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Aging Oil-Water Interfaces with Asphaltene and Demulsifier Adsorption: Interface Rheology and Heterogeneity

A dissertation submitted in partial satisfaction
of the requirements for the degree

Doctor of Philosophy
in
Chemical Engineering

by

Chih-Cheng Chang

Committee in charge:

Todd Squires, Chair
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September 2019

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May 2019

Aging Oil-Water Interfaces with Asphaltene and Demulsifier Adsorption: Interface
Rheology and Heterogeneity

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by

Chih-Cheng Chang

For my grandmother,
who always supported me and became an angel during my
graduate program.

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- **Chih-Cheng Chang**, Ian Williams, Arash Nowbahar, Vincent Mansard, Jodi Mecca, Kathryn A. Whitaker, Adam K. Schmitt, Christopher J. Tucker, Tom H. Kalantar, Tzu-Chi Kuo and Todd M. Squires, The effect of ethylcellulose on the rheology and mechanical heterogeneity of asphaltene films, *Langmuir*, submitted
- **Chih-Cheng Chang**, Arash Nowbahar, Vincent Mansard, Ian Williams, Jodi Mecca, Adam K. Schmitt, Tom H. Kalantar, Tzu-Chi Kuo, and Todd M. Squires, Interfacial Rheology and Heterogeneity of Aging Asphaltene Layers at the Water/Oil Interface, *Langmuir*, Volume 34, 2018, Pages 5409-5415
- Subrata Das, **Chih-Cheng Chang**, Che-Yuan Yang, Sudipta Som, Chung-Hsin Lu, Microemulsion-derived ZrO₂:Ce³⁺ + nanoparticles: Phase transformation and photoluminescence characterization, *Materials Characterization*, Volume 106, 2015, Pages 20-26
- **Chih-Cheng Chang**, Che-Yuan Yang, Chung-Hsin Lu, Preparation and photoluminescence properties of Sr₄Al₁₄O₂₅:Eu²⁺ phosphors synthesized via the microemulsion route, *Journal of Materials Science Materials in Electronics*, Volume 24, Issue 5, 2013, Pages 1458-1462

- Tsai-Ta Lai, **Chih-Cheng Chang**, Che-Yuan Yang, Subrata Das, Chung-Hsin Lu, Influence of Bi₂O₃ ux in the structural and photoluminescence properties of SrAl₂O₄:Eu²⁺ phosphors, *Ceramics International*, Volume 39, Issue 1, January 2013, Pages 159163

Presentations

- **Chih-Cheng Chang**, Arash Nowbahar, Vincent Mansard, Jodi Mecca, Adam Schmitt, Tom Kalantar, Tzu-Chi Kuo, and Todd Squires, Aging oil-water interfaces with asphaltene adsorption: interface rheology and heterogeneity, 2018 AIChE Annual Meeting, Pittsburgh, 2018
- **Chih-Cheng Chang**, Arash Nowbahar, Vincent Mansard, Jodi Mecca, Adam Schmitt, Tom Kalantar, Tzu-Chi Kuo, and Todd Squires, Aging oil-water interfaces with asphaltene adsorption: interface rheology and heterogeneity, 90th ACS Colloid & Surface Science Symposium, Cambridge, 2016
- **Chih-Cheng Chang**, Arash Nowbahar, Vincent Mansard, Jodi Mecca, Adam Schmitt, Tom Kalantar, Tzu-Chi Kuo, and Todd Squires, Aging oil-water interfaces with asphaltene adsorption: interface rheology and heterogeneity, AIChE Annual Meeting, San Francisco, 2016

Abstract

Aging Oil-Water Interfaces with Asphaltene and Demulsifier Adsorption: Interface
Rheology and Heterogeneity

by

Chih-Cheng Chang

Asphaltenes are surface-active molecules which naturally appear in the crude oil. They can adsorb at the water-oil interface and form a viscoelastic film, which stabilizes emulsion drops and makes water-oil separation extremely challenging. These emulsion drops can cause serious problems in the petroleum industry, so the understanding of the asphaltene film and a reliable method to enhance water-oil separation needs to be established.

In this study, we apply the interfacial shear rheology on the water-oil interface to characterize the adsorption of asphaltene. Generally, the evolving asphaltene adsorption results in the increase of interfacial stiffness and brings a transition from viscous-dominated to more viscoelastic response to the interface. However, significant variation in the rheological evolution is observed between the nominally-identical experiments. The direct visualization of the interface reveals the mechanical heterogeneity appearing at the evolving film, from both micron and millimeter scale. This heterogeneity seems to be an inherent feature of the asphaltene film and impact the coalescence of asphaltene-stabilized emulsion drops. In addition, we also reveal that the asphaltenes interfacial rheology can be impacted by the chemical and physical parameters of the experiment. The oil composition such as aromatic fraction, bulk asphaltene composition and the choice of model oil can all influence the evolving rheology. Furthermore, the water-oil geometry, selection

of rheometry probes and the way conducted shear rheology can also vary the measured rheological response. Our results thus reveal a more complex adsorption process and interfacial structure than that reported in the literature and provide a deep understanding of how to control the asphaltene adsorption.

The asphaltene-stabilized emulsions are often demulsified by the chemical demulsifier. The second focus in this dissertation is investigating how the various chemical demulsifiers impact the asphaltene interfacial rheology. We first examine ethylcellulose (EC) as a model demulsifier using two different mechanisms. The ‘premixed’ experiment allows asphaltene and EC concurrently adsorb, showing that EC can disrupt asphaltene adsorption and retard the stiffening of interfacial film. The experiment of introducing EC to aged asphaltene layer, on the other hand, characterizes that EC softens the stiff layer formed prior to the addition of demulsifier. From the direct visualization of the heterogeneous structure, we further reveal that EC acts inhomogeneously and soften the relatively soft region at the interfacial film initially. This mechanism might impact the demulsification process and provide a new insight into the emulsion destabilization. The influence of chemical architecture on the rheological response of demulsifier is also investigated. We utilized a series of EO-PO-EO block copolymers to the two mechanisms described in the EC experiment. The high molecular weight is found to decrease the ability of demulsifier on preventing asphaltene from forming an viscoelastic layer at the low concentration but generates no significant change on softening the aged asphaltene layer. High hydrophilic-lipophilic balance (HLB) can better prevent asphaltene from adsorption, but poor ability to soften the aged asphaltene layer. These results can provide systematic information to guide the design of demulsifier which can provide a particular rheological response at the interface, facilitating the demulsification process.

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Chapter 1

Introduction

1.1 Project motivation: The problem of water-in-crude-oil emulsions

The extraction and processing of crude oil often results in the water existing in the crude oil[1]. For example, the water flooding process injects water into the stratum to extract crude oil out of the ground[2]. Due to the growing market demand, more and more crude oil is extracted from deep-water environments. [3] Oil sand is another important source of crude oil, for which Clark Hot Water Extraction process (CHWE) is widely used for the commercial recovery.[4, 5] This process crashes and mixes the oil sands with hot water to extract the oil layer by the density difference. As a result, water is typically unavoidable in the petroleum industry.

Although water and crude oil are two immiscible fluids, natural surfactants such as asphaltenes, resins, and fine particles in the crude oil can adsorb at water-oil interfaces and stabilize water as an emulsion[6], introducing difficulties for the water-oil separation. These water-in-crude-oil emulsions have the scale of 1-10 μm [7], which is thermodynam-

ically unstable but kinetically stable due to these surfactants. Class of these surfactants, asphaltenes are believed to have the largest effect on emulsion stability[8, 9], which attract our interest in this study.

The remaining water in bitumen causes several problems. Firstly, dissolved ions such as sodium, iron, and chloride in the water-in-oil emulsion poison catalysts used in the refinery process[10]. The ions dissolved in water can also react to form corrosive components such as hydrochloric acid when they encounter high temperature and pressure during refining[11]. In addition, the emulsified water increases the overall volume[12] and the viscosity of crude oil[13]. More energy is thus required for the transportation of crude oil if emulsion exists.

Since the presence of water causes these issues, strict regulations require the water content in crude oil to be lower than 0.5 % [14]. If more than 0.5 % water exists in crude oil, pipeline transportation is prohibited[15]. As a result, understanding how the water-in-oil emulsion is stabilized and how to destabilize the emulsion to enhance water-oil separation is important for improving crude oil extraction and processing efficiency.

1.2 Introduction of asphaltene

Of all the natural surfactants that exist in crude oil, we focus on studying the main stabilizer, asphaltene, in order to understand the stabilization mechanism of the water-in-oil emulsion. Asphaltenes are a class of macromolecules found in crude oil, which are soluble in toluene but insoluble in light alkanes such as n-heptane and n-pentane[16, 17]. Thousands of distinct molecular structures have these solubility properties and are classified as asphaltenes[18, 19]. A previous study conducted by Schuler *et al.* used atomic force microscopy (AFM) and scanning tunneling microscopy (STM) to probe the atomic structure of asphaltene molecules, and confirmed that they are composed of diverse

chemistries[19]. Therefore, investigating the asphaltene-stabilized water-in-oil emulsion via chemical methods has proven challenging due to their complicated composition. Representative asphaltene structures are shown in Fig. 1.1[20]. Asphaltene molecules typically contain polycyclic aromatic hydrocarbons(PAHs) with peripheral alkanes[21, 22]. Their molecular weights usually range from a few hundred to thousands of daltons[23, 24], and the size of asphaltene molecules is usually around 1 nm[20].

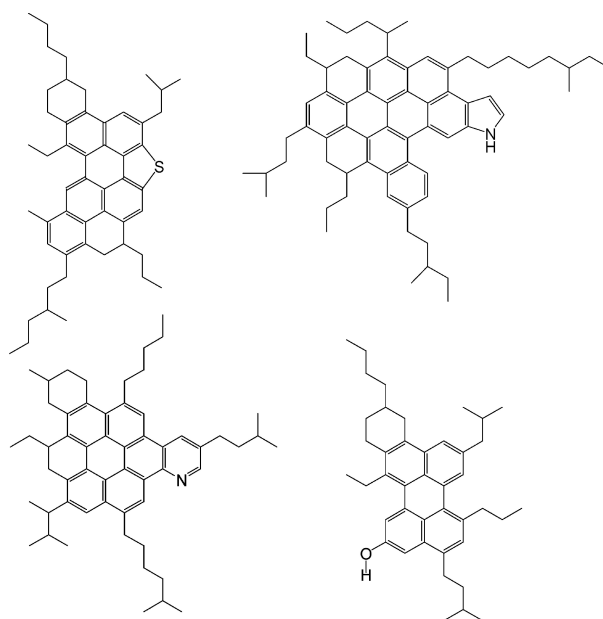


Figure 1.1: The four representative asphaltene structure, adapted from Mullins[20]

Individual asphaltene molecules can aggregate into a bigger structure. The Yen-Mullins model describes the hierarchical architecture of asphaltene molecules when the concentration increases in the bulk oil phase[20, 16], shown in Fig.1.2. Asphaltene molecules first self-aggregate to become ‘nanoaggregates’ with aggregation numbers around 6. The size of nanoaggregates is around 2 nm, as measured by small-angle-X-ray scattering (SAXS) and small-angle neutron scattering (SANS)[25, 26]. The formation of nanoaggregates is attributed to the dipole-dipole intermolecular attraction between PAHs in the interior structure. Brought together by this attractive force, the asphaltene molecules

can then $\pi - \pi$ stack into nanoaggregates with these PAHs. However, the attractive force decays as a function of distance like r^{-6} , and the exterior alkane substituents also provide steric repulsion to prevent more PAHs embedded in the molecular structure. The balance between dipole-dipole interaction and steric repulsion thus results in low aggregation number of nanoaggregates[20, 16]. When the asphaltene concentration increases to the critical nanoaggregation concentration (CNC), the formation of nanoaggregates halts. The value of the CNC can vary from 50 to 150 mg/L [27, 28] depending on the source of asphaltene. The CNC can be measured by AC/DC-conductivity measurements [29, 30], NMR studies [31], and centrifugation [32].

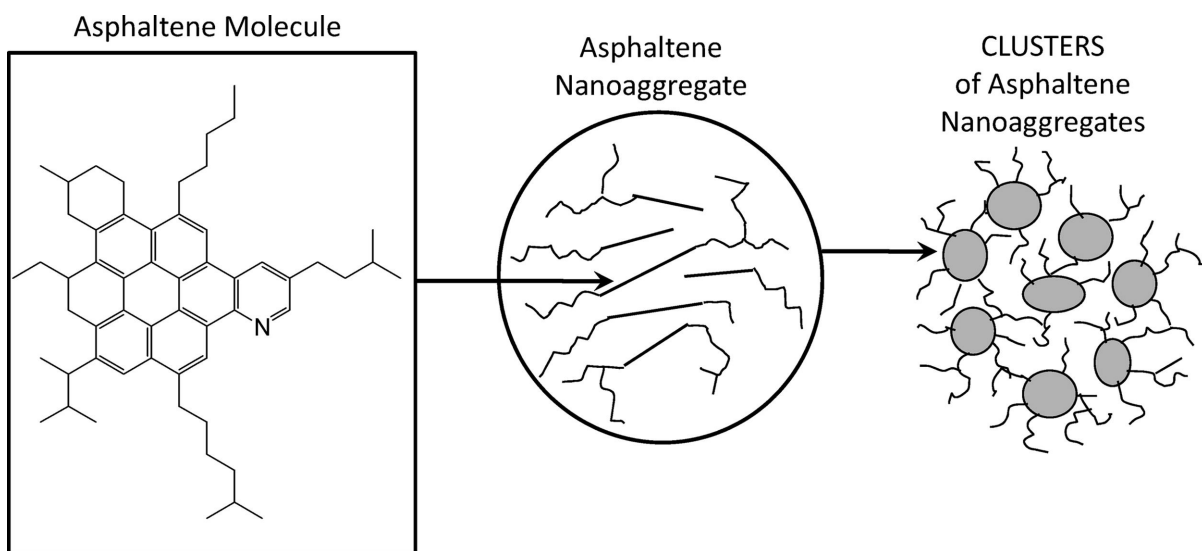


Figure 1.2: The Yen-Mullins model, adapted from Mullins[20]

When the asphaltene concentration increases further, asphaltene nanoaggregates form secondary aggregates with around 8 nanoaggregates[20]. Cluster formation is a reaction-limited interaction, which is different from nanoaggregate formation, which is diffusion-limited[33]. The size clusters is around 5 nm[30, 34], which is larger than nanoaggregates, but smaller than asphaltene flocs (300 nm to micron)[20]. As a result, the chemical characterization of asphaltenes become more challenging due to the self-aggregation of

the asphaltene molecules. We thus focus on using physical methods to investigate the stabilization mechanism.

1.3 Asphaltene interfacial layer

In addition to describing the asphaltene self-aggregation in the bulk fluid, the Yen-Mullins model can also be applied to describe the asphaltene interfacial structure. Asphaltenes are around to adsorb at the interface as molecules, rather than aggregates, by comparing the size of asphaltene molecule and the average cross-section area occupied by adsorbing species measured via surface tension measurement.[35] Sum frequency generation (SFG) vibrational spectroscopy suggests that the PAHs of asphaltene molecules orient in the interface with their aliphatic chains perpendicular to the water surface [36].

The exact interfacial structure formed by asphaltene molecules is still under debate. Pauchard et al. argue that the asphaltene molecules form a single layer without cross-linking, like 2D random close packing of polydispersed disks at water-oil interfaces[37]. However, different studies report that asphaltenes form a cross-linked, gel-like structure layer at the water-oil interface [38, 39, 12], and hypothesize that the cross-linked asphaltene is the origin of the viscoelasticity of the water-oil interface[39].

As the asphaltene concentrations increased, different asphaltene structure are observed. These can also be related to the Yen-Mullins model. Nanoaggregates are found to appear at the interface when the concentration is higher than the critical nanoaggregate concentration(CNAC).[40] Molecular dynamics simulations show that asphaltenes first self-assemble into nanoaggregates in the bulk, and these nanoaggregates pin perpendicularly to the interface, forming fence-like structures as a protective film[41]. Brewster angle microscopy (BAM) further shows that when the concentration of asphaltene is increased, the asphaltene adsorbed at the interface evolves from relatively homogeneous

nanoaggregates to more heterogeneous clusters.[42] In summary, although the field agrees that asphaltenes adsorb at water-oil interface and promote emulsion stability, the architecture of asphaltenes at the interface is complicated, with different possible structures that may arise depending on a number of factor- asphaltene source, oil composition and aging time.

1.4 Surfactant adsorption at fluid-fluid interface

When water and oil phases come into contact, they form an interface at an energetic penalty. This is because the molecules at the interface experience intermolecular attractive force towards the bulk. The surface tension γ is the energy required to create excess surface area between two immiscible fluid-fluids.

Surfactants are molecules that typically have a hydrophobic head (oil-soluble) and hydrophilic tail (water-soluble), making them amphiphilic. When the bulk fluid contains amphiphilic surfactants, these surfactants preferentially adsorb at the interface/surface since part of surfactant is energy-unfavorable in the bulk fluid. The adsorbed surfactant decreases the surface tension and thus stabilizes the fluid-fluid interface. The reduced surface tension due to the adsorbed surfactant is called surface pressure π . This surface pressure is also equal to the free energy required to compress the surfactant layer.

The hydrophilic-lipophilic balance (HLB) [43] characterizes the affinity of a surfactant to water and oil phases respectively. HLB ranges from 0-20, and is given by:

$$\text{HLB} = 20 * \frac{M_h}{M}, \quad (1.1)$$

where M_h is the molecular weight of hydrophilic component, and M is the molecular weight of the overall surfactant. When $\text{HLB} \leq 10$, the surfactant is more hydrophobic;

when the $\text{HLB} > 10$ the surfactant is more hydrophilic.

Oil-soluble surfactants prefer to adsorb at the water-oil interface with the hydrophilic part buried in the water phase. However, the adsorption of surfactant decreases the entropy of the molecule, since they lose access to the micro-states in the bulk phase[44]. Competition between these two mechanisms gives an equilibrium isotherm that relates surface concentration Γ to bulk concentration C .

The equilibrium between bulk concentration and surface concentration depends on the chemical potential of the surfactant, which is the free energy required to insert one molecule into bulk phase or to interface[44]. For a dilute, ideal surfactant in the bulk fluid, the chemical potential μ_b is:

$$\mu_b = \mu_b^0 + k_b T \ln \left(\frac{C}{C_0} \right), \quad (1.2)$$

where μ_b^0 is the reference chemical potential at concentration C_0 . The chemical potential μ_s of a dilute, ideal surfactant in the interfacially adsorbed state is

$$\mu_s = \mu_s^0 + k_b T \ln \left(\frac{\Gamma}{\Gamma_0} \right), \quad (1.3)$$

where μ_s^0 is a reference chemical potential at surface concentration Γ_0 . When the concentration of surfactant in the bulk and at the interface reaches equilibrium, $\mu_s = \mu_b$. The Henry isotherm is obtained when both bulk and interfacial surfactant are ideal (Eq 1.2 and 1.3), giving

$$\Gamma = \left(\frac{\Gamma_0}{C_0} \right) \exp \left(\frac{\mu_b^0 - \mu_s^0}{k_b T} \right) C = K^{ideal} C, \quad (1.4)$$

where K^{ideal} is the equilibrium constant. The surface pressure associated with Henry isotherm is given by derivative of interfacial free energy with respect to area, holding T

and number of surfactant constant:

$$\pi = k_b T K^{ideal} C \quad (1.5)$$

Surfactant that are not dilute and non ideal, different isotherms arise. [45]

In addition to deviating from ideality while adsorbed on the interface, surfactants can also exhibit non-ideal behavior in the bulk fluid. For example, surfactants can spontaneously self-aggregate to form micelles above the critical micellization concentration (CMC). [46] At equilibrium, the chemical potential of surfactant on the surface μ_s and in the bulk μ_b are equal to the chemical potential of a surfactant in a micelle $\mu_{micelle}$ [44] Adding more surfactant results in the formation of more micelles rather than increasing bulk and interfacial concentration. As a result, surface concentration and surface tension remain constant, when the bulk concentration C of surfactant exceeds CMC.

Immiscible fluid-fluid interfaces can sometimes show instability driven by mass transport of solute from one liquid to another. Sternling and Scriven [47] attributed this hydrodynamic instability to the chemical potential difference between the two non-equilibrium phases. When the fluid containing solute or surfactant has a higher viscosity and lower diffusivity compared with the other fluid, the adsorbed concentration at the region must also change, subsequently changing interfacial tension. Concentration differences generate interfacial tension gradients, driving Marangoni flows that amplify the initial disturbance under certain conditions.

Interfacial turbulence and ultra-low or negative surface tension are believed to be related to the mechanism of spontaneous emulsification. [48] However, Silva et al. [49] found that spontaneous emulsification can even occur in systems with appreciable surface tension. Bochner et al. [50] recently showed that, water-toluene-asphaltene interface can spontaneously generate stable water-in-oil emulsion drops near interface. They argue the

reason is that interfacial layer can spontaneously curve to let more asphaltene molecules adsorb to the interface, decreasing the free energy.[51]

1.5 Stabilization mechanism of water-in-oil emulsion

Asphaltenes are known to be strongly surface-active, and to therefore form interfacial layers at the water-oil interface, resulting in stable water-in-oil emulsion [35, 52, 9]. Many hypothesize that asphaltenes can form viscoelastic, cross-linked or gel-like interfacial films that resist deformation, retard fluid drainage and act as physical barriers to droplet coalescence[53, 12, 54, 39, 38]. However, emulsion stability is a complex phenomenon that involves multiple mechanisms, and connecting emulsion stability to interfacial rheology remains correlative rather than directly proven.

The relationship between emulsion stability and interfacial properties, including elasticity, viscosity, steric repulsion, and Marangoni effect, are widely discussed[55, 56, 57, 54]. Regarding interfacial elasticity, recent research conducted by Harbottle *et al.* suggests that interfacial elasticity enhances emulsion stability, as the mobility of molecules at the surface is reduced within the solid-like films inhibiting coalescence. This hypothesis is based on the comparison of coalescence time and surface shear elasticity for asphaltene stabilized emulsions.[57] Clearly, the elastic film of the emulsion drops needs to be ruptured in order to coalesce with other drops. It therefore seems reasonable to expect interfaces with strong surface elasticity to resist coalescence strongly. In addition, a highly elastic interfacial layer makes the drops difficult to compress and deform, which prevents coalescence.[56]

Interfacial viscosity was also hypothesized to provide additional resistance to the interfacial film drainage [58, 59]. When two emulsion drops contact, flow generated at the interface sweeps the surfactant away, which makes the interfacial layer thinner (drainage)

and eventually coalesces the emulsion drops. A correlation between interfacial viscosity and the emulsion stability was shown by Pandey *et al.*[60]. However, other reports conversely shows viscosity is not related to emulsion stability[55]. Recently, sensitive measurements made by Zell *et al.*[61] found that all soluble small molecule surfactants(of those tested) are surface shear inviscid, irrespective of their efficiency in stabilizing foams and emulsions. Clearly, much remains to be discovered about the role of interfacial viscoelasticity in emulsion stability.

In addition to interfacial viscoelasticity, steric repulsion can also contribute to emulsion stability. The adsorbed surfactant layer can generate repulsive force between the emulsion drops to repel the emulsion drops[62], working as a physical barrier [63, 64]. This physical barrier, for example, can be the hydrophobic tail or hydrophilic head of surfactant which separates oil and water respectively from the emulsion drops.

During thinning or draining of the interface, the surfactants are driven away from the center of the draining film. This flow generates gradients of surfactant and concentration. The Marangoni effect causes these gradients of surfactant concentration and surface tension to exert a stress back towards the center of the film, retarding coalescence[58]. Thus, the Marangoni effect can hamper the deformation of the interface and contribute to the emulsion stabilization.

In summary, the mechanical properties of interfacial layers is believed to correlate with emulsion and foam stability[55, 65, 57, 54]. In this study, we will focus on how asphaltene impacts the interfacial shear viscoelasticity, and also how emulsion drop dynamics change when these asphaltene molecules adsorb at the interface.

1.6 Interfacial rheology of asphaltene film

Interfacial rheology quantifies how interfacial fluid flows and deforms under excess mechanical stress. It is widely utilized to characterize the viscoelasticity of a surfactant layer at the water-oil interface[61, 66, 67]. From the previous discussion, investigating the rheological properties of adsorbed asphaltenes at the water-oil interface is important for understanding the stability of emulsion droplets and also the mechanical properties of the film.[35]

The rheological properties of an interface can be measured by monitoring its response to dilational[68, 69, 70] or shear deformation[71, 52, 72, 73]. Dilational rheology measures the response of a surface to a change of area and therefore surface concentration. This deformation introduces complexities due to the consolidation of asphaltenes, the molecular exchange between the bulk and the interface, and the Marangoni effect.[74] These features thus bring a challenge when one wants to extract a particular contribution from the obtained rheological response. Compared with dilational rheology, shear rheology is usually obtained by rotating a probe to shear the interface without changing the surface area and allows the extraction of interfacial properties with less perturbation.

Bicone [71, 52, 72] and double wall ring (DWR) [57, 73, 75] geometries have been widely used to measure shear rheology of asphaltene layers at water-oil interfaces under various conditions. Several general features have been found in the literature. Fan *et al.* investigated how the properties of bulk oil impact the asphaltene interfacial rheology using a bicone geometry and found that higher asphaltene concentration and lower aromaticity results in higher interfacial viscoelasticity.[71] Harbottle *et al.* observed a transition from viscous-dominated to elastic-dominated shear response for an aging asphaltene film between water and bulk oil phase with asphaltene. [57] The influence of the aqueous phase has also been studied by Verruto *et al.*, suggesting that the addition of electrolyte

can retard the adsorption of asphaltene due to the screening effect[72]. In addition, a model asphaltene was often used to simplify the complexity of the asphaltene[76]. The corresponding rheology for the model asphaltene molecule was also widely studied[73, 75].

In conclusion, asphaltene adsorption at the water-oil interface has been shown to qualitatively increase the interfacial complex modulus $|G_s^*|$ and to result in a transition from viscous, liquid-like interface to a more elastic, solid-like interfacial film[71, 72, 73, 75]. The rheology measurements of the asphaltene film vary depending on asphaltene composition[73, 75, 77] and concentration[71], aromaticity of oil phase[71], and aqueous properties.[72]

1.7 Interfacial rheology: Sensitivity and heterogeneous structure

Interfacial rheology studies of asphaltene films introduce challenges on comparing results quantitatively due to the different experimental conditions and sources of asphaltene used in these studies. In addition, the sensitivity limit of the shear geometry used in the literature is usually on the order of $\mu\text{Ns/m}$ [78, 79], such as the interfacial shear rheometer (ISR, 1 $\mu\text{Ns/m}$) and double-wall ring (5 $\mu\text{Ns/m}$). To the best of our knowledge, more sensitive geometries like the deep-channel surface viscometer (0.1 $\mu\text{Ns/m}$)[80] and microbutton (0.01 $\mu\text{Ns/m}$) have not been applied to asphaltene interfacial rheology[81]. The rheology measurements in the literature often produce no measurable rheology at the early stage of asphaltene adsorption or even no measurable rheology within the particular experimental conditions, such as the study using pure aromatic solvent as the oil phase.[71] This ‘no measurable rheology’ might just be a rheological response lower than the sensitivity limit of the rheometer. As a result, we want to use a more sensitive

microrheometry to understand the rheological properties of the asphaltene film, and also to systematically investigate how experimental conditions impact asphaltene adsorption.

Furthermore, larger-scale structural heterogeneities exist in asphaltene films at the air-water interface, as revealed by atomic force microscopy (AFM)[15, 82, 83], fluorescence techniques[84], and Brewster angle microscopy (BAM)[85]. These heterogeneities are hypothesized by Fan *et al.* to reflect the formation of nanoaggregates and clusters described in the Yen-Mullins model[85]. Although these studies were performed at the air-water surface, rather than the oil-water interface, these micron-scale asphaltene aggregates have been proven to exist in asphaltene films[7]. Since the scale of these aggregates is comparable to that of emulsion drops that typically exist in crude oil, such structural and/or rheological heterogeneities might impact emulsion coalescence and stability. In addition, interfacial rheology measurements conducted in the literature typically use millimeter-scale probes, thus coarse-graining and overlooking the influence of structural heterogeneities.

Recent research conducted by Lin *et al.* combines interfacial imaging with macroscopic rheological measurements, revealing a connection between asphaltene mechanical structure and the rheological response[86]. The structure of aggregates and wrinkles can be linked to the shear thinning response, fracture and yielding of asphaltene films, indicating that morphological heterogeneity on the mechanical structure can indeed determine rheology. As a result, in addition to a more sensitive measurement, we also want to track the evolution of interfacial mechanical structure simultaneously, to better provide an overall understanding of the asphaltene structure and rheology.

1.8 Demulsification

Understanding the interfacial properties of the asphaltene layer is our first step towards investigating the treatment of water-in-crude oil emulsions. In order to enhance water-oil separation, demulsification is needed to destabilize the water-in-oil emulsion. Demulsification can be achieved by enhancing flocculation and coalescence of the emulsion drops[14]. In the flocculation process, the emulsion droplets physically adhere to each other without coalescing. Flocculation occurs when emulsion droplets attract each other by van der Waals forces. Demulsifier molecules can enhance flocculation by adsorbing onto emulsion droplets and form bridges that hold multiple emulsion drops as a single aggregate. The flocculation of emulsion drops depends on the viscosity of fluid, density difference between water and oil, temperature and water cut[17]. Flocculation can also increase the probability of coalescence, and accelerate sedimentation.

In contrast to flocculation, wherein emulsion droplets keep their identity, coalescence occurs when two droplets emerge to form a larger droplet due to the protective film rupture. Coalescence is composed of several steps[87]. Droplets need to first approach each other, and draining fluid between the drops. When two drops compress each other, the local surface area increases and the surfactant layer at the interface spreads more thinly, which results in an uncovered region at the surface so the dispersed phases can bridge. This process is irreversible and decreases the total number of emulsion droplets. Coalescence can be influenced by the rate of flocculation, the viscoelasticity of the protective film, interfacial tension, oil viscosity and water cut.[17]

Ostwald ripening occurs in polydisperse emulsions. When emulsion drops have different sizes, mass transfer takes place between the small emulsion drop and the large emulsion drop. This is because the concentration of dispersed phase at the emulsion drop surface is inversely proportional to the radius of curvature[88], which makes a larger emulsion

drop more energy-favorable than the smaller drop.

Chemical[89], mechanical[90], electrical[91], and thermal[92] methods are widely used in industry to destabilize emulsions and promote water-oil separation. Pure physical processes precipitate emulsions by gravity (or some other force) to separate water and oil, and have usually high cost and low efficiency. For example, settling tanks require large volumes and construction costs, and are not available everywhere due to the location of mining operations[93]. Compared to physical methods, chemical demulsifiers provide an more effective, economic and convenient method to destabilize emulsions since they can work as a ‘drop-in’ process without additional capital cost[94, 95]. In practice, a combination of chemical and electrical/mechanical methods is used in industrial separations.[17, 13] Various polymeric demulsifiers have been reported, including polysiloxane[96], alkylphenol polyalkoxylated resins[13], polyurethanes[13], and PO-EO block copolymers [97, 98, 99, 100, 101]. In addition to polymeric demulsifiers, ionic liquid[102, 103, 104] and nanoparticles[105] can also be the candidates as effective demulsifiers.

Chemical demulsifiers are usually amphiphilic molecules and more surface-active than asphaltenes, so they can competitively adsorb at the interface[106, 107]. They are believed to weaken or displace interfacial films formed at the water-oil interface[108, 109, 110, 54, 111], which results in a change in interfacial tension, viscoelasticity and thickness of the asphaltene interfacial film[15, 14, 112]. The demulsifiers are also shown to change the bulk rheological properties of the oil phase. With increasing amount of emulsion drops, the yield stress of the oil phase is increased[113] Adding demulsifier can further increase the yield stress and viscosity of the oil phase[114, 94].

The demulsifier performance can be tuned by varying HLB number[115]. In addition, the demulsification performance can also depends on the position of hydrophobe and hydrophile, demulsifier concentration, molecular weight and temperature [116]. These

factors will be discussed in the following section through the discussion of series of EO-PO block copolymers.

1.9 Ethylcellulose: Sample demulsifier

Ethylcellulose (EC, shown in Fig. 1.3) is an effective demulsifier which has been investigated recently using various techniques, such as simple bottle tests[83, 117], micropipette experiments[118], microfluidics[119], contact angle measurements[120, 121], atomic force microscopy(AFM)[111] and molecular dynamics simulation[41]. The structure of EC is composed of a series of repeating rings connected by an oxygen atom. Each ring has one oxygen atom and five carbon atoms, and three carbon connecting ethyl or hydroxyl group. The cellulose backbone is hydrophilic and the ethyl substituents are hydrophobic, making EC amphiphilic.

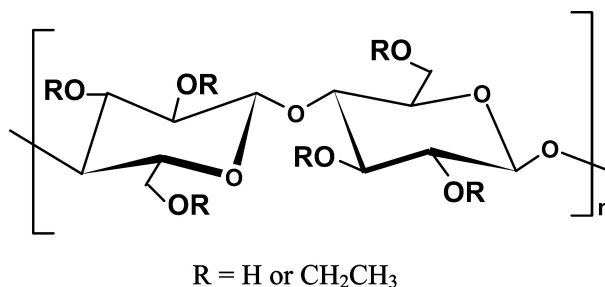


Figure 1.3: Structure of ethylcellulose, adapted from Feng *et al.*[83]

Interfacial tension measurements reveal that EC has a higher affinity for the interface than asphaltene[83], so they compete for adsorption. In addition, EC also has the ability to increase the compressibility of asphaltene interfacial film[111]. The film thickness measurement by ellipsometry and wet-ability measurement further reveal that EC can displace surface-active material at the interfacial film[111, 120]. By increasing EC concentration, mutually repulsive asphaltene-coated emulsion drops can be driven to adhere

and even coalesce[122], observed from the micropipette measurement. EC is thus believed to enhance water-oil separation by flocculation-assisted coalescence. Furthermore, the demulsification performance of EC has been shown to depend on its hydrophilic-lipophilic balance (HLB) and molecular structure.[122].

Although EC has been identified as an effective demulsifier and its influence on the asphaltene film is widely investigated, there are still some issues remaining. From the hypothesized relationship between the interfacial rheology and emulsion stability, it is prudent to characterize the influence of EC on the rheological properties of an asphaltene film, and its consequent effect on demulsification. However, to the best of our knowledge, little research has focused on this aspect of EC behavior[110]. Moreover, the AFM measurements have shown that when EC is added on the asphaltene interfacial film, EC can break interfacial structures inhomogeneously[118, 111]. The heterogeneity in the mechanical structure is already reported to impact the rheology of the interfacial film[86]. We want to build the connection between interfacial rheology evolution and heterogeneous breaking to further understand the mechanism of EC softening the asphaltene interfacial film.

1.10 EO-PO block copolymer: Structural effect on demulsification

Although EC is an effective demulsifier for the water-in-crude-oil emulsion, EC is economically not efficient for crude oil treatment. A more cost-friendly and effective demulsifier needs to be developed for the industrial demand. To guide the strategy for designing the demulsifier, we focus on how the chemical structure of demulsifiers impacts its performance on the interface. In this study, we use a series of EO-PO block copoly-

mers to investigate how the chemical architecture of demulsifiers impact their abilities on preventing asphaltene adsorption and interacting with pre-existing asphaltene film. These EO-PO block copolymers are commercially available and widely used in emulsification/demulsification, lubrication, foaming, and detergency application[123]. They are composed of hydrophilic polyoxyethylene (EO) and hydrophobic polyoxypropylene (PO) units, making the copolymer amphiphilic. The architecture of EO-PO block copolymer can vary by simply synthesizing the polymers with various amount of EO and PO groups[124].

