



Correlating asphaltene fractions instability with the predominance of archipelago-type molecules

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*Erro! A referência de hiperlink não é válida.

Abstract

Analyzing unstable asphaltene fractions is essential for the comprehension of the mechanisms involved in their auto-association behavior. Herein, a fractionation methodology capable of separating the most unstable asphaltene species is presented. Then, asphaltenes were fractionated and analyzed by Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). The results show higher contents of archipelago-type asphaltenes in the most unstable fractions isolated by the fractionation methodology. Also, the content of heteroatoms O and S was higher in the most unstable fractions. Therefore, the results indicate that polar archipelago asphaltene species as the main ones responsible for asphaltene instability.

Keywords

Asphaltene's instability; archipelago-type asphaltenes; structural characterization of asphaltenes.

Introduction

Asphaltenes can precipitate by pressure changes and/or by mixing incompatible fluids, leading to costly flow restrictions in oil production [1,2]. Therefore, knowing the composition of the most unstable samples is fundamental to the understanding of the mechanisms involved in asphaltenes precipitation.

To accomplish this task, FT-ICR mass spectrometers are essential due to their capacity of analyzing even the most complex samples [3]. Even so, fractionating asphaltenes into sub-fractions of reduced complexity is required for an in-deep analysis of the samples.

Herein, a fractionation method based on solubility mechanisms capable of separating the asphaltene species prone to aggregate is presented. Then, asphaltenes were fractionated and characterized by FT-ICR MS using laser desorption/ionization (LDI) for avoiding capillary obstructions during analysis, as previously described [4].

There is still no consensus about the role of the island and archipelago structures in asphaltene's stability. Some studies indicate the island-type molecules as the main ones responsible for asphaltene aggregation due to the $\pi - \pi$ interactions favored in these structures [5,6]. On the other hand, other studies point to the archipelago-type structures as the main responsible for asphaltene's instability [7-9]. Therefore, through the results, we intend to

establish correlations between asphaltene structures and stability.

Methodology

Asphaltenes were precipitated from a crude oil by using n-heptane (n-C7) as previously reported [4]. Next, the asphaltenes were submitted to Soxhlet extraction, as illustrates Fig. (1). Then, five asphaltene sub-fractions were separated by the following eluents: acetone, acetonitrile (ACN), heptane (Hep), heptane/toluene (1:1, v/v), and toluene (Tol).

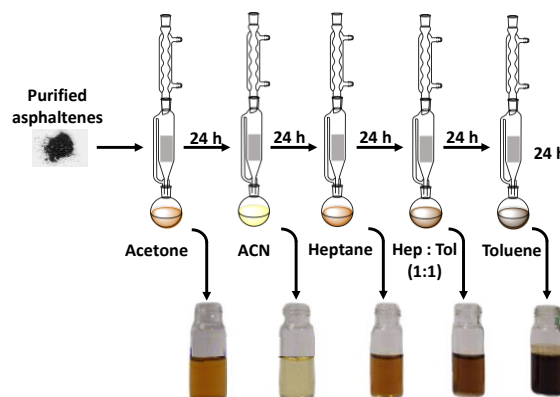


Figure 1. Asphaltene fractionation scheme.

The sample's stability was evaluated by TurbiscanLab analysis as previously described [4]. For this, solutions were prepared in mixtures of

heptane/toluene containing 10, 30, 50, 70, and 90% heptane (v/v). Finally, the samples were characterized by LDI (+) FT-ICR MS. The data was acquired using the following laser power from 17 to 24% and 15 to 400 laser shots, according to the ionization efficiency of each sample.

Results and Discussion

Acetone was first used for removal of the most ionizable species. Next, acetonitrile was employed for the extraction of porphyrins that may be present in the sample. Then, heptane was used for extracting low polarity asphaltenes [8]. Although asphaltenes are defined as insoluble in these solvents, in a Soxhlet apparatus, they are capable of extract less insoluble compounds [4]. Also, as shown in Fig. (2), these solvents extracted the more ionizable species that may cause ion suppression in MS analysis, limiting the characterization of asphaltene samples. In sequence, the use of the heptane/toluene mixture resulted in the extraction of 78.6% of the sample. Even so, species more prone to aggregate remained insoluble, being extracted only in the last fraction.

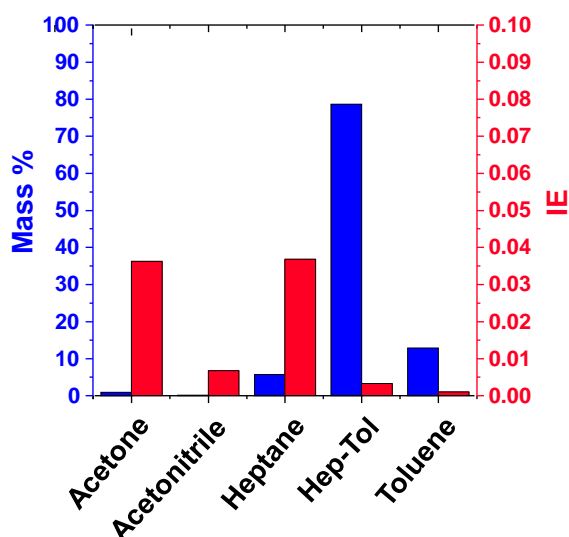


Figure 2. Mass recovery (%) and ionization efficiency for the asphaltene sub-fractions.

