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Demulsification mechanism of asphaltene-stabilized water-in-oil emulsions by a polymeric EO-PO demulsifier

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Abstract

The demulsification mechanism of asphaltene stabilized water-in-toluene emulsions by an ethylene-oxide/propylene oxide (EO/PO) based polymeric demulsifier was studied. Demulsification efficiency was determined by bottle tests and correlated to the physicochemical properties of asphaltene interfacial films after demulsifier addition. From bottle tests and droplet coalescence experiments, the demulsifier showed an optimal performance at 2.3 ppm (mass basis) in toluene. At high concentrations, the demulsification performance deteriorated due to the intrinsic stabilizing capacity of the demulsifier, which was attributed to steric repulsion between water droplets. Addition of demulsifier was shown to soften the asphaltene film under (i.e. reduce the viscoelastic moduli of asphaltene films) both shear and compressional interfacial deformations. Study of the micro and macro structure, and the chemical composition of asphaltene film at the toluene-water interface after demulsifier addition demonstrated gradual penetration of the demulsifier into the asphaltene film. Demulsifier penetration in the asphaltene film changed the asphaltene interfacial mobility and morphology, as probed with Brewster Angle and Atomic Force Microscopy.

Keywords: petroleum emulsions, demulsification, ethylene oxide-propylene oxide demulsifier, asphaltenes, interfacial film rheology.

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1.   Introduction

The formation of stable water-in-oil (W/O) emulsions during bitumen extraction poses operational problems, such as rag layers[1] that create bottlenecks in gravity separation vessels. In addition, the high salt concentration in any retained water in the overflow oil promotes corrosion of downstream process equipment and catalyst poisoning[2]. Bitumen is a mixture of complex natural chemical components of largely unknown molecular structures, among which asphaltenes play a major role in stabilizing W/O emulsions[3]. Research conducted using the thin liquid film balance technique has shown that asphaltenes form aggregates that are capable of flocculating water droplets but hinder their coalescence by retarding the intervening liquid film drainage, producing steric repulsion and forming rigid skins at the oil-water interface[4-6].

Polymeric demulsifiers are commonly used to address emulsion stability issues and separate water from oil. Separation of water from oil can occur by flocculation and/or coalescence of the water droplets, to form larger water droplets that readily separate from the oil. However, to achieve a free water layer under the separation zone, droplet coalescence should be the dominant destabilizing mechanism. While flocculation can promote coalescence by enhancing the contact between water droplets[7], flocculated water droplets can also be stabilized by steric forces that resist thin liquid film drainage[8]. Although flocculants are often used to separate water from oil emulsions, the use of coalescers is preferable as it reduces oil losses to the phase-separated underflow aqueous phase[9].

Coalescers destabilize emulsions by three major mechanisms: 1) they exhibit greater interfacial activity compared with the stabilizing species, and can thus penetrate stabilizing films at the oil-water interface[10, 11]; 2) they disrupt and soften (i.e. lower the viscoelastic moduli) the stabilizing interfacial film[10, 12, 13]; and 3) they suppress interfacial tension gradients which are responsible for emulsion stabilization by the Marangoni effect[14]. When demulsifier molecules penetrate the bitumen or asphaltene stabilized films, the structure and mechanical properties of the film can change. For example, ethyl-cellulose (EC) was shown to modify the interfacial film texture[12] and produce fractures within the film[15]. Those fractures have been identified to provide favorable zones for drop-drop coalescence.

However, drop-drop coalescence in a separation vessel is a dynamic process where droplets undergo shear and compressional deformations[16]. Those deformations and the mobility of

stabilizing species are dependent on the drop-drop contact force and droplet interfacial rheology. As a result, studying shear and compressional rheology of oil-water interfacial films would shed light on the mechanism of emulsion stability and hence demulsification[17-19]. Different studies have shown that demulsifiers soften (i.e. lower the viscoelastic moduli) interfacial films under compression[10, 12]. However little research has considered the shear rheological properties of interfacial stabilizing films[13], and only one study has correlated emulsion stability by surface active biopolymers to high shear and compressional elasticity of the interfacial film[16]. The relationship between the demulsifier performance and interfacial rheology has been recognized[20-22], but never investigated systematically for an important class of EO-PO based polymer demulsifiers at toluene-water interfaces.

Extensive research has been conducted using a variety of chemical demulsifiers, including ethyl-cellulose[10, 23], non-ionic surfactants[24], and EO-PO demulsifiers[25-30] to assess the relationship between the structure, composition, molecular weight, and demulsifier performance. Studies conducted using a broad array of EO-PO demulsifiers showed that at a low dosage, demulsifiers of higher hydrophilicity are more effective than those of lower hydrophilicity[26, 27, 29]. The effect of the demulsifier concentration on demulsification performance has frequently been investigated. It was established that beyond an optimal dosage, the performance of a demulsifier can either plateau (type I behaviour) or degrade (type II behaviour, also known as overdose), resulting in an increase in the emulsion stability. Type I behaviour has been reported for EC[31] and for some EO-PO demulsifiers[27, 32-34], while overdose was observed for octylphenyl-polyethoxylates and sodium bis(2-ethylhexyl)sulfosuccinate demulsifiers[35], commercial demulsifiers[36-38], polyoxyalkylates[9], diethanolamines[15] and some EO-PO demulsifiers[27, 39]. These demulsifiers act either as flocculants or coalescers[41]. Overdose for flocculating demulsifiers, such as polyoxyalkylates[9] and diethanolamines[15], was attributed to the low density of formed flocs[9] as a result of electrosteric repulsion[15]. Studies conducted using a wide array of coalescer type EO-PO polymer demulsifiers demonstrated a correlation between the hydrophilicity of EO-PO demulsifiers and their demulsification efficiency, with hydrophilic demulsifiers showing overdose effects at high concentrations[27]. Such studies generated critical information on the effect of the demulsifier composition and structure on its performance. However, the mechanisms of overdose by coalescer type demulsifiers remains to be explored.

Studies relating emulsion stability to the mechanical properties and morphology of asphaltene interfacial films are very limited and have only been conducted at the air-water interface[40, 41]. Although not directly related to emulsion films, studies on air-water interfaces laid the foundation in the context of new approaches to investigate stabilization mechanisms. The current study represents the first of its kind to relate the dewatering efficiency and the overdose of an EO-PO demulsifier to the interfacial shear and the compressional rheological properties of the films, and to their morphological structure studied by Brewster Angle Microscopy (BAM). Macroscopic observations were supplemented by molecular level morphologies of interfacial films transferred on silicon wafers by Langmuir-Blodgett method and determined by Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM). Finally, X-ray Photoelectron Spectroscopy (XPS) was used to study the change in chemical composition of asphaltene films upon the addition of the demulsifier.

2.   Materials and methods

2.1.   EO-PO demulsifier

An EO-PO block-copolymer demulsifier was provided by Baker Hughes and used throughout this study. The demulsifier had a star-like structure of five arms, a molecular weight of ~12,000 g/mol and an EO content of 35% (number of EO% per mole). The EO groups in the structure conferred hydrophilic properties and the PO groups added hydrophobic properties to the demulsifier molecule. The amphiphilicity of the demulsifier enabled preferential sorption at the oil-water interface, exceeding the interfacial activity of the stabilizing species (Figure 1). The relative solubility number (RSN) of the demulsifier was determined to be 18 following a standard protocol[42].

2.2.   Solvents and water

HPLC grade toluene and pentane (Fisher Scientific, Canada) were used as received. The water used throughout this study was purified with a Millipore system and had a resistivity of 18.2 mΩ/m (Milli-Q water).

2.3.   Asphaltenes precipitation

C5 asphaltenes were extracted from coker feed bitumen (Syncrude, Canada) using a standard protocol of excess pentane[43]. Briefly, bitumen was dissolved in HPLC grade pentane at a 1:40

bitumen to pentane volume ratio (one part bitumen and 40 parts pentane) for 24 hrs. The mixture was then filtered and washed with excess pentane until the eluent was clear. The precipitated asphaltenes were then dissolved in toluene and the toluene-insoluble solids that originate from the bitumen were removed by 30 min centrifugation at 20,000 RCF (Relative Centrifugal Force). The asphaltenes were obtained after the evaporation of toluene and storage in a desiccator. The same asphaltene batch was utilized in all the tests reported here.

