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University of Alberta

Interfacial Behavior of De-asphalted Bitumen

by

Zhoulin Yan ©

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of Master of Science

in

Chemical Engineering

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ABSTRACT

The stability of water-in-diluted-bitumen emulsions is directly related to properties of surface active species at the diluted bitumen/water interface. In addition to asphaltenes, the present work shows that surface-active components are present in de-asphalted bitumen.

The change of interfacial tension, measured with a de-Nouy ring tensiometer, was used to study the properties of adsorbed species at the interface of water and diluted de-asphalted bitumen, bitumen and asphaltene respectively. Interfacial tension measurement results indicated that de-asphalted bitumen contained surface-active components that can lower the interfacial tension of the de-asphalted bitumen/water interface. At relatively high de-asphalted bitumen concentrations in hexane and toluene, critical micelle concentrations may have been reached.

The roles of various components of bitumen in stabilizing water-in-bitumen emulsions were also investigated. It was observed that de-asphalted bitumen doesn't stabilize water-in-bitumen emulsions. Asphaltenes were found to stabilize emulsions more effectively than whole bitumen, hereby indicating that the presence of small molecules such as resins and aromatics in bitumen weakens the stability of water-in-bitumen emulsions. Asphaltenes and solids were found to be the main stabilizers for water-in-bitumen emulsions.

ACKNOWLEDGEMENT

First of all, I am very grateful to my supervisors, Dr. Jacob H. Masliyah and Dr. Janet A.W. Elliott, for their guidance and encouragement throughout this work. Much of the work in this thesis has benefited from discussions with them. I feel very lucky to have had the opportunity to be associated with them over this time. I am indebted to them for their immeasurable help and financial assistance; and for suffering through the many drafts of this thesis, and tirelessly telling me to be confident.

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Finally, I wish to thank my parents for supporting me coming to Canada and encouraging me to overcome every difficulty in my life. Special gratitude is to my husband. Marrying him was the sweetest episode of my life in U of A.

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CHAPTER 1.

INTRODUCTION

1.1 Oil Sands

As main energy resources, oil and gas have played important roles in the last century. With increasing consumption, less and less oil and gas are left in large easily developed pools. In the future, more and more oil and gas will inevitably come from heavy oil and oil sands, which are technologically challenging resources [Yarranton, 1997].

Oil sand is also known as tar sand. It consists of a mineral sand matrix impregnated with bitumen—a heavy and viscous carbonaceous material [AOSTRA, 1991]. The size of oil sands deposits varies. So far, the Athabasca deposit, located in northeastern Alberta, Canada, is the largest known deposit in the world. It covers an area of 46,800 square kilometers and is estimated to contain 137 billion cubic meters (862 billion barrels) of oil [AOSTRA, 1991]. The oil-bearing formation has a thickness of about 45 meters [AOSTRA, 1991].

There are two kinds of oil sand, "oil-wet oil sand" and "water-wet oil sand". In an oil sand formation, if individual sand particles are in direct contact with bitumen, the oil sand is called "oil-wet oil sand". If sand particles and bitumen are separated by a water layer, they form "water-wet oil sand". In the latter case, the bitumen is in contact only with the water, and not with the sand particles themselves, which is illustrated schematically in Figure 1-1. The different structures of the two kinds of oil sands make a difference from a processing point of view. Bitumen from water-wet oil sand is ready to be extracted using the Clark Hot Water Process. "Oil sand from the Athabasca deposit is water-wet, whereas many other deposits, such as those in Utah, Alabama and California are oil-wet" [AOSTRA, 1991].

The oil sands currently mined in the Athabasca deposit consist of approximately 85% sand, silts and clays, 5% water, 10% bitumen and less than 1% particulate organic material that is insoluble in organic solvents [Strausz,1989; Long *et al.*,1994]. In some areas the formation water can be salty with very high chloride concentrations [Long *et al.*, 1994]. During the extraction process, as shown in Figure 1-2, the original oil sands mined from deposits are sent to a tumbler where the bitumen is separated from the sand grains and bitumen-air attachment takes place. The produced slurry containing water, aerated bitumen and solids is fed to a primary separation vessel where the bitumen rises to the top of the vessel forming froth. The froth from the primary separation vessel contains approximately 60% bitumen, 30% water and 10% sands. This froth is then diluted with naphtha, heated and de-aerated and is sent to an inclined plate settler followed by centrifuges to separate the water and nearly all solids from the diluted bitumen. However, it has been found that the diluted bitumen leaving the last centrifuge bank, at position A in Figure 1-2, still contains 3 to 5% water and 0.5% solid particles. This water is in the form of small water droplets that do not coalesce easily. The water and the diluent in the bitumen are removed in a diluent recovery unit (DRU) while the salts in the water stay in the produced bitumen, called coker feed bitumen, which is ready to be upgraded. The salts can cause corrosion when they contact the hot metal processing facilities in the downstream upgrading processes.

