#### THE UNIVERSITY OF CALGARY

#### **Role of Asphaltenes and Resins**

#### in the Stabilization of Water-in-Hydrocarbon Emulsions

by

**Oiga Victorovna Gafonova** 

**A THESIS** 

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#### ABSTRACT

Water-in-crude oil emulsions are often an undesired byproduct of petroleum production and processing. Emulsions increase the volume and viscosity of oil which add significantly to operating costs. Water-in-crude oil emulsion can also form during oceanic oil spills impending clean up operations. It is well established that the stability and treatment of these emulsions mainly depend on the presence of a rigid film on the emulsion interface. It is believed that this film is composed of naturally occurring crude oil constituents, such as asphaltenes, resins and fine solids.

In this thesis, the role of asphaltenes, resins and native solids in stabilizing water-inhydrocarbon oil emulsions was investigated by measuring the interfacial composition and stability of model emulsions composed of water with mixtures of toluene, heptane, asphaltenes, resins and solids. It was found that the amount of asphaltenes adsorbed on the emulsion interface increased as the asphaltene bulk concentration increased. However, emulsion stability decreased over the same concentration range. These results suggest that asphaltenes change configuration on the interface. The addition of either a good solvent or resins was found to reduce asphaltene adsorption and to reduce emulsion stability. Resins were able to completely replace asphaltenes on the interface at high concentrations. Native solids were found to have no affect on asphaltene adsorption but to significantly enhance emulsion stability.

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## **LIST OF SYMBOLS**

- A Interfacial area per molecule (m<sup>2</sup>)
- $A_w$  Surface area of an emulsion (m<sup>2</sup>)
- C Concentration (kg/m<sup>3</sup>)
- C<sub>A</sub>° Concentration of asphaltenes in the continuous phase before emulsification (kg/m<sup>3</sup>)
- $C_A^{eq}$  Concentration of surface-active asphaltenes at equilibrium (kg/m<sup>3</sup>)
- d Diameter (m)
- ds Sauter mean diameter (m)
- F Number Frequency
- g Gravitational constant (m/s<sup>2</sup>)
- M Molar mass (g/mol)
- m Mass (kg)
- N Total number of drops
- N<sub>A</sub> Avogadro's number
- Q Volumetric flow rate (m<sup>3</sup>/s)
- R Universal gas constant (J/mol·K)
- R<sub>s</sub> Particle radius (m)
- T Temperature (K)
- t Time (s)
- v Velocity (m/s)
- V Volume (m<sup>3</sup>)
- X Fractional asphaltene concentration

#### Greek Symbols

Γ	Mass surface coverage (mol/m <sup>2</sup> )
Г′	Molar surface coverage (mol/m <sup>2</sup> )
ρ	Density (kg/m <sup>3</sup> )
σ	Interfacial tension (mN/m)

μ	Fluid viscosity (Pa·s)
θ	Fractional surface coverage

## **Subscripts**

Asphaltenes
Emulsion droplet
Heavy liquid phase
i <sup>th</sup> asphaltene component
Interface
Light liquid phase
Total mixture
Resins
Solid
Total emulsion

### **CHAPTER 1**

#### **INTRODUCTION**

#### **1.1 GENERAL DESCRIPTION**

The formation of water-in-crude oil emulsions is one of the problems that petroleum producers have to deal with during oil recovery, treatment and transportation. Produced water can come either from the original reservoir water saturation, or as a result of secondary or tertiary production methods. In refining processes, water comes either as result of "washing out" of contaminants present in crude oil, or as the result of steam injection to improve fractionation. While water and oil can initially be present as independent phases, agitation and shearing forces in the wellbore, chokes, valves, pipelines and pumps enhances mixing, causing the formation of crude oil emulsions.

Emulsions are undesirable because the volume of dispersed water occupies space in processing equipment and pipelines, increasing capital and operating costs. Furthermore, the physical properties and characteristics of oil change significantly upon emulsification. The density of emulsion can increase from 800 kg/m<sup>3</sup> for the original oil to 1030 kg/m<sup>3</sup> for the emulsion. The most significant change is observed in viscosity, which typically increases from a few mPa·s or less to about 1000 mPa·s (Fingas et al., 1993).

Produced water has a high concentration of chloride salts, which can lead to scaling, corrosion problems, and catalyst poisoning in the refining equipment. In order to eliminate

salt from the oil before it is refined, emulsions undergo a desalinating process. In this process, the crude oil and produced water are deliberately mixed with fresh water ("wash water") and emulsified. Then the desalter emulsions are broken and the majority of the salt and water is separated from the oil. The separation of desalter emulsions is very difficult since most of these emulsions are very stable. Furthermore, some of the oil stays trapped in the emulsion and causes sludge generation (McLean and Kilpatric, 1997).

Another problem associated with water-in-crude oil emulsions is their formation during oceanic oil spills. Agitation from the action of waves, wind and currents leads to emulsification of the oil spilled in the ocean. These emulsions significantly increase the quantity and viscosity of the spilled material. The amount of water in the emulsions can make up between 60 to 80 volume percent of the emulsion, increasing the volume of spilled pollutant 3-5 times the original size (Fingas, 1995). The high viscosity of the emulsion effectively changes spilled oil from a liquid to a semisolid material. This solid-like behavior highly complicates and increases the cost of cleanup operations.

In order to minimize production problems associated with crude oil emulsions and meet environmental concerns, petroleum operators need to prevent their formation or to break them. In some cases when the formation of emulsions is a result of poor operation practices, it is possible to prevent emulsion formation. However, in many instances emulsion formation is inevitable. The exclusion of water during recovery from the oil wells and prevention of agitation is difficult or impossible to achieve, and emulsions must be treated.

The treatment of water-in-crude oil emulsions involves the application of chemical, thermal, electrical process, or their combinations. It is based on the principle of coalescing dispersed water droplets into larger droplets. Eventually, a separate water phase is formed. In order to bring about coalescence of water-in-oil emulsions, a rigid interfacial film surrounded the water droplets must be weakened or broken. This is often accomplished by applying heat and/or by adding properly selected chemicals. The later are referred to as dehydration chemicals or demulsifiers. Their effectiveness depends on the composition of the oil in the bulk phase and on the interface.

As will be discussed later, the film encapsulating the water droplets is formed by adsorbed solid particles or surface-active materials. The rigidity and structure of this film determines the stability of the emulsion. Unfortunately, since crude oil is an extremely complex mixture of many thousand of compounds, it is difficult to identify the role of any of these compounds in crude oil emulsion stabilization. Despite extensive research, even the composition of the interfacial film is poorly understood. Therefore, it is almost impossible to predict the performance of demulsifiers or other treatment methods. In most cases, emulsifiers are selected by trial and error, and crude oil emulsion resolution is still more of an art than a science.

Nevertheless, some progress has been made in the understanding of water-in-crude oil emulsions. The rigid interfacial film surrounded water droplets is believed by many researchers to be composed predominantly of asphaltenes, resins and/or fine solids (Strassner, 1968; McLean and Kilpatric, 1997; Yan et. al., 1999). Asphaltenes are defined as a solubility class of petroleum; that is they are soluble in toluene but insoluble in n-heptane or n-pentane. Resin molecules are soluble in both types of solvents. Asphaltenes are composed of polyaromatic hydrocarbons that consist of condensed aromatic rings and aliphatic side chains along with a variety of functional groups. Resins are composed of molecules with similar structure, but lower molecular weight, fewer functional groups, and a higher hydrogen/carbon ratio.

Resins and asphaltenes are considered to be surface-active (Sheu et al., 1995; Ese et al., 1998). This may allow them to accumulate on the water/oil interface where they form a rigid film. The behavior of asphaltenes and resins in crude oil is still poorly understood. Asphaltenes are known to self-associate in crude oil (Koots and Speight, 1975). It is also proposed that resin molecules may adsorb on the associated asphaltenes and form aggregates (Dickie and Yen, 1967). Therefore, asphaltenes and resins may adsorb on the interface as independent molecules, or different types of aggregates. It has been observed that asphaltene concentration, the resin/asphaltene ratio, and asphaltene solubility in the continuous oil phase of an emulsion are the primary factors governing the stability of water-in-crude oil emulsions (McLean and Kilpatrick, 1995; Ese at al., 998). However, it

is still not clearly known what role resins and asphaltenes play in the formation of interfacial film and hence in water-in-crude oil emulsion stabilization.

Fine solids, such as sand, clay, silica and organic particles are also able to stabilize emulsions (Menon et al., 1988; Yan et al., 1995). However, the role of solids and the mechanism of their action in crude oil emulsion stabilization is only partly understood.

#### **1.2 OBJECTIVES**

The key to understanding the role of asphaltenes, resins and solids in the emulsion stability is to determine what is adsorbing on the emulsion interface. Hence, the main objective of this study is to measure the composition of the interfacial film formed by asphaltenes and resins; that is, to determine mass of surface-active compounds per area of the water/oil emulsion interface. These data may provide information in what form asphaltenes and resins adsorb on the interface.

The determination of the interfacial composition can be conducted at various bulk oil phase compositions, such as different solvents, asphaltene and resin concentrations, and resin/asphaltene ratios in the continuous phase. A comparison of the interfacial composition at various conditions can provide more insight on the mechanism of emulsion stabilization by asphaltenes and resins.

Finally, the stability of the asphaltene and/or resin water-in-oil emulsions can be related to the interfacial composition. The comparison of emulsion stability at different continuous phase composition is another good tool for understanding the behavior of asphaltenes and resins on the emulsion interface.

While the main goal of this study is to investigate the role of asphaltenes and resins in the stabilization of emulsions, the role of native solids in emulsion stabilization will be also considered. It is known that asphaltenes removed from bitumen by precipitating them with a solvent contain some solid material (Yarranton, 1997). Therefore solids present in the asphaltene fraction may interfere with the adsorption of asphaltenes and/or resins on the emulsion interface. Moreover, the solids may overshadow the stabilization capacity of asphaltenes and resins. Therefore, the role of native solids in emulsion stabilization needs to be examined. This can be done by comparing the interfacial composition and emulsion stability of emulsions prepared with and without solids.

In summary, the objectives of the study are restated below:

- 1. To measure the interfacial composition (the mass per area) of the emulsions stabilized by asphaltenes and resins
- 2. To relate the interfacial composition to the continuous oil phase composition (asphaltene and resin concentration, solvent type, and asphaltene/resin ratio)
- 3. To relate interfacial composition and emulsion stability
- 4. To examine the role of solids in emulsion stabilization

To avoid the complexity of a bitumen system, model emulsions were used to measure the interfacial composition and emulsion stability. The dispersed phase in the model emulsions was prepared from the de-ionized water. The oil continuous phase in these emulsions contained various concentrations of asphaltenes, resins and solids, dissolved in mixtures of toluene and heptane. Asphaltenes and resins were extracted from Athabasca and Cold Lake bitumens.

A combination of interfacial tension, emulsion drop size distribution and continuous oil phase composition measurements was used to determine the interfacial film composition. The interfacial tension measurements were used to identify the average area per molecule on the water/oil interface. The area per molecule was determined from the slope of the plot of interfacial tension versus the log concentration of the surface-active material.

The other necessary data are the surface area of the emulsions and the total mass of asphaltenes and resins on the interface. The surface area of model emulsions was calculated from the water volume and the Sauter mean diameter of the water droplets. The Sauter mean diameter was determined from drop size distributions observed with an invert microscope equipped with a video camera and image analysis software.

The mass of material on the interface was determined from the change in bulk phase concentration upon emulsification. The concentration of asphaltenes and resins in the continuous phase after emulsification was measured by collecting continuous phase samples, evaporating the solvent and weighing asphaltene-resin-solid residue. The combination of surface area and continuous phase concentration measurements was used to determine the interfacial composition in terms of mass per area. The results were used to construct an appropriate adsorption model of asphaltenes and resins on the emulsion interface.

#### **1.3 THESIS STRUCTURE**

This thesis is separated into six chapters. Chapter 2 serves as a general introduction to the subject of water-in-crude oil emulsions. The first section of this chapter reviews the basic emulsion principles with a main focus on factors controlling the stability of emulsions. Following that is a section describing characterization of the asphaltenes and resins, with the main focus on the mechanisms of their association and surface-active properties. Following that, a section provides a description of the research conducted in the area of crude oil emulsions.

Chapter 3 describes the experimental work used to obtain results for this study. This includes: separation of asphaltenes, resins, and solids from the bitumen, interfacial tension measurements of the asphaltenes and resins, model emulsions preparation, drop size analysis, stability tests, and gravimetric determination of adsorbed asphaltenes and resins on the emulsion interface.

Chapter 4 summarizes the results obtained from the interfacial tension measurements for mixtures of varying composition of asphaltenes, resins, toluene, heptane and water. The interfacial tension measurements were used to test a micellization in these mixtures, as well to determine the interfacial areas for the asphaltenes and resins.

The main findings of this research are presented in Chapter 5. In particular, the effect of solids content, asphaltene and resin concentration, and solvent composition on the interfacial composition and stability of model water-in-heptol emulsions is assessed.

Chapter 6 summarizes the conclusions of the study and provides recommendations for additional research required to further characterize stability mechanisms of water-in-crude oil emulsions.

#### **CHAPTER 2**

#### LITERATURE REVIEW AND BACKGROUND

#### **2.1 INTRODUCTION**

Crude oil emulsions vary widely in their physical properties and stability characteristics. Although surface phenomena determine the fundamental properties of petroleum emulsions in terms of stability and drop size distribution, the bulk composition of the crude oil also plays an important role in crude oil emulsion characteristics. Hence, in order to investigate crude oil emulsions, it is both necessary to understand the fundamental concepts involved in emulsion formation and to know the properties and composition of crude oil. The first and second sections of Chapter 2 provide a necessary background for understanding petroleum emulsions. The first section sets out the basic principles of colloidal science involved in emulsions within the context of their applicability to petroleum emulsions. The second section of this Chapter provides a detailed characterization of crude oil and its components. The third and final section is a discussion of the research done in the area of crude oil emulsions.

#### **2.2 EMULSION CHARACTERISTICS**

#### 2.2.1 Basic Principles of Emulsion Formation

Emulsions have long been a subject of study, since they are widely present in everyday life. We are all acquainted with food emulsions (i.e. milk, butter, and mayonnaise) and cosmetic emulsions (i.e. creams, lotions, and shampoos). In the petroleum industry many stages of oil recovery and treatment processes, such as oil-sands extraction, reservoir fluid flow, refining processes, and transportation through pipelines, are often accompanied by emulsion formation. Water-in-oil emulsions also form during oceanic oil spills and are known as "chocolate mousse" based on their appearance.

An emulsion is defined as a mixture of two immiscible liquids where one of the phases is dispersed in the other in a form of droplets. The dispersed phase is often referred to as the internal phase, and the continuous phase is called the external phase. For the petroleum industry, the two immiscible liquids are usually water and crude oils or refined hydrocarbons.

Depending on which phase is continuous or dispersed the following two types of emulsions may be distinguished:

- Oil-in Water (O/W) (for oil dispersed in water)
- Water-in-Oil (W/O) (for water dispersed in oil)

The more common emulsion formed in the petroleum industry is the water-in-oil type, which is often referred to as a regular emulsion. An oil-in-water emulsion is often called a reverse emulsion. More complex multiple water-in-oil-in-water (W/O/W) and oil-in-waterin-oil (O/W/O) emulsions may also form. A multiple W/O/W emulsion contains water droplets dispersed in oil droplets, which are in turn dispersed in a continuous water phase. Some examples of occurrence and type of emulsions in petroleum industry are presented in Table 2.1.

Occurrence	Usual Type
Well-head emulsions	W/O
Oil sand flotation process, froth	W/O or O/W
Oil spill mousse emulsions	W/O
Heavy pipeline emulsions	O/W
Oil sand flotation process slurry	O/W
Emulsion drilling fluid, oil-emulsion mud	O/W
Emulsion drilling fluid, oil-base mud	W/O
Asphalt emulsion	<b>O/W</b>
Enhanced oil recovery in situ emulsions	O/W

 Table 2.1. Examples of Emulsions in the Petroleum Industry (Schramm, 1992)

The natural tendency of most immiscible water/oil mixtures is to form two separate liquid phases. Therefore, to create an emulsion, the oil and water must be agitated with sufficient energy to disperse one phase in the other. The greater the energy, the smaller the drop size of the dispersed phase.

Water-oil mixtures tend to form separate phases because an oil-water interface carriers excess energy. The energy arises because oil and water molecules are brought into contact

at the interface and are no longer surrounded by like molecules. The energy is manifested as an interfacial tension which is a 2D analogue of pressure. An oil-water mixture tends to minimize the energy by minimizing its interfacial area. First, the dispersed phase droplets have spherical form and second, the droplets tend to coalesce into larger droplets eventually leading to complete phase separation. In order to maintain an emulsion a third agent is required that adsorbs on the interface and prevents coalescence. Such agents are known as emulsifiers.

In summary, three conditions are necessary for the formation of the either of the emulsion types:

- 1. The presence of two immiscible or mutually insoluble liquids
- 2. The introduction of agitation sufficient to disperse one liquid in the other
- 3. The presence of an emulsification agent

#### 2.2.2 Emulsifying Agents

Emulsifiers are compounds, which adsorb on the interface where they reduce interfacial tension and may form a viscous layer. Both layer formation and reduced interfacial tension increase emulsion stability.

Solid particles, such as silica, clay and wax, can act as emulsifiers. They adsorb on the interface and create a structural barrier. Their presence at the interface also prevents the thinning of the liquid film between droplets. Both effects prevent drops from fusing together. In the petroleum industry solids-stabilized emulsions are often encountered

during separation of oil from wastewater, separation of fines from shale oil, and during the extraction of bitumen from oil sands (Sanford, 1983; Menon et al., 1985).

The ability of solids to stabilize emulsions has been known for a long time. Pickering (1907) and Briggs (1921) found that for solids to act as emulsifying agents, solid particles must collect at the interface and they must be wetted by both the oil and water phases (i.e., both phases have a strong affinity for maximizing interfacial contact with the solid). This condition implies that the solid must have a contact angle in the region of 90° at the three phase (oil / water / solid) contact line. The strength of affinity to one of the phases determines the type of emulsion. For example, a water-in-oil emulsion forms when the particle has more affinity to oil. Here, the particles on the interface will reside mostly in the oil and will form a steric barrier on the surface of water droplets. Hence, water droplets are stabilized.

In order to collect on the interface, the particles also must be very small relative to the droplet size of the emulsified phase (the particle should be at least 100 times less then diameter of emulsion droplet (Kitchner et al., 1968)). When particles are small the radius of curvature of the meniscus between the particles is small, and the force of attraction between particles is large. That is, the smaller particles form a more coherent film on the interface, which increases emulsion stability.

The most commonly known emulsifiers are surfactants. A surfactant molecule consists of two parts each having an affinity to a different phase. Most surfactants contain polar hydrophilic groups or "heads", and hydrophobic non-polar organic "tails", containing 10 or more carbon atoms. The polar head groups of the surfactant molecule may be either ionic or nonionic in nature. The most commonly known nonionic groups are polyoxyetethylene moieties,  $-(C_2H_4O)_x$ , where x ranges from 3 to 20. Ionic groups may be either cationic (i.e. quaternary ammonium groups  $-NH_3^+$ ), anionic (i.e. sulfate  $-SO_4^-$ , sulfonate  $-SO_3^-$ , and carboxylate  $-CO_2^-$ ), or zwitterionic, where both positively and negatively charged groups are present (Hiemenz and Rajagopalan, 1997). Surfactants adsorb on an water/oil interface in such a way that the polar groups are incorporated into the water while the hydrocarbon part of the molecule is oriented away from the water.

For water-in-oil emulsions, a surfactant with a large tail (for example a polymer surfactant) can form a physical or steric barrier on the interface and stabilize the emulsion. When the surfactant covered water droplets approach each other, the outermost layer begin to overlap. The ensuing repulsion forces prevent droplets approaching close enough to coalesce.

For oil-in-water emulsions, surfactants stabilize emulsions by means of a charge stabilization mechanism. In a high dielectric medium, such as water, the surface of oil droplets becomes charged due to the presence of adsorbed surfactants with various ionic groups on their interface. The droplets attract the counter-ions from the water medium, but those of the same charge (co-ions) are repelled. The charged surface plus the neutralizing shell consisting of the excess counter-ions is known as the electrical double layer. The counterion shell may be quite diffuse depending on the influence of the electrical forces and thermal motion. Therefore, the droplets may act as charged spheres at finite separation distances. The overlap of the electrical double layers causes an electrostatic repulsive force between the droplets. If the force is strong enough it will prevent droplets from approaching each other and coalescing.

#### 2.2.3 Emulsion Stability and Destabilization

Most emulsions are not thermodynamically stable because increasing the interfacial area between two liquid phases increases the system free energy. As mentioned previously, an emulsion tends to minimize its free energy by minimizing its interfacial area through coalescence of the dispersed droplets. However, if emulsifiers are present, the emulsion may exhibit an apparent stability. An emulsion is deemed stable when the number, spatial arrangement and size distribution of droplets in the emulsion are not changing within the given time interval. If an emulsion is unstable, rearrangements of droplets occur and the emulsion may separate into two bulk liquids.

