

Asphaltene Aggregation: Techniques for Analysis

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ABSTRACT

The study of asphaltene colloidal properties is motivated by their propensity to aggregate, flocculate, precipitate, adsorb onto interfaces and, hence, pose considerable challenges for the petroleum industry. Asphaltenes are defined as the toluene (or benzene) soluble, yet *n*-heptane (or *n*-pentane) insoluble, portion of crude oil. The “solubility class” definition of asphaltenes generates a broad distribution of molecular structures that vary greatly among crude sources. Asphaltenes are generally characterized by fused ring aromaticity, small aliphatic side chains, and polar heteroatom-containing functional groups (e.g., carboxylic acids, carbonyl, phenol, pyrroles, and pyridines) capable of donating or accepting protons inter- and intra-molecularly. Molar H/C ratios between 1.0–1.2 and N, S, and O content of a few weight percent suggest that the asphaltene backbone mostly contains fused aromatic carbon interspersed with occasional polar functional groups. The most plausible mechanisms of asphaltene aggregation involve dispersion interactions between aromatic rings, polar and hydrogen bonding interactions between heteroatoms, and other charge transfer interactions. Understanding asphaltene chemistry and the fundamental mechanisms of colloid formation has been the driving force behind much petroleum research of the last half-century.

Key Words: Asphaltenes; Near-infrared spectroscopy; Pulsed-field gradient spin echo nuclear magnetic resonance; Small-angle neutron scattering; Vapor pressure osmometry.

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INTRODUCTION

This article discusses four instrumental techniques used to study asphaltene aggregation: near-infrared (NIR) spectroscopy, pulsed-field gradient spin echo nuclear magnetic resonance (PFG-SE NMR), vapor pressure osmometry (VPO), and small-angle neutron scattering (SANS). A brief introduction to each technique is provided, with particular emphasis on applications and recent findings.

INSTRUMENTAL TECHNIQUES

Near-Infrared Spectroscopy

The NIR spectroscopic region of the electromagnetic spectrum spans the wavelength range from 780 to 2500 nm—the most prominent absorption bands associated with the overtones or combinations of stretching vibrations from carbon–hydrogen bonds. Such vibrational modes are described theoretically using an anharmonic oscillator model. NIR spectra also possess a background elevation due to light scattering by particles and aggregates. NIR experiments are relatively simple, time efficient, and non-invasive. The NIR technique can quickly and accurately identify variations in asphaltene aggregation behavior with changes in temperature, pressure, solvent conditions, and with dopant addition; however it is still unclear whether it can quantitatively determine aggregate sizes.^[1,2] For example, Auflem et al. performed NIR experiments to study the disintegration of North Sea asphaltenes (0.125 wt%) dissolved in 70/30 *n*-heptane/toluene by adding various amphiphiles and naphthenic acids as a function of concentration.^[1] Changes in asphaltene aggregate size were observed as a decrease in the optical density at 1600 nm. Aske et al. pressurized North Sea crude oil (~0.8 wt% asphaltenes) to 300 bar and then depressurized in incremental steps with NIR spectra recorded at each pressure.^[2] The aggregation onset pressure, as well as changes in the fluid compressibility and aggregate size, were determined from multivariate analysis of the NIR spectra. Furthermore, re-pressurization showed reversibility of the crude oil aggregates to their original aggregate size after 72 hr at 300 bar.

Pulsed-Field Gradient Spin Echo Nuclear Magnetic Resonance

PFG-SE NMR is a non-invasive, relatively fast instrumental technique to probe molecular self-diffusion coefficients using magnetic field gradients of varying strength to effect large signal attenuation. Asphaltene polydispersity can be accounted for in the data analysis by assuming a log-normal distribution of diffusion coefficients. A log-normal distribution is reasonable because diffusion coefficients are positive-definite and may vary over several orders of magnitude. Deuterated solvents are typically used to prevent signal attenuation from proton spin–spin relaxation. Östlund et al. studied the self-diffusion of Venezuelan asphaltenes (0.044 to 5 wt%) in *d*-toluene.^[3] Fitting the signal attenuation in the range from 0.7 to 1.9 ppm provided a polydispersity



($\sigma \sim 0.6$) that was concentration independent. A median diffusion coefficient, D_m , in the order of 1×10^{-10} to 2×10^{-10} m²/sec monotonically decreased with increasing concentration, indicating an increase in the average aggregate size. Model fitting of the diffusion coefficients based on particle geometry and concentration suggested that asphaltene aggregates could not be spherical in shape, because of large obstruction effects. Instead, a disc-like structure was proposed. In another study, deuterated *n*-pentane and *n*-heptane (≤ 30 wt%) were added to Venezuelan asphaltenes (3.7 wt%) in *d*-toluene and *d*-ethylbenzene.^[4] Non-linear increases in D_m with flocculant concentration were observed that could not be attributed to changes in the solvent viscosity alone. For example, D_m of asphaltenes in toluene increased from ca. 1.15×10^{-10} m²/sec with no flocculant added to 1.35×10^{-10} m²/sec at 30% pentane. The polydispersity of the solute increased from $\sigma = 0.6$ to 0.7 at the highest flocculant concentration, further suggesting that *n*-alkane addition was inducing flocculation. Sjöblom et al. showed that PFG-SE NMR is applicable to study the interactions of asphaltenes with various additives, such as naphthenic acids, which serve to solvate asphaltenes and decrease aggregate sizes.^[5]

Vapor Pressure Osmometry

VPO takes advantage of the change in vapor pressure when a small amount of solute is added to a pure solvent. The VPO measuring chamber consists of a solvent reservoir with two wicks providing a saturated solvent atmosphere around two thermistors. Condensation of solvent from the atmosphere into an asphaltene solution placed at one thermistor releases heat and increases the thermistor temperature until the solution vapor pressure matches the pure solvent. Subsequent small voltage changes induced at the thermistor are related to the number-averaged molar mass of the solute. Due to differences in vapor pressure, VPO measurements are limited to single solvent solutions and are impractical for the study of whole crudes. Yarranton et al. observed the molar masses of Athabasca and Cold Lake bitumen asphaltenes in toluene and 1,2-dichlorobenzene increased with concentration to a limiting value of 10–20 g/L (~ 1 –2 wt%).^[6] Figure 1 shows the VPO molar mass of Athabasca C7-asphaltenes in 1,2-dichlorobenzene at two different temperatures. Linear extrapolation (75°C) at concentrations below 3 g/L suggested monomer molar masses of ca. 1000 g/mol. The molar mass at high concentration approached 6000 g/mol, a value indicative of an aggregate with approximately six monomers. The degree of asphaltene association varied with solvent polarity and temperature with no clear indication that asphaltenes were completely dissociated in the low concentration limit. Spiecker et al. performed VPO measurements on whole asphaltenes and their more and less soluble subfractions in toluene at 53°C.^[7] So-called “soluble” and “precipitate” fractions were generated by asphaltene precipitation in heptane–toluene, with the “precipitate” fraction accounting for the least soluble 30–40% of the whole asphaltenes by mass. The apparent molar masses of the “precipitate” fraction (12,000–17,000 g/mole) from B6 crude oil were substantially higher than the corresponding “whole” and “soluble” asphaltenes (2500–3500 g/mole) due to significant polar and H-bonding interactions among the asphaltene monomers in the absence of the solvating character of the complementary more soluble fraction.



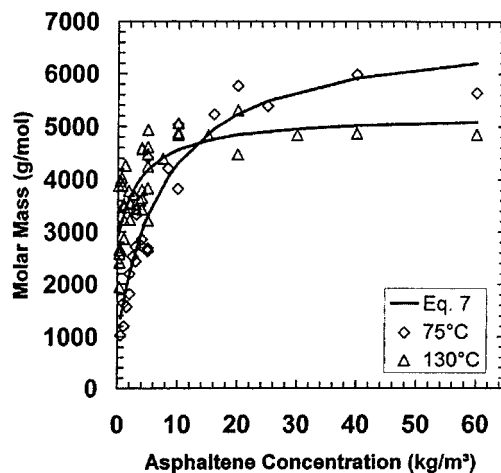


Figure 1. VPO molar masses of Athabasca C7-asphaltenes in 1,2-dichlorobenzene. [Reproduced with permission from *Ind. Eng. Chem. Res.* 2000, 39(8), 2916–2924. Copyright 2000 Am. Chem. Soc.]

