



Structural characterization of asphaltenes enriched in island and archipelago motifs by LDI (+) FT-ICR MS

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Abstract

Nowadays it is widely accepted that island and archipelago-type molecules coexist in asphaltene samples. However, investigating the predominance of molecules from the island and/or archipelago model remains challenging. Besides the high complexity, asphaltenes often precipitate during analysis, causing damage to equipment's. In this context, laser desorption ionization (LDI) is presented here as a viable alternative for analyzing even the most unstable samples. In addition, collision-induced dissociation (CID) was employed for the structural characterization of asphaltenes. Using these tools, it was possible to characterize asphaltene sub-fractions enriched in island and archipelago motifs in a much easier way, without the occurrence of any capillary obstructions.

Keywords

Asphaltenes; FT-ICR MS; laser desorption ionization.

Introduction

Two models describe the aromatic nuclei's nature in asphaltenes. The island-type molecules consisting of a single aromatic core, and the archipelago-type structures containing at least two aromatic nuclei linked by alkyl bridges.

Recent studies have demonstrated that the predominance of island and/or archipelago structures is sample dependent [1,2]. However, the analytical tool can favor the detection of one type of structure, leading to wrong conclusions. In this context, Chacón-Patiño et al [1]. developed a fractionation method for separating asphaltenes according to their structural characteristics. Then, the samples were characterized by Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) using atmospheric pressure photoionization (APPI). In addition, infrared multiphoton dissociation (IRMPD) was employed for structural characterization. Although IRMPD are effective, this dissociation experiment requires modifications on commercial FT-ICR MS instruments. On the other hand, all commercial FT-ICR mass spectrometers can perform collision-induced dissociation (CID) experiments. Therefore, using CID experiments would be much easier to implement.

In addition, recurrent deposit formation in the APPI fused silica capillary during ionization of the asphaltene sub-fractions have been reported. Therefore, analyzing samples with the greater

tendencies to aggregate is arduous [1]. Asphaltene deposition in capillaries reflects asphaltene deposition in reservoirs, wells, pipes, pumps, etc. Hence, analyzing the most unstable samples is fundamental to understanding why asphaltenes precipitate. Hence, it is essential the search for suitable ionization sources.

Given this background, the use of laser desorption ionization (LDI) is proposed here, as an alternative for analyzing asphaltenes, avoiding obstructions and equipment damage. Therefore, herein we applied LDI and CID experiments to simplify the access to chemical information about asphaltene samples through FT-ICR MS analyses.

Methodology

Asphaltenes were precipitated from a Brazilian oil using n-heptane as previously reported [3]. The fractionation of asphaltenes was carried out based on a procedure published elsewhere [1]. In brief, asphaltenes adsorbed on silica were submitted to Soxhlet extraction using the following eluotropic series: acetone, acetonitrile (ACN), heptane (Hep), heptane/toluene (1:1, v/v), toluene (Tol), THF, and THF/MeOH (4:1, v/v).

All samples were analyzed by LDI (+) FT-ICR MS. The positive mass spectra were acquired in the range of 200-1000 m/z for Full Scan and 100-1000 m/z for CID. The source was set at 17.0 lp, and 15-400 laser shots according to the ionization

efficiency of the samples. For CID experiments it was applied collision energies from 25 to 35 V.

Equations

The differences in ionization efficiencies of the species present in complex samples, as asphaltenes, direct impacts MS analysis. In this context, it has been shown that there is a relation between the ionization efficiency (IE) and the number of laser shots (LS) needed to ionize the samples [4]. It was noted that, as higher the EI, is lower the LS is required for accumulate a target number of ions. This relation is demonstrated in Eq. (1).

$$IE \propto \frac{1}{LS} \quad (1)$$

Results and Discussion

Equation 1 was used to calculate the IE for all sample analyzed. As shown in Fig. (1), the analysis of the crude oil, maltenes, occluded compounds removed from unclean asphaltenes and purified asphaltenes emphasize the importance of purifying asphaltenes before asphaltenes characterization.

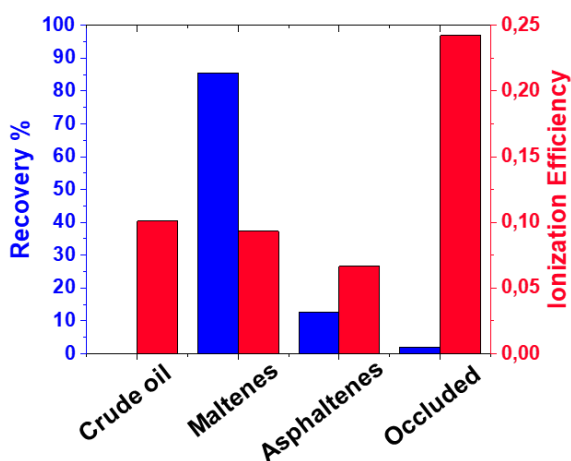


Figure 1. Mass recovery (%) and ionization efficiencies calculated for the crude oil, maltenes, purified asphaltenes and occluded compounds.

