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Investigation of Interfacial and Rheological Properties of Asphaltenes at Solid-Liquid and Liquid-Liquid Interfaces

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ABSTRACT

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Asphaltenes are surface-active polyaromatic molecules in crude oil that are known to deposit onto surfaces of pipelines and stabilize water-in-oil droplets by flocculating at interfaces, resulting highly viscous emulsions. This has led to significant flow assurance problems in oil production. Therefore, a thorough investigation of the behavior of asphaltene aggregation at interfaces is needed. Microfluidic devices are used as a novel methodology for probing asphaltene deposition and asphaltene-stabilized emulsions. In particular, homogeneous and porous-media microfluidic designs are developed to represent various flow conditions typical of that found in oil flow processes. A variety of factors influencing asphaltene deposition are investigated, including asphaltene solubility, chemical dispersants, the presence of the brine, and solvent effects. Furthermore, the property of asphaltenes at interfaces is characterized using interfacial rheology and chemical analysis. By understanding the nature and the behaviors of asphaltenes at interfaces, we improve our ability to design cost effective mitigation strategies. This includes the development of a new generation of chemical inhibitors/demulsifiers and improved methods for prevention and treatment of this problem.
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Chapter 1

Introduction

1.1. Motivation and Objective

Flow assurance is defined as the ability to produce multiphase fluids from reservoirs to processing plants in an economically and technically feasible way. Asphaltenes have been referred to as the “cholesterol of petroleum”, since they can precipitate out of crude oils and adsorb at interfaces. Severe asphaltene problems often arise in the porous media near the wellbore region, where significant changes in shear rates occur. As a result of these flow changes, nano- and micro-aggregates of the destabilized asphaltenes form in the crude oil. Additionally, if the pressure, the temperature, or the compositions of the crude oil varies, the solubility parameter of the oil will be changed and asphaltenes can be destabilized. In particular, pipeline fouling has been reported to be a result of CO₂ injection in Enhanced Oil Recovery (EOR) and mixing various crude oil streams. Flow assurance in the oil and gas industry has been focused on preventing asphaltene deposition and asphaltene-induced emulsification (Figure 1.1). Therefore, in this
thesis, a combined platform consisting of microfluidics and interfacial rheological measurements is used to offer greater understanding in better designing the solutions to asphaltene-related flow assurance problems.

Figure 1.1 (a) Asphaltene deposition in the pipeline. (b) Asphaltene-stabilized water-in-oil emulsions. Scale bar is 50 µm.

1.2. Definition of Asphaltenes

Crude oil is composed of maltenes and asphaltenes. Maltenes can further be separated into saturates, aromatics, and resins. Generally, asphaltenes are defined as the species in crude oils that are soluble in aromatics (i.e. toluene), and insoluble in n-alkanes (i.e. n-heptane).\(^{17}\) This definition is also called SARA (saturates, aromatics, resins, and asphaltenes) fractionation.\(^ {18,19}\) Asphaltenes are also known to be the most polarizable, heaviest, and strongly associating component in crude oil.\(^ {17,20}\) The specific molecular structure of asphaltene molecules cannot be uniquely defined due to their general classification by solubility. Recently, the molecular structure of asphaltenes is proposed to be island or archipelago shapes. Mullins \textit{et al.} proposed a modified Yen-Mullins model
concluding that island asphaltenes are dominant,\textsuperscript{5} showing that the size of an asphaltene molecule is around 1.5 nm. In the dissolved phase, asphaltene molecules will form nanoaggregates, with a size of about 2 nm, equivalent to an aggregation number of approximately six.\textsuperscript{5} A larger cluster with aggregation number of eight will form with the size around 5 nm as shown in Figure 1.2. Also, Bruno \textit{et al.} used atomic force microscopy and molecular orbital imaging by scanning tunnelling microscopy to prove the Yen-Mullins model and they first time observed directly the archipelago asphaltenes (Figure 1.3).\textsuperscript{21}

![Figure 1.2 Yen–Mullins model.](image)

On the other hand, asphaltene structure is further found to be a continuum of island and archipelago motifs by Fourier transform ion cyclotron resonance mass spectrometry and infrared multiphoton dissociation.\textsuperscript{22} It is hypothesized that the dominant structure (island or archipelago) depends on the asphaltene samples. Advances in asphaltene chemistry lead to promising ways to explore the solutions to flow assurance problems.
1.2.1. Asphaltene Deposition

Asphaltenes are known to exist in the oil as nanoaggregates and the dominant interaction between asphaltenes is van der Waals attraction. Destabilization of these stable nanoaggregates occurs when physicochemical conditions are altered. Attraction between nanoaggregates increases resulting in micro-aggregation. The combination of destabilization and micro-aggregation is defined as precipitation. During the precipitation, asphaltenes tend to either deposit on the surface or form larger particles. This deposition can cause flow assurance problems in pipelines and near-wellbore regions by plugging small pore throats via the mechanical trapping or depositing on rock surfaces. Both plugging and non-plugging depositions contribute to the permeability reduction within the porous media. Depending on the local flow velocity gradients, asphaltene deposits can be mobilized from non-plugging deposits to later contribute to mechanical trapping and plugging of the porous media, which further depicts the complexity of asphaltene deposition to flow assurance.

To tackle this problem, the scenario of deposition is considered as the particle/colloid deposition that particles transport by the bulk fluid and attach on the
surface in this thesis. Two steps for asphaltene deposition are required: first, asphaltene aggregates transport from the bulk solution to the solid surface by both convection and diffusion from Brownian motion and fluid flow. After the aggregates transport near the surface, colloidal interactions are dominant in determining if the aggregates would attach on the surface. These interactions mainly depend on the solution chemistry as well as the surface properties of the aggregate and the surface. The interactions consist of several components, including electrical double layer, van der Waals, steric forces which are within a short range between the aggregate and the surface. Figure 1.4 illustrates that a particle transported near the surface of a collector and attach on the surface depending on the colloidal interactions.

Figure 1.4 Illustration of the particle transportation by convection-diffusion effect and attachment by colloidal interactions.

Previous studies have examined the arterial deposition of asphaltenes in glass and stainless steel capillary pipes. Diffusion is usually assumed to be an important mechanism leading to asphaltene deposition. Nabzar et al. proposed a colloidal model for
asphaltene deposition in the diffusion-limited and shear-limited regimes. Vargas et al. proposed that there is a competition between the flocculation and deposition of asphaltenes in the oil well production. It is thought that asphaltenes will either aggregate to form large colloidal systems that can readily flow through the pipe, or deposit onto the surface. Asphaltene deposition in porous media has been less investigated, and various deposition mechanisms such as the hydrodynamic bridging must be considered. Coreflood tests have been widely utilized to analyze the effects of miscible and immiscible fluid injections on the permeability impairment and formation damage. However, only macroscopic properties, such as the permeability reduction from asphaltene deposition, can be obtained, but the dynamics for asphaltene precipitation and deposition within porous media has not been visualized at the pore scale. Moreover, limited literatures studied the interaction between asphaltenes and solid surfaces during the deposition. Recently, microfluidic devices have been adopted to provide insights into oil flow processes. The asphaltene contents in crude oil samples have been characterized using glass microfluidic devices. A microfluidic packed bed reactor has been developed to study the kinetics of asphaltene deposition and dissolution in a porous media system. An in-depth understanding on how the combination of fluid transport and colloidal interactions influences their deposition at the pore-scale has not been reached. Therefore, the porous media micromodel is used.

1.2.2. Asphaltene-Stabilized Emulsions

Asphaltene-stabilized water-in-oil emulsions cause fluids in oil production process to be highly viscous, which demands more power and costs for transportation. Moreover, these
stable emulsions make separation of water and oil for high quality oil very difficult. This also results in detrimental disasters for the environment. In this case, asphaltenes are the surface active agents for stabilizing emulsions against water droplets coalescing in refining and extraction processes. They are typically thought of as sheet-like structures with heteroatoms embedded (N, O, and V) in the center of the sheet and aliphatic chains on the of the molecule as shown in Figure 1.3. Because of these heteroatoms and rings, the center is more hydrophilic, while the aliphatic chains cause the sides are hydrophobic. A detailed review article by Kilpatrick et al., described the stabilization of water-in-oil emulsions, and concluded that there are sub-fractions of asphaltenes that are acidic or multiprotic. This suggests that electrostatic interactions govern the adsorption at the interface, as shown in Figure 1.5. Therefore, the salt ions found in brine provide a shielding effect on the long-range interactions. Certain asphaltenes are treated as amphiphilic molecules.

![Figure 1.5](image)

Figure 1.5 Electrostatic attractions between asphaltenes (a) No salt. (b) With salt and possible screening effect.
The interfacial properties of asphaltenes have been widely studied recently by varying the surface and bulk concentration, aromaticity of the solvent, pH, and salinity. In particular, the salinity effect on the asphaltenes at oil-water interfaces is known to be a determining factor in asphaltene adsorption onto the interface. Zhang et al. used micropipette technique to study the coalescence of two asphaltene-stabilized emulsions and found that increasing the concentrations of CaCl$_2$ and NaCl facilitated coalescence of emulsions. Ions can have strong interactions with carboxyl groups and enhance the coalescence between two interfacial layers. Chen et al. used AFM to measure the force between two oil droplets in brine and found that the addition of Ca$^{2+}$ ions changed the conformation of asphaltenes at oil-water interfaces, reducing the critical force load required for coalescence to occur. With adsorbed asphaltenes, coalescence is inhibited sterically and showing an adhesion process during the separation of two droplets, as shown in Figure 1.6. Mohammad et al. used a Langmuir surface balance to determine that the interfacial elasticity is dependent on the concentrations and spreading volumes of both asphaltenes and resins. Alvarez et al. utilized a Langmuir trough with different spreading volumes to analyze the elasticity of this thin film. In essence, higher amounts of asphaltenes on the interface resulted in a more elastic film. Also, after some compression-expansion cycles, a hysteresis phenomenon was found. The potential mechanism is that upon compression the strong attractive forces cause irreversible aggregation, as shown in Figure 1.7. However, these results do not include shear stresses, which would be more representative of real systems where flows in the pipeline undergoes large shear stress. Moreover, adsorbed asphaltenes are typically reported to form a cross-linked network at the interface offering mechanical resistance during the
coalescence between emulsions.\textsuperscript{58} Hence, the rheology of this system needs to be characterized.

Figure 1.6 AFM technique to measure the loaded force during coalescence. With adsorbed asphaltenes, coalescence is inhibited sterically and showing an adhesion process during the separation of two droplets.

Figure 1.7 Hysteresis for compression-expansion cycles for asphaltene

Rheology is a well-established and interdisciplinary subject for extracting and interpreting responses from material deformation. The viscoelastic response is often
described by frequency-dependent storage and loss shear moduli which are commonly measured by oscillatory strain. Nevertheless, conventional rheometers are not useful for delicate and heterogeneous samples such as protein-lipid membranes and fluids in biological cells.\textsuperscript{57,59} However, for this conventional rheometer, the information from the bulk phase might dominate that from the interface. Also, visualizing the microstructure of the asphaltene network during the experiment is important to understand the rheological responses. Therefore, the interfacial rheometer with a double-wall ring geometry combined with a modified Langmuir trough to visualize the interface during the measurement is used.

### 1.3. Thesis Structure

This thesis demonstrates results showing the behaviors of asphaltenes at the solid-liquid and liquid-liquid interfaces. Chapter 2 describes materials and methods, such as microfluidics and various measurements to study interfacial properties of asphaltenes. Chapter 3 demonstrates the solubility effect of the oil on the hydrodynamics of asphaltene aggregates in deposition. Chapter 4 further describes the alteration of the colloidal interactions between asphaltenes by the addition of chemical dispersants. Chapter 5 depicts that the dispersants are able to destabilize the network of adsorbed asphaltenes at interfaces by a combined measurement for viscoelasticity of the asphaltenes with the visualization of the microstructure. Chapter 6 demonstrates a method to combine microfluidics and dilatational rheology in studying \textit{in situ} coalescence process of emulsification/demulsification of the asphaltene-stabilized emulsions in the presence of non-ionic surfactants and demulsifiers. Chapter 7 extends the knowledge of
asphaltene deposition and the measurements of the interfacial properties in studying the behaviors during the deposition of asphaltene-stabilized emulsions. Chapter 8 summarizes the thesis and proposes the future directions.
Chapter 2

Materials and Methods

2.1. Materials

All chemicals were of reagent grade (purity ≥ 95%) purchased from Sigma-Aldrich and used without further purification. Deionized water (18.2MΩ·cm) was used. Commercial dispersants, such as $p$-dodecylphenol (purity ≥ 96.5%) [Pfaltz & Bauer (Connecticut, USA)], $p$-hexylphenol (98%), $p$-octylphenol (99%), $iso$-dodecylphenol were reagent grade (purity ≥ 99%) [Sigma-Aldrich (Missouri, USA)] and used as is. These various dispersants were premixed into the oils at the concentration of 0.01 wt%, characteristic of what would typically be used in field applications. A gravimetric and spectroscopic measurement\textsuperscript{60} on the oils confirmed that the dispersants did not precipitate additional asphaltenes from the oils.
2.1.1. Preparation and Characterization of Model Oil and Crude Oil

2.1.1.1. Model Oils

The model oils composed of toluene and asphaltenes were used in the deposition, interfacial rheology, and coalescence experiments to reduce the influence of complex components typically found in the crude oil. The asphaltenes were extracted by \( n \)-pentane from bitumen samples from the Middle East with an asphaltene concentration greater than 20 wt\% (Chapter 3) and from Canada (Chapter 4 and Chapter 5). The extracted asphaltenes were then slowly dissolved in toluene at 90 °C in a 40-kHz ultrasonic bath (VWR) for a minimum of 30 minutes until a desired asphaltene concentration was achieved.

Model oil used to stabilize emulsions in Chapter 6 are made from asphaltenes extracted from a Canadian heavy crude oil (15.45% asphaltenes) using the ASTM 863-69 standard. In order to mimic the crude oil, this study was performed using heptol (mixture of \( n \)-heptane and toluene). The extracted asphaltenes were dispersed in heptol and sonication was used to facilitate the dispersion. 2 w\% asphaltenes dispersed in 40 vol\% \( n \)-heptane and 60 vol\% toluene (C40 model oil) and 2 w\% asphaltenes dispersed in 50 vol\% \( n \)-heptane and 50 vol\% toluene (C50 model oil) were used as model oils (Table 2.1).
Table 2.1 Composition of C40 and C50 model oils.

<table>
<thead>
<tr>
<th>Model oils</th>
<th>Model oil Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>C40 model oil</td>
<td>2% asphaltene dispersed in 40% heptane and 60% toluene</td>
</tr>
<tr>
<td>C50 model oil</td>
<td>2% asphaltene dispersed in 50% heptane and 50% toluene</td>
</tr>
</tbody>
</table>

We used a non-ionic surfactant ($C_{12-15}E_7$) having a HLB equal to 12.2 favoring the formation of oil-in-water emulsions. The composition of the microemulsion (ME) was 23 w% of $C_{12-15}E_7$, 23 w% isopropyl alcohol, 39 w% Milli-Q water and 15 w% d-limonene. Upon dilution in the aqueous phase, this ME forms d-limonene swollen micelles. An equivalent surfactant solution (SURF) was prepared replacing the amount of d-limonene by water. Three different demulsifiers, EO-PO, APA (alkoxylated polyamine) and PE (polyester polyol) were tested. Microemulsions were formulated without and with demulsifiers (replacing water by the amount of demulsifier added). A detailed composition of the SURF and the different ME’s is shown in Table 2.2. d-Limonene was obtained from Florida Chemical.
Table 2.2 Detailed composition of surfactant solution (SURF) and microemulsions (ME) with and without demulsifiers.

<table>
<thead>
<tr>
<th>Aqueous Treatments</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microemulsion (ME)</td>
<td>23 w% of C_{12-15}E_7, 23 w% isopropyl alcohol, 39 w% Milli-Q water and 15 w% d-limonene</td>
</tr>
<tr>
<td>Surfactant (SURF)</td>
<td>23 w% of C_{12-15}E_7, 23 w% isopropyl alcohol, 54 w% Milli-Q water</td>
</tr>
<tr>
<td>5w% EO-PO ME</td>
<td>23 w% of C_{12-15}E_7, 23 w% isopropyl alcohol, 5w% EO-PO, 34 w% Milli-Q water and 15 w% d-limonene</td>
</tr>
<tr>
<td>5w% APA ME</td>
<td>23 w% of C_{12-15}E_7, 23 w% isopropyl alcohol, 5w% APA, 34 w% Milli-Q water and 15 w% d-limonene</td>
</tr>
<tr>
<td>5w% PE ME</td>
<td>23 w% of C_{12-15}E_7, 23 w% isopropyl alcohol, 5w% PE, 34 w% Milli-Q water and 15 w% d-limonene</td>
</tr>
<tr>
<td>10w% EO-PO ME</td>
<td>23 w% of C_{12-15}E_7, 23 w% isopropyl alcohol, 10 w% EO-PO, 29 w% Milli-Q water and 15 w% d-limonene</td>
</tr>
</tbody>
</table>

2.1.1.2. Crude Oils

Properties of crude oil S and crude oil C, at 1 atm and 23 °C are listed in Table 2.3 after pretreatment by centrifuge to remove existing solids and water. Before the experiment, the crude oil used was sonicated to minimize the potential asphaltene aggregation. Moreover, the asphaltene in the crude oil C was precipitated by \textit{n}-heptane and characterized by energy-dispersive X-ray spectroscopy (EDX) as listed in Table 2.4. Zeta potential measurements in various brine conditions were performed using Delsamax Pro (Beckman Coulter). Samples were prepared by adding 0.2 mL of the oil-heptane mixture in 10 mL of the brine. The vial was tightly sealed by Teflon tape, alumina foil, and parafilm tape, and then followed by sonication for 40 min to disperse the mixture in the brine.
Table 2.3 Properties of Crude Oil

<table>
<thead>
<tr>
<th>Source</th>
<th>Oil S</th>
<th>Oil C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>0.826</td>
<td>0.885</td>
</tr>
<tr>
<td>Viscosity (cP)</td>
<td>5.36</td>
<td>22</td>
</tr>
<tr>
<td>Saturates (wt %)</td>
<td>69.60</td>
<td>48.6</td>
</tr>
<tr>
<td>Aromatics (wt %)</td>
<td>22.02</td>
<td>31.8</td>
</tr>
<tr>
<td>Resins (wt %)</td>
<td>7.17</td>
<td>15.5</td>
</tr>
<tr>
<td>C5 asphaltenes (wt %)</td>
<td>1.21</td>
<td>4.1</td>
</tr>
<tr>
<td>Water content (wt %)</td>
<td>-</td>
<td>0.03</td>
</tr>
<tr>
<td>Onset (vol%)</td>
<td>43</td>
<td>45</td>
</tr>
</tbody>
</table>

Table 2.4 Asphaltene Characterization

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C (wt%)</td>
<td>77.80</td>
</tr>
<tr>
<td>N (wt%)</td>
<td>3.59</td>
</tr>
<tr>
<td>O (wt%)</td>
<td>9.78</td>
</tr>
<tr>
<td>Fe (wt%)</td>
<td>2.68</td>
</tr>
<tr>
<td>Ca (wt%)</td>
<td>1.58</td>
</tr>
<tr>
<td>V (wt%)</td>
<td>4.52</td>
</tr>
</tbody>
</table>
2.2. Methods for the Study of Asphaltene Deposition

2.2.1. Microfluidics

Microfluidic systems provide a fast and well-controlled platform to study flow processes within porous media, and to date, has been successfully applied to various crude oil and asphaltene systems. The typical length scales of microfluidic devices match the representative pore sizes of the near-wellbore region and reservoir rock, and its transparency allows processes to be visualized. The direct visualization capacity provide a platform for studying asphaltene deposition dynamics in great detail. Additionally, the high surface-to-volume ratio in microfluidic devices gives rise to a highly controllable measurement for studying particle-surface interactions and provides a high-throughput platform for efficient screening of dispersants. Deposition is a result of competition between surface adsorption and erosion. Adsorption is dominated by the diffusion of small asphaltene particles to the surface, but erosion is governed by the shear forces exerted by fluid convection acting on the deposited aggregates as well as the colloidal interactions between aggregates and surfaces.

