

The National IOR Centre of Norway

# Lanthanide ester complexes for SWCTT

Project 2.5.2 and 2.5.5

Project manager: Tor Bjørnstad

Postdoc: Mahmoud Ould Metidji

Other key personnel: Alexander Krivokapic, Laura Ferrando-Climent, Mario Silva and Sissel O. Viig

Project duration: 5 years

## Final Project Report

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List of abbreviations:

**DOTA:** 1,4,7,10-Tetraazacyclododecane-1,4,7,10-tetraacetic acid

**DOTAGA:** 2,2',2''-(10-(2,6-Dioxotetrahydro-2H-pyran-3-yl)-1,4,7,10-tetraazacyclododecane-1,4,7-triyl)triacetic acid

**DTPA:** Diethylenetriamine pentaacetic acid

**PCTA:** 3,6,9,15-Tetraazabicyclo[9.3.1]pentadeca-1(15),11,13-triene-3,6,9-triacetic acid)

**DMSO:** Dimethyl sulfoxide

**Ln:** Lanthanide

**UPLC:** Ultra-Performance Liquid Chromatography

**GC-MS:** Gas Chromatography – Mass Spectrometry

**LC-MS:** Liquid Chromatography – Mass Spectrometry

**SoR:** Residual Oil Saturation

**TRF:** Time-Resolved Fluorescence

**PITT:** Partitioning Interwell Tracer Test

**SWCTT:** Single-Well Chemical Tracer Test

**K-value:**  $K = \text{concentration of tracer in the oil phase} / \text{concentration of tracer in the aqueous phase at partition equilibrium}$

### 1. Executive summary

Tracer technology for well experiments is one of very few applicable technologies for collection of unique dynamic data of reservoir flows. Two main tracer tests are commonly used for reservoir characterization: (i) the Single-Well Chemical Tracer Test (SWCTT) and (ii) the InterWell Tracer Test (IWTT) which includes Partitioning Interwell Tracer Tests (PITT). SWCTT and PITT are intended to monitor the residual oil saturation (SoR) in the near-well and interwell regions, respectively.

The concept of using a new class of potentially partitioning *fluorescent* tracers for SWCTT tests was introduced at the start of this project. The tracer is a chemical complex formed by an organic chelate former and a fluorescent metallic center (mainly a lanthanide ion). The results have shown that it was possible to functionalize the chelate with an ester function to form a desired hydrolyzing compound and, at the same time, theoretically increase the affinity of the final complex for the oil phase.

The present study in collaboration with University of Lyon allowed to establish the complexation strategies and characterization tools for detecting and quantifying the tracers. Especially, High-Performance Liquid Chromatography (HPLC) coupled with a Time-Resolved Fluorescence (TRF) detection unit allowed separating the different partitioning compounds and their passive form with a

high specificity in the synthesis reaction mixture. A series of water-oil partitioning tests have been carried out using synthetic production water and both synthetic oil and a crude oil from the Norwegian continental shelf.

Against the expectation, close to 100% of the ester tracer was found in the aqueous phase after contact with the oil. This result has been confirmed for two tracers with different ester chain length (ethyl ester and butyl ester). Moreover, the LC-MS characterization provided a better understanding about the environment of the metallic ion. This shows that the original negative charge of the lanthanide complex, also after esterification, has not become sufficiently neutralized at the applied reaction conditions. Hence, the final goal of this project has not been reached within its timeframe and economic resources.

## 2. Introduction and background

Single-Well Chemical Tracer Test (SWCTT) is the most widespread method to determine residual oil saturation (SoR). SoR is one of the key parameters to obtain an accurate dynamic model of mature reservoirs where a high amount of oil is possibly trapped by the capillary forces [1]. Evaluating the SoR after secondary and/or tertiary recovery allows estimating the remaining oil-reserves, thus contributing to the establishment of the best production strategy for further EOR/IOR operations.

SWCTT is a well-known technique introduced in 1971 by Deans (Exxon) [2]. It is based on the use of tracers which form true solutions both in the oil (immobile phase) and the water (mobile phase). In practice, reactive esters such as ethyl acetate are injected in one well after injection of several pore volumes of water to displace all the mobile oil. It should be noticed that at this stage, the reservoir is cooled down due to the water injections and the temperature may drop down by few tens of degrees. The temperature increases over time to reach the initial value. The rate of this phenomenon depends on the rock-fluid heat exchange coefficient, nature of the rock and the temperature of the injecting fluid.

After injection of the primary tracer which is a water/oil partitioning compound, the well is shut in, thus allowing for hydrolysis of the ester compound to take place. Hydrolysis is stopped when about 50 % of the ester have reacted [3] as determined beforehand in laboratory calibration experiments. To keep the testing economically viable, the tracers are selected based on their hydrolysis rates that are used to determine the shut-in time [4]. A typical full SWCTT examination campaign takes up to two weeks, thus involving esters with ideal hydrolysis degradation half-lives between 1.5 and 7 days, within the test conditions of pH and temperature [5]. The hydrolysis rate is determined using static batch experiments in the lab under the relevant conditions of temperature and pH. The ideal scenario of a SWCTT involves stable conditions (pH and T) during the timescale of the test as the hydrolysis rate of an ester depend exponentially on the temperature, and is also a strong function of pH, thus influencing indirectly the SoR estimation [5].

The hydrolysis of the primary injected tracer (ester) leads to an alcohol, which is a pure water-solvable compound, and an acid which is also a purely water-solvable compound, if the pH of the bulk is higher than the product of the acidity constant ( $pK_a$ ) of the acid. During back-production, the chromatographic separation between the remaining primary tracer and the generated secondary alcohol compound enables a fairly accurate determination of the SoR using the laboratory-determined K-value of the primary phase-partitioning tracer. The accuracy of the test will strongly depend on the stability of the reservoir conditions during its execution. As already mentioned, the partition

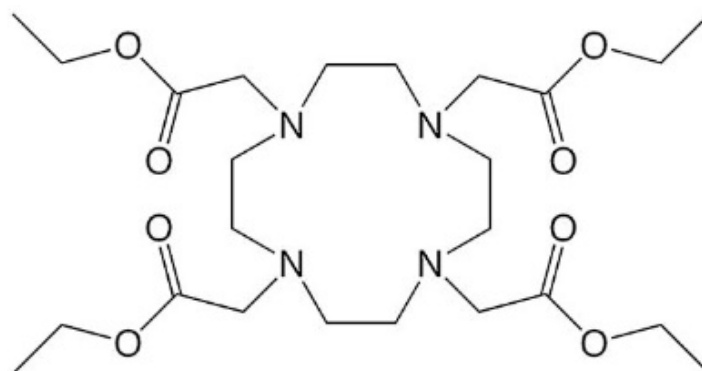
equilibrium is dependent on both pH and temperature. Thus, any variations in these parameters during the test can significantly impact the results and the interpretation of the data [6].

In most cases, traditional SWCTT tracers are monitored by gas chromatography (GC). This technique suffers from several limitations for on-field implementation such as (i) running costs, (ii) difficulty to monitor in real-time, (iii) requires highly qualified operators and relatively high detection limits for the most common tracers [7]. The possibility of using Time-Resolved Fluorescence coupled with the use of long-lived emission (phosphorescent) tracers has been introduced previously [8]. This technique appears very promising regarding: (i) the improvement of the analytical detection limits of the tracers (low-ppb range), (ii) the easier and faster implementation, (iii) the lower operating costs and (iv) the possibility to run the analysis on-site or even on-line [7, 8].

#### *Background: use of Ln-complexes as water tracers*

Due to their unique electronic configuration  $[Xe]4f^n$ , the trivalent ions of the lanthanides ( $Ln^{3+}$ ) display long-lived and narrow-line emission bands in the UV-visible region under UV excitation [9, 10]. In the last decade several groups have worked on the protection or shielding of lanthanide ions with organic chelates to: (i) prevent water molecules from entering the coordination sphere of the ion and (ii) allow the indirect excitation of the lanthanide through a ligand displaying a stronger absorption (enhanced excitation efficiency). Furthermore, the design of the organic "shell" gives access to a wide range of possibilities to obtain a fluorescent structure adaptable to a multitude of environments.