The sample's stability was evaluated using the optical analyzer known as TurbiscanLab. Samples prepared in solutions of heptane/toluene containing up to 50% of heptane (v/v) showed low instability indexes (II). On the other hand, for solutions containing higher proportions of heptane, Fig. (3) shows high II for the toluene extracted sample.

Fig. 4 shows the weighted average of N/C, O/C, and S/C ratios for the asphaltene subfractions. Note the higher O/C, and S/C ratios calculated for the most unstable fraction, extracted in toluene. Also, attention is drawn to the lower S/C ratios detected in the most stable fractions, extracted in acetonitrile and heptane. Therefore, the results highlight the important role of sulfur species in the

aggregation of asphaltenes. Further, such results are in agreement published studies [10,11].

Finally, Tandem MS analysis were performed for differentiating asphaltene fractions enriched in island and archipelago-type molecules. Collision-induced dissociation (CID) and Infrared multiphoton dissociation (IRMPD) experiments have been successfully employed in revealing structural details about asphaltene samples [4,8,12]. Herein, we intend to perform CID experiments to investigate whether the predominance of island or archipelago structures could be related to the stability in asphaltene fractions.

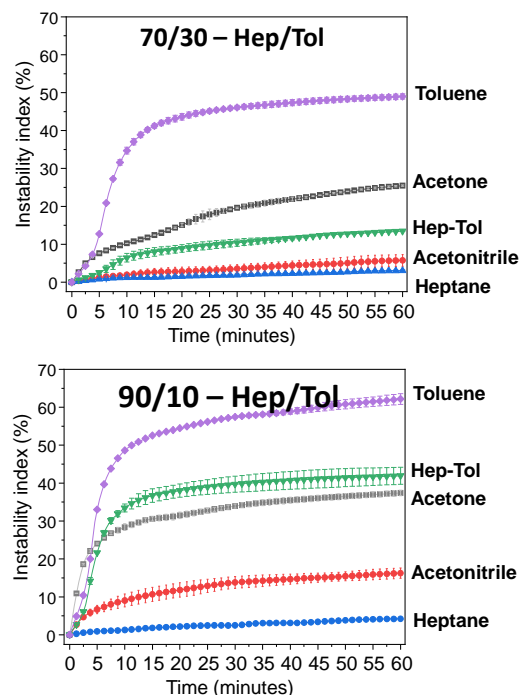


Figure 3. Instability indexes (II) for the asphaltene sub-fractions prepared in heptane/toluene solutions containing 70 and 90% (v/v) heptane.

Therefore, LDI (+) FT-ICR MS/MS experiments were performed for three selected mass regions, m/z 375, 428, and 515 ± 10 Da. Then, the results were used for calculating the percentages of archipelago-derived fragments, as described previously described [4]. For this, the sum of total abundances of product ions from all classes was equaled to 100%. Then, the proportions of product ions derived from the cleavage of alkyl bridges between aromatic cores in archipelago-type precursors was calculated. The results shown in Fig. (5) are not quantitative, however, they can be used to compare the abundances of archipelago-derived fragments detected between the extracted fractions.

Note the higher percentages of archipelago-derived fragments for the last fraction, extracted with toluene (Fig. 5). Also, the toluene extracted sample exhibited higher II. Therefore, the results may indicate a correlation between the high instability of this fraction with high proportions of

archipelago-type molecules. The same can be said about the heptane/toluene extracted sample as this sample showed the second-highest instability, and the second high proportions of archipelago-derived fragments. However, as the acetone extracted sample presented lower proportions of archipelago-derived fragments, the structural motif cannot be considered the only contributing factor for the instability of asphaltenes. On the other hand, note that the S/C ratios are higher for the most unstable fractions, including for the acetone extracted sample. Then, the results indicate that asphaltene instability may be also correlated with high S/C ratios.

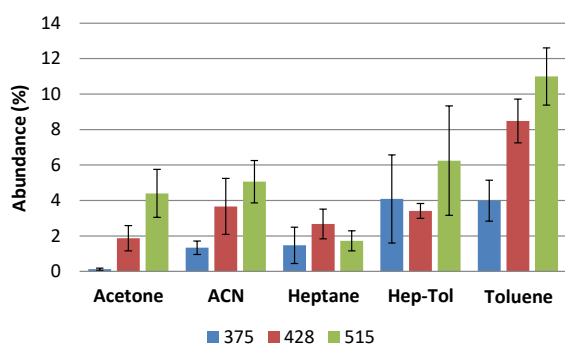


Figure 5. Relative abundances (%) of product ions resulting from the cleavage between aromatic nuclei in archipelago-type structures. Error bars show the standard deviation of measurements made in triplicate.

Conclusions

The fractionation methodology was effective in separating the most unstable asphaltenic species in the last fraction extracted using toluene. Further, the methodology was able to extend the characterization of asphaltene samples by removing the most easily ionizable species in the first fractions. Then, LDI (+) FT-ICR MS analysis was employed in the characterization of the asphaltene sub-fractions. By the results it was seen higher S/C ratios in the less stable fractions. Finally, it was verified greater abundances of archipelago-derived fragments in the most unstable subfractions. Therefore, there are indications that sulfur-containing archipelago species may play a major role in asphaltene aggregation.

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Responsibility Notice

The authors are the only responsible for the paper content.

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