To mimic the porous media in the near-wellbore region, a homogeneous pore-network of circles was designed so that the diameter of the circular posts and the smallest pore-throat spacing are both 125 μm, as shown in Figure 2.1b. All microfluidic devices were made of NOA-81 (Norland Optical Adhesive), a thiolene photopolymer with known solvent resistance and temperature tolerance. Standard lithography protocols were followed to fabricate an SU-8 2015 (Microchem Corp) photoresist template that was a 20-micron tall positive relief of the porous media pattern. Afterward, liquid
polydimethylsiloxane (PDMS) elastomer base (Sylgard 184, Dow Corning), mixed in a 10:1 weight ratio with the curing agent, was poured onto the SU-8 template, cured at 60 °C, and removed to form a negative relief of the porous media pattern. Subsequently, NOA-81 was poured on the negative relief as well as a blank PDMS layer, and both were cured under a UV-lamp. Both the NOA-81 porous media patterned layer and the blank NOA-81 base were then released from the PDMS. The blank NOA-81 base was mounted on a clean glass slide, and finally the patterned NOA-81 layer and the blank base were bonded with O₂ plasma. A representative microfluidic device with fittings is shown in Figure 2.1c. The length of the porous media (L_p) is 10 mm. The permeability of the porous media is around 5.23 Darcy, similar to that of a sand pack or a gravel pack. The surface contact angle of the NOA microchannel was 79.50°±2.67°, which is slightly water-wet, measured by the sessile drop method (KSA CAM 200). Each microfluidic device was used only once per experiment.
Figure 2.1 (a) Schematic of the experimental setup. (b) SEM image of the porous media used to study asphaltene deposition. (c) A complete NOA-81 microchannel. The white scale bars are 200 μm for (b) and 1.0 cm for (c).

All experiments were performed under ambient conditions with a fixed temperature of 23 °C. The oils and precipitant (n-heptane) were injected separately by syringe pumps (Harvard Apparatus PHD 2000) mixing at a T-junction (IDEX, MicroTee Assy PEEK-1/16 in), and the mixture subsequently flowed through the porous media microchannel where the asphaltene deposition was observed via a video optical microscopy. The total flow rate of the fluid mixture was fixed at $Q = 60 \, \mu$L/min, which corresponds to an equivalent superficial velocity $u = 0.028 \, m/s$. The time between the mixing tee and porous media is around two minutes. The microfluidic device was staged on an inverted microscope (Olympus IX 71), as shown in Figure 2.1a, and the visualization of the deposition process was recorded using a high-speed CMOS camera (Phantom V4.3, Vision Research, Inc.). A differential pressure transducer (Validyne P610) was connected to the microchannel to measure the pressure drop across the porous media.

2.2.2. Data Analysis

The experimental images were processed using ImageJ\textsuperscript{73} and Python image-processing module scikit-image.\textsuperscript{74} The procedure was to first identify the location of each post in the porous media by image registration and then determine the pixel count associated with asphaltene deposition around each post by image thresholding using Otsu’s method.\textsuperscript{75} Next, the pixel count was converted to a coverage area and multiplied by the microchannel height, $h = 20 \, \mu$m, to obtain an average asphaltene deposition volume. The
mass of deposition, \( m_d \), was calculated by multiplying the deposition volume by the average asphaltene density \( \rho = 1200 \text{ kg/m}^3 \). Finally the average deposition over multiple posts was determined. Note, this calculation assumes that the asphaltene deposition spans across the microchannel.

### 2.2.3. Flow/Aggregate Correlation

Since solvent solubility and dispersants alter asphaltene aggregate size, deposition can be described in terms of the Péclet number \( (Pe) \), which accounts for the relative contributions from convection and diffusion, with limitation that the particles are in the vicinity of an individual post, which acts as the collector surface, and within the size range of 0.1 – 10 \( \mu \text{m} \).\(^{76}\) The asphaltene aggregate size, obtained from DLS, is used to calculate the Péclet number by Eq. 2.1-2.2 to analyze the relative convection-diffusion ratio:\(^{67,76-78}\)

\[
Pe = \frac{2uR_p}{D_{BM}} \tag{2.1}
\]

\[
D_{BM} = \frac{k_BT}{6\pi\mu R_p} \tag{2.2}
\]

where \( R_p \) is the average radius of asphaltene aggregate, \( D_{BM} \) is the Brownian diffusivity (\( \text{m}^2/\text{s} \)) assuming a spherical aggregate which is supported by our SEM measurements, \( u = 0.028 \text{ m/s} \) is the superficial velocity, \( \mu \) is the dynamic viscosity of the oil-precipitant mixture, and \( k_B = 1.38 \times 10^{-23} \text{ (m}^2 \cdot \text{kg})/(\text{s}^2 \cdot \text{K}) \) is the Boltzmann constant.
2.2.4. Numerical Simulation on Flow through Porous Media

To obtain the insight into the velocity field and the shear rate inside the porous media microfluidic channel during asphaltene deposition experiments, a numerical model based on the Lattice-Boltzmann method (LBM) is performed. The present model describes the steady flow of fluids in a representative elementary volume (REV) of the homogeneous porous media pattern. The LBM simulation is carried out in two dimensions. Because the depth of the microchannel is much smaller than the width/length of it, the 2-D calculation should be close to the real scenario. An open source code, Palabos (http://www.palabos.org/) was adapted to perform the LBM simulation. A real picture of the REV from the deposition experiment was first digitalized to a binary mask to be used as the simulation domain, in which both the stationary circular grain and the asphaltene deposits was treated as solid wall with no-slip boundary conditions. The constant average injection velocity was set at the inlet of the REV domain, periodic boundary conditions was set at both upper and lower sides of the REV domain, and a pressure outlet boundary condition was set at the outlet of the REV domain. The time-transient LBM simulation was performed until the relative error between time steps was less than $10^{-4}$, at which we concluded the steady state had been reached. Finally, the simulation data was analyzed in the ParaView software from which the velocity field and the shear rate distribution was calculated and plotted.
2.3. Methods for the Study of Asphaltene-Stabilized Emulsions

2.3.1. Microfluidics

Microfluidic experiments (Chapter 6) were run at 20°C using the setup shown in Figure 2.2. A microfluidic design similar to that of Krebs et al. was used; however, only one T-junction and one outlet were used to inject the two phases. The width of the channel and the collision chamber was 100 μm and 500 μm, respectively, the height of the channel was 50 μm. The coalescence rate of the emulsion drops was studied in the collision chamber upon injection of the continuous phase (model oil) and the dispersed phase (SURF and ME) using two syringe pumps (Harvard Apparatus PHD 2000). The flow rate of the dispersed phase was fixed at 1 μl/min and 8 μl/min for the continuous phase. Before starting the microfluidic experiment, the model oil was flowed through the device for about one hour to make it visually oil wet. The microfluidic device was positioned on a Keyence digital microscope, and the visualization of coalescence was recorded by a high-speed Keyence VH-Z20R camera. The experimental images were processed using Image J.
Figure 2.2 Schematic of the microfluidic experimental setup. The red rectangle represents the recording region.

2.3.2. Interfacial Shear Rheology

Surface viscoelasticity has been identified as one of the determining factors controlling coalescence when the rupture of the isolated films between two emulsions occurs.\textsuperscript{80} Therefore, understanding of the interfacial rheology is important when studying emulsion stability. The rheology of asphaltenes at various interfaces (Chapter 5) were investigated with an AR-G2 stress-controlled rheometer with an interfacial rheology cell described by Vandebril \textit{et al.} (inner radii are 31 mm for the subphase and 30 mm for the upper phase, and outer radii are 39.5 mm for the subphase and 40.5 mm for the upper phase), based on a double-wall ring geometry (TA instruments).\textsuperscript{81} The rheometer has been modified to allow visualization of the interface during experimentation.\textsuperscript{82} Asphaltenes at an air-water interface are prepared by dropwise spreading of the mixture of asphaltene solution (20 vol\%) with \textit{n}-heptane (80 vol\%), which precipitates a significant fraction of the asphaltenes from the solution. Evaporation time for \textit{n}-heptane and toluene is at least 20 mins.\textsuperscript{42,83,84} Decane is chosen as the oil phase since it is a “poor” solvent for the asphaltenes; therefore, asphaltenes will be driven to the oil-water interface. Asphaltenes at oil-water interfaces were prepared two ways, as shown in Figure 2.3: 1) spreading 4mL of \textit{n}-decane dropwise onto the asphaltene layer formed at the air-water interface described previously (decane-water interface with the aggregation in the air, DW-a) or 2) spreading 4mL of \textit{n}-decane dropwise onto the water subphase and then injecting the asphaltene solution at the decane-water interface (decane-water interface with the
aggregation in decane, DW-d). Two methods were chosen since asphaltenes are known to trap solvents, which may alter their interfacial activity.

Figure 2.3 Illustration of the preparation of the asphaltene film for the interfacial rheological measurements.

For interfacial shear rheology, a shear deformation at the interface was applied while the interfacial area remained constant. Shear viscosity of the interface was obtained from steady shear experiments. Surface viscosity was measured at a single shear rate, ranging from 0.001 to 1 s\(^{-1}\), for at least 15 mins for each shear rate. A new interface was prepared after a set of steady shear rates. The temperature was held constant at 23°C. The surface viscosity can be modeled as a function of shear rate, as shown in Eq. 2.3:

\[ \eta(\dot{\gamma}) \propto \dot{\gamma}^k \]  

(2.3)

where \( \eta \), \( \dot{\gamma} \), and \( k \) are surface viscosity, shear rate, and a constant, respectively. When \( k \) is less than 0, then the interface shows a shear-thinning behavior. Additionally, when \( k \) <
-1, the interface shows solid and yielding behavior with the assumption that the steady-state shear stress is independent of shear rate.\textsuperscript{85,86}

Sagis and Fischer previously demonstrated the use of strain amplitude-sweep experiments to study complex fluid-fluid interfaces.\textsuperscript{87} Here, small-amplitude-oscillatory-shear (SAOS) experiments were conducted on asphaltenes at interfaces. A new interface was prepared each time. A sinusoidal shear strain was applied to the interface at an angular frequency, $\omega = 1 \text{ rad}\cdot\text{s}^{-1}$ and strain amplitudes, ranging from 0.01\% to 10\%; for frequency-sweep experiments, the angular frequency ranged from 0.1 rad\cdot s$^{-1}$ to 10 rad\cdot s$^{-1}$ with strain amplitude being 0.05\%. The storage modulus, $G'$, and loss modulus $G''$, which describe the elasticity and viscosity of the interface, are derived from the resulting out-of-phase response.\textsuperscript{85,88}

Interface images were captured using a CCD camera (Pixellink PI-E531MU) and analyzed using ImageJ (NIH).\textsuperscript{73} The complex shape of the asphaltene microstructure was quantitatively described by the fractal dimension and the effective aggregate size. Fractal dimension was calculated by the built-in box counting method.\textsuperscript{89} Moreover, the effective aggregate size was calculated by fitting the interfacial area of asphaltenes into a defined circle with diameter.

A typical experimental image before processing is shown in Figure 2.4a. The uneven illumination background was extracted by Gaussian blur filter (Figure 2.4b) and removed from the original picture (Figure 2.4c). The image was further de-noised by Bandpass filter (Figure 2.4d). The contrast of image was then optimized using the built-in function “Brightness/Contrast” in Fiji. (Figure 2.4e) To measure the fractal dimension and the area of the aggregates, the grayscale image was thresholded to become black and
white. (Figure 2.4f) At last, the black and white image was skeletonized using the built-in function in Fiji to measure the backbone fractal dimension of the links. (Figure 2.4g)

Figure 2.4 Image processing procedures. (a) Original image. (b) Background. (c) Image without background. (d) After bandpass filter. (e) After brightness/contrast. (f) After thresholding. (g) After skeletonized.

The rheology (Chapter 7) was investigated on an ARES-G2 strain-controlled rheometer using a double-wall ring geometry. The asphaltene film was prepared by spreading 10 mL of crude oil-heptane mixture as the oil top phase on the water sub-phase. The ratio between oil and heptane was taken as 55 vol% to 45 vol%, consistent with the conditions in the microfluidic micromodels. The time sweep was operated with 1 % strain amplitude and 1 Hz frequency. The range of frequency was chosen from 0.01 to 1 Hz with 1 % strain amplitude, and the range of strain amplitude was from 0.1 to 10 % with 1 Hz frequency.
2.3.3. Dilatational Rheology and Interfacial Tension

Interfacial tension (IFT) and dilatational viscoelastic properties were measured using a commercial pendant drop tensiometer (Teclis). A freshly formed oil drop was formed at the end of an inverted needle tip inside a cuvette filled with the aqueous solution. Both dynamic and equilibrium IFTs are shown in this study. Dynamic IFT measurements started as soon as the drop was formed and continued for 5000 seconds. Equilibrium IFT values were recorded when the change in IFT remained nearly almost constant, below 0.1 mN/m during a 10-minute measurement period. To measure the dilatational viscoelastic properties, the oil drop was oscillated at different amplitudes and frequencies to change the surface area (A) in order to be in the linear regime. This area deformation leads to a sinusoidal change in the surface tension (dγ). The densities of the oil and the aqueous phase were measured using a densimeter (Anton Paar DMA 4500 M).

The dilatational modulus can be given by Eq. 2.4:

\[ \varepsilon^* = \frac{d\gamma}{d \ln A} = \frac{A d\gamma}{dA} \] (2.4)

For viscoelastic interfaces, the dilatational modulus is a complex number, with real and imaginary components, defined as follows in Eq. 2.5:

\[ \varepsilon^* = \varepsilon' + i\varepsilon'' \] (2.5)

where \( \varepsilon' \) is the interfacial elastic modulus and \( \varepsilon'' \) is the viscous modulus. The viscoelastic properties were measured using 10% area variation (linear regime) and a frequency of 0.5Hz.
2.3.4. Langmuir Trough and Brewster Angle Microscopy (BAM)

Interface preparation is similar to that of the interfacial rheology. Surface pressure compression-expansion curves of the various interfaces were obtained using a KSV 2000 (KSV Instruments Ltd., Finland), which has the effective surface area of 75,900 mm. Compression-expansion experiments of the interface were performed at a fixed speed of 1500 mm$^2$•min$^{-1}$ and the constant temperature of 23°C was controlled by a circulating water bath (F25 Julabo, Kutztown, PA). This trough is made of Teflon and the moving barriers comprise of Delrin, a hydrophilic material that could prevent the water passing beneath the barriers. The surface pressure is measured by Wilhelmy plate, which is generally consist of thin platinum coupled with an electrobalance. The trough is combined with Brewster angle microscopy (BAM) (Accurion, GmbH, Germany) to monitor the asphaltene microstructure.

Brewster Angle Microscopy (BAM) is a technique that is used to visualize organization of molecules at the air-water interface based on index of refraction differences. Basically, refraction and reflection of lights are expected to occur when shooting a laser beam at the interface. However, there is no reflection of the incident light from the interface under the Brewster angle. Brewster angle can be calculated from Eq. 2.6.

$$\tan \theta_B = \frac{n_s}{n_a}$$

(2.6)

where $\theta_B$ is Brewster angle; $n_s$ and $n_a$ are refractive index of subphase and air, respectively. For the air-water interface, Brewster angle is equal to 53.1 degree. Therefore, the signal from water would exhibit a minimum value, and water will show
the darkness in the image with this angle. Once an asphaltene thin film forms at the air-water interface, this film will reflect the incident light, and those structures at interface can be detected. Real-time structure changes at the interface can be monitored.

2.3.5. Bottle Tests

The emulsion bottle test used in this study consists in mixing different ratio of water to oil under a specific shear rate in a small vial. The phase separation of the two phases was monitored over time to determine the emulsion stability. A ratio of 2:1 model oil to aqueous phase was used. A spinning blade attached to a 4000 Dremel Rotary tool was used to prepare the emulsions under rotating speed of 5000 rpm for 60 seconds. The emulsion bottle tests are usually performed at higher temperature to be representative of bottom-hole temperatures. The separation was monitored over time at room temperature, same temperature as microfluidic experiments.
Chapter 3

Examining Asphaltene Solubility on Deposition in Model Porous Media

3.1. Introduction

Asphaltenes are destabilized by the decrease in solubility of the oil when physicochemical conditions altered. Theoretically, various equations of state or mixing free energy models, such as the Flory-Huggins theory, have been utilized to describe the solubility and oil-asphaltene bulk-phase equilibria.\textsuperscript{17,91,92} Experimentally, refractive index measurements in capillary tubes have been used to describe the trends of asphaltene solubility change.\textsuperscript{20,28} This chapter describes the solubility effect on the change in hydrodynamics of the asphaltene aggregates during the deposition process in the vicinity of the surfaces in micromodels, especially within a model system consisting asphaltenes and toluene. We investigate the dynamics of asphaltene deposition after destabilization by the precipitant of \textit{n}-heptane in a microfluidic channel of porous media with a high-
speed optical microscopy. Model oil with a specific asphaltene content is investigated in the experiments leaving out other intrinsic components in crude oils which disturb the asphaltene stability.\textsuperscript{93-95} The solubility parameter of the oil-precipitant mixture is calculated to generalize the effects of oil-precipitant concentration ratio. The resulting asphaltene aggregates are further characterized by their Péclet number for the analysis of deposition dynamics. The deposition rate is found to vary with precipitant fractions nonlinearly. The pressure drop across the porous media is measured to correlate the deposition dynamics with a permeability reduction. The velocity and shear rate profiles within a typical pore space are obtained to explain the pore-scale dynamic of the depositing process based on the convection-diffusion effect. The remainder of this chapter is divided into three sections. Presentations and discussions of the experimental observations and the associated calculations are shown in the next section. Some concluding remarks are presented in the end.

3.2. Results and Discussions

3.2.1. Asphaltene Precipitation

Determining asphaltene precipitation is a key step prior to studying asphaltene aggregation and deposition. The amount of precipitated asphaltenes after mixing with \textit{n}-heptane was measured using the “indirect method”, a combination of gravimetric and spectroscopic techniques developed by Tavakkoli \textit{et al.}\textsuperscript{96} (Figure 3.1).
Figure 3.1 Asphaltene precipitation ratio results from the indirect method for the model oil mixed with \(n\)-heptane. Precipitation onset occurs at 37.74 vol% of \(n\)-heptane. The average standard deviation (ASD) of absorbance is 1.74%. (■) The absorbance at 1100 nm (●) The ratio of precipitation.

To generalize the properties of the oil-precipitant mixture, the solubility parameter using the volumetric mixing rule is calculated. The solubility parameter is derived by Hildebrand and defined as the square root of the cohesive energy density.\(^97\) The solubility parameter (\(\delta\)) can be used to explain asphaltene phase behavior. C. M. Hansen et al. (1969) defined the solubility parameter for non-polar fluids shown in Eq. 3.1.\(^98\) The solubility parameter for pure asphaltene ranges from 19 to 24 MPa\(^{0.5}\).\(^99\)

\[
\delta = \sqrt{\text{Cohesive energy density}} = \sqrt{-\frac{U^{rms}}{v}} \tag{3.1}
\]

where \(U^{rms}\) is the residual internal energy which is obtained by subtracting the ideal gas contribution from that of the real fluid, and \(v\) is the pure liquid volume.
J. Buckley et al. (1999) proposed to use the index of refraction to calculate the solubility parameter by Eq. 3.2-3.3.\textsuperscript{100}

\[ \delta = 52.042 F_{RI} + 2.904 \]  
\[ F_{RI} = \frac{n^2 - 1}{n^2 + 2} \]  

where \( n \) is the refraction index.