A promising group of groundwater tracers are lanthanide ions chelated by molecules such as DTPA and DOTA derivatives [11-14]. This is particularly true in the case of DOTA complexes. These have high thermodynamic stability (logarithm of stability constant  $K$  have values between 23 and 25). This prevents any transmetalation phenomenon to occur significantly and enables a higher solubility and stability of the lanthanide ions in formation water [15]. The use of DOTA-Lanthanide (DOTA- $Ln$ ) complexes as tracers for water flow in oil reservoirs was previously patented by our partner in the project University of Lyon [8]. The 3<sup>rd</sup> example of the patent describes the preparation of a partitioning tracer: Tetraethyl 2,2', 2'', 2''' - (1,4,7,10-tetraazacyclododecane-1, 4,7,10-tetrathyl) tetraacetate (DOTA-Et) associated with Europium (III). The ligand is represented below (Figure 1).



*Figure 1: Tetraethyl 2,2', 2'', 2''' - (1,4,7,10-tetraazacyclododecane-1, 4,7,10-tetrathyl) tetraacetate (DOTA-Et)*

The synthesis consisted of mixing 979 mg of esterified DOTA (Figure 1) ligand in water with 662 mg of  $EuCl_3 \cdot 6H_2O$ , and the mixture was left for almost 6 days at 80°C under stirring. Results showed that the final compound was fully hydrolyzed. The obtained compound was diluted 100 times in a sample of production water and a water/oil partitioning test was performed using a crude-oil (50/50 v/v). Time-

resolved fluorescence (TRF) measurements were performed in the aqueous phase before and after the partitioning experiments (Figure 2).

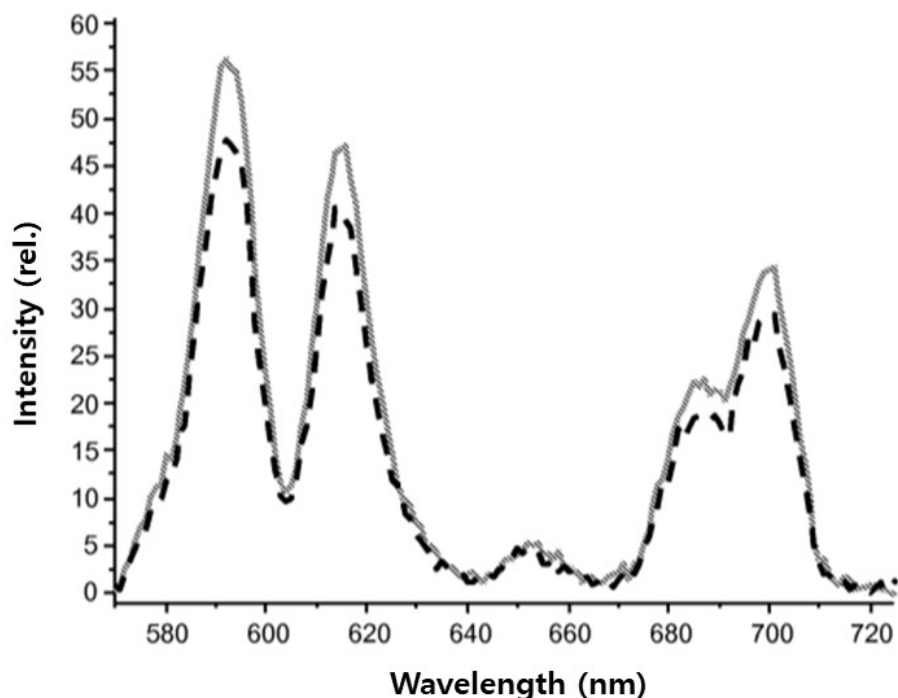


Figure 2: TRF measurements of DOTA-Et-Eu were performed with excitation at 395nm ( $4f \rightarrow 4f$  transition) before (gray line) and after (dashed line) partitioning test.

The fluorescence intensity dropped after contact with oil which might indicate that the final product(s) is (are) partially partitioning or exhibiting surface activity towards the hydrocarbon phase (surfactant like behavior). Moreover, for a mixture of different fluorescent species, TRF alone is not sufficient to study the products unless a purification step is applied after synthesis to isolate each form of the complex (excitation/emission and lifetime).

The present study aims at functionalizing DOTA-Ln complexes to obtain a set of phase-partitioning tracers for SoR determination in SWCTT operations. To achieve this, attempts were made to esterify the DOTA-Ln complexes with hydrocarbon chains with different lengths (number of carbon atoms).

In theory, the affinity of the tracer towards the oil phase depends on the hydrocarbon chain length in the tracer compound (methyl ester, ethyl ester, etc.). To orient the esterification on one specific carboxylic acid group, the glutamic acid form of the DOTA can be used (DOTAGA; Figure 3). It is further assumed that the fifth carboxylic function of the DOTAGA molecule is more reactive due to the steric conformation of the molecule (however, there is a lack of literature on this point). The desired compound should be in the monoester form since a mixture of polyesters will be more complex and more time and cost consuming to analyze in produced water. Regarding the similar reactivity of the carboxylic groups, the mono-esterification is more challenging than the formation of the whole esterified compound. The polyester form of DOTA (DOTA-Et; Figure 1) is already commercialized (CheMatech, France) contrarily to the monoester form.

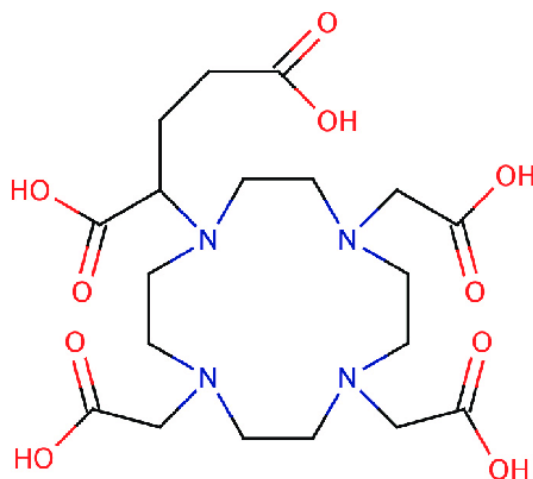


Figure 3: Representation of DOTAGA

As the esters are hydrolysed, the acid formed provides a stronger chelation for the europium by creating coordination bonds. This phenomenon results in a progressive removal of water molecules close to the lanthanide; this in turn increases the luminescence quantum yield and the lifetime of the complex.

The quantifiable changes in the lifetime of the complexes makes it possible to differentiate the ester from the acid versions of the chelates. This can be performed by fitting the experimentally determined lifetime of the mixture with the following equation:

$$I = \alpha_1 \cdot \exp\left(-\frac{t}{\tau_1}\right) + \alpha_2 \cdot \exp\left(-\frac{t}{\tau_2}\right) \quad \text{Eqn.1}$$

where  $I$  = intensity,  $t$  = running time,  $\tau_1$  = the lifetime of the ester,  $\tau_2$  = the lifetime of the acid version of the chelate, and  $\alpha_1$  and  $\alpha_2$  factors which depend on the concentration ratio between the ester and the acid.

Solving this equation then gives direct access to the fractional contribution of each component through the following equation:

$$f_i = \frac{\alpha_i \cdot \tau_i}{\sum_j \alpha_j \cdot \tau_j} \quad \text{Eqn.2}$$

This set of equations makes it possible to identify and quantify both the ester and the acid with a single lifetime measurement.

Objectives of the project:

- Establish strategies for a reproducible synthesis method of a phase-partitioning lanthanide complexes (of a majority of the same monoester) by using a new family of compounds (based on DOTAGA-monoalkyl esters-Ln).

- Qualify hydrolysis rate, K-values (water/oil partition coefficient) and stability at reservoir conditions.
- Establish methods to uniquely characterize the obtained products during synthesis and after hydrolysis in waters with relevant mineral compositions added.

### 3. Experiments and Results

#### 3.1. Materials and Methods

The two-step strategy employed to create the DOTAGA-monoalkyl ester complex with  $\text{Ln}^{3+}$  consists of i) synthesizing the desired ligand and ii) perform the lanthanide ion complexation afterwards.

