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Study of Brazilian asphaltene aggregation by Nuclear Magnetic Resonance spectroscopy

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HIGHLIGHTS

- ^{1}H and ^{13}C NMR for discrimination of asphaltenes from three different oils.
- Aggregation of asphaltenes by diffusion-ordered NMR spectroscopy (DOSY).
- Correlation between continental and archipelago model and asphaltene aggregation.

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ABSTRACT

Nuclear Magnetic Resonance experiments were used to study the relationship between the structural type (continental or archipelago) and aggregation properties of three different asphaltenes (asph_A, asph_B and asph_C). Diffusion-ordered NMR spectroscopy (DOSY) was applied to investigate the diffusion coefficients. The self-diffusion of the asphaltene aggregates was investigated in the concentration range of 0.01–10% of each asphaltene in deuterated toluene. Data obtained from ^{1}H and ^{13}C NMR indicate that asph_B has a predominantly continental type of structure. This contributes to different properties of aggregation. DOSY shows the presence of three aggregates, with three different diffusion coefficients, called nanoaggregate, microaggregate and macroaggregate.

1. Introduction

Oil is a complex mixture of organic molecules, mainly composed of carbon and hydrogen atoms. For its potential energy to be used to the maximum extent, it must be processed and converted conveniently for the purpose of obtaining the greatest possible quantity of good quality products, and thus greater commercial value. Achieving this goal, with the lowest operational costs, is the basic guideline of refining [1].

The concern for the lack of light, heavy and extra heavy oils have stirred great interest in the petroleum industry. The main problem when processing heavy and extra heavy oils lies in the deposition of organic compounds. Among the groups of compounds that undergo deposition during processing, refining and transportation, the asphaltenes are highlighted as the most important. Asphaltenes are classified by their solubility and comprise a very large set of organic compounds which are insoluble in organic solvents such as pentane (C5) and heptane (C7), and soluble in solvents such as benzene, toluene and pyridine [2].

Asphaltenes are composed of molecules of high molecular weight which contain polycondensed aromatic rings with aliphatic chains attached to them. Usually, they also contain heteroatoms such as oxygen, nitrogen and sulfur, and some metals such as nickel and vanadium can also be observed. These metals can be complexed into porphyrin structures that poison catalysts in the hydroprocessing process, for example [3]. At low concentrations, the asphaltenes form nanoaggregates increase the size as they increase concentration, as much as to flocculate and precipitate [4].

To avoid precipitation during the processing of oil and so as to minimize the harm caused by asphaltenes, it is necessary to understand the behavior and structure of this class of compounds [4]. Despite the fact that it has been studied for decades, all the properties of asphaltenes have been object of debate. Even with all the research done on this topic, information such as molecular weight, size, shape and structural data are not yet clearly established. Several techniques have been applied in the study of asphaltenes such as: size exclusion chromatography (SEC) [5–7], mass spectrometry

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(MS) [8], small-angle X-ray scattering (SAXS) [9], small-angle neutron scattering (SANS) [10,11], scanning electron microscopy (SEM) [12] and Nuclear Magnetic Resonance (NMR) [13].

In recent decades, NMR has been widely used as a tool in the study of petroleum and its derivatives [14]. Obtaining ^{1}H and ^{13}C NMR spectra allows the direct determination of a series of structural parameters such as the fraction of aromatic carbons, carbon bounded to an alkyl chain and their respective percentage of substitution in this system [15]. The development of new NMR techniques, such as diffusion ordered spectroscopy (DOSY) [16] based on the sequence of pulsed field gradient (PFG) [17,18], has been shown to be an excellent tool in the elucidation of complex mixtures.

The DOSY experiment results in a two-dimensional spectrum (2D), where one of the axes is present in the chemical shift component which belongs to the mix and, in another dimension, molecular diffusion of a given compound that comprises the mixture [17,18]. The DOSY technique has been employed in the study of mixtures [19], polymers [20], in the study of protein [21] and in drug delivery [22]. The diffusion coefficient extracted from the two-dimensional DOSY spectrum gives us important information about the size and state of aggregation of asphaltenes [23]. Durand et al. use the DOSY technique in the study of asphaltenes from three different sources and different behaviors are observed for the three asphaltenes depending on their chemical composition, which result in two states of aggregation, called nanoaggregate and macroaggregate [23].

The present paper is a study on the physical and chemical behavior of three asphaltenes obtained from oils extracted from Brazilian wells with DOSY NMR technique. With this aim, asphaltenes were diluted in various concentrations in deuterated toluene and spectra were correlated with their respective states of aggregation. The diffusion properties were highly dependent on the concentration and type of oil used for the generation of asphaltenes.