This method is based on the assumption that dominant interaction forces are London dispersion forces. London dispersion interactions is occurred because of induced polarization. The London desorption of a substance can be determined by the wavelength dependence of the refractive index. From this definition, this method can only be used to describe interactions without hydrogen bonding and non-polar interactions. Changing the solubility parameter alters the interactive forces between asphaltenes. Several groups have adopted the solubility parameter to describe the properties of the oil-precipitant-solvent systems.\textsuperscript{101-103} The solubility parameter of our model oil was measured and calculated from its refractive index. Refractive indices were measured by a refractometer (Anton Paar WR) under the wavelength of sodium D line (589.3 nm) with an accuracy of \( \pm 1 \times 10^{-4} \) nD and a measuring range of 1.30 to 1.72 nD. The solubility parameter at each volume ratio of \( n \)-heptane varied from 17.01 MPa\textsuperscript{0.5} at 40 vol% to 15.8 MPa\textsuperscript{0.5} at 80 vol% (see the Figure 3.2 and Table 3.1).
Figure 3.2 Solubility parameter of the oil-heptane mixture at different volume ratio of heptane.

Table 3.1 Properties of oil-precipitant mixture for each ratio of \( n \)-heptane

<table>
<thead>
<tr>
<th>Oil (vol%)</th>
<th>C7 (vol%)</th>
<th>Density (kg/m(^3))</th>
<th>Viscosity (cP)</th>
<th>Re</th>
<th>Pe</th>
<th>Solubility parameter (MPa(^{0.5}))</th>
<th>Mass flow rate of injected precipitates ((\mu)g/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>40</td>
<td>795.4</td>
<td>0.51</td>
<td>8.03</td>
<td>1.0\times10^4 – 4.7\times10^4</td>
<td>17.01</td>
<td>1.75</td>
</tr>
<tr>
<td>55</td>
<td>45</td>
<td>781.7</td>
<td>0.50</td>
<td>8.19</td>
<td>1.7\times10^4 – 6.5\times10^4</td>
<td>16.86</td>
<td>8.34</td>
</tr>
<tr>
<td>50</td>
<td>50</td>
<td>772.8</td>
<td>0.48</td>
<td>8.53</td>
<td>1.9\times10^4 – 1.3\times10^5</td>
<td>16.71</td>
<td>13.41</td>
</tr>
<tr>
<td>45</td>
<td>55</td>
<td>762.2</td>
<td>0.47</td>
<td>8.71</td>
<td>3.3\times10^4 – 5.2\times10^5</td>
<td>16.55</td>
<td>15.74</td>
</tr>
<tr>
<td>40</td>
<td>60</td>
<td>755.1</td>
<td>0.46</td>
<td>8.90</td>
<td>2.3\times10^4 – 1.9\times10^6</td>
<td>16.40</td>
<td>15.16</td>
</tr>
<tr>
<td>35</td>
<td>65</td>
<td>746.3</td>
<td>0.45</td>
<td>9.10</td>
<td>9.3\times10^4 – 1.8\times10^6</td>
<td>16.25</td>
<td>13.77</td>
</tr>
<tr>
<td>30</td>
<td>70</td>
<td>739.7</td>
<td>0.44</td>
<td>9.31</td>
<td>1.5\times10^5 – 2.8\times10^6</td>
<td>16.10</td>
<td>12.24</td>
</tr>
<tr>
<td>20</td>
<td>80</td>
<td>724.3</td>
<td>0.42</td>
<td>9.75</td>
<td>1.5\times10^5 – 3.5\times10^6</td>
<td>15.80</td>
<td>8.63</td>
</tr>
</tbody>
</table>

3.2.2. Deposition Rate of Asphaltenes in Porous Media

Representative images of asphaltene deposition for varying \( n \)-heptane volume fractions at a fixed injection volume are shown in Figure 3.3. The flow is from left to right and the
front (left) side of the post makes the first contact with the incoming fluid mixture. The volume fraction of n-heptane in the mixture, \( \varphi_h = \frac{Q_{heptane}}{Q} \), varied from 40% to 80%.

The experimental time \( t \) at different \( \varphi_h \) also varied from 10-30 minutes so that the total oil injection volume \( V_{oil} = (1 - \varphi_h)Qt \) remains constant. The particle size distribution (PSD) is obtained from the Dynamic Light Scattering (DLS) measurements (See Figure 3.4). At \( n \)-heptane volume fractions \( \varphi_h < 50\% \), submicron asphaltene aggregates are present. Upon increasing \( \varphi_h \), the mean aggregate size increases and micron-sized aggregates dominate at \( \varphi_h > 65\% \). PSD is further used to calculate the range of Péclet numbers, using Eq. 2.1-2.2, for each volume fraction to compare the relative ratios of convection to diffusion (See Table 3.1).

Figure 3.3 Images of asphaltene deposition in a homogeneous porous media. (a) 50 (b) 55 (c) 60 (d) 65 (e) 70 (f) 0 vol% of n-heptane. Flow is from left to right. The white scale bar is 500 \( \mu \)m and the black scale bar is 100 \( \mu \)m. The vol% of \( n \)-heptane alters the mean
asphaltene aggregate size, which in turn alters the relative ratio of convection to diffusion as characterized by the range of Péclet numbers (Pe). (a) Pe = 1.9 \times 10^4 - 1.3 \times 10^5 (b) Pe = 3.3 \times 10^4 - 5.2 \times 10^5 (c) Pe = 2.3 \times 10^4 - 1.9 \times 10^6 (d) Pe = 9.3 \times 10^4 - 1.8 \times 10^6 (e) Pe = 1.5 \times 10^5 - 2.8 \times 10^6

A range of Péclet numbers is provided to illustrate the relative contributions of convection and diffusion, whereby the convection becomes more dominant at higher \( \varphi_h \). Optical microscopy images show that when \( \varphi_h > 50\% \), asphaltenes deposit on each post in a cone-like pattern against the direction of fluid flow, as shown in Figure 3.3a. At higher \( \varphi_h \), the cone shape continues to be a characteristic of the deposition pattern in the front of the post and the deposition on the backside of the post is observed. Of particular interest is the variation in the aspect ratio of the cone-shape. After \( \varphi_h > 70\% \), significant bridging is observed between the posts, as shown in Figure 3.3e. For \( \varphi_h = 40\% \), an insignificant amount of deposition of the submicron aggregates is observed (data not shown).
Figure 3.4 Particle size distribution obtained by DLS measurements. (a) 40 (b) 45 (c) 50 (d) 55 (e) 60 (f) 65 (g) 70 (h) 80 vol% of heptane.

The mass ratio of deposited asphaltenes versus precipitated asphaltenes is used to quantify the asphaltene deposition rate, $\dot{m}_d$. Figure 3.6a shows the deposition mass $m_d$ (in $\mu$g) with respect to the precipitated asphaltenes mass $m_i$ (in mg) in the mixtures passing through. For each $\varphi_h$, the total asphaltene content in the model oil and the ratio of precipitates remain constant, hence $m_i$ increases linearly with time, $m_i = \dot{m}_i t$, and $\dot{m}_d$ is obtained from a linear regression on the $m_d - m_i$ curve (Figure 3.6a). As previously described, the precipitation onset occurs at
\( n \)-heptane volume fraction \( \phi_{\text{onset}} = 37.74\% \), above which asphaltenes begin to precipitate into submicron- or micron-sized aggregates due to decreased solubility.\(^9^4\)

Since \( \phi_h = 40\% \) is just above the onset point, the aggregates are nanosized, so the time required to form deposit far exceeds the residence time in our microfluidic channel. Interestingly, from \( \phi_h = 40 - 65\% \), the deposition rate increases and then decreases. It has been reported that the structure of the precipitates alters from nanoaggregates to fractal-like micron-sized aggregates\(^9^4\), where there is a competition between the deposition and convection within the fluid. Finally, the deposition rate increases again from \( \phi_h = 70 - 80\% \), due to the increasing size of asphaltene aggregates. Also, at \( \phi_h > 70\% \), the deposition occurs rather rapidly due to the bridging between posts. The measured pressure drop across the porous media increases as a result of the reduced permeability by asphaltene deposits (See Figure 3.5). Overall, three stages of the asphaltene deposition can be identified as a function of Péclet number (Pe): 0 - 55\% (small Pe, diffusion-dominated), 55 - 65\% (intermediate Pe, shear removal), and 70 - 80\% (large Pe, bridging), and the detailed analysis of deposition dynamics around a single post is discussed in the following section.
Figure 3.5 The normalized permeability reduction curve with 70 vol% of heptane.

The permeability reduction in porous micromodels due to asphaltene deposition is shown in Figure 3.5. The injected mixture is 70 vol% of n-heptane and 30 vol% of the oil. The permeability reduced to ~13% of initial value after injected 1500 µl of the mixture. Permeability is calculated from Eq. 3.4.

\[
Q = -\frac{kA}{\mu L_p} \Delta P
\]  

Eq. 3.4 is Darcy’s law where \( k \) is permeability, \( \Delta P \) is pressure drop, and \( L_p \) is the length of the porous media.
Figure 3.6 (a) Asphaltene deposition with different volume ratios of n-heptane. Here we assume the average density of asphaltenes is 1200 kg/m$^3$ (b) The asphaltene deposition rate (µg/mg), which is the slope of a linear fitting from (a), versus the concentration of n-heptane (vol%) with corresponding Péclet numbers.

3.2.3. Dynamics of Asphaltene Deposition onto a Post

The asphaltene deposition observed is characteristic of particle deposition profiles previously observed with micron-sized latex particles around a single cylindrical post by varying the Péclet number.$^{78}$ For $\phi_h = 50\%$, the deposit takes on a broad cone-like shape ($\text{Pe} = 1.9 \times 10^4 - 1.3 \times 10^5$, Figure 3.3a). The sub-micron asphaltene aggregates more readily deposit at the stagnation region in front of the post and grows against the direction
of flow via convection and diffusion. The cone elongates and narrows at $\varphi_h = 55\%$ (Pe = $3.3 \times 10^4 - 5.2 \times 10^5$, Figure 3.3b). The cone is blunted and shortened due to a competition between deposition and erosion for $60\%$ (Pe = $2.3 \times 10^4 - 1.9 \times 10^6$, Figure 3.3c). Vincent et al. also observed a similar deposition profile with micron-sized polystyrene colloids for various convection-diffusion conditions.\textsuperscript{77} Finally, for $\varphi_h = 70 - 80\%$ (Pe = $10^5 - 10^6$), the bridging of asphaltene deposits across posts occurs for larger asphaltene aggregates. As soon as the bridging occurs, it continues to entrain precipitated asphaltenes. Hu et al. described that mechanical entrapment is the dominant mechanism for insoluble asphaltene deposition in a packed-bed device.\textsuperscript{40,41}

![Figure 3.7 The dynamics of the deposition growth at the pore scale.](image)

Figure 3.7 The dynamics of the deposition growth at the pore scale. (a) cone-like, 50 vol\% (b) finger-like, 55 vol\% (c) tip-like, 60 vol\% of $n$-heptane. The white line is the initial stage. The red line is at 100s. Orange line is at 200s. The yellow line is at 300s. The green line is at 400s. The scale bar is 50 µm.

The dynamics of the deposition growth is governed by the relative contributions between convection and diffusion. The deposition profiles of the asphaltene aggregate at various points on the timeline are shown in Figure 3.7. The profile for $\varphi_h = 50\%$ shows that the deposition grows against the fluid flow and broadens laterally, forming a characteristic wide cone-like deposit. With increasing Péclet numbers, the deposit profile evolves into an elongated and narrower shape for $\varphi_h = 55\%$ as the deposition accumulates more in the stagnation region of the flow. The deposition dominates the
erosion resulting in the highest deposition rate in the first stage ($\varphi_h = 0 - 55\%$), and the deposition rate also increases with more precipitated asphaltenes by lowering the solubility of the mixture. At this stage, the removal effect is not significant due to relatively small Péclet number. Previous studies also mentioned that the submicron aggregates are the main contribution to the surface deposition. At $\varphi_h = 60\%$, a blunt tipped deposit is observed due to a balance between deposition and erosion.

The velocity and shear profiles around a characteristic asphaltene deposit on a single post for $\varphi_h = 50, 55$ and $60\%$ are simulated using the Lattice-Boltzmann method and plotted in Figure 3.8 to better elucidate the local flow patterns around the deposited asphaltenes. The deposition grows in the stagnation region (shown in blue) at the centerline of the post against the fluid flow direction. It can be observed that the highest shear rate (shown in red) appears near the edges of the deposit, where there is a competition between the deposition growth and the shear removal resulting in a cone-like deposition profiles. Also, in the high-velocity region asphaltene particles are carried downstream by the flow and therefore not able to diffuse onto the post surface.
Figure 3.8 Profiles of velocity and shear rate around representative asphaltene deposits at 50, 55 and 60 vol% of \(n\)-heptane. Velocity: (a) 50 vol\% (b) 55 vol\% (c) 60 vol\%. Shear rate: (d) 50 vol\% (e) 55 vol\% (f) 60 vol\%. The white area is the post. The brown area is the deposit.

3.3. Summary

The effect of asphaltene solubility on its deposition is examined with porous media microfluidic devices. We demonstrate that the deposition dynamics vary significantly with different concentrations of \(n\)-heptane (a well-characterized asphaltene precipitant). We associate the difference in deposition profiles to changes in the particle size distribution and corresponding Péclet number with varying \(n\)-heptane concentration. Finally, we analyze our results of pore-scale visualization with velocity and shear rate profiles near the deposit from numerical simulations to better understand the effect of deposited asphaltenes on depositing ones. Once the deposit is formed, the depositing
tendency is to grow against the flow direction (in the low-shear zone) rather than laterally (in the high-shear zone).

To solve asphaltene problems, fundamental understanding of asphaltene behaviors at micro-scale is needed. Well-defined mechanisms behind the deposition can be further incorporated into deposition simulators to accurately predict flow assurance problems and guide the design of remediation strategies.
4.1. Introduction

The colloidal interactions are further investigated after the role of the hydrodynamics of asphaltene aggregates is studied. Dispersants alter the interaction by offering the steric repulsion in the system, and the use of dispersants is to prevent the asphaltene deposition. Common solutions utilized to tackle deposition problem include mechanical removal using scrapers or solvent washing in the wellbore and near-wellbore region. Additionally, preventive chemical additives, such as asphaltene inhibitors or dispersants, have been proposed to be injected into the wellbore and formation. Inhibitors can be used to shift the thermodynamic conditions required for asphaltene precipitation versus dispersants prevent destabilized asphaltene agglomerates from flocculating and
aggregating with the goal of keeping asphaltenes suspended in the crude oil so that they can be carried by the flow instead of depositing onto the surface or plugging pore throats. 107–112 Previous studies of low-molecular-weight alkylbenzene-derived amphiphile dispersants investigate the influence of both the polarity of head groups and length of the alkyl tail on stabilizing asphaltenes under the scenario that polar moiety attaches to asphaltenes, and alkyl tails offer steric repulsion. 107,108 Bulk studies of alkylphenol dispersants on the asphaltene aggregation in heptane/toluene (Heptol) solutions evaluated dispersant effectiveness in terms of delaying the precipitation onset and reducing aggregate size. 113 The effectiveness of dispersants is typically characterized by quantifying the concentration of suspended asphaltenes in the solution using turbidity measurements and dispersancy tests by transmittance under static conditions. 107,108,113–118 However, the performance of dispersants under complex flow conditions is difficult to predict solely from static dispersancy tests. Without considering hydrodynamic effects on asphaltene aggregates, these chemical dispersants may worsen deposition and hasten flow assurance problems in the field. 119 Although commercially available alkyl-phenols have demonstrated various successes as asphaltene dispersants, it is not clear how these chemicals influence plugging and non-plugging asphaltene deposition processes. Therefore, it is important to study the performance of asphaltene dispersants under flowing conditions in porous media and integrate these studies with conventional dispersancy tests to form a multifaceted screening platform to better understand the influence of chemical additive injections for flow assurance.

In this chapter, dispersants alter the size and the intermolecular interactions between asphaltene aggregates; hence influencing both the diffusion and shear removal
regarding the deposition process. Therefore, we studied the deposition kinetics of asphaltenes under the influence of dispersants with dynamic flow conditions in porous media microfluidic devices. In particular, we identified how various chemical dispersants changes the effective asphaltene size and intermolecular interactions, which in turn alters the deposition and shear removal tendencies. A microfluidic device was used to analyze different asphaltene deposition growth rates and morphologies and provides further insight how altering the chemical interactions among asphaltenes can lead to worsening deposition in porous media.

4.2. Results and Discussions

4.2.1. Asphaltene Aggregation with Dispersants

The required amount of anti-solvent to induce asphaltene precipitation is a measure of the stability of the asphaltenes in the oil phase. Titration with $n$-heptane combined with gravimetric and spectroscopic measurements was used to determine that the instantaneous precipitation point of asphaltenes from the model oil occurred at 45 vol% of $n$-heptane. It is important to note that previous research has shown that this phase separation is a dynamic process, which indicates that the instantaneous precipitation point is time-dependant.\textsuperscript{120,121} Therefore, the instantaneous precipitation point measured occurred at within 10 minutes, the timescale for which oil would contact the porous media. Asphaltenes were forced to precipitate out of the model oil by mixing with $n$-heptane at the volumetric ratio of 20:80, which was well above the instantaneous precipitation point. Zeta potential and dynamic light scattering (DLS) measurements were
performed using a Delsamax Pro (Beckman Coulter) instrument to estimate the effective size and the charge of asphaltene aggregates in the absence and presence of the various dispersants. Samples were prepared by adding the oil-heptane mixture first to ethanol and then further diluted with DI water. The final volumetric ratio of oil-heptane mixture to ethanol-water mixture was 1 to 40. The time between the sample preparation and measurement was fixed at approximately 10 minutes. The average results were listed in Table 4.1. SEM images also confirmed that the aggregates are globular. (Figure 4.1)

![SEM images](image)

Figure 4.1 SEM images for asphaltene aggregates. (a) No dispersant. (b) $p$-hexylphenol. (c) $p$-octylphenol. (d) $p$-dodecylphenol. (e) iso-dodecylphenol. Scale bar is 5 µm.

The tendency for asphaltene aggregation is investigated by varying the chain length of the alkyl tail on the dispersant. These chemicals have a phenol head group and an alkyl tail. It is thought that the alkyl tail increases the steric repulsion between asphaltene aggregates, as shown in Table 4.1, where smaller aggregates form in the presence of dispersants with longer chain lengths. Goual et al. also studied the effects of alkylphenols on asphaltene aggregation and found that aggregates became smaller and
filamentary because alkylphenols attached to the surface of asphaltene aggregates, which increased steric interactions. Chang et al. conducted a systematic investigation of the effect of dispersants having various functional groups and lengths for the alkyl tail on solubilized asphaltenes. It was found that a longer alkyl tail better stabilized asphaltenes in the solution.

Table 4.1 Characterization of Asphaltene Aggregates Precipitated from Model Oil with \textit{n}-Heptane and Dispersants

<table>
<thead>
<tr>
<th>Dispersant</th>
<th>Zeta Potential (mV)</th>
<th>Particle Size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No dispersant</td>
<td>-35 ± 19</td>
<td>1.05 ± 0.22</td>
</tr>
<tr>
<td>\textit{p}-Hexylphenol (pC6)</td>
<td>-30 ± 5</td>
<td>0.73 ± 0.12</td>
</tr>
<tr>
<td>\textit{p}-Octylphenol (pC8)</td>
<td>-29 ± 8</td>
<td>0.59 ± 0.18</td>
</tr>
<tr>
<td>\textit{iso}-Dodecylphenol (isoC12)</td>
<td>-28 ± 6</td>
<td>0.26 ± 0.18</td>
</tr>
<tr>
<td>\textit{p}-Dodecylphenol (pC12)</td>
<td>-25 ± 3</td>
<td>0.27 ± 0.17</td>
</tr>
</tbody>
</table>

4.2.2. Deposition Rate and Morphology of Asphaltenes in Micromodel

Asphaltene deposition from model oils with and without the presence of the dispersants was further examined. The representative deposition profiles in porous media are shown in Figure 4.2. The mass flux of precipitated asphaltenes was approximately 24 g/(s·m²). In the absence of the precipitant, shown in Figure 4.2a, asphaltenes remain soluble in the oil phase and flow within the porous media without depositing. In the presence of the precipitant, \textit{n}-heptane, a cone-shaped deposit is observed to form at the front of the posts, against the flow direction as well as the rear of the posts, as shown in Figure 4.2b. In the
presence of $p$-hexylphenol and $p$-octylphenol, the asphaltene deposits tend to form blunter cone-shape, resulting in a wide streamlined shape, as shown in Figure 4.2c – 4.2d versus in the presence of $p$-dodecylphenol and $iso$-dodecylphenol, a smaller streamlined deposit is observed in front of the post. Furthermore, the deposition on the rear-side of the post is significantly reduced in the presence of dispersants.