##### *Strategy point 1: Preparation of monoalkyl ester ligand*

The esterification of DOTAGA anhydride with an alcohol leads to the formation of two regioisomers (1 and 2; Figure 4). However, the asymmetry of the anhydride ring leads to favouring of one of the regioisomers over the other due to steric hindrance [16].

The DOTAGA-anhydride compound was provided as a gift by the team of Professor Olivier Tillement (Lyon1 University), which is our partner in the project. Butanol (99.7% for HPLC) and ethanol (purity GC 99.5%) were purchased from Merck.  $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$  salt (99.9%) was purchased from Merck. DOTAGA-ethyl ester (compound A) and DOTAGA-butyl ester (compound B) were synthesized under reflux with an excess of alcohol (butanol or ethanol). Reactions were performed in round-bottom flasks by dissolving 50 mg of DOTAGA-anhydride in 30 mL of ethanol (reflux at 82°C) or in 30 mL of butanol (reflux at 122°C). After 16 hours, reaction mixtures were evaporated on a rotary evaporator device until obtaining dry powders (40°C/40 mbar for A; 50°C/20 mbar for B). After dilution in water, the obtained products were analysed by ultra-performance liquid chromatography (UPLC) and liquid

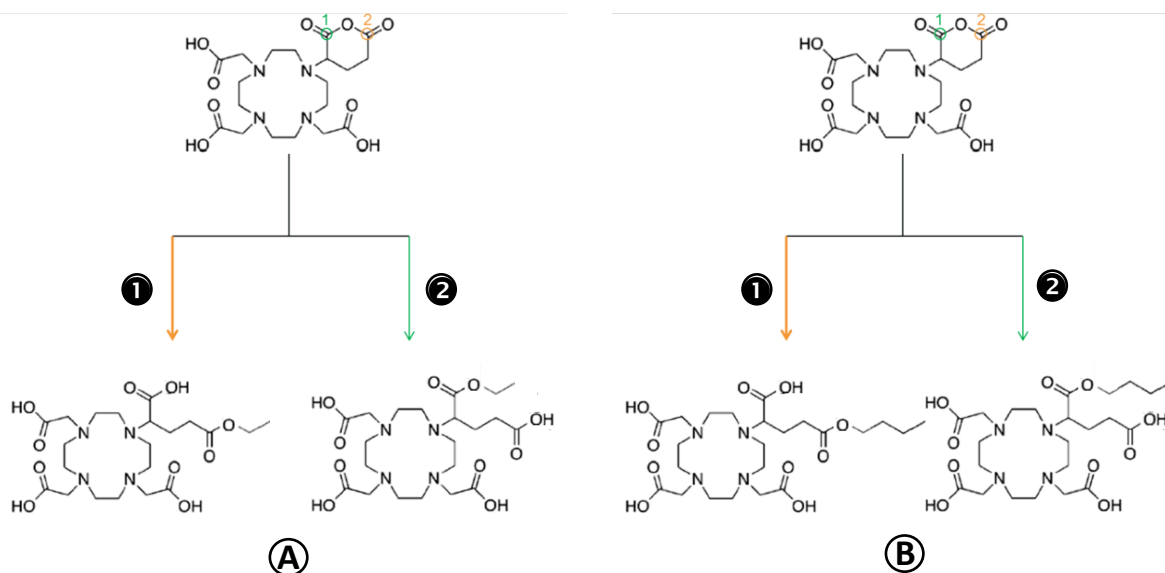


Figure 4: Reaction scheme of DOTAGA-anhydride with ethanol and butanol, formation of two regioisomers of DOTAGA-monoethyl ester (A) and DOTAGA-monobutyl ester (B).

chromatography in combination with mass spectrometry (LC-MS).

### *Strategy point 2: Complexation reactions*

The lanthanide ion must be complexed in a very controlled condition since any presence of water combined with temperature will lead to the hydrolysis of the ester. In addition, the complexation of a lanthanide ion by a DOTAGA or a derivative in water requires pH adjustment and heating (70 °C) and may take up to 2 weeks [17]. Therefore, we have chosen to perform complexation of the Ln<sup>3+</sup> in dimethyl-sulfoxide (DMSO) or alcohol (EtOH<sub>abs</sub> or BuOH<sub>abs</sub>). The complexation process can be followed by recording the lifetime of the fluorescence, which tends to increase with the reduction of water molecules in the lanthanide coordination sphere. This is due to the replacement of H<sub>2</sub>O molecules by the chelating functions. For a complex formed by Tb<sup>3+</sup> and DOTA this value can increase up to 2 ms while the lifetime of free terbium ions is around 0.4 ms [18]. However, for a more complex mixture of fluorescent species (more than three or four compounds) the lifetime may give a qualitative information but do not allow to conclude uniquely on the stability of the complex.

#### *Complexation in DMSO*

DMSO was used to preserve the ester form. The first step consists of mixing 20 mg of DOTAGA-ethyl ester solution with 4 mL of DMSO with addition of a few grains of a molecular sieve. At the same time ethylenediamine tetra-acetic acid (EDTA), diethylenetriamine penta-acetic acid (DTPA) and DOTAGA terbium complexes are synthesized by diluting respectively 12, 16 and 20 mg of pure complexing agent compounds (Sigma-Aldrich) in 4 mL of DMSO. The fluorescence lifetime of the lanthanide in water are well described in the literature contrarily to those in DMSO, and the use of EDTA, DOTAGA and DTPA will give a reference for the experiment [18]. The terbium source was prepared by dissolving 40 mg of TbCl<sub>3</sub>·6H<sub>2</sub>O in 8 mL of DMSO with molecular sieves added. The complexation was performed by mixing 1 mL of terbium solution with 1 mL of solutions of each of the complexing agents and with a reference sample with 1 mL of DMSO without complexing agents. Fluorescence measurements including accumulation of lifetime and excitation spectra were performed by focusing on the emission at 545 nm, which is the most intense emission peak of terbium.

#### *Complexation in alcohol and UV/TRF-HPLC analysis*

The experiments were performed by mixing 3 mg of the desired ligand mixture (DOTAGA-mono ethyl- or monobutyl ester) with 8 mg of TbCl<sub>3</sub>·6H<sub>2</sub>O in 2 mL of the corresponding alcohol to prevent transesterification (ethanol for ethyl ester and butanol for butyl ester). The reactions were performed in sealed ampoules for 24 h at 100 °C. 100 µL of the obtained samples were evaporated at 100 °C in open vials and 1 mL of the eluent used as mobile phase in the HPLC (water with 0.1 % (v/v) H<sub>3</sub>PO<sub>4</sub>; pH 2.5) was added before UV/TRF-HPLC analysis. The chromatographic separation was achieved with a mobile phase consisting of 0.1 % H<sub>3</sub>PO<sub>4</sub> in MilliQ water within the first 3 minutes followed by a gradient of up to 90 % of methanol at t<sub>r</sub> = 10 min. The free ligands (without terbium) were analysed in parallel.

#### *Partition experiments of DOTAGA-monoethyl ester-Ln and DOTAGA-monobutyl ester-Ln*

The partitioning tests were carried out using a volumetric ratio of oil:water = 1:1. In the standard procedure, 500 µL of a model production water (Table1) containing 0.2 ppm of tracer is mixed with 500 µL of a synthetic oil or with a crude-oil from a Norwegian oil field (Norne Oil).



Table 1: Salt content of the synthetic production water (PW).

Conditions	Electrolyte	Concentration
T = 20 °C pH 7	NaCl	40.0 g/L
	KCl	0.63 g/L
	MgCl <sub>2</sub>	2.54 g/L
	NaHCO <sub>3</sub>	0.21 g/L
	Na <sub>2</sub> SO <sub>4</sub>	0.04 g/L

The samples were shaken vigorously, and 100 µL of the aqueous phase were sampled after 5 minutes. The aqueous phase was directly injected in the HPLC without any pre-treatment.