2.4.   Interfacial tension

Interfacial tension measurements were conducted to assess the activity of individual components and the potential for the demulsifier to penetrate an interfacial preformed asphaltene film. Two types of interfacial tension were measured, namely the static and the dynamic interfacial tension. The equilibrium toluene-water interfacial tension was measured using the Du Noüy ring technique (Kruss, K12, Germany). The measurement was repeated periodically until the interfacial tension change remained below 0.1 mN/m during a 30 min measurement period. The interfacial tension of water and asphaltenes in a toluene solution was measured for an asphaltene concentration range from 10^{-3} g/L to 10^2 g/L (equivalent to ⁓1 ppm to ⁓10^5 ppm in toluene), while the demulsifier concentration in the toluene phase ranged between 0.06 ppm to 288.4 ppm.

To elucidate the adsorption kinetics of asphaltenes and demulsifier at the toluene-water interface and to probe their ability to compete for such interface, the dynamic toluene-water interfacial tension was measured for asphaltenes (0.25 g/L, 332 ppm) and demulsifier (0.3 ppm and 1.2 ppm) and then for a mixed system (equivalent concentrations) using the pendant drop technique (Theta Optical Tensiometer, Attension, Finland). For the mixed system, asphaltenes were first adsorbed to the interface for 30 min, after which the demulsifier was injected in the toluene phase while continuously measuring the interfacial tension. All the interfacial tension measurements were conducted at room temperature (23°C) and atmospheric pressure.

2.5.   X-ray Photoelectron Spectroscopy

Chemical composition of the interfacial films was characterized using X-ray Photoelectron Spectroscopy (XPS). Films of asphaltenes (produced by spreading 100 □L of 1g/L asphaltene in toluene solution, cf. section 2.9), pure demulsifier, and mixed systems (with demulsifier added at 2.3 ppm and 11.5 ppm, based on the mass of toluene phase) were transferred onto gold substrates using the method described in section 2.11. The XPS measurements were performed on a Kratos

Ultra instrument at the Alberta Centre for Surface Engineering and Science (ACSES), University of Alberta. The base pressure in the sample analytical chamber was maintained lower than 1 x 10^{-8} torr. A monochromatized Al Kα x-ray source (hν=1486.6 ev) was used. The spectral resolution of the instrument was 0.55 eV for Ag_{3d} and 0.70 eV for Au_{4f} peaks. The spot size of analysis was set to 300 x 700 μm. Survey scans spanned a binding energy range from 1100 to 0 eV. The spectra were collected with an analyzer pass energy of 160 eV and a step of 0.4 eV. For high resolution spectra, the pass energy was set at 20 eV and the step at 0.1 eV, with dwell time of 200 ms. The number of scans for high resolution spectra was determined according to the spectrum intensities of the elements to be analyzed. An electron flood neutralizer was used to compensate sample charging. Instrument software Vision2 was used to calculate the composition with relative sensitivity factor (RSF) of Scofield and Shirley background from the high-resolution spectra.

2.6.   Bottle tests

Bottle tests were conducted to assess the potential of the demulsifier to destabilize asphaltene-stabilized emulsions. Asphaltenes were dissolved in toluene at 0.25 g/L (~332.6 ppm), assisted by sonication to ensure complete dissolution. W/O emulsions were prepared with 60 vol.% asphaltene in toluene solution and 40 vol.% water, homogenized for 5 min at 30,000 rpm using a Powergen 100 homogenizer (Fisher Scientific). The average drop size of the resultant emulsion was 22 □m, as determined by optical microscopy images (Axiovert 200, Zeiss). The prepared emulsions were transferred to settling tubes. The radius of the settling tube was 0.5 cm and the total volume of the emulsion was 20 mL, resulting in an initial emulsion depth of ~13 cm. Demulsifier was added drop-wise to the desired concentration between 0.1 and 288.4 ppm (based on the mass of the toluene phase) and the emulsion was hand-shaken for 1 min to aid dispersion of the demulsifier throughout the emulsion. The settling tubes were then positioned vertically and the height of the continuous water phase resolved was measured periodically during 90 min, assessing the ability of the demulsifier to promote water droplet coalescence. A control test conducted in the absence of demulsifier addition confirmed that the emulsion was stabilized by 0.25 g/L asphaltene (equivalent to 332.6 ppm) in toluene solution. Bottle tests were also conducted with demulsifier only in the toluene phase with the same mixing time and water content used in the control tests conducted with asphaltenes only, to determine if the demulsifier had intrinsic stabilizing properties.

2.7. Micropipette experiments

Micropipette experiments were conducted to investigate the effect of demulsifier addition on the coalescence of asphaltene-stabilized water droplets. Three systems were analyzed: 1) asphaltene-stabilized emulsions without demulsifier addition; 2) asphaltene-stabilized emulsions with 2.3 ppm demulsifier addition (optimal dosage determined by bottle tests); and 3) asphaltene-stabilized emulsions with 28.8 ppm demulsifier addition (concentration at which overdose was observed). Emulsions were prepared using procedures identical to those described previously for bottle test experiments (cf. Paragraph 2.6). The prepared emulsions were transferred into the glass sample cell of the micropipette apparatus. The cell was mounted onto an optical microscope (Axiovert 200, Zeiss). Using a micropipette mounted on a three dimensional micro manipulator, an emulsified water droplet was picked up and held at the tip of the micropipette by a low suction pressure applied to the micropipette. Another emulsified water droplet was picked up in a similar manner by a second micropipette in an axial alignment with the first micropipette, manipulated to enable a direct "head-on" contact between the two water droplets of approximately the same size. The applied force was maintained for 1 min. The probability of coalescence is defined as the ratio of the number of contacts in which coalescence was observed to the total number of contacts (30 for each system considered) measured. Further details regarding the micropipette technique can be found elsewhere[44, 45].

2.8. Shear rheology: Double Wall Ring geometry

An AR-G2 controlled stress rheometer (TA Instruments, USA) with a Double Wall Ring (DWR) geometry was used to measure the shear viscoelastic properties (G': elastic and G": viscous) of an asphaltene-stabilized interfacial film. The formation and subsequent breakdown of the interfacial film by demulsifier addition were monitored. The viscoelasticity of the interfacial film was determined from the harmonic oscillation in both stress and strain while keeping the interfacial area constant. Applying a sinusoidal strain deformation (γ) of fixed amplitude to the interfacial film produced a sinusoidal shear stress (σ) response separated by a phase angle, δ. The strain deformation applied and the stress responses are given by:

$$\gamma(t) = \gamma_0 \sin(\omega t) \tag{1}$$

$$\sigma(t) = \sigma_0 \sin(\omega t + \delta) \tag{2}$$

where ω is the angular frequency, while σ_0 and γ_0 are the maximum stress and strain, respectively. From the theory of the complex shear modulus, $|G*| = \dfrac{\sigma_0}{\gamma_0}$, the elastic (G') and viscous (G") components of the interfacial film are given by Equations 1 and 2. To ensure that the technique measures the integral structural properties of the film, it is essential to conduct the measurement below a critical strain (γ_{CR}). This condition is defined as the linear viscoelastic region where the shear moduli, G' and G'', are independent of the applied strain.

For the current study the angular frequency and strain were fixed at 0.5 Hz and 0.8%, respectively. All experiments were conducted at a temperature of 23°C, kept constant using a Peltier plate. Time sweep measurements over several hours allowed tracking the development in the viscoelastic properties of an interfacial asphaltene film. At the critical condition G' $\approx$ G", a 1000 ppm demulsifier stock solution was added drop-wise to obtain a final demulsifier concentration of 2.3 ppm and 34.6 ppm in toluene. The shear rheological response of the film was continually measured at 30 s intervals, until steady-state conditions were attained. Further details regarding this technique can be found elsewhere[46].

2.9.   Langmuir trough: pressure-area isotherms

The compressional behavior of interfacial films at the toluene-water interface was characterized by interfacial pressure−area (π-A) isotherm measurements using a Langmuir trough. To study competitive adsorption of asphaltenes and demulsifier, π-A isotherms were collected for: i) asphaltenes in toluene alone; ii) demulsifier in toluene alone; and iii) mixed system of asphaltene and demulsifier in toluene. The Langmuir trough experiments were conducted using a computer controlled KSV trough (Biolin Scientific, Finland) with a trough area of 170 cm^2. The interfacial pressure was measured using a paper Wilhelmy plate sensor (Biolin Scientific, product id. KN 0005). In the presence of interfacial material, the interfacial pressure (π) represents the change in interfacial tension (IFT) relative to the clean interface (IFT$_0$), and is given by:

$$\pi = ITF_0 - ITF \tag{3}$$

Prior to each measurement the trough was carefully cleaned with toluene, acetone, and Milli-Q® water. The lower part of the trough was filled with 120 mL of Milli-Q® water as the sub-phase. The trough was considered clean when the pressure sensor reading was < 0.1 mN/m with the

water phase being compressed to an area of 12.5 cm^2. The balance was zeroed at the clean air-water interface prior to forming films at the toluene-water interface. This procedure allowed for obtaining information regarding the interfacial tension in the presence of asphaltenes and demulsifier. After setting the interfacial pressure to zero, 100 μL of 1g/L asphaltene in toluene solution was evenly spread at the air-water interface using a Hamilton gastight syringe, while the trough area was wide-open. After asphaltene addition the solvent was evaporated completely over 20 min to allow for the formation of a uniform asphaltene film at the air-water interface. Finally, 100 mL of toluene was added as the top-phase. After equilibrating the film for 30 min compression was initiated.