Figure 4.2 Deposition profiles with and without dispersants in homogeneous porous media taken at 900s near the inlet. (a) Only oil. (b) No dispersant. (c) $p$-hexylphenol (d) $p$-octylphenol (e) $p$-dodecylphenol (f) $iso$-dodecylphenol. Scale bar is 200 µm, and the scale bar in the inset is 100 µm. Flow is from left to right.

The averaged deposition is quantified in Figure 4.3a, where the deposition rate, the ratio of the coverage of deposited asphaltenes and time, is shown in Figure 4.3b and results from the pressure drop measurements are provided in Figure 4.3c. Model oils with $p$-hexylphenol or $p$-octylphenol show higher overall deposition rates than the no-dispersant experiment. Initially, model oils with $p$-dodecylphenol or $iso$-dodecylphenol also show a higher deposition rate, but the deposition rate then reduces; hence the overall deposition is lower than the no-dispersant case.
The Péclet number (\(Pe\)), based on average aggregates size, is calculated to correlate the properties of the flow to the aggregation.\textsuperscript{67,77,78} Particularly, previous research has shown that stable asphaltenes are present in oil and deposit on the surface as aggregates in the colloidal size range.\textsuperscript{4} The no-dispersant case has the highest \(Pe\) (\(1.7 - 4.2 \times 10^5\)). With dispersants, \(Pe\) decreases since the aggregate size decreases. Specifically, \(Pe\) ranges from \(4.0 \times 10^4 - 1.7 \times 10^5\) for \(p\)-hexylphenol, \(3.0 \times 10^4 - 1.3 \times 10^5\) for \(p\)-octylphenol, \(2.1 \times 10^3 - 4.0 \times 10^4\) for \(p\)-dodecylphenol, and \(2.6 \times 10^3 - 4.0 \times 10^4\) for \textit{iso}-dodecylphenol. With a higher \(Pe\), the increased local shear stress exerted on the aggregate is expected to lead to erosion of the asphaltene aggregates\textsuperscript{67}, leading to the sharper-cone shape observed in Figure 4.2b. In the experiments with \(p\)-hexylphenol and \(p\)-octylphenol, asphaltene deposition increases due to decreased shear stress and increased possibility of attachment due to higher diffusion. However, the deposition rate significantly dropped with both \(p\)- and \textit{iso}-dodecylphenol, even though the relative ratio of convection to diffusion is the smallest for these dispersants. One possibility is the attractive intermolecular interactions governing asphaltene aggregates have weakened, so that shear stress is better able to erode and shear off these “softened” deposited asphaltenes from the porous media. Further discussion of this possibility will be explored in the following sections. Non-uniform axial deposition profiles are observed along the length of the flow direction, as shown in Figure 4.4. The reason this occurs is that the asphaltene concentration is being depleted over the distance, which in turn decreases the mass transfer coefficient through the porous media. In Figure 4.4a, the variation between first-half and second-half sections is not as obvious as Figure 4.4b. For larger asphaltene aggregates, the mass transfer entrance region is longer due to lower diffusivity.\textsuperscript{23} Therefore, the deposition profile in
the presence of \( p \)-octylphenol has a more prominent difference between these two sections since the concentration of destabilized asphaltenes decreased faster within the entrance region of the porous media.

Figure 4.3 (a) Deposition curves with and without dispersants. The green line represents the oil in the absence of dispersants, black line for \( p \)-hexylphenol, red line for \( p \)-octylphenol, blue line for \( p \)-dodecylphenol, and brown line for \( iso \)-dodecylphenol. (b)
The deposition rate obtained from the linear regression of curves in Figure 3a. (c) The pressure drop measured with flow tests.

![Figure 4.4 Deposition profiles with and without p-octylphenol in taken at 900s. (a) No dispersant. (b) p-octylphenol. Scale bar is 500 µm. Flow is from left to right. The white dotted line separates the section near the inlet and the section near the outlet.](image)

4.2.3. Pore-Scale Visualization of Asphaltene Deposition with Dispersants

The dynamics of the asphaltene deposition at the pore scale are illustrated by deposition growth profiles in Figure 4.5. Previously, we observed asphaltene deposits form sharper cone-like deposits on the posts when Pe increased. This sharp-cone shape enables a higher shear flow around the deposit, resulting in a competition between attachment and detachment of aggregates. Furthermore, this cone-shape is also present for short times (300s) when octylphenol and dodecylphenol are also added to the model oil. The deposition profile is altered at longer times (600s) in the presence of dispersants in which the deposits experience enhanced detachment. The centerline of the deposits for all three conditions are continuously growing and eroded when confronting the incoming fluid, resulting in a non-linear growth of the asphaltene deposit around a given post. To further
investigate the characteristic shape of the deposits (streamlined shape) at the pore scale, local flow patterns (the velocity and shear rate profiles of the deposits) are plotted by a Lattice-Boltzmann method, as shown in Figure 4.6. High-velocity fluid flow zones are found at the north and south regions of the post ($y = 45-90 \mu m$), suggesting a higher shear removal effect. The locations between posts ($x = 0-100 \mu m$ and 200-250 $\mu m$) show the highest velocity. The streamlined shape formed between these two high-velocity zones ($x = 100-200 \mu m$) is due to the fluid stagnation region near the post. High shear rates are also found at the interface of the deposit and flowing fluid, resulting in a strong competition between attachment and detachment. However, enhanced local shear stress is not able to explain the decrease in the overall deposition rate for $p$- and iso-dodecylphenol. Hence, the intermolecular interactions between asphaltenes in the presence of dispersants are discussed in the following section.

Figure 4.5 Schematic dynamics of asphaltene deposition growth with and without dispersants. (a) No dispersant (b) $p$-octylphenol (c) iso-dodecylphenol. Red line is for 300s. The yellow line is for 600s. Scale bar is 100 $\mu m$. 
Figure 4.6 Velocity profile and shear rate around representative asphaltene deposits for no dispersant, p-octylphenol, and iso-dodecylphenol. Velocity profile: (a) no dispersant, (b) p-octylphenol, and (c) iso-dodecylphenol. Shear rate: (d) no dispersant, (e) p-octylphenol, and (f) iso-dodecylphenol. The white area is the post. The brown area is the deposit.

4.2.4. Forces between Asphaltene Aggregates

A schematic illustrating the key factors causing asphaltene attachment and erosion is shown in Figure 4.7. Our hypothesis is that the dispersants increase the steric repulsion between asphaltene aggregates, which influences deposition in two competing ways. The first is by reducing the aggregate size, the relative effect of shear stress is decreased but the aggregate diffusion is increased. The second is by altering the strength of the intermolecular interactions which weakens their attachment to other aggregates and the porous media surface, resulting in “softer” deposited asphaltenes that are easier to remove by shear forces exerted by flow. The former will cause more deposition while the latter will cause less deposition. Slightly increasing the steric repulsion between asphaltene aggregates cannot sufficiently weaken the aggregate adhesion; hence, octylphenol and dodecylphenol results in more deposition in the porous media. However,
significantly increasing the repulsion between aggregates will more readily enable erosion, leading to less asphaltene deposition. After understanding the deposition tendency for the various dispersants, intermolecular forces are analyzed to better examine the hypothesis.

![Diagram showing the effect of dispersants on aggregate detachment](image)

**Figure 4.7** Illustration of detachment of deposited aggregates with 2D velocity distribution with corresponding streamlines.

Asphaltene self-association is governed by the van der Waals attraction with a major contribution from dispersion forces due to induced polarization.\textsuperscript{35,123} The dispersion interaction potential ($\Phi$) in an interacting system is the product of the effective Hamaker constant ($A$) and a function of the geometry of the system. (Eq. 4.1)

$$\Phi = A \cdot f(\text{geometry})$$  \hspace{1cm} (4.1)

In a system of two macroscopic materials and a given medium, the pair-wise summation is commonly utilized to calculate the effective Hamaker constant.\textsuperscript{124–126} Here, the interacting system (subscript ama) consists of asphaltenes in bulk solution (subscript a), medium (subscript m), and asphaltenes adsorbed onto a surface.\textsuperscript{127} If the Hamaker
constants for the bulk asphaltenes and adsorbed asphaltenes are assumed to be similar, then the effective Hamaker constant can be calculated as:

\[ A_{ama} = \left( \sqrt{A_a} - \sqrt{A_m} \right)^2 \]  

(4.2)

where \( A_a \) and \( A_m \) are Hamaker constants of the bulk asphaltenes and bulk medium solution, respectively. The Hamaker constant of a pure material can be calculated by Eq. 4.3 with the assumption that the dispersive energy component is the main contribution to the surface energy, which is a good assumption for these experiments due to lack of the hydrogen bonding in solvents (\( n \)-heptane and toluene):

\[ A_m = 24\pi L_0^2 \gamma_s \]  

(4.3)

where \( L_0 = 0.165 \text{ nm} \) is defined as the characteristic distance between interacting molecules, and \( \gamma_s \) is the surface energy. The calculated Hamaker constant (\( A_a = 5.73 \times 10^{-20} \text{ J} \)) was obtained from Gonzalez et al. who used the Lifshitz theory towards a system of asphaltenes. The Hamaker constant of the medium (\( A_m = 4.22 \times 10^{-20} \text{ J} \)) was calculated with the measured surface energy (\( \gamma_s = 20.5 \pm 0.06 \text{ mN/m} \)), where the surface tension was measured using a force tensiometer (K100, KRÜSS, GmbH). The effective Hamaker constant of the interacting system (\( A_{ama} \)) was estimated to be \( 1.14 \times 10^{-21} \text{ J} \) using Eq. 4.2. Previously, Fotland et al. studied van der Waals forces between asphaltenes by altering the medium with different ratios of \( n \)-pentane and benzene. They found that the effective Hamaker constant was reduced with a smaller fraction of \( n \)-pentane, which also explained experimental observations that precipitation is directly correlated to the ratio of precipitant in the solution. Additionally, Wang et al. analyzed the interaction forces of asphaltene surfaces in heptane-toluene mixtures using atomic
force microscopy (AFM). They found that the interaction are mainly due to van der Waals attractive forces when asphaltenes were in a solvent with high volume ratio of n-heptane, which is similar to the conditions reported here.\textsuperscript{129}

To study the attachment and removal of asphaltenes, the attraction and repulsion are estimated as follows. The attraction of asphaltenes to the post is assumed to be a system with a particle and a planar surface in contact with a distance \((D)\), and the attractive force \((F_A)\) can be described by Eq. 4.4.\textsuperscript{126}

\[
F_A = \frac{A_{ama}R_p}{6D^2}
\] (4.4)

Since dispersants are known to increase the steric repulsion between asphaltene aggregates by adsorbing onto the asphaltenes, then this steric repulsion has a significant impact on erosion of asphaltene deposited.\textsuperscript{107,108,113,115} To evaluate the steric repulsive forces \((F_s)\), we use the force-distance profile between a particle and a repulsive surface, which is shorter than two times of the thickness of the adsorbed layer, \((D < 2L)\), estimated by Eq. 4.5.\textsuperscript{126,130,131}

\[
F_s(D) = 2\pi R_p \left(\frac{k_B T}{s^3}\right) \left\{ \frac{8L}{5} \left[ \left(\frac{2L}{D}\right)^{\frac{5}{4}} - 1 \right] + \frac{8L}{7} \left[ \left(\frac{D}{2L}\right)^{\frac{7}{4}} - 1 \right] \right\} \text{ for } D < 2L
\] (4.5)

where \(s\) is the average distance between attachment points\textsuperscript{132}, \(L\) is the thickness of the adsorbed dispersant layer. The first term in Eq. 4.5 is the osmotic repulsion from the overlap of steric surfaces which increases the osmotic pressure and the second term is associated with the loss of entropy associated with adsorption.\textsuperscript{130} The distance between attachment points \((s)\) was estimated with the method by Rahme et al\textsuperscript{132}, which is the
square root of the surface area for the asphaltene aggregate per dispersant molecule, and the distances were 6.55 nm for \( p \)-hexylphenol, 7.05 nm for \( p \)-octylphenol, and 7.95 nm for \( p \)-dodecylphenol with the assumption that all the dispersants in the oil adsorbed on asphaltenes. The thickness of the adsorbed layer \( (L) \) was taken as size of the dispersant, and they were estimated to be 1.18 nm for \( p \)-hexylphenol, 1.39 nm for \( p \)-octylphenol, and 1.89 nm for \( p \)-dodecylphenol by Gaussian G09.D1. The volume and the surface area of an asphaltene molecule were estimated by Eq. 4.6 and Eq. 4.7. The distance between attachment points was estimated by Eq. 4.8 with the assumption of a spherical shape for the asphaltene aggregate.

\[
V_A = \frac{M_w}{\rho_A \cdot N_A} \tag{4.6}
\]

\[
A_s = \left(36\pi V_A^2\right)^{\frac{1}{3}} \tag{4.7}
\]

\[
s = \left(A_s \cdot \frac{\text{mole of asphaltenes}}{\text{mole of dispersants}}\right)^{\frac{1}{2}} \tag{4.8}
\]

where \( V_A \) is the volume of an asphaltene molecule, \( M_w \) is the molecular weight of the asphaltene aggregate (4000 g/mol), \( \rho_A \) is the density of the asphaltene (1.2 g/cm\(^3\)), \( N_A \) is the Avogadro number, and \( A_s \) is the surface area of the asphaltene aggregate. Electrostatic repulsion is neglected because most of the solvents used as the medium are non-polar (\( n \)-heptane and toluene) and the measured zeta potential for asphaltenes with different dispersants are in a similar range, suggesting that the electrostatic repulsion between asphaltene aggregates are not a dominant factor. The combination of attraction and repulsion forces for different dispersants is plotted in Figure 4.8.
Retention of aggregates on the surface is presented in two situations. Aggregates can adhere to either favorable sites (depositing without repulsive forces) or unfavorable sites (with the secondary minimum or overcoming the repulsive barrier staying with the primary minimum). Irreversible deposition occurs at the primary minimum. The combined value of the barrier and the secondary minimum represents the energy for an aggregate to deposit in the primary minimum. Reversible deposition was reported for aggregates depositing with the secondary minimum.\textsuperscript{133–136} In Figure 8, the maximum value of the energy barrier increases and the depth of the secondary minimum decreases when the length of the alkyl tail on the dispersant is increased. For aggregates with dodecylphenol, the energy barrier for irreversible deposition is the highest, and the depth for the reversible process is the shallowest. To further estimate the potential convection effect discussed in previous sections with the interacting forces, the depth of the secondary minimum (reversible deposition) is plotted with the hydrodynamic force as a function of the size of the aggregate. The hydrodynamic force is estimated as the drag force assuming the particle rolling and sliding are the main contributions to the removal as shown in Eq. 4.9.\textsuperscript{137}

\[ F_d = 1.7(6\pi)\mu R_p^2\dot{\gamma} \]  

(4.9)

The shear rate (\(\dot{\gamma} \sim 8400\) or 1350 \(1/s\)) is estimated as (\(\sim 6u/h\)) where \(h\) is the height of the channel or the distance between posts (the pore size).\textsuperscript{138} This drag force balances the adhesion force from the secondary well. In Figure 4.9, the crossover between the drag force based on the height and the secondary minimum shifts with increasing the length of the alkyl tail. This explains the drop in the deposition rate for
dodecylphenol. The drag force is also calculated based on the pore size but no crossover is obtained. However, this estimation requires further consideration, including the deformability of the aggregates (changing the contact area) and other removal factors such as lift forces. Therefore, more investigations into the rheological properties of asphaltenes and other forces resulted from hydrodynamics are required to analyze the deposition process.

Figure 4.8 Approximation of the interaction between an asphaltene aggregate and an asphaltene-deposited surface with dispersants. The inset plot is the zoom-in graph of Figure 8. Black line represents $p$-hexylphenol, red dashed line is $p$-octylphenol, and blue dotdashed line is $p$-dodecylphenol.
Figure 4.9 The depth of the secondary minimum and the hydrodynamic force are functions of the size of the asphaltene aggregate. The black line represents $p$-hexylphenol, red dashed line is $p$-octylphenol, and blue dotdashed line is $p$-dodecylphenol. The orange dotted line represents the hydrodynamic force based on the height of the micromodel and aqua dotted line is the hydrodynamic force based on the pore size calculated from Eq. 4.9.

Microfluidic investigation on the effect of dispersants was also extended to crude oil S, which include asphaltenes along with saturates and resins. The deposition profiles with and without the presence of $p$-octylphenol or $p$-dodecylphenol are shown in Figure 4.10 with the elapsed time of 600 and 1200 seconds. The no-dispersant case forms a cone-shape deposition profile, as was observed in the model oil deposition. The profiles in the presence of dispersants show more streamlined shapes, as shown in Figure 4.10e and Figure 4.10f. This streamlined shape is possibly caused by a smaller effective aggregate size. This dynamic growth of deposition is quantified, as shown in Figure 4.11. More deposition is obtained with the presence of dispersants, the same trend as observed in the model oil tests. However, the addition of $p$-dodecylphenol caused more deposition than the case with the presence of $p$-octylphenol. There are two possible reasons for this difference. First, there is a significant amount of saturates in crude oil S, which increases the Hamaker constant for the system. $^{128,129}$ Hence, the steric repulsion provided by adsorbed dispersants are not strong enough to easily disrupt the deposited asphaltenes due to shear flow. Second, the combination of resins in the crude oil and dispersants stabilize the asphaltenes better in the crude oil compared to the model oil, resulting in even smaller aggregates and less hydrodynamic erosion. Therefore, a higher deposition rate is observed with the presence of $p$-dodecylphenol in crude oil S.
Figure 4.10 Deposition profiles of crude oil S with and without the presence of dispersants taken at 600s for (a)(b)(c) and 1200s for (d)(e)(f). (a) and (d) are no-dispersant cases. (b) and (e) are for \( p \)-octylphenol. (c) and (f) are for \( p \)-dodecylphenol. Scale bar is 500 µm. Flow is from left to right.

