Relaxometric Study Concerning the Action of A Complexant Agent on Petroleum

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Abstract: Applying a complexant agent to the contention and bioremediation of petroleum spills, although important for industry, is very rare. Therefore, the aim of this paper is to present a study concerning the influence of a complexant agent, namely chitosan, on petroleum using time-domain nuclear magnetic resonance (TD-NMR). Alterations in the transverse relaxation time (T_2) values and peak areas were observed, inferring that the interaction of the complexant agent with petroleum causes destabilization, precipitation of chemical compounds and separation of phases (water and oil). Thus, a novel application involving this spectroscopic technique in the energy field is presented.

Keywords: Petroleum, chitosan, low field NMR.

1. INTRODUCTION

The discovery of new reservoirs and the increase in petroleum production makes the topic, petrochemical accidents, a major concern around the globe. Some disasters such as Exxon Valdez in 1989 in Alaska, Prestige in 2002 on the coast of Spain, BP British in the Golf of México in 2010, and recently in the Guanabara Bay in the Brazil, show the environmental impact caused by petroleum spills [1-4].

There are countless reasons why millions of gallons of petroleum are spilled in offshore environments around the world. These include the improper storage of petroleum tankers and operational errors that lead to irreparable damage to marine flora and fauna [1-7].

Modern techniques such as top kill (which consists of injecting fluid of water, clay and other substances into reservoirs to equilibrate pressure and avoid leaks) is often implemented in large environmental accidents to avoid petroleum spills [8].

Therefore, physical, chemical and biological processes are used to remove, recover and degrade the oil. However, the application of a complexant agent to the contention and bioremediation of petroleum is rare.

Thus, using substances which can interact with petroleum has become a viable and ecologically sustainable alternative. Such substances can provide a rapid response to the progression of a petroleum spill, preventing it from spreading to areas not yet contaminated.

The copolymer, chitosan, constituted by the β-(1→4) link between units 2-amino-2-deoxy-D-glucopyranose and residues of 2-acetamido-2-deoxy-D-glucopyranose, is a chemical derivate obtained from the alkaline deacetylation reaction of chitin, which is naturally found on the walls of some fungi and in most crustaceans and insects [9-12]. This biomaterial has kindled great interest in the scientific community because of its property of complexation and biosorption, especially in contrast to more traditional competitors such as coal and activated carbon [13].

The possibility of acting as a complexant is an intrinsic feature of chitosan due to its high interaction with water molecules, which is proportioned by the large number of hydroxyl groups found in its glycosidic units [9,11,14].

This biopolymer is widely applied as a nontoxic flocculent to treat organically polluted wastewater [15,16]. This application is possible because it has high proportions of amino functions that provide sites of complexation with many heavy metals [11,12,16-18]. However, to the best of our knowledge, no studies have been done to research the action of this biomaterial in petroleum by time-domain nuclear magnetic resonance (TD-NMR).

The TD-NMR spectrometer consists of a magnet that produces an inhomogeneous magnetic field with a frequency of up to 42.5 MHz for the proton (^{1}H) [19]. The main advantages of this technique are the low cost, non-destructiveness, as well as the easy and rapid use [20].

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Accordingly, the results obtained from TD-NMR are time constants from exponential decay curves, which reflect the relaxation that occur in the system. The longitudinal relaxation time, abbreviated as T_1, describes the return of magnetization over the z-axis due to the change in energies between spins and lattice. The relaxation time that involves the disappearance of magnetization in the transverse plane is called transverse relaxation time, T_2 [21-23]. The exponential decay curves can be inverted by a mathematical process called inverse Laplace transform (ILT). The importance of this process is to provide distribution curves that reflect the different chemical environments inside the system [24].

The use of TD-NMR has been considered in a variety of studies concerning the viscosity of petroleum and porosity of rocks, measurement of water content in petroleum emulsions, oilseed and fruit ripening [25-28].

