UNIVERSITY OF CALGARY

Effect of Surfactants on Asphaltene Interfacial Films and Stability of Water-in-Oil Emulsions

by

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A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE
DEGREE OF MASTER IN SCIENCE

DEPARTMENT OF CHEMICAL AND PETROLEUM ENGINEERING

CALGARY, ALBERTA
APRIL, 2009

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Abstract

Undesirable water-in-oil emulsions often form during oil processes. Chemical treatment is a common method for breaking down these emulsions; however, this technique is not always effective. In order to improve the chemical treatment of emulsions, it is useful to have an understanding of emulsion stability. The stability of water-in-oil emulsions depends in part on the surface properties. The surface is composed of natural material present in the produced oil, such as asphaltenes, resins, clays and surfactants, which adsorb on the water-oil interface. Asphaltenes play an important role in stabilizing the emulsion since they irreversibly adsorb at the interface of the water droplets and form a steric barrier or rigid skin that prevents coalescence. An effective demulsifier must disrupt this film in order to accelerate coalescence. However, the chemical treatment design is still done by trial and error partly because the effect of surfactants on interfacial films is poorly understood.

This thesis focuses on emulsions stabilized by asphaltene films. It was previously found that the stability of these emulsions could be predicted from both the compressibility and crumpling film ratio of irreversibly adsorbed asphaltene films. In this study, the effect of surfactants on asphaltene interfacial films is analyzed through the change in film properties. Surface pressure isotherms were measured at 23^{o}C for model interfaces between aqueous surfactant solutions and asphaltenes dissolved in toluene and heptane:toluene mixtures. Compressibility, crumpling film ratio and surface pressure were determined from the surface pressure isotherms. The stability of water-in-oil emulsions was determined for the same systems based on the free water resolved after repeated treatment involving heating at 60^{o}C and centrifugation. Experimental variables included concentration of asphaltenes (5 and 10 kg/m^3), concentration and type of surfactant (Aerosol OT, nonylphenol ethoxylates, dodecylbenzene sulfonic acids, sodium naphthenate) and aging time (from 10 min to 4 h). The effect of surfactants on film properties and emulsion stability was found to divide in two distinct behaviours. 1) surfactants that formed reversible films and destabilized emulsions and 2) surfactants that maintained the irreversible adsorption at the interface and could enhance emulsion stability.

Acknowledgements

I would like to express my sincere and deepest gratitude to my supervisor, Dr. H.W. Yarranton for his excellent guidance, encouragement and valuable advice during my Master's degree program. I also wish to thank Ms. Elaine Baydak for all her assistance and the great help that she provided during the experimental work.

I wish to thank Syncrude Canada Ltd. for the financial support and for providing the bitumen samples for the experimental work as well as Champion Technologies Ltd. for providing surfactant samples.

I thank the administrative and technical staff of the Department of Chemical and Petroleum Engineering for all their assistance throughout the duration of my master's studies.

I am grateful to the Asphaltene and Emulsion Research members at the University of Calgary for their support and assistance.

Finally, I would like to thank my family which is always encouraging and supporting me every moment.

Dedication

To my mom, Marlene Gonzalez, who always gives me all her support.

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A_t	total interfacial area (mm^2)
A_n	surface area per molecule (m^2/molecule)
b	radius of curvature at the apex of a drop
C_i	interfacial compressibility (m/mN)
C_A	asphaltene molar concentration (mol/m^3)
C	bulk surfactant concentration
d_{32}	Sauter mean diameter (m)
d	drop diameter (m)
f	frequency
g	gravity acceleration (9.8 m/s^2)
K	partition Coefficient
m_A	mass of asphaltenes (kg)
R_1	radius of curvature in x-z plane
R_2	radius of curvature in y-z plane
t	time (hr)
V	volume

Greek symbols

Γ_A	mass surface coverage (kg/m^2)
Γ	interfacial tension (mN/m)
γ	Interfacial tension (mN/m)
ΔP	pressure difference between phases (N/m^2)
θ	angle between R_2 and z-axis (°)
π	surface pressure (mN/m)
ρ	fluid density (kg/m^3)

Subscripts

‘0’	pure or initial
‘1’	component 1
‘2’	component 2
eq	equilibrium
‘i’	i^{th} drop
‘o’	Oil
‘w’	water

Abbreviations

‘AEP’	surfactant added after emulsion preparation
‘AOT’	aerosol OT
‘CP’	continuous phase
‘CR’	crumpling point
‘DBSA-B’	dodecylbenzene sulfonic acid branched
‘DBSA-L’	dodecylbenzene sulfonic acid linear
‘Heptol’	mixture of heptane and toluene
‘IFT’	interfacial tension
‘NEO’	nonylphenol ethoxylates
‘NEO-10’	nonylphenol ethoxylate with 10 ethoxy groups in the molecule
‘NEO-15’	nonylphenol ethoxylate with 15 ethoxy groups in the molecule
‘NEO-30’	nonylphenol ethoxylate with 30 ethoxy groups in the molecule
‘PR’	phase transition
‘SN’	sodium naphthenate

1. INTRODUCTION

Water-in-oil emulsions are known to form during crude oil production, oil sands extraction processes, and oil spills in aquatic environments. Often, these water-in-oil emulsions are undesirable since they can cause several problems including: 1) production of an off-specifications crude oil (high solids and water content, >0.5%); 2) corrosion and catalyst poisoning in pipes and equipment for water settling; and 3) environmental issues when oil spills occur over water (*e.g.* rivers and oceans). Treatment of these water-in-crude oil emulsions is still a challenge in the petroleum industry due to their high stability.

The stability of water-in-crude oil emulsions depends in part on the irreversible adsorption of asphaltenes at the oil-water interface (McLean & Kilpatrick. 1997). Asphaltenes create a steric barrier around the water droplets which prevents coalescence and hinders water separation from the emulsion (Yarranton *et al.* 2007b). Additionally, other natural materials present in oil sands, such as resins, clays and surfactants (*e.g.* naphthenic acids) also adsorb on the water-oil interface. When other material is adsorbed along with the asphaltenes, emulsion stability may increase, decrease, or not change at all. Depending on the emulsion stability, which is related to interfacial composition and film properties, water separation might take from minutes to years.

When water-in-crude oil emulsion formation and stabilization take place, additional treatments are required to break the emulsion and accelerate water separation. Along with heating, chemical treatment with demulsifiers (surface active agents) is the most common process for breaking emulsions; however, this technique is not always effective. The effect of demulsifiers on the surface of the emulsified water droplets in diluted bitumen is not well understood. In order to improve the chemical treatment for these emulsions, it is useful to have an understanding of the factors that contribute to the stabilization or destabilization of emulsions.

Previous work has shown that emulsion stability depends on the interfacial rheological properties such as interfacial elasticity, compressibility and crumpling film ratio (Yarranton *et al.* 2007a). Interfacial compressibility and crumpling film ratio were evaluated through surface pressure isotherms measured using a drop shape analyzer. It was shown that asphaltenes created a cross-linked network on the interface favouring the formation of a low compressibility film. It was also found that a low interfacial compressibility and high crumpling film ratio promoted emulsion stability.

When a surfactant is added to a water-in-crude oil emulsion, it must disturb the interface in order to destabilize the emulsion (Grace. 1992). However, it is not well understood how a surfactant affects the water-oil interface or how it enhances or decreases emulsion stability. In other words, how the interfacial rheological properties change with surfactant addition is still unclear. It is likely that the surfactant molecules replace asphaltenes on the interface. Hence, the interfacial film is weakened (becomes more compressible) as more surfactant molecules adsorb on the interface instead of asphaltenes. Weaker films are believed to favour coalescence and hence more unstable emulsions.

Numerous studies in this area have been based on empirical field results, usually with trial and error treatments using different concentrations and types of surfactants. Other studies have attempted to analyze film properties such as interfacial tension and elasticity. Nonetheless, the understanding of surfactant effects on asphaltene film properties and the relationship with emulsion stability is still lacking. This work attempts to have a better understanding of the surfactant phenomena in asphaltene films and emulsion stability. This thesis investigates the effect of different surfactants on interfacial film properties in the presence of asphaltenes and relates these effects to emulsion stability.

1.1. Objectives

The primary objective of this work is to investigate the effect of surfactants on interfacial films and the stability of water-in-oil emulsions stabilized by asphaltenes. Film properties included interfacial compressibility, crumpling film ratio, and surface pressure (interfacial tension). Film properties were determined from surface pressure isotherms. The emulsion stability was defined by the percentage of free water resolved (percentage of the initial water) from the emulsion after centrifugation and heating treatment. Model systems, consisting of asphaltenes and solvent (toluene or heptol), were used for most of the experiments. Some diluted bitumen systems were also analyzed to compare between model and real systems.

The specific objectives of this work are as follows:

1. Determine surface pressure isotherms for asphaltene-surfactant films using a drop shape analyzer.
2. Determine the effect of each surfactant on film properties and compare with asphaltene-only films.
3. Determine the effect of surfactant concentration and structure in asphaltene model systems.
4. Assess emulsion stability for asphaltene model systems with surfactants and compare with systems with only asphaltenes.
5. Correlate film properties with emulsion stability for asphaltene model systems in the presence of surfactants.
6. Analyze the effect of surfactant on film properties and emulsion stability in some diluted bitumen systems and compare with asphaltene model systems.

1.2. Thesis Structure

This thesis is separated into five chapters. Chapter 2 presents the basic concepts to understand water-in-crude oil emulsions. Crude oil and surfactant chemistry is introduced. Emulsions and their stabilizing and breaking mechanism are described. Finally, the role of surfactants as demulsifiers in the oil industry is reviewed.

Chapter 3 describes the experimental methods, materials, and instrumentation required to achieve the proposed objectives. This includes:

- interfacial tension and surface area measurements to build surface pressure isotherms.
- description of the instrument used for interfacial tension measurements (drop shape analyzer).
- description of drop shape analysis to calculate interfacial tension.
- experimental techniques for emulsion preparation and analysis (drop size distributions and mass on the interface).
- the procedure for the emulsion stability test in which the free water resolved from the emulsion is determined after a destabilization treatment.

Chapter 4 shows the main results obtained in this research. The effect of seven different surfactants on film properties with asphaltene model systems is discussed. The effect of concentration and surfactant structure in asphaltene model systems is analyzed. The relationship between emulsion stability and interfacial properties such as compressibility, surface pressure, and crumpling ratio is also discussed. Film properties and emulsion stability for some diluted bitumen systems with surfactants are also presented in order to compare with a whole crude oil.

Chapter 5 summarizes the finding of this work and presents recommendations for future research.

2. LITERATURE REVIEW

In this chapter, crude oil properties are briefly reviewed with a focus on heavy oil. The background needed for understanding emulsions and emulsion stability is provided as well as basic concepts of emulsion treatment.

2.1. CRUDE OIL BASIC CONCEPTS

2.1.1. Composition and Classification

Crude oil is a mixture of hundreds of thousands of different hydrocarbons as well as other components such as sulphur, nitrogen, oxygen and sometimes organometallics at low concentrations (Gruse. 1960). Its composition varies according to the origin of the crude oil. Petroleum can be classified in several ways; for example, by its physical properties (*e.g,* specific gravity, viscosity), elemental composition (*e.g,* amount of carbon, hydrogen, sulphur, nitrogen), carbon distribution, distillation curve, nature of the residue after distillation (*e.g.* paraffinic, naphthenic, aromatic, asphaltic), or solubility class (SARA fractionation into saturates, aromatics, resins and asphaltenes). The classification into conventional oil, heavy oil, or bitumen is based on physical properties as indicated with the UNITAR classification given in Table 2-1.

Table 2-1. UNITAR classification of oils by their physical properties at 15.6°C (Gray. 1994).

	Viscosity **mPa.s**	**Density** **Kg/m^3**	**API Gravity** **°API**
Conventional oil	<10^2	< 934	
Heavy oil	10^2 - 10^5	934 – 1000	20 - 10
Bitumen	>10^5	>1000	<~10

Heavy oils and bitumens are often characterized using SARA analysis; that is, the fractionation of the oil into the solubility/adsorption classes of saturates, aromatics, resins and asphaltenes. The SARA fractionation scheme is described in Figure 2-1. Saturates are the nonpolar material in the crude oil including linear, branched and cyclic saturated hydrocarbons. Aromatics are those components that contain one or more aromatic rings. Resins and asphaltenes are similar to aromatics but are larger, contain more fused aromatic rings, and contain more heteroatoms (Fan *et al.* 2002).

Typical SARA analyses for different heavy oils and bitumens are shown in Figure 2-2. The asphaltenes and resin content of each heavy oil and bitumen exceeds 40 wt%, significantly higher than in conventional oils. Asphaltenes are of particular interest in this work because they are known to stabilize water-in-oil emulsions (McLean & Kilpatrick. 1997, Sheu & Shields. 1995, Taylor *et al.* 2002, Yarranton *et al.* 2000).

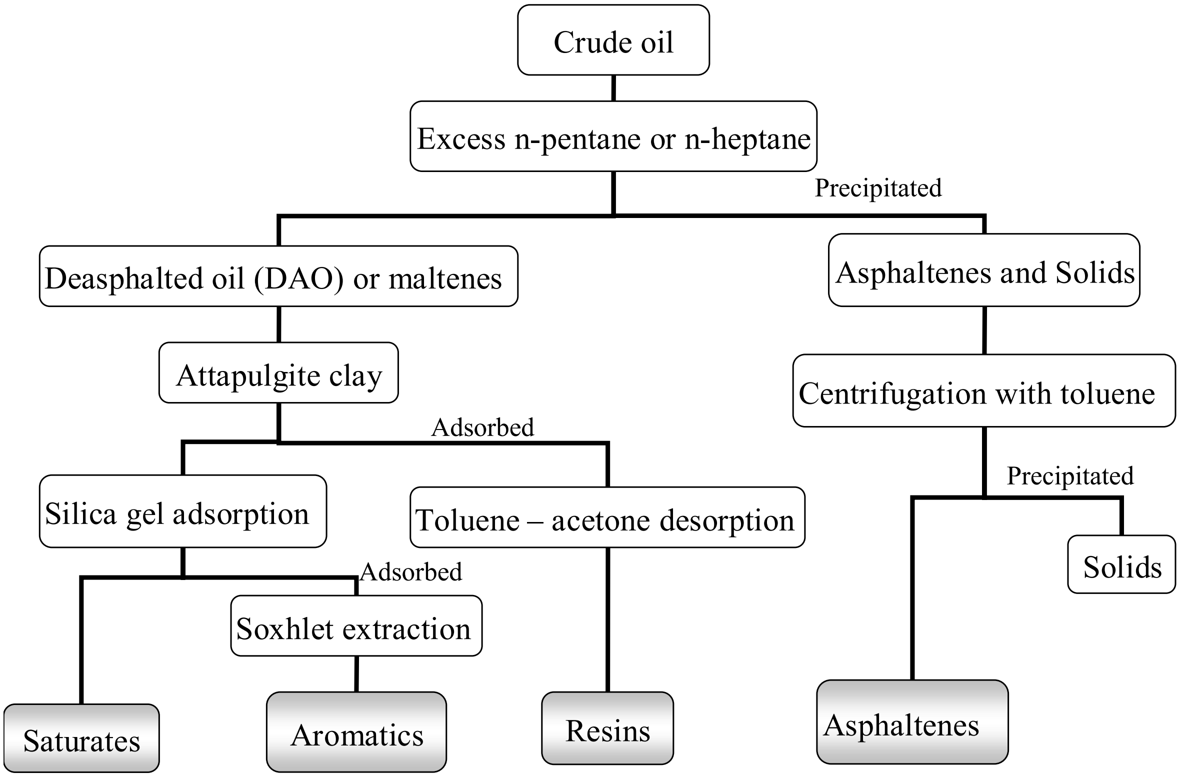


Figure 2-1. SARA fractionation scheme.

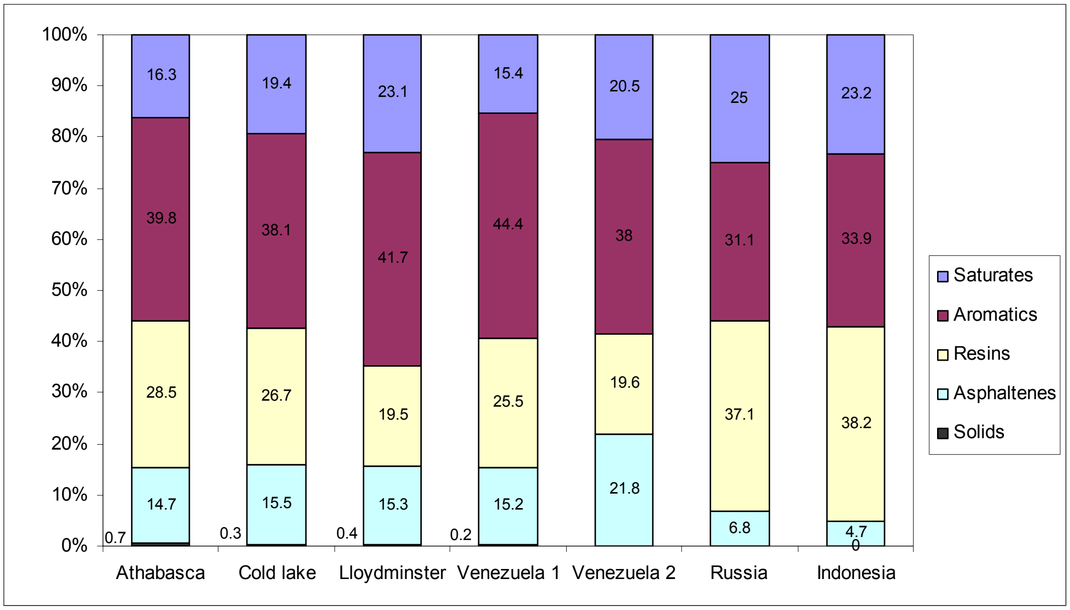


Figure 2-2. Composition of different heavy oils (Lloydmister, Russia and Indonesia) and bitumens (Athabasca, cold lake, Venezuela 1 and 2.) in base of SARA fractionation (Data from Akbarzadeh *et al.* 2004).

2.1.2. Asphaltenes in Bitumen

Asphaltenes are known to be large, polar, polynuclear molecules consisting of condensed aromatic rings, aliphatic side chains and various heteroatom groups (Payzant *et al.* 1991). Asphaltenes are soluble in aromatic solvents such as toluene, but precipitates in excess amounts of aliphatic solvents such as *n*-pentane and *n*-heptane (*e.g,* 40 parts of aliphatic solvent for 1 part of bitumen). Hence, asphaltenes are not a pure component but rather a solubility class of materials. They are a mixture of tens of thousands of different species. Their elemental composition varies somewhat from source to source and molecular structures have been difficult to determine.

2.1.2.1. Asphaltene Structure

The asphaltene structure is unknown but two types of structures have been postulated: (1) “continent” structure and (2) “archipelago” structure. The continent structure consists on a large aromatic or “continent” structure and alkyl branches, Figure 2-3. This model is based on x-ray diffraction measurements of solid asphaltenes (Dickie & Yen. 1967). This particular hypothetical continent structure has a formula of $C_{84}H_{100}N_2S_2O_3$, with a H/C ratio of 1.19 and a molecular weight of 1276 g/mol.

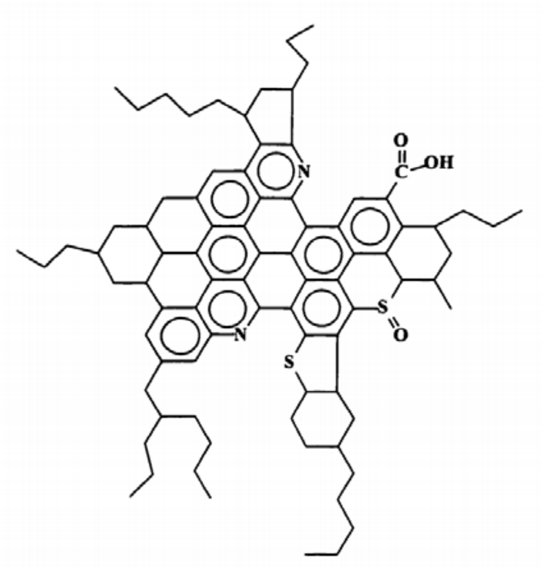


Figure 2-3. Continent structure of asphaltene molecule.

Strausz *et al.* (1992) proposed a so-called “archipelago” structure that consists of small aromatic islands connected by alkyl bridges. This structure is based on chemical and thermal degradation studies. Figure 2-4 shows a slight modification of the first model proposed also by Strausz in 1992.

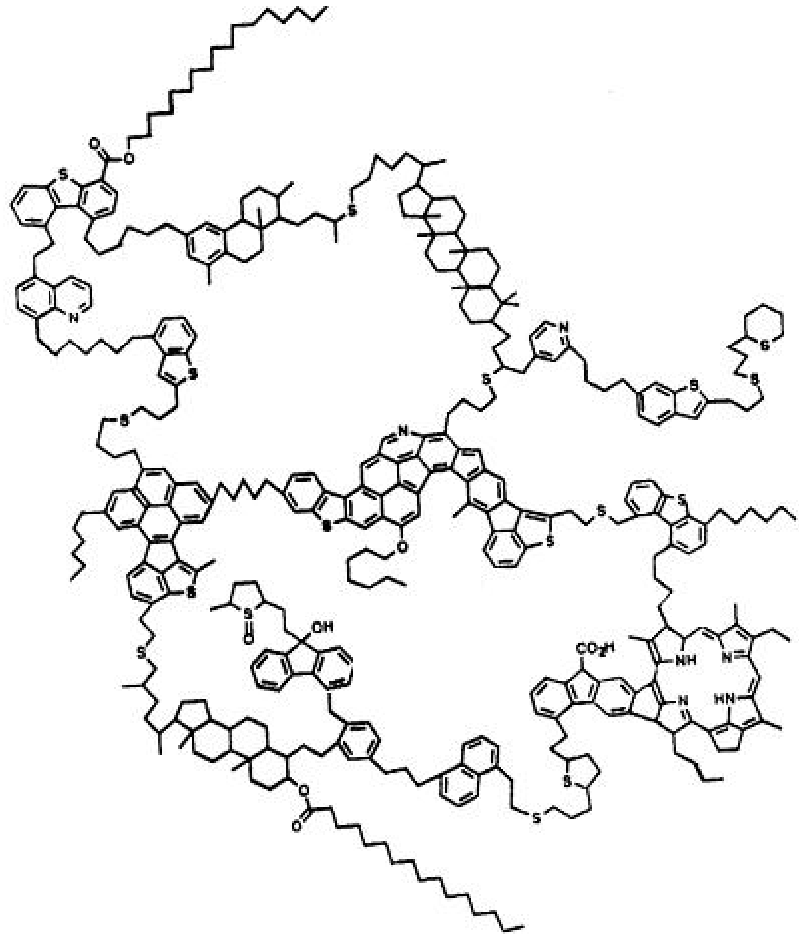


Figure 2-4. Proposed two-dimensional Asphaltene molecule from Athabasca Bitumen, archipelago structure (Murgich *et al.* 1999).

The hypothetical archipelago molecule proposed by Murgich *et al.* (1999) has a formula of $C_{412}H_{509}S_{17}O_9N_7$, with a H/C ratio of 1.23 and a molecular weight of 6239 g/mol. Note that there are some uncertainties in the structure due to assumptions made during its construction which are described in Strausz *et al.*, 1992. It has also been found that the molecular weight of an average asphaltene monomer is in the order of 1000 g/mol (Yarranton. 2005), less than the molecular weight of the hypothetical molecule. The molecular weight of the hypothetical structure is similar to that of a self-associated asphaltene. Monomer structures may resemble polynuclear-based fragments of the structure shown in Figure 2-4.

It is still debated which of the proposed structures is most representative. However, the archipelago structure is the most consistent with the observed reaction products from upgraded residues which are rich in asphaltenes (Gray. 1994).

2.1.2.2. Asphaltene Self-Association

Asphaltene self-association has been observed with a number of techniques including molar mass measurements which demonstrated that the apparent molar mass of asphaltenes increases with asphaltene concentration (Sztukowski *et al.* 2003) what indicates association of asphaltene monomers.

The structure of the asphaltene molecular aggregates is also still debated but the various proposed structures fall into two main categories: (1) colloidal aggregates and (2) oligimer-like macromolecules. The colloidal model proposed that asphaltenes consist of stacked aromatic sheets attracted by π-π acid-base and/or hydrogen bonding (Yen. 1974). The small stacks of asphaltenes are assumed to be dispersed in a crude oil by resins. This model follows from the continent structure of asphaltene monomers and is supported by small-angle neutron scattering measurements indicating structures of approximately 30 nm length scale (Dickie & Yen. 1967). Recently, this interpretation of the SANS data has been challenged (Sirota. 2005). Acoustic and nanofiltration experiments indicate smaller structures in the macromolecular scale (Zhao & Shaw. 2007).

The oligimer model assumes that asphaltene association is analogous to polymerization and that the macromolecules are in solution in the crude oil containing multiple active sites (heteroatoms and aromatic clusters). Unlike colloids, the size of the macromolecular aggregate is expected to increase with asphaltene concentration as observed with vapour pressure osmometry (Agrawala & Yarranton. 2001, Evdokimov *et al.* 2003), a common method to measure molar mass. Agrawala *et al.* (2001) found that an asphaltene association model based on an analogy to linear polymerization fit the molar mass data well. Calorimetry experiments confirmed the free energy of association predicted with this model (Merino-Garcia & Andersen. 2005).

Sztukowski *et al.* (2003) demonstrated that the asphaltene aggregates adsorb at the oil-water interface in water-in-hydrocarbon emulsions. The thickness of the adsorbed layer was shown to be proportional to the average apparent molar mass of the aggregates and increased with concentration as the apparent molar mass increased. This observation is consistent with the oligimer model.

2.1.2.3. Surface Activity of Asphaltenes

Asphaltenes have a large hydrocarbon skeleton but contain a variety of polar heteroatom groups which include oxygen, nitrogen, or sulfur. The hydrocarbon skeleton is hydrophobic while the polar groups are hydrophilic. The presence of both hydrophobic and hydrophobic groups on single molecule makes asphaltenes surface active; that is, they tend to adsorb at the water-oil interface with hydrophobic groups aligned in the organic phase while the hydrophilic groups are aligned in the aqueous phase. Interfacial tension (IFT) measurements have confirmed that asphaltenes adsorb at the water-oil interface lowering the interfacial tension in the same manner as surfactants (Mohamed *et al.* 1999, Schildberg *et al.* 1995, Yarranton *et al.* 2000).

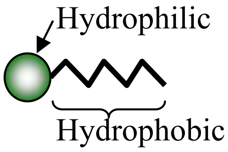
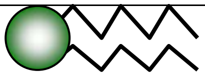
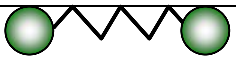
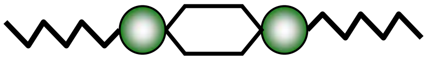
2.2. SURFACTANTS

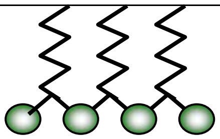
2.2.1. Definition and Structure

Surfactants, or surface active agents, are organic compounds that significantly reduce interfacial tension. They have at least one hydrophobic (water-fearing) group and one hydrophilic (water-loving) group in the molecule. In other words, one part has an affinity for nonpolar media and the other one has an affinity for polar media.

The hydrophilic and hydrophobic part of the surfactant molecule may be configured in different ways. For example, a surfactant molecule can have one hydrophilic head and one hydrophobic tail (Table 2-2a), one hydrophilic head and two hydrophobic tails (Table 2.-2b), one hydrophobic tail terminated at both ends by hydrophilic groups (Table 2-2c), more than one hydrophilic and hydrophobic groups linked in the same molecule by covalent bonds (polymeric surfactants, Table 2-2e) (Karsa. 2006).

Table 2-2. Surfactant structures (Gecol. 2006).

Surfactant structure		Example
a		Soap (Sodium salt of fatty acids) Alkyltrimethylammonium salts Polyoxyethylene alkyl ether Alkyldimethylamine oxide
b		Alkylbenzene sulfonate Phospholipids Alkyl secondary amines
c		Bolaform quaternary
d		Gemini phosphate esters

e		Polymeric alkyl phenol ethoxylates Silicone polymeric surfactants Polyester surfactants

2.2.2. Classification of Surfactants

The hydrophilic group of the surfactant molecule may carry a negative charge, a positive charge, both positive and negative charges, or no charge at all. These are classified respectively as anionic, cationic, amphoteric (or zwitterionic), and non-ionic surfactants.

- Anionic: dissociate such that the hydrophilic head is negatively charged.
- Cationic: dissociate in water such that the hydrophilic head is positively charged.
- Amphoteric/zwitterionic: dissociate in water and depending on pH, the hydrophilic head has positive, negative or both positive and negative charges
- Non-ionic: do not dissociate in water and the hydrophilic head is neutral

More details about these surfactants are provided in Appendix A.

2.2.3. Surfactant Properties.

The relative size and shape of the hydrophilic and hydrophobic parts of the surfactant molecule determine many of its properties. The principal properties that characterize surfactant behaviour such as critical micelle concentration, solubility and Krafft point, cloud point, phase inversion temperature, HLB and surfactant adsorption and surfactant partition are presented briefly in this section.

2.2.3.1. Micelles and Critical Micelle Concentration

When surfactant molecules reach a sufficient concentration in an aqueous phase, they can form aggregates such that the hydrocarbon tails cluster together inside the aggregate while with the head groups are oriented toward the aqueous solution forming a polar shell (Carale *et al.* 1994), see Figure 2-5. In this way, the hydrophilic head groups reside in an aqueous environment while the hydrophobic tail groups reside in an organic environment. This configuration minimizes the free energy of the solution. These aggregates are called micelles and the concentration at which they form is the critical micelle concentration (CMC). At the CMC, there is equilibrium between monomers of surfactant (and counterions in the case of ionic surfactants) and monodisperse micelles. In nonaqueous media (*e.g.* oil) surfactant molecules aggregate with their polar heads together in the micellar core and their tails in the organic continuous phase .Water is solubilized in the core of these structures known as reverse micelles (terminology used for emphasizing the difference from aqueous micelles). Although micelles and reverse micelles are surfactant structures, their properties and mechanisms by which they form are not necessarily the same. The shape of the micelles (aggregation in aqueous phase) depends on the surfactant properties (*e.g.* size of the head group). The aggregation in nonpolar media (reverse micelles) differ in several important aspects from aggregation in water (micelles); for example, reverse micelles form smaller aggregates than micelles, with fewer molecules per aggregate; also, reverse micelles form in a stepwise process rather than a series of reactions that are underwent during micelle formation.

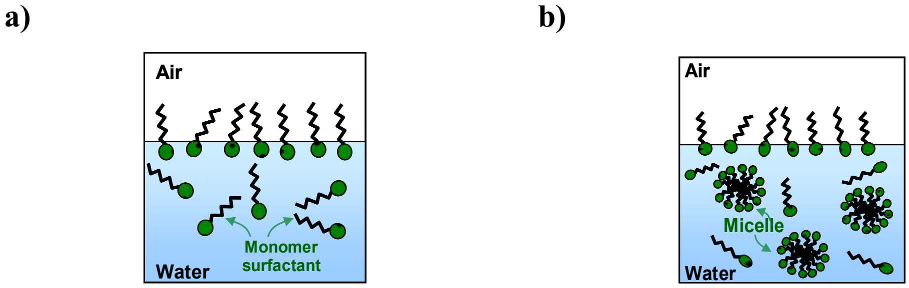


Figure 2-5. Aqueous surfactant solution a)below the cmc, b)above the cmc.

Figure 2-6 shows how properties of aqueous surfactant solution change markedly above and below the CMC. The change in properties occurs both because larger structures have formed and because the concentration of free surfactant molecules is nearly constant above the CMC. For example, surface and interfacial tension become constant after the CMC is reached because the micelles are not surface active and the interfacial tension only depends on the concentration of free surfactant. Hence, the maximum reduction in surface or interfacial tension is reached at the CMC.

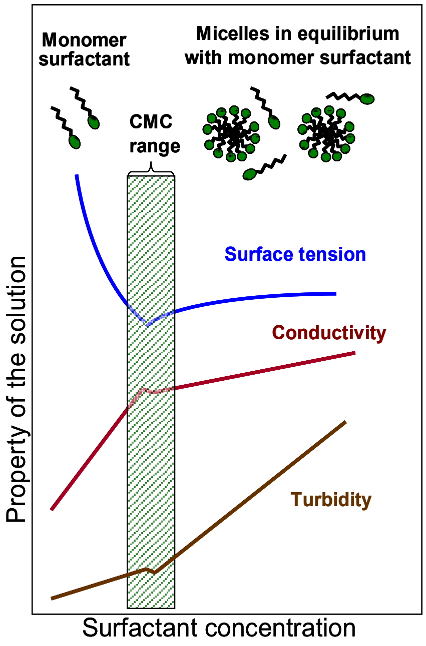


Figure 2-6. General changes in some physical properties of a surfactant aqueous solution in the neighbourhood of CMC.

2.2.3.2. Krafft Point

The Krafft point (or Krafft temperature) is related to the change of surfactant solubility with temperature. The solubility might be very low at low temperature and then increases by an order of magnitude over a relatively narrow temperature range. This increase in solubility is a result of micelle formation (Lindman. 2001) and is termed the "Krafft phenomenon". The Krafft point has rarely been observed for nonionic surfactants (Pandit *et al.* 1995, Wang *et al.* 2008).

2.2.3.3. Cloud Point

Heating a non-ionic surfactant solution may cause the solution to strongly scatter light over a range of temperatures; that is, the solution becomes "cloudy." It is a measure of the inverse solubility of the surfactant with temperature. At some temperature, there is separation between a surfactant-rich phase and a surfactant-poor phase. Cloudiness is the evidence of an onset of separation of the solutions (Lindman. 2001). Above the cloud point the surfactant solubility decreases and it becomes ineffective as a surfactant (Schramm *et al.* 2003).

2.2.3.4. Phase Inversion Temperature (PIT)

An emulsion consists of one of the immiscible liquids dispersed as fine drops in the other phase. When a surfactant is present, the phase that is dispersed depends either on the relative affinity of the surfactant to the respective phases or on the order of the addition of the phases making the emulsion. For example, a surfactant with a high affinity for water at low temperatures will form an oil-in-water emulsion. However, when the conditions of the emulsion are changed, phase inversion may occur (the continuous phase becomes the dispersed phase and *vice versa*). For example, changing the temperature changes the surfactant's relative affinity to each phase, causing phase inversion. The temperature at which the surfactant or emulsifier shifts its preferential solubility from water to oil (or *vice versa*) was defined by Friberg as phase inversion temperature or PIT (Brooks *et al.* 1998).

2.2.3.5. Partitioning of the Surfactant

Partitioning of the surfactant refers to the distribution of the monomeric surfactant into the water phase and the oil phase. The surfactant will distribute between the two phases according to its respective solubility in each phase. The partitioning coefficient is defined as (Pollard *et al.* 2006):

$$K_{ow} = C_o/C_w;\ K_{wo} = C_w/C_o \qquad \textbf{Equation 2-1}$$

where K is the partition coefficient, C_o and C_w is the concentration of surfactant in the oil phase and in the water phase, respectively. Note that the partition coefficient is based on the concentration of free surfactant in each phase and cannot be used with total concentrations above the CMC.

Some studies have been made in order to determine partitioning coefficients of different surfactants in water and different oil phases. The partition coefficient can be affected by ionic strength, pH, type of oil, cosolvents (Pollard *et al.* 2006), temperature and surfactant composition at the interface (BenGhoulam *et al.* 2004). For nonionic surfactants, it was observed that the partitioning coefficient between water and oil, K_{wo}, was greater than unity for the surfactants with more than 10 ethylene oxide units, which confer high water solubility (BenGhoulam *et al.* 2004).

2.2.3.6. Hydrophilic – Lipophilic Balance HLB

HLB is an empirical quantity used to define the polarity or solubility of surfactants. It has an arbitrary scale, typically from 1 to 20, in which a low HLB number means low solubility in water and a high HLB number means high solubility in water. HLB is also used to describe the application of surfactant as shown in Table 2-3. However, creating an emulsion on the basis of HLB alone does not necessarily mean that the emulsion will be stable.

Table 2-3. Application of surfactants according with their HLB value (Becher. 1967).

Range	Application
3 - 6	Water-in-oil emulsifier
7 – 9	Wetting agent
8 – 15	Oil-in-water emulsifier
13 – 15	Detergent
15 – 18	Solubilizer

The HLB may be determined either on analytical or composition data (Becher. 1967, Brooks *et al.* 1998). Some expressions for calculating the HLB for different surfactants are given in Table 2-4.

Table 2-4. Prediction of HLB for some surfactants.

Expression	
For fatty acid esters $HLB = 20\left(1 - \frac{S}{A}\right)$	S = Saponification number A = Acid number of the fatty acid
For fatty acid ester which saponification number is not practical to obtain $HLB = \frac{E+P}{5}$	E = weight per cent of oxyethylene content P = weight per cent of polyol content
Materials where only ethylene oxide is used to produce the hydrophilic group (e.g. E =the weight per cent of polyeoxyethylene) $HLB = \frac{E}{5}$	E = weight per cent of polyeoxyethylene (ethylene oxide groups) in the surfactant.

2.2.3.7. Hydrophilic – Lipophilic Deviation (HLD)

Hydrophilic-lipophilic deviation, HLD, is an improved version of HLB. HLD takes into account not only the surfactant by itself but also the nature of the oil, aqueous phase salinity, presence of alcohol as cosurfactant, temperature, and pressure (Rondon *et al.* 2006). HLD is a dimensionless expression of the surfactant affinity difference, SAD, which is defined as the variation of the chemical potential, μ, when a molecule of surfactant is transferred from oil to water. The typical expression for chemical potential of an ideal surfactant solution is defined as $\mu = \mu^{*} + RT \ln X$, where μ^{*} indicates the standard chemical potential of the surfactant in some reference state (superscript *). At equilibrium, where the surfactant distributes in the water and oil phase, the expression for chemical potential is given by (Salager. 2006):

$$\mu^{oil} = \mu^{*O} + RT \ln X_S^O = \mu^{water} = \mu^{*W} + \ln X_S^W \qquad \textbf{Equation 2-2}$$

where X is the surfactant composition in the oil (superscript O) and water (superscript W) phase . Rearranging equation 2-2

$$\Delta\mu^{*}_{O \to W} = \mu^{*W} - \mu^{*O} = RT \ln \left[\frac{X_S^O}{X_S^W} \right] \qquad \textbf{Equation 2-3}$$

where $\Delta\mu^{*}_{O \to W}$ is defined as the variation of the chemical potential, μ, when a molecule of surfactant is transferred from oil to water or SAD. SAD = $\Delta\mu^{*}_{O \to W}$ will be zero when the surfactant equally distributes in the oil and water phase. Rearranging Equation 2-3, with concentrations instead of compositions, and combining with Equation 2-1, an expression for SAD with partition coefficients is given by:

$$SAD = \Delta\mu^{*}_{O\rightarrow W} = \mu^{*W} - \mu^{*O} = RT\ln\left[\frac{K_{ow}}{K^{*}_{ow}}\right]$$ **Equation 2-4**

HLD is a dimensionless form of SAD and is given by:

$$\mathrm{HLD} = SAD/RT$$ **Equation 2-5**

It was also found that HLD can be written as a linear form of the different formulation variables such as salinity, temperature, structure of the surfactant (*e.g.* degree of ethoxylation for non-ionic surfactants). The expression depends on the type of surfactant used. Some expressions for HLD are given in Salager (2006).

When the water/oil ratio is close to unity, the type of emulsion expected will be oil-in-water for positive values of HLD and the emulsion expected will be water-in-oil for negatives values of HLD. Minimum emulsion stability is expected at HLD=0.

2.2.3.8. Adsorption at the Interface

Surfactant molecules at low concentrations in aqueous solutions exist as monomers or free molecules. These free molecules adsorb at the interface forming a monolayer and lowering the interfacial tension. In this way, the polar groups reside in the aqueous phase and the hydrophobic groups reside in the non-aqueous phase, minimizing the free energy of the system. Adsorption of surfactant may occur at a liquid/liquid interface, liquid/solid interface, or air/liquid interface.

Several factors may affect surfactant adsorption, for example, molecular structure and concentration of surfactant, aging time, temperature, type of oil, nature of the surface which the surfactant is in contact with, co-surfactant and/or co-solvent addition, presence of impurities or other components such as solids, electrolytes, and salt. Surface active molecules can also be oriented and packed in different ways on the surface. Depending on surfactant molecules orientation and confinement at the interface, the emulsion stability will change.

2.2.3.9. Surface/Interfacial Tension Reduction

Reduction of interfacial tension depends directly on the replacement of molecules of solvent at the interface by surfactant molecules. This results in an excess of surfactant on the interface and changes in the energy of the interface due to changing interaction forces.

