

DEVELOPMENT OF SOME NEW AZA AND THIA COMPLEX AS ALTERNATIVE TRACERS FOR OIL RESERVOIRS

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ABSTRACT

A promising group of non-sorbing tracers are lanthanide ions complexed to organic anions, which yield a negatively charged complex. Besides, this lanthanide ion could be chosen which, in its non-complexed form, is very insoluble in groundwater and thus no severe background concentrations problem would arise. The lanthanide elements may be used as tracers since they present good solubility in water, when complexed, and the nuclides have high neutron cross sections, they may be used as activable tracers under neutron irradiation in order to evaluate the efficiency of the petroleum production processes. For this purpose, tracers must be soluble in the aqueous phase and be insoluble in the organic phase, they also must not be adsorbed on the internal microporous rock formations and be easily detectable. Lanthanide complexes with DTPA and thiodicarboxylic acid ligands are an alternative to the development of these novel tracers since their properties may be chemically adjusted.

1. INTRODUCTION

Nowadays petroleum is one of the most important natural resources of the world, since it is one of the main primary sources of energy and also raw material for many different products. It can be found accumulated in the subsoil, and it was produced from the remaining portions of animals and vegetables, in a process that took millions of years to be concluded.¹ Initially, only a small fraction of the oil contained in a reservoir (about 25%) can be extracted, and for this reason fluids are injected in the deposit to increase the recovery of the remaining quantity, this process, called Secondary Recovery.¹ The fluid most commonly injected is water which should be previously treated so that no physical or chemical alterations occur in the reservoir. The efficiency of the water flow process highly depends on the rock characteristics. It will generally be less efficient if heterogeneities are present in the reservoir, such as permeability barriers which prevent a good displacement of the petroleum by the injected water^{2,3}. Generally, the injected fluid is labeled with a tracer (radioactive or non-radioactive) and the produced fluid from the well(s) of interest is sampled and analyzed to determine the tracer response. A variety of materials have been used as a water tracer in early works on streams, underground caverns, groundwater and oilfields.¹

A tracer is any substance which, when incorporated in the mass of a system (an industrial process, an environmental compartment, a living organism, etc) allows the investigation of its behavior in a particular physical, chemical, biological, or of another natural process. The most important characteristic of tracers is that they behave as close as possible to the material to be studied and they possess characteristics that make them detectable even if in low concentrations. The most used non-isotopic water tracers consist of specific chemical compounds soluble in water, easily identifiable and which can be measured by means of high sensitivity analytical techniques. They may be organic, ionic or dye compounds.³The isotopic tracers can be divided in four groups: purposely added radioactive tracers; activable tracers (formed by non-radioactive nuclides whose concentration is determined through neutron activation analysis); natural radioactive tracers and stable isotopes from water elements. The group of activable tracers is of great interest, since they can be introduced in the system to be studied in their inactive state and then sampled and dosed through neutron activation. Besides, they might eliminate the biggest problem involving radioactive tracers in field works: the safety of high activities handled under relatively precarious conditions, the possible radioisotopes decay during long work, as well as the logistic difficulties involved in the transport of radioactive materials to isolated regions, sometimes in the oceans⁴. Based on tracer behavior, certain transport parameters within the reservoir may be assumed. In other words, based on an appropriate interpretation of the transference functions between the injection and the production well, evinced by results obtained in experiments with tracers, it is possible to diagnose possible inefficiencies in the secondary recovery process and to take the adequate decisions to correct their causes⁴.

1.1. TRACER BEHAVIOR IN PETROLEUM RESERVOIRS

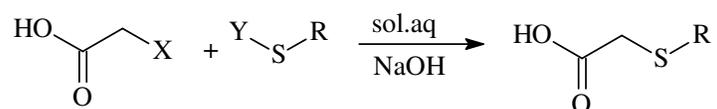
The fluid flow is anisotropic in most reservoirs. The structures of the reservoir are often extended in layers containing significant heterogeneities which lead to directional variations in the flow extension. And in this point the tracer technology plays an important role, the tracer movement reflects the movement of injected fluid. It is important to make sure that the tracer properties are as similar as possible to the characteristics of the ideal tracer.³ In order to be applied as a tracer, a certain compound must fulfill a series of requirements, depending on the desired purpose. Tracers applied to study the water behavior inside the reservoir, must follow water molecules without being restrained in the rocky surfaces (phenomenon named sorption) or partitioned within the organic phase.³