Recently, Morgan *et al.* applied TD-NMR to develop a viscosity model on base transverse relaxation time (T_2) for petroleum with viscosity ranging from 23.75 to 1,801.09 mPa.s and API gravity from 16.8 to 30.6 [29]. Other authors have used chemometric tools in experimental data of ^{1}H NMR spectroscopy and low field NMR to obtain the "chemical signature" of crude oils from different reservoirs and also for predicting API gravity and viscosity [30-31].

Therefore, this paper presents a novel application for this spectroscopic technique in the energy field, which consists of studying the action of a complexant agent on petroleum, using only relaxometric measurements.

2. EXPERIMENTAL SECTION

2.1. Complexant Agent

2.5 g of biopolymer chitosan acquired from Sigma-Aldrich with a high degree of purity was used in this research.

2.2. Petroleum Samples

The petroleum samples were provided by Petrobras S/A. Before carrying out TD-NMR experiments, all samples were placed in polyethylene bottles and sealed to minimize the risk of loss of light fractions of petroleum. Interaction experiments were performed using 25.00 g of petroleum. The characterizations of the petroleum samples were performed according to ASTM-D 7042-12 for viscosity and ASTM-D 4007-11 to determine the content of basic sediment and water (BSW) [32-33].

The criteria adopted to choose the samples for NMR analysis were the primary features, among them API (American Petroleum Institute) gravity, as well as low and high values of BSW.

API gravity calculated using the ASTM-D 4052-11, classified these samples into the following: heavy (°API < 22.30), medium (22.30 < °API < 31.10) and light (°API ≥ 31.10) [34].

Table **1** presents data from the chemical and physical characterization of eight samples of heavy and medium petroleum used in this research. The viscosity values of petroleum changed between 58.11 and 2131. 44 mm^2 s^{-1} (measured at 20ºC), the density varied from 0.9164 to 0.9530 g cm^{-3} (measured at 20ºC), the BSW values varied between 0.20% and 36.00% (v/v) and the API gravity varied from 17.0 to 22.9. The variations in these physical properties prove that these samples were supplied from different exploration wells.

It is important to mention that the first seven samples listed in Table **1** were dehydrated according to ASTM-D 4007-11 in order to study the behavior of the complexant agent on the dehydrated oil and water, separately [33].

2.3. Petroleum Fractions

Petroleum 8 in Table **1** was used to produce fractions, because of the small amount of water and

Table 1: Physical Properties of Petroleum Used in the Research

Petroleum	ºAPI	Viscosity (mm^2 s^{-1})	Density (g cm^{-3})	BSW (v/v)
1	20.1	553.63	0.9330	9.00
2	19.7	651.82	0.9355	36.00
3	17.0	673.93	0.9530	12.00
4	18.2	2131.40	0.9450	12.00
5	20.0	528.01	0.9342	26.32
6	19.6	671.12	0.9363	10.00
7	19.7	581.50	0.9357	8.00
8	22.9	58.11	0.9164	0.20

Table 2: Physical Properties of Fractions Obtained from Fractioned Distillation of Petroleum 8

Fraction	T_{cut} (°C)	Density (g cm^{-3})	Color
1	80	0.6598	Colorless
2	170	0.7811	Light Brown
3	240	0.8420	Dark brown
4	350	0.8992	Green
5	380	0.9104	Dark green

salts. The large amounts of these substances can cause damage to the distillation tower [35].

This petroleum was distilled according to the ASTM-D 2892-11 method. Five fractions with colors varying from colorless to dark green (Table **2**) were produced and investigated by TD-NMR. About 25.00 g of petroleum fractions were used in this study.

Figure **1** shows the visual aspect of the two fractions obtained from distillation. In low boiling points, as in Figure **1a**, the fraction is colorless due to the paraffinic nature, however the color observed in Figure **1b** is dark brown because of the predominance of heavier compounds, such as aromatics. Therefore, the colors can provide an indicative of the chemical composition with respect to the hydrocarbon categories [30,36-38].

