Experimental report

26/02/2019

Proposal:	**9-10-1531**	**Council:**	4/2017

Title: Investigating the structure and stabilisation mechanism of asphaltenesubfractions

Research area: Chemistry

This proposal is a new proposal

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Samples:
toluene-d
heptane-d
heptane-h
asphaltene whole fraction
asphaltene fractions
toluene-h

Instrument	Requested days	Allocated days	From	To
D33	0	2	07/04/2018	09/04/2018
D11	0	0		
D22	2	0		

Abstract:

Asphaltenes are polyaromatic species present in crude oil which are defined as soluble in aromatic solvents and insoluble in n-alkanes. The asphaltene structure depends upon the source of crude, but generally comprises a range of structures e.g. condensed aromatic (and non-aromatic) rings with aliphatic side chains and hetero groups. There is significant research interest in asphaltenes involving aggregation at solid-liquid and liquid-liquid interfaces. Such phenomena can result in problems such as fouling of heat exchangers and blocking of pipes.

Model asphaltene structures have been produced to explain such aggregation. Molecular dynamic simulation has suggested a core-shell structure with an aromatic core and an aliphatic shell. The problematic asphaltene sub-fraction has recently been isolated and differences between this and whole asphaltenes observed.

The proposed SANS experiment will determine the self-assembled structure of model asphaltene and contrast this with the behaviour using whole and sub-fractions of asphaltene (in solution and at the oil-water interface). Elucidating the mechanism of aggregation will have a significant impact on crude oil recovery/ refining.

Investigating the structure and stabilisation mechanism of asphaltene subfractions

BALLARD, HARBOTTLE, DOWDING, QIAO, XU, CATTOZ

Asphaltenes are polyaromatic species present in crude oil which are defined as soluble in aromatic solvents (such as toluene) and insoluble in n-alkanes (pentane, heptane). The research objective was to study the colloidal sizes and shapes (nanoaggregates, nanoclusters) of whole asphaltenes (WA) extracted from two crude oils and then further separated using our newly proposed e-SARA method. E-SARA separates the most interfacially active asphaltenes (IAA), which have partitioned at an oil-water interface, from the remaining asphaltenes (RA) which remain in the solvent following emulsification. The effect of asphaltene concentration and solvent aromaticity on the asphaltene aggregates was considered in the study. Measuring the aggregates of the different asphaltenes using D33 has provided us with new insights regarding asphaltene aggregates size and shape and when correlated to elemental composition and molecular structures will elucidate the key asphaltene properties that govern aggregation and routes for asphaltenes growth.

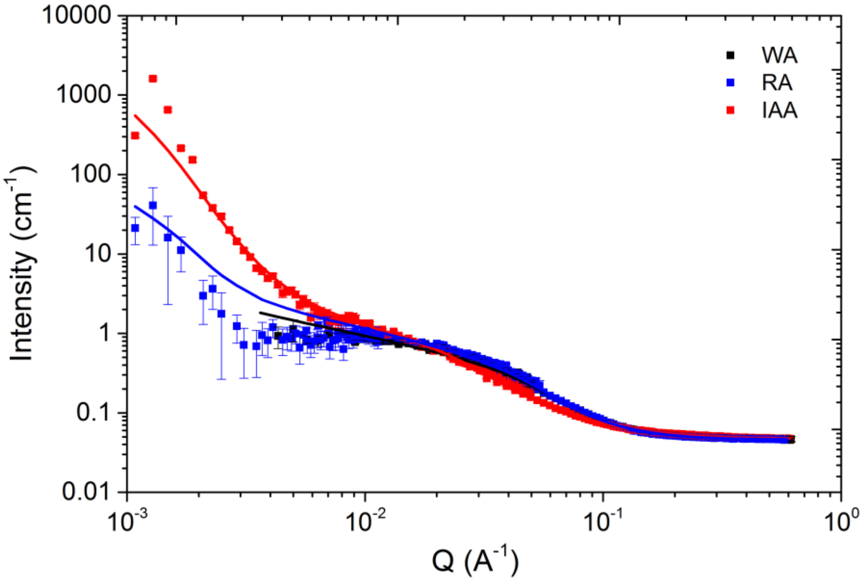

Figure 1. SANS data for 5 g/L WA, RA and IAA fractions in toluene. Guinier-Porod fits shown by the solid lines.