#### *LC-MS characterizations*

The complexes diluted in water (not more than two hours prior the analysis) were analyzed, without pre-treatment, by LC-MS (high-resolution MS) to obtain information on the structure of the formed complex and increase the comprehension of results from the partitioning experiments. The UPLC system was coupled with high resolution mass spectrometry (QExactive Orbitrap from Thermo Fisher Scientific®). A C<sub>18</sub> reversed-phase column, BEH (1.7 µm, 150 mm) from Waters®, was used for the chromatographic separation. An elution gradient mode was utilized based on an aqueous solution of 0.1 % formic acid (A) and an organic phase with 100 % of methanol (B). Starting conditions were 100 % of A within the first 3 minutes, - thereafter increasing to 90 % of B until 10 minutes of elution. The MS analysis was performed with an electrospray ionization (ESI) interface in positive (3.5 kV) ionization mode. For the MS detection, the acquisition method was performed in full scan mode with a resolution of 70 000 at 200 Da, in the range of 100-800 Da.

#### *Hydrolysis rate / Stability at reservoir conditions*

The hydrolysis rate of DOTAGA-monoethyl ester-Tb was studied at 50, 70 and 100 °C. The tracer is prepared to a concentration of 2 ppm in a synthetic production water (Table1). The 2 ppm solution is divided into 25 samples of 1.5 mL and the stability test is performed in sealed glass vials. The samples were recovered at different times and kept at -20°C until the analysis could take place. Each set of samples (50, 70 and 100°C) was left at ambient temperature for 30 minutes prior the analysis and all samples were analyzed consecutively. The tracer quantification was performed by TRF-HPLC using an isocratic mode (30 % MeOH / 70 % water at 0.1 % phosphoric acid). The HPLC elution peak corresponding to the monoester complex DOTAGA-monoethyl ester-Tb was centered at 5.43 minutes on the TRF chromatogram.

### 3.2. Results and discussion

#### *DOTAGA-monoalkylester ligands synthesis*

Samples from the laboratory synthesis with the expected compounds A (ethyl ester) and B (butyl ester) were analysed by HPLC-UV (Agilent Technologies 1290 Infinity II) with UV detection at 210 nm. Chromatographic separation was achieved with the column Waters "ACQUITY UPLC BEH" reversed-phase C<sub>18</sub> 1.7 µm packed column. The mobile phase consisted of buffered water (0.1 % H<sub>3</sub>PO<sub>4</sub>) within the first 3 minutes followed by a gradient up to 90% of methanol at t<sub>r</sub> = 10 min. The chromatograms obtained showed that the reaction leads to the formation of secondary products which can be related to the formation of di-, tri-, tetra- and penta-esters compounds.

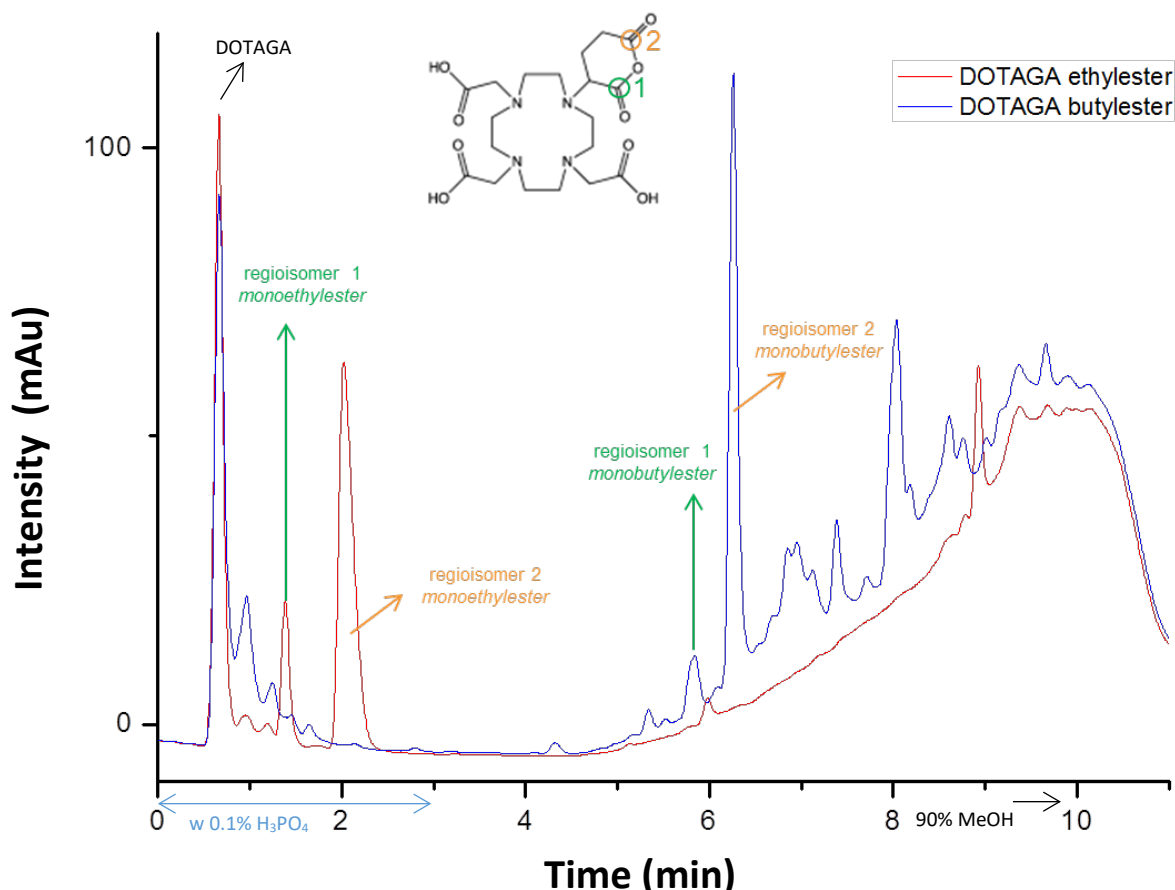


Figure 5: UPLC-UV chromatograms for DOTAGA-ethyl ester experiment (red line) and DOTAGA-butyl ester experiment (blue line).

The peak at  $t_r = 0.66$  min can be attributed to the unreacted DOTAGA or the DOTAGA acid from already hydrolysed DOTAGA-ester. DOTAGA is mostly polar and hydrophilic due to the 5 carboxylic acid functions contained within its structure. The esterification leads to the formation of more hydrophobic compounds as observed on the chromatograms with the appearance of peaks at  $t_r = 1.37, 2.01, 5.98$  and  $8.91$  min for the DOTAGA-ethyl ester (A). For the DOTAGA-butyl ester (B), the chromatogram reveals more than the expected five peaks, however compounds at  $t_r = 5.80, 6.25$  and  $8.04$  seem to be synthesized with the greater yield. Furthermore, depending on the regioisomer (nucleophilic attack on  $C_1$  or  $C_2$ ) the polarity of the DOTAGA can be affected and lead to the formation of many different combinations and, therefore, to different retention times between two regioisomers.

The results were confirmed by LC-MS (UPLC-QExactive from Thermo Fisher Scientific<sup>®</sup>) and published in a conference paper [19].

#### Complexation of $Ln^{3+}$ : DMSO

Fluorescence lifetime measurements for the emission band at 545 nm were performed on the samples with an excitation wavelength at 265 nm.

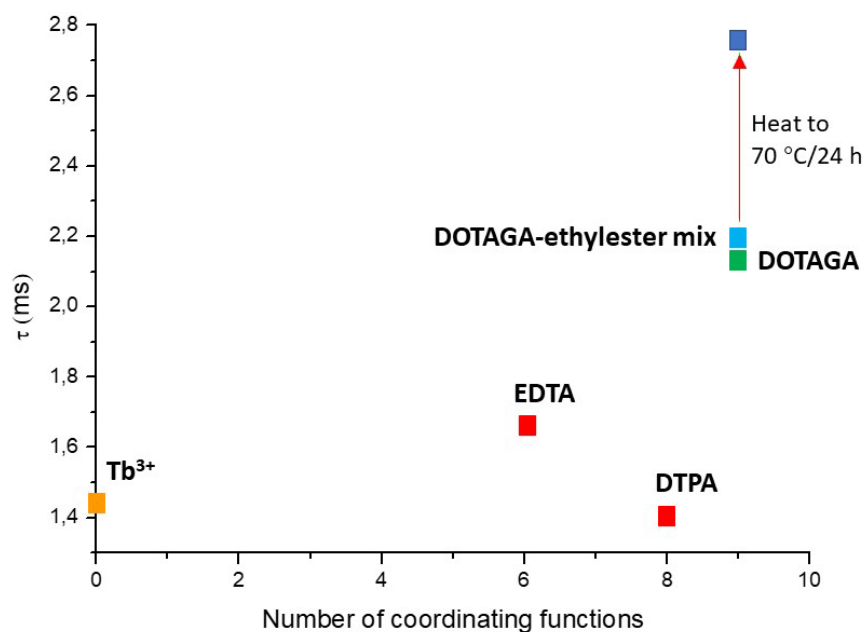


Figure 6: Fluorescence lifetime obtained for the different complexes of terbium in DMSO