To elucidate the effect of the demulsifier on the physical properties of asphaltene interfacial films, a diffusion protocol was used by introducing the demulsifier to the toluene top-phase. After topping the interfacial asphaltene film with 100 mL of toluene, the demulsifier was added in the toluene top-phase at the desired concentration (0.2 – 288.4 ppm of the toluene top- phase). 30 min demulsifier diffusion was allowed before compression. This diffusion time was selected to reflect the typical residence time of demulsification in real oil field applications. As a control test, the demulsifier solution was added to the toluene top-phase in the absence of asphaltene interfacial films.

In order to evaluate if the interfacially active species in the system (demulsifier and asphaltenes) were reversibly or irreversibly adsorbed to the interface, wash-off experiments were conducted. In wash-off experiments, asphaltene and demulsifier films were produced and compressed as described above. After the films were compressed to an area of 12.5 cm^2, the toluene top-phase was exchanged with fresh toluene while keeping the barriers closed. The barriers were subsequently expanded at a speed of 5 mm/min, and the films equilibrated for 30 min (first wash-off). Following this equilibration time, the films were compressed again and the wash-off process was repeated (second wash-off).

A reference isotherm was collected at a clean toluene-water interface. The pressure measured at a clean toluene-water interface was equal to 11 mN/m, with minimal changes (less than 0.7 mN/m) upon compressing the area from 170 cm^2 to 12.5 cm^2. All experiments were conducted at room temperature, and the interfacial films were compressed at 10 mm/min for each barrier, following a previously published protocol[10].

2.10. Brewster Angle Microscopy

Brewster Angle Microscopy (BAM) was used to image the morphology of an interfacial film in situ, without the need to transfer the film to a solid substrate. An advantage with this technique is that the morphological changes of asphaltene films after demulsifier addition could be imaged without disturbing the films to determine the film-breaking mechanism in real time. In this technique the interfacial film is illuminated by a laser at the Brewster angle (θ_B). At this angle s-polarized light (i.e. the light perpendicular to the incident plane) can be reflected to the detector solely from the interface, not by the bulk phases below or above it. As a result, the images collected reflect the characteristic features of the interface. The BAM (Model EP3, Accurion GmbH, Germany) used in this study was equipped with light guides and a CCD camera to image films at the toluene-water interface at a magnification of 5X. Images were collected using EP3View2.x software (Accurion GmbH, Germany). The trough used for these experiments had a fixed area of 28 cm^2, at which all images were captured.

To form an asphaltene interfacial film at the oil-water interface, 30 mL of the aqueous phase was first added to the trough, followed by spreading 50 □L of 1 mg/mL asphaltene in toluene solution at the air-water interface. After 20 min evaporation, 100 mL toluene top-phase was added gently along the sidewall of the trough to prevent any disturbances of the interface. Asphaltene interfacial films were first equilibrated for 45 min and imaged at an angle of incidence (AOI) of 42°, while the polarizer and analyzer were set to 10°. With the drop-wise addition of demulsifier at 0.2 to 288.4 ppm (based on the mass of toluene phase), the mechanism by which the asphaltene film was modified and the time frame in which such changes occurred were analysed by collecting interfacial images at desired time intervals. In order to elucidate a possible dependence between demulsifier concentration and film structure, images were also taken for pure demulsifier films. Demulsifier films were produced with the drop-wise addition of demulsifier-in-toluene solutions and imaged using the same setup conditions as previously described.

2.11. Langmuir-Blodgett film deposition

Langmuir-Blodgett (LB) films were transferred from the oil-water interface onto either silicon (for AFM measurements) or gold wafers (for XPS measurements). The wafers were first cleaned in a 1:1 toluene and acetone mixture by sonication for 30 min and subsequently soaked in 1 N

HCl solution for a further 15 min to remove any surface contaminants. Asphaltene, demulsifier and mixed films were prepared following the procedure outlined in section 2.9. Films were transferred onto the silicon or gold substrates by first compressing the interfacial area to 40 cm^2 at a speed of 10 mm/min per barrier, followed by pulling the wafer upwards at a speed of 5 mm/min, while maintaining a constant interfacial pressure through a computer controlled feedback system. The transfer ratio, which is defined as the ratio between the decrease in the area of the interfacial layer to the area of the film transferred over the substrate, was close to unity in all cases.

2.12. Atomic Force Microscopy Imaging

Atomic Force Microscopy (AFM) images of LB films deposited on silicon wafers were obtained using an Agilent 5500 AFM (Agilent Technologies, Inc., USA) operating in AC mode in air. The substrates were fixed using double-sided tape on a sample platform, which was magnetically held in place on the AFM sample stage. Silicon cantilevers (ACT-200, Applied NanoStructures Inc., USA) with a nominal resonance frequency of 200-450 kHz and nominal spring constants of 25-75 N/m were used for imaging at a scan rate of 1 Hz. AFM imaging was carried out at room temperature (~20°C). The vendor-supplied SPM software was used to control the probe and scan the sample. The roughness (Sq) was calculated from AFM images using Picoimage basic v.5.1 software (Agilent Technologies, Inc.) using the following equation:

$$Sq = \sqrt{\frac{1}{N}(Z - \bar{Z})^2} \qquad\qquad (4)$$

where N is the number of points analyzed, Z is the height of each point and $\bar{Z}$ is the average height of the N points analyzed.

2.13. Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) micrographs of LB films were obtained using a Hitachi S-2700 SEM equipped with a Princeton gamma tech IMX digital imaging system. The accelerating voltage used was 10 KV.

3.   Results and Discussion

3.1. Interfacial tension. The equilibrium interfacial tension of a clean toluene-water interface was measured using the Du Nüoy ring technique to be 36.2 mN/m. The equilibrium toluene-water interfacial tension in the presence of asphaltenes and/or demulsifier is given in Figure 1a. The data reveal that at equivalent concentrations in toluene, the demulsifier molecules are more interfacially active than asphaltenes. This result indicates that the demulsifier has the potential to compete with the asphaltenes for the toluene-water interface, disrupting the asphaltene network.

To further probe the ability of the demulsifier to penetrate interfacial asphaltene films, the dynamic interfacial tension was measured before (asphaltene aging) and after demulsifier addition (Figure 1b). After 30 min asphaltene aging, 0.3 ppm demulsifier was added drop-wise to the toluene phase, causing a gradual decrease in the interfacial tension. The slope of the interfacial tension vs. time curve of the mixed system became very close to the slope of the interfacial tension curve measured for the pure demulsifier, indicating similar adsorption kinetics. Such characteristic behavior would confirm that the demulsifier molecules are effectively penetrating the asphaltene film network. The dynamic interfacial tension of the droplet after demulsifier addition was not the same as the interfacial tension value for the pure demulsifier (0.3 ppm) over one and a half hour observation period. This result indicates that both asphaltenes and demulsifier were adsorbed at the toluene-water interface after one and a half hour demulsifier was introduced in the system. Observations were not conducted for longer time periods, and complete penetration of demulsifier after one and a half hour cannot be discounted.

Experiments were also conducted with 1.1 ppm demulsifier in the toluene phase (data not shown). In this case, the reduction in the interfacial tension and hence the penetration kinetics of demulsifier into the asphaltene film were found to be much faster as compared with the case of 0.3 ppm demulsifier. Dynamic interfacial tension measurement with higher demulsifier concentrations could not be conducted, as the low interfacial tension would promote droplet streaming from the needle tip. For this reason, the kinetics of demulsifier penetration into the asphaltene film network at demulsifier dosages greater than 1.1 ppm in toluene were probed using shear rheology.

While interfacial tension is a measure of the molecules ability to lower the interfacial energy of the system, it does not necessarily link directly to demulsification performance, with many

studies showing a lack of agreement between demulsification performance and interfacial tension reduction by demulsifier addition[27, 28, 47].

3.2. XPS. To verify that the demulsifier could penetrate oil-water interfacial asphaltene films, asphaltene films transferred from oil-water interface by Langmuir-Blodgett (LB) method without and with demulsifier addition were analyzed by XPS. For comparison, the interfacial films of demulsifier alone were also analyzed by XPS. The results showed an oxygen to carbon (O/C) atomic ratio of 0.042 for asphaltene films, in agreement with the results from previous studies[48, 49]. In contrast, a much higher O/C atomic ratio of 0.363 was obtained for the demulsifier films due to the presence of the EO and PO groups (Table 1). The O/C atomic ratio for the asphaltene LB interfacial films in the presence of the demulsifier fell between the values of the asphaltenes and demulsifier (Table 1), indicating penetration of the demulsifier into the asphaltene films. Since the measured O/C atomic ratio of the asphaltene film in the presence of the demulsifier is much lower than the value of the demulsifier film, it is reasonable to conclude that at the demulsifier concentrations tested, the demulsifiers could only partially displace the asphaltenes from the interface. Dynamic interfacial tension data, obtained by adding demulsifier at concentrations of 0.3 ppm and 1.1 ppm in toluene, also indicated that in the mixed systems of asphaltenes and demulsifier, both asphaltenes and demulsifier were adsorbed at the interface. At demulsifier dosages higher than 1.1 ppm in toluene, dynamic interfacial tension measurements could not be conducted because of very low interfacial tension that caused the droplet to stream out from the needle. At such dosages the hypothesis of partial displacement is supported by comparing the Langmuir isotherms and the AFM images of films formed by pure demulsifier with that obtained by demulsifier diffusion into asphaltenes formed at toluene-water interface. Significant differences in both isotherms and images were observed, suggesting adsorption of both demulsifier and asphaltenes at the toluene-water interface, as will be further discussed in sections 3.5 and 3.6.

3.3. Bottle tests and micro-pipette experiments. While the interfacial tension and XPS results have confirmed the sorption of the demulsifier molecules at the asphaltene stabilized oil-water interface, such sorption does not necessarily translate to demulsifier performance. Bottle tests were conducted to assess the demulsification performance. Without demulsifier addition, emulsions remained stable for more than 1 day (data not shown). The results obtained with demulsifier addition are shown in Figure 2. The performance of the demulsifier reached its

optimum at 2.3 ppm concentration in the toluene phase, with ˜80% of the free water resolved after 15 min gravity separation. At 11.5 ppm demulsifier addition in toluene, the volume of free water resolved reached ˜80% after approximately 80 min gravity separation. Furthermore, with 28.8 ppm demulsifier addition, only 30% free water was resolved even after 90 min gravity separation. Upon addition of demulsifier at 57.7 ppm or higher in the toluene phase, the emulsions were observed to be extremely stable with no free water resolved after 90 min separation (Fig. 2a) and even after 24 hr gravity separation (data not shown). These results demonstrate that the demulsifier is only effective at low dosages.

To determine if the demulsifier alone can stabilize the W/O emulsion, bottle tests were conducted with pure demulsifier. The results in Figure 2b show that emulsions were unstable when demulsifier was added at the optimal dosage of 2.3 ppm in toluene. At higher concentrations ($\geq$ 11.5 ppm) however, the demulsifier displayed increasing stabilizing potential up to 230.7 ppm, at which the emulsion remained stable (no free water) over the 90 min test. The data confirms that the reduction in dewatering performance at higher demulsifier concentration (chemical overdose) results from the inherent stabilizing capacity of the demulsifier molecule.

To further study the role of demulsifier concentration on destabilizing and stabilizing droplets, the probability of coalescence of asphaltene-stabilized emulsion water droplets was determined by micropipette technique without and with demulsifier addition in toluene. Typical images of coalescing and non-coalescing water droplets in the micropipette experiments are shown in Figure 2. The results showed a significant increase in the probability of coalescence from 0.09 to 0.85 upon addition of 2.3 ppm demulsifier in toluene, and then a significant decrease from 0.85 to 0.25 with a further increase in demulsifier addition from 2.3 ppm to 28.8 ppm. These results clearly illustrate the detrimental effect of demulsifier overdose. The micropipette results are in excellent agreement with the bottle test data shown in Figure 2, in which sample images of coalescing and non-coalescing droplets are also shown.

3.4. Shear rheology. With interfacial rheology known to affect the stability of emulsion droplets[17, 18], the shear rheological properties of asphaltene films at the water-oil interface before and after demulsifier addition were measured using the DWR geometry. The viscoelastic properties of the interface were measured as a function of aging time as the asphaltenes diffused towards and adsorbed at the water-toluene interface. With gradual accumulation of asphaltenes to the toluene-water interface, the interface transitioned from a viscous to an elastic dominant

microstructure. With particular focus on the effect of demulsifier addition, the first 6000 s of interfacial aging are not shown. Readers are referred to the following papers for the characteristic aging of an asphaltene film as measured by shear.[13] [46]

Once the condition G' = G'' was met the demulsifier was added at 2.3 ppm (optimum dosage from the bottle tests) and 34.6 ppm (overdose). When the elastic contribution is substantial, asphaltenes are intimately linked and form a cohesive interfacial network. To assess demulsifier performance in penetrating and breaking the cohesive network of asphaltenes, the shear viscoelastic moduli were measured continuously.

Upon addition of 2.3 ppm demulsifier in toluene, both viscous and elastic shear moduli of the interfacial film decreased as shown in Fig. 3 (a). The elastic modulus decreased to an unmeasurable value within 10 min and the viscous modulus decreased to a value equivalent to that of "clean" toluene-water interface after approximately 30 min. At higher demulsifier concentration (34.6 ppm) a similar response for the viscoelastic moduli was measured albeit the kinetics of film disruption was accelerated as shown in Fig. 3 (b). Interestingly, from shear rheology one would be inclined to believe that a higher concentration of demulsifier would support improved dewatering, with faster film disruption kinetics. However, the bottle test and micropipette data presented within this work would not support such a statement. The end condition of both systems studied were equivalent, with G' = 0 N/m and G'' = 4.5 x 10^{-5} N/m. With the G'' contribution equivalent to that of a "clean" water-toluene interface, the response would suggest that the asphaltene interconnected network has been sufficiently disrupted (G' = 0 N/m) and the remaining interfacial species offer no resistance to shear. To confirm the interfacial shear rheology of the demulsifier molecule, a study was conducted in the absence of asphaltenes. Adding 57.6 ppm demulsifier to a toluene top-phase, the G'' and G' (= 0 N/m) remain unchanged (cf. Figure 3). While the technique is useful to study the breakdown kinetics of an asphaltene-stabilized interface, the technique alone is limited when trying to understand the mechanism for overdose.

3.5. Pressure-area isotherms. While interfacial shear rheology can provide information on the kinetics of asphaltene-stabilized film disruption, the technique appears limited when predicting overall demulsification performance. A second deformation of the interface that can contribute to droplet stability is the compressional response of the interfacial film.[18] Specifically, low

interfacial film rigidity under compression is reported to favor droplet coalescence[50, 51]. Interfacial pressure-area (π-A) isotherms were measured to probe the effect of demulsifier addition on the behaviour of asphaltene-stabilized interfacial films. For comparison, demulsifier π-A isotherms in the absence of asphaltenes were also measured. The π-A isotherms of asphaltenes, demulsifier and their mixture at the toluene-water interface are given in Figure 4a.

The results in Figure 4a show that at the maximum trough area of 170 cm^2, demulsifier addition to the system caused a significant increase in the interfacial pressure, corresponding to a decrease in the interfacial tension (cf. Eq. 3), as previously shown in Figure 1a. At low demulsifier concentration (0.2 ppm) the interfacial tension of the mixed system was intermediate between the interfacial tension of the two interfacially active species (asphaltenes and demulsifier), once again confirming partial substitution of the asphaltene film. At higher demulsifier concentrations the interfacial tension measured for the mixed system was close to that measured for pure demulsifier. These results once again indicate penetration and potentially more complete displacement of the asphaltenes film. Similar results were obtained in studies conducted with ethyl-cellulose[31].