No radioisotope species acts as an ideal tracer hence its selection should be carried out according to the characteristics of the process to be studied⁵. A promising group of non-sorbing tracers are metal ions strongly complexed to organic anions, which yield a negatively charged complex. Besides, this metal ion could be chosen which, in its non-complexed form, is very insoluble in groundwater and thus no severe background concentrations problem would arise.⁶ The lanthanide elements may be used as tracers (activable) since they present good solubility in water, when complexed, and the nuclides have high neutron cross sections, which allow their detection in extremely low concentrations by means of the Neutron Activation Analysis (NAA)⁷. Nevertheless, it is important to point out that for them to behave as good tracers the ideal is that they might behave similarly to water and that there is no partition in any other phase, unless this can be quantified⁵.

2. METHODOLOGY

2.1. Synthesis of Thiodicarboxylic acids (TD)⁸

These compounds have the general formula R-S-Y-COOH, at the present time they are proceeding basically according with the reaction:



General reaction procedure: addition of the alpha-halogen substituted acid, which was dissolved in an aqueous NaOH solution, to the corresponding thiolates (Y-S-R) also dissolved in NaOH, followed by magnetic stirring at room temperature for 20 to 34 h (or, alternatively, reflux during 8 h). Then diluted H₂SO₄ was added to the reacting system until pH = 2. If no immediate precipitation occurs, the reacting mixture is thrice extracted with dichloromethane (3 x 100 mL) and ethylic ether (3 x 100 mL). In the later case the whole organic extract is dried with anhydrous sodium sulfate, filtrated to eliminate the drying agent, and concentrated in a rotary evaporator. The dried and pure ligands have been obtained as colorless solids with a yield ranging from 63% to 91%. The obtained thiodicarboxylic acids were then characterized through spectrometric techniques by means of Infrared (IR) and Nuclear Magnetic Resonance of hydrogen (¹H-NMR) and of carbon- 13 (¹³C-NMR), as it is shown in Figure 1 seen below:

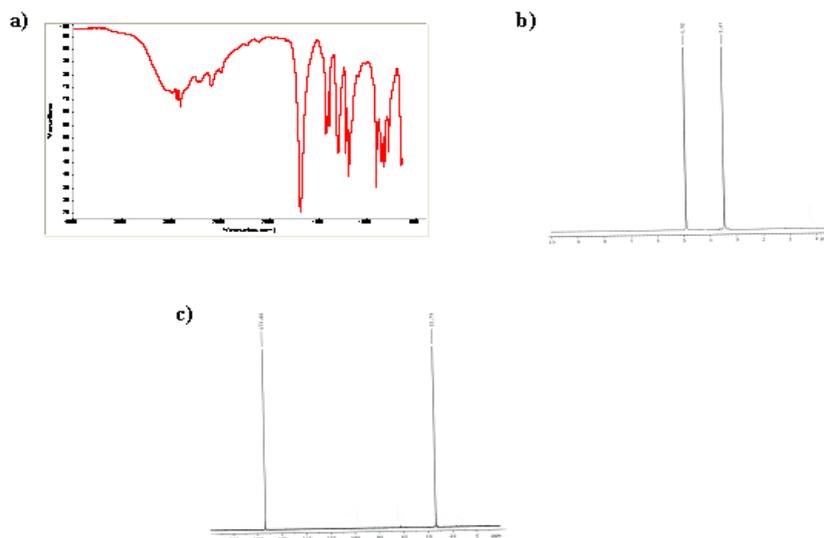
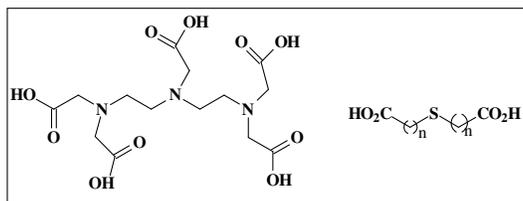


Figure 1. Spectra of thiodicarboxylic acids: a) Infrared (IR), b) Nuclear Magnetic Resonance of hydrogen (NMR of ^1H) and c) NMR of ^{13}C .