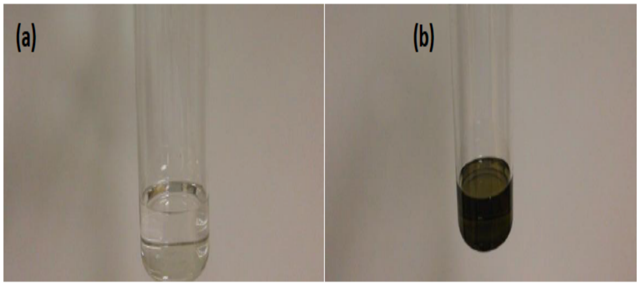

Figure 1: Typical petroleum fractions obtained from fractioned distillation of petroleum sample 8. In (**a**), the fraction with a paraffinic nature can be observed, commonly found in lighter fractions. In (**b**), the fraction with an aromatic nature can be seen, commonly found in denser compounds.

2.4. TD-NMR Measurements

The NMR measurements presented in this work were obtained using a Maran Ultra-2 NMR spectrometer from Oxford Instruments Ltd. operating at a Larmor frequency of 2.2 MHz for the hydrogen nucleus (^{1}H).

The samples for the NMR analysis were placed inside glass tubes. Before each experiment, the samples were stabilized at 27.5^{0}C. The temperature was monitored using an optical thermometer (FOT Lab Kit Fluoroptic Thermometer, manufactured by LUXTRON). After stabilization, chitosan in powder form was added.

Studies were conducted to determine the longitudinal relaxation time (T_1) by the inversion-recovery pulse sequence for all systems with the aim of estimating the value of recycle Delay (RD) and avoid the saturation of the NMR signal.

NMR experiments using the Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence to measure T_2 were carried out with the aim of verifying the sensitivity of the technique to detect alterations in the relaxation time in the presence of the complexant agent.

The CPMG pulse sequence was applied with pulses of 180° and 90° with time duration of 16.4 µs and 8.2 µs, respectively. The following parameters were used during the acquisition: relaxation delay with values in the range of 4 to 15 s, number of echoes between 8,192 and 32,768, the number of scans equal to 8, and finally, the time delay between pulses was fixed at 200 ms. The decay curves presented in this work and the areas of peaks were obtained using the software Origin® 8.0. The decay of the echo for the samples was inverted by applying ILT using the WinDXP® 3.0 software to obtain distribution curves. All analyses were performed in triplicate with a relative error lower than 3%. Finally, the T_2 values corresponded to the peak maximum in the distribution curve from ILT.

As discussed in the literature, the values of T_1 and T_2 are very close in the liquid medium, particularly for low magnetic fields [21-23]. In this paper, T_2 values were used for analysis because CPMG is considerably faster that the inversion recovery sequence.

3. RESULTS AND DISCUSSION

3.1. Addition of Complexant Agent to Petroleum

Analyses from typical T_2 distribution curves in Figures **2a** and **b** show that petroleum has two distinct

