Evaluation of Demulsifiers by Modified Thin Liquid Film Technique

By

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Abstract

The formation of stable water-in-oil emulsions during oil sands extraction process causes a number of operational issues, such as equipment corrosion, storage and transportation problems. One common method for emulsion breakup in industry is to use chemical demulsifiers. The chemical demulsifiers decrease the stability of water-in-oil emulsions associated with the properties of the thin liquid films formed between two closely approached water droplets. In this thesis, the Thin Liquid Film Technique and the novel Modified Thin Liquid Film Technique were introduced to generate the intervening liquid films from droplet-droplet interactions for demulsification study. For the first time a systematic comparison between two demulsifiers addition protocols was conducted using EC300 as demulsifiers to clarify the possible effect of order of demulsifier addition on demulsification. The comparison of premixing system and dosing system showed that modified thin liquid film technique can more closely mimic the real demulsification process in industry and can be used to study the molecular mechanism of how demulsifiers break interfacial films. The measurement of film stability against coalescence after adding different demulsifiers showed that EC300 and EC4 have slightly greater but very similar film breaking performance, despite of their dramatically different molecular weights. The film breaking efficiency of EO-PO 86H was lower than EC300 and EC4, but greater than EO-PO 16H, both being commercial demulsifiers. However, the concentration window of EO-PO for breaking the film was much wider than that of EC. The morphology of diluted bitumen films after dosing EC300 revealed the penetration into the diluted bitumen-water interface, causing asphaltene aggregation and forcing the interfacial film rupture into small fragments. High concentration of EC300 can form films with greater thickness, leading to overdose of the demulsifier.

This study shows that film breaking efficiency of demulsifiers is concentration-dependent and closely related to emulsion destabilization. This finding as well as the mechanisms of demulsification and overdose effect revealed from this work are required to be carefully considered when designing new demulsifiers or applying current demulsifiers to dewatering of water-in-petroleum emulsions.

Preface

This thesis is an original work by Xinrui Ma. No part of this thesis has been previously published.

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Firstly, I would like to take this opportunity to deeply thank my supervisor, Professor Zhenghe Xu for his guidance and support throughout this project. This work cannot be accomplished without his knowledge, detailed guidance and encouragement. I appreciate his instructions, which opened a door for me to understand how engineers work and think.

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Chapter 1 Introduction

1.1 Oil Sands Process

Worldwide population increase and rapid economic growth have stimulated demand of energy resources.[1] With the rapid depletion of conventional petroleum deposits, unconventional resources especially Canadian oil sands reserves have become increasingly important and have received more worldwide attentions.[2] Canadian oil sands are one of the largest unconventional oil reserves, with a total amount of 1.7 trillion barrels of bitumen in place.[3] The mineable oil sands ores in Alberta, which has the largest Canadian oil sands deposit, contain approximately 7~14% bitumen, 83-88% mineral solids and 3-5% water by weight.[4] Bitumen has very high viscosity and normally an API gravity less than 10.

Due to the difference in depth of oil sands formations, two main methods are used to extract bitumen from oil sands ore: open pit mining for resources within 75 m depth from the surface and in-situ production for deeper resources (over 75 meters underground). In the following sections, more details about these two techniques will be described as follows.

1.1.1 Open Pit Mining

The oil sands ores located 50 to 75 m underground, which account for about 20% of total oil sands reserves, are accessible with open pit mining techniques.

The generalized process of bitumen extraction for mineable oil sands ores is shown in Figure 1-1.

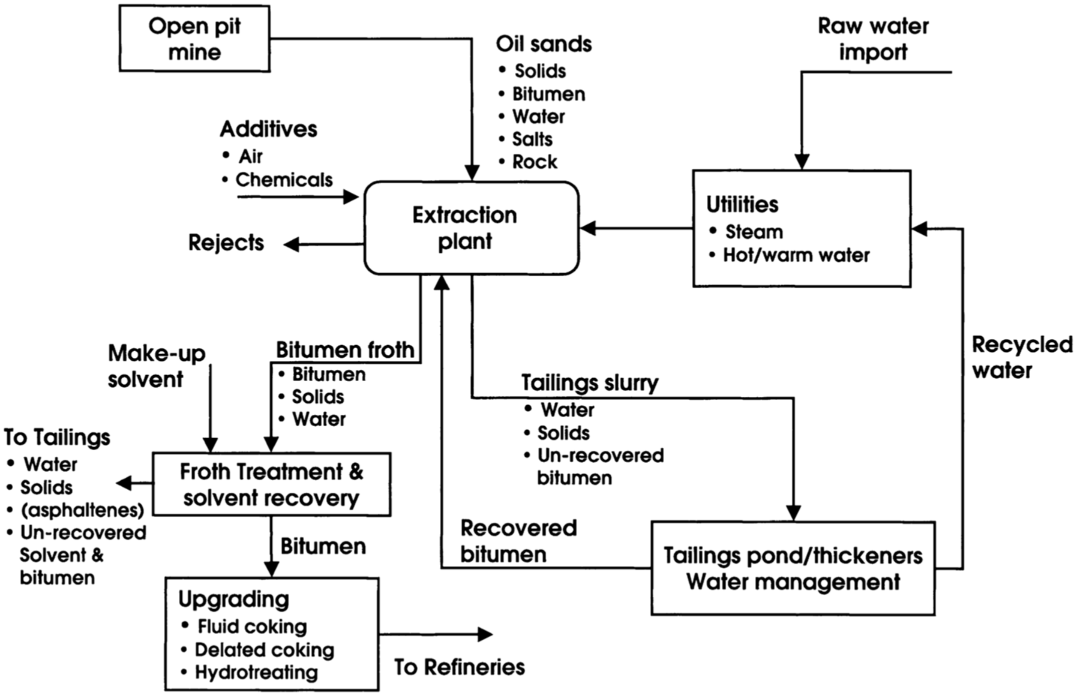


Figure 1-1 Generalized process diagram of bitumen production using water-based extraction method. Reprinted with permission from “Understanding Water-Based Extraction from Athabasca Oil Sands” Copyright (2004) The Canadian Journal of Chemical Engineering.[4]

In surface mining extraction process, the first step is to transport the oil sands ores mined to crushers, where large clumps are crushed to get more contact area for the next process. Then hot water and chemicals are added to prepare slurry for hydrotransport. Once the slurry is sent to extraction plant, it is diluted with more hot water and fed into a large gravity separation vessel, where bitumen is separated from water and solids, on the top of slurry as bitumen froth. Bitumen froth typically contains around 60% bitumen, 30% water and 10% solids by weight. The bottom part is tailings slurry, which mainly contains water, solids and a small amount of unrecovered bitumen. The tailings are sent to tailings pond or thickeners for further treatment, while the bitumen froth is fed into froth treatment vessels.

The froth treatment requires solvents to reduce bitumen viscosity for rejection of water and solids, so that bitumen can meet the specifications for upgrading.

1.1.2 SAGD Technique

The oil sands resources located deeper than 75m underground, which account for around 80% of total oil sands reserves, are accessible by in-situ production techniques, with Steam Assisted Gravity Drainage (SAGD) being the most widely used technique.

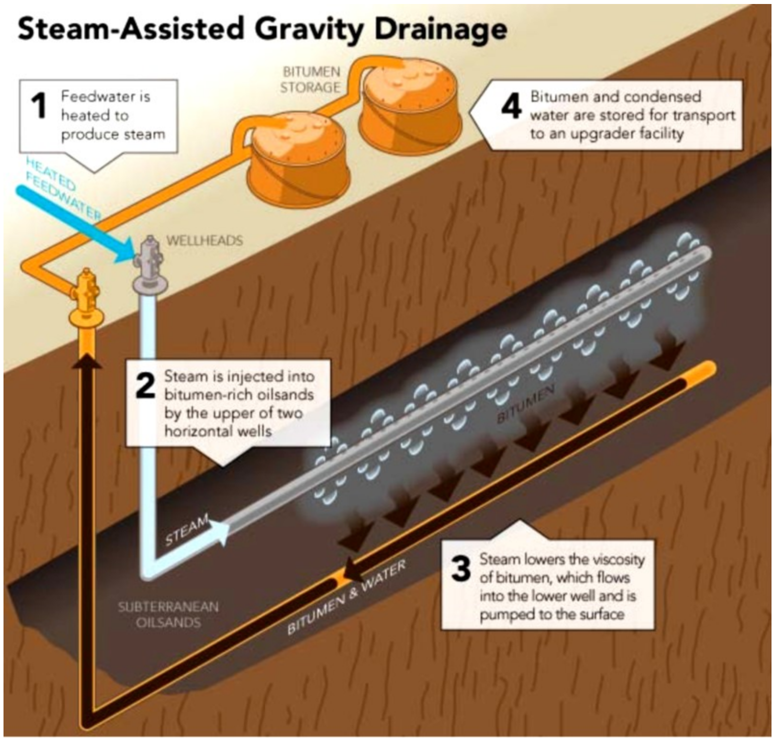


Figure 1-2 Schematic diagram of Steam Assisted Gravity Drainage (SAGD) process. Reprinted with permission from “Talk about SAGD”.[5]

The process of SAGD technique is shown in

Figure 1-2. In a typical SAGD operation, a pair of parallel horizontal wells are drilled towards the bottom of oil sands formation, with one around 5 m above the other. High pressure steam generated from natural gas heating of water is continuously injected into the upper well through pipelines to reduce the viscosity of bitumen in place. With temperature increasing, the bitumen becomes more fluid and drains into the lower well, where it is pumped out to the surface for further processing. Water condensed is recycled for new steam generation after extensive treatment. For this in-situ method, it requires a large amount of hot water and natural gas.[6]

1.2 Froth Treatment

The bitumen froth obtained from extraction process requires further treatment to reject extra water and solids before the bitumen can be sent to upgraders or sold to the market. The removal of water and solids from bitumen froth is accomplished with a hydrocarbon-based gravity separation process, which requires addition of light hydrocarbon solvents to reduce viscosity and enhance the density difference between the oil phase and aqueous phase.

There are two major types of froth treatment methods used in the oil sands industry: naphthenic process and paraffinic process. This classification is based on the types of solvent used to dilute bitumen froth.

1.2.1 Naphthenic Froth Treatment

Naphthenic froth treatment (NFT) is a conventional froth treatment process, which has been used and modified by Syncrude, Suncor, CNRL, etc. In this process, a relatively low solvent-to-bitumen ratio is employed. Figure 1-3 shows a schematic of a typical two-stage naphthenic froth treatment process.[7] In this process, naphtha is added to reduce viscosity and density of bitumen and demulsifiers are used to break up emulsion droplets for more effective separation. After settling, the preliminarily cleaned bitumen froth is fed into a multistage centrifugation process to further remove solids and free water. The final bitumen product after froth treatment is called diluted bitumen. The diluted bitumen products still contain about 1-2% water and 0.5-1% fine solids.[8] After recovery of naphtha, the bitumen is sent to an on-site upgrader, where it is converted into synthetic crude oil and then transported to refineries.

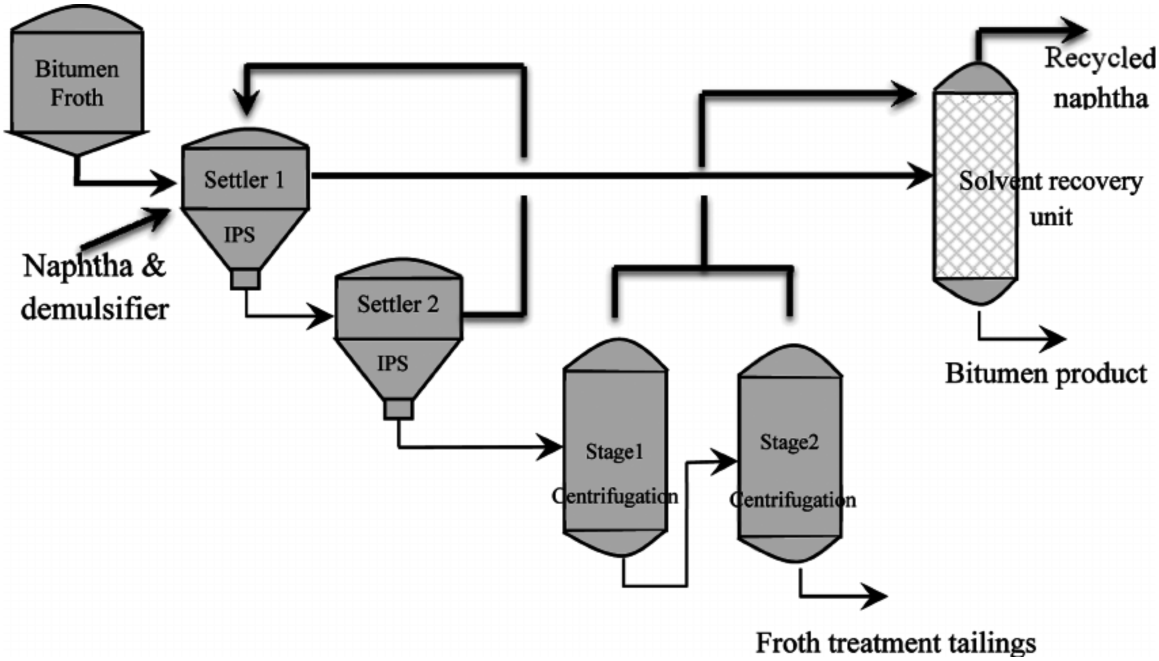


Figure 1-3 Generalized schematics of a typical two-stage naphthenic bitumen froth treatment process. Reprinted with permission from “Froth Treatment in Athabasca Oil Sands Bitumen Recovery Process: A Review”. Copyright (2013) American Chemical Society.[7]

It is really challenging to remove the residual water and fine solid particles in the diluted bitumen, as the water has been emulsified with the solids in micro scale, as shown in Figure 1-4. This residual water containing a lot of chloride salts with solids and some other dissolved substances in diluted bitumen can cause serious problems for the downstream upgraders, such as corrosion of equipment, catalyst deactivation and some safety problems. Many companies have made great efforts to modify the NFT process to improve the quality of final diluted bitumen product.