2.2. Lanthanoid complexation

The two ligands tested thus far were: DTPA - diethylenetriaminopentaacetic acid and thiodicarboxylic acid (TD), whose structural formulas are as following:



The complexation can be confirmed by the melting point analysis, since the free ligands, DTPA and TD respectively, have lower melting points (m.p.= 220 and 122 °C) than the corresponding complexes which have melting points > 200 °C. In fact, the complexation occurrence was checked by infrared spectrometry. The spectra of the above aminopolycarboxylic and thiodicarboxylic acids show absorption bands at the 1700-1600 cm⁻¹ wave number range. It can be seen in Figures 2 and 3, that this band shifts to a lower range in the case of europium complexed with DTPA and thiodicarboxylic acid.

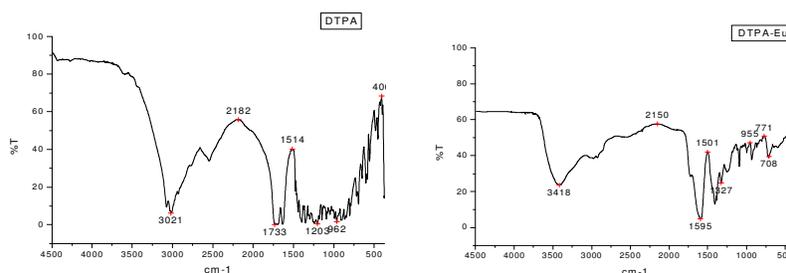


Figure 2. Infrared spectra of DTPA and Eu-DTPA (1:1)

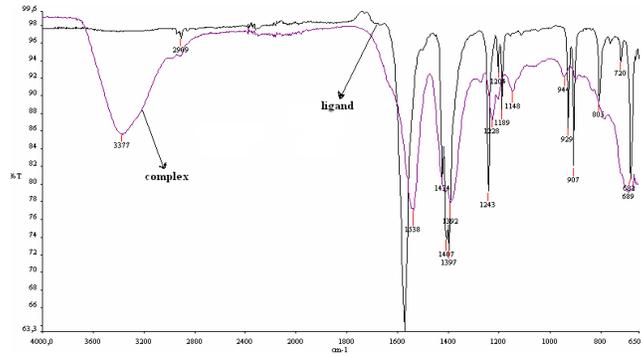


Figure 3. Infrared spectra of Thiodicarboxylic acid and complex Eu-Thiodicarboxylic (1:1)

2.3. Analysis in bench test with a core sample

The lanthanide concentration for Neutron Activation Analysis (NAA) was determined before and after contact with the phases of the system. In the case of tracer partition between water and a solid, the process is called sorption (comprising adsorption and desorption). The bench test with a core sample showed a possible adsorption of the tracer in the solid phase, see Figure 4:

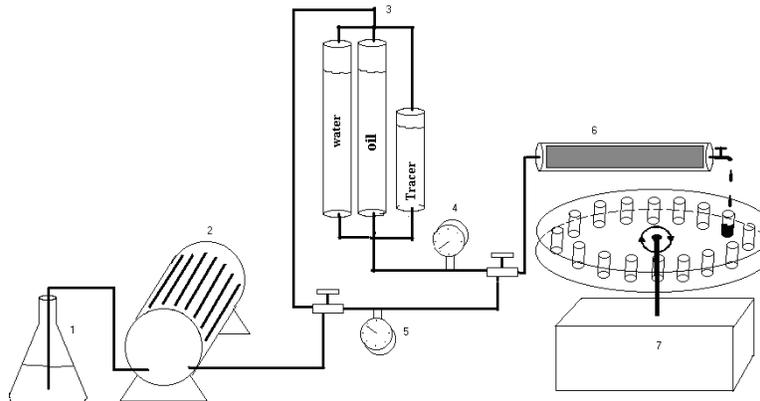
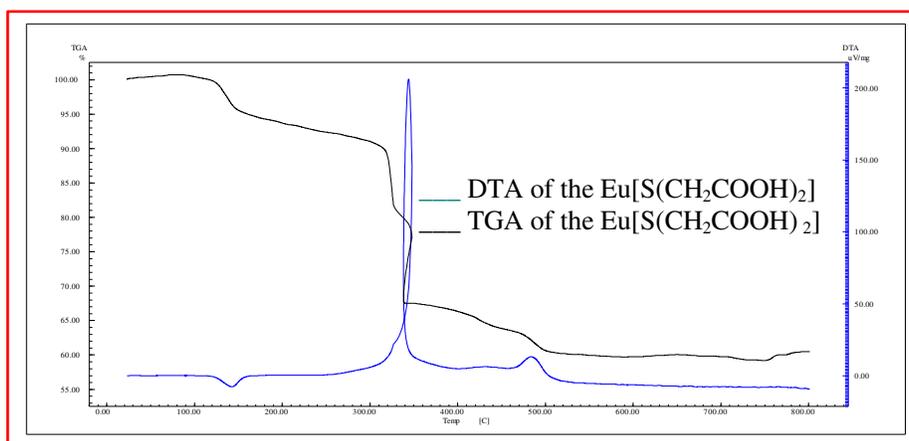


