

Analysis of molecular weight distribution of asphaltene heptol sub-fractions by laser-induced acoustic desorption/Fourier transform ion cyclotron resonance mass spectrometry

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Heavy petroleum fractions usually contain constituents capable of self organization commonly referred to as asphaltenes. The complex behavior of this fraction has contributed to uncertainties in the determination of some of its most important properties, such as the distribution of molecular weights (MW). This parameter is very important because it is required to determine a molecular structure and correlate it to physical properties. Two main types of measurements: mass spectrometry and molecular diffusion, produce the most consistent evidence on asphaltene molecular weight and size.

In this work, we employed laser-induced acoustic desorption (LIAD) [1] to analyze asphaltenes from Brazilian vacuum residues (VR) obtained from two off-shore fields A and B, that have similar elemental compositions and considered as rich in asphaltenes (around 9% by weight) [2]. Samples were evaporated into a dual-cell Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR) where the neutral asphaltene molecules were ionized by electron bombardment, a universal ionization method that ionizes all organic compounds. VRs A and B were fractionated by a modified IP-143 method, using mixtures of heptane and toluene in different concentrations, as precipitation solvents. Samples were heated gently until they became fluid and homogenized before an aliquot was taken. Approximately 1 g of sample was weighed for each analysis. The solvent employed was a mixture of n-heptane, reagent grade, 99,5%, and toluene, reagent grade, (referred to as "heptol"), in proportions that vary between 0% v/v ("pure" asphaltene), and 30% v/v of toluene in the heptol mixture (asphaltene are completely soluble in higher concentrations of toluene). The efficiency of fractionation was monitored by the asphaltene content of each fraction while chemical properties of sub-fractions are reflected by their ¹H chemical shifts. Results have been discussed in a previous paper [2].

LIAD/ICR/MS [3] experiments were run as following: asphaltene solutions were prepared by dissolving ~1 mg of the sample in ~10 mL of CH₂Cl₂ or CS₂. The CH₂Cl₂ solution was electrospray deposited on a 12.7 μm thick, 2 cm diameter round Ti foil situated on a platform. Alternatively, a drop of the hot CS₂ solution was placed onto a Ti foil on a hot plate (50°C). Both methods of sample deposition left

a thin film of the asphaltene on the surface of the foil. Each Ti foil with the sample was mounted onto a LIAD probe and inserted into the FT-ICR mass spectrometer. The LIAD technique employs laser-generated acoustic waves to evaporate thermally labile and/or nonvolatile samples as intact neutral molecules into the mass spectrometer from the front side (sample side) of a 12.7 μm thick Ti foil when the backside of the foil is irradiated by pulses of laser light. A high-power LIAD probe ("fiberless" probe) was used in this work [1]

Our results are consistent with experiments run on model compounds [3] and show that asphaltenes from VR-A (A-0%) fall in the MW range of around 500-1000 Da and sub-fractions A-10% and A-20% are very similar in MW distributions. There are however, some important differences. Average MW for A-10% is similar to that of asphaltenes before fractionation, or A-0%, while MW for A-20% is slightly higher. It is also important to point out that some of the peaks found in A-0% also appear in A-10% while others appear in A-20%. This means that sub-fractionation led to a distribution of constituents with varying degrees of aromatic content, as shown by ¹H NMR [2]. On the other hand, heavier constituents are found in the less soluble fraction. VR-B asphaltenes show a MW distribution that is completely different from that of VR-A asphaltenes. They tend to have a heavier character, but fall in similar MW ranges, between 600 and 1100 Da. LIAD/EI mass spectra measured for A and B asphaltenes and their sub-fractions show that they are made up of hundreds of constituents but none of them falling above 1100 Da, with maxima around 750-800 Da. The MS results also confirm those observed by NMR [2]. In spite of their similar elemental compositions VRs A and B contain distinct structures and were extracted into heptanes/toluene mixtures to a different extent.

References

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