In the presence of surfactants at the interface, the resulting interaction forces are between: polar surfactant head with water molecules, hydrocarbon surfactant tail with oil molecules, water with oil molecules, and oil with water molecules, Figure 2-7. The last two interactions are present in the gaps between surfactant molecules. These are also the only two interactions when there is no surfactant present at the interface (Figure 2-7a). The attraction forces between the surfactant with the two liquid molecules (Figure 2-7b) are much stronger than the attractive forces between the two liquid molecules themselves (Rosen. 2004). Consequently, there is a free energy reduction due to stronger attraction when surfactant molecules are brought to the interface. This reduction in free energy manifests as a lowering of the interfacial tension.

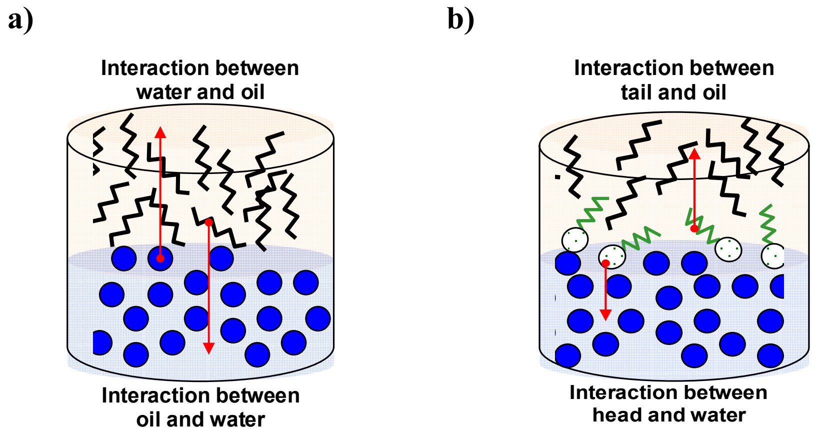


Figure 2-7. Representation of the interface of two immiscible liquids a) without surfactant b) in the presence of surfactant.

When comparing the performance of surfactants in reducing surface or interfacial tension, both the efficiency and effectiveness of surfactants are considered where:

- efficiency refers to the bulk phase concentration of surfactant needed to reduce the surface or interfacial tension by 20 mN/m (C20). The value of surface coverage, Γ, with this reduction is usually close to its maximum.
- effectiveness means the maximum reduction in surface or interfacial tension that can be obtained. This value is reached at the critical micelle concentration (CMC) of the surfactant.

2.3. WATER-IN-CRUDE OIL EMULSION CHARACTERISTICS

2.3.1. Classification

An emulsion is a mixture of two immiscible liquids (*e.g.* water and oil) in which one liquid is dispersed in the form of droplets into the other liquid (continuous phase). Classification of the emulsions depends on which phase is the “droplet phase,” or dispersed phased.

- Water-in-oil emulsions – w/o : oil is the continuous phase and water is the droplet or dispersed phase
- Oil-in-water emulsions – o/w : water is the continuous phase and oil droplets are the dispersed phase.
- Multiple emulsions – w/o/w or o/w/o: when droplets are dispersed in other dispersed droplets; for example, water-oil-water, indicates that water droplets are dispersed inside oil droplets which are dispersed in a continuous water phase

In the petroleum industry, some emulsions are undesirable while others are desirable. An example of some of these emulsions is given in Table 2-5. In some cases, even desirable emulsions become undesirable at the end of the process and need physical and/or chemical treatment to speed up the separation of the water from the oil.

Table 2-5. Some desirable and undesirable emulsions (Schramm & Kutay. 2000).

	Type of emulsion
Undesirable	
Well-head emulsions	W/O
Fuel oil emulsions	W/O
Oil flotation process froth emulsions	W/O or O/W
Oil flotation process diluted froth emulsions	O/W/O
Oil spills mousse emulsions	W/O
Desirable	
Heavy oil pipeline emulsions	O/W
Oil flotation process emulsions	O/W
Emulsion drilling fluid: oil-emulsion mud	O/W
oil-base mud	W/O
Asphalt emulsion	O/W
Enhance oil recovery in situ emulsions	O/W
Fuel-oil emulsion (70% heavy oil)	O/W

2.3.2. Emulsion Stability

Emulsions are thermodynamically unstable because they have an excess of interfacial free energy (excess of energy due to the creation of larger surface area in the system) as the contact area between the two immiscible phases increases. As a result, there is a tendency to reduce the contact area between the phases. However, the processes involved to reduce contact area might be very slow and the emulsion becomes kinetically stable for hours, days, or even years.

Formation of stable emulsions needs a surface active agent as an emulsifier, in combination with mechanical shear. The emulsifying agent, or surfactant, has two main functions, (1) to allow emulsion formation, and (2) provide stability to the emulsion (Walstra. 1993). The mechanical shear is required to create dispersed droplets in the first place.

The main mechanisms stabilizing emulsions are electrostatic stabilization, steric stabilization and the Plateau-Marangoni-Gibbs effect.

- Electrostatic stabilization: This includes the electrostatic repulsive force when the electrical double layers of two particles overlap (Hiemenz & Rajagopalan. 1996). For water-in-crude oil emulsions, electrostatic forces are weak enough to neglect it because the continuous oil phase has a low dielectric constant and thus a low ion concentration (Yarranton *et al.* 2007a).
- Plateau-Marangoni-Gibbs effect: This accounts for the surface tension gradients during film rupture. During film rupture, the local surface is extended. In this area, the surface tension is temporarily higher than the adjacent part of the film causing interfacial tension gradients. The interfacial tension gradient causes flow of the surfactant along the surface of a droplet and drives droplets away from each other (Walstra. 1993). Depending on the size of the surface and the size of the "local extended area", re-equilibration between the extended area and the adjacent film will be fast or slow. This mechanism is also dependent on the film thickness and drain velocity of the fluid (continuous phase) between the particles.

- Steric stabilization or a steric barrier refers to adsorbed material around the dispersed droplets in the emulsion. This material will form a physical barrier around those dispersed droplets (e.*g.* Figure 2-8). For example, when polymers adsorb on the surface, a physical layer is formed. This layer may mask the attraction between particles and make emulsions stable against aggregation and/or coalescence (Hiemenz & Rajagopalan. 1996). The steric barrier may also arise from rigid films that slow the drainage of the film between droplets so that film rupture and coalescence are prevented. For water-in-crude oil emulsions, this barrier may be made of asphaltenes, fine solids, coarse clays, resins, naphthenic acids, and other natural or added surfactants (Sztukowski & Yarranton. 2004).

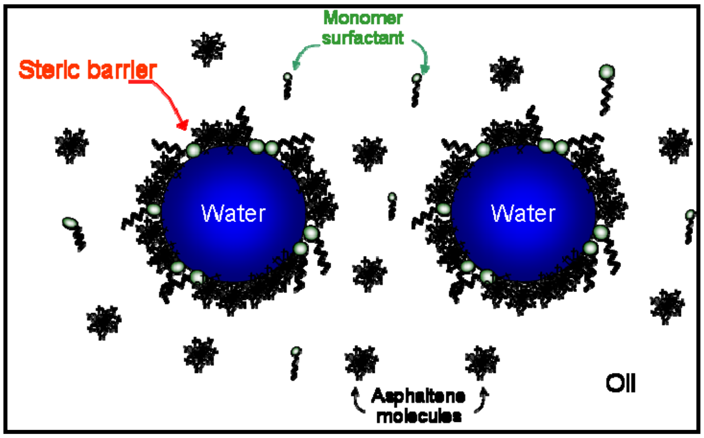


Figure 2-8. Schematic representation of steric stabilization of water droplets in water-in-oil emulsions by asphaltene and surfactant molecules.

In water-in-crude oil emulsions, asphaltenes are believed to be an important factor contributing to the stabilization of these emulsions (Gafonova & Yarranton. 2001, McLean & Kilpatrick. 1997, Sheu & Shields. 1995, Taylor *et al.* 2002). It has been shown that asphaltene aggregates adsorb on the interface and over time laterally interact on the interface forming a rigid film that provides high emulsion stability (Yarranton *et al.* 2007b). Stable incompressible non-relaxing films act as a mechanical barrier to coalescence (Jones *et al.* 1978, Mohammed *et al.* 1993). Various properties of these films have been studied such as interfacial tension, surface pressure, interfacial viscosities and interfacial viscoelastic parameters. Some of these properties are described in the next section.

There are several factors involved in emulsion stability and Schramm (2003) summarized these factors as follows:

- *low interfacial tension* makes it easier to form and maintain large interfacial areas
- *electric double layer repulsion* reduces the rates of aggregation and coalescence
- *surface viscosity* retards coalescence
- *steric repulsion* reduces the rates of aggregation and coalescence
- *small volume of dispersed phase* reduces the rate of aggregation
- *bulk viscosity* reduces the rate of creaming and aggregation
- *small density difference between phases* reduces the rate of creaming and aggregation
- *dispersion force attraction* increases the rates of aggregation and coalescence

2.3.3. Interfacial Properties and Compressibility of Asphaltene Films in Water-in-Oil Emulsions

Some studies show that asphaltenes make rigid films in water-in-oil emulsions. These asphaltene films create a barrier around the water droplets that prevents coalescence and make very stable emulsions. Moran *et al.* (1999) studied the film rigidity of water-in-diluted bitumen emulsions. They observed that the film crumpled when it was compressed. The crumpling of the film is evidence of the formation of rigid skins around the water droplets that resist deformation of these droplets. Similar behaviour has been observed in other studies (Aske *et al.* 2002, Mohammed *et al.* 1993, Nordli *et al.* 1991, Sztukowski *et al.* 2003, Yarranton *et al.* 2007a, Zhang *et al.* 2003).

The occurrence of crumpling in asphaltene films suggests that asphaltenes are irreversibly adsorbed at the interface. Irreversible adsorption means that once asphaltene aggregates are adsorbed at the oil/water interface, they do not leave the interface upon compression of the film. When the asphaltene film undergoes compression, the adsorbed asphaltene aggregates are forced closer together on the interface and eventually, the film becomes completely packed, very rigid, and resistant to coalescence. The change in film properties can be assessed from the compressibility of the film, given by (Gaines. 1978):

$$c_I\left(\frac{m}{mN}\right)=\frac{1}{A}\frac{dA}{d\pi}=\frac{d\ln A}{d\pi} \qquad \textbf{Equation 2-6}$$

where c_I is the interfacial compressibility in m/mN, A is the interfacial area and π is the surface pressure what is defined as the difference between interfacial tension of the pure solvent, γ_o, and interfacial tension of an asphaltene film, γ.

Yarranton *et al.* (2007b) used surface pressure isotherms to show that the film compressibility decreased as the surface area of asphaltene films was compressed. Upon further surface compression, the film collapsed indicating that the film had become incompressible. An example of a surface pressure isotherm for irreversibly adsorbed asphaltenes is shown in Figure 2-9. Note that in this figure, the surface area is expressed as the surface film ratio (FR); that is, the ratio between the initial surface area of the asphaltene film, A_o, and the surface area after the asphaltene film was compressed, A (Film Ratio=A/A_o).

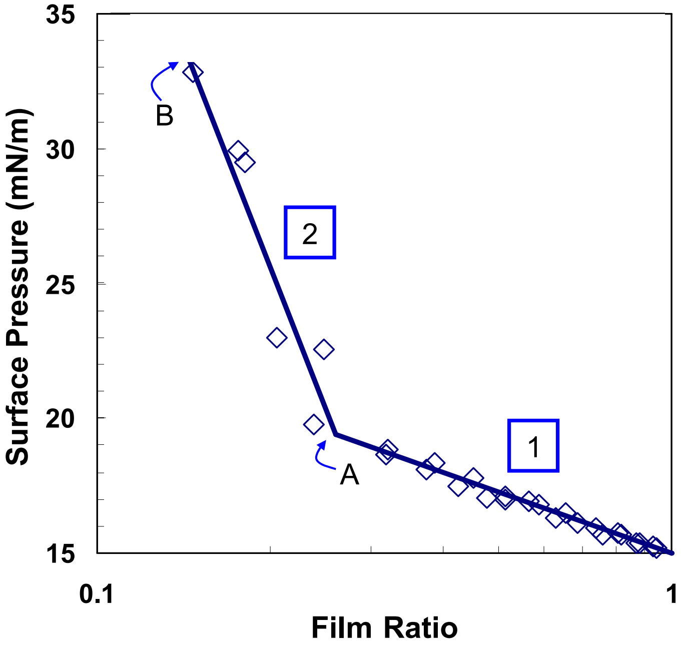


Figure 2-9. Interfacial pressure isotherm. 1= phase one, 2= phase 2, A= phase change, B = crumpling point.

There are four important phenomena to observe in Figure 2-9. The initial film (Film Ratio=1) has a “high” compressibility. The compressibility is constant until the film ratio is substantially reduced. The film behaves like a two-dimensional liquid (Phase 1). As film compression progresses, a phase change (A) occurs and a Phase 2 appears with very low compressibility. Upon further compression, a crumpling point (B) is reached when the film cannot be compressed anymore and crumples under the compressive force.

Asphaltenes are irreversibly adsorbed at the interface, that is, asphaltenes do not leave the interface when the surface is compressed. During coalescence, the total surface area of the droplets is reduced. As coalescence progresses, the asphaltene film is compressed, the film compressibility (c_I) decreases and there is more resistant to coalescence. Once the crumpling point is reached, coalescence appears to stop and the film becomes incompressible. At this point, a very stable emulsion is obtained.

Yarranton *et al.* (2007b) correlated the asphaltene interfacial properties with coalescence rate of the model emulsions. It was found that the rupture rate decreased exponentially to near zero after 4 to 8 hours of aging. Using the data from the surface pressure isotherms (compressibility of the two phases, phase change film ratio, crumpling phase ratio) and rupture rate, a model was developed. The model successfully predicted experimental data for drop growth indicating that the coalescence of water droplets in asphaltene-stabilized emulsions is governed by the compressibility of the asphaltene interfacial films.

2.3.4. Asphaltene Film Properties and Emulsion Stability

Asphaltene film properties (*e.g.* compressibility, crumpling, elasticity, interfacial tension) are governed by several factors such as temperature, aging time, chemistry of the solvent, asphaltene concentration, and other surface active components in the crude oil (*e.g.* resins and naphthenic acids). Some of these factors may enhance emulsion stability by increasing the rigidness of the film or the cohesion of asphaltenes at the oil/water interface. For example, aging has been shown to increase emulsion stability (Figure 2-10) because aged films have lower compressibilities (Nordli *et al.* 1991, Urrutia. 2006). Addition of a poor solvent for asphaltenes (*e.g.* *n*-heptane) also increases the stability of emulsion (Figure 2-11) as asphaltenes are more difficult to displace from the interface (Urrutia. 2006). Note, in Figures 2-10 and 2-11, the emulsion is unstable at low asphaltene concentrations because there is insufficient asphaltene to stabilize the interface.

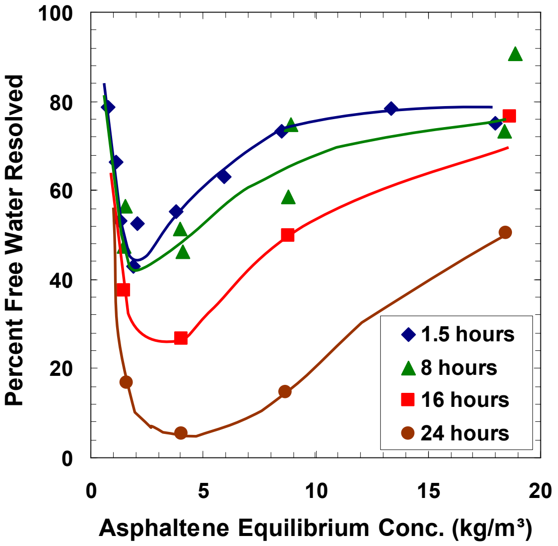


Figure 2-10. Effect of aging at 23°C prior to treatment on the free water resolved from emulsions prepared from 25/75 heptol and treated (after aging) for 1.5 hours at 60°C (Yarranton *et al.* 2007a).

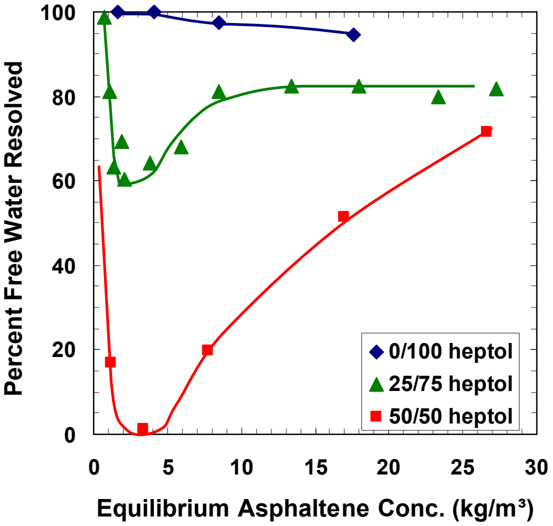


Figure 2-11. Effect of solvent in emulsion stability after 8 hours of treatment at 60°C of emulsions prepared from water and solutions of 5, 10, and 20 kg/m³ asphaltenes in toluene, 25/75 and 50/50 heptol at 23°C (Yarranton *et al.* 2007a).

In previous work, Yarranton *et al.* (2007b) developed a relationship between emulsion stability (water resolved from the emulsion) and film properties (interfacial compressibility and crumpling film ratio), Figure 2-12. The correlation confirms that the compressibilities of the interfacial films are the key factors in the stability of emulsions stabilized by asphaltenes. Yarranton *et al.* (2007b) defined a "capacity of coalescence" as the product of interfacial compressibility, c_i, and the capacity of compression what is defined as: 1-CR, where 1 is the initial film ratio and CR is the crumpling film ratio. This criterion provided an acceptable indicator for emulsion stability in which stable and unstable emulsion were identified in Figure 2-12 with a threshold around 0.2. Note this threshold only applies to the particular emulsion systems; however, the correlation could be used as a comparative test; for example, of the effect of different demulsifiers.

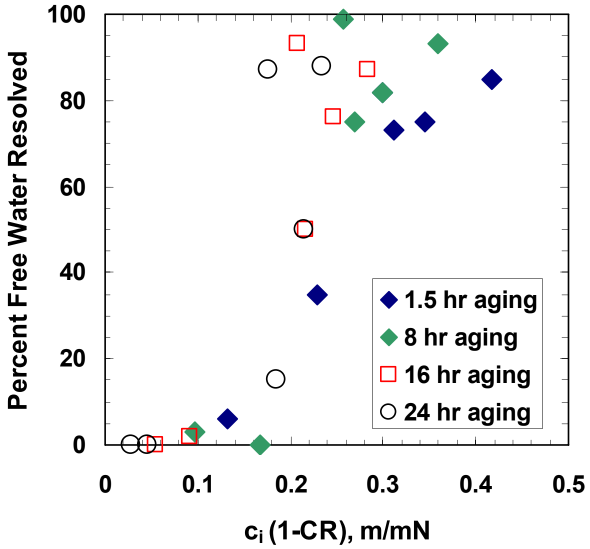


Figure 2-12. Relationship between free water resolved from emulsions at 60°C and C_I(1-CR) determined at 23°C (5, 10, and 20 kg/m³ asphaltenes in toluene, 25/75 and 50/50 heptol). Note that the open symbols indicated that the crumpling film ratio was measured directly but extrapolated from a plot of CR versus time.

2.4. BREAKING EMULSIONS

Emulsions are thermodynamically unstable although they are frequently kinetically stable for months or years. Water-in-crude oil emulsions must be treated to speed up phase separation (Aveyard R. *et al.* 1990). However, consistently breaking emulsions is still a challenge for the petroleum industry due to several factors such as differences in composition, origin (Hannisdal *et al.* 2007), and type of treatment of the crude oil. The mechanisms and methods of breaking emulsions are explained below.

2.4.1. Emulsion Breakdown Mechanisms

There are four main mechanisms responsible of breaking emulsions, or in other words, separating the two immiscible phases, (1) creaming/sedimentation, (2) coalescence, (3) flocculation/aggregation and (4) Ostwald ripening. They are described below.

2.4.1.1. Creaming and Sedimentation:

Creaming means the rise or floating of the oil droplets of an oil-in-water emulsion due to the difference in densities between the oil and water, Figure 2-13a. In a water-in-oil emulsion, the water droplets settle to the bottom, and this process is named sedimentation, Figure 2-13b. Both creaming and sedimentation can be affected by reducing or increasing the density difference of the two phases respectively, slowing down or speeding up the two processes (Buzzacchi *et al.* 2006). Creaming and sedimentation do not directly cause phase separation but act to bring droplets closer together.

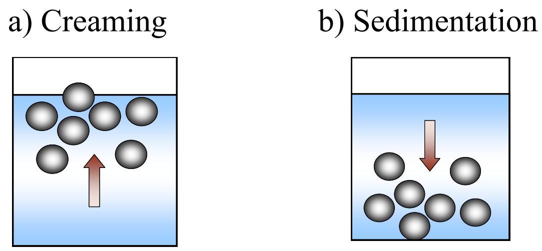


Figure 2-13. Representation of (a) creaming and (b) sedimentation processes.

2.4.1.2. Coalescence:

In coalescence, two single droplets (or more small particles) merge and make a single new larger drop. During coalescence, two droplets approach each other (Figure, 2-14a) due to convection of creaming. As they approach, their surface may deform and create planar surfaces between the two droplets. At the same time, the liquid between the two droplets begins to drain allowing the droplets to approach even closer (Figure 2-14b). During drainage, the surface material spreads and gaps with less interfacial material are formed on the surface. Bridges between droplets can form from the gaps (Figure 2-14c) and then fusion of the two droplets occurs (Figure 2-14d).

An important fact in coalescence is that the total surface area is reduced or compressed when a large particle is formed from fusion of smaller particles (Hiemenz & Rajagopalan. 1996). In order to achieve the coalescence of emulsified water droplets in water-in-crude oil emulsions, the stabilizing material on the interface, such as asphaltenes, solids, resins, waxes and natural surfactants, should be replaced or removed to make weaker films for coalescence to occur.

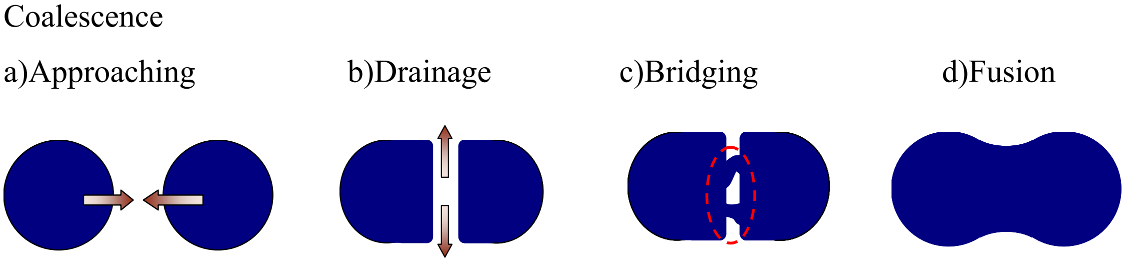


Figure 2-14. Steps in Coalescence.

2.4.1.3. Flocculation/Aggregation:

Flocculation occurs when particles join together, but there is no rupture of the droplet's film and the particles remain separated by a thin layer of continuous phase, Figure 2-15a. For example, a polymer solution is added to the system at low concentrations, bridging flocculation may occur. The polymer chain forms bridges bringing together more than one particle, Figure 2-15b. At moderate or high polymer concentration an effect called depletion flocculation begins to have an influence. In this case, free polymer molecules, which surround the two particles are excluded. Hence, there is an osmotic pressure force on all sides of the particles except where they approach each other from the space between the particles and as a consequence there is a net force of attraction between the two particles (Hiemenz & Rajagopalan. 1996). Flocculation does not directly cause phase separation but accelerates creaming and brings droplets closer together.

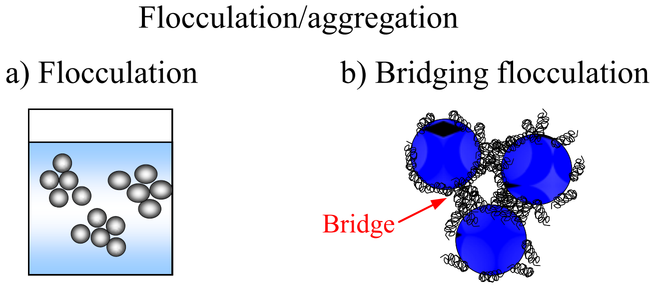


Figure 2-15. Representation of flocculation/aggregation (a) flocculation (b) bridging flocculation.

2.4.1.4. Ostwald Ripening:

Ostwald ripening results from molecular diffusion because of differences of concentration. The surface concentration of the dispersed phase material is higher at the surface of small droplets because the Laplace pressure is higher. Hence, material contained in small droplets diffuses through the continuous phase to the larger drops. This phenomenon produces a general increase in the size of the emulsion droplets (Binks. 1998).

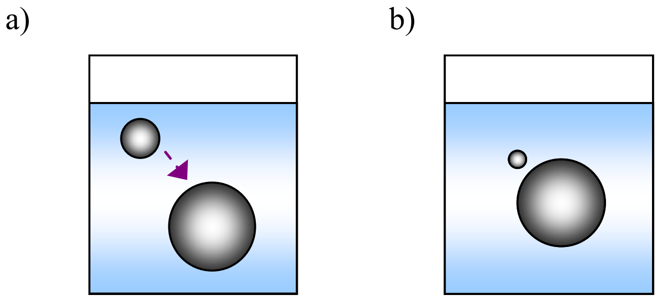


Figure 2-16. Representation of Ostwald ripening mechanism.

2.4.2. Methods of Breaking Water-in-Crude Oil Emulsions

There are different methods for breaking emulsions. Some of the most important methods used for many years are described below:

- Gravity-settling: the emulsions are allowed to cream or sediment under normal gravity. The creaming/sedimentation brings the dispersed phase droplets closer together promoting coalescence. In some processes, centrifugation is used to achieve more rapid and closer contact of droplets.

- Dilution: Changing the physical characteristics of an emulsion by the addition of diluents or water reduces the viscosity of the continuous phase and contributes to coalescence. The type of solvent also affects the emulsion stability since solvents change the solubility of interfacial material. Some organic solvents may dissolve the emulsifier interfacial material, thinning the film and making it easier for the water droplets to coalescence. For example, for water-in-crude oil emulsions, it has been shown that addition of toluene after emulsification makes weaker films promoting coalescence. This was observed through an increment of additional 30% free water resolved when toluene was added (Sztukowski & Yarranton. 2005). On the other hand, if the solvent reduces the solubility of the interfacial material, the emulsion may become more stable. For example, the addition of heptane after emulsification made more stable emulsions. Dilution also affects dispersed solids and can lead more or less stable emulsions depending on concentration and adsorption of solids.

- Thermal treatment: Increasing the temperature of the emulsion decreases the viscosity of the crude oil which increases both the water-settling rates and drainage rates. High temperature may also reduce rigidity of the interface what makes easier for the droplets to coalesce when they collide. Additionally, higher thermal energy accelerates collision rates between droplets. All these factors reduce emulsion stability. However, heating can increase the loss of light ends from the crude oil which would increase the density of the crude oil adversely affecting gravity settling (Kokal & Al-Juraid. 1998).

- Electrical Treatment: Applying electrical fields that promote coalescence is also called electrocoalescence. These fields assist small water droplets to fuse more quickly into larger ones. In the electric field, droplets deform as they approach each other. With the elongation and deformation of droplets, coalescence occurs more rapidly (Less *et al.* 2008). This method is considered an alternative to thermal and chemical treatment. However, it is not well understood how to modify or adapt this method to different emulsion properties (Lundgaard *et al.* 2006) in order to make an efficient and economically viable process every time.

- Chemical treatment: Chemicals are added to promote flocculation, create a more compact emulsion, or promote coalescence. The selection of a chemical or group of chemicals for emulsion breaking must be preceded by valid test procedures and a thorough understanding of the treating system and the petroleum company's objectives. If the applied chemicals do not have a broad treating range, fluctuating overtreatment and undertreatment conditions will reduce the performance considerably. The cost-effectiveness of chemical emulsion-breaking programs is dependent on proper chemical selection and application. A detail description of chemical treatment is given in Section 2.5.

Often a combination of these methods is used for breaking emulsions. For example, a combination of heat and chemical aids eliminates or neutralizes the effects of emulsifying agents in most oilfield applications (Grace. 1992).

2.5. SURFACTANTS AS DEMULSIFIERS

Demulsifiers are a mixture of chemicals that contain solvents (*e.g.* benzene, toluene, xylene, short-chain alcohols, and heavy aromatic naphtha) and surfactants that work as promoters for flocculation, coalescence or wetting agents.

2.5.1. Historical Development

A list of the demulsifiers used in the petroleum industry is shown in Table 2-6. The development of new demulsifiers has enabled lower dosages and better performance.

Table 2-6. Summary of demulsifier changes in the petroleum industry (Staiss *et al.* 1991)

Time Period	**Typical concentration**	**Chemical type**
1920s	1000 ppm	Soap, salts of naphthenic acids, aromatic and alkylaromatic sulphonates
1930s	1000 ppm	Petroleum sulphonates, mahogany soaps, oxidized castor oil, and sulphosuccinic acid esters
Since 1935	500 to 1000 ppm	Ethoxylates of fatty acids, fatty alcohols and alkylphenols
Since 1950	100 ppm	Ethylene oxide/propylene oxide copolymers, p-alkylphenol falmaldehyde, resins with ethylene/propylene oxides modifications
Since 1965	30 - 50 ppm	Amine oxylates
Since 1976	10 -30 ppm	Oxalkylated, cyclic p-alkylphenol formaldehyde resins and complex modifications
Since 1986	5 – 20 ppm	Polyesteramines and blends

Anionic surfactants made by saponification, soaps, were the first demulsifiers used; however, they were not useful in saline oil field waters because multi-valent ions like calcium and magnesium caused some water insolubilities in these soaps. Long-alkyl-chain sulfonates replaced soaps; however, they may undergo hydrolysis so pH control is necessary. Nonionic agents, generally have a better performance than anionic and cationic surfactants.

With the introduction of ethylene/propylene oxide, very active molecules at the water/oil interface became available. This chemical group offers a wide variety of demulsifiers such as fatty acids, fatty alcohols and alkylphenol ethoxylates. Additionally, it has been found that polyesteramines (derived from ethylene-propylene oxide block) have the ability to adhere to natural substances (organic and inorganic material) that stabilize emulsions and improved demulsification performance (Mikula & Munoz. 2000).

Nowadays, demulsifier development is based in making polymeric surfactants (*e.g.* EO/PO-block copolymer and their variants) with complex structures, but with high interfacial activity. Also, the development of different synergistic blends (mixtures of several surfactants with different chemical structures) is constantly being explored for tailoring demulsifiers.

2.5.2. Chemical Demulsification Theories and Studies

Demulsifiers are surfactants with the ability to destabilize water-in-oil emulsions. They promote the aggregation and coalescence of the water droplets in order to separate the water from the oil. Demulsifier performance is affected by several factors such as oil type, oil viscosity, presence and wettability of solids, size distribution of the water phase (Mikula & Munoz. 2000).

The chemical demulsifier is thought to destabilize water-in-crude oil emulsions by causing a disintegration of asphaltene layer at the interface (Jones *et al.* 1978). They will orient at the oil/water interface and replace the interfacial material stabilizing emulsions such as asphaltenes and natural surfactants (Kang *et al.* 2006, Zaki *et al.* 2000). Also it is assumed that demulsifiers break the association at the interface. In general, it is accepted that demulsifiers affect the interfacial rheological properties and disrupt the rigid film (Eley *et al.* 1987, Kim & Wasan. 1996, Zhang *et al.* 2003).

Kang *et al.* (2006) studied the change in interfacial elasticity. He found that regardless of the type of demulsifier, low interfacial elasticity can improve demulsifier efficiency. Note, low elasticity corresponds to high compressibility.

Zhang *et al.* (2003) studied the interfacial behaviour of monolayers of asphaltenes and a polymeric demulsifier. Using surface pressure isotherms at the air-water and oil-water interface, they found that the monolayer of asphaltene and demulsifier had gas-like, liquid-like, and solid-like phases; however, there was no clear phase transition between them. The film did not collapse abruptly.

Singh (1994) found that an appreciable reduction of surface pressure is correlated with a good demulsifier performance. In general, emulsion stability increased as the surface pressure increased. It is also believed that good demulsifier performance is achieved with demulsifiers with high-partition coefficient and high surface activity. These demulsifiers cross the interface and diffuse into the water phase breaking the film and destabilizing the emulsion (Aveyard *et al.* 1990, Krawczyk *et al.* 1991, Nurxat-Nuraje *et al.* 1999, Zhang *et al.* 2003); However, Zhang (2003) found that once asphaltenes and demulsifier spread at the oil (mixture of heptane and toluene) /water interface, they did not migrate into either of the bulk phases.

The composition and nature of crude oil make it very complicated to predict the behaviour of demulsifiers in every field. No demulsifier can be applied to break all types of crude oil emulsions (Kang *et al.* 2006). One demulsifier may work perfectly in one field with a specific type of oil but its effectiveness could be limited with another type of oil at another field. This issue makes the study of demulsifiers interesting as it is important to identify why demulsifiers work perfectly in some fields with certain types of oil but not in others.

2.6. Chapter Summary

Water-in-crude oil emulsions are very often formed in the petroleum industry. These emulsions form as a result of mixing of water and crude oil during processing; they may become very stable due to the presence of natural surface active materials in the crude oil such as asphaltenes, resins, native solids and clays and indigenous surfactants (*e.g.* naphthenic acids). These components are able to adsorb at the oil-water interface and form a "skin" or physical barrier which prevents coalescence of the water droplets.

Asphaltenes, or a fraction of asphaltenes, are believed to be one of the principal components stabilizing emulsions. They are able to form "skins" or interfacial film with high interfacial elasticity and low capacity for compression. In the coalescence of water droplets, the interface is constantly compressed and the adsorbed material undergoes a gradual rearrangement creating more rigid skins and increased resistance to deformation. During interfacial compression, the capacity for film compression significantly decreases until the film "crumples". It was shown that for asphaltene films, coalescence stopped when the film reached the crumpling point since the film no longer had capacity for compression.

When other surface active components are present along with asphaltenes, it is believed that they compete with the asphaltenes to adsorb at the interface. Depending on this competition and the interactions between asphaltenes and the other components at the interface, the surface active components may enhance or decrease emulsion stability. However, the effect of surfactants in asphaltene films and their relationship with emulsion stability remains unclear.

3. EXPERIMENTAL METHODS

This chapter describes the experimental methods for measuring rheological properties of interfacial films and emulsion stability when additives are present in asphaltene stabilized emulsions. The materials and instrumentation required to perform the measurements are described in Section 3.1. The rheological interfacial properties were assessed through surface pressure isotherms by measuring interfacial tension and surface area during compression steps, as is explained in Section 3.2. Surface pressure isotherms yield information on the film properties of water-oil interfaces such as interfacial tension, interfacial compressibility, and crumpling point. Emulsion stability was evaluated by measuring the amount of free water resolved from the emulsion over time after intervals of centrifugation and heating at 60°C (Section 3.3). Finally, the amount of asphaltenes on the interface was determined from a mass balance on prepared emulsions and drop size measurements (Section 3.4).

3.1. Materials

3.1.1. Chemicals

Commercial *n*-heptane, 98% purity, and technical grade toluene were purchased from ConocoPhillips and Univar, respectively. *n*-Heptane was used to precipitate asphaltenes and toluene was used to remove solids from the precipitated asphaltenes. Both were used for emulsion preparation . Analytical solvents used for dynamic surface pressure isotherm experiments were certified *n*-heptane, 99.4%, and Omnisolv toluene, 99.99%, purchased from Fisher Scientific and VWR, respectively. Mixtures of X vol% *n*-heptane and Y vol% toluene, described as X:Y heptol, were used for the dynamic surface pressure isotherm experiment and the emulsion preparation.

Sodium hydroxide (NaOH) 1M and hydrochloric acid (HCl) 1M were used to prepare high and low pH solutions, respectively. The pH of the solutions were measured using a Corning 308 hand-held pHmeter. Reverse Osmosis water was supplied by the University of Calgary water plant.

3.1.2. Athabasca Bitumen and its Asphaltene Fraction

Athabasca coker-feed bitumen was Plant Seven solvent-removed froth product from Syncrude Canada Ltd. Asphaltenes were precipitated from the bitumen and separated from any non-asphaltene solids using a previously established procedure (Sztukowski & Yarranton. 2005) which is described below. Asphaltenes were precipitated from the same bitumen source for all the experiments.

3.1.2.1. Asphaltene-Solid Precipitation

As mentioned in Chapter 2, asphaltenes are a solubility class which is insoluble in a paraffinic solvent such as *n*-pentane or *n*-heptane, but soluble in aromatic solvents such as toluene. To precipitate asphaltenes, *n*-heptane was added to the bitumen in a 40:1 (cm^3/g) solvent-to-bitumen ratio. The mixture was sonicated in an ultrasonic bath for 45 to 60 minutes to obtain a homogeneous mixture. The solvent-bitumen mixture was left in contact for 24 hours. The supernatant was slowly filtered through a Whatman #2, 24 centimetre diameter filter paper. Approximately 20 vol% remained unfiltered at the end. Additional *n*-heptane was added to the remaining solution at a 4:1 (cm^3/g) solvent-to-original bitumen ratio and sonicated for 45 minutes. The solution was left overnight and then filtered through the same filter paper. After filtration, the filter paper with asphaltenes was left to dry for four days. The asphaltenes precipated with *n*-heptane still contain some solids and were labelled as C7 asphaltenes-solids. The average yield of C7 asphaltenes-solids was 16.0wt%.

3.1.2.2. Solids removal

For solids removal, a previously established centrifugation technique (Sztukowski & Yarranton. 2005) was used. A solution of approximately 10 g/L of C7 asphaltenes-solids in toluene was prepared, usually by dissolving two grams of C7 asphaltenes-solids in 200 mL of technical toluene and sonicating for twenty minutes. After settling for 50 minutes, the solution was centrifuged for six minutes at 4000 rpm and the supernatant decanted. The solvent in the supernatant was evaporated off over 3 days until the mass of the residue no longer changed. The dry residue was labelled as C7 asphaltenes-solids free. Any fine solids that remained in the asphaltenes after the above procedure have been shown to have no significant effect on the surface pressure isotherms and emulsion stability results (Sztukowski & Yarranton. 2005). All the experiments were performed with these solids free asphaltenes.

The residue from the centrifuge tube was dried to determine the mass of the non-asphaltene solids. The average solids content of the C7 asphaltenes-solids was 2.8wt%. These asphaltenes were stored in a glass container which was left in a desiccator; they were only removed from the desiccator to take samples needed for performing the experiments. C7 asphaltenes-solids were used during the surface pressure isotherms experiments and emulsion stability tests which are explained in the next sections.

3.1.3. Surfactants

Aerosol OT, 98% purity, was purchased from Aldrich Chemical Company, Inc. Champion Technologies, Ltd. provided the nonylphenol ethoxylate surfactants (10, 15 and 30 moles of ethylene oxide), and dodecylbenzene sulfonic acid surfactants (DBSA-Linear and DBSA-Branched). Sodium naphthanate was made by Acros Organics, purchased from Fisher Scientific.

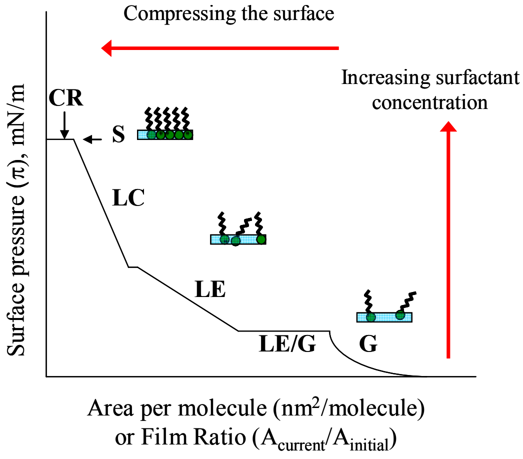
3.2. Dynamic Surface Pressure Isotherms

Surface pressure is the reduction of surface/interfacial tension due to the presence of surface active agents on a surface between two fluids, and is defined as (Hiemenz & Rajagopalan. 1996),

$$\pi = \gamma_o - \gamma$$ **Equation 3-1**

where π is the surface pressure, γ_o is the interfacial tension of the pure solvent (in the absence of an adsorbed layer, no surface active agent), and γ is the interfacial tension with an adsorbed layer.

Surface pressure, π, describes the behaviour of surface active molecules on a surface. Its magnitude depends on both the amount of material adsorbed on the surface and the area over which the surfactant is distributed. Surface pressure isotherms (π-A) are a representation of two-dimensional phase behaviour of an irreversibly adsorbed monolayer in which the surface active agent remains on the surface even during compression. As shown in Figure 3-1, the phase behaviour of an irreversibly adsorbed surfactant monolayer ranges from low values of π at very low concentration of surfactant on the surface (gas-like distribution of surfactant), to high values of π, when the surface area is reduced and surfactant molecules are very closely packed (solid-like distribution of surfactant). A number of liquid and solid-like phases can be observed as the film is compressed. If the film is compressed sufficiently, a maximum surface pressure is reached at a maximum packing (minimum area per molecule). If the film is compressed beyond this point, it buckles and the surface pressure remains constant. This point is termed the crumpling point. At the crumpling point, the monolayer collapses because the surfactant confinement forces are too strong on the packed surface.