Stability of emulsions is a relative concept. Depending on the particular emulsions, the time interval at which emulsion remains stable can vary from a few seconds to years. In different processes there are different specifications for stability. In the case of cosmetic and food emulsions, it is beneficial for the producer that the emulsified system retains high stability. In the petroleum industry, emulsion stability may or may not be desired. Emulsion stability is affected by many factors, such as the properties of initial phases, drop size, temperature, amount and nature of emulsifier. A desired stability of an emulsion may be achieved by varying these factors.

If an emulsion is not treated, a certain amount of water will separate from the oil by natural processes of emulsion destabilization: creaming or sedimentation, flocculation, coalescence and Ostwald ripening. These processes affect emulsions in different ways. Creaming and flocculation do not change the drop size distribution, but change the spatial arrangements within it, while coalescence and Ostwald ripening cause a change in the size distribution of the droplets, but may not affect the spatial arrangements. Each process is described below.

Destabilization of an emulsion due to flocculation, coalescence and creaming is determined by the shape of the interaction energy potential curve presented in Figure 2.1. This particular example indicates the short-range interactions between emulsion droplets that are described by the DLVO theory of colloidal stability. In this theory, developed by Derjaguin, Landau, Verwey, and Overbeek, the total energy of interaction is the sum of the London-van der Waals attractive energy and electrical double layer repulsive energy between particles. The total energy of the interaction forces in Figure 2.1 is characterized by the existence of a maximum and a primary minimum at close separation distances, as well as a secondary minimum at large separation distances. The maximum represents the repulsive energy barrier to coalescence. The primary and the secondary minima represent the separation distances where droplets are able to flocculate.

#### Creaming / Sedimentation

Under the influence of gravity, separation occurs when there is a difference between the density of the dispersed and the continuous phases. In case of W/O emulsion, if the density



Figure 2.1 Potential energy curve between two droplets showing van der Waals and electrostatic potentials (Robins et al., 1998)

of water is greater, droplets of water sink through the medium. This process is known as sedimentation. In O/W emulsions the equivalent rise of oil drops is known as creaming. Creaming and sedimentation are reversible processes and the initial emulsion condition can be reestablished by applying gentle agitation of the mixture. Creaming/sedimentation bring droplets into closer contact and can be an important step in breaking emulsions. Creaming/sedimentation will occur in all emulsion systems except those with very diffuse double layer where electrostatic repulsion dominates.

#### **Flocculation**

Flocculation is the process where droplets form aggregates without the rupture of the stabilizing layer on the water/oil interface. The formation of aggregates leads to enhanced creaming, since droplets rise faster as the effective radius increases. Flocculation can either be a reversible process, occurring in the secondary minimum of interaction energy profile (Figure 2.1), or an irreversible process, occurring at the primary minimum. Flocculation is enhanced in polydisperse systems since the difference in moving speed of larger and smaller drops increases the probability of aggregation

#### Coalescence

Creamed or flocculated droplets may undergo coalescence – the process in which two or more droplets fuse and form a single larger droplet. Coalescence changes the drop size distribution and ultimately leads to complete phase separation. The probability of two approaching droplets coalescing is determined by the behavior of the thin film trapped between the two droplets. When the film has thinned to some critical thickness, it ruptures and the droplets coalesce. There are many factors affecting film thinning and rupture, such as the density and viscosity of the liquid phases, the droplet size, the concentration and type of the emulsifying agent, and the forces acting on the interface (Menon and Wasan, 1985). Coalescence is the most important factor in treating crude oil emulsions.

#### Ostwald Ripening

Any droplet in an emulsion may undergo Ostwald ripening. The ripening involves mass transfer between droplets of different curvature through their surrounding continuous medium. The concentration of the dispersed phase material at the surface of a drop is inversely proportional to the radius of the curvature. Hence large droplets have less surface concentration in comparison with small droplets. Mass transfer occurs along the concentration gradient from small droplets to large droplets. That is, small droplets shrink and eventually disappear while large droplets increase in size. This process leads to a change in the drop size distribution. However, it is a very slow process and can be neglected in most practical applications.

#### **2.2.4 Emulsion Treatment Methods**

Methods of emulsion breaking are designed to facilitate drop coalescence and usually creaming/sedimentation as well. This is achieved by combination of physical (gravitational, thermal and electrical) and chemical methods.

Many emulsion treatments involve heating. Heating has several effects that increase coalescence. It reduces the viscosity of the oil. This allows a water droplet to settle more
rapidly and enhances thinning between colliding droplets. Heating also increases the droplets' molecular movement and intensifies their collisions. Heating can also enhance the action of demulsifiers, causing them to work more efficiently. However, the drawback of the method is the high cost of heating up liquid phases. It can also cause a significant loss of lower-boiling point hydrocarbons. The remaining oil has lower API gravity, which in turn leads to lower value of the oil.

Electrostatic methods of emulsion treatment are only used for water-in-oil emulsions. An applied electrical field causes the water droplets to become polarized and align themselves with the lines of electric force. This alignment places the positive and negative poles of the droplets in close proximity to each other. The induced dipole creates an attractive force drawing the droplets together. The electric field also distorts and thus weakens the interfacial film probably by reorienting the polar surfactant molecules. The induced attractive force and weakened film enhance coalescence.

The action of chemical demulsifiers is based on counteracting or displacing emulsion stabilizers. For demulsifiers to work they must reach the oil/water interface, migrate to the protective film surrounded the emulsified droplets, and displace or minimize the effect of the emulsifying agent at the interface. This leads to the coalescence. Chemical emulsion breakers are usually specific for each particular site or type of crude oil. Since the number of indigenous emulsifiers in crude oils is large, the number of demulsifier combinations is also numerous. Most demulsifiers used in breaking crude oil emulsions are blends of the following types of compounds: polyglycols and polyglycol esters, low-molecular and highmolecular resin derivatives, sulfonates, polymerized oils and esters, alkanolamine condensates, oxylkylated phenols, and polyamine derivatives (Grace, 1992). These variations in chemical properties provide a wide range of demulsifier actions. However, the mixing of various demulsifiers should be done with care to ensure compatibility of its ingredients with each other. An incompatible combination may cause the opposite effect and increase emulsion stability.

In general, emulsion breaking processes combine the methods described above in three main stages. First, an emulsion is destabilized by applying heat or various chemicals to weaken the interfacial film surrounded the water droplets. Second, an application of moderate agitation or an electrical field intensifies the contact rate of the dispersed droplets. This increases coalescence and leads to the formation of larger droplets. Third, the coalesced droplets are separated from the continuous phase by providing sufficient settling time and arranging a flow pattern that induces settling.

The treatment of "chocolate mousse" water-in-oil emulsions formed during oil spills requires the initial mechanical skimming of the mousse using specially designed skimmers. The skimmed emulsions are than treated in a similar way as other crude oil emulsions, particularly by applying chemicals and/or heating.

In petroleum production, different environments, varieties of crude-oil types and emulsions, make each emulsion breaking process unique. However, chemical demulsification is the most widely applied method of treating crude-oil emulsions. This treatment method is attractive for oil producers for many reasons. Chemical application is easy and reasonably inexpensive. Demulsifiers can even be added prior to emulsification in order to inhibit emulsion formation. Chemical additives minimize the use of heat and reduce settling time. They provide a flexible method of emulsion resolution, since the additives can be easily adjusted to changes in emulsion or crude oil characteristics. The cost-effectiveness of chemical methods for emulsion breaking depends on proper chemical selection and application. Nonetheless, most chemical treatments are designed based on experience because no methods are available to predict emulsifier performance a priori. The optimization of chemical treatment requires a proper understanding of not only of demulsifiers but also of the properties of the naturally occurring emulsifiers that stabilize the emulsions in the first place.

# **2.3 CRUDE OIL COMPOSITION**

# **2.3.1 Classification of Petroleum Fractions**

It is well known that crude oil is one of the most complex mixtures of organic compounds. Its composition can vary significantly based on its reservoir's place of origin, age and depth (Speight, 1991). Crude oils mainly consist of carbon and hydrogen although there are some heteroatoms present, such as oxygen, sulfur and nitrogen, as well as structures with incorporated metallic molecules such as vanadium, nickel and iron. There is a wide variation in physical properties from the lighter oils to the bitumens. For this reason several classification systems of petroleum were proposed based on different criteria: density (specific gravity or API gravity), viscosity, boiling cut, H/C ratio, heteroatom content, and solubility class. The classification of interest here is the solubility class. The most commonly used solubility classes are saturates, aromatics, resins and asphaltenes. The method of dividing crude oil into these four classes is called SARA fractionation, based on the first letters in the name of the classes. SARA fractionation is illustrated in Figure 2.2.

In the first step, the crude oil is deasphalted by mixing 40:1 volume ratio of pentane to bitumen. The precipitated fraction of the bitumen is the asphaltenes. At the next step, the deasphalted oil is separated into saturates, aromatics and resins using clay-gel adsorption chromatography. In this method, resins adsorb on Attapulgus clay, aromatics adsorb on silica gel, and saturates elute directly. The aromatics and resins are then removed using a mixture of solvents of equal volume ratio, i.e. toluene/pentane and toluene/acetone respectively. The SARA analysis of typical Alberta oil sand bitumens is shown in Table 2.2. A more detailed description of the SARA fractionation method is given in the Chapter 3.

	Athabasca	Cold Lake
Asphaltenes (wt %)	17.28	15.25
Resins (wt %)	25.75	24.81
Aromatics (wt %)	39.7	39.2
Saturates (wt %)	17.27	20.74

Table 2.2 SARA Fractionation of Alberta Oil Sands Bitumens (Peramanu et al., 1998)



Figure 2.2 Schematic of SARA fractionation of crude oils

As SARA fractions are solubility classes and are separated by their physical behavior rather than their chemical nature, each of the fractions consists of thousands of molecular species with various properties and chemical structures. Nonetheless, each class contains characteristic types of molecular species.

The composition and structure of the saturate and aromatic fractions of crude oils are well defined in comparison with asphaltenes and resins, due to their relative simplicity. The saturates consist mostly of alkyl cycloalkanes ranging from one to five rings (Strausz, 1989). In Alberta and Cold Lake bitumen the di- and tricyclic compounds are predominant. The aromatic fraction consists of homologues of mono, di- and tri-nuclear aromatic series. The sulfur compounds are represented by benzo-, dibenzo-, naphtobenzothiophenes and alycyclic sulfides. Nitrogen compounds are present in the form of carbazoles, benzolquinolines and their higher aromatic derivatives. Since the research is concerned with asphaltenes and resins, their chemistry is reviewed in more detail.

# 2.3.2 Asphaltenes

Asphaltenes are dark brown to black amorphous powders, have a specific gravity just above unity, and molar masses of 1000 to 10,000 g/mol (Speight, 1994). They are the most aromatic and highest molar mass fraction of oil. It is believed that asphaltenes strongly influence some physical properties of petroleum, especially specific gravity and viscosity.

## 2.3.2.1 Asphaltene Elemental Composition

The elemental composition of asphaltene molecules is quite well determined. Summarized data on asphaltenes from crudes of different origin shows that the variation in the elemental composition from one oil to another is not significant (Table 2.3). For example, as was reported by Moschopedis and Speight (1976), the H/C ratios of asphaltenes are usually in the range of  $1.15 \pm 0.05$  %. The constancy of this ratio has led to a general belief that asphaltenes do have a characteristic chemical composition and structure, which may permit a more meaningful description than that of just a solubility class. The nitrogen content is also somewhat similar (0.6 %-3.3 %). The most variations are seen in oxygen content (0.3%-4.9%) and sulfur content (0.3%-10.3%). This may be due to reactions between petroleum and oxygen or sulfur (and sulfur-containing materials) present in crude oil (Speight, 1994). Asphaltenes also contain metals, including nickel, vanadium and iron.

#### 2.3.2.2 Asphaltene Molecular Structure

Although the elemental composition of asphaltenes is quite well determined none of the molecules from the asphaltene fraction have been positively identified. There is still no single view regarding the structural characteristics of these compounds. However, certain generalities have been noted from available analytical data.

The information obtained by use of infrared and nuclear magnetic resonance spectroscopic techniques (Speight et al., 1972; Yen, 1979; Strausz, 1989) indicated that asphaltenes contain condensed aromatic rings with short aliphatic saturated side chains and polar heteroatoms, such as oxygen, nitrogen, and sulfur distributed in various locations. The

condensed aromatic ring systems may contain about 6 rings, or can be much larger and comprise up to 20 rings.

# Table 2.3 Elemental Composition of Various n-Pentane and n-Heptane Precipitated Asphaltenes (Speight, 1991)

	Canada		I	ran	Kuwait		
	n-pent	n-hept	n-pent	n-hept	n-pent	n-hept	
Carbon (wt %)	79.5	78.4	83.8	84.2	82.4	82.0	
Hydrogen (wt %)	8.0	7.6	7.5	7.0	7.9	7.3	
Nitrogen (wt %)	1.2	1.4	1.4	1.6	0.9	1.0	
Oxygen (wt %)	3.8	4.6	2.3	1.4	1.4	1.9	
Sulfur (wt %)	7.5	8.0	5.0	5.8	7.4	7.8	
H/C Ratio	1.21	1.16	1.07	1.00	1.14	1.07	
N/C Ratio	0.013	0.015	0.014	0.016	0.009	0.010	
O/C Ratio	0.036	0.044	0.021	0.012	0.014	0.017	
S/C Ratio	0.035	0.038	0.022	0.026	0.034	0.036	

Investigation of functional groups and the location of heteroatoms in asphaltenes was mainly done by mass and nuclear-magnetic resonance spectrometry. Oxygen has been identified in various functional groups, such as hydroxyl in phenols, alcohols and carboxylic acids, carbonyl in esters, ketones, and in form of ethers in heterocycles (Bestougeff and Byramjee, 1994; Moschopedis and Speight, 1976). Data on Athabasca asphaltenes indicated that about 75 % of the oxygen is concentrated in the hydroxyl functional group (Bestougeff and Byramjee, 1994).

Moschpedis and Speight (1976) suggested that nitrogen occurs in carbozoles and amides. A small amount of nitrogen is present in porphyrin complexes. Sulfur is present as part of heterocycles, such as benzothiophenes, and naphthene benzothiophenes. Sulfur may also occur in other forms such as alkyl-alkyl sulfides, alkyl-aryl sulfides and aryl-aryl sulfides (Yen, 1974). It has been shown that majority of metal atoms (especially nickel and vanadium) are included in petroporphyrins (Yen, 1974; Strausz, 1989). However, it is still unknown if the porphyrins are an integral part of the asphaltene structure (Speight, 1991).

Based on the determined polyaromatic structures and functional groups which exist in asphaltene molecules, some researches have attempted to create an "average molecular structure" and assign specific molecular configurations to asphaltene constituents (Strausz et al., 1989, 1992; Murgich et al., 1999). An example of the hypothetical representations of an asphaltene molecule is shown in Figure 2.3. However, the complexity of this petroleum fraction makes the determination of a suitable molecular model a very difficult task. There is no guarantee that the model is a true representation of an asphaltene molecule. Hence molecular models have limited significance for understanding the chemical nature of asphaltenes. They can also be misleading, especially when there is uncertainty in molar mass data (Storm et al., 1994; Speight, 1994).



Figure 2.3 Hypothetical representation of an average asphaltene molecule (Strausz et al., 1992)

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#### 2.3.2.3 Asphaltene Molar Mass

Speight and co-workers (1985) published an overview of the numerous techniques used for asphaltene molar mass determination. They reported that different analytical techniques display a discrepancy in measured molar mass of over two orders of magnitude (from 600 to 300,000 g/mol) as shown in Table 2.4. There are several reasons for this huge variation. Since the asphaltene system is polydispersed, different analytical techniques give a different average molar mass, (e.g. mass average versus number average molar mass). Another source of discrepancy is the variation in the conditions of the experiments.

Molar mass measurements from solution techniques like vapour pressure osmometry (VPO) indicate that the asphaltene molar mass depends on solvent, temperature and asphaltene concentration (Moschopedis and Speight, 1976). These observations indicate that asphaltenes have some form of the association in many solvents, especially at high asphaltene concentrations and low temperatures.

The difference in molar masses obtained by using different techniques, solvents and temperature indicates that the careful choice of experimental conditions and methods are extremely important in obtaining meaningful results. Vapour pressure osmometry (VPO) and gel-permeation chromatography (GPC) are the two most commonly used methods nowadays. However some research indicates that polynuclear aromatic structures of asphaltenes cause them to adsorb on polysterene gel, which makes GPC invalid (Wiehe et al., 1996). Furthermore, GPC needs calibration since molar mass is usually obtained in polystyrene molar mass equivalents. Most researchers accept VPO to be the most accurate

method when a good solvent, such nitrobenzene or dichlorobenzene is used (Moschopedis and Speight, 1976; Wiehe et al., 1996).

Table 2.4	Average	Molar	Mass	Of	Asphaltenes	from	Several	Crudes	Determined	by
Different l	Experime	ntal Me	ethods	(M	loschopedis a	n <mark>nd</mark> Sp	peight, 1	976)		-

Method	Molar Mass (g/mol)
Ultracentrifugation	20,000 - 30, 000
Osmotic pressure	20,000 - 80, 000
Ultrafiltration	80,000 - 140, 000
Boiling point elevation	2,500 - 4, 000
Freezing point depression	600 - 6000
Vapour pressure osmometry	1,000 - 8, 000
Viscosity	900 – 2, 000
X-ray Diffraction	40, 000

It has been concluded that the measured molar mass from 10,000 to 100,000 g/mol or more is the measured molar mass of asphaltene aggregates rather than molecules. Strausz (1989) reported the average molar mass, measured by VPO for Athabasca asphaltenes is  $\sim$ 3600 g/mol. It is considered now that the molar masses of asphaltene molecules ranges from 1000 to 10,000 g/mol (Speight, 1994).

# 2.3.3 Resins

The content of resins in crude oils ranges from 2-40 wt %. Koots and Speight (1975) observed that the resin content of a crude oil is higher but proportional to the asphaltene

concentration. Crude oils with a small amount or no asphaltenes have a lower concentration of resins than those with larger amount of asphaltenes.

Resins are dark brown or black, semi-solid, very adhesive materials, have a specific gravity near unity, and molar mass ranging from 500 to 2000 g/mol. The molecular species within the resins are similar to those in the aromatics. However resins species have higher molar mass, greater polarity, lower H/C ratio, and higher heteroatom content than the aromatics. In fact, aromatics, resins and asphaltenes can be considered as a continuum of molecular species where molar mass, polarity and heteroatom content increase from aromatics to resins to asphaltenes.

# 2.3.3.1 Resin Elemental Composition

The resin fraction consists of carbon  $(85 \oplus 3 \text{ wt \%})$ , hydrogen  $(10.5 \pm 1 \text{ wt \%})$ , oxygen  $(1.0 \oplus 0.2 \text{ wt \%})$ , and nitrogen  $(0.5 \oplus 0.15 \text{ wt \%})$ . The content of these elements in resins of various crudes varies over a narrow range. The widest range is observed in sulfur content (0.4 to 5.1 wt %) (Speight, 1991). In general, the heteroatom content of resins is less than that of asphaltenes (Koots and Speight, 1976). The elemental composition of petroleum resins from various crude oil is shown in Table 2.5.

Resins have a much higher H/C ratio than asphaltenes, which indicates that they are less aromatic than asphaltenes. Asphaltenes are presumed to be a maturation products of resins; in the maturation process the cyclic portion of resin molecules undergoes aromatization (Speight, 1991).

	Canada	Iraq	Italy	Kuwait	USA
Carbon (wt %)	86.1	80.4	79.8	83.1	85.1
Hydrogen (wt %)	11.9	10.7	9.7	10.2	9.0
Oxygen (wt %)	1.1	2.4	7.2	0.6	0.7
Nitrogen (wt %)	0.5	0.7	trace	0.5	0.2
Sulfur (wt %)	0.4	5.8	3.3	5.6	5.0
H/C Ratio	1.66	1.59	1.46	1.47	1.27
O/C Ratio	0.009	0.022	0.067	0.005	0.006
N/C Ratio	0.005	0.007	-	0.005	0.002
S/C Ratio	0.002	0.027	0.030	0.025	0.022

 Table 2.5 Elemental Composition of Petroleum Resins (Speight, 1991)

# 2.3.3.2 Resin Molecular Structure and Molar Mass

Structural studies of resin molecules have not been as intensive as they have been for asphaltenes. Originally resins were presented either as long paraffinic chain molecules with naphthenic rings in the center, or as condensed aromatic and naphthenic ring systems with heteroatoms scattered in different locations (Speight, 1991) (Figure 2.4). Now it is generally believed that resin molecules are composed of a highly polar end group, which may incorporate oxygen, sulfur or nitrogen, and a long non-polar paraffinic group (Hammami et al., 1998). Nitrogen is present in resins in the form of pyrrole and indole groups. Infrared spectroscopic data also indicated the presence of ester, ketone and acid functional groups. Sulfur is present in form of cyclic sulfides.