Figure 4.11 Asphaltene deposition from crude oil in the microfluidic porous media plotted with time with and without the presence of dispersants. The green line represents the crude oil in the absence of dispersants, red dashed line for \( p \)-octylphenol, and blue dotdashed line for \( p \)-dodecylphenol.
4.3. Summary

Microfluidic devices offer a well-controlled platform to analyze the relative effects of convection-diffusion and intermolecular forces resulting from chemical injections on the asphaltene deposition. In general, smaller asphaltene aggregates are better able to resist shear flows from the fluid, increasing its probability for deposition. Injection of chemical dispersants effectively reduces their size and resulting in higher initial deposition rates; however, these chemical dispersants alter the intermolecular interactions. Stronger repulsive interactions result in “softer aggregates” that are readily eroded in shear flow after deposition, thereby lowering the overall deposition rate. This is observed for the case with dodecylphenol dispersants and model oil, where the deposited asphaltenes for easily removed by shear forces due to higher repulsive interactions, which eventually resulted in a lower overall deposition rate. Furthermore, in crude oil systems that include saturates and resins, the asphaltenes are not as easily destabilized compared to the model oil system. The saturates in crude oil increase the attractive Hamaker constant for the asphaltene aggregates, while the resins combined with dispersants reduce the effective aggregate size.
Chapter 5

Combined Interfacial Shear Rheology and Microstructure Visualization of Asphaltenes at Air-Water and Oil-Water Interfaces

5.1. Introduction

Dispersants are designed to prevent destabilized asphaltene agglomerates from flocculating and aggregating as mentioned in Chapter 4. Asphaltenes are also known to be surface-active and assemble at oil-water and air-water interfaces, often forming an interfacial film. This also leads to flow assurance problems, such as difficulty in transporting highly viscous fluids or separating phases in stabilized water-in-oil emulsions.\textsuperscript{141,142} Furthermore, tailings/wastewater containing bitumen and crude oil that are discharged into tailing ponds often deposit and form a film on the pond.\textsuperscript{143,144} Therefore, understanding of the interfacial properties of the surface-active species in the presence of dispersants is essential for recovery and remediation of oils.
In the last two decades, the interfacial viscoelasticity of asphaltenes have been studied, including air-water\textsuperscript{42,57,83,143,145–151} and oil-water interfaces with either air\textsuperscript{47,84,152,153} or oil induced aggregation\textsuperscript{44,46,48,142,154–158} as well as oil-water interfaces with asphaltenes in the dispersed phase.\textsuperscript{50,158,159} These studies have shown that the conditions by which the asphaltene film forms at the interface determines its rheological responses. Asphaltenes at a heptol-water interface are found to be more compressible than those at an air-water interface.\textsuperscript{84,152,154} The rigidity of the film is reduced when maltenes or other demulsifiers are mixed with asphaltenes at the interface, which is thought to reduce the attractive interactions between asphaltenes.\textsuperscript{42,145} The addition of solvents to these interfaces alters the interparticle aggregate interactions. It has been observed that low-aromaticity solvents (more aliphatic molecules) increased the attractive interactions, thereby decreasing the time required to saturate the interface with asphaltenes.\textsuperscript{155}

A Langmuir trough with an existing double wall ring rheometer is modified to perform \textit{in situ} visualization of asphaltene aggregation at air-water and oil-water interfaces while under strain. We relate the observed microstructure of asphaltenes at interfaces with their rheological behavior and in the presence of various chemical dispersants. This allows us to simultaneously visualize dynamic aggregation of asphaltenes at interfaces under various strain conditions. The rheological response is correlated with the microstructure to design more effective chemical additives to mitigate asphaltene related flow assurance problems, and to develop improved remediation methods to recovery discharged oils and bitumen in tailing ponds.
5.2. Results and Discussions

5.2.1. Surface Pressure - Area Compression-Expansion Curves of Asphaltenes at Air-Water Interfaces

Asphaltenes at the air-water interface were subject to two cycles of compression-expansion experiments using a Langmuir trough to obtain plots of surface pressure versus area (Figure 5.1a). Also, the corresponding BAM images are shown in Figure 5.1b. In the presence of asphaltenes, the surface pressure was initially negligible, and then upon compression, the surface pressure began to rise once asphaltenes came into closer contact (Figure 5.1b1 and Figure 5.1b2). The trough area at which this rise occurred corresponds to is 600 cm$^2$ and considering the mass of the asphaltenes added to the interface was 280 µg, surface pressure started to increase at 0.46 µg•cm$^{-2}$. Further compression resulted in increasing surface pressure, indicative of a 2D continuous “skin” of asphaltenes (Figure 5.1b3). As the trough area was further decreased, and surface pressures increased above 35 mN•m$^{-1}$, as a result of asphaltenes jamming together. Compression of this solid film resulted in instabilities, such as surface wrinkling and multilayer aggregates (Figure 5.1b4). Erni et al. previously reported temporal alteration of wrinkling and buckling of oil drops in the water solution as a function of oil solubility. They observed a rigid layer at the oil-water interface and concluded that both interfacial compression and shear elasticity were responsible for surface wrinkling. Theo et al. described that wrinkles appeared when particle-laden interfaces were unable to rearrange in-plane, causing them to deform out-of-plane. This also corresponded to the rigidity of the interface. Pauchard et al. also observed
wrinkles of asphaltenes at interfaces using contracting pendant drop experiments and proposed that this phenomenon was a transition to a glassy interface, comparable to a gelling process.\textsuperscript{162} For our asphaltene layer, a max surface pressure was obtained at 48 mN•m\(^{-1}\) before reaching the limit of the trough compression.

Similar profiles were observed for asphaltenes in the presence of \(p\)-octylphenol and \(p\)-dodecylphenol as shown in Figure 1a, where the rise occurred at 0.46 \(\mu\)g•cm\(^{-2}\); however, the surface pressure associated with asphaltenes jamming were lower as a result of smaller asphaltene aggregates that caused the interface to become more compressible. Furthermore, surface pressure under identical surface coverage decreased following the order of asphaltenes without dispersants, with \(p\)-octylphenol, and with \(p\)-dodecylphenol, such that surface pressure was measured as 32.1, 21.6, and 15.3 mN•m\(^{-1}\) respectively when the coverage was 0.7 \(\mu\)g•cm\(^{-2}\) (the blue dashed line as shown in Figure 5.1a). These results indicated that asphaltenes were less capable of reducing the excess free energy of the surface in the presence of the chemical dispersants. As previously described, alkylphenols have been reported to attach onto the periphery of asphaltenes, saturating the H-bond sites (polar moiety) and the alkyl tail further offered more hydrophobicity, suggesting these asphaltenes were less likely to adsorb on the water subphase.\textsuperscript{113} Also, there was a large hysteresis upon expansion, where the surface pressure decreases rapidly to zero, due to irreversible aggregation of the asphaltenes at the interface and possible loss of asphaltenes from the interface. The second (and subsequent) cycles showed a much smaller hysteresis. (Figure 5.1a, inset plot)
Figure 5.1 Behaviors and morphology of asphaltenes at air-water interfaces with a Langmuir trough. (a) Compression-expansion experiments. The inset plot is the second cycle. (b) Brewster Angle Microscopy (BAM) images for asphaltenes at air-water interface without dispersants under varying surface pressure. (b1) 0.05 (b2) 3 (b3) 25 (b4) 38 mN•m⁻¹. The scale bar is 100 μm.

5.2.2. Interfacial Rheology of Asphaltenes at Air-Water Interface

Rheological behavior of asphaltenes at the air-water interface was examined by steady-shear and SAOS experiments with two surface coverages (0.5 and 4 μg•cm⁻² asphaltenes). The results of the steady-shear viscosity, η, showed characteristic shear-thinning behavior
at both coverages (Figure 5.2a and 5.2b). The data was fit to Eq. 2.3 and the power law exponent was obtained. The exponent, $k$, was determined to be $-0.82 \ (0.5 \ \mu g \cdot cm^{-2})$ and $-1.91 \ (4 \ \mu g \cdot cm^{-2})$, respectively. Additional surface coverage increased the yielding behavior of the interface. Furthermore, asphaltenes mixed with $p$-octylphenol and $p$-dodecylphenol showed lower surface viscosity and a less yielding behavior, with $k$ values being respectively $-0.69$ and $-0.61 \ (0.5 \ \mu g \cdot cm^{-2}),$ $-1.8$ and $-1.57 \ (4 \ \mu g \cdot cm^{-2}).$ Dispersants decreased the yielding behavior of the interface likely by disrupting the association of asphaltenes. Goual et al. also showed that in the presence of alkylphenols, asphaltene aggregates were observed to be filamentary instead of globular.\textsuperscript{113}

![Rheological behavior of asphaltenes at air-water interfaces.](image)

Figure 5.2 Rheological behavior of asphaltenes at air-water interfaces. Steady-shear viscosity and dynamic viscosity: (a) $0.5 \ \mu g \cdot cm^{-2}$ and (b) $4 \ \mu g \cdot cm^{-2}$. Strain amplitude-sweep experiment: (c) $0.5 \ \mu g \cdot cm^{-2}$ and (d) $4 \ \mu g \cdot cm^{-2}$. Black circles correspond to the interface without dispersants, squares are in the presence of $p$-octylphenol, and triangles are in the presence of $p$-dodecylphenol. Averaged $G_0'$ for (c) low coverage $= 0.23 \pm 0.02$ (without dispersants), $0.12 \pm 0.04 \ (p$-octylphenol) and $0.004 \pm 0.007 \ \text{N} \cdot \text{m}^{-1} \ (p$-dodecylphenol). Averaged $G_0'$ for (d) high coverage $= 0.85 \pm 0.07 \ (without \ dispersants), 0.71 \pm 0.05 \ (p$-octylphenol) and $0.28 \pm 0.05 \ \text{N} \cdot \text{m}^{-1} \ (p$-dodecylphenol).
Furthermore, strain amplitude-sweep results are also shown for these two surface coverages in Figure 5.2c and Figure 5.2d. The rheological response for two coverages varies significantly with strain amplitude. With increasing the surface coverage, both $G'$ and $G''$ increased. At the lower coverage, both $G'$ and $G''$ remained constant at smaller strain amplitudes and decreased monotonically at larger strain amplitudes. At the higher surface coverage, the interface was more sensitive and brittle to the strain amplitude, and both moduli decreased with increasing strain amplitude. Also, the linear viscoelastic (LVE) regime indicated a more ductile structure at the lower surface coverage (wider LVE) than the higher coverage (narrower LVE). These results will be discussed with corresponding observed microstructures.

In the presence of $p$-octylphenol, both moduli slightly decreased, while with $p$-dodecylphenol both moduli significantly decreased. Also, a similar trend with dispersants was observed in frequency-sweep experiments as shown in Figure 5.3. This response is likely due to phenol molecules disrupting the asphaltene self-association properties, which in turn decreased the elasticity of the asphaltene interface.\textsuperscript{113,163} Also, the responses from frequency-sweep experiments showed that the viscoelastic layer (frequency-dependent) was altered to a solid (frequency-independent) film with a higher coverage. Of particular interest is the response with $p$-dodecylphenol at the lower surface coverage that $G''$ was slightly higher than $G'$, indicative of a more viscous interface. One possible explanation is that the longer alkyl tail on $p$-dodecylphenol destabilized the association of asphaltenes more readily. However, at the higher coverage, $G'$ was significantly higher than $G''$, suggesting a more elastic interface. In this regard, alkyl tails offer greater steric repulsion at the lower surface coverage while they may be more
entrained into the multilayer aggregates at the higher surface coverage, shown in Figure 3h and discussed in the following section.

![Figure 5.3](image)

**Figure 5.3** Frequency-sweep rheological results for 0.5 $\mu$g•cm$^{-2}$ and 4 $\mu$g•cm$^{-2}$ of asphaltenes at air-water interface. (a) Elastic modulus. (b) Viscous modulus. Circles, squares, and triangles are for no additive, $p$-octylphenol, and $p$-dodecylphenol, respectively. Orange symbols are for 0.5 $\mu$g•cm$^{-2}$, and black symbols are for 4 $\mu$g•cm$^{-2}$.

The microscopy images showed the morphological difference between two coverages, where the lower coverage was an asphaltene skin that appeared uniform in greyscale (Figure 5.4a) while the higher coverage showed jammed multilayer aggregates and surface wrinkling corresponding to a more rigid and solid interface (Figure 5.4b), which is consistent with the solid response from SAOS results. Tchoukov *et al.* proposed that asphaltenes form a multilayer structure at the oil-water interface based on interferometry measurements.\textsuperscript{58} Pauchard *et al.* also described the formation of multilayer asphaltene network is possible due to interactions between the alkyl chains.\textsuperscript{164} The asphaltene skin at the low coverage behaved less shear-thinning at a shear rate of 1 s$^{-1}$.
and remained unchanged from the microscopy (Figure 5.4e). This observation also indicates that the asphaltene skin could possibly reorganize during the experimentation, characteristic of a ductile behavior (wider LVE). However, the skin ruptured for the high surface coverage (Figure 5.4f). Multilayer structure remained unaltered, even in the presence of $p$-octylphenol and $p$-dodecylphenol (Figure 5.4c, 5.4d, 5.4g and 5.4h) at both shear rates of 0.001 and 1 s$^{-1}$. Erni et al. also found that by having a solid yielding layer at air-water interfaces resulted in a shear-thinning response with fractured interface. This fractured layer further gave rise to shear localization, where the interface is only deformed near a spinning disk.$^{165}$ The empirical Cox-Merz rule, as shown in Eq. 5.1, which equates the dynamic viscosity, $|\eta^*(\omega)|$ and steady-shear viscosity, $\eta(\dot{\gamma})$, was also checked.$^{166}$

\[ |\eta^*(\omega)| = \eta(\dot{\gamma}) \text{ with } \dot{\gamma} = \omega \]  

(5.1)

For our asphaltene layer, the Cox-Merz rule is not obeyed, with a significant deviation between dynamic and steady-shear viscosity, as shown in Figure 5.2a and 5.2b. Steady-shear viscosity consistently showed lower values than dynamic viscosity. This measured difference further confirmed that the yielding and highly shear-thinning behavior in steady-shear experiments was caused by the fractured interface with the possibility of shear localization, as shown in Figure 5.4f. Moreover, fractured interfaces are not able to reorganize readily, which explains the high sensitivity (narrower LVE) in strain amplitude-sweep experiments when the mechanical strength of the interfacial layer is non-uniform.
Figure 5.4 Optical microscopy images of asphaltene microstructure at air-water interfaces. (a) Interface at rest for surface coverage of 0.5 µg/cm² shows a uniform asphaltene “skin”. (b) The interface at rest for surface coverage of 4 µg/cm² shows a wrinkled asphaltene skin coexisting with multilayer asphaltene aggregates. Asphaltene under the shear rate of 1 s⁻¹ at (e) 0.5 µg/cm² remain unchanged from microscopy and show a fracture in the skin caused by shear stress at (f) 4 µg/cm². Asphaltene interfaces for surface coverage of 4 µg/cm² at shear rates of (c) 0.001 and (g) 1 s⁻¹ in the presence of p-octylphenol, and (d) 0.001 and (h) 1 s⁻¹ in the presence of p-dodecylphenol. The total strain is around (a) 0, (b) 0, (c) 0.9, (d) 0.9, (e) 2500, (f) 2500, (g) 2500, and (h) 2500. The scale bar is 50 µm.

5.2.3. Interfacial Rheology of Asphaltenes at Oil-Water Interface

As previously mentioned, a DW-a layer (asphaltenes at the decane-water interface with the aggregation in the air) was prepared by adding decane to an existing asphaltene film at an air-water interface versus a DW-d layer (asphaltenes at the decane-water interface with the aggregation in decane) was prepared by first forming a decane-water interface and then injecting the asphaltene solution into the subphase. The microscopy images of asphaltenes at the high coverage are shown in Figure 5.5. This high coverage was studied to determine the behavior of the multilayer asphaltene aggregates at oil-water interfaces versus air-water interfaces. The general size and close-packed morphology of multilayer...
structure for DW-a (Figure 5.5a) are similar to the one at an air-water interface. However, the surface wrinkling of asphaltenes at air-water interfaces was not observed. Though decane is a poor solvent for asphaltenes, the interface may be able to relax due to some solubilization of the asphaltenes into decane. This is supported by Pauchard *et al.* showed using pendant drop, surface wrinkles in compressed asphaltene films relaxed when an equilibrium surface pressure was established between adsorption and desorption of asphaltenes from the interface.\(^{162}\) Also, Samaniuk *et al.* suggested another possible explanation where the hydrophobic components of asphaltenes resulted in repulsive interactions with hexadecane while attractive interactions in the air.\(^{156}\)

The asphaltene film of DW-d (Figure 5.5b) appeared morphologically different than that observed at either of an air-water or a DW-a interface. Though the multilayer asphaltene islands of DW-d are similar in size to those observed at an air-water interface, they were less tightly packed compared to asphaltenes at an air-water or a DW-a interface. As shown in the inset, the DW-a aggregate shows a finer grain-like structure with a smooth edge, while DW-d aggregates appear to be more fractal-like with a coarser-grain appearance and rough edges. Since the asphaltene solution was injected directly into a decane-water interface, the solvent aggregated with asphaltenes cannot easily evaporate. Gawrys *et al.* used Small-Angle-Neutron-Scattering (SANS) to show that solvent entrainment resulted in a 30 - 50% swelling of asphaltene aggregates.\(^{167,168}\) Swollen asphaltenes entrained with solvents at the interface were unable to form tightly packed layer. Moreover, Duerr-Auster *et al.* studied the aggregation-dependent rheological behaviors of polyglycerol fatty acid ester (PGE), and found that the number of the intermolecular junction points in the structure under varying aggregation process
determined the rheological response. A single layer microstructure which aggregated in the air majorly due to the attractive interactions of the alkyl chains showed a lower viscoelastic modulus, while a bilayer structure formed during the adsorption process showed a higher modulus. However, the amount of adsorbed surfactants depended on the adsorption time resulting in a difficult comparison between two aggregation processes. In our work, the amount of adsorbed asphaltenes for two methods (aggregation in the air or decane) is similar due to the limited solubility of asphaltenes in decane. Therefore, the determining factor in the rheological response is the intermolecular junction points. In the asphaltene aggregation in decane, solvents are trapped in the structure possibly resulting in less junction points, while the aggregation in the air causes more compact structure and more connections.\(^{169}\) In the presence of the two phenols, the aggregates were dispersed across the interface as shown in Figure 5.5c and 5.5d. Since the phenols decreased the tendency for asphaltenes to self-associate, the resulting microstructure was more of a fractal structure across the interface. Interfaces of asphaltenes with and without dispersants are illustrated in Figure 5.5e. Asphaltene aggregates consisting of nanoaggregates adsorbed on the subphase forming a densely packed interfacial layer without dispersants, while asphaltene nanoaggregates are more sparsely distributed with dispersants since dispersants are designed to have a polar head attaching on nanoaggregates and a tail offering steric repulsions.\(^{107,108,113}\)
Figure 5.5 Asphaltenes at decane-water interfaces. (a) DW-a in the red-dotted box. (b) DW-d in the blue box. (c) DW-d with p-octylphenol. (d) DW-d with p-dodecylphenol. (e) Illustration of the asphaltenes at interfaces with and without dispersants. All are 4 $\mu$g•cm$^{-2}$. The total strain is 0 for all. The scale bar is 50 $\mu$m.

The rheological data of asphaltenes without dispersants at air-water and decane-water interfaces for the higher surface coverage is shown in Figure 5.6. DW-a ($k = -0.59$) and DW-d ($k = -0.66$) both behaved with a characteristic shear-thinning response, and $k$ is much smaller than that obtained at air-water interfaces (microstructures as shown in Figure 5.2b and 5.2f). The Cox-Merz rule is also not obeyed as shown in Figure 5.6a. Complex dynamic viscosity is generally higher than steady-shear viscosity, especially
asphaltenes without dispersants at the air-water interface discussed in the previous section. However, the dynamic viscosity of DW-a and DW-d are closer to the steady-shear viscosity. The possible explanation is discussed later with microscopy images (Figure 5.8) under shear stress. Strain amplitude-sweep results for the various interfaces are shown in Figure 5.6b. The decane-water interface showed much lower moduli than the air-water interface. Reynaert et al. also measured aggregated colloidal particles at air-water and decane-water interfaces, and found that the complex viscosity of an air-water interface was much higher than a decane-water interface when varying the surface coverage.\textsuperscript{170}
Figure 5.6 Rheological properties of asphaltenes at various interfaces without dispersants at a surface coverage of 4 µg•cm⁻². (a) Steady-shear viscosity and complex dynamic viscosity of different interfaces. (b) SAOS for different interfaces. Black squares, red diamonds, and blue circles are for asphaltenes at the air-water interface, DW-a, and DW-d, respectively. Averaged $G_0'$ for (b) = 0.85 ± 0.07 (asphaltenes at air-water interface), 0.016 ± 0.004 (DW-a) and 0.015 ± 0.003 N•m⁻¹ (DW-d).