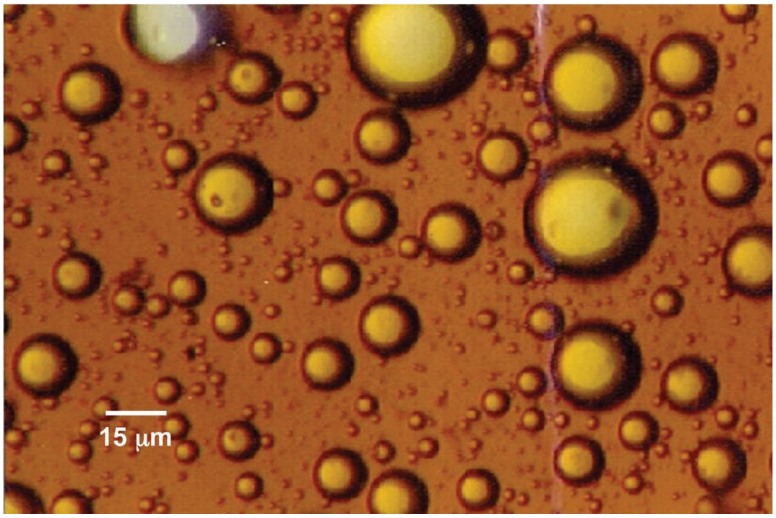


Figure 1-4 Photomicrograph of a water-in-oil emulsion. Reprinted with permission from "Crude-Oil Emulsions: A State-Of-The-Art Review". Copyright (2005) SPE Production & facilities. [9]

1.2.2 Paraffinic Froth Treatment

Paraffinic froth treatment is a relatively new method and currently used by Shell Albian Sands and Imperial Oil.[10] In this process, paraffinic solvent is used as the diluent. In this process a higher solvent-to-bitumen ratio is employed, which causes asphaltene rejection from bitumen. As asphaltene precipitation is accompanied by the formation of aggregates with fine solids and emulsified water droplets, this method produces a very clean final diluted bitumen product.[8] Furthermore, asphaltenes are also major materials that contribute to high viscosity of bitumen, meaning that asphaltene rejection can lower the viscosity of final diluted bitumen product, which is good for downstream upgraders. However, the high solvent-to-bitumen ratio may also result in more solvent loss, increase operation cost and cause more environmental problems.[11]

The main difference between naphtha based froth treatment and paraffinic froth treatment is the choice of solvent used in the process. With paraffinic diluents, a clean diluted bitumen product can be obtained, but bearing the loss of diluents and some other safety problems. In contrast, the quality of diluted bitumen from naphthenic froth treatment can be relatively poor since it contains some residual water and solids. Great efforts have been made to reduce residual water and solids content in final diluted bitumen product. However, it is not easy as residual water typically exists in the form of emulsified droplets of high stability. One way that has been widely used in industry to remove the residual water is to use demulsifiers to break up emulsion droplets and speed up water separation from the final product.

1.3 Objectives and Outline of the Thesis

The objective of this thesis is to study and evaluate different chemical demulsifiers on the interfacial film level. Using Thin Liquid Film (TLF) technique and Modified Thin Liquid Film (MTLF) technique, the behaviour of different demulsifiers and demulsification efficiency on W/O emulsion films obtained from diluted bitumen solution will be evaluated. The MTLF technique allows evaluation of different demulsifier addition methods. The thesis also aims at gaining new understanding of demulsification mechanisms through studying the properties of the thin liquid films formed between two water droplets.

Although much effort has been made to study chemical demulsifiaction, the effective water removal in petroleum industry is still a major problem. It is important to have a better understanding about the demulsification mechanism on the interfacial level, in order to enhance demulsification efficiency and design more effective demulsifiers.

The thesis consists of 5 chapters and a brief summary of each chapter is described below:

Chapter 1 gives a brief description of the two oil sands extraction methods, i.e., open pit mining and in-situ production, as well as two types of froth treatment process.

Chapter 2 reviews the literature on water-in-oil emulsion and the role of thin liquid film, techniques to measure intervening film properties, application of thin liquid film technique to oil sands extraction, and chemical demulsification.

Chapter 3 describes the materials and experimental setup of the thin liquid film technique and modified thin liquid film technique used in this thesis.

Chapter 4 compares the effect of two demulsifier addition systems using EC300. Film behaviors and lifetimes are investigated and the demulsification mechanism on interfacial level is determined and discussed. The demulsification efficiency of four kinds of demulsifiers is determined via modified thin liquid film technique to develop this technique into a method to evaluate chemical demulsifiers' performance. Two types of EC and two kinds of EO-PO were used in this research.

Chapter 5 provides a summary of the major conclusions from this research and recommends some future work.

Chapter 2 Literature Review

2.1 Water-in-Oil Emulsion and Thin Liquid Film

An emulsion is a dispersion of two immiscible or partially immiscible liquids.[12] The water-in-oil emulsion defines water as dispersed phase and oil as continuous phase. For oil sands industry, water-in-oil emulsions are common but undesirable, because they can cause corrosion in equipment and other transportation problems. Chemical and/or thermal treatments are often applied to removing the containing water, as the emulsified water can hardly be removed from oil with gravity settling alone. The most important property of emulsion encountered in oil sands industry is its stability. The emulsion can be stabilized by a third constituent, known as emulsifier or emulsifying agent, which has three main classes: surfactants, macromolecules and fine solids.[13]

The surfactants or macromolecules stabilize emulsions through adsorption of emulsifiers onto water-oil interface, thus decreasing the interfacial tension and providing electric charges to emulsion droplets or forming steric stabilization layer around droplets.[13] The emulsion stabilized by fine solids is well known as Pickering emulsion. In many cases, the solid-stabilized emulsions have extreme stability, as the solid particles attached on to the water-oil interface can form a steric barrier to prevent coalescence.[14-16] The water-in-diluted bitumen emulsions that formed in oil sands extraction process are known to be stabilized by some interfacial active materials, such as asphaltenes, naphthenic acid, resins and fine solids.[17-20] Despite of decades of effort, the exact molecular stabilization mechanism of W/O emulsions in petroleum industry has not been fully understood. However, it has been generally accepted that the stability of water-in-oil emulsion is governed by the properties of a rigid, viscous film around water droplets that prevent their coalescence.[21-26] The film is part of the continuous liquid phase (i.e. oil for water-in-oil emulsions) between dispersed droplets (i.e. water droplets for water-in-oil emulsions). When two water droplets approach each other, the oil between two water droplets will drain and the film will become increasingly thinner and change into a flat film. The curvature change of the interface occurs when two water droplets are at a small distance (typically within hundreds of nanometers) and can interact with each other. Thus, a capillary pressure difference which arises between the flat film and the meniscus will force the oil phase to further drain out of the film. During this drainage process, the droplets can interact via many kinds of surface forces, such as van de Waals forces (attractive), electrical double layer repulsive forces, steric forces, etc. Normally, all these forces per unit area are called disjoining pressure, which is used to express the actual pressure on the interfacial film. The disjoining pressure can be either negative or positive, which determines film stability. If the disjoining pressure is negative, the strong attractive forces will cause continuous film drainage until the film ruptures, followed by droplets coalescence. The similar situation will also happen when the disjoining pressure is positive but less than the attractive capillary pressure. On the contrary, the strong repulsive force can obviously increase the film stability, as the disjoining pressure can balance the capillary pressure. With the increasing disjoining pressure, a uniform film forms and droplets remain stable when the disjoining pressure equals the capillary pressure.[15]

Figure 2-1 describes the formation of thin films between two water droplets in oil, as well as the relationship between film stability and droplets coalescence. From this figure, it can be seen that the properties of water-oil interfacial films have significant influence on emulsions stability. There are several techniques available to study the properties of interfacial film, which will be described in detail below.

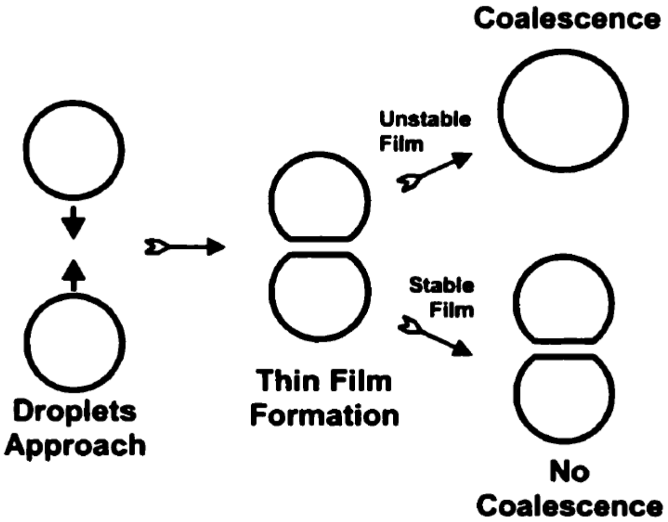


Figure 2-1 Schematics of thin liquid film formation between two water droplets in water-in-oil emulsion and its relationship with emulsion stability. Reprinted with permission from "Colloidal Interactions in Water in Diluted Bitumen Emulsions".[27]

2.2 Techniques to Study Intervening Liquid Films

2.2.1 Micropipette

Micropipette is a novel technique to study the interface of emulsion droplets on micro-scale via visual observation. This technique was first introduced by Yeung et al., in which small suction pipettes were used to grab emulsion droplets and conduct mechanical experiments in-situ, thus providing a better understanding on emulsion systems.[28] The micropipette technique is an ideal tool to study individual emulsion droplets. With this technique, the interfacial tension and emulsion stability can be measured directly on micro-sized emulsion droplets. Moran and Czarnecki[29] combined micropipette technique with a maximum bubble pressure method to measure interfacial tension on individual micron-sized droplets and obtained consistent results when comparing with literature value. Using micropipette technique, Gao et al. studied the role of asphaltenes and maltenes in stabilizing water-in-heptol (a mixture of heptane and toluene at a 4:1 volume ratio) diluted bitumen emulsions.[30] The interfacial adsorption behavior, rigidity of emulsified water droplet surfaces and its stability against coalescence were observed and recorded in their work to analyze the interfacial property of water-in-diluted oil droplets. They found that asphaltenes dissolved in heptol were the main contributor to form steric layer at the oil-water interface that stabilized water droplets, while water droplets in diluted maltenes coalesced readily.

2.2.2 Atomic Force Microscope (AFM)

Atomic force microscope (AFM) is a kind of scanning probe technique, which can reach a high resolution of nanometer scale. The AFM technique has been applied in a wide range of disciplines, including surface chemistry, telecommunications, biological, chemical and energy industries, etc. This technique has also been extensively used to study colloidal forces between different oil sands components, such as oil sand solids and oil droplets as well as the thin film formed between two emulsion droplets. Using AFM technique, Wang et al. measured the colloidal forces between asphaltene surfaces immersed in toluene, in order to better understand the stabilization mechanism of water-in-crude oil emulsions.[31] In their work, two methods were used to coat asphaltenes on silica surfaces: Langmuir-

Blodgett deposition technique and dip-coating method. They found that the repulsive forces between two asphaltene-in-toluene surfaces were steric force in nature and the measured force agreed well with polymer scaling theory of noncharged macromolecules. In another paper, Wang et al. further found that there is a long-range repulsion of steric nature in good solvent such as pure toluene and the repulsive forces changed to attractive van der Waals forces with increased heptane content in heptol, leading to asphaltene precipitation.[32]

2.2.3 Surface Force Apparatus (SFA)

The surface force apparatus (SFA) is an instrument developed to measure surface forces between two surfaces, in which one surface is held by a spring and the other can be moved towards and away from the surface on the spring. Surface forces measured using SFA such as van der Waals forces, electrostatic forces, steric interactions and capillary forces have been extensively reported in the literature, including many studies on colloidal forces in the oil sands area. Using SFA, Vuillaume et al. compared the interactions between mica surfaces across a diluted bitumen and different asphaltene solutions.[33] The experiment showed that the interactions between adsorbed layers had considerable differences due to different compositions. Their studies of the systems confirmed that the adsorbed layer from a crude oil had significantly different molecular structure and molecular weight from that remained in toluene solutions. In the work by Wang et al., they used the combination of N-(1-hexylheptyl)-N0-(5-carboxylicpentyl) perylene-3,4,9,10-tetracarboxylic bisimide (C5Pe) as model compound of asphaltenes to study possible molecular interactions of asphaltenes in different solvents.[34] SFA was used to investigate the adsorption behaviors and interaction forces between model compound C5Pe and the model clay (mica) in toluene and heptane solutions. The results indicated that the repulsive force for the interaction between two mica surfaces across the C5Pe-in-toluene solution was shown to originate from a steric force and its distance profiles can be described by AdG scaling theory over both short and long distances.

2.3 Application of Thin Liquid Film Technique to Studying Oil Sands Extraction Emulsion Systems

When two water droplets in a water-in-oil emulsion approach each other within a small distance, a thin liquid film forms between them, as shown in Figure 2-2a.

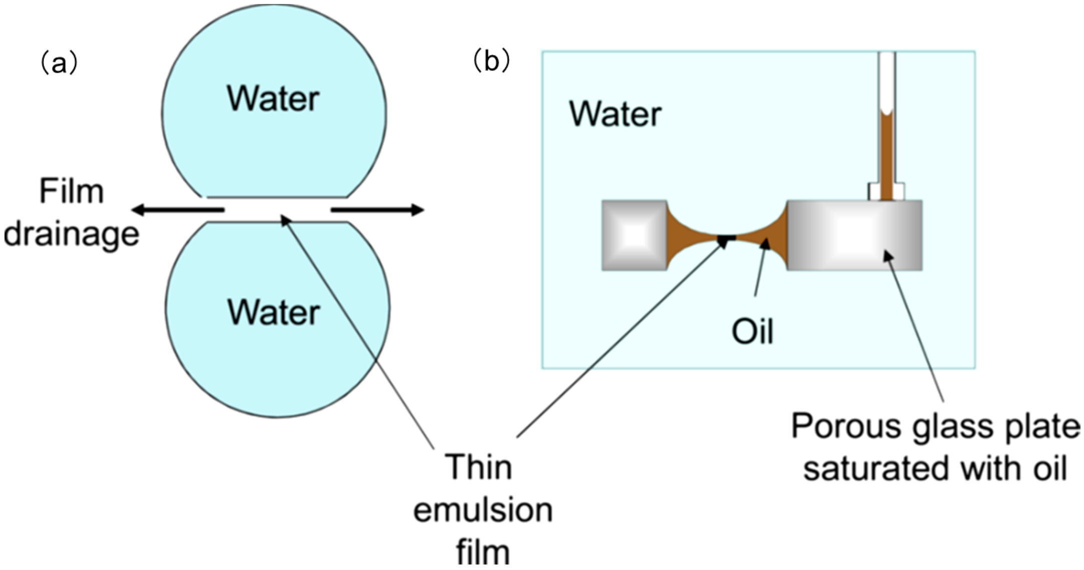
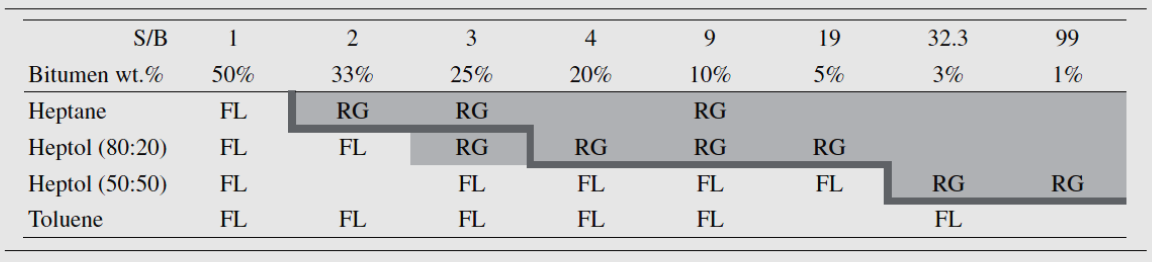


Figure 2-2 Formation of thin liquid film (a); and Principles of thin liquid film technique (b). Reprinted with permission from "Possible role of asphaltenes in the stabilization of water-in-crude oil emulsions." Copyright (2012) American Chemical Society.[35]

The properties of the thin oil layer separating two approaching water droplets in water-in-oil emulsion play a key role in emulsion stabilization. The thin liquid film (TLF) technique is a convenient and direct method to probe properties of the adsorption layer on oil-water interface and further understand the interactions between emulsion droplets.[36-38] As shown in Figure 2-2b, the TLF technique can mimic the real emulsion condition to create a similar film in the thin film measurement cell and provide large amount of information about film drainage kinetics, film thickness and surface forces responsible for film stability. This technique has been widely used to study thin film properties of foams and oil-in-water emulsions.[37] But recently, the TLF technique was adapted by Khristov et al. to study water-in-diluted bitumen emulsions to address the undesirable emulsion problems faced during oil sands extraction process.[35,39-41] The previous work using TLF technique to solve problems encountered in oil sands industry provided helpful information about emulsion stabilization mechanism. Khristov et al. systematically studied the water-in-diluted bitumen emulsion films using the thin liquid film-pressure balance technique (TLF-PBT).[39] They found that the lifetime and properties of water-in-diluted bitumen emulsion film strongly depend on the solvent type and dilution ratio. For heptane diluted bitumen system, black systems containing trapped liquid within the film formed following formation of black spots in the film. Furthermore, a 'network' of spots was formed for certain unknown reasons at heptane-to-bitumen mass ratio from 10:1 to 15:1. On the contrary, the images obtained from toluene-diluted-bitumen films showed change of these films to stable, thinner, uniform grey films.