Various structural effects are studied through the EO-PO block copolymer to characterize how they influence the demulsification efficiency of the water-in-oil emulsion. For example, the effect of HLB is investigated by varying the ratio of EO and PO component to tune the HLB of demulsifiers. High HLB is found to enhance the ability to remove emulsion and water-oil separation. [100, 124]. However, low EO ratio is also reported to enhance the demulsification[125]. Molecular weight is another factor studied in the literature. Feng *et al.* shows that higher molecular weight can better flocculate and coalesce emulsion drops.[118] The series of commercial demulsifiers investigated by Wu *et al.* show that the low-molecular-weight (< 4000 Da) can only remove 10% water from crude-oil emulsion in the dosage of 300-400 ppm. They thus claimed high-molecular-weight demulsifier with 7500-15000 Da can remove emulsion effectively[126]

The molecular architecture can also influence demulsifier performance even if the demulsifiers have similar HLB or molecular weight. For example, sequential block copolymer EO – PO – EO (Pluronic) is shown to be better than reverse sequential block copolymer PO – EO – PO on demulsification, and high EO ratio cannot compensate this position effect[100]. Dendrimer copolymers are suggested to exhibit better demulsification ability than linear copolymers[127, 128], since the dendrimer might flocculate the emulsion drops more efficiently than the linear copolymer. This feature increases the chance

of dendrimer to enhance emulsion drops coalescence.[128]

In addition to the intrinsic properties of the demulsifier, the concentration (dosage) of demulsifier also impact the efficiency of demulsification. The performance of demulsification usually increases when the concentration of demulsifier is increased. However, when the concentration reaches a particular value, even higher concentration either cannot further be improved (Type I behavior) or decrease the demulsifier performance (Type II behavior, overdose)[93]. EC is shown as Type I behavior[118], and EO-PO block copolymer can show either type I[94, 93, 128] or type II[124]. The mechanism of the overdose might be attributed to the amphiphilic nature of demulsifier which can also stabilize the emulsion[124], but these bottle tests suggests that an optimal demulsifier concentration exists for efficient demulsification.

Although the relation between molecular structure and demulsifier performance is widely studied, most of the studies are conducted only by the bottle test. The impact of HLB and molecular weight on interfacial properties is rarely studied. A polymeric demulsifier is shown to decrease the rigidity of the asphaltene interfacial film and change the packing of asphaltene aggregates at interface[15], and only one study uses an EO-PO block copolymer to examine its influence on the shear and dilational rheology[54]. To the best of our knowledge, there is no systematic study on how the molecular structure impacts interfacial rheology. As a result, we want to test various EO-PO demulsifiers on the asphaltene interfacial film to investigate how the molecular structure of demulsifier influences the interfacial property.

1.11 Overview of the dissertation

We have introduced the problem of water-in-crude oil emulsion, the main emulsion stabilizer asphaltene, emulsion stabilization mechanism, the study of asphaltene inter-

facial film which stabilize the emulsion, and demulsifier which destabilize the emulsion in chapter 1. Chapter 2 summarizes the main technique of interfacial rheology we used, including the interfacial shear microrheometry (microbutton), how we utilize the image analysis to analyze the heterogeneous structure at the interface, and how to measure macro-rheology and heterogeneous structure using the rheometer. Chapter 3 focuses on the pure asphaltene adsorption, without varying any experimental parameters such as asphaltene concentration and oil composition, to have an initial understanding about how asphaltene adsorption impacts the interfacial rheology and structure, which stabilize the emulsion drop. Chapter 4 studies how the sample demulsifier ethylcellulose (EC) prevents asphaltene from forming a stiff layer and soften the pre-existing asphaltene layer. The impact of EC on emulsion drop and bulk rheology is also investigated. Chapter 5 starts to characterize the possible parameters which can influence asphaltene adsorption, including the selection of model oil composition, asphaltene concentration, the aromatic fraction of oil phase, asphaltene aggregates, and the measuring parameter such as frequency and strain. Chapter 6 utilizes various PO-EO-PO block copolymers as demulsifiers to prevent asphaltene adsorption and soften the asphaltene layer to quantify how molecular structure impacts the demulsifier performance on the interfacial layer. Chapter 7 concludes the results from this study.

Chapter 2

Interfacial shear rheology

2.1 Interfaical shear microrheometry: Microbutton

2.1.1 Design of microbutton probes

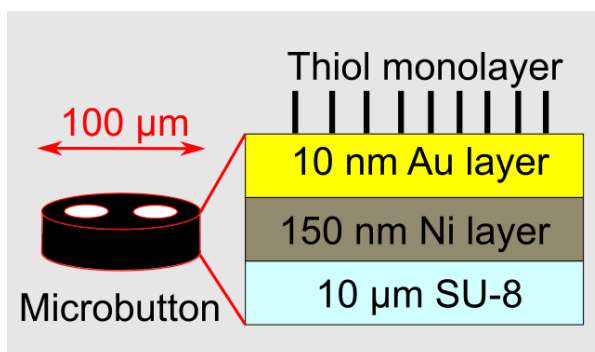


Figure 2.1: Side-view of the microbutton. SU-8 forms the hydrophilic base. Nickel layer makes the microbutton ferromagnetic. Gold facilitates the attachment of hydrophobic thiol monolayers to make the microbutton amphiphilic.

Interfacial microrheology is measured using the ferromagnetic microbutton technique described in the previous work of Squires group[81, 129, 61, 66]. The $100\mu\text{m}$ diameter microbuttons used in this study are composed of multiple layers as illustrated in Fig. 2.1. A $10\ \mu\text{m}$ thick SU-8 photoresist (MicroChem Corp.) layer composes the hydrophilic

side of the microbutton. The photoresist layer is coated with a 150 nm nickel layer to provide ferromagnet, and another 10 nm gold layer is coated to anchor the hydrophobic thiol monolayer (1H, 1H, 2H, 2H, perfluorooctanethiol). The four layers of microbutton result in an amphiphilic, ferromagnetic probe that can attach at the water-oil interface and responds to the magnetic field applied by the external electromagnets.

2.1.2 Electromagnetic array

In order to generate a magnetic field for applying torque on the microbutton, we designed an electromagnetic array depicted as Fig. 2.2. A pair of oppositely aligned electromagnets (1a and 1b) are connected in series and used to apply a sinusoidal magnetic field torquing the probe and shearing the interface. Electromagnets 2a and 2b are used to translate and align the microbutton. The current in the electromagnet is controlled by the custom Labview software.

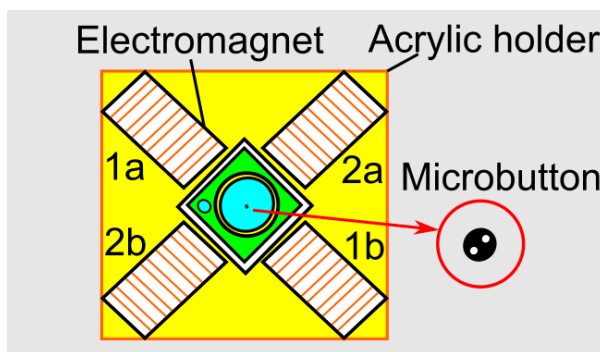


Figure 2.2: Top view schematic of the electromagnetic array around the sample cell with microbutton.

2.1.3 Oil-on-water interface and sample cell

For measuring the interfacial rheology between water and oil phases, a stable oil-water interface with microbutton needs to be established. The oil-on-water interface is

formed by a custom sample cell shown in Fig.2.3. The Delrin container has two connected channels. 200 μl of the deionized water is first injected through the side channel and pins by the Teflon tape at the top of the center channel, forming a flat water surface. A microbutton is then placed on the water surface and its magnetic moment is calibrated by drag resistance provided by water. Finally, 40 μl of the oil phase is gently added on top to form the oil-water interface. A cover glass is placed on the acrylic wall to prevent evaporation. After each measurement, the sample cell is cleaned using toluene, isopropyl, alcohol and water.

2.1.4 Water-on-oil interface and sample cell

In addition to the oil-on-water interface, we also design a sample cell for forming stable water-on-oil interface in order to investigate the gravity effect on asphaltene adsorption. The water-on-oil interface is obtained by modifying the oil-on-water sample cell illustrated in Fig. 2.3. Figure 2.4 (a) first shows how we established a water-on-air interface. One end of the acrylic-made capillary is sealed by the cover glass to form a dead-end capillary. This diameter of the capillary is smaller than the capillary length of the water. After the water is filled in the capillary, the microbutton is deposited on the water surface. The dead-end capillary is then placed on the Delrin sample cell and the capillary force hold water in the capillary. After the water-on-air interface is established on the Delrin sample cell, oil is injected through the side channel by a transfer pipette, shown in 2.4 (b). The level of the oil phase is raised carefully to contact with water phase, forming stable water-on-oil interface.

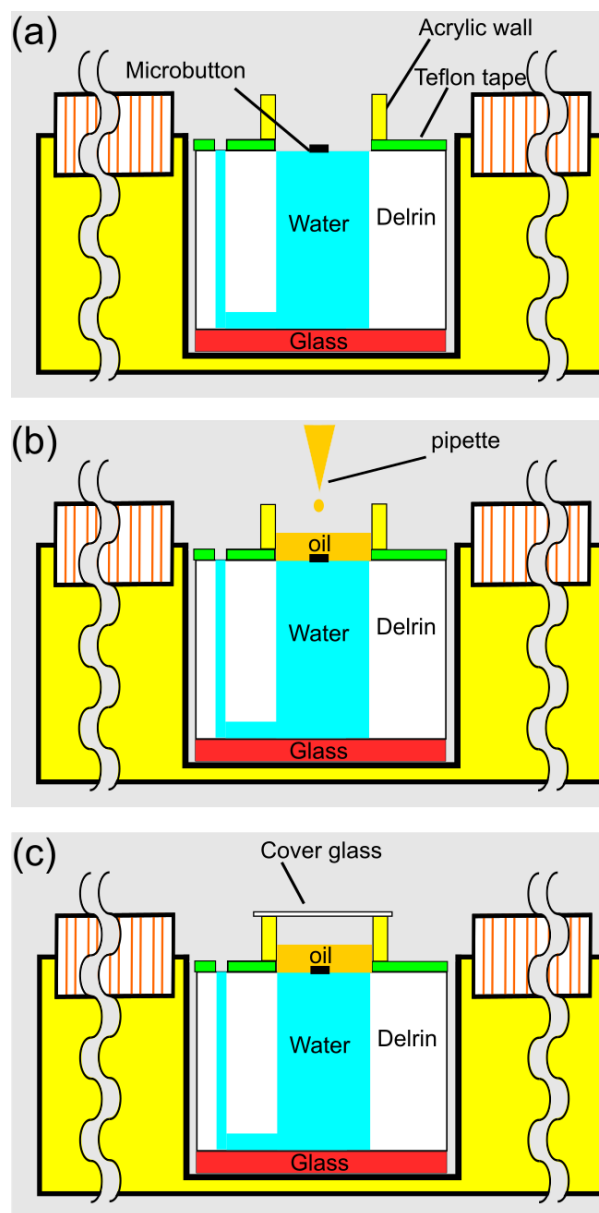


Figure 2.3: Side view of the oil-on-water sample cell. The water level in the central channel is pinned by the Teflon tape and controlled via the side channel. The microbutton is first placed in the central channel and oil phase is added from the top by a transfer pipette. The acrylic wall and cover glass prevent evaporation.

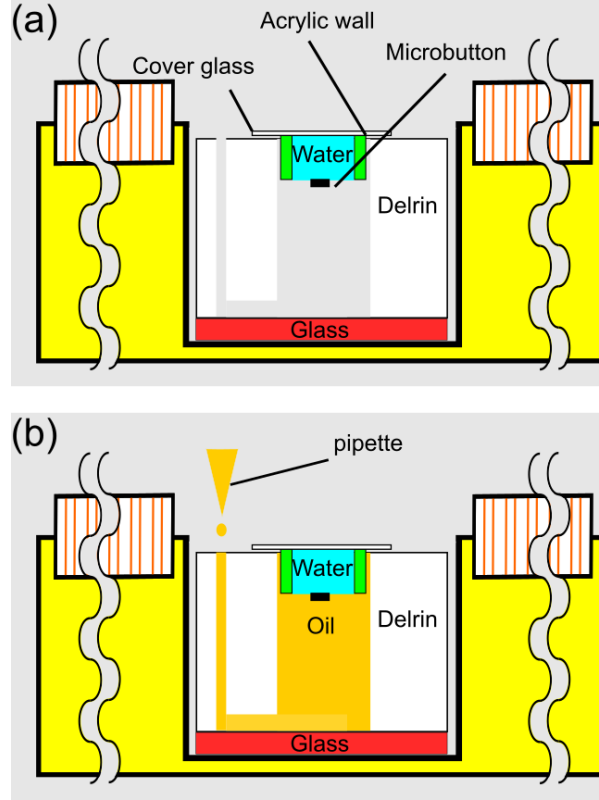


Figure 2.4: Side view of the water-on-oil sample cell. The water is pinned by a acrylic wall with one side sealed by cover glass, and the microbutton is placed on the water phase. The whole geometry is then placed on the main channel and the oil phase is injected from side channel to let water and oil contact.

2.1.5 Rheology measurement: Theory

We designed a custom Labview program to control the alternating current passed through electromagnets 1a and 1b for generating a sinusoidal magnetic field, $B = B_0 e^{i\omega t}$ to rotate the microbutton. The interfacial layer and microbutton are visualized by a bright-field microscope (Eclipse 80i, Nikon) connected to a CCD camera (CV-A10CL, JAI) to record images. If the imposed magnetic field is aligned perpendicular to the magnetic moment of the probe, $\vec{m}$, The magnitude of the torque applied to the microbutton, Γ , is:

$$\Gamma = \left| \vec{m} \times \vec{B} \right| \approx m B_0 e^{i\omega t} \quad \text{for } \vec{m} \perp \vec{B}. \quad (2.1)$$

If the angle between magnetic field and magnetic moment is not perpendicular but a value χ between 0 and $\pi/2$, Γ is then corrected by $\sin \chi$. The two ‘buttonholes’ of the microbutton are tracked to record its oscillating angular displacement, $\Delta\theta(t)$:

$$\Delta\theta(t) = \Delta\theta_0 e^{i(\omega t - \delta)}, \quad (2.2)$$

where $\Delta\theta_0$ is the amplitude of the angular displacement and δ is the phase lag relative to the applied torque depending on the interfacial properties. The complex rotational drag resistance, ξ_R^* , is then obtained by:

$$\xi_R^* = \frac{mB_0 e^{i\delta}}{i\omega \Delta\theta_0}, \quad (2.3)$$

The rotational drag resistance includes the contributions from the bulk phases and the interface. The relative magnitudes of interfacial drag and bulk phase drag can be characterized by the Boussinesq number, which is:

$$Bo = \frac{\eta_s}{\eta a}, \quad (2.4)$$

where a is the radius of the microbutton, η_s is the interfacial viscosity and η represents the sum of the viscosities of water and oil phases.

When $Bo \ll 1$, bulk phase drag dominates the contribution, and the rotational resistance is given by $\xi_R = 16\eta a^3/3$ [130]. This relation facilitate the calibration of magnetic moment by comparing the apparent drag resistance at the clean water-air surface in the low Boussinesq number limit and bulk viscosity of water. Equating equation (2.3) to ξ_R in the limit of $Bo \ll 1$ and rearranging gives

$$m = \frac{16\eta a^3 \omega \Delta\theta_0}{3B_0 \sin \delta}. \quad (2.5)$$

After the magnetic moment is calibrated, oil phase contacts with water and asphaltene start to adsorb. When the surface-active material adsorbs and interface becomes stiffer, where drag along the probe perimeter dominates and $Bo \gg 1$, the drag resistance approaches the limit $\xi_R = 4\pi\eta_s a^2$ [130]. Equating this form of ξ_R with equation 2.3 gives another expression for the complex interfacial viscosity, η_s^* ,

$$\eta_s^* = \frac{mB_0 e^{i\delta}}{i\omega \Delta\theta_0 4\pi a^2}, \quad (2.6)$$

this can be related to the interfacial complex modulus, G_s^* , via:

$$G_s^*(\omega) = i\omega\eta_s^*(\omega) = G' + iG'' = \frac{mB_0}{4\pi a^2 \Delta\theta_0} (\cos \delta + i \sin \delta). \quad (2.7)$$

$|G_s^*|$ quantifies the stiffness of the interface, and δ characterizes its viscous or elastic nature. When $\pi/4 < \delta < \pi/2$, the interface behaves more like a viscous liquid, while $0 < \delta < \pi/4$ represents more elastic behavior. For most of the experiments described in this study, the frequency is fixed at 1 Hz and the magnetic field amplitude, B_0 , is maintained at a small angular strain $\Delta\theta_0$ ($0.3\% \pm 0.02\%$, or $\sim 1^\circ$) to prevent damage or yielding of the interfacial layer.

2.1.6 Rheological measurement: Practical calculation and error analysis

In this section, we describe how to extract the function of magnetic field and angular displacement in equation 2.1 and 2.2 from the signal we obtained and how to estimate the error of measurement. When the microbutton is sheared sinusoidally, we first record angular displacement $\Delta\theta(t)$ and magnetic field $B(t)$ as a function of time. In order to extract the amplitude and phase angle of $\Delta\theta(t)$ and $B(t)$, least squared root method is

applied to fit $\Delta\theta(t)$ and $B(t)$ by a sinusoidal curve $y(t)$.

For any sinusoidal curve $y(t)$, we first linearize the function as:

$$y(t) = X\hat{\beta} = a \sin(\omega t) + b \cos(\omega t) + c \quad (2.8)$$

where X is the matrix of $\sin(\omega t)$, $\cos(\omega t)$ and constant and $\hat{\beta}$ is the matrix of the fitted parameter a , b and c . If there are n sampling points for $y(t)$, the residual of the fitting become:

$$R^2 = \sum_i^n [y_i - (a \sin(\omega t_i) + b \cos(\omega t_i) + c)]^2 \quad (2.9)$$

To apply the least square root method, the derivatives of R^2 with respect to a , b , and c are calculated:

$$\frac{\partial R^2}{\partial a} = -2 \sum_i^n [y_i - (a \sin(\omega t_i) + b \cos(\omega t_i) + c)] \sin(\omega t_i) \quad (2.10)$$

$$\frac{\partial R^2}{\partial b} = -2 \sum_i^n [y_i - (a \sin(\omega t_i) + b \cos(\omega t_i) + c)] \cos(\omega t_i) \quad (2.11)$$

$$\frac{\partial R^2}{\partial c} = -2 \sum_i^n [y_i - (a \sin(\omega t_i) + b \cos(\omega t_i) + c)] \quad (2.12)$$

a , b , and c can be determined when the above three derivatives are equal to zero:

$$a \sum_i^n \sin^2(\omega t_i) + b \sum_i^n \sin(\omega t_i) \cos(\omega t_i) + c \sum_i^n \sin(\omega t_i) = \sum_i^n y_i \sin(\omega t_i) \quad (2.13)$$

$$a \sum_i^n \sin(\omega t_i) \cos(\omega t_i) + b \sum_i^n \cos^2(\omega t_i) + c \sum_i^n \cos(\omega t_i) = \sum_i^n y_i \cos(\omega t_i) \quad (2.14)$$

$$a \sum_i^n \sin(\omega t_i) + b \sum_i^n \cos(\omega t_i) + cn = \sum_i^n y_i \quad (2.15)$$

These equations can be re-written in the matrix form as:

$$\begin{bmatrix} \sum_i^n \sin^2(\omega t_i) & \sum_i^n \sin(\omega t_i) \cos(\omega t_i) & \sum_i^n \sin(\omega t_i) \\ \sum_i^n \sin(\omega t_i) \cos(\omega t_i) & \sum_i^n \cos^2(\omega t_i) & \sum_i^n \cos(\omega t_i) \\ \sum_i^n \sin(\omega t_i) & \sum_i^n \cos(\omega t_i) & n \end{bmatrix} \begin{bmatrix} a \\ b \\ c \end{bmatrix} = \begin{bmatrix} \sum_i^n y_i \sin(\omega t_i) \\ \sum_i^n y_i \cos(\omega t_i) \\ \sum_i^n y_i \end{bmatrix} \quad (2.16)$$

Simplify above equation, we obtain:

$$V\hat{\beta} = K \quad (2.17)$$

Using Cramer's rule, we can solve $\hat{\beta}$ (namely, a , b , and c). The amplitude of $y(t)$, y_0 , is:

$$y_0 = \sqrt{a^2 + b^2} \quad (2.18)$$

so the amplitude of angular displacement $\Delta\theta_0$ and magnetic field B_0 can then thus be obtained from calculating a , b and c with respect to the angular displacement and magnetic field signal. The phase of $y(t)$, δ_y , can also be derived as:

$$\delta_y = \cos^{-1} \frac{a}{\sqrt{a^2 + b^2}} \quad (2.19)$$

the phase lag δ between angular displacement and magnetic field is $|\delta_B - \delta_{\Delta\theta}|$. The equation of magnetic field and angular displacement in equation 2.1 and 2.2 can then be obtained from the signal we record.

In order to estimate the goodness of the fitting, the variance of $\hat{\beta}$ is calculated:

$$\text{var}(\hat{\beta}_j) = \frac{R^2}{n - m} \left([X^T X]^{-1} \right)_{jj} = \frac{R^2}{n - m} (V^{-1})_{jj} \quad (2.20)$$

where $m = 3$ for three fitted parameter a , b , and c and j can be 1, 2 and 3 with respect to a , b , and c . With the variance of each component of $\hat{\beta}$, we can then get the standard deviation σ for each parameter σ_a , σ_b and σ_c , and quantify the uncertainty of $\Delta\theta(t)$ and $B(t)$.

The uncertainty of $\Delta\theta(t)$ and $B(t)$ contribute to the uncertainty of rheological measurement. For any function $Q(a, b, \dots, z)$, if the uncertainties (standard deviation) in $a, b, \dots, z$ are independent, then the uncertainty (standard deviation) in $Q(a, b, \dots, z)$ is

$$\sigma_Q = \sqrt{\left(\frac{\partial Q}{\partial a} \sigma_a \right)^2 + \dots \left(\frac{\partial Q}{\partial z} \sigma_z \right)^2} \quad (2.21)$$

so the standard deviation for the rheological measurement such as $|G_s^*|$ and δ can thus be obtained through σ_A , σ_B and σ_C with respect to $\Delta\theta(t)$ and $B(t)$. In the study, we trust the rheological response when the stand error is under 10% of the measured value.

2.2 Stain tracking and mechanical heterogeneity

2.2.1 Particle tracking at water-oil interface

The C7 asphaltenes form natural aggregates at the water-oil interface which can be tracked by particle tracking algorithm[131], enabling the analysis of the interfacial angular strain field. In experiments without aggregates, we instead disperse polyethylene particles (Cospheric, diameter 1 to 4 μm) on the water surface as artificial tracers before water and oil contact, to facilitate the study of strain field. We first obtain the angular

displacement $\Delta\theta(t, r)$ as a function of time for each identified particles located at distance r from the center of the microbutton. A fast Fourier transform (FFT) is then used on $\Delta\theta(t, r)$ to extract the amplitude as a function of frequency. The amplitude at driving frequency we apply on the microbutton (usually is 1 Hz) is selected as the displacement amplitude $\Delta\theta$ for this aggregate or particle. By calculating $\Delta\theta$ for all the tracers at the interface, we can then map the spatial distribution of interfacial angular strain around the microbutton probe. This strain field mapping reveals mechanical heterogeneities within the interfaces.

2.2.2 Strain decay for a rotating cylinder

The interfacial strain field obtained by tracking the asphaltene aggregates or particles can encode a map of the stiffness near the probe, from which we can detect mechanical structure of the interfacial film.

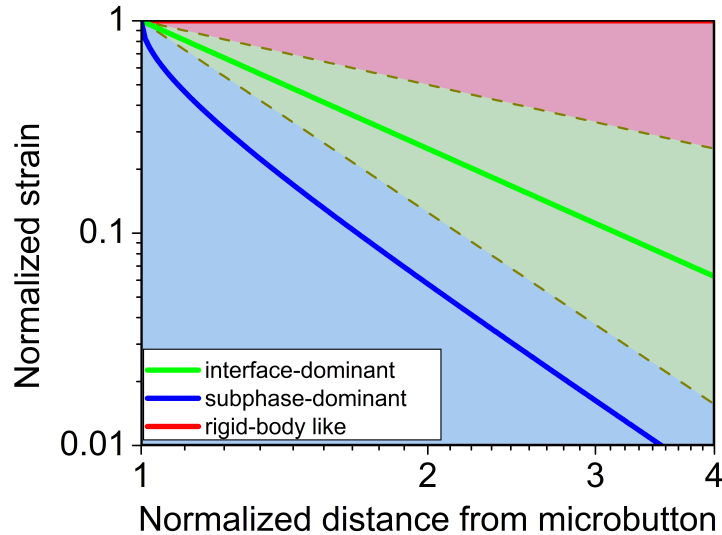


Figure 2.5: Strain decay from a rotating cylinder. Red, green and blue lines are the theoretical curves for rigid-body, interface-dominated, and bulk-phase-dominated behavior respectively. The dark yellow dashed lines divide the strain field into three qualitative regions representing the three different dynamic behaviors.

Goodrich[132] derived the Boussinesq-number-dependent strain field for a rotating disk at an interface. For a homogeneous interface, three ideal cases can appear: interface-dominated drag ($Bo \gg 1$), bulk-phase-dominated drag ($Bo \ll 1$), and rigid-body rotation. When the drag on the disk is dominated by the interface, the angular strain decays as

$$\frac{\Delta\theta(r)}{\Delta\theta_0} = \left(\frac{r}{a}\right)^{-2}, \quad (2.22)$$

where $\Delta\theta(r)$ is the amplitude of angular displacement at a distance r from the probe center. When there is no surface-active material at the interface or slip between interfacial layer and the probe, the drag is bulk-phase-dominated. The strain decay for this case becomes

$$\frac{\Delta\theta(r)}{\Delta\theta_0} = \frac{2}{\pi} \left[\frac{r}{a} \sin^{-1} \frac{a}{r} - \left(1 - \frac{a^2}{r^2}\right)^{\frac{1}{2}} \right], \quad (2.23)$$

which is approximated for $r \gg a$ by:

$$\frac{\Delta\theta}{\Delta\theta_0} \rightarrow \frac{4}{3\pi} \left(\frac{r}{a}\right)^{-3} \quad (2.24)$$

When surface-active material forms a rigid structure that attaches to the probe, the interface does not shear, and the surrounding structure behaves as rigid body. In this case, no angular strain decay is observed.

Figure 2.5 illustrates the sample figure for the azimuthal-averaged strain decay. The theory profile for rigid-body, interface-dominated and bulk-phase-dominated strain are depicted as red, green and blue lines respectively. Dashed lines are drawn between rigid-body, interface-dominated, and bulk phase-dominated decay to define distinct qualitative behaviors according to:

$$\frac{\Delta\theta}{\Delta\theta_0} > \left(\frac{r}{a}\right)^{-1}, \text{ (rigid-body, red zone)} \quad (2.25)$$

$$\left(\frac{r}{a}\right)^{-1} > \frac{\Delta\theta}{\Delta\theta_0} > \left(\frac{r}{a}\right)^{-3}, \text{ (interface-dominated, green zone)} \quad (2.26)$$

$$\frac{\Delta\theta}{\Delta\theta_0} < \left(\frac{r}{a}\right)^{-3}, \text{ (bulk phase-dominated, blue zone)} \quad (2.27)$$

Through measuring azimuthal-averaged strain decay and comparing our observations to these three ideal cases, we can reveal the overall mechanical structure at the water-oil interface.

2.2.3 Map of mechanical heterogeneity

The azimuthal-averaged strain decay only reveals the overall property of the interface. If the interface is not homogeneous, this azimuthal-averaged strain decay can not reflect the real mechanical structure at the interface. To further elucidate the heterogeneity, we map the strain amplitude associated with aggregate or particle to visualize the rheological heterogeneity. Local stiffness is encoded in an apparent decay exponent, n_{app} , at the location of each aggregate or particle:

$$n_{app} = \frac{\log\left(\frac{\Delta\theta}{\Delta\theta_0}\right)}{\log\left(\frac{r}{a}\right)}, \quad (2.28)$$

calculated as though the strain decays with power-law relation. If a region displays perfectly rigid-body, interfacial-dominated, or bulk phase-dominant behavior, n_{app} is 0, -2, or -3 respectively. To simplify the mapping, we discretise n_{app} by labeling the local stiffness to be rigid-body if $n_{app} > -1$, interface-dominated if $-3 < n_{app} < -1$ and bulk phase-dominated if $n_{app} < -3$, which respect to the red, green and blue region in Fig. 2.5. The identified aggregates or particles generate the Voronoi cell at the interface. The interfacial area in the Voronoi cell belonging to each aggregate is then colored according

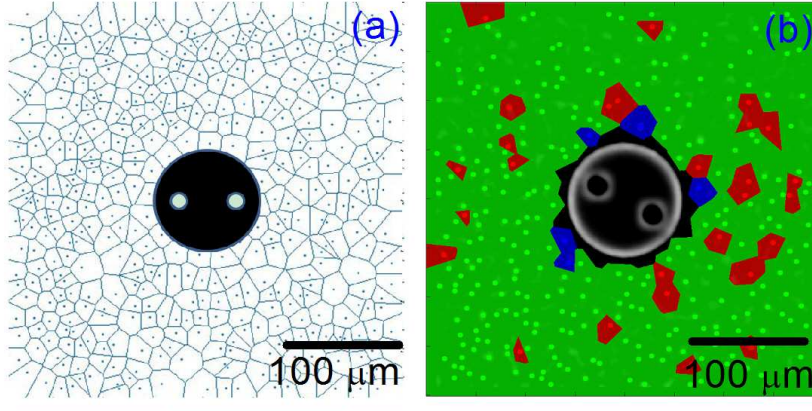


Figure 2.6: (a) Voronoi construction obtained from the particle positions. (b) Example maps of local stiffness for water-oil interface. Red, green and blue represent rigid-body, interface-dominated and bulk phase-dominated regions. The scale bar in the lower right corner represents 100μm.

to this mapping. Red, green and blue represent rigid-body, interface-dominated and bulk phase-dominated rheology respectively. An example of Voronoi cell and heterogeneous color map is shown in Fig.2.6

2.3 Interfacial shear macrorheometry: Rheometer with double wall ring

2.3.1 AR-G2 magnetic bearing rheometer with double wall ring

The microbutton microrheometry quantify the micron scale rheology and mechanical structure. In addition, although microbutton is more sensitive than most of the commercial rheometer, the microbutton encounter the upper limit of measurement since the current cannot exceed 2 amperes. This feature makes microbutton unable to track the late stage of asphaltene adsorption since the interfacial film is too stiff and no distinguishable angular displacement can be observed.

In order to characterize the interface at the larger scale and late stage of asphaltene

adsorption, a macrorheometry is needed. The AR-G2 Magnetic Bearing Rheometer is the commercial instrument built by TA instrument, shown in Fig. 2.7. This rheometer



Figure 2.7: Rheometer and the double wall ring. The photo is adapted from TA instrument website

is a combined motor and transducer instrument, which can rotate a shaft by applying the torque produced through the induction motor. Various geometries such as cone and plate, Couette, bicone, and double wall ring can be connected to the shaft for measuring the bulk or interfacial shear rheology. The double wall ring (DWR) geometry we use in this study is established by Vandebriel *et al.* [79] and commercialized as a part of AR-G2 rheometer. The DWR is a platinum-made ring with a radius of 35 mm, and the cross section of DWR is square-edged so the ring can pin the water-oil interface. The design of the ring geometry minimizes the contact area per perimeter so high Bo can be obtained for measuring interfacial shear rheology. [79] The sensitive limit of the double wall ring, however, is $5 \mu\text{Ns/m}$, which is less sensitive than the microbutton (0.01 Ns/m). But the

motor enable rheometer to characterize the interface when the interfacial layer is stiffer than the upper limitation of microbutton.

To form the stable oil-on-water interface with the ring pinning the interface, the water phase is first injected into the Delrin sample cell through the transfer pipette. The edge of the sample cell can pin the water surface so the curvature of the water surface can be adjusted manually. After a flat water surface is obtained, the ring is then placed on the water surface and the water phase is adjusted again to maintain a flat surface. 3 ml oil phase is then deposited from the top of the ring uniformly and carefully over the whole sample cell to get the stable water-oil interface

2.3.2 Custom visualization for macrohreometry

The microbutton microrheometry can measure rheology and track the evolution of mechanical heterogeneous structure at the interface simultaneously due to the visualization of the interface. For the rheometer and DWR, the visualization of water-oil interface is obtained by a home-made optical microscope and camera system shown in Fig. 2.8

The Delrin sample cell for forming the water-oil interface is re-made using the laser cutting technique. In order to facilitate the imaging system, the bottom of the sample cell is made by transparent acrylic plate and sealed with Delrin part using ultraviolet light adhesive (NOA 81, Norland Products). A custom lamp and two lenses with different focal length are built at the top of the sample cell to apply Kohler illumination on the water-oil interface. The two aperture in the lighting system can control the intensity and the size of lighting at the interface.

An infinity-corrected 4x Nikon objective is placed under sample cell to observe the interface. The tube lens followed by the objective focuses the image at the sensor of the CCD camera. The magnification of the image can be controlled by using a tube lens with

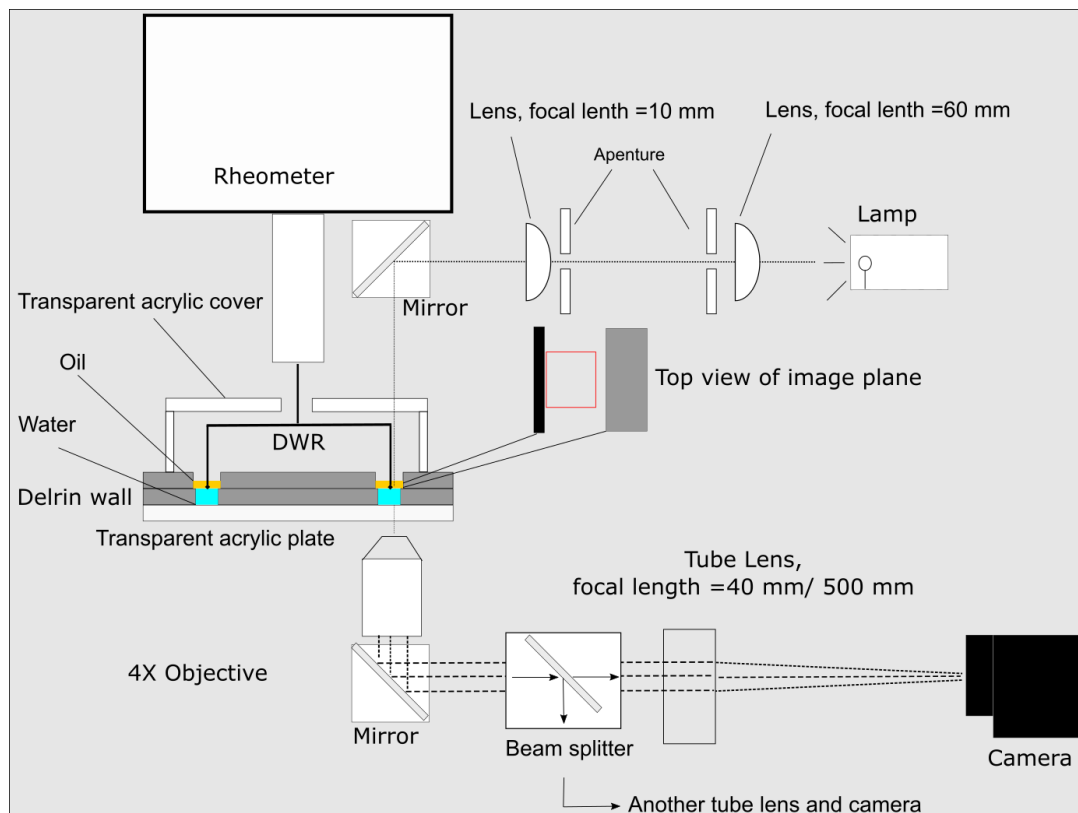


Figure 2.8: Rheometer and visualization setup. A set of lamp, lens and aperture is built on the top of water-oil sample cell to illuminate the interface. The sample cell is re-made and using transparent acrylic as the bottom plate to facilitate the visualization. A system of objective and tube lens is built under the sample cell to focus the image of the interface into the CCD camera. A beam splitter is placed between mirror and tube lens to separate the image to another tube lens with different focal length to visualize the interface with two different magnification simultaneously.

