H5. A SANS STUDY OF THE ADSORBED ASPHALTENE LAYER IN WATER-IN-HYDROCARBON EMULSIONS

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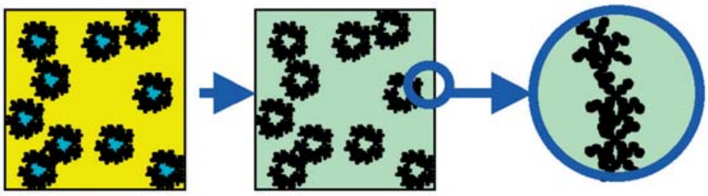
During oil production, crude oils are typically produced as water in crude oil (w/o) emulsions, which are often very stable. Among the indigenous natural surfactants contained in the crude oils, asphaltenes and resins are known to play an important role in the formation and stability of w/o emulsions [1]. Until now, the stability of the oil/water interface, and particularly the contribution of asphaltene, has been studied mainly from a rheological point of view [2]. Correlations between stability and mechanical properties of the interfaces have been highlighted. Nevertheless, less is the knowledge about the structural organisation of the molecules at the interface and the link between the structure at the local scale and the stabilization mechanisms [3].

We present a new and original method to visualize the interfacial film in liquid-liquid petroleum emulsion by SANS measurements. Though the droplet size is micronic, one structure in the system is a few nanometer, which the water-oil interface, and also some 10 nm asphaltene large fractal-like aggregate present in the oil [4] can be linked to this interface. Neutron scattering is here used at its best, owing to contrast matching of the two liquid phases: by adjusting the scattering length density of the aqueous to the one of the organic phase, we measure the residual scattering contribution of the interface only. Emulsions are water in oil (xylene) mixtures stabilized by asphaltenes, which are the higher molecular mass, the denser, the more polar and aromatic components of crude oils. We showed the possibility to reach to the local structure of the interface (size, composition) and to the linkage of asphaltene aggregate structures between bulk and interface.

To make SANS measurements accurate and meaningful, a specific protocol is used. Asphaltene is dissolved into xylene, and the solution is mixed with water; after the emulsion process (strong stirring), two liquids phases appear, a packed droplet water phase and a supernatant, which separates by decantation. A specific attention was made to know precisely (by weighing) the volumic fractions of oil and water in each phases. It allowed us to measure independently the scattering from the initial asphaltene solution, from the surpernatant and from the packed droplet water phase. The oil phase is a mixture of normal and deuterated xylene, the water phase is a mixture of normal and deuterated water. Depending on the deuterated species fractions, we can separate the scattering contribution of the different components of the system. Special care (figure 1) was made in the banks measurements (incoherent scattering and residual asphaltene bulk scattering) to background subtraction to be sure to get the interface scattering.



Scheme 1. The use of neutrons: inner and outer scattering densities are matched, and one look at the scale of the interface.

By matching the asphaltene signal, we can see the water droplets scattering contribution and have an access to the quantity of interface. Systematic experiments were performed by varying the amount of resins (which is related to the size of asphaltenes aggregates), the pH of the aqueous phase, which change the asphaltenes-asphaltenes interactions and the ageing times of the emulsions, to study slowing down effects.

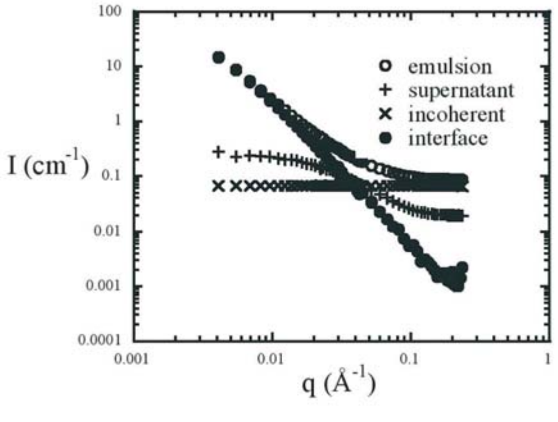


Figure 1. Specific treatment of emulsion measurements in the two liquid phase matching contrast condition to extracted the interface scattering signal after subtraction of the contributions of both incoherent scattering and asphaltene bulk scattering.

From bulk SANS measurements in initial solutions and supernatant, we can deduce radius of gyrations and molecular mass of asphaltene aggregates using the Zimm approximation. We observe a systematic decrease of theses quantities after the emulsification process (table 1). This suggested a preferential localisation of the large aggregates in the interface.

Asphaltenes Aggregates	R_g (Å)/M_w(g.mol^{-1}) before emulsification (initial solution)	R_g (Å)/M_w(g.mol^{-1}) after emulsification (supernatant)
Small	66 / 9.76.10^4	61/ 9.79.10^4
Medium	84 / 1.81.10^5	74 / 1.45.10^5
Large	106 / 3.02.10^5	90 / 2.37.10^5

Table 1. Variation of the size and of the mass of the asphaltene aggregates before and after emulsification.

The interface scattering signal obtained after subtraction of background shows a decrease of the intensity as q-2 which is the sign of the scattering of two dimensional objects (figure 2).

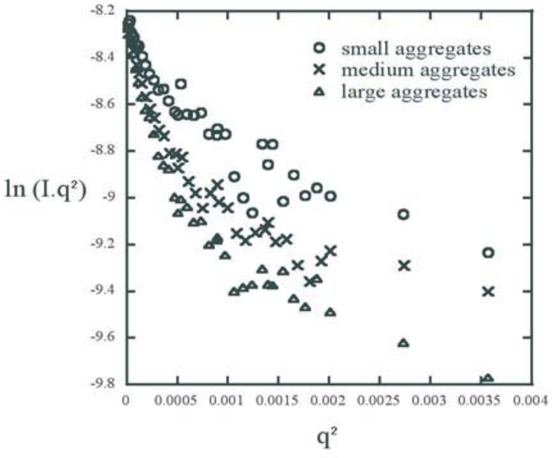


Figure 2. The interface scattering, in a log (q^{2}I (q)) versus q^2 plot: the thickness of the interface is given by the slope of the curves assuming a flat disk model.

The signal could be analysed using a simple flat disk model from which we could extract the thickness of the interface. The most important result is that the thickness of the interface is directly correlated to the asphaltene aggregate sizes in bulk: The larger the aggregates in bulk, the thicker the interface. Measurements in asphaltene matching conditions displays a Porod law, as expected, with a specific surface yielding the water droplets radius, in situ. Coupling these values with independent asphaltene adsorb amount in grams per grams of water droplets, using classical adsorption measurement methods, permit to calculate the quantity of molecules in grams per surface unit. The obtained adsorption values are consistent with a structural organization of aggregates as a mono layer at the interface. The stability of the emulsion could be analysed with a simple criterion: the quantity of water resolved after centrifugation and discussed as function of the structural parameter of the interface [5]. The main conclusions could be summarizing as follows: the interface is stabilized by the larger asphaltene aggregates, organized as a monolayer. The thickness of the interface is directly correlated to the asphaltene size in bulk and the larger is the layer the more stable is the emulsion; the lower is the quantity of resolved water after centrifugation. Increasing the pH of the aqueous phase (from neutral to basics values) seems to contribute to the ionization of the polar fraction of the aggregates. This changes the interaction between aggregates inside the layer, which becomes more repulsive, and induced a decreasing of the number of objects per surface unit and in fact, of the emulsion stability.

To conclude, we have demonstrated the capacity of SANS measurement to characterize the structure of liquid-liquid interface in the case of petroleum emulsion and the links between this organization at the local scale and the stability of the emulsions. From a larger point of view, this demonstrates the ability of SANS to study macro emulsions and would be applied to a large panel of experimental systems.

[1] Sjöblom J., Aske N., Auflem I.H., Brandal O., Havre T.E., Saether O., Westvik A., Johnsen E.E., Kallevik H. *Advances in Colloid and Interface Science* **2003**, 100-102, pp. 399-473

[2] Bourriat P., Kerri El N., Graciaa A., Lachaise J. *Langmuir* **2004**, 20, pp 7459-7464

[3] Czarnecki J., Moran K. *Energy & Fuel* **2005**, 19, pp 2074-2079

[4] Fenistein D., Barré L., Broseta D., Espinat D., Livet A., Roux J.-N., Scarcella M. *Langmuir* **1998**, 14, pp 1013-1020

[5] Jestin J., Simon S., Barré L., in prepar. for *Langmuir*