To gain better understanding of surface forces that stabilize the thin liquid films, Taylor et al. measured disjoining pressure isotherms for water-in-toluene diluted bitumen and water-in-diluted asphaltene emulsion systems.[40] The similar disjoining pressure isotherms obtained from these two systems suggest that the surface active materials from asphaltenes fraction of bitumen may be mainly responsible for film and emulsion stability. The results showed that films were more stable at high concentrations for both bitumen and asphaltene. These previous studies demonstrated that solvent-to-bitumen ratio (S/B) had a significant effect on film lifetime and thickness of water-in-diluted bitumen emulsions. Tchoukova et al. conducted a systematic study on the effect of S/B and solvent aromaticity on film behaviours.[42] They found a critical solvent-to-bitumen (S/B) dilution ratio in an aliphatic solvent (e.g. heptane/heptol) diluted bitumen solution, at which film behavior changed abruptly, while the films formed by toluene diluted bitumen were able to remain flexible in most cases. The relationship between film transition from flexible to rigid interface and solvent quality is summarized in Table 2-1.

Table 2-1 Summary of observed transition from fluid to rigid interfaces as solvent aromaticity changes. The thick line in the table represents the critical S/B ratio as reported. Reprinted with permission from "Study of water-in-oil thin liquid films: Implications for the stability of petroleum emulsions".[42]



S/B	1	2	3	4	9	19	32.3	99
Bitumen wt.%	50%	33%	25%	20%	10%	5%	3%	1%
Heptane	FL	RG	RG		RG			
Heptol (80:20)	FL	FL	RG	RG	RG	RG		
Heptol (50:50)	FL		FL	FL	FL	FL	RG	RG
Toluene	FL	FL	FL	FL	FL		FL	

Above critical S/B ratio, film became extremely rigid and stable thickness increased significantly. Furthermore, some new asphaltene aggregates formed in the film, as precipitated asphaltenes had already been removed initially. The results indicate that stable films were observed in aromatic solvent or aliphatic solvent with low S/B ratio. The quantitative measurement of critical S/B ratios for films in heptol (mixture of heptane and toluene) showed that the critical S/B ratios for stable films agreed with the values from emulsion stability studies. The authors mapped out regions of stable film against coalescence in bitumen concentration and toluene content in heptol solutions diagram, as shown in Figure 2-3.

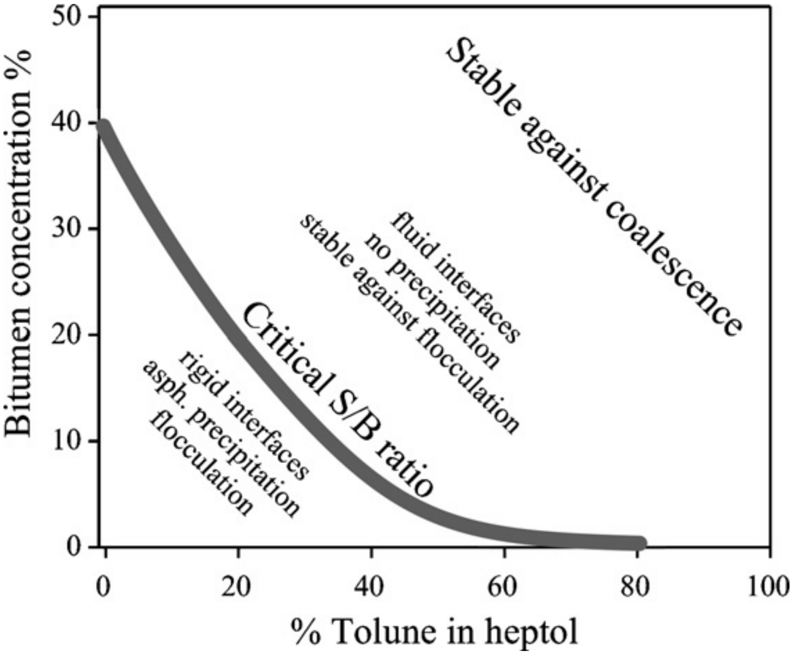


Figure 2-3 Summary of water-in-diluted bitumen emulsion film stability against coalescence and flocculation for different bitumen concentrations and solvent compositions. Reprinted with permission from "Study of water-in-oil thin liquid films: Implications for the stability of petroleum emulsions".[42]

To further understand the exact role of different bitumen fractions, Tchoukov et al. used TLF technique to measure the film lifetime, film thickness and film drainage kinetics of water-in-oil emulsion films formed by bitumen, asphaltenes and maltenes in toluene solutions.[41] The lifetime results showed that asphaltenes can stabilize thin films at relatively low concentrations (0.5-2 g/L), while the equivalent concentrations of asphaltenes in bitumen were much higher (10-50 g/L). Equilibrium film thicknesses of films stabilized by asphaltenes (40-90 nm) were much thicker than maltene films (~10 nm), indicating significantly different stabilization mechanisms between these films. The drainage of thin liquid films stabilized by asphaltenes was significantly slower than that stabilized by bitumen and maltenes. The drainage kinetics of the film formed from asphaltene solutions did not fit well known Stokes-Reynolds-Young-Laplace model. A comparison of film drainage kinetics of films obtained from 10 g/L asphaltenes, 50 g/L maltenes and 59 g/L bitumen diluted in toluene solutions and their schematic mechanism are shown in Figure 2-4. These differences in film properties among asphaltenes, bitumen and maltenes were believed to be related to asphlatene aggregation. They found that the asphaltenes formed a 3-dimensional "gel-like" network structure in poor solvent, which could stabilize the formed protective intervening liquid films against coalescence, while for bitumen diluted in good solvent, asphaltene aggregation was suppressed and a viscoelastic layer was formed at oil-water interfaces.

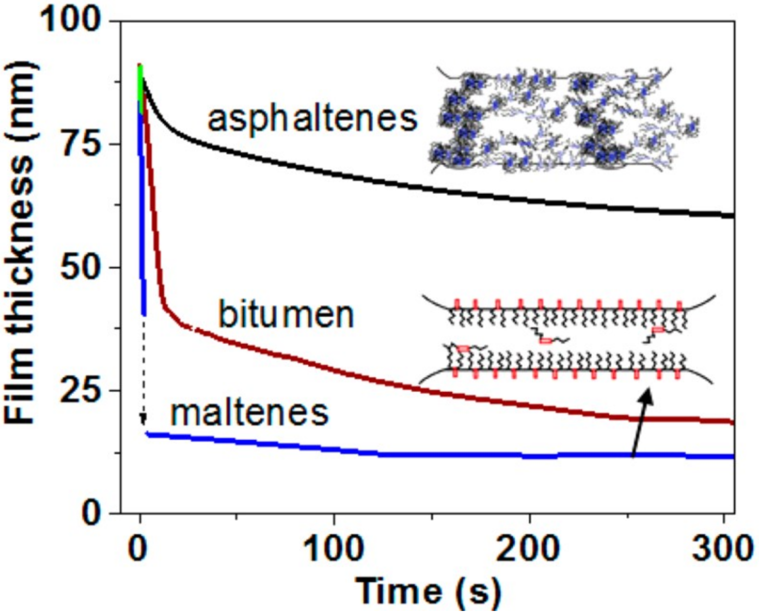


Figure 2-4 Comparison of film thickness obtained from 10 g/L asphaltenes, 59 g/L bitumen, and 50 g/L maltenes in toluene solutions and their schematic mechanisms. Reprinted with permission from "Role of Asphaltenes in Stabilizing Thin Liquid Emulsion Films". Copyright (2014) American Chemical Society.[41]

2.4 Chemical Demulsification

2.4.1 Demulsifiers

To break up the water-in-crude oil emulsions, a variety of techniques have been used, such as centrifugation, sonication, chemical demulsification, etc.[43-45] As one of the most efficient and economical method, chemical demulsification has drawn wide attention and has been extensively used in petroleum industry.

The chemical additives used to destabilize emulsions are typically polymeric surfactants of different molecular weights, which are known as demulsifiers. It has been well accepted that demulsifiers should have a stronger affinity to the oil-water interface than the original surface active materials, e.g., asphaltenes, and thus can weaken the interfacial films and induce coalescence of water droplets.[46,47] A number of demulsifiers have been developed, such as acid- or base- catalyzed phenol-formaldehyde polymers, epoxy polymers and silicone copolymers as well as some commercial demulsifiers, polyoxyalkylates, diethanolamines, ethylene oxide (EO)/propylene oxide (PO) copolymer demulsifiers, etc.

EO-PO demulsifiers are commercially available and have been widely used in petroleum industry. The amphiphilicity of EO-PO demulsifiers from hydrophilic ethylene oxide (EO) groups and hydrophobic propylene oxide (PO) groups provided them stronger adsorption at the oil-water interface than the original interfacially active species. Extensive research on their demulsification mechanism and relationship between the structure, molecular weight, RSN of EO-PO demulsifiers and demulsification performance has been conducted.[43,48-52]

Previous studies showed that, at low dosage of EO-PO demulsifiers, the more hydrophilic demulsifier had higher demulsification efficiency than the one with lower hydrophilicity.[49,50] Kailey et al. studied properties and performance of three EO-PO demulsifier blends and the individual components.[53] The results indicated an additive RSN of blends, which can be estimated from the individual RSN values. In addition, the dehydration efficiency of EO-PO blends is higher than their individual components, indicating synergistic interactions among mixed demulsifiers. Kailey and Feng studied the relationship between demulsification performance and RSN, EO content, PO content, and molecular weight using six EO-PO samples from two families.[54] The results indicated cross-linked EO−PO copolymers of higher molecular weight and more EO−PO branches had higher dehydration efficiencies of demulsifiers containing less than 40% of EO. Pensini et al. studied EO-PO demulsification mechanism of water-in-toluene diluted asphaltene emulsions using a number of techniques, including AFM, Langmuir-Blodgett, BAM, Shear Rheology, etc.[55] They reported that EO-PO used in their work could effectively replace asphaltenes at the interface, penetrate and soften asphaltene films due to stronger interfacial activity of EO-PO demulsifiers than asphaltenes. However, high concentration of EO-PO caused formation of thick films, which would likely increase steric repulsion between water droplets and prevent them from coalescence, thus showing overdose effect.

In recent years, a cost-effective and biodegradable polymer, ethylcellulose (EC) was found to be effective in destabilizing water-in-diluted bitumen emulsions.[56] By using in-situ micropipette apparatus, the demulsification process of two water droplets with EC was directly and visually investigated.[57,58] They found that the addition of EC could significantly reduce the interfacial tension of diluted bitumen-water interface. The AFM imaging of films transferred by Langmuir-Blodgett method showed disruption of the interfacial asphaltene films. They concluded that EC can destabilize water-in-diluted bitumen through both flocculation and coalescence of water droplets. Hou et al. studied the effect of EC on interfacial films formed by surface active materials from bitumen through Langmuir trough technique, polarization modulation infrared reflection absorption spectroscopy (PMIRAS) and film thickness measurement.[59] The results indicated that EC irreversibly adsorbed at the oil-water interface and caused a more compressible interfacial film, thus resulting in coalescence of water droplets.

2.4.2 Mechanisms Involved in Chemical Demulsification

The detailed mechanism of chemical demulsification is still subjected to much debate. However, there are a few general conclusions for how chemical demulsifiers can destabilize emulsions.[60] Some demulsifiers possess greater interfacial activity than natural stabilizers from original emulsion at the oil-water interface and can thus displace them.[59,61] The displacement will then change the structure and mechanical properties of the original interfacial film and cause film disrupted or softened, leading to conditions beneficial to water droplets coalescence.[58,62,63] In addition to displacing the stabilizing species at the interface and rupturing or weakening the rigid film, some chemical demulsifiers can suppress buildup of preventive interfacial layers, e.g., inhibiting interfacial tension gradients.[64] Therefore, the ideal demulsifiers should possess both abilities of displacing natural stabilizing materials and supressing the formation of interfacial films.

Although considerable efforts have been made to study chemical demulsifiaction, the effective water removal in petroleum industry remains a problem. It is important to have a better understanding on the demulsification mechanism of the interfacial level, in order to enhance demulsification efficiency and design more effective demulsifiers.

Chapter 3 Materials and Methods

3.1 Materials

3.1.1 Demulsifiers

Ethylcellulose (EC) samples (EC4 and EC300) were purchased from Sigma-Aldrich and used as received. The molecular structure of ethyl cellulose (EC) is shown in Figure 3-1. The viscosity of 5 wt.% EC4 and EC300 in 80:20 toluene/ethanol (v/v) solution was determined to be 4 cP and 300 cP, respectively. The molecular weight of EC4 and EC 300 determined by intrinsic viscosity measurement was 46 kDa and 182 kDa, respectively.[56]

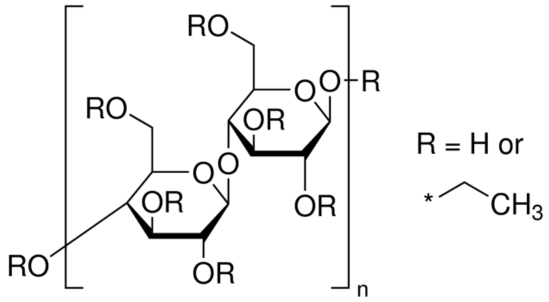


Figure 3-1 Molecular structure of ethyl cellulose (EC).

Properties of EC4 and EC300 are shown in Table 3-1. The EC samples were dissolved into toluene solution at the concentration of 0.1mg/ml and 1 mg/ml under stir for 24h prior to use.

Table 3-1 Properties of EC300 and EC4.