Lifetime measurements (Figure 6) show an increase from EDTA (1.66 ms) to DOTAGA (2.2 ms) which tend to confirm that the terbium is well complexed in all cases. The DOTAGA and DOTAGA-ethyl ester complexes of terbium display a lifetime close to 2.2 ms which is encouraging for the study. However, the lifetime measured for the reaction mixture can give an indication only, but it is not representative for the stability of the monoethyl ester complex. 0.5 mL of DOTAGA- $Tb^{3+}$  and DOTAGA-ethyl ester- $Tb^{3+}$  were placed at 70°C for 24h. The lifetime for the DOTAGA-ethyl ester- $Tb^{3+}$  increase from 2.2 to 2.7 ms with the temperature treatment indicating increased complexation strength.

The use of Time-Resolved Fluorescence to characterize the tracers can only be considered for a more advanced step of the study. In fact, at this stage we need to separate the different forms to study specifically the desired compounds. Hence, we have tried to analyze the two complexes DOTAGA- $Tb^{3+}$  and DOTAGA-ethyl ester- $Tb^{3+}$  by UPLC-UV and UPLC-MS after the heating treatment. However, the presence of DMSO was problematic for the liquid chromatography (UV detection) characterization. One hypothesis was that even after high dilution in water the DMSO absorbs to strongly the UV light in a similar range that the target compounds. An observation was also that the products were not well separated in presence of DMSO.

#### *New methodology to separate and qualify the new set of tracers: HPLC-TRF*

The reaction mixtures after complexation in alcohols were characterized by HPLC. The use of time-resolved fluorescence for detecting the different forms of the complex (esters, acidic) allows a very high specificity. The analysis of the DOTAGA-monoethyl ester- $Tb$  complex is given as an example in Figure 7. A sample of free ligand (DOTAGA-monoethyl ester) was analyzed and compared to the complex.

The UV chromatogram in black (solid line) represents the free ligands sample mixture and the peaks at  $t_r=0.9;1.6$  and 2.6 min can be attributed to the unreacted DOTAGA and to DOTAGA-monoethyl ester

regioisomer 1 and 2, respectively (Figure 7). The black dashed line represents the UV chromatogram of the complexation mixture. As can be seen on the time-resolved fluorescence chromatogram in blue and the UV chromatogram (dashed black line), after complexation of the terbium the two regioisomers are retained from 5 to 6 minutes longer than the free ligands. The two regioisomer free-ligands are clearly seen in the water fraction (0 to 3 minutes, Figure 5).

#### Partitioning tests and LC-MS characterizations

Static (batch type) partitioning tests were performed to determine the partition coefficients (K-value) of the new tracers. The results obtained for the complex DOTAGA-monoethyl ester-Tb are given as an example in Figure 8.

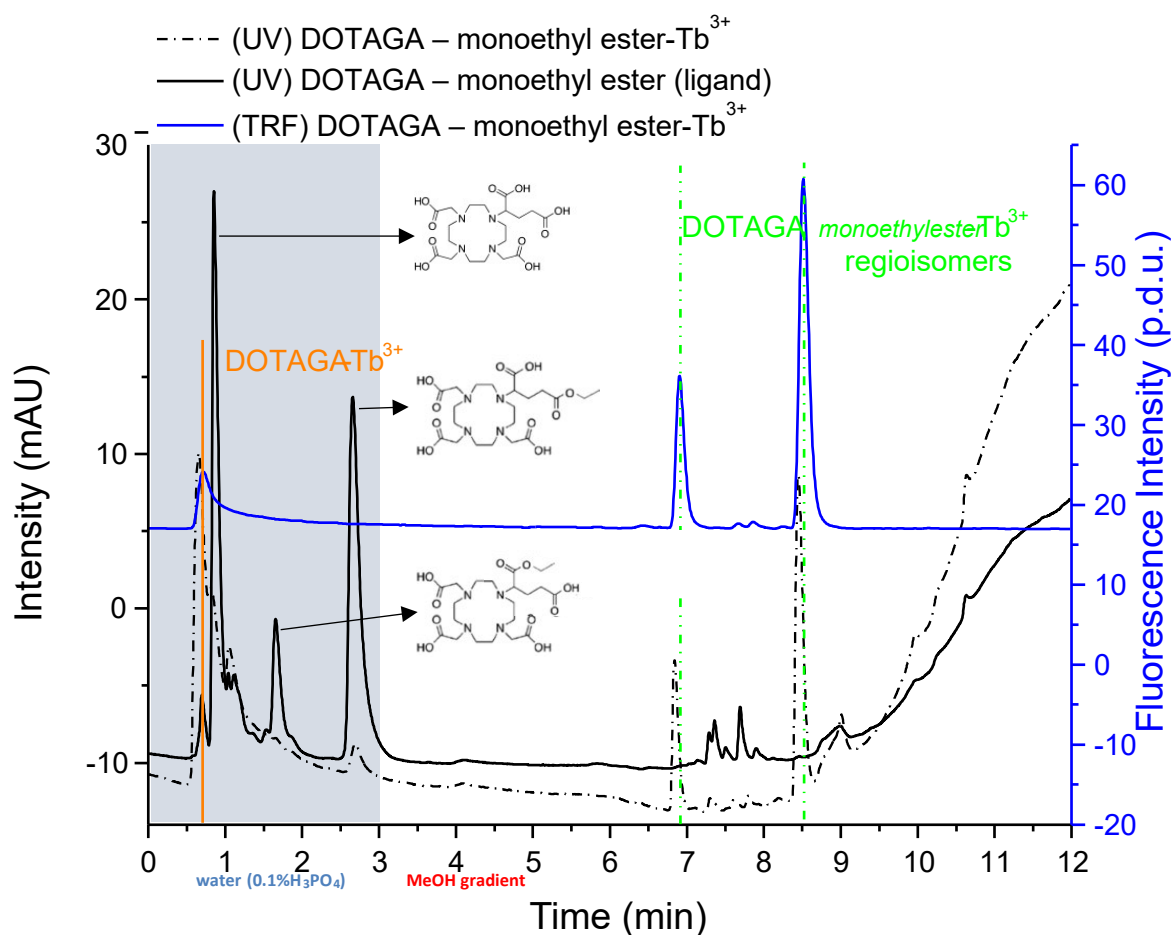


Figure 7: HPLC chromatograms of the ligand DOTAGA-monoethyl ester and of the reaction mixture containing the  $[Tb(DOTAGA\text{-monoethyl ester})(H_2O)]^{1-}$  and a fraction of unreacted DOTAGA with  $Tb^{3+}$ . Detected by: (blue chromatogram for the complex) Time-Resolved Fluorescence (0.1 ms delay; 5 ms gate; excitation 220 nm; emission 545nm) and by (black chromatograms complex and ligand) UV detection.

