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Asphaltene-stabilized emulsions: an interfacial rheology study

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ABSTRACT

In the current study, we consider the rheological properties of an asphaltene-stabilized water-oil planar interface. Using rheological techniques we are able to measure time-dependent changes of the interfacial film mechanical properties. To elucidate the critical role of interfacial rheology we have directly compared rheology measurements to single droplet-droplet coalescence times measured using our in-house built Integrated Thin Film Drainage Apparatus (ITFDA). In all interfacial aging experiments, step-change behaviour in the droplet coalescence time is measured with the coalescence time increasing from a few seconds to no coalescence. Correlating the rheology and droplet coalescence data we identify that the condition for no coalescence corresponds to a shear rheological property $G' > G''$.

We extend the study to consider the disruption of asphaltene-stabilized films following the introduction of an emulsion breaker, ethyl-cellulose (EC). At low demulsifier concentration (0.2 ppm), the asphaltene-stabilized emulsion is very stable with less than 20% water drop out. The prolonged stability corresponds well to the interconnected network of asphaltenes as visualized by Brewster Angle Microscopy and the strongly elastic film. In contrast, at a slightly higher demulsifier concentration (1 ppm), the emulsion is considerably less stable (~50% water drop out), forming an island-like film of asphaltenes which exhibits viscous dominant properties and no measurable elastic contribution, $G' = 0$ mN/m.

KEYWORDS Asphaltenes, droplet stability, interfacial rheology, ethylcellulose, demulsification

INTRODUCTION

The formation of stable water-in-oil emulsions is often an undesirable consequence of crude oil extraction. The transport of two immiscible fluids and their mixing in high shear zones can form tight emulsions that are difficult to separate. Micron-sized droplets can often be carried over in the oil phase creating concern for downstream operations due to the high chloride content which resides in the water. Poor separation of micron-sized droplets results from the inability to coalesce and increase the droplet size in the separator. The mechanism of droplet stabilization remains an area of significant scientific interest with particular focus on the various sub-fractions

of crude oil, in particular; asphaltenes, surfactants and fine particles.² The current study focuses on the interfacial activity and film formation of asphaltenes.

Asphaltenes are the heavy components of crude oil which are defined by a solubility class, soluble in aromatic solvents (toluene, benzene) and insoluble in n-alkanes (pentane, heptane). Many studies have shown that the aromatic core is aligned parallel to the water-oil interface and asphaltenes can aggregate to form large clusters through a range of mechanisms including aromatic π - π stacking and hydrogen bonding.² Their interfacial activity and ability to form a film at the water-oil interface has been confirmed as a mechanism which prevents droplets coalescing. However, the mechanical properties of those films have received little attention and it is those properties that will enable better understanding of the stabilization mechanism and hence, the ability to efficiently and reliably promote droplet coalescence and rapid dewatering.

The study provides a unique insight into the critical mechanical properties of asphaltene-stabilized films which govern the stability of petroleum emulsions.

Materials and Methods

Asphaltenes are extracted from Athabasca bitumen following the standard protocol.¹ Asphaltene dispersions were prepared in two solvents (toluene and heptol 1:1 by volume) to determine the effect of solvent aromaticity on interfacial activity and the rheological properties of the adsorbed film. A novel demulsifier, ethylcellulose (EC 300, Mw = 182 kDa), was purchased from Sigma Aldrich and used as received without further purification.

Interfacial shear rheometer: AR-G2 controlled stress rheometer with double wall ring geometry (DWR) was used to measure the time-dependent viscoelasticity of the asphaltene film. The measurement was conducted in the linear viscoelastic region at constant frequency (0.5 Hz) and constant strain (0.8%). To load the sample, 19.2 mL of Milli-Q water was first pipetted into the Delrin® trough before the square-cut geometry was positioned at the air-water interface. Finally, the asphaltene dispersion (15 mL) was gently pipetted onto the water and the measurement trough sealed to minimize solvent evaporation.

Integrated thin film drainage apparatus (ITFDA): a droplet coalescence device has been built in-house to measure the ‘real’ coalescence time by measuring the force of interaction between two contacting droplets.^{1, 3} Both measurement techniques (rheology and ITFDA) provide equivalent oil phase volume to interfacial area ratio and hence allow the direct comparison of interfacial film rheology and droplet stability. Figure 1 below shows a trace of the interaction force as two droplets interact and eventually coalesce.

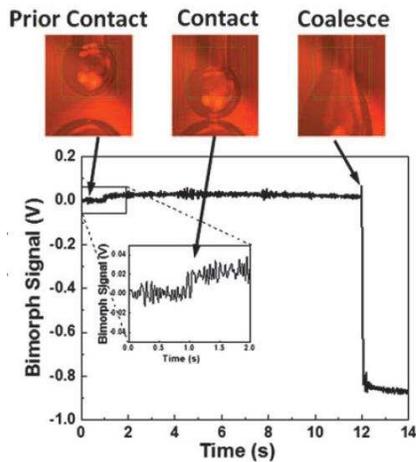


Figure 1 Bi-morph trace for two interacting droplets. Prior to contact the bimorph = 0 V. Upon contact and slight displacement (effective droplet overlap) the bimorph voltage increases and remains steady until droplet coalescence and a catastrophic reduction in the bimorph voltage. The time between first contact (+ve voltage) and voltage reduction is identified as the 'real' droplet coalescence time.¹