Chemical	Ethoxyl%	MW	HLB
EC300	48	182,000	7.9
EC4	48	46,000	7.9

Two EO-PO block copolymer demulsifiers (86H and 16H) were provided by Baker Hughes and used as received. EO content (number of EO per mole) for both 86H and 16H was 35%. The molecular weight of 86H and 16H was 12311 and 6145 Da, respectively. The relative solubility numbers (RSN) of these two demulsifiers 86H and 16H were 18.07 and 16.92, respectively. RSN is an important character for a nonionic surfactant. Similar to HLB value, RSN can be used to indicate hydrophilicity, with a higher number indicating a more hydrophilic product and more preferable for aqueous phase. The RSN was determined by a standard procedure.[54]

EO-PO 86H and 16H are of a star-like structure with five and three arms, respectively. Detailed information of EO-PO 86H and 16H are summarized in Table 3-2. Similar to EC, the EO-PO samples were also dissolved in toluene solution at the concentration of 0.1 mg/ml and 1mg/ml under stir for 24h prior to use.

Table 3-2 Properties of EO-PO 86H and EO-PO 16H.

Chemical	EO%	Arm Number	RSN	MW
EO-PO 86H	35	5	18.07	12311
EO-PO 16H	35	3	16.92	6145

3.1.2 Solvents and Solution Preparation

Toluene (Optima, Fisher Scientific Canada), n-heptane (HPLC grade, Fisher Scientific Canada) and acetone (Optima, Fisher Scientific Canada) were used as received. Heptol (80:20) prepared by mixing heptane and toluene in the volume ratio of 80:20 was used as the major solvent in this thesis.

The aqueous phase was simulated industrial water, prepared by dissolving 0.012M $NaHCO_3$, 0.004M Na_2SO_4 and 0.014M NaCl in 1L Milli-Q water of 18.2 MΩ·cm at 25°C.

All the salts used here were purchased from Fisher Scientific Canada and of A.C.S. grade. The simulated industrial water used in this thesis can provide similar ionic strength and pH (~8.5) as Syncrude plant recycle water.

Vacuum distillation feed bitumen was provided by Syncrude Canada Ltd. Bitumen was diluted with heptol (80:20) solution with a solvent to bitumen ratio of 1 (50 wt.% bitumen). The mixture of bitumen and heptol was shaken for around 4h to ensure complete mixing. The diluted bitumen solution prepared using this procedure was used throughout the study.

To remove fine solids and precipitates, the prepared bitumen in heptol solution was centrifuged at 14,000g and18 °C for 60min. This sample is referred to as centrifuged diluted bitumen.

3.2 Thin Liquid Film Technique

3.2.1 Experimental Setup

Thin liquid film technique was used to probe the demulsification efficiency and interfacial properties of emulsion films. This technique provides a convenient and direct method to study both drainage kinetics of thin liquid films and surface forces between two droplets as in a sandwiched model system. In our case, it is a thin oil layer between two water phases, which is similar to the real W/O emulsion system.[36,65,66] This technique has an accuracy of about 2 nm for the thickness measurement of common emulsion films. A schematic diagram of thin liquid film apparatus is shown in Figure 3-2.

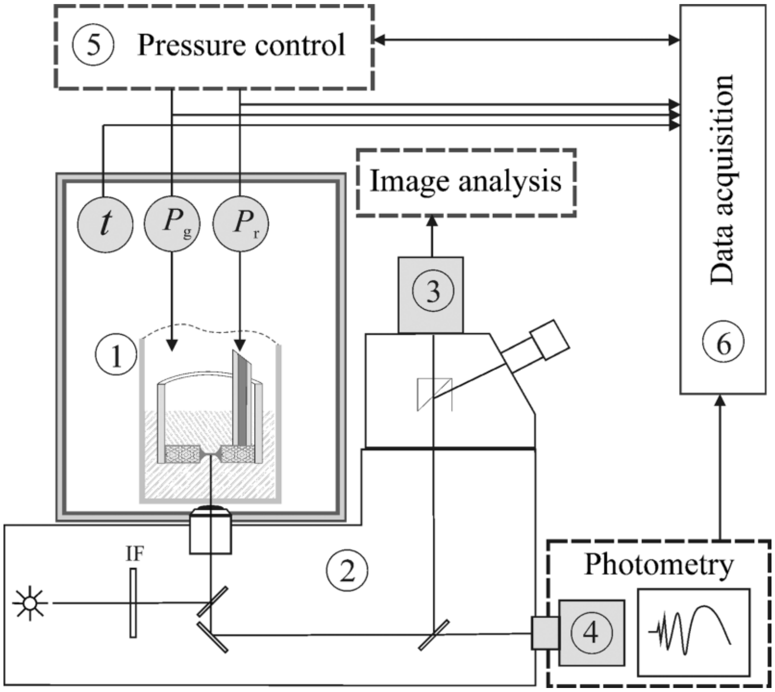


Figure 3-2 Experimental setup of thin liquid film apparatus: (1) Scheludko Exerowa cell; (2) Carl Zeiss Axio Observer inverted microscope; (3) Leica DFC500 CCD Camera; (4) Hamamatsu Si photodiode; (5) PSD/2 Hamilton Syringe Drive, Omega PX143 Pressure transducer; (6) NI Data acquisition system with LabVIEW. Reprinted with permission from "Study of water-in-oil thin liquid films: Implications for the stability of petroleum emulsions".[42]

In our cases, W/O emulsion films were generated in the Scheludko Exerowa cell.[36,66] The cell has a porous glass disc with a 0.8 mm diameter hole in the center. To form a W/O emulsion film, the porous glass holder was initially soaked in an oil phase for 10 min and then immersed into water-filled cell to allow the oil-water interface in full contact. By decreasing the pressure in the capillary P_r, the oil phase in the porous glass disc was withdrawn slowly through the capillary. When the two biconcave meniscuses were close enough, a liquid film formed in the center of the hole. The cell was placed in a thermostatted chamber to maintain a constant temperature as well as prevent stray light from entering the optical path. The film drained under the pressure differential from the curvature of the interface and disjoining pressure. The drainage process was observed in the reflected light with the Carl Zeiss Axio Observer inverted microscope which was placed under the metal chamber. A Leica DFC500 chargecoupled device (CCD) camera of high spatial resolution and high sensitivity was equipped to record film drainage process. Image analysis was performed by ImageJ software. To measure the film thickness, an HBO lamp was used as light source, a low-noise Hamamatsu photodiode as a detector, with a green interference filter was used to create monochromatic light. The film thickness was calculated using the equation derived by Scheludko and Platikanov[67]:

$$h = \left(\frac{\lambda}{2\pi n_{\mathrm{f}}}\right) \arcsin\left(\frac{\Delta}{1 + [4N/(1-N)^2][1-\Delta]}\right)^{1/2} \tag{1}$$

where $\Delta = (I - I_{min})/(I_{max} - I_{min})$ and $N = (n_f - n_s)^2/(n_f + n_s)^2$, h is the calculated film thickness, I is the intensity of reflected light from thin liquid film, I_{max} and I_{min} are the maximum and minimum of light intensity, n_f and n_s correspond to the refractive indexes of the thin film liquid and the surrounding water phase, respectively, and λ is the wavelength of the monochromic light.

Pressure P_g and P_r measured by a pressure transducer from Omega can be controlled by a Hamilton Syringe Drive-PSD/2 to manipulate the film diameter and thickness. A custom-designed National Instrument (NI) LabVIEW program was used to acquire the data and control the experiment.

3.2.2 Procedures of TLF Technique

For each experiment, the porous glass disc was made hydrophobic by immersing it in 20% dichlorodimethylsilane (>99.5%, Fluka) in toluene solution for 24 h. The cleaned porous glass disc was then soaked in the studied solution for 10 min before being immersed in simulated process water. Upon the contact of the solution with water, we started to count the ageing time, i.e., the time that the cell was left to equilibrate oil-water contact. Except for the experiments to study ageing effect, the ageing time was kept for 45-60 min. Once the water and oil phase were contacted, a thick film of oil sandwiched between two water phases was formed in the hole of the porous disc. After specified ageing time, a thin oil film was formed and adjusted to a desired radius by changing the pressure in the capillary. Microscopic images of the thin film and film lifetime were recorded. After each experiment, the cell was washed with toluene and acetone in an ultrasonic bath and then placed into an oven to dry. Piranha solution was also used to further clean the demulsifier residue in the porous glass disc.

3.3 Modified Thin Liquid Film (MTLF) Technique

To study films formed from a mixture of diluted bitumen and demulsifier, the film features were based on the premixed solution with added demulsifier, which was different from the real demulsification process. In practice, the oil-water interfacial film has been formed prior to demulsifier addition into the emulsion solution, so that demulsifier has to experience diffusion and competition processes for demulsification. However, the traditional TLF technique does not allow such process to be studied where the concentration and composition of oil phase in the middle of sandwich model could be changed. Therefore, to simulate the real demulsification process, a modification to the current thin liquid film technique has been introduced.

3.3.1 Modified Scheludko-Exerowa Cell

The novelty of MTLF technique is the introduction of a dosing system to allow demulsifier addition after film is formed and aged for certain time. Figure 3-3 shows schematics of the modified Scheludko-Exerowa cell. The Scheludko-Exerowa cell was modified by opening an outlet and adding a spout-like glass cylinder with a rubber cap on it to make the system gas tight. A micro-syringe is used to punctuate the cap and inject a certain amount of demulsifier solution into the porous glass disc. The other parts of the experimental setup are the same as TLF technique described in section 3.1. This simple modification makes it feasible to deposit demulsifier solutions or some other substances into the system at any chosen time.

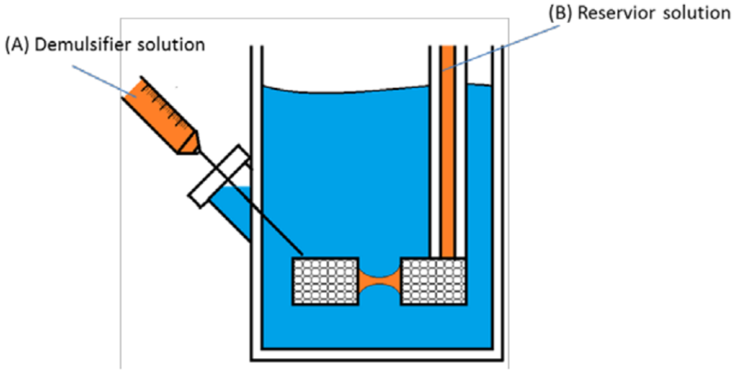


Figure 3-3 Schematics of the modified Scheludko-Exerowa cell. Reprinted with permission from “Bitumen fractions responsible for stabilizing water in oil emulsions”[68]

3.3.2 Procedures of MTLF Technique

In this experiment, a water-in-diluted bitumen film was formed using the procedure described in section 3.2.2. The morphology and lifetime of the thin liquid film were recorded. After a desired time, the film was reverted to a thick film by pushing oil liquid from the capillary back into the porous glass disc. After that, demulsifier solution in the micro-syringe was dispensed into the small droplets (~2uL) and deposited onto the porous glass disc. The demulsifier solution was dosed into the film with these small droplets absorbed into the oil phase in the capillary due to the hydrophobic treatment of porous glass disc and capillary force. To dispense the demulsifier into oil phase uniformly, the droplets should be deposited at different locations near the center of the hole on glass disc. The oil phase and demulsifier solution droplets can be mixed by withdrawing and pumping oil liquid in the capillary into the disc. In each experiment, at least five times of mixing processes were conducted to ensure well mix of demulsifier in oil liquid film. The thin liquid film was then generated and film properties were studied using the procedures described above.

The final concentration of demulsifiers in the thin liquid film (C_d) was calculated using the following formula:

$$C_d = \frac{V_{d0} \cdot C_{d0}}{V_{d0} \cdot \rho_{d0} + m_r} \qquad （2）$$

where C_{d0} is the concentration of demulsifier in the original demulsifier solution, V_{d0} is the volume of demulsifier solution added, ρ_{d0} is the density of the original demulsifier solution and m_r is the total mass of the oil liquid, including both oil in the glass plate and in the capillary. It should be noted that the local concentration of demulsifier would be higher than the value calculated using equation 2. Unfortunately, the actual concentration in the film cannot be determined as the actual volume of thin liquid oil film and oil in the capillary is not known.

Chapter 4 Results and Discussion

The dewatering process of water-in-oil emulsions in petroleum industry is often conducted through water droplets coalescence, which strongly depends on thin liquid film stability between oil-water interfaces. In the thin liquid film technique, the film stability against coalescence is evaluated by lifetime of thin film, which is the time measured from film formation to film rupture. Based on the results from previous study, films that can survive for more than 25 min are considered stable.[41]

In this chapter, a formula to form stable water-in-diluted bitumen emulsion film is determined in order to further study the effect of demulsifiers on thin liquid film. Two different demulsifier addition systems (premixing system and dosing system) are compared to understand the interactions between demulsifier and interfacially active materials from diluted bitumen. Two kinds of demulsifiers EC with different molecular weights are evaluated via dosing system to study the film stability and properties. To further understand demulsification performance and mechanism on thin liquid films, two commercial demulsifiers of EO-PO are used in our experiment.

4.1 Diluted Bitumen Films

To understand the effect of demulsifiers on physical properties of thin liquid emulsion film, a formula that can form a stable water/diluted bitumen/water film was determined. 50 wt.% bitumen in 80:20 heptol solution was used throughout this study, as the film formed by this solution can survive for more than 25 min as described in the work of Tchoukova et al.[42]

As shown in Figure 4-1, the film drainage process proceeds in three stages. (1) A dimple shape appeared. (2) The dimple drained out into a meniscus in less than one minute due to pressure difference between concave and convex and disjoining pressure. (3) The film continued to drain into a film of relatively homogeneous film thickness. This drainage process agrees with the results from previous studies.[42]

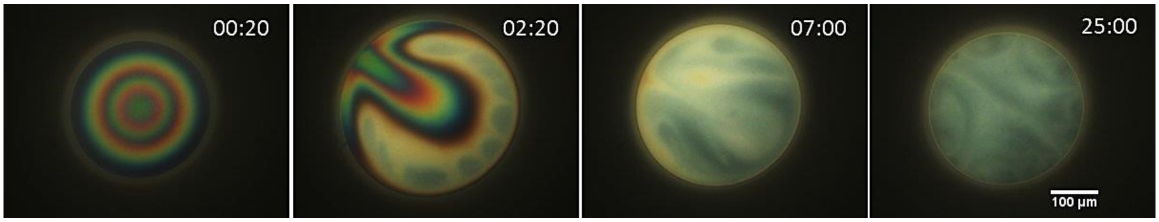


Figure 4-1 Film drainage of water-in-diluted bitumen emulsion film (50 wt.% bitumen in 80:20 heptol). The scale bar is 100 μm and stamps show the time after film formation in minutes:seconds.

After the film drainage of diluted bitumen film was analyzed, the effect of centrifuging the diluted bitumen and ageing time on film lifetime and properties was studied in detail. Films formed from diluted bitumen before and after centrifugation as well as samples aged for 1 hour and 3 hours were compared in this work. The results showed that films can survive for more than 25 minutes for all the cases and no significant difference in film morphology was observed. To simplify film system and focus on the study of demulsifiers, centrifuged diluted bitumen samples were used throughout the experiment.

4.2 Two Demulsifier Addition Systems

4.2.1 Premixing System

In premixing system, demulsifier EC300 was first mixed well with diluted bitumen and the mixture was then used as oil phase to form thin liquid film. Different ageing times were studied to determine ageing effect and explore demulsification mechanisms.