**Figure 2.4** Hypothetical representation of an average resin molecule (Speight, 1991)

Magnetic resonance data indicated that resins molecules are much smaller than asphaltenes (Speight, 1991). Furthermore the determined molar mass of the resins fraction is lower than that of the asphaltenes. The comparison of literature data demonstrates that resin molar mass does not appear to vary with method or experimental conditions. It is likely that the molar masses of resins determined by different methods can be considered as a true molar masses (Speight, 1991). The molar masses of resins derived from different crude oils are present in Table 2.6.

 Table 2.6 Average Molar Mass of Resins from Several Crudes (Speight, 1991;

 Peramanu et al., 1998)

Source	Molar Mass (g/mol)
Canada – Athabasca (Peramanu et al., 1998)	947
Canada – Cold Lake (Peramamu et al., 1998)	825
Iraq <i>(Speight, 1991)</i>	791
Italy (Speight, 1991)	812
United States (Speight, 1991)	845
Kuwait (Speight, 1991)	860

# 2.3.4 Asphaltenes and Resins as Surface-Active Materials

As was indicated above both asphaltene and resins molecules have various oxygen, sulfur, and nitrogen functional groups as well as aromatic structures with long aliphatic side chains. These functional groups are hydrophilic and the hydrocarbon structure is hydrophobic. This resembles the molecular structure of surfactants, described earlier. This similarity in structure leads to the assumption that asphaltenes and resins are surface-active.

To date, there are only few published studies on the interfacial properties of resins with respect to the water/oil interface. However, Murzakov et al. (1980), and Layrisse et al. (1984) proposed that due to the presence of heteroatom functional groups, especially acid groups, resins are surface-active compounds.

Asphaltene surface activity has been investigated more intensively. An important step in this research was the separation of asphaltenes according to their chemical functions, i.e. on acidic, basic, amphoteric and neutral compounds. Asphaltenes were separated into these subfractions by cation and anion resin chromatography (Kisilew, 1979), and silica gel chromatography (Ramlajak et al., 1979). The presence of non-neutral molecules is indicates that asphaltenes are likely to be surface active.

Asphaltene surface activity is clearly demonstrated by reduction in interfacial tension with an increase in asphaltene content (Rogacheva et al., 1980; Khulbe et al., 1988; Sheu et al., 1995; Marques et al., 1997; Yarranton, 1997). Acevedo et al. (1992, 1995) and Sheu and Shields (1995) observed that the reduction in interfacial tension of asphaltenes dissolved in toluene over water is highest at high and low pH. This indicates that both acidic and basic groups participate in the interaction on the interface. Surface activity of asphaltenes was also confirmed by adsorption of asphaltenes on hydrophilic surfaces (Gonzalez et al., 1994). Interestingly, that the curve of IFT of asphaltenes dissolved in toluene versus pH parallels to that of crude oils (Acevedo et al., 1992). This leads to conclusion that asphaltenes are the key surface-active materials in crude oils.

#### 2.3.5 Asphaltene and Resin Association

The behavior of asphaltene and resins in crude oil and various solutions is the most intriguing issue in asphaltene research at present. Many researchers believe that asphaltenes are able to self-associate, based largely on molar mass measurements, as was mentioned previously. However, there is no common opinion on the nature of the association. The proposed models fall into two major categories: colloidal models and thermodynamic molecular models. The first group considers asphaltene associates to be colloid particles dispersed in the oil medium by resins, which surround the asphaltene molecules. The second approach treats asphaltenes as solvated, macromolecular solutes and regards the resins parts as an independent component of the solvent medium.

#### 2.3.5.1 Colloidal Models

The first model of asphaltene aggregation was proposed more than half a century ago by Dutch scientists Nellensteyen (1938), and Pfeiffer and Saul (1939). According to their theory asphaltenes are solvated in the oil by non-asphaltenic molecules (usually resins) and form "micelles", or more properly colloids (Figure 2.5). Resins, acting as peptizing agents, maintain the asphaltenes in a crude oil in a colloidal dispersion as opposed to a solution.



Figure 2.5 Pfeiffer-Saal model of an asphaltene-resin complex

Dickie and Yen (1967) postulated that asphaltenes are present in the center of micelles as clusters rather than as single molecules. Their model is based on X-ray diffraction data of solid asphaltenes. They suggested that asphaltene colloids are the aggregation of stacks of polycyclic aromatic compounds. The elementary unit of the stack is disk-like particle with a flat central part composed from fused aromatic rings, and periphery made up of naphtenic rings and aliphatic chains. On average, five particles are held together by  $\pi$ - $\pi$  bonds. Lin et al. (1991) later proposed that polycyclic aromatic cores are connected by sulfide, ether, aliphatic and naphtenic linkages. Yen (1974) reported that interplanar and aliphatic spacing were equal to 0.35 and 0.5 nm respectively (Figure 2.6). Later X-ray diffraction experiments by Siffert (1984) indicated the similar lattice spacing between asphaltene molecules.

The size and shape of asphaltic clusters were also studied by small angle X-ray scattering (Storm et al., 1991; Herzog et al.; 1988; Kim and Long, 1977; Sirota, 1998) and small angle neutron scattering techniques (Sheu et al., 1995; Overfield et al., 1989; Ravey et al., 1988). The proposed structure of asphaltene colloids based on these studies is contradictory. Herzog et al. (1988) presented evidence that asphaltenes in benzene exist as discs-like macromolecules of about 0.34 nm in thickness and radii in the range of 1.3-80 nm. Similar results were obtained by Acevedo and co-workers (1995) using gel-permeation chromatography. Ravey et al. (1988) observed a discotic shape for asphaltene aggregates with radii in the interval 0.6-80 nm and thickness of about 0.6-0.8 nm. Reerink (1973) using viscosity and electron microscopy measurements proposed a flat ellipsoidal shape of asphaltene aggregates, while Overfield et al. (1989) proposed rod-like particles.

Sheu et al. (1991), and Storm et al. (1991) observed spherical or disk-like asphaltene aggregates in solution with radii of 5 nm.

The role of resins in asphaltene aggregation is controversial. In the colloidal model, the presence of resins is necessary for the dispersion of asphaltenes. Moreover, some researchers indicate that resins of one crude oil do not contribute to the solubility of the asphaltenes from another crude oil. This may occur because the resins have selectivity for some adsorption sites on the asphaltene molecules (Koots and Speight 1976; Murgich et al. 1999). However, Sheu et al. (1992), observed that asphaltenes alone were able to form stable aggregates in organic solution without presence of resins. Hence, the presence of resins is not necessary for asphaltenes to form dispersed aggregates.

The mechanism of asphaltene-asphaltene and asphaltene-resins molecular aggregation is still poorly understood. Few interaction mechanisms have been proposed. It has been suggested that asphaltene stacking is caused by  $\pi$ - $\pi$  interactions between delocalized electrons in fused aromatic ring core (Dickie and Yen 1967). Hydrogen bonding is another mechanism of asphaltene self-association that has also been proposed as an important mode in asphaltenes-resins interactions (Strausz 1989). In this mechanism, the association occurs due to donor-acceptor interaction with phenolic or alcoholic OH and carbozole or porphyrins NH groups acting as hydrogen donors, and basic nitrogen and aromatic rings acting as hydrogen acceptors. Another mechanism could be metal-electron interactions between heavy metal ions such as vanadium and nickel and electron pairs in pyrrolic or porphyrin functional groups.



Figure 2.6 Dickie-Yen model of an asphaltene colloid

As opposed to the model of Yen, Speight proposed that asphaltenes exist in petroleum micelles not as stacks of molecules, but rather as single asphaltene molecules surrounded by resins. Interfacial tension measurements indicate a change in the slope of the interfacial tension on a plot of interfacial tension vs. asphaltene concentration (Speight 1991; Sheu et al. 1992). This can be evidence of the association of asphaltenes into true surfactants-like micelles. Andersen and Birdi (1991) suggested that asphaltenes form reversed micelles, with polar moieties associated in the center of micelle, surrounded by the nonpolar parts of the same molecule. They determined the endothermic heat of demicellization of asphaltene micelles.

# 2.3.5.2 Thermodynamic Molecular Model

Hirschberg et al. (1984) proposed an alternative model in which asphaltenes are seen as a single lumped fraction of the oil. In this model the asphaltene monomer corresponds to the asphaltene sheet defined by Yen. Asphaltene phase separation is modeled in the same way as other hydrocarbon phase separations usually using equation of state or regular solution theory. Hirschberg et al. (1984) later expanded his theory proposing that the "pure" asphaltenes aggregate by a linear "polymerization" process. In the crude oil the polymerization is reduced by the asphaltene-resin association.

To date, there is insufficient evidence to prove or discount any of the proposed models. It is still not clear in which form asphaltenes and resins are present in solution. Some models incorporate ideas of both thermodynamic and colloidal models. Kawanka et al. (1988) suggested that it may be possible that asphaltenes are present in crude oil partly as dissolved molecules and partly as asphaltene clusters, suspended by resin molecules adsorbed onto the asphaltene surface. This hypothesis is supported by the observed wide range of asphaltene sizes.

## **2.4 CRUDE OIL EMULSION STUDIES**

# 2.4.1 Historical Overview

Oil producers first became interested in crude oil emulsions around ninety years ago (Cottrell 1911). At the time, oil exploration progressed from eastern Pennsylvania fields to the western regions of the United States, which produced heavier crude oil, and emulsion formation became a serious problem. At first, the emulsified mixture of crude oil and water, or as it was called the "cut oil", was considered "a necessary evil" (Dow 1926). There was no method known for emulsion treatment, and the cut oil was drained into the nearby streams. This practice caused severe water pollution and was soon prohibited by government authorities. Consequently, it was decided to burn the cut oil. This method was extremely wasteful since the amount of emulsified oil was quite large (occasionally as high as 90 per cent) especially in heavy oil fields. Therefore, oil producers started to seek methods for preventing emulsion formation or more efficiently treating the emulsions.

It was observed that in sump tanks water and oil naturally separated with free oil floating on the surface. Some attempts were made to skim the oil from specially constructed sumps; a process called "sunning the oil". Later it was discovered that heating the cut oil in the sumps increased the separation of an emulsion. Oil producers also started to use the electric dehydration process invented by Cottrell (1911), and in some cases centrifuging. Later, attempts were made to use chemicals in emulsion resolution. Barnickel (1921) developed a method, named Tret-O-Lite, which involved the use of a special mixture of chemicals for the dehydration of cut oil. This method was a vast improvement in efficiency over other methods of treatment.

With the implementation of different methods of emulsion treatment, it was observed that the emulsions formed from oils of different origin had different properties. A treatment method that was successful for one emulsion was often useless for others. It was found that emulsion properties and methods of treatment correlated to the paraffin and naphthene content, the A.P.I. gravity, the viscosity, and the asphaltic content or carbon residue of the oil (Dow 1926).

However, a literature review of crude oil emulsion studies reveals a lot of contradictory observations on seemingly similar systems. These discrepancies in many cases result from the variation of crude oil origin, properties and composition. As a result, there is still a little fundamental understanding of crude oil emulsions which would provide oil producers with any meaningful information for the optimization of emulsion treatment methods. Therefore companies and institutions concerned with crude oil emulsions have carried out independent studies of particular emulsion treatment problems. Nonetheless, some generally applicable information has been obtained from research on crude oil emulsions, much of it focusing on the role of the interfacial film and asphaltenes in emulsion stability.

### 2.4.2 Investigation of the Interfacial Film Formation

Recent studies of crude oil emulsions from the Norwegian Continental Shelf examined the difference in stability of emulsions from various crude oils (Johansen et al. 1989). Their work indicated that emulsion stability only correlated directly with oil viscosity. It was observed that emulsion stability increases with increasing viscosity of crude oil. Comparison with other physicochemical properties showed only a weak correlation with emulsion stability. However, a number of other studies indicate that the correlation to viscosity is likely an indirect measure of a more relevant property such as the strength of the interfacial film.

Interfacial rheology (Strasner 1968; Graham 1983) and electron micrography (Eley et al. 1976) measurements revealed the presence of a rigid interfacial film on the oil-water interface. It was proposed that this film is a major factor in the stabilization of water-in-oil emulsions. The formation of the film was attributed to presence of natural emulsion stabilizers found in crude oil, such as metal porphyrins (Canevari et al. 1997; Twardus 1980), waxes (Mackay 1987; Birdie et al. 1980; Graham 1988; Bobra et al. 1992), organic acids (Siefert et al. 1969; Acevedo et al. 1999), finely divided sand, clay particles (Menon et al. 1988; Yan et al. 1999) and paraffinic solids (Puskas et al. 1996). However, among them, asphaltenes, resins, and fine solids have been proposed to play the most important role in rigid film formation and emulsion stability. This assumption has been supported by numerous studies, as discussed below.

# 2.4.2.1 Effect of Solids on the Interfacial Film Formation

Heavy crude oils are often produced with solids, such as ashes, silts, clays and other mineral particles. Solids are also a problem in the bitumen extraction from the oil sands. In this process the concentration of solids might be as high as 85%. The ability of solids to stabilize emulsions has been known for a long time (Pickering 1907). However, little work was done on the role of solids in crude emulsion stabilization.

A brief review of some research done on this topic can be found in Levine et al. (1985), Menon et al. (1988) and Yan et al. (1999). As was described in the previous section, for solids to stabilize emulsions, they have to be wetted by both the oil and water phases. The wettability is determined by the surface energies at oil-water, water-solid and oil-solid interfaces. These surface energies in turn depend on the presence of surface-active species at the interface. Since asphaltenes are surface active, their presence in crude oil might affect the adsorption of solids on the interface. It was found that in crude oil systems the wettability is a strong function of the concentration of adsorbed asphaltenes on the particles (Sanford 1983; Menon et al. 1988). Yan and Masliyah (1994) indicated that fine particles with various contact angles can be obtained by adsorbing different amount of asphaltenes onto the particle surface. The adsorption of asphaltenes renders initially hydrophilic particles hydrophobic to the point where they stabilize water-in-oil emulsions.

The size of solids is also a very important factor in solid-stabilized emulsions. As was indicated previously, solids have to be very small compared with the droplet size. The role of solid size in crude oil emulsion stabilization was recently investigated by Yan et al.

(1999). In their study of water-in-diluted Athabasca bitumen emulsions, they found that finely divided solids present in the bitumen greatly increased emulsion stability. Particles larger than 8  $\mu$ m did not affect emulsion stability. The major role in emulsion stabilization was attributed to fine particles less than in 0.5  $\mu$ m diameter.

In general, the literature review indicates that there is a little evidence that solids can stabilize water-in-oil emulsions independently. However, due to interaction with polar surface-active materials present in crude oil, particularly asphaltenes, solids can adsorb on the interface and increase emulsion stability.

# 2.4.2.2 Effect of Asphaltenes and Resins on the Interfacial Film Formation

As was described earlier, it was proposed that both asphaltenes and resins are surface active, can adsorb on the water/oil interface, and may stabilize emulsions. The adsorption of asphaltenes on the emulsion interface is also supported by other studies. Measurements of interfacial viscoelastic properties led Eley et al. (1987) to conclude that the very high surface viscosities and elasticities found in crude oil emulsions is a consequence of a threedimensional network of asphaltenes adsorbed at the interface. The creep curves were found to exhibit dilatancy, with the shape of the curve depending on the concentration of asphaltenes at the interface. Mohammed et al. (1993) observed that the viscosity of the oilwater interface increases with time. They proposed that the increase in viscosity is due to adsorption of higher molar mass species, such as asphaltenes over a period of hours. During this time asphaltenes rearrange themselves and form more packed structures. This increases the rigidity of interfacial film. However, the form in which asphaltenes and resins adsorb on the water/oil interface is also a challenging issue. As was previously discussed, asphaltenes and resins may exist in crude oil in three different forms, independent molecules, asphaltene-resins colloids, or true surfactant-like micelles. The form in which asphaltenes and resins adsorb on the emulsion interface depends on the form at which they exist in solution. However, the form in which asphaltenes and resins exist in a crude oil is still unknown. Hence the determination of the interfacial composition of crude oil emulsion is complicated.

Many researchers believe that colloidally dispersed asphaltenes will form a more stable emulsion than a molecular solution of asphaltenes (Sjoblom et al. 1990; McLean and Kilpatrick 1997). Further Eley et al. (1988) determined that asphaltenes stabilize water-inoil emulsions if they are near or above the point of incipient flocculation. It has been suggested that they collect in the interface in the form of fine solid particles or asphalteneresin colloids (McLean and Kilpatrick 1997; Acevedo et al. 1992; Oetter et al. 1994). The adsorption of these aggregates on the interface leads to the formation of a threedimensional cross-linked network and strong interfacial films. Siffert et al. (1984) believed that asphaltene particles are regularly stacked in lamellar structures, resembling surfactant liquid crystals. However, Yarranton (1997) showed that asphaltenes at low concentrations (< 2% w/w) can stabilize emulsions as independent molecules.

In the recent work done by Ese et al. (1998) the influence of Northern Sea, European and Venezuelan crude oils asphaltenes and resins on the properties of interfacial film was studied by means of Langmuir-Blodgett technique. Their findings support the idea that asphaltenes form rigid films on the interface, which led to emulsion stability. The observed decrease in film compressibility with increased surface pressure was proposed to be due to interactions between the rigid aromatic parts of the asphaltenes. The determined interfacial molecular area for asphaltenes was equal to 80-100  $A^2$ . The presented results are more consistent with molecular rather that colloidal asphaltenes.

The interfacial film between water and bitumen was recently investigated using the thin liquid film pressure balance technique (Khristov et al. 1999). Their studies of water/diluted bitumen/water emulsion films demonstrated that at lower dilution of bitumen with toluene (3:1 toluene: bitumen), the film had a multilayer structure, but in more dilute solutions (> 20:1 toluene: bitumen) the film had a bilayer structure with a film thickness of 15 nm (7.5 nm per layer). These dimensions are more consistent with molecular asphaltenes.

# 2.4.3 Effect of Crude Oil Composition and Properties on Emulsion Stability

In parallel to the aforementioned studies some scientists have used emulsion stability experiments to understand crude oil emulsions and interfacial film formation as a function of crude oil composition and conditions. In these studies, emulsions were either prepared from the whole crude oil, or made from extracted fractions of crude oil. The composition and method of preparation of these emulsions varied significantly. Some emulsions were made with distilled water, while others were composed of brine containing various inorganic salts. The organic phase contained different solvents, such as heptane, hexane, toluene, decane, dodecane and their mixtures as well as various crude oil fractions. Different separation procedures were used to obtain surface-active fractions. A review of these studies also showed that the presence of solids in crude oil was not taken into consideration. As was described earlier solids commonly present in crude oil can affect emulsion stability. Their effect can overshadow the effect of other crude oil fractions on emulsion stability.

As a result of the above-mentioned discrepancies, these studies can be considered only as a guide, providing qualitative information. In general the research has focused on the role of pH, solvents, and asphaltene/resins ratio in emulsion stability.

## 2.4.3.1 Effect of PH

The pH of the water in an emulsion can be expected to affect both the quantity and type of material on the water/oil interface. As was described earlier, interfacial tension of crude oil changes with pH in the same way as interfacial tension of asphaltenes in solvents does. This is attributed to the amphoteric nature of asphaltene molecules. The changing of the pH values causes the ionization of acidic and basic groups in asphaltene molecule, which changes the strength of the interfacial film. Further investigations indicated that adjustment of pH indeed changed emulsion stability.

Strassner (1968) determined that for each crude oil-brine system there exists an optimum pH, at which maximum emulsion breaking occurs. The optimum pH depends on crude oil and brine composition. Neustadter and co-workers (1979) investigated the viscoelastic properties of emulsions composed from Iranian heavy, Kuwait and Forties crudes. They

found that at neutral pH the interfacial film exhibited the highest viscoelasticity, and the emulsion was the most stable. In the work done by Johansen et al. (1988) emulsions exhibited stability at very high and very low pH values, and intermediate pH value caused instability. However, McLean and Kilpatric (1997) showed that at pH 10 and 12 emulsions were relatively unstable. At low pH values their emulsions were highly stable. This can be explained by the potential absence of strong basic groups in the crude oil asphaltenes used for their studies. Overall the observed findings suggest that the effect of pH strongly depends on the origin of crude oil, and there is no straight-forward data which would tell at what pH a given emulsion is the most or least stable.