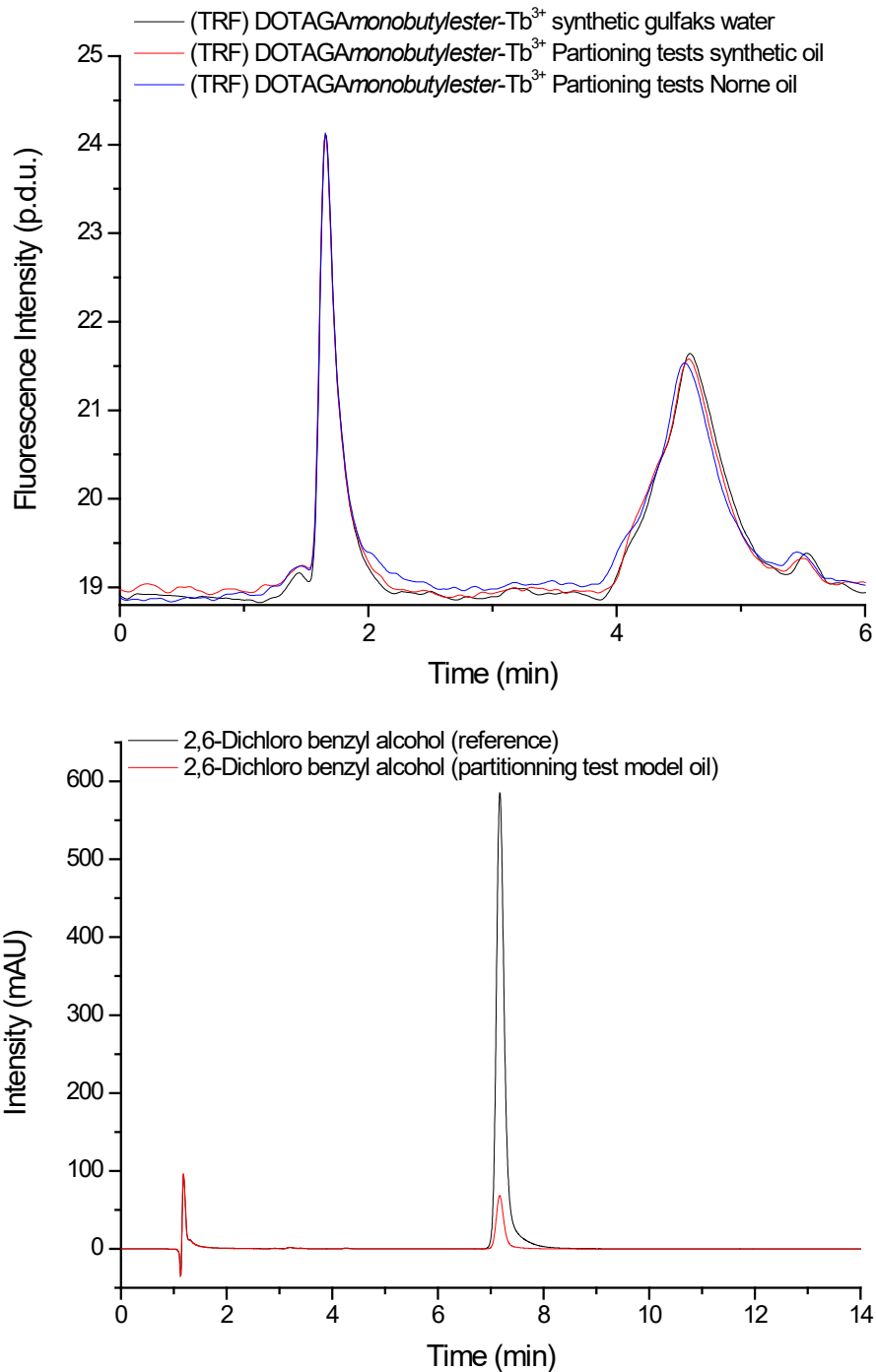


Figure 8: HPLC chromatograms of: (top)  $[Tb(DOTAGA\text{-}monobutylester)(H_2O)]^{1-}$  partitioning test with synthetic production water (pH 7) with: (red) model oil, (blue) crude-oil and (black) reference (bottom) partitioning test under the same conditions (synthetic production water; 50/50 (v/v) O/W) of 2,6-Dichloro benzyl alcohol acid used as a reference partitioning tracer to validate the protocol.

The chromatograms presented in Figure 8 (top figure: blue, black and red lines) were obtained from the aqueous phase analysis containing the complex DOTAGA-*monobutylester*-Tb. No significant changes (beyond the experimental error) in the complex concentration were observed during the partitioning test using the synthetic production water at pH7 in contact with two different organic fluids (crude-oil and model oil). The experimental procedure was evaluated by testing the 2,6-

dichlorobenzyl alcohol, known as a partitioning tracer, under the same conditions (Figure 8 bottom). The results suggest that the DOTAGA-*monobutylester*-Tb complex is exclusively hydrophilic, or has very little lipophilicity, despite of the attempt of increasing its affinity with the oil phase by esterification.

*Structure determination by LC-MS: Analysis of reference and water in contact with oil.*

The compounds are ionized in the ESI probe after leaving the chromatographic system (column). In the acidic conditions of the mobile phase combined with the electric potential of the ESI, protonation will occur in the ester group bound. However, the desired monoester was not found on the Total Ion Chromatogram (TIC) when extracting the ion-chromatogram using this mass (terbium mass added to DOTAGA-*monobutylester* mass with four additional H<sup>+</sup>; Figure 9 center). In a second approach, the ion-chromatogram was extracted from the TIC using a mass corresponding to the monoprotonated DOTAGA-*monobutylester*-Tb (neutralization of the three positive charges of the terbium) (Figure 9 right).

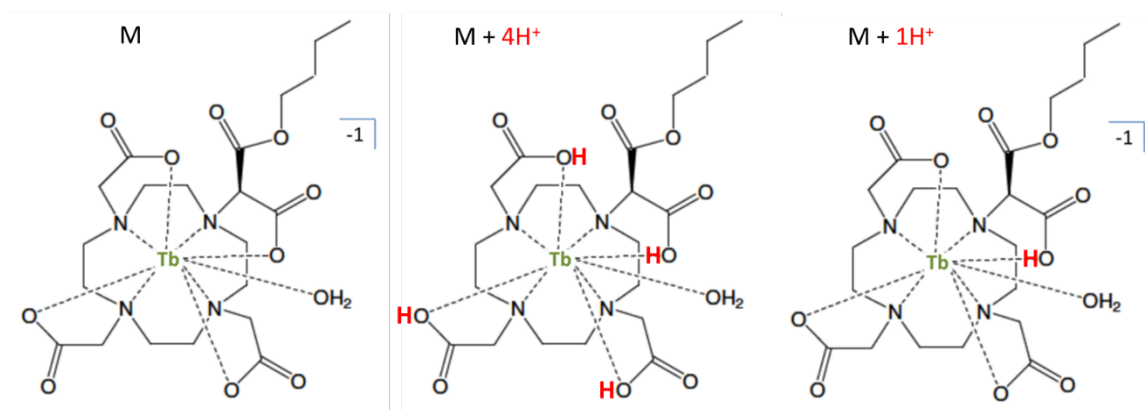


Figure 9: Possible forms of the complex DOTAGA-*monobutylester*-Tb under the chromatographic conditions investigated by extracting the ion-chromatograms from the TIC using the corresponding masses ( $M$ ,  $M+4$  and  $M+1$ ).

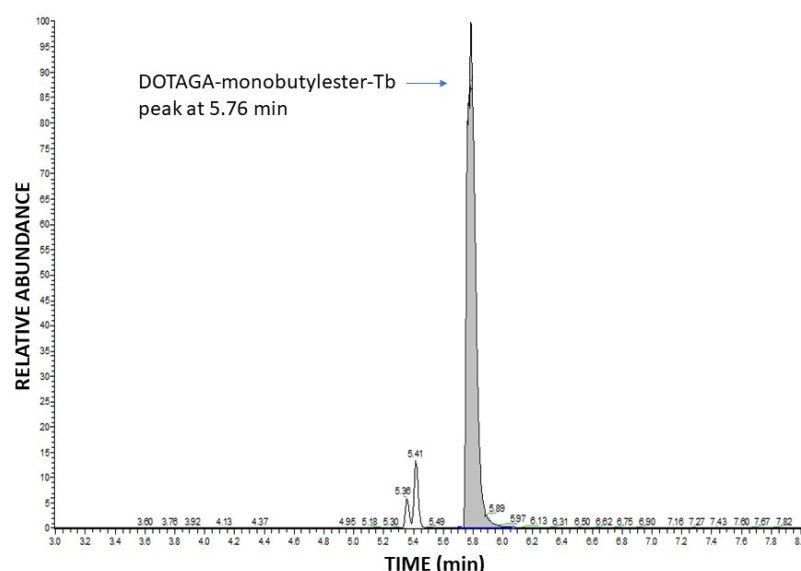


Figure 9: Extracted ion-chromatogram of the DOTAGA-*monobutylester* for a  $m/z= 689.1769-689.19251$  (form with three acidic groups complexing the terbium and one protonated).