Droplet stability and interfacial rheology: Figure 2 compares the interfacial rheology of an asphaltene film formed at the planar water-oil interface to the droplet coalescence time. Initially, the films are viscous dominant with $G'' > G'$ ($t = 0$ hrs, $G' = 0$ mN/m). Continual accumulation of the asphaltene molecules at the water-oil interface leads to the onset of an elastic contribution, $G' > 0$ mN/m. Dependent on the solvent condition, initial bulk asphaltene concentration and interfacial aging time, the mechanical property of the film may become elastically dominant ($G' > G''$). Comparing the time-dependent change in the film viscoelasticity, it becomes apparent that there is minimal resistance to droplet coalescence when $G'' \gg G'$ and the droplets remain stable when $G' > G''$. Further investigation of the elastically dominate films by strain sweep measurements confirmed the presence of a substantial shear yield stress in the order of 10^4 N/m² that prevents mobility and rupture of the interfacial film.

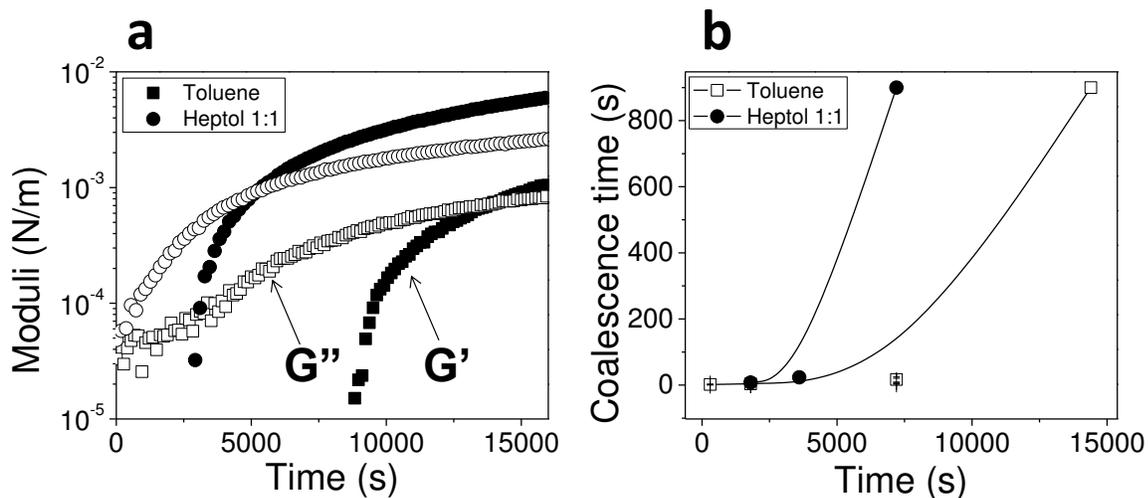
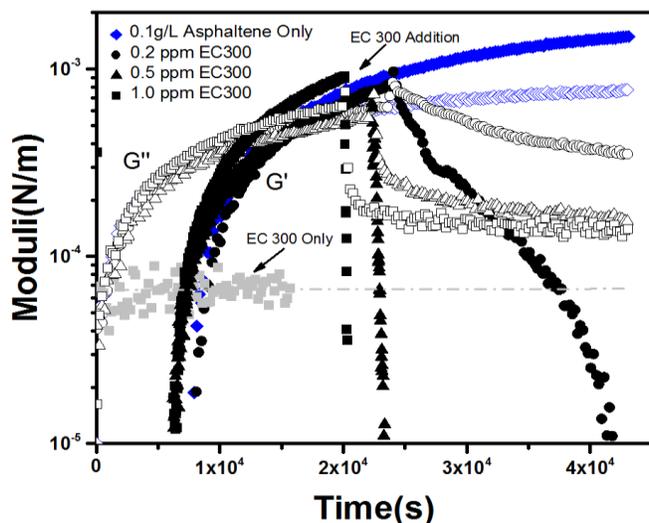


Figure 2 a) Time-dependent viscoelastic properties of an asphaltene-stabilized film under different solvent conditions. b) Droplet coalescence times as a function of droplet aging and solvent aromaticity. Asphaltene concentration = 0.4 g/L.¹

Demulsification: To overcome the high yield stress it is essential to disrupt the asphaltene-stabilized film using larger (space spanning), more interfacially active molecules. Figure 3 shows the characteristic rheological aging profile up to the condition $G' > G''$. Different concentrations of demulsifier are then added to the oil phase and the rheological properties measured with time. Clearly the demulsifier molecules are able to partition in the film and most importantly diminish



the elasticity of the film. The increase in the rate of droplet coalescence, corresponding with a reduction in the film elasticity is confirmed using the ITFDA, where in the absence of EC the droplets remained stable (> 200 s) but rapidly coalesced (0.14 s) in the presence of 1 ppm EC.

FIGURE 3 Time-dependent breakdown of a rigid interfacial film ($G' > G''$) after the addition of EC 300 (0.2, 0.5 and 1.0 ppm).

CONCLUSIONS

- Asphaltenes adsorb at the oil-water interface to form an interfacial film that is resistant to shear;
- Shear yield stress must be overcome to mobilize the interfacial film;
- Novel demulsifier EC is capable of displacing asphaltenes at the oil-water interface;
- Shear elasticity is diminished and the interfacial films become mobile upon EC addition, promoting coalescence.

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