Similarly, Fig. (2) reinforce the importance of fractionating asphaltenes for a complete characterization, as the species extracted in acetone presented higher ionization efficiencies that could cause ionic suppression in MS analyses. Structural characterization of the asphaltene sub-fractions was performed by LDI (+) FT-ICR MS/MS. For this, the m/z 428 ± 10 Da was selected in the quadrupole and submitted to CID experiments. The results shown the coexistence of island and archipelago molecules in all fractions, however, archipelago structures have been mostly detected in the fractions extracted with heptane/toluene, toluene, and toluene/THF. On the other hand, island structures were majoritarian detected in the

THF and THF/MeOH extracted fractions, as seen in Fig. (3).

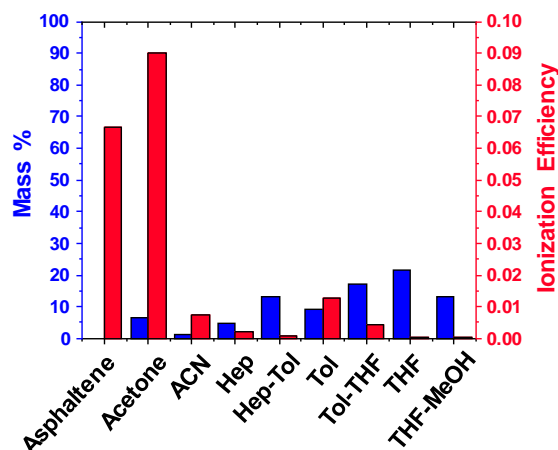


Figure 2. Mass recovery (%) and ionization efficiencies calculated for the asphaltene sub-fractions.

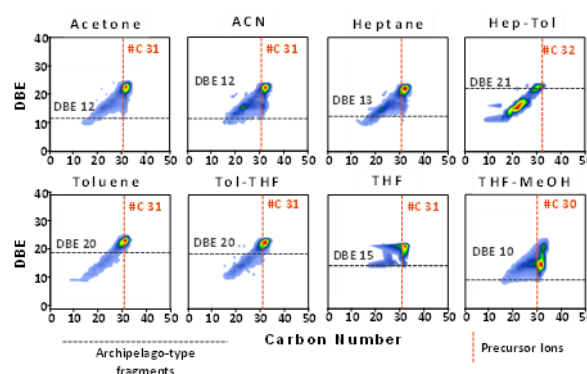


Figure 3. Plots of DBE versus carbon number for precursor and fragment ions.

Interestingly, in samples where island and archipelago motifs coexist, fragmentation of large molecules reveals more significant loss of DBE; in other words, large m/z ranges seem to contemplate more archipelago structures (See Fig. (4)).

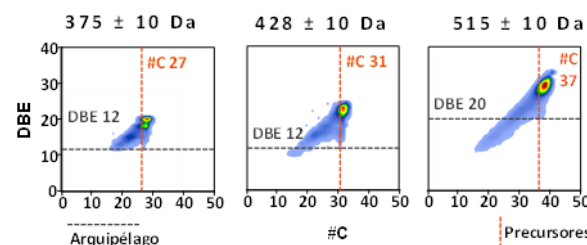


Figure 4. Plots of DBE versus carbon number for precursor and fragment ions detected in the acetone extracted fraction.

Finally, the LDI (+) FT-ICR MS data revealed that the eight sub-fractions analyzed can be assembled in three main groups. The first comprises the acetone, acetonitrile, and heptane fractions, mainly composed of island-type asphaltenes with pericondensed structures. The second group

comprises the heptane/toluene, toluene, and toluene/THF fractions, mainly composed of archipelago-type asphaltenes. Then, the third group comprehends the THF and THF/MeOH fractions, predominantly composed of island-type asphaltenes with cata-condensed structures. Therefore, a sample of each group was chosen as the main representative of each group. Thus, an in-deep analysis of the fragmentation profiles was used in the proposition of structures for the most abundant precursor ions detected in the acetone, toluene, and THF/MeOH fractions. Figure 5 shows theoretical structures proposed for the most abundant ions detected in these fractions in the mass ranges of 365-385 and 418-438 Da.

