}$  (*i.e.* close to the demixion concentration) in the organic phase. In these polymetallic aggregates (mainly bi, tri and tetra-metallic aggregates), the neodymium cations

are bonded by bridging nitrates ions (3 per  $\text{Nd}^{3+}$ ) and surrounded by TODGA extractant (2 per  $\text{Nd}^{3+}$ ) and water molecules (1 to 2 per  $\text{Nd}^{3+}$ ).

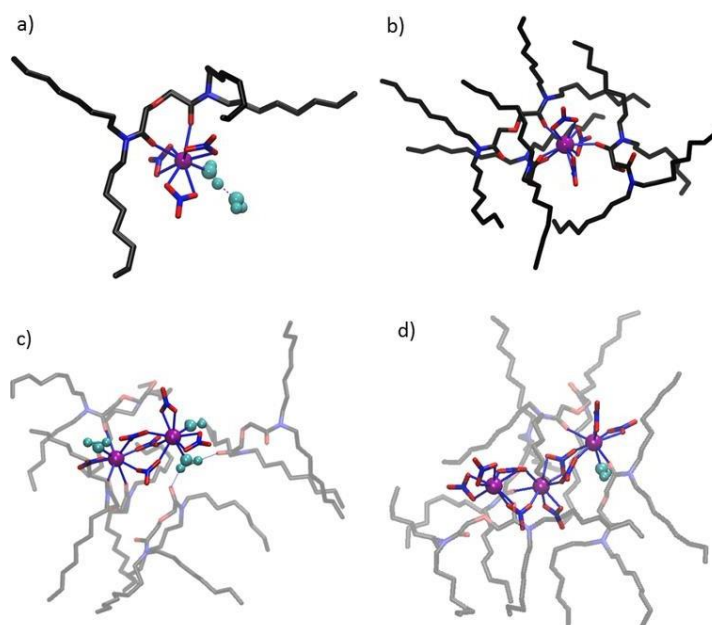


Figure 10: representative structures observed in the TODGA 0.2M simulations after extraction of neodymium nitrate. Neodymium: purple, carbon atoms in black, nitrogen atoms in blue and oxygen atoms in red. TODGA hydrogen atoms are not represented, water molecules are represented in cyan

### **TODGA 0.2M + 5% 1-Octanol in n-heptane**

For a similar neodymium concentration in the organic phase, the introduction of  $0.32 \text{ mol.L}^{-1}$  1-octanol ( $0.2 \text{ mol.L}^{-1}$  TODGA + 5%  $v_{ol}$  1-octanol) decreases the number of polymetallic aggregates: for  $[\text{Nd}]_{org} = 0.063 \text{ mol.L}^{-1}$  the proportion of monometallic complexes raises to 34% (14% without 1-octanol). The size of the polymetallic aggregates also decreases: almost no aggregates with more than 3 neodymium are formed. The radial distribution function of the octanol oxygen atoms centered on Nd(III) shows that, on the average, each Nd(III) is bonded to 1 octanol molecule, decreasing the number of water molecules in the cation first coordination sphere.

Surprisingly, increasing the neodymium concentration in this  $0.2 \text{ mol.L}^{-1}$  TODGA + 5%  $v_{ol}$  1-octanol organic phase does not lead to an increase of the aggregation: on the contrary, the

number of monometallic complexes even increase to 45%, and the number of larger aggregate decreases in favor of the smaller bimetallic aggregates.

Octanol molecules are included in these aggregates, replacing the few water molecules that were bonded to the neodymium cation in the organic phase without 1-octanol. The presence of these octanol molecules stabilizes the aggregates, increases the solubility of the aggregates in the organic phase and avoids their coalescence, preventing the demixion of the organic phase at higher  $\text{Nd}(\text{NO}_3)_3$  concentration. 1-octanol is therefore not a “simple” phase modifier since it takes part directly in the complexes or aggregates structure and enhances their solubility by addition of aliphatic chains near the extracted cation.

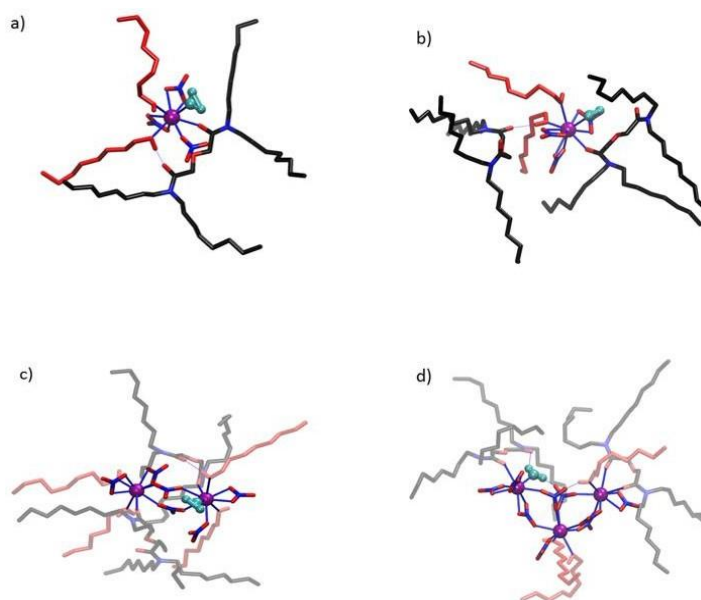


Figure 11: Representative structures observed in the TODGA 0.2 mol.L<sup>-1</sup> + 5%<sub>vol</sub> 1-octanol simulations after extraction of neodymium nitrate. Neodymium: purple, carbon atoms in black, nitrogen atoms in blue and oxygen atoms in red. TODGA hydrogen atoms are not represented; 1-octanol molecules are represented in red, water molecules are represented in cyan.