Therefore, in order to avoid potential corrosion problems, it is desirable to either prevent the formation of the water-in-diluent-bitumen emulsion or to remove the water droplets from the diluted bitumen.

Understanding water-in-bitumen emulsions is important for other aspects of processing. For example, bitumen trapped in tailing emulsions leads to lost profit and causes environmental problems.

1.2 Classification of Petroleum Fractions

Crude petroleum is composed of compounds with different boiling temperatures that can be separated into various generic fractions by distillation and by fractionation [Speight, 1991]. Since it is impractical to classify them by composition, some other criteria are used to classify petroleums such as physical properties, atomic H/C ratio, heteroatom content, boiling cut, and solubility class. Petroleum boiling cuts are given in Table 1-1 [Gray, 1994] and solubility classes are shown in Figure 1-3 [Strausz, 1989]. The most commonly used solubility classes of petroleum are: asphaltenes, resins, aromatics and saturates. Asphaltenes are the class of highest molecular weight and are the most highly polar fraction. They are soluble in toluene but insoluble in alkanes. When any chemical or physical disturbances are introduced into a petroleum system, it is the higher molecular weight constituents that will be most seriously affected [Mushrush and

Speight, 1995].

Petroleum from different sources that exhibits different behavioral characteristics is often difficult to define with any degree of precision. There is a wide variation in the properties of petroleum and the proportions in which the different constituents occur will also vary widely. Some crude oils have higher proportions of the lower boiling point constituents, whereas others (such as bitumen) have higher proportions of the higher boiling point constituents (often called the "asphaltic components" or "residuum"). These higher boiling point constituents often bring problems during recovery and refining operations. The asphaltene content of different kinds of crude oils are illustrated in Table 1-2 [Speight, 1996]. For heavy oils and bitumens, the asphaltene content largely determines the properties of the oil.

1.3 Bitumen

Athabasca bitumen is used in this study. The composition and properties of most Alberta bitumens are summarized in Table 1-3.

The molecular composition of the Alberta bitumens can be easily described using their solubility classes. The saturates and aromatics are relatively simple classes. The saturates fraction is composed of "alkyl cycloalkanes of 1 to 6 rings (approximately 17% of the bitumen)" [Yarranton, 1997]. The aromatic fraction of bitumens consists mainly of "monoaromatic (approximately 10% of the bitumen), di- and tri-nuclear aromatic hydrocarbons (approximately 9% of the bitumen)" [Yarranton, 1997]. Although both the saturates and the aromatics are complex mixtures containing many unidentified components, each class has distinct types of molecular species.

Resins are mixtures of heterocyclics (40% of the bitumen) and a small amount (1-2% of the bitumen) of carboxylic acids. There are many heteroatom homologous series in the resins [Yarranton, 1997]. Although the molecular species of the resins are similar to the heteroatom species in the aromatics, the resin species have higher molar mass, greater polarity and lower H/C ratios. The difference between resins and aromatics is not as clear as that between saturates and aromatics [Yarranton, 1997]. The chemical species of resins resemble those of asphaltenes. However, asphaltenes have lower H/C ratios and higher molar mass and heteroatom content than resins [Koots and Speight, 1975].

By definition, asphaltenes are a solubility class that is precipitated from petroleum by the addition of an excess amount of an alkane such as hexane or heptane [Speight *et al.*, 1994]. Using ruthenium-ion-catalyzed oxidation, Strausz *et al.*[1992] identified many asphaltene elemental structures and gave a hypothetical structure of the asphaltene molecule, which is shown in Figure 1-4. The elemental formula of this hypothetical asphaltene molecule is $C_{420}H_{496}N_6S_{14}O_4V$ [Strausz *et al.*, 1992].