The images shown in Figure 4-2 (A) and (B) are films in the same experiment with different ageing times. With low concentration of EC300, (e.g. 1ppmw), aging time showed no significant effect on lifetime and morphology of films formed from premixed solutions of diluted bitumen and EC300. Both films drained quickly and were very unstable, rupturing within 30 seconds. Some white dots appeared in the film and became more visible with increasing demulsifier concentration.

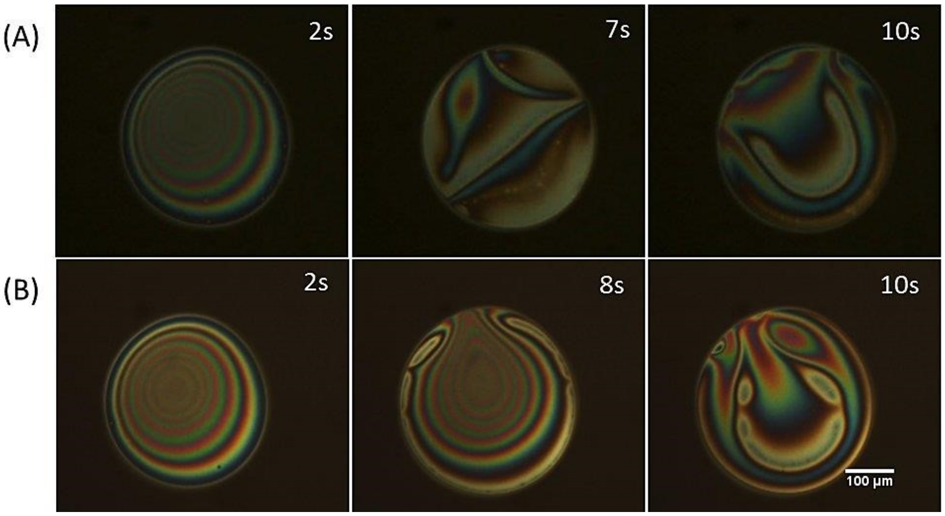


Figure 4-2 Film drainage of mixture of 1 ppmw EC300 with 50 wt.% bitumen in 80:20 heptol aged for 1h (A) and 3h (B). The scale bar is 100 μm and stamps show the time after film formation in seconds.

On the contrary, films formed from mixture of diluted bitumen and high concentration of EC300 showed very different lifetime and features at different ageing time. Figure 4-3 shows the film drainage of mixture of diluted bitumen and 197 ppmw EC300 in the same experiment after ageing for 1 hour (A) and 3 hours (B). Film in Figure 4-3A was formed 1 hour after initial oil-water interface contact. The film drained relatively slowly and could survive for around 3 minutes. With increasing ageing time, the film did not drain into meniscus but formed some black areas, representing thinner areas in the film.

After the film in Figure 4-3A ruptured, the diluted bitumen solution in the capillary was slowly pushed back into the disc to form a thick film again. Then this oil-water interface was left to contact for another ageing time. After being aged for 3 hours, the film in Figure 4-3B was formed. The film was far more stable, which could survive for more than 25 minutes. The black areas which were similar to Figure 4-3A appeared in the film and finally occupied the whole film except some dimples trapped inside, indicating the presence of some immobile areas. Meanwhile, the white spots became much clearer. These white spots were the areas with greater film thickness, which were probably caused by small aggregates. Based on the report of Tchoukov et al., these white spots are most likely the asphaltene aggregates from diluted bitumen.[41] The images in Figure 4-3 indicate that high concentration of EC300 allows EC300 more competitively to diffuse and adsorb to the interface with the increased ageing time. The additional ageing time can also facilitate the aggregation in diluted bitumen.

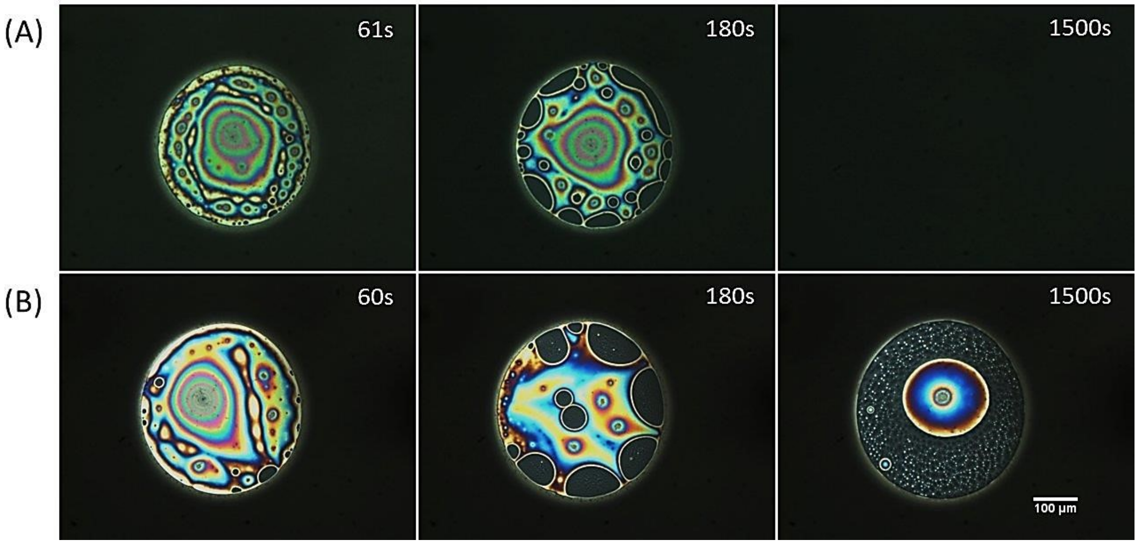


Figure 4-3 Film drainage of mixture of 197 ppmw EC300 with 50 wt.% bitumen in 80:20 heptol aged for 1h (A) and 3h (B). The scale bar is 100 μm and stamps show the time after film formation in seconds.

To evaluate the thin film stability against coalescence, film lifetime was measured. Films that can survive for more than 25 minutes were considered stable. The lifetimes of films formed from the mixture of EC300 and diluted bitumen after being aged for 1h and 3h are shown in Figure 4-4. For unstable films, 6 films were measured for each concentration to obtain the standard deviations, while 3 times were measured for films that did not rupture within 25 minutes. For concentrations of EC300 below 30 ppmw, films aged for both 1 hour and 3 hours ruptured within 30 seconds after the film formation, which indicate EC300 below 30 ppmw could efficiently prevent the formation of stable interfacial films with a negligible effect of film ageing time on film lifetime. The film lifetimes increased slightly, but still within 1 minute with increasing EC300 concentration from 30 ppmw to 65 ppmw. The difference in film lifetime between different ageing times increased gradually. However, the films aged for 1 hour and 3 hours showed very different lifetimes, forming stable films after aged for 3 hours with above 200 ppmw EC300 addition. For low concentrations, the competitive adsorption of EC300 with the interfacially active components in diluted bitumen causes asphaltenes aggregation and makes films less stable. At high concentration EC300 addition, excessive EC300 at the diluted bitumen-water interface could stabilize the interfacial film to some extent. Those findings were consistent with the previous results from Hou et al.[59]

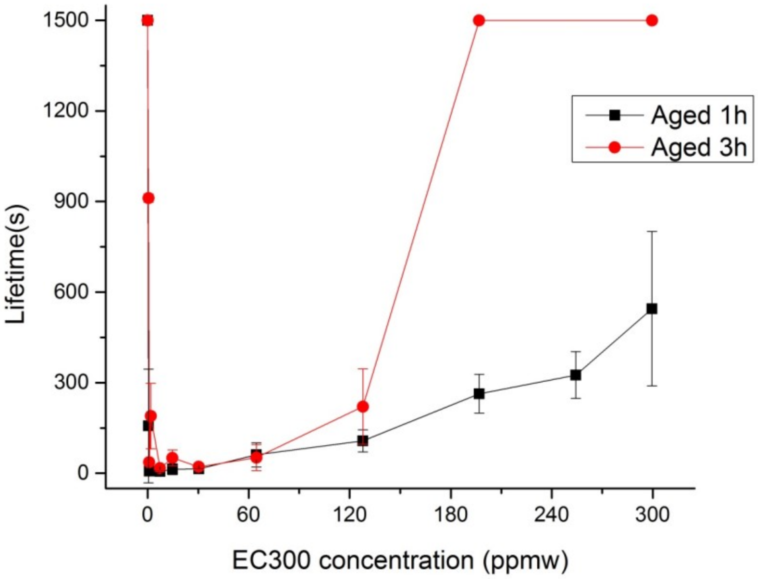


Figure 4-4 Lifetime of films obtained from mixture of EC300 and 50 wt.% bitumen in 80:20 heptol as a function of EC300 concentration after the film being aged for 1h and 3h.

4.2.2 Dosing System

To further simulate the real dewatering process, a novel modified thin liquid film technique was introduced, in which demulsifier EC300 was added into an already formed diluted bitumen film. The morphology of films formed via dosing system with different EC300 concentrations showed interesting features. As shown in Figure 4-5a, the addition of low concentration of EC300 (i.e. 10 ppmw) to diluted bitumen film led to a very unstable film with lifetime less than 30 seconds. Although some small aggregates appeared in the film, the film still could form a dimple of regular shapes. With increasing EC300 concentration to 39 ppmw, the film changed dramatically to be thick and inhomogeneous, as shown in Figure 4-5b. Due to uneven film thickness, the film became colorful, which was caused by the increasing amount of aggregates of different sizes in the film. When 102 ppmw EC300 was dosed into the diluted bitumen film, the film became stable again and the change of the film features can be divided into several stages, as shown in Figure 4-5c. Initially, a colourful film of uneven thickness with lots of aggregates formed. Then a new thin liquid film layer formed quickly beneath the initial film. Although the film kept draining, it still trapped a few dimples inside. Finally, the film cracked into two domains: a thinner region and a thicker region. Feng et al. reported similar findings on AFM images of LB films formed at the heptol-water interface.[58] They showed that the addition of EC could partially break interfacial films, forming heterogeneous interface with a few micro-domains of greater film thickness. Although AFM imaging and thin liquid film technique are on different scales, they showed similar phenomenon. The change of the domains from immobile to mobile at the interface suggests a significant modification of the oil-water interface by demulsifiers to a state where asphaltene aggregates can no longer attach firmly to the interface.

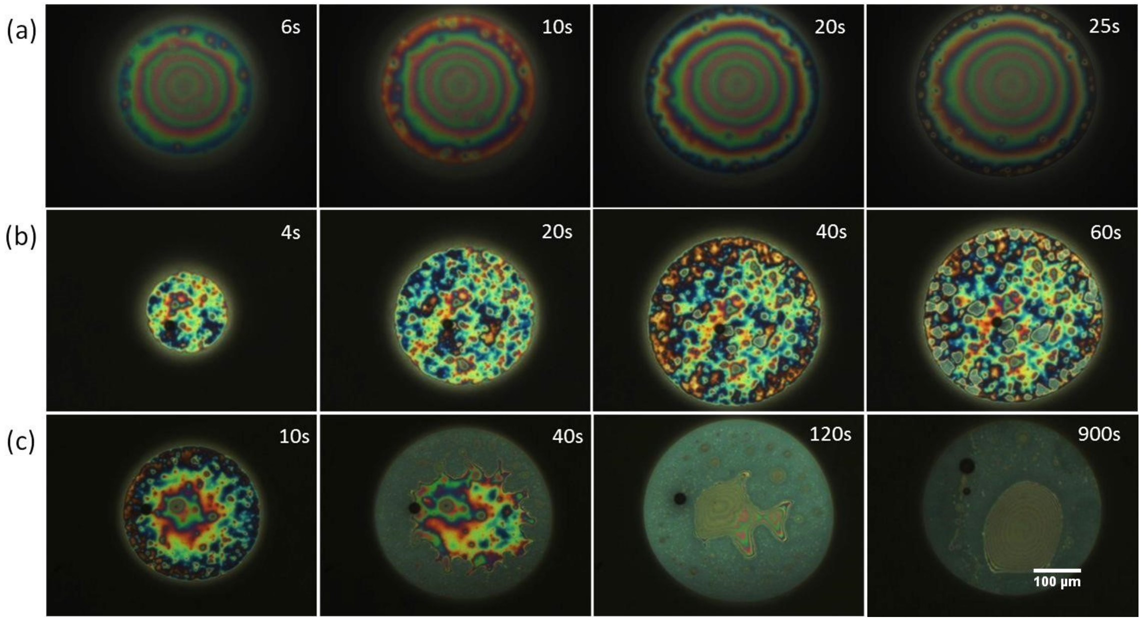


Figure 4-5 Film drainage of dosing different concentrations of EC300 into 50 wt.% bitumen in 80:20 heptol film at 10 ppmw EC300 (a); 39 ppmw EC300 (b) and 102 ppmw EC300 (c). The scale bar is 100 μm and stamps show the time after film formation in seconds.

To better understand the film behavior with EC300 addition, we investigated drainage of films formed from EC in 80:20 heptol and toluene solutions. As shown in Figure 4-6, 200 ppmw EC300 in both toluene and 80:20 heptol solutions can stabilize the film on its own, but showed very different film behaviors. The film formed from EC300 in 80:20 heptol shown in Figure 4-6a was highly heterogeneous and almost identical to the new film layer formed in the film of Figure 4-5c, while the film formed from EC300 in toluene shown in Figure 4-6b was relatively homogenous. Therefore, we could conclude that when high concentration of EC300 was added into the diluted bitumen film, part of EC300 competed with asphaltene, while extra EC300 formed a new film layer at the oil-water interface on its own with great stability. The steric interaction between EC300 molecules in the EC film and at the original oil-water interface led to a stable film, even when the original film layer was cracked. Pensini et al. reported in the work of studying demulsification mechanism of EO-PO demulaifiers that high concentration of demulsifiers preferred to form thick films, which would likely increase steric repulsion between water droplets and prevent them from coalescence, thus showing the overdose effect.[55]

The quality of solvent can significantly affect the film behavior of films formed by EC300. As shown in Figure 4-6a, the film from EC300 in 80:20 heptol solution formed a number of aggregates and trapped some small dimples inside, indicating some immobile areas in the film, while the film of EC300 in toluene solution as shown in Figure 4-6b was homogenous. That means the aggregates appeared in film of dosing high concentration of EC300 into diluted bitumen were caused by both asphaltene and EC300 aggregation due to poor solvent quality of heptol.

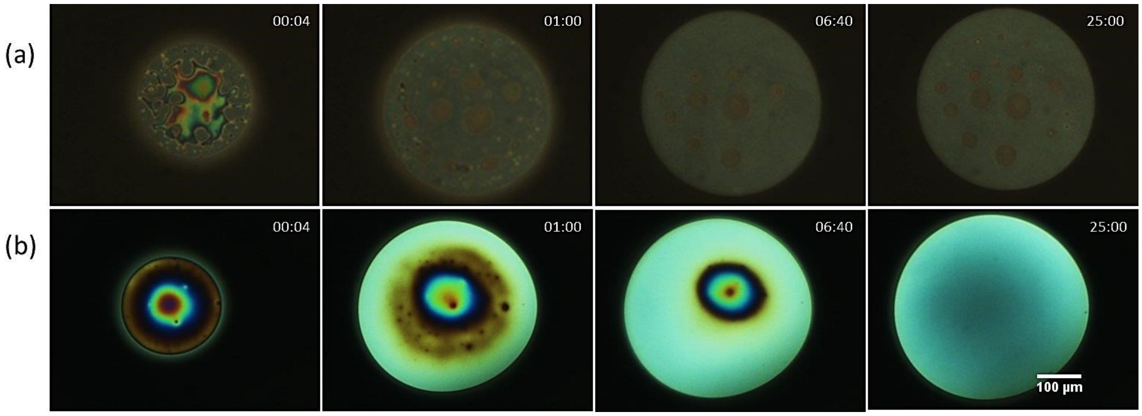


Figure 4-6 Film drainage of EC300 in different solvents. (a) 200 ppmw EC300 in 80:20 heptol solution; and (b) 196 ppmw EC300 in toluene solution. The scale bar is 100 µm and stamps show the time after film formation in minutes:seconds.