The shear-thinning behavior of decane-water interfaces with dispersants is shown in Figure 5.7. With possible desorption of asphaltenes into decane, dispersants were able to disrupt the association of asphaltenes and fluidize the film. This phenomenon also differentiated the influence of dispersants on the steady-shear viscosity, whereby those
with a longer alkyl tail caused the asphaltene layer to become more fluidic. (Figure 5.7a) For DW-d, the behavior of the steady-shear viscosity with and without dispersants was similar. One possible reason is that alkylphenols can partition into the decane phase, thus reducing the interactions between alkylphenols and asphaltenes at the interface. (Figure 5.7b)

![Figure 5.7](image)

Figure 5.7 (a) Steady-shear viscosity of DW-a. (b) Steady-shear viscosity of DW-d. Both are for 4 µg•cm⁻². Circles, squares, and triangles are for asphaltenes without dispersants, with p-octylphenol, and with p-dodecylphenol, respectively. Red represents DW-a, and blue represents DW-d.

As shown in Figure 5.8a, under a shear rate of 1 s⁻¹, the multilayer structure formed on the DW-a separated producing several smaller aggregates at the interface, while no
fracture was observed compared to asphaltenes at air-water interfaces. This implies that attractive interactions governing the multilayer structure are much weaker compared to those at air-water interfaces, and the skin around the multilayer structure is able to reorganize during deformation. Interestingly, for DW-d, shown in Figure 5.8b, the multilayer aggregate was dispersed. The governing hypothesis is that solvent entrapment in the DW-d aggregates allows them to be more readily disrupted under a shear stress. Furthermore, the size of shear-dispersed asphaltenes decreased with \( p \)-octylphenol (Figure 5.8c), and even smaller with \( p \)-dodecylphenol (Figure 5.8d). In the absence of a fractured interface for both DW-a and DW-d, the possibility of shear localization does not exist, resulting in a less shear-thinning response. These observations could also explain that dynamic viscosity is closer to steady-shear viscosity for decane-water interfaces than the air-water interface, as shown in Figure 5.6a. Shear-induced deformation of the asphaltene layer with dispersants is also shown in Figure 5.8e, illustrating that under shear stress, aggregates are dispersed at the interface.
Figure 5.8 Asphaltenes under the shear rate of 1 s\(^{-1}\) at (a) DW-a without dispersants, (b) DW-d without dispersants, (c) DW-d with \(p\)-octylphenol, and (d) DW-d with \(p\)-dodecylphenol. (e) Demonstration of asphaltenes at interfaces before and after shear. All are 4 \(\mu\)g•cm\(^{-2}\). The red-dotted box represents DW-a, and blue box represents DW-d. The total strain is around 2500 for all. The scale bar is 50 \(\mu\)m.

The rheological properties of the elastic interface have been predicted by the scaling law derived from the concept of the elastic links between aggregates by Shih \textit{et al.} for polymer gels.\textsuperscript{171} Reynaert \textit{et al.} used this scaling law, shown in Eq. 5.2, to characterize 2D particulate suspensions:\textsuperscript{170}

\[
G' \sim \phi^p \sim \phi^{d+\frac{D_{bb}}{d-D_f}} \tag{5.2}
\]
where $G'$ is the elastic modulus, $\varnothing$ is the concentration, $n$ is the power law exponent, $d$ is the dimension of the Euclidean space, $D_f$ is the fractal dimension of the aggregate network, and $D_{bb}$ is the fractal dimension of the backbone of the network. The fractal dimension of the asphaltene aggregates at various interfaces can be calculated under different shear rates, as shown in Figure 5.9. The fractal dimension of the multilayer aggregates at the air-water interface remained fairly constant at values between 1.6-1.7 for $D_f$ and 1.4-1.6 for $D_{bb}$ across various shear rates. For DW-a and DW-d, the fractal dimension decreased to 1.3-1.5 for $D_f$ and 0.9-1.4 for $D_{bb}$, representing that the interface became more dispersed. (Figure 5.9a and Figure 5.9b) The power law exponent, $v$, was within the range of 8.9-9.9 for the air-water interface. Reynaert et al. also obtained 8.2 for the network comprised of polystyrene micrometer particles at the air-water interface, which is comparable to our results. The power law exponent decreased with higher shear rates, which matches the decrease of the surface viscosity. (Figure 5.9c) Moreover, the effective aggregate size was estimated. (Figure 5.9d) The average size at the air-water interface remained fairly constant but has a large standard deviation while aggregates at the decane-water interface decreased in size with increasing shear stress. Additionally, DW-d aggregates were smaller than DW-a aggregates.
Figure 5.9 (a) Fractal dimension of the interfaces with different conditions. (b) Fractal dimension of the backbone of the aggregate network. (c) The power law exponent under various shear rates. (d) The effective aggregate size of the interfaces with different conditions. Black circles correspond to the interface without dispersants, squares are in the presence of \textit{p}-octylphenol, and triangles are in the presence of \textit{p}-dodecylphenol. Black solid symbols are for the air-water interface. Red solid symbols are for DW-a. Blue open symbols with a dotted line are for DW-d.

5.3. Summary

Simultaneous analysis of the asphaltene microstructure at interfaces and the corresponding rheological responses was obtained using an interfacial rheometer with the double-wall ring geometry. This method offers a platform to examine the correlation of the asphaltene microstructure to its rheology. Air-water and decane-water interfaces with
the aggregation in the air and in decane have been measured. Elastic films, multilayer aggregates, surface wrinkles, and dispersed aggregates were observed. Of particular interest is asphaltenes at the higher surface coverage of 4 \mu g\cdot cm^{-2}, where multilayer aggregates and wrinkles were observed. Fractures were observed during steady-shear experiments, which matches the highly yielding trend with the exponent, \( k < -1 \). Adding decane as the upper phase altered the asphaltene layer causing surface wrinkles to disappear. Multilayer aggregates were more readily dispersed under the application of a shear stress. The effect of dispersants was also studied and showed that the layer became less elastic. The scaling theory for the correlation between elasticity of the structure and rheological properties was examined. The change of the power law exponent (obtained from the visualization) matched the trend of rheological properties. When the layer was dispersed, the surface viscosity decreased. With the understanding of the correlation of asphaltene microstructure to the rheological responses, the development of a more effective demulsifiers and methods to accelerate the coalescence of the water-in-oil emulsions as well as an improved method for the remediation to recovery crude oil and bitumen discharged in tailing ponds are facilitated.
A Combined Microfluidic and Interfacial Rheological Investigation of the Coalescence of Asphaltene-Stabilized Emulsions

6.1. Introduction

Emulsification/demulsification of asphaltene-stabilized emulsions is further studied along with the knowledge of the interfacial properties of asphaltenes obtained from Chapter 5. For produced oilfield emulsions, three types of emulsions can be encountered; water-in-oil, oil-in-water and multiple emulsions. Typically, water-in-oil emulsion is the most common in the oilfield. The amount of water that emulsifies with crude oil varies significantly from one well to another. These emulsions must be treated to remove the dispersed water and associated inorganic salts to meet crude oil specifications for transportation, storage, and export and to reduce corrosion and catalyst poisoning in downstream processing facilities. Crude oil emulsions are often very stable for hours.
or even for days, which make them very difficult to break due to the presence of surface-active components in crude oils, such as asphaltenes and resins. Asphaltenes (the most polar component of the crude oil) are soluble in toluene and insoluble in n-alkanes, such as \( n \)-pentane and \( n \)-heptane. These molecules may adsorb at the oil-water interface and form rigid skins reducing coalescence significantly between emulsion drops.\(^{44,174}\)

Emulsion destabilization occurs by way of several processes: sedimentation or creaming, Ostwald ripening\(^{175}\), and coalescence. Chemical demulsifiers such as polyols, ethoxylated phenolic/formaldehyde resins, ethoxylated phenols, alkoxylated amines, polyamine derivatives and sulfonic acid salts are typically used to destabilize water-in-oil emulsions.

Common use levels range from 1 ppm up to 500 ppm and depend on emulsion stability, fluid properties, and environmental conditions. The interfacial activity of these demulsifiers must be high enough for them to penetrate interfacial films.\(^{176}\) They are thought to suppress the interfacial tension gradient while the stabilizing species are expelled from the center of the film, thus accelerating the rate of film drainage and promoting coalescence. Demulsifiers might also disrupt and soften (i.e., lower the interfacial viscoelastic moduli) the stabilizing interfacial layer, causing its rupture, thus enabling the separation of the emulsified water from the crude oil.\(^{177}\)

Different studies using a Langmuir film balance have shown\(^{178,179}\) that demulsifiers significantly reduce the rigidity of the interfacial layer under compression, facilitating the coalescence of water droplets upon collision with each other. Different experimental methods can be used to test the efficiency of demulsifiers such as centrifugation, microscopic methods, micropette experiments and application of electric field.\(^{180,181}\) In the oil and gas industry, the emulsion bottle test is typically used as a screening tool in field application to test...
emulsion tendencies and select the most efficient demulsifier for destabilizing crude oil emulsions. The details of the test procedure vary somewhat depending upon the materials available at a particular oilfield operation. The disadvantage of this test is that it requires large quantities (50mL) of crude oils for each test, which are oftentimes scarce or costly. Microfluidics can provide a better understanding of emulsification/demulsification mechanisms and offer *in-situ* visualization of the coalescence phenomena using a very small amount of crude oil and water (on the order of microliters). Well-controlled and high-throughput microfluidic devices have been utilized to provide insights into the physicochemical hydrodynamics of oil-related issues including flow assurance and enhanced oil recovery (EOR)\textsuperscript{15,67,68,182–184}. Recent studies have described the emulsification/demulsification process of model systems using microfluidics. Christopher *et al.* investigated the collision of water and water/glycerol droplets dispersed in silicone oil with no surfactant added using microfluidic T-junctions. They observed different responses to droplet collision events at microfluidic junctions depending on the initial droplet size and flow conditions (coalescence, splitting, and slipping).\textsuperscript{185} Krebs *et al.* also utilized microfluidic devices consisting of a collision chamber for direct observation of collision and coalescence events between hexadecane droplets dispersed in water with no added surfactant. The coalescence rate and contact time were measured *in situ*, which could reveal the film drainage process of the continuous phase between the droplets.\textsuperscript{79,186,187}

To our knowledge, very limited literature studied emulsification/demulsification processes of crude oil or model crude oil emulsions or the effect of demulsifiers on emulsion stability using microfluidic devices.\textsuperscript{188} In this study, we investigate emulsion
stability of model crude oil emulsions by measuring the coalescence rate using a microfluidic T-junction. In parallel, we measured the dilatational interfacial viscoelastic moduli and attempted to correlate them to the emulsion stability. The use of microfluidics to study emulsification/demulsification will be very advantageous to investigate crude oil emulsions. It will provide valuable information usually collected using several experimental techniques such as emulsion type, presence or not of fines at the interface, droplets size and coalescence rate using very small volumes of both aqueous and crude oil phases.

6.2. Results and Discussions

The onset of the asphaltene precipitation was determined to be around 45 vol% of \( n \)-heptane and 55 vol% of toluene. C40 and C50 model oils were below and above the onset of precipitation, respectively. The chemical composition of the model oils are listed in Table 2.1. One model oil drop containing an air bubble was placed between a glass slide and a cover slip and the air-oil interface was visualized using a Leica microscope. For C40 model oil, no asphaltene aggregates were observed at the air-oil interface. However, for C50 model oil, a significant amount of asphaltene aggregates was observed at the interface due to asphaltene precipitation (Figure 6.1).
6.2.1. Coalescence Rate using Microfluidics

Monodisperse emulsions were prepared using a microfluidic T-junction. Depending on the composition of the aqueous phase, different coalescence rates were observed. Representative images of low and high coalescence rates are shown in Figures 6.2a and 6.2b. Black arrows are used to indicate the flow direction of the emulsion drops, entering from the inlet, traveling through the collision chamber and finally exiting from the outlet. For high coalescence rate, emulsion drops came into contact with each other, coalesced and merged to form a single emulsion drop after a short contact time as they moved toward the outlet.
Figure 6.2 Examples of high and low coalescence rates. (a) High coalescence rate (b) Low coalescence rate. Black arrow is the flow direction. Scale bar is 500 µm.

The coalescence rate was calculated to study the demulsification process using Eqns 6.1 and 6.2:

\[ R_c = \frac{n_c}{A_t t_{exp} n_T} \]  
\[ n_c = \sum_{i}^{j} n_{c,ij} \]  

where \( R_c \) is the coalescence rate \((m^{-2} \cdot s^{-1})\), \( n_c \) is the number of the coalescence events, \( A_c \) is the monitored area \((m^2)\), \( t_{exp} \) is the experimental time \((s)\), and \( n_T \) is the total number of initial emulsion drops formed during the experimental time.
For stable emulsions, no coalescence was observed between the emulsion drops even after a long contact time. For unstable emulsions, a high number of coalescence events were recorded (average ~1000 coalescence events) and analyzed.

For C40 model oil and DI water, the measured coalescence rate was high meaning that the water-in-oil emulsion was unstable, while the coalescence rate measured for C50 model oil and DI water was low; probably due to the different state of asphaltene aggregation (precipitated asphaltenes, as shown in Figure 6.1) and their ability to stabilize water-in-oil emulsions (Figure 6.2). It has previously been shown that the most stable emulsion is observed when the conditions are close to the onset of asphaltene precipitation.\textsuperscript{93} Less surface-active asphaltenes will aggregate and precipitate while highly surface-active asphaltenes will adsorb at the interface resulting in a more rigid and irreversible adsorbed layer preventing emulsion coalescence.\textsuperscript{52} It has also been proposed that there is an optimum solvent aromaticity for asphaltene aggregates to stabilize emulsions with mechanical resistance close to precipitation conditions and the differing asphaltenes chemistry from one crude oil to another change drastically the amount of precipitated asphaltenes and their aggregation potential.\textsuperscript{43,172} Spieker \textit{et al.} studied emulsion stability versus n-heptane and toluene concentrations for four different crude oils using centrifugal separation method. They observed that polar asphaltenes form stable emulsions up to nearly 100% toluene over a large range of solvent conditions.\textsuperscript{43,93} Whereas, the relatively nonpolar asphaltenes form weak emulsions at high toluene concentration and stabilize only emulsions at toluene concentrations close to the solubility boundary (40-50% toluene). For C40 model oil and above 0.01% of SURF, the emulsion became very stable and no coalescence between emulsion drops was observed.
The composition of the solutions is listed in Table 2.2. \( \text{C}_{12-15}\text{E}_7 \) is a hydrophilic surfactant (HLB=12.2) and should stabilize oil-in-water emulsions. The natural surfactants of the crude oil (asphaltenes and resins) actuate as lipophilic emulsifiers (low HLB). We attributed the stability of the water-in-oil emulsion to the formation of a mixed layer of \( \text{C}_{12-15}\text{E}_7 \) and asphaltenes (mixing rule, HLB blend) stabilizing the emulsion. The emulsions made using ME were less stable than the ones made with SURF alone, up to a concentration of 0.1% of ME. We suggest that the d-limonene contained in the microemulsion (ME) diffuses to the interface and softens the layer of adsorbed asphaltenes increasing emulsion coalescence. Above 0.1% ME, the emulsion became stable and no coalescence was observed probably due to the increase of \( \text{C}_{12-15}\text{E}_7 \) concentration within the ME, counteracting the effect of d-limonene and increasing therefore the emulsion stability. It was reported that the addition of resins and solvent such as toluene destabilize emulsions, increasing the amount of separated water.\(^{172}\) However for C50 model oil, emulsion stability was not affected by the presence of d-limonene, probably due to the high rigidity of the asphaltenic film.
Figure 6.3 Coalescence rate of emulsion drops as a function of surfactant or ME concentrations (▲) C40 model oil and DI water. (Δ) C50 model oil and DI water (●) C40 model oil and surfactant solutions (■) C40 model oil and ME solutions (○) C50 model oil and surfactant solutions. (□) C50 model oil and ME solutions.

The coalescence rates for the ME with and without 5w% of EO-PO (5w% EO-PO ME) with both C40 and C50 model oils are shown in Figure 6.4. The coalescence rate was increased significantly by the addition of the demulsifier at 0.2% (5w% EO-PO ME) for C40 model oil. Follotec et al. measured the efficiency of the demulsification using four triblock copolymers (hydrophilic-hydrophobic-hydrophilic) and claimed that shorter chain lengths within the hydrophobic components were very efficient to destabilize water-in-oil emulsions. In fact, they will contribute to the nucleation of holes within the oil layer, breaking it and destabilizing the emulsions. However, for C50 model oil, the coalescence rate remained unchanged for all studied concentrations (5w% EO-PO ME) due to the higher stability of the emulsion. Hence, the percentage of the demulsifier was
increased to 10 w% within the ME (10w% EO-PO ME) as shown in Figure 6.5. Emulsion stability remains high up to 0.1% (10 w% EO-PO ME) for both C40 and C50 model oils. At a concentration equal to 0.15% (10 w% EO-PO ME), the coalescence rate increases significantly and reaches the same value for both model oils. Above 0.15%, the coalescence rate starts to decrease. This is known as demulsifier overdose where beyond an optimal dosage, the performance of the demulsifier starts to lose efficacy leading to stable emulsion formation. Overdose is generally attributed to the adsorption of a monolayer of the demulsifier at the interface by displacing the indigenous crude oil surfactant layer. Overdose was also observed with other hydrophilic EO-PO polymer demulsifiers at high concentrations.  

![Coalescence rate as a function of ME concentrations with and without demulsifier for both model oils.](image)

Figure 6.4 Coalescence rate as a function of ME concentrations with and without demulsifier for both model oils. (■) C40 model oil and ME (□) C50 model oil and ME (●) C40 model oil and 5w% EO-PO ME (○) C50 model oil and 5w% EO-PO ME.
Images showing the time sequence of the emulsion drops coming into contact, coalescing and then merging to form a single drop as they travel through the collision chamber are shown in Figure 6.6. Coalescence type 11 means the coalescence event happened between two first generation emulsion drops as they enter the collision chamber. Whereas coalescence type 12 means the coalescence happened between the newly formed emulsion drop and another first generation drop. The cascade between the drops will continue as the emulsion travel through the collision chamber and different coalescence type will occur such as 13, 14, 23 etc.

The influence of different demulsifiers on the coalescence rate of the emulsion drops was investigated. The coalescence distribution for each demulsifier was plotted in Figure 6.7. The demulsifier with highest efficiency in destabilizing emulsions shows a wider distribution of the coalescence types. EO-PO and APA showed wider coalescence distribution than PE. However, PE shows the highest ratio for the coalescence type 11. When only first generation drops (type 11) coalesced without further coalescence, the coalescence rate is low as shown in the inset plot in Figure 6.7. The efficiency of a demulsifier depends strongly on the crude oil type; asphaltenic versus paraffinic, API gravity and TAN number. Several other parameters such as salinity, temperature etc can affect the demulsifier performance.

A good correlation between the emulsion bottle tests and the microfluidics was observed as shown in Figure 6.5. Using the emulsion bottle test, the destabilization of the emulsion with the addition of 0.2% (10w% EO-PO ME) was observed and more than 85% of the emulsified water was resolved after just 10 minutes with C50 model oil (right
This result is consistent with the high coalescence rate of the emulsion drops using microfluidics.

Figure 6.5 Coalescence rate as a function of ME concentrations. (■) C40 model oil and ME solutions (□) C50 model oil and ME solutions (▲) C40 model oil and 10w% EO-PO ME solutions (Δ) C50 model oil and 10w% EO-PO ME solutions. The emulsion bottle tests correspond to C50 model oil and DI water (left inset) and C50 model oil and 0.15% 10w% EO-PO ME (right inset).
6.2.2. Dynamic IFT and Dilatational Viscoelastic Properties

6.2.2.1. Without Demulsifier (SURF and ME)

The dynamic IFT was measured between C40 model oil and both SURF and ME solutions at three different concentrations (0.025, 0.1 and 0.2%), as shown in Figure 6.8. For the SURF solutions, IFT was observed to decrease as a function of surfactant concentration over time. The slow decrease in IFT over time is probably due to the
reorganization of the asphaltenes at the interface. However, for the ME solutions, an instantaneous decrease in the IFT was observed. This significant change in IFT behavior was probably due to the d-limonene diffusing into the water-oil interface, softening the asphaltene layer and thereby accelerating their reorganization at the interface. When C50 model oil was used, a small difference in the dynamic IFT between the surfactant and the ME was observed. For this model oil, asphaltenes are in a precipitated form exhibiting much larger and compact aggregates, which make their penetration and softening by d-limonene much more difficult.