Asphaltene molecular weights, measured with vapor pressure osmometry, are dependent not only on the nature of the solvent but also on the solution temperature [Moschopedis *et al.*, 1976]. Data show that asphaltenes form molecular aggregates, even in dilute solution, and that this association is influenced by solvent polarity, asphaltene concentration, and the temperature [Speight, 1996]. As a matter of fact, the means by which the asphaltenes remain dispersed in the oil medium is not currently understood and has been the focus of many studies by geochemists, chemists and engineers.

An early hypothesis of the physical structure of petroleum suggested that asphaltenes are the centers of micelles. These micelles are formed by adsorption of maltenes or even of part of the maltene fraction onto the surfaces or into the interiors of the asphaltene particles, see Figure 1-5 [Speight, 1996]. Thus, in this model, the nuclei are surrounded first by those substances with greater molecular weight and the most pronounced aromatic nature. The lighter constituents of lesser aromatic nature are situated in the outer layers of the nucleus. The transition to the intermicellular phase is continuous. It is further suggested that asphaltene-asphaltene clusters form the micelle, although other options such as asphaltene-resin clusters are also possible. This model is usually called the colloidal model [Pfeiffer and Saal, 1940].

X-ray diffraction data suggest that the polynuclear aromatic asphaltene core is composed of agglomerated stacks and that each stack consists of up to 6 molecules [Dickie and Yen, 1972]. The stacks are held together by π-π bonding and physical constraints. In solution, the same stacks are believed to form, yielding a colloid with a diameter of about 3 nm as well [Dickie and Yen, 1972].

Another model that describes the asphaltene association in bitumen is the micelle model.

It resembles the colloidal model except that the asphaltenes are dispersed as molecules rather than colloidal stacks. Hence, the resins in the natural crude solvate asphaltene molecules which are modeled as surfactants. Experimental observation and interfacial tension measurement suggest that asphaltenes form micelles at higher concentration [Cimino *et al.*, 1995].

1.4 Stability and Interfacial Properties of Water-in-Oil Emulsions

1.4.1 Water-in-Oil Emulsions

"An emulsion is a dispersion of droplets of one liquid in another one with which it is incompletely miscible" [Israelachvili, 1994]. If the emulsion is stable, the droplets will remain dispersed for a long period of time. Whether or not a stable emulsion is desired depends on the particular application. In food production, it is important to keep emulsions stable for long shelf-life. On the other hand, in the oil sand industry it is desirable to decrease the stability of water-in-crude-oil emulsions in order to obtain water-free hydrocarbon product. Water-in-crude-oil emulsions in the oil processing industries are considered to be harmful for a variety of reasons. The salts contained in the emulsified water can cause corrosion upon contact with hot metal surfaces. In the offshore production of crude, where space on platforms is limited, the processing facilities involving separators and coalescers should be as efficient as possible. As well, the water-in-crude oil emulsions formed in oceanic oil spills can make clean up more difficult and therefore lead to environmental damage [Mackay *et al.*, 1973].

Though the stability of water-in-oil emulsions is of much interest to industry, few facts are known about it. Most research so far has relied on visual observations. It is known that the water droplets are 2-5 microns in diameter and that the emulsion remains dispersed in aromatic solvents even when centrifuged at high speed but flocculates in aliphatic solvents and is easily settled [Yarranton, 1997]. It is generally believed that some components in the oil phase including asphaltenes, clays and silica partially coated with organic material may act as stabilizers. It is also believed by some that the stability of most of the water-in-oil emulsion systems is due to the formation of a rigid, highly condensed film at the oil-water interface formed by adsorption of asphaltenes [Blair, 1960]. Recently it was found that only asphaltenes far from the precipitation point were capable of stabilizing emulsions. That is, only soluble, surface active asphaltenes stabilized the emulsions [Yarranton, 1997].

1.4.2 Interfacial Properties of Emulsions

Generally, two pure, immiscible phases do not form a stable emulsion. Only when a third component, particularly a surfactant, is added into the system, is it possible to form a stable emulsion. One way of measuring the effect of a surfactant is to examine the interfacial tension of the two phases making up the emulsion. When a surface-active species is added to a system, the surfactant molecules will adsorb at the interface and decrease the interfacial tension. This phenomenon may be used as an indication of the presence of surface-active species.

