



Advances in Asphaltene Petroleomics. Part 2: Selective Separation Method That Reveals Fractions Enriched in Island and Archipelago Structural Motifs by Mass Spectrometry

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Introduction

Advances in FT-ICR MS enable molecular-level characterization of asphaltenes. These analyses usually reveal compounds that are highly aromatic/alkyl-deficient, supporting the classical “island” model of asphaltene structure. However, recent works that combine chromatographic separations with mass spectrometry for petroleum characterization have shown that differences in ionization may greatly affect the analysis. Simply, compounds that ionize with greater efficiency are preferentially observed and mask the detection of poorly ionized species. Asphaltenes are not immune to this phenomenon. Importantly, asphaltenes generated by different precipitants exhibit different monomer ion yields (ionization efficiencies). This work focuses on the development of an extrography fractionation that selectively targets the removal of asphaltene species that exhibit high monomer ion yields and, thus, restrict mass spectral characterization of less efficiently ionized species.

Experimental

Positive atmospheric pressure photoionization (+ APPI) coupled to 9.4 T FT-ICR mass spectrometry was used to analyze extrography fractions derived from petroleum asphaltenes.

Results and Discussion

Silica gel is used as the stationary phase, and a unique solvent series separates asphaltenes based on their interaction with the silica surface, which was later determined to depend heavily upon the structure as well as monomer ion yield. The first two solvents (acetone and acetonitrile) isolate compounds that most efficiently produce monomeric asphaltene ions and, thus, cause bias in mass spectrometric analyses of whole asphaltenes. Subsequently, a solvent polarity gradient is used, with n-heptane, toluene, tetrahydrofuran, and methanol, to separate remnant asphaltene compounds on the basis of polarity and structure. The results demonstrate that mass spectrometry of whole asphaltenes does not reveal the complete molecular composition but rather preferentially exposes highly aromatic, alkyl-deficient, island-type structures. Early eluting fractions are shown to resemble the composition of the whole asphaltene and are enriched in island structures, whereas the analysis of later-eluting fractions reveals archipelago structural motifs as well as species with atypical asphaltene molecular compositions. We also demonstrate that, as molecular weight increases, the asphaltenes exhibit increased contributions of archipelago structural motifs. Higher mass ions, even from asphaltene fractions enriched in island structures, exhibit fragmentation pathways that originate from archipelago structures.

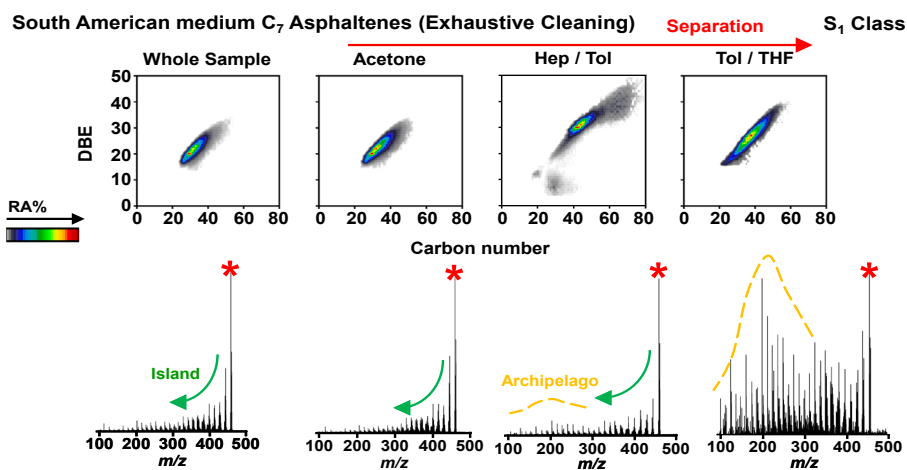


Fig 1. Upper panel: DBE vs. carbon number plots for the extrography fractions from South American Medium asphaltenes. Lower panel: IRMPD fragmentation mass spectra of precursor ions at m/z 453-457.

Conclusions

The island model is not the dominant structure of asphaltenes. It coexists with abundant archipelago structures, and the ratios of each are sample-dependent.

Acknowledgements

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Reference

[1] Chacón-Patiño M.L., *et al.*, Energy Fuels 2018, **32**(1), 314-328 (2018).