### **TODGA 0.2M + DMDOHEMA 0.5M in n-heptane**

The addition of 0.5 mol.L<sup>-1</sup> DMDOHEMA as an alternative of 1-octanol (0.2 mol.L<sup>-1</sup> TODGA + 0.5 mol.L<sup>-1</sup> DMDOHEMA) and for a comparable neodymium concentration (0.06 mol.L<sup>-1</sup>) decreases drastically the aggregation: in this case, 73% of the  $\text{Nd}(\text{NO}_3)_3$  present in the organic

phase are included in monometallic complexes. The DMDOHEMA extractant truly act as a co-extractant: DMDOHEMA molecules are involved in the complexation of the Nd(III) cation, replacing TODGA extractants.

The loading capacity of this organic phase is much higher than the two previous ones, and even for  $[\text{Nd}]_{\text{org}} = 0.093 \text{ mol.L}^{-1}$ , the size of the aggregates remains small (around 80% of the neodymium form mono or bimetallic complexes or aggregates). This aggregate size reduction is concomitant with a reduction of the aggregates polar core size reduction, which consequently reduces the attraction between these polar cores, and therefore the possible coalescence of these aggregates. The DMDOHEMA extractant is here the major one (its concentration is more than twice higher than the TODGA one), therefore, even if TODGA molecules are still present in all the aggregates, the organic phase structure is here imposed by the DMDOHEMA extractant (and not TODGA).

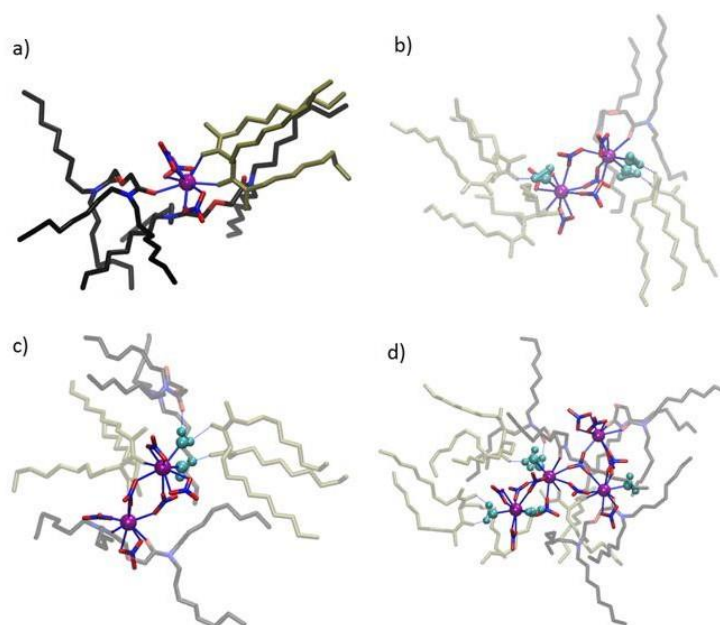


Figure 12: Representative structures observed in the TODGA 0.2 mol.L<sup>-1</sup> + DMDOHEMA 0.5 mol.L<sup>-1</sup> simulations after extraction of neodymium nitrate. Neodymium: purple, carbon atoms in black, nitrogen atoms in blue and oxygen atoms in red. TODGA and DMDOHEMA hydrogen atoms are not represented, DMDOHEMA molecules are represented in light brown, water molecules are represented in cyan.

#### 4. CONCLUSION

Combining experimental and theoretical characterization of the solutions provided a better description of organic solutions of separation processes. The characterization of organic phases containing either TODGA 0.2 mol.L<sup>-1</sup>, TODGA 0.2 mol.L<sup>-1</sup> + 5% vol 1-octanol (corresponding to 0.32M) or TODGA 0.2 mol.L<sup>-1</sup> + 0.5 mol.L<sup>-1</sup> DMDOHEMA, in *n*-heptane has been performed, allowing to better understand the role of phase modifier (octanol) or co-extractant (DMDOHEMA) in organic solutions.