# 2.4.3.2 Effect of Solvents

Some researchers have been trying to relate the influence of various organic solvents on emulsion stability (Bobra et al. 1992; Mclean and Kilpatrick 1997; Ese et al. 1998; Eley et al. 1988). Work done by Bobra et al. (1992) indicates that the increasing of alkane content in the oil phase of emulsions increases their stability. However, emulsions made only from 100% alkane solvent in their oil phase exhibited no stability. Bobra et al. (1992) observed that stability of the emulsions depends on the solubility parameter of aromatic solvents. When the solubility parameter of the solvent decreases (e.g. the oil is more aromatic), the oil forms more stable emulsions. Results from their studies also indicated that model oils have a stronger tendency to form stable emulsions as the molar mass of the alkane solvent increases. Kilpatrick et al. (1997) studied the influence of solvents of various aromaticity and structure including benzene, toluene, xylene, ethylbenzene, tetr-butyl benzene, and cymene on emulsion stability. His results indicate that the more aromatic solvents (i.e. with the highest content of the aromatic carbon) are more effective in destabilizing emulsions. Singh et al. (1999) studied the effect of fused ring aromatic solvents (i.e. methyl-naphthelyne, phenanthridine, and phenanthrene) on stability of emulsion and concluded that the higher the aromaticity of the solvent the greater the ability of the solvent to destabilize emulsions.

Ese et al. (1998) and Yarranton et al. (2000) linked the change of emulsion stability with the degree of various asphaltene solubility in different solvents. Yarranton et al. (2000) changed the ratio of alkane to aromatic solvent in the model oil emulsions, and determined that only soluble asphaltene are surface-active and only a certain fraction of the soluble asphaltenes is surface-active. The amount of surface-active asphaltenes depends on alkaneto-aromatic ratio of solvent. Ese et al. (1998) investigated the film formed by spreading of asphaltenes and resins from toluene, hexane and their mixtures. Their studies showed that increased surface concentration of asphaltenes is necessary to achieve a film of similar stability when changing the solvent from pure toluene to pure hexane. Their data indicated that solvents have less influence on the resins than on the asphaltenes.

## 2.4.3.3 Effect of Asphaltene/Resin Ratio

Many researchers have been trying to relate the emulsion stability to the asphaltene/resin ratio. Bobra et al. (1992) indicated that resins alone can act as effective emulsifiers. They

also showed that the range of alkane to aromatic solvents at which stable emulsions are produced is the largest for asphaltene containing oils. When asphaltenes and resins are both present, the range is larger than for either resins or asphaltenes alone. However, Mouraille et al. (1998) presented contradictory results. The authors pointed out that too much resins destabilizes emulsions. The investigation of the film formed by the adsorption of asphaltene/resin mixture indicated that resins start to predominate the film properties when their content exceeds 40% (Ese et al. 1998).

Khristov et al. (1999) indicated that a combination of asphaltenes and resins at a ratio of 3:1 (asphaltene: resin) resulted in the most stable emulsion. McLean and Kilpatric (1997) found that the same 3:1 asphaltene/resin ratio correlated to the highest emulsion stability. Schroling and co-workers (1999) showed that as the ratio of the asphaltenes to resins increases the stability of emulsions in terms of flocculation decreases. They found that stability of emulsion is the highest with an asphaltene/ resin ratio of 1. As seen from this observation the asphaltene/resin ratio influences emulsion stability. However, more information needs to be obtained to quantify this relationship.

### **2.5 CHAPTER SUMMARY**

The formation of water-in-crude oil emulsions is often encountered in the petroleum industry in both production and refining segments. Their formation occurs as a result of agitation of normally immiscible oil and water and their stabilization by a wide variety of emulsifying agents present in crude oil. To achieve a desired product quality and meet

environmental concerns, it is often necessary for oil producers to treat these emulsions. Chemical demulsification, such as addition of surfactants, is the most widely applied method of treating water-in-crude oil emulsions. Typically, the added surfactants replace the native stabilizers on the interface with a surfactant layer which is less resistant to coalescence. Treatments can fail when the added surfactant does not sufficiently replace native emulsion stabilizers. In order to devise an optimum treatment it is necessary to understand the emulsion stabilization mechanisms and properties of the naturally occurring emulsifiers that stabilize the emulsions in the first place.

The extensive research in this area revealed that the stability of water-in-crude oil emulsions is mainly determined by the presence of a rigid interfacial film on the water/oil interface. It was proposed that this film is composed of naturally occurring crude oil compounds, mainly asphaltenes, resins and/or solid particles. However, the role which each of these compounds plays is still poorly understood. Most of the reviewed studies provide qualitative information in this area. Moreover, the comparison of the literature revealed a lot of discrepancies.

Investigation of the asphaltene and resin properties revealed that they are surface-active and are able to adsorb on the water/oil interface. However, the form in which this compounds adsorb on the interface is still an unresolved issue. Various studies suggest that asphaltenes and resins adsorb on the interface in the form of a monolayer or a multilayer of independent molecules and/or asphaltene-resin aggregates. There is some evidence that emulsions formed from asphaltene/resin mixtures can be more stable that those formed from asphaltenes or resins alone. On the other hand, resins have also been shown to reduce emulsion stability. It was also observed that the stability of emulsions and rigidity of the interfacial film depends on the pH, aliphatic and aromatic solvent content, and asphaltene/resin ratio in the crude oil. The studies indicated that varying these factors may change the solubility of asphaltenes and resins, which in turns affect emulsion stability. The combined effect of all these factors has yet to be determined.

Investigation of the role of solids in stabilization of crude oil emulsions indicated that naturally occurring fine solid particles significantly increase emulsion stability. The presence of fine solids was not accounted for in many studies of other crude oil components. Hence, there is a need for a systematic study of the role of asphaltenes, resins, and native solids in emulsion stability.
### **CHAPTER 3**

#### **EXPERIMENTAL METHODS**

#### **3.1 INTRODUCTION**

As was stated in Chapter 1, the main objective of this project is to determine the interfacial composition of the asphaltene/resin stabilized emulsions and to relate the interfacial composition to bulk oil phase composition and emulsion stability. The effect of fine solids present in crude oil on the emulsion stability will be also examined.

The necessary experimental data to determine the interfacial composition (i.e. asphaltene/resin monolayer, multilayer, or aggregate) are the interfacial area of the emulsion, the total mass of the asphaltenes and resins adsorbed on the emulsion interface, and the area per molecule occupied by the asphaltenes and resins on the water/oil interface. The interfacial area of the emulsion can be determined from the drop size distribution of an emulsion. The total mass of the asphaltenes and resins on the interface can be obtained from the gravimetric analysis of the continuous phase of an emulsion. The asphaltene and resin surface areas can be determined from the interfacial tension measurements. The interfacial tension can also be used to assess the ability of the asphaltenes and resins to form micelles. Finally, stability tests of emulsions are conducted in order to relate the interfacial composition and micelle formation to emulsion stability. The next few sections provide detailed descriptions of the required materials, procedures and theory.

#### **3.2 MATERIALS**

The asphaltenes and resins used in these experiments were extracted from Athabasca and Cold Lake bitumens. Oil sand coker-feed Athabasca bitumen, supplied by Syncrude Canada Ltd, has had most of the sand and water removed and is ready for upgrading. The Cold Lake bitumen, obtained from Imperial Oil Ltd. of Canada, is recovered by steam injection from an underground oil reservoir and has been treated to remove most of the sand and water. Reagent grade acetone, n-heptane and n-pentane were obtained from VWR. Distilled water used for interfacial tension measurements was obtained from Sigma Aldrich Company. Distilled water used for emulsions was supplied by the University of Calgary water plant.

#### 3.2.1 Terminology

As described previously, crude oils and bitumens contain asphaltenes, resins, aromatics, saturates and suspended fine solids. Asphaltenes are defined as the fraction of bitumen that is insoluble in an alkane but soluble in toluene. In order to extract asphaltenes from the bitumen, they are precipitated with n-heptane or n-pentane. When asphaltenes are precipitated from bitumen, any solids present in bitumen will coprecipitate (Yarranton, 1997). The solids include material such as ash, fine clays and some adsorbed hydrocarbons which are insoluble in toluene. The mixture of asphaltenes and solids which precipitate directly from the bitumen is here referred to as "asphaltenes", unless otherwise noted.

Asphaltenes from which solids have been removed are referred to throughout this report as "solids-free asphaltenes", also unless otherwise noted.

#### 3.2.2 Fractionation of Bitumen into Solubility Classes

The separation of Athabasca and Cold Lake bitumens into saturates, aromatics, resins and asphaltenes was performed using the SARA fractionation method (modified ASTM D2007 procedure). A flowsheet of the extraction technique is shown in Figure 2.2. In the SARA fractionation method, asphaltenes are removed by precipitation with n-pentane. The deasphalted bitumen is further separated into saturate, aromatic and resin fractions using clay-gel adsorption chromatography. Saturates, aromatics and n-pentane extracted asphaltenes were not used in the experiments; however, their separation is a required step in the resin extraction.

#### 3.2.2.1 Extraction of Asphaltenes

Bitumen was dispersed in n-pentane or n-heptane with a concentration of one gram of bitumen to 40 mL of precipitant. The reported density of the Athabasca bitumens at 20 °C is approximately 1000 kg/m<sup>3</sup> (Peramanu et al., 1998), therefore the volume ratio of bitumen to precipitant was 1:40. The mixture was then sonicated in an ultrasonic bath for 45 minutes and left to settle overnight. After settling the mixture was sonicated again for 20 minutes. The precipitated asphaltenes were filtered on medium porosity Whatman Grade 2 filter paper (porosity–8µm). The collected asphaltenes were mixed again with 1:4 volume ratio of original bitumen to n-pentane or n-heptane, sonicated for 45 minutes and left

overnight. The asphaltenes were then filtered again and dried at 45°C under vacuum until the solvent had completely evaporated. The asphaltene-solids fraction was considered dry when the change in mass was less than 0.1% over a 24 hour period.

For the SARA fractionation method, n-pentane is used as the precipitant. However, nheptane precipitated asphaltenes were used for the emulsion experiments, since most literature data are based on n-heptane extracted asphaltenes.

#### 3.2.2.2 Extraction of Resins

The mixture of deasphalted bitumen and n-pentane collected during a SARA asphaltene extraction was placed in a rotary evaporator to remove the pentane from the supernatant. The small amount of deasphalted bitumen that remained after the evaporation was poured into a sample jar and placed inside a vacuum oven at 45 °C to remove the remaining solvent. The solvent was considered to be completely removed when the change in mass of deasphalted bitumen was less than 0.1 % over a 24 hour period.

Five grams of deasphalted bitumen were dissolved in 500 mL of pentane and transferred to the adsorption column. The adsorption column consisted of two identical glass sections assembled vertically. The lower section contained 200 g of activated silica gel and 50 g of freshly activated Attapulgus clay on top of the gel. The upper part was charged with 150 g of Attapulgus clay with glass wool on top of the clay. Resins were adsorbed on the Attapulgus clay, while aromatics were adsorbed on silica gel. The remaining saturates eluted directly and were collected in a flask. To remove the aromatics, 1600 mL. of toluene and pentane (50:50 vol. ratio) was fed into the column. The eluted aromatics were collected in a flask. For the complete removal of aromatics from silica, the lower section of column was detached and refluxed with 200 mL of toluene for 2 hours. The resin fraction was collected by washing the upper section with 400 mL. of toluene and acetone (50:50 vol. ratio). The saturates, aromatics and resins were then recovered by evaporating the solvents using rotary evaporators. The residue from the rotary evaporator was placed in the vacuum oven at 45 °C until there was no change in mass. The mass fractions of saturates, aromatics, and resins of the Athabasca and Cold Lake bitumens obtained in the present work are reported in Table 3.1. The average yield of SARA fractionation was in a range of 92-95%. The loss in yield was attributed to resins that remained adsorbed in the clay section of fractionation column. It is known that resins are able adsorb strongly, therefore the missing 5-8% in yield was attributed to the resin fraction.

Fractions (mass %)	Athabasca	Cold Lake
Asphaltenes	17.1	16.8
Resins	26.8	25.8
Aromatics	39.8	39.1
Saturates	16.3	18.3
<b>Coarse Solids</b>	7.5	2.4

Table 3.1 SARA Fractions and Solids Content in Athabasca and Cold Lake Bitumens

#### 3.2.3 Preparation of Solids-Free Asphaltenes

#### 3.2.3.1 Removal of Coarse Solids

The asphaltene-solids were dissolved in toluene at a volume ratio of 100:1 toluene:asphaltene. The mixture was sonicated for 20 minutes to ensure that all the asphaltenes were dissolved. The mixture was then centrifuged at 3500 rpm (1750 g) for 5 minutes. The supernatant liquid was recovered and evaporated until only dry asphaltenes remained.

The size of solids settled at the bottom of the centrifuge tube can be estimated from Stoke's law, assuming spherical geometry:

$$v = \frac{2Rs^2(\rho_x - \rho_l)w^2x}{9\mu}$$
(3.1)

In this equation, v (m/s) is the velocity of particle, Rs (m) is the diameter of the solid particle,  $\rho_r$  and  $\rho_l (kg/m^3)$  are the densities of the particle and liquid phase respectively,  $\mu$ (*Pa*·s) is the fluid viscosity, and w (m/s) is the centrifuge angular velocity, x (m) is the distance of particle from the axis of rotation.

Taking the viscosity of toluene as equal  $5.87 \cdot 10^{-4}$  Pa·s, the density of solid (i.e clay and silica particles) as 2000-2200 kg/m<sup>3</sup>, the length of the centrifuge tube as 10 cm, the residence time in the tube as 5 minutes, and the centrifuge acceleration ( $w^2x$ ) as 1750g

m/s<sup>2</sup>, the estimated diameter of settled solids ranged from 0.7 to 1  $\mu$ m. This analysis indicates that this method can remove solids of higher than 1  $\mu$ m diameter. Solids removed by this method shall be referred to as the "coarse solids". The coarse solids content in the Athabasca and Cold Lake Bitumens is reported in Table 3.1.

#### 3.2.3.2 Removal of Fine Solids

Asphaltenes free of fine solids were obtained in two ways: by filtration and by precipitation methods.

The filtration method involves two steps. Initially, coarse solids were removed from asphaltene-solids by dissolving them in toluene and centrifuging as described above. Next, the supernatant liquid was filtered with under vacuum through a 0.5  $\mu$ m Metrigrad Glass fiber filter (Pall Corporation). The filtrate was placed in a vacuum oven at 45°C and left until the change in mass of asphaltenes was less than 0.1% over a 24 hour period.

The precipitation method is based on the fact that solids are removed with the precipitation of asphaltenes from a mixture of heptane and toluene. It has been observed that solids coprecipitate with the asphaltenes that first come out of solution, perhaps because they act as nucleation sites (Yarranton, 1997). Hence, with the addition of sufficient heptane to cause a small fraction of asphaltenes to precipitate from a toluene/asphaltene mixture, most or perhaps all of the solids can be removed as well. Here, a 55:45 heptane to toluene volume ratio was used. At this ratio, according to asphaltene solubility data (Yarranton, 1997), approximately 2 % wt. of Cold Lake and Athabasca asphaltenes precipitate.

Initially, 5 g of asphaltenes were dissolved in 225 cm<sup>3</sup> of toluene and sonicated for 20 minutes to ensure complete mixing. A volume of 275 cm<sup>3</sup> of heptane were then added to the mixture. The concentration of asphaltene-solids in the heptol was 10 kg/m<sup>3</sup>. The mixture of heptol and asphaltene-solids was then sonicated in an ultrasonic bath for 45 minutes and left to settle overnight. After settling, the mixture was sonicated again for 10 minutes. After sonication the mixture was poured into centrifuge tubes and centrifuged at 3500 rpm for 5 minutes. The solids and the small amount of co-precipitated asphaltenes remained at the bottom of the centrifuge tubes. The supernatant liquid was poured off and evaporated until only dry asphaltenes remained. The solids-free asphaltenes from the supernatant were further used for emulsion experiments. The amount of solids extracted by this method is around  $7 \pm 0.5$  wt. % and around  $3\pm 0.5$  wt. % of asphaltenes for Athabasca and Cold Lake bitumens, respectively.

#### **3.3 INTERFACIAL TENSION EXPERIMENTS**

Interfacial tensions of asphaltenes, resins and their mixtures against water were measured with a *Kruss Model DVT-10 Drop Volume Tensiometer*. All measurements were taken at 22°C. The schematic of the drop volume apparatus is shown in Figure 3.1. For the interfacial tension measurements between two liquids the denser liquid is placed in a glass

tube. A liquid with lesser density is pumped by a syringe pump at a constant flow rate through a thin wall capillary connected to the bottom of the glass tube. The flow rate is controlled with a Harvard Apparatus Model 44 syringe pump accurate to  $\pm 1\%$ . The pumped liquid detaches from the capillary into the denser continuous phase as a series of drops. The detachment of a drop occurs when the buoyancy force acting on the drop equals the interfacial energy acting on the perimeter of the capillary tip. In the following experiments, distilled water was the continuous phase and mixtures of asphaltenes and resins in heptane and toluene, were the drop-forming phase. The detached drops are detected by a photodiode detector positioned above the capillary. A timer is started after the detachment of the first drop and the time between subsequent drops passing the detector is measured. Since the flow rate is constant, the time interval between drops can be converted to the volume of each drop. Hence, the interfacial tension can be calculated as follows:

$$\sigma = \frac{V_{drop}(\rho_h - \rho_l)g}{\pi d} = \frac{Q(\rho_h - \rho_l)gt}{\pi d}$$
(3.2)

where  $V_{drop}$   $(m^3)$  is the drop volume at detachment, Q  $(m^3/s)$  is the volumetric flow rate, t(s) is the time from initiation to detachment of each drop, g  $(m/s^2)$  is the gravitational acceleration, d (m) is the diameter of the capillary tip, and  $\rho_h$  and  $\rho_l$   $(kg/m^3)$  are the densities of heavy and light phases respectively. Note that the mixture density must be used in equation 3.2. Ideal mixing was assumed for all cases in this work. Asphaltene and resin densities of 1200 kg/m<sup>3</sup> and 998 kg/m<sup>3</sup> (Peramanu et al., 1999), respectively were used in all calculations.

The IFT values measured with the drop volume tensiometer is generally accurate to  $\pm$  0.1mN/m. To confirm the accuracy of the measurements a series of interfacial tension experiments were performed with pure solvents. The results are compared with literature values in Table 3.2. The deviation between experimental and literature values was found to be within  $\pm$  2% in all cases.

	Interfacial Tension (mN/m)			
Solvent	Drop Volume Method	Literature Values (Li, 1992)		
n-heptane	49.5	50.1		
toluene	35.9	35.8		
benzene	34.7	34.0		

Table 3.2 Interfacial Tension of Organic Solvents versus Distilled Water

The drop volume tensiometer has some limitations. High viscosities (above 20,000 mPa·s) change the adherence force invalidating equation 3.2. As liquid viscosity increases the flow rate must be decreased in order to ensure valid results. At a flow rate above  $2 \text{ cm}^3/\text{h}$  the inertial force becomes significant and equation 3.2 is no longer valid.



Figure 3.1 The schematic of the drop volume apparatus used for the interfacial tension measurements (DVT-10 Users Manual, 1994)

The drop volume tensiometer measures the IFT at different flow rates, in effect at different contact times between the two phases, i.e. dynamic interfacial tension. Surface active materials require a finite time to diffuse to an interface and reach equilibrium. In this technique, the time for a drop to detach from the capillary tip is insufficient for the interface to reach the equilibrium.

It would require a large number of experiments to obtain equilibrium interfacial tensions for the range of conditions investigated in the present work. As will be discussed in the next chapter, our interest is in the slope of the interfacial tension. Yarranton et al., (2000) showed that equilibrium interfacial tensions are not required when obtaining the slope of asphaltene-toluene mixtures versus increasing asphaltene concentration for flow rates ranging from 0.25 to  $1.5 \text{ cm}^3$ /h. They showed that the slopes of the interfacial tensions differed at mostly by 8.5 % from the equilibrium slope. Yarranton et al., (2000) used a flow rate of  $1.0 \text{ cm}^3$ /h for all their subsequent measurements. The same flow rate is used for the present work.

#### **3.4. EMULSION EXPERIMENTS**

#### 3.4.1. Determination of the Mass Surface Coverage of Asphaltenes and Resins

The amount of asphaltenes and resins on the water/oil interface of an emulsion can be calculated from the Sauter mean diameter of the emulsion and gravimetric analysis of the continuous phase. To simplify the explanation, the mass of asphaltenes will be used as an example.

The total asphaltene mass surface coverage,  $\Gamma_A$  is simply the total mass of the asphaltenes on the interface  $m_I(g)$ , divided by the surface area of an emulsion  $A_w$   $(m^2)$ :

$$\Gamma_A = \frac{m_I}{A_w} \tag{3.3}$$

Therefore, it is necessary to determine  $m_I$  and  $A_w$ .

 $A_w$  can be found from the Sauter mean diameter, a measurable quantity. The Sauter (surface-volume) mean diameter ds, is calculated from the drop size distribution,  $d_i$  of an emulsion measured with optical microscopy as follows:

$$ds = \frac{\sum F_{i} d_{i}^{3}}{\sum F_{i} d_{i}^{2}}$$
(3.4)

where  $F_i$  is the drop number frequency.