Figure 4. Experimental model with core sample: water reservoir (1), constant outflow pump (2), recipient for storing the tracer solution (3), pressure gauges (4,5), core sample (6), sample collection system (7).

Tritium was used for comparison since it behaves a nearly ideal tracer and is a reference for the evaluation of the performances of the other tracers. The tritium analyses were carried out by means of the Liquid Scintillation technique.

3. RESULTS AND DISCUSSION

The stability of the lanthanide complexes (Eu, La, Dy and Tb) with the ligand thiodicarboxylic acid was determined using thermogravimetric analysis (TGA), in dynamic air atmosphere at heating rate of 10 °C/min and temperature range of 20-800 °C, the results



obtained in the thermogravimetric analysis (TGA) is shown in Figure 5 and 6 see below:

Figure 5. Thermogravimetric analysis with Eu-Thiodicarboxylic acid

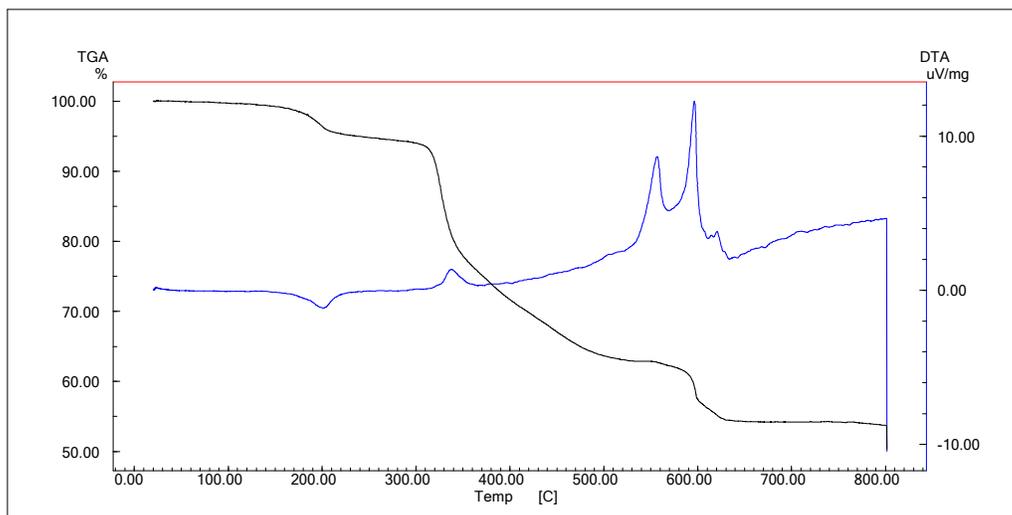


Figure 6. Thermogravimetric analysis with La-Thiodicarboxylic acid

The results of this thermal analytical technique confirm an effective complexation between the ions and the ligand. According to the thermogravimetric analysis, the complex $\text{Eu}[\text{S}(\text{CH}_2\text{COOH})_2]$ is stable up to approximately 120°C , and $\text{La}[\text{S}(\text{CH}_2\text{COOH})_2]$ is stable up to approximately 135°C , a very important feature to test this complexes as tracer in oil reservoirs, where the temperature is around 70°C . It can be also seen that the decomposition process occurs in five stages with an extremely exothermic effect, in the temperature range $320\text{-}360^\circ\text{C}$. The complex $\text{Eu}[\text{S}(\text{CH}_2\text{COOH})_2]$ at 345°C release of energy of 5985 kJ mol^{-1} (7.6 kJ g^{-1}), this energy is almost twice of the quantity released by detonation of the TNT (4.18 kJ g^{-1}). While the complex $\text{La}[\text{S}(\text{CH}_2\text{COOH})_2]$ in 338°C release of energy of $96,5 \text{ kJ mol}^{-1}$. Similar observations were found in the case of complexes $\text{Dy}[\text{S}(\text{CH}_2\text{COOH})_2]$ and $\text{Tb}[\text{S}(\text{CH}_2\text{COOH})_2]$.

In order to determine the occurrence of a partition for a solid, tritium and the complexes were simultaneously injected in the body test apparatus. The results obtained in the core sample bench test experiment for the solution of the tracer Eu-DTPA and tritium are shown in Figure 7 see below:

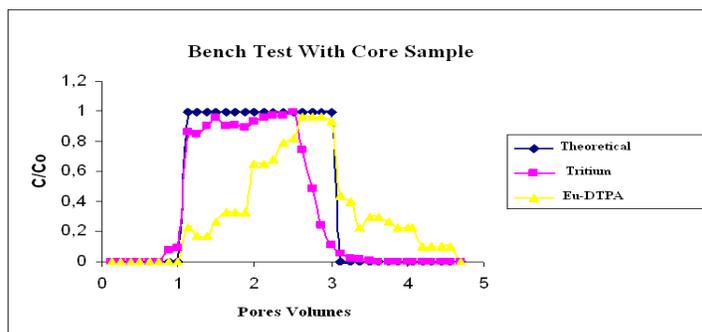


Figure 7. Bench test with tritium + Eu-DTPA