The lifetime of films formed by EC300 in 80:20 heptol solution is shown in Figure 4-7. For the solution with EC300 concentration 73 ppmw, the water-EC300 in heptol-water film ruptured rapidly within 10 seconds. With increasing EC300 concentration to 127 ppmw, the film stability was slightly increased, resulting in a lifetime of around 2 minutes. Further increasing EC300 concentration to more than 200 ppmw led to formation of stable film, showing a lifetime of more than 25 minutes, which indicates the ability of EC300 to stabilize film on its own. This result further confirms the reason of overdose effect.

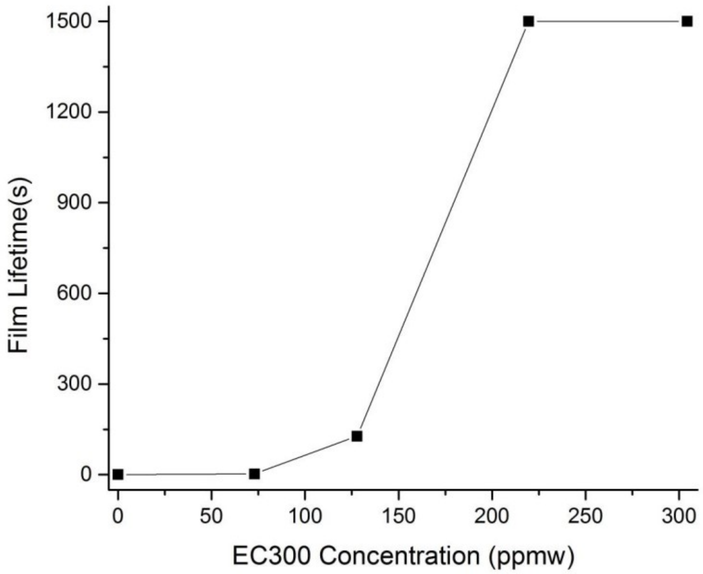


Figure 4-7 Lifetime of films formed from EC300 in 80:20 heptol solutions as a function of EC300 concentration.

Figure 4-8 shows the film lifetime after adding different amount of EC300 into already formed diluted bitumen films. Although the film formed by diluted bitumen solution is stable, which can survive for more than 25 min, very low dosage of EC300 (e.g. 1 ppmw) can reduce its film lifetime to less than 30 seconds. For concentration below 71 ppmw, EC300 can efficiently break the film within a very short period of time. However, further increase in EC300 concentration increased film lifetime to some degree, i.e., becoming less effective in breaking already formed bitumen films. This overdose phenomenon indicates that EC300 can stabilize film on its own, which agrees with the results shown in Figure

4-7. With low concentration addition, EC300 caused asphaltene aggregation and destabilized the water-in-diluted bitumen emulsions, while the addition of high concentration EC300 resulted in thick films, which would likely increase steric repulsion between the water droplets and prevent coalescence, thus showing overdose effect.

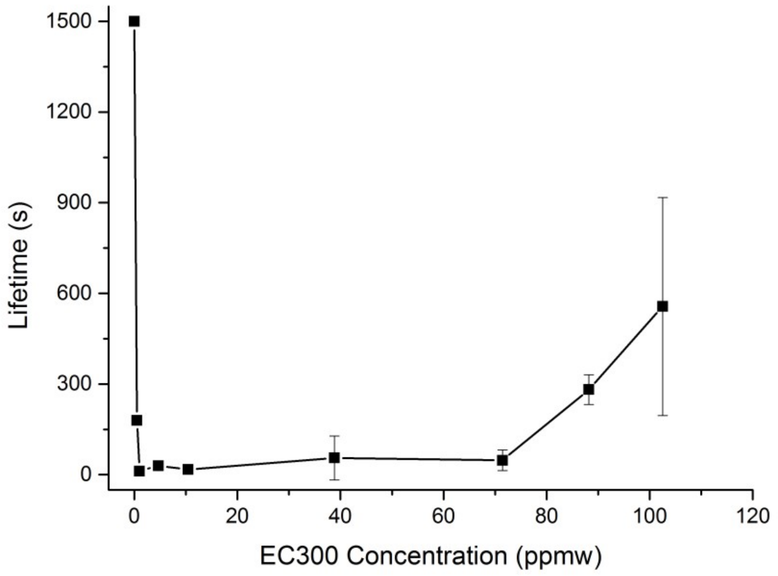


Figure 4-8 Lifetime of films obtained from dosing EC300 into films formed by 50 wt.% bitumen in 80:20 heptol as a function of EC300 concentration.

Figure 4-9 compares lifetime of films formed from 50 wt.% bitumen in 80:20 heptol change with different EC300 dosages by premixing and dosing protocols. The results illustrated similar film breaking efficiency of EC300 at low concentration (i.e. lower than 70 ppmw) for both premixing dosing protocols, reducing film lifetime to less than 1 minute, as EC300 could diffuse quickly to the interfacial layers and thus accelerate film coalescence. In contrary, for high concentration of EC300, especially when overdose phenomena occurred of 80 ppmw, the dosing protocol appears to be more sensitive to overdose, showing a much weaker ability to break the films. It appears that local high concentration of EC300 in dosing system could facilitate EC300 to form its own film quickly while competing with the surface active materials at the oil-water interface. Such local concentration difference between these two EC300 addition protocols led to the observed film behavior that stable thin liquid film could be obtained at a lower EC300 concentration with dosing protocol than with premixing protocol.

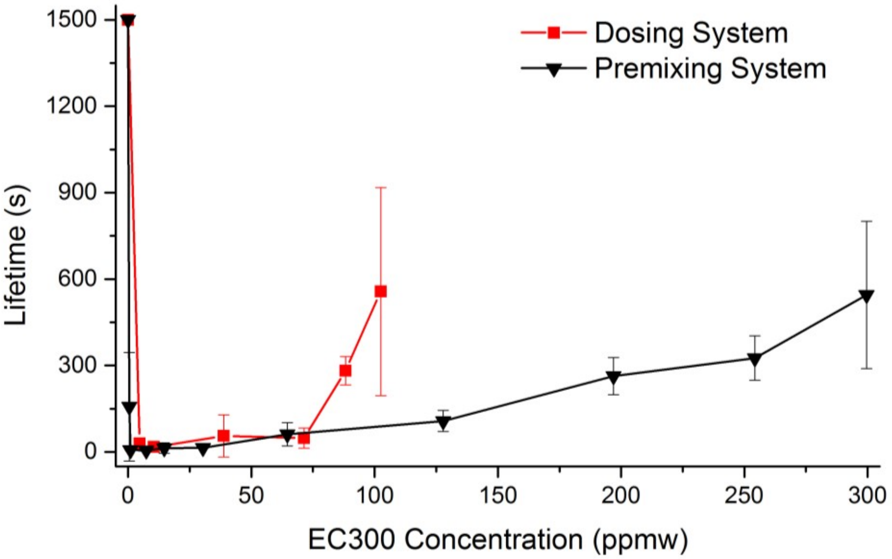


Figure 4-9 Lifetime of films obtained from dosing protocol and premixing protocol as a function of EC300 concentration.

4.3 Evaluating Demulsification Efficiency Using MTLF Technique

Using the modified thin liquid film technique, we further studied the behavior of films formed by 50 wt.% bitumen in 80:20 heptol after dosing with different demulsifiers, in an attempt to investigate whether MTLF technique could be used to evaluate the performance of demulsifiers.

4.3.1 Comparison between EC300 and EC4

In this set of experiments, two kinds of EC (EC4 and EC300) with the same ethoxyl content but different molecular weights were used. After adding EC4 into diluted bitumen film via dosing protocol in MTLF technique, the film showed different behaviors from EC300. As shown in Figure 4-10, the film morphology at low EC4 concentration was similar to that of EC300. The most important difference is for the high concentration of EC4 that there was no new film layer and cracked layer did not form in the film, as shown in Figure 4-10c. Instead, the film continued to drain and formed a thin and uniform film. This finding suggests that the lower molecular weight EC4 improved its ability to be incorporated into the original interfacial film. The diluted bitumen film after dosing 210 ppmw of EC4 remained stable, having a lifetime longer than 25 min. Another different aspect shown in Figure 4-10b is that the liquid in the film after dosing 50 ppmw EC4 was very flexible and could drain into regular shape dimple, even for films of initially uneven thickness.

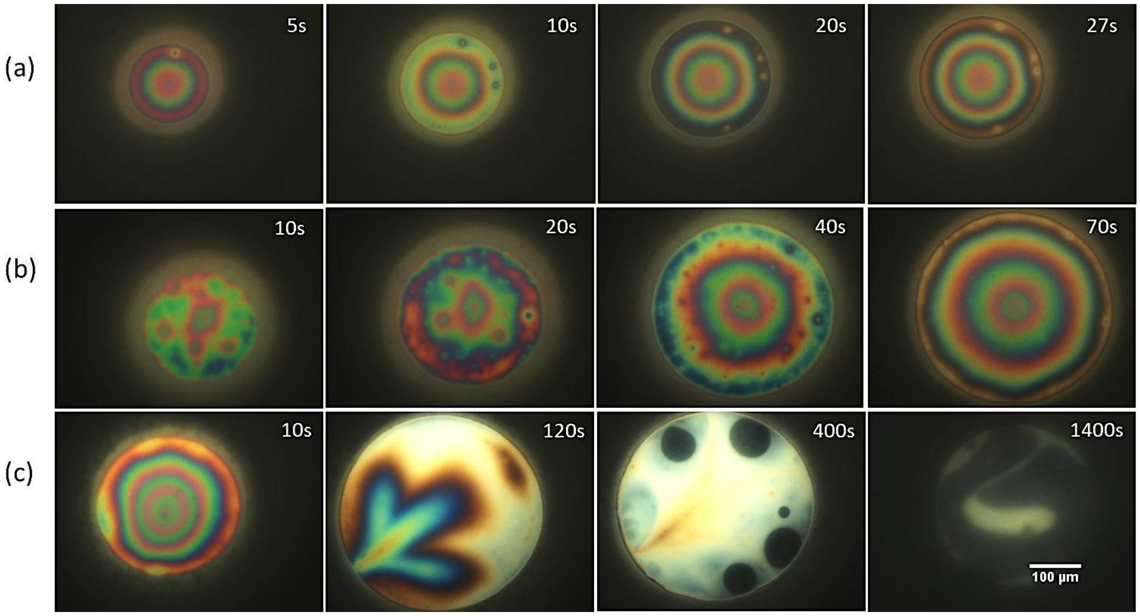


Figure 4-10 Film drainage of dosing different concentrations of EC4 into 50 wt.% bitumen in 80:20 heptol solutions. (a) 10 ppmw EC4; (b) 50 ppmw EC4; and (c) 210 ppmw EC4. The scale bar is 100 μm and stamps show the time after film formation in seconds.

To understand the film behavior of EC4, films from 210 ppmw EC4 in 80:20 heptol and toluene solutions were formed and recorded, as shown in Figure 4-11. Similar to films formed from EC300 in heptol and toluene solutions, films formed from EC4 in both solutions can survive for more than 25 min, and the aromaticity of solvent determined whether aggregates formed initially. It can be seen from Figure 4-11a that the film drained quickly into a flexible and uniform film with small dimples trapped inside within 1 second for EC4 in 80:20 heptol. The film in Figure 4-11b formed by EC4 in toluene also drained quickly but finally resulted in a very thin film. When high concentration of EC was added into diluted bitumen film, the film stability and features were dominated by the nature of EC.

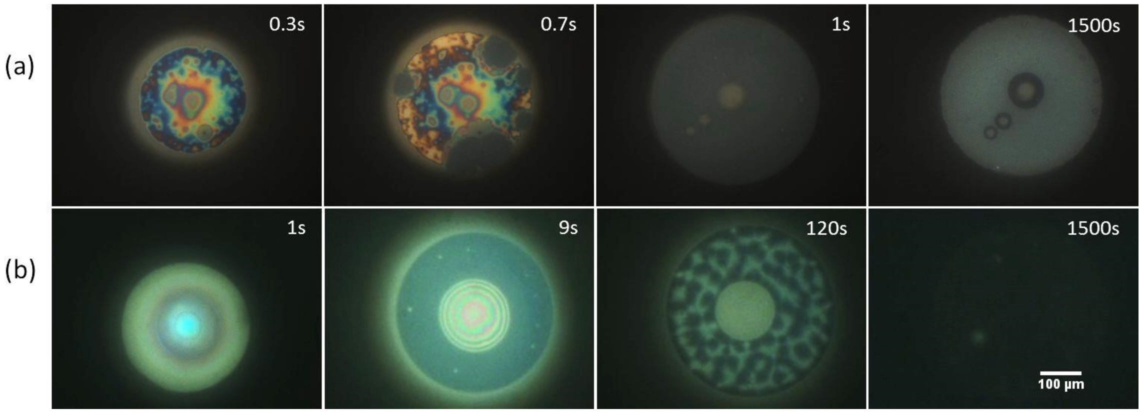


Figure 4-11 Film drainage of 210 ppmw EC4 in (a) 80:20 heptol and (b) toluene.

Figure 4-12 shows the change of film lifetime with dosing different concentrations of EC4 into the films formed from 50 wt.% bitumen in 80:20 heptol. The addition of 1 ppmw EC4 could efficiently break the diluted bitumen film, resulting in film lifetime of less than 30 seconds. However, further increase in EC4 dosage weakened its ability to break the interfacial film, with lifetime around 70s for 50 ppmw and 144s for 87 ppmw. When the concentration of EC4 was increased to 200 ppmw, the diluted bitumen showed great stability again with lifetime longer than 25 min.

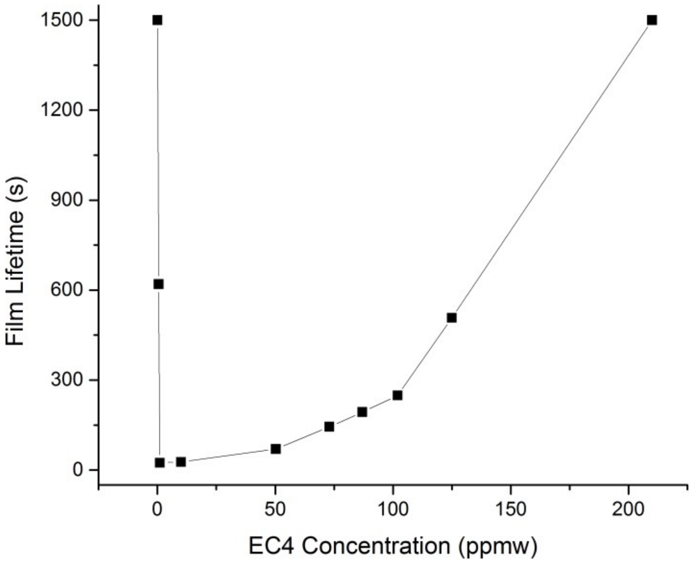


Figure 4-12 Lifetime of films obtained by dosing EC4 into the films formed from 50 wt.% bitumen in 80:20 heptol as a function of EC4 concentration.