The Sauter mean diameter, ds, provides the relationship between the total volume of water,  $V_w$ , in the emulsions and the surface area of the water droplets. The total volume of the dispersed water is related to the distribution of drop diameters in the emulsion as follows:

$$V_{w} = \frac{\pi N}{6} \sum F_{i} d_{i}^{3}$$
 (3.5)

where N is the total number of drops.

The total surface area of emulsion is the surface area of water drops,  $A_w$ , and is related to the distribution of drop diameters by:

$$A_{w} = \pi N \sum F_{i} d_{i}^{2}$$
 (3.6)

An expression for the emulsion surface area is found by combining equations 3.4-3.5 and is given by:

$$A_{w} = \frac{6V_{w}}{ds}v = \frac{2Rs^{2}(\rho_{x} - \rho_{i})w^{2}x}{9\mu}$$
(3.7)

The remaining unknown,  $m_{I}$ , can be determined from concentration measurements. Upon emulsification, asphaltenes partition between the emulsion interface and the continuous phase. Consequently, the asphaltene concentration in the continuous phase becomes less than its initial value. The mass of asphaltenes on the interface,  $m_{I}$  can be found from a material balance.

$$m_{l} = m_{l} \left(1 - \frac{C_{A}^{eq}}{C_{A}^{0}}\right)$$
 (3.8)

where  $m_t$  is the total mass of asphaltenes in the emulsion,  $C_A^{\ 0}$  is the initial asphaltenes concentration in the continuous phase prior to emulsification and  $C_A^{\ eq}$  is the new equilibrium asphaltene concentration in the bulk phase. Substituting equations 3.7 and 3.8 into equation 3.3 gives:

$$\Gamma_{A} = \frac{m_{t}(1 - \frac{C_{A}^{eq}}{C_{A}^{0}})}{6V_{w}}$$
(3.9)

#### **3.4.2 Preparation of the Model Emulsions**

The continuous (oil) phase of the model emulsions was made from asphaltenes, resins, and toluene and heptane mixtures in different ratios. The mixture of toluene and heptane will henceforth be referred to throughout this thesis as "heptol". The composition of the heptol will be presented as the volume percent of toluene indicated in brackets. For example, heptol containing 75 vol % toluene and 25 vol % heptane is presented as heptol (75 vol % toluene).

To prepare an emulsion, a known amount of asphaltenes and resins was dissolved in toluene. The solution was stirred in a sonic mixture for 20 minutes. Heptane was added after asphaltenes and resins were completely dissolved in the toluene. The mixture was again sonicated for five minutes to ensure homogeneity.

The prepared oil phase was then processed with a CAT-520D homogenizer with a 17 mm flat rotor generator configuration at 17,000 rpm. During mixing a given amount of dispersed water phase was added dropwise to the system. After all the water had been added, the mixing continued for five minutes at the same speed. It was determined that the minimum mean drop diameter generated by this homogenizer is 7  $\mu$ m which corresponds to the Sauter mean diameter of 8.8  $\mu$ m. The amount of water in all the emulsions was 40 vol %.

#### 3.4.3 Emulsion Drop Size Distribution Analysis

Drop size analysis was used in order to calculate the total area of an emulsion. These calculations are based on the determination of the Sauter mean diameter, as described in Section 3.4.1. To perform a drop size analysis, model water-in-heptol emulsions were allowed to stand under the influence of gravity for 1.5 hours. During this time, emulsions creamed and separated into an emulsion layer on the bottom and a clear continuous phase on top. After this period, a drop of emulsion phase was placed by pipette onto a hanging drop slide. In order to achieve a uniform distribution of the emulsion sample on the slide

some continuous phase was also added. A slipcover was then placed on the sample. The emulsion samples were analyzed using a *Carl Zeiss Axiovert S100* inverted microscope equipped with a video camera. Images from the microscope were captured on a computer and drop size distributions were then measured using *Image Pro* image analysis software. Examples of some emulsion images and drop size distributions are shown in Figures.3.2 and 3.3.

The determination of emulsion drop sizes by optical microscopy is widely used in emulsion studies. However, this method has some drawbacks. It is very sensitive to sampling error because relatively few droplets are being examined. Some droplets, especially with large diameter, can be distorted and broken during collection onto the microscope slide. Therefore, the obtained Sauter mean diameter can be underestimated. Small droplets can be hidden under large ones, or large droplets can settle to the bottom of the slide leaving small droplets suspended (Orr, 1985). A general guideline is that a measurement of 149 particles gives a drop size cumulative distribution with a 10 % error. The measurement of 740 particles gives 5 % error and the measurement of 4256 particles reduces the error to 2.5 % (Dixon, 1969). In the present work 400 drops were used to obtain drop size distributions, giving an expected error of 5-10 %.

For the accurate determination of the asphaltene and resin mass on the emulsion interface, it is important that the surface area of emulsions (drop size distribution) doesn't change over the time when the concentration measurements are taken. In the current work,



Figure 3.2 Images of model water-in-heptol (50 vol% toluene) emulsions stabilized by asphaltenes ( $\phi_w = 0.40$ ) *a*)  $C_A^0 = 1 \text{ kg/m}^3$ , *b*)  $C_A^0 = 2 \text{ kg/m}^3$ , *c*)  $C_A^0 = 10 \text{ kg/m}^3$ 



Figure 3.3 Drop size distributions of water-in-heptol (50 vol % toluene) emulsions stabilized by Athabasca asphaltenes ( $\phi_w$ =0.40)

emulsions that show no change in the drop size distribution over 2 hours under normal gravity condition are used for the gravimetric analysis. Yarranton et al., (1999) showed that in the emulsions stabilized by asphaltenes there is only a small change in the drop size distribution for at least 24 hours. No resolved water is observed in these emulsions even after several months under normal gravity.

#### **3.4.4 Emulsion Gravimetric Analysis**

#### 3.4.4.1 Determination of Asphaltene Concentration in Emulsion and Continuous Phases

To perform a gravimetric analysis, emulsions were allowed to stand after preparation for one and a half hours. Due to creaming, the emulsions separated into a continuous phase on top and an emulsion layer on the bottom. The continuous phase was than poured into a graduated cylinder and its volume measured. It was then poured into a round-bottom flask and placed into a rotary evaporator, allowing the toluene-heptane solvent to evaporate until only asphaltenes were left in the flask. The asphaltenes were dried under nitrogen in a vacuum oven at 60 °C, after which their weight was determined gravimetrically. The balance was accurate to  $\pm 0.002$  g.

The concentration of asphaltenes in the continuous phase is the gravimetrically determined weight of asphaltenes divided by the measured volume of supernatant. The mass of asphaltenes in the continuous phase is the concentration in the continuous phase multiplied by the total volume of the continuous phase. The mass of asphaltenes on the interface is the difference between the initial mass of asphaltenes and the mass of asphaltenes in the continuous phase. From repeated measurements, the standard deviation was found to be  $\pm 0.0007 \text{ mg/m}^2$ . Hence this gravimetrical measurements yields the mass of asphaltenes on the interface accurate to a  $\pm 0.0012 \text{ mg/m}^2$  (a 95 %. confidence interval).

## 3.4.4.2 Determination of Asphaltene and Resin Concentration in Asphaltene/Resin Mixtures

When emulsions were prepared from a mixture of asphaltenes and resins it was necessary to determine the mass and the ratio of these fractions on the emulsion interface. The total mass of the asphaltene-resin mixture remaining in the continuous phase after emulsification was determined gravimetrically as described above. Asphaltenes were then separated from the mixture by precipitation with n-heptane. The dry asphaltene-resin mixture was dissolved in 30 cm<sup>3</sup> of n-heptane and poured into a preweighed centrifuge tube. The mixture was sonicated for one hour and allowed to settle overnight. After settling it was sonicated again for 15 minutes and centrifuged for 10 minutes at 3500 rpm. The supernatant containing the resin fraction was poured into a preweighed beaker and set aside in order to most of the heptane to evaporate. The beaker was placed into the vacuum oven at 45°C until complete drying had occurred. The mass of resins was than determined gravimetrically. The centrifuge tube containing the precipitated asphaltenes was also placed in the vacuum oven and the mass of dried asphaltenes was determined. The material balance of the asphaltene-resin mixture was checked. Only results where the material balance closed to within 10% are reported. The mass of asphaltenes and resins on the interface is calculated as previously described for the asphaltenes.

One problem is that the presence of resins may affect the solubility of the asphaltenes. On other words, not all of the asphaltenes may precipitate in heptane if resins are also present. Therefore, to check the accuracy of the separation method, the method was applied to control samples with known amount of asphaltenes and resins. The results of this experiment indicated that this gravimetrical method yields asphaltene masses accurate to 17 %.

#### 3.4.5 Stability Tests

The stability of the emulsions was determined visually by measuring the water separated from the emulsion as a function of time. Some of the emulsions investigated in this research were extremely stable and didn't separate under normal gravity conditions. In order to enhance the separation of water centrifugation and heating of emulsion were employed. The same treatment was applied to all the emulsions presented in this thesis.

Immediately after emulsification, the samples were transferred into 15 cm<sup>3</sup> graduated centrifuge tubes. The tubes were closed with caps to prevent solvent evaporation and centrifuged for 5 minutes at 4000 rpm (1780 g) and placed in a constant temperature water bath at 60°C. After a period of 2 hours the emulsions were centrifuged for five minutes and the amount of resolved water measured. The centrifuge tubes were returned to the heating bath for another period of two hours, and than centrifuged before measuring the amount of resolved water. This procedure was repeated until most of the water was separated. The heating/centrifuging time applied to an emulsion sample is referred to as

destabilization time. The amount of resolved water was reported as the percent of total water volume contained in the given emulsion sample. The reported values are accurate to  $\pm$  11 vol.% water resolved. Examples of destabilization over time of model water-in-heptol emulsions are shown in Figure 3.4.

Note that after 8 hours, the procedure was stopped and the samples stored at room temperature overnight. No significant charge in free water or drop size distribution was observed overnight. The treatment was resumed the next morning. Stability time was measured as if there was no break; that is, the first time of the next day was taken as 8 hours. While this approach is acceptable to establish general trends, almost all comparisons presented in the thesis are made after less than 8 hours of destabilization time.



**Figure 3.4** The percentage of water resolved from model water-inheptol (50 vol % toluene) emulsions stabilized by Athabasca asphaltenes and asphaltene/resin mixtures as a function of time

## **CHAPTER 4**

# INTERFACIAL TENSION MEASUREMENTS OF ASPHALTENES, RESINS AND THEIR MIXTURES

#### **4.1 INTRODUCTION**

As described previously, it has been reported that asphaltenes and resins are surface active, and therefore are able to adsorb on the water/oil interface (Sheu et al., 1995, Ese et al., 1998, Yarranton et al., 2000). It is believed that asphaltene and resin molecules have a similar structure, except that resins have lower molar mass, heteroatom content and aromaticity. Therefore, resin molecules may occupy less area on the water/oil interface. In addition, it was proposed that resins are more surface active (decrease surface tension more) than asphaltenes (Yan et al., 1999). Hence, asphaltene and resin composition on the interface may be different from that in the continuous oil phase. It was also proposed that asphaltenes and resins may interact and form micelles (Storm et al., 1995). Micelle formation can lead to a different interfacial composition and emulsion stability. In addition, it is known that asphaltenes precipitated from bitumen may contain some solid particles, such as sand, clay and silica (Yarranton et al., 1997; Yan et al., 1999). It is of interest to determine if the solids affect asphaltene adsorption on the water/oil interface.

#### 4.1.1 Theory

In a dilute solution, the molar surface area,  $\Gamma'$ ,  $(mol/m^2)$  can be obtained from the plot of interfacial tension versus the natural logarithm of solute concentration according to Gibbs equation:

$$\Gamma' = \frac{(d\sigma / d \ln C)}{-RT}$$
(4.1)

where R (J/mol·K) is the universal gas constant, T (K) is temperature,  $\sigma$  (N/m) is the interfacial tension, and C (kg/m<sup>3</sup>) is the concentration of the surface active materials in the bulk phase.

For a pure surfactant system the plot of interfacial tension (IFT) versus logarithm of the solute concentration is linear once the interface becomes saturated with the solute molecules. The molecular surface area is constant and can be found from the slope of this plot. With mixed surfactants (such as asphaltenes and resins) similar plots are obtained (Campanelli et al., 1999).

The average area per molecule on the interface (i.e. molecular cross-section) is the ratio of molar surface area to Avogadro's number:

$$A = \frac{1}{\Gamma' N_A}$$
(4.2)

IFT measurements have also been performed in order to characterize the onset of the micellization of the asphaltenes and resins, i.e. the critical micelle concentration (CMC). This method has been widely used for the determination of CMC in aqueous solutions of surfactants. Surfactant molecules, as was described in the Chapter 2, are characterized by the presence of hydrophilic head and hydrophobic tail in their structure. This dual nature allows the surfactant molecules to self-associate and form micelles. A micelle is a surfactant aggregate in which the hydrocarbon tails are concentrated towards the center of the aggregate and the polar head groups are aligned near the surface. These types of micelles occur when water is the continuous phase, so that the hydrophilic groups reside in the water. In oils, surfactants form reverse micelles. The formation of micelles occurs above a certain concentration of surfactant in solution, known as the critical micelle concentration or CMC. Initially, the adsorption of surfactant molecules on the interface lowers IFT. However, above the CMC, each additional surfactant molecule is incorporated not on the interface but into micelles. Hence, the IFT of the system no longer changes. As shown in Figure 4.1, the CMC can be detected by looking for the break in slope in a plot of IFT versus log surfactant concentration.

#### 4.1.2 Results

Interfacial tensions were measured for the range of asphaltene and/or resin concentrations in heptol solutions of varying composition. In the following discussion, interfacial tension refers to interfacial tension versus water (of a given hydrocarbon solution). The composition of the heptane/toluene solution will be further referred to as heptol.



Figure 4.1 Surface tension of asphaltene solution in pyridine over water (Sheu et al., 1995)

The IFT of asphaltenes, resins and their mixtures versus the natural log of their concentration in heptol are illustrated in Figures 4.2-4.5. The surface coverage,  $\Gamma'$ , and interfacial area per molecule, A, of asphaltenes, resins and asphaltene-resin mixtures were calculated from the slopes of interfacial tensions versus the natural log of concentration of the surface active material, as described in Chapter 3. The calculated slope,  $\Gamma'$ , and, A, are presented in Tables 4.1-4.4. To estimate the accuracy of the measurements two identical runs each consisting of 5 data points were repeated. The results were found to be accurate to about  $\pm 10$  %. The results for each component and their mixtures are discussed below.

#### **4.2 ASPHALTENES**

The interfacial tension of Athabasca asphaltenes dissolved in heptol of 25, 50, 62.5, 75 and 100 vol% toluene were measured at asphaltene concentrations ranging from 0.5 to 50 kg/m<sup>3</sup>. For all five heptol systems, the interfacial tension of the asphaltene-toluene-heptol systems decreases monotonically as asphaltene concentration increases. Moreover, the measured interfacial tensions appear to decrease linearly with an increase in log concentration of asphaltenes. This behavior suggests that there is no micelle formation. Yarranton et al., (1999) also observed no micelle formation for Athabasca asphaltenes dissolved in toluene and 1,2-diclorobenzene in the concentration range of 0.05 to 100 kg/m<sup>3</sup>.

	Slope	Г	Α
	(mN/m)	(10 <sup>-6</sup> mol/m <sup>2</sup> )	( <b>nm</b> <sup>2</sup> )
Asphaltenes	-1.45	0.58	2.84
1:3 R:A	-1.46	0.60	2.82
1:1 R:A	-1.51	0.61	2.72
3:1 R:A	-1.87	0.76	2.20
Resins	-1.97	0.80	2.09

# Table 4.1 Measured Slopes and Calculated Molecular Dimension of the Athabasca Asphaltenes, Resins, and Asphaltene/Resin Mixtures in Toluene

 Table 4.2 Measured Slopes and Calculated Molecular Dimension of the Athabasca

 Asphaltenes, Resins, and Asphaltene/Resin Mixtures in Heptol (75 vol% Toluene)

	Slope	Γ	A	
	( <b>m</b> N/m)	(10 <sup>-6</sup> mol/m <sup>2</sup> )	(nm²)	
Asphaltenes	-2.09	0.84	1.97	
1:3 R:A	-2.12	0.86	1.94	
1:1 R:A	-2.42	0.98	1.70	
3:1 R:A	-3.28	1.33	1.25	
Resins	-4.01	1.62	1.02	

	Slope	Γ	A
	( <b>m</b> N/ <b>m</b> )	(10 <sup>-6</sup> mol/m <sup>2</sup> )	(nm²)
Asphaltenes	-2.09	0.85	1.96
1:3 R:A	-2.12	0.86	1.94
1:1 R:A	-2.46	1.00	1.6 <b>7</b>
3:1 R:A	-3.59	1.45	1.15
Resins	-4.11	1.66	1.00

 Table 4.3 Measured Slopes and Calculated Molecular Dimension of the Athabasca

 Asphaltenes, Resins, and Asphaltene/Resin Mixtures in Heptol (62.5 vol% Toluene)

#### Table 4.4 Measured Slopes and Calculated Molecular Dimension of the Athabasca Asphaltenes, Resins, and Asphaltene/Resin Mixtures in Heptol (50 vol% Toluene)

[	Slope	Γ	Α
	(mN/m)	(10 <sup>-6</sup> mol/m <sup>2</sup> )	(nm²)
Asphaltenes	-2.15	0.87	1.91
1:3 R:A	-2.57	1.04	1.60
1:1 R:A	-2.80	1.13	1.47
3:1 R:A	-3.71	1.50	1.11
Resins	-4.28	1.73	0.96

Table 4.5 Asphaltene and Resin Interfacial Tension in Heptol of Different Composition,  $(C_{A,R}=10 \text{ kg/m}^3)$ 

Heptol Composition	Asphaltene IFT	Resin IFT	Difference in IFT
	(mN/m)	(mN/m)	(mN/m)
Toluene	29.6	27.4	2.2
Heptol (75 vol% toluene)	30.3	23.6	6.7
Heptol (62.5 vol% toluene)	32.4	23.6	8.8
Heptol (50 vol% toluene)	31.4	21.5	10.0



Figure 4.2 Interfacial tension of Athabasca asphaltenes, resins and asphaltene/resin mixtures in toluene over water



Figure 4.3 Interfacial tension of Athabasca asphaltenes, resins and asphaltene/resin mixtures in heptol (75 vol% toluene) over water



Figure 4.4 Interfacial tension of Athabasca asphaltenes, resins and asphaltene/resin mixtures in heptol (62.5 vol% toluene) over water



Figure 4.5 Interfacial tension of Athabasca asphaltenes, resins and asphaltene/resin mixtures in heptol (50 vol% toluene) over water

The effect of solvent composition (vol% toluene in heptol) on the interfacial behavior of asphaltenes is illustrated in Figures 4.6-4.7. As seen in Figure 4.6 the slopes of interfacial tension measured in heptol of 50, 62.5 and 75 vol% toluene differ from each other only by about 2 %, while the slope observed for 100 vol% toluene is 31-33 % higher than for the mixtures when heptane is present. The smaller slope in the solvent containing 100 vol% toluene indicates that the interfacial molar area of asphaltenes is bigger than in the solvents containing heptane.

The interfacial molar area calculated from the slopes is as follows: 2.84 nm<sup>2</sup> in 100 vol% toluene, and 1.97 nm<sup>2</sup> in 75 vol% toluene (Figure 4.7). With the further addition of heptane the area decreases only slightly to 1.91 nm<sup>2</sup> in heptol (50 vol% toluene). The average surface areas of asphaltene molecules, as summarized in Tables 4.1-4.4, are close to the values of 1.8-2.2 nm<sup>2</sup> reported by Yarranton et al., (1997). The results are also in a good agreement with the values of 2.53 – 5 nm<sup>2</sup> calculated from surface tension data. (Taylor, 1992, Bhardwaj and Hartland, 1994, Yan et al., 1999).

The decrease in the molar surface area with the addition of heptane to the solvent can be explained in two possible ways. One possibility is that the smaller asphaltene molecules are adsorbed preferably on the water/oil interface in solvent containing heptane. Alternatively, the addition of heptane could also change the configuration of the molecules on the interface, leading to a smaller area occupied per molecule. Hence, this change in


Figure 4.6 Effect of solvent composition on the interfacial tension of Athabasca asphaltenes in heptol over water



Figure 4.7 Effect of solvent composition on the interfacial area of Athabasca asphaltenes and resins

configuration could lead to formation of a thicker layer on the interface. These possibilities will be considered in more detail in the next chapter.