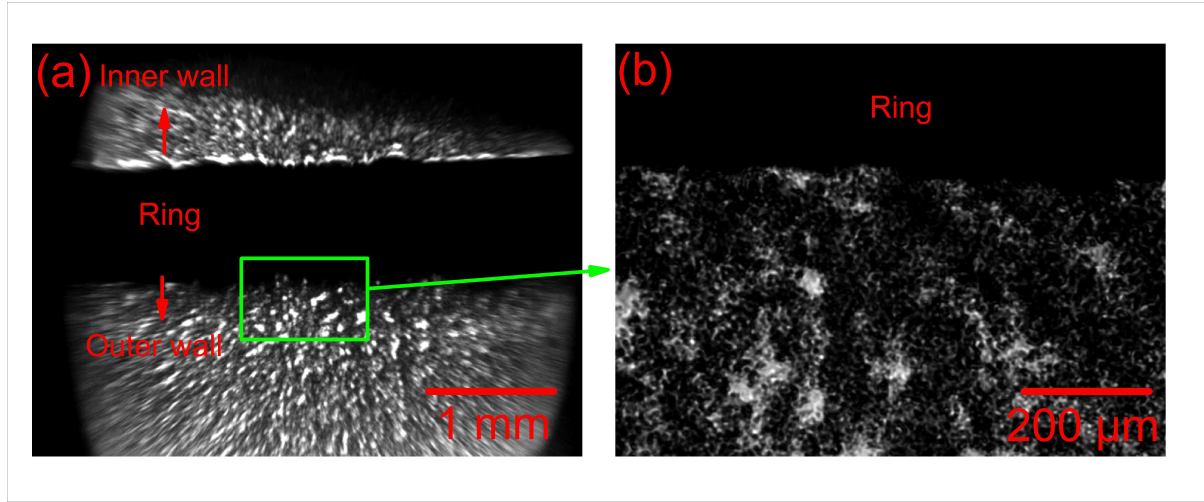


Figure 2.9: Visualization of DWR and asphaltene interface using (a) tube lens with 40 mm focal length and (b) tube lens with 500 mm focal length simultaneously. (b) is the interface in the green square in (a)

different focal length. A beam-splitter is placed between the tube lens and objective to separate the image to another tube lens and camera for visualizing the same interface with different magnification. Figure 2.9 shows the sample visualization of the water-oil interface with asphaltene aggregates. The two photos (a) and (b) of Fig. 2.9 are the images obtained simultaneously through tube lens with focal length 40 mm and 500 mm respectively. The green box in Fig. 2.9 (a) points out the region shown in Fig. 2.9 (b). With tube lens with shorter focal length, the magnification of the image is smaller and wider interface can be observed.

2.3.3 Heterogeneity analysis for macrorheometry

The mechanical heterogeneity of the water-oil interface is analyzed through a similar idea as microbutton rheometry shown in the previous section. The theoretical curve of strain decay for rigid-body, interface-dominant and bulk-phase dominant rotation is calculated by Vandebriel *et al.* [79] and re-plotted in Fig. 2.10. Red, green and blue curves in Fig. 2.10 represent rigid-body, interface-dominated and bulk-phase dominated

behavior respectively. We use the two dark yellow line to separates the three characteristic behaviors at the interface, which are:

$$\frac{\Delta\theta}{\Delta\theta_0} > \left(\frac{r}{a}\right)^{-4.5}, \text{ (rigid-body, red zone)} \quad (2.29)$$

$$\left(\frac{r}{a}\right)^{-4.5} > \frac{\Delta\theta}{\Delta\theta_0} > \left(\frac{r}{a}\right)^{-18}, \text{ (interface-dominated, green zone)} \quad (2.30)$$

$$\frac{\Delta\theta}{\Delta\theta_0} < \left(\frac{r}{a}\right)^{-18}, \text{ (bulk phase-dominated, blue zone)} \quad (2.31)$$

The apparent decay exponent n_{app} define in equation 2.28 of each aggregate is also calculated to visualize the local stiffness at the water-oil interface for DWR geometry. To simplify the mapping, we discretise n_{app} by labeling the local stiffness to be rigid-body if $n_{app} > -1$, interface-dominated if $-3 < n_{app} < -1$ and bulk phase-dominated if $n_{app} < -3$, which respect to the red, green and blue region in Fig. 2.10. The Voronoi cell belonging to each aggregate is also colored according to this mapping. Red, green and blue represent rigid-body, interface-dominated and bulk phase-dominated rheology respectively.

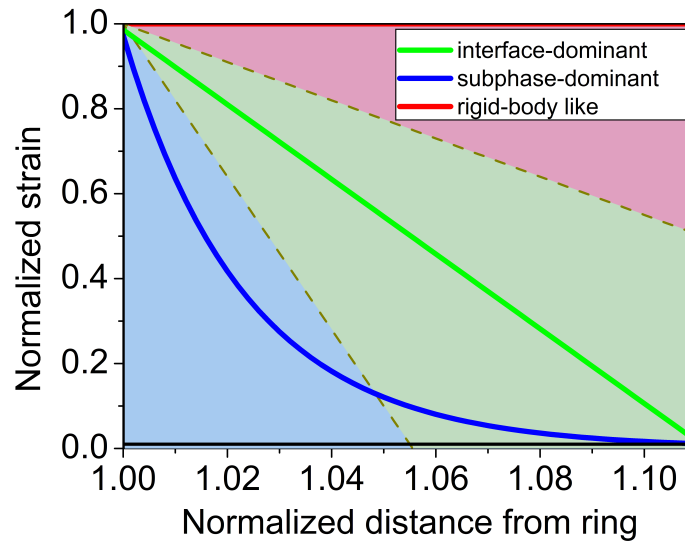


Figure 2.10: Strain decay for the DWR geometry. Red, green and blue lines are the theoretical curves for rigid-body, interface-dominated, and bulk phase-dominated behavior respectively. The dark yellow dashed lines divide the strain field into three qualitative regions representing the three different dynamic behaviors.

Chapter 3

Interfacial rheology and heterogeneity of asphaltene adsorption at water-oil interface

3.1 Overview

In this chapter, we first study the pure asphaltene adsorption at the oil-on-water interface using C7 asphaltene in the decane-toluene mixture ‘dectol’. The composition of oil phase (e.g. the concentration of asphaltene, ratio of aromatic solvent and aliphatic compound) and the parameter of experimental apparatus (e.g. frequency and strain of oscillation) are fixed in this chapter. With this model system, we can have an initial understanding of asphaltene adsorption and its property at the water-oil interface. We will discuss the parameters which impact the asphaltene adsorption in chapter 5.

The microbutton rheometry is first used to study how the asphaltene adsorption influences the interfacial stiffness and viscoelasticity on the micron scale. In order to reveal the mechanical structure of the interfacial film during the rheological measurement,

we develop the algorithm based on strain decay to analyze the visualization of the water-oil interface along with rheology measurement. The double wall ring rheometry is then applied to reveal the interfacial rheology and heterogeneous structure in the millimeter scale, and the result is compared to that of micron scale observed using microbutton rheometry. In order to investigate the role of rheology on emulsion stabilization, a simple drop coalescence experiment is designed to correlate the interfacial rheology and drop coalescence dynamic when the interface ages with asphaltene in different time scale.

3.2 Materials

The oil phase ‘dectol’ used in this chapter is composed of toluene (Sigma-Aldrich, HPLC grade, purity=99.9%) and decane (Sigma-Aldrich, anhydrous, purity $\geq 99\%$) at a volume ratio of 1 to 4 and contains 0.1 wt% C7 asphaltene. The C7 asphaltene is precipitated by n-heptane (Sigma-Aldrich, anhydrous, purity $\geq 99\%$) from bitumen (Alberta, Canada). 1 g bitumen is first dissolved in 40 ml n-heptane and agitated on a horizontal shaker for 2 hours. The solution is then filtered by Whatman Grade 4 filter paper, and the asphaltene is washed by n-heptane until the rinses are clear. The asphaltene solid is further dried by vacuum to remove the residual n-heptane.

The C7 in dectol is prepared by dissolving asphaltenes in toluene and sonicating for 10 minutes. Decane is then mixed with C7 in toluene and the whole solution is sonicated again for a further 10 minutes. The aqueous phase is deionized water (Milli-Q, with resistivity 18.2 M Ω cm and total organic carbon < 5 ppb). Since the oil phase contains less toluene, asphaltenes precipitate in the oil phase, solutions are sonicated for 10 minutes before water and oil contact. Asphaltene solutions are discarded 12 hours after preparation to avoid long-term degradation such as the oxidation reported in the literature[133, 77]

3.3 Microrheology: Aging of asphaltene adsorption at water-oil interface

We first study the impact of asphaltene adsorption on the mechanical properties of the oil-on-water interface, using microrbutton and the sample cell illustrated in Fig. 2.3. Figure 3.1(a) shows the evolution of complex modulus $|G_s^*|$ in seven different experimental trials. Each experiment is prepared following the identical procedure described in the previous section, and all trials stiffen to $|G_s^*| \sim 10 \mu\text{N/m}$ in 5-10 minutes. The rheology measurement stopped when the probe no longer responds detectably to the maximum applied current because the software can no longer extract reliable sinusoidal strain. The maximum measurable $|G_s^*|$ varies trial by trial due to variations in magnetic moment m between microbuttons.

Although all the trials exhibit stiffening, qualitative and quantitative differences in the adsorption rate and the scaling of $|G_s^*|$ with t can still be observed. Three qualitatively different behaviors are evident. For group 1 (red curves), $|G_s^*|$ exhibits a power-law increase when the interface is aging. Exponential growth occurs initially for group 2 (green curves), however, a discontinuous change following a kink in the evolution is observed. Group 3 (black curves) shows the complex modulus to increase exponentially as a function of time. Although these trials are prepared following by the identical procedure, these qualitative differences imply that simple mechanism is not able to describe asphaltene adsorption at the water-oil interface. In the following section, we will show that the interfacial layer in group 2 and 3 reflect strong mechanical heterogeneity, whereas the layers in group 1 are relatively homogeneous around the microbutton.

Research in the literature suggests that the asphaltene interfacial layers transit from viscous-dominated shear rheology to a more viscoelastic response when they age[57, 73, 75, 52]. This observation is consistent with Fig 3.1(b). Although there are some variations

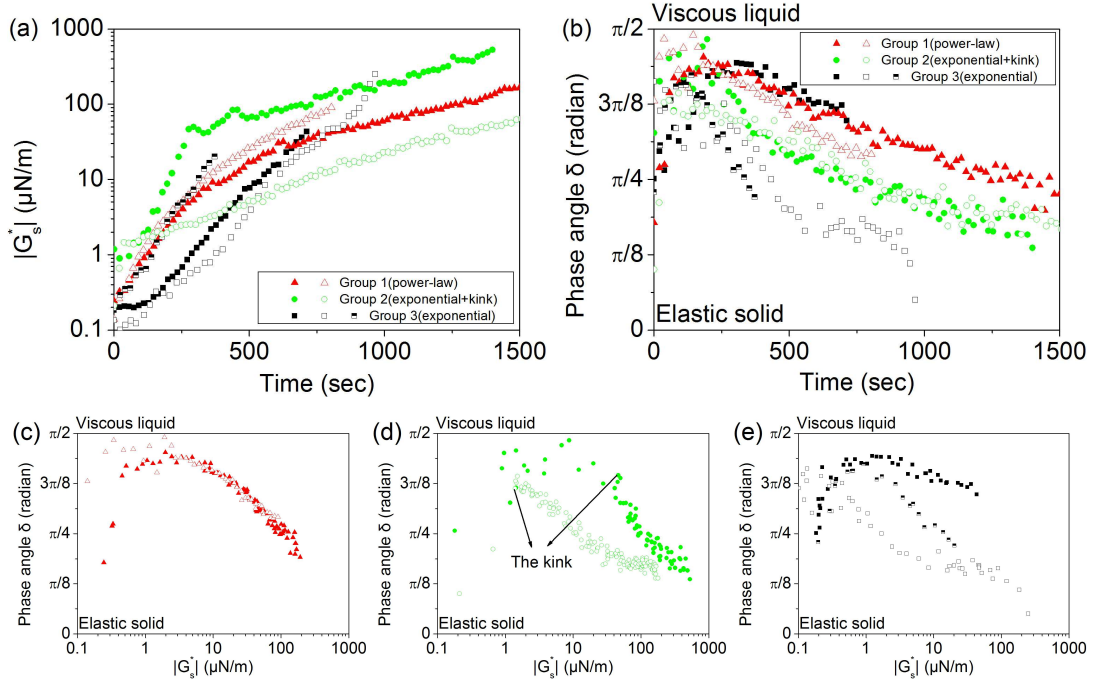


Figure 3.1: The rheology measurement at dectol-on-water interface with pure asphaltene adsorption. (a) Magnitude of the interfacial complex modulus of dectol-on-water interface with 0.1 wt% C7 asphaltene in the oil phase for 7 trials prepared identically. Group 1 (red points), group 2 (green points) and group 3 (black points) show a power-law increase, exponential increase with kink, and exponential increase respectively. (b) Evolution of phase angle of the dectol-on-water interface with 0.1 wt% C7 asphaltene in the oil phase of 7 trials prepared identically. (c), (d) and (e) Phase angle as a function of $|G_s^*|$ for group 1, 2 and 3.

at the initial stage of adsorption, the qualitative evolution of the phase angle, δ , shows viscous-liquid like response ($\delta \approx \pi/2$) at early times followed by an increase in elasticity (decrease in δ) as asphaltenes adsorb. However, similar to the case with $|G_s^*|$, there are quantitative inter-group and intra-group differences.

Figure 3.1(c), (d) and (e) shows that the evolution of viscoelasticity during adsorption cannot be described by a unique relationship between δ and $|G_s^*|$. Qualitatively, δ increases at an early time when $|G_s^*|$ is low then decreases when the interface ages and becomes increasingly elastic. Nevertheless, these features still differ from trial to trial. For example, Fig. 3.1(e) shows that phase angles of group 3 decrease differently in each

of the three experiments. This observation implies that even interfaces whose $|G_s^*|$ evolve in a similar way may have qualitatively different structures. In experiments showing a kink in the evolution of $|G_s^*|$ [Fig. 3.1 (d)], δ shows a sharp transition concurrent with a kink, and subsequently decreases rapidly with $|G_s^*|$. Interestingly, the two experiments which exhibit power law stiffening [Fig. 3.1 (c)], both of which show similar evolution in δ , suggest that these interfaces might be similar in both rheology and structure. The inconsistency in rheological evolution indicates that additional variations exist between experiments which are not captured by $|G_s^*|$ alone, requiring more detailed investigation.

3.4 Heterogeneity analysis of asphaltene layer

We first hypothesize the inconsistency in the rheology measurements can be attributed to the variation of the mechanical structure near the microbutton probe. In order to reveal the mechanical structure, the strain decay is applied to analyze the visualization we obtained along with the rheology measurement. Figure 3.2(a) shows the azimuthal-averaged strain decay measured in the group 1 experiment (red open triangles in Fig. 3.1 at 350 sec), in which $|G_s^*|$ exhibits a power-law growth. The interface is separated to eight different sectors and the corresponding strain decay of each sector is calculated. Data in all four chosen sectors collapse onto the theoretical profile, indicating interfacial-dominated behavior in these regions. The close agreement throughout the interfaces indicates a homogeneous, isotropic asphaltene layer near the probe. The other four sectors which are not plotted also collapse, supporting this interpretation.

On the contrary, Fig. 3.2(b) reveals the severe anisotropy in the strain decay for a group 2 experiment (green open circles in Fig. 3.1 at 350 sec), wherein $|G_s^*|$ increases exponentially following by a kink. The four strain decays of chosen sectors do not collapse, nor do they fit any theoretical lines. Two strain decays exhibit a primarily rigid-body

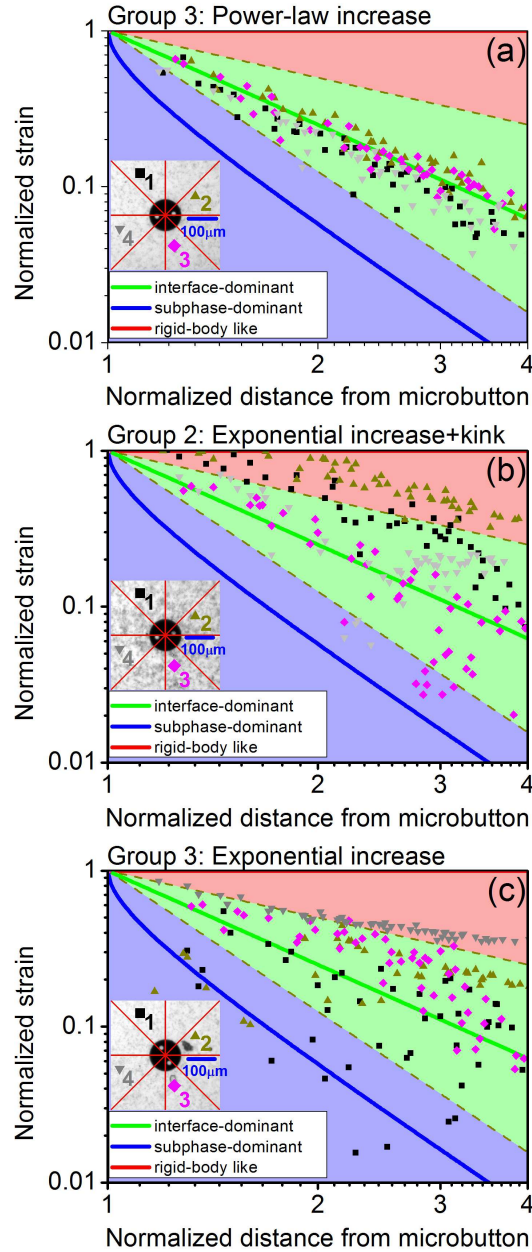


Figure 3.2: Azimuthal-averaged strain decay measured in four distinct angular sectors near the microbutton after 350 sec of asphaltene adsorption for (a) a homogeneous layer showing a power-law increase in $|G_s^*|$ (Group 1), (b) a heterogeneous layer showing an exponential increase in $|G_s^*|$ followed by a kink (Group 2) and (c) a heterogeneous layer showing an exponential increase in $|G_s^*|$ (Group 3). Red, green and blue lines are the theoretical curves for rigid-body, interface-dominated, and bulk phase-dominated behavior respectively. The dark yellow dashed lines divide the strain field into three qualitative regions representing the different dynamic behaviors. Inset: visualization of the water-oil interface showing the microbutton, the four sectors are labeled with the corresponding symbols. The artificial red lines divide the interface into eight angular sectors.

response, while the other two are scattered in the interface-dominated region. This inconsistency of strain decay suggests that the interface in the former sectors is stiffer than in the latter, a clear signature of rheological heterogeneity.

Fig. 3.2(c) illustrates another anisotropic strain decay measured in a group 3 experiment (black half open rectangles in Fig. 3.1 at 350 sec), which shows an exponential increase in $|G_s^*|$. Strain decays in three sectors are scattered between the interface and bulk phase dominated regions, while data from the fourth decays linearly in the rigid-body region. As previously, this indicates heterogeneous interfacial rheology.

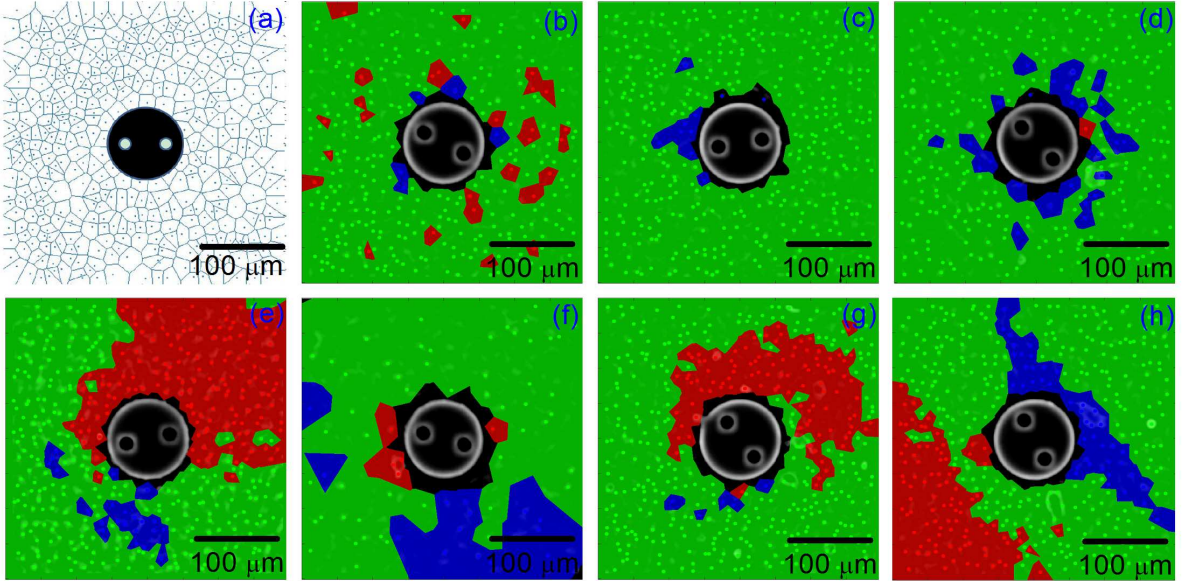


Figure 3.3: The map of local stiffness at asphaltene film (a) Example Voronoi construction obtained from aggregate positions. (b)-(h) Maps of local stiffness after 350 sec of asphaltene adsorption according to the discretization of n_{app} . (b) and (c) show experiments for which $|G_s^*|$ follows a power law, (d) and (e) depict interfaces showing an exponential increase in $|G_s^*|$ followed by a kink, and (f), (g) and (h) represent interfaces showing exponential growth of $|G_s^*|$. Red, green and blue represents rigid-body, interface-dominated and bulk phase-dominated regions. The scale bar in the lower right corner represents 100μm.

Since the interfacial structure is inhomogeneous and the azimuthal-strain decay can no longer reflect the property at the interface, we use the apparent decay exponent defined in equation 2.28 to map the local stiffness at the interface. Figure 3.3 shows the local

stiffness maps for all experiments when asphaltene adsorb for 350 seconds based on the discretization of n_{app} . Red, green and blue represent rigid-body, interface-dominated and bulk phase-dominated regions. Figure 3.3 (a) illustrates a sample map of Voronoi construction formed by the identified asphaltene aggregates at the interface. Figure 3.3 (b)-(c), (d)-(e), and (f)-(h) show the maps of groups 1, 2 and 3, respectively, which correspond to the experiments showing power-law increase, exponential growth followed by a kink, and exponential increase in $|G_s^*|$. The strain decays in Fig. 3.2 (a), (b) and (c) are mapped in Fig. 3.3 (c), (e) and (h). From the maps of Fig. 3.3, significant variations exist between experiments after the identical adsorption time. Figure 3.3 (b) and (c) confirm that power law growth of $|G_s^*|$ corresponds to fairly homogeneous interfaces, which is consistent with the isotropic strain decay in Fig. 3.2 (a) and similar rheological response in 3.1 (c). By contrast, Fig. 3.3 (e) and (h) show the coexistence of rigid-body, interface-dominated and bulk phase-dominated regions. This heterogeneity results in the anisotropic and scattered strain decays of Fig. 3.2 (b) and (c). In conclusion, the local stiffness maps reveal significant heterogeneity in adsorbed asphaltene films over tens of microns. This observation supports our hypothesis that the heterogeneous local stiffness near the probe gives rise to intra- and inter-group variations in the rheological measurements.

Figure 3.3 only demonstrate the intra-trail difference in the mechanical structure with an identical time of adsorption. In order to investigate how the general structure evolves when asphaltenes adsorb, the area fractions for rigid-body, interface-dominated and bulk-phase dominated regions for each trial are averaged based on the function of time. Figure 3.4 show this average time evolution for asphaltene adsorption experiments using three trials in which the measurements are still available after around 1500 sec adsorption. The area fraction evolutions for each individual trial is shown in Figs. 3.5. The pure C7 adsorption shows a fast initial increase in the interface-dominant region from around 70%

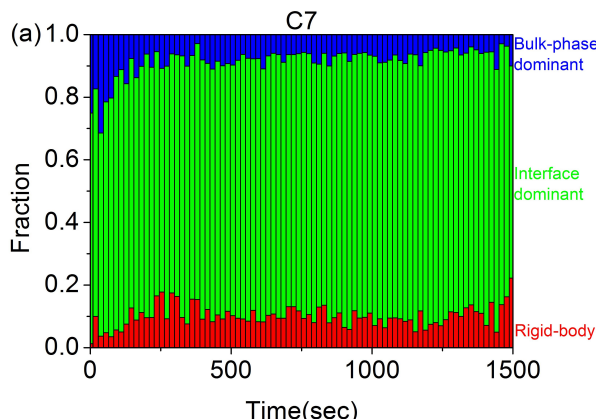


Figure 3.4: Average evolution of average area fraction of rigid-body (red), interface-dominated (green) and bulk-phase dominated (blue) regions for (a) C7 only, (b) EC only and (c) premixed C7 and EC interface.

to 90% of the interfacial area. The bulk-phase-dominated area correspondingly decreases from around 25% to 5% and a small increase in rigid area is suggested. This trend indicated that during C7 asphaltene adsorption, more surface active material adsorb and form stiff structure at the water-oil interface. Nevertheless, Fig. 3.5 suggest that the evolution of mechanical structure still varies trial by trial, indicating that the adsorption is not a homogeneous process.

3.5 Discussion of asphaltene adsorption

The asphaltene films have been studied using interfacial shear rheology previously for experiments performed by the bicone geometry[71, 52, 72] and a double wall ring geometry[57, 73, 75] but with different asphaltenes and oils. The increasing modulus and the transition from viscous-dominated to elastic-dominated behavior reproduce the results in the literature. However, the material differences between their studies make any quantitative comparison challenging. It is likely that the properties of an asphaltene film and the dynamics of its formation depend strongly on the solvent composition, water

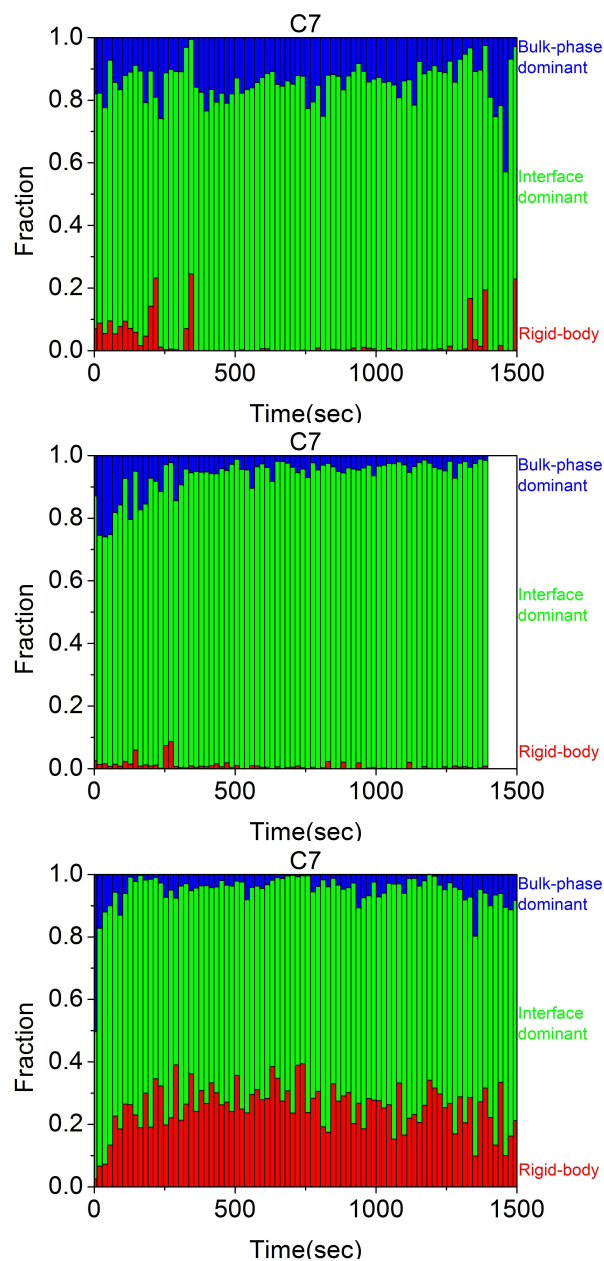


Figure 3.5: Area fraction evolution of rigid-body(red), interface-dominant(green) and bulk-phase dominant(blue) region for the pure C7 interface.

composition, asphaltene concentration and composition. These effects will be studied in the following section.

In addition to the oil composition, the difference on rheometry probe also brings a difficulty to compare our result to the literature. Rheological measurements are inherently influenced by the length scale of the probe. The radius of the bicone and double wall ring geometries employed in other experiments are 34 mm and 35 mm respectively, which are significantly larger than the 50 μm microbutton. This feature might limit the detection of these micron-scale rheological heterogeneities. If the scale of heterogeneity is only 10-100 μm in size as shown in Fig. 3.3, the influence of heterogeneity on this scale is effectively averaged out in macroscopic measurements using the bicone or double wall ring. However, in the following section, we will prove that the heterogeneity actually exist also in the scale of millimeter, but this feature is never reported in the literature.

Moreover, the smaller probe is more sensitive to lower moduli. In order to interpret drag resistance from both bulk and interface as an interfacial modulus, measurements must be made at high Boussinesq number, which is inversely proportional to the dimensions of the probe. The micron size of microbutton allows us to obtain reliable measurements of small moduli early in the adsorption process. Conversely, because larger forces can be applied, larger probes can measure higher moduli. The microbutton technique has an upper limit in the measurable modulus which is restricted by the maximum current we can pass through the electromagnets. If the stiffness of the asphaltene layers still continue to increase after microbutton encounters the maximum measurable modulus, which means that the adsorption proceeds is beyond the experimental duration, the microbutton measurement does not represent asphaltene films at adsorption equilibrium. In the following section, the issue of asphaltene film equilibrium will be investigated using identical C7 solution and DWR geometry.

The other issue is whether the scale of rheology measurement and emulsion drop

dynamic is comparable. The size of stable water-in-oil emulsion droplets is usually 1-10 μm [7]. Rheological studies in the literature typically use millimeter-sized or larger probes, which are sensitive only to interfacial properties on these much larger length scales. By using the microbutton, we can resolve mechanical heterogeneities at the ~ 10 μm scale, which are inaccessible to macroscopic rheometry. Since the length scales of mechanical heterogeneity and the emulsion drop size are comparable, it is plausible that the interfacial asphaltene films that form on emulsion droplets is not always homogeneously stiff, and may in fact vary between droplets. This may impact the dynamics and stability of water-in-oil emulsions since the adsorbed asphaltene layer is not isotropically strong enough to prevent the drop coalescence. Our study thus provides microscopic insight into the stabilization and/or destabilization of the water-asphaltene-oil system. We will try to correlate the rheology property and emulsion drop coalescence dynamic in the following section.

3.6 Macrorheology and heterogeneity: Comparing the large and small scale

We have investigated the asphaltene adsorption using the micron-scale rheometry, revealing the increasing stiffness and heterogeneous structure when asphaltene layer ages at the water-oil interface. Since there is a limitation of measurement for microbutton rheometry, we use rheometer with double wall ring (DWR) geometry to probe the interfacial rheology of the asphaltene film in a larger (millimeter) scale. Although DWR is not as sensitive as microbutton, the rheometer can apply higher torque on the probe to study the stiff interfacial film at the late stage of asphaltene adsorption. The visualization is also recorded simultaneously along with rheology measurement using the

apparatus described in Fig.4.7.

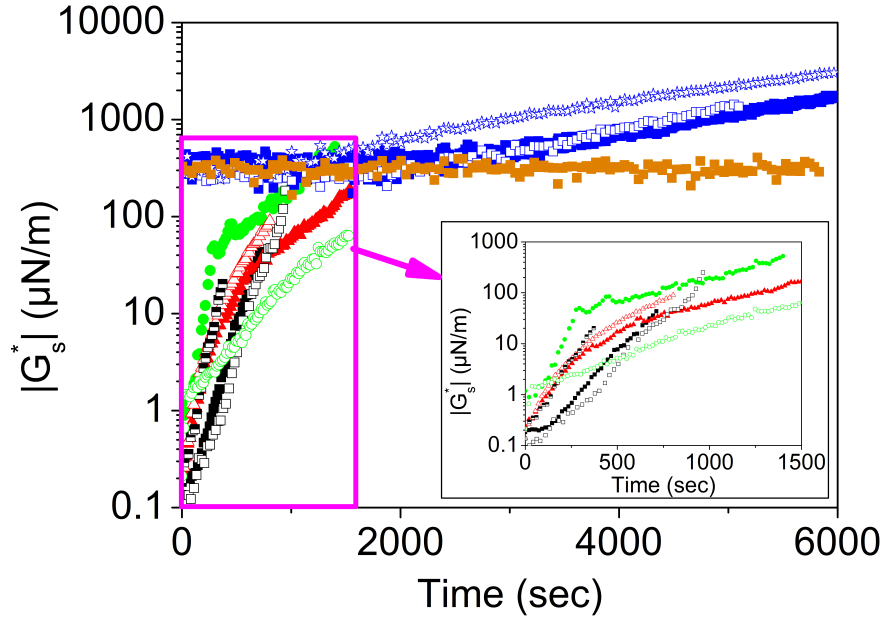


Figure 3.6: Magnitude of the interfacial complex modulus of dectol-on-water interface with 0.1 wt% C7 in bulk oil phase using DWR apparatus (blue curves) and microbutton apparatus (black, green and red, identical data as Fig. 3.1). The dark yellow line represents the measurement of clean-dectol-on-water interface without C7, indicating the lower limitation of measurement for DWR geometry. The inset shows a zoom-in data derived from microbutton apparatus, same figure as Fig. 3.1.

Figure 3.6 depicts the evolution of complex modulus $|G_s^*|$ at the dectol-on-water interface with 0.1 wt% C7 (blue filled, open and star symbol) and without asphaltene (dark yellow) in the bulk oil phase. The rheological measurements using microbutton rheometry shown in Fig. 3.1 are also illustrated in Fig.3.6 and the inset as black, green and red curves. When there is no asphaltene in the bulk dectol phase, $|G_s^*|$ remains around 200 to 400 $\mu\text{N/m}$, revealing the lowest limitation of DWR geometry. Phase angle δ is not shown for DWR rheometry since at the lowest limit of measurement there is still relatively high G' exist which interrupting the calculation of δ . When the oil phase contains 0.1 wt% C7, the stiffness of interface remains at the same level as limitation of

measurement at the early stage of asphaltene adsorption, implying the interfacial stiffness is smaller than that DWR can detect. The interfacial stiffness becomes distinguishable from the lower limit of measurement and starts to increase after around 2000 sec. This result indicates that interface still becomes stiff from a macroscopic point of view, but DWR meets the challenging on tracking the initial stage of asphaltene adsorption. The DWR measurement further shows that the interface can be stiffer than 3000 $\mu\text{N/m}$, suggesting that when the microbutton reach the limitation of measurement (around 500 $\mu\text{N/m}$), the interfacial stiffness keep increasing to the value higher than the upper limit of measurement. However, no steady state can be found even after 6000 sec of asphaltene adsorption. In addition, comparing the time scale and the scale of $|G_s^*|$ of microbutton and DWR rheometry, microbutton is proven to be more sensitive than DWR so it is able to track the initial stage of adsorption, but DWR can better track the late stage of adsorption when interface is stiffer than around 500 $\mu\text{N/m}$ compared with the microbutton rheometry.