Phases in a surface pressure isotherm

G : Gas-like
LE : Liquid expanded
LC : Liquid condensed
S : Solid-like
CR: Crumpling point

Figure 3-1. Surface pressure versus area, π-A, isotherm and monolayer phenomena (Hiemenz & Rajagopalan. 1996).

While reversibly adsorbed monolayers do not crumple, they too can show an increase of surface pressure upon compression. For both reversible and irreversible films, the change in surface pressure with a reduction in surface area is expressed in terms of compressibility, given by (Gaines. 1978):

$$C_i = -\frac{1}{A_t}\frac{dA_t}{d\pi} = -\frac{d\ln A_t}{d\pi}$$

Equation 3-2

where C_i is the interfacial compressibility (m/mN), A_t is the total surface area, and π is the surface pressure. The interfacial compressibility is a two-dimensional analog of the bulk compressibility of a fluid which relates pressure change to a change in volume. The compressibility can be calculated for each interfacial phase as the slope of the surface pressure versus the logarithm of A_t.

In this work, surface pressure isotherms were built through stepwise interfacial tension and surface area measurements of an oil drop immersed in an aqueous phase. The oil phase consisted of a known mass of asphaltenes or bitumen dissolved in toluene or mixtures of toluene and *n*-heptane. The aqueous phase consisted of pure water or a known mass of surfactant dissolved in water. The stepwise measurements were performed after a series of interfacial compressions in which small amounts of fluid from the oil drop were withdrawn producing a reduced surface area. A silhouette of a pendant oil droplet surrounded by a transparent aqueous phase was captured and the oil drop shape was analysed via digital processing with an "IT Concept drop shape analyser" which determines the interfacial tension and surface area, as explained below. A detail explanation of the procedure to built the surface pressure isotherms is given in Section 3.2.3.

3.2.1. Principles of Drop Shape Analysis

The shape of a droplet at the tip of a capillary is governed by the balance between interfacial and gravity forces. The interfacial tension tends to give a spherical shape to the drop whereas gravity elongates the drop. The interfacial tension is computed using the Laplace-Young equation and the equilibrium between interfacial tension and gravity forces acting on the drop.

The Laplace-Young equation describes a spherical droplet which is formed in the absence of any external field such as gravitational, magnetic or electrical fields. This equation accounts for pressure drop across a curved interface. The simple form of the Laplace-Young equation states the relationship between the interfacial pressure of the drop, ΔP, with the interfacial tension, γ, and radii of curvature, R, through the following expression (Erbil. 2006):

$$\Delta P = P_{interior} - P_{exterior} = \gamma\left(\frac{2}{R_{sph}}\right)$$ **Equation 3-3**

However, in order to describe three-dimensional objects, for example non-spherical bubbles and drops, two radii of curvature are needed and Equation 3-3 becomes

$$\Delta P = P_{interior} - P_{exterior} = \gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$$ **Equation 3-4**

Figure 3-2 shows the profile for an axisymmetric pendant drop in which the radii of curvature R_1 and R_2 of equation 3-4 are illustrated.

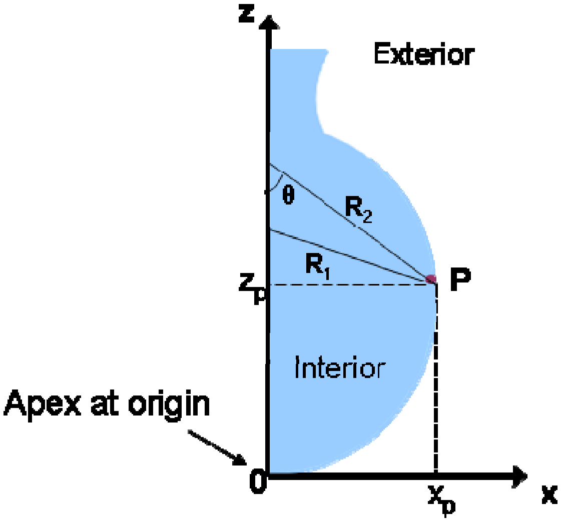


Figure 3-2. Illustration of an axisymemetric pendant drop and its coordinates for drop shape analysis.

In Figure 3-2, P is a point on the interface of the droplet, R_1 is the radius of curvature in the x-z plane, R_2 is the radius of curvature in the y-z plane, and θ is the angle between R_2 and the z-axis. Interior and exterior refer to two different fluids, with densities of $\rho_{interior}$ and $\rho_{exterior}$, respectively.

Now, the hydrostatic forces acting at Point P provide another expression for ΔP (Erbil.2006):

$$\Delta P = P_{interior} - P_{exterior} = \Delta P_{APEX} + \Delta\rho g z \qquad \textbf{Equation 3-5}$$

where $\Delta\rho$ is the density difference between fluids, $\Delta\rho = \rho_{exterior} - \rho_{interior}$. At the apex there is symmetry and $R_1 = R_2$ or $R_{apex} = R_{sph}$. Equation 3-4 is applied at the apex and substituted into Equation 3-5 to obtain:

$$\Delta P = \left(\frac{2}{R_{apex}}\right) + \frac{\Delta\rho g z}{\gamma} = \left(\frac{1}{R_1} + \frac{1}{R_2}\right) \qquad \textbf{Equation 3-6}$$

Since Point P may vary with z, the two radii of curvature, R_1 and R_2 may also vary. Accordingly, the following expressions for R_1 and R_2 are obtained from analytical geometry (Erbil 2006):

$$\frac{1}{R_1} = \frac{d^2z/dx^2}{\left[1 + (dz/dx)^2\right]^{3/2}} \qquad \textbf{Equation 3-7}$$

$$R_2 = \frac{x}{\sin\theta} \qquad \textbf{Equation 3-8}$$

The radii of curvature, R_1 and R_2, are determined from Equations 3-7 and 3-8 and the value of interfacial tension, γ, can be computed with Equation 3-6 by iteration to find the value that best fits the equation. The inputs to this equation are fluid densities and local gravity. The drop shape analyser uses the same approach but with curvilinear coordinates.

3.2.2. Drop Shape Analyser

All interfacial measurements were performed on a IT Concept Drop shape analyser using Tracker software. The instrument is composed of five major parts: 1) syringe piston actuator, 2) sample cell, 3) light source, 4) lens and CCD camera and 5) instrument control with a personal computer and a manual motor control, see Figure 3-3.

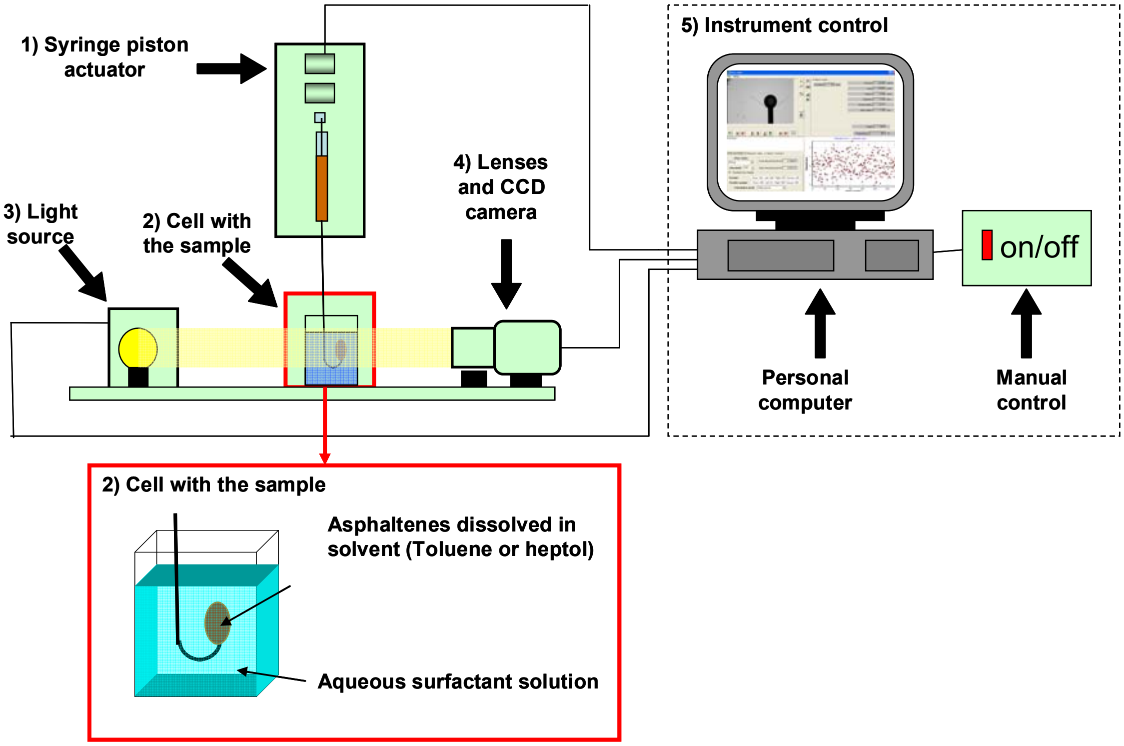


Figure 3-3. Drop Shape Analyser (DSA) Configuration.

The configuration of a drop can be either pendant (hanging) or sessile (rising from the base) depending on the densities of the two fluids. A sessile drop is the configuration used in this work. For the drop shape measurements of interfacial tension, a syringe is fit with a U-shaped needle and is loaded with a less dense fluid; for example, asphaltenes or bitumen dissolved in toluene or heptol (less dense than an aqueous phase). The syringe is fitted in a motor drive (Figure 3-3, Part 1) and the tip of the U-shaped needle is positioned in a quartz cuvette and immersed in the aqueous phase (Figure 3-3, Part 2). An oil drop is formed at the tip of the needle. The light source, Part 3 in Figure 3-3, uniformly illuminates the oil droplet formed at the tip of needle and the CCD camera, Part 4, captures the droplet profile. The image can be analysed using the drop shape analysis software to determine the interfacial tension, drop surface area, and drop volume. The whole instrument is placed over anti-vibrational bench to prevent disturbances during the measurements.

The drop shape analyser has three modes of calculation: high-precise, precise, and normal. These calculation modes account for the precision in which the Laplace-Young equation (Equation 3-6) is solved and the number of iterations per second. In other words, it allows specifying the accuracy and speed of the calculation. High-precise and precise mode allow a very high precision and performs up to 20 and 15 iterations per second, respectively. Normal mode allows a slightly less precise measurement and performs up to 10 iterations per second. In this work, the high precise mode was used for taking the measurements.

3.2.3. Surface Pressure Isotherm Experimental Procedure

The preparation of the solutions and of the apparatus and the procedure to measure interfacial tension and surface area are described below.

3.2.3.1. Preparation of Solutions

To prepare the asphaltene solution, a given mass of asphaltenes was dissolved with a given volume of toluene or heptol and sonicated for up to 20 minutes depending on the concentration. Urrutia (2007) showed that asphaltene concentration had little effect on surface pressure isotherms (asphaltene concentrations between 1 and 20 kg/m^3) and almost no effect changing from 10 to 20 kg/m^3. On the other hand, emulsion stability had a minimum usually between 5 and 10 kg/m^3 asphaltene equilibrium concentration (Sztukowski & Yarranton. 2005). According with Urrutia (2007) and Sztukowski (2005) results, asphaltene concentrations of 5 and 10 kg/m^3 were selected in this work.

Heptol was prepared with toluene volume fraction of 1, 0.75 and 0.5. Toluene is a good asphaltene solvent, the addition of heptane allowed to analyze the effect of poorer solvent in asphaltene films. The bitumen solutions were prepared at a dilution ratio of 9 parts solvent to 1 part of Athabasca bitumen. Bitumen solutions were also sonicated to ensure homogeneity. Fresh solutions were prepared daily to avoid aging effects.

For the surfactant solutions, surfactant was weighed and dissolved in an appropriate mass of water and sonicated until complete dissolution. For low concentrations of surfactant (<10 ppm), a dilution from a more concentrate solution was made. The surfactant concentrations were between 1 ppm to 5000 ppm (0.5wt%). All the concentrations were selected to be below the critical micelle concentration.

Before performing an experiment, each of the two phases were saturated with the other phase. This involved adding two drops of each phase into the other phase and letting the solutions sit for 60 to 90 minutes to equilibrate. This saturation procedure was performed in order to eliminate diffusion effects during the interfacial tension measurements.

3.2.3.2. Preparation of the Drop Shape Analyser

In order to take accurate and reproducible measurements, the drop shape analyser and its accessories had to be rigorously cleaned. The syringe, needle and cuvette were carefully washed sequentially with *n*-heptane, *2*-propanol, and toluene. The parts were then dried with vacuum and rinsed with reverse osmosis water.

To verify the cleanliness of the instrument, the interfacial tension of a pure solvent, for example analytical toluene, was taken and compared with its literature value. The average interfacial tension for toluene versus water obtained with the drop shape analyser was 36.0 ± 0.3 mN/m at 23^{o}C in comparison with a literature value of 35.8 mN/m at 25^{o}C (Li & Fu. 1992) which gives a percentage deviation of 0.9%.

3.2.3.3. Interfacial Tension and Surface Area Measurements

The oil solution (dissolved asphaltenes or bitumen) was loaded into a syringe with a U-shaped needle and was immersed in aqueous surfactant solution contained in a cuvette. A droplet was formed at the tip of the needle. The volume of the drop was selected to be small enough to remain on the tip of the needle throughout the experiment but large enough to provide a reasonable number of compression steps in order to build the surface pressure isotherm. The drop volumes ranged from approximately 5 to 8 μL. The oil droplet was aged for 10, 30, 60 or 240 minutes. After aging, a stepwise compression was performed by withdrawing fluid from the droplet. At every step, the interfacial tension and drop surface area was measured and recorded. Compression steps ended when crumpling was observed or the drop was so small that an accurate measurement was not possible. Most experiments were performed twice to ensure repeatability. The statistical analysis is provided in Appendix F. In general, the total average percentage error for initial compressibility was 20.8% with a minimum error of 0.3% and a maximum error of 60%. The average absolute error for crumpling film ratio was ±0.040.

Figure 3-4 shows a series of compression steps until the visual crumpling point was observed or the droplet was too small for further measurements.

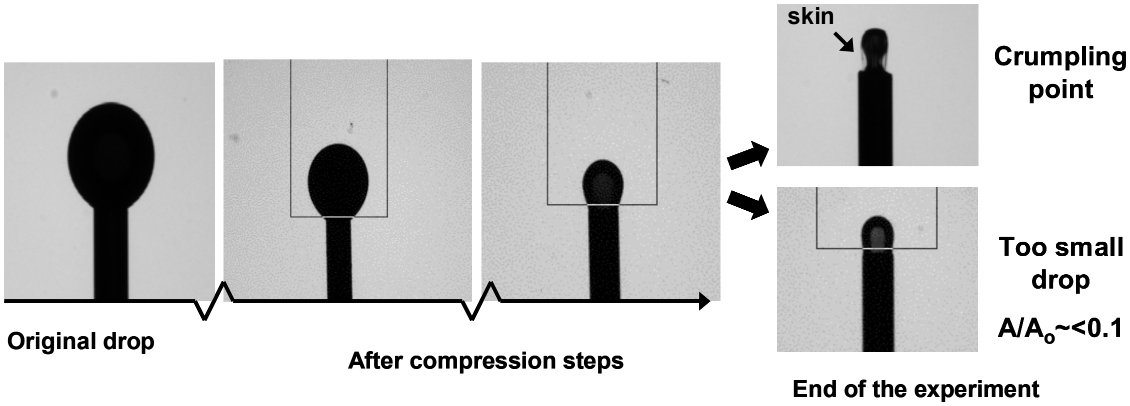


Figure 3-4. Compression steps during surface pressure isotherm experiments.

3.3. Emulsion Stability

To determine emulsion stability, water resolved from an emulsion was measured as function of time after a repeated treatment of heating and centrifugation. The procedure is described below.

3.3.1. Emulsion Preparation Procedure

Model emulsions were prepared with an organic phase of asphaltenes or bitumen with heptane and toluene, and an aqueous surfactant solution. 30 mL of organic phase was mixed for 5 minutes with 20 mL of aqueous surfactant solution to prepare an emulsion with a water ratio of 40vol%. The aqueous surfactant solution was slowly added to the oil phase while vigorously mixing with a *CAT*-520D homogenizer equipped with a 17 mm rotor at 17000 rpm.

3.3.2. Stability Test Procedure

For emulsion stability tests, the emulsion was first allowed to settle for 1.5 hours following homogenizing. After settling, two phases separated in most of the systems: a continuous phase (oil phase) and a concentrated emulsion. In some systems, an aqueous phase also settled out indicating that the emulsion was unstable. The continuous or oil phase was decanted. Both the concentrated emulsion and aqueous phase, if present, were used for the stability tests.

For emulsion drop size experiments, the emulsion was settled from 0.5 hours up to 24 hours depending on the stability of the system. For surfactants that effectively destabilized emulsions at short times, the drop size experiment was only done with shorter settling times. Otherwise, the continuous phase (CP) was decanted and the concentrated emulsion was used for measuring the drop sizes.

The concentration of asphaltenes in the continuous phase was also required. The volume of the decanted continuous phase was measured. The solvent was then evaporated until only asphaltene remained and the mass of the asphaltene residue was measured. The equilibrium concentration of asphaltenes in the continuous phase after emulsification (C^{eq}) is simply given by (Sztukowski 2005):

$$C^{eq} = \frac{mass(g)}{VolumeCP(mL)}$$ **Equation 3-9**

The concentrated emulsion and the free water, if present, were transferred to 12 mL graduated-centrifuge tubes and capped to prevent evaporation of the oil phase. The tubes were centrifuged for 5 minutes at 4000 rpm corresponding to 1640 RCF. After this first centrifugation, the separated phase volumes were recorded. This first centrifugation, immediately after settling, corresponded to time zero in the emulsion stability test. After the first centrifugation, the tubes were placed in a water bath for two hours at 60^{o}C and then centrifuged again. The separated phase volumes were recorded after every centrifugation. This procedure was repeated up to 24 hours or until there was no additional phase separation. The free water resolved is reported as a percentage of the total water in a given emulsion. The emulsion stability with aqueous surfactant solution in the emulsion was compared with the corresponding system of pure water to determine how emulsion stability changed when additives were added. Some experiments were performed at least twice to ensure repeatability. The statistical analysis is provided in Appendix F. In general, the emulsion stability tests with surfactants were highly reproducible giving errors (vol% free water) of ±2% for 100 ppm AOT systems, ±1.9% for 10 ppm NEO systems, ±7.6% for 100 ppm NEO systems and ±3.9% for 0.1wt% SN systems.

The emulsion stability test for systems with additives was always compared with stability test for a system with only asphaltenes (no surfactant) as reference line. One of the most common systems used as a referemce was 5 g/L asphaltenes in 25:75 heptol. Figure 3-5 shows the error bars for the average of three repeat runs. The repeats were performed on the same batch of asphaltenes over the course of several weeks.

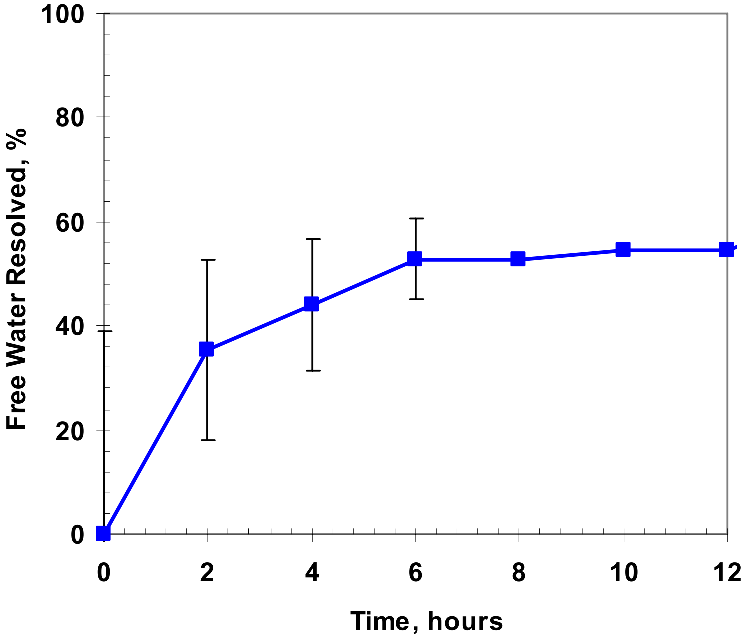


Figure 3-5. Emulsion stability test for 5g/L asphaltenes in 25:75 heptol and repeatability analyzes through error bars. Note, repeats were not performed for the data after 6 hours.

3.4. Emulsion Drop Size and Surface Coverage

3.4.1. Emulsion Drop Size

After the emulsion settling time, explained in the last section, a drop of the concentrated emulsion was placed onto a hanging-drop-glass slide along with a few drops of continuous phase. The sample was observed through a Carl Zeiss Axiovert S100 inverted microscope equipped with video camera and AxioVision Release 4.6.3 analysis software. Several images were collected of each sample, an image example is shown in Figure 3-6. In this work, approximately 500 to 700 water droplets were analysed to determine the Sauter mean diameter, d_{32}, which is defined as (Erbil 2006):

$$d_{32} = \frac{\sum_{i=1}^{N} f_i d_i^3}{\sum_{i=1}^{N} f_i d_i^2}$$ **Equation 3-10**

where f_i is the frequency and d_i is the diameter of the i^{th} droplet.

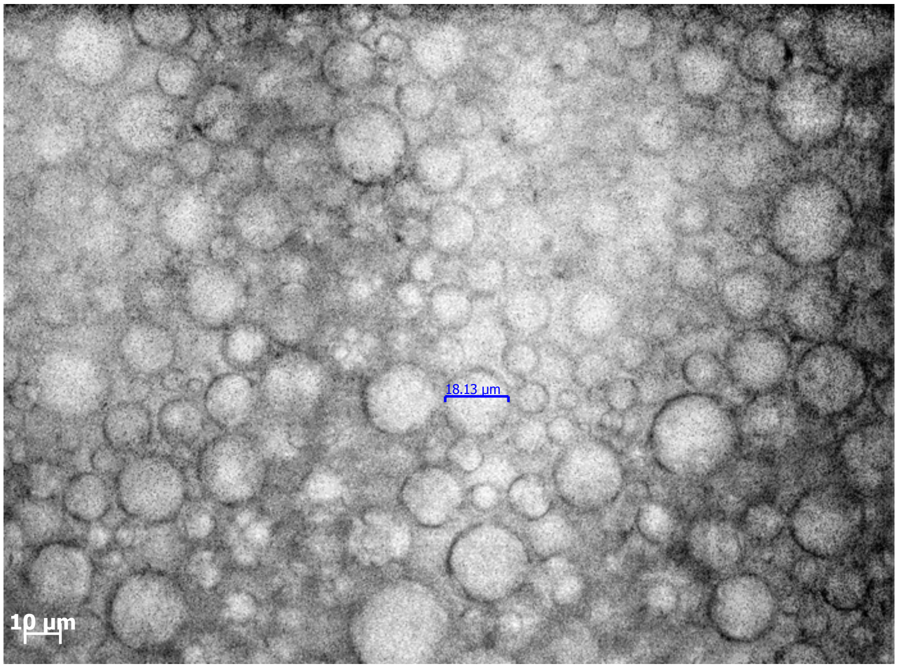


Figure 3-6. Micro picture of a water-in-oil emulsion with 5 kg/m^3 of asphaltene in toluene and 100 ppm of AOT aqueous solution at 8 hour of aging. Blue line is the diameter, d_i=18.13 µm, of one of the droplets.

3.4.2. Asphaltene Surface Coverage Calculation

Determination of asphaltene surface coverage was performed with an established procedure (Gafonova & Yarranton. 2001). Two experimental measurements are needed to determine asphaltene surface coverage, 1) the equilibrium concentration of asphaltenes in the continuous phase and 2) the Sauter mean diameter of the water droplets in the emulsion. These two measurements were described earlier. The calculations are described below.

The surface coverage of an emulsion interface is defined as (Erbil 2006),

$$\Gamma_A = \frac{m_{AI}}{A} \qquad \textbf{Equation 3-11}$$

where m_{AI} is the mass of asphaltenes adsorbed in the interface and A is the total area of the interface. The mass of asphaltenes adsorbed on the interface is found by an asphaltene mass balance (Gafonova & Yarranton. 2001),

$$m_{AI} = m_{AT} - m_{ACP} \qquad \textbf{Equation 3-12}$$

where m_{AT} is the total mass of asphaltenes on the emulsion and m_{ACP} is the mass of asphaltenes in the continuous phase after settling time. The total mass of asphaltenes in the emulsion is a known amount since the emulsion was prepared under a specified composition and it is related to the initial asphaltene concentration of the emulsion by (Gafonova & Yarranton. 2001),

$$m_{AT} = C_A^o V_{cp} \qquad \textbf{Equation 3-13}$$

where is the C_A^o is the initial asphaltene concentration (kg/m^3 of g/mL) in the emulsion and V_{cp} is the total volume (m^3 or mL) of continuous phase (oil phase) in the emulsion. Most emulsions contained 20 mL of the oil phase.

The mass of asphaltenes remaining in the continuous phase after settling time is also related to asphaltene concentration by (Gafonova & Yarranton. 2001),

$$m_{ACP} = C_{ACP}^{eq.} V_{cp}$$ **Equation 3-14**

where $C_{ACP}^{eq.}$ is the asphaltene concentration in the continuous phase (g/mL) after settling time and it is called equilibrium asphaltene concentration. The total volume of the continuous phase (oil phase), V_{cp}, is the same defined in Equation 3-13.

The mass of asphaltenes on the interface is related to initial and equilibrium asphaltene concentration by combining Equations 3-12 to 3-14 (Gafonova & Yarranton. 2001):

$$m_{AI} = m_{AT}\left(1 - \frac{C_{ACP}^{eq.}}{C_A^o}\right)$$ **Equation 3-15**

The other variable in Equation 3-11 is the total surface area which is related to the total volume of the dispersed phase (aqueous phase, V_w) and Sauter mean diameter (Equation 3-10) by:

$$A = \pi \sum_{i=1}^{N} f_i d_i^2 = \pi \left(\frac{\sum_{i=1}^{N} f_i d_i^3}{d_{32}} \right) = \frac{6V_w}{d_{32}}$$ **Equation 3-16**

With Equations 3-15 and 3-16, the surface coverage in Equation 3-11 is computed using experimental variables.

4. FILM PROPERTIES AND EMULSION STABILITY

As discussed in Chapter 2, the stability of water-in-oil emulsions stabilized by asphaltenes is related to the compressibility and crumpling ratio of the asphaltene film at the water-oil interface. When surfactants are added to the system, they disturb the asphaltene film and modify the interfacial properties such as the interfacial tension, compressibility, and crumpling ratio of the film.

Previously (Yarranton *et al.* 2007a,Yarranton *et al.* 2007b), the effects of solvent and asphaltene concentration were analyzed for model systems. Figure 4-1 shows how the film is more rigid as the heptane ratio in the solvent increases. More rigid films have lower compressibilities (steeper slopes in the surface pressure isotherm) and higher crumpling ratios. Higher surface pressures (lower interfacial tensions) were also observed as the heptane content increased. Note, the film properties were not sensitive to temperature up to at least 60°C. Figure 4-2 shows that these stronger films correlate to more stable emulsions (less free water).

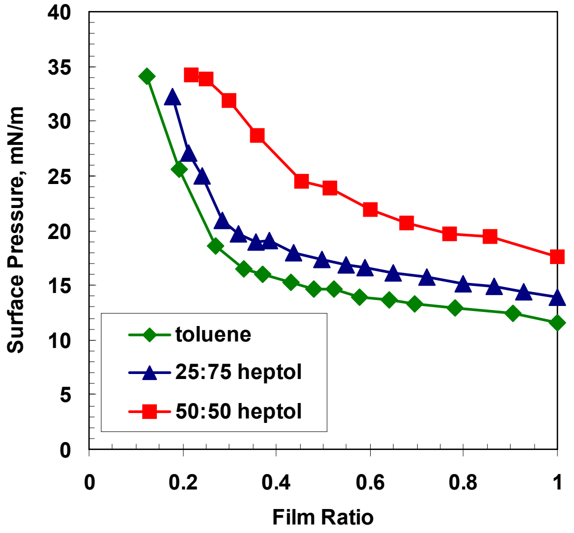


Figure 4-1. Surface pressure isotherms for solutions of 10 kg/m^3 asphaltenes in toluene and heptane versus water at 23°C.

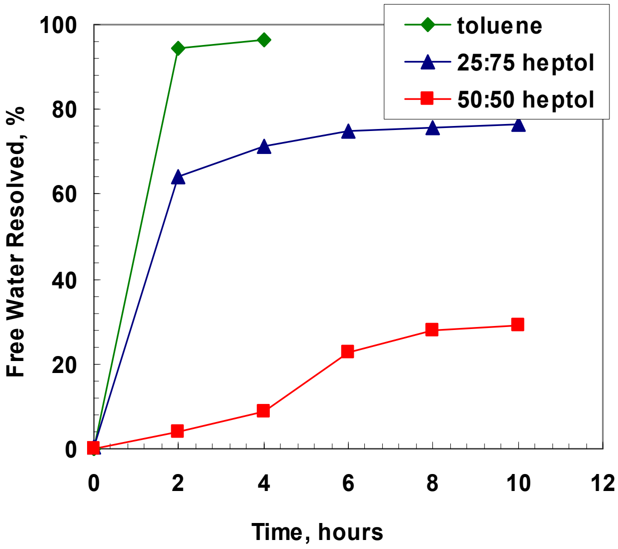


Figure 4-2 . Emulsion stability for solutions of 10 kg/m^3 asphaltenes in toluene and heptane and 40 vol% water at 60°C.

This chapter focuses on the effect of surfactants on asphaltene film properties and the stability of water-in-oil emulsions. Surface pressure isotherms are analyzed to determine the compressibilities and crumpling film ratios of the interfacial films. A comparison is made between asphaltene films alone and asphaltene films with additives in order to determine the change in the interfacial properties due to the presence of additives. Emulsion stability is assessed for the same systems in order to identify how the additive modified film properties affect emulsion stability.

Seven different additives were investigated in this work: Aerosol OT, three types of nonylphenol ethoxylate, NEO, (10, 15 and 30 ethoxy groups in the molecule), two types of dodecylbenzene sulfonic acid (DBSA-linear and DBSA-branched), and sodium naphthenate, SN. Aerosol OT, NEO and DBSA are the simplest structures within their family of surfactants and are widely use in commercial applications. Sodium naphthenate was investigated as well because it is present in bitumen extraction processes as a reaction product of naphthenic acids (natural component) and sodium hydroxide (added during bitumen processing). Note, the data for sodium naphthenate, DBSA-L, and DBSA-B were collected by Elaine Baydak (Baydak. 2008).

The additives were found to divide into two distinct behaviours: 1) additives that created reversible films; 2) additives that maintained irreversible asphaltene films. An example of each type of additive is shown in Figure 4-3. NEO-30 (diamonds) forms a film with high compressibility and no crumpling point. The absence of a crumpling point indicates a “reversibly” adsorbed film where the additive can leave the interface when the interface is compressed. DBSA-B (triangles) does not eliminate the crumpling point indicating that the film remains “irreversibly” adsorbed. These two types of additive effects are discussed separately below.

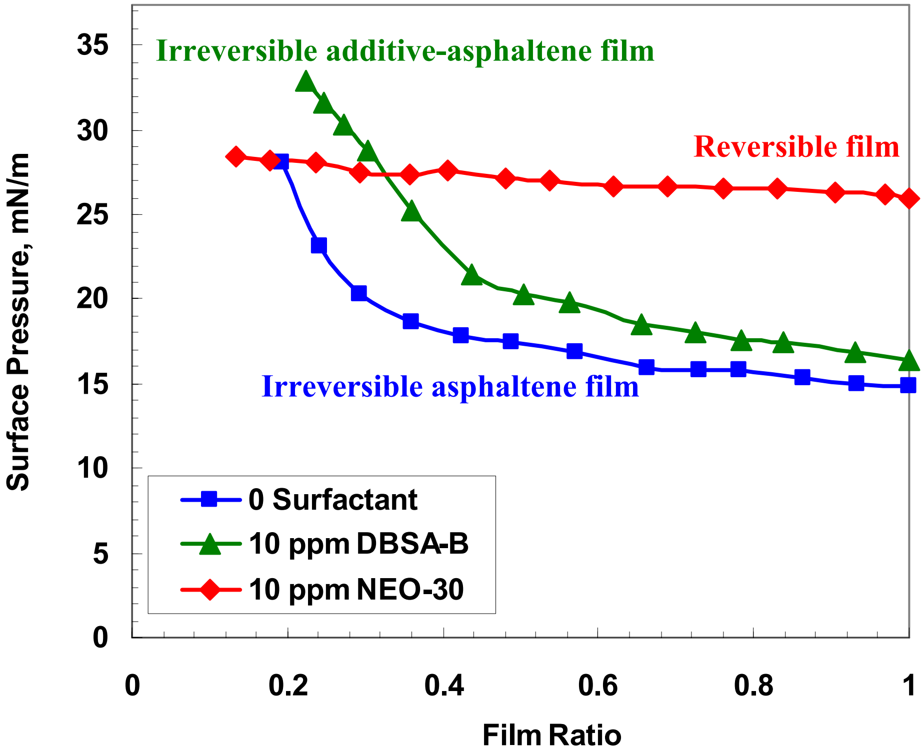


Figure 4-3. Comparison of surface pressure isotherms between reversible and irreversible films for solutions of 10 kg/m³ asphaltenes in 25:75 heptol versus aqueous phase. Films were aged for 1 hour at 23°C.

Note that the aging time for the asphalente-additive films is presented at one hour of aging. The aging effect was analyzed from 10 minutes to 240 minutes and it was found that the film properties do not significantly change with time, especially after 1 hour of aging. An example of the aging effect is presented in Appendix G.

4.1. Additives that Form Highly Compressible and Reversible Films.

Aerosol OT and nonylphenol ethoxylates (10, 15 and 30 ethoxy groups in the molecule) were found to form reversible and highly compressible films when added to solutions of asphaltenes in 25:75 heptol. AOT was investigated at 100 and 500 ppm in solution with 5 and 10 kg/m^3 asphaltenes in toluene, 25:75 and 50:50 heptol. Three nonylphenol ethoxylates were examined (10, 15, or 30 ethylene oxide groups per molecule) each at 10 and 100 ppm concentration with 10 kg/m^3 asphaltene in 25:75 heptol.

4.1.1. AOT Model Systems

Figure 4-4 shows the effect of AOT concentration on film properties in the model systems of asphaltenes in 25:75 heptol. The following observations were made:

2. the interfacial compressibility (Ci) increased as AOT concentration increased. Ci increased from 0.189 m/mN for an asphaltene film to 0.541 and 0.855 m/mN at AOT concentrations of 100 and 500 ppm, respectively.
3. the crumpling ratio decreased at 100 ppm AOT concentration, at 500 ppm AOT, no crumpling was observed.
4. the surface pressure increased (interfacial tension decreased) as AOT concentration increased.

One interpretation of these observations is that the AOT replaces the asphaltenes on the interface. Figure 4-5 compares surface pressures of AOT and asphaltene films with surface pressures of pure AOT films at 500 ppm. As the AOT concentration increases, the surface pressure increases (interfacial tension decreases) indicating that the more surface active AOT is replacing asphaltenes at the interface. The pure AOT films all have very high compressibility and no crumpling ratio indicating that the AOT molecules freely leave the interface when it is compressed; that is, the AOT is reversibly adsorbed. At 500 ppm AOT, the asphaltene-AOT film is nearly identical to the pure AOT film and appears to be reversibly adsorbed.

At 100 ppm AOT, the asphaltene-AOT film had properties intermediate between the pure AOT and pure asphaltene films. The film was more compressible than the pure asphaltene film but at least some of the film remained irreversibly adsorbed so that a transition to Phase Two with low compressibility occurred and a crumpling point was reached. The AOT and asphaltene molecules likely compete to adsorb at the interface. At 100 ppm, a mixture of asphaltenes and AOT is adsorbed at the interface. By 500 ppm, there is sufficient AOT to dominate the interface.

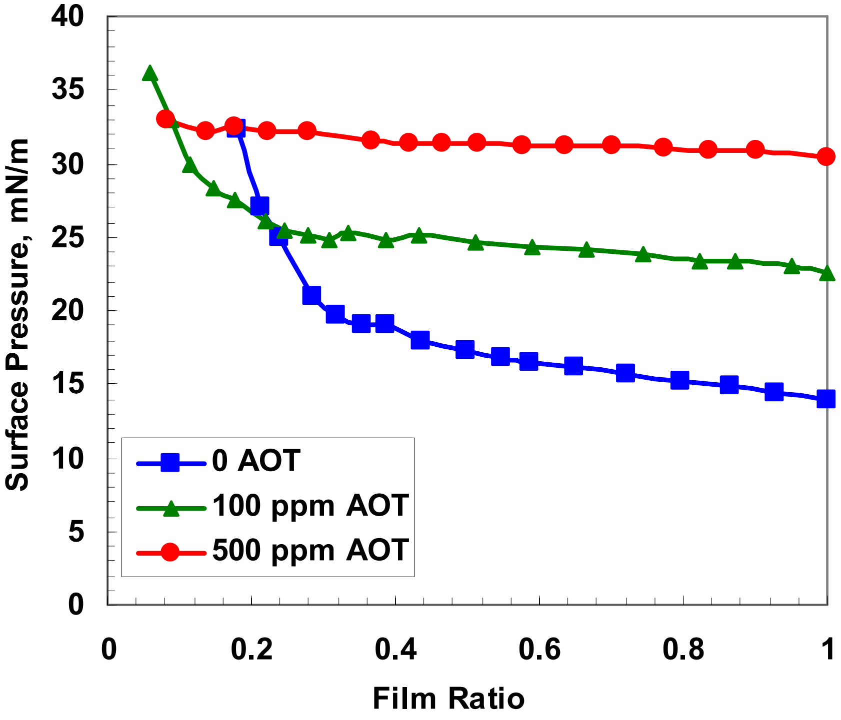


Figure 4-4. Effect of AOT on surface pressure for solutions of 5 kg/m³ asphaltenes in 25:75 heptol versus water. Films were aged for 1 hour at 23°C.

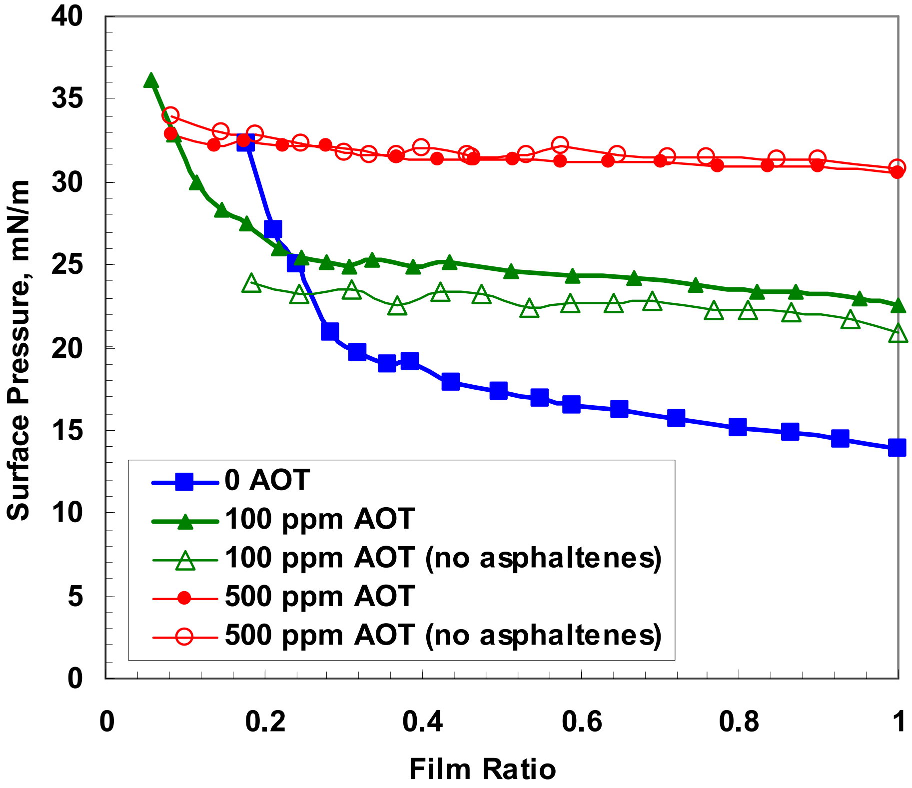


Figure 4-5. Comparison of surface pressure isotherms for solutions with and without 5 kg/m³ asphaltenes in 25:75 heptol versus aqueous solution. Films were aged for 1 hour at 23°C.