The results of wash-off experiments are shown in Figure 4b. Wash-off experiments conducted with pure demulsifier showed that the interfacial pressure, as measured with the barriers fully expanded, decreased when the toluene top-phase was exchanged with fresh toluene following the first compression (first wash-off). The interfacial pressure is related to the interfacial tension (cf. Eq. 3), and the measured decrease in the pressure after wash-off corresponds to an increase in the interfacial tension. Such an increase indicates that the molecules at the interface can desorb [52-54]: the data thus shows that the demulsifier could partially desorb from the toluene-water interface after compression. When the toluene top-phase was exchanged a second time (second wash-off) the interfacial pressure changes were negligible, suggesting that part of the demulsifier molecules were irreversibly adsorbed at the toluene-water interface. Dissimilar to demulsifier, asphaltenes could not be washed off the interface (data not shown), consistent with previous studies[55]. Wash-off data at the toluene-water interface explain the characteristic features of the isotherms, as will be discussed below.

The increase in pressure upon compression was small for pure demulsifier films, at all demulsifier concentrations. The rationale for the limited increase in the pressure upon film

compression can be two-fold: 1) The film formed by the molecules present at the oil-water interface is soft (i.e. the compressional viscoelastic moduli are low); 2) The molecules are reversibly adsorbed at the oil-water interface, and desorb when the interfacial film is compressed. Wash-off experiments suggest that both mechanisms were relevant, and that while some demulsifier molecules desorbed from the interface, others remained adsorbed onto it upon film compression, exhibiting soft film behaviour. It is noted that in Langmuir trough experiments the compressional viscoelastic moduli were not measured. However, the compressional viscoelastic moduli are qualitatively related to the slope of the Langmuir trough isotherms, since the compressional viscoelastic moduli are proportional to the ratio between the change in pressure versus the change in the area to which the interfacial films are compressed ($\Delta\pi/\Delta A$)[56]. When this ratio is high, the compressional isotherms measured with the Langmuir trough have a steep slope, indicating significant compressional viscoelastic moduli in comparison to films of small ratios which are typical of soft films (i.e. films having low compressional viscoelastic moduli and relatively "flat" compressional isotherms).

The isotherm measured for a mixed system of asphaltene and low demulsifier concentration (0.2 ppm) displayed a behaviour that was between that of pure asphaltenes and demulsifier. Specifically, the increase in the pressure upon compression was limited at large interfacial areas (low compression), and the slope of the π-A isotherm resembled that of the pure demulsifier isotherm. These results suggest that asphaltene molecules had been partially displaced from the toluene-water interface and demulsifier dominated the compressional behaviour of the system. However at smaller compressional areas the slope of the π-A isotherm increased, suggesting that asphaltenes molecules that had not been displaced by the demulsifier were tightly squeezed and resisted the compressional force. Therefore, with 0.2 ppm demulsifier added, at low compression the demulsifier molecules dominate the interfacial properties, but at high compression the interfacial properties are dominated by the asphaltenes. Interestingly this system would correspond to poor dewatering performance. At the optimum dewatering condition (demulsifier concentration = 2.3 ppm) the situation is somewhat different and the two π-A isotherms (asphaltene + demulsifier, and demulsifier only) were similar and displayed soft film characteristic as the interfacial area was reduced to 12.5 cm^2. It is often discussed that interfacial film rigidity (compressional and shear) is responsible for the enhanced stability of asphaltene stabilized emulsions[4, 5 46]. Hence, film softening by demulsifier addition would promote

favorable conditions for emulsion separation[57]. The data obtained with 2.3 ppm demulsifier would indicate that film softness under different levels of compression promotes dewatering. However, at demulsifier concentrations above the optimal the two π-A isotherms measured for asphaltene + demulsifier and for demulsifier only were also similar, displaying soft film behaviour. These results show that the rheological data is somewhat limited when trying to explain the overdose phenomena. Therefore mechanisms other than rheology contribute to the stabilizing potential observed during overdose.

It is noted that in the Langmuir trough experiments demulsifier was added to the system after 30 minute asphaltene film aging. It is reported that the characteristics of asphaltene films are time dependent, and that the shear[58] and the compressional viscoelastic moduli[59] of asphaltene films increase in time (i.e. asphaltene films become more rigid) due to rearrangement and further association of the asphaltene molecules at the interface. It is therefore possible that different minimal demulsifier dosages are required to soften to the same extent the asphaltene films aged for different periods of time. However, the trends discussed above would not be altered: regardless of aging time, higher demulsifier dosages soften asphaltene films more effectively than lower demulsifier dosages under both shear and compression conditions, which will not change the general correlation between the coalescence of water droplets and the interfacial film rheology: film softening is beneficial and necessary for coalescence, but it may not be sufficient.

3.6. Morphology of the films at toluene-water interface. Imaging of interfacial asphaltene films was conducted to visually observe the impact of demulsifier on asphaltene film morphology, and to better understand the ability of demulsifier to penetrate asphaltene films and alter their structure. BAM images of spread asphaltene films at the air-water interface revealed island-like structures (Fig. 5), in agreement with previously published data[60-62]. In previous studies the morphology of asphaltene films was probed in situ with BAM at the air-water interface[41, 60-62], while asphaltenes films at the toluene-water interface have been previously imaged after being transferred onto solid substrates (LB films) [55, 57, 63]. In the current study, after the toluene (good solvent) top phase was gently added, the cracks in the film were observed to "heal" (Fig. 5), to form a homogeneous film. When the toluene-water interface was imaged in situ using BAM, the films interfacial features were not mobile, suggesting that the asphaltenes formed an interconnected, rigid-like film. This visual observation is in good agreement with the

results from the shear rheology and π-A isotherm measurements discussed in the previous sections.

In the demulsifier concentration range 0.2 ppm to 28.8 ppm the asphaltene film structure appeared unchanged when observed at the toluene-water interface at 5X magnification (Figure 6). Asphaltene film morphology at the lower demulsifier concentration was further studied using AFM, which enabled surface features to be observed at the nano-meter scale resolution (Figure 7). While BAM showed no measurable differences in the asphaltene film morphology, on visual inspection the film mobility was observed to increase after demulsifier addition. This mobility is in agreement with the drastic reduction in the film shear elasticity after 2.3 ppm demulsifier addition as shown in Figure 3 (a) and with film softening under compression shown in Figure 4. In addition to the film mobility, the interface was observed to change position (lower z-axis position) and shape from an approximately flat to a convex film, due to the decrease in the interfacial tension. The change in the interfacial shape became more substantial at higher demulsifier concentrations. At concentrations greater than 28.8 ppm demulsifier in toluene, aggregates of several microns in diameter were observed to form at the toluene-water interface (Fig. 6). The morphology of asphaltene films further changed at higher demulsifier concentrations, acquiring a visible texture contrasting the smooth films observed at lower demulsifier concentration (Fig. 6). The observed changes in the film morphology and mobility at low demulsifier concentrations occurred within a few minutes following demulsifier addition, while the changes were instantaneous at higher demulsifier concentrations.

BAM images of pure demulsifier films at the toluene-water interface were also considered. These images showed the formation of smooth films in the demulsifier concentration range 0.2 ppm to 28.8 ppm (Fig. 6), whereas at concentrations greater than 28.8 ppm aggregates were clearly visible at the toluene-water interface (Fig. 6). The population of the aggregates at the interface increased progressively when increasing the demulsifier concentration in toluene from 28.8 ppm to 288.4 ppm (Fig. 6), leading to the formation of densely packed networks having a 3-Dimensional appearance. SEM images of LB films deposited after diffusion of 288.4 ppm demulsifier in toluene confirmed the presence of large irregular structures at the toluene-water interface (Fig. 8).

The presence of such structures suggests that steric forces can be responsible for the observed overdose effect and for the intrinsic stabilizing capacity of demulsifier at high concentrations in toluene. Such a hypothesis is in agreement with the results of previous studies that demonstrated the important role of steric repulsion in the interactions between polymer-coated surfaces[64, 65], and in the stability of emulsions[66] and foams[67] in the presence of EO-PO co-polymers.

