Characterization of Asphaltenic “Solid” Deposits and Asphaltene Rich Phases in Hydrocarbons

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Introduction

Preliminary conventional small-angle x-ray scattering (SAXS) experiments were conducted in conjunction with coordinated phase behavior and calorimetric measurements as part of a larger, long-term study aimed at understanding the structures of neat asphaltenes and asphaltenes in their native hydrocarbon media and in hydrocarbon solvents. Despite the importance of asphaltenes and their properties in petroleum and natural gas production and refining, their properties are poorly understood. Moreover, the models for predicting molecular nanoscale and macroscopic properties, which are based on diverse physical and chemical arguments, also remain speculative, since validation techniques are unavailable. For example, diverse “average” models for molecular structure have been proposed (Fig. 1), even for the same or closely related materials and both micelles and nanoparticles are proposed at the supramolecular level on the basis of such models.

Supramolecular behaviors predicted on the basis of these models frequently do not agree with experimental data. For example, recent work at Argonne [3] suggests that asphaltenes from Maya, Khafji, and Irianian light crudes, when present at low concentrations in decalin, begin as large, extended fractal networks at room temperature. With increasing temperature, the networks break down, and the mixtures become nearly homogeneous self-solutions. The observed transition temperatures vary from asphaltene to asphaltene but are sharp. Proposed supramolecular models do not exhibit such sharp transitions from one behavior to another.

Coordinated data sets that capture the relevant physics and chemistry at the molecular, nano, micro, and macro length scales for neat asphaltenes and asphaltene + solvent mixtures are needed so that proposed models can be evaluated. The first hypothesis to be tested was whether or not asphaltenes with the same molecular characteristics exhibit the same supramolecular properties. Key results from these preliminary SAXS experiments are reported on here in this brief summary.

Methods and Materials

Maya and Athabasca asphaltenes were selected for the preliminary study because of the similarity of their average submolecular structures. Results from their elemental and C13 nuclear magnetic resonance (NMR) analyses, as well as their mean molar mass as determined from vapor pressure osmometry (VPO), are presented in Table 1. The infrared spectra for the two asphaltenes, reported on elsewhere [4], show the equally close agreement of the oxygen distribution among functional groups. Neat samples of these asphaltenes, samples of the native oils, and samples of asphaltenes in solvent solutions were prepared and transferred to 3-mm-diameter by 0.28-mm-thick borosilicate NMR tubes, which were then sealed under vacuum. In addition to standards, samples prepared and conditions investigated included these:

- Maya crude + n-dodecane (C12) and 1-methyl-naphthalene (1-MN) (50-310°C)
- Athabasca vacuum bottoms (ABVB) + C12 and 1-MN (50-310°C); ABVB and Maya C7-asphaltenes + C12 and 1-MN (50-310°C)
- ABVB, ABVB asphaltene, and Maya asphaltene coking (200-425°C)

Samples spanned a range of compositions from 1% asphaltenes in solvent to neat asphaltenes. The ABVB and Maya crudes are made of 32% and 15% asphaltenes, respectively. SAXS emissions were evaluated at 20°C intervals in the temperature windows indicated at a variety of exposure times by using the BESSRC sector 12 facilities at the APS.

FIG. 1. Diverse average molecular structures proposed for athabasca bitumen fractions. Structure on left is from Ref. 1; the structure on right is from Ref. 2.
TABLE 1. Molecular characterization of asphaletenes selected for the preliminary study.

<table>
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<tr>
<th>Parameter</th>
<th>Ref. 5</th>
<th>Ref. 6</th>
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<tr>
<td></td>
<td>ABVB Asphaltenes</td>
<td>Maya Asphaltenes</td>
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<tr>
<td>Elemental composition, wt%</td>
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<tr>
<td>Carbon</td>
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<tr>
<td>Molar mass</td>
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<td>NMR aromatic carbon functional groups</td>
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<td>R-CH3</td>
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</table>

where the x-ray beam comprised synchrotron radiation (8.5-23.0 keV). The samples were held at each temperature for 15 minutes before the data were acquired, except in the coking experiments, where the samples were analyzed as soon as a temperature was reached.

Results

The key findings from the analyses listed above are summarized in Figs. 2 and 3. The average scatter energy, the fractal dimension of large scatters, and the apparent heat capacity for ABVB asphaltenes as functions of temperature are shown in Fig. 2. The dashed curve in the apparent heat capacity graph [Fig. 2(c)], is based on the Einstein equation for structured solids [7]. It is evident that at low temperatures, ABVB asphaltenes behave as a structured solid within the error of the calorimetric measurements. This result is supported by the fractal dimension data [Fig. 2(b)], where a fractal dimension of 3 is found for ABVB asphaltene at low temperatures. At room temperature and above, ABVB asphaltene are subject to reversible endothermic and exothermic transitions. The endotherm is associated with a general reduction in SAXS emissions [Fig. 2(a)], over the Q range of 0.005 to 0.18, whereas the exotherm is associated with a destructuring of the asphaltene. The fractal dimension of the large scatters drops from 3.0 to 2.3 in the temperature range from 400 to 550K. At temperatures higher than ~ 610K, asphaltene begin to react irreversibly to form coke as the principal product. Average SAXS emissions for ABVB asphaltene increase and then decrease as they are heated through this temperature range [Fig. 3(a)], whereas the fractal dimension increases [Fig. 3(b)]. The average SAXS emissions and the fractal dimension for Maya asphaltene follow opposing trends in the same temperature interval, and although it is not shown in this report, the calorimetric behavior of Maya asphaltene differs from that of Athabasca asphaltene as well.
FIG. 2. (a) Average SAXS scatter energy, (b) fractal dimension, and (c) apparent heat capacity for Athabasca asphaltenes.

FIG. 3. Comparison between the (a) average SAXS emissions and (b) the fractal dimension for Athabasca and Maya asphaltenes.

Discussion

Athabasca and Maya asphaltenes have nearly identical values for standard measurements such as elemental composition and molecular substructure, yet they exhibit radically different behaviors at the supramolecular level. This pivotal result provides a clear illustration that standard techniques applied for asphaltene analysis cannot yield information that can predict the supramolecular behavior of neat asphaltenes and, while not addressed here, asphaltenes in solvents. This unexpected result poses a number of challenges for scientists and engineers in the petroleum sector. These challenges include determining how to characterize asphaltenes and what basis to use for creating predictive models for asphaltene precipitation and phase behavior.

We have begun to address aspects of these issues that may help move the field to move forward. We
are currently focusing on the interpretation of SAXS and small-angle neutron scattering (SANS) data to obtain detailed supramolecular structural information across broad concentration ranges without making a priori assumptions about asphaltenes, which remain an ill-defined petroleum fraction. It is currently not clear whether SAXS can be used to provide unambiguous size, concentration, and shape measurements for nanoscale particles where the shape is not known a priori.

Acknowledgments

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References