The dilatational elastic and viscous moduli were measured using the pendant drop tensiometer, as shown in Figure 6.9. The elastic modulus decreased significantly as a function of the SURF and ME concentrations for both model oils, whereas the viscous modulus remained almost the same at all concentrations. The coalescence rate was observed to decrease as the concentration of SURF and ME was increased, which is the opposite of the trend observed for interfacial elasticity.

The unexpected trend between the elasticity data and coalescence rate can be explained by the following reasons. For the demulsification experiments, the time scale for two emulsion drops to travel through the collision chamber, come into contact with each other and coalesce was less than a minute. However, dilatational viscoelastic measurements were performed after 5000 seconds, a much longer time scale than the microfluidic experiments. This allowed the adsorbed asphaltenes to rearrange and/or consolidate (interfacial rigid layers formation) at the water-oil interface which might completely change the elasticity of the adsorbed asphaltic layer. In addition, elasticity
measurements at the water/oil interface were performed by oscillating the surface of the oil drop surrounded by an excess of aqueous phase whereas coalescence occurred by merging two water drops separated by an oil layer to form a single drop. The different time scales, interfaces and mechanisms could explain the unexpected trend between the interfacial elasticity and emulsion stability. Dicharry et al. studied the stability of water-in-oil emulsions made using different distilled fractions of a crude oil. They found that the stability of these emulsions did not correlate with the elasticity modulus values where the fractions deprived of asphaltenes produced less stable emulsions than the crude oil, though their elasticity modulus was higher.

6.2.2.2. With Demulsifier (10w% EO-PO ME)

Figure 6.10 shows the equilibrium IFT values measured between both model oils and 10 wt% of EO-PO ME. The IFT was observed to decrease as a function of ME concentration for both model oils with the addition of EO-PO, confirming the penetration of the EO-PO demulsifier into the interfacial asphaltenic layer. A larger decrease of the IFT was observed for C40 model oil compared to C50 model oil. The viscoelastic moduli of both model oils/ME and 10w% EO-PO ME interfaces were measured (Figures 6.11a and 6.11b). At lower concentrations (lower than 0.05%), the measured interfacial viscoelastic moduli increased for C40 model oil and 10w% EO-PO ME compared to ME. This result is consistent with the decrease of coalescence rate where an increase in the interface rigidity and viscosity will stabilize the emulsion. Above 0.1%, the elastic modulus became slightly lower than the one without the demulsifier, and the rate of emulsion coalescence increased significantly. However, the magnitude of increase of the
coalescence rate could not be related to the small decrease in elasticity, probably due to the contribution of other mechanisms to the emulsion stability and/or the formation of a rigid layer at the interface over longer time scales. For C50 model oil, the interfacial elasticity did not change for all ME concentrations with and without the demulsifier.

Figure 6.7 Coalescence rate distribution of various type of coalescence events. (■) C40 model oil and 5w% EO-PO ME (■) C40 model oil and 5w% APA ME (■) C40 model oil and 5w% PE ME. The inset plot is the coalescence rate for each demulsifier.
Figure 6.8 Dynamic IFT between model oils and surfactant and ME solutions. (a) C40 model oil/ SURF (b) C40 model oil/ ME (c) C50 model oil/SURF and (d) C50 model oil/ME.

Figure 6.9 Elastic and viscous moduli as a function of surfactant and ME concentrations.
Figure 6.10 IFT between C40 and C50 model oils and ME solutions with and without EO-PO demulsifier.

Figure 6.11 Elastic and viscous moduli as a function of surfactant and ME concentrations with and without EO-PO demulsifier.
6.3. Summary

We have demonstrated the use of microfluidic devices to visualize in-situ emulsification and demulsification of asphaltene-stabilized water-in-oil emulsions. The emulsion stability was increased above the onset of precipitation of the asphaltenes contained in the model oil. For C-40 model oil, the addition of ME showed a larger emulsion destabilization compared to \( \text{C}_{12-15}\text{E}_7 \) up to a concentration equal to 0.1%. Above 0.1%, the emulsion became very stable for both ME and \( \text{C}_{12-15}\text{E}_7 \). For C-50 model oil, the emulsion was already very stable and the addition of either ME or \( \text{C}_{12-15}\text{E}_7 \) did not affect it. Three different demulsifiers, EO-PO, APA and PE were added to destabilize the water-in-oil emulsion. EO-PO was by far the most efficient demulsifier for both C40 and C50 model oils. Bottle tests results were found to be consistent with the coalescence rate of emulsion drops measured using microfluidics. The dynamic interfacial tension (IFT) measured between C40 model oil and the ME reached equilibrium faster than the one measured with \( \text{C}_{12-15}\text{E}_7 \). We attributed this result to the d-limonene diffusing into the interfacial film, softening the asphaltenes layer and thereby accelerating their reorganization at the interface. No correlation was observed between the dilatational viscoelasticity and the coalescence rate of the emulsion drops probably due to the formation of asphaltenic rigid layers at longer time scale. This study used model oils emulsions which are easier to demulsify than oilfield emulsions containing supplementary chemicals such as scale and corrosion inhibitors, biocide, \( \text{H}_2\text{S} \) scavenger and clay control additives added into the oil well during extraction operations. Next step will be to look at using different crude oils and investigating the effect of not just
asphaltenes on the stability of the water-in-oil emulsions but also other crude oil components such as paraffin, saturates and naphthenic acids.
Chapter 7

Deposition and Oil-Brine Interfacial Rheology of Asphaltene-Stabilized Emulsions

7.1. Introduction

A combined platform consisting of microfluidics and interfacial rheology is also used to investigate the deposition process in the presence of asphaltene-stabilized emulsions. Water is unavoidable during oil production and asphaltenes are known to stabilize water-in-oil emulsions. A detailed review by Kilpatrick et al. describes on the stabilization of water-in-oil emulsions, and concluded that there are sub-fractions of asphaltenes that are acidic or multiprotic surface-active molecules that readily adsorb onto the interface.\(^{43}\) Therefore, the impact of water on asphaltene deposition becomes essential;\(^{177,193}\) however, this impact is still unclear.\(^{194-196}\)

Wang et al. investigated the impact of water on deposition and observed that pressure drop decreased with the addition of water into the capillary deposition flowloop.\(^{194}\) Aslan
and Firoozabadi also found a decreasing pressure drop using a pipe line system, and proposed that the formation of H-bonds between water and asphaltene molecules inhibited deposition. Hu et al. proposed that beyond the solubility limit of water, emulsions can be stabilized by indigenous surface-active components in the oil; the emulsions then block the porous media by mechanical entrapment and cause significant pressure drop. Below the solubility limit, water can prevent asphaltene aggregation and further reduce the pressure drop. The reported pressure drops are representative of deposition based plugging in systems containing water, but the measured changes have been reported to behave differently. Moreover, the impact of brine on asphaltene deposition remains unclear. Early observations by Wang et al. noted that asphaltenes tend to deposit more in the presence of brine and ions, especially with Fe$^{3+}$ and Al$^{3+}$, but the full implications are not known. As a result, better understanding of the mechanism of asphaltene deposition in the presence of water/brine is required.

In the presence of water and brine, surface-active asphaltenes become significantly important. Therefore, the interfacial properties of asphaltenes have been widely studied recently by varying the surface and bulk concentration, aromaticity of the solvent, pH, and salinity. In particular, the salinity effect on the asphaltenes at oil-water interfaces is known to be a determining factor in asphaltene adsorption onto the interface. Zhang et al. used micropipette technique to study the coalescence of two asphaltene-stabilized emulsions and found that increasing the concentrations of CaCl$_2$ and NaCl facilitated coalescence of emulsions. Potential determining ions can have strong interactions with carboxyl groups and enhance the coalescence between two interfacial layers. Chen et al. used AFM to measure the force between two oil droplets in brine and
found that the addition of Ca$^{2+}$ ions changed the conformation of asphaltenes at oil-water interfaces, reducing the critical force load required for coalescence to occur.\textsuperscript{54} In this regard, a well-controlled platform is needed to investigate the interfacial phenomena of asphaltenes.

We therefore turn to microfluidic micromodels to investigate the impact of water on the deposition of asphaltenes. As previous shown, the deposition profile of asphaltenes in the absence of additional water is characteristic broad, narrow, or shortened cone-like shapes in model porous media due to the competition between adsorption and erosion depending on the relative ratio of convection and diffusion.\textsuperscript{67,68} However, crude oils containing excess water have different deposition profiles when emulsions are depositing onto the rock surface. In this chapter, asphaltenes are shown to act as an adhesive agent between emulsion droplets and between emulsions and solid surfaces. Therefore, in addition to mechanical entrapment of emulsions, we propose a new mechanism of permeability reduction, whereupon asphaltene-stabilized emulsions can adhere to solid surfaces, thereby reducing permeability of the porous media significantly. Moreover, the salinity effect on asphaltenes was investigated by both microfluidics and interfacial rheology.
7.2. Results and Discussions

7.2.1. Impact of Water Content on the Blockage of the Porous Media

Representative images of the deposition profile of asphaltene-stabilized emulsions with varying water contents are shown in Figure 7.1. The mixture was injected from left to right, and the leading edge of the post (on left) came into contact with emulsions and asphaltenes first. The volumetric ratio of oil to precipitant was 55% to 45%, which is close to the condition for asphaltene precipitation. Water was premixed with the oil by a stir bar, with weight percentages varying from 0.03 (dissolved water), 0.5, 2, 4, 10, to 20 wt% in the oil-water mixture. The experimental images were processed using ImageJ to obtain the size distribution of emulsions. As previously shown in chapter 3, without additional water, asphaltenes deposit in narrow, cone-like shapes, dominated by the convection-diffusion effect due to the competition between adsorption and erosion as illustrated in Figure 7.1a. In the presence of additional water, emulsions significantly alter the deposition dynamics and reshape the deposits. It is clear that emulsions adhere to or become trapped in asphaltene deposits, showing significant stability in the micromodel. Tchoukov et al. also mentioned that asphaltenes can form a gel-like layer at the interface to prevent emulsions from coalescing when asphaltenes are in a condition of poor solubility in the oil. Moreover, the gel-like film of the emulsion was reported to promote the flocculation of asphaltene-stabilized emulsions. In this work, these emulsions act as the depositing micro-particles contributing to the deposition process, and deposited asphaltenes behave as the adhesive between emulsions and surfaces. The hypothesis is that deposited asphaltenes increase the van der Waals attraction in the
emulsion-surface system. Therefore, the Hamaker constants of these interacting systems are investigated using Eq. 7.1 to Eq. 7.4. The calculated $A_{ama}$ is $4.3 \times 10^{-22} J$ and $A_{wmn}$ is $5.3 \times 10^{-23} J$, indicating that the van der Waals attraction between asphaltene-stabilized water droplets and asphaltene-coated surfaces have stronger attraction than between pure droplets and blank NOA 81 surfaces. This result matches the observation that asphaltenes are acting as the adhesive in the process of emulsion deposition.

$$A_{ama} = (\sqrt{A_a} - \sqrt{A_m})^2$$ (7.1)

$$A_{wmn} = (\sqrt{A_w} - \sqrt{A_m})(\sqrt{A_n} - \sqrt{A_m})$$ (7.2)

where $A_{ama}$, $A_{wmn}$, $A_a = 5.7 \times 10^{-20} J$ and $A_n = 4.7 \times 10^{-20} J$ are Hamaker constants of the system with asphaltene-stabilized water droplets and asphaltene-coated surfaces, the system with pure droplets and blank NOA 81 surfaces, asphaltene, and the NOA 81 surfaces, respectively. $A_n = 24\pi L_0^2 \gamma_{s,n}$ where $L_0 = 0.165 \text{ nm}$ is defined as the characteristic distance between interacting molecules and $\gamma_{s,n} = 22.83 \pm 0.46 \text{ mN/m}$ is the surface energy of NOA 81 surface.$^{200,201}$

$$A_{wmw} = (\sqrt{A_w} - \sqrt{A_m})^2$$ (7.3)

where $A_w = 3.7 \times 10^{-20} J$ and $A_m$ (obtained using Eq. 7.4) are Hamaker constants of water and the oil-heptane mixture, respectively.$^{206}$

$$A_m = \phi_o A_o + \phi_h A_h$$ (7.4)
where $A_o = 5.0 \times 10^{-20}J$ and $A_h = 4.5 \times 10^{-20}J$ are Hamaker constants of oil and the heptane, respectively.\textsuperscript{203,206} $\varnothing_o = 0.55$ and $\varnothing_h = 0.45$ are volumetric ratio of oil and heptane in the oil-heptane mixture.

When the water concentration increases, the mechanism of the blockage of the micromodel switches from adhesion to a combination of adhesion and hydrodynamic bridging. Dressaire and Sauret reviewed several clogging mechanisms (blockage of the microchannel) in microfluidic systems and proposed that blockages can be categorized into sieving, bridging, and aggregation (adhesion in this paper). These mechanisms vary with several factors including the ratio of particle diameter ($D$) and channel width ($W$), the particle volume fraction in suspension ($\varnothing$), and interactions between particles or particle and surfaces. Sieving requires $D \geq W$, low $\varnothing$, and steric repulsion between particles. Bridging requires the conditions of $D \leq W$, large $\varnothing$, and steric repulsion. Adhesion requires $D \leq W$, low $\varnothing$, and attraction between particles or particle and surfaces.\textsuperscript{202} In this study, the ratio ($D/W$) is less than 1, indicating bridging and adhesion are dominant factors. In Figure 7.1b and 7.1c, the deposition is still dominated by adhesion of asphaltenes and emulsions. When more water is introduced to the system, as shown in Figure 7.1d – 7.1f, emulsions become larger and the deposition becomes dominated by hydrodynamic bridging, and a preferred flow path is formed. The size distribution of emulsions is shown in Figure 7.2 showing that larger emulsions were obtained with increasing water contents.
Figure 7.1 Representative images of the emulsion deposition profile with varying water contents with injected 900 µl of the mixture. (a) 0.03, (b) 0.5 wt%, (c) 2 wt%, (d) 4 wt%, (e) 10 wt%, and (f) 20 wt% of water in the oil. The white scale bar is 500 µm, and the black scale bar is 100 µm. The flow direction is from left to right.

To monitor this complex deposition process, the pressure drop across the porous media is measured as shown in Figure 7.5a. In general, the pressure drop increases with increasing water contents in the oil, suggesting the formation of more blockages in the porous media. In particular, the pressure drop in the presence of 2 wt% water increases to approximately 8 times higher than the pressure drop in the absence of additional water and 40 times higher with existing 20 wt% water. This increased pressure drop was also observed using the micro-packed bed, and the proposed mechanism is emulsions blocking the porous media. However, no adhesion of emulsions was mentioned in the literature.\textsuperscript{197} Here, with pore-scale visualizing capability, the adhesion and bridging of emulsions in porous media is observed, and is seen to result in increased pressure drops. On the other hand, decreased pressure drop in the presence of water has been reported in the capillary flowloop or pipeline systems.\textsuperscript{194,195} This decreased trend was possibly caused by the strong erosion from the flow of the fluid. In addition, in the absence of
stagnation region in their systems (the front of the post in porous media), emulsions were not able to stay in the low-velocity area.

Figure 7.2 Droplet size distribution. (a) 0.5 wt%, (b) 2 wt%, (c) 4 wt%, (d) 10 wt%, and (e) 20 wt% of water in the oil.

Figure 7.3 Droplet size distribution with 2 wt% of (a) 1 mM NaCl, (b) 1 mM CaCl₂, (c) 100 mM NaCl, and (d) 100 mM CaCl₂ solution in the oil.
Figure 7.4 Droplet size distribution with 10 wt% of (a) 1 mM NaCl, (b) 1 mM CaCl₂, (c) 100 mM NaCl, and (d) 100 mM CaCl₂ solution in the oil.

Using Darcy’s Law, permeability reduction can be calculated as a function of measured pressure drops as seen in Eq. 7.5. Permeability reduction as a function of the ratio between added water and dissolved water (0.03 wt%) from the corresponding pressure drop is calculated from Eq. 7.5 is demonstrated in Figure 7.5b. A decreased tendency is observed in the presence of a higher amount of water in the oil. A schematic of the switching mechanism is shown in Figure 7.5c.

\[
Q = -\frac{kA}{\mu L_p} \Delta P
\]  \hfill (7.5)

where \( k \left( \text{m}^2 \right) \) is permeability, \( Q \left( \text{m}^3/\text{s} \right) \) is the flow rate of the fluid, \( \Delta P \left( \text{N/m}^2 \right) \) is pressure drop, \( A \left( \text{m}^2 \right) \) is the cross-section area of the channel, and \( L_p \left( \text{m} \right) \) is the length of the porous media.
Figure 7.5 (a) Pressure drop results for deposition of emulsions. (b) Permeability reduction as a function of the ratio between added water and dissolved water for around 700 s experimental time. (c) Demonstration of the switching mechanism from adhesion to bridging with increasing water.

Dynamics of the emulsion deposition process for adhesion and bridging are presented in Figure 7.6. Upon first contacting the surface of the post, emulsions adhere to the post surface with less erosion in the stagnation region as mentioned in previous studies.\textsuperscript{67,68} The north and south regions of the post are closer to other posts resulting in higher fluid flow velocity and shear rate. Therefore, nearly no asphaltenes and emulsions are observed in these regions, as shown in Figure 7.6a – 7.6c. In the adhesion process, emulsions first adsorb onto the surface (Figure 7.6a) and are stabilized by incoming depositing asphaltenes (Figure 7.6b). Subsequent emulsions adhere to the existing deposit, establishing a larger formation (Figure 7.6c). For the bridging process, large emulsions
first adhere to the surface or form a temporary bridge between posts when most of the emulsions are removed by the flow (Figure 7.6d). Bridges are altered by the flow before asphaltenes stabilizing the blockage (Figure 7.6e). Finally, the depositing asphaltenes fill up the space between emulsions and develop a stable network (Figure 7.6f).

![Figure 7.6 Dynamics of the deposition of emulsions with 2 wt% (a)(b)(c) and 20 wt% (d)(e)(f) of water. The time lengths are 60 s for (a)(d), 180 s for (b)(e), and 360 s for (c)(f). Scale bar is 100 µm. The grey area represents the posts.]

7.2.2. Salinity Effect on Deposition Behavior

The impact of the salinity on the deposition during the adhesion stage is shown in Figure 7.7 and Figure 7.8. Deposition profiles are reshaped and show more hydrodynamic bridging compared to Figure 7.1c. Generally, the size of emulsions in the presence of salts becomes larger than without salts. This alteration of size gives rise to both stronger erosion and more chances to form bridges in the porous media. Deposition is still dominated by adhesion in the presence of 1 mM NaCl, as highlighted in the green dotted box (Figure 7.7a). However, with 100 mM NaCl (Figure 7.7c) and 1 mM CaCl\textsubscript{2} (Figure 7.7b), as well as 100 mM CaCl\textsubscript{2} (Figure 7.7d), the size of the emulsion was larger,
causing lower probability of adhesion (less deposition). However, a few bridges as emphasized in blue boxes are observed. From previous studies, the deposition is found to be determined by the local flow field and fluid properties.\textsuperscript{67,68} The Péclet number was utilized to examine the convection and diffusion on the deposition process. The shape of the deposit became narrower with higher Péclet number, due to stronger erosion in the absence of additional water. In this regard, the Péclet number becomes higher in the presence of NaCl and CaCl\textsubscript{2}. The size distribution is shown in Figure 7.3, illustrating the larger emulsions in the presence of NaCl and CaCl\textsubscript{2}. Therefore, less deposition is observed. This effect can also be seen in the results of pressure drop measurements as illustrated in Figure 7.8. A decreasing trend for pressure drop is found with higher salt concentrations for both NaCl (Figure 7.8a) and CaCl\textsubscript{2} (Figure 7.8b). The corresponding permeability reduction is calculated after the discussion for the influence of salinity on the bridging stage. The schematic of the switching deposition behavior of emulsions from adhesion to a combination of stronger erosion and bridging with increasing salinity is shown in Figure 7.8c.
Figure 7.7 Salinity effect on deposition profile for 2 wt% solution. (a) 1 mM NaCl (b) 1 mM CaCl₂ (c) 100 mM NaCl (d) 100 mM CaCl₂. Scale bar is 500 µm.

