

Characterization of asphaltenes separated physically and chemically using small-angle X-Ray scattering

Jesús Amundaraín, John Shaw*

^a Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta, T6G 2V4
(* corresponding author: jmsshaw@ualberta.ca)

Asphaltenes, an ill-defined self-assembling fraction of hydrocarbon resources such as reservoir fluids and bitumen, present numerous challenges for production, transport, and refining. In this work, Athabasca asphaltenes were characterized using small-angle X-ray scattering (SAXS) with synchrotron radiation. The analysis of the aggregates involved the study of their size and structure.

Two separation methods were used to partition asphaltenes: chemical precipitation of asphaltenes from Athabasca vacuum residue (AVR) using n-pentane; physical separation using nanofiltration of Athabasca bitumen through zirconia membranes with a 20 nm average pore size [1]. Extracted samples were added to two solvents: 1-methylnaphthalene and n-dodecane. SAXS images were obtained over the temperature and asphaltene composition ranges, 50-310 °C and 1-8 wt. %, respectively.

All SAXS measurements were performed on the APS BSSERC-CAT 12-ID-C beamline at the Argonne National Laboratories. The beamline optics were adjusted for an X-ray energy of 18 keV. SAXS images were collected at a camera distance of 3.7 m, corresponding to a q-range of 0.005-0.2 Å⁻¹.

Two approaches were taken in the analysis of the SAXS spectra. A model-independent approach was used to provide radii of gyration and scattering coefficients; while model-dependent fitting was used to estimate particle size distribution assuming aggregates are spherical. Key illustrative examples are reported here.

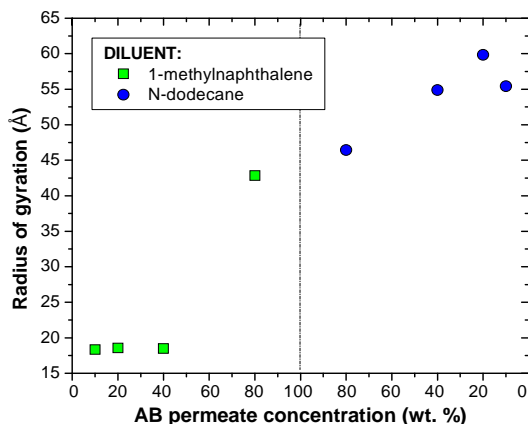


Fig. 1. Effect of solvent type and AB permeate concentration on radius of gyration for asphaltenes.

Fig. 1 shows the radii of gyration for AB permeate (10.4 wt. % asphaltenes) obtained from the

nanofiltration experiments and diluted in 1-methylnaphthalene and n-dodecane. Aggregates are smaller on dilution with 1-methylnaphthalene and larger in n-dodecane. A clear transition is observed for the mean aggregate size at 50 % AB permeate in 1 methylnaphthalene. Otherwise, small changes in the solvent environment lead to small changes in aggregate size. Although not shown, the radii of gyration were found to be independent of temperature over the range of temperatures investigated. The scattering coefficient was also largely independent of temperature, at fixed composition, as shown in Fig. 2.

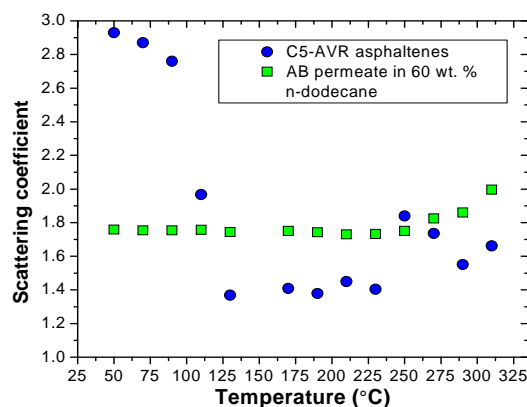


Fig. 2. Temperature dependence of the scattering coefficient for 4 wt. % asphaltenes in n-dodecane.

Scattering coefficients of chemically separated asphaltenes (Fig. 2) showed strong temperature dependence even at fixed composition, unlike the physically separated asphaltenes. The high scattering coefficients observed at low temperatures are associated with closely packed structures, whereas low scattering coefficients observed at higher temperatures are associated with more open structures. The transition in scattering behavior occurs in a temperature range where chemically-separated Athabasca pentane-asphaltenes undergo a phase transition [2, 3].

These and additional examples demonstrate that the aggregation properties of asphaltenes in diluted native hydrocarbon fluids differ markedly from chemically separated asphaltenes in pure solvents.

References

- [1] Zhao, B., Shaw, J.M., (2007) Energy & Fuels 21, 2795-2804.
- [2] Maham, Y., et al. (2005) Fluid Phase Equilibria 227, 177-182.
- [3] Fulem, M., et al. (2008) Fluid Phase Equilibria 272, 32-41.