Heavy Petroleum Composition 3. Asphaltene Aggregation

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Results and Discussion

Molecular characterization of asphaltenes by conventional analytical techniques is challenging due to their compositional complexity, high heteroatom content, and asphaltene aggregate formation at low concentration. Thus, most common characterization techniques rely on bulk properties or solution-phase behavior (solubility). Proposed over 20 years ago, the Boduszynski model proposes a continuous progression in petroleum composition (molecular weight, structure, and heteroatom content) as a function of atmospheric equivalent boiling point. Asphaltenes, defined by their insolubility in alkane solvents, accumulate in high boiling fractions and form stable aggregate structures at low (ppb) concentrations, far below the concentration required for most mass analyzers. Here, we present direct mass spectral detection of stable asphaltene aggregates (see Figure 1) at lower concentration than previously published, and observe the onset of asphaltene nanoaggregate formation by time-of-flight (TOF) mass spectrometry. We conclude that a fraction of asphaltenes must be present as nanoaggregates (not monomers) in all atmospheric pressure and laser-based ionization methods. Thus, those methods access a subset of the asphaltene continuum.

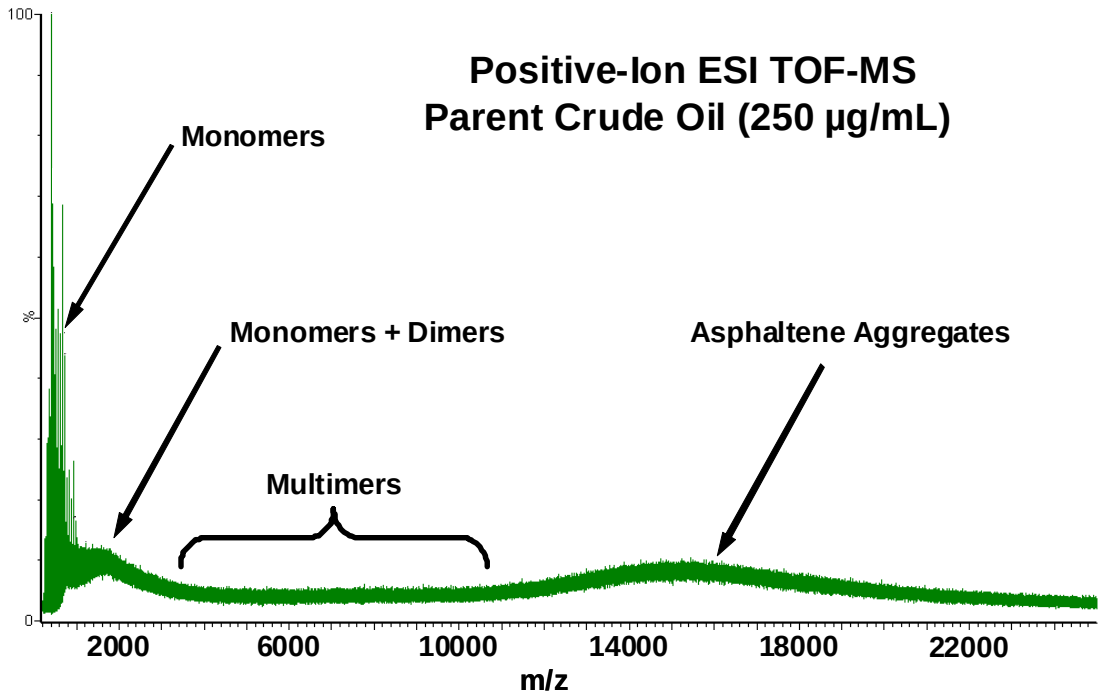

Figure 1. Positive-ion electrospray ionization time-of-flight mass spectra acquired with the Manitoba TOF instrument for a Middle Eastern heavy crude oil complexed with silver triflate (50:50 toluene:MeOH).

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References

[1] McKenna, A. M., *et al*., Energy & Fuels, **27**, 1246-1256 (2013).