For the core test runs, the entrance and exit functions of both tritium and the complexed lanthanide did not coincided completely, which shows there were no delays with respect to tritium, that is, the absence of adsorption of the complex by the rock walls. Anyway, these data demonstrate the possible applicability of Eu-DTPA complex as tracers for petroleum reservoirs.

4. CONCLUSION

The occurrence of the complexation of the ligands with lanthanide ions can be confirmed by means of the Infrared (IR) spectrometry that indicated the band shifts of the characteristic carbonyl band to lower ranges. The characterization of the complexes Eu-thiodicarboxylic acid and La-thiodicarboxylic acid by thermogravimetric analysis (TGA) corroborates an effective complexation between the metals and the ligand and it is noteworthy that the complexes are stable up to approximately 120°C, a very important feature to test this complex as tracer in oil reservoirs, where the temperature is around 70°C. The results of both analytical techniques confirm an effective complexation between the metals and the ligand.

The results of the core tests, determined for two analytical techniques: Neutron Activation Analysis (NAA) for the lanthanide complexes, plus the Liquid Scintillation Spectrometry (LSS) for the tritium water injected simultaneously as Eu-DTPA reference tracer, showed:

- 1) there is an almost null percentage of complexed lanthanides dissolved in aqueous solution;
- 2) small evidence of sorption of the tracers on the internal surfaces of the rock formation pores since there was no displacement between the complexed lanthanide and reference tracer responses, whose behavior reflects faithfully the water flow outlet.

With these results two features of a good tracer were fulfilled: a behavior as similar as possible as the fluid whose behavior it tracers (water) and detectability even if only in low concentrations. The similar behavior reproduction of tritiated water by the tracers tested in the core runs are one of the inside a shielding of europium by the ligand DTPA.

The partition process of the tracer on the oil/water interface should now be carried out to be simulated by physical analogue of the Flow Injection Analysis (FIA), by usual partition coefficient determination techniques. Experiments in real petroleum fields should now be carried out to evaluate the performance *in situ* of the Eu-DTPA complex in reservoirs during the injection water process, as a final step their homologation as activable tracers to estimate the efficiency of the secondary recovery of petroleum.

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