Since surfactants can self-associate, above a critical concentration, called the critical micelle concentration (cmc), surfactant molecules aggregate to form micelles. As the concentration of non-associated surfactant molecules is constant, beyond the cmc, the interfacial tension does not change with the increase of the surfactant concentration. This property is often used to characterize the surface activity of surfactants.

Experimental studies showed that the interfacial tension of an organic solvent and water decreases through the addition of asphaltenes to the organic solvent [Sheu *et al*, 1992]. When asphaltene concentration in the solvent is at a certain level, the critical micelle concentration is reached [Sheu *et al.*, 1992]. Therefore asphaltenes can be considered to be a surfactant in organic mixtures. On the other hand, asphaltene molecules at an interface may participate in steric stabilization as well. The retraction of an aged pendant drop of crude oil in water has demonstrated the existence of rigid interfacial films in water-in-crude-oil emulsions [Strassner, 1968; Kimbler *et al.*, 1966; Taylor, 1992]. By investigating the behavior of pentane-precipitated asphaltene and resin films, three types of film and film behavior are described. They are: solid films that form a relatively insoluble skin; highly mobile films that pack under compression to give a momentary distortion of the drop but rapidly redistribute and return the drop to the symmetrical shape and transition films that showed no distortion under drop contraction.

Although the rheology of the interface is as important as its interfacial tension, it is not the main concern of the present work.

1.5 Objectives

The purpose of this thesis is to study the nature of the stability of water-in-bitumen emulsions. One way to contribute to the understanding of water-in-bitumen emulsions is to understand roles of different bitumen components in stabilizing the water/bitumen interface. Because bitumen is very complex, many of its components could potentially affect the stability of water-in-bitumen emulsions. In this thesis, we will mainly study the roles of asphaltenes and de-asphalted bitumen (that is the components of bitumen remaining after asphaltenes are removed) in stabilizing water-in-bitumen emulsions. Although asphaltenes have been studied extensively, emulsion studies on the components that coexist with asphaltenes in bitumen have been neglected. The study of de-asphalted bitumen hopefully will contribute to the understanding of the behavior of the diluted bitumen /water interface. Therefore, the objectives of this thesis are to:

1. Measure the interfacial tension of water in contact with hex-tol (a mixture of hexane and toluene) diluted asphaltenes, de-asphalted bitumen and bitumen respectively; and compare the surface activities of the three systems by analyzing the interfacial tension measurement results.
2. Examine the stability of water-in-bitumen, water-in-asphaltene and water-in-de-asphalted bitumen emulsions; investigate the role of de-asphalted bitumen in stabilizing the water/bitumen interface; compare the roles of asphaltenes and solids in stabilizing the water/bitumen interface.

1.6 Terminology

- Bitumen:

The original coker feed bitumen that is ready for upgrading. It may contain some fine solids but it is water-free.

- Solids-free bitumen :

When bitumen is dissolved in toluene, solids are the only insoluble component. By filtering off the solids, solids-free bitumen is obtained. The filtration is performed with either 0.22 μm filter paper or 8 μm filter paper as indicated in the text.

- De-asphalted bitumen:

When bitumen is dissolved in excess hexane, asphaltenes and solids will precipitate. De-asphalted bitumen is the material left in the supernatant other than the solvent hexane. De-asphalted bitumen is considered to be free of solids.

- DB:

An abbreviation of de-asphalted bitumen.

- DB-solids:

De-asphalted bitumen with reintroduced dispersed solids obtained from the bitumen.

- Asphaltene-solids:

When asphaltenes are precipitated from bitumen, solids, including ash, fine clays and some adsorbed hydrocarbons also precipitate. The mixture of asphaltenes and solids that first precipitates is referred to as "asphaltene-solids".

- Asphaltene(s):

Asphaltenes free of solids. The solids are filtered off by 0.22 μm filter paper.

- Asphaltenes-free bitumen:

De-asphalted bitumen with reintroduced dispersed solids obtained from the bitumen.

- Hex-tol (a:b):

Hexane and toluene with the volume ratio of hexane to toluene being a:b. When a:b=1:1, the (a:b) portion is omitted.

- Water-in-bitumen emulsion:

An emulsion that is made by dispersing water into a solution that is made up of bitumen and hex-tol.

- Water-in-asphaltene emulsion:

An emulsion that is made up by dispersing water into a solution of asphaltene and hex-tol.

- Water-in-de-asphalