610e From Oblate Cylinders to Elastic Films: a Neutron Scattering and Dilatational Rheology Investigation of Asphaltene Self-Assembly in Solution and at the Oil/Water Interface

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Asphaltenes, a crude oil constituent defined as the n-heptane insoluble/toluene soluble fraction, comprise the heaviest, most polar, and heteroatomically rich fraction, and are believed to consist of polycondensed carbon rings, interconnected by aliphatic chains. Their chemistry and topology enables self-assembly into interfacially active aggregates. Small angle neutron scattering (SANS) was performed at the IPNS (Argonne National Laboratory, Argonne, IL) on asphaltenes dispersed in model oils (toluene, heptane/toluene blends). Analysis of SANS data was performed using several non-geometric methods including Guinier, Zimm, and small-particle mass fractal models in addition to mono- and polydisperse cylinder geometric models. An oblate cylinder with radius polydispersity, described by a Schultz distribution, demonstrated the best ability of the models tested to recover the R_G and I_o obtained by the well-accepted Guinier analysis. Reduced chi-squared analysis strengthens the support for utilization of such a form factor over a larger q range than those applicable in the non-geometric models. Additionally, information obtained in a geometric form factor fit enables further characterization, including solvent entrainment, aggregate molecular weight, and even interaggregate interactions (via the second virial coefficient).

Asphaltenic aggregates are known to diffuse to oil/water interfaces, where they adsorb and rearrange molecularly into elastic films that impede coalescence, stabilizing the water-in-oil emulsions that create industrial processing and transport problems. Resins comprise a surface-active crude oil fraction that disrupts intraaggregate interactions and solvates asphaltenic aggregates. Their presence reduces emulsion stability compared to asphaltene-only systems. We employed dilatational rheology to probe the elastic nature of such interfacial films using an oscillating drop tensiometer for asphaltene-only and asphaltene/resin model oils. The dilatational modulus (ε) of aging films formed with asphaltene-only model oils monotonically increased with time to an apparent equilibrium modulus, which differed for asphaltenes of unique chemistry. The stabilizing film of an aging asphaltene/resin model oil droplet in water exhibited a time-dependent local maximum in ε. This behavior has also been reported for water-in-asphaltene/resin model oil emulsion stability tested by the critical electric field (CEF) technique. These observed phenomena are similar to the “Vroman effect,” observed in competitive protein adsorption. One plausible explanation is that resin-solvated asphaltenic aggregates are able to diffuse and adsorb to the interface more quickly than larger pure asphaltenic aggregates, but then a molecular rearrangement occurs in which resins assume the monolayer position and displace the asphaltenes, thereby reducing the stability and the dilatational elasticity.