The average molar mass of asphaltenes can be estimated from the calculated surface coverages, the density, and an assumed spherical geometry as follows:

$$M_{i} = \frac{\pi}{6} \rho_{i}^{3/2} A_{i} N_{A}$$
 (4.3)

where  $M_i$  and  $\rho_i$  are the molar mass and density, respectively of the interfacially active component,  $A_i$  is the molar interfacial area and  $N_A$  is the Avagadro's number. Asphaltene density of 1200 kg/m<sup>3</sup> was used (Yarranton et al., 1996). The calculated asphaltene monomer molar masses of the Athabasca asphaltenes are given in Table 4.6. These data are also in a good agreement with the values of 1800-4000 g/mol asphaltene molar masses reported in literature (Yarranton et al., 1996; Peramanu et al., 1998). The apparent change in molar mass with the solvent probably indicates that the spherical geometry assumption is not adequate or that molecules of different size are adsorbing.

## **4.3 SOLIDS-FREE ASPHALTENES**

The interfacial tension of solids-free asphaltenes in heptol (50 vol%) toluene was measured and compared to the interfacial tensions of asphaltenes containing solids in the same

## Table 4.6 Calculated Molar Masses of the Athabasca Asphaltenes in Heptol of Different Composition

Heptol Composition	Molar Mass (g/mol)		
Toluene	2600		
Heptol (75 vol% toluene)	1500		
Heptol (62.5 vol% toluene)	1490		
Heptol (50 vol% toluene)	1430		

# Table 4.7 Calculated Molar Masses of the Athabasca Resins in Heptol of Different Composition

Heptol Composition	Molar Mass (g/mol)
Toluene	1640
Heptol (75 vol% toluene)	560
Heptol (62.5 vol% toluene)	540
Heptol (50 vol% toluene)	510
Heptane	500

solvent as shown in Figure 4.8. This figure indicates that the removal of solids has no significant effect on the interfacial tension of asphaltenes. Hence, it appears that the presence of solids does not affect the adsorption of asphaltenes on the interface.

## 4.4 RESINS

The interfacial tensions of resins were measured in heptol containing 0, 25, 50, 62.5 and 75, 100 vol% toluene with resin concentrations ranging from 0.5 to 25 kg/m<sup>3</sup>. The comparison of resin and asphaltene interfacial tensions (Fig. 4.2-4.5) clearly demonstrates that resins are more surface active (decrease surface tension more) than asphaltenes in all solvent systems. This correlates well with the interfacial tension data obtained by Yan et al., (1999). The interfacial tension of resins decreases linearly with the logarithm of resin concentration. Again, this suggests that there is no micelle formation within the measured range of concentrations.

The larger slope of the resin interfacial tensions suggests that resins are smaller molecules than the asphaltenes. The average molar mass of resins was calculated from the molar surface coverages. These data are presented in Table 4.7. Again, spherical geometry was assumed and a resin density of 1000 kg/m<sup>3</sup> (Peramanu et al., 1998) was used. The calculated molar masses are in a range from 500 to 1640 g/mol, which is smaller that the average molar mass of asphaltene molecules. The obtained resin molar masses are in good



Figure 4.8 Effect of removing solids on interfacial tension of Athabasca asphaltenes in heptol (50 vol% toluene) over water

agreement with the data reported by Peramanu et al., (1998) and Speight, (1991) as discussed in Chapter 2.

A comparison of the resin interfacial area per molecule in the various heptol systems indicates that the addition of heptane has a similar effect on resins as on the asphaltenes. The resin interfacial area in heptol (75 vol% toluene) is 50 % smaller than that in pure toluene. The further addition of heptane up to and including pure heptane solvent changes area only by 7 %. The comparison of solvent effect on the interfacial area of resins and asphaltenes is shown in Figure 4.7. As with asphaltenes, the addition of heptane may cause the preferable adsorption of smaller resin molecules and/or it may change the configuration of resin molecules on the interface.

## 4.5 MIXTURES OF ASPHALTENES AND RESINS

As stated above, resins reduce IFT more than asphaltenes. Therefore, it is expected that resins would predominantly adsorb on the water/oil interface so as to minimize the energy of the system. The analysis of the combination of the two fractions indicates that the interfacial tensions of the resin-asphaltene mixtures is between that of asphaltenes and resins alone. Apparently, both resins and asphaltenes adsorb on the water/oil interface roughly in proportion to their bulk phase composition. We also observe a linear decrease in the interfacial tension of asphaltenes and resin mixtures along a measured range of 55

concentrations (Fig. 4.2-4.6). Hence, the interfacial composition appears invariant at a given asphaltene: resin ratio. The linearity also indicates that there is no micellization in the asphaltene-resin mixtures.

An estimate of asphaltene and resin composition on the interface can be made given these assumptions:

- 1. Asphaltenes and resins have the same surface average area per molecule in their mixtures as asphaltenes and resins alone.
- 2. Heptane and toluene do not adsorb on the interface
- 3. The area fraction of the asphaltenes,  $\theta_A$ , is directly proportional to the mass fraction of the asphaltenes.

Then the asphaltene fractional surface coverage,  $\theta_A$ , can be found from a material balance on the interface:

$$\theta_A = \frac{A_{mix} - A_R}{A_A - A_R} \tag{4.4}$$

Where  $A_A$  and  $A_R$  are the average interfacial area of asphaltene and resin molecules, respectively, and  $A_{mix}$  is the interfacial molecular area in asphaltene-resin mixtures. The results are illustrated graphically in Figure 4.9 which shows the mass fraction occupied by asphaltenes for various heptol systems versus the fractional asphaltene concentration in the continuous phase,  $X_A$ , where:



Figure 4.9 Relationship of interfacial composition to bulk phase composition for Athabasca asphaltenes and resins in heptol.

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$$X_{\mathcal{A}} = \frac{C_{\mathcal{A}}}{C_{\mathcal{A}} + C_{\mathcal{R}}}$$
(4.5)

Figure 4.9 indicates that both resins and asphaltenes adsorb on the water/oil interface. At intermediate  $X_{A}$ , the interfacial composition is almost proportional to the bulk phase composition. At  $X_A$  below 0.3, the resins dominate the interface. However, when  $X_A$  exceeds 0.5 asphaltenes predominantly adsorb on the interface (except in heptol (50 vol% toluene)). This result contradicts the expectation that resins will dominate the interface and it suggests that a mechanism other than minimization of IFT controls the interfacial composition. One possibility is that asphaltenes cross-link on the interface and bind each other in place preventing resins from replacing the asphaltenes on the interface. Asphaltenes do not dominate in heptol (50 vol% toluene) possibly because the difference between asphaltene and resin interfacial tensions is greatest in this solvent (Tables 4.4- 4.5). The driving force to minimize interfacial energy may be sufficient to overcome the tendency of asphaltenes to cross-link and dominate the interface.

## 4.6 COMPARISON WITH COLD LAKE ASPHALTENES AND RESINS

Interfacial tension measurements were also made for the Cold Lake asphaltenes, resins and their mixtures dissolved in heptol (50 vol% toluene) and toluene. The results are presented in Figures 4.10-4.11. Again, the linearity in the plots of interfacial tension versus log concentration



Figure 4.10 Interfacial tension of Cold Lake asphaltenes, resins and asphaltene/resin mixtures in heptol (50 vol% toluene) over water



Figure 4.11 Interfacial tension of Cold Lake asphaltenes, resins and asphaltene/resin mixtures in toluene over water

indicates no evidence of micelle formation for all range of asphaltene/resin concentrations in all heptol systems.

The calculated surface coverages,  $\Gamma'$ , of asphaltenes, resins and asphaltene-resin mixtures, the calculated interfacial area per molecule, A, and molar masses (Tables 4.8-4.9), demonstrate the similarity between the Cold Lake and the Athabasca fractions. As shown in Figure 4.12, the plot of the mass fractions of asphaltenes versus fraction of the asphaltene concentration in the continuous phase follows the same trend for the Cold Lake asphaltenes. The observed similarities suggest that it may be possible to apply the results for the Athabasca bitumens to other Western Canadian bitumens.

## 4.7 APPLICABILITY OF THE INTERFACIAL TENSION STUDIES TO EMULSION STABILITY

The resin and asphaltene composition on the water/oil interface determined by interfacial tension experiments indicates that resins are present on the interface in all cases. However, as will be discussed in Chapter 5, measurements of the emulsion interfacial composition show that no resins are present on the water/oil interface, except at very high resin concentrations

The linearity in the plots of the interfacial tension versus log concentration of the asphaltene/resin mixtures suggests that the composition on the interface is the same at all

	Toluene			Heptol (50 vol% Toluene)		
	Slope (mN/m)	Г (10 <sup>-6</sup> mol/m <sup>2</sup> )	A (nm <sup>2</sup> )	Slope (mN/m)	Г (10 <sup>-6</sup> mol/m <sup>2</sup> )	A (nm <sup>2</sup> )
		Co	ld Lake			
Asphaltenes	-1.49	0.60	2.76	-2.21	0.89	1.86
1:3 R:A	-1.53	0.61	2.70	-2.80	1.13	1.47
1:1 R:A	-1.60	0.65	2.57	-2.89	1.17	1. <b>42</b>
3:1 R:A	-1.99	0.80	2.07	-3.73	1.50	1.10
Resins	-2.01	0.81	2.05	-4.10	1.65	1.00
		Ath	abasca			
Asphaltenes	-1.45	0.58	2.84	-2.15	0.87	1.91
1:3 R:A	-1.46	0.60	2.82	-2.57	1.04	1.60
1:1 R:A	-1.51	0.61	2.72	-2.80	1.13	1.47
3:1 R:A	-1.87	0.76	2.20	-3.71	1.50	1.11
Resins	-1.97	0.80	2.09	-4.28	1.73	0. <b>96</b>

Table 4.8 Measured Slopes and Calculated Molecular Dimension of the Cold Lake and Athabasca Asphaltenes, Resins, and Asphaltene/Resin Mixtures in Toluene and Heptol (50 vol% toluene)

Table 4.9 Calculated Molar Masses of the Cold Lake and Athabasca Asphaltenes and Resins in Toluene and Heptol (50 vol% Toluene)

Heptol Composition	Molar Mass (g/mol)			
Asphaltenes	Cold Lake	Athabasca		
Toluene	2490	2600		
Heptol (50 vol% toluene)	1370	1430		
Resins	Cold Lake	Athabasca		
Toluene	1590	1640		
Heptol (50 vol% toluene)	540	510		



Figure 4.12 Relationship of interfacial composition to bulk phase composition for Cold Lake and Athabasca asphaltenes and resins in toluene and heptol (50 vol% toluene)

measured concentrations of asphaltenes and resins in the bulk phase and that it depends on the asphaltene/resin ratio in the bulk phase. However, the emulsion experiments indicated that the interfacial composition changes depending on the concentration of resins in the continuous phase, rather than the asphaltene/resin ratio.

This discrepancy could be explained by the difference in the state of water/oil interfaces in emulsion phase and in interfacial tension apparatus. The interfacial tension measurements are taken on a static or expanding interface. In the emulsion under investigation, the interface contracts as coalescence occurs. It is known that asphaltenes are able to interact with each other and form aggregates. Therefore, it is possible that asphaltene molecules cross-link when they adsorb on the water/oil interface. It is believed that resin molecules are not able to interact and cross-link with each other. Therefore, when the interface contracts, independent resin molecules may be ejected from the water/oil interface and cross-linked asphaltenes remain.

## **4.8 CHAPTER SUMMARY**

Interfacial tension measurements indicate that while both asphaltenes and resins are surface active and adsorb on the water/oil interface; resins exhibit higher surface activity than do asphaltenes.

A comparison of the interfacial tension between asphaltenes and solids-free asphaltenes shows that solids do not affect adsorption of asphaltenes on the water/oil interface.

The interfacial tension measurements show no evidence of micelle formation for asphaltenes, resins or their mixtures.

The addition of heptane to a mixture of toluene and asphaltenes or resins causes a decrease in the average interfacial area of both asphaltene and resin molecules. The decrease in area can be explained either by adsorption of smaller molecules in the solvent containing more heptane or by a change in configuration of asphaltenes and resins on the interface with the addition of heptane.

The interfacial tensions of resin-asphaltene mixtures indicate that both asphaltenes and resins are present on the interface, although asphaltenes dominate at medium or high asphaltene/resin ratios. As will be discussed later, the interfacial tension results for asphaltene/resins mixtures may not be applicable to emulsions, because IFT measurements involve a static or expanding interface whereas emulsions have contracting interfaces.

## **CHAPTER 5**

## ROLE OF ASPHALTENES, RESINS AND SOLIDS IN WATER-IN-HEPTOL EMULSION STABILIZATION

## **5.1 INTRODUCTION**

The objective of the research presented in Chapter 5 is to investigate what role asphaltenes, resins and solid particles play in stabilizing emulsions. Their role is examined by measuring the interfacial composition and stability of model emulsions composed of the mixtures of asphaltene-solids, resins and solids-free asphaltenes of various composition in toluene/heptol solutions.

While the primary focus of this work is on the role of asphaltenes and resins, native solids must be accounted for because they are often associated with asphaltenes and can affect emulsion stability. Therefore, the stability of emulsions prepared with solids-free asphaltenes or asphaltene-solids is compared.

The main experiments deal with asphaltenes. The mass of the adsorbed asphaltenes is measured at different asphaltene concentrations in the continuous phase and adsorption isotherms of asphaltenes on the emulsion interface are constructed. The effect of the solvent on the stabilization of emulsions by asphaltenes is also examined. The change in the amount of adsorbed asphaltenes and emulsion stability with a change in solvent reveals some details on the asphaltene phase behavior on the emulsion interface. Finally, the role of resins in stabilizing emulsions is considered. The stability and adsorption isotherms of emulsion prepared with various asphaltene/resin ratios are compared with the one obtained for pure asphaltenes.

## **5.2 ROLE OF SOLIDS**

It is important to recognize that asphaltenes precipitated from bitumen contain some other insoluble material. This material, here referred to as "solids", can contain sand, clay, silica and organic particles (Menon et al., 1988; Yan et al., 1995). The recent studies of Yan et al. (1999) demonstrated that solids play a significant role in stabilizing water-in-crude oil emulsions. If solids increase emulsion stability, their effect can overshadow the stabilization properties of asphaltenes and resins in crude oil emulsions. Yan et al.'s results also revealed that the role which solids played in stabilizing emulsions is affected by the size of the solids. Therefore in the present study, it was necessary to assess the role of solids and the solid particle size on model emulsion stability.

In order to investigate the role of solids and the effect of their size on emulsion stability, model water-in-heptol emulsions containing asphaltene-solids (AS), asphaltenes with only coarse solids removed (ACS) and solids-free asphaltenes (AFS) were prepared and their stability compared. Recall from Chapter 3 that ACS are obtained by removing "coarse" solids with a diameter greater than 1  $\mu$ m by centrifuging. AFS are obtained by removing "fine" solids using either by precipitation

with asphaltenes or filtration through 0.5-µm porosity filter paper. These two methods also remove "coarse" solids. Hence, asphaltenes obtained this way are termed "solids-free".

The role of solids can be investigated by comparing the stability of emulsions prepared with and without solids. For this comparison, all of the emulsions were prepared with an initial concentration of 5 kg/m<sup>3</sup> asphaltene material in the hydrocarbon phase. The hydrocarbon phase consisted of heptol containing 50 vol% toluene. In order to compare emulsion stability, the same standard stability test (described in Chapter 3) was performed with these emulsions. The percent of resolved water was measured for all emulsions at a destabilization time of 6 hours. The results from this study are presented in Figure 5.1(a).

As shown in Figure 5.1 (a), for the emulsion prepared from ACS, approximately 10 vol% of water was resolved after 6 hours of destabilization. This stability is very similar to the stability of emulsions prepared from AS, in which about 6 vol% of water was resolved. The emulsion prepared from AFS in which fine solids were removed by filtration has approximately 50% free water resolution in 6 hours. This indicates that this last emulsion is much less stable than emulsion prepared with AS and ACF. This comparison clearly illustrates that the effectiveness of solids in stabilizing water-inheptol emulsions depends on their size. According to these experiments, fine solids in a range of 0.5-1  $\mu$ m in diameter significantly increase emulsion stability. It should be

also noted that the filter may capture solid particles smaller than 0.5  $\mu$ m. Therefore, we can only conclude that particles less that 1  $\mu$ m effectively stabilize emulsions. Similar results were obtained by Yan et al., (1999) as shown in Figure 5.1(b). In their study of water-in-diluted bitumen emulsions, it was shown that solids larger than 8  $\mu$ m were unable to stabilize emulsions, while fine solids in a range of 0.22–8  $\mu$ m in diameter effectively stabilized these emulsions.

The third type of solids-free emulsions was prepared from AFS in which fine solids were removed by precipitation of a small fraction of the asphaltenes. The stability tests of emulsions prepared from these asphaltenes resulted in approximately 50 vol % of water resolution after 6 hours (Fig. 5.1(a)). This stability is similar to the stability of emulsion prepared with 0.5- $\mu$ m filtered asphaltenes. This indicates that the precipitation of asphaltenes results in fine solids removal from crude oil systems. However, it should be noted that by removing solids by precipitation method, we also remove 2% of the asphaltenes. The similarity in stability of emulsions prepared with 0.5- $\mu$ m filtered and precipitated solids-free asphaltenes suggests that this small asphaltene fraction does not affect emulsion stability. It is very time consuming to extract significant quantities of 0.5- $\mu$  m filtered asphaltenes. Therefore, in the present research, the solids-free emulsions were prepared with the solids-free asphaltenes obtained by the precipitation method rather than by the filtration method.



Figure 5.1 (a) Effect of solids in stabilizing model water-in-heptol (50 vol% toluene) emulsions ( $\phi_w=0.40$ ;  $C_A^0=5$  kg/m<sup>3</sup>; destabilization time = 6 hours)



Figure 5.1 (b) Effect of solids in stabilizing water-in-diluted bitumen emulsions (Yan et al., 1999)

As stated above, solids-free emulsions are much less stable than emulsions with solids. When determining the asphaltene and resin surface coverage it was necessary to work with stable emulsions. Therefore, the majority of the experiments were conducted with emulsions made of asphaltenes containing solids. The results of these experiments were later compared with solids-free samples. The results will be discussed in next few sections. Note that, in the subsequent sections of this thesis, asphaltenes containing solids will be referred to as "asphaltenes", unless otherwise noted.

As indicated by the interfacial tension results of asphaltene-solids and solids-free asphaltenes in Chapter 4, the presence of solids does not affect the adsorption of asphaltenes on the water/oil interface. To confirm if this is true in emulsion interfaces, a series of emulsion stability tests were conducted with emulsions of the same composition containing either asphaltene-solids or solids-free asphaltenes. As will be discussed in the next sections, the results of these tests indicated that the presence of solids does not effect the adsorption of asphaltenes and resins on the interface, but it may misrepresent the role of asphaltenes and resins in emulsion stabilization.

### **5.3 ROLE OF ASPHALTENES**

Numerous studies suggest that asphaltenes are able to stabilize water-in-oil emulsions by adsorbing on the water/oil emulsion interface and creating a rigid film which prevents drop coalescence (McLean et al., 1997, Ese et al., 1998, Yarranton, 1997). However, as was described in Chapter 2, the composition and structure of the interfacial film formed by asphaltenes is still unknown. It is proposed that asphaltenes may adsorb on the interface in the form of colloidal aggregates, or as monolayer or multilayer of molecules. In addition, asphaltenes may adsorb on the emulsion interface in several different forms, depending on asphaltene concentration or solvent composition.

One of the ways to determine how asphaltenes adsorb on the interface is to measure the mass of the asphaltenes on the emulsion interface. In the current research, the amount of asphaltenes adsorbed on the emulsion interface,  $m_i$ , was determined from gravimetric analysis, as described in Chapter 3. The resulting adsorption isotherms relate the mass of adsorbed asphaltenes in model water-in-heptol emulsions to concentration in the continuous phase. The asphaltene concentrations in the continuous phase ranged from 2 to 50 kg/m<sup>3</sup>. To further understand the role of asphaltene in emulsion stabilization, the mass of asphaltenes on the emulsion interface was also related to stability of the model emulsions of the same composition. The role of solvent composition was investigated by performing gravimetric analysis and stability tests with model emulsions in which heptol contained 50 vol% and 75 vol% toluene.

### 5.3.1 Asphaltene Adsorption on the Emulsion Interface

The adsorption isotherm of asphaltenes in the model water-in-heptol emulsions (50 vol% toluene) emulsion is shown in Figure 5.2 (a). The adsorption isotherm is plotted in terms of asphaltene mass per area,  $\Gamma_A$ , of the emulsion interface versus initial asphaltene concentration in the bulk phase,  $C_A^{0}$ . The adsorption isotherm has two



Figure 5.2(a) Surface coverage of Athabasca asphaltenes on water-in-heptol (50 vol% toluene) emulsion interface as a function of initial asphaltene cocentration

distinct parts. At  $C_A^0$  below 4 kg/m<sup>3</sup>, the asphaltene surface coverage is constant and equal to approximately 4 mg/m<sup>2</sup>. Above this concentration  $\Gamma_A$  follows the form of a Langmuir adsorption isotherm. Surface coverage sharply increases until  $C_A^0$  is about 40 kg/m<sup>3</sup> and then plateaus reaching its limiting value of approximately 11 mg/m<sup>2</sup>.