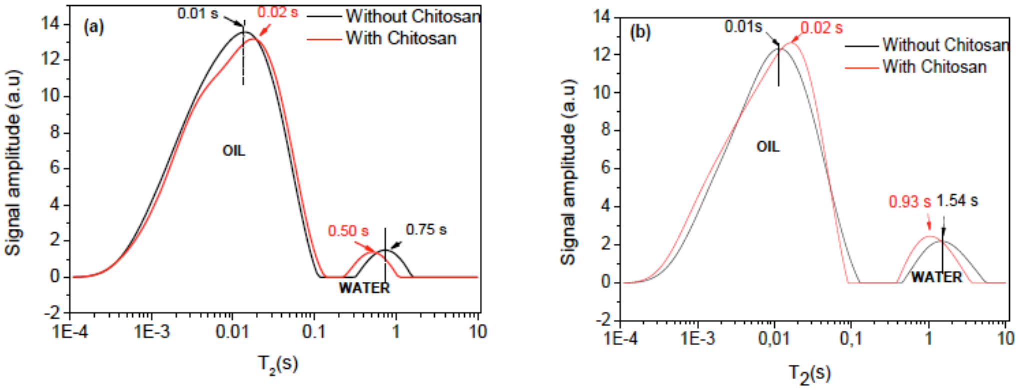

Figure 2: T_2 distribution curves showing two environments in the petroleum. The environment on the left, belonging to oil, presents lower T_2 values. The environment on the right, belonging to emulsified water, has higher T_2 values. The effect of adding chitosan to petroleum sample 1 (a) and petroleum sample 2 (b) in both environments is shown. The physical properties of these two samples are depicted in Table **1**.

spin populations, where the left peak refers to the oil and the right peak refers to the emulsified water.

The presence of the complexant agent caused a displacement of T_2 for higher values in the oil peak. These alterations will be analyzed in more detail in the next sections. Concerning the presence of chitosan in the water environment, displacement to smaller T_2 took place. This occurred due to the complexation of metals present in emulsified water and strong interactions with water molecules, such as hydrogen bonding [16-18]. In these cases, the T_2 values corresponded to the maximum of the distribution curve obtained. In relation to the area peak, a reduction in water was observed, whereas for oil the changes in the area were insignificant.

3.2. Interaction Provided by the Complexant Agent Concerning Water from Petroleum Dehydration

This section specifically relates the interaction between the complexant agent and water from the dehydration of petroleum. The dehydration processes produces water with high salinity (around 300,000 mg kg^{-1}) due to several metallic ions and residual petroleum. These components directly affect the T_2 values [39].

Figures **3a** and **b** show typical T_2 values obtained for the water from the petroleum dehydration of samples 1 and 2.

In these cases, the results indicated that for the chemical environment belonging to the water from petroleum 1 and 2, there was a reduction in the T_2 of 0.58 s (Figure **3a**) and 0.91 s (Figure **3b**), respectively. It can be inferred that the amino groups in the complexant agent can connect and bind with the metals forming complexes and precipitates, as can be seen in Table **3**, which are based on the data in the reduction of the area [10,15,17]. However it is important to mention that there are no direct relations between the reduction in the area and the physical and

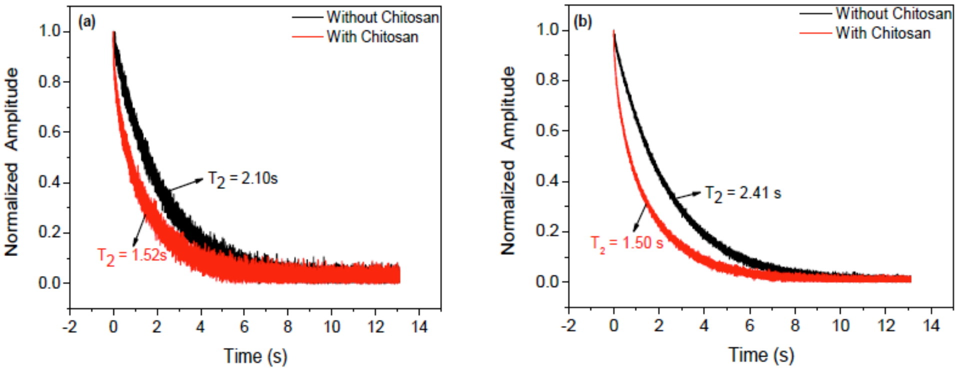

Figure 3: Comparison of results of interactions provided by chitosan (red line) on the water from the dehydration process of petroleum sample 1 (**a**) and petroleum sample 2 (**b**). In this Figure, it is important to note the difference between the ratio signal/noise of samples due to the dehydration process.

chemical properties of petroleum due to the high complexity of this system.