Nevertheless, from the three different trials shown in Fig. 3.6, there are still quantitative differences between each trial prepared by the identical procedure. This result suggests that heterogeneity might still exist in the macroscopic (millimeter) scale. In order to reveal the macroscopic mechanical heterogeneity at the dectol-asphaltene-water interface, Fig. 3.7 illustrates the map of local stiffness when asphaltene ages at the interface, using the n_{app} calculation defined in equation 2.29 to 2.31. Figure 3.7 (a) re-plots a trial shown in Fig.3.6 and points out the 5 sampling time chosen for analyzing the local stiffness. At the beginning of adsorption (Fig.3.7 (b)), the interface remains mostly as the bulk-phase-dominant region with only some fraction of interface-dominant region at the interface. When asphaltenes adsorb for 2200 sec, the more interface-dominant region is observed in Fig. 3.7 (c), indicating that the formation of stiff asphaltene film. Figure 3.7 (d)-(f) further shows that when the asphaltenes keep aging on the interfacial

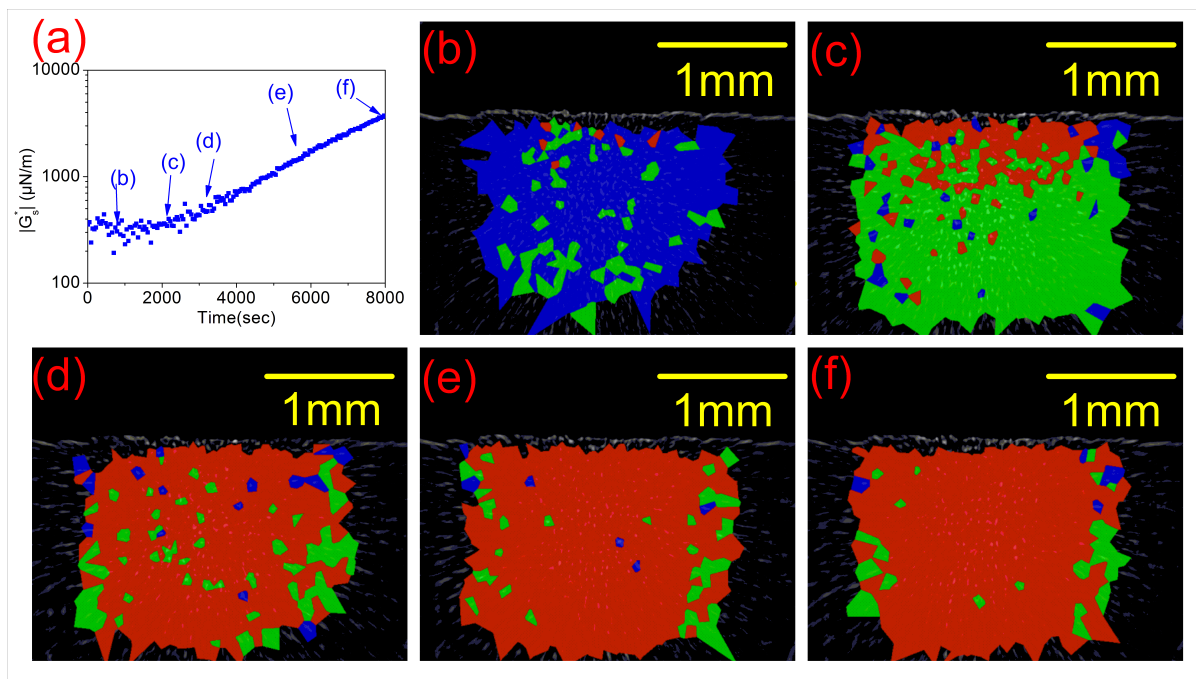


Figure 3.7: (a) Interfacial rheology of the dectol-on-water interface with 0.1 wt% C7 in the oil phase (blue filled symbol in Fig. 3.6) using DWR rheometry. (b)-(f) Evolution of mechanical local stiffness when C7 aged at the interface. Red, green and blue cell represent rigid-body, interface-dominated and bulk phase-dominated behavior respectively.

film, asphaltenes form a rigid chunk on the interface and result in the high drag resistance measured by the DWR rheometry. Figure 3.7 proves the existence of macroscopic mechanical heterogeneity, which explaining the quantitative difference between each experimental trial prepared by the identical procedure. The evolving interfacial structure also agrees with the average evolution local stiffness illustrated in Fig.3.4. Asphaltene adsorption has been shown gradually generate stiff but heterogeneous structure at the water-oil interface, microscopically and macroscopically.

3.7 Aging asphaltene layer and emulsion stability

We have investigated the mechanical property of the asphaltene layer formed at the water-oil interface, showing that asphaltenes form a heterogeneous stiff layer both microscopically and macroscopically. In order to correlate the mechanical property, we measure and the real emulsion drop coalescence dynamic, a drop coalescence experiment is designed for the current water-oil interface we study. Figure 3.8 illustrates the apparatus for observing multiple water drop coalescence simultaneously at the dectol-on-water interface with 0.1 wt% C7 asphaltene in the bulk oil phase. A series of acrylic-made wells is sandwiched by two hydrophobic glass slides coated with trichloro(1H,1H,2H,2H-perfluorooctyl)silane (Sigma-Aldrich, 97%). Water is first injected into each well through a transfer pipette and the height of the water phase in each well is adjusted to a similar level in each well. Dectol with 0.1 wt% C7 is then injected into each well to form a stable dectol-on-water interface. After the interface is aged with asphaltene for a period of time, we use a glass capillary connected with a syringe pump (New Era Pump Systems Inc., NE-1800) to carefully form and place a millimeter scale water drop at the water-oil interface. A CCD camera (Thorlabs, DCU223C) with a zoom lens(Thorlabs, MVL7000) is applied to observe the side-view of 12 wells simultaneously, obtaining the photos as shown in Fig. 3.8. The identical experiment is conducted 10 times in order to obtain the statistic distribution of coalescence time from 120 measurements, and two different aging time scale are investigated. This apparatus allows us to study when the asphaltene form a stiff layer at the interface, whether this viscoelastic film can prevent another water drop coalescence with the bulk water phase.

Figure 3.9 depicts the distribution of drop coalescence time for the water drop staying at the dectol-on-water interface with asphaltene adsorbing for 80 sec(red) and 1080 sec(blue). When asphaltene is aged for only 80 sec, 85% drops coalesce with bulk water

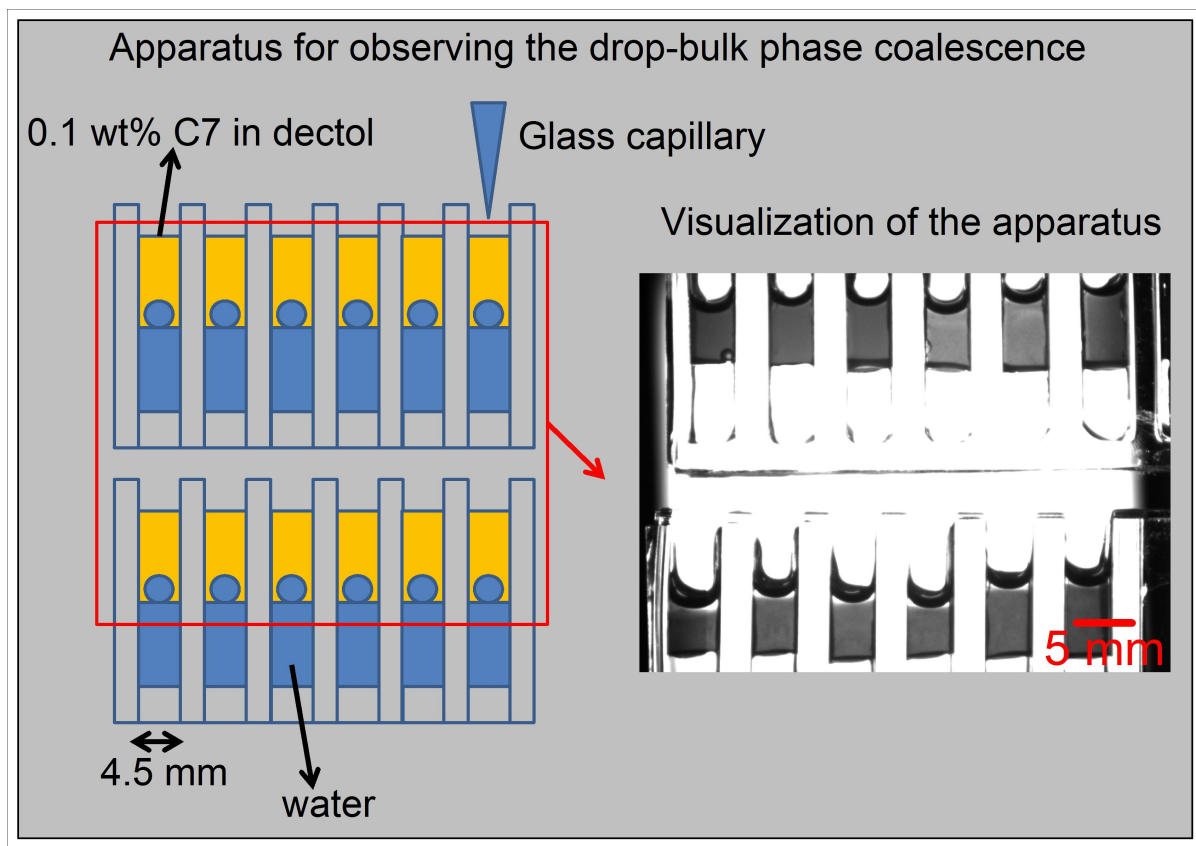


Figure 3.8: Apparatus for observing drop-bulk phase coalescence. A series of acrylic-made well is sandwiched by two hydrophobic glass slides. Water and C7 in dectol are injected respectively through a transfer pipette. After asphaltene adsorb for a particular period of time, a glass capillary connected with syringe pump is applied to place a water drop in each well carefully and a CCD camera is used to observe count the coalescence time scale in each well.

phase in 200 sec, and no drops can stay at the interface without coalescence longer than 2200 sec. However, when the asphaltenes have aged for 1080 sec before the water drop is deposited at the dectol-on-water interface, the distribution is more dispersed compared with that of 80 sec aging. Only around 20% drops coalesce with the bulk water phase in 200 sec, and around 20% drop can stay at the interface without coalescence longer than 2200 sec. From the rheological measurement, we conducted previously, Fig. 3.1 shows that when the dectol-on-water interface age with 0.1 wt% C7, $|G_s^*|$ increase around 2-3 orders of magnitude and interfacial film transfer from viscous-dominated response to more

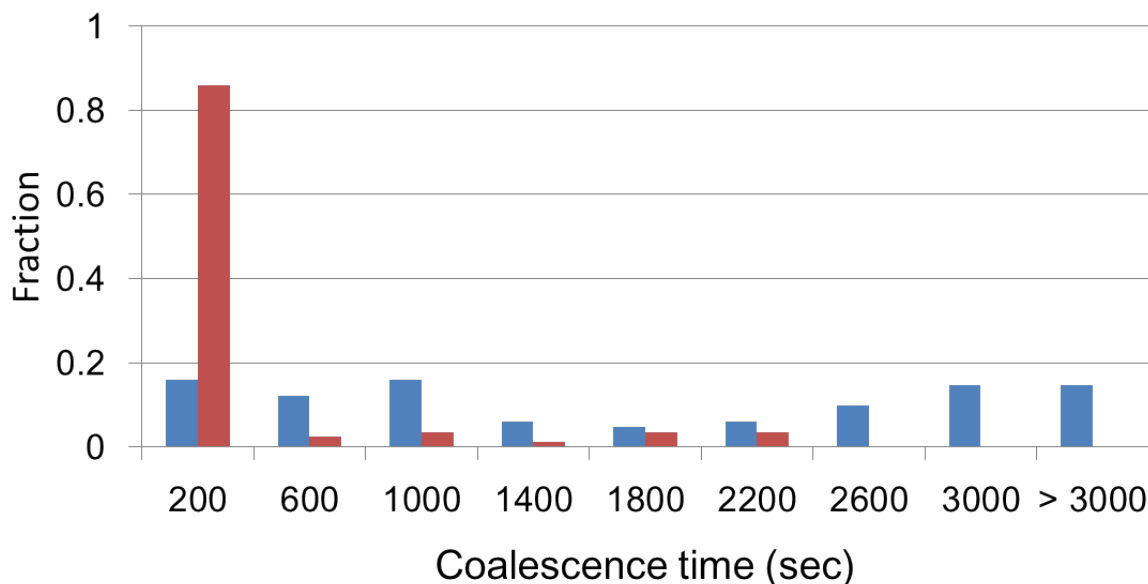


Figure 3.9: Distribution of coalescence time for a water drop at the dectol-on-water interface with 0.1 wt% C7 aged for 80 sec (red) and 1080 sec(blue).

viscoelastic response. The shift of coalescence time distribution in Fig.3.9 and rheological measurement in Fig. 3.1 implies that when asphaltenes form viscoelastic stiff film the dectol-on-water interface, this film can significantly prevent another drop coalescing with the water phase protected by the asphaltene film. Moreover, the disperse distribution of long adsorption time might be attributed to the heterogeneous structure at the water-oil interface formed by asphaltene, although no direct heterogeneity analysis is conducted in this experiment. If the drop stays at a relatively weak region, the drop can coalesce with the bulk phase easily since the local asphaltene layer is not strong enough to prevent drop coalesce. In the next chapter, we will further study the hypothesis that mechanically heterogeneous structure impacts the dynamic of the interface using the sample demulsifier ethylcellulose (EC).

3.8 Conclusion

We have investigated the physical property of the asphaltene interfacial film at the dectol-on-water interface. The microbutton rheometry reveals that asphaltenes form a viscoelastic stiff film at the interface, and asphaltene adsorption can increase the stiffness for 3 order of magnitude in 1000 sec. However, a quantitative difference of rheological measurement can be found between each trial prepared by the identical experimental procedure. The strain analysis proves the existence of micron-scale mechanical heterogeneity at the dectol-on-water interface near the microbutton probe, explaining the irreproducible rheological measurement we found. The evolution of local stiffness shows that asphaltene can gradually form stiff structure and cover the whole interface. Using DWR rheometry, we further show that the asphaltene interfacial films still stiffen after reaching the limitation of measurement of the microbutton rheometry, and no steady state can be found even after 6000 sec adsorption. The millimeter-scale mechanical heterogeneity is characterized by DWR rheometry, indicating the heterogeneous interfacial structure can be observed from both microscopic and macroscopic scale. By conducting the drop coalescence experiment, we build the correlation between the interfacial rheology and drop coalescence dynamic of asphaltene film. The viscoelastic stiff film formed by asphaltene can efficiently prevent coalescence happening between the water drop and bulk water phase. However, the coalescence seems to be impacted by the mechanically heterogeneous structure formed by asphaltene.

Chapter 4

The impact of sample demulsifier ethylcellulose (EC) on asphaltene adsorption

4.1 Overview

In this chapter, we focus on testing how the sample demulsifier ethylcellulose (EC) influences the asphaltene interfacial film. Interfacial shear microrheology and the strain analysis are utilized for quantifying the effect of EC in two different mechanisms and compared to pure asphaltene adsorption. EC is first premixed with C7 asphaltene in the dectol to investigate how EC interrupts asphaltene adsorption at the dectol-on-water interface. The second study is introducing EC on the pre-existing asphaltene layer at the interface to probe how EC softens the stiff asphaltene layer. With the knowledge of EC in the microscopic point of view, the macroscopic impact of EC on aged asphaltene interfacial film is then studied by DWR rheometry, also from both rheology and mechanical heterogeneity point of view. After investigating the impact of EC at the dectol-water

interface, we then study how EC change the emulsion drop size and the bulk rheological property of emulsion solution, to clarify the rule of EC besides its influence at the water-oil interface.

4.2 Material and experimental setup

C7 asphaltene is identical to that studied in the previous chapter. Ethylcellulose (EC, STD-100, Dow Chemical) has number-average molecular weight 57000 g/mol and weight-average molecular weight 179000 g/mol[134]. The oil phase is still dectol as used in the last chapter, which is the mixture of toluene (Sigma-Aldrich, HPLC grade, purity=99.9%) and decane (Sigma-Aldrich, anhydrous, purity $\geq 99\%$) at a volume ratio of 1 to 4. Three different oil phases are considered in this chapter: 0.1 wt% C7 asphaltene, 0.01 wt% EC, and a mixture of 0.1 wt% C7 and 0.01 wt% EC. These oil phases are prepared by first dissolving C7 and/or EC in toluene and sonicating for 10 minutes. Decane is then added into the solution and the whole solution is sonicated for an additional 10 minutes. Immediately prior to a measurement, the solution is again sonicated for 10 minutes to disperse any asphaltene aggregates. The aqueous phase is deionized water (Milli-Q, resistivity 18.2 M Ω cm).

We study the effect of EC on rheology using two different experimental procedure. Figure 4.1 (a) shows a “premixed” C7 and EC solution concurrently adsorb to the interface, which characterizes how EC prevent C7 from forming the viscoelastic stiff layer. The formation of the dectol-on-water interface with premixed EC and C7 is followed by the identical procedure as pure C7 adsorption illustrated in Fig. 2.3. Figure 4.1 (b) depicts another ‘post-mixed’ experiment which introduces EC to an aged asphaltene layer. This experiment investigates the ability of EC on softening the pre-existing stiff layer. The introduction of EC is achieved by first adding 40 μ l of oil containing 0.1 wt%

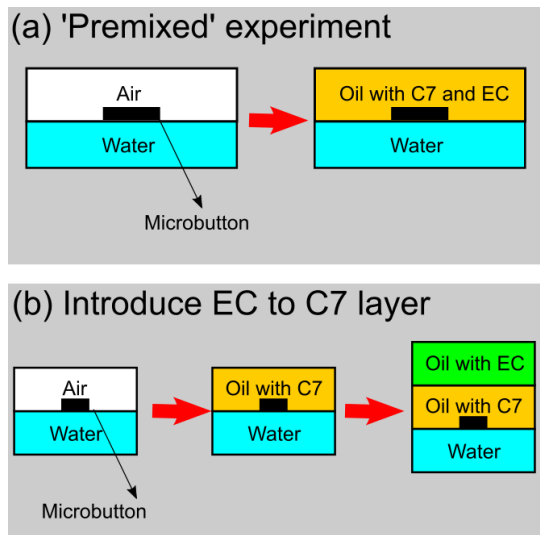


Figure 4.1: (a) The ‘premixed’ experiment. An oil phase containing both C7 and EC is placed on top of the water, forming an oil-water interface onto which asphaltene and EC adsorb simultaneously. (b) EC is introduced to a pre-existing C7 layer. Firstly, oil containing only C7 is placed on water and an asphaltene film is allowed to form. Subsequently, the second layer of oil containing EC is carefully added, allowing the EC to interact with a preformed C7 layer.

C7, allowing the asphaltene film to form and age to the limitation of measurement, then subsequently depositing an additional 40 μ l of oil containing 0.01 wt% EC.

4.3 Concurrent adsorption of asphaltene and ethylcellulose

4.3.1 Rheological measurement

We first investigate how EC influences C7 asphaltene adsorption when both component are present in solution and concurrently adsorb to the interface. Figure 4.2 shows $|G_s^*|$ and δ as a function of time for dectol-on-water interface containing 0.1 wt% C7 (black), premixed 0.1 wt% C7 and 0.01 wt% EC (red) and 0.01 wt% EC (green) in the bulk oil phase. A representative curve of C7 adsorption shows that C7 stiffen interface

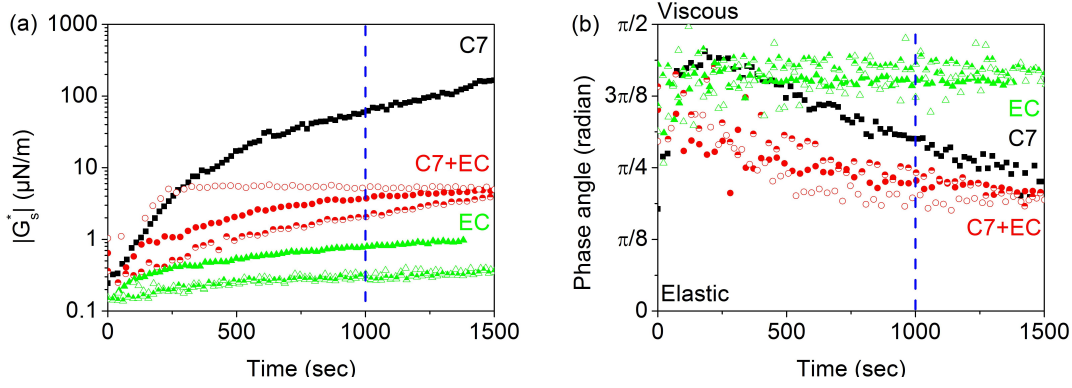


Figure 4.2: (a) Evolution of the magnitude of the interfacial complex modulus when the oil phase contains 0.1 wt% C7 asphaltene (black), 0.1 wt% C7 and 0.01 wt% EC (red) and 0.01 wt% EC (green). (b) Evolution of the phase angle in the same experiments. Blue dashed line represents the sampling time in Figure 4.3.

by 1000-fold in 1500 seconds, with phase angle δ decreasing steadily, indicating that the interface transits from a viscous- to a more elastic-dominated response. In the previous chapter, we have shown that the stiffening of the interface when asphaltene adsorbs can vary from experiment to experiment due to the mechanical heterogeneity on the probe length scale. However, the qualitative trend of increasing stiffness and elasticity is reproducible and robust. As a result, we chose this representative curve to characterize the effect of EC.

Compare with the stiffening interface with C7 adsorption, qualitatively different behavior is observed for EC only solutions in dectol(green). Namely, the interfacial stiffness increases only 5-10 times over 1500 seconds as EC adsorbs, and retains a viscous-dominated nature ($\delta(t) \sim \frac{\pi}{2}$). When EC is premixed with C7 in the oil phase, however, $|G_s^*|$ show an intermediate behavior. This is accompanied by a transition from viscous- to elastic-dominated nature, much like pure C7.

The interfacial rheological measurement with EC and C7 concurrent adsorption imply that EC does not entirely prevent C7 adsorption. If EC adsorb quickly to the interfacial layer, and this EC layer excludes C7 further adsorbs, the corresponding viscoelastic re-

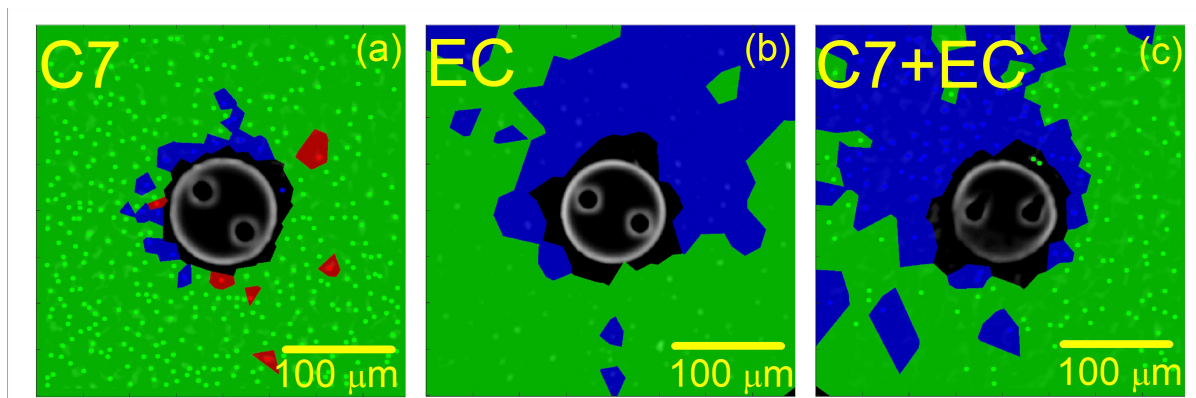


Figure 4.3: Local mechanical character of aged interfaces after 1000 seconds of adsorption of (a) C7, (b) EC, and (c) mixed C7 and EC. Red, green and blue represent rigid-body, interface-dominated, and bulk phase-dominated rotation respectively.

sponse would resemble that of the pure EC layer. However, this is not the case. When C7 and EC adsorb concurrently, the rheological response evolves like to pure C7, although with reduced overall stiffness. We interpret these data as suggesting that EC slows asphaltene adsorption, and/or interferes with asphaltene structure formation. Nevertheless, asphaltenes do adsorb and occupy the significant interfacial area. Consequently, after comparable adsorption times, we measure stiffnesses which are intermediate between pure C7 and pure EC but exhibit a viscoelastic nature comparable to pure C7.

Although the pure C7 and premixed C7 and EC solution demonstrate qualitatively different nature compared with pure C7 adsorption, one can still observe quantitative variation between the trials conducted using identical oil composition. From the previous study of C7 adsorption, we found the mechanical heterogeneity at the interfacial structure is responsible for this variation of rheology measurement. In order to verify the existence of heterogeneity in these two systems, the strain analysis is needed to provide a detailed understanding of the interfacial structure.

4.3.2 Study of local structure

Since the rheology measurement with EC still shows quantitative variation between trials prepared by identical procedure, we then apply the strain analysis on the visualization recorded with rheology measurement simultaneously. Figure 4.3 maps the apparent decay exponent, n_{app} , defined in equation (2.28), corresponding to the rheological measurements in Fig. 4.2 after 1000 seconds of adsorption. For the representative asphaltene layer we chose (black rectangles in Fig. 4.2 (a)), Fig. 4.3 (a) shows the local rheological character at the interface primarily interface-dominated, indicating that adsorbed asphaltene forms a stiff interfacial layer responsible for the high drag resistance measured in Fig. 4.2 (a). Figure 4.3 (b) illustrates n_{app} for pure EC adsorption (red closed circles in Fig. 4.2 (a)). EC adsorption forms a heterogeneous film mixed with more bulk-phase-dominated and interface-dominated regions compared with pure C7 adsorption. This characteristic implies that some regions of a pure EC interface have less surface-active material and/or weaker interfacial structure than other regions, and the whole interface around the probe remains relatively soft, resulting in the relatively lower $|G_s^*|$ measured in Fig. 4.2 (a).

Figure 4.3 (c) shows n_{app} obtained from the concurrent adsorption of C7 and EC (green closed triangles in Fig 4.2 (a)). This mixed system also exhibits coexistence of bulk-phase-dominated and interface-dominated regions, indicating that EC can prevent C7 from forming a stiff interfacial layer. The observed heterogeneity explains the variations in $|G_s^*|$ between nominally identical experiment prepared by identical procedure, since the measured $|G_s^*|$ depends on the locally rheological environment near the microbutton probe. Furthermore, this rheological heterogeneity can explain the lower overall $|G_s^*|$, compared with pure C7 adsorption, since bulk-dominated regions offer less resistance to interfacial shear. Figure 4.3 (b) and (c) also suggest that EC can create soft regions

whether or not C7 is present. That $|G_s^*|$ is higher when both C7 and EC adsorb than EC adsorb, implies that the interface-dominated regions in the premixed experiments might be stiffer than those resulting from pure EC adsorption. However, since the strain analysis only reveals the relative contribution of drag resistance from bulk and interface, a further quantitative correlation between strain analysis and rheology measurement is challenging.

Consequently, from the map of local stiffness shown in Fig. 4.3, it is clear that when C7 and EC adsorb simultaneously, EC retards C7 adsorption and forms a softer interfacial layer than pure C7 adsorption. Furthermore, whenever EC is adsorbed, the interface is mechanically heterogeneous, consisting of softer bulk-phase-dominated and stiffer interface-dominated regions on the length scale of microbutton probe.

In order to assess the generality of these observations, we consider the time evolution of the averaged area fractions of rigid-body behavior, interface-dominated and bulk-phase dominated regions in multiple experiments prepared by the identical procedure. Figure 4.4 show the average time evolution for each of the distinct adsorption experiments (pure C7, pure EC, and premixed C7 and EC, the data of pure C7 is identical to Fig. 3.4). The area fraction evolutions for each individual experiment are shown in Figs. 3.5, 4.5 and 4.6.

For the pure C7 adsorption, as we discussed in the previous chapter, Fig. 4.4 (a) shows a fast initial increase in interface-dominant area and gradual bulk-phase-dominated area. A small amount of rigid area also appears when asphaltenes adsorb. In comparison, pure EC adsorption (Fig. 4.4 (b)) reveals no rigid regions appear but only bulk-phase-dominated and interface-dominated area are found. Notably, however, the interface-dominated area fraction increases steadily and slowly from approximately 60% to 80%. Finally, Fig. 4.4 (c) illustrates this evolution for premixed C7 and EC. Bulk-phase-dominated and interface-dominated regions coexist, and a slow increase in the

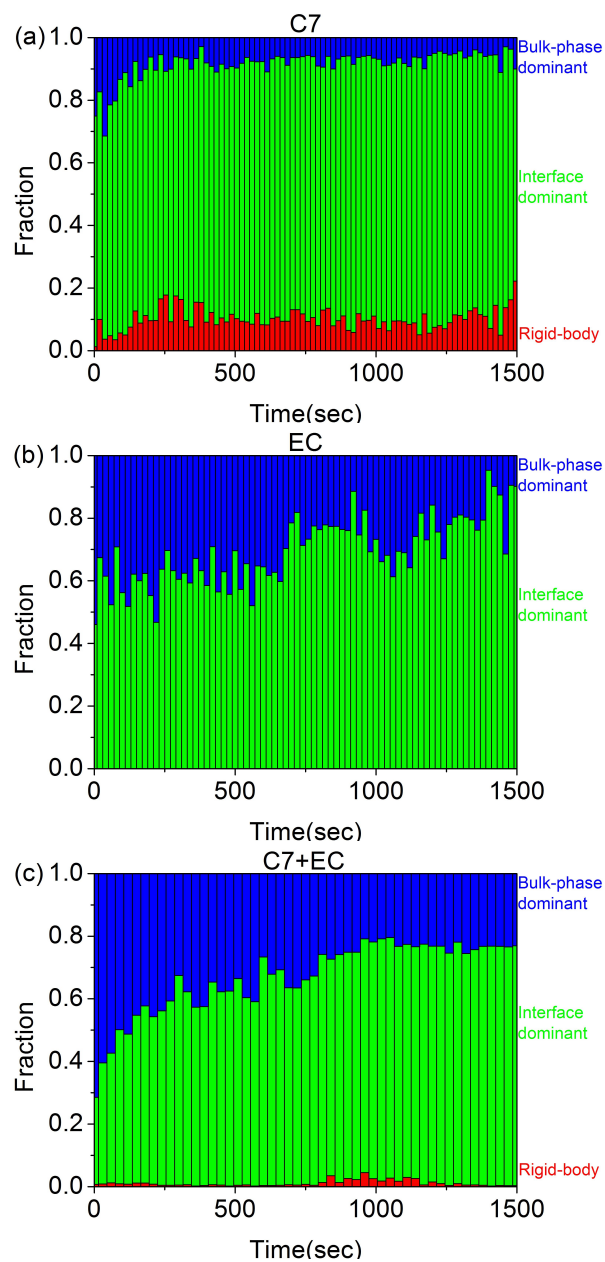


Figure 4.4: Evolution of average area fraction of rigid-body (red), interface-dominated (green) and bulk-phase dominated (blue) regions for (a) C7 only, (b) EC only and (c) premixed C7 and EC interface.

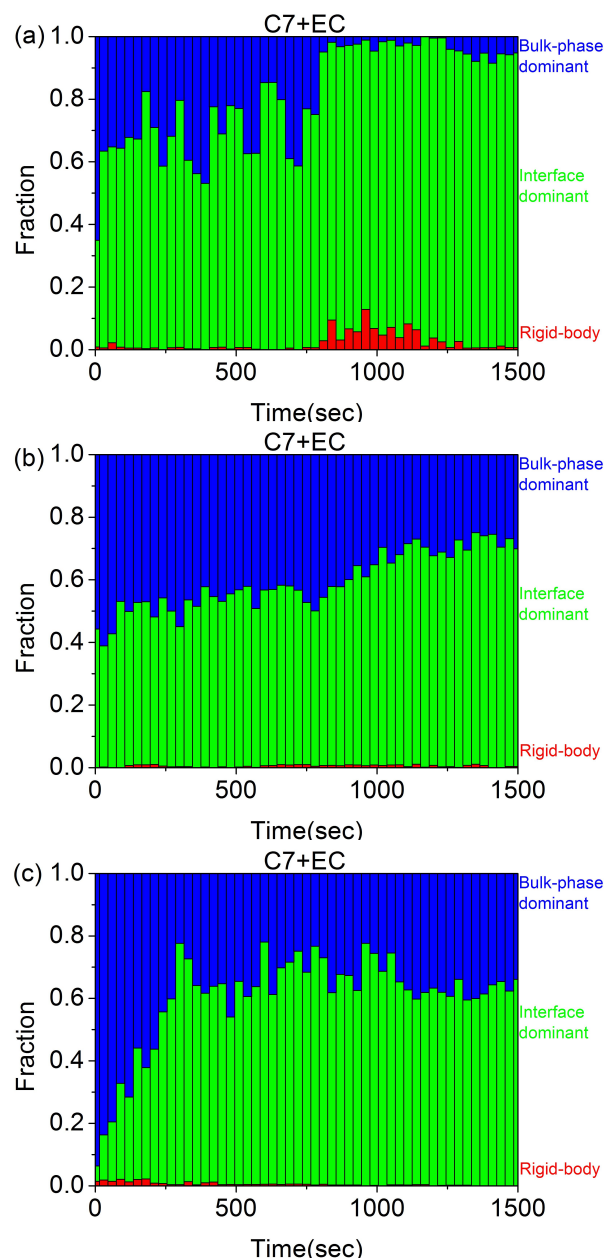


Figure 4.5: Area fraction evolution of rigid-body(red), interface-dominant(green) and bulk-phase dominant(blue) region for the premixed C7 and EC interface. (a), (b), and (c) represent the closed, open, half-open red curve in Fig. 4.2 respectively.