In that case an intense retention peak centered on 5.76 minutes was observed confirming that under the applied chromatographic conditions the lanthanide ionic center is complexed by three carboxylic acids from the DOTAGA-monobutylester (Figure 10).

The additional carboxylic acid, protonated in the chromatographic conditions, is most likely unprotonated under the partitioning test conditions (pH7) and provide a negative charge that may partially explain the exclusive hydrophilic behavior. Furthermore, the extracted ion-chromatogram for the di-ester compound DOTAGA-dibutylester-Tb reveals four isomers at a significantly lower concentration than the monoester form (Figure 11).

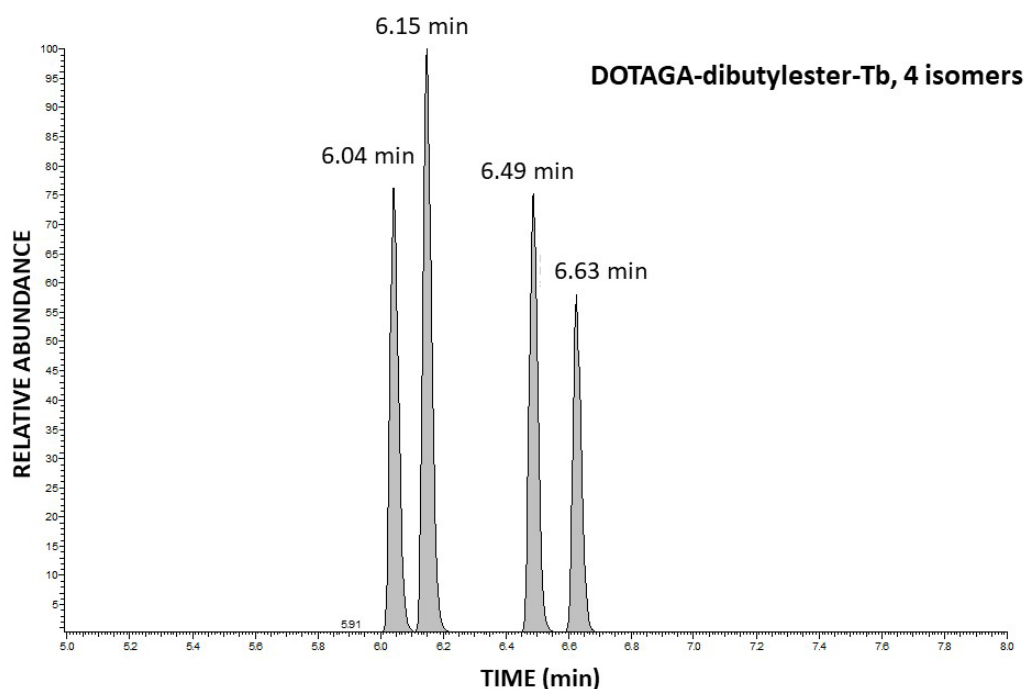


Figure 10: Extracted ion-chromatogram of the DOTAGA-dibutylester for a  $m/z= 745.23654-745.25687$  (form with three acidic group complexing the terbium and one protonated)

The comparison of the signals before and after contact with oil reveals that none of the diester isomers were partitioning. The measured intensities were  $5.25 \times 10^8$  and  $5.02 \times 10^8$ , respectively. This clearly shows that adding hydrophobic functions on the chelate via esters is not sufficient to adjust the partitioning behavior of the complex. In fact, the new ester tracers are exclusively hydrophilic at pH around 7 due to global negative charges, meaning they do not dissolve in the hydrocarbon phase. However, chromatographic retention times suggest they exhibit a “surfactant-like” behavior. Other strategies using more hydrophobic ligands and neutral final complexes, are subjects for future explorations.

However, as a spin-off, the sensitivity of the new tracers toward temperature might be relevant for improving SoR determination and more generally collect *in-situ* temperature data [5].

#### *Hydrolysis rate / Stability under reservoir conditions*

The DOTAGA-monobutylester-Tb concentration as function of the temperature (50, 70 and 100°C) was studied in a synthetic PW. The hydrolysis of the ester follows a simple and approximate exponential decay consistent with first order kinetics shown for the three studied temperatures in Figure 12.

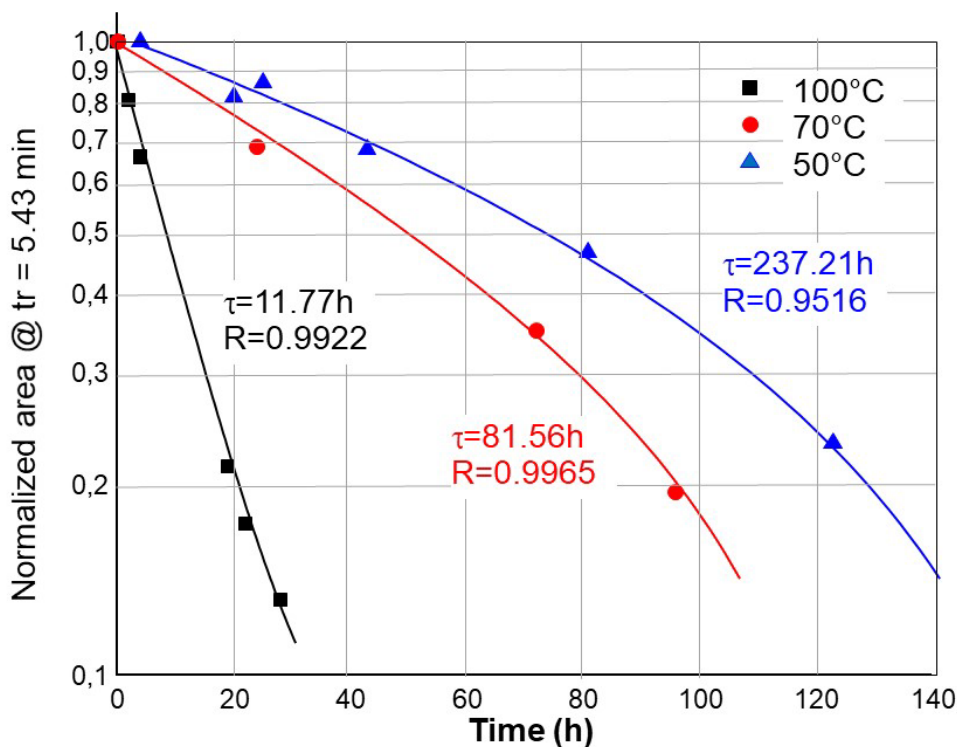


Figure 11: Diagram representing the absolute area of the elution peak at  $t_r = 5.43$  min (for the DOTAGA-monobutylester-Tb concentration) as function of time for three temperatures 50, 70 and 100 °C. Monoexponential regressions were used to determine the half-life ( $\tau$ ). The Y-axis is presented using a logarithmic scale.

The half-lives for hydrolysis of the DOTAGA monobutylester-Tb at 50, 70 and 100 °C were 9.8, 3.4, and 0.5 days, respectively. The displayed half-lives are particularly suited for the timeframe of most of the common SWCTT approaches where reservoir temperatures are generally ranging between 60 and 100°C. Increasing the length of the ester chain might lead to increase in the half-life. In fact, a higher steric hindrance has been shown to slow the attack of the ester by a molecule of water.

#### 4. Conclusion(s)

The goal of the present study was to establish methods for synthesis and characterization strategies for a new set of long-lived fluorescent tracers for SWCTT and SoR estimation. The two-step protocol consisted of: (i) synthesizing the ligand and (ii) complexation of the Ln ions in controlled conditions.

The use of DOTAGA-anhydride as reactant allowed obtaining two potential ligand candidates for forming the targeted complexes. The successful synthesis of DOTAGA-monoethylester and DOTAGA-monobutylester have been evidenced and proven by HPLC-UV and UPLC-MS.

The complexation of Terbium (III) by the new synthesized ligands was performed in DMSO and in excess alcohol. The reactional mixtures were not purified leading to the formation of complex mixtures of different fluorescent products (mono-, di-, tri- esterified compounds and other by-products). Thus, the characterization of the fluorescent tracers by only fluorescence spectroscopy becomes very difficult. This was especially the case of the complexes obtained in DMSO.