Since the addition of AOT increases the film compressibility and either decreases or eliminates the crumpling point, AOT is expected to decrease the stability of emulsions stabilized by asphaltenes. Pure AOT in heptol was found to create completely unstable emulsions. Hence, if AOT does indeed replace asphaltenes at the interface, completely unstable emulsions are expected at 500 ppm AOT. Figure 4-6 shows the emulsion stability for asphaltene model systems with AOT surfactant. As predicted, the addition of AOT decreased the stability of the emulsion and completely destabilized the emulsions at 500 ppm AOT.

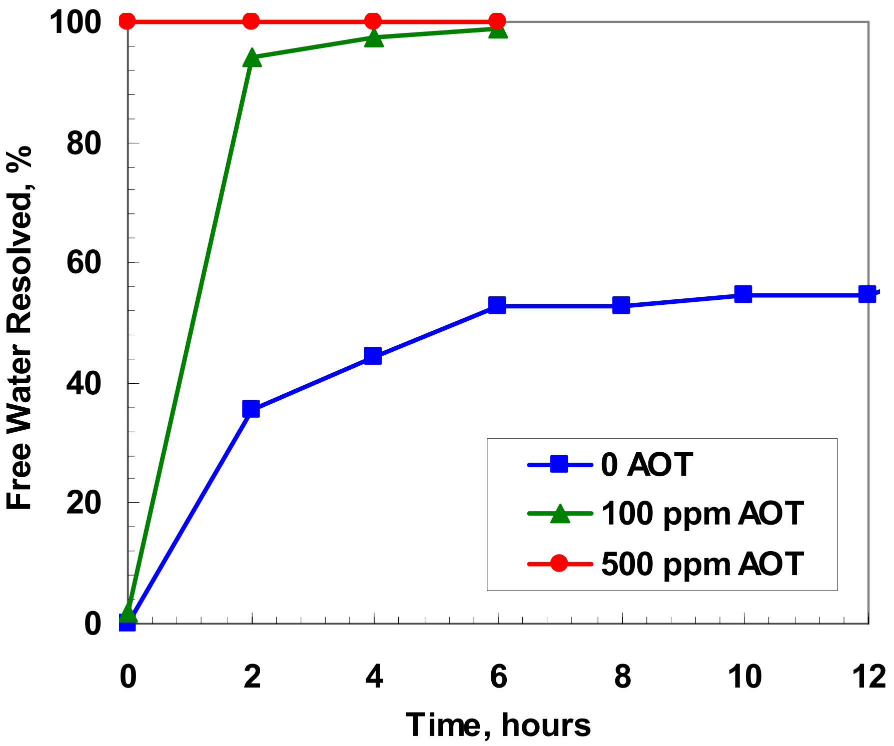


Figure 4-6. Effect of AOT on emulsion stability for solutions of 5 kg/m³ asphaltenes in 25:75 heptol at 60°C. Emulsions contained 40 vol% water.

Note, the above results were obtained when AOT and asphaltenes were added to the solution before emulsification. In demulsification applications, the surfactant is added after the emulsions already exist. Figure 4-7 shows that, except at time zero, the same effect on emulsion stability was observed when AOT was added after the emulsion was prepared (open triangles). At time zero, there was more free water when the surfactant was added after emulsification. Part of this water was the water in the aqueous surfactant solution (15 vol% of the total water) which was not emulsified with this procedure. However, an additional 25% resolved at time zero suggested that adding water when the emulsion was already formed accelerates coalescence. The added water goes through the emulsion in the form of big droplets with a high surfactant concentration. The high local concentration of surfactant might facilitate coalescence of water droplets in the vicinity. The added water may also swell some of the emulsified water promoting rapid coalescence of larger water droplets.

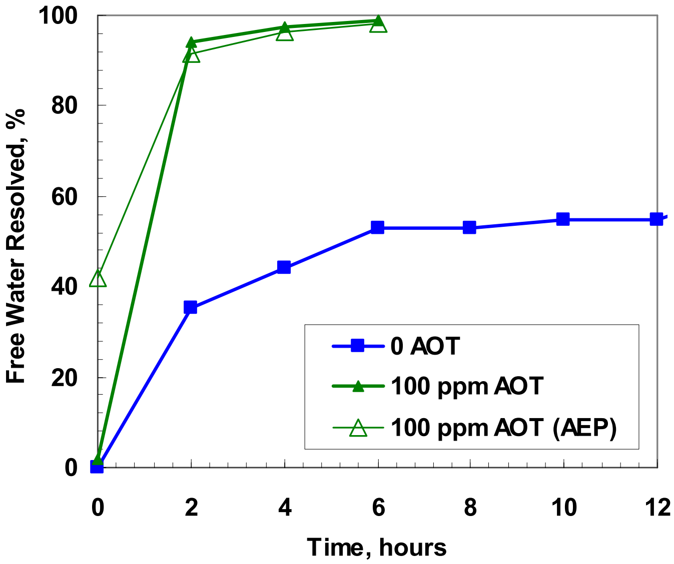


Figure 4-7. Comparison of order of AOT addition on emulsion stability for solutions of 5 kg/m³ asphaltenes in 25:75 heptol at 60°C. Emulsions contained 40 vol% water. (AEP : surfactant added after the emulsion was prepared).

4.1.2. AOT Diluted Bitumen Systems

Figures 4-8 and 4-9 show the surface pressure isotherms and the emulsion stability test for systems with diluted bitumen and AOT. AOT had the same effect on diluted bitumen systems as the model systems; that is, adding AOT increased the film compressibility, decreased the crumpling ratio, increased surface pressure (lowered interfacial tension), and created less stable emulsions. Again, it appears that AOT replaces asphaltenes at the interface, creating reversibly adsorbed films, and destabilizing the emulsions.

A difference in emulsion stability from asphaltene model systems was that at time zero, free water was resolved from bitumen systems with surfactants. A possible explanation for this is that some other material competed with asphaltenes to adsorb on the interface. Some of this material might not be irreversibly adsorbed and may contribute destabilizing the emulsion. For example, it has been found that adsorption of resins tended to destabilize emulsions (Sztukowski *et al.* 2003). The combination of surfactant and resins may create even less stable emulsions. However, at two hours treatment emulsions in bitumen are generally more stable than in the model systems, perhaps because the fluid viscosity is higher. Higher continuous phase viscosity slows the drainage between approaching droplets and therefore retards coalescence. After longer times of treatment, bitumen emulsions were still resolving water and they became less stable than the model systems. This observation supports the idea that relatively slow drainage velocity between the water droplets slows but does not stop coalescence. Note, at 4:1 dilution, the bitumen emulsions were more stable than the 9:1 diluted emulsions (Appendix E), again supporting the idea that continuous phase viscosity plays a role.

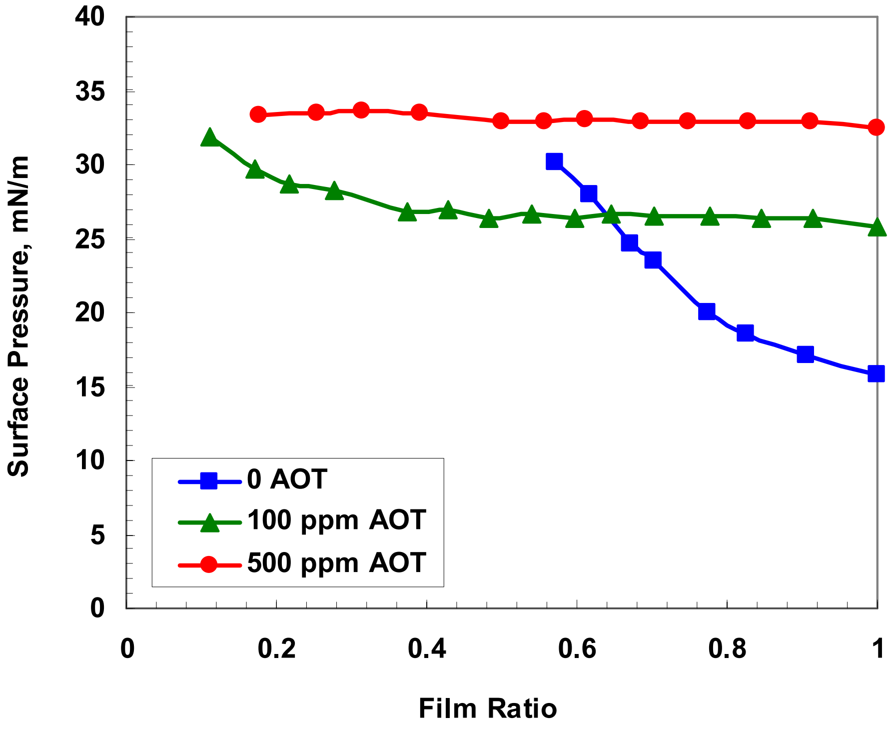


Figure 4-8. Effect of AOT on surface pressure for a 9:1 dilution of Athabasca bitumen in 25:75 heptol at 23°C versus aqueous solution. Films were aged for 1 hour.

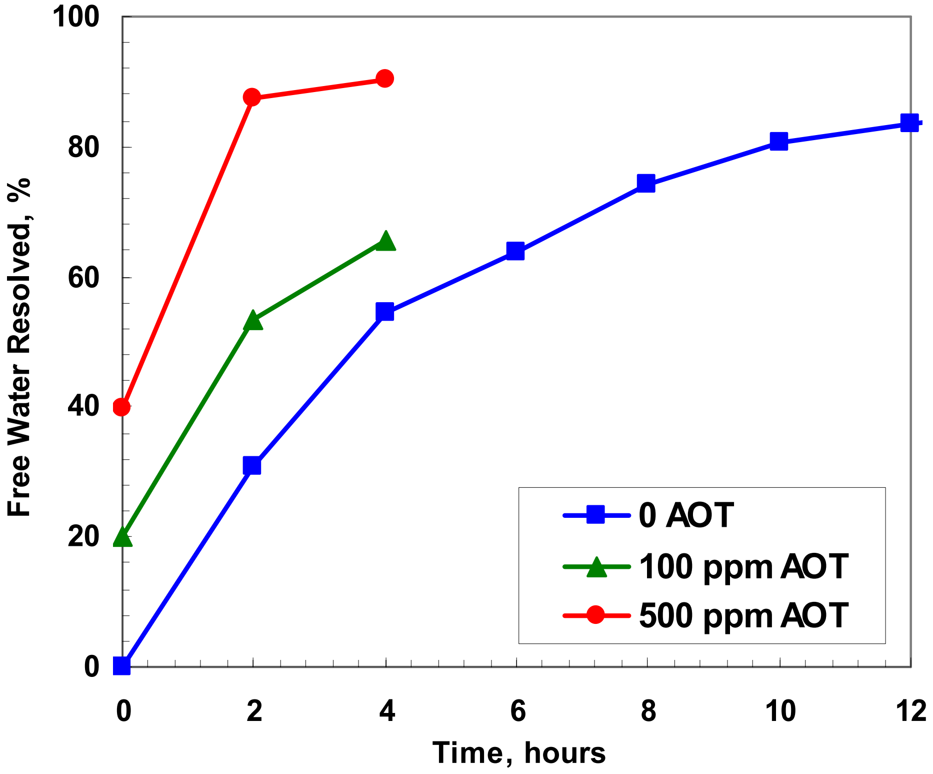


Figure 4-9. Effect of AOT on emulsion stability for a 9:1 dilution of Athabasca bitumen in 25:75 heptol at 60°C. Emulsions contained 40 vol% water.

4.1.3. Nonylphenol Ethoxylate Model Systems

Similar results to AOT model systems were obtained for nonylphenol ethoxylate surfactants, although at lower concentrations, as shown in Figure 4-10 and 4-11. Figure 4-10 shows that at just 1 ppm of NEO-15 surfactant, there was a decrease in film compressibility and lowering of interfacial tension. However, the emulsion stability was only slightly affected in comparison with the asphaltene-only film, Figure 4-11. It appears that 1 ppm of NEO-15 does not sufficiently weaken the film to significantly increase coalescence. Note that the crumpling ratio is barely affected indicating that the film remains irreversibly adsorbed.

At 10 ppm, NEO-15 created almost completely reversible films and formed less stable emulsions resolving 90% of the emulsified water (at 2 hours of treatment). At 100 ppm of NEO-15, the film was completely reversible and the emulsion almost completely unstable resolving 75% emulsified water at time zero and 96% at 2 hours of treatment. These results suggest that 100 ppm of NEO surfactant was enough to replace asphaltenes on the interface and effectively destabilized the emulsions.

The same trends in film properties and emulsion stability with additive concentration were observed for NEO-10 and NEO-30. In all cases, as the additive concentration increased, film compressibility increased, crumpling film ratio decreased, interfacial tension decreased, and emulsion stability decreased. Data are provided in Appendix C.

Note that at low film ratios (FR ~ 0.2) there is a slight decrease in surface pressure which is an experimental effect. The interface is sensitive to some experimental variables such as the rate at which fluid is withdrawn form the droplet during each step when the droplet is very small. As the compression steps were manually performed, there is no control in the exact amount withdrawn from the droplet and therefore some variation in the measured interfacial tension can occur at low film ratios.

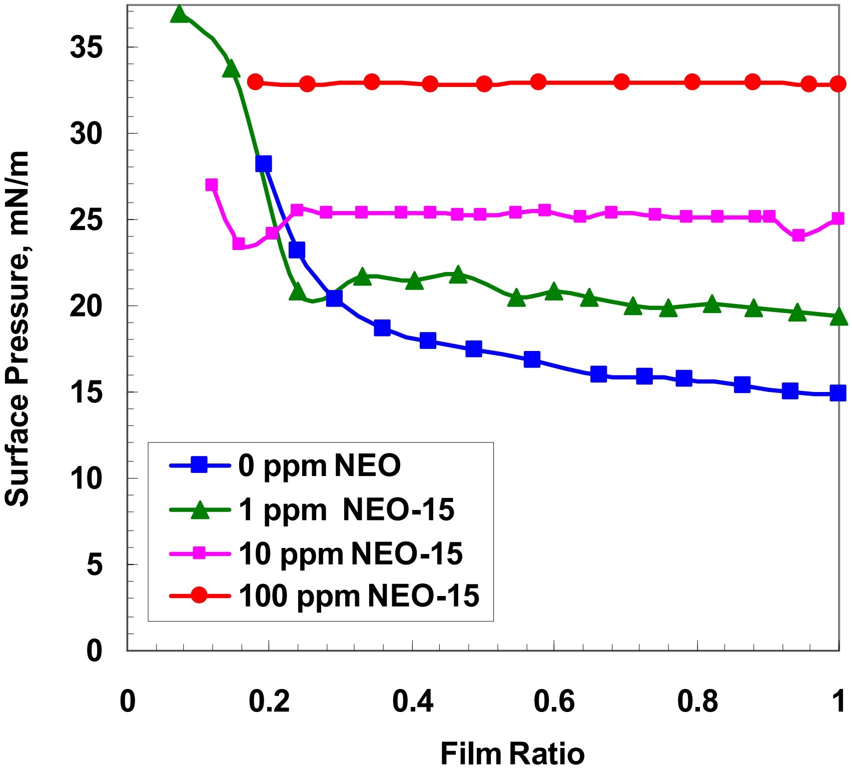


Figure 4-10. Effect of concentration for Nonylphenol Ethoxylate 15 (NEO-15) on solutions of 10 kg/m^3 asphaltenes in 25:75 heptol versus aqueous surfactant solutions. Films were aged for 1 hour at 23^{o}C.

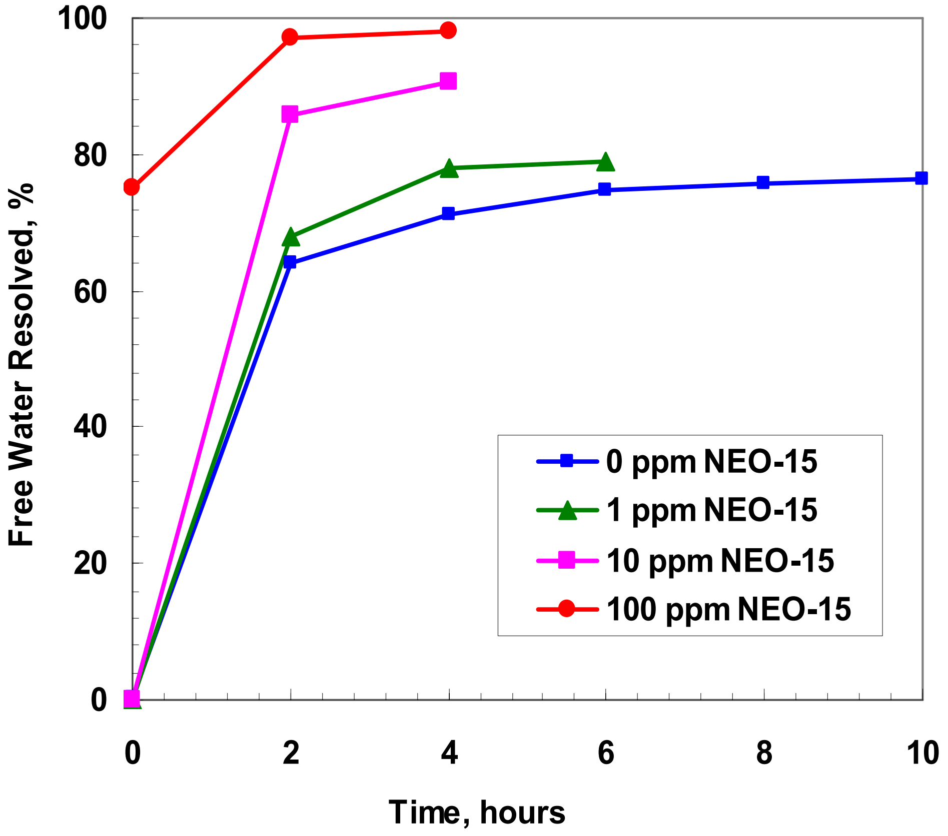


Figure 4-11. Effect of concentration for Nonylphenol Ethoxylate 15 (NEO-15) on emulsion stability for solutions of 10 kg/m³ asphaltenes in 25:75 heptol versus aqueous surfactant solutions at 60°C. Emulsions contained 40 vol% aqueous solution.

Figure 4-12 shows that isotherms with 100 ppm of NEO surfactants and asphaltenes in heptol are very similar to pure NEO with heptol (without asphaltenes). These results are again consistent with competitive adsorption and the replacement of asphaltenes with the additive. NEO-15, which is not shown in Figure 4-12, has properties intermediate between NEO-10 and NEO-30.

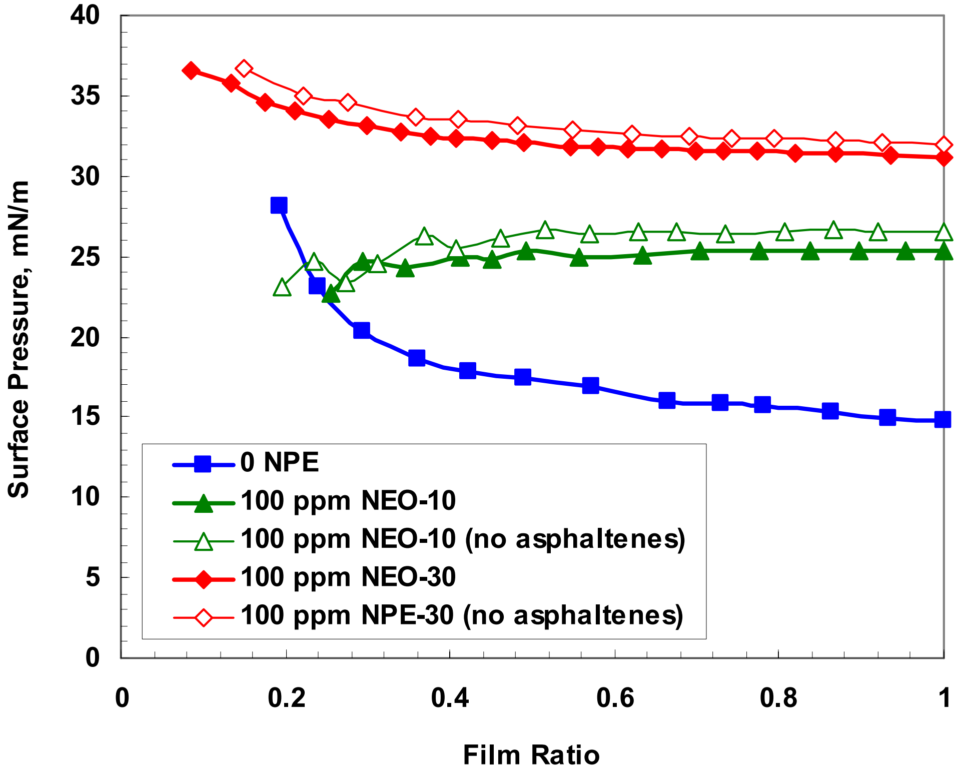


Figure 4-12. Comparison of surface pressure isotherms for systems with and without asphaltenes in 25:75 Heptol versus nonylphenol ethoxylates (NEO) 10 and 30 in water. Films were aged for 1 hour at 23°C.

Figures 4-13 and 4-14 show the effect of the number of ethoxy groups (increasing the size of the polar head group) on film properties and emulsion stability, respectively. Increasing the number of ethoxy groups increased compressibility, decreased the crumpling ratio, significantly reduced the interfacial tension, and decreased emulsion stability. In other words, the effect of increasing the number of ethoxy groups is similar to increasing the concentration of the additive. This observation suggests that increasing the polarity of this additive increases its surface activity allowing it to compete more effectively to adsorb at the interface. Kang *et al.* (2005) showed that, for crude oil emulsions with kerosene and water in a 1:1 v/v ratio, both the rate of film thinning and dewatering increased as the ethoxy number increased. Kang *et al.* (2005) results are also consistent with the idea that increasing the number of ethoxy groups enhances the adsorption of the additive, weakening the films, and destabilizing the emulsions. Rondon *et al.* (2006) also observed similar results for NEO over a range of ethoxy group between 4.75 and 20. They found that the emulsions were all destabilized by an additive concentration of 10 to 100 ppm with lower concentrations required for higher numbers of ethoxy groups.

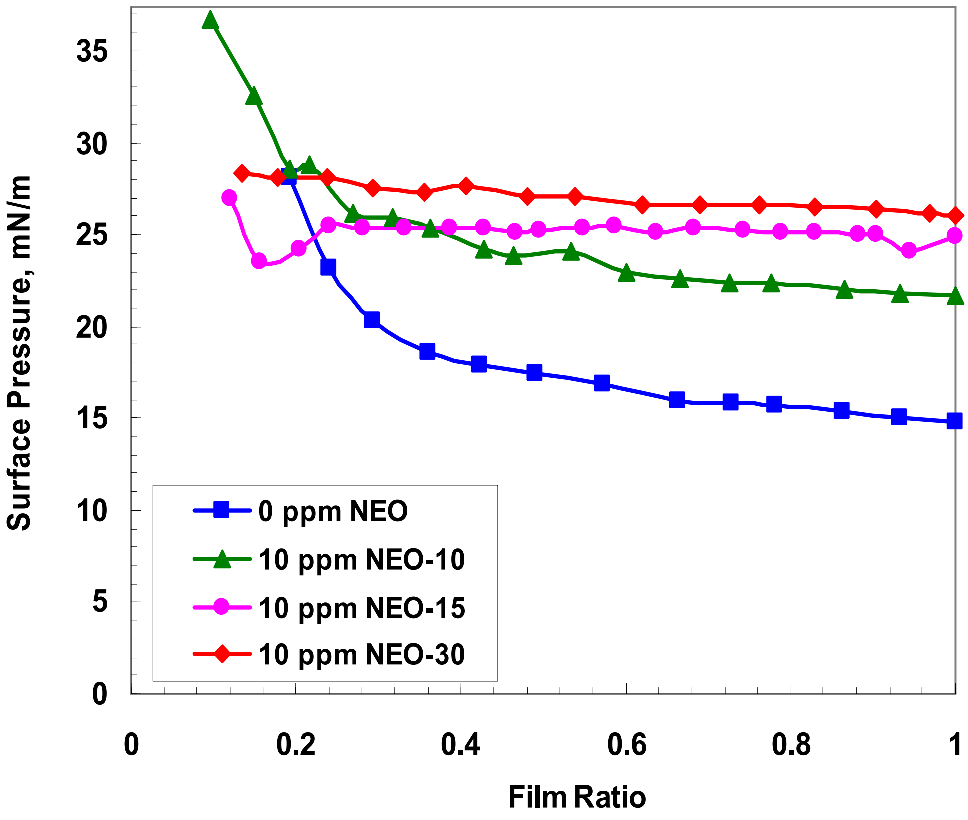


Figure 4-13. Effect of structure for Nonylphenol Ethoxylate (NEO) 10, 15 and 30 on surface pressure for solutions of 10 kg/m³ asphaltenes in 25:75 heptol versus aqueous surfactant solution. Films were aged for 1 hour at 23°C.

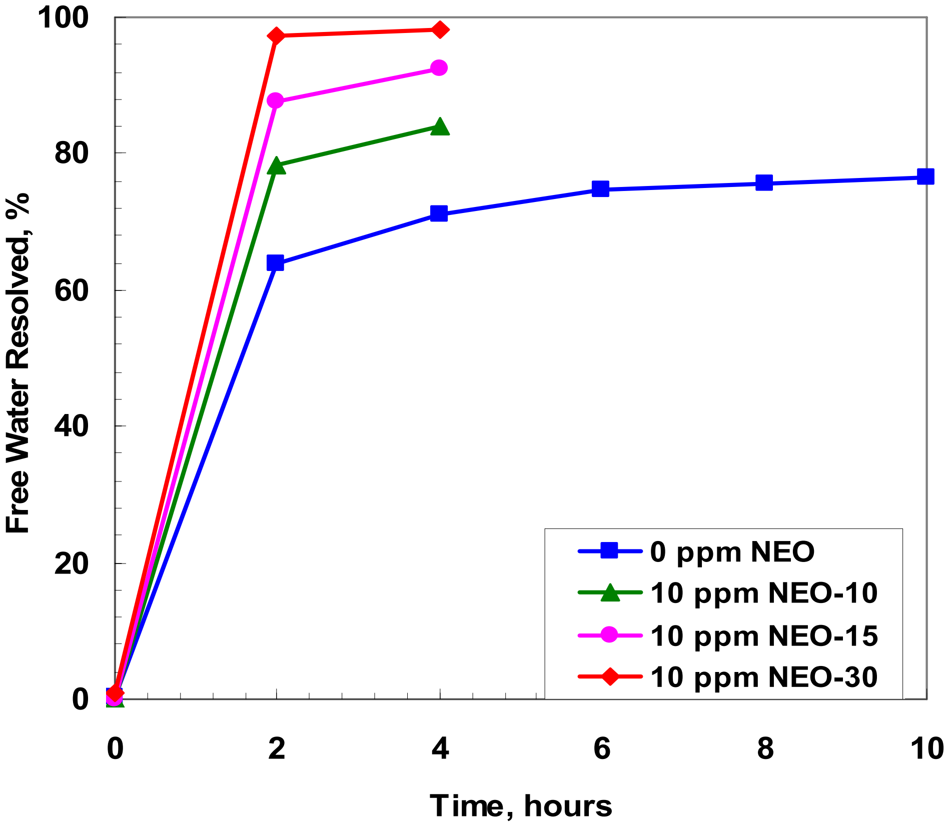


Figure 4-14. Effect of number of ethoxy groups in Nonylphenol Ethoxylate (NEO-10, NEO-15 and NEO-30) on emulsion stability for solutions of 10 kg/m³ asphaltenes in 25:75 heptol at 60°C. Emulsions contained 40 vol% aqueous surfactant solution.

Note, that in the same manner as AOT, NEO surfactants were added to the aqueous phase before emulsification. Figure 4-15 compares the emulsion stability when the additive is added before (closed symbols) and after (open symbols) emulsification. Changing the order of additive addition has little effect on emulsion stability. As with AOT, adding surfactant after emulsion preparation had some difference in the water resolved at time zero. As with AOT, the water that is part of the added surfactant solution report as free water and there may also be some early coalescence as the result of swelling the emulsified water droplets.

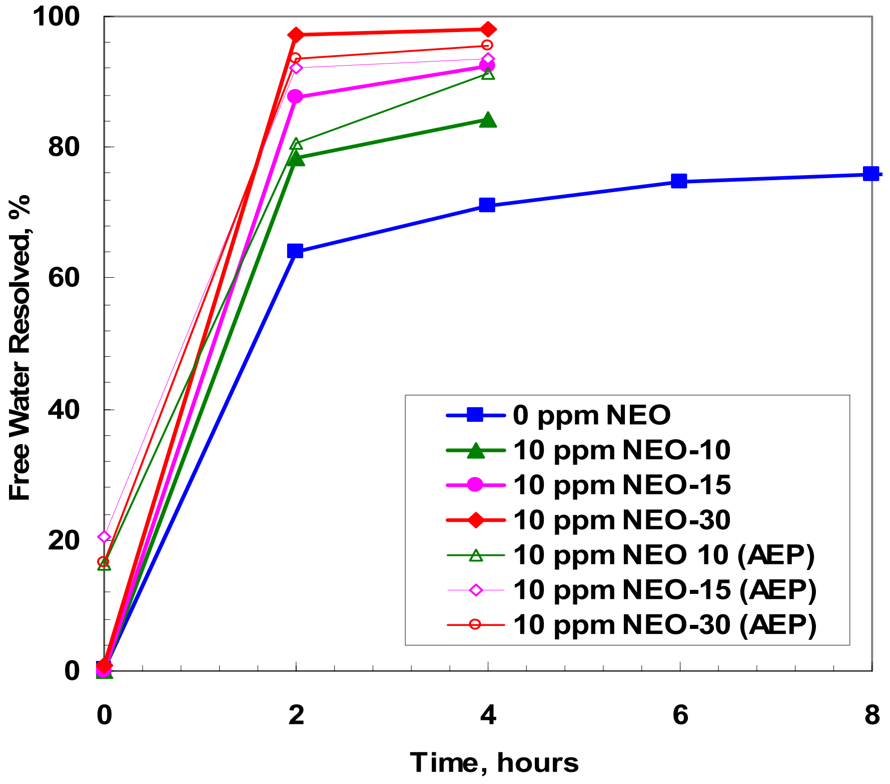


Figure 4-15. Comparison of order of NEO surfactants addition on emulsion stability for solutions of 10 kg/m³ asphaltenes in 25:75 heptol at 60°C. Emulsions contained 40 vol% water. (AEP : surfactant added after the emulsion was prepared).

Figures 4-16 and 4-17 compare the effect of AOT and NEO-30 at a concentration of 100 ppm on film properties and emulsion stability, respectively. All of the NEO additives weakened the films and destabilized the emulsions more effectively than AOT at a given additive concentration. For example, only 10 ppm of NEO-30 (open diamonds) was required to completely destabilize the emulsion compared with over 100 ppm for AOT. In this case, NEO-30 had lower interfacial tension (higher surface pressure) than AOT, that is, NEO-30 had higher surface activity than AOT. As NEO-30 is more surface active, it adsorbs more efficiently on the interface, hence, lower concentrations than AOT were needed to destabilize emulsions.

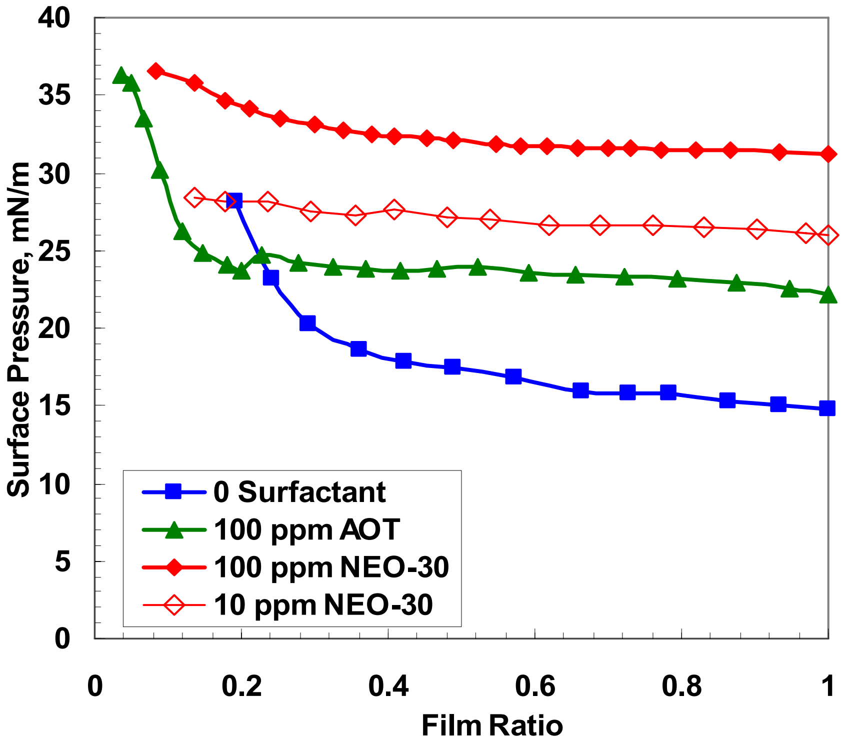


Figure 4-16. Comparison of surface pressure isotherms between AOT and NEO-30 for solutions of 10 kg/m³ asphaltenes in 25:75 heptol versus aqueous surfactant solution. Films were aged for 1 hour at 23°C.

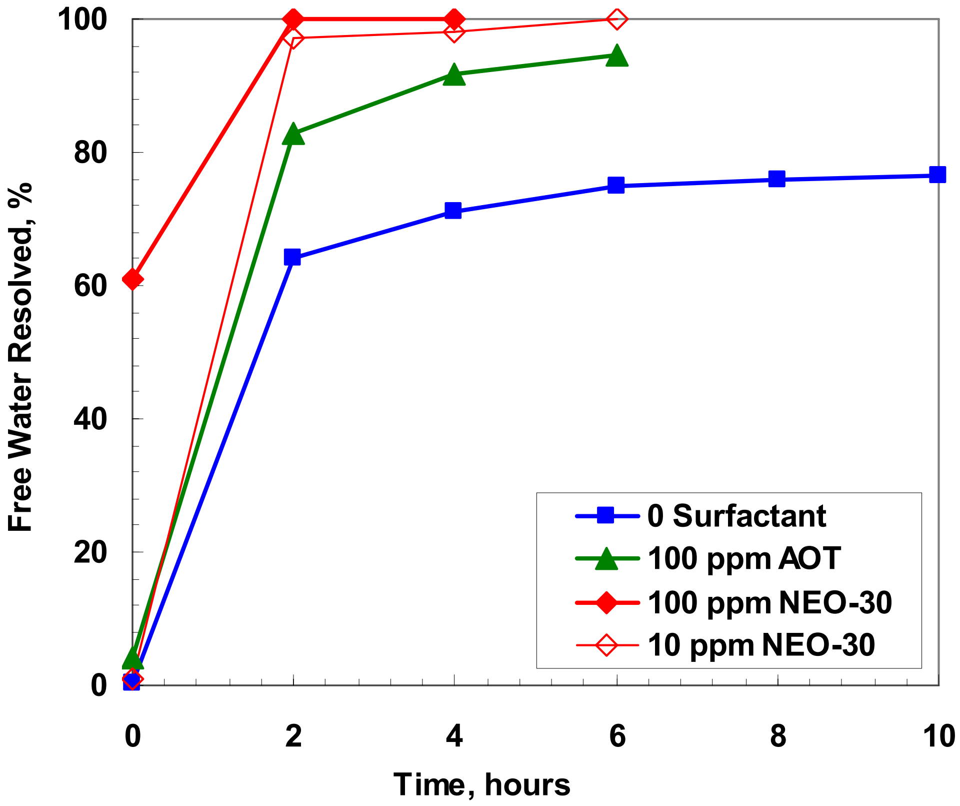


Figure 4-17. Comparison of AOT and NEO-30 at 100 pmm on emulsion stability for solutions of 10 kg/m³ asphaltenes in 25:75 heptol at 60°C. Emulsions contained 40 vol% aqueous solutions.

4.1.4. Nonylphenol Ethoxylate Diluted Bitumen Systems

Figure 4-18 shows that nonylphenol ethoxylates weaken bitumen films and create reversibly adsorbed films at 100 ppm concentrations. Figure 4-19 shows that the weaker films correspond to less stable water-in-diluted bitumen emulsions.

The main difference between asphaltene model systems and diluted bitumen systems with NEO was that some water resolved at time zero for bitumen emulsions; that is, free water was present after initial settling and one centrifugation without heating the emulsions. Bitumens contain significant amounts of resins which are also surface active and are known to create weaker emulsions than asphaltenes (Sztukowski & Yarranton. 2005) . It is likely that the interfacial films formed in bitumen contain both asphaltenes and resins. These weaker films may require less additive to restore reversibility. Interestingly, while these emulsions are initially less stable, their stability after treatment (2 hours and longer) is greater than observed for asphaltene films at the same additive concentration. It is possible that the higher viscosity of the diluted bitumen contributes to emulsion stability by inhibiting film drainage between approaching droplets. Increased emulsion stability was also observed for a lower dilution ratio (higher viscosity in the continuous phase) in diluted bitumen systems with no additives (data are shown in Appendix E).

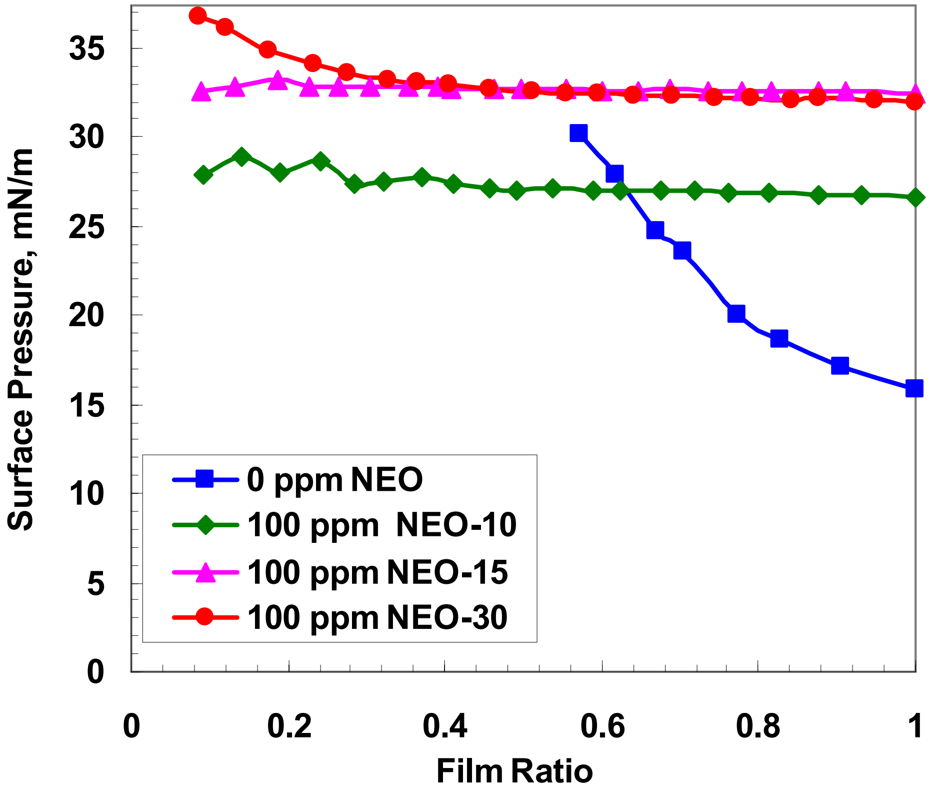


Figure 4-18. Effect of Nonylphenol ethoxylates (NEO) 10, 15 and 30 on surface pressure isotherms for a 9:1 dilution of Athabasca bitumen in 25:75 heptol versus aqueous surfactant solution at 23°C. Films were aged for 1 hour.

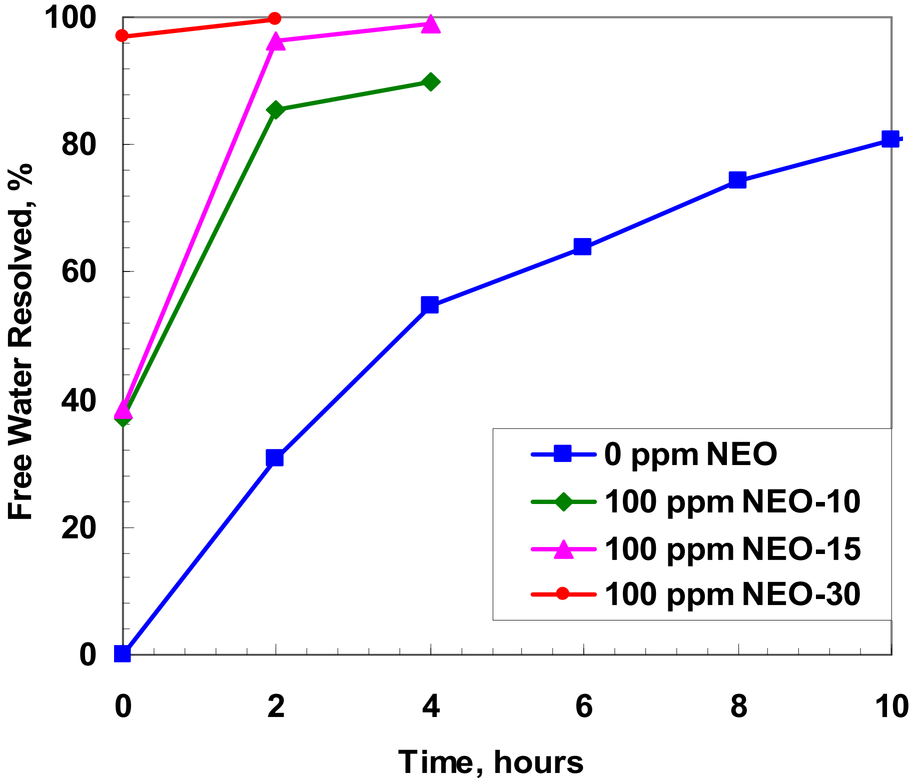


Figure 4-19. Effect of Nonylphenol ethoxylates (NEO) 10, 15 and 30 on emulsion stability for a 9:1 dilution of Athabasca bitumen in 25:75 heptol at 60°C. Emulsions contained 40 vol% water.