Figure 4-13 compares the lifetime change of diluted bitumen film after dosing different concentrations of EC300 and EC4. Despite of the large difference of molecular weight, EC300 and EC 4 presented very similar film breaking efficiency. EC300 showed a slightly stronger ability to break diluted bitumen film than EC4 at 0.5 ppmw, lowering film lifetime to around 3 min and 10 min, respectively. However, both of their optimal concentrations were at 1 ppmw, at which diluted bitumen film broke in less than 30 seconds. Overdose effect was observed when the concentration was increased to 75 ppm for EC4 and 90 ppm for EC300. Feng et al. reported results of water content as a function of EC dosage, illustrating similar demulsification efficiency for the EC4 and EC300 which have drastically different molecular weight (46 000 vs 182 000 Da).[56]

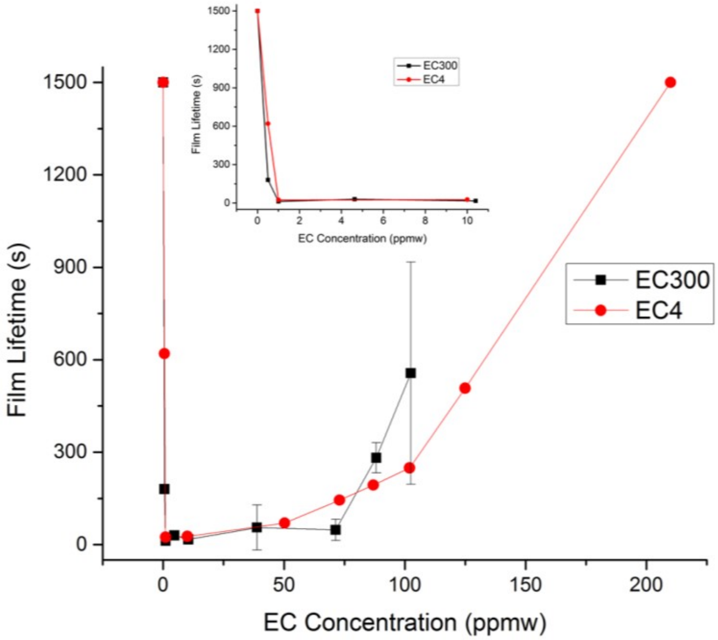


Figure 4-13 Lifetime of films obtained from dosing EC300 and EC4 into the films formed by 50 wt.% bitumen in 80:20 heptol as a function of EC concentration.

4.3.2 Comparison between EO-PO 86H and EO-PO 16H

EO-PO, another type of demulsifiers commercially available was also evaluated by the MTLF technique. Figure 4-14 shows film drainage processes after dosing 100 ppmw EO-PO 86H and EO-PO 16H into diluted bitumen films. The addition of EO-PO 86H with higher molecular weight and more arm numbers resulted in the formation of much more inhomogeneous films than the films with 16H addition. It seems that some aggregates of 86H demulsifier were formed, but they were not sufficient to stabilize the film.

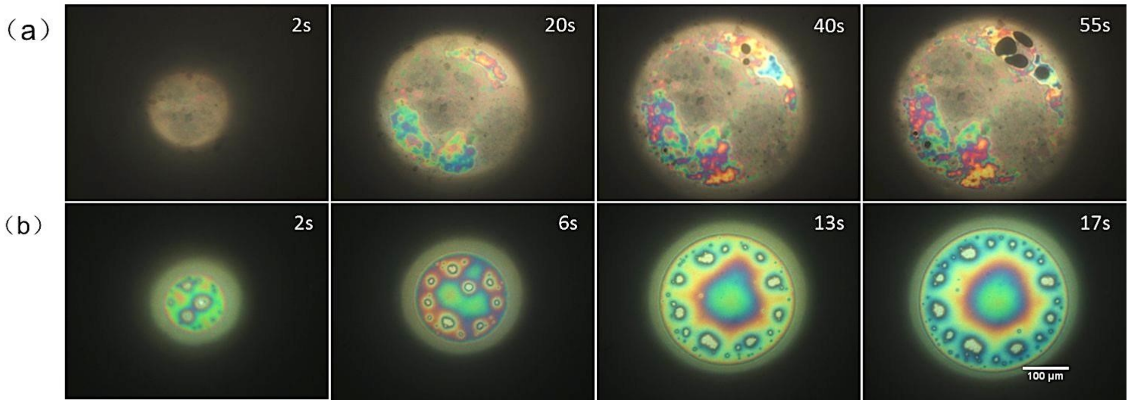


Figure 4-14 Film drainage of dosing 100 ppmw (a) EO-PO 86H and (b) EO-PO 16H into films formed by 50 wt.% bitumen in 80:20 heptol. The scale bar is 100 μm and stamps show the time after film formation in seconds.

The lifetime change between EO-PO 86H and EO-PO 16H is compared in Figure 4-15. Neither 1 ppmw 86H nor 1 ppmw 16H was able to shorten the film lifetime. At the concentration of 5 ppmw, 86H reduced the lifetime of diluted bitumen film to around 12 min, while the film lifetime after adding EO-PO 16H was around 20 min. This finding means that for low concentration of EO-PO, 86H was more efficient than 16H for breaking oil-water films. This trend applied to EO-PO concentrations less than 100 ppmw. Such difference can be explained by the increased molecular weight of 86H.

A lot of research has been conducted for the correlation between the molecular weight of demulsifiers and their corresponding demulsification performance. A direct relationship had been established.[19,54,69,70] Wu et al. investigated the effect of varying molecular weights on the performance of a number of demulsifiers.[43] They concluded that the EO-PO copolymers with RSN values 7.5-12.5 and molecular weights 7500-15000 Da had the highest efficiency for dewatering water-in-diluted bitumen emulsions. Kailey and Feng found that the dewatering efficiency of EO-PO demulsifiers had the same trend with their molecular change, e.g., increasing molecular weight resulted in higher dewatering efficiency. Another reason that can explain the higher film breaking ability is the increased polymer arm numbers of EO-PO 86H. Kailey and Feng also observed that the EO-PO copolymers with five branches had better dehydration efficiency than those with three branches, indicating that demulsifiers of more arm numbers have higher dehydration ability.[54] The knowledge obtained in this study can provide useful ideas for selecting suitable demulsifiers to destabilize water-in-oil emulsions.

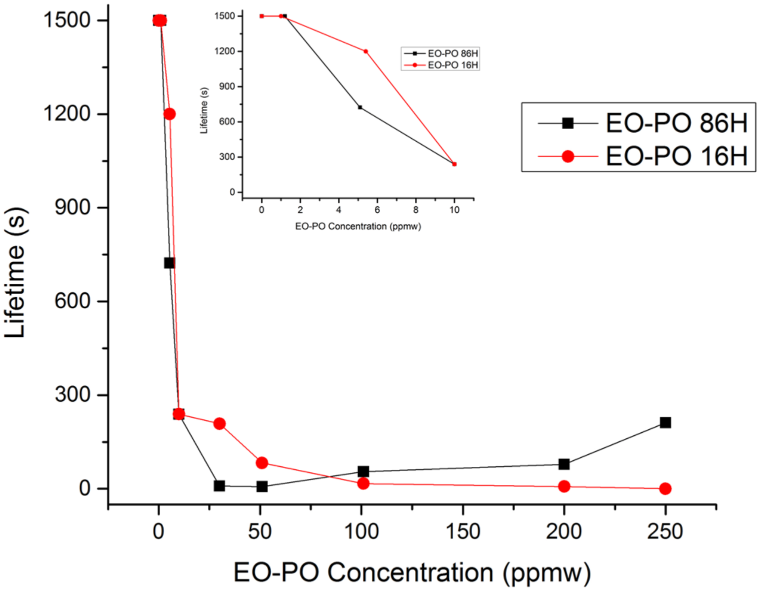


Figure 4-15 Lifetime of films obtained from dosing EO-PO 86H and EO-PO 16H into the films formed by 50 wt.% bitumen in 80:20 heptol as a function of EO-PO concentration.

4.3.3 Comparison between EC and EO-PO

Figure 4-16 shows the lifetime changes of diluted bitumen films after different demulsifiers were dosed into the system, including EC300, EC4, EO-PO 86H and EO-PO 16H. From this figure, we can see that both EC300 and EC4 were more efficient to break interfacial films than EO-PO, achieving film break at low concentration of demulsifiers addition. After adding 1 ppmw demulsifiers for example, EC300 and EC4 can shorten film lifetime to less than 30 seconds, while the film lifetimes of adding both EO-PO 86H and 16H were more than 25 min. To reach that efficiency, the concentrations of EO-PO 86H and 16H should be around 30ppm and 50 ppm, respectively. Therefore, the film breaking efficiency of these four demulsifiers were in the order of EC300 > EC4 > EO-PO 86H > EO-PO 16H. However, different with EC, the EO-PO used in this work had a much wider concentration window for effective demulsification, which means EO-PO can work in a wide range of concentrations for film breaking without overdose effect.

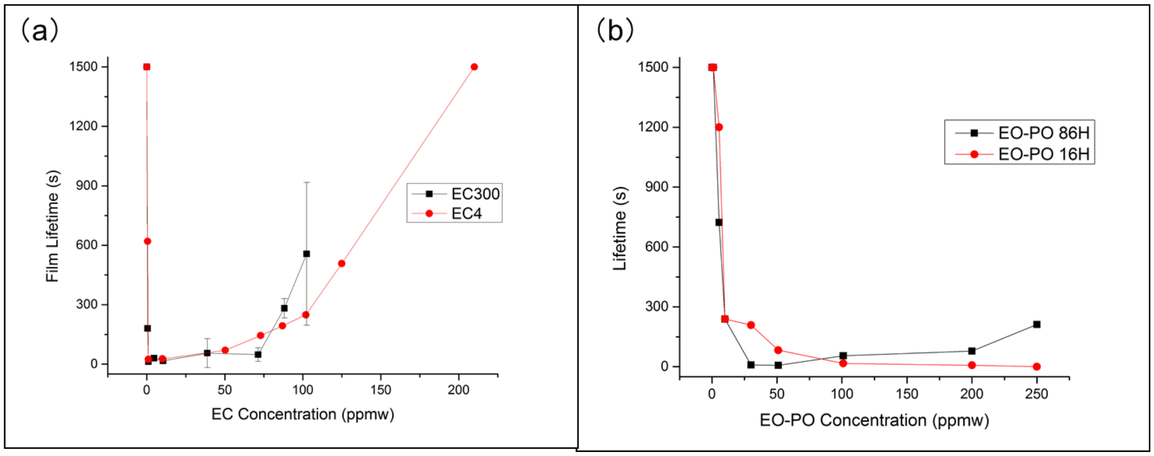


Figure 4-16 Lifetime of films obtained from dosing demulsifiers (a) EC300 and EC4 and (b) EO-PO 86H and EO-PO 16H into films formed by 50 wt.% bitumen in 80:20 heptol as a function of demulsifiers concentration.

Chapter 5 Conclusions and Future Work

5.1 General Conclusions

Studies relating demulsification efficiency and mechanism to stability and morphology of intervening thin liquid films formed by droplet-droplet interactions are very limited. Most studies have mainly been conducted at air-water interface, which is very different from the real emulsion situation.[59,71] Another aspect normally happened in demulsification study, for instance the interfacial tension measurement, is that the demulsifiers are mixed with active materials from the oil phase to proceed further experiment, which also cannot mimic the real demulsification process.[53,58]

In this thesis, the Thin Liquid Film Technique and Modified Thin Liquid Film Technique were introduced to generate the intervening liquid films from droplet-droplet interactions for demulsification study. For the first time a systematic comparison between two demulsifiers addition protocols was conducted using EC300 as demulsifiers to clarify the possible effect of order of demulsifier addition on demulsification. The results showed that although EC300 obtained similar film breaking efficiency below concentration of 70 ppm from these two protocols, dosing protocol showed more sensitivity to overdose effect than premixing protocol. The differences in film morphology from these two protocols showed that the dosing protocol can reflect both competition process and displacement process, while only competition process can appear in the premixing system. This finding suggests that the Modified Thin Liquid Film technique can more closely mimic the real demulsification process in industry and can be used to study the molecular mechanism of how demulsifiers interact with oil-water interface and break the thin liquid films, while the Thin Liquid film technique can only be used to study systems with fixed constituents.

Using EC300 as a chemical demulsifier, the demulsification mechanism was studied via designing premixing system and dosing system. When low concentration of EC300 was added, the diluted bitumen film drained quickly, and was destructed in a short time as EC300 penetrated the diluted bitumen-water interface and caused asphaltene aggregation. The formation of stable films of 200 ppmw EC in heptol solution confirmed that EC300 can stabilize the film on its own, and explained the overdose phenomena that appeared when adding high concentration of EC300 into diluted bitumen film.

The demulsification performance of EC300, EC4, EO-PO 86H and EO-PO 16H in destabilizing the films of water-in-80:20 heptol diluted bitumen emulsions was evaluated by measuring the film lifetime. At low usage of demulsifier, EC300 showed a slightly greater efficiency than EC4 and both EC300 and EC4 showed greater film breaking ability than EO-PO 86H and EO-PO 16H, but with narrow concentration window. In comparison of EO-PO 86H with EO-PO 16H, EO-PO 86H with higher molecular weight and more arm numbers could destabilize the diluted bitumen films at a lower demulsifier concentration. However, 16H showed a wider concentration window for film breaking than 86H. In conclusion, the film break efficiencies of these four demulsifiers were in the order of EC300 > EC4 > EO-PO 86H > EO-PO 16H.

Although the modification for thin liquid film technique proves important for dmeulsifiaction study, it remains challenging to the measure the exact concentration of demulsifiers in the oil film. Increasing the times of mixing and decreasing the size of demulsifier solution droplets can be beneficial to homogenize demulsifier distribution. Another aspect we can count on is to control the amount of diluted bitumen solution initially. If the diluted bitumen solution can cover the porous glass disc with little extra amount in capillary, the errors of using equation 2 to calculate the concentration of demulsifiers in the oil films will be much smaller. Expert practice of MTLF technique will be needed to make this condition work.

This study shows that film breaking efficiency of demulsifiers is concentration-dependent and closely related to emulsion destabilization. This finding as well as the mechanisms of demulsification and overdose effect revealed from this work are required to be carefully considered when designing new demulsifiers or applying current demulsifiers to dewatering of water-in-petroleum emulsions.

5.2 Recommendations for Future Work

In our work, we observed that the films from demulsifers in different solvents showed very important and characteristic features. To gain better understanding on mechanism of demulsification by demulsifiers, it would be valuable and can provide more insights for formulation determination of demulsifiers in petroleum industry to establish systematic work about film thickness, morphology and stability of demulsifiers with different chemical nature as well as demulsifiers in solvents of different aromaticities.

