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Possible role of asphaltenes in stabilization of water–in–crude oil emulsions

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According to the widely accepted paradigm, asphaltenes are the main stabilizing agent for water-in-crude oil (W/O) emulsions. This notion is supported by numerous experimental observations; see [1] and the references therein. However, contrary to popular belief, asphaltenes are only weakly surface active and, due to their high affinity to the oil phase, have very low HLB values. Therefore, asphaltenes cannot stabilize emulsions the way typical emulsifiers do.

The mechanisms by which asphaltenes may be involved in W/O emulsion stabilization are still not well understood. Substantial new knowledge has been gained from studies related to the extraction of bitumen from the oil sands of northern Alberta. Because the density of bitumen is very close to that of water, a light hydrocarbon solvent has to be added to bitumen in order to lower the density and viscosity of the oil phase, thus facilitating dewatering operations. Studies on the impacts of the solvent-to-bitumen ratio and solvent composition have provided important insights into W/O emulsion stabilization mechanisms. The most important finding is that there is a critical solvent-to-bitumen ratio, or critical dilution, at which the properties of the system drastically change [2,3]. Critical dilution, which coincides with the onset of asphaltene precipitation, depends on the solvent composition. Below critical dilution, the oil/water interface is flexible and very stable W/O emulsions are readily formed. Above critical dilution, the oil/water interface is rigid and W/O emulsion droplets flocculate. This finding led to a new commercial froth treatment technology.

The properties of the thin oil films that separate adjacent water droplets play a key role in the stability of the emulsion as a whole. Microinterferometric thin liquid film techniques have been widely used for studies of foams, O/W emulsions, and, recently, petroleum W/O emulsions [4].

Figure 1 shows thinning of a film made from a 5% solution of bitumen in ‘heptol 80:20’ (a mixture of heptane and toluene at 80:20 by volume), centrifuged at 20,000g, allowed to age overnight, and centrifuged again. Emulsion films prepared from this solution were very stable and homogeneous. All such films prepared above critical dilution behaved the same way.

Film drainage initially follows the prediction of the Reynolds law (dotted line in Fig. 1) until the film is about 65 nm thick, at which point drainage stops. The film is much thicker than that for 50% bitumen in heptol 80:20 (below critical dilution). This finding is counterintuitive — reducing the bitumen concentration and rejecting a significant amount of asphaltenes (a potential stabilizer) increases the film thickness. Although this result would be unexpected based on thin-film theory in the literature, it agrees well with studies of water/diluted bitumen interfaces and supports the notion that only a small subfraction of the total asphaltenes is responsible for emulsion stabilization [3]. The formation of asphaltene nano-aggregates and their further assembly into larger moieties continues over time [5]. The build-up of a network on a length scale comparable to the film thickness may result in non-Newtonian behaviour of the liquid forming the film. Our estimations show that the Bingham yield stress of such a liquid may be too small to be measured by conventional rheological instruments but large enough to prevent drainage of the thin oil film separating water droplets, thus effectively stabilizing the emulsion.

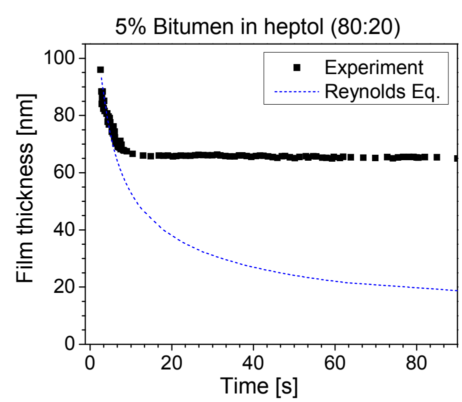

Fig. 1. Film thinning for 5% bitumen in heptol 80:20 (above critical dilution)

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