Small-Angle Neutron Scattering

SANS is used to deduce sizes and morphologies of colloidal aggregates in solution. Proper analysis of SANS scattering intensity curves provides values for aggregate radius of gyration (R_g), molar mass, and apparent “fractal” dimension. Molar masses are weight-averaged and may be biased toward the presence of a small number of high mass aggregates in solution. SANS studies typically employ selective solvent deuteration to maximize the coherent scattering contrast between the solvent and solute. Perhaps the major drawback of SANS is the monetary cost of deuterated solvents and the limited availability of beamtime at national laboratories. Nevertheless, numerous studies have been performed over the past decade to probe the effects of concentration, solvent, temperature, and various additives on asphaltene aggregation behavior. For example, Roux used SANS to study temperature and concentration effects on the structure of Safaniya asphaltenes in toluene.^[8] Aggregate R_g values were nearly constant (~ 70 Å) at asphaltene volume fractions less than 3–4%, indicating that asphaltenes did not dissociate with dilution to $\sim 0.3\%$ v/v. Aggregate R_g and molar mass decreased with increasing concentration (>3 –4% v/v) due to aggregate interpenetration. Fenistein et al. performed SANS analysis on dilute solutions ($\sim 3\%$ v/v) of Safaniya asphaltenes dissolved in d-toluene with varying d-heptane concentration (0–45% v/v).^[9] R_g values increased with heptane content from 69 to 144 Å and molecular weights increased from 90 to 570 kDa. Apparent “fractal” dimensions of ~ 2 obtained from the scaling behavior of the scattering intensity at intermediate wavevectors suggested that asphaltenes form highly porous aggregates consistent with the so-called “archipelago” model of asphaltenes in which the monomer molecular structure is comprised of fused-ring aromatic moieties connected by aliphatic and heteroatomic groups. The aggregate depicted in Fig. 2(c) is consistent with the observed fractal-like dimensions as the “scatterers” in a SANS experiment contain some percentage of entrained deuterated solvent in the interstitial space that does not give rise to scattering contrast.