To increase understanding of the role of the demulsifier at lower concentrations, LB films of asphaltene + demulsifier, asphaltenes without demulsifier and pure demulsifier were deposited onto silica wafers for nano resolution analysis by AFM and SEM. AFM measurements allowed quantitative determination of nanometer resolution roughness of interfacial films (defined in Eq. (4)), with the values being given in Table 2. As shown in Fig. 7, asphaltene films were fairly homogenous, with small aggregates uniformly distributed on the surface. The surface had a roughness of approximately 1 nm. These results are in agreement with the results reported in previous studies[55, 57]. The addition of demulsifier at 0.2 ppm in toluene had a marginal effect on the morphology and roughness of asphaltene films as shown in Fig. 7. Increasing the demulsifier concentration to 2.3 ppm (i.e., at the optimal dosage determined in the bottle tests) or even higher significantly changed the morphology of the asphaltene film, as shown in Fig. 7 and Fig. 8. Specifically, addition of 2.3 ppm or 5.7 ppm demulsifier in toluene induced the formation of spherical aggregates, sparsely distributed on an otherwise smooth surface, but had a negligible effect on the roughness of asphaltene films as shown in Table 2. Such aggregates could be a result of the aggregation from asphaltenes that were displaced from the interface, which was preferentially occupied by the demulsifier. This hypothesis is in agreement with the results from the interfacial tension measurement and XPS analysis of the interfacial LB films that indicated partial asphaltene displacement. Similar findings were reported from previous studies on displacement of stabilizing asphaltene or bitumen films from the interface by other polymeric demulsifiers[15, 23], including EC[10, 45]. Specifically, previous studies conducted using EC showed that EC preferential adsorption onto the oil-water interface caused bitumen or asphaltenes to segregate into micro-domains surrounded by EC[10, 45].

LB interfacial films of demulsifiers diffused to the clean toluene-water interface (in the absence of asphaltenes) were imaged for comparison. The morphology of films obtained with pure demulsifier differed from those obtained when demulsifier was diffused into the interface where asphaltenes films were already formed. This result suggests that both the demulsifier and the

asphaltenes were present at the interface, as previously discussed (cf. sections 3.1 and 3.2). The roughness of demulsifier films without asphaltenes was small (0.4 nm) at a demulsifier in toluene concentration up to 28.8 ppm (Table 2, and Fig. 7), at which point an overdose was observed and the demulsifier had intrinsic stabilizing capacity. These results show that roughness was not the cause for the overdose effects. It is important to note that the AFM images can only be analyzed to obtain the roughness, but not the absolute thickness of the transferred LB interfacial film. Therefore, the smoothness of pure demulsifier films at demulsifier concentrations up to 28.8 ppm (at which the overdose occurred) does not contradict the hypothesis that steric repulsion caused by demulsifier film thickening may stabilize emulsions at high demulsifier concentrations in toluene.

It should be noted that the asphaltene stabilized toluene-water interface certainly differs in many ways from "real" diluted bitumen-water interfaces. Nevertheless, using asphaltene in toluene as a model for diluted bitumen allowed us to probe the critical role of asphaltenes in stabilizing water in diluted bitumen and demulsifiers in breaking such stable emulsions. As shown in this work, the importance of film rigidity and rheology, and the role played by additional factors such as steric forces were highlighted from studying this model system. The observations from our work shed valuable lights on the stability of petroleum emulsions and demulsification, with a major finding in overdose of demulsifiers and corresponding over dose mechanisms that may encounter in real systems. This work represents a first step towards understating the stability of real water-in-diluted bitumen emulsions and demulsification.

4. Conclusions

The performance of an EO-PO demulsifier in the dewatering of asphaltene-stabilized water-in-oil emulsions was studied by bottle tests and coalescence measurements of emulsified water droplets in toluene using the micropipette technique. The properties of interfacial asphaltene films were probed through a number of techniques, including surface tension, shear rheology, interfacial pressure-area isotherms, chemical composition, and nano and micro morphology.

Bottle tests and micropipette experiments showed an optimal performance of the demulsifier at 2.3 ppm in toluene. At higher concentrations, the performance degraded, indicating an overdose of the demulsifier used. The observed optimal performance of the demulsifier was explained on

the basis of asphaltene film softening (i.e. of the reduction of the viscoelastic moduli) under shear and compression, while the overdose was attributed to steric repulsion between water droplets.

Asphaltenes stabilize water-in-oil emulsions by forming rigid skins at the oil-water interface. The demulsifier used in this study was more surface active than asphaltenes, and thus competed effectively with asphaltenes for the interface, penetrating asphaltene films and softening them under shear and compression. The softness of asphaltenes films was found to increase with increasing demulsifier addition up to 288.4 ppm in toluene, leading to faster kinetics of asphaltene film penetration at higher demulsifier dosages. However, high demulsifier concentrations are likely to produce thick films, which would possibly increase steric repulsion between water droplets and prevent the droplets from coalescing.

This study shows that demulsification involves a complex interplay of concentration-dependent competing mechanisms, all of which must be taken into consideration to fully understand dewatering performance and the design of demulsifiers.