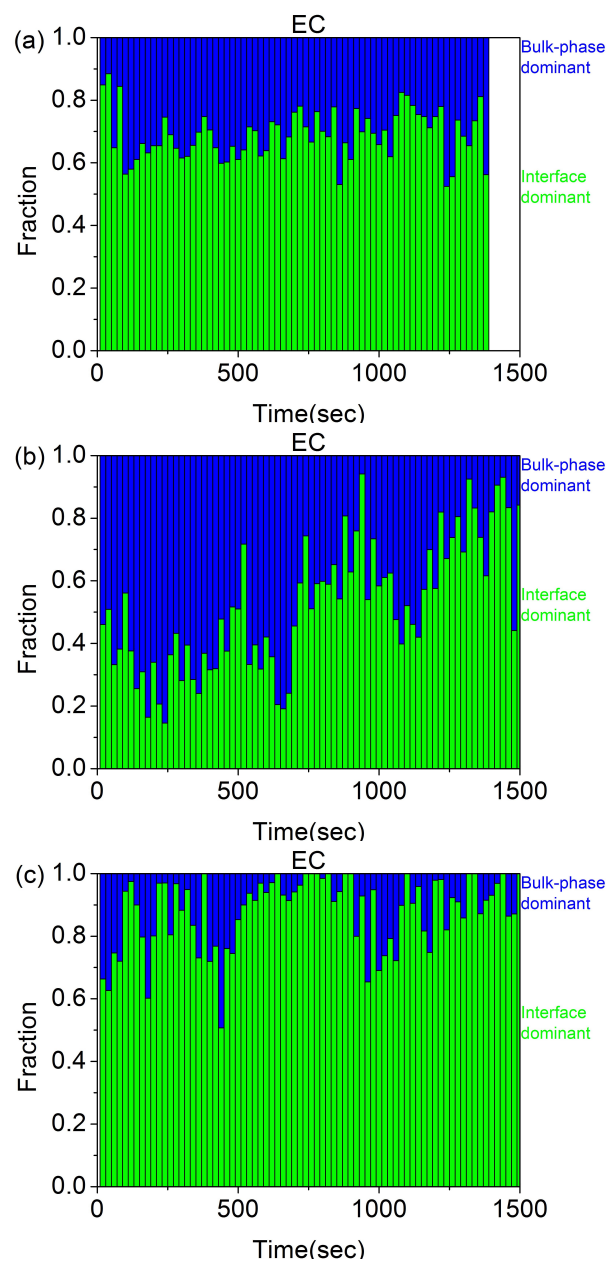


Figure 4.6: Area fraction evolution of rigid-body(red), interface-dominant(green) and bulk-phase dominant(blue) region for the pure EC interface. (a), (b), and (c) represent the closed, open, half-open green curve in Fig. 4.2 respectively.

proportion of interface-dominated area from around 30% to 70% is measured. Compare the increase rate of the interface-dominated area between pure C7 adsorb and concurrent adsorption of EC and C7, pure C7 occurs significantly faster than that of C7 and EC adsorb concurrently. This difference suggests that the presence of EC does indeed retard asphaltene adsorption. That the end-state in the mixed system consists, on average, of a significantly larger proportion of bulk-phase-dominated area and reduced rigid area compared to the pure C7 experiments supports our speculation that, in addition to its retarding effect, EC modifies and weakens the structure of the overall asphaltene film. Thus, both our hypotheses are supported, and the effect of EC on the C7 film appears to be two-fold: EC both slows asphaltene adsorption and alters its interfacial structure.

4.4 Drop-in ethylcellulose on aged asphaltene layer

4.4.1 Rheological measurement

After demonstrating the influence of EC on C7 adsorption when they adsorb simultaneously from a premixed solution, we now study the effect of adding EC to the aged C7 asphaltene layer using the procedure described in Fig. 4.1 (b). Figure 4.7 depicts how $|G_s^*|$ and δ evolve before and after a 0.01 wt% EC solution is introduced to the asphaltene layer formed by adsorption from a 0.1 wt% C7 solution. The C7 adsorption is initially monitored until $|G_s^*|$ reaches the upper limit of measurement, depending on the magnetic moment of the probe, and then EC solution is introduced from the top of the oil phase (which we call $t = 0$). The large symbols at $t < 0$ reflects the rheology as pure C7 adsorb, whereas the small symbols at $t > 0$ show the rheological evolution after adding EC.

Figure 4.7 (a) shows $|G_s^*|$ are weakened by 1-3 orders of magnitude after introducing EC to an aged C7 layer. Following the initial decrease, however, qualitative variation

arises between these experiment prepared by the identical procedure. One interface (purple) gradually recovers to relatively high $|G_s^*|$, one (red) appears arrested at an intermediate $|G_s^*|$, while some interfaces (blue, orange and green) continue to soften.

Figure 4.7 (b) demonstrates that, in all experiments, the phase angle δ increases immediately after depositing EC on the aged asphaltene layer, which corresponds to the loss of elasticity. Following the immediate increase, δ remains high in those experiments for which $|G_s^*|$ continues to decrease (blue, orange and green), suggesting that more liquid-like behavior is maintained for these experiments. This behavior contrasts with the experiments for which $|G_s^*|$ recovers or appears arrested (red and purple), since in these experiments δ slowly decreases, indicating that the interface transits back towards an elastic response. As a result, the recovery of $|G_s^*|$ at the late stage of EC introduction is associated with a recovery of elastic behavior. From the rheology study, we have shown that EC successfully softens the aged C7 asphaltene layers, however, with qualitative and quantitative variations after the initial softening. This variation likely reflects the heterogeneity of the asphaltene film based on our previous strain analysis from pure C7 adsorption, with certain areas of the asphaltene layer more susceptible to penetration and disruption by EC than others.

4.4.2 Dynamic of local stiffness during softening process

In order to investigate the varying effect of EC at the aged asphaltene layer, we utilize the mechanical heterogeneity for analyzing the evolution of local structure when EC interact with asphaltene layer. Fig. 4.8 shows maps of local stiffness in a particular experiment (orange data in Fig. 4.7) before and after depositing EC. Figure 4.8 (a) re-plots $|G_s^*|(t)$ for this experiment, emphasizing the early stages of EC interaction, and pointing out the 5 points considered in panels (b-f). Figure 4.8 (b) shows the map

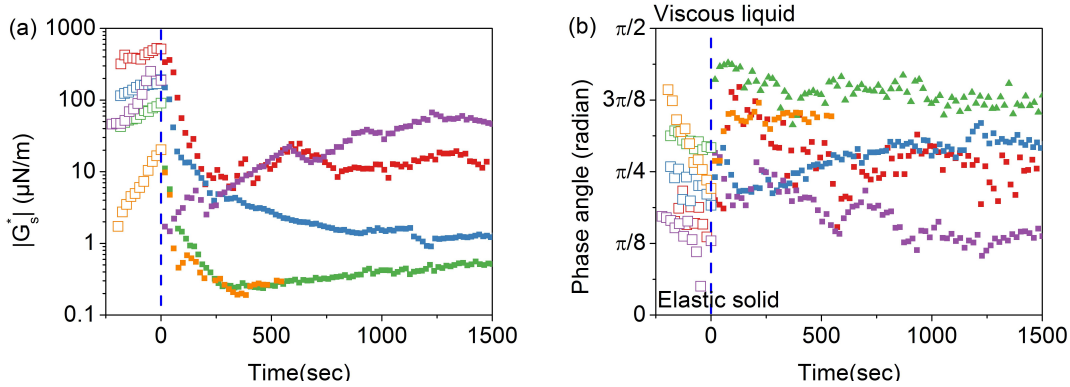


Figure 4.7: (a) Evolution of the magnitude of the interfacial complex modulus when a 0.01 wt% EC solution is deposited above an aged asphaltene interface formed from a 0.1 wt% C7 solution. EC is introduced at $t = 0$. (b) Evolution of the phase angle in the same experiments. Large (small) symbols show quantities before (after) EC addition. Different colors represent different trials prepared by identical procedure.

of n_{app} immediately before EC is introduced and (c)-(f) show the evolution of local stiffness. As evident from Fig. 4.8 (b), prior to the addition of EC, the interface is mechanically heterogeneous with a scar-like weak region near the microbutton and a rigid-body behavior region in the lower left of the probe. After EC is introduced, EC appears to adsorb to and expand the pre-existing soft, bulk-phase-dominated region as shown in Fig. 4.8 (c), (d) and (f). When this inhomogeneous softening process occurs, $|G_s^*|$ decreases as the drag resistance in the vicinity of the microbutton decreases. After EC interact with the interface for around 500 sec, Fig. 4.8 (f) indicates that interface-dominated regions gradually recover, but the region near the microbutton probe still remains soft.

The evolution of mechanical structure in Fig. 4.8 implies that EC preferentially interacts regions which are already soft. EC may more easily disrupt, penetrate or expand pre-existing weak regions at the asphaltene film. The recovery of the interface-dominated region might be attributed to the bulk C7 adsorption back into the soft region created by EC, or that a restructuring of the interfacial layer occurs. This recovery might

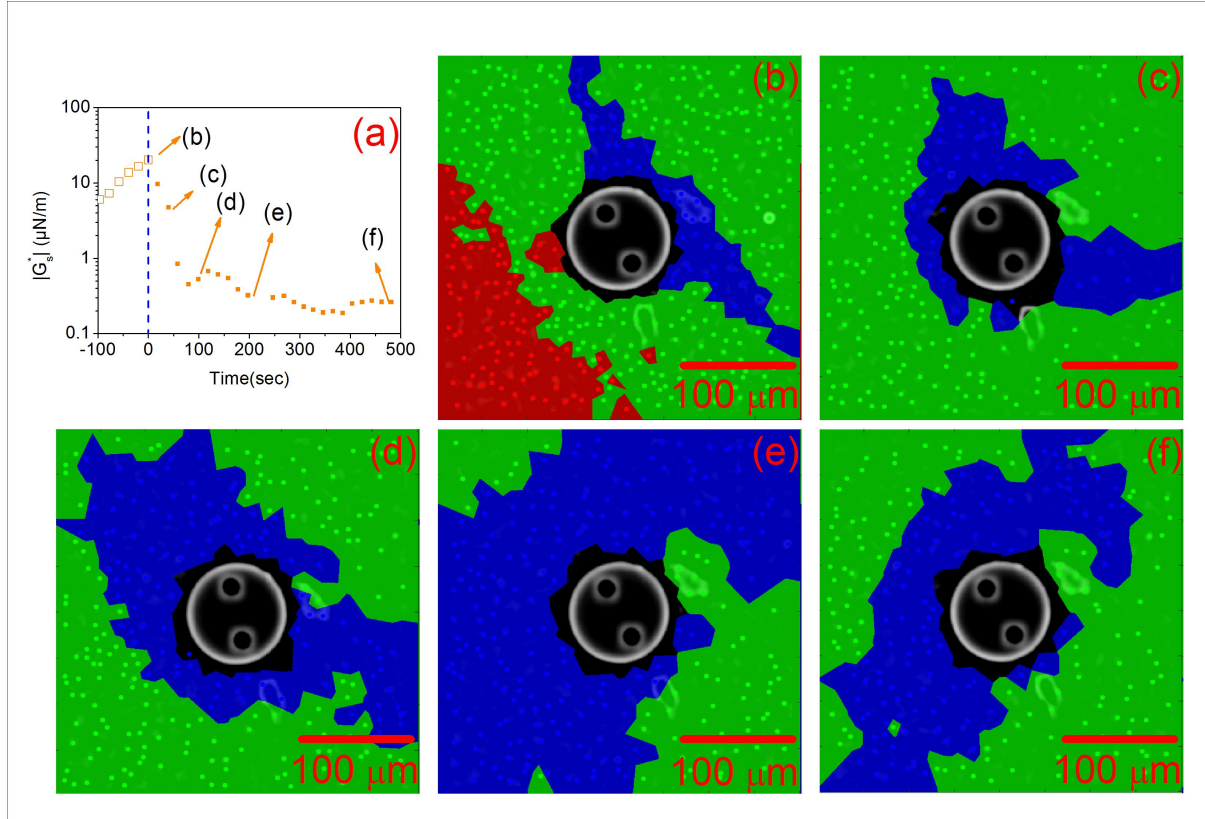


Figure 4.8: (a) Interfacial rheology of the water-oil interface when adding 0.01 wt% EC on aged asphaltene layer. EC is introduced at $t = 0$. (b) Mechanical local stiffness before adding EC. (c)-(f) Evolution of mechanical local stiffness after adding EC. Red, green and blue cell represent rigid-body rotation, interface-dominated rotation and bulk phase-dominated rotation respectively.

increase or prevent further decreasing the film stiffness.

The sample evolution shown in 4.8 demonstrates the impact of EC for a particular interface. To reveal the general evolution of mechanical structure when EC is introduced, we average the instantaneous area fractions of bulk-phase-dominated, interface-dominated and rigid-body-like regions obtained from the five experiments prepared by identical procedure in which EC is added to a pre-existing asphaltene layer at $t = 0$. This averaged evolution is shown in Figure 4.9, and the evolution of each trial is shown in Fig. 4.10. The interface-dominated and rigid-body fraction decrease rapidly when EC is introduced, while the bulk-phase-dominated regions increase. After the initial expansion

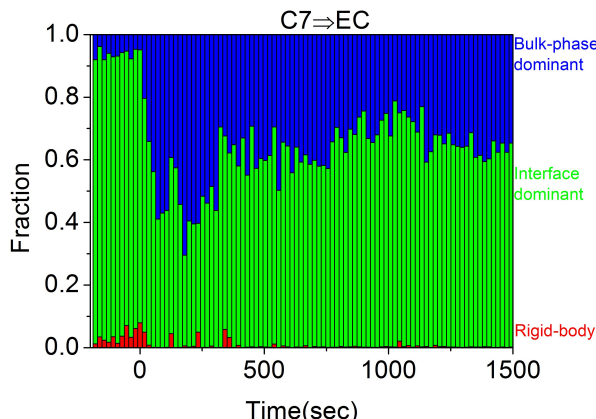


Figure 4.9: Evolution of average area fractions of rigid-body (red), interface-dominated (green) and bulk-phase-dominated (blue) regions after introducing 0.01 wt% EC on aged C7 layer. EC is deposited at $t = 0$. Data are an average of five identically prepared experiments.

of bulk-phase-dominated regions and associated softening on the stiffness, the interface slowly begins to recover towards a more interface-dominated drag resistance. This trend supports the generality of the progression we observed in the local stiffness maps in Fig. 4.8, and explains the rheology evolution in Fig. 4.7.

Although the general trend appears robust, qualitative differences in evolution are observed between these nominally-identical trials. Those experiments in which interfacial stiffness increases after its initial drop (red and purple curve in Fig. 4.7) exhibit a much faster recovery of the interface-dominated area fraction compared to the experiments in which interfacial stiffness continues to decrease over a much longer period (blue and green data in Fig. 4.7). It is likely that the differences in the mechanical stiffness near the microbutton determine the differences in the measured rheology.

4.5 Macroscopic view of interfacial softening process

We have utilized the microbutton rheometry to reveal how EC soften the interfacial layer and break the mechanical structure inhomogeneously. Since the microbutton can

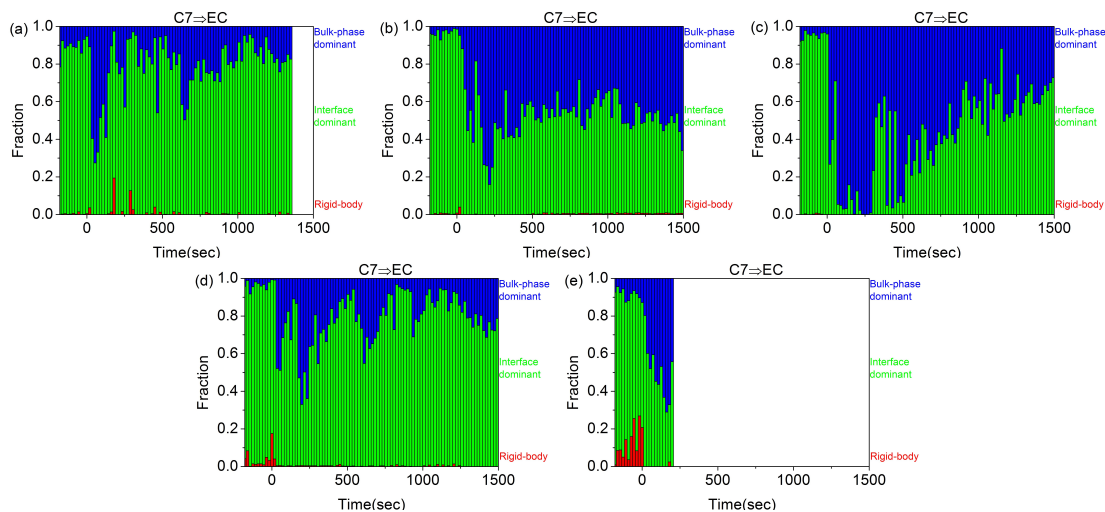


Figure 4.10: Area fraction evolution of rigid-body(red), interface-dominant(green) and bulk-phase dominant(blue) region for the interface with C7 before and after adding EC. (a), (b), (c), (d) and (e) represent the red, blue, green, purple and orange curve in Fig. 4.7 respectively. EC is deposited at $t = 0$.

only reveal the micron-scale structure locally near the microbutton probe, we want to further probe the effect of EC on the macroscopic scale. The DWR rheometry is used for this rule, which enables the macroscopic observation of the asphaltene mechanical structure and rheology measurement to be obtained simultaneously. We first demonstrate a reference experiment of depositing clean dectol at the aged asphaltene layer to characterize the physical disruption when we add additional oil phase on the aged asphaltene layer. With this reference experiment, we can then introduce dectol with EC to characterize the effect of EC.

The experiment of introducing new oil phase is operated by first adding 3 ml dectol contains 0.1 wt% C7 on the top of water phase and letting the interface aging for 3000 sec to form a stiff layer at the interface. After interface becomes stiff, we deposit another 3 ml clean dectol or dectol with 0.01 wt% EC from the top of the C7 oil phase. The ratio of the C7 oil phase and new oil phase is kept at 1 to 1, identical to that of microbutton experiment we conducted previously.

Figure 4.11 depicts the interfacial rheology at the dectol-on-water interface with depositing a new layer of dectol containing no EC (green curve) and 0.01 wt% EC (red curve) on the aged C7 layer. The green curve in Fig. 4.11 suggests that the physical disruption resulted from adding a new oil phase does not soften the asphaltene interfacial layer, and the interfacial layer still keeps stiffening after the bulk oil phase is diluted. Compare with adding clean dectol, when the new oil phase contains 0.01 wt% EC, $|G_s^*|$ still increases initially after addition, however, $|G_s^*|$ still drops gradually after 2000 sec addition. The decrease of $|G_s^*|$ indicate that EC can still soften the asphaltene layer macroscopically, but no an instantaneous decrease of $|G_s^*|$ can be found as microbutton rheometry.

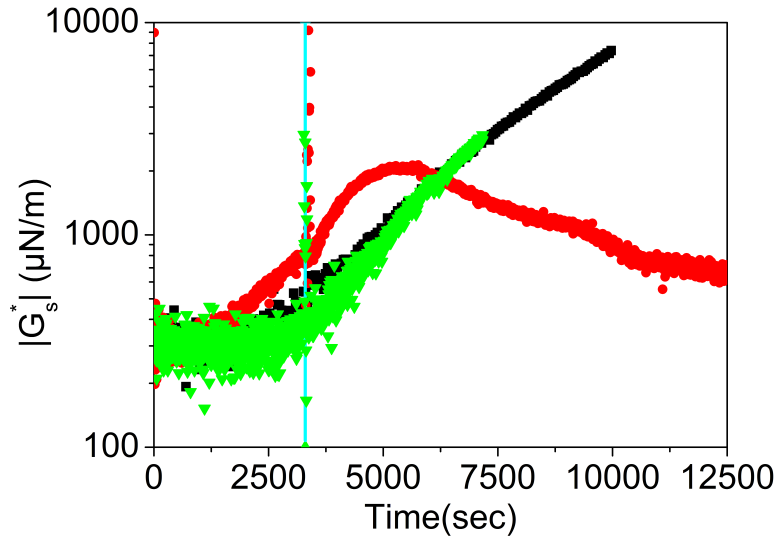


Figure 4.11: Magnitude of the interfacial complex modulus when a 3 ml 0.01 wt% EC in dectol solution (red) and clean dectol (green) is deposited above an aged asphaltene interface formed by a 0.1 wt% C7 solution. New oil phase is introduced at $t = 3000$ sec. Black curve is the reference curves which represents interface ages with 0.1 wt% C7 in dectol without adding new oil phase.

The delay of $|G_s^*|$ decrease might attribute to the higher stiffness of interface when we introduce EC to DWR geometry compared with microbutton experiment since we can only deposit EC when the interfacial film is stiff enough to characterize the effect

of EC from the lower limit of DWR measurement. This limitation of technique results in stronger asphaltene film than that of microbutton rheometry, so EC might need more time to soften the interface film and cause the delay of $|G_s^*|$ we observe.

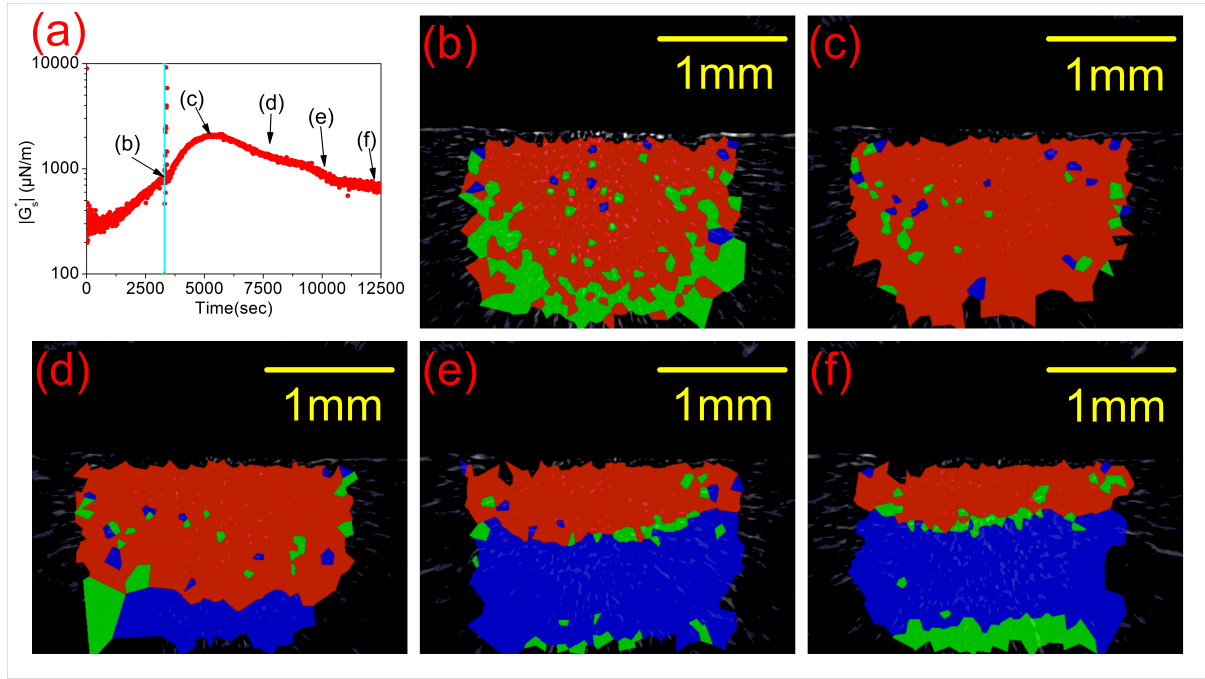


Figure 4.12: (a) Interfacial rheology of the water-oil interface when adding 3 ml 0.01 wt% EC on aged asphaltene layer. EC is introduced at $t = 3000$ sec. (b) Mechanical local stiffness before adding EC. (c)-(f) Evolution of mechanical local stiffness after adding EC. Red, green and blue cell represent rigid-body rotation, interface-dominated rotation and bulk phase-dominated behavior respectively.

The microbutton rheometry shows that the map of the mechanical structure at the interface reflects how EC soften and break the asphaltene layer microscopically. The similar algorithm is applied to DWR rheometry for revealing the macroscopic view of EC dynamic at the water-oil interface. Figure 4.12 illustrates the macroscopic evolution of local stiffness when EC is deposited at the aged asphaltene layer. We first re-plot the rheology data (red curve of Fig. 4.11) in Fig. 4.12 (a) and points out the 5 points considered for local stiffness in Fig. 4.12 (b) to (f). Before the addition of EC, the interfacial layer is mechanically heterogeneous with most of the interfacial structure be-

has as rigid-body and some interface-dominated region. Only a small amount of soft (bulk-phase-dominated) region exist. This stiff structure in Fig. 4.8 and higher $|G_s^*|$ both agree with our previous claim that the interfacial layer in DWR is stronger than that we observed in the microbutton rheometry.

When EC is deposited at the interface, Fig. 4.12 (c) reveals that the fraction of rigid-body region at the interface still increase compared with that of the interface before adding EC. This increase of rigid-body region is consistent with the increase of $|G_s^*|$ after depositing EC on the asphaltene layer. When the interface keeps aging with EC, Fig.4.12 (d), (e) and (f) shows that EC gradually generate bulk-phase-dominant region at the interface, which explaining the decrease of $|G_s^*|$ in Fig. 4.12 (a). At the end of the experiment, Fig. 4.12 (e) shows that there is still part of rigid-body region attaches to the ring, which still provides drag resistance and prevents $|G_s^*|$ decrease to the level of the clean water-dectol interface.

In conclusion, the map of mechanical stiffness successfully fits the measured rheology and explains the different responses between DWR and microbutton rheometry. EC has been shown to efficiently create soft region at the interface, from microscopic and macroscopic point of view, using the map we developed in Fig. 4.12 and Fig. 4.8. Moreover, the mechanical of asphaltene layer seems to strongly impact the ability of EC on softening the interface. If the asphaltene layer is stiff enough, EC needs more time to soften and break the asphaltene layer and create a weak region at the interface.

4.6 The impact of EC on emulsion property

4.6.1 Emulsion preparation

We have demonstrated that EC can successfully soften the stiff asphaltene layer at

the water-oil interface. In order to correlate the interfacial property we measured to the emulsion drop dynamic, the water-in-dectol emulsion coated with asphaltene is prepared for characterizing the influence of EC. Water is mixed with 0.1 wt% C7 in dectol at a volume ratio of 1 to 9. The mixed water and oil solution is then sonicated for 15 sec using ultrasonicator (Model 705 Sonic Dismembrator, Fisher Scientific) to form stable emulsion drops. For characterizing the impact of EC on emulsion solution, water is mixed with the dectol contains 0.1 wt% C7 and 0.01 wt% EC at a volume ratio of 1 to 9, and sonicated following the identical procedure as preparing the asphaltene-coated water-in-oil emulsion. The obtained asphaltene-coated emulsion and emulsion treated with EC are observed using the optical microscope for size distribution study and sheared by rheometer with cone-and-plate geometry to characterize bulk rheology property.

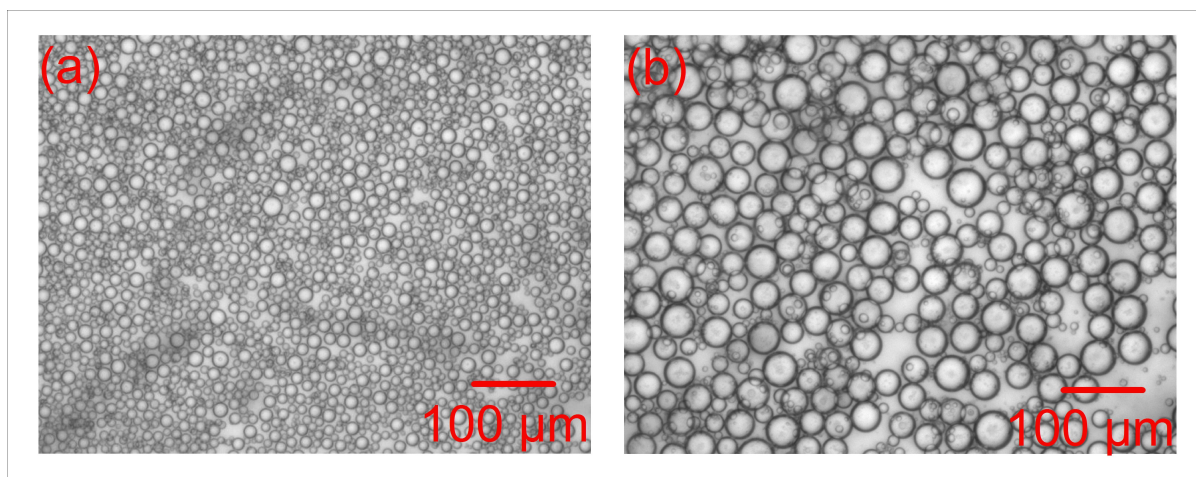


Figure 4.13: Images of water-in-dectol emulsion with (a) 0.1 wt% C7 and (b) premixed 0.1 wt% C7 and 0.01 wt% EC in the bulk oil phase.

4.6.2 Impact of EC on emulsion drop size

Figure 4.13 shows the sample image of the water-in-dectol emulsion prepared by (a) 0.1 wt% C7 and (b) mixed 0.1 wt% C7 and 0.01 wt% EC. When the oil phase contains only asphaltene, the existence of asphaltene can result in monodisperse, micron-size water

drops in the oil phase. However, when the oil phase contains 0.01 wt% EC, the emulsion droplet become larger and more polydisperse compared with that of pure asphaltene emulsion.

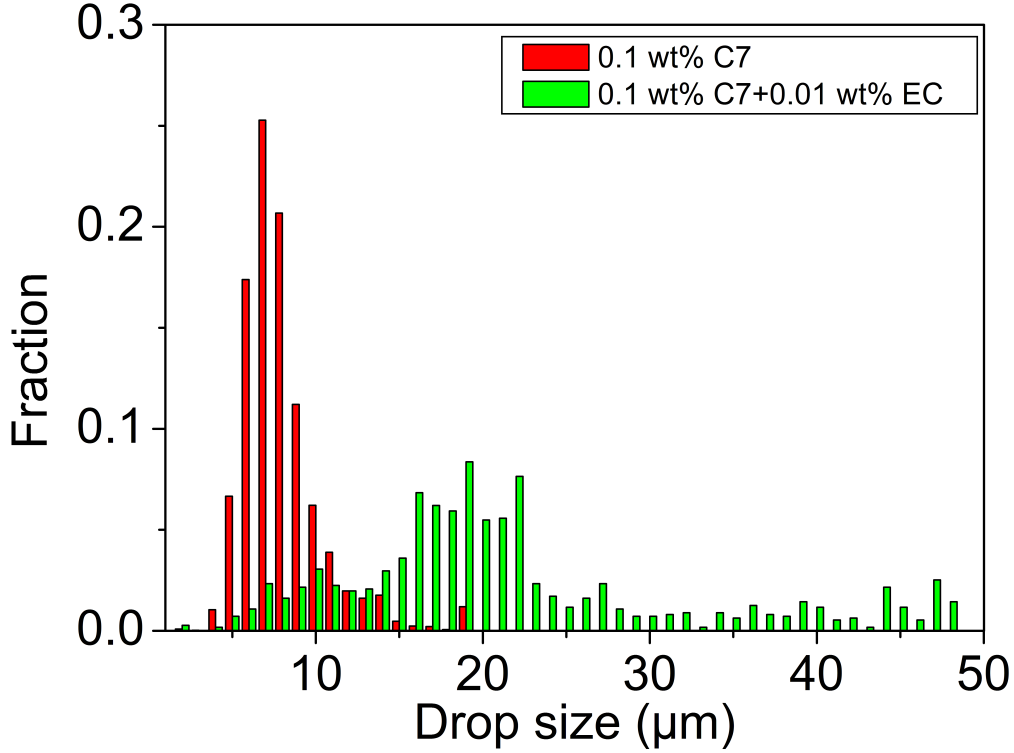


Figure 4.14: Distribution of water-in-oil emulsion drop size for oil phase contains 0.1 wt% C7 (red) and 0.1 wt% C7 and 0.01 wt% EC (green)

The photos of water-in-dectol emulsion are further analyzed by the custom Matlab program using circle finding technique to obtain the size distribution of emulsion drops. Figure 4.14 depicts the distribution of emulsion drop size with 0.1 wt% C7 only (red) and mixed 0.1 wt% C7 and 0.01 wt% EC (green) in the oil phase. The distribution is calculated by measuring 1000 emulsion droplets for each emulsion solution. For C7 only emulsion, the mean of drop size is $7.9 \mu\text{m}$, and coefficient of variation is 0.31. For C7 and EC emulsion, however, the mean of drop size is increased to $20.6 \mu\text{m}$, and coefficient of

variation becomes 0.54. The drop size analysis suggests that, with the viscoelastic stiff layer formed by asphaltene, the emulsion remains stable and a uniform, micron size can be maintained. When EC appears in the oil phase and create a relatively soft interfacial layer, the drops become less stable and coalescence happens easily, which result in the larger average size and more polydisperse emulsion drops.

4.6.3 Impact of EC on the bulk rheology of emulsion solution

In addition to the size of emulsion drop, the physical property of the bulk oil phase is also influenced by the emulsions and EC. Here, we use rheometer with cone and plate geometry to examine how emulsion droplets and EC change the rheological property of the oil phase. For the oil phase used in the bulk rheology study, we vortex the bulk oil for 10 sec prior to the measurement in order to disperse the emulsion in the oil phase.

Figure 4.15 (a) depicts the shear viscosity of dectol as a function of shear rate for dectol with 0.1 wt% C7 without emulsion (black), dectol with 0.1 wt% C7 emulsion (red) and dectol with 0.1 wt% C7 and 0.01 wt% EC emulsion (green). For dectol without

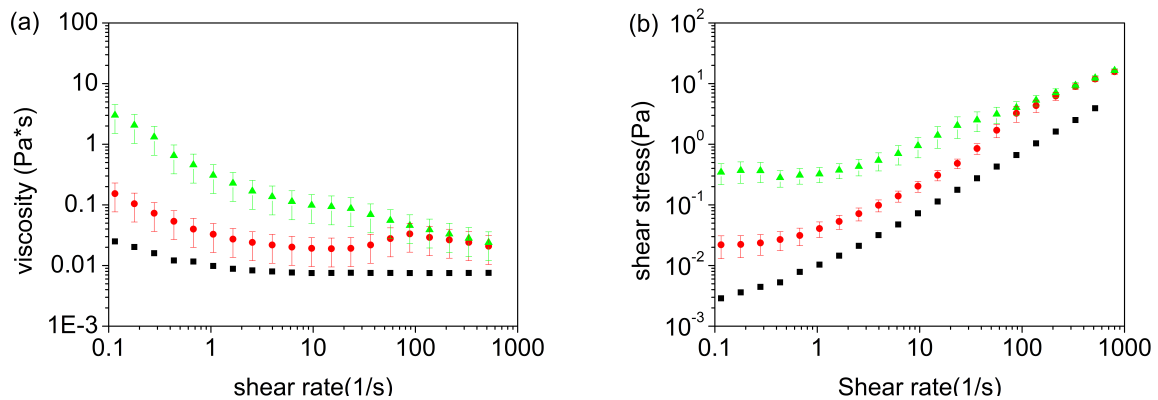


Figure 4.15: (a) Shear viscosity and (b) shear stress as a function of shear rate for dectol with 0.1 wt% C7 only (black), dectol with emulsion contains 0.1 wt% C7 and dectol with emulsion contains 0.1 wt% C7 and 0.01 wt% EC

emulsion, the viscosity of oil phase is nearly independent from the shear rate. When

there are emulsion droplets coated with asphaltene existing in the oil phase, the viscosity is increased for an order of magnitude. In addition, the viscosity starts to depend on the shear rate we applied on the emulsion solution. The green curve in Fig. 4.15 indicates that EC can further increase the viscosity of the bulk oil phase with emulsion. The emulsion solution with both C7 and EC also shows significant shear-thinning behavior compared with the oil phases without EC or emulsion.