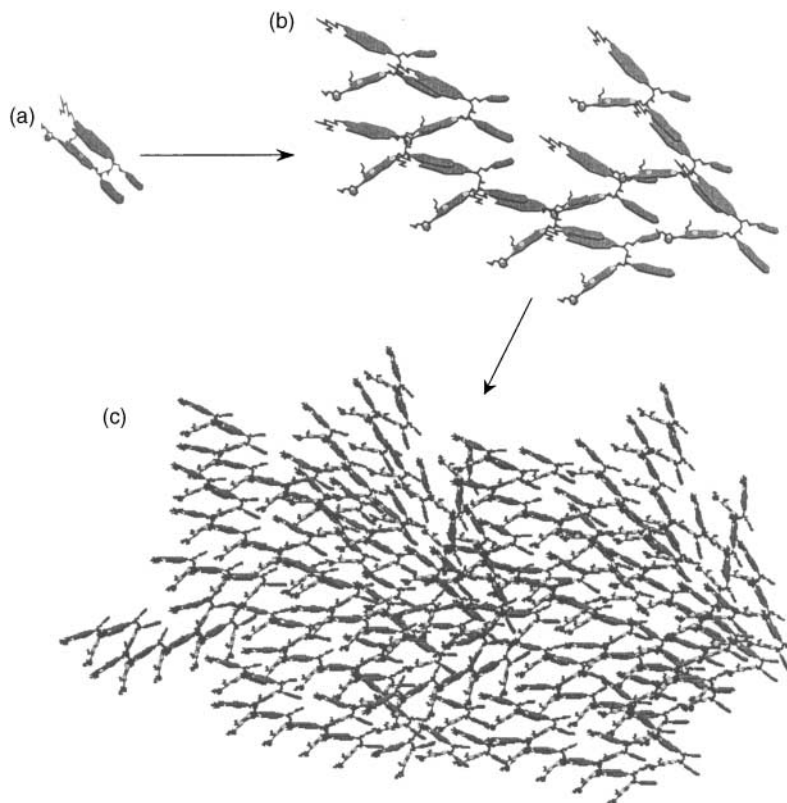


Figure 2. Schematic illustration depicting (a) an asphaltene monomer; (b) an asphaltene aggregate with size ca. 3–4 nm, molecular weight ca. 20–25 kDa, and apparent “fractal” dimension between 1–2; and (c) an asphaltene aggregate with size ca. 12–15 nm, molecular weight ca. 200–400 kDa, and apparent “fractal” dimension between 2–2.5.

Spiecker et al. performed SANS analysis on dilute solutions (~ 1 wt%) of “whole,” “soluble,” and “precipitate” asphaltene fractions in deuterated heptane/toluene solutions.^[7] Enhancement of polar and π -bonding interactions for the less soluble subfractions indicated by elemental analysis results was reflected by the large aggregate sizes for B6 “precipitate” asphaltenes compared to the “whole” and “soluble” fractions in Fig. 3. The less soluble (i.e., “precipitate”) subfractions contributed the majority of species responsible for asphaltene aggregation. In another study, SANS measurements were performed on 1% wt asphaltene solutions in mixtures of heptane toluene at various resin-to-asphaltene mass ratios.^[10] The correlation length of the soluble aggregates decreased with increasing resin content to a minimum value of ca. 20 Å, presumably corresponding to a asphaltene monomers or small oligomers solvated by resins. Aggregate size increased with resin content in the presence of insoluble asphaltenes, as more polar material was dissolved into solution. Upon dissolution of the insolubles, additional resins served to decrease the correlation length.



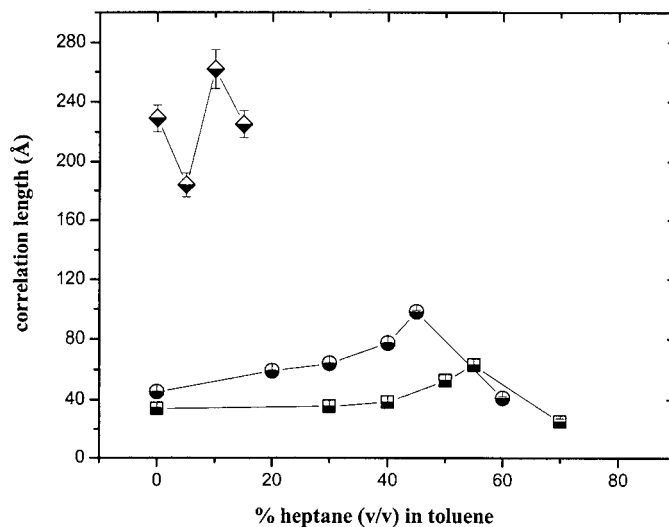


Figure 3. Aggregate sizes B6 precipitate (\diamond), whole (\bullet), and soluble (\blacksquare) asphaltene fractions (1 wt%) as a function of d-heptane content in d-toluene. Correlation length (ξ) scales with radius of gyration (R_g) according to the relation: $\xi = R_g/\sqrt{3}$.

CONCLUSIONS

This article has provided an introduction to four different, yet complementary, experimental methods used to study asphaltene aggregation behavior: NIR spectroscopy, PFG-SE NMR, VPO, and SANS. These methods represent a small subset of those currently employed by researchers in petroleum science and engineering. While each technique has its own advantages and disadvantages, all provide valuable insight into the fundamental mechanisms driving asphaltene colloidal behavior.

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