This shape in the adsorption isotherm can be explained as the follows. The surface area (drop size distribution) in emulsions is determined by the amount of asphaltenes and/or mixing conditions. At low asphaltene concentrations there are insufficient asphaltenes to cover the surface area of the approximately 10  $\mu$ m droplets generated by the homogenizer. Yarranton et al., (2000) showed that these emulsions coalesce until monolayer surface coverage is achieved. As more asphaltenes are added, more of the surface area of the 10  $\mu$ m droplets is covered by asphaltenes and less coalescence occurs. As a result the Sauter mean diameter decreases as shown in Figure 5.2 (b). At higher asphaltene concentrations, (above 4 kg/m<sup>3</sup>), the drop size distribution becomes governed solely by mixing conditions. In other words, there is no coalescence and the Sauter mean diameter becomes constant as indicated in Figures 5.2 (b). Therefore, above C<sub>A</sub><sup>0</sup> of 4 kg/m<sup>3</sup> the interfacial area is fixed. With a fixed interface, asphaltenes are able to adsorb in greater amounts as shown in Figure 5.2(a).

An adsorption isotherm such as the one shown in Figure 5.2(a) is more meaningfully plotted against *equilibrium* asphaltene concentration in the bulk phase. This



Figure 5.2 (b) Sauter mean diameter of Athabasca asphaltenes in water-in-heptol (50 vol% toluene) emulsions ( $\phi_w$ =0.40)

equilibrium asphaltene concentration is calculated by rearranging equation 3.9 in Chapter 3:

$$C_{A}^{eq} = C_{A}^{0} \left(1 - \frac{m_{I}}{m_{e}}\right)$$
(5.1)

As can be seen in Figure 5.3, all the data now collapses into a smooth curve.

The adsorption isotherm of asphaltenes is in a good agreement with the results obtained by Ese at el., (1998) The asphaltenes surface coverage measured by the Langmuir-Blodgett film technique ranged from 6 to 8 mg/m<sup>2</sup> at  $C_A^0$  equal from 1 to 8 kg/m<sup>3</sup>. Ese at el. also observed an increase in the surface coverage with an increase in the bulk asphaltene concentration.

An increase in the asphaltene mass on the interface can be explained in three ways. The first explanation assumes that at higher bulk phase concentration, asphaltene molecules undergo a conformation change allowing more compact packing of molecules on the interface. This leads to a higher surface coverage. The observed plateau at high  $C_A^{eq}$  indicates that asphaltenes achieve the maximum packing on the interface. The build-up of interfacial material may possibly create a stronger and more rigid interfacial barrier. Therefore, it can be expected that the emulsions prepared with the higher asphaltene concentration would be more stable. This can be verified by



Figure 5.3 Adsorption isotherm of Athabasca asphaltenes on water-in-heptol (50 vol% toluene) emulsion interface

comparing the stability of emulsions (percent of the resolved water) prepared from different asphaltene concentrations in the continuous phase.

The second possibility is that larger asphaltene molecules adsorb preferentially. At low concentration, there are insufficient large molecules to saturate the interface. At higher concentration, the interface becomes saturated with large molecules and the mass surface coverage plateaus.

The third possibility assumes that asphaltenes form a multilayer on the interface. This concept, however, is not immediately acceptable, because the observed adsorption isotherm reaches a marked plateau, or tends towards a limiting value. Moreover, we observe no inflection point except at low asphaltene concentrations, which would indicate the formation of the first or any subsequent layer. Some researches, however, in studying polymer adsorption, indicate that the absence of a point of inflection does not necessarily exclude the possibility of multiplayer formation (Kipling, 1965). However, the stability results presented later suggest that the increase in mass is due to conformation change rather than multilayer formation or selective adsorption.

#### 5.3.2 Correlation between Adsorption Isotherm and Emulsion Stability

The stability of water-in-heptol (50 vol% toluene) emulsions as a function of  $C_A^{eq}$  is illustrated in Figure 5.4(a). These results were obtained at a destabilization time of 16 hours. Figure 5.4(a) shows that the stability of emulsions increases as the asphaltene concentration in the continuous phase increases from about 2 to 10 kg/m<sup>3</sup>.



Figure 5.4 (a) Emulsion stability of Athabasca asphaltenes in water-inheptol (50 vol% toluene) emulsions ( $\phi_w$ =0.40; destabilization time=16 hours)

With the further addition of asphaltenes in the continuous phase, the stability changes only slightly. The observed increase in emulsion stability with an increase of the asphaltene concentration has three possible explanations.

The first possibility is that the observed increase in emulsion stability may be related to a decrease in the drop size with an increase in  $C_A^{eq}$ . As stated in Chapter 2, smaller drops coalesce less readily and emulsions containing drops of lesser diameter are more stable. As seen from Figure 5.4(b), the Sauter mean diameter of emulsions decreases with an increase in asphaltene concentration. The comparison of the Sauter mean diameter and emulsion stability in Figure 5.4 (b) shows a very good correlation between these two trends. At  $C_A^{eq}$  less than 5 kg/m<sup>3</sup>, the emulsion stability increases as ds decreases. At higher asphaltene concentrations both the Sauter mean diameter and the emulsion stability changes only slightly. This correlation shows that an increase in emulsion stability at low asphaltene concentrations may be attributed to the change in the mean emulsion drop size.

A second possibility is that the increase in emulsion stability is explained by an increase of the asphaltene mass on the interface. As was demonstrated by the asphaltene adsorption isotherm in Figure 5.3, the asphaltene surface coverage,  $\Gamma_A$ , increases with an increase of  $C_A^{oq}$ . The higher surface coverage may create a stronger interfacial barrier and increase emulsion stability. The comparison of the asphaltene



Figure 5.4 (b) Correlation between the Sauter mean diameter and emulsion stability of Athabasca asphaltenes in water-in-heptol (50 vol% toluene) emulsions ( $\phi_w$ =0.40; destabilization time=16 hours)

adsorption isotherm and emulsion stability is shown in Figure 5.4 (c). It's clearly seen that as  $\Gamma_A$  increases emulsion stability also increases. However, emulsion stability increases until  $C_A^{eq}$  reaches concentrations of 10-15 kg/m<sup>3</sup> while  $\Gamma_A$  continues to increase until double that concentration. Also note that, as the asphaltene concentration increases from 1 to 5 kg/m<sup>3</sup>, emulsion stability increases by a factor 3 whereas  $\Gamma_A$ increases only by about 50% (from 4 to 6 mg/m<sup>2</sup>). This suggests that at low asphaltene concentrations the increase in emulsion stability is not related to  $\Gamma_A$ . At higher  $C_A^{eq}$ (above 5 kg/m<sup>3</sup>) an increase in stability may be caused either by the accumulation of the asphaltenes on the interface or due to reduction in the emulsion drop size.

The third possible explanation for the increase in emulsion stability involves the fine solid particles associated with the asphaltenes. As discussed in the previous section, these particles are capable of stabilizing emulsions. An increase in the asphaltene concentration in the continuous phase also leads to an increase in solids content in the continuous phase. Hence, the growth in the emulsion stability can also be caused by an increase in the concentration of the fine solid particles in the emulsion. To isolate the role of solids, adsorption isotherm, drop size distribution and stability were measured for emulsions containing solids-free asphaltenes. This will be discussed in the next section.



Figure 5.4 (c) Correlation between adsorption isotherm and emulsion stability of Athabasca asphaltenes in water-in-heptol (50 vol% toluene) emulsions ( $\phi_w$ =0.40; destabilization time= 16 hours)
5.3.3 Adsorption Isotherms and Emulsion Stability of Solids-Free Asphaltenes The comparison of the adsorption isotherms and emulsion stability of solids-free asphaltenes and asphaltene-solids in heptol (50 vol% toluene) is presented in Figure 5.5. As this figure indicates, the adsorption isotherm of solids-free asphaltenes is almost identical to that of asphaltenes containing solids. This suggests that solids do not affect asphaltene adsorption. Recall from Chapter 4 that the interfacial tensions of asphaltene-solids and solids-free asphaltenes also showed that solids do not interfere with the adsorption of asphaltenes on the water/oil interface. The measurement of the Sauter mean diameter of water-in-heptol emulsions (50 vol% toluene) stabilized by solids-free asphaltenes also indicated that asphaltene-solids and solids-free emulsions have an identical drop sizes. This again supports the argument that solids do not affect the asphaltene adsorption. This may indicate that solids do not stabilize emulsions by adsorbing on the emulsion interface. Possibly they are trapped between emulsion droplets, thus preventing coalescence.

Although the adsorption isotherms and the Sauter mean diameters for solids and solidsfree asphaltenes were nearly identical, the trends in stability for these two types of emulsions have a significant difference. With an increase in the asphaltene concentration in the continuous phase from 1 to 5 kg/m<sup>3</sup>, the stability of both types of emulsions increases. However, above 5 kg/m<sup>3</sup>, the emulsions containing solids-free asphaltenes exhibit a reduction in stability, while the stability of asphaltene-solids emulsions increases. The observed maximum in emulsion stability of solids-free emulsions indicates that emulsion stability is governed by two opposing mechanisms.



Figure 5.5 Effect of removing solids on the adsorption isotherm and emulsion stability of Athabasca asphaltenes in water-in-heptol (50 vol% toluene) emulsions ( $\phi_w$ =0.40; destabilization time=4 hours)

From these observations it follows that the initial sharp increase in emulsion stability at low  $C_A^{eq}$  (observed for both types of emulsions) is due to the reduction of drop sizes in the emulsions. An increase of the stability of asphaltene-solids emulsions at  $C_A^{eq} > 5$  kg/m<sup>3</sup> is due to an increase in the amount of solids particles. The stability trend of the solids-free sample indicates the true effect of the asphaltenes without the overshadowing effect of the solids.

In summary, the data for the solids-free emulsions demonstrate that while there is an increase in the asphaltene surface coverage, there is a reduction in the emulsion stability with an increase in  $C_A^{eq}$  above 5 kg/m<sup>3</sup>. This unexpected behavior contradicts the argument that accumulation of the asphaltenes on the interface would lead to the creation of a stronger, thicker interfacial barrier, that increases emulsion stability. This behavior is difficult to explain if we assume that asphaltenes form a multilayer on the interface at high bulk phase concentrations. It is also difficult to explain if larger molecules saturate the interface at high concentration. In either case, a thicker more rigid interface is expected and hence greater stability.

Although it is not clear why this behavior is observed, one possible interpretation is that the rheology of the interface changes with a change in molecular conformation. At low asphaltene concentrations and consequently low surface coverage molecules are spread out on the interface. In this position, molecules may have many points of attachment on the interface, as shown in Figure 5.6 (a). At high asphaltene concentrations, molecules may change their alignment on the interface so that they become attached at



Figure 5.6 Possible configurations of asphaltene molecules on the emulsion interface

one or only a few points per molecule. In the latter arrangement much more material can be attached to a given surface area (Figure 5.6 (b)). When molecules are attached to the interface at only one point, they are more extended into the continuous phase and may be more mobile than when attached at several points. This more mobile interface may present a reduced barrier to coalescence. When molecules attached at several sites, the interface may be more rigid, and the emulsion more stable. Similar observations were made in studies being currently conducted at the University of Alberta by Taylor (2000). His measurements of the film properties formed by asphaltenes indicate that the film was rigid at  $C_A^{eq}$  below 15 kg/m<sup>3</sup> and fluid above this concentration.

# 5.3.4 Effect of the Solvent Composition on the Asphaltene Adsorption and Emulsion Stability

To investigate the effect of solvent composition on the interfacial adsorption of asphaltenes, gravimetric analysis, drop size measurements and stability tests were performed with water-in-heptol (75 vol% toluene) emulsions ranging from a  $C_A^0$  of 2 to 40 kg/m<sup>3</sup>. Figure 5.7 (a) compares the adsorption isotherms and emulsion stability curves obtained for these emulsions to those results obtained for water-in-heptol (50 vol% toluene) emulsion. With a better solvent (heptol (75 vol% toluene)), the asphaltene adsorption is less for the whole range of measured concentrations. The decrease in the asphaltene surface coverage with an increase in the heptane content in the solvent was also observed by Ese et al. (1998) from the Langmuir-Blodget film experiments. The comparison of the resolved water shows that the stability of water-in-heptol (75 vol% toluene) is also less for all measured range of asphaltenes

concentrations. However, both the adsorption and the stability curves of these two emulsion types follow the same trend.

Figure 5.7 (b) compares the Sauter mean diameter of these two types of emulsions. The comparison indicates that at  $C_A^{eq}$  less than 5-10 kg/m<sup>3</sup> the Sauter mean diameter of water-in-heptol (75 vol% toluene) emulsion is higher than in emulsion made with heptol (50 vol% toluene). Above this  $C_A^{eq}$  diameters of both emulsions are almost identical. Once again, at low asphaltene concentrations, emulsion stability appears to be governed by emulsion drop sizes. The formation of larger droplets in heptol (75 vol% toluene) leads to less stable emulsions.

At higher asphaltene concentration, the further reduction in stability of emulsions containing 75 vol% toluene may be related to the change of the asphaltene adsorption on the emulsion interface. Both asphaltene surface coverage and emulsion stability decreases in a better solvent (75 vol% toluene). The most plausible explanation for these findings is that in a better solvent asphaltene molecules are more solvated. The mechanism of a solvent action can be better explained by analogy with a polymer solution. In polymer solutions, the solute is often described as a random coil in which the domain of the molecule contains both polymer segments and solvent molecules. The energy of the interactions between solvent molecules and polymer chain segments determines the degree of solvent embodiment in the molecule domain and the spatial extension of the polymer molecules. A solvent in which solvent-solute interactions are



(\$\$\phi\_w=0.40; destabilization time=16 hours) isotherm and emulsion stability of Athabasca asphaltene emulsions Figure 5.7 (a) Effect of solvent composition on the adsorption



Figure 5.7 (b) Effect of solvent composition on the Sauter mean diameter of Athabasca asphaltenes in water-in-heptol emulsions ( $\phi_w$ =0.40)

favored, is called a "good solvent". A good solvent swells the coil dimensions. In a "poor" solvent solute-solute contacts are favored and the coils shrink (Hiemenz et al., 1997).

An increase in the toluene content in heptol increases the "goodness" of the solvent. Asphaltene molecules become solvated to a higher degree. The solvated molecules occupy a larger area and are more loosely packed on the interface, as shown in Figure 5.6 (c). Recall that the interfacial data of Chapter 4 also showed an increase in the surface area of asphaltene molecules with an increase in the toluene content. The looser packing of asphaltenes on the interface explains the decrease in mass surface coverage.

Furthermore, in a better solvent, the strength of interactions between asphaltene and solvent molecules is more than between two asphaltene molecules. Therefore, in a better solvent, asphaltenes may be less cross-linked with each other, making the interface less rigid and the asphaltenes more mobile. Hence, emulsions stabilized by asphaltenes are less stable at higher toluene: heptol ratios. Similar results were observed in the case of polymer adsorption. It was determined that polymer surface coverage is less and polymer desertion is easier in a better solvent (Kipling, 1965).

To further investigate the effect of solvent composition, asphaltene adsorption and stability experiments should be done with other heptane/toluene ratios. However, there are two problems with this. On one hand, an increase in toluene content makes emulsion very unstable. On the other hand, at a toluene content below 50 vol% asphaltenes precipitate. Therefore, it was impossible to perform a gravimetric analysis on emulsions with other heptol compositions.

Despite these limitations for the gravimetric analysis, the role of solvent content was further investigated by conducting stability tests for emulsions prepared with various heptol compositions. All stability tests were conducted where  $C_A^{0}$  was equal to 5 kg/m<sup>3</sup>. The amount of resolved water was measured at a destabilization time 6 hours for all emulsions. These tests were performed for both solids and solids-free asphaltene emulsions. The results of these tests are illustrated in Figure 5.8, where the percentage of resolved water in emulsion is plotted against the volume percent toluene in the heptol. Figure 5.8 clearly shows that the heptol composition significantly affects emulsion stability. The comparison of solids-free emulsions and emulsions containing solids indicates that stability curves of these two types of emulsions follows the same trend.

The plots are characterized by a maximum in stability at around 50 vol % toluene in the solvent. The maximum stability indicates that the effect of solvent composition is governed by two opposing trends. The right side of the curve shows that an increase in the toluene content destabilizes emulsions. This again can be explained by the solvating effect of the "good" solvent, as described previously. The left side of the curve shows that a decrease in stability occurs when there is an increase in the heptane content in the solvent. This decrease in stability is caused by the precipitation of



Figure 5.8 Effect of solvent composition on the stability of water-inheptol emulsions containing Athabasca asphaltene-solids and solids-free asphaltenes ( $\phi_w$ =0.40; C<sub>A</sub><sup>0</sup>=5 kg/m3; destabilization time= 6 hours)

asphaltenes from the heptol containing more than 50 vol% of heptane. Yarranton et al. (1997, 1999) showed that the precipitated asphaltenes are not able to adsorb on the water/oil interface. Hence, when asphaltenes precipitate, the amount of asphaltenes which are able to adsorb on the interface decreases. This reduces emulsion stability.

The precipitation of asphaltenes explains why for heptol containing less than 40 vol% toluene the stability of solids-free emulsions is the same as in emulsions containing solids, while at heptol with more than 40 vol% of toluene the stability of solids-free emulsions is less than in emulsions containing solids. As discussed previously, solids-free emulsions are less stable than with solids. However, asphaltenes precipitated from solution act as a collector of solids, as shown in section 5.1. Therefore with heptol containing about 40 vol% toluene, solids are removed from solution and both systems are effectively solids-free.

The observed effect of solvent composition on emulsion stability is in a good agreement with the results obtained by McLean and Kilpatrick, (1998) for asphaltenes derived from Arabian and Venezuelan crude oils. The comparison of their data and the present work is presented in Figure 5.9.

## 5.3.5 Characterization of the Adsorbed Asphaltenes

The Athabasca asphaltenes isolated from the emulsion phase were characterized by elemental analysis and compared with the original Athabasca asphaltenes used for preparation of the model oil emulsions. The elemental analysis of the asphaltenes was



**Volume Percent Toluene in Solvent Mixture** 

Figure 5.9 The correlation of emulsion stability to the fraction of the interfacially active asphaltenes available to adsorb on the interface at various heptol compositions ( $\phi_w$ =0.40; C<sub>A</sub><sup>0</sup>=5 kg/m3; destabilization time= 6 hours)

conducted at analytical laboratory at Syncrude Canada. The results are presented in Table 5.1

The comparison of heteroatom content in the two types of asphaltenes reveals that interfacially active asphaltenes contain more sulfur and oxygen heteroatom groups, and therefore they are more polar. The H/C shows that the asphaltenes from the emulsion phase are more aromatic and/or condensed. The result suggests that those asphaltenes with the most hydrophobic groups or greater hydrophilic/hydrophobic contrast are the most surface active.

The results are in a good agreement with the data obtained by McLean and Kilpatric, (1997). Their data are also presented for comparison in Table 5.1.

# 5.3.6 Comparison of Athabasca and Cold Lake Asphaltenes

The adsorption of Cold Lake asphaltenes and emulsion stability was also investigated. The gravimetric analysis and stability tests were performed for asphaltene dissolved in heptol (50 vol% toluene) in a concentration range of 2 to 50 kg/m<sup>3</sup>. The obtained results are compared with Athabasca asphaltenes.

Figure 5.10 presents the adsorption isotherms of Athabasca and Cold Lake asphaltenes. The figure indicates that the adsorption of Cold Lake asphaltenes is less than that of Athabasca asphaltenes. However, the shape of the adsorption isotherm is identical.

	Present Work		Literature (McLean and Kilpatric, 1997)		
	Original asphaltenes (Athabasca)	Emulsion phase	Original asphaltenes (Arab Heavy)	Emulsion phase	Continuous phase
Carbon (wt%)	76.9	76.1	-		
Hydrogen (wt%)	7.77	7.52	-	-	-
Nitrogen (wt%)	1.16	1.14	0.94	0.93	1.01
Sulfur (wt%)	6.70	7.03	7.17	7.21	6.72
Oxygen (wt%)	7.47	8.21	-	-	-
H/C	1.21	1.19	1.11	1.08	1.2
V (ppm)	929	1000	667.6	619.8	520.4
Ni (ppm)	379	404	352.1	430.9	329.9
Al (ppm)	8720	6700	_	-	-
Fe (ppm)	6660	5340	_	-	-
Si (ppm)	12000	9500	-	-	-
Ti (ppm)	1 <b>92</b> 0	1520	_	-	-

Table 5.1 The elemental analysis of original asphaltenes and asphaltenes adsorbed on the emulsion interface

The stability of Athabasca and Cold Lake asphaltene emulsions versus  $C_A^{eq}$  is compared in Figure 5.11. This figure indicates that stability of Cold Lake asphaltene emulsions is much less than in Athabasca asphaltene emulsions. Moreover, above 10 kg/m<sup>3</sup> the emulsions prepared with Cold Lake asphaltenes exhibit a reduction in stability, while the stability of Athabasca asphaltene emulsions increases. However, the trend observed with Cold Lake asphaltenes emulsions is similar to that observed for a



Figure 5.10 Adsorption isotherms of Cold Lake and Athabasca asphaltenes on water-in-heptol (50 vol% toluene) emulsion interface  $(\phi_w = 0.40)$ 

solids-free Athabasca asphaltene emulsions. Recall from Chapter 3, that the solid content in Cold Lake asphaltenes is almost three times less than in Athabasca asphaltenes. Therefore, the discrepancy in emulsion stability can be caused by the low amount of solid particles in Cold Lake asphaltenes.

