On the Size Distribution of Self-Associated Asphaltenes

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Results and Discussion

Various experimental techniques were applied to a single source asphaltene sample under the same experimental conditions, to reveal the possible size distributions of asphaltene monomers and aggregates. The asphaltene sample was divided into solubility cuts by selective precipitation in solutions of heptane and toluene. Asphaltene self-association was assessed through a combination of density, vapor pressure osmometry (VPO), elemental analysis, Fourier transform-ion cyclotron resonance (FT-ICR) mass spectrometry, and time-resolved fluorescence emission spectra measurements for each cut. The physical dimensions of the asphaltenes were assessed by small angle x-ray scattering (SAXS), dynamic light scattering (DLS), membrane diffusion, Rayleigh scattering, and nanofiltration measurements. Molecular and nanoaggregate dimensions were also investigated through a combination of interfacial tension, interfacial adsorption, and surface force measurements. All of the measurements indicated that approximately 90 wt % of the asphaltenes self-associate. Ultrahigh resolution FT-ICR MS (**Figure** 1) suggests that the nonassociated asphaltenes are smaller and more aromatic than bulk asphaltenes, indicating that the associating species are larger and less aromatic. On the basis of vapor phase osmometry, the average monomer molecular weight was approximately 850 g/mol, whereas the molecular weight of the nanoaggregates extended to at least 30,000 g/mol with an average on the order of 10,000 to 20,000 g/mol. SAXS and DLS gave molecular weights 10 times larger. The physical dimensions of the nanoaggregates were less than 20 nm based on nanofiltration and with average diameters of 5 to 9 nm based on diffusion and Rayleigh scattering. SAXS and DLS gave average diameters of 14 nm and indicated that the nanoaggregates had loose structures. Film studies were consistent with the lower molecular weights and dimensions and also demonstrated that asphaltene monolayers swell by a factor of 4 in the presence of a solvent. The most consistent interpretation of the data is that asphaltenes form a highly polydisperse distribution of loosely structured (porous or low fractal dimension) nanoaggregates.

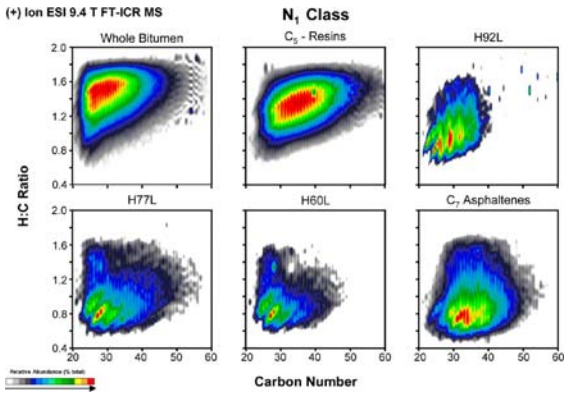

Figure 1. Whole bitumen and C_5-resins report H/C ratios in agreement with reported bulk property measurements for maltenes (H/C ratio 1.2 to 2), whereas fractions report lower H/C ratios (0.6 to 1.0) for species within the same heteroatom class. Importantly, the observed species represent only a subset of molecules that remain monomeric at sample concentrations required for all mass spectral characterization.

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References

[1] Yarranton, H.W. *et al.*, Energy & Fuels., **27**, 5083-5106 (2013)