2. Experimental section

2.1. Extraction of asphaltenes

The three different samples of asphaltenes were obtained from crude petroleum by precipitation with n-heptane (30 mL/g of oil), washed in a soxlhet system using the same solvent. The crude precipitated was filtered and solubilized in toluene. After solubilization, the solution was evaporated to obtain the asphaltene, according to ASTM 6560-00. Asphaltene extraction and quantification were carried out in triplicate.

2.2. ^{1}H and ^{13}C nuclear magnetic resonance

The ^{1}H and ^{13}C NMR spectra of asphaltenes were performed on a Varian VNMRS 400 spectrometer, operating at 9.4 T, using a 5 mm BroadBand $^{1}H/X/D$ NMR probe. The ^{1}H NMR experiments were performed at 25 °C, using 20 mg of asphaltene diluted in 0.6 mL of a solution of 50 mM of $Cr(acac)_3$ in deuterated chloroform. Tetramethylsilane (TMS) was used to reference the chemical shifts. A spectral width of 6410.3 Hz with a relaxation delay of 1.5 s and 512 scans were accumulated, with a pulse flip angle of 90° (12.7 ms). For the ^{13}C NMR, the same solution used in the ^{1}H NMR experiments was employed, with a spectral width of 25510.2 Hz, a relaxation delay of 15 s and 20,000 scans, with a pulse flip angle of 90° (9.5 ms). The decoupler mode was set to inverted gated to avoid the nuclear Overhauser enhancement effect (NOE).

The NMR spectra of the three asphaltenes were separated in specific chemical shift regions by the type atoms (aromatic and aliphatic) and the integration of the signals provided comparable information about the molecular structural parameters. Those parameters allowed us to correlate the asphaltene structure with its aggregation properties.

2.3. DOSY NMR

For the DOSY experiments, a wide range of concentrations (0.01–10%) were prepared, using deuterated toluene (99.5% D) as solvent. The experiments were performed on a Varian 400 MHz spectrometer, equipped with a 5 mm BroadBand $^{1}H/X/D$ probe, generating an 18 G cm^{-1} field strength.

The *Doneshot* sequence was employed to measure the self-Diffusion of the aggregates, using 25 linear steps from 0 to 18 G cm^{-1}. The gradients were calibrated according to the manufacturer, using the HOD/D_2O (99%) standard solution at 25 °C. In the *Doneshot* sequence, the gradient pulse duration (δ) ranged between 1.5 and 3 ms and the diffusion delay (Δ) varied between 0.05 and 0.45 s. The spectra were acquired at 25 °C with a relaxation delay of 30 s and pulse duration of 12.7 μs (90°).

3. Results and discussion

3.1. Sample characterization

For this study, four oils obtained from four different oil wells were employed, namely oil_A, oil_B, oil_C and oil_D. Table 1 shows properties of these oils such as viscosity and density. Table 1 also shows the average content of asphaltene, obtained from ASTM 6560-00 standard procedure. The term average was employed because the extraction of asphaltene from oil was done in triplicate.

In Table 1 one can notice that the asphaltene content increases with the decrease of °API of the origin oil. This is due to the fact that oils with less °API are those with higher density and, consequently, more polar fraction in its constitution. Asphaltenes are known to represent the most polar parts of oil. Thus, for oils with lower °API (heavier), we expect to obtain greater amount of asphaltenes.

3.2. Chemical composition

Table 2 shows the chemical composition of each asphaltene, called asph_A, asph_B and asph_C obtained respectively from oils_A, B and C. In the elemental analysis of Table 2, we can see that the relationship between the three different asphaltenes is very similar regarding contents of hydrogen and nitrogen. However, the carbon, oxygen and sulfur content is smaller in asph_C. Another important point to be mentioned is the quantities of Ni and V metals in the samples. One can see an increase in the asphaltene nickel content as we move from the light oil to the heavy one. The inverse relationship could be observed for vanadium, which is present in higher amount in the asphaltene obtained from the lighter oil. The amount of heteroatoms and metals described has been taken into account in the study of asphaltenes, once these

Table 1
Detailed characterization of oils used for asphaltenes extraction.

Property	Oil_A	Oil_B	Oil_C	Oil_D
°API	17.3	22.0	13.5	29.0
Density 20 °C (g cm^{-3})	0.9469	0.9180	0.9721	0.8779
Viscosity at 20 °C (mm^2 s^{-1})	2406.1	196.04	82163	59.795
Viscosity at 40 °C (mm^2 s^{-1})	519.39	62.332	7384.2	21.427
Viscosity at 50 °C (mm^2 s^{-1})	279.14	34.496	2827.3	15.107
Average content of asphaltene (wt.%)	2.23	0.41	7.63	–[a]

[a] Values below the detection limit of the method.