Figure 4.15 (b) illustrate the shear stress as a function of the three different oil phases discussed in Fig. 4.15 (a). The shear stress at the low shear rate points out that the emulsion drops can provide the yield stress to the oil phase, and EC can further increase the yield stress of the oil phase. In order to quantify the yield-stress and shear-thinning property of the oil phase, we utilize Herschel-Bulkley model [135] to fit the shear stress curve shown in Fig. 4.15:

$$\sigma = \sigma_y + K\dot{\gamma}^n \quad (4.1)$$

where σ is the shear stress, σ_y is yield stress, K is the consistency index, n is flow index. When $n = 1$ the fluid is Newtonian, $n < 1$ is shear-thinning, $n > 1$ is shear-thickening. For the oil phase only contains C7 without emulsion, $\sigma = 0.0076\dot{\gamma}$, indicating the oil phase is Newtonian and no yield stress can be found. When asphaltene-coated emulsion exists in the oil phase, $\sigma = 0.0235 + 0.0175\dot{\gamma}^{1.072}$, revealing that yield stress appear but the oil phase still remains as closed to the Newtonian fluid. This measurement implies that emulsion might aggregate or flocculate together slightly which provide the weak yield stress to the oil phase. If EC also exist the emulsion solution, $\sigma = 0.227 + 0.113\dot{\gamma}^{0.776}$. This result indicates that the yield stress is significantly increased and oil phase become a shear-thinning fluid. When EC exists in the oil phase, EC can bridge and flocculate emulsion drops[83], which might result in the further increase of the yield stress we observe. After the shear rate increases, the network build by EC breaks and the viscosity

starts decreasing. As a result, the flow behavior becomes more similar to that of emulsion without EC at the high shear rate. This increase of yield stress due to the addition of demulsifier is also reported in the [113, 114, 94]. The bulk rheology study reveals that in addition to the impact on the interfacial property, EC also modifies the bulk properties of the oil phase with the asphaltene-coated emulsion. The addition of EC enhance emulsion drops coalescence and seems to also flocculate and/or build the network between the emulsion drop to modify the bulk rheology property of the oil phase. The rule of demulsifier in the asphaltene-water-oil emulsion is not only on the interfacial property, but a more complicated mechanism is involved.

4.7 Conclusion

We have investigated how the sample demulsifier ethylcellulose (EC) impact the asphaltene interfacial film and the emulsion property. When EC concurrently adsorb with asphaltene, EC can prevent C7 asphaltene from forming a viscoelastic stiff layer at the water-oil interface. EC also has the ability to soften the pre-existing asphaltene layer and removing the elasticity of the interfacial film. The strain analysis reveals that if there is soft region already at the asphaltene film before EC is introduced to the asphaltene layer, EC can first soften the layer from that region and further weaken the interface inhomogeneously. DWR rheometry shows that EC can soften the asphaltene layer from a macroscopic point of view, creating a millimeter scale soft region at the interface. From the emulsion dynamic point of view, EC is found to increase the emulsion drop size and polydispersity of the emulsion drop. In addition to the influence on the interfacial property, EC can also introduce yield stress of bulk emulsion solution, which might attribute to the network formed by EC between emulsion drops. This study shows that the demulsifier can have multiple rules at both the interfacial and the bulk property, a

single property is not enough to describe the demulsification of the asphaltene-water-oil emulsion.

Chapter 5

The chemical and physical factors impact asphaltene interfacial rheology

5.1 Overview

We have investigated the asphaltene adsorption at a single system using 0.1 wt% C7 asphaltene in dectol. However, the property of the asphaltene film strongly depends on the chemical composition of the oil phase, and how the measurement is conducted can also impact the result we obtained. In this chapter, we investigate the possible factors which can influence the asphaltene interfacial rheology to give a deep understanding of this phenomena. The chemistry of oil composition is first studied to reveal its impact on asphaltene adsorption. Two different oil phase are investigated with identical asphaltene concentration and aromatic fraction, which are a decane-toluene mixture (‘dectol’) and isopar-aromatic-200 mixture (‘isomatic’), in order to reveal how the choice of model oil phase influence the rheology. After investigating the choice of model oil, asphaltene

concentration is then varied from 0.5 wt% to 0.01 wt% in isomatic to characterize the impact of concentration gradient on asphaltene adsorption. The aromatic fraction of the oil phase can influence the solubility of asphaltene in the oil phase and thus the affinity of asphaltene to the interface. We use oil phases with 20 vol% aromatic fraction (‘bad solvent’) and 80 vol% aromatic fraction (‘good solvent’) to investigate the effect of aromatic fraction in the oil phase.

With the study of oil phase chemistry, we then elucidate how the experimental apparatus and operation influence the rheological response physically. The water-on-oil and oil-on-water rheological measurements are compared to probe how asphaltene aggregates and gravity influence the formation of the interfacial film. The frequency sweep is conducted to investigate the rheological property over the long and short time period. Finally, a linear viscoelasticity region of asphaltene interfacial film is studied by the strain sweep test to confirm the validation of our previous study.

5.2 Materials and experimental setup

The C7 asphaltene is identical to that utilized in the previous study, which is obtained by precipitating using n-heptane (Sigma-Aldrich, anhydrous, purity $\geq 99\%$) from bitumen (Alberta, Canada). Two different model oil phases are considered in this study. The oil phase ‘dectol’ is composed of toluene (Sigma-Aldrich, HPLC grade, purity=99.9%) as aromatic composition and decane (Sigma-Aldrich, anhydrous, purity $\geq 99\%$) as aliphatic composition, identical to the previous study. The other oil phase ‘isomatic’ is the mixture of isopar (isoparaffinic hydrocarbon, ExxonMobil) as aliphatic composition and aromatic-200 (ExxonMobil) as aromatic composition. The C7 in dectol/isomatic is prepared by first dissolving asphaltenes in toluene/aromatic-200 and sonicating for 10 minutes. Decane/isopar is then mixed with C7 in toluene/aromatic-200 and the whole solution is

sonicated again for a further 10 minutes. Prior to the rheology measurement, the solution is sonicated again to disperse the asphaltene aggregates in the oil phase. The aqueous phase is deionized water (Milli-Q, with resistivity 18.2 M Ω cm and total organic carbon < 5 ppb).

In this study, the asphaltene concentration and the aromatic fraction of the oil phase are varied to tune the chemistry of the oil phase. Asphaltene concentration is varied from 0.5 wt% to 0.01 wt%, and aromatic fraction is varied from 20 vol% aromatic (bad solvent) solvent to 80 vol% aromatic fraction (good solvent). For the oil phase contains 20 vol% aromatic solvent, asphaltene aggregates form due to the low solubility in the oil phase. In order to characterize the influence of asphaltene aggregates, an aggregates-free C7 in the bad solvent is prepared and compare to the original solvent. The aggregates-free isomatic or dectol is obtained by centrifuging the oil phase and extracting the supernatant as the new oil phase without aggregates.

The oil-on-water and water-on-oil geometry used in this study are described previously in Fig. 2.3 and 2.4. The frequency sweep and strain sweep experiment is conducted by varying the frequency and the amplitude of the current through the electromagnet during asphaltene adsorption.

5.3 The choice of model oil phase: Isomatic and dectol

We first study how the choice of model oil phase influence the asphaltene adsorption using decane-toluene mixture ‘dectol’ and isopar-aromatic-200 mixture ‘isomatic’. Isopar and decane form the aliphatic compound of oil phases, while toluene and aromatic-200 compose the aromatic components. The aromatic fraction of both oil phases are fixed

at 20 vol% and asphaltene concentration is 0.1 wt%, so we can focus on the influence of different oil molecules on the rheology.

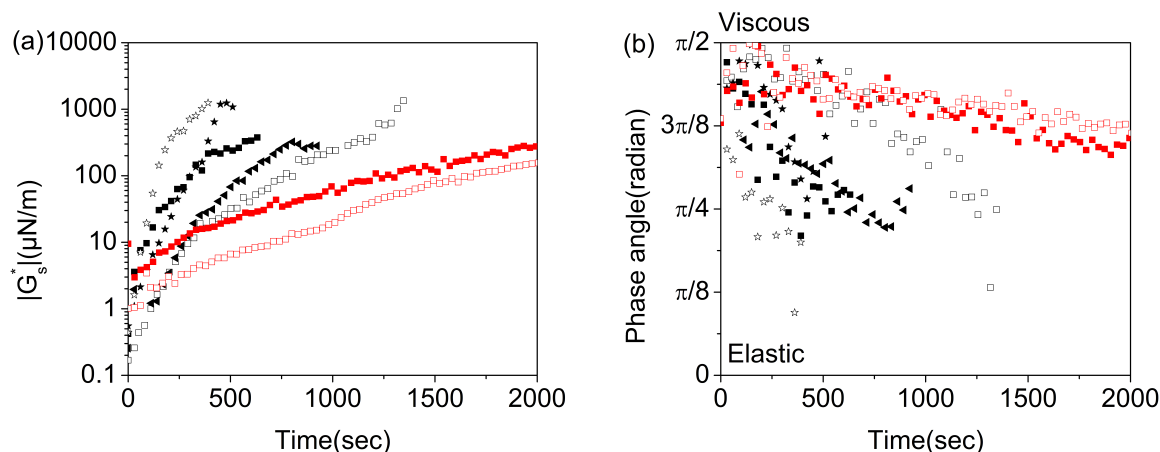


Figure 5.1: The influence of model oil molecules on interfacial rheology. (a) Magnitude of the interfacial complex modulus when the oil phase contains 0.1 wt% C7 asphaltene in dectol (black) and isomatic (red). Different symbols represent different trials prepared by the identical procedure. The aromatic ratio for both oil phases are fixed at 20 vol%, geometry is oil-on-water. (b) Evolution of the phase angle in the same experiments.

The evolution of interfacial stiffness and phase angle for 0.1 wt% C7 asphaltene in dectol and isomatic are illustrated in Figure 5.1. Figure 5.1(a) shows that, although significant variation between the trials of dectol can be observed, the stiffening rate of dectol is qualitatively faster than that of isomatic. Figure 5.1 (b) demonstrates the transition from viscous-dominated response to viscoelastic response of dectol and isomatic. Dectol shows faster transition compared to the isomatic. When C7 adsorbed from dectol, the interface becomes viscoelastic between 500 sec to 1000 sec. However, for the isomatic, even after 2000 sec the interface still behave similarly to the viscous liquid.

Figure 5.1 reveals that although the asphaltene concentration and aromatic fraction remains identical, changing the model oil can still significantly vary the rate of forming viscoelastic asphaltene film at the interface. This phenomenon might be attributed to the different diffusivity of asphaltene in both oil phases. Asphaltene in dectol might diffuse

faster than that in isomeric, which results in the faster formation of a stiff layer.

5.4 Bulk asphaltene concentration: Concentration gradient between bulk and interface

The impact of asphaltene bulk concentration on rheology is studied by dissolving the various amount of asphaltene in the ‘bad’ isomeric (20 wt% aromatic fraction) using oil-on-water geometry. We compare three different asphaltene concentration: 0.01 wt% (cyan), 0.1 wt% (pink) and 0.5 wt% (orange) in Fig. 5.2 to quantify how the bulk concentration impacts the asphaltene adsorption.

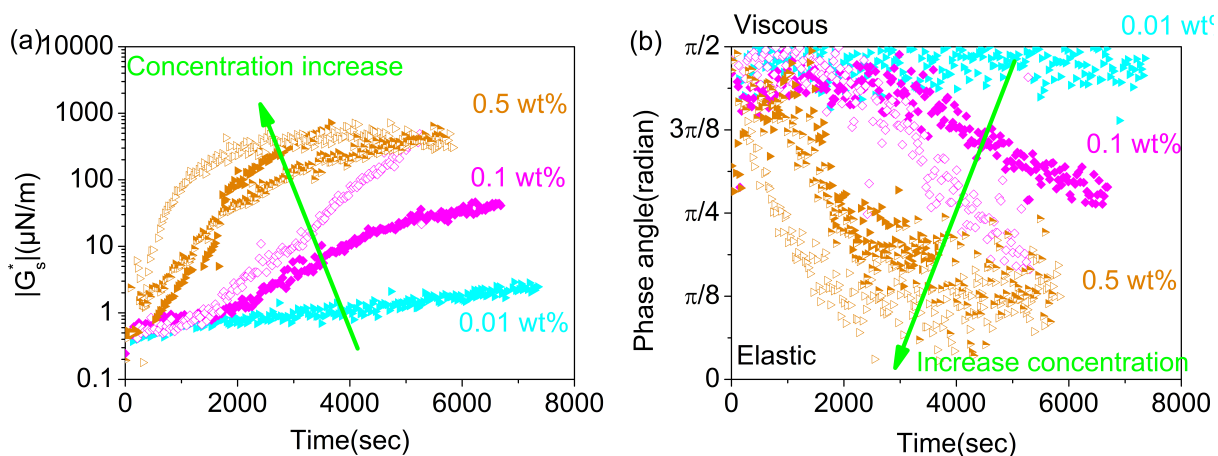


Figure 5.2: (a) Magnitude of the interfacial complex modulus when the oil phase contains 0.5 wt% (orange), 0.1 wt% (pink) and 0.01 wt% (cyan) C7 asphaltene in isomeric. Different symbols represent different trials prepared by the identical experimental procedure. Aromatic ratio for oil phases are fixed at 80 vol%, geometry is oil-on-water (b) Evolution of the phase angle in the same experiments.

Figure 5.2 (a) shows that with higher C7 concentration, the stiffening rate of interfacial layer becomes faster. When the concentration is 0.5 wt%, $|G_s^*|$ increase around 2-3 orders of magnitude in 2000 sec and reaches a plateau. For 0.1 wt% C7, although significant variation exists between the two trials we measured, $|G_s^*|$ still increase slower

compared to that of 0.5 wt%. When the concentration is further decreased to 0.01 wt%, $|G_s^*|$ only increase around 5 times higher in 7000 sec measurement. Figure 5.2 (b) illustrates that when C7 concentration is increased, the asphaltene layer can transit to more elastic-dominant response faster. For 0.5 wt% C7, δ decrease to around $\pi/8$ in 4000 sec, indicating a elastic-dominated response. When C7 concentration is decreased to 0.1 wt%, δ decrease slower and only reach around $\pi/4$ in 5000 sec. The δ of 0.01 wt% C7 remains as viscous-dominated response in 7000 sec measurement.

The higher C7 bulk concentration has been shown to increase the stiffening of the interface and result in a faster transition from viscous-dominated response to more viscoelastic response. This faster stiffening and appearance of elasticity might attribute to the higher concentration gradient between bulk and interface, which result in faster asphaltene adsorption to the interface and thus the formation of the interfacial film is accelerated.

5.5 Aromatic fraction: The solubility of asphaltene

The asphaltenes are defined as the class of molecules which are soluble in aromatic solvent but not solvable in n-alkane. Changing the aromatic fraction of the bulk oil phase can thus vary the solubility of asphaltene in the oil phase and perhaps the affinity of asphaltene to the interface. The ‘good isomatic’ (80 vol% aromatic-200) and ‘bad isomatic’ (20 vol% aromatic-200) are used to probe the impact of solubility on asphaltene adsorption. C7 concentration is fixed at 0.1 wt% in this study, and oil-on-water geometry is utilized.

Figure 5.3 (a) depicts the evolution of $|G_s^*|$ with good and bad isomatic. For the good isomatic, $|G_s^*|$ remains below 1 $\mu\text{N}/\text{m}$ in the first 2000 sec and increase gradually later. The stiffening rate of the interface is significantly increased when the aromatic

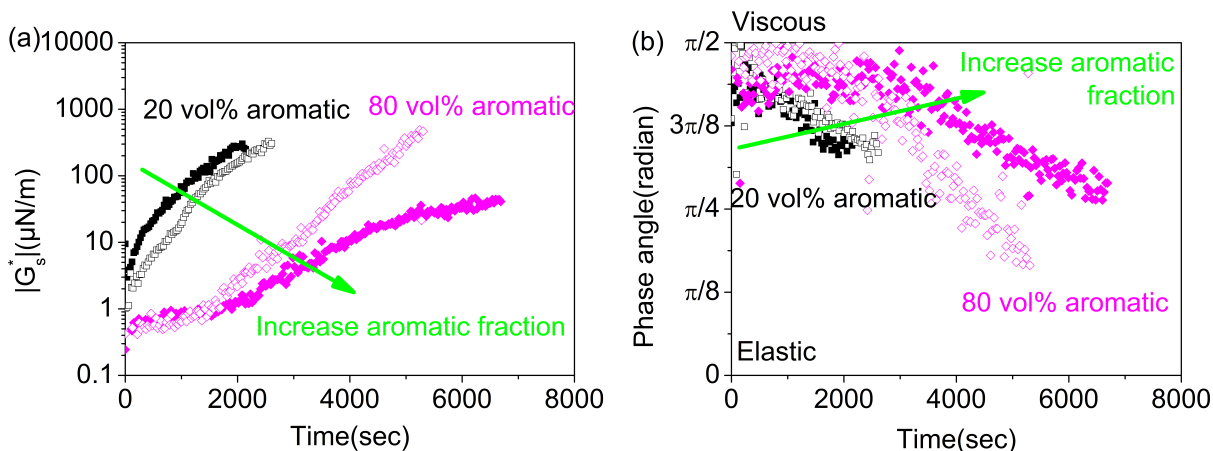


Figure 5.3: The influence of aromatic fraction on asphaltene interfacial rheology (a) Magnitude of the interfacial complex modulus when the oil phase contains 0.1 wt% C7 asphaltene in isomatic. Aromatic ratio for oil phases is 20 vol% (black) 80 vol% (pink), respectively. Geometry is oil-on-water. (b) Evolution of the phase angle in the same experiments.

fraction is decreased. For the bad isomatic with only 20 vol% aromatic fraction, $|G_s^*|$ can increase to around 300 $\mu\text{N/m}$ in 2000 sec, which is 100 times higher than that of the good isomatic. Figure 5.3 (b) shows that δ of the interface with good isomatic remains as the viscous-dominated response in the first 2000 sec, but still transit to the level of the viscoelastic structure after around 5000 sec. However, bad isomatic shows no delay initially and elasticity appear faster compared with good isomatic.

The rheological difference between the good and bad isomatic indicates that the asphaltene adsorption is significantly delayed when the bulk aromatic fraction is increased, but varying the aromatic fraction cannot totally prevent the formation of the viscoelastic stiff structure at the water-oil interface. That the increasing aromatic fraction delays asphaltene adsorption agrees with the study in the literature.[8, 136] Increasing the aromatic fraction in the oil phase might result in the higher affinity of asphaltenes to dissolve in the oil phase rather than adsorb to the interface, which cause slower stiffening and viscoelastic transition in the good solvent.

5.6 Gravitational effect: Influence of asphaltene aggregates

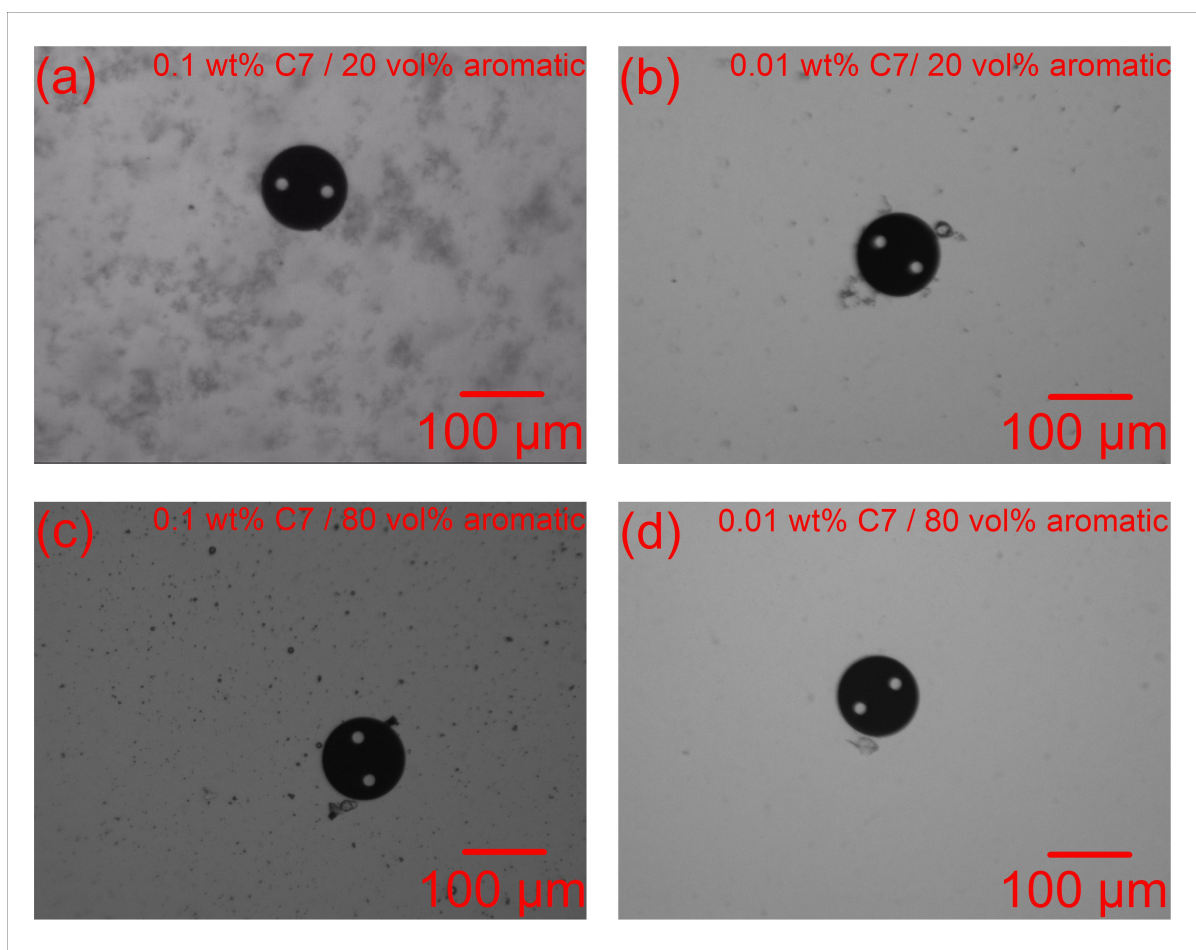


Figure 5.4: Visualization of the water-dectol interface with (a) 0.1 wt% C7 with 20 vol% toluene, (b) 0.01 wt% C7 with 20 vol% toluene, (c) 0.1 wt% C7 with 80 vol% toluene and (d) 0.01 wt% C7 with 80 vol% toluene. All interfaces are aged for 3000 sec.

When the asphaltene concentration is over the precipitation onset, asphaltene can form natural aggregates in the bulk oil phase. These aggregates precipitate at the oil-on-water interface, which works as natural tracers to facilitate strain analysis. Figure 5.4 shows a sample image of aged asphaltene interfacial film with various bulk oil phases.

The number of asphaltene aggregates decrease when the asphaltene concentration decrease and aromatic fraction increase. Figure 5.4 thus confirms that the appearance of asphaltene aggregates can be attributed to the excess asphaltene over the solubility of the oil phase.

In order to quantify the impact of asphaltene aggregates at the water-oil interface, we use two different ways to avoid aggregates appearing at the interface. The first way is reversing the interface from the oil-on-water to water-on-oil interface, for which the aggregates precipitate to the bottom of the sample cell rather than the interface due to the gravity. We can then compare the interfacial rheology at oil-on-water interface and water-on-oil interface to characterize the rule of aggregates. The detail of oil-on-water and water-on-oil experimental apparatus are depicted in Fig. 2.3 and Fig. 2.4. The second way is removing the aggregates before water and oil contact by centrifuging the bulk oil phase and extracting the supernatant. This way is more convenient than reversing the interface. In practice, we combine these two methods to give a deep understanding of how aggregates impact the interfacial rheology.

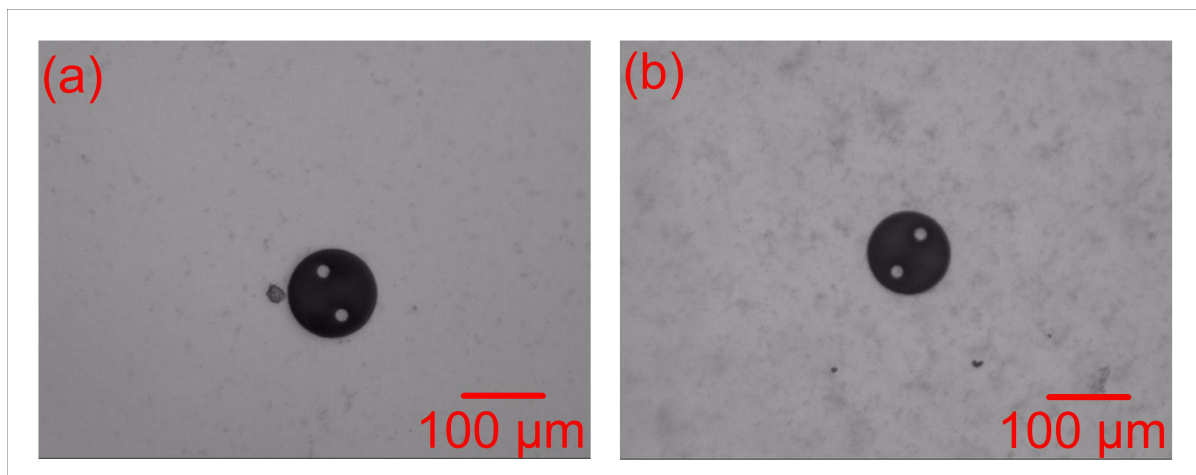


Figure 5.5: Visualization of (a) water-on-oil and (b) oil-on-water interface. Both interfaces are aged for 3000 sec, and the bulk oil phases are both composed of 0.1 wt% C7 and good dectol (20 vol% aromatic)

Figure 5.5 represents the visualization of water-on-oil and oil-on-water interface after 3000 sec aging. The oil phase contains 0.1 wt% C7 in bad dectol (20 vol% aromatic fraction) so aggregates form in the bulk oil phase. For the water-on-oil interface, the asphaltene aggregates precipitate to the bottom of the sample cell, so no visible aggregates can be observed compared to that of oil-on-water interface. This result confirms that reversing the water-oil interface can efficiently avoid asphaltene aggregates appear at the interface.

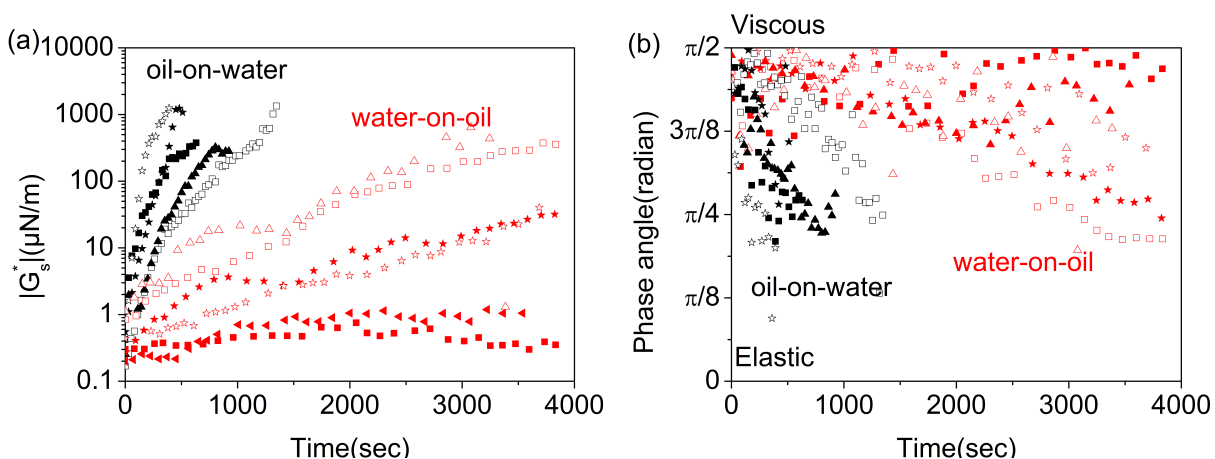


Figure 5.6: Comparison of water-on-oil and oil-on-water interfacial rheology. (a) Magnitude of the interfacial complex modulus of oil-on-water (black curves) and water-on-oil (red curves) interface with 0.1 wt% C7 asphaltene in the bad dectol (20 vol% aromatic fraction) (b) Evolution of the phase angle in the same experiments.

Figure 5.6 shows the interfacial rheology of the water-on-oil and oil-on-water interface. The $|G_s^*|$ and δ of two apparatus are quantitatively different. The water-on-oil apparatus shows a slower increase of interfacial stiffness and transition from viscous-dominated response to viscoelastic response than that of oil-on-water apparatus. Moreover, the rheology of water-on-oil apparatus is more dispersed compared with oil-on-water geometry.

Although Fig. 5.6 shows a significant difference between oil-on-water and water-on-oil interfacial rheology, one might question whether gravity or the position of aggregates is the reason of different rheology. In order to further confirm the exact role of aggregates

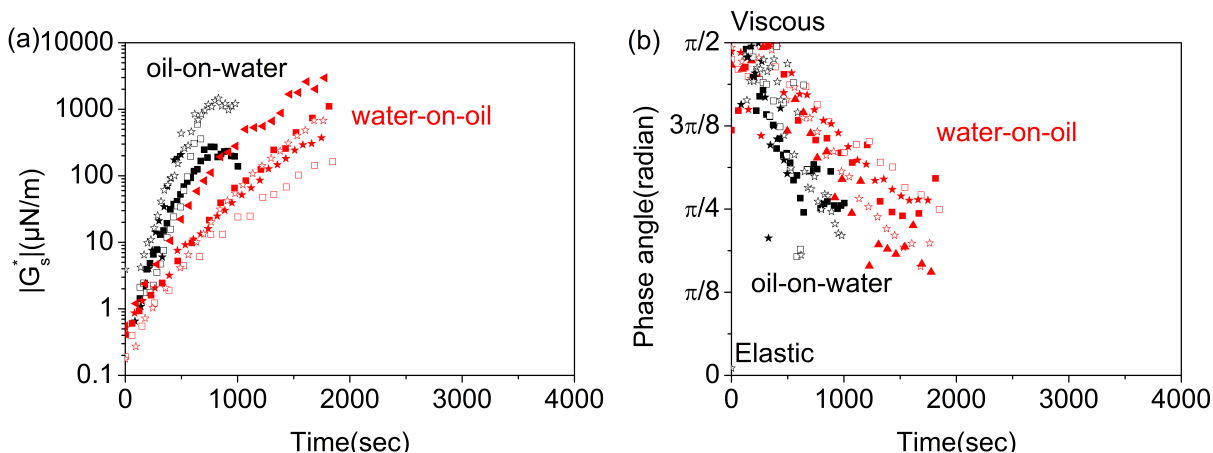


Figure 5.7: Comparison of water-on-oil and oil-on-water interfacial rheology without aggregates existing in the system. (a) Magnitude of the interfacial complex modulus of oil-on-water (black curves) and water-on-oil (red curves) interface with 0.1 wt% C7 asphaltene in the bad dectol (20 vol% aromatic fraction). Aggregates are removed prior to the water-oil contact by centrifugation (b) Evolution of the phase angle in the same experiments.

in the difference of Fig. 5.6, we then use the oil phase without asphaltene aggregates (the supernatant of 0.1 wt% C7 in bad dectol) to repeat the experiment. If both apparatus still show different response without aggregates existing in the system, gravity can then be attributed to the difference shown in Fig. 5.6. Figure 5.7 shows the rheological measurement of water-on-oil and oil-on-water interfaces without asphaltene aggregates in the whole system. The bulk dectol phase is composed of 0.1 wt% C7 and 20 vol% toluene, but aggregates are removed by centrifugation. Compare to the result in Fig. 5.6, $|G_s^*|$ and δ of both oil-on-water and water-on-oil in Fig. 5.7 are more similar. This result indicates that the position of the asphaltene aggregates rather than gravity effect are the reason of different rheological response in Fig. 5.6.

After confirming that the existence of aggregates at the interface does impact the rheology, we then try to compare the rheology of identical apparatus but different oil phases to further investigate the role of asphaltene aggregates. Figure 5.8 compare the interfacial rheology of oil-on-water interface with and without asphaltene aggregates in

the whole system. When the asphaltene aggregates precipitate to the interface, the aggregates show no significant impact on the rheology, both the $|G_s^*|$ and δ . However, for the water-on-oil apparatus, Fig. 5.9 depicts that the rheological response is more dispersed with aggregates, and the formation of a viscoelastic stiff layer is delayed significantly.

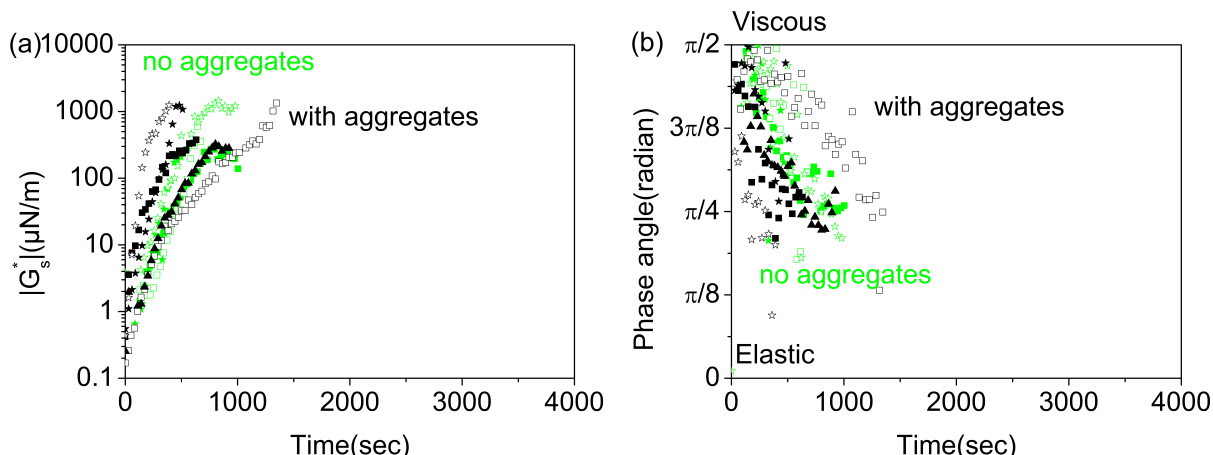


Figure 5.8: The different oil-on-water interfacial rheology for interface with and without aggregates. (a) Magnitude of the interfacial complex modulus of the oil-on-water interface with 0.1 wt% C7 asphaltene in the dectol (20 vol% aromatic fraction) (black curves), and identical experiment but aggregates are removed prior to the water-oil contact (green curves). (b) Evolution of the phase angle in the same experiments.

From the comparison shown above, the asphaltene aggregates might work as a nucleation point which can attract more asphaltene molecules to form aggregates. For the water-on-oil apparatus, the asphaltene aggregates precipitate to the bottom of the sample cell, driving more asphaltene molecules going to the bottom of sample cell rather than adsorbing at the interface. On the contrary, when the oil-on-water apparatus is applied, the asphaltene aggregates precipitate to the interface. This mechanism still drive asphaltene adsorbing to the interface, so no significant difference on the rheology as Fig. 5.9 can be found in Fig. 5.8. When most of the asphaltenes aggregates are removed prior to water-oil contact, the water-on-oil and oil-on-water rheology become more similar than that of oil phase with aggregates, since no aggregates interfere with

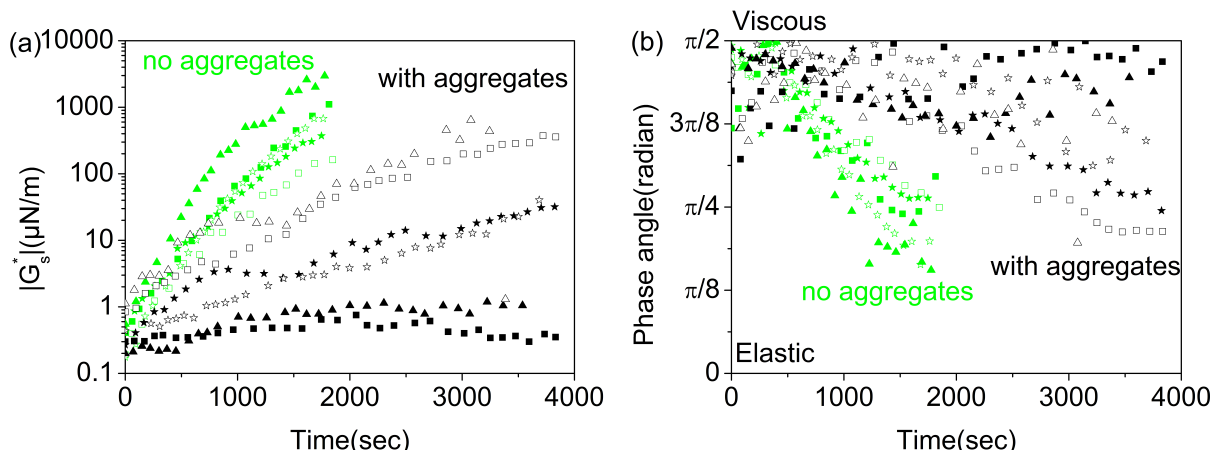


Figure 5.9: Comparison for the existence of aggregates for water-on-oil interfacial rheology. (a) Magnitude of the interfacial complex modulus of water-on-oil interface with 0.1 wt% C7 asphaltene in the bad dectol (20 vol% aromatic fraction) (black curves), and identical experiment but aggregates are removed prior to the water-oil contact (green curves). (b) Evolution of the phase angle in the same experiments.

the adsorption mechanism.