The complexation in alcohol yielded a reactional mixture easily characterizable by HPLC. A new protocol of characterization by HPLC-TRF was developed allowing the fast and easy identification and quantification of the targeted complexes in the mixtures with a high specificity. The results were confirmed by UPLC-MS. This method has produced valuable knowledge on the structure of the complex (DOTAGA-monobutyl ester). Under the chromatographic conditions, three of the carboxylic acid groups were bound to the  $Tb^{3+}$  cation, and the fourth carboxylic group seemed to be protonated.

Static partitioning experiments performed in synthetic production water and pure water using two different oils (crude-oil and synthetic oil) have evidenced that the obtained tracers were exclusively hydrophilic. This could be explained by the global negative charge, i.e. the fourth carboxylic group has not been protonated during the partitioning tests at pH7. Additionally, the DOTAGA-alkyl esters are constituted of a relatively high fraction of significantly electronegative atoms (such as oxygen and nitrogen). As a speculation, these enhance the polarity of the structure and probably lead to the presence of strong hydration "sphere" that further prevents the transfer of the ester from an aqueous to a hydrocarbon phase.

Results from the stability experiments performed with synthetic production water at 70°C with two weeks contact time showed hydrolysis kinetics well suitable for a SWCTT for the [DOTAGA-butyl ester- $Tb$ ] $^{1-}$  tracer. The lack of sufficient water/oil partitioning could possibly be remediated by a longer hydrocarbon ester chain and more acidic conditions. However, as the hydrocarbon ester length increases, the hydrolysis rate will probably decrease. Thus, the time needed for a SWCTT due to increased shut-in time will possibly become unacceptably long.

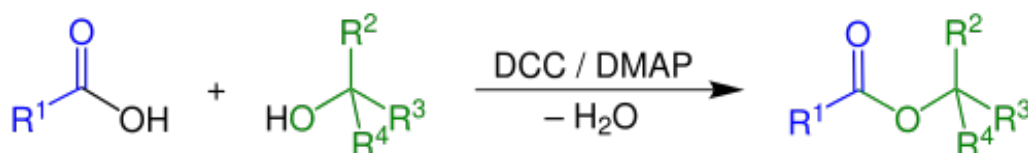
Finally, the UPLC-MS characterizations have also evidenced the presence of the DOTAGA-tri-butyl ester- $Tb$  form. Even with three esters on the molecule, the partitioning tests have shown no presence of the compound in the oil phase. This observation hardens the assumption that the originally charged complexes are not neutralized in the production water. For the success of the original project idea, neutral complexes should be obtained under relevant (relatively to the reservoir) pH conditions. This should be the case of the [DOTA-monoester- $Ln$ ] $^0$ , however, attempts to produce this complex have not been successful so far.

## 5. Future work/plans

*Ln-Complex for SWCTT: partnership with University of Lyon*

Until now, the approaches to synthesize the partitioning lanthanide complexes were based on the use of a dodecane tetraacetic acid (DOTA) ligand derivative called DOTA-GA (Glutamic Acid). As explained above, this resulted in a final complex which was likely negatively charged having no water/oil partitioning behavior.

A new proposed synthesis route is based on the modification of a DOTA ligand to obtain a neutral lanthanide complex using the Steglich esterification method [20], known for being milder than the classical Fisher esterification [21]. The reaction is based on the protection of the 3 carboxylic acids of the DOTA by complexation on the lanthanide ion (neutral complex), the 4<sup>th</sup> acid is supposedly more reactive. It is also possible to esterify the DOTA and then complex the metal ion in alcohol. The reaction uses di-cyclohexylcarbodiimide (DCC) as a coupling agent and 4-dimethylaminopyridine as a catalyst (DMAP).



Monoesters of DOTA are currently being prepared using the Steglich esterification by Lyon University, our partner in the project. It should be noticed that the first observation is that the 4<sup>th</sup> carboxylic function of the DOTA doesn't seem to be very reactive, but more characterizations have to be performed (HPLC-TRF and UPLC-MS). The synthesis aims at obtaining at least four different esters from the ethyl- to the octyl-ester. The products will be characterized with the new methodology developed within the scope of this project (HPLC-TRF) and UPLC-MS for confirming the formation of the desired esters. The study aims at clarifying what are the key parameters that govern the partitioning behavior of such tracers. Static partitioning will be systematically performed using a synthetic oil and a crude oil from the Norwegian continental shelf to study the influence of the ester chain length on the partitioning coefficient.

*Spin-off: Real-time PITT Monitoring*

Another sub-task in the project will be to evaluate the potential use of Ln-complexes for PITT applications. In that case, two tracers are co-injected (phase partitioning and passive water tracer) and the two tracers have to be non-reactive, i.e. not degrade. The DOTA derivative called PCTA (3,6,9,15-Tetraazabicyclo[9.3.1]pentadeca-1(15),11,13-triene-3,6,9-triacetic acid, Figure 13) seems to be very promising (high quantum yield, neutral charge, affinity with oil). This ligand is commercially available. Hence, finding a way to modify this compound could lead to a new series of partitioning tracers for PITT.

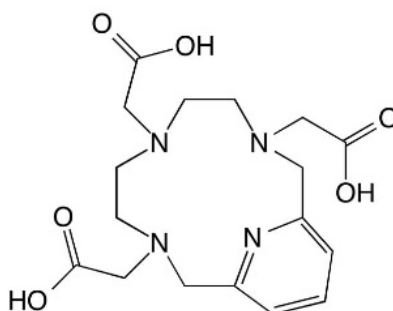


Figure 13: Representation of PCTA

## 6. Dissemination of results from start of this R&D subject

Brichart, T.B., Ould Metidji, M., Ferrando-Climent, L. and Bjørnstad, T.: *New Fluorescent Tracers for SWCTT*, in *IOR 2017 - 19th European Symposium on Improved Oil Recovery*, EAGE, Editor. 2017, EAGE: Stavanger, Norway.

Brichart, T.: *Final Project Report for the postdoc period of Thomas Brichart*, NIOR, 2018:  
 \*Task 2.5.1. *Development of nanoparticle tracers based on C-dots for interwell applications*  
 \*Task 2.5.2. *Single-Well Chemical Tracer Technology, SWCTT.*

Ould Metidji, M.: *IOR Center mid-2017 Activity Report*, NIOR, August 2017, 17 pp.:  
 \*Task 2.5.1. *Development of nanoparticle tracers based on C-dots for interwell applications*  
 \*Task 2.5.2. *Single-Well Chemical Tracer Technology, SWCTT.*

Ould Metidji, M: "IOR Center 2017 Activity Report, August 2017 to December 2018", NIOR, January 2018, 11 pp.:

- \*Task 2.5.1. *Development of nanoparticle tracers based on C-dots for interwell applications*
- \*Task 2.5.2. *Single-Well Chemical Tracer Technology, SWCTT.*

Ould Metidji, M: "IOR Center 2018 Activity Report, January 2018 to December 2018", NIOR, August 2018, 11 pp.:

- \*Task 2.5.1. *Development of nanoparticle tracers based on C-dots for interwell applications*
- \*Task 2.5.2. *Single-Well Chemical Tracer Technology, SWCTT.*

T.B. Brichart, M.O.M. Ould Metidji\*, L.F. Ferrando-Climent & T. Bjørnstad: "New Fluorescent Tracers for SWCTT", presented at IOR NORWAY 2017 – 19th European Symposium on Improved Oil Recovery, 24-27 April 2017, Stavanger, Norway

Lawrence Cathles and Mahmoud Ould Metidji: "Multicomponent tracer methods to assess fracture controlled flow tens of meters from the wellbore and a proposed field test", presented at NIOR 2018 Workshop, 23 April 2018, Stavanger, Norway

Ould Metidji, M., Silva, M., Krivokapic, A. and Bjørnstad, T.: "Synthesis and Characterization of a Reactive Fluorescent Tracer and its Possible Use for Reservoir Temperature's Data Collection", Paper n°156, presented at the 20<sup>th</sup> European Symposium on Improved Oil Recovery, Pau, France, 8-11 April, 2019.

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