The demulsifiers used in this work were all studied individually, however, in industry, blends of three or more kinds of demulsifies were synergistically used together to obtain better dewatering efficiency, compared with simple addition of individual components. Therefore, the Modified Thin Liquid Film technique could be applied to rapidly evaluate the performance of demulsifiers and properties of blends of individual components with different chemical nature and different mixing ratio.

In addition, to investigate more details of film disruption with demulsifiers addition, film thickness can be measured quantitatively and calculation of disjoining pressure can be conducted to understand more about interaction forces between two water droplets in diluted bitumen solutions during coalescence process. Furthermore, interfacial tension measurement can be used to compare the interfacial adsorption ability, and interfacial shear rheology can be introduced to study the mechanical property changes of the "protective skin" formed by the continual accumulation of asphaltenes at the oil-water interface after demulsifier addition. The combination of these results and information from modified thin liquid film technique can provide a better understanding of demulsification mechanisms of water-in-oil emulsions in petroleum industry.

The remaining solids in diluted bitumen product can stabilize emulsion in a different way as stabilizers in bitumen, known as pickering emulsion. With the MFTL technique, we can study the demulsification efficiency of different EC and EO-PO demulsifiers on pickering emulsion systems to confirm whether EC type demuldifiers still have higher film breaking efficiency than EO-PO type demulsifiers, thus moving forward the commercial application of EC type demulsifiers in petroleum industry.

References

1 Sieminski, A. International Energy Outlook. *Energy Information Administration (EIA)* (2014).

2 Jackson, P. M. & Eastwood, K. M. Finding the critical numbers: what are the real decline rates for global oil production. *CERA, Private Report–Client Services, Cambridge, MA, USA* (2007).

3 *Oil Sands Facts and Stats* <http://www.energy.alberta.ca/OilSands/pdfs/FactSheet_OilSands.pdf> (2015).

4 Masliyah, J., Zhou, Z. J., Xu, Z., Czarnecki, J. & Hamza, H. Understanding water‐based bitumen extraction from Athabasca oil sands. *The Canadian Journal of Chemical Engineering* **82**, 628-654 (2004).

5 Glassman, D., Wucker, M., Isaacman, T. & Champilou, C. The water-energy nexus. *Adding Water to the Energy Agenda, A World Policy Paper, EBG Capital, Environmental Investments* (2011).

6 *Talk about SAGD*, <http://www.energy.alberta.ca/OilSands/pdfs/FS_SAGD.pdf> (2013).

7 Rao, F. & Liu, Q. Froth treatment in Athabasca oil sands bitumen recovery process: a review. *Energy & Fuels* **27**, 7199-7207 (2013).

8 Long, Y., Dabros, T. & Hamza, H. Stability and settling characteristics of solvent-diluted bitumen emulsions. *Fuel* **81**, 1945-1952 (2002).

9 Kokal, S. L. Crude oil emulsions: A state-of-the-art review. *SPE Production & Facilities* **20**, 5-13 (2005).

10 Romanova, U. G., Yarranton, H. W., Schramm, L. L. & Shelfantook, W. E. Investigation of oil sands froth treatment. *The Canadian Journal of Chemical Engineering* **82**, 710-721 (2004).

11 Madge, D. N. & Garner, W. N. Theory of asphaltene precipitation in a hydrocarbon cyclone. *Minerals Engineering* **20**, 387-394 (2007).

12 Lissant, K. J. Emulsions and emulsion technology. *Soil Science* **120**, 160 (1975).

13 Berg, J. C. *An introduction to interfaces & colloids: the bridge to nanoscience*. (World Scientific, 2010).

14 Chevalier, Y. & Bolzinger, M.-A. Emulsions stabilized with solid nanoparticles: Pickering emulsions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **439**, 23-34 (2013).

15 Masliyah, J., Czarnecki, J. & Xu, Z. Handbook on theory and practice of bitumen recovery from Athabasca oil sands. *Vol. I. Theoretical basis* (2010).

16 Vignati, E., Piazza, R. & Lockhart, T. P. Pickering emulsions: interfacial tension, colloidal layer morphology, and trapped-particle motion. *Langmuir* **19**, 6650-6656 (2003).

17 McLean, J. D. & Kilpatrick, P. K. Effects of asphaltene solvency on stability of water-in-crude-oil emulsions. *Journal of Colloid and Interface Science* **189**, 242-253 (1997).

18 Yan, Z., Elliott, J. A. W. & Masliyah, J. H. Roles of various bitumen components in the stability of water-in-diluted-bitumen emulsions. *Journal of colloid and interface science* **220**, 329-337 (1999).

19 Wu, X. Investigating the stability mechanism of water-in-diluted bitumen emulsions through isolation and characterization of the stabilizing materials at the interface. *Energy & Fuels* **17**, 179-190 (2003).

20 Kilpatrick, P. K. Water-in-crude oil emulsion stabilization: Review and unanswered questions. *Energy & Fuels* **26**, 4017-4026 (2012).

21 Siffert, B., Bourgeois, C. & Papirer, E. Structure and water-oil emulsifying properties of asphaltenes. *Fuel* **63**, 834-837 (1984).

22 Nordli, K. G., Sjöblom, J., Kizling, J. & Stenius, P. Water-in-crude oil emulsions from the Norwegian continental shelf 4. Monolayer properties of the interfacially active crude oil fraction. *Colloids and Surfaces* **57**, 83-98 (1991).

23 Sheu, E. Y., Maureen, M., Storm, D. A. & DeCanio, S. J. Aggregation and kinetics of asphaltenes in organic solvents. *Fuel* **71**, 299-302 (1992).

24 Mohammed, R. A., Bailey, A. I., Luckham, P. F. & Taylor, S. E. Dewatering of crude oil emulsions 1. Rheological behaviour of the crude oil-water interface. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **80**, 223-235 (1993).

25 Yeung, A., Dabros, T., Czarnecki, J. & Masliyah, J. 1990 edn 3709-3723 (The Royal Society).

26 Yarranton, H. W., Hussein, H. & Masliyah, J. H. Water-in-hydrocarbon emulsions stabilized by asphaltenes at low concentrations. *Journal of Colloid and Interface Science* **228**, 52-63 (2000).

27 Taylor, S. D. *Colloidal interactions in water-in-diluted-bitumen emulsions*. (2003).

28 Yeung, A., Dabros, T., Masliyah, J. & Czarnecki, J. Micropipette: a new technique in emulsion research. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **174**, 169-181 (2000).

29 Moran, K. & Czarnecki, J. Competitive adsorption of sodium naphthenates and naturally occurring species at water-in-crude oil emulsion droplet surfaces. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **292**, 87-98 (2007).

30 Gao, S., Moran, K., Xu, Z. & Masliyah, J. Role of bitumen components in stabilizing water-in-diluted oil emulsions. *Energy & Fuels* **23**, 2606-2612 (2009).

31 Wang, S., Liu, J., Zhang, L., Xu, Z. & Masliyah, J. Colloidal interactions between asphaltene surfaces in toluene. *Energy & Fuels* **23**, 862-869 (2008).

32 Wang, S., Liu, J., Zhang, L., Masliyah, J. & Xu, Z. Interaction forces between asphaltene surfaces in organic solvents. *Langmuir* **26**, 183-190 (2009).

33 Vuillaume, K. & Giasson, S. Interactions between mica surfaces across crude oil and asphaltene solutions. *The Journal of Physical Chemistry C* **113**, 3660-3665 (2009).

34 Wang, J. *et al.* Molecular interactions of a polyaromatic surfactant C5Pe in aqueous solutions studied by a surface forces apparatus. *The Journal of Physical Chemistry B* **116**, 11187-11196 (2012).

35 Czarnecki, J., Tchoukov, P. & Dabros, T. Possible role of asphaltenes in the stabilization of water-in-crude oil emulsions. *Energy & Fuels* **26**, 5782-5786 (2012).

36 Sheludko, A. Thin liquid films. *Advances in Colloid and Interface Science* **1**, 391-464 (1967).

37 Platikanov, D. & Exerowa, D. 6 Thin liquid films. *Fundamentals of Interface and Colloid Science* **5**, 1-91 (2005).

38 Exerowa, D., Kruglyakov, P. M., Möbius, D. & Miller, R. Foam and foam films: theory. *Experiment Application, Marcel Dekker, New York* (1998).

39 Khristov, K., Taylor, S. D., Czarnecki, J. & Masliyah, J. Thin liquid film technique-application to water–oil–water bitumen emulsion films. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **174**, 183-196 (2000).

40 Taylor, S. D., Czarnecki, J. & Masliyah, J. Disjoining pressure isotherms of water-in-bitumen emulsion films. *Journal of Colloid and Interface Science* **252**, 149-160 (2002).

41 Tchoukov, P. *et al.* Role of asphaltenes in stabilizing thin liquid emulsion films. *Langmuir* **30**, 3024-3033 (2014).

42 Tchoukov, P., Czarnecki, J. & Dabros, T. Study of water-in-oil thin liquid films: Implications for the stability of petroleum emulsions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **372**, 15-21 (2010).

43 Wu, J., Xu, Y., Dabros, T. & Hamza, H. Effect of demulsifier properties on destabilization of water-in-oil emulsion. *Energy & Fuels* **17**, 1554-1559 (2003).

44 Al-Sabagh, A. M., El-Din, M. R., Morsi, R. E. & Elsabee, M. Z. Demulsification efficiency of some novel styrene/maleic anhydride ester copolymers. *Journal of Applied Polymer Science* **108**, 2301-2311 (2008).

45 Zhang, L. Y., Xu, Z. & Masliyah, J. H. Langmuir and Langmuir-Blodgett films of mixed asphaltene and a demulsifier. *Langmuir* **19**, 9730-9741 (2003).

46 Lissant, K. J. Demulsification; Industrial Applications. (1983).

47 Solovyev, A., Zhang, L. Y., Xu, Z. & Masliyah, J. H. Langmuir films of bitumen at oil/water interfaces. *Energy & Fuels* **20**, 1572-1578 (2006).

48 Zaki, N. N., Abdel-Raouf, M. E. & Abdel-Azim, A. A. Propylene oxide-ethylene oxide block copolymers as demulsifiers for water-in-oil emulsions, II. Effects of temperature, salinity, pH-value, and solvents on the demulsification efficiency. *Monatshefte für Chemie/Chemical Monthly* **127**, 1239-1245 (1996).

49 Wu, J., Xu, Y., Dabros, T. & Hamza, H. Effect of EO and PO positions in nonionic surfactants on surfactant properties and demulsification performance. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **252**, 79-85 (2005).

50 Xu, Y., Wu, J., Dabros, T., Hamza, H. & Venter, J. Optimizing the polyethylene oxide and polypropylene oxide contents in diethylenetriamine-based surfactants for destabilization of a water-in-oil emulsion. *Energy & Fuels* **19**, 916-921 (2005).

51 Ramalho, J. B., Ramos, N. & Lucas, E. The influence of some interfacial properties of PEO-b-PPO copolymers on dewatering of water-in-oil asphaltene model emulsions. (2009).

52 Abdel - Azim, A. A. A., Zaki, N. N. & Maysour, N. E. S. Polyoxyalkylenated amines for breaking water-in-oil emulsions: effect of structural variations on the demulsification efficiency. *Polymers for Advanced Technologies* **9**, 159-166 (1998).

53 Kailey, I., Blackwell, C. & Behles, J. Collaborative interactions between EO-PO copolymers upon mixing. *Industrial & Engineering Chemistry Research* **52**, 17913-17919 (2013).

54 Kailey, I. & Feng, X. Influence of structural variations of demulsifiers on their performance. *Industrial & Engineering Chemistry Research* **52**, 785-793 (2013).

55 Pensini, E. *et al.* Demulsification mechanism of asphaltene-stabilized water-in-oil emulsions by a polymeric ethylene oxide–propylene oxide demulsifier. *Energy & Fuels* **28**, 6760-6771 (2014).

56 Feng, X., Xu, Z. & Masliyah, J. Biodegradable polymer for demulsification of water-in-bitumen emulsions. *Energy & Fuels* **23**, 451-456 (2008).

57 Feng, X. *et al.* Mechanistic study on demulsification of water-in-diluted bitumen emulsions by ethylcellulose. *Langmuir* **26**, 3050-3057 (2009).

58 Feng, X. *et al.* Effect of hydroxyl content and molecular weight of biodegradable ethylcellulose on demulsification of water-in-diluted bitumen emulsions. *Industrial & Engineering Chemistry Research* **50**, 6347-6354 (2011).

59 Hou, J., Feng, X., Masliyah, J. & Xu, Z. Understanding interfacial behavior of ethylcellulose at the water–diluted bitumen interface. *Energy & Fuels* **26**, 1740-1745 (2012).

60 Sjöblom, J., Söderlund, H., Lindblad, S., Johansen, E. J. & Skjärvö, I. M. Water-in-crude oil emulsions from the Norwegian continental shelf. *Colloid and Polymer Science* **268**, 389-398 (1990).

61 Fan, Y., Simon, S. & Sjöblom, J. Chemical destabilization of crude oil emulsions: effect of nonionic surfactants as emulsion inhibitors. *Energy & Fuels* **23**, 4575-4583 (2009).

62 Ese, M. H., Sjöblom, J., Djuve, J. & Pugh, R. An atomic force microscopy study of asphaltenes on mica surfaces. Influence of added resins and demulsifiers. *Colloid and Polymer Science* **278**, 532-538 (2000).

63 Fan, Y., Simon, S. & Sjöblom, J. Interfacial shear rheology of asphaltenes at oil–water interface and its relation to emulsion stability: influence of concentration, solvent aromaticity and nonionic surfactant. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **366**, 120-128 (2010).

64 Kim, Y. H. & Wasan, D. T. Effect of demulsifier partitioning on the destabilization of water-in-oil emulsions. *Industrial & Engineering Chemistry Research* **35**, 1141-1149 (1996).

65 Leermakers, F., Eriksson, J. C. & Lyklema, H. 4 Association colloids and their equilibrium modelling. *Fundamentals of Interface and Colloid Science* **5**, 1-123 (2005).

66 Exerowa, D. & Kruglyakov, P. M. (Elsevier, Amsterdam, 1998).

67 Scheludko, A. & Platikanowa, D. Utersuchung dunner flussiger schichten auf quecksilber. Kolloid Zeitschrift and Zeirschrift Fur Polymer **175**, 150 (1961).

68 Yang, F. *Bitumen fractions responsible for stabilizing water in oil emulsions*, (2016).

69 Rosen, M. J. Surfactants and interfacial phenomena (2nd end.) Wiley. *New York*, 39-55 (1989).

70 Al-Sabagh, A. M., Maysour, N. E., Naser, N. M. & El-Din, M. R. N. Synthesis and evaluation of some modified polyoxyethylene-polyoxypropylene block polymer as water-in-oil emulsion breakers. *Journal of Dispersion Science and Technology* **28**, 537-545 (2007).

71 Hua, Y. & Angle, C. W. Brewster angle microscopy of Langmuir films of athabasca bitumens, n-C5 asphaltenes, and SAGD bitumen during pressure–area hysteresis. *Langmuir* **29**, 244-263 (2012).