Table 3: Results Showing the Reduction in the Peak Area of Water from Petroleum Dehydration after the Action of about 2.5 g of Complexant Agent

Sample	Percentage of reduction in the area
1	22.31%
2	23.21%
3	25.18%
4	20.40%
5	22.56%
6	24.45%
7	32.14%

Moreover, it was noted that the signal/noise ratio obtained in Figure **3a** is lower than in Figure **3b**, because the petroleum dehydration process did not supply the same amount of water for all samples, as this amount is dependent on BSW (see Table **1**). Finally, the black line in both Figures shows that the water from petroleum 1 has T_2 value equal to 2.10 s, whereas the water from petroleum 2 relaxes in 2.41 s. It can be concluded from this result that the water from petroleum 1 has lower T_2 due to a high amount of paramagnetic ions and salts present in its aqueous phase.

3.3. Interaction Provided by the Complexant Agent in the Chemical Environment of the Oily Phase from Petroleum Dehydration

In this section, the action provided by the complexant agent only concerning the oily phase is analyzed. The results presented in Figure **4a** and **b** show soft alterations in this system after adding chitosan. Therefore, to prove the effect of chitosan specifically in this system, a more in-depth investigation was carried out applying the complexant agent to petroleum fractions.

3.4. Interaction Provided by the Complexant Agent Concerning Petroleum Fractions

A relaxometric study on the fractions presented in Table **2** was conducted to evaluate the interaction caused by the complexant agent in this system and to clarify their action on the oily phase. As described by Riazi in 2005, fractions consist of several functional groups such as phenol, carboxylic acid, alcohol and others. Such substances can be sites of interaction with the complexant agent [36].

The reduction in the area observed after adding the complexant agent was attributed to the emergence of a precipitate of chitosan and heavy fractions that did not emit a signal in the TD-NMR. This precipitate did not emit a NMR signal due to the low molecular mobility, which provides T_2 values lower than the dead-time of the spectrometer.

The results in Figure **5a** show that T_2 is 1.80 s with and without the addition of chitosan in fraction 1 (distilled to final boiling point equal to 80 ^{o}C). However, for fraction 5 (distilled to final boiling point equal to 380 ^{o}C) without chitosan, the T_2 is 0.03 s and with the complexant agent, the value was displaced to 0.04 s. Due to the paraffinic nature and consequent small reactivity of fraction 1, the chitosan did not cause alterations in relaxation time. However, fraction 5 has

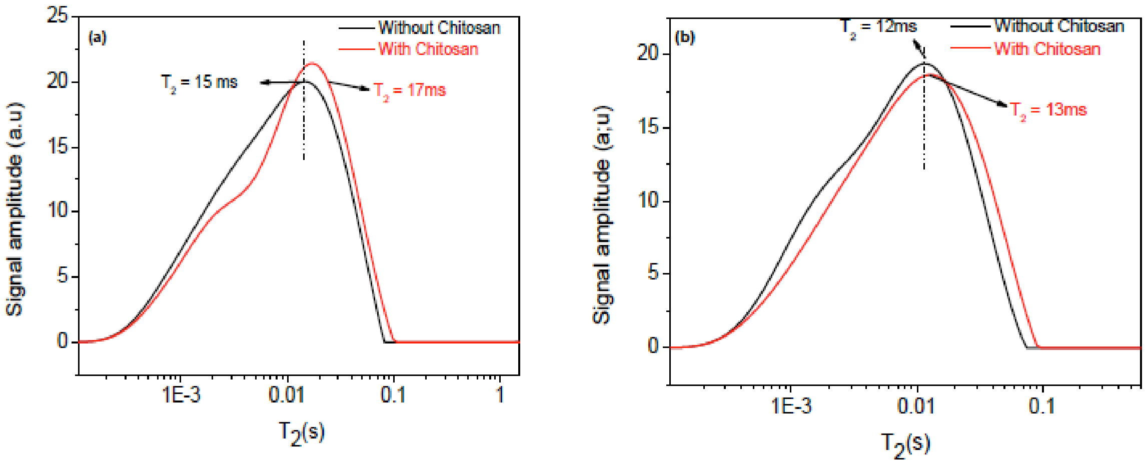

Figure 4: Comparison of the influence of complexant agent chitosan (red lines) from T_2 distribution curves obtained from the ILT process to the dehydrated petroleum sample 1 (**a**) and dehydrated petroleum sample 4 (**b**). In this Figure, the soft displacement for higher values after action of the complexant agent can be observed.