4.1.5. Summary of Additives that Form Reversible Films

AOT and NEO surfactants had the following effects:

1) At low concentrations (<500 ppm AOT, <100 ppm NEO), additives increased interfacial compressibility and decreased crumpling film ratios. Both factors decreased emulsion stability. At high concentrations (500 ppm AOT, 100 ppm NEO), additives eliminated the crumpling point and created completely reversible films (infinite interfacial compressibility). These factors effectively destabilized emulsions. Reversible films were formed when surfactant molecules replaced asphaltenes at the interface.

2) Less concentration of the surfactants with larger polar head groups was needed to effectively destabilize emulsions. For example, 100 ppm of AOT was required to achieve same effects as 10 ppm of NEO-30. Similarly, lower concentrations of NEO-30 were required to destabilize emulsions compared with NEO-10.

3) The same trends were observed in diluted bitumen systems with small differences attributed to presence of resins and a more viscous continuous phase.

4.2. Additives that Maintain an Irreversible Asphaltene Film

Sodium naphthenate and dodecylbenzene sulfonic acid, linear and branched, were found to maintain the irreversibility of asphaltene films and form relatively low compressibility films when added to solutions of asphaltenes in toluene, 25:75 and 50:50 heptol. Sodium naphthenate was investigated at 1000 ppm (0.1wt%) and 5000 ppm (0.5wt%) in solution with 5 and 10 kg/m^3 asphaltenes in toluene, 25:75 and 50:50 heptol. Both the linear (DBSA-L) and the branched (DBSA-B) forms of DBSA were studied at concentrations of 10 and 100 ppm (aqueous phase) in solutions of toluene, 25:75 heptol, 50:50 heptol and asphaltene concentrations of 5 and 10 kg/m^3, all at 23°C.

As will be discussed, the behaviour of sodium naphthenate depends on pH. Also, the DBSA additives are part of an acidic solution with pH as low as 3.3. pH affects the interfacial properties of asphaltene films and the stability of the corresponding emulsions. Therefore, to assess the effect of these additives baseline data for asphaltene films and emulsions at the appropriate pH are required.

4.2.1. Effect of pH on Asphaltene Model Systems

High pH (7 to 10):

Figure 4-20 shows a comparison on film properties in model systems of asphaltenes in toluene of pH 7 and pH 10. The effect of high pH was to lower the interfacial tension (higher surface pressure) to approximately 4 mN/m. The compressibility and crumpling film ratio barely changed. Compressibilities for pH 7 and pH 10 were 0.233 and 0.221 m/mN, respectively. The crumpling film ratios were 0.10 and 0.09 for pH 7 and pH 10, respectively.

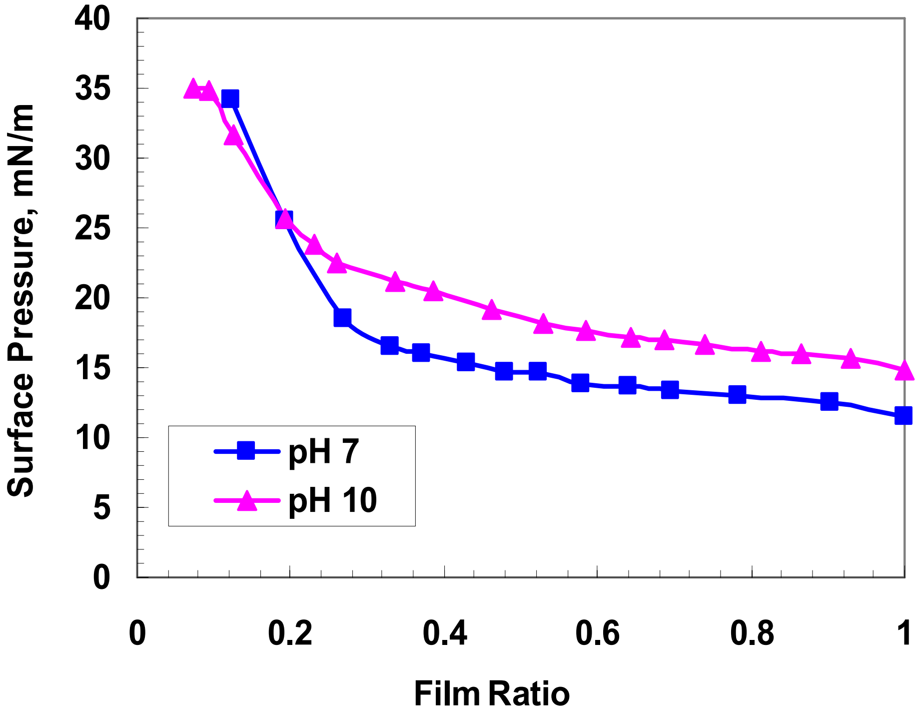


Figure 4-20. Effect of high pH on surface pressure for solutions of 5 kg/m³ asphaltenes in toluene versus water at pH 7 and pH 10. Films were aged for 1 hour at 23^{o}C.

Since the change from pH 7 to pH 10 had no large effect on compressibility (slope of the surface pressure isotherm) and crumpling ratio, high pH was not expected to change the stability of the emulsion. However, Figure 4-21 shows that more stable emulsions were formed at pH 10. A possible explanation is that lower interfacial tension contributes to emulsion stability. The lowering of the interfacial tension might be attributed to a molecular reorganization at the interface.

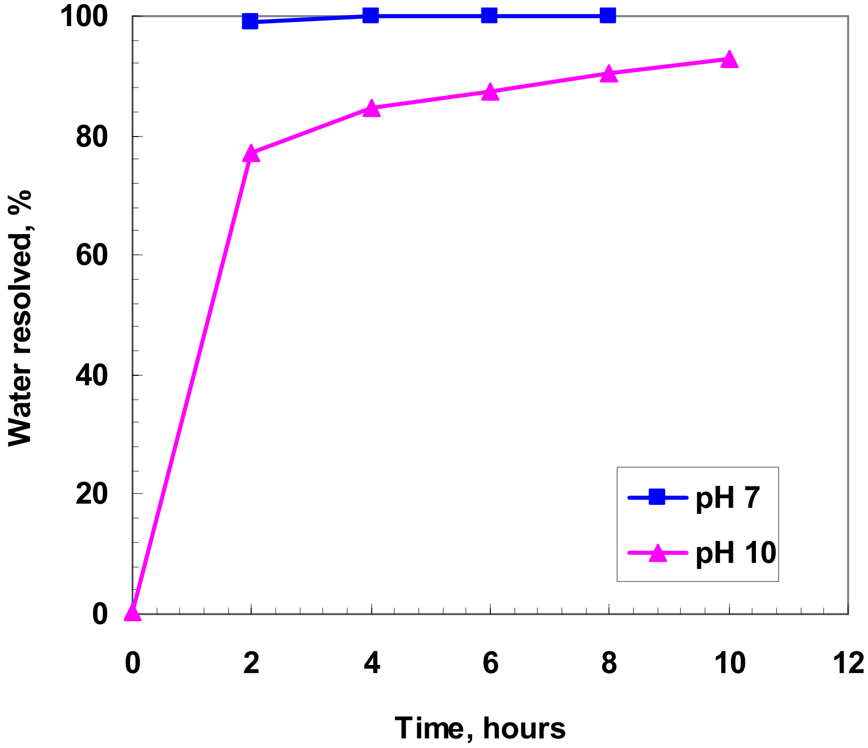


Figure 4-21. Effect of high pH on emulsion stability for solutions of 5 kg/m³ asphaltenes in toluene with water at pH 7 and pH 10 at 60°C. Emulsions contained 40 vol% water.

When heptane was added to systems with pH 7 and pH 10, the film properties were not affected as in toluene systems, Figure 4-22. Note, that in toluene increasing pH form 7 to 10, shifts interfacial tension up by ~4 mN/m. Changing the solvent from toluene to 25:75 heptol had almost identical effect, see Figure 4-1. It is possible that adding heptane already increased the asphaltene surface coverage so that a pH change has little additional effect. Figure 4-23 shows that emulsion stability decreased at pH 10. It is not clear why emulsion stability decreased at high pH in this case.

Note that emulsion stability increased in comparison with systems with only toluene at the same respective pH (Figures 4-21 and 4-23). This followed the same trend than for only asphaltene systems in which emulsion stability increased as heptane was added to the systems.

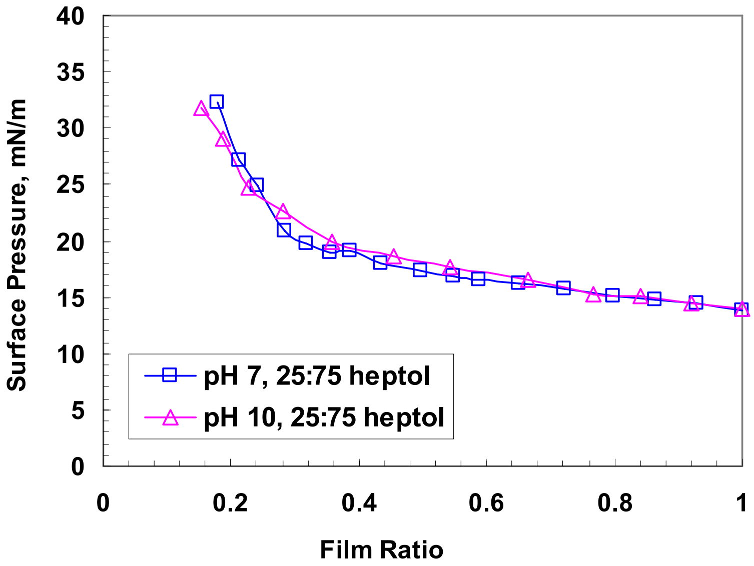


Figure 4-22. Effect of high pH on surface pressure for solutions of 5 kg/m³ asphaltenes in 25:75 heptol versus water at pH 7 and pH 10. Films were aged for 1 hour at 23°C.

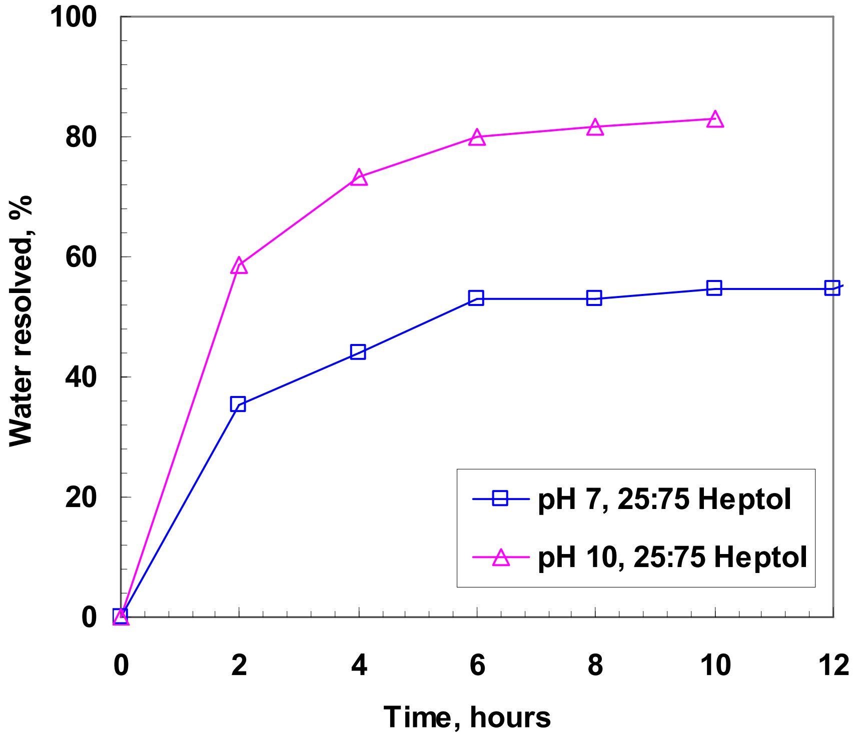


Figure 4-23. Effect of high pH on emulsion stability for solutions of 5 kg/m³ asphaltenes in 25:75 heptol with water at pH 7 and pH 10 at 60°C. Emulsions contained 40 vol% water.

Low pH (3.3 to 7):

Figure 4-24 shows the surface pressure isotherms for model systems with 10 kg/m^3 of asphaltenes at low pH. At low pH crumpling film ratios significantly increased and compressibility decreased, that is, more rigid films were formed. There was little change in film properties from pH 4.5 to 3.3 although the films appear to be weakest at pH 4.5. Poteau *et al.* (2005) observed that at both low and high pH, the elastic compression modules increased which corresponds to lower compressibility as observed in this work.

A possible explanation for the increased film rigidity at low pH is that asphaltene functional groups may become charged, enhancing asphaltene surface activity (Poteau. *et al.* 2005). As asphaltenes become more surface active, a larger mass of asphaltenes may adsorb on the interface, leading to a more rigid film. As well, more surface active asphaltenes may become more strongly bound to the interface; that is, they become more irreversibly adsorbed. A similar example is the increased irreversibility of asphaltene films in heptane because heptane is a poor solvent for asphaltenes and therefore forces the asphaltenes to adsorb more strongly. The mass of asphaltenes adsorbed on the interface was measured and was found to increase from $1.62 \cdot 10^{-3}$ g/m^2 at pH 7 to $2.46 \cdot 10^{-3}$ g/m^2 at pH 3.3. Data for mass on the interface for different systems are provided in Appendix D.

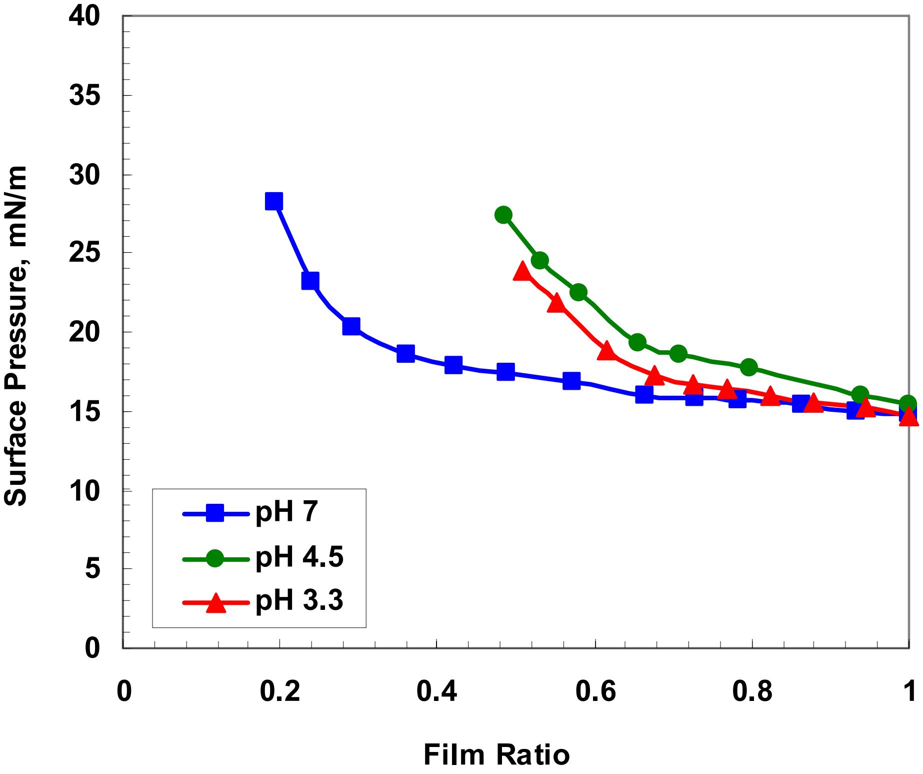


Figure 4-24. Effect of low pH on surface pressure for solutions of 10 kg/m³ asphaltenes in 25:75 heptol versus water at pH 7, pH 4.5 and pH 3.3. Films were aged for 1 hour at 23°C.

Figures 4-25 shows the effect of low pH on emulsion stability for model systems with 10 kg/m³ of asphaltenes. As was expected the emulsion stability increased for pH 3.3 since the film was more rigid. However, the emulsion stability at pH 4.5 was the same as at pH 7. The trends in emulsion stability at an asphaltene concentration of 5 kg/m³ are even more challenging to interpret, Figure 4-26. Although the film properties followed the same trend as at 10 kg/m³ (stronger films at lower pH), the emulsion stability decreased at lower pH. Note, error bars were included on these plots because the stability data for some pH where close together and yet different beyond the scatter in the data.

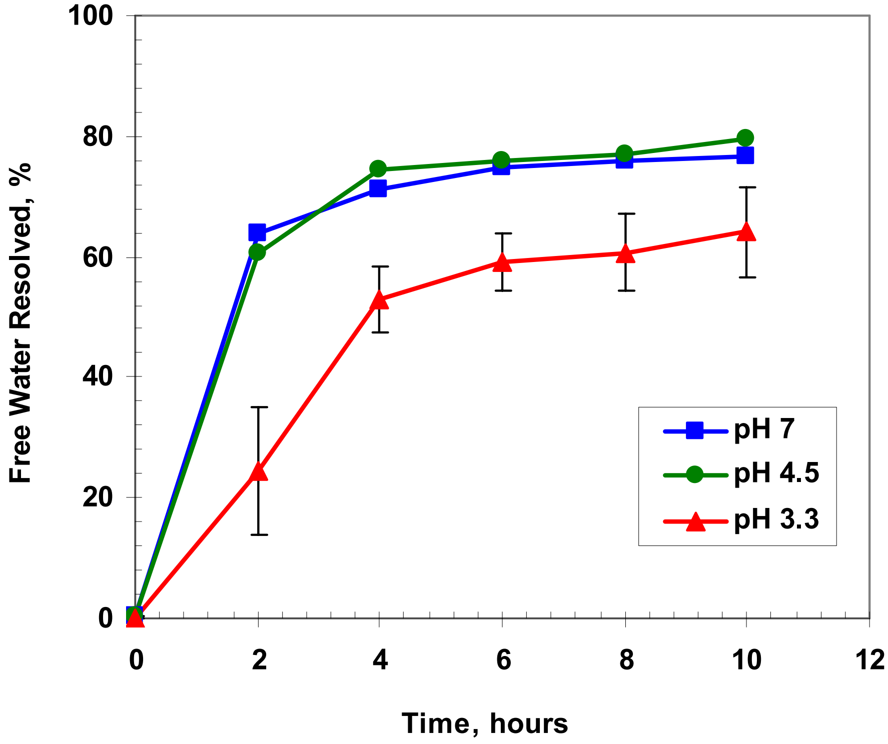


Figure 4-25. Effect of low pH on emulsion stability for solutions of 10 kg/m³ asphaltenes in 25:75 heptol with water at pH 7, pH 4.5 and pH 3.3 at 60°C. Emulsions contained 40 vol% aqueous solution.

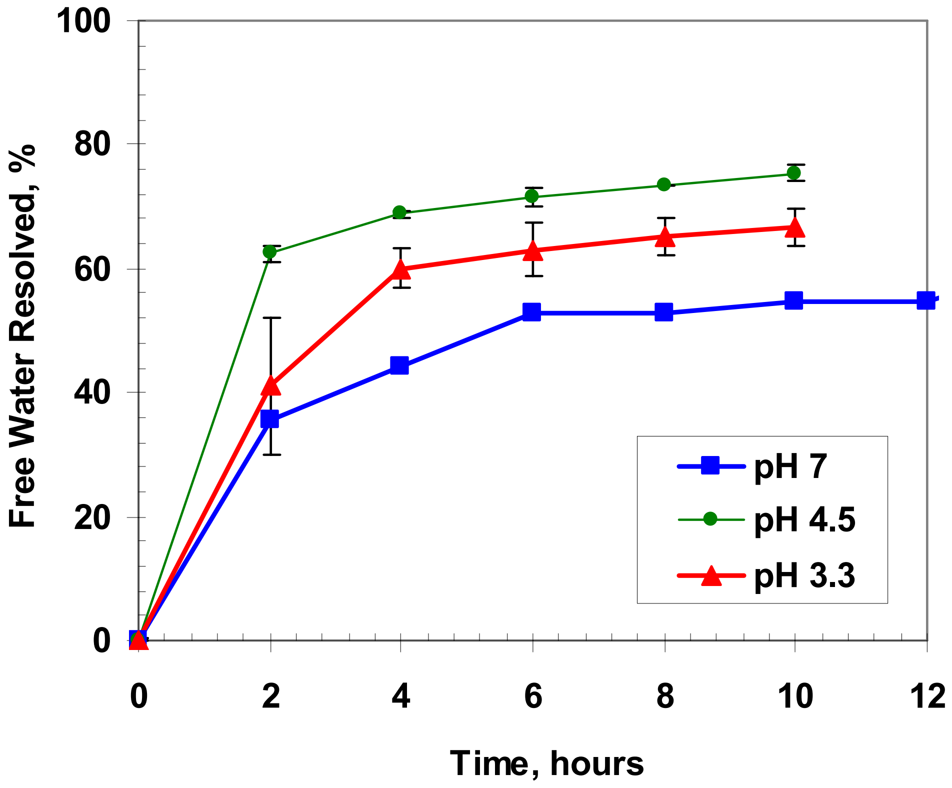


Figure 4-26. Effect of pH on emulsion stability for solutions of 5 kg/m³ asphaltenes in 25/:75 heptol with water at pH 7, pH 4.5 and pH 3.3 at 60°C. Emulsions contained 40 vol% water.

A possible explanation to decreased emulsion stability at low pH might be an effect of higher temperature on asphaltene films at low pH. In the original experiments, film properties were measured at 23°C. Film properties at low pH were reanalyzed at the same temperature than the emulsions stability tests (60°C). Figure 4-27 shows that high temperature (60°C) at low pH (pH 3.3) significantly decreased the crumpling film ratio. Note that this effect was not observed at pH 7 in which the film properties were similar at 23°C and 60°C. Decreasing crumpling film ration means that the film had more capacity to be compressed. It is likely that asphaltenes, at low pH and high temperature, are able to rearrange on the surface decreasing the surface coverage per molecule; it allows more compression of the film. However, stronger films were observed at both 23°C and 60°C. These film properties have a poor correlation with emulsion stability.

Some of the following issues might play a role affecting the relationship between film properties and emulsion stability:

- pH may increase mobility of asphaltene aggregates on the surface. Mobility along with centrifugal forces in the stability tests, favours displacement of asphaltenes during drainage in coalescence and decrease emulsion stability.
- temperature effect which increased capacity of film compression at low pH. This favours coalescence and less stable emulsions.

It is unclear what mechanisms are involved at low pH with asphaltene films and emulsion stability. More research is needed to clarify this mechanism.

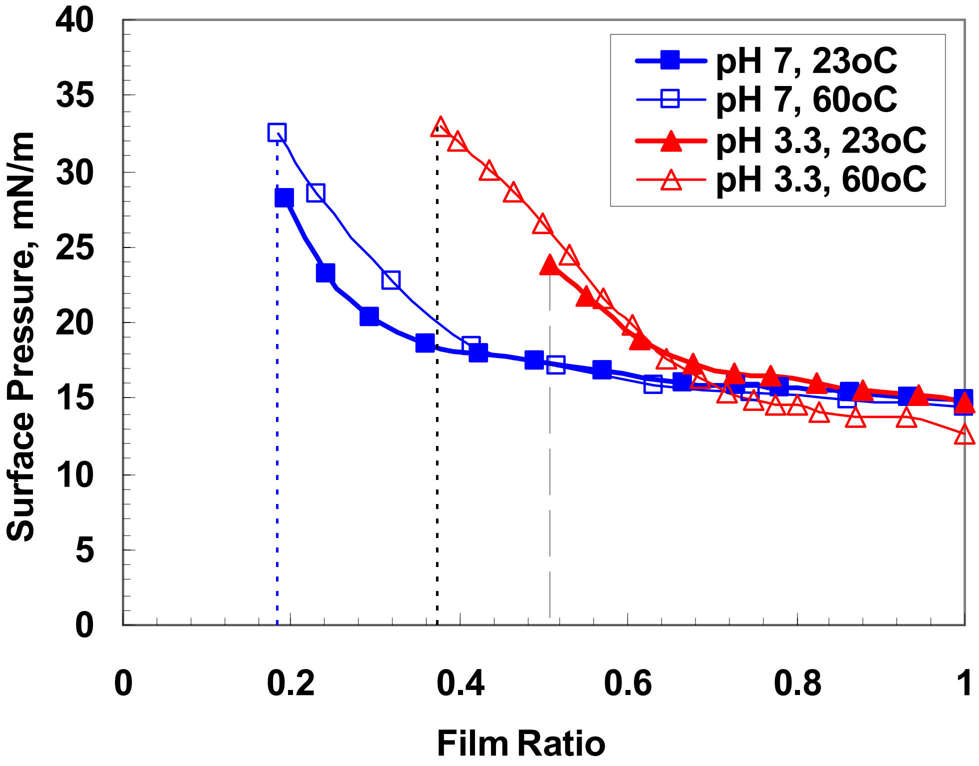


Figure 4-27. Effect of temperature on surface pressure isotherms for solutions of 10 kg/m³ asphaltenes in 25:75 heptol versus water at pH 7 and pH 3.3. Films were aged for 1 hour at 23°C and 60°C.

4.2.2. Effect of Low pH on Diluted Bitumen Systems

The effect of pH was also examined for diluted bitumen systems at low pH. Figure 4-28 shows that for a 9:1 dilution of Athabasca bitumen at low pH, compressibility decreased, the crumpling point slightly decreased as well as the interfacial tension. In general, the film properties seem very similar at low pH and at pH 7 in contrast to asphaltene model systems where the crumpling point significantly decreased at low pH.

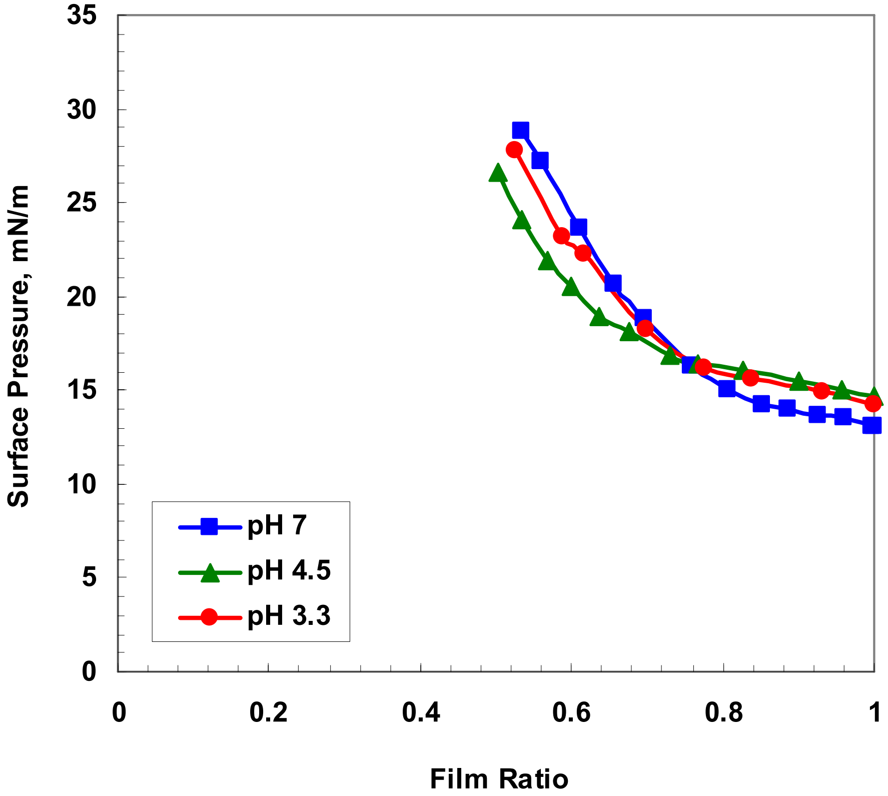


Figure 4-28. Effect of pH on surface pressure isotherms for a 9:1 dilution of Athabasca bitumen film with 25:75 heptol versus water at pH 7, 4. 5 and 3.3. Films were aged for 1 hour at 23°C.

Interestingly, when Athabasca-diluted-bitumen isotherms at pH 3.3 and pH 4.5 are compared with asphaltenes isotherms at the same pH, the surface pressure isotherms are very similar as shown in Figure 4-29. However, the surface pressure isotherms at pH 7 are different, Figure 4-30. This observation suggests that at neutral pH other bitumen constituents influence the film properties but at low pH the films are dominated by asphaltenes. General data for diluted bitumen systems with no additives are provided in Appendix E.

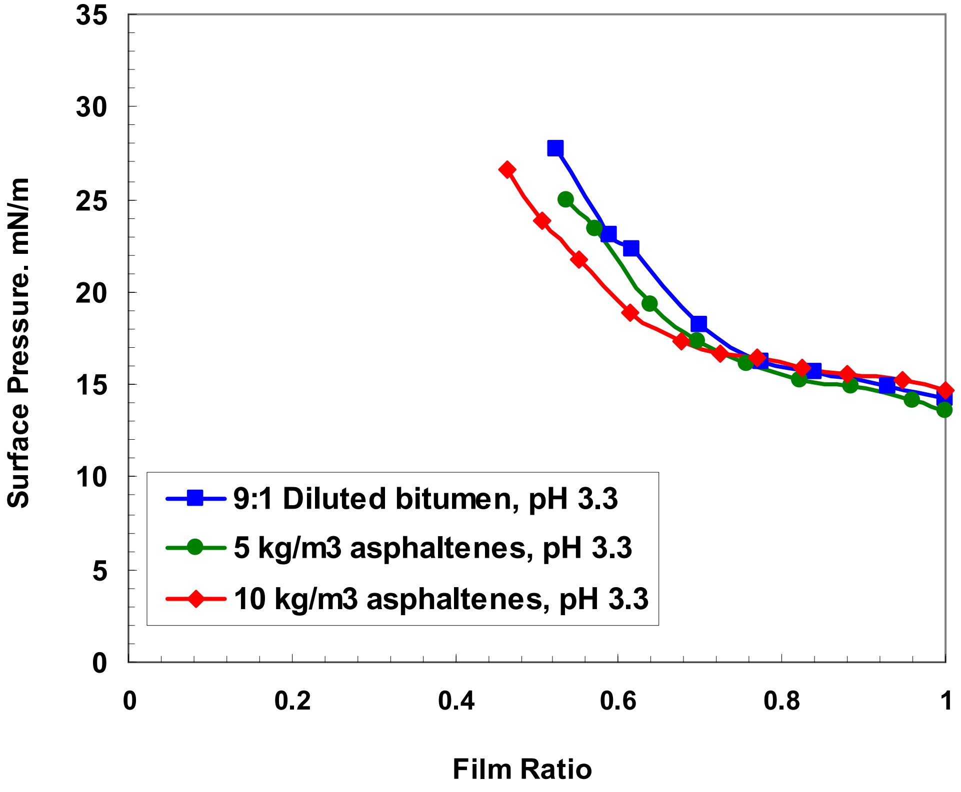


Figure 4-29. Comparison of surface pressure isotherms between asphaltanes films and a 9:1 dilution of Athabasca bitumen film with 25:75 heptol versus water at pH 3.3. Films were aged for 1 hour at 23°C.

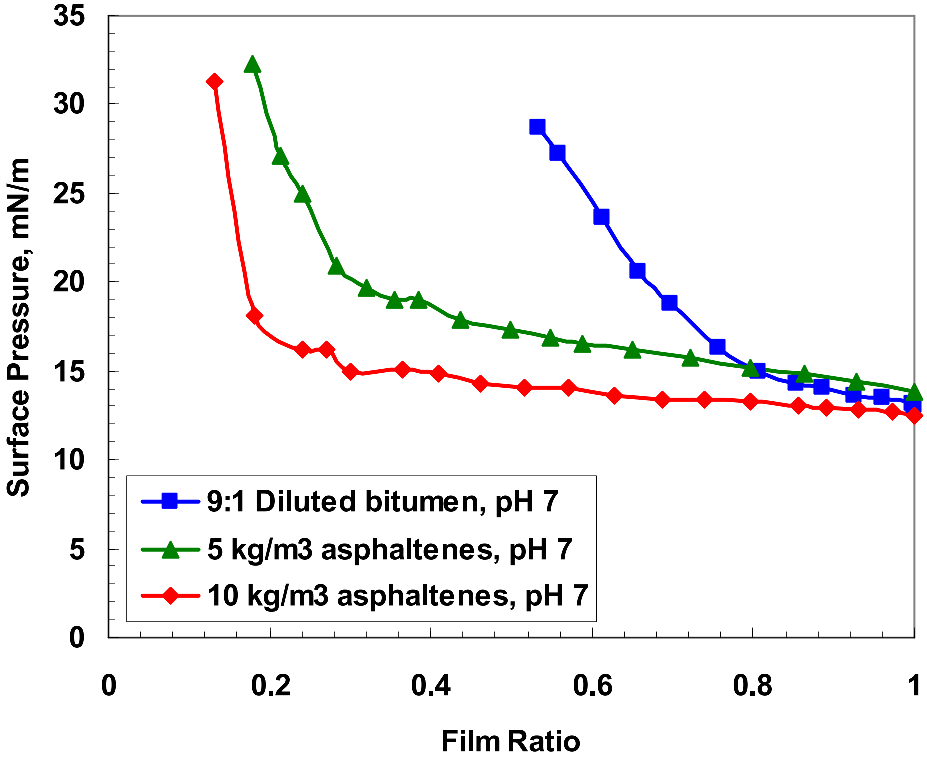


Figure 4-30. Comparison of surface pressure isotherms between asphaltanes films and a 9:1 dilution of Athabasca bitumen film with 25:75 heptol versus water at pH 7. Films were aged for 1 hour at 23°C.

Figure 4-31 shows that emulsion stability was reduced at low pH in diluted Athabasca bitumen systems. Part of the explanation may be the reduction in film compressibility at low pH. However, the correlation of emulsion stability with film properties at low pH is poor as was found with asphaltene model systems.

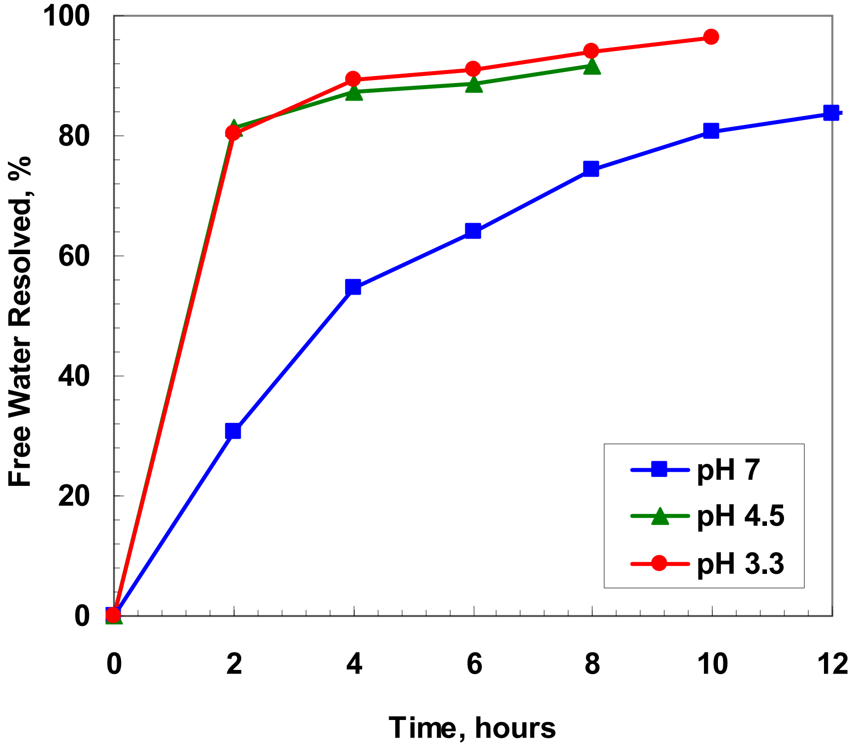


Figure 4-31. Effect of pH on emulsion stability for solutions of diluted Athabasca bitumen in 25:75 heptol with water at pH 7, pH 4.5 and pH 3.3 at 60°C. Emulsions contained 40 vol% aqueous solution.

4.2.3. Sodium Naphthenate Model Systems

As mentioned in Appendix B, sodium naphthenate (SN) is a product of the reaction of naphthenic acid with a base, in this case, NaOH (Table 4-1, Reactions “a” and “b”). Once the sodium naphthenate is formed, it dissociates in aqueous phase solution, Table 4-1, Reaction “c”. The carboxylate ($C_nH_{(2n+z)}COO^-$) is the surface active form of SN.

Table 4-1. Equilibrium reaction of naphthenic acids and its naphthenates

a) Acid dissociation:	$C_nH_{(2n+z)}COOH$	$\longleftrightarrow$	$CnH_{(2n+z)}COO^- + H^+$
b) Reaction with a base:	$C_nH_{(2n+z)}COO^- + NaOH$	$\longleftrightarrow$	$C_nH_{(2n+z)}COONa + OH^-$
c) SN dissociation:	$C_nH_{(2n+z)}COONa$	$\longleftrightarrow$	$C_nH_{(2n+z)}COO^- + Na^+$

The pH of the SN solutions ranged from pH 7 up to pH 8.6. In the following discussion, the results are compared with a zero SN baseline at pH 7. The change in baseline film properties and emulsion stability between pH 7 and pH 10 was relatively small (see Figures 4-20 and 4-22) and therefore the differences between pH 7 and 8.6 are expected to be very small.

Figures 4-32 shows the effect of sodium naphthenate on the film properties for systems of 5 kg/m³ asphaltenes in toluene. At 0.01wt% (~100ppm) SN, there was not a significant effect on film properties. The films weakened slightly at 0.1wt% (~1000 ppm). SN At 0.5wt% (~5000 ppm) the film had less capacity for compression (crumpling film ratio increased) but higher initial compressibility. Surface pressure increased (interfacial tension decreased) significantly with increasing SN concentration above 0.01 wt%. Note that the concentration of SN in the Figures is expressed as wt% instead of ppm for convenience (smaller numbers in legends).

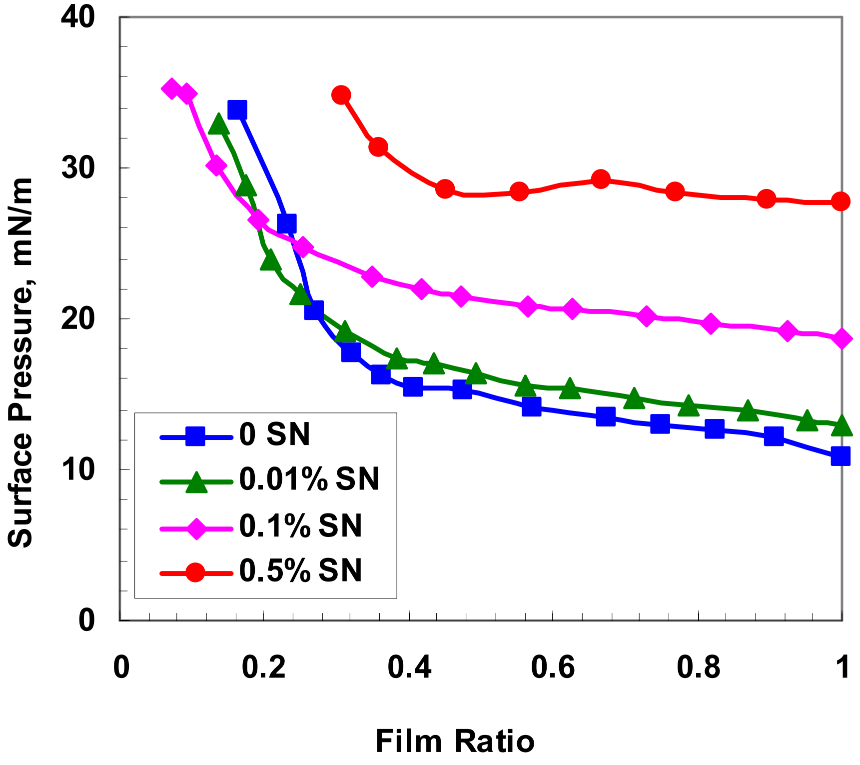


Figure 4-32. Effect of sodium naphthenate on surface pressure for solutions of 5 kg/m^3 asphaltenes in toluene versus aqueous surfactant solutions. Films were aged for 1 hour at 23^{o}C.