In a favorable (purely aromatic) solvent, Fig. 1 shows measurable differences between the IAA fraction and the RA, WA fractions. Similarity between RA and WA is not unexpected since approximately 98% of the WA fraction is composed of RA. The low Q range (<0.01 A^{-1}) shows a higher intensity for the IAA fraction suggesting a greater proportion of larger aggregates. Using the Guinier-Porod model, it was possible to determine the radius of gyration (R_g) and the fractal dimension (D_F) for each asphaltene fraction, see Fig. 2.

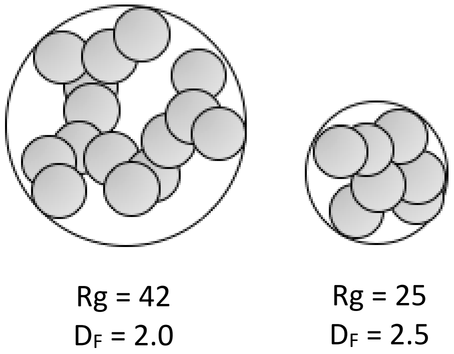

Figure 2. Schematic representation of a typical IAA (left) and RA (right) aggregate based on the Guinier-Porod model fits. Individual asphaltene molecules represented by spherical bodies.

In addition to the different asphaltene fractions the solvent aromaticity was also considered, changing the solvent from a very good solvent (toluene) to a poorer solvent (3:2 heptol, heptane to toluene volume basis). All experiments were conducted at 5 g/L. In the high Q range, Fig. 3 shows nanoaggregates with a size that is independent of the solvent aromaticity, and the Guinier-Porod fit results in an R_g of 25 Å and a fractal dimension of 2.5 for all three samples. However, in the low Q range the scattering intensity increases in the poorer solvent suggesting a greater number of nanoclusters. The asphaltenes R_g increases in the following order toluene < 1:1 heptol < 3:2 heptol. This data suggests that solvent aromaticity does not influence the formation of nanoaggregates but does contribute to the formation of nano-clusters (likely formed by the interaction of nanoaggregates).

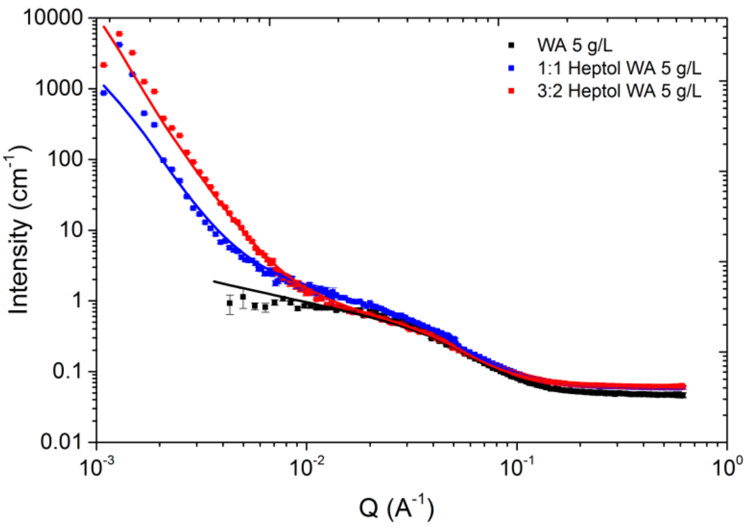

Figure 3. 5 g/L Colombian heavy crude oil asphaltenes dispersed in toluene (black), 1:1 heptol (blue) and 3:2 heptol (red).

Further comments:

Studying asphaltenes at the oil-water interface was also proposed. However, there were some issues with emulsion separation and droplet settling. An attempt was made to measure the scattering from settled samples to determine the thickness of the stabilizing film. Data analysis is currently ongoing. Possible future neutron studies could involve the interaction of asphaltene nanoaggregates with additives and / or asphaltene adsorption at a solid/liquid interface.