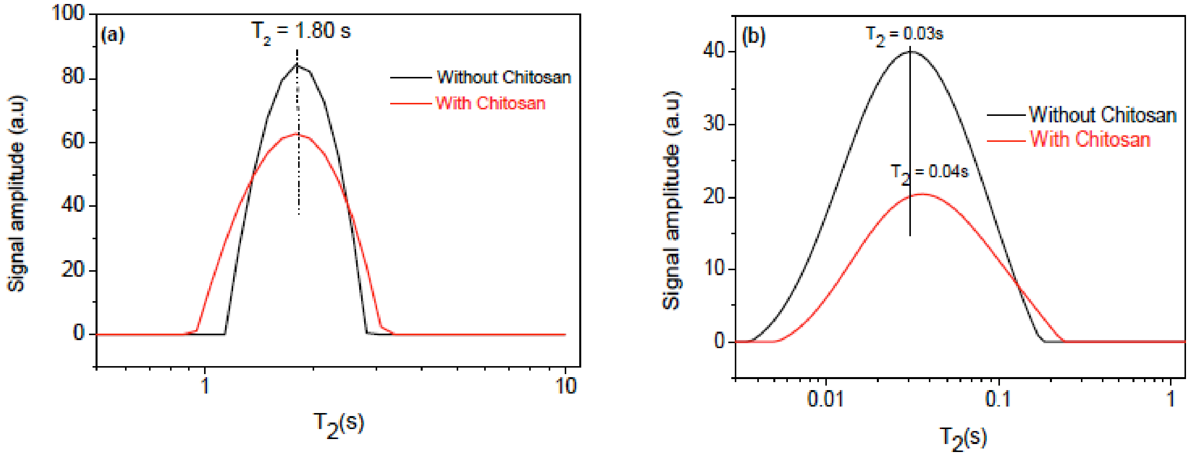

Figure 5: Comparison between T_2 distribution curves for fractions samples. In (**a**), the influence of the complexant agent chitosan on the lighter fraction, rich in paraffinic compounds, can be observed. In (**b**), the influence by chitosan on the denser fraction, rich in naphthenic compounds, can be seen. Moreover, the difference between the T_2 values, 1.80 s (lighter fraction) and 0.03 s (denser fraction) can be clearly seen in this Figure. This difference reflects the nature of these compounds.

Table 4: Percentage of Reduction in the Area Caused by Chitosan in the Petroleum Fractions with a Different Density

Sample	Percentage of reduction in the area	Density (g cm^{-3})
1	5.67%	0.7282
2	30.00%	0.7811
3	51.50%	0.8420
4	53.00%	0.8992
5	69.33%	0.9104

denser compounds (for example, aromatics) which interact with chitosan and change the T_2 values.

The results in Table **4** show that the reduction in the area is correlated with the density of the petroleum fraction. There was a reduction from 5% (fraction 1, lighter) to 70% (fraction 5, denser). This result shows the light displacement observed for higher values in the oily phase.

4. CONCLUSIONS

Adding chitosan to petroleum reduced the T_2 values from the chemical environment concerning emulsified water due to the complexation of metals in this environment. Relaxometric studies show that the complexant agent (chitosan) had a strong interaction with chemical compounds present in the denser fractions of the oily phase, leading to destabilization and precipitation, and consequently a reduction in the peak area. Finally, the results obtained from applying biopolymer and TD-NMR concluded that this technique could be a new way to understand and monitor petroleum spills in water.

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SUPPLEMENTAL MATERIALS

The supplemental materials can be downloaded from the journal website along with the article.

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