Figure 4-33 shows emulsion stability increased with increasing SN concentration. A possible explanation is that the significant reduction in interfacial tension increased emulsion stability. Since the films remained irreversibly adsorbed, the effect of decreased interfacial tension dominates.

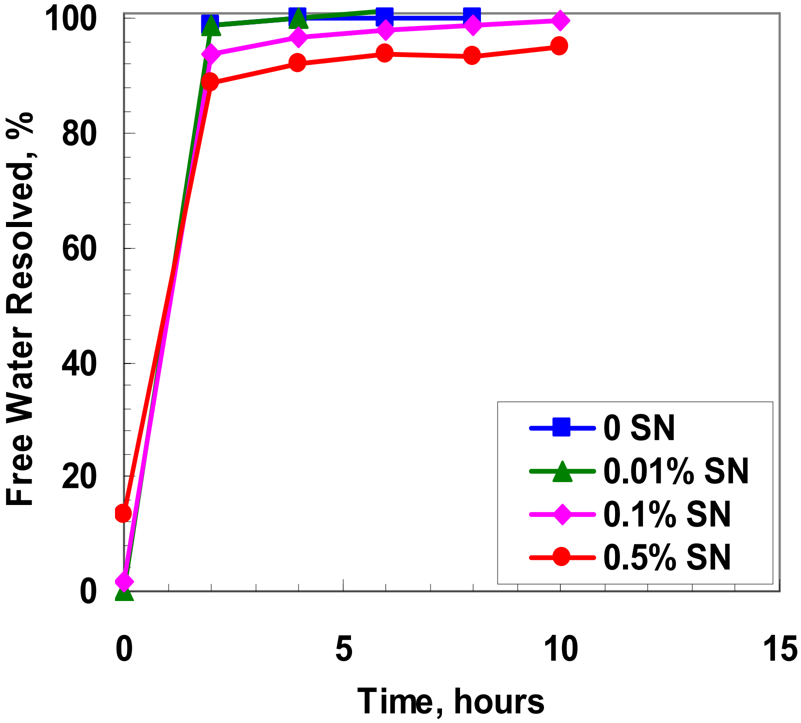


Figure 4-33. Effect of sodium naphthenate on emulsion stability for solutions of 5 kg/m³ asphaltenes in Toluene at 60°C. Emulsions contained 40 vol% aqueous surfactant solution.

Figures 4-34 and 4-35 show the effect of sodium naphthenate on the film properties and emulsion stability when heptane is added in a heptane:toluene ratio of 25:75 to systems of 5 kg/m^3 asphaltenes. As for the model systems with toluene, at 0.01 wt%SN there is almost no effect on film properties. Weaker films and reduced interfacial tension were observed at 0.1 and 0.5wt% SN. In this case, even 0.01 wt% SN significantly reduced emulsion stability. Emulsion stability increased slightly as the SN concentration increased above 0.01 wt%.

Figures 4-36 shows that the same trends in film properties occur for 5 kg/m^3 of asphaltenes in 50:50 heptol. However, for this system, the emulsion stability decreased not only in comparison with only asphaltene systems but also when the SN concentration increased. Results for sodium naphthenate model systems with 10 kg/m^3 of asphaltene, showed the same trend at each heptol ratio but the change in emulsion stability was even more noticeable as the sodium naphthenate concentration increased.

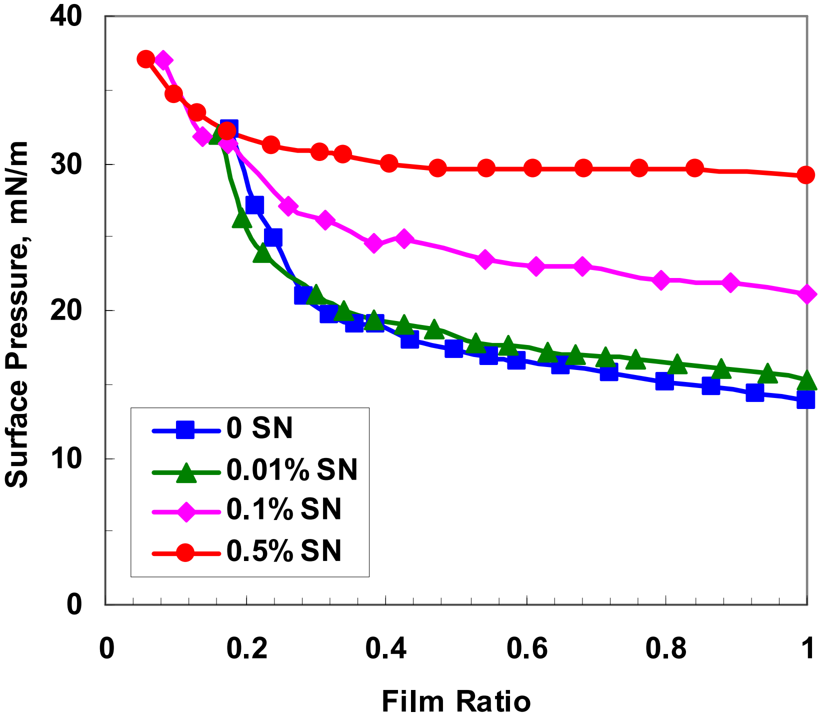


Figure 4-34. Effect of sodium naphthenate on surface pressure for solutions of 5 kg/m^3 asphaltenes in 25:75 heptol versus aqueous surfactant solutions. Films were aged for 1 hour at 23^{o}C.

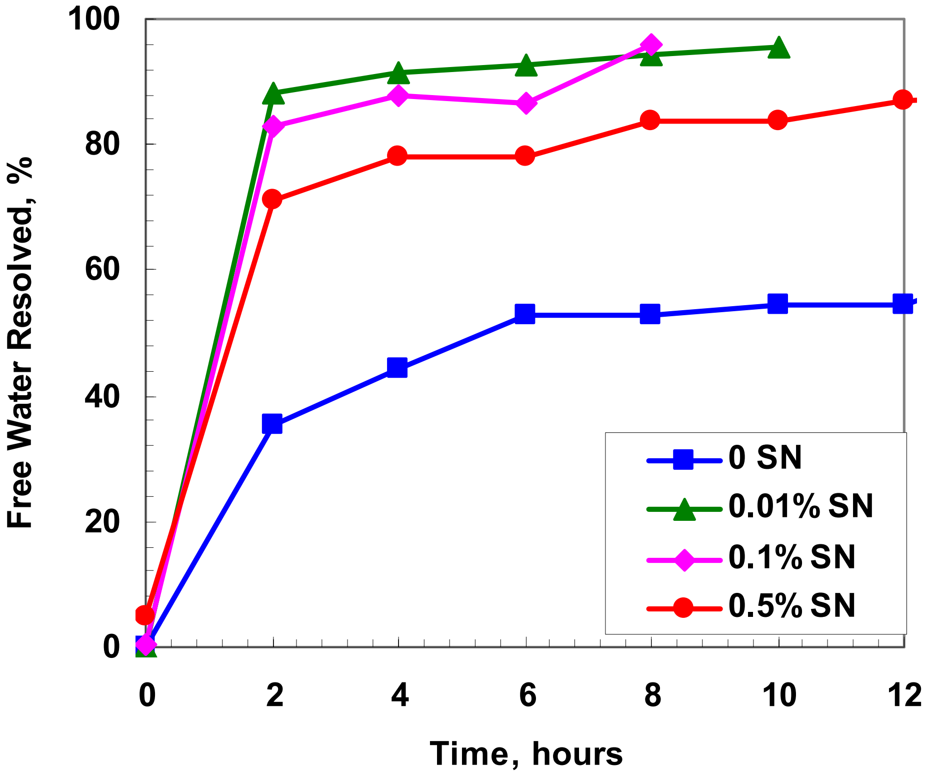


Figure 4-35. Effect of sodium naphthenate on emulsion stability for solutions of 5 kg/m³ asphaltenes in 25:75 heptol at 60°C. Emulsions contained 40 vol% aqueous surfactant solution.

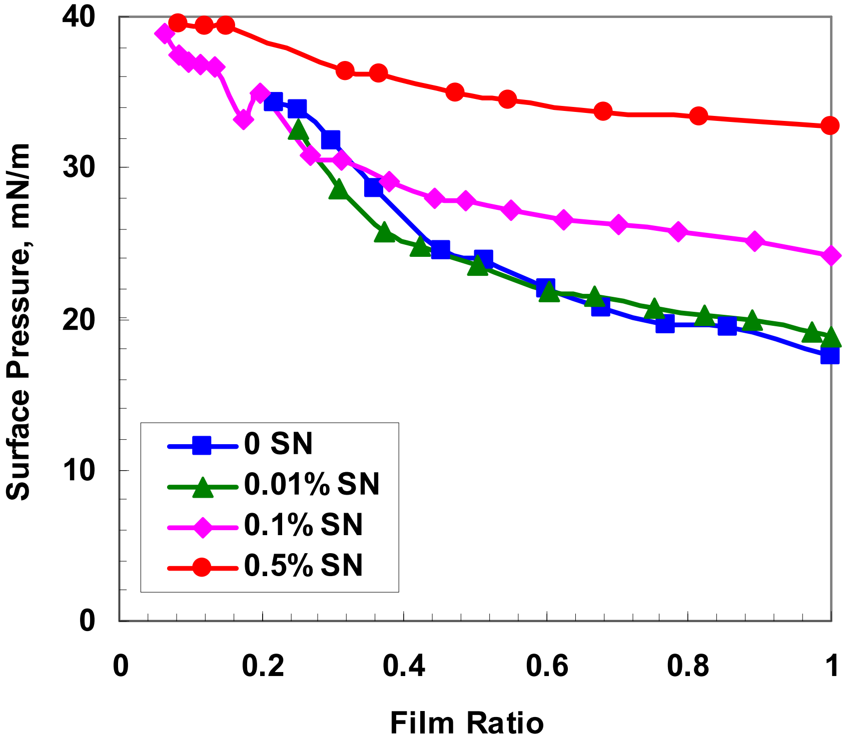


Figure 4-36. Effect of sodium naphthenate on surface pressure for solutions of 5 kg/m³ asphaltenes in 50:50 heptol versus aqueous surfactant solutions. Films were aged for 1 hour at 23°C.

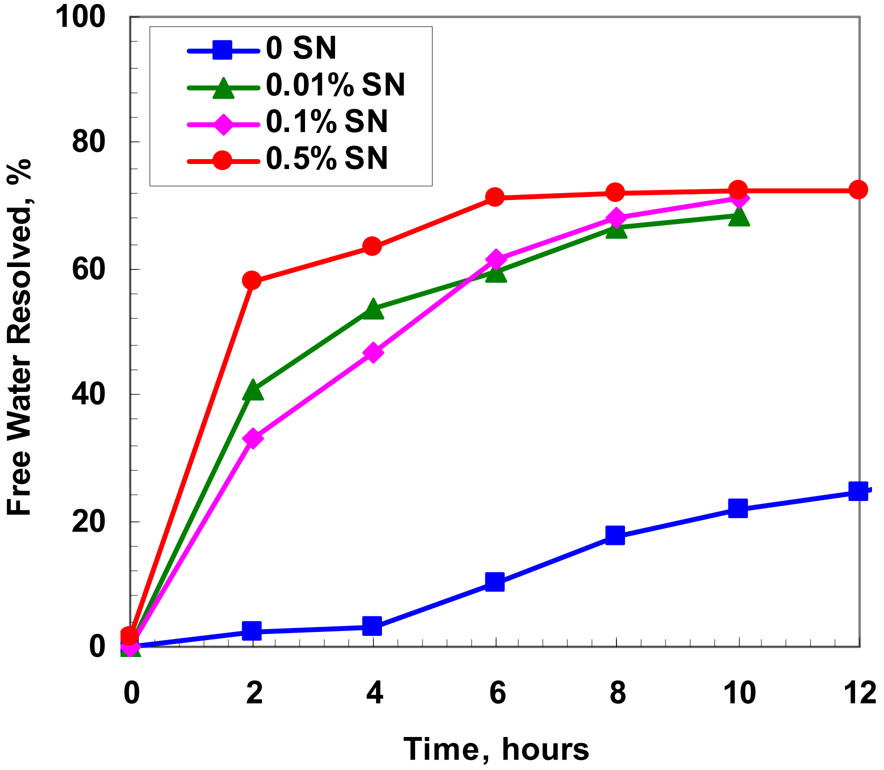


Figure 4-37. Effect of sodium naphthenate on emulsion stability for solutions of 5 kg/m³ asphaltenes in 50:50 heptol at 60°C. Emulsions contained 40 vol% aqueous surfactant solutions.

The correlation of film properties and emulsion stability was poor when SN concentration increased and emulsion stability increased as well. Perhaps SN molecules are also irreversibly adsorbed as asphaltenes do. With irreversible adsorption, SN molecules remain on the interface during compression which favours steric repulsion (skin formation) and emulsion stability. Moran & Czarnecki (2007) observed skin formation in presence of sodium naphthenates which is a result of irreversible adsorption. Part of the explanation may also be a balance between weaker films but lower interfacial tension.

Varadaraj & Brons (2007) showed that lower interfacial tension for different naphthenic acids exhibited higher surface excess concentrations, that is, a larger amount of molecules are present on the interface. Similar behaviour was observed for polydisperse ethoxylate alcohol surfactant in which more favourable interfacial aggregation lead to lower interfacial tensions (Varadaraj *et al.* 1991). It is possible that SN molecules adsorb in the space left between adsorbed-asphaltene-aggregates causing the lowering of the interfacial tension due to adsorption of SN on the interface. In general, the effect of SN on emulsion stability appears to correlate most with interfacial tension.

4.2.4. Dodecylbenzene Sulfonic, Acid Linear and Branched, Model Systems

A complication with DBSA was that the solutions have low pH and asphaltene films are sensitive to low pH. All of the results with DBSA were compared to asphaltene films without DBSA but at the same pH obtained with the DBSA solutions. The pH's at 10 ppm and 100 ppm DBSA (both linear and branched) were 4.5 and 3.3, respectively.

Figure 4-38 shows the film properties for DBSA linear (DBSA-L) for model systems with 5 kg/m^3 asphaltenes. Addition of DBSA-L increased the interfacial compressibility (Table 2-4), decreased the crumpling film ratio, and decreased interfacial tension. These results indicate that DBSA-L weakened the films but did not create completely reversible films. Although DBSA-L weakened the films, it produced more stable emulsions, as shown in Figure 4-39. Similar results were obtained for DBSA-B. The interfacial films were weaker at higher DBSA-B concentration, Table 4-3 and Figure 4-40, and yet the emulsion stability increased, Figure 4-41.

Table 4-2. Compressibilities for DBSA-L for solutions of 5 kg/m^3 asphaltenes in 25:75 heptol versus aqueous solution. Film aged 1 hour at 23^{o}C.

Dose (ppm)	Compressibilities (m/mN)	
	pH 4.5	pH 3.3
0	0.189	0.189
10	0.22	--
100	--	0.37

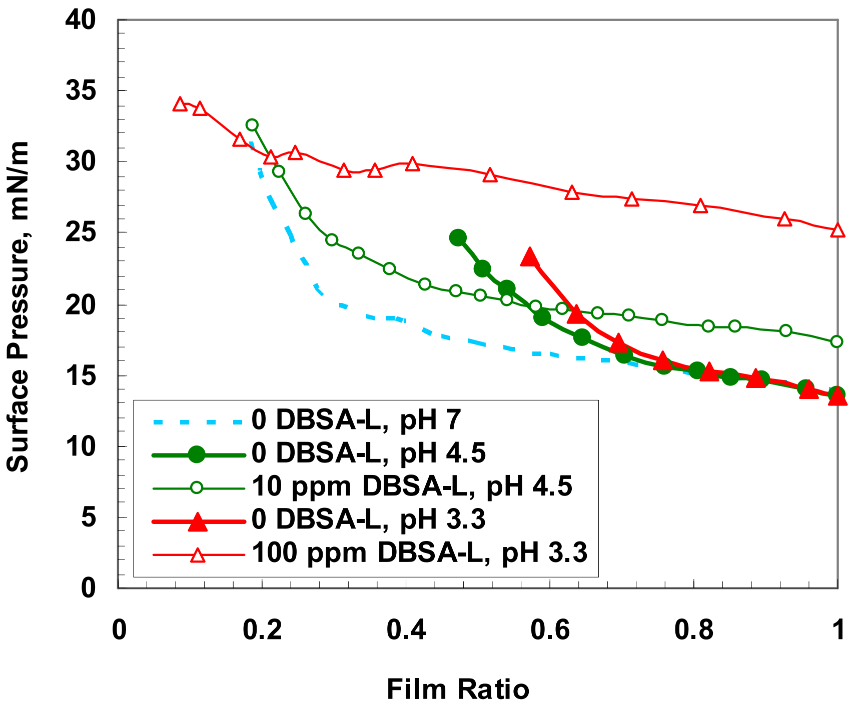


Figure 4-38. Effect of DBSA-Linear on surface pressure for solutions of 5 kg/m³ asphaltenes in 25:75 heptol versus aqueous solution. Films were aged for 1 hour at 23°C.

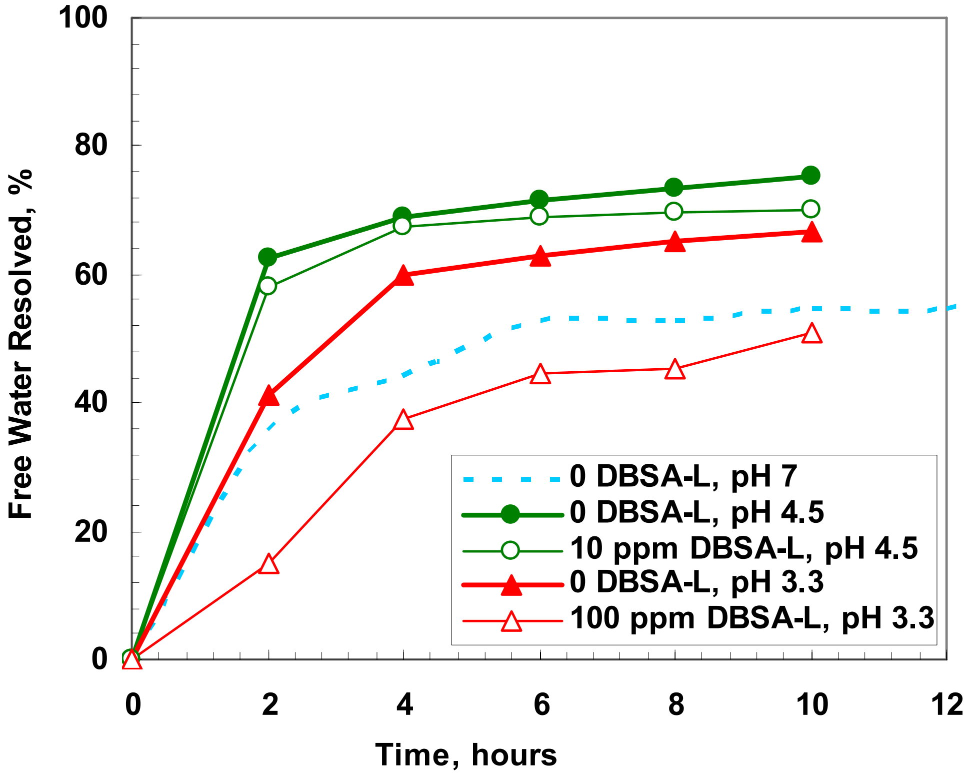


Figure 4-39. Effect of DBSA-Linear on emulsion stability for solutions of 5 kg/m³ asphaltenes in 25:75 heptol at 60°C. Emulsions contained 40 vol% aqueous solution.

Table 4-3. Compressibilities for DBSA-B for solutions of 10 kg/m³ asphaltenes in 25:75 heptol versus aqueous solution. Films aged 1 hour at 23°C.

Dose (ppm)	Compressibilities (m/mN)	
	pH 4.5	pH 3.3
0	0.11	0.16
10	0.17	--
100	--	0.47

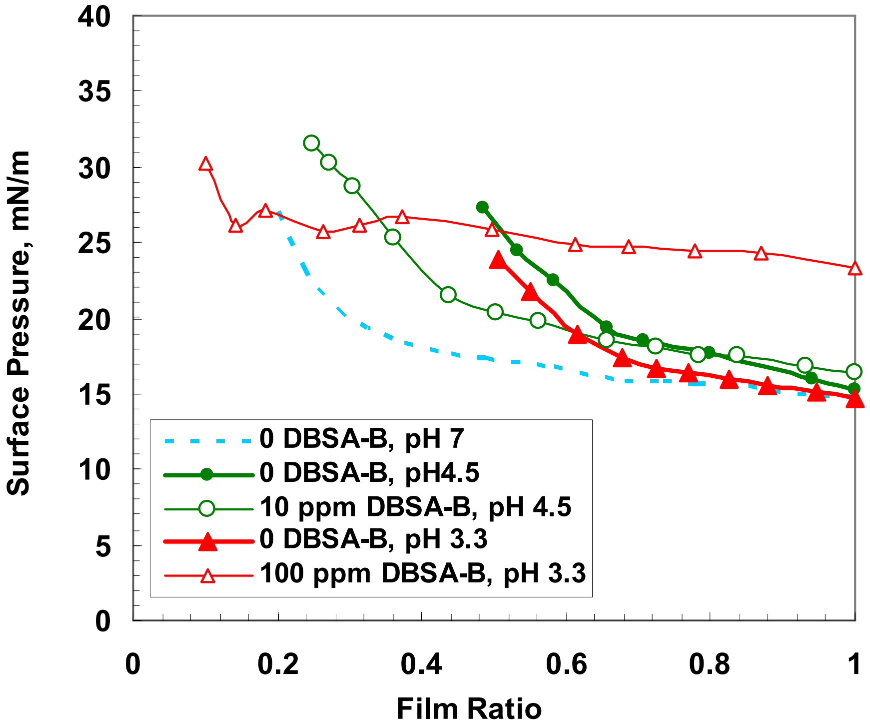


Figure 4-40. Effect of DBSA-Branched on surface pressure for solutions of 10 kg/m³ asphaltenes in 25:75 heptol versus aqueous solution. Films were aged for 1 hour at 23°C.

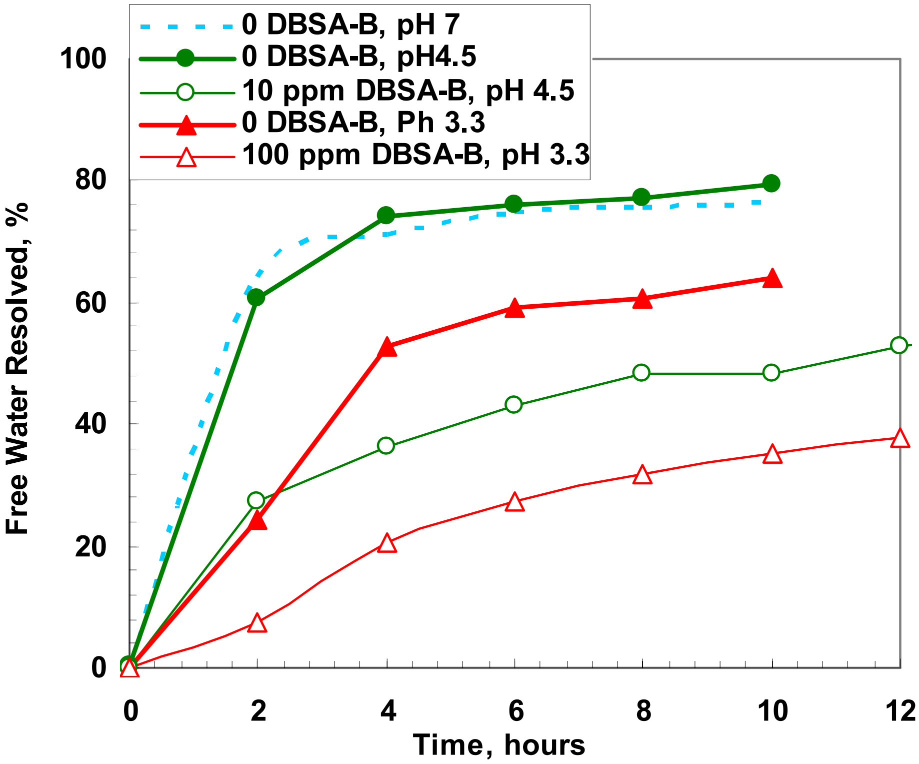


Figure 4-41. Effect of DBSA-Branched on and emulsion stability for solutions of 10 kg/m³ asphaltenes in 25:75 heptol at 60°C. Emulsions contained 40 vol% aqueous solution.

In almost all cases where emulsion stability increased even though the films were weakened, there was a reduction in interfacial tension (higher surface pressure). For both DBSA and sodium naphthenate, emulsion stability appears to correlate most with interfacial tension.

DBSA is known to disperse and stabilize asphaltenes from precipitation (Sjoblom *et al.* 2003). The mechanism of DBSA asphaltene stabilization is assumed to be the strong interaction between the sulfonic acid head group and basic material in the asphaltene molecule. It can be suggested that DBSA associates with asphaltenes aggregates on the interface instead of replacing them

4.2.5. Dodecylbenzene Sulfonic Acid, Linear and Branched, Diluted Bitumen Systems

For diluted bitumen systems in the presence of DBSA, the baselines for film properties and emulsions stability are those of the corresponding pH of DBSA solutions: pH 4.5 for 10 ppm of DBSA and pH 3.3 for 100 ppm of DBSA.

Figure 4-42 shows that adding DBSA-L at 10 ppm weakened the film only a small amount; while adding 100 ppm of DBSA-L significantly weakened the film but did not completely restore reversibility. Figure 4-43 shows the effect of DBSA-L on emulsion stability. First note that adding DBSA shifts emulsion stability simply because the pH changes. Adding 10 ppm of DBSA-L slightly increased emulsion stability relative to the baseline at the same pH even though it had little effect on film properties and interfacial tension. Adding 100 ppm of DBSA-L had little effect on emulsion stability even though it had a significant effect on film properties. In this case, the emulsions are already very unstable and there is little opportunity for further destabilization. Also, the reduction in interfacial tension may counterbalance the weakening of the film, as was observed with the model systems.

Similar results were obtained for DBSA-Branched. Adding DBSA-B weakened the films, Figures 4-44, but increased emulsion stability, Figure 4-45. Again, it appears that the lowering of interfacial tension is the dominant mechanism when the films remain irreversibly adsorbed.

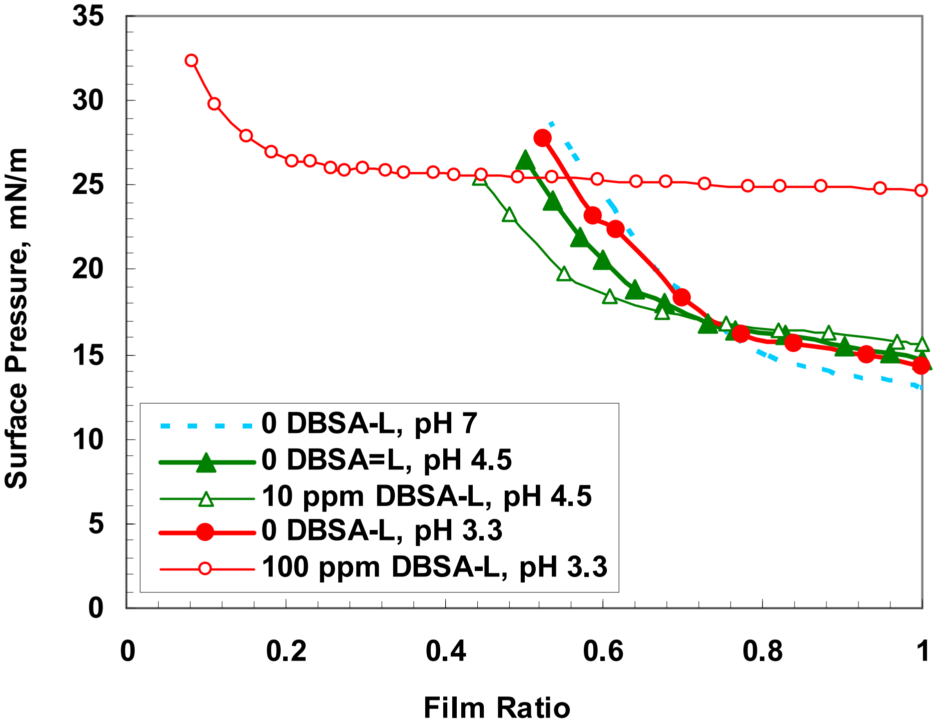


Figure 4-42. Effect of DBSA-L on surface pressure for a 9:1 dilution of Athabasca bitumen with 25:75 heptol at 23°C. Films were aged for 1 hour at 23°C.

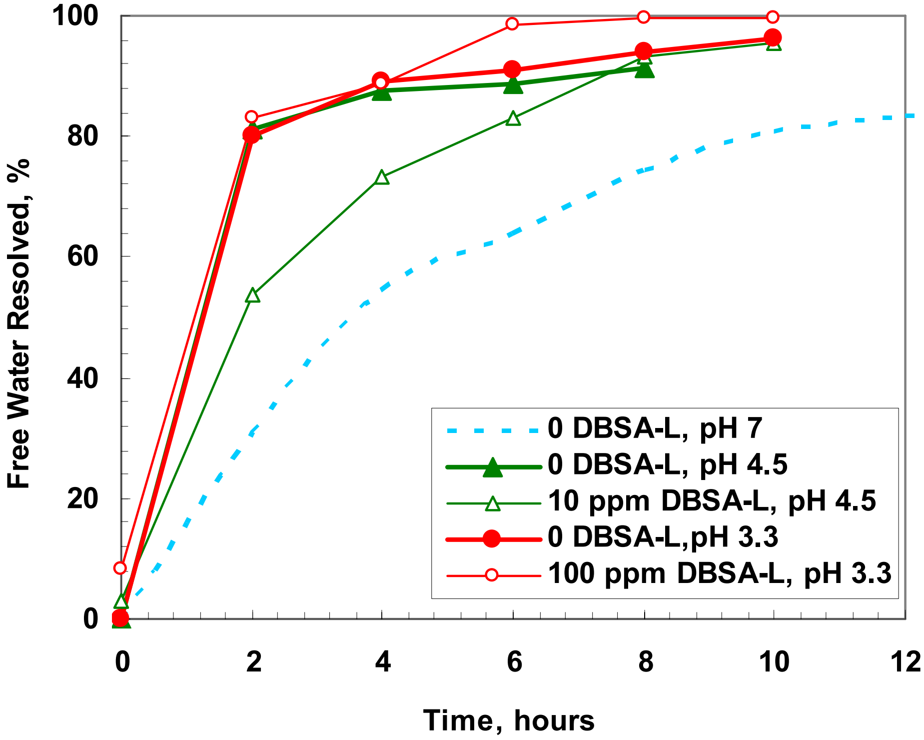


Figure 4-43. Effect of DBSA-L on emulsion stability for a 9:1 dilution of Athabasca bitumen with 25:75 heptol at 60°C. Emulsions contained 40 vol% aqueous solution.

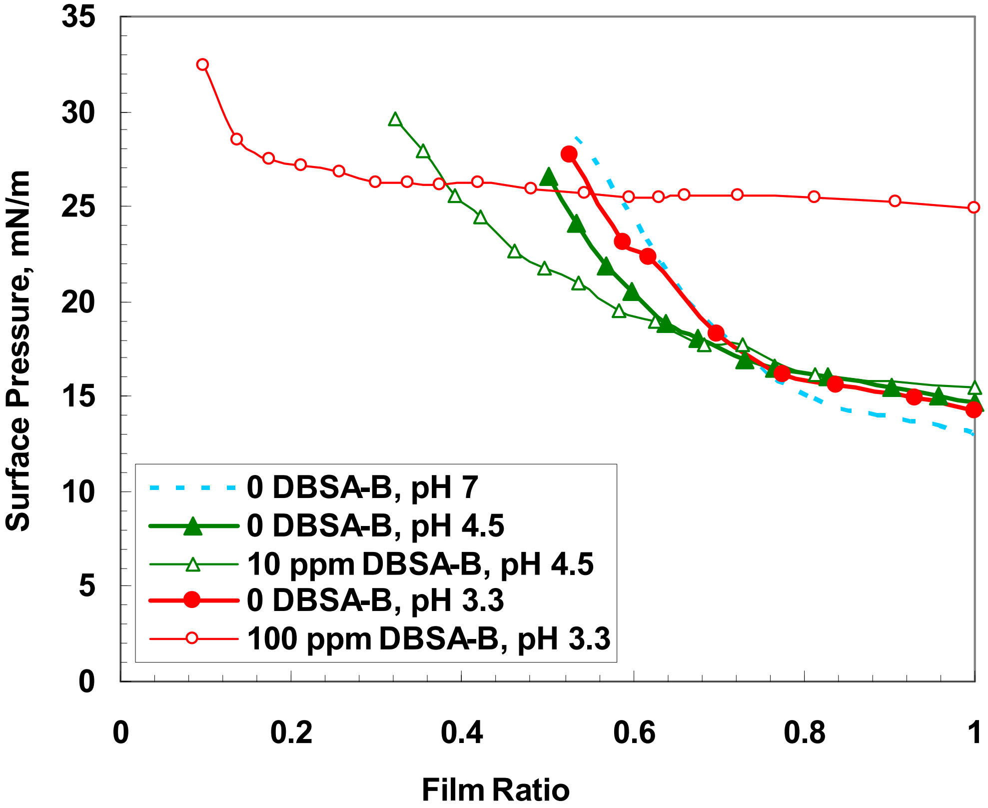


Figure 4-44. Effect of DBSA-B on surface pressure for a 9:1 dilution of Athabasca bitumen with 25:75 heptol at 23°C. Films were aged for 1 hour.

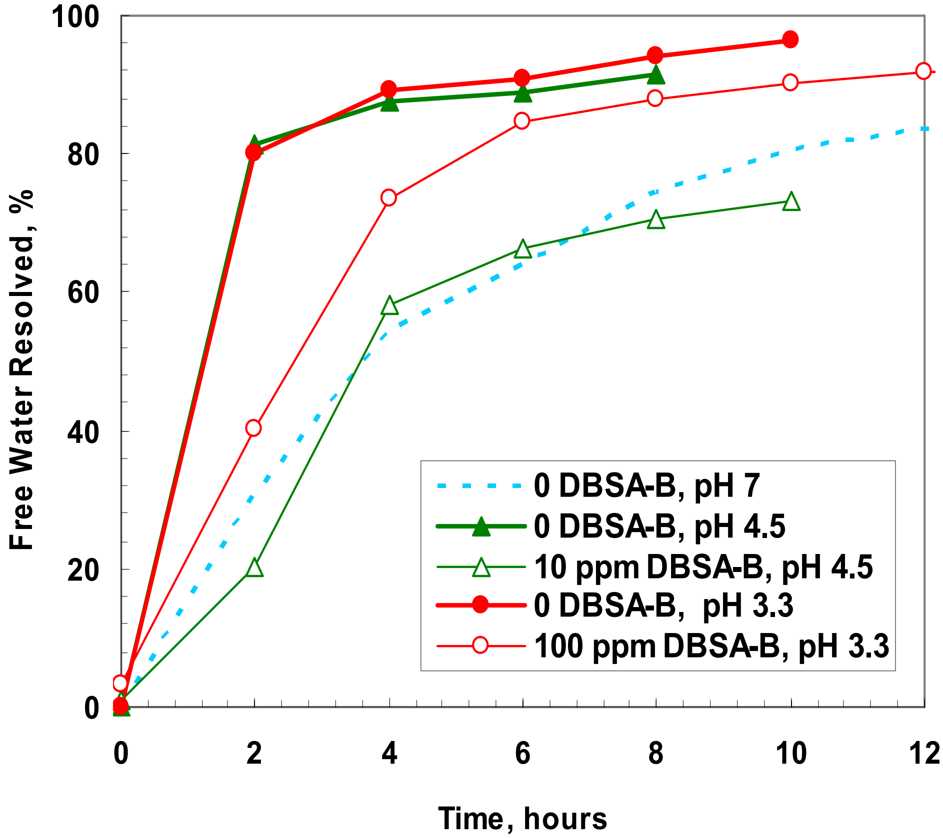


Figure 4-45. Effect of DBSA-B on emulsion stability for a 9:1 dilution of Athabasca bitumen with 25:75 heptol at 60°C. Emulsions contained 40 vol% aqueous solution.

4.2.6. Summary of Additives that Maintain an Irreversible Film

The effect of sodium naphthenate and dodecylbenzene sulfonic acids on film properties and emulsion stability can be summarized as follow:

1) Both surfactants increased interfacial compressibility. Although SN and DBSA increased compressibility, not all systems did form reversible films (infinite compressibility). All systems had crumpling point but, the crumpling film ratio was lower than for asphaltene-only systems. Both SN and DBSA lowered interfacial tension (increased surface pressure). All these factors confirmed that DBSA and SN were adsorbed along with asphaltenes and maintained an irreversible film.

2) With SN systems, the emulsions were less stable than for asphaltenes-only systems; as SN concentration increased, emulsion stability also increased. With DBSA, emulsion stability was greater than for asphaltene-only systems and also increased with concentration. In both cases, mores stable emulsions were observed for weaker films. In these cases, interfacial tension decreased suggesting that the lowering of interfacial tension was the main mechanism affecting emulsion stability. Lower interfacial tension reduces the driving force for coalescence and increases emulsion stability.

4.3. Correlation of Emulsion Stability to Film Properties

The additives were observed to have three major effects:

1. to decrease crumpling film ratio (CR).
2. to decrease interfacial tension, γ (increase surface pressure, π)
3. to increase compressibility of the film (C_i).

It was empirically found that the stability of the emulsions (% of water resolved) tested, correlated reasonably well to the crumpling ratio and interfacial tension (surface pressure). A first attempt to correlate emulsion stability data with film properties was made by Yarrranton *et al* (2007b) with the following correlation parameter: $C_i(1\text{-}CR)$. This parameter was used only for asphaltene films without additives and correlated well with emulsion stability data. This correlation was described in Section 2.3.4 and Figure 2-12. For asphaltene-additive films the same correlation was tested but it failed for systems with low interfacial tension. The new stability parameter was then defined including crumpling point and interfacial tension (surface pressure):

$$SP = CR^{0.5}\left(\frac{\pi}{\gamma_0}\right) = CR^{0.5}\left[1-\left(\frac{\gamma}{\gamma_0}\right)\right] \qquad \textbf{Equation 4-1}$$

where SP is the stability parameter, *CR* is the crumpling ratio, π is the surface pressure and γ and γ_o are the interfacial tension of the sample (in presence of asphaltenes and/or surfactant) and pure solvent, respectively. The emulsion stability (% of water resolved) was plotted as function of the stability parameter SP as shown in Figure 4-46.

The expression was tested with different exponents for the crumpling film ratio. At low exponents (*e.g.* 0.1) the values for SP spread out from 0.3 to 0.8. At high exponents (*e.g.* 1), the values for SP grouped between zero and 0.2. A clear and sharp transition from low to high stability emulsions was observed when the crumpling film ratio was raised to the power of 0.5.

When reversible films are formed and they do not exhibit a crumpling point, the crumpling film ratio, CR, is zero and the stability parameter, SP, becomes also zero. Hence, unstable emulsions (high percentage of free water) are expected to correlate to zero values of SP. These results matched with stability emulsion data in which at zero SP, unstable emulsions were obtained (see Figure 4-46). When irreversible films are formed, SP is non-zero and will increase as the interfacial tension decreases. Hence, more stable emulsions (lower free water) are expected to correlate to a higher value of SP. The interfacial tension ratio ($\pi/\gamma_o = 1-\gamma/\gamma_o$) grouped the data in a sharp trend which included all the data points for unstable and stable emulsions. Further adjustment of the interfacial tension ratio did not improve the correlation. Figure 4-46 shows that the percentage of free water does indeed correlate to SP. The correlation is very steep and there is some scatter and therefore its predictive capability is limited. Nonetheless, the correlation does confirm that both interfacial tension (surface pressure) and crumpling film ratio are key factors in the stability of these emulsions.