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Figures
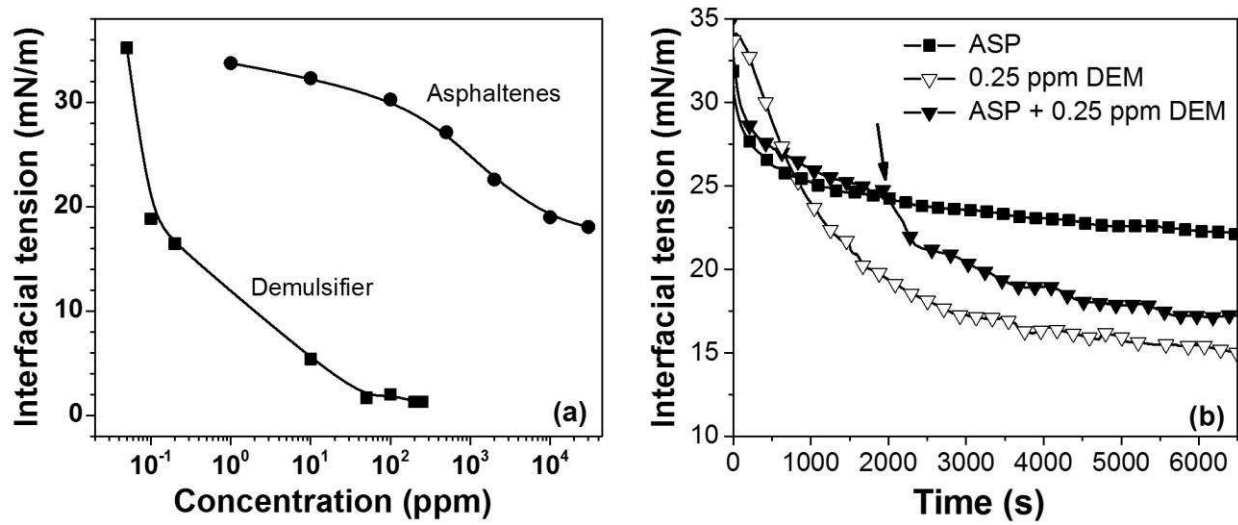
Figure 1. Equilibrium interfacial tension of asphaltenes and demulsifier at different concentrations of demulsifier in toluene (based on the toluene phase mass) (a); dynamic interfacial tension for asphaltenes, pure demulsifier and mixed system (b). The arrow indicates the time when demulsifier was injected in the cuvette (30 min). Asphaltenes and demulsifiers are abbreviated as "ASP" and "DEM", respectively in the legend.
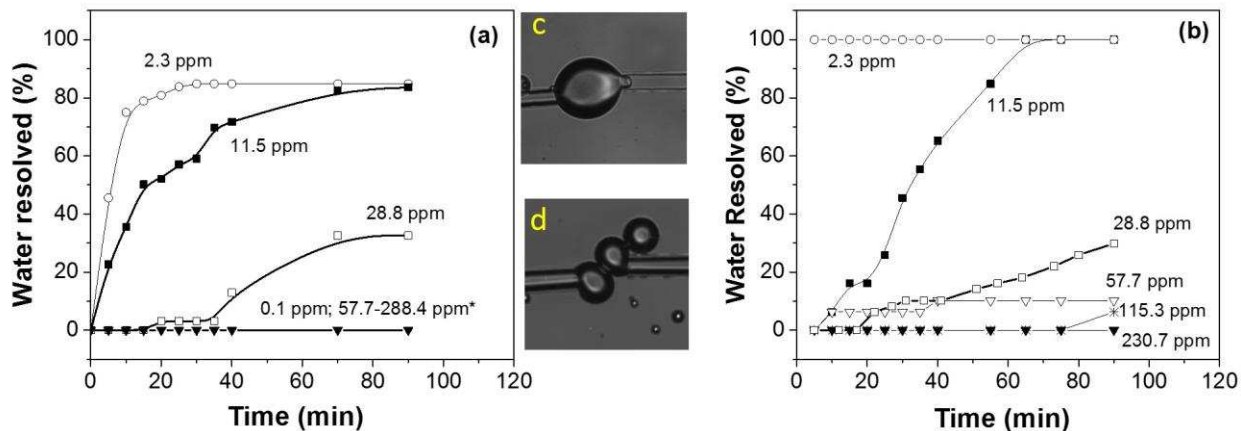
Figure 2. Water resolved in bottle tests upon addition of demulsifier at different concentrations (based on the mass of toluene phase) to asphaltene stabilized emulsions (a) and in emulsions where only the demulsifier was present (b). Examples of coalescing (c) and non-coalescing (d) water droplets manipulated using micropipettes are shown adjacent to Figure 2 (a). *It is noted that upon addition of demulsifier at 57.7 ppm or higher in the toluene phase, the emulsions were stable with no free water resolved even after 24 hr gravity separation.
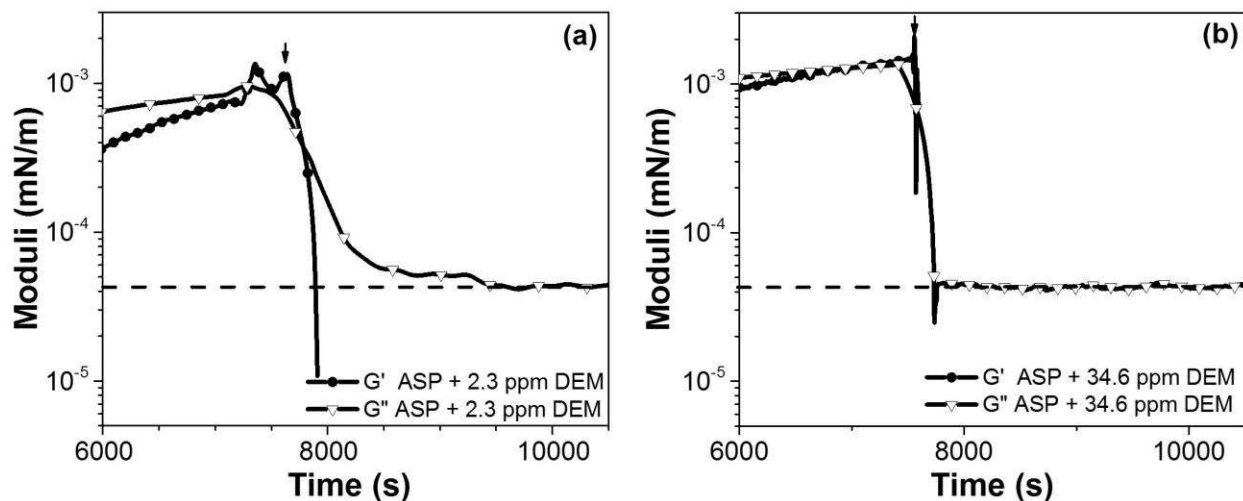
Figure 3. Shear elastic (G') and viscous (G") moduli obtained for asphaltene films prior and after addition of demulsifier at 2.3 ppm (a) and 34.6 ppm in the toluene phase (b). The arrow indicates the time at which the demulsifier was added. Asphaltenes and demulsifiers are abbreviated as "ASP" and "DEM", respectively in the legend. The dashed line represents the viscous modulus of a clean toluene-water interface or of the toluene-water interface when demulsifier was added at 57.6 ppm in toluene (G'= 0 N/m).
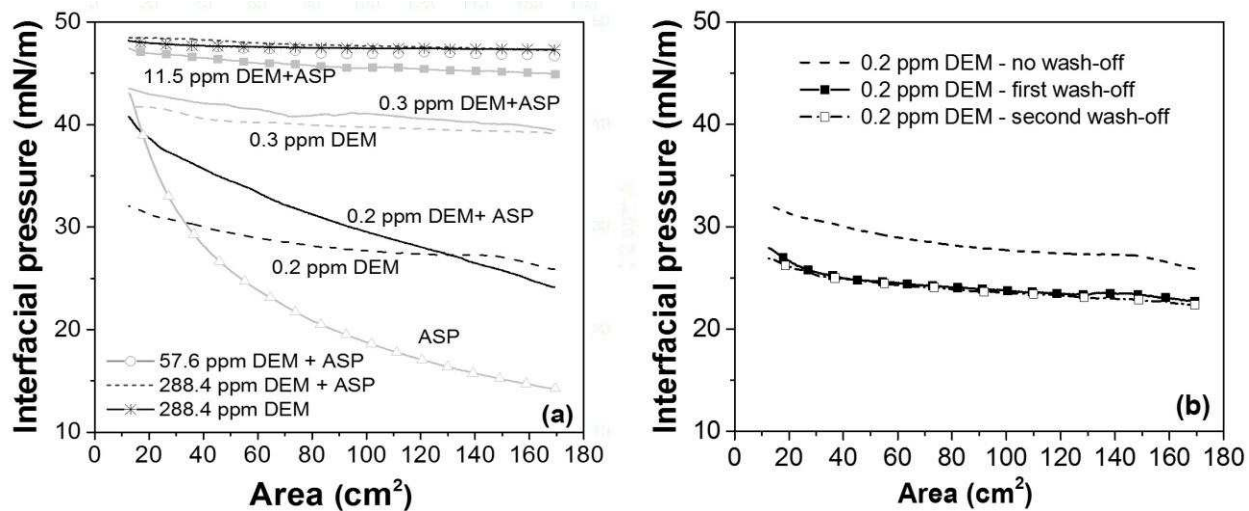
Figure 4. Comparison of π-A isotherms obtained for asphaltene, demulsifier and their mixture at the toluene-water interface (a), and isotherms measured for demulsifier at 0.2 ppm concentration in toluene before and after wash-off of the toluene top-phase (b). In the legend asphaltenes and demulsifier are abbreviated with "ASP" and "DEM", respectively. The demulsifier concentrations given in ppm are based on the mass of toluene.