Figure 7.8 Pressure drop across the porous media for 2 wt% solution with (a) NaCl and (b) CaCl₂. (c) Demonstration of the switching mechanism from adhesion to stronger erosion and bridging with increasing salinity in the adhesion stage.

The deposition tendency in the presence of salts is further investigated in the bridging stage. The behavior is not changed significantly by salinity effect and the dominating mechanism is still the bridging as shown in Figure 7.9. With both 1 mM NaCl (Figure 7.9a) and CaCl₂ (Figure 7.9b), the profiles are similar to Figure 7.1e. However, emulsions become larger and tend to form bridges more easily in the porous media in the presence of both 100 mM NaCl (Figure 7.9c) and CaCl₂ (Figure 7.9d). The size distribution is demonstrated in Figure 7.4 where after the addition of salts, emulsions become larger. Also, the corresponding pressure drop is illustrated in Figure 7.10a -
7.10b. An increasing trend of measured pressure drop is observed with higher concentrations of NaCl (Figure 7.10a) and CaCl₂ (Figure 7.10b). The schematic of the stronger bridging with increased salinity is shown in Figure 7.10c. Calculated permeability reduction for 0.03, 2, and 10 wt% water in the presence of NaCl and CaCl₂ is shown in Figure 7.11. Generally, a decreasing trend for the permeability is seen with increasing water content as discussed in Figure 7.5b. However, the salt concentration plays different roles in deposition tendency. In the adhesion stage, increased permeability is found with increasing the salt concentration, while in the bridging stage, decreased permeability is obtained. The major contribution of salinity to the deposition was found to be the alteration of the size of emulsions. Moreover, the changes in the size of the emulsions before depositing on the surface are dominated by the interfacial properties of asphaltenes adsorbing at the oil-water interface. Therefore, a greater understanding of asphaltenes with salts at interfaces is important and is discussed in the following section.

Figure 7.9 Salinity effect on deposition profile for 10 wt% solution. (a) 1 mM NaCl (b) 1 mM CaCl₂ (c) 100 mM NaCl (d) 100 mM CaCl₂. Scale bar is 500 µm.
Figure 7.10 Pressure drop for the salinity effect for 10 wt% (a) NaCl solution, and (b) CaCl$_2$ solution. (c) Demonstration of the deposition behavior with increasing salinity in the bridging-dominated stage.

Figure 7.11 Permeability reduction for the salinity effect for around 700 s experimental time. The inset is the zoom-in plot for 10 wt% water.
7.2.3. Interfacial Rheology of the Asphaltene Film

The interfacial rheology of asphaltenes adsorbing at oil-brine interfaces is investigated by varying both the type of salt and the bulk concentration (NaCl: 1, 100, and 1000 mM; CaCl₂: 1 and 100 mM) as shown in Figure 10. We find that in general, the moduli decreases with increasing salt concentration. This reduction enhances the coalescence of water droplets, resulting in larger emulsion size. Chávez-Miyauchi *et al.* studied interfacial shear rheology of crude oil-brine interface, and found that under high salinity, the elasticity of the interface decreases when ions reduced the attractions between polar components. During the time-dependent consolidation process of the asphaltene layer (Figure 7.12a and Figure 7.12d), both elastic and viscous moduli increase and reach a relative equilibrium for all measurements except 100 mM CaCl₂ (Figure 7.12d). This result indicates that adsorbed asphaltenes reorganize at the interface with time. Also, this much lower modulus suggests that the structure of asphaltenes with CaCl₂ is not as robust as the layer forming under other conditions. On the contrary, the viscoelastic response for asphaltenes with NaCl shows a weak dependence on the concentration even with 1000 mM NaCl (Figure 7.12a). In the strain amplitude-sweep experiment, the linear viscoelastic (LVE) regime is relatively similar in the presence of various concentrations of NaCl (Figure 7.12b). On the other hand, the LVE becomes narrower with increasing concentrations of CaCl₂, and especially the LVE is much narrower with 100 mM CaCl₂ (Figure 7.12e). Furthermore, in the frequency-sweep measurement, a weak dependence on the concentration of NaCl is also obtained (Figure 7.12c). For both salts, under 0.05
Hz, the interfaces show a relatively viscous behavior, and the layer becomes more elastic with increasing frequency (Figure 7.12c and Figure 7.12f).

![Figure 7.12 The rheological behavior of the asphaltene film with varying salinity. Time sweep are (a) NaCl and (d) CaCl$_2$. Strain sweep are (b) NaCl and (e) CaCl$_2$. Frequency sweep are (c) NaCl and (f) CaCl$_2$.](image)

More details of the interfacial properties can be obtained from frequency-sweep results. Verruto *et al.* mentioned that a consolidated asphaltene interfacial layer results in weak frequency-dependence as shown in Eq. 7.6 with the power exponent ($n$) being $0 < n < 1$.\(^\text{44}\)

$$G', G'' \propto \omega^n$$  \hspace{1cm} (7.6)

Samaniuk *et al.* also mentioned that the results of frequency-sweep experiments can be used to predict if the layer is undergoing a glass transition showing that there are three stages. If $n > 2$ in Eq. 7.6, the layer is behaving like liquid, it is viscoelastic and
shear-thinning if $0 < n < 2$, and the layer is in a glassy state if $n < 0$. From Table 7.1, the power exponents are relatively in a similar range, and behaved as a consolidated and viscoelastic layer, indicating the layer is possibly undergoing a glassy transition that asphaltene network is changing from a viscoelastic and more amorphous film to a more glassy state.

Table 7.1 Power Exponent ($n$) and Zeta Potential ($\zeta$)

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<th>DI Water</th>
<th>NaCl</th>
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<td></td>
<td>1mM</td>
<td>100mM</td>
<td>1000mM</td>
</tr>
<tr>
<td>$n$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\gamma$</td>
<td>0.45</td>
<td>0.46</td>
<td>0.46</td>
</tr>
<tr>
<td>$\eta$</td>
<td>0.31</td>
<td>0.33</td>
<td>0.30</td>
</tr>
<tr>
<td>$G_0'$ (mN/m)</td>
<td>19 ±2</td>
<td>17 ±3</td>
<td>12 ±2</td>
</tr>
<tr>
<td>$\zeta$ (mV)</td>
<td>-94 ±4</td>
<td>-95 ±3</td>
<td>-48 ±4</td>
</tr>
</tbody>
</table>

Furthermore, the zeta potential is measured to examine the theory that ions reduce the possible electrostatic attractions from polar moiety of charged asphaltenes. The zeta potential of asphaltenes in various brines and DI water is thus listed in Table 7.1. This result clearly shows that zeta potential is neutralized in the presence of NaCl and CaCl$_2$. Increased salinity reduces the potential significantly and possibly screen the electrostatic attractions between charged asphaltenes at the interface. In particular, the influence of increased concentration of CaCl$_2$ on the neutralization is more prominent. These results are consistent to the interfacial behaviors obtained in rheology that increased
concentration of CaCl$_2$ causes lower interfacial viscoelasticity and a more unstable structure.

### 7.3. Summary

Asphaltene-related flow assurance problems are widely known for the plugging of pipelines, formation damage, and the stabilization of undesirable viscous emulsions. In this study, we showed that water-in-oil emulsions can enhance asphaltene deposition and cause more significant blockage in model porous media. In the presence of additional water, water-in-oil emulsions form and reshape the deposit, changing the deposition mechanism from adhesion to hydrodynamic bridging. Increased pressure drop and more severe permeability reduction occur with increasing water contents. The dynamics of the deposition process show that emulsions adhere to the surface or first form a temporary bridge, with incoming asphaltenes further stabilizing the emulsions. Furthermore, emulsions are larger in the presence of NaCl and CaCl$_2$, resulting in higher Péclet number and stronger erosion in the adhesion-dominated stage, which eventually causes less permeability reduction. While in the bridging-dominated stage, larger emulsions block the porous media more easily, causing higher pressure drops and permeability reduction. Therefore, the size of the emulsion is essential to the deposition process.

Interfacial rheology measurements were made to investigate the impact of salinity on the asphaltene layer at the interface, which is important for coalescence between water droplets. Viscoelasticity decreases with the increasing salt concentration, indicating a weak layer at the interface, resulting in coalescence and larger emulsions. In
particular, the increased concentration of CaCl$_2$ causes more reduction in the modulus. Significant neutralization in zeta potential by salts suggests a screening effect on the electrostatic attraction between charged asphaltenes at the interface, which eventually results in a weak asphaltene layer. This combined platform of microfluidics and interfacial shear rheology offers greater understanding to better design the solutions to asphaltene-related flow assurance problems.
Chapter 8

Conclusion and Future Directions

8.1. Summary of Results

Here we present a novel methodology for probing asphaltene deposition and asphaltene-stabilized emulsions using microfluidic devices. In particular, we considered homogeneous and porous-media microfluidic designs to represent various flow conditions typical of that found in oil flow processes. A variety of factors influencing asphaltene deposition are investigated, including solubility effect, commercial chemical dispersants, the presence of the brine, and solvent effects. Furthermore, we also characterized the properties of asphaltenes at interfaces by interfacial rheology and chemical analysis. By understanding the nature and the behaviors of asphaltenes at interfaces, we increase our ability to design cost effective mitigation strategies that includes the development of a new generation of asphaltene deposition inhibitors/demulsifiers and improved methods for prevention and treatment of this problem.
8.2. Suggestions for Future Work

8.2.1. Solvent Washing of Asphaltene Deposits

The deposition process is investigated by examining both the hydrodynamics and colloidal interactions that govern asphaltene transport. Dispersants are used to change the colloidal interactions and prevent the deposition. However, if asphaltenes attached onto the pipeline surfaces, remediation methods need to be implemented. Solvents are often the first course of action. Injecting different washing solvent with various solubility parameters has demonstrated some success.

Asphaltenes have different fractions in crude oils (from higher solubility parameter to lower solubility parameter, asphaltenes: 19-24MPa$^{0.5}$). Let’s assume there are three fractions, which are higher, medium, and lower solubility parameter asphaltenes). Each fraction of asphaltenes which have already deposited on the surfaces has its own tendency to dissolve in solvents (mixture of toluene and heptane, toluene: 18.2MPa$^{0.5}$, n-heptane: 15.2MPa$^{0.5}$).

When deposits are washed by good solvent, lower and medium solubility parameter asphaltenes will dissolve first and make the washing solvent a better one to remove ones with a higher solubility parameter. However, if deposits are washed by poor solvent first, this solvent can only remove lower solubility parameter asphaltenes (which might be able to remove the medium ones, but not enough to remove higher solubility asphaltenes). Therefore, even washed by good solvent after poor solvent, the higher ones remain. Asphaltene deposits in the microchannel are easier to re-dissolve in the toluene-heptane (v:v=1:1) mixture (good solvent, solubility parameter is 16.7MPa$^{0.5}$). However,
if deposits were washed with (v:v=1:2) TH-mixture (poor solvent, solubility parameter is 16.19MPa$^{0.5}$) followed by good solvent, some of them still cannot be removed as shown in Figure 8.1 using oil A. The properties of the crude oils are listed in Table 8.1. Two crude oils are used here. Oil A is from the Middle East and Oil C is from Gulf of Mexico.

![Figure 8.1 Washing effect.](image)

**Table 8.1 Crude Oil Properties**

<table>
<thead>
<tr>
<th>Property</th>
<th>Oil A</th>
<th>Oil C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, g/cc</td>
<td>0.841</td>
<td>0.885</td>
</tr>
<tr>
<td>Viscosity, cP</td>
<td>6.5</td>
<td>22</td>
</tr>
<tr>
<td>Saturates, wt%</td>
<td>73.8</td>
<td>48.6</td>
</tr>
<tr>
<td>Aromatics, wt%</td>
<td>20.2</td>
<td>31.8</td>
</tr>
<tr>
<td>Resins, wt%</td>
<td>5.6</td>
<td>15.5</td>
</tr>
<tr>
<td>n-C$_5$ Asphaltenes, wt%</td>
<td>0.4</td>
<td>4.1</td>
</tr>
</tbody>
</table>
To detect the subtle composition changes in the asphaltenes, a confocal laser scanning microscopy (Carl Ziess LSM 510) is utilized. In fluorescence studies, a laser excitation wavelength of 488 nm was chosen for FITC ($\lambda_{\text{Ex}}=494.5$ nm, $\lambda_{\text{Em}}=519$ nm). A series of experiments shown in Figures 8.2 to 8.4 demonstrate that asphaltenes, resins, maltenes have a high intensity of fluorescence at a 488nm excitation wavelength measured by spectrofluorometer (SPEX FluoroLog-3). At an excitation wavelength of 410nm, the C5-7 asphaltene shows little fluorescence. Also, at an excitation wavelength of 580nm, no fluorescence emission is observed. Confocal laser scanning microscopy provides z-scanning, this capability allows us to analyze the profile of asphaltene deposition in the depth direction of the microchannel.

![Emission Curve (excitation 410nm)](image)

Figure 8.2 Fluorescence emission curve for excitation wavelength 410nm.
Figure 8.3 Fluorescence emission curve for excitation wavelength 488nm.

Figure 8.4 Fluorescence emission curve for excitation wavelength 580nm.
Figure 8.5 shows measured pressure drop for the washing effect with oil C for both 70 and 80 vol% of \(n\)-heptane. For both volumetric ratios of \(n\)-heptane, the washing effect is observed.

![Pressure drop for oil C with the washing effect](image)

Figure 8.5 Pressure drop for oil C with the washing effect.

Figure 8.6 and Figure 8.8 demonstrate the visualization of the washing effect indicating for 60, 70, and 80 vol% of \(n\)-heptane, the washing effect exists while with 80 vol% of \(n\)-pentane, the washing effect is not significant. Asphaltenes with a lower solubility parameter are easier to precipitate by a precipitant with a lower solubility parameter, and the solubility parameter of \(n\)-pentane is 14.4 MPa\(^{0.5}\) and 15.2 MPa\(^{0.5}\) for \(n\)-heptane. Therefore, the poor solvent can dissolve the asphaltenes with a lower solubility parameter and further remove the remaining asphaltenes. Figure 8.7 and Figure 8.9 illustrate the fluorescence of the trapped oil in the deposit. Before washed by the poor solvent, the green fluorescence representing the trapped oil is observed significantly, but after washed by the poor solvent and the good solvent, green fluorescence became difficult to be detectable. (The light intensity is increased by 60%)
Figure 8.6 Visualization of asphaltenes in the micromodel before and after a good solvent and followed by a poor solvent for the oil C.

Figure 8.7 Confocal laser scanning to study the composition and microstructure of the deposit before and after a good solvent and followed by a poor solvent for the oil C.

Figure 8.8 Visualization of asphaltenes in the micromodel before and after a good solvent and followed by a poor solvent for the oil A.
Figure 8.9 Confocal laser scanning to study the composition and microstructure of the deposit before and after a good solvent and followed by a poor solvent for the oil A.

A future work in this study is to use quartz crystal microbalance with dissipation (QCM-D)\textsuperscript{95,207} to investigate the mass and the tightness of deposited asphaltenes remaining on the surface. Also, more chemical analyses are required to understand the chemical properties of these various asphaltenes with different solubility parameters.

8.2.2. Fractionation of Asphaltenes

Previous section has described the importance to understand the chemical properties of each subfraction of asphaltenes. As mentioned in Chapter 2 that there is still a controversy on the structure of the problematic asphaltenes as shown in Figure 8.10.
Here, we present a study of the dynamics of asphaltene deposition in porous media using microfluidic devices. A model oil containing 0.1 wt% dissolved asphaltenes in toluene was mixed with \( n \)-heptane, a known asphaltene precipitant, and flowed through a representative porous media microfluidic chip. Each asphaltene fraction is obtained by the fractionation of the solids from Petrophase 2017. The solid is dissolved in a variety of solvents, and followed by an extraction process developed by Florida State University, each fraction is further characterized by Fourier transform ion cyclotron resonance mass spectrometry and infrared multiphoton dissociation.\(^2\) Acetone-dissolved fraction mostly contains island-type asphaltenes, and follow the order of heptol, tol, tol:THF, and THF, the ratio of archipelago-type asphaltenes in each fraction increases.

Asphaltene deposition tendency and morphology were recorded and analyzed as a function of chemical structure. Deposition tendency is found to be higher with increasing the ratio of archipelago-type of asphaltenes as shown in Figure 8.11. The whole sample represents the solid from Petrophase 2017, which behaves between island-type and archipelago-type. Island-type asphaltenes are found to have less deposition and the shape

Figure 8.10 Demonstration of island- and archipelago-type asphaltenes.
of the deposit is more fractal showing a possible diffusion-dominated deposition as shown in Figure 8.12. These results suggest that island-type asphaltenes stabilize the other fractions during the deposition process.

![Graph showing coverage of deposited asphaltenes](image)

**Figure 8.11** The coverage of the deposited asphaltenes in the micromodel.

![Microscope images of deposited asphaltenes](image)

**Figure 8.12** The deposition profile of the deposited asphaltenes in the micromodel.
8.3. Conclusion

This thesis provides key insights in the interfacial and rheological behaviors of asphaltenes using microfluidics, interfacial rheology, and various chemical analyses. At solid-liquid interfaces, physicochemical properties (transport from the bulk solution to the solid surface and attachment onto the solid surface by colloidal interactions) are investigated to study asphaltene deposition. The transportation of the aggregates is studied by changing the convection and diffusion, which is characterized by $Pe$ number. Decreased solubility parameter of the oil increases the van der Waals attractions between the aggregates resulting in larger aggregates. These larger aggregates enhance the erosion by reducing the diffusion coefficient and increasing the hydrodynamic forces exerted on the aggregate. Chemical dispersants are utilized to alter the colloidal interactions between the aggregate and the solid surface during the attachment by offering the steric repulsion. This repulsion force also decreases the aggregate size. The combination of smaller aggregate size and steric repulsion force results in increased deposition rate but softer asphaltene deposits.

At liquid-liquid interfaces, asphaltenes tend to form a cross-linked microstructure showing significant viscoelastic responses in the rheological measurements. Chemical dispersants are also found to decrease the viscoelasticity of the asphaltene network using interfacial shear rheology, and asphaltenes are visualized in a more dispersed morphology at the interface. Microemulsions containing d-limonene and demulsifiers are also used to change the interactions between asphaltenes to destabilize the asphaltene-stabilized water-in-oil emulsions. Dilatational rheology is used to study the effects of the
microemulsion and demulsifiers, but no clear correlation is found between dilatational surface elasticity and the coalescence rate between the water-in-oil emulsions generated in a microfluidic T-junction. In addition to the chemical effect on adsorbed asphaltenes at the liquid-liquid interface, the presence of brine ions has an influencing role in offering a shielding effect of the electrostatic interactions on readily adsorbed asphaltenes. Also, asphaltenes are found to act as an adhesive agent to stick water-in-oil emulsions onto the solid surface by increasing the surface energy of the solid surface.

Finally, the molecular structure of asphaltenes is essential to study the remediation process and the prevention of asphaltene deposition. Washing solvents with various solubility parameters have different abilities to dissolve asphaltenes. Washed by a lower solubility solvent could possibly cause unexpected remaining deposits even after washed by a higher solubility washing solvent. Deposition of various asphaltene subfractions obtained and fractionated from the solids of Petrophase 2017 shows that a mixture of archipelago- and island-shape asphaltenes has a higher deposition rate than island-shape-dominated asphaltenes. By understanding the nature and the behaviors of asphaltenes at interfaces, we improve our ability to design cost effective mitigation strategies. This includes the development of a new generation of chemical inhibitors/demulsifiers and improved methods for prevention and treatment of this problem.
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