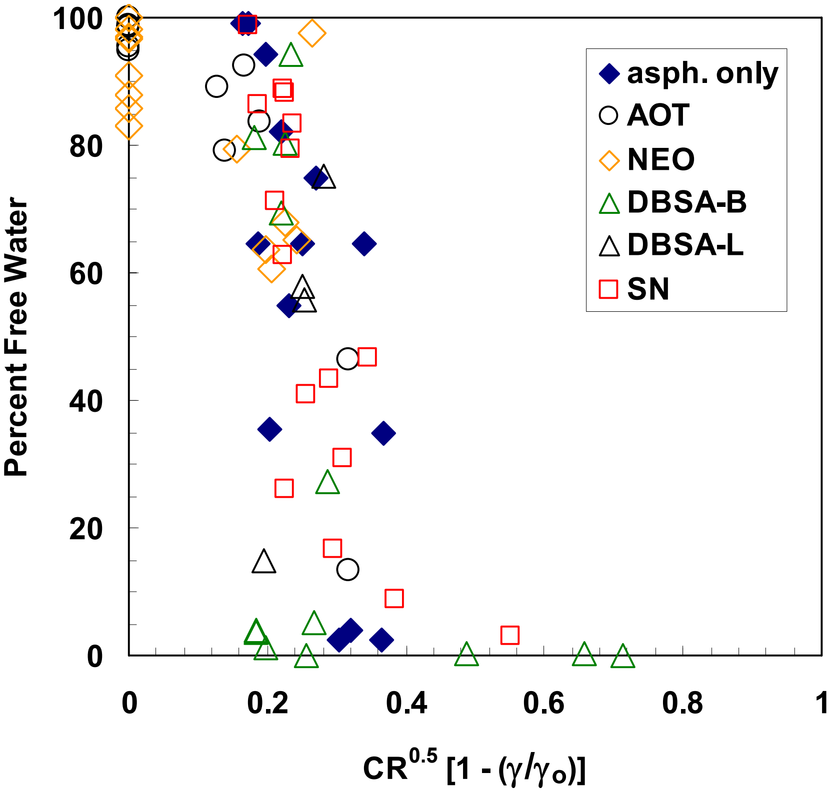


Figure 4-46. Correlation of emulsion stability to crumpling ratio and interfacial tension using the stability parameter SP.

As was mentioned previously, interfacial compressibility, C_i, is also an important property in emulsion stability so the correlation factor is modified to include the interfacial compressibility. Usually, crumpling film ratio and compressibility are inversely related in emulsion stability; for example, for stable emulsions high crumpling film ratios and low compressibilities are expected. Therefore, the inverse of the interfacial compressibility, C_i, was introduced into the correlation factor. A weighting factor of 3 was found to provide reasonable results in which 73% of the unstable emulsion data (>60vol% free water resolved) fell in the unstable region. The modified correlation factor, *SP**, is given by:

$$SP^* = CR^{0.5}\left[1-\left(\frac{\gamma}{\gamma_0}\right)\right]\left[1+\left(\frac{1}{3\cdot C_i}\right)\right] \qquad \textbf{Equation 4-2}$$

Figure 4-47 shows the new relationship for emulsion stability and the modified correlation parameter. It is now possible to identify unstable emulsions below a threshold value of *SP** = 0.5. Between SP* 0.5 and 0.65, there is a transition pattern to stable emulsions (dotted lines in Figure 4-47). Above SP* = 0.65, the emulsions are stable. The improved correlation suggests that interfacial compressibility is also an important property in emulsion stability with both asphaltenes and additives on the film.

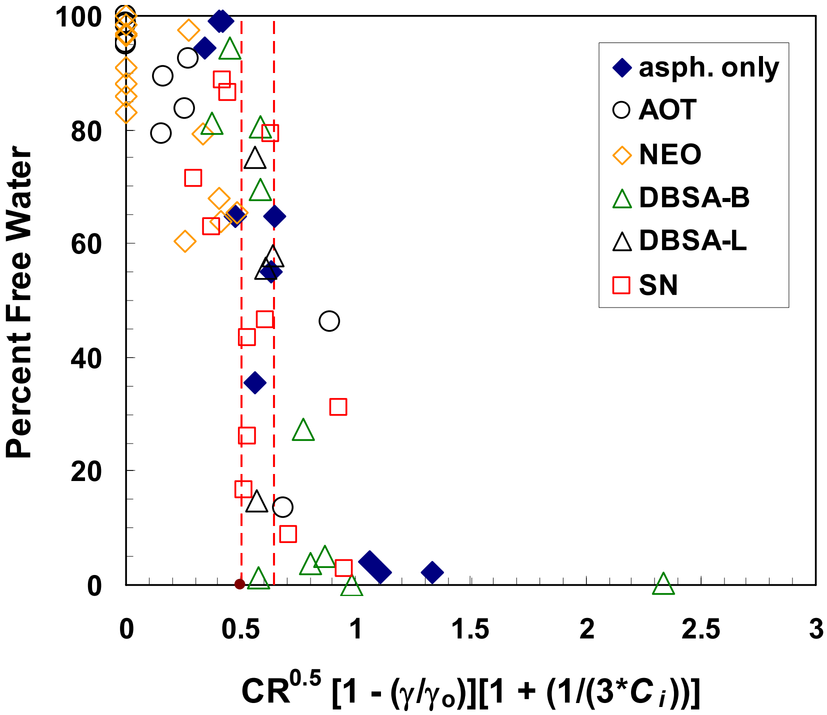


Figure 4-47. Correlation of emulsion stability to crumpling ratio, interfacial tension and interfacial compressibility using the modified stability parameter SP^*.

5. CONCLUSIONS AND FUTURE WORK

The principal objective of this study was to investigate the effect of surfactants on interfacial film properties and relate them to the stability of water-in-oil emulsions stabilized by asphaltenes. The conclusions from this work and recommendations for future research in the area are presented below.

5.1. Thesis Conclusions

1. Surface pressure isotherms were used to evaluate the effect of additives in asphaltene films. The surfactants exhibited two behaviours, surfactants which were able to form reversible or high compressible films, and surfactants which maintained irreversible adsorption at the interface.

2. In general, surfactants that formed reversible or high compressible films increased compressibility, increased surface pressure and decreased or eliminated the crumpling point. The compressibility of these films was very high and in some cases was infinite. These effects indicated that the film weakened as a consequense of replacement of asphaltene aggregates by surfactant molecules at the interface. Weaker films favoured coalescence and decreased emulsion stability.

3. Surfactants which failed to reverse asphaltene adsorption or, in other words, maintained the irreversibly adsorption at the interface, in most cases significantly reduced interfacial tension. This suggested that surfactant molecues did not replace asphaltenes on the film, but at most adsorbed along with asphaltenes at the interface. Both irreversible adsorption and lowering of the interfacial tension could enhance emulsion stability.

4. The film properties of model systems were related to emulsion stability. It was found that additives that form reversible films were effective demulsifiers destabilizing emulsions. Likewise, surfactants that maintained the irrevesible adsoption could enhance emulsion stability.

5. Aerosol OT and nonylphenol ethoxylate surfactants formed reversible or high compressible films. These surfactants proved to be effective demulsifiers destabilizing water-in-oil emulsions. Sodium naphthenate, DBSA-L and DBSA-B maintained irreversible films. These surfactants enhanced emulsion stability through lowering of interfacial tension.

6. The same trends were observed in diluted bitumen systems as in asphaltene-solvent systems for each surfactant. This indicated that asphaltenes or components within asphaltenes fractions were stabilizing the water-in-diluted bitumen emulsions.

5.2. Recommendations for Future Work

This research study provided a better understanding of the role of surfactants stabilizing or destabilizing water-in-crude oil emulsions. However, other questions arose from the presented results. The following are recommendations for future research.

1. This work showed that surfactants had two key effects on film properties; however, these effects were not related to surfactant chemistry. Molecular structure details such as size of the molecule, size ratio of head and tail groups, polarizability, HLB or molecular weight could be related to demulsifier performance and effects on film properties. Relating the demulsifier performance to its chemical structure may be useful for more effective tailoring of demulsifier treatments.

2. In this study, film properties were related to emulsion stability for asphaltene model system with surfactants. It would be interesting to determine a coalesence model to predict emulsion stability for these systems.

3. Other components within bitumen such as resins, solids, and clays have been shown to adsorb at the interface and change the film properties. It would be interesting to investigate the effect of resins and solids in asphaltene model emulsions when surfactants are present. It would provide results about real systems in the oil field and possible unexpected interaction behaviours.

4. In real applications, multiple benefits are sought in demulsification treatments. For example, removal of water from the oil phase accompanied by clean water phase with no oil after the demulsification treatment. Hence, a variety of surfactant blends are made and used in the field to achieve more than one task at the same time. Study of different surfactant blends on film properties and emulsion stabitily could identify the synergies or competing effects of different additives. These studies are usuful since blends of surfactants may have different and unexpected effects than the single components within the blend.

5. So far in this study, pH effects on asphaltene films were only examined briefly. However, much information is still unknown about the mechanism of pH effects on asphaltene films. In industrial applications, basic or acidic surfactants are added during chemical oil treatments changing the overall pH of the system. A more thorough study of the pH effect on asphaltene films would be important to understand how pH modifies emulsion stability and coalescence in demuslfication treatments.

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APPENDIX A - CLASSIFICATION OF SURFACTANTS

A.1. Anionic Surfactants

Anionic surfactants are commonly used in cleaning applications such as detergents and shampoos. These surfactants have a good ability to emulsify oily soils into wash solutions and can lift soils from surfaces (Hibbs. 2006). Anionic surfactants can be classified according to their polar group as follows:

- *Soaps* are the most common surfactant for detergents and cleaners in some countries. They are also widely used in body care and cosmetics products. Soaps are mainly produced from coconut oil, palm kernel oil and tallow. They can be produced by the neutralization of fatty acids or by the saponification process.
- *Alkyl Sulfates* are very important in the textile industry. Their surface active characteristics are dominated by the alkyl chain length and structure. Some examples of this type are sodium dodecyl sulphate and sodium lauryl sulphate (alkyl ethoxy sulfate).
- *Alkyl Carboxylates* have a carboxylic group as the hydrophilic part of the molecule. They do not hydrolyse as alkyl sulfates do. They show excellent dispersing and emulsifying properties.
- *Sulfonate* surfactants are distinguished between aromatic sulfonates (alkyltoluene, alkylxylene, alkylnaphthalene, alkylbenzene) and aliphatic sulfonates (α-olefin sulfonates, alkane sulfonates, sulfosuccianates).
- Petrolsulfonate are produced through treatment of petroleum fractions with high content of aromatic hydrocarbons. They are used as additives for lubricants and oil fuels and corrosion inhibition.
- Alkylbenzene sulfonates are the main surfactant used in household cleaners, detergents and sanitary formulations. The surface activity of this

type of surfactant depends on the water solubility and the length of the alkyl chain.

- *Oleofinesulfonate* are a complex mixture of isomeric alkenesulfonates and hydroxyalkanesulfonates. In general, this type of surfactant is a blend of different surfactants. They have excellent water solubility and soil removal ability. Oleofinesulfonate are also good detergents and tend to form stable foams.
- Sulfosuccinates are produce from mono- or dialkyl esters of succinic acid. Their surface activity depends on the hydrocarbon chain length. Sulfosuccinates with hydrocarbon length less than C10 exhibit good water solubility. They are very useful in emulsion polymerization process for their efficiency lowering the interfacial tension. Some important sulfosuccionates are di-2-ethylhexyl sulfosuccinate, diisodecyl sulfosuccinate, diisooctyl sodium sulfosuccinate.

A.2. Cationic Surfactants

Cationic surfactants have a positively charged hydrophilic group. The surfactants in this class are dominated by positively charged nitrogen as the core hydrophile. Cationic surfactants are mostly all amino-based surfactants. An important application is in fabric softening. Cationic surfactants are also used for surface treatment in which they assist in deposition on to surfaces.

The adsorption on surfaces accounts for other applications as biocides or disinfectants (*e.g.* amines and dialkyl ammonium quaternaries), road construction, agricultural formulation for improving herbicides and pesticides (*e.g.* poltethoxy fatty amines, quaternary ammonium salts, amine oxides). The majority of produced amines originate from natural fats and oils, alpha-olefins and fatty alcohols which are the main source for cationic surfactants (Steichen. 2001). Some of the most common cationic surfactants are

- Secondary and tertiary amines produce by reduction of a fatty nitrile (*e.g.* Alkyltrimethylammonium chloride, Dialkyldimethylammonium chloride)
- Quaternary ammonium compounds produce for a fatty nitrile. The amine is produced first (tertiary amine) and then quaternized to produce the quaternary ammonium compound (*e.g.* alkyldimethylammonium – quaternaries)
- Quaternized amidoamines and imidazolines, and their ethoxylated derivatives are produced directly from fats, oils or fatty acids without a nitrile intermediate.

A.3. Zwitterionic/Amphoteric Surfactants

Zwitterionic surfactants contain at least one negative and one positive charge in the molecule at the same time, with both charges neutralizing each other internally under normal conditions. Amphoteric surfactants exhibit a varying charge from positive to amphotheric (both positive and negative at the same time) to just negative depending on the pH of the solution. The hydrophilic head is positive in acidic solutions (cationic), negative in alkaline solutions (anionic) and both negative and positive charges in an intermediate pH. Due to their ability to support both positive and negative charge, amphoteric surfactants usually have large head groups (Floyd *et al.* 2001). The most common examples of zwitterionic surfactants are betaines and for amphoteric are aminoethylethanolamine-derived.

- Carboxybetaines/alkyl betaines are also call betaines which refers to trimethylglycine , Figure 2-5. In this type of surfactantas, the positive charge is located at a quaternary nitrogen atom, and the negative charge at a carboxylic group (e.g. N,N,N-trimethylglycine). alkyl betaines surfactants are formed by replacing one methyl group in N,N,N-trimethylglycine by an alkyl chain. If another functional group replaces the carboxylic group, it is indicated in the name of the betaine, for example, sulfobetaine phosphobetaine.

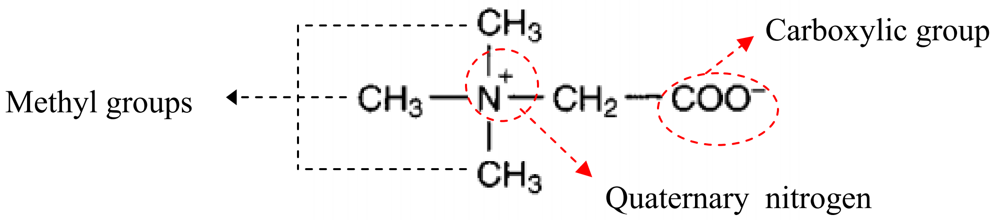


Figure A-1. Structure of trimethylglycine

- Aminoethylethanolamine-derived amphoterics are mainly used in personal care formulation. Usually, this type of surfactant is a complex mixture of different components and impurities which varies with the production parameters. Some examples in this group are amphomonoacetates and amphodiacetates.

A.4. Non-Ionic Surfactants

Non-ionic surfactant usually refers to derivatives of ethylene oxide (EO), Figure A-2a, and/or propylene oxide (PO), Figure A-2b, with an alcohol containing an active hydrogen atom, Figure A-3. However, other types such as alkyl phenol, sugar esters, alkanolamides, amine oxides, fatty acids, fatty amines and polyols are also produced.

Figure A -2. a) Ethylene oxide structure, b) propylene oxide structure.

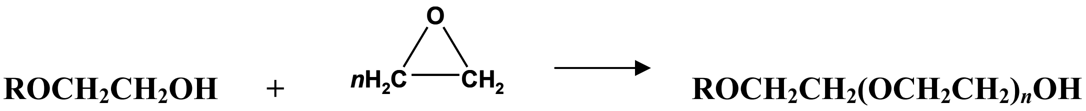


Figure A-3. Example of the reaction of the hydroxyl group (alcohol) with ethylene oxide to form a non-ionic surfactant.

Some common non-ionic surfactants are mentioned below (Cox. 2001).

- Alcohol ethoxylates are widely used in laundry detergents and as a cosurfactant with anionic surfactant for dishwashing liquids. An advantage of this alcohols is their structure flexibility in terms of carbon chain length (C6 to C20+), carbon chain distribution (single homologues or various blends), feedstock source (petrochemically or oleochemically based), the degree of minor (methyl) branching , ethoxy chain length and distribution (ethoxymer distribution refers to unethoxylated or not reacted feedstock, for example, free alcohol in alcohol ethoxylates).
- Alkylphenol ethoxylate is based on nonylphenol with different numbers of ethylene oxide groups. An advantage of alkylphenol ethoxylates is that they are essestially free of alkylphenol.
- Ethylene oxide/propylene oxide block copolymers are very low-foaming surfactants. They are used are thickening and gelling agents. Increasing the ethylenoxide content increases water solubility and reduces wetting.
- Alkylpolyglycosides (APGs) are high-foaming surfactants. Increasing the alcohol chain lengh increases surface activity but decreases water solubility and foaming.
- Amine oxides are the reaction products of tertiary amines and hydrogen peroxide. They are neutral at neutral pH but in acidic environment, amine oxides are cationics. They are based on C12-C18 alkyldimethylamines.
- Amine ethoxylates are widely used as corrosion inhibitors (oilfield applications), emulsifiers (asphalts) and wetting agents processing.
- Methyl ester ethoxylates have very similar properties to alcohol ethoxylate but as yet are not commercialised. They have a lower tendency to gel however they are unstable a high pH (around 9) where they hydrolyse.

APPENDIX B - PROPERTIES OF SURFACTANT USED IN THIS WORK

B.1. Aerosol OT

Aerosol OT or AOT is a type of aliphatic sulfonates (sulfosuccinate). Sulfosuccinates are chemically stable and due to ester likages, they will hydrolyze at extremes of pH and with elevated temperature (Hibbs. 2006). These surfactants are known as excellent solubilising and emulsifying agents. AOT is particularly known for being a good microemulsifier.

Chemical structure:

AOT is a dichain (two tails) anionic surfactant as Figure B-1 shows.

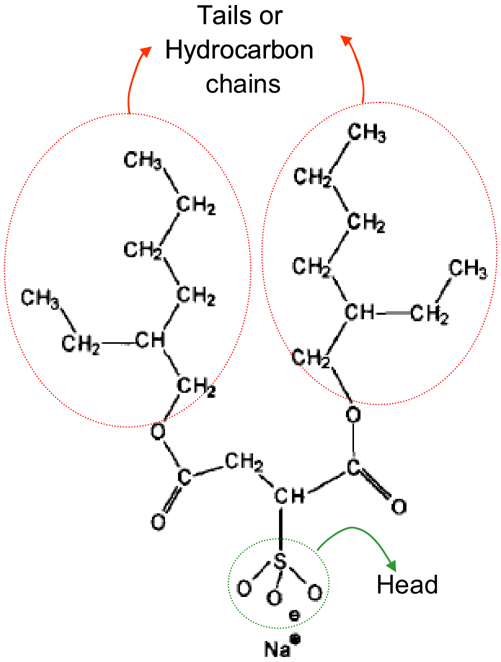


Figure B-1. Structure of the AOT molecule (Li *et al.* 1998).

Molecular weight, CMC and HLB for AOT

Table B-1. AOT Properties.

	CMC (mM)	MW	CMC (g/L)	HLB
AOT	2.2	444.55	0.978	20

*(Nave *et al.* 2000)

Partitioning

When the surfactant concentration is below its critical micelle concentration, the monomer surfactant distributes between the water and oil phase. AOT has the particular property of distributing strongly in the water phase even though AOT is slightly soluble in water and very soluble in alkanes (Binks. 1993).

Surface coverage:

Some studies have shown that the surface coverage of AOT monomer changes with concentration. However, most of the publications reported the surface coverage at the CMC. In the literature the concentrations are reported as a fraction of the CMC, so that, a CMC value of 0.978 g/l was used to determine the area per molecule at the interface as function of AOT concentration in ppm, Figure B-2.

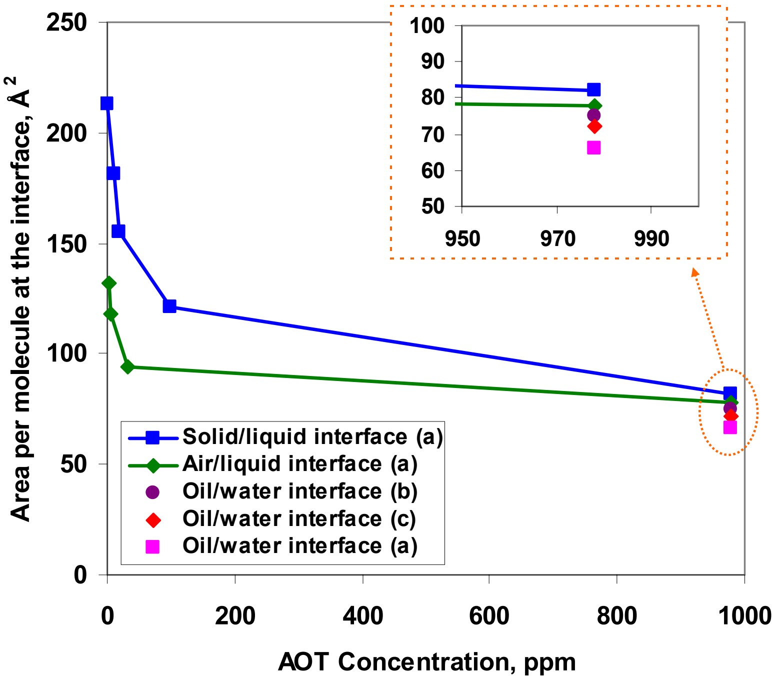


Figure B-2. Surface coverage of AOT at and below the CMC. Source (a) (Li *et al.* 1998); (b) (Nave *et al.* 2002); (c) (Li *et al.* 1998).

The difference of the surface coverage at the CMC depends on the type of oil used, experimental method and the way to calculate the surface coverage from the experimental data. However, most of the values fall between 72 and 82 A^2 at the CMC.

B.2. Nonylphenol Ethoxylates

The properties of nonylphenol ethoxylates, NPE, change with varying the number of ethoxylate groups. NPE up to about the 12-mole ethoxylate are liquid at room temperature. As more ethylene oxide is added to the NPE structure, some physical properties change. For example, the cloud point increases thereby changing the solubility of different components in NPE surfactants. Flash point and fire point also rise with the addition of ethylene oxide. The solidification point decreases until around 50% ethylene oxide in the NPE molecule, higher content of ethylene oxide increases the solidification point. NPE surfactants containing above 75 per cent ethylene oxide are solids at room temperature. NPE surfactants become water soluble when they contain about 50 per cent of ethylene oxide, the larger the amount of ethylene oxide the better the water solubility (Porter. 1991). Around 50 per cent ethylene oxide in the NPE molecule gives the maximum surface-tension reduction (Lange. 1967).

Chemical structure of NPE:

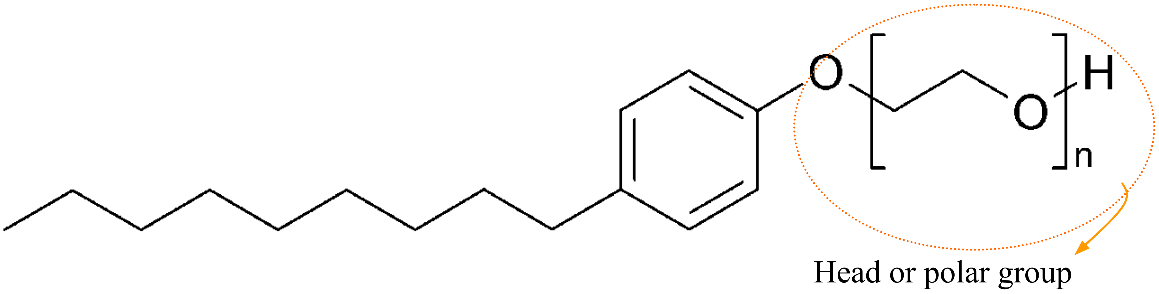


Figure B-3. Molecular structure of nonyl phenol ethoxylate with n ethoxy grups (n=number of ethylene oxide groups in the molecule).

Molecular weight, CMC and HLB according with the degree of ethoxylation:

Table B-2. Properties for NPE depending on the degree of ethoxylation (Porter. 1991).

Surfactant	CMC (µM)	Molecular weight	CMC (g/l)	HLB
NP + 10 EO	75	644	0.048	13.4
NP + 15 EO	87	864	0.075	15
NP + 30 EO	153	1553	0.237	17.2

Polarizability

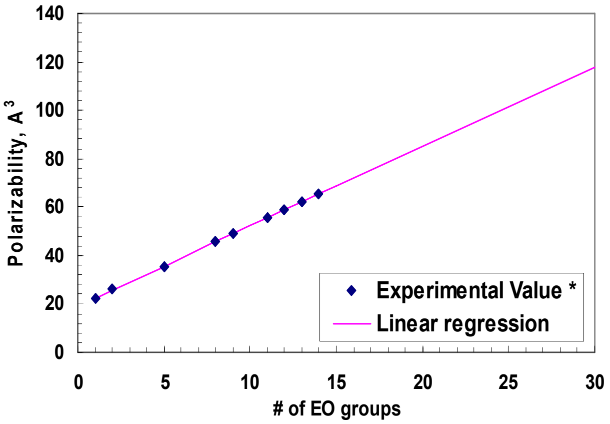


Figure B-4. Change on polarizability with increasing the number of ethoxy group in the molecule.

Partitioning

It has been found that partition coefficient for noionic surfactants is low and even lower for less polar solvent. Nonionic surfactants distributed in favor of the more polar organic phase due to their ability to participate in hydrogen bonding as acceptors (Pollard *et al.* 2006), for example, for systems such as water-toluene or water-heptane, it is easier for nonionic surfactant distribute to the toluene phase than to the heptane phase as the polarity parameter for toluene is 9.9 and for heptane is 1.2.

B.3. Naphthenic Acid and Naphthenate Salt

Naphthenic acids are carboxylic acids present in crude oils that exhibit high viscosities. When the pH increases the acid groups dissociate and react with metal ions to form the corresponding naphthenate. Naphthenic acids and their naphthenate are amphiphilic molecules which tend to accumulate ate the interface between the oil and water phase.

There is no a general estructure for naphthenic acids their naphthenate, in general they are aliphatic molecules with hydrocarbon chains of at least five carbons, typically C15 to C17 and at least one terminal carboxylic group.

Chemical structure

The general formula of carboxylic acids is

$C_nH_{2n+z}O_2$

Where n is the carbon number, z is the number of hydrogen lost for each saturated ring structure in the molecule

Various series are indicated: straight chain(z=0), one ring (z=-2), two ring (z=-4)three rings (<z=-6) structures, etc. With a range of carbon numbers from about 10 to 30 and of z number from 0 to -6.

Some structure of different naphthenic acids, Abietic acid, Figure B-5, 5β-Cholanic acid, Figure B-6 and C80 isoprenoid (ARN acid or tetraacid), Figure B-7, are shown below.

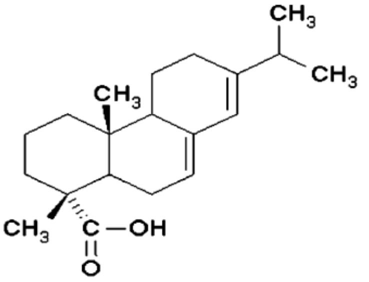


Figure B-5. Structure of Abietic acid**.** (Varadaraj & Brons. 2007)

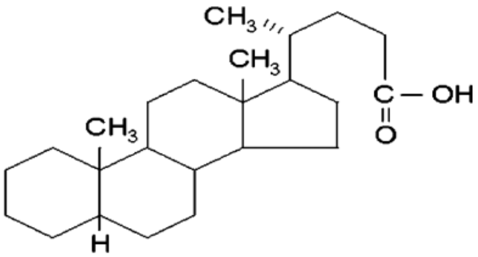


Figure B-6. Structure of 5β-Cholanic acid

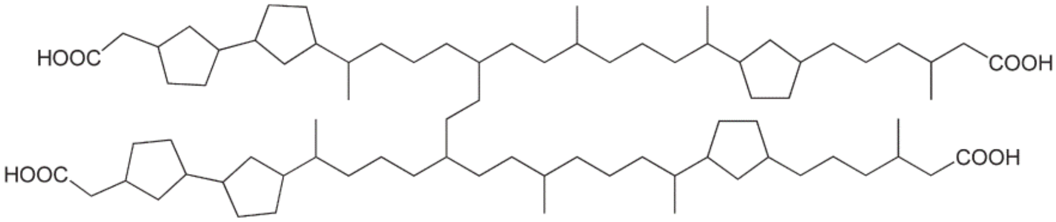


Figure B-7. Structure of C80 isoprenoid (tetraacid or ARN acid) (Magnusson *et al.* 2008).

Extracted-crude oil naphthenic acids are usually a mixture of different carboxylic acids. This mixture might be described as a mixture of components mainly with carbon number between C10-C50 and 0 to 6 fused rings, most which are saturated, and the carboxylic group is attached to a ring through a shore side chain (Robbins, 1998). It has been found that crude oil naphthenic acids contain the COOH group attached to primary, secondary or tertiary carbons (Varadaraj & Brons. 2007).

When naphthenic acids react to the metal ion, their naphthenate is formed when the hydronium is replace by the metal ion in the molecule (e.g. sodium myristate,C14, and sodium palmitate,C16). For example, sodium naphthenate (SN) is a product of the reaction of naphthenic acid with a base. In the oil industry NaOH is a very common base used during oil prossesing. Table B-3 present each reaction and equilibrium to the obtain the salt, Sodium naphthenate from the acid.

Table B - 3. Reactions of naphthenic acid and sodium naphthenate.

a) Acid dissociation:	**$C_nH_{(2n+z)}COOH$**	$\longrightarrow$	**$CnH_{(2n+z)}COO^{-}$ + H^{+}**
b) Reaction with a base:	**$C_nH_{(2n+z)}COO^{-}$ + NaOH**	$\longrightarrow$	**$C_nH_{(2n+z)}COONa$ + OH^{-}**
c) SN dissociation:	**$C_nH_{(2n+z)}COONa$**	$\longrightarrow$	**$C_nH_{(2n+z)}COO^{-}$ + Na^{+}**

Table B-4. Properties of different naphthenic acids.

	Abietic	**5β-Cholanic**	**Crude oil NA**	**C80/ARN**
MW	302	360	from 250 to 750	
Area/molecule ($Å^2$)			31 to 71 (a) 113 to 152 (b)	200
Area/mol ($Å^2$)	160	252	38	
Energy of adsorption (kJ/mol) *	-14.3	-28.4	-19.4	

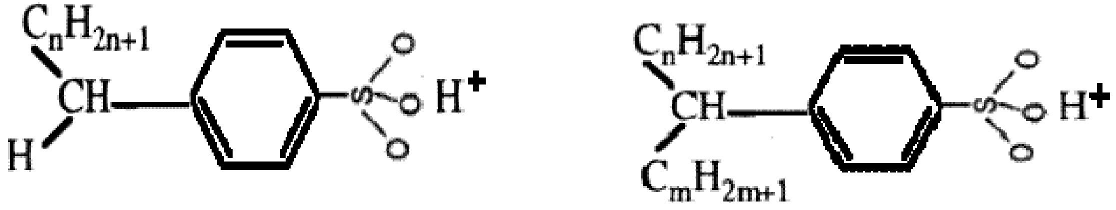
(a) at pH=11 in oil-in-water emulsions (Havre *et al.* 2002)

(b) at water-toluene interface (Ovalles *et al.* 1998)

B.4. Dodecylbenzene Sulfonic Acid

DBSA is within the group of alkyl benzene sulfonates. The fact that there is a benzene sulfonate (sulphur atom link to an aromatic ring) makes the surfactant quite stable. There are different variations of the alkyl group such as the chain length (C8 up to C15) and substitution of the benzene ring in different positions which can affect some physical properties of the surfactant (Porter. 1991). The acids are soluble in water and soluble/dispersable in organic solvents. DBSA is also used for retardation of asphaltene precipitation in crude oils. In this work, tow DBSA configurations are used, one with a linear chain (DBSA-Linear) and one with a branched chain (DBSA-Branched). These are shown in Figure B-8.

Chemical structure:



a)

b)

Figure B-8. Chemical structure of DBSA. a) linear alkyl chain (Chang & Fogler. 1993); b) branched alkyl chain (Chen & Hsiao. 1999). (n+m-1 = 12, number of C in the chain).

Table B-5. Properties of DBSA.

Surfactant	CMC (%wt)	Molecular weight	HLB
DBSA-Branch	0.11	326.5	
DBSA-Linear	0.59		

Surface coverage:

DBSA-Linear = 2.96×10^{-6} mol/m^2 (Abdel-Khalek *et al.* 1999).

It has been found that p-alkylbenzenesulfonic acid is effective stabilizer of asphaltenes in alkane solvents (Hu & Guo. 2005) and it is used to inhibit asphaltene precipitation, that is, they may shift the offset of asphaltene precitpitation. The main effect for shifting offset of asphaltene precipitation is to provide a steric-stabilization layer around asphaltenes.

Chang & Fogler. (1993) showed tht the strength of the p-alkylbezenesulfonic group is so great that it can undergo almost irreversible acid-base interaction with asphaltenes by donating its proton to the C=C bonds and/or specific basic groups of asphaltenes. As a consequence the headgroup is irreversible attached to asphaltenes.

APPENDIX C - EFFECT OF CONCENTRATION OF NEO-10 AND NEO-30 ON FILM PROPERTIES AND EMULSION STABILITY

C.1. Nonylphenol Ethoxylate with 10 ethoxy groups, NEO-10.

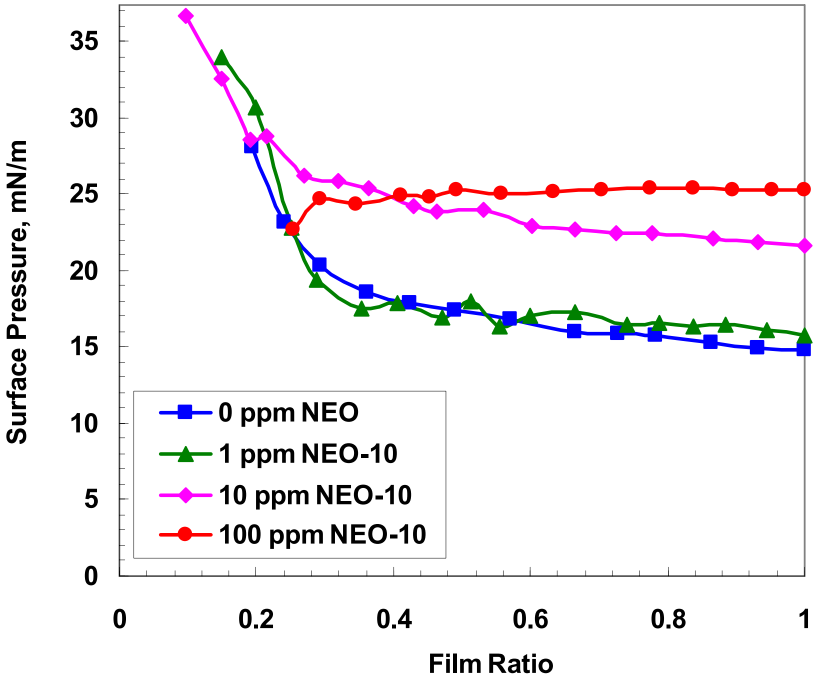


Figure C-1. Effect of concentration for Nonylphenol Ethoxylate 10 (NEO-10) on solutions of 10 kg/m³ asphaltenes in 25:75 heptol versus aqueous surfactant solutions. Films were aged for 1 hour.

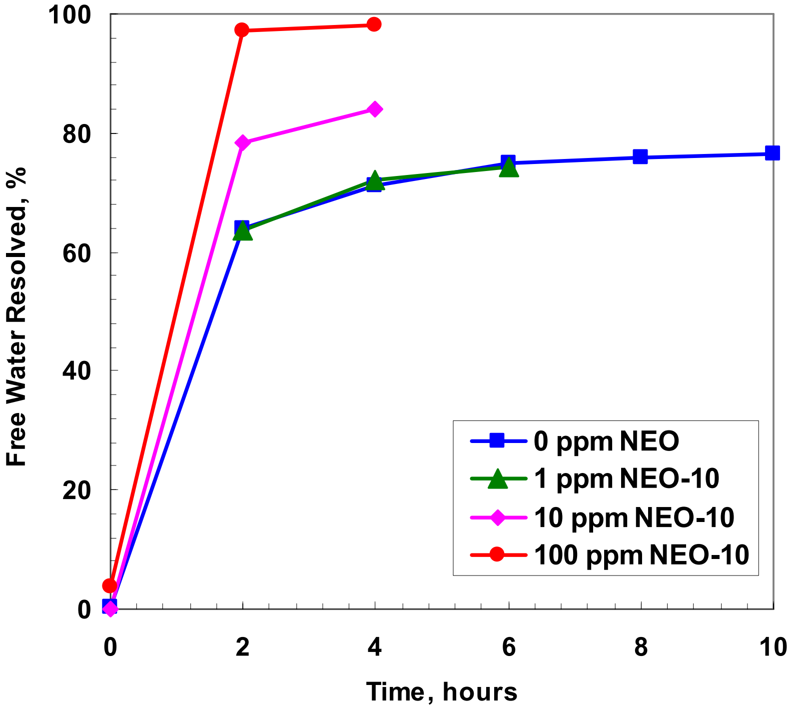


Figure C-2. Effect of concentration for Nonylphenol Ethoxylate 10 (NEO-10) on emulsion stability for solutions of 10 kg/m³ asphaltenes in 25:75 heptol versus aqueous surfactant solutions. Emulsions contained 40 vol% aqueous solution.

C.2. Nonylphenol Ethoxylate with 30 ethoxy groups, NEO-30.

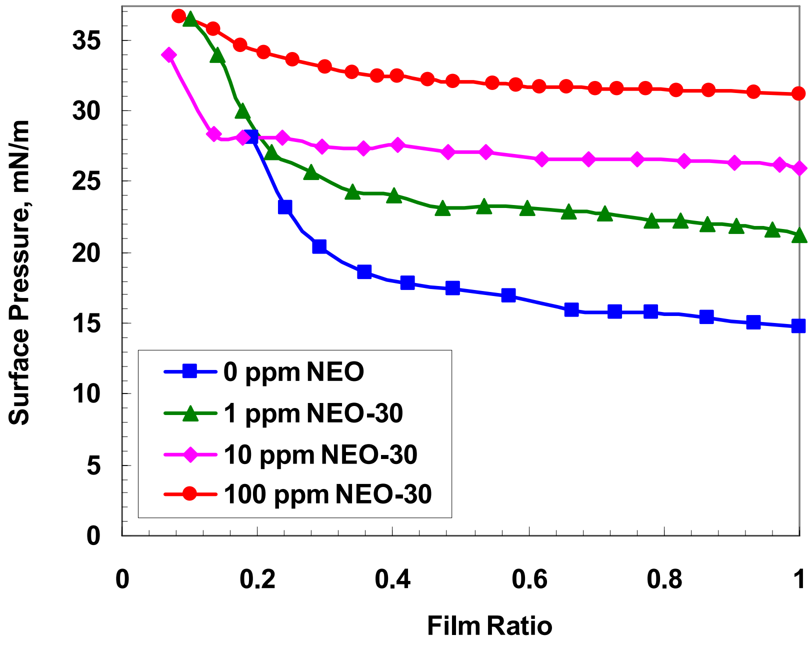


Figure C-3. Effect of concentration for Nonylphenol Ethoxylate 30 (NEO-30) on solutions of 10 kg/m³ asphaltenes in 25:75 heptol versus aqueous surfactant solutions. Films were aged for 1 hour.

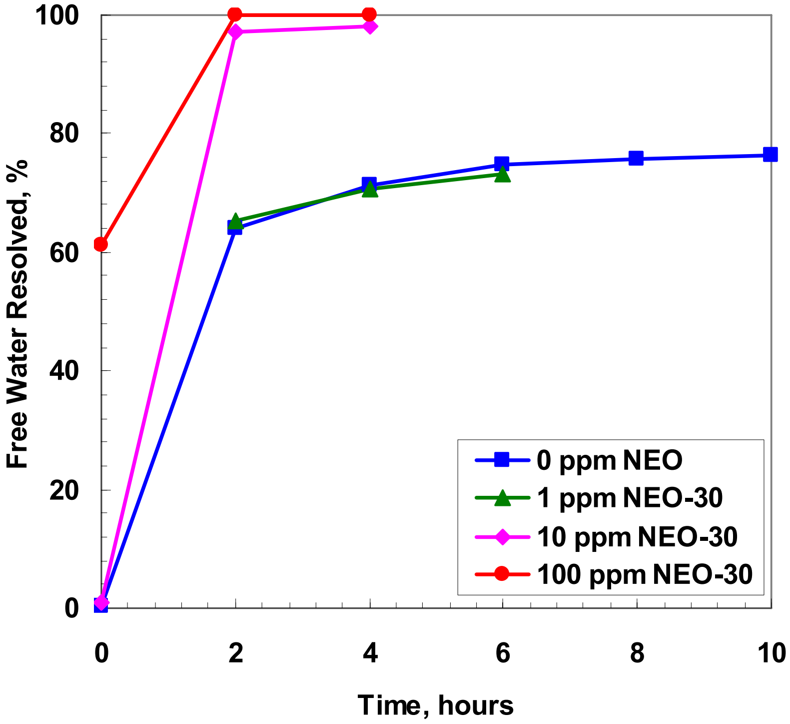


Figure C-4. Effect of concentration for Nonylphenol Ethoxylate 30 (NEO-30) on emulsion stability for solutions of 10 kg/m³ asphaltenes in 25:75 heptol versus aqueous surfactant solutions. Emulsions contained 40 vol% aqueous solution.