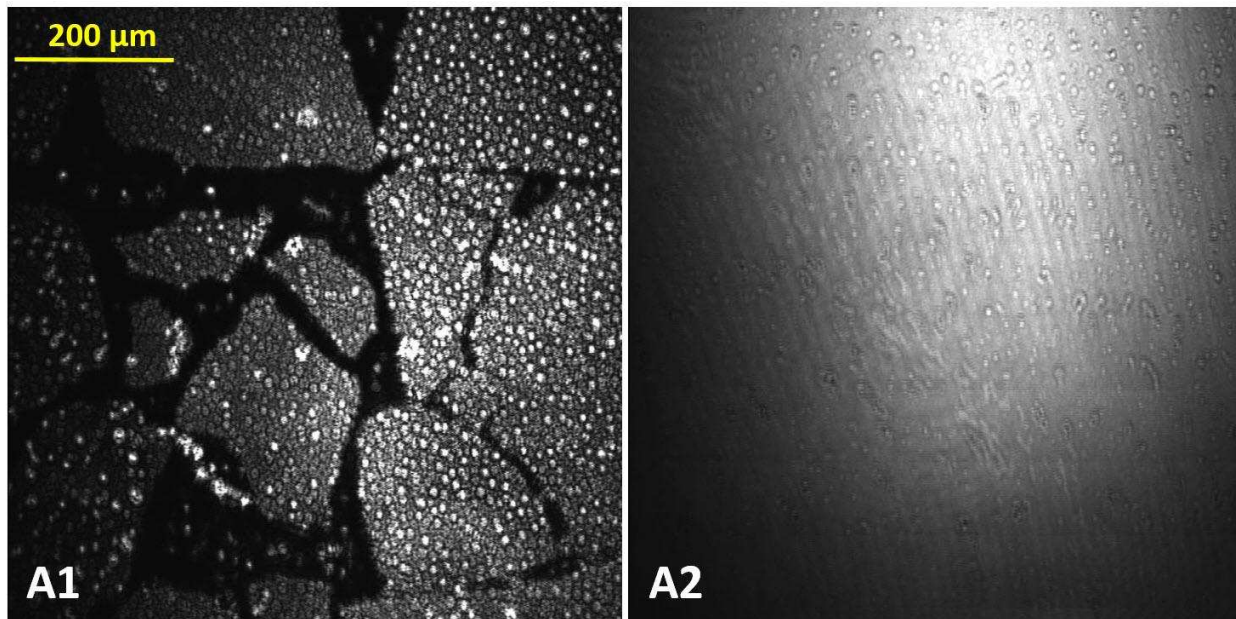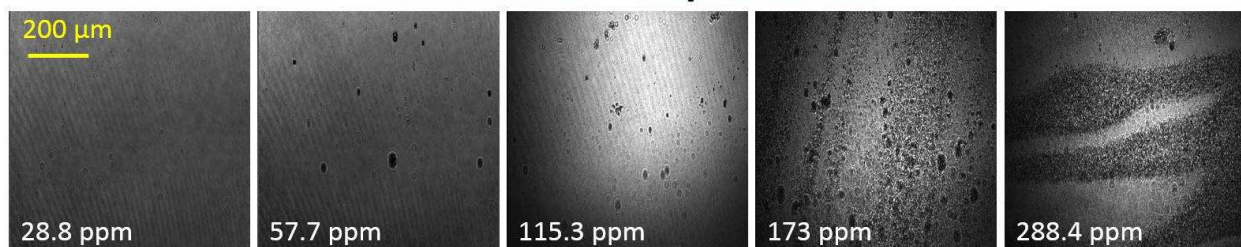
Figure 5. BAM images of asphaltenes without demulsifier at the air-water (A1) and toluene-water interface (A2).
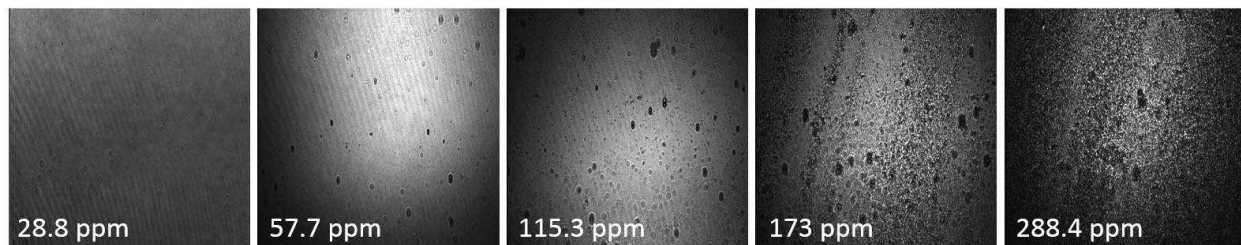
Figure 6. BAM images of asphaltenes after addition of the demulsifier (top row) and of pure demulsifier films (bottom row) at different concentrations in toluene. Demulsifier films formed with demulsifier concentrations in toluene below 28.8 ppm appeared smooth and similar to those formed with 28.8 ppm demulsifier concentrations in toluene. Such images are not shown here for brevity. The size of BAM images is 800 ☐m X 800 ☐m.
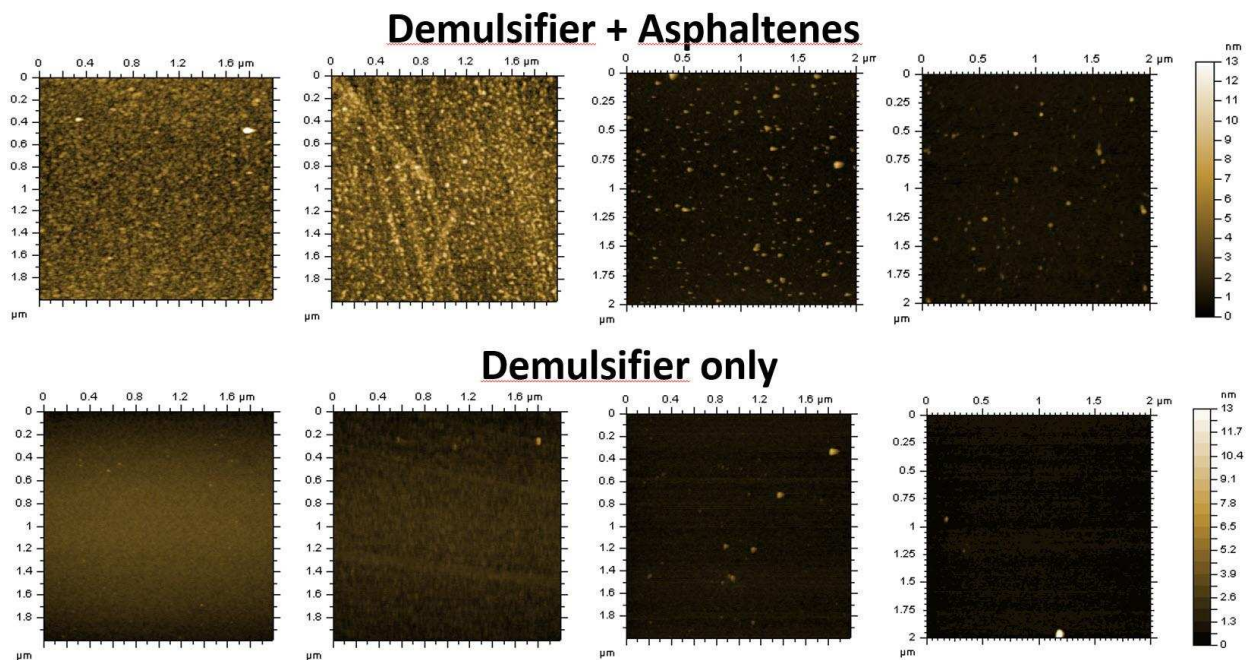
Figure 7. AFM images of asphaltene films after addition of demulsifier at different concentrations in toluene (top row) and of pure demulsifier toluene-water interfacial LB films at different concentrations in toluene (bottom row). The image of pure demulsifier at 10 ppm was similar to the one obtained at 28.8 ppm, and is not shown here for brevity. The color bar indicates the height scales (in reference to the lowest point of the sample): the brighter the color of the area, the higher the topology, with the brightest color representing 13 nm.
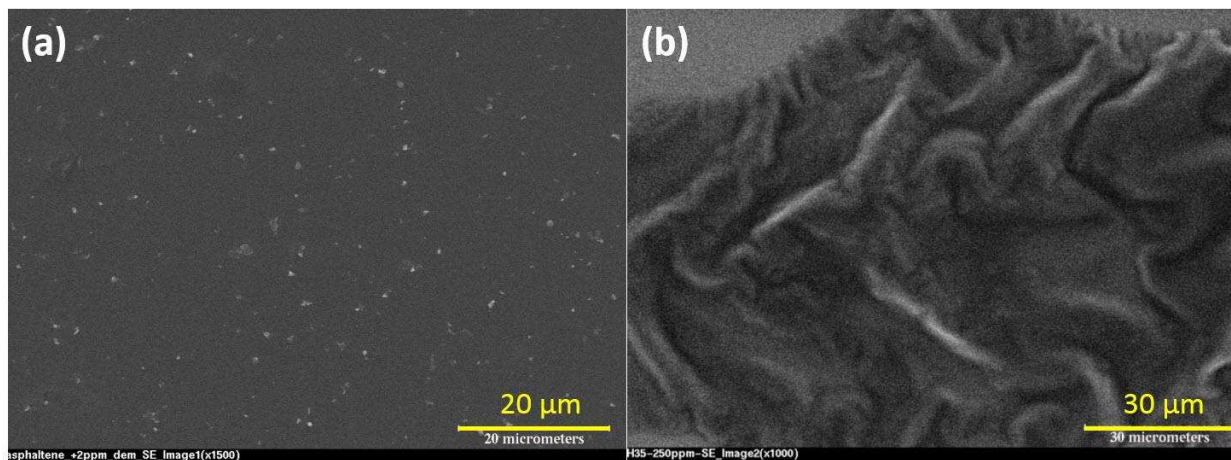
Figure 8. SEM images of asphaltene toluene-water ınterfacial LB films with 2 ppm (a), and SEM image of a pure demulsifier film produced by diffusing 250 ppm of demulsifier in toluene (b).

Tables

Table 1. Oxygen to carbon (O/C) atomic ratio of different LB films, obtained by XPS analysis.

Sample	O/C atomic ratio
Asphaltenes*	0.042
Demulsifier (2.3 ppm in toluene)	0.363
Asphaltenes+2.3 ppm demulsifier in toluene	0.133
Asphaltenes+11.5 ppm demulsifier in toluene	0.157

*Films formed with the spreading method (cf. section 2.9)

Table 2. Roughness of LB films before and after demulsifier addition, determined by quantitative AFM imaging. All demulsifier concentrations expressed in ppm are based on the mass of toluene phase.

Type of film	Roughness (nm)
Asphaltene	1.1
Asphaltene + 0.2 ppm demulsifier	1.0
Asphaltene + 2.3 ppm demulsifier	1.1
Asphaltene + 5.8 ppm demulsifier	0.9
2.3 ppm, 11.5 ppm and 28.8 ppm demulsifier	0.4