Heavy Petroleum Composition 4. Asphaltene Compositional Space

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Results and Discussion

Asphaltenes and maltenes are defined operationally by solubility (in, e.g., heptane). Asphaltenes self-associate in solution and form putative nanoaggregates, composed of approximately six to ten asphaltene monomers per subunit. Bulk measurements indicate that asphaltenes are more aromatic than maltenes, and contain more heteroatoms and metals (nitrogen, sulfur, oxygen, nickel and vanadium). Numerous direct imaging, molecular diffusion, and mass spectral results agree that asphaltenes and maltenes are defined by similar, overlapped carbon number ranges, drastically restricting the acceptable carbon number and aromaticity "compositional space" for asphaltene compounds. Current mass spectral results (see also parts I, II, and III of this series) establish a continuum in petroleum structure and composition in support of the Boduszynski model, and confirm that asphaltene molecules share carbon number range with their maltene counterparts, but are simply more aromatic. Thus, the compositional space for maltenic and monomeric asphaltene species is now known. Part III provided evidence for asphaltene aggregate formation at concentrations below that required for most mass spectral analyses, suggesting that at these concentrations, most of the asphaltenes are locked in aggregate structures and therefore undetected as monomers. Here, Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry results confirm that asphaltenes and maltenes of the same heteroatom class exhibit higher aromaticity than maltenes of the *same carbon number*, limited by the highest possible aromaticity for a stable *planar* aromatic structure, and clearly differentiates asphaltene and maltene monomeric molecular compositions (see Figure 1).

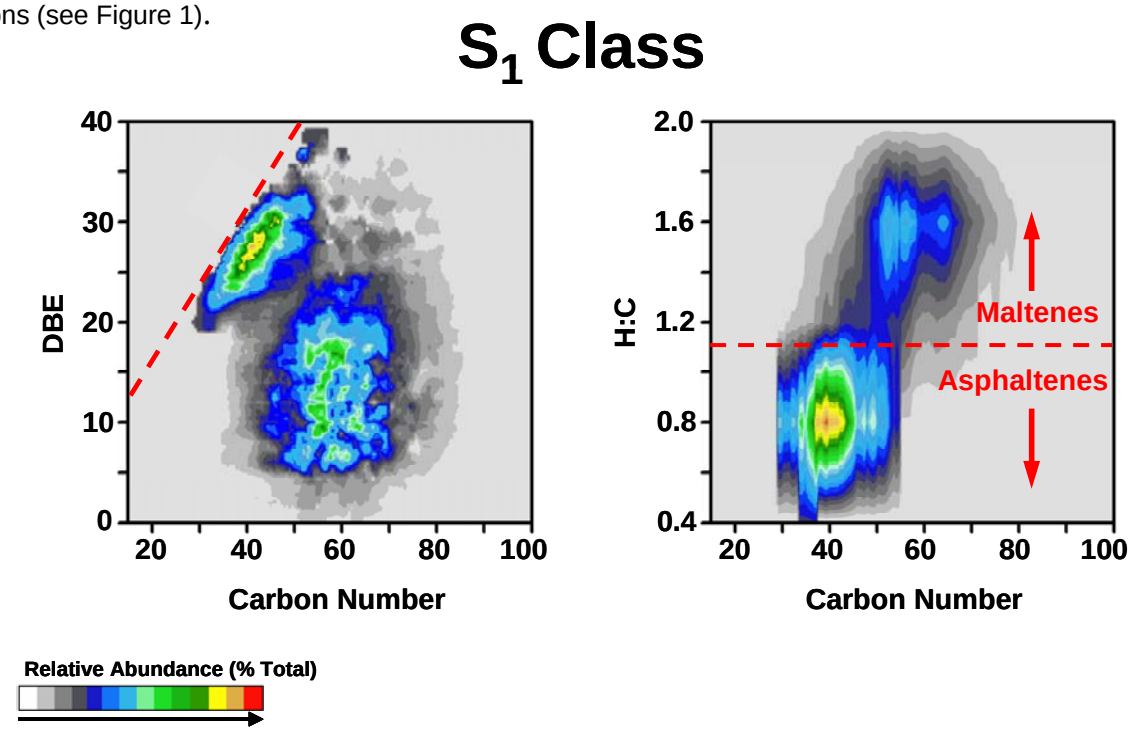

Figure 1. Composite isoabundance-contoured plots of DBE versus carbon number (left) and H:C ratio versus carbon number (right) for members of the S_1 class for the asphaltene and maltene fractions of Middle Eastern heavy crude, 593^+ °C residue, obtained by positive-Ion APPI 9.4 T FT-ICR MS.

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References

[1] McKenna, A. M., *et al*., Energy & Fuels, **27**, 1257-126 (2013).