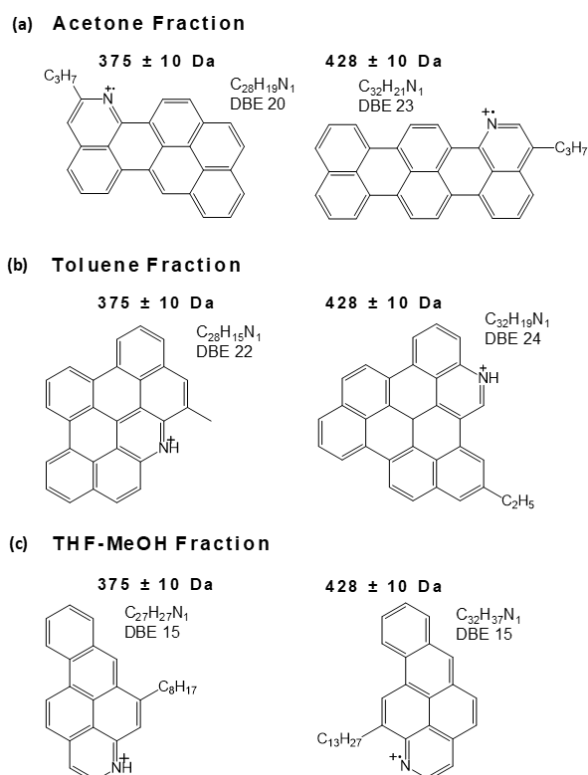


Figure 5. Theoretical structures proposed for the most abundant molecular formulas identified in the fractions (a) acetone, (b) toluene, and (c) THF/MeOH in the ranges of m/z 375, and 428 ± 10 Da.

Figure 6 shows the theoretical structure proposed for the most abundant precursor ions detected in the acetone, toluene, and THF/MeOH samples in the mass range of 505-525 Da. As discussed, more extensive mass ranges seem to contemplate more archipelago structures invent in samples enriched in island-type molecules. Therefore, the structures proposed in Fig. (6) agree with these findings.

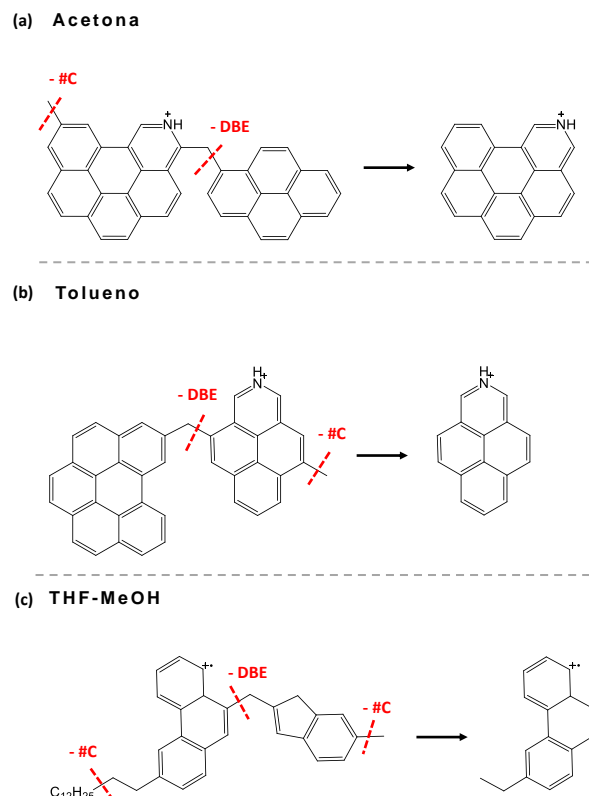


Figure 5. Theoretical structures proposed for the most abundant molecular formulas identified in the fractions (a) acetone, (b) toluene, and (c) THF/MeOH in the range of m/z 515 ± 10 Da.

Conclusions

The applicability of LDI (+) FT-ICR MS analysis to characterization of unstable asphaltene fractions was demonstrated without the occurrence of any capillary obstructions. In addition, CID experiments were successfully used for structural characterization of samples enriched and island and archipelago motifs.

Initially, an oil and its fractions were characterized. The differences in ionization efficiencies highlighted the importance of purifying asphaltenes before MS analysis.

The purified asphaltenes were fractionated according to their structural motifs. The ionization efficiencies reinforced the importance of fractionating asphaltenes to achieve a complete characterization. Then, through LDI (+) FT-ICR MS and MS/MS analysis it was verified the separation of samples according to their structural characteristics.

Finally, the results allowed the proposition of theoretical structures for the most abundant and representative structures detected in the analyses.

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Responsibility Notice

The results described in this work are published ([10.1016/j.fuel.2022.124418](https://doi.org/10.1016/j.fuel.2022.124418)).

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