A more meaningful comparison is on a solid-free basis. The percent resolved water for emulsions stabilized by the Athabasca and Cold Lake solids-free asphaltene versus  $C_A^{eq}$ is compared in Figure 5.11. The stability of the two emulsions is identical. The similarity in stability curves and in adsorption isotherms indicates that Cold Lake and Athabasca asphaltenes exhibit the same general behavior. This was also supported by the interfacial tension measurements discussed earlier in Chapter 4.

## **5.4 ROLE OF RESINS**

As described in Chapter 2, the role of resins in the stabilization of water-in-oil emulsions is unclear. Some researchers indicate that resins alone can act as effective emulsion stabilizers (Bobra et al., 1992). Some evidence suggests that the adsorption of resin/asphaltene aggregates on the emulsion interface makes the most stable emulsions. It has also been shown that resin/asphaltene ratio in the continuous phase is an important factor in crude oil emulsion stability (McLean and Kilpatrick, 1997). However, there is some evidence that the adsorption of resins on the emulsion interface makes in the emulsion interface makes in the emulsion interface makes in the emulsion interface is some evidence that the adsorption of resins on the emulsion interface destabilizes emulsions (Ese at al., 1998; Mouraille et al., 1998; Yan, et al., 1998). In spite of the discrepancies in the literature, the observed data indicates that resins



Figure 5.11 Stability of emulsions containing Athabasca and Cold Lake asphaltenes in heptol (50 vol% toluene) ( $\phi_w$ =0.40; destabilization time=6 hours)

independently or thorough their interactions with asphaltenes play an important role in the stability of water-in-oil emulsions. Therefore, one of the objectives of the current work was to determine the role of resins in the stability of water-in-heptol emulsions, containing asphaltenes.

The methods used in this investigation were similar to the one used in the case of pure asphaltenes, described in the previous section. This investigation was conduced by measuring the interfacial composition and the stability of emulsions prepared with different resin/asphaltene ratios (R:A) in the continuous phase. The model water-in-heptol emulsion used in this study were prepared with R:A ratios in the continuous phase of 1:3, 1:1, and 2:1. The total initial (asphaltene + resin),  $C_{A+R}^{0}$ , concentration in the continuous phase ranged from 2 to 40 kg/m<sup>3</sup>.

### 5.4.1 Stability of Emulsions Containing Asphaltene/Resin Mixtures

The results of stability tests of emulsions containing 1:3, 1:1, and 2:1 R:A ratios in the continuous phase are compared with the stability of emulsions containing only asphaltenes and are plotted in Figure 5.12. To better demonstrate the effect of resins, the percentage of resolved water in the emulsions is plotted against the equilibrium asphaltene concentration in the continuous phase,  $C_a^{eq}$ . In all cases, emulsion stability increases at  $C_A^{eq}$  in a range from 2 to 5 kg/m<sup>3</sup>. Above 5 kg/m<sup>3</sup> we observe that the stability of the emulsions decreases. The initial increase is caused by decreasing the Sauter mean diameter, as previously discussed. The subsequent decrease in stability is partly due to change in the asphaltene configuration, as was discussed in Section 5.2.3.



Figure 5.12 Stability of emulsions containing Athabasca asphaltene/resin mixtures of various composition in heptol (50 vol% toluene) ( $\phi_w$ =0.40; destabilization time=6 hours)

Figure 5.12 indicates that the stability of all the emulsions containing resins is much less than those containing only asphaltenes for the whole range of measured concentrations. Furthermore, the emulsions become less stable as the R:A ratio increases. The observed decrease in emulsion stability could be due to the fact that the addition of resins dilutes the amount of solids in the continuous phase. Recall, that the asphaltenes in these emulsions contain some solids. An emulsion prepared with 1:1 R:A and  $C_{A+R}^0$  of 20 kg/m<sup>3</sup> has half as much asphaltenes, and consequently solids, as an emulsion prepared only with asphaltenes at  $C_A^0$  20 kg/m<sup>3</sup>. However, if solids were the main factor, the stability of emulsions prepared with 1:1 R/A and  $C_{A+R}^0$  of 20 kg/m<sup>3</sup> and emulsions containing only asphaltenes at  $C_A^0$  10 kg/m<sup>3</sup> should be the same. Figure 5.12 shows that the stability of the emulsion containing resins is less than in emulsions prepared with only asphaltenes. Hence, solids cannot be the main factor. The effect of solids dilution can also be tested by conducting the stability tests of solids-free emulsions.

The stability plots of solids-free emulsions prepared with 1:3, 1:1, and 2:1 R:A mixtures dissolved in heptol (50 vol % toluene) are shown in Figure 5.13. This figure indicates that the stability of emulsions containing resins is much less than in emulsions prepared only with solids-free asphaltenes. The stability of the emulsions also decreases with an increase in R:A ratio, similar as observed in Figure 5.12. Hence, it is clear that the emulsion destabilization by resins is independent of the decrease in solid concentration in these emulsions. Of course, in the solids containing emulsions the solids are partly responsible for emulsion stabilization and they may obscure trends.

However, the comparison of the stability plots presented in Figures 5.12 and 5.13 shows that the consistent patterns are emerging in emulsions prepared with and without solids.

One explanation for the decrease in emulsion stability is that resins adsorb on the emulsion interface and displace the asphaltenes. This displacement would change the properties of the emulsion interface leading to emulsion destabilization. This mechanism is consistent with the interfacial tension measurements of resins, described in Chapter 4. It was found that resins decrease interfacial tension more than the asphaltenes and therefore could tend to displace the asphaltenes on the interface. The proposed mechanism can be tested by measuring the interfacial composition of emulsions prepared with resin/asphaltene mixtures in the continuous phase.

Unfortunately, emulsions containing resins are extremely unstable, as was shown in Figures 5.12 and 5.13. It is important that emulsion drops do not rupture during the drop size distribution measurements. In the case of emulsions containing mixtures of resins and asphaltenes, the only stable emulsions contained a 1:3 R:A ratio dissolved in heptol (50 vol % toluene). As shown in Figure 5.14, the drop size distribution of these emulsions didn't change in a two-hour period. In emulsions with higher R:A ratios and in all solids-free emulsions, the rupture of drops was observed during microscopy measurements. Nonetheless, gravimetric measurements were performed for these



Figure 5.13 Emulsion stability of emulsions containing solids free Athabasca resin/asphaltene mixtures ( $\phi_w$ =0.40; destabilization time=4 hours)

emulsions. The measured interfacial compositions for these emulsions can be considered only as a rough estimate. However, some trends can be distinguished from these results and will be discussed below.

# 5.4.2 Adsorption Isotherms of Asphaltenes in Emulsions Containing Asphaltene/Resin Mixtures

Figure 5.15 shows the adsorption isotherms of asphaltenes in emulsions containing 1:3 R:A ratio versus  $C_A^{eq}$  in a range from about 5 to 30 kg/m<sup>3</sup>. The adsorption isotherm of pure asphaltene-solids is also shown for comparison. Figure 5.15 indicates that the asphaltene surface coverage,  $\Gamma_{A_0}$  is less in asphaltene/resins emulsions containing 1:3 R:A than in emulsions prepared with asphaltenes alone for the whole range of  $C_A^{eq}$ . The shapes of the adsorption isotherms are also different. In the asphaltene/resin emulsions  $\Gamma_A$  increases, at  $C_A^{eq}$  from about 5 to 30 kg/m<sup>3</sup>, and decreases above 30 kg/m<sup>3</sup>, while in emulsions containing asphaltenes alone asphaltene surface coverage increases in the whole concentration range. The measurement of the resin mass on the emulsion interface in the asphaltene/resin emulsions indicated that no resins are present on the interface at  $C_A^0$  below 20 kg/m<sup>3</sup>. Only above this concentration the presence of resins is observed. A similar trend was observed in the adsorption isotherms of emulsions at higher R:A ratios. The asphaltene adsorption isotherm in emulsions with 1:1 R:A is shown in Figure 5.15. Recall that due to experimental difficulties this adsorption isotherm indicates only a trend, and not the true interfacial composition. This figure shows that  $\Gamma_A$  increases at  $C_A^{eq}$  from about 5 to 20 kg/m<sup>3</sup>, and decreases



Figure 5.14 Drop size distributions of water-in-heptol (50 vol % toluene) emulsions stabilized by Athabasca asphaltene/resin mixture  $(C_{A+R}^{0} = 20 \text{ kg/m3}; \text{R}:A=1:3; \phi_w=0.40)$ 



Figure 5.15 Adsorption isotherm of Athabasca 1:1 and 1:3 asphaltene/resin mixtures and asphaltenes on water-in-heptol (50 vol% toluene) emulsion interface ( $\phi_w = 0.40$ )

until it reaches 0 at  $C_A^0$  equal 20 kg/m<sup>3</sup>. As in the case of the 1:3 R:A ratio resins were found on the emulsion interface only at  $C_A^0$  above 20 kg/m<sup>3</sup>.

In summary, the emulsion stability trends show a decrease in emulsion stability with an increase in resin concentration in continuous phase. The adsorption isotherm indicates that resins decrease the amount of asphaltenes on the interface. At the same time resins do not adsorb on the emulsion interface, except at high resin concentrations. The observed trends in the emulsion stability and in the adsorption isotherms suggest that resins weaken the interfacial barrier and destabilize emulsions by acting as a good solvent. The effect of solvent "goodness" on the asphaltene adsorption was already discussed in the case of emulsions containing asphaltenes alone in Section 5.3.4. Recall from this section, that an increase in the toluene content in heptol caused a decrease in the asphaltene surface coverage and in the emulsion stability. Similar trends are observed in emulsions containing resins.

It is likely that resin molecules have a closer chemical structure to the structure of asphaltene molecules, than have toluene molecules. Therefore, the resin-asphaltene interactions might be even stronger than toluene-asphaltene interactions and resins might be a better solvent for asphaltenes than toluene. This can explain why resins destabilize emulsions at low concentrations. Also recall, that resins are surface-active and able to adsorb on the water/oil interface. At high resin concentrations, when the asphaltene molecules are highly solvated and their cross-linking is sufficiently weakened, resins, may be able to replace asphaltenes on the interface. Hence, at high resin concentrations asphaltene surface coverage decreases to zero and resins start to dominate the emulsion interface.

### 5.5 CHAPTER SUMMARY

The results presented in this chapter indicate that solids, asphaltenes and resins play an important role in the stabilization of the model water-in-heptol emulsions.

It was found that naturally occurring solids significantly increase emulsion stability. The increased stability was attributed to solids less than 1  $\mu$ m in diameter. These solids were found to precipitate with asphaltenes. Hence, they may obscure the stabilization effect of the asphaltenes in emulsions. This was observed when the stability trends of Athabasca and Cold Lake solids-free and asphaltene-solids were compared. Therefore, the presence of solids should always be considered for asphaltene stabilized emulsions. It was also shown that solids have no affect on the asphaltene adsorption. This can possibly indicate that solids stabilize emulsions not by adsorbing on the interface, but by being trapped between droplets, thus preventing drops coalescence.

The investigation of the interfacial composition of the asphaltene-stabilized emulsion revealed that asphaltenes adsorb on the water/oil emulsion interface. The elemental analysis of the adsorbed asphaltenes indicated that asphaltenes with the most hydrophilic groups or the greatest hydrophobic/hydrophilic contrast preferably adsorb on the emulsion interface.

The asphaltene adsorption isotherm for asphaltene bulk concentrations up to 40 kg/m<sup>3</sup> was constructed. At low concentrations (less than 4 kg/m<sup>3</sup>) asphaltenes appear to form a monolayer on the emulsion interface with a mass surface coverage of about 4 mg/m<sup>2</sup>. At higher concentrations, the surface coverage increases until it reaches a limiting value of about 12 mg/m<sup>2</sup> at concentrations of 10-20 kg/m<sup>3</sup>. It appears that the increasing surface coverage corresponds to the conformation change of asphaltene molecules on the emulsion interface. At higher asphaltene bulk concentration they change the configuration from planar to a more compressed "vertical" state. This configuration allows more compact packing of asphaltene molecules, thus increasing mass surface coverage.

This change in asphaltene configuration also causes emulsion destabilization. It was observed that at asphaltene bulk concentration above 5-10 kg/m<sup>3</sup> the stability of solids-free asphaltene emulsions is reduced. The configuration change of asphaltene molecules from planar to a compressed vertical state reduces the number of sites for attachment to the emulsion interlace. Hence, each molecule may be more easily displaced from the interface and therefore a less rigid interface is formed that is less resistant to coalescence.

It was shown that in a better solvent asphaltene surface coverage is reduced. The results demonstrate that the asphaltene surface coverage is approximately 20% less in the heptol (75 vol% toluene) than in the heptol (50 vol% toluene). Emulsion stability also decreased in better solvents. This can possibly be explained by the "solvating" effect of the good solvent. A good solvent surrounds asphaltene molecules, thus creating looser packing of asphaltenes on the interface, and less rigid interface. Consequently we observe a reduction in the asphaltene surface coverage. In a better solvent the strength of the asphaltene-solvent interactions becomes stronger than the asphaltene-asphaltene interactions. This makes asphaltene molecules more mobile and interface less rigid. This reduces emulsion stability.

In poorer solvents the precipitation of asphaltenes reduced emulsion stability. It was observed that emulsion stability decreased as more asphaltenes precipitated. This indicates that precipitated asphaltenes do not participate in stabilizing emulsions. Precipitation removes asphaltenes available for adsorption on the interface, thus destabilizing emulsions.

In all cases, resin addition decreased emulsion stability. At low resin concentration, they decrease the amount of asphaltenes adsorbed on the interface by acting as a good solvent for the asphaltene molecules. At high resin concentrations (above 20 kg/m<sup>3</sup>) they replace asphaltenes on the interface and significantly reduce emulsion stability.

# **CHAPTER 6**

# **CONCLUSIONS AND RECOMMENDATIONS**

The main objectives of this thesis were to measure the interfacial composition of the emulsions stabilized by asphaltenes and resins and to relate this composition to the continuous oil phase composition (asphaltene and resin concentration, solid content, solvent type, and asphaltene/resin ratio) and emulsion stability. The conclusions reached through this study are presented below, followed by the recommendations for future work on crude oil emulsions.

# **6.1 CONCLUSIONS**

### Asphaltenes:

• The interfacial tension and gravimetric experiments showed that asphaltenes adsorb on the water/oil emulsion interface. The asphaltene mass surface coverage has been obtained for asphaltenes concentration in the continuous phase up to 40 kg/m<sup>3</sup>. Asphaltenes mass on the emulsion interface increased with asphaltene concentration and reached a plateau at concentrations of 10-20 g/L. The amount of asphaltene adsorption increased from approximately 4 to 12 mg/m<sup>2</sup>. The limiting value depends on the solvent and the asphaltenes. An increase of the asphaltene mass on the interface is likely due to change in the configuration of the asphaltenes on the interface. At low asphaltene concentration they appear to spread out on the interface in a more planar form and at high concentration they appear to align into more compressed "vertical" configuration.

- The stability of solids-free and asphaltene-solids stabilized emulsions increased at asphaltene concentration up to 10 kg/m<sup>3</sup>. An increase in stability at low concentration corresponds to a decrease in a droplet diameter. Smaller drops coalesce less readily and lead to more stable emulsions.
- Above 10 kg/m<sup>3</sup>, there was a slight decrease in emulsion stability in solids-free systems. The emulsion stability does not appear to change at this concentration range for emulsions prepared with asphaltene-solids. The discrepancy in the stability trends between these two systems is probably due to the overshadowing effect of solids.
- The decrease in stability can be explained by a configuration change of the asphaltenes on the interface. An increase in the asphaltene concentration leads to increase of the asphaltene mass on the interface. Higher adsorption indicates smaller interfacial area per molecule and potentially fewer sites of attachment to the interface. With less attachment the molecule may be easier to displace from the interface and hence the emulsion is less stable.

• The elemental analysis of the adsorbed asphaltenes revealed that asphaltenes which are more aromatic and have more sulfur and oxygen heteroatom groups are adsorb preferentially on the emulsion interface.

## Solvent:

- The asphaltene surface coverage decreases in a better solvent. In a better solvent asphaltene molecules have stronger interactions with solvent molecules and are more solvated. The solvated molecules occupy larger area and are more loosely packed on the interface. This explains the decrease in the asphaltene mass surface coverage and reduction in emulsion stability.
- Emulsion stability is also reduced in a better solvent. In a "good" solvent asphaltene molecules are likely less cross-linked with each other and more mobile, creating a less rigid interface. This makes emulsion drops easier to coalesce and the emulsion less stable.
- The precipitation of asphaltenes in a poor solvent also reduces emulsion stability. Emulsion stability decreases as more asphaltenes precipitate. Precipitated asphaltenes do not appear to participate in stabilizing emulsions. Hence, in effect, precipitation removes stabilizing asphaltenes.

#### <u>Resins</u>

Resins are interfacially active but do not stabilize emulsions. In all cases, resin addition
decreased emulsion stability. They destabilize emulsions by acting as a very good
solvent for the asphaltenes. This decreases the amount of asphaltenes adsorbed on the
interface. At high concentrations, they replace asphaltenes on the interface.

## <u>Solids:</u>

 It was found that naturally occurring fine solids less than 1 µm in diameter significantly increase stability of model emulsion, however they have no effect on the asphaltene adsorption on the water/oil interface.

## **6.2 FUTURE WORK AND RECOMMENDATIONS**

The ultimate goal of this research project is to establish a relationship between crude oil composition and water-in-oil emulsion stability. Determination of this relationship is a necessary step in designing effective emulsion treatments associated with crude oil production and oil spills. The increased knowledge in this area can be particularly useful for designing predictive models of demulsifier performance and dosages. It can also be helpful in predicting the outcome of mixing oils from different sources. The results so far confirm that the addition of a good solvent, already used in Syncrude froth treatment process, does help to destabilize water-in-oil emulsions. However, the results suggest that a potentially more efficient treatment methods could be designed based on the removal of

solids, for example by precipitating a small fraction of asphaltenes. These treatments could reduce the operating costs and mitigate the environmental consequences of emulsion formation.

While this research project unveiled some important issues in crude oil emulsion stability, many new questions arose. The answer to these questions would greatly increase the understanding of the crude oil emulsion stability. Presented below are some recommendations for future research in the area of crude oil emulsions.

- 1. During this project gravimetric analysis and stability tests were performed only with "fresh" emulsions (i.e. emulsions were investigated after one and half-hour after preparation). However, some studies indicate that the interfacial viscoelastic properties and emulsion stability change with the emulsion aging (Sjöblom et al., 1995). This change is possibly caused by the accumulation of the asphaltene on the interface or change in the configuration over time. The aging processes can be directly investigated by measuring the interfacial composition and stability of the aged emulsions.
- 2. Another step in the investigation can be to analyze the model emulsions prepared with recombined original crude oil fractions of various compositions. That is, aromatic and saturate fractions can be used instead of heptane and toluene.

- 3. Indirect evidence from this work suggest that the asphaltenes undergo a conformation change on the interface with a change in the asphaltene bulk concentration or solvent composition. At present the explanations are only speculative. More information can be obtained by conducting rheological measurements of the emulsion interface. This way, the conformation change could by confirmed directly.
- 4. This project showed that fine solids effectively stabilize water-in-oil emulsions. However, the mechanism of solid stabilization remains unclear. It is not known whether solids adsorb on the interface or remain trapped between droplets. It is also not known how many solids are needed to stabilize emulsions. This question could be investigated by conducting stability tests with emulsions prepared with various solid concentrations. Cryogenic, confocal or scanning electron microscopy may help to determine the position of solids relative to the interface.
- 5. The analysis performed in this work showed that the elemental composition of the adsorbed asphaltenes is different from that of the asphaltenes remaining in the continuos phase. These asphaltenes could be characterized for their acidic, basic and amphoteric content, functional groups, as well as molar mass. This information could be a useful guide for finding appropriate chemicals to target specific asphaltene functional groups and prevent strong film formation.
6. Finally, only two Alberta bitumens were examined for this research project. In order to generalize the results, it is necessary to investigate other crude oils from various locations. Also it would be of interest to investigate the emulsions prepared with mixed crude oils as refinery desalters always deal with mixed feeds.

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