Figure 5.10 depicts the water-on-oil and oil-on-water rheology for the isomatic oil phase contains 0.1 wt% C7 and 80 vol% aromatic-200 (good solvent). Not surprisingly, since there are no aggregates in the oil phase, the water-on-oil and oil-on-water apparatus demonstrate similar response on both $|G_s^*|$ and δ , agreeing with the result in Fig. 5.7. From the above study, we have confirmed that the aggregates can result in a strong variation on asphaltene adsorption under particular experimental condition. If the oil phase is composed of enough aromatic solvent and no aggregates appear, a more reproducible rheological property can be obtained. This result motivates us choosing good isomatic as the new model oil phase in order to quantify the performance of demulsifiers.

5.7 Frequency-dependent rheology

We have investigated how the chemistry of the oil phase influence the asphaltene adsorption at the water-oil interface. However, the rheology property also depends on how

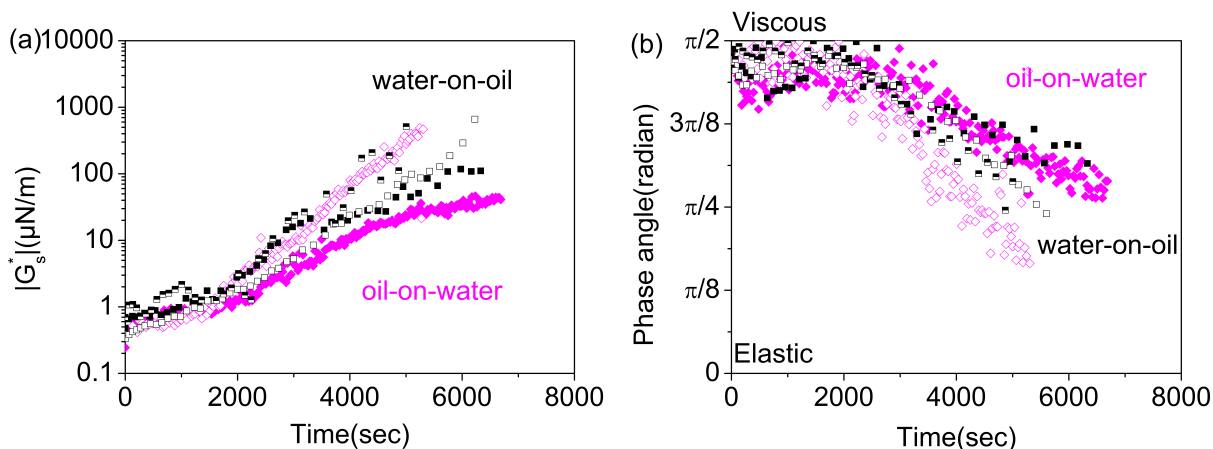


Figure 5.10: The different water-on-oil interfacial rheology for the oil phase with and without aggregates. (a) The magnitude of the interfacial complex modulus of the oil-on-water (pink curves) and water-on-oil (black curves) interface with 0.1 wt% C7 asphaltene in the good isomeric (80 vol% aromatic). (b) Evolution of the phase angle in the same experiments.

the interfacial structure relax after applying the stress. Characterizing the viscoelastic property in different period of time thus facilitate a better understanding of the structure of asphaltene film. In order to probe the rheological property of asphaltene interfacial film in different period time, the frequency sweep is conducted during asphaltene aged at the water-isomeric interface. Frequency is swept between 1 Hz, 0.5 Hz, 0.1 Hz and 0.01 Hz for an identical interface. The experimental apparatus used in this study is water-on-good-isomeric interface with 0.1 wt% C7.

Figure 5.11 (a) shows that $|G_s^*|$ can decrease around 1 order of magnitude when the frequency of stress is decreased from 1 Hz to 0.01 Hz. This result reveals that the interfacial complex modulus is dependent on the relaxation time which the structure can interact when the stress is applied. Figure 5.11 (b) further points out that the asphaltene layer remains viscous-dominated response in the first 2000 sec, no matter which frequency is applied. This viscous-dominated responses at early stage suggest that only the interfacial viscosity increase before 2000 sec, which results in the increase of

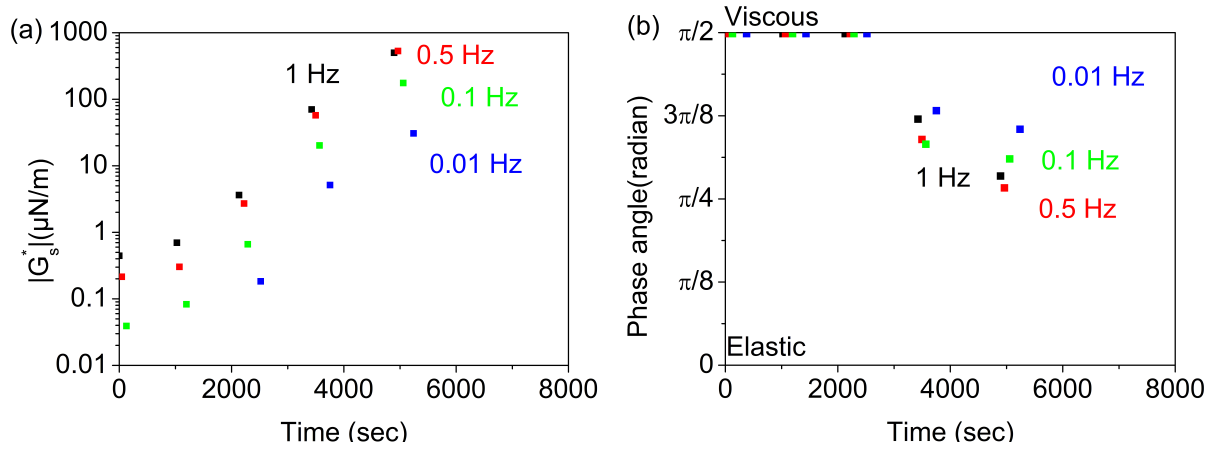


Figure 5.11: Apply frequency sweep experiment when asphaltene layer ages. (a) The magnitude of the interfacial complex modulus when the oil phase contains 0.1 wt% C7 asphaltene in isomatic. Frequency is switched between 1 Hz (black), 0.5 Hz (red), 0.1 Hz (green), and 0.01 Hz (blue) during the measurement Geometry is water-on-oil. (b) Evolution of the phase angle in the same experiments.

$|G_s^*|$ in Figure 5.11 (a). When the interface is aged and elasticity appears, asphaltene interfacial film shows more viscous-dominated response in the low-frequency mode. This liquid-like behavior over the long time period indicates that the asphaltene interfacial layer is a viscoelastic liquid material.

Figure 5.12 further shows G' and G'' as a function of frequency when interface ages. This figure is re-plotted using the identical result from Fig. 5.11. From Fig. 5.12 (a), no measurable G' appear before 2000 sec. Both G' and G'' increase when interface ages and show a dependence on the frequency applied. To quantify the frequency-dependence of the asphaltene film, we derive the apparent power law exponent n using following equation to fit G' , G'' , and $|G_s^*|$:

$$G \sim f^n \sim \omega^n \quad (5.1)$$

where f is the frequency and ω is the angular frequency we apply, and the result is plotted in Fig. 5.12 (b). n is found to be near 1 before 2000 sec for G'' , namely, G'' is pro-

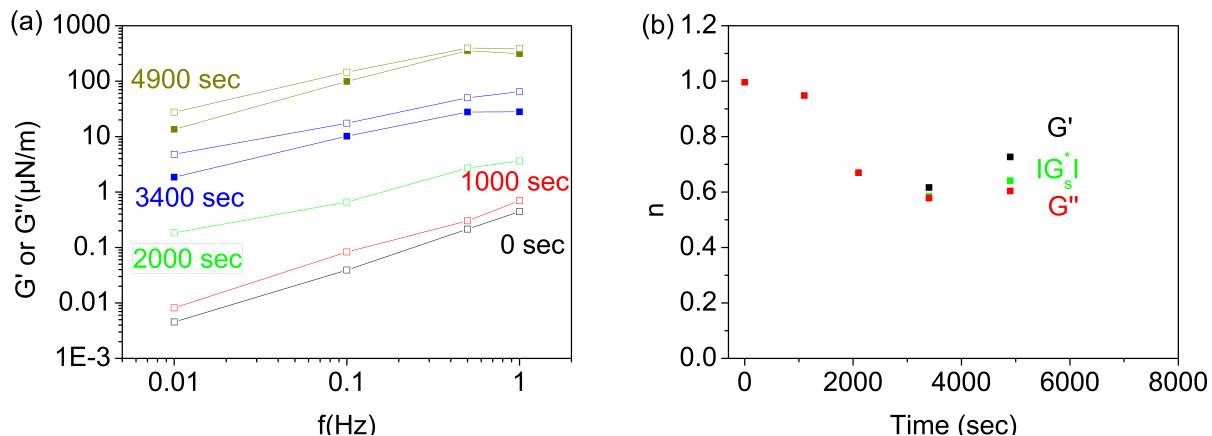


Figure 5.12: (a) Frequency sweep of G' and G'' when the water-isomastic interface is aged with 0.1 wt% C7 asphaltene for 0 sec (black), 1000 sec (red), 2000 sec (green), 3400 sec (blue) and 4900 sec (dark yellow). Filled and open symbols represent G' and G'' respectively. (b) Power-law exponent for G' (black), G'' (red) and $|G_s^*|$ (green) as a function of frequency.

portional to frequency, $G''(\omega) \sim \omega \eta_s$. This relation suggests that the interface remains a pure viscous-liquid response, and viscous modulus is contributed by the surface viscosity η_s as described in Eq. 2.7. When the interface is aged for 5000 sec, the modulus still shows frequency-dependence, but the apparent decay exponents are smaller than 1. This evolution suggests that when the interface ages and becomes stiff, the influence of structural relaxation on the rheological property decrease, but it still impact the rheological response.

5.8 Linear viscoelasticity of asphaltene film

We have revealed how the structure relaxation impacts the rheological property of the asphaltene layer. Another factor which can impact the rheology is the strain responding to the stress we applied. The rheological measurement requires small enough strain to maintain the structure at near equilibrium. Namely, the strain should stay in the linear viscoelastic region so the measurement does not break or yield the asphaltene structure.

In order to study the linear viscoelastic region of the asphaltene film, Fig. 5.13 illustrates the G' and G'' as a function of strain when the interface is aged for 3000 sec. The experimental apparatus is water-on-good-isomastic with 0.1 wt% C7. Both G' and G'' remains unchanged when the strain is smaller than 3%, and the interface starts yielding when strain is higher than 3%. This result confirms that the strain we apply during microbutton measurement ($\sim 0.3\%$) is at the region of linear viscoelasticity.

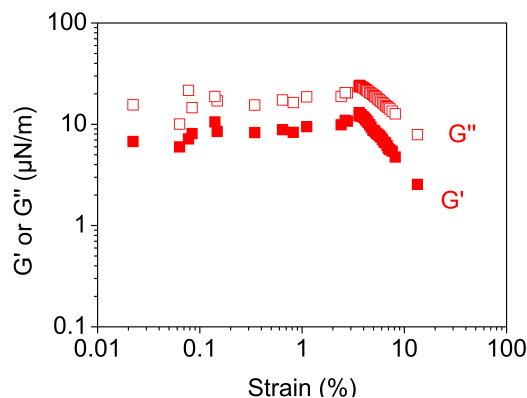


Figure 5.13: Strain sweep of G' and G'' when the water-isomastic interface is aged with 0.1 wt% C7 asphaltene for 3000 sec. Filled and open symbols represent G' and G'' respectively.

5.9 Conclusion

We have investigated the chemical and physical factors which can influence the interfacial rheology when asphaltene adsorb at the water-oil interface. The chemistry of oil composition is shown to impact asphaltene adsorption strongly. Different oil phases are shown to influence the asphaltene adsorption even with identical aromatic fraction and asphaltene concentration, which might be attributed to different diffusivity of asphaltene in different oil phases. Higher asphaltene concentration in the bulk oil phase can increase the stiffening rate of interfacial layer, which seems to correlate with higher concentra-

tion gradient between bulk and the interface. When the aromatic fraction of oil phase increase, the asphaltenes dissolve easily in the oil phase and thus has a lower affinity to the water-oil interface. This results in slower stiffening rate and also slower transition from viscous-dominated behavior to viscoelastic behavior of the interfacial film.

In addition to the chemistry of the oil phase, the asphaltene aggregates appear in the low aromatic fraction (bad isomeric, 20% aromatic fraction) can also impact the rheology within the particular condition. The asphaltene aggregates seem to form the nucleation point, not at the interface, which results in relatively slower adsorption at the interface. This issue can be avoided by removing the aggregates from bad isomeric or using the oil phase without asphaltene aggregates (good isomeric, 80 vol% aromatic fraction). For the oil phase without aggregates, oil-on-water and water-on-oil rheological measurement are similar, and a more reproducible rheological response can be obtained. This result indicates that gravity does not impact the asphaltene adsorption. The frequency and strain sweep provides a deep understanding of the property of the interfacial film. The asphaltene interfacial film shows liquid-like behavior over a long time period. To maintain the measurement in the linear viscoelastic region, the strain of rheological measurement should be kept less than 3%. The study in this chapter provides an overall understanding of how to control the asphaltene adsorption and suggest the strategy if we want to establish a more reproducible system to test the effect of various demulsifiers.

Chapter 6

Study of demulsifier structure

6.1 Overview

We have utilized the sample demulsifier, ethylcellulose (EC) to investigate how the demulsifier delays asphaltene adsorption and softens the pre-existing asphaltene layer. However, although EC significantly destabilizes the interface and enhance emulsion coalescence, EC is economically inappropriate for the industrial using and a new demulsifier is needed. In order to develop a new demulsifier, we want to establish a strategy to guide the design of the demulsifiers. As a result, this chapter focuses on how the demulsifier structure impacts its performance on preventing asphaltene from forming a stiff layer and softening the pre-existing asphaltene interfacial film. We want to test how the property of demulsifiers, such as molecular weight and hydrophilic-lipophilic balance(HLB), impact the performance of demulsifier.

The 0.1 wt% C7 in good isomatic (a mixture of 20 vol% and isopar and 80 vol% aromatic-200) is chosen in this chapter as the model oil phase, using microbutton rheometry and water-on-oil sample cell. We first improve the method for introducing demulsifier to the aged asphaltene layer using the water-on-oil apparatus. The $\text{PO}_{14} - \text{EO}_9 - \text{PO}_{14}$

(2150) block copolymer is studied as a reference of demulsifier performance for the following study of PO – EO – PO triblock copolymers. PO₂₀ – EO₁₃ – PO₂₀ (3100) is then studied to probe how the demulsifiers with identical HLB but different molecular weight impact the demulsifier performance at the interface. Finally, we use PO₁₃ – EO₂₂ – PO₁₃ (2650) to probe how the length of hydrophile influence the demulsifier performance under the different mechanism.

6.2 Reference experiment: The water-on-clean-isomastic interface

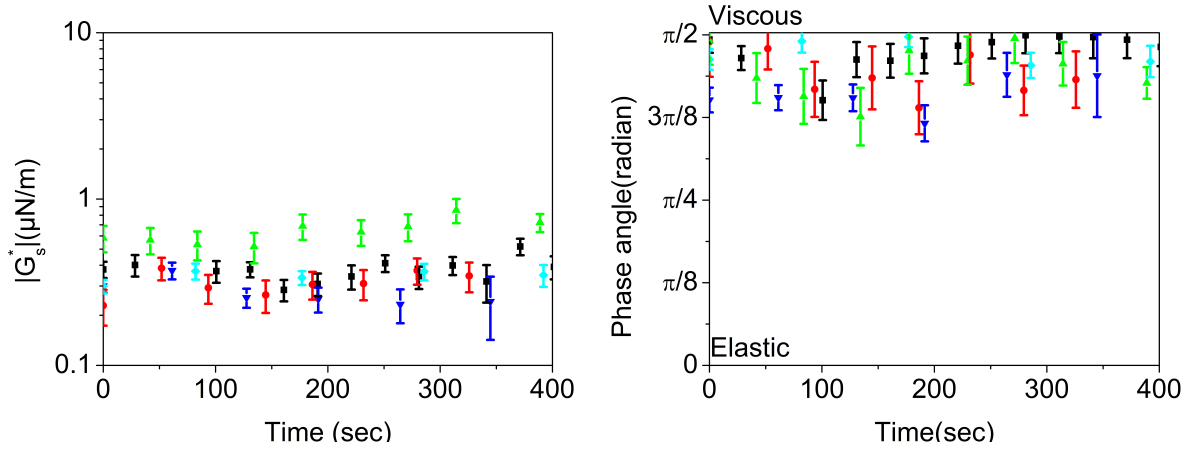


Figure 6.1: Reference rheological study of clean water-on-isomastic interface. (a) Magnitude of the interfacial complex modulus of water-on-good-isomastic interface. Different colors represent different trials conducted by identical experimental apparatus. (b) Evolution of the phase angle in the same experiments.

The rheology of clean isomastic-water interface is first studied to provide a baseline of the rheological response. Figure 6.1 depicts $|G_s^*|$ and δ of water-on-clean-isomastic of 5 different trials prepared by identical experimental apparatus. The average value of $|G_s^*|$ for water-on-clean-isomastic interface is $0.45 \pm 0.16 \mu\text{N/m}$, while the average of phase angle δ is 1.47 ± 0.10 radian. In the following result of this chapter, we choose the up-limit

of $|G_s^*|$, $0.61 \mu\text{N/m}$, and the low-limit of δ , 1.37 as the reference line of clean isomeric response. When $|G_s^*|$ is below the baseline or δ is over the baseline, the response will be considered similar to the clean-water-isomeric interface without any surface-active material adsorption.

6.3 Improved method to introduce demulsifier: The separable water-on-oil phases

The method of introducing demulsifier to the aged asphaltene layer we described previously in Fig. 4.1 actually encounters a non-controllable mechanism. When the new oil phase is deposited from the top of the pre-existing oil phase, the demulsifier needs to diffuse to and mix with another oil phase, and eventually adsorb the interface. This process is not controllable and hard to be quantify. In order to introduce demulsifier using a more controllable method, we develop a new experimental procedure using the water-on-oil geometry illustrated previously in Fig. 2.4.

Figure 6.2 (a) shows the procedure for injecting the premixed C7 asphaltene and demulsifier oil phase into the sample cell to form stable water-on-oil interface, which allowing C7 and demulsifier adsorb to the interface simultaneously. The premixing experiment does not encounter any further physical disruption after the water and oil contact, and the adsorption mechanism is similar to that of oil-on-water geometry we have shown previously. Figure 6.2 (b) depicts the new procedure to introduce demulsifier to pre-existing C7 layer. The demulsifier is introduced by removing the bulk oil phase with C7 asphaltene only and inject a new oil phase with both C7 asphaltene and demulsifier into the sample cell. This oil phase exchanging procedure prevents the issue of mixing two different oil phases, and the bulk asphaltene concentration in the new oil

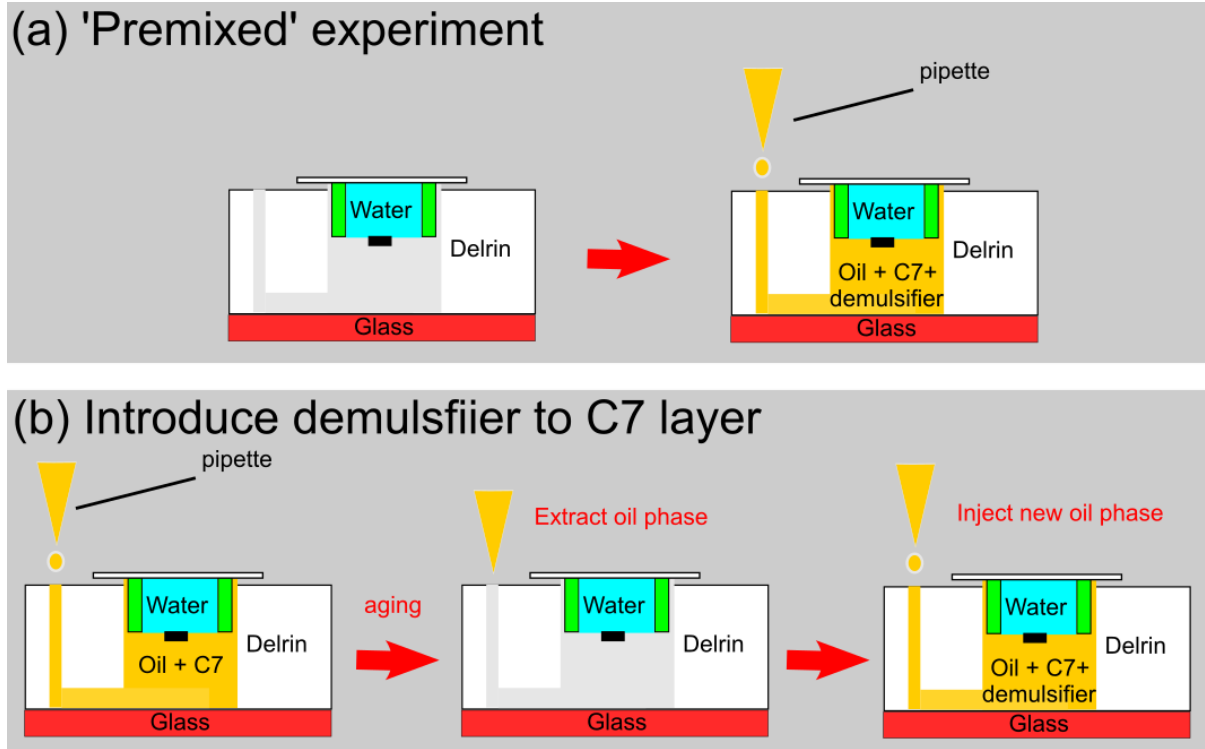


Figure 6.2: Procedure of characterizing demulsifier on interfacial rheology using water-on-oil geometry. (a) The 'premixed' experiment. An oil phase containing both C7 and demulsifier is injected through the side channel of the sample cell, and the level of the oil phase is raised carefully to form a stable water-on-oil interface which asphaltene and demulsifier adsorb simultaneously. (b) The experiment of introducing demulsifier to C7 layer. Firstly, the oil phase with C7 contacts with water to form an aged C7 layer at the water-on-oil geometry. Secondly, oil with C7 is extracted and a new oil phase with both C7 and demulsifier is re-injected through the side channel, allowing demulsifier to interact with a preformed C7 layer.

phase is maintained as that of the old oil phase.

In order to quantify the physical disruption on the aged asphaltene layer during exchanging the bulk oil phase, Fig. 6.3 and Fig. 6.4 illustrate how the rheology change when the new bulk oil phase contains only clean isomeric and isomeric with identical asphaltene concentration as the old oil phase, respectively. The oil phase is exchanged when the interface is aged for around 3300 sec. Figure 6.3 shows that, when the bulk isomeric with 0.1 wt% C7 asphaltene is exchanged by the clean isomeric without asphaltene, $|G_s^*|$ decrease around 1 order of magnitude right after the bulk oil phase is exchanged and no

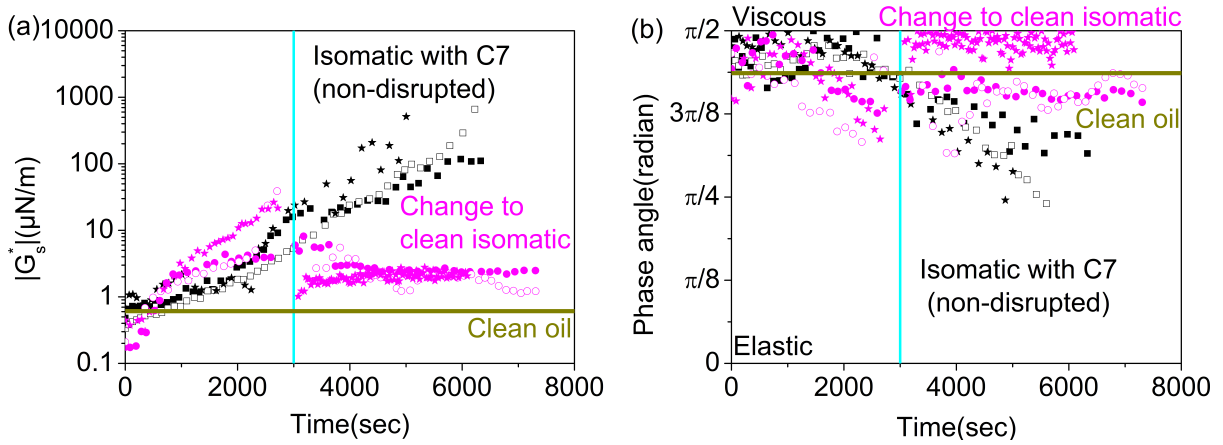


Figure 6.3: The influence of reducing bulk C7 concentration on interfacial rheology. (a) The magnitude of the interfacial complex modulus of water-on-oil interface with 0.1 wt% C7 asphaltene in the good isomastic (black) and interface with exchanging the oil phase from 0.1 wt% C7 asphaltene in the good isomastic into clean isomastic (pink). The cyan line represents the time of exchanging the oil phase, and the dark yellow line represents the level of water-clean-isomastic response. Different symbols in identical colors represent different trials conducted by identical experiment procedure. (b) Evolution of the phase angle in the same experiments.

further change of $|G_s^*|$ can be observed. The corresponding elasticity of the interfacial layer is also decreased and remains nearly unchanged after exchanging the oil phase. Figure 6.4 shows how the interfacial rheology evolve at water-on-isomastic interface when the bulk oil phase is exchanged by the new isomastic with identical concentration of C7. After the oil phase is exchanged, $|G_s^*|$ does not decrease as the experiment using clean isomastic. However, $|G_s^*|$ keep increasing and its evolution is similar to the non-disrupted water-on-isomastic interface with 0.1 wt% C7. The elasticity of the interfacial layer also keeps increasing, similar to the non-disrupted interface.

The result of Fig. 6.4 indicates that when the bulk C7 concentration remains unchanged, the physical disruption during exchanging the oil phase does not break the interfacial film. However, when the bulk C7 concentration decrease, the interfacial layer is softened and lose the elasticity. Part of the adsorbed asphaltene might desorb from the interface and re-dissolve back into the clean isomastic, weakening the structure at

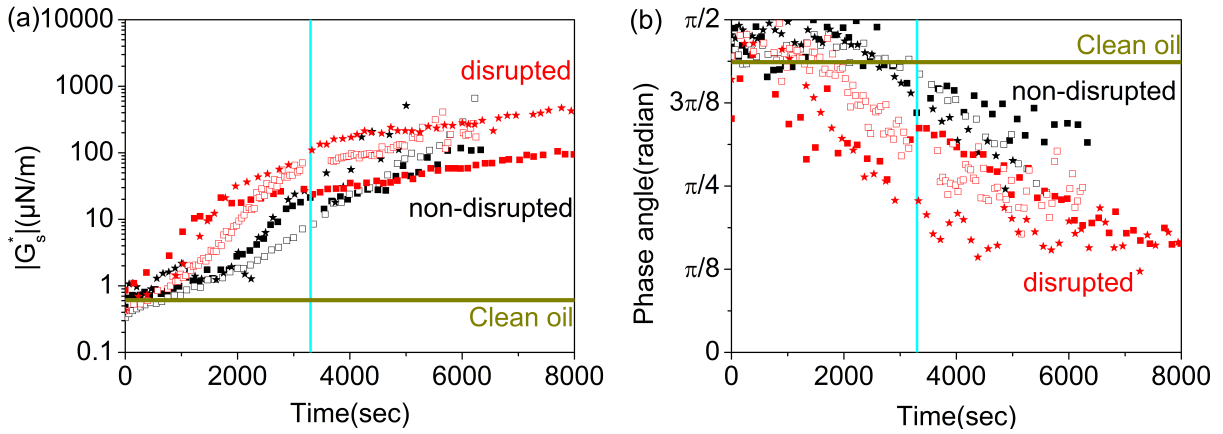


Figure 6.4: The influence of physical disruption from exchanging oil phase on rheology. (a) The magnitude of the interfacial complex modulus of the water-on-oil interface with 0.1 wt% C7 asphaltene in the isomastic (black) and interface encountering removing and re-injecting identical isomastic with 0.1 wt% C7 asphaltene (red). The cyan line represents the time of exchanging the oil phase, and the dark yellow line represents the level of water-clean-isomastic response. Different symbols in identical colors represent different trials conducted by identical experiment procedure. (b) Evolution of the phase angle in the same experiments.

the interface. To characterize the influence of demulsifier at the interfacial layer, the C7 concentration in the bulk oil phase should remain constant. As a result, in the following study when demulsifiers are introduced to the aged asphaltene layer, the new oil phase is composed of premixed demulsifier and identical C7 concentration as the oil phase. The good isomastic (20 vol% isopar and 80 vol% aromatic-200) is used as a model oil phase, and the C7 asphaltene concentration is fixed at 0.1 wt%. The red curves in Fig. 6.4 are utilized as the reference experiment to indicate the rheology evolution when the new exchanging oil phase contains no demulsifier.

6.4 PO₁₄ – EO₉ – PO₁₄ (2150) triblock copolymer

6.4.1 Concurrent adsorption of C7 and 2150

The PO – EO – PO triblock copolymers are utilized to probe the structure effect since they are commercially available and the structural can be varied easily.[123, 124] We first study the concurrent adsorption of PO₁₄ – EO₉ – PO₁₄ (2150) demulsifier and C7 asphaltene as a reference performance of PO – EO – PO triblock copolymer. Figure 6.5 depicts the interfacial rheology of the water-on-oil interface with premixed 0.1 wt% C7 and various concentrations of 2150 in the good isomeric.

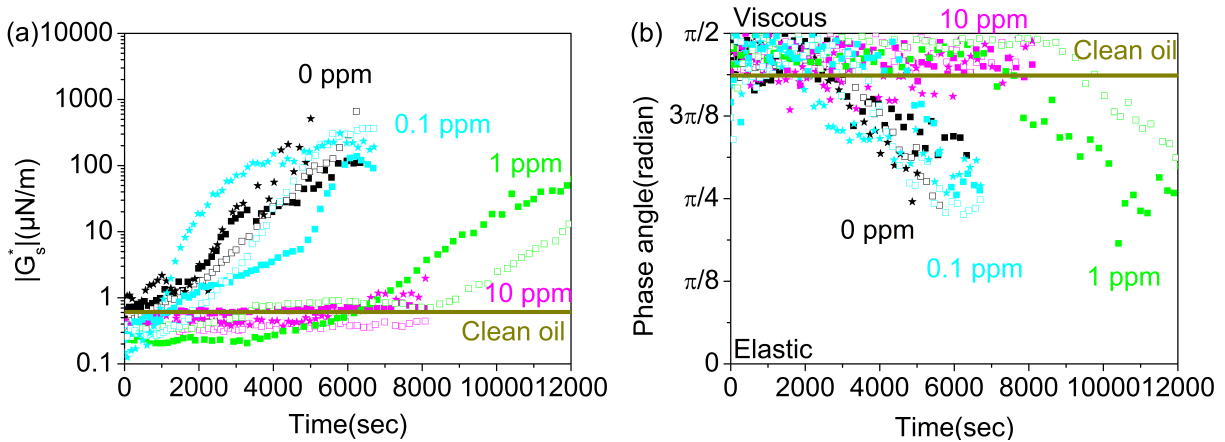


Figure 6.5: Concurrent adsorption of C7 and 2150 demulsifier and its impact on the interfacial rheology. (a) The magnitude of the interfacial complex modulus when the oil phase contains 0.1 wt% C7 asphaltene only (black), premixed 0.1 wt% C7 and 0.1 ppm 2150 (cyan), 1 ppm 2150 (green) and 10 ppm 2150 (pink). The dark yellow line represents the level of water-clean-isomeric response. Geometry is water-on-oil interface, and different symbols in identical colors represent different trials conducted by identical demulsifier concentration. (b) Evolution of the phase angle in the same experiments.

When the concentration of 2150 is 10 ppm (pink curves), 2150 significantly prevent asphaltene forming a stiff and viscoelastic layer at the water-on-isomeric interface. However, when the concentration of 2150 is decreased to 1 ppm (green curves), the stiffness and elasticity start to increase beyond the region of clean isomeric-water interface after

6000 sec adsorption, meaning 2150 delay but not prevent the formation of the stiff viscoelastic film. When the concentration is further decreased to 0.1 ppm (cyan curves), the premixed 2150 and C7 shows a similar increase of the interfacial stiffness and viscoelasticity transition to that of interface with 0.1 wt% C7 only (black curves). This experiment asserts that 2150 demulsifier can prevent or delay asphaltene forming stiff and viscoelastic layer at the water-isomatic interface, but the performance depends strongly on the concentration of demulsifier.

6.4.2 Impact of 2150 on the aged asphaltene layer

After investigating the ability to prevent asphaltene from forming stiff layer for 2150 demulsifier, we then study how 2150 soften the pre-existing asphaltene film. Figure 6.6 depicts the rheology of the water-on-good-isomatic interface when the bulk oil phase is exchanged from 0.1 wt% C7 only to premixed 0.1 wt% C7 and various concentrations of 2150. The oil phase is exchanged when the interface is aged for around 3300 sec.

For the new oil phase containing with 10 ppm 2150 (pink curves), 2150 significantly decreases the stiffness by around 2 order of magnitude and removes the elasticity of the interfacial film right after the oil phase is exchanged. When the 2150 concentration is decreased to 1 ppm (green curves), the stiffness does not decrease instantly and significantly as that of 10 ppm, but a slight suppression or no increase on the stiffness is observed. 1 ppm 2150 further stops the transition from viscous-dominated response to viscoelastic response, but the elasticity remains similar to that before exchanging the oil phase. When the concentration is decreased again to 0.1 ppm (cyan curves), the interfacial stiffness and elasticity keep increasing as the reference experiment without demulsifier (red curves). The experiments in Fig. 6.6 and 6.5 shows that 1 ppm is the threshold for 2150 demulsifier to have the ability on softening the C7 interfacial layer and preventing C7

from forming the stiff layer at the water-isomastic interface. With enough concentration, 2150 is proven as an efficient additive to soften C7 layer and prevent C7 from forming stiff layer.