Without metallic cation, in 0.2 mol.L<sup>-1</sup> TODGA solution in *n*-heptane, small aggregates containing mainly two or three TODGA molecules represent 74 % of the extractants. These results are consistent with literature data.<sup>15, 50, 51</sup> Using vapor pressure osmometry and small-angle neutron scattering, but without take into account the polydispersity of species, Yaita et al. suggested a mixture of monomers and dimers and Nave et al. a mixture of monomers with tetramers for TODGA solution in alkane after contact with water or weakly acidic aqueous phases. The extraction of Nd(NO<sub>3</sub>)<sub>3</sub> by this organic phase leads to complexes or aggregates where each neodymium is surrounded by water molecules, nitrate ions, and several TODGA extractants with some in the cation second coordination sphere. MD simulation results showed that neodymium cations are surrounded in average by 2 to 4 TODGA, 3 nitrate ions and 1 to 2 water molecules. Simulations showed as well that polymetallic species (aggregates) may be formed in the organic phase, even for low neodymium concentrations. An increase of Nd(III) concentration results in an increase of the aggregates sizes that can lead to a third phase formation, in agreement with the experimental results.

Without metallic cation, adding 5% vol 1-octanol (0.32 mol.L<sup>-1</sup>) to 0.2 mol.L<sup>-1</sup> TODGA solution in *n*-heptane leads to the formation of mixed aggregates that contain 1 to 3 TODGA and 1 to 4 octanol molecules. These mixed aggregates (which represent 60% of the TODGA molecules)

solvate more water than the aggregates formed with TODGA only. In the organic phases containing  $0.2 \text{ mol.L}^{-1}$  TODGA and  $0.5 \text{ mol.L}^{-1}$  DMDOHEMA, the DMDOHEMA extractants drive the organization: all the aggregates contain at least one DMDOHEMA molecule. Some aggregates containing only DMDOHEMA are even observed. Each of them solvates water molecules.

After  $\text{Nd}(\text{NO}_3)$  extraction, and for a similar neodymium concentration, the ESI-MS studies in presence of 5% vol. 1-octanol or  $0.5 \text{ mol.L}^{-1}$  DMDOHEMA show that the number of TODGA decreases around each neodymium. Mixed complexes or aggregates are formed, with at least one TODGA molecule remaining in the cations first coordination sphere. The MD simulations indicates the formation of complexes and aggregates including both TODGA + 1-octanol (in presence of 5% vol of 1-octanol) and TODGA + DMDOHEMA (in presence of 0.5M DMDOHEMA). In presence of octanol, some 1-octanol molecules replace water molecules in the cation first coordination spheres. Octanol molecules act as a co-surfactant, improving the solubility of the neodymium species in the organic phase, but with a direct contribution in the aggregates structures. With  $0.5 \text{ mol.L}^{-1}$  DMDOHEMA in the organic phase, the MD simulations show that DMDOHEMA molecules replace partially TODGA in the cation first coordination sphere. In the aggregates, the phase modifier (octanol) replaces water molecules, whereas the co-extractant replaces the other extractant.

Intrinsically, 1-octanol and DMDOHEMA have much lower interactions with  $\text{Nd}(\text{III})$  than TODGA: alcohol are less polar than amide, and DMDOHEMA extracts much less neodymium than TODGA (at low nitric acid concentration  $D_{\text{Nd}}$  is around 100 times smaller for an organic phase with  $[\text{DMDOHEMA}] = 0.7\text{M}$  than an organic phase with  $[\text{TODGA}] = 0.1\text{M}$  <sup>6, 11, 79</sup>). However, these results show that at the concentrations used in the i-SANEX and EURO-GANEX processes ( $0.32\text{M}$  1-octanol or  $0.5\text{M}$  DMDOHEMA respectively), these molecules

both interact directly with the extracted salts in the organic phase, modifying the structure of the neodymium species, and improving their solubility in this organic phase. In other words, the TODGA extractant, which remains in the cation first coordination sphere in both cases, preserves its significant role in the complexation/selectivity of the cations, but both 1-octanol and DMDOHEMA have a significant role in the speciation of these cations in the organic phase.

Since the end of the 1990s, progress in understanding third phase formation has been driven by direct determination of molecular aggregation obtained via small-angle X-rays and neutron scattering.<sup>45-49</sup> The surfactant approach provided a better understanding taking into account the presence of aggregates in the organic solutions. Simultaneous detection of small- and wide-angle X-ray scattering (SWAXS) allow to obtain a spatial description of species from a few angstroms up to a few tens of nanometers<sup>58</sup>. Due to high extractant and solute concentrations and the polydispersity of the aggregates, classical analysis of SWAXS data is not well adapted. Combining experimental characterization with MD simulation allowed to overcome this limitation and provided a better understanding of the complex structure of the organic phase in solvent extraction system with a complete description of the organization at both molecular and supramolecular scales. In particular, the role of phase modifier added in organic solutions to prevent the third phase formation is better understood. In conclusion, this study shows the interest of investigating the speciation both at a molecular and at a supramolecular scale. This methodology could be applied to other complex chemical systems after extraction of high concentration of solute such as for example the characterization of light and heavy phases formed after third phase formation.

## **ACKNOWLEDGMENTS**

We thank Bruno Corso for technical help and Olivier Diat for fruitful exchange of views.



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