APPENDIX D - ASPHALTENE SURFACE COVERAGE

D.1. Aerosol OT

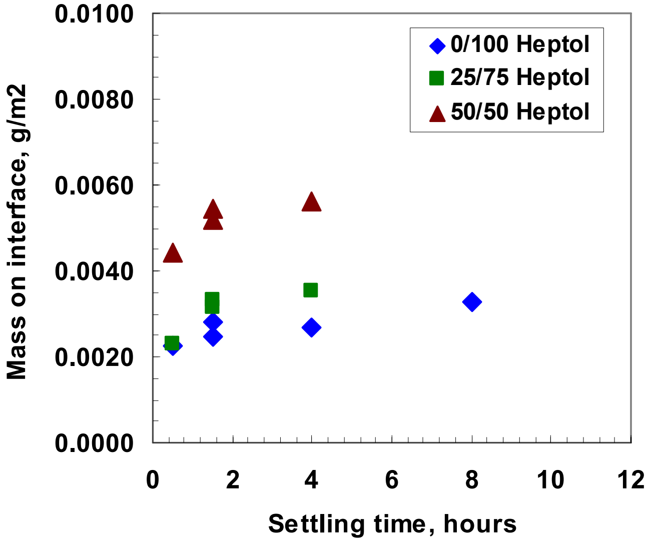


Figure D- 1. Surface coverage for 5 kg/m^3 asphaltene and 100 ppm AOT in the aqueous phase.

D.2. Sodium Naphthenate

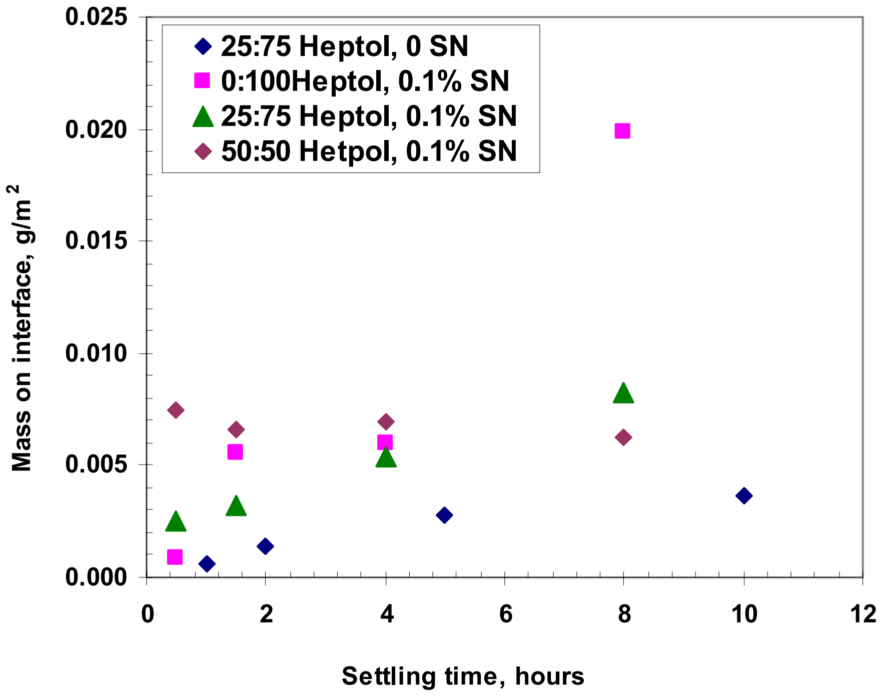


Figure D-2. Surface coverage for 5 kg/m^3 asphaltene and 0.1wt% sodium naphthenate in the aqueous phase.

D.3. DBSA-Branched

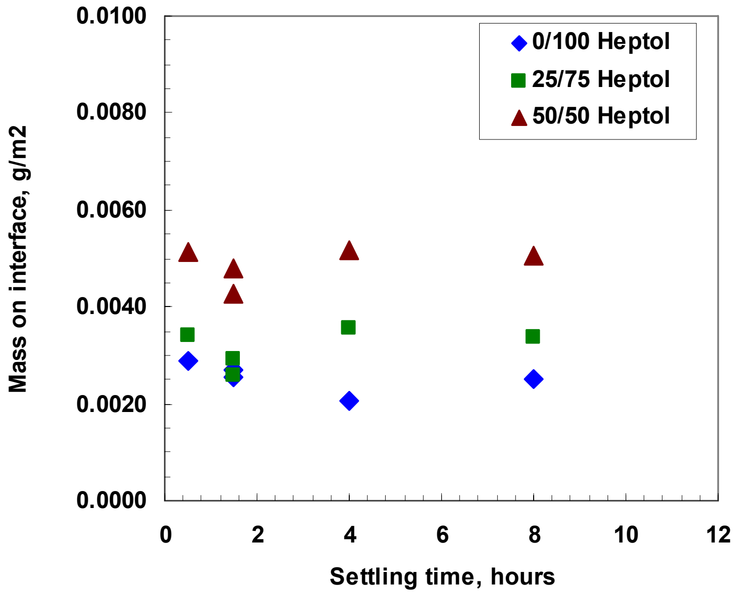


Figure D- 3. Surface coverage for 5 kg/m^3 asphaltene and 10 ppm DBSA-branched in the aqueous phase.

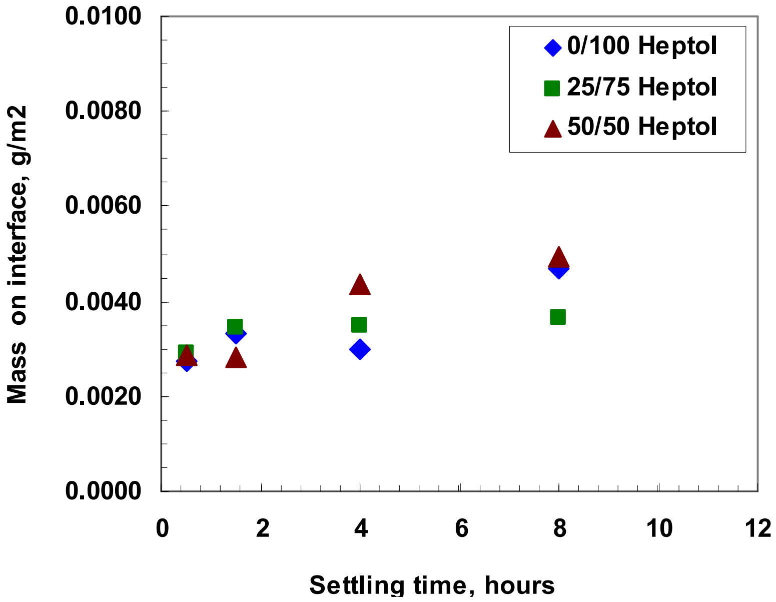


Figure D-4. Surface coverage for 5 kg/m^3 asphaltene and 100 ppm DBSA-branched in the aqueous phase.

D.4. DBSA-Linear

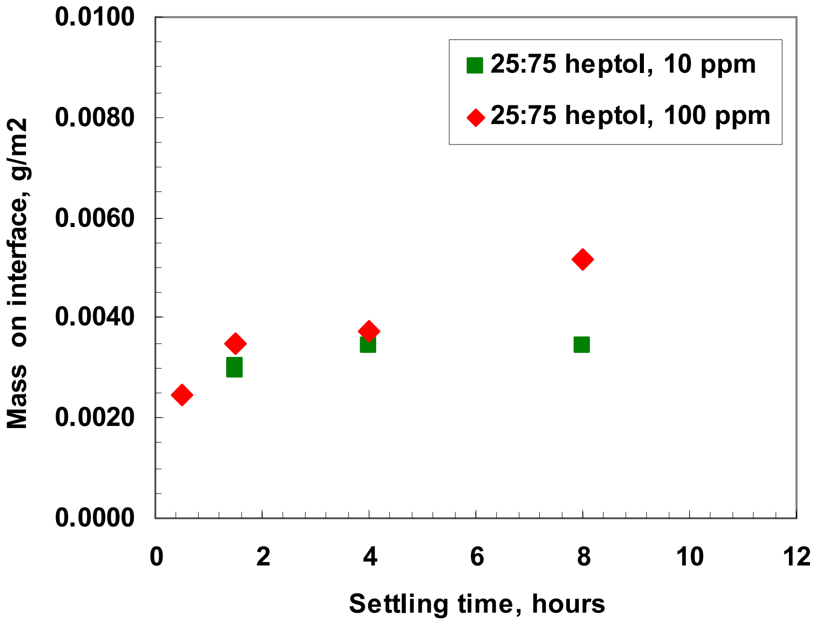


Figure D-5. Surface coverage for 5 kg/m^3 asphaltene in 25:75 heptol with 10 and 100 ppm DBSA-Linear in the aqueous phase.

APPENDIX E RESULTS WITH DILUTED BITUMEN SYSTEM

Surface pressure isotherms and emulsion stability tests were performed for diluted Athabasca bitumen with and without the additives. The results for diluted Athabasca bitumen without additive are reported in this appendix.

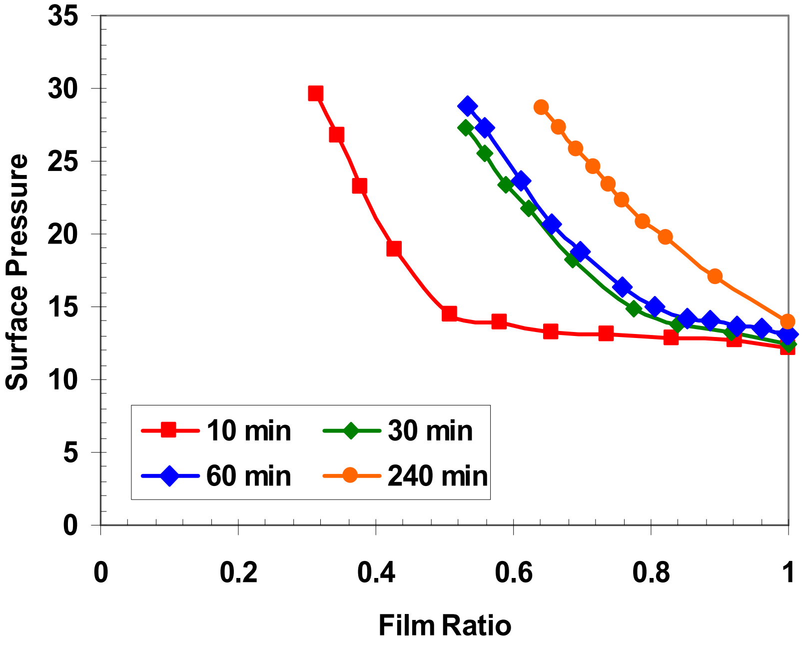


Figure E-1. Effect of aging on surface pressure for 9:1 dilution of Athabasca bitumen in 25:75 heptol at 23°C.

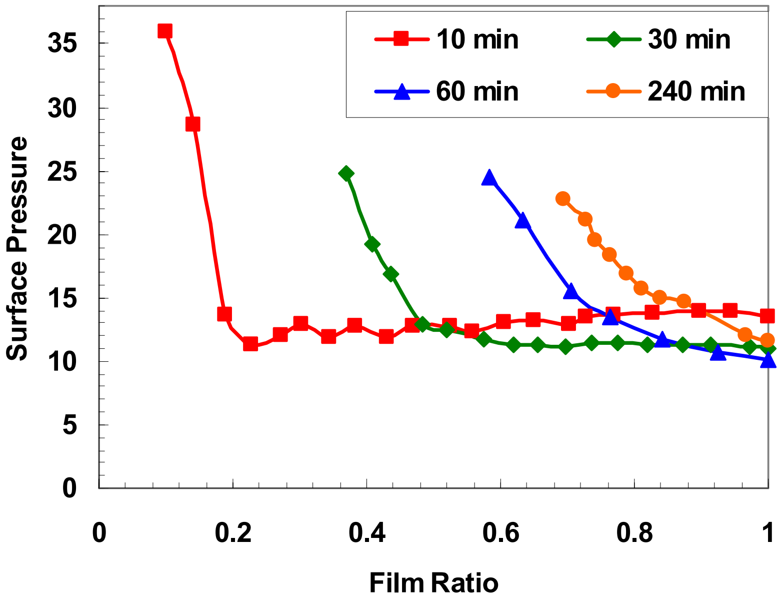


Figure E-2. Effect of aging on surface pressure for and 4:1 dilution of Athabasca bitumen in 25:75 heptol at 23°C.

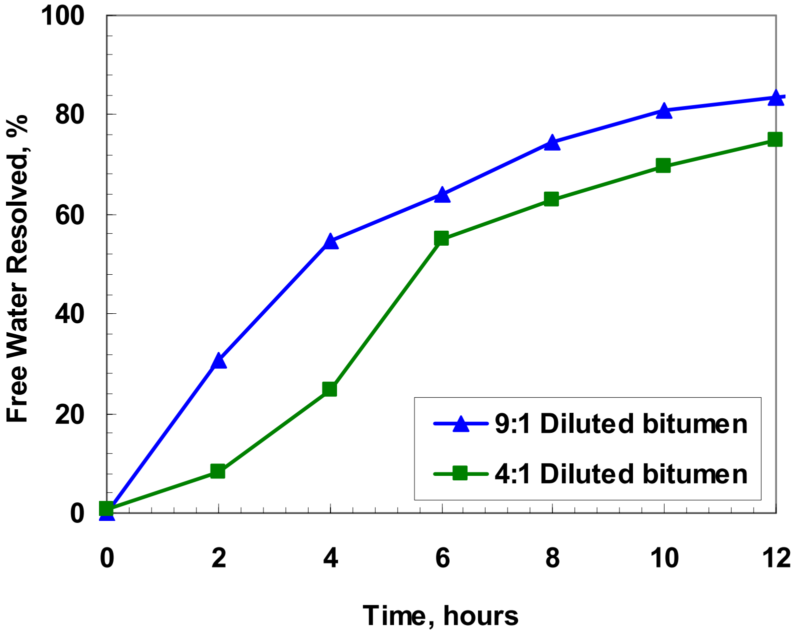


Figure E-3. Emulsion stability for 9:1 and 4:1 dilution of Athabasca bitumen in 25:75 heptol at 60°C. Emulsions contained 40 vol% of water.

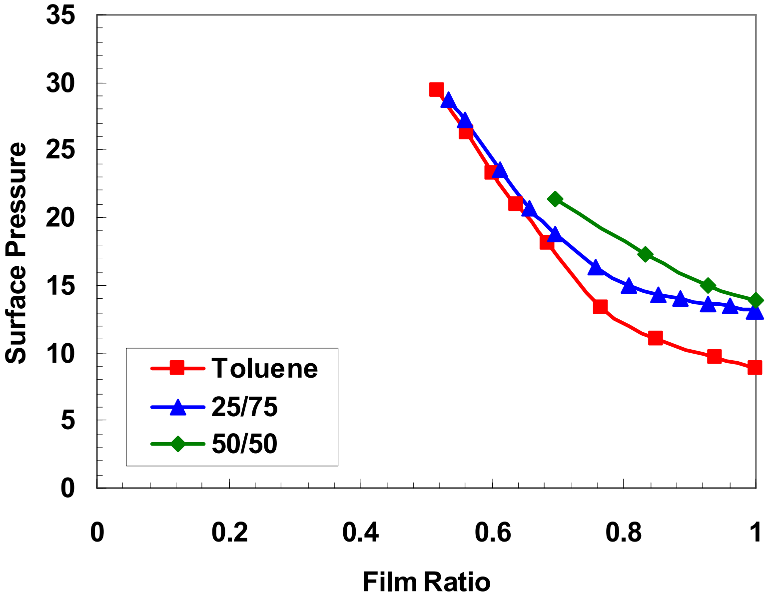


Figure E-4. Effect of solvent on surface pressure for 9:1 dilution of Athabasca bitumen with 1h aging at 23°C.

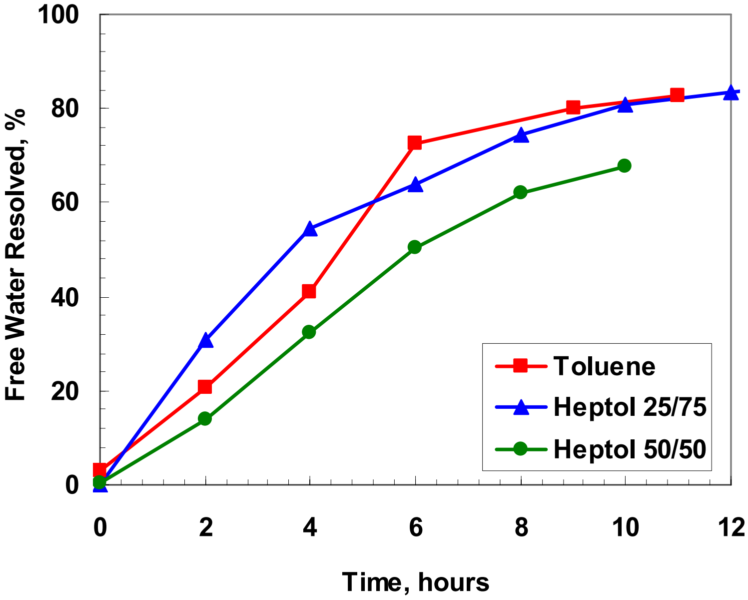


Figure E-5. Effect of solvent on emulsion stability for 9:1 dilution of Athabasca bitumen at 60°C.

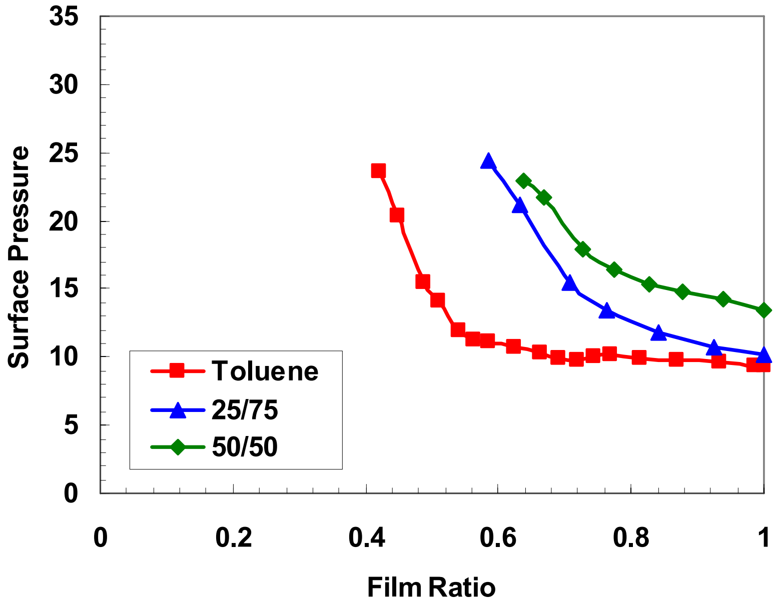


Figure E-6. Effect of solvent on surface pressure for 4:1 dilution of Athabasca bitumen with 1h aging at 23°C.

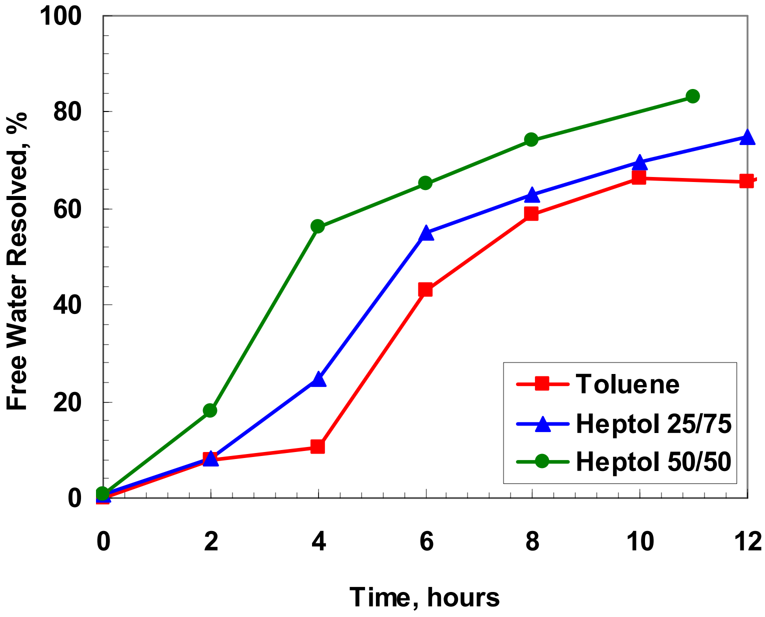


Figure E-7. Effect of solvent on emulsion stability for and 4:1 dilution of Athabasca bitumen at 60°C.

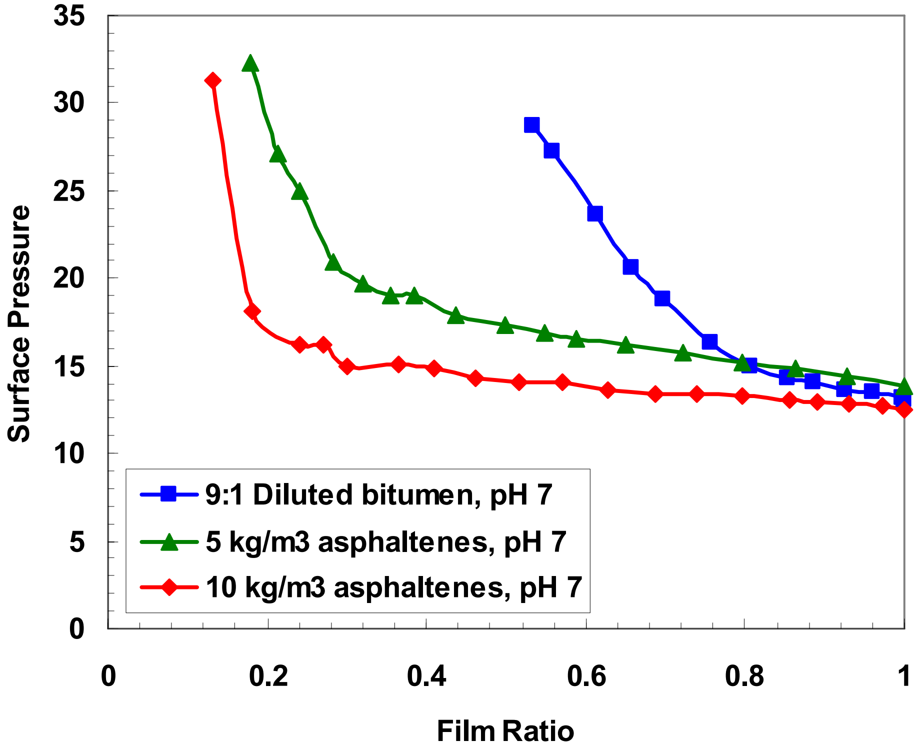


Figure E-8. Comparison between bitumen (9:1 dilution ratio) and asphaltene (5 and 10 kg/m^3) in 25:75 heptol surface pressure isotherms at pH 7. Films were aged 1 hour at 23^{o}C.

APPENDIX F - ERROR ANALYSIS

The sample mean $\bar{y}$ of a sample of n observations is defined as

$$\bar{y} = \frac{\sum_{i=1}^{n} y_i}{n} \qquad \textbf{Equation F-1.}$$

where y_i is each measured data in the sample.

The variability of scatter in the data is described by the sample standard deviation, s, defined by

$$s = \sqrt{\frac{\sum_{i=1}^{n}\left(y_i - \bar{y}\right)^2}{n-1}} \qquad \textbf{Equation F-2}$$

In the current work, the mean of the population, μ, and the population standard deviation are unknown and the number of observations is small ($n \leq 5$). Hence, t-distribution is employed to determine the confidence interval as follow,

$$\bar{y} - t_{(\alpha/2,v)}\frac{s}{\sqrt{n}} \leq \mu \leq \bar{y} + t_{(\alpha/2,v)}\frac{s}{\sqrt{n}} \qquad \textbf{Equation F-3}$$

where $\nu = n - 1$ and $\alpha = 1 -$ (%confidence/100). In the current work, a confidence interval of 80% was utilized in all the error analyzes. Hence, $\alpha = 0.2$

F.1. Interfacial Compressibility

Table F-1. Reproducibility analysis for compressibility data in asphaltene model systems with 100 ppm of AOT.

Asphaltene model systems	**Time min**	**No. of data**	**Mean m/mN**	**Standard deviation**	**±Error m/mN**	**% Error**
5 kg/m^3						
Toluene						
	60	2	1.339	0.381	0.443	33.1
	240	2	0.479	0.096	0.111	23.2
25-75						
	10	2	0.913	0.065	0.075	8.2
	30	2	0.801	0.007	0.008	1.0
	60	2	0.657	0.164	0.191	29.1
	240	2	0.507	0.138	0.161	31.8
50-50						
	10	2	0.343	0.101	0.117	34.1
	30	2	0.201	0.022	0.026	12.9
	60	2	0.183	0.004	0.004	2.2
	240	2	0.117	0.009	0.010	8.5
				Average error	**±0.115 m/Nm**	**18.4%**
10 kg/m3						
Toluene						
	240	2	0.784	0.129	0.150	19.1
25-75						
	10	2	1.726	0.815	0.948	54.9
	30	2	1.478	0.716	0.833	56.4
	60	2	1.032	0.169	0.197	19.1
	240	2	0.706	0.211	0.245	34.7
50-50						
	10	2	0.858	0.006	0.007	0.8
	30	2	0.553	0.196	0.228	41.2
	60	2	0.376	0.125	0.145	38.6
	240	2	0.183	0.032	0.038	19.1
				Average error	**±0.310 m/Nm**	**31.7%**

Table F-2. Reproducibility analysis for compressibility data in asphaltene model systems with 0.1wt% sodium naphthenate.

Asphaltene model systems	**Time min**	**No. of data**	**Mean m/mN**	**Standard deviation**	**±Error m/mN**	**% error**
5 kg/m3						
Toluene						
	10	2	0.322	0.044	0.051	15.8
	30	2	0.305	0.001	0.001	0.3
	60	2	0.289	0.069	0.080	27.7
	240	2	0.229	0.041	0.048	21.0
25-75						
	10	3	0.312	0.066	0.076	24.4
	30	3	0.277	0.013	0.016	5.8
	60	3	0.237	0.023	0.027	11.4
	240	3	0.227	0.006	0.006	2.6
50-50						
	10	2	0.234	0.018	0.021	9.0
	240	2	0.134	0.016	0.019	14.2
				Average error	**±0.034 m/Nm**	**13.2%**

Table F-3. Reproducibility analysis for compressibility data in asphaltene model systems with 0.5wt% sodium naphthenate.

Asphaltene model systems	**Time min**	**No. of data**	**Mean m/mN**	**Standard deviation**	**±Error m/mN**	**% error**
5 kg/m^3						
Toluene						
	10	2	0.696	0.363	0.422	60.6
	30	2	0.364	0.021	0.024	6.6
	60	2	0.338	0.031	0.036	10.7
	240	2	0.280	0.015	0.018	6.4
				Average error	**±0.034 m/Nm**	**21.1%**

Total Average % error : 20.8 %

F.2. Crumpling Film Ratio

Table F-4. Reproducibility analysis for crumpling film ratio data in asphaltene model systems with 100 ppm AOT.

Asphaltene model systems		Time min	No. of data	Mean	Standard deviation	±Error
5 kg/m^3						
	25:75					
		240	2	0.082	0.012	0.027
	50:50	10	2	0.091	0.046	0.101
		30	2	0.132	0.011	0.023
		60	2	0.178	0.003	0.006
		240	2	0.239	0.025	0.054
					Average error	**±0.042**
10 kg/m^3						
	25:75					
		240	2	0.079	0.0001	0.0003
	50:50	30	2	0.090	0.014	0.031
		60	2	0.148	0.035	0.075
		240	2	0.241	0.043	0.094
					Average error	**±0.050**

Table F-5. Reproducibility analysis for crumpling film ratio data in asphaltene model systems with 0.1wt% sodium naphthenate.

Asphaltene model systems	Time min	No. of data	Mean	Standard deviation	±Error
5 kg/m^3					
Toluene					
	10	2	0.041	0.002	0.005
	30	2	0.064	0.009	0.020
	60	2	0.093	0.002	0.005
	240	2	0.170	0.022	0.049
25:75					
	10	3	0.052	0.021	0.023
	30	2	0.074	0.003	0.006
	60	3	0.103	0.023	0.025
	240	2	0.181	0.031	0.067
50:50	10	2	0.122	0.016	0.034
	240	2	0.2795	0.057	0.125
				Average error	**±0.036**

Total Average absolute error: ± 0.040

F.3. Emulsion Stability

Table F-6. Reproducibility analysis for emulsion stability data in 25:75 heptol asphaltene model systems.

Asphaltene model systems	**time**	**No. of data**	**Mean vol%**	**Standard deviation**	**±Error vol%**
5 kg/m^3 24:75 heptol					
	2	2	47.72	17.36	20.19
	4	2	53.08	12.62	14.68
	6	2	58.43	7.87	9.15
				Average error	**±14.7 vol%**
10 kg/m^3 25:75 heptol					
	0	5	0.19	0.46	0.38
	2	5	63.98	19.85	16.33
	4	5	71.16	16.36	13.46
	6	5	74.83	14.26	11.73
	8	4	75.74	14.42	11.86
	10	4	76.49	13.97	11.49
				Average error	**±10.9 vol%**

Table F 7. Reproducibility analysis for emulsion stability data in asphaltene model systems with 100 ppm AOT.

Asphaltene model systems	**time**	**No. of data**	**Mean vol%**	**Standard deviation**	**±Error vol%**
5 kg/m^3 25:75 heptol					
	2	2	96.53	3.21	3.74
	4	2	98.39	1.28	1.50
	6	2	99.43	0.51	0.60
				Average error	**±2.0 vol%**

Table F 8. Reproducibility analysis for emulsion stability data in asphaltene model systems with 10 ppm NEO surfactants.

Asphaltene model systems	time	No. of data	Mean vol%	Standard deviation	±Error vol%
10 kg/m^3					
25:75 heptol					
NEO-10	0	2	0.00	0.01	0.01
	2	2	78.43	1.76	2.05
	4	2	84.13	4.09	4.76
NEO-15	0	2	0.00	0.00	
	2	2	87.56	2.48	2.88
	4	2	92.44	2.64	3.08
NEO-30	0	2	0.85	1.20	1.39
	2	2	97.27	0.90	1.04
	4	2	98.12	0.30	0.35
				Average error	**±1.9 vol%**

Table F 9. Reproducibility analysis for emulsion stability data in asphaltene model systems with 100 ppm NEO surfactants.

Asphaltene model systems	time	No. of data	Mean vol%	Standard deviation	±Error vol%
10 kg/m^3					
25:75 heptol					
NEO-10	0	2	3.70	0.74	0.86
	2	2	97.24	0.54	0.63
NEO-15	0	2	68.68	8.99	10.45
	2	2	98.74	2.39	2.78
NEO-30	0	2	61.10	24.14	28.08
	2	2	100.00	2.51	2.92
				Average error	**±7.6 vol%**

Table F 10. Reproducibility analysis for emulsion stability data in 25:75 heptol asphaltene model systems with pH=4.5 in the aqueous phase.

Asphaltene model systems	time	No. of data	Mean vol%	Standard deviation	±Error vol%
5 kg/m^3					
25:75 heptol					
	0	4	0.07	0.15	0.12
	2	4	62.06	1.16	0.95
	4	4	68.64	0.38	0.31
	6	4	71.21	1.43	1.17
	8	2	73.37	0.01	0.01
	10	2	75.42	1.19	1.38
				Average error	**±0.7 vol%**

Table F-11. Reproducibility analysis for emulsion stability data in 25:75 heptol asphaltene model systems with pH=3.3 in the aqueous phase.

Asphaltene model systems	time	No. of data	Mean vol%	Standard deviation	±Error vol%
5 kg/m^3					
25:75 heptol					
	0	3	0.11	0.19	0.21
	2	3	41.03	10.97	11.97
	4	3	60.09	3.24	3.54
	6	3	63.02	4.32	4.71
	8	2	65.09	2.98	3.99
	10	2	66.75	2.99	3.99
				Average error	**±4.7 vol%**
10 kg/m^3					
25:75 heptol					
	0	2	0.17	0.23	0.27
	2	2	24.44	10.42	12.12
	4	2	52.82	5.40	6.28
	6	2	59.03	4.83	5.61
	8	2	60.73	6.47	7.53
	10	2	64.11	7.37	8.57
				Average error	**±6.7 vol%**

Table F 12. Reproducibility analysis for emulsion stability data in asphaltene model systems in toluene and 0.1wt% sodium naphthenate.

Asphaltene model systems	time	No. of data	Mean vol%	Standard deviation	±Error vol%
5 kg/m^3					
Toluene					
	0	2	1.15	0.88	1.03
	2	2	90.20	5.44	6.32
	4	2	93.45	4.80	5.58
	6	2	95.14	4.42	5.14
	8	2	97.68	1.78	2.07
	10	2	98.96	0.98	1.14
				Average error	**±3.5 vol%**
10 kg/m^3					
Toluene					
	0	2	1.01	1.42	1.66
	2	2	59.78	4.30	5.00
	4	2	70.33	4.65	5.41
	6	2	81.09	0.20	0.23
	8	2	84.46	2.43	2.83
	10	2	86.20	1.47	1.71
				Average error	**±2.8 vol%**

Table F 13. Reproducibility analysis for emulsion stability data in asphaltene model systems in 25:75 heptol and 0.1wt% sodium naphthenate.

Asphaltene model systems	**time**	**No. of data**	**Mean vol%**	**Standard deviation**	**±Error vol%**
5 kg/m^3					
25:75 heptol					
	0	2	0.41	0.58	1.04
	2	2	83.02	5.13	9.18
	4	2	87.93	5.25	9.39
	6	2	86.70	4.59	8.22
	8	2	95.79	1.18	2.11
	10	2	98.48	2.63	4.71
				Average error	**±5.8 vol%**
10 kg/m^3					
25:75 heptol					
	0	3	0.54	0.74	0.80
	2	3	47.36	7.40	8.03
	4	3	69.23	2.47	2.68
	6	3	82.35	3.89	4.22
	8	3	85.34	2.86	3.10
	10	3	87.39	1.58	1.72
				Average error	**±3.4 vol%**

Table F 14. Reproducibility analysis for emulsion stability data in asphaltene model systems in 50:50 heptol and 0.1wt% sodium naphthenate.

Asphaltene model systems	**time**	**No. of data**	**Mean vol%**	**Standard deviation**	**±Error vol%**
5 kg/m^3					
50:50 heptol					
	0	4	0.07	0.14	0.12
	2	4	17.13	18.72	15.35
	4	4	24.75	25.74	21.11
	6	4	32.58	34.57	28.35
	8	4	37.81	35.48	29.09
	10	4	39.84	36.48	29.92
				Average error	**±20.7 vol%**
10 kg/m^3					
50:50 heptol					
	0	4	0.42	0.83	0.68
	2	4	8.74	6.91	5.66
	4	4	16.19	12.03	9.86
	6	4	33.39	26.96	22.10
	8	4	38.32	26.26	21.53
	10	4	42.66	28.73	23.56
				Average error	**±13.9 vol%**

Table F 15. Reproducibility analysis for emulsion stability data in asphaltene model systems with 100 ppm DBSA-Branched.

Asphaltene model systems	**time**	**No. of data**	**Mean vol%**	**Standard deviation**	**±Error vol%**
10 kg/m^3					
25:75 heptol					
	0	2	0	0	
	2	2	7.40	5.11	5.95
	4	2	20.71	8.80	10.23
	6	2	27.52	12.16	14.14
	8	2	31.87	11.20	13.03
	10	2	35.29	10.69	12.43
	12	2	37.79	8.89	10.34
				Average error	**±11.0 vol%**

APPENDIX G - EFFECT OF AGING FOR AOT-ASPHALTENE FILMS

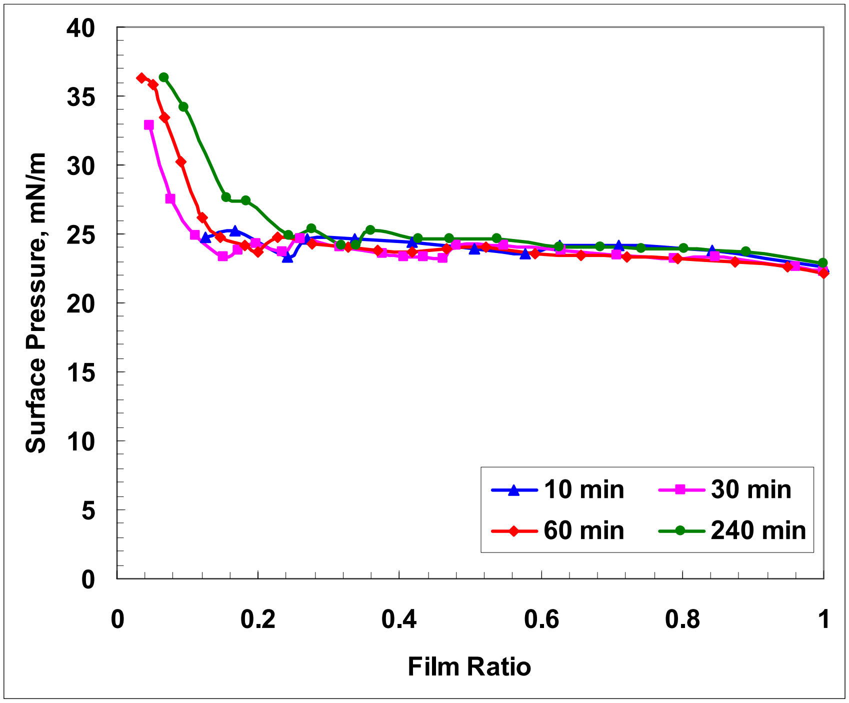


Figure G -1. Effect of aging in the surface pressure isotherm for 10 kg/m^3 asphaltenes in 25:75 hetpol and 100 ppm AOT aqueous surfactant solution.

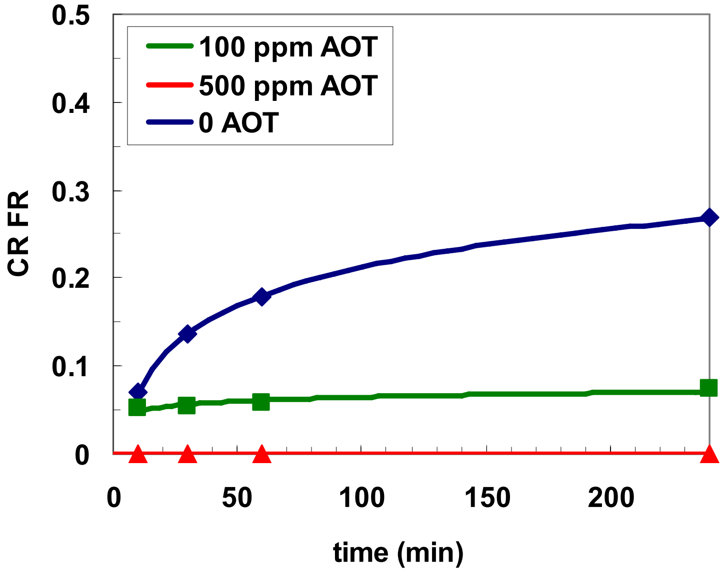


Figure G-2. Effect of aging on Crumpling point for 10 kg/m^3 asphaltenes in 25:75 hetpol and AOT aqueous surfactant solution.

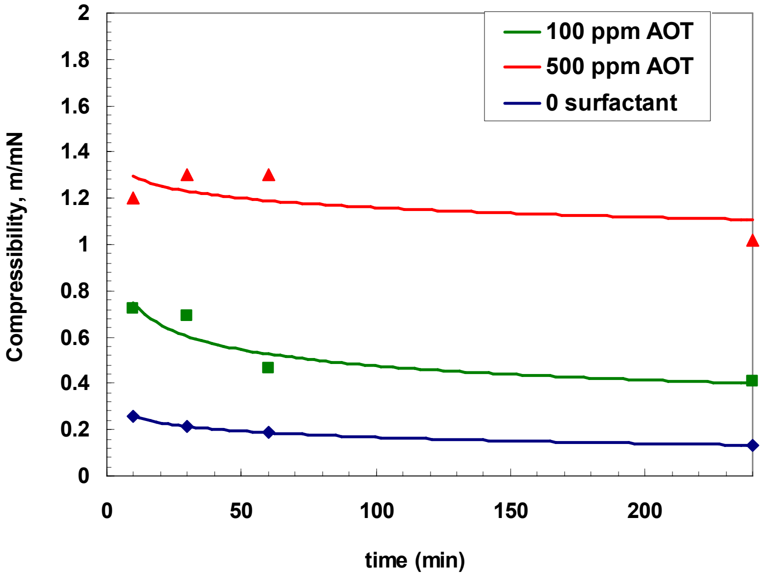


Figure G*3. Effect of aging on interfacial compressibility for 10 kg/m^3 asphaltenes in 25:75 hetpol and AOT aqueous surfactant solution.