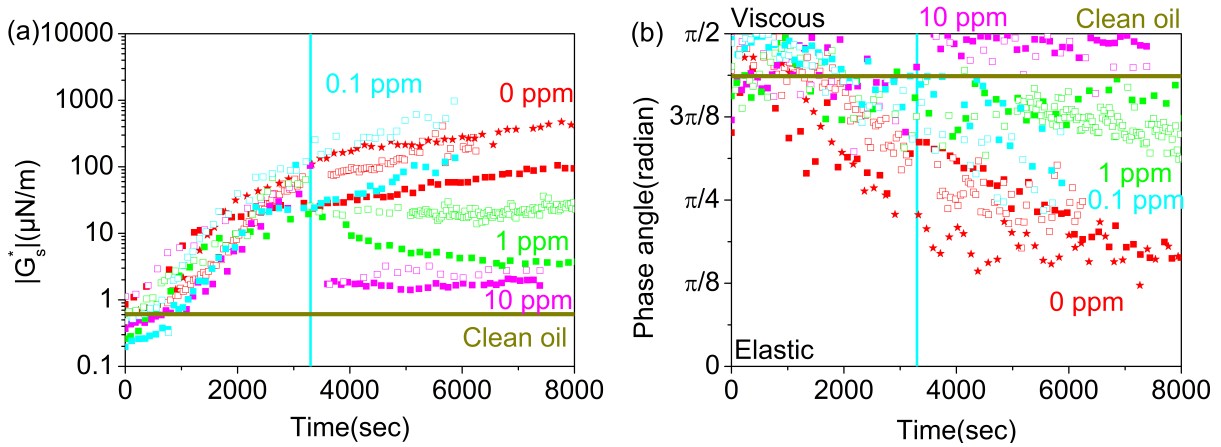


Figure 6.6: The impact of 2150 demulsifier on aged asphaltene layer. (a) The agnitude of the interfacial complex modulus evolution at the water-on-oil interface when 0.1 wt% C7 in isomastic is replaced by 0.1 wt% C7 in isomastic with 0.1 ppm 2150 (cyan), 1 ppm 2150 (green) and 10 ppm 2150 (pink). Different symbols in identical colors represent different trials conducted by identical experiment setup. The cyan line at 3000 sec represents the time of exchanging the oil phase, and the dark yellow line represents the level of water-clean-isomastic response. The red symbols are reference experiment of replacing oil phase by identical 0.1 wt% C7 in isomastic, showing the physical disruption during exchanging the oil phase. (b) Evolution of the phase angle in the same experiments.

6.5 Effect of molecular weight: $\text{PO}_{20} - \text{EO}_{13} - \text{PO}_{20}$ (3100) triblock copolymer

6.5.1 Concurrent adsorption of C7 and 3100

The first factor of demulsifier structure we want to investigate is whether the molecular weights of the demulsifiers influence their performance at the interface. To probe the impact of molecular weight on demulsifier performance, $\text{PO}_{20} - \text{EO}_{13} - \text{PO}_{20}$ (3100)

triblock copolymer is chosen to compare with $\text{PO}_{14} - \text{EO}_9 - \text{PO}_{14}$ (2150) demulsifier. 3100 has higher molecular weight but identical hydrophilic-lipophilic balance (HLB) as 2150. The 3100 demulsifier thus keeps identical affinity to the interface as 2150 and allow us to elucidate the contribution of demulsifier.

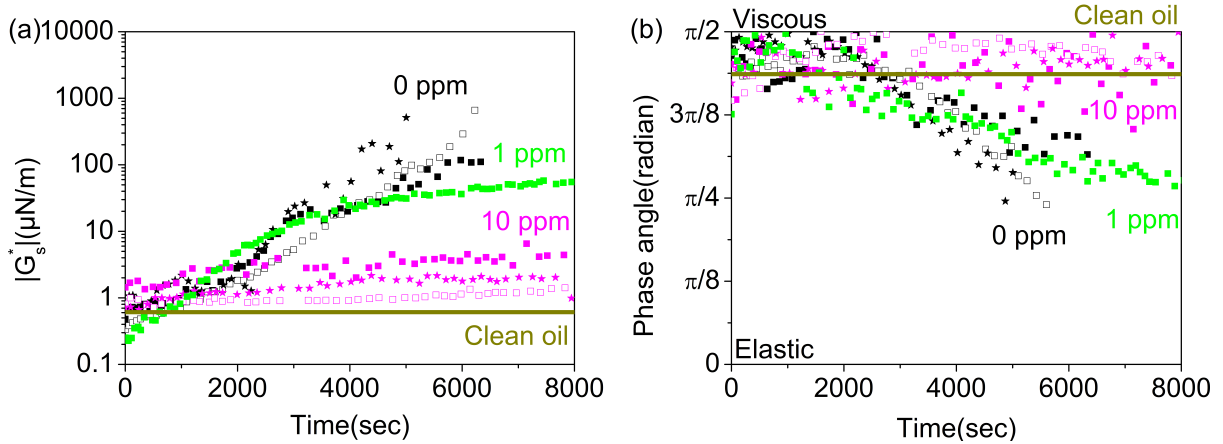


Figure 6.7: Concurrent adsorption of C7 and 3100 demulsifier and its impact on the interfacial rheology. (a) The magnitude of the interfacial complex modulus when the oil phase contains 0.1 wt% C7 asphaltene (black) , premixed 0.1 wt% C7 and 1 ppm 3100 (green) and premixed 0.1 wt% C7 and 10 ppm 3100 (pink). The dark yellow line represents the level of water-clean-isomastic response. Geometry is the water-on-oil interface, and different symbols in identical colors represent different trials conducted by identical experiment setup. (b) Evolution of the phase angle in the same experiments.

Figure 6.7 illustrates the interfacial rheology of water-on-good-isomastic interface with premixed 0.1 wt% C7 and various amount of 3100 demulsifiers in the bulk oil phase. When the bulk oil phase contains 10 ppm 3100 (pink curves), $|G_s^*|$ only increase around 5 times in the 8000 sec adsorption and the interface remains mostly viscous-dominated response like the clean water-isomastic interface. This result suggests that 10 ppm 3100 successfully prevent C7 from forming a stiff and viscoelastic layer at the water-isomastic interface.

However, when the concentration of 3100 is decreased to 1 ppm (green curve), $|G_s^*|$ increase initially as the interface without demulsifier in the first 4000 sec, and then remains

at a relatively low value compared with that of pure C7 interface. The corresponding elasticity of 1 ppm 3100, however, increases when the interface aging similar to the interface without demulsifier. This result indicates that 3100 need concentration higher than 1 ppm to efficiently prevent asphaltene from forming a viscoelastic stiff layer at the water-isomastic interface.

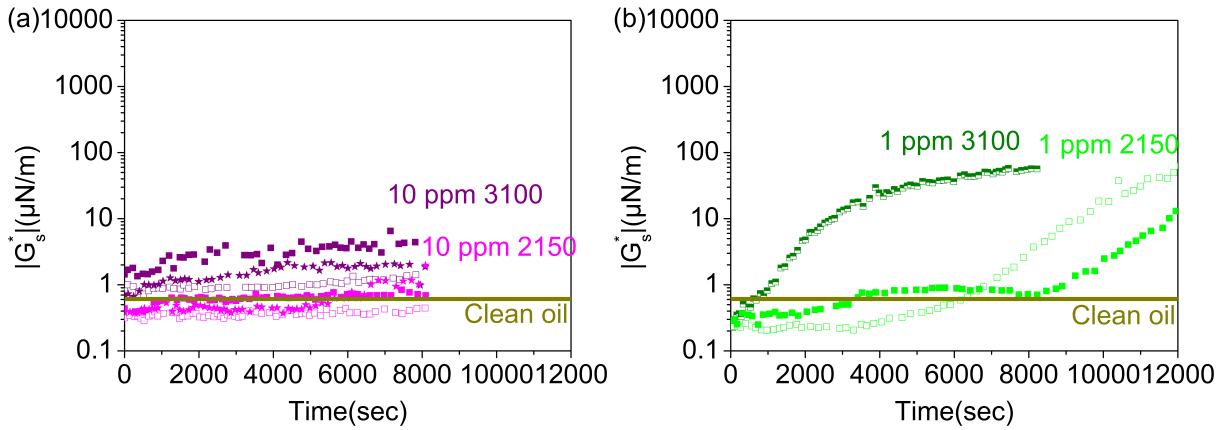


Figure 6.8: Comparison of 2150 and 3100 demulsifier on preventing asphaltene adsorption. Figures illustrate the magnitude of the interfacial complex modulus when the oil phase contains premixed 0.1 wt% C7 asphaltene with (a) 10 ppm 2150 (pink) or 10 ppm 3100 (purple), (b) 1 ppm 2150 (green) or 1 ppm 3100 (dark green). The dark yellow line represents the level of water-clean-isomastic response.

Figure 6.8 compares the rheological measurement with premixed 0.1 wt% C7 asphaltene and various concentration of 2150 or 3100 in the good isomastic. When the oil phase contains 10 ppm demulsifier, Fig. 6.8 (a) shows that both 3100 (purple) and 2150 (pink) efficiently prevent C7 from forming stiff layer at the water-on-good-isomastic interface. $|G_s^*|$ of these two experiments both increase around 5 times during 8000 sec and are below $10 \mu \text{ N/m}$. However, when the concentration of demulsifier decrease to 1 ppm, 2150 (green) shows better performance compared with 3100 (dark green) on preventing C7 forming a stiff layer. The 2150 demulsifier can suppress $|G_s^*|$ at the value near clean water-isomastic interface for 6000 sec and then gradually increase $|G_s^*|$ to the level

of 100 $\mu\text{N/m}$ after 12000 sec, while $|G_s^*|$ of interface with 3100 already stiffen to 100 $\mu\text{N/m}$ in 6000 sec adsorption. Figure 6.8 thus suggests that when the HLB keep identical, demulsifier with a higher molecular weight at low concentration can not reach the same performance as the demulsifier with smaller molecular weight. The 2150 demulsifier might have higher affinity than 3100 when there is 1 ppm demulsifier in the bulk oil phase, so 2150 can better prevent asphaltene further adsorbing at the interface than 3100 demulsifier.

6.5.2 Impact of 3100 on the aged asphaltene layer

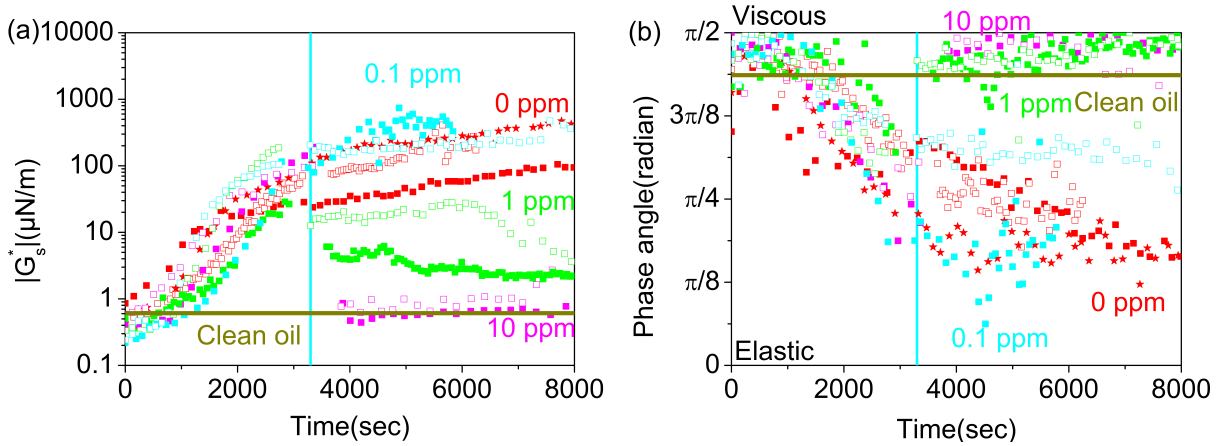


Figure 6.9: The impact of 3100 demulsifier on the aged asphaltene layer. (a) The magnitude of the interfacial complex modulus evolution at the water-on-oil interface when 0.1 wt% C7 in isomastic is replaced by 0.1 wt% C7 in isomastic with 0.1 ppm 3100 (cyan), 1 ppm 3100 (green) and 10 ppm 3100 (pink). Different symbols in identical colors represent different trials conducted by identical experiment setup. The cyan line at 3000 sec represents the time of exchanging the oil phase, and the dark yellow line represents the level of water-clean-isomastic response. The red symbols are reference experiment of replacing oil phase by identical 0.1 wt% C7 in isomastic, showing the physical disruption during exchanging the oil phase. (b) Evolution of the phase angle in the same experiments.

After investigating how 3100 demulsifier delays C7 from forming a stiff and viscoelastic layer, we then probe the ability of 3100 on softening the aged asphaltene film. Figure

6.9 shows how the interfacial rheology at the water-on-good-isomastic interface evolves when the bulk oil phase is exchanged from 0.1 wt% C7 only to premixed 0.1 wt% C7 and various concentration of 3100. 10 ppm 3100 (pink curves) is found to decrease the interfacial stiffness for 2 order of magnitude right after the oil phase is exchanged. The corresponding interfacial elasticity also disappeared after interfacial film contacting new oil phase with 10 ppm 3100. When the 3100 concentration is decreased to 1 ppm (green), 3100 gradually decreases the interfacial stiffness, but $|G_s^*|$ is still higher than that of 10 ppm after 3100 interacting with interfacial film for 5000 sec. The phase angle of the interface, however, instantly move to the level of the viscous-dominated region. For the experiment with 0.1 ppm 3100 in the new oil phase (cyan curves), the interfacial stiffness and elasticity both increase after exchanging the oil phase, indicating this amount of demulsifier is not enough to soften the interfacial film. The result in Fig. 6.9 reveals that 1 ppm is the threshold for 3100 demulsifier to be able to soften the interfacial film. When the 3100 concentration is increased, 3100 can better soften the aged interfacial layer.

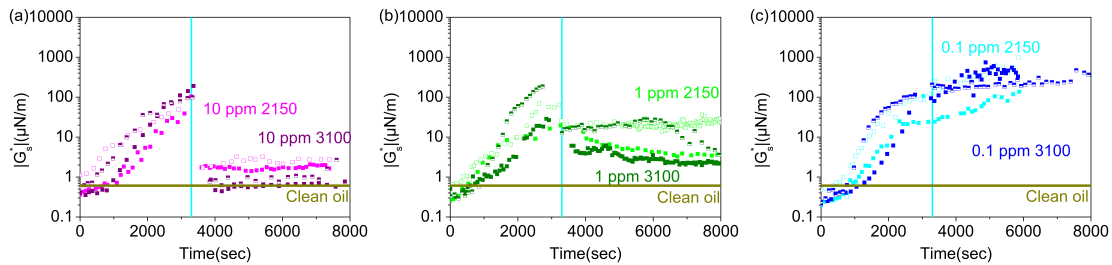


Figure 6.10: The ability of 2150 and 3100 demulsifier on softening the aged asphaltene layer. The figures illustrate the magnitude of the interfacial complex modulus evolution of the water-on-oil interface when 0.1 wt% C7 in isomastic is replaced by 0.1 wt% C7 in isomastic premixed with (a) 10 ppm 2150 (pink) or 10 ppm 3100 (purple), (b) 1 ppm 2150 (green) or 1 ppm 3100 (dark green) and (c) 0.1 ppm 2150 (cyan) or 0.1 ppm 3100 (blue). Different symbols in identical colors represent different trials conducted by identical experiment setup. The cyan line at 3000 sec represents the time of exchanging the oil phase, and the dark yellow line represents the level of water-clean-isomastic response.

Figure 6.10 compare the ability to soften asphaltene interfacial film for 2150 and 3100

demulsifier. For 10 ppm demulsifier in the new oil phases, both demulsifiers decrease 2-3 order of magnitude of $|G_s^*|$ right after exchanging the oil phase. When the concentration of demulsifier is decreased to 1 ppm, both demulsifier show either gradually decrease or no further increase on the interfacial stiffness. This result indicates that 1 ppm is the threshold that both demulsifiers can start impacting the interfacial layer. The 0.1 ppm 2150 and 3100 both can not soften the interfacial layer, so $|G_s^*|$ keep increasing after exchanging the oil phase. Figure 6.10 suggests that when the molecular weight of demulsifier change but keep HLB identical, the ability to soften interfacial film remains similar. This result is different from what we observed in Fig.6.8, which indicates that 2150 can better prevent asphaltene from forming a stiff layer. In conclusion, when demulsifiers with identical HLB, the molecular weight of demulsifier seems to only impact its ability on preventing C7 forming a stiff layer at the water-oil interface, but no significant difference can be found on the ability to soften pre-existing asphaltene layer.

6.6 Length of hydrophile: $\text{PO}_{13} - \text{EO}_{22} - \text{PO}_{13}$ (2650) triblock copolymer

6.6.1 Concurrent adsorption of C7 and 2650

With the knowledge of how the molecular weight contributes to the demulsifiers performance on the interface, we then study how HLB, the relative affinity to the water and oil phases, impacts the demulsifier performance. The $\text{PO}_{13} - \text{EO}_{22} - \text{PO}_{13}$ (2650, HLB= 8) triblock copolymer is chosen and compared with $\text{PO}_{14} - \text{EO}_9 - \text{PO}_{14}$ (2150, HLB= 4) block copolymer to probe how the higher length of hydrophile but similar length of hydrophobe influence demulsifier performance.

Figure 6.11 depicts the rheology of water-on-good isomeric interface aging with pre-

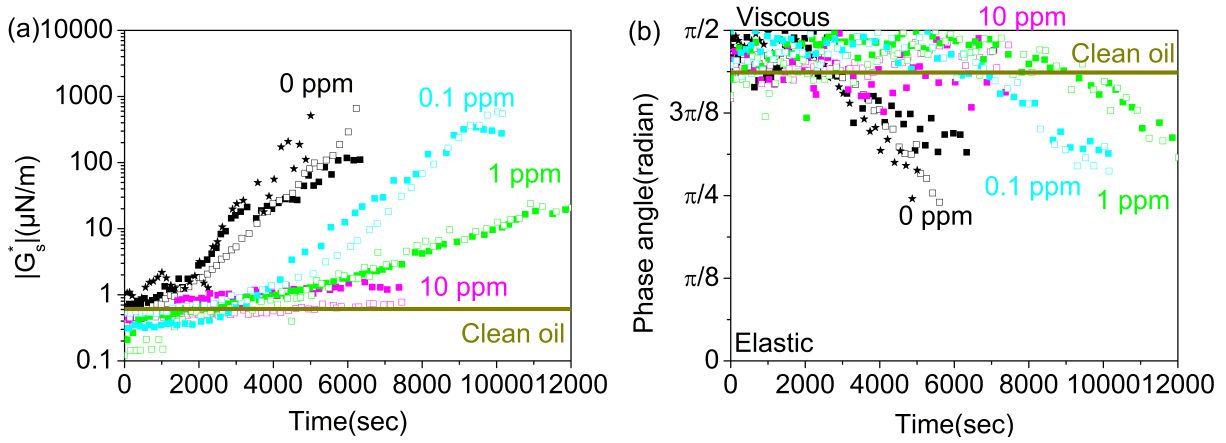


Figure 6.11: Concurrent adsorption of C7 and 2650 demulsifier and its influence on interfacial rheology. (a) The magnitude of the interfacial complex modulus when the oil phase contains 0.1 wt% C7 asphaltene (black) , premixed 0.1 wt% C7 and 0.1 ppm 2650 (cyan), premixed 0.1 wt% C7 and 1 ppm 2650 (green) and premixed 0.1 wt% C7 and 10 ppm 2650 (pink). The dark yellow line represents the level of water–clean-isomastic response. Geometry is water-on-oil interface, and different symbols in identical colors represent different trials conducted by identical experiment setup. (b) Evolution of the phase angle in the same experiments.

mixed 0.1 wt% C7 and various amount of 2650 demulsifier. With 10 ppm 2650 (pink curves) in the bulk oil phase, $|G_s^*|$ only slightly increase for 5 times and no elasticity can be found during 8000 sec adsorption. When 2650 concentration is decreased to 1 ppm (green curves), the stiffening rate and viscoelasticity transition are still delayed compared with the pure C7 adsorption. $|G_s^*|$ stays at the level of clean isomastic interface for 3000 sec, and gradually increase to around 20 $\mu\text{N/m}$ after 12000 sec adsorption. δ remains similar as clean-water-isomastic interface until 10000 sec and then starts to drop to the level of $5\pi/16$, indicating that the elasticity appears. For bulk oil phase contains 0.1 ppm 2650 and 0.1 wt% C7 (cyan), $|G_s^*|$ stays at the region of clean-water-isomastic interface for 3000 sec and shows similar increase rate as pure C7 adsorption. The corresponding δ , however, remains in the region of clean isomastic-water interface for 6000 sec, and elasticity starts to appear. The series of experiments using 2650 indicate that even the concentration of 2650 is decreased to 0.1 ppm, 2650 can still delay the formation of the

viscoelastic layer. Not surprisingly as other demulsifiers we investigate, the performance of demulsifier also depends on their bulk concentration.

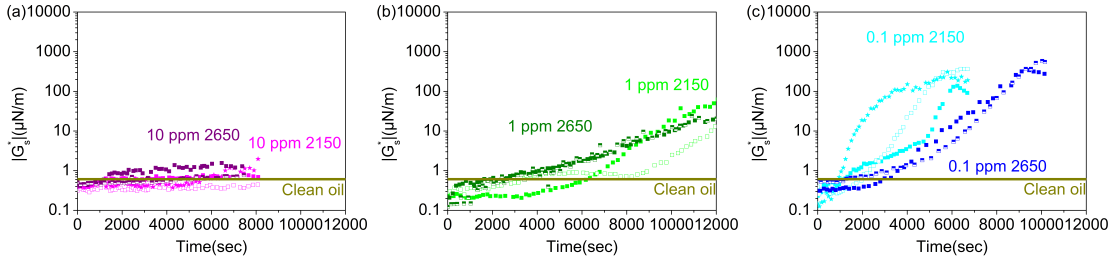


Figure 6.12: Interfacial rheology with 0.1 wt% C7 and various concentration of 2150 or 2650 demulsifier in the isomastic. The figures illustrate the magnitude of the interfacial complex modulus when the oil phase contains premixed 0.1 wt% C7 asphaltene with (a) 10 ppm 2150 (pink) or 10 ppm 2650 (purple), (b) 1 ppm 2150 (green) or 1 ppm 2650 (dark green), and (c) 0.1 ppm 2150 (cyan) or 0.1 ppm 2650 (blue). The dark yellow line represents the level of water-clean-isomastic response.

Figure 6.12 illustrates the rheological response of water-on-good-isomastic interface with premixed C7 and (a) 10 ppm, (b) 1 ppm and (c) 0.1 ppm 2150 or 2650 in the oil phase. 10 ppm 2150 (pink curves) and 2650 (purple curves) both prevent C7 from forming stiff layer and $|G_s^*|$ remains nearly at the level of clean isomastic. 1 ppm 2150 (green) and 2650 (dark green) show similar increase rate of $|G_s^*|$, and $|G_s^*|$ of the two cases gradually increase to around 20 $\mu\text{N/m}$ after 12000 sec adsorption. However, when the demulsifier concentration is decreased to 0.1 ppm, 2650 (blue curves) shows a slower increase rate of $|G_s^*|$ compares with 2150 (cyan curves). Figure 6.12 thus suggests that 2650 can better prevent C7 from forming a stiff layer at the water-oil interface than 2150 at low concentration.

6.6.2 Impact of 2650 on the aged asphaltene layer

Since the longer hydrophile (2650 demulsifier) shows better performance on preventing stiff layer formation than demulsifier with shorter hydrophile (2150 demulsifier), we then

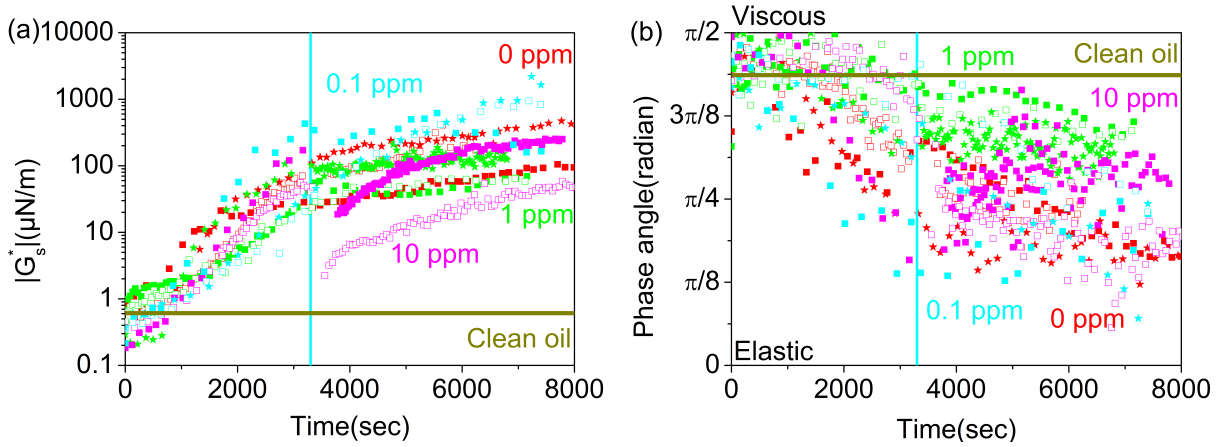


Figure 6.13: The influence of 2650 demulsifier on the interfacial rheology of asphaltene interfacial film. (a) The magnitude of the interfacial complex modulus evolution of the water-on-oil interface when 0.1 wt% C7 in isomastic is replaced by 0.1 wt% C7 in isomastic with 0.1 ppm 2650 (cyan), 1 ppm 2650 (green) and 10 ppm 2650 (pink). Different symbols in identical colors represent different trials conducted by identical experiment setup. The cyan line at 3000 sec represents the time of exchanging the oil phase, and the dark yellow line represents the level of water-clean-isomastic response. The red symbols are reference experiment of replacing oil phase by identical 0.1 wt% C7 in isomastic, showing the physical disruption during exchanging the oil phase. (b) Evolution of the phase angle in the same experiments.

study how the length of hydrophile impact the ability of demulsifier on softening the asphaltene film. Figure 6.13 depicts the interfacial rheology evolve at the water-on-good-isomastic interface when the bulk oil phase is exchanged from 0.1 wt% C7 only to premixed 0.1 wt% C7 and various amount of 2650. With 10 ppm 2650 in the new bulk oil phase (pink curves), 2650 slightly decrease $|G_s^*|$ right after exchanging the oil phase, but $|G_s^*|$ still increase and recover to the value before exchanging the oil phase after demulsifier interacting with asphaltene layer for 5000 sec. When the 2650 concentration is decreased to 1 ppm (green curves), $|G_s^*|$ slightly increase and δ slightly decrease from the value before exchanging the oil phase, indicating 2650 cannot soften the interface anymore. For 0.1 ppm 2650 (cyan curves), $|G_s^*|$ and δ keep increasing as the reference experiment without demulsifier.

Figure 6.14 compares the rheological response at the water-on-good-isomastic interface

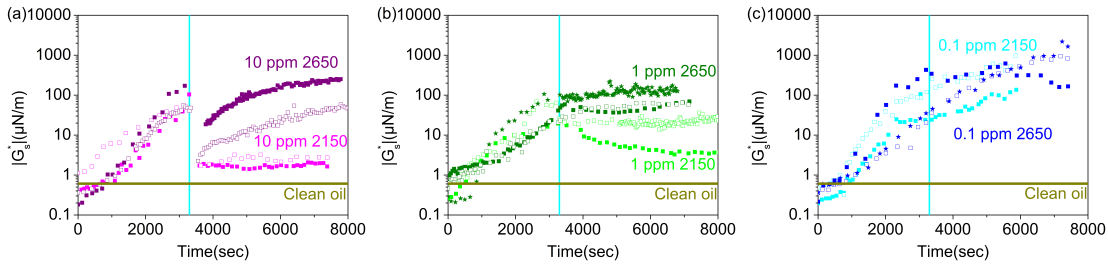


Figure 6.14: The influence of 2150 and 2650 demulsifier on the interfacial rheology of the asphaltene film. The figures illustrate the magnitude of the interfacial complex modulus evolution of the water-on-oil interface when 0.1 wt% C7 in isomatic is replaced by (a) 0.1 wt% C7 in isomatic premixed with 10 ppm 2150 (pink) or with 10 ppm 2650 (purple), (b) 0.1 wt% C7 in isomatic premixed with 1 ppm 2150 (green) or with 1 ppm 2650 (dark green), and (c) 0.1 wt% C7 in isomatic premixed with 0.1 ppm 2150 (cyan) or with 1 ppm 2650 (blue). Different symbols in identical colors represent different trials conducted by identical experiment setup. The cyan line at 3000 sec represents the time of exchanging the oil phase, and the dark yellow line represents the level of water-clean-isomatic response.

after exchanging the bulk oil phase from 0.1 wt% C7 to premixed 0.1 wt% C7 and different concentration of 2150 or 2650 demulsifier. Both 10 ppm 2650 (purple curves) and 2150 (pink curves) can decrease interfacial stiffness right after exchanging the oil phase. However, 2150 can prevent interfacial stiffness recover back to the level before exchanging the oil phase, but interfaces with 2650 gradually recover to the stiffness before 2650 interacting with the asphaltene layer. For 1 ppm demulsifier, 2150 gradually decrease the interfacial stiffness or at least prevent $|G_s^*|$ from further increasing (green curves), but 2650 (dark green curves) result in a slight increase of $|G_s^*|$ after the oil phase is exchanged. When the concentration is further decreased to 0.1 ppm, both 2150 (cyan curves) and 2650 (blue curves) show a similar increase of stiffness after exchanging the oil phase.

The comparison in Fig. 6.14 suggests that 2150 can better soften the asphaltene interfacial film than 2650 when concentration is higher than 1 ppm. When the length of hydrophile is increased, 2650 demonstrates a better ability to prevent asphaltene form-

ing stiff layer but poor ability to soften on the pre-existing asphaltene layer. We thus hypothesize the effect of longer hydrophile on the two different mechanisms we test. For demulsifier with shorter hydrophile (2150), the demulsifier is more soluble in the oil phase. When demulsifier concurrently adsorbs with asphaltene, less 2150 adsorb to the interface than 2650, which results in the worse performance of 2150 on the premixed experiment shown in Fig. 6.12. However, when the demulsifier is introduced to the pre-existing asphaltene layer, the demulsifier with shorter hydrophile (2150) can squeeze to the weak region of asphaltene film using less energy compared with 2650. As a result, 2150 can better soften the interfacial layer than in 2650.

6.7 Conclusion

We have investigated how the chemical architecture of demulsifiers impact their performance on the interfacial rheology using a series of PO – EO – PO triblock copolymer and two different mechanisms (premixing and exchanging oil phase). When the molecular weight of the copolymer is increased but HLB keep identical, PO₂₀ – EO₁₃ – PO₂₀ (3100) triblock copolymer prevent asphaltene from forming stiff layer worse than low-molecular-weight PO₁₄ – EO₉ – PO₁₄ (2150), but the ability on softening pre-existing interfacial film remains unchanged. When HLB of demulsifier is increased, PO₁₃ – EO₂₂ – PO₁₃ (2650) depicts better performance on preventing C7 forming stiff layer than low-HLB PO₁₄ – EO₉ – PO₁₄ (2150) block copolymer, but the ability on softening interfacial film of 2650 is worse than that of 2150. We hypothesize that the shorter hydrophile results in better solubility in the oil phase so the demulsifier cannot prevent or compete adsorption of asphaltene when they adsorb simultaneously. However, the shorter hydrophile takes less energy to squeeze into the weak region on the interface, which results in better performance on softening the pre-existing asphaltene film. This study thus provides an

initial guide of selecting chemical architecture for designing a demulsifier to destabilizing the asphaltene-coated water-in-oil emulsion.

Chapter 7

Conclusion

We have established a systematical method to probe the interfacial rheology and the mechanical heterogeneous structure simultaneously, for studying the asphaltene adsorption and demulsifier interaction at the water-oil interface. Chapter 2 first demonstrates the microbutton microrheometry and corresponding sample cell to form a stable water-on-oil or oil-on-water interface, enabling the characterization of asphaltene interfacial film. An algorithm based on the strain decay from the rheological probe is established to reveal the local stiffness near the probe, which provides the map of mechanical structure with the rheology information. This rheology-mechanical structure mapping technique is also established on the macrorheometry, using the commercial AR-G2 rheometer with double wall ring (DWR) instrument.

Chapter 3 starts an initial investigation of pure ‘C7’ asphaltene adsorption using a model decane-toluene (‘dectol’) system. The C7 adsorption increases the stiffness of the interface and transit the interface from viscous-dominated behavior to a more viscoelastic response. The microbutton and DWR can characterize the asphaltene film at the initial stage and late stage respectively due to their sensitive nature. However, we observed quantitatively variation between nominally-identical trials prepared by the same

experimental procedure. The map of the mechanical structure reveals that this irreproducibility issue is attributed to the mechanical heterogeneous structure formed near the rheometry probe. In addition, this heterogeneous feature can be observed from both the micron and millimeter scale, indicating a more complicated adsorption mechanism than that reported in the literatures. Our custom drop coalescence experiment further shows that the viscoelastic stiff layer formed by asphaltene is related to the enhanced emulsion stability.

In Chapter 4, we utilize a model demulsifier ethylcellulose (EC) to interrupt the asphaltene interfacial film. EC is found to both prevent asphaltene from forming the viscoelastic stiff layer at the water-oil interface and soften the pre-existing aged asphaltene layer. The map of the heterogeneous structure further reveals that EC can prevent asphaltene from forming stiff structure and soften the asphaltene layer from the relatively soft region, suggesting a new understanding of how demulsifier impacts the asphaltene layer. This softening process is also observed in the micron and millimeter scale. In addition to the interfacial rheology, the bulk rheology suggests that EC provide emulsion solution yield stress and shear-thinning feature, which might be the EC network formed between the emulsion drops.

With the initial understanding of asphaltene adsorption and the possible role of demulsifier at the interface, we then focus on how the asphaltene adsorption can be impacted by the chemical and physical parameters. Chapter 5 systemically studies the asphaltene adsorption under different condition. The selection of the oil phase is first shown to influence the stiffening rate of asphaltene film, from the comparison of dectol and a mixture of isopar and aromatic-200 ‘isomatic’. Low aromatic fraction and high bulk asphaltene concentration are both able to enhance the formation of viscoelastic stiff asphaltene layer at the interface. When the asphaltene concentration is higher than the solubility limit of the oil phase, asphaltene can form micron-scale aggregates. These

asphaltene aggregates are found to increase the irreproducibility of the rheology measurement when they appear not at the interface. If the oil phase contains no aggregates a more reproducible experiment can be obtained. Gravity is proven to be irrelevant to the asphaltene adsorption, from the comparison of water-on-oil and oil-on-water geometry. In addition to these parameters, we also confirm that the asphaltene layer shows a viscoelastic liquid nature in the long period of time. Linear viscoelastic region of the asphaltene layer is found to be lower than 3 % of the strain.

The relationship between chemical structure and demulsifier performance is studied through the series of EO-PO-EO triblock copolymer. With a more controllable method introducing demulsifier to the aged asphaltene layer, we conducted a systematical characterization of demulsifier concentration and architecture from the rheological point of view. When the hydrophilic-lipophilic balance (HLB) keeps unchanged, demulsifier with higher molecular weight needs higher concentration to prevent asphaltene from forming the viscoelastic layer. However, molecular weight results in not distinguishable difference on the ability to soften aged asphaltene layer. The higher HLB demulsifier is shown to demonstrate a better ability to prevent C7 from forming stiff layer but worse performance on softening the aged layer. These studies provide useful information for one wants to design a new demulsifier which can result in a particular rheological response at the water-oil interface with asphaltene.

To summary, our research provides a detailed understanding of asphaltene-stabilized water-in-oil emulsion from the interfacial rheological point of view. We also study how the demulsifiers prevent the formation of these asphaltene film, and how the demulsifiers break the asphaltene structure already exists at the interface. We hope our work can guide the industry about the nature of asphaltene film and the strategy to design the demulsifier for treating these asphaltene-stabilized emulsions, facilitating the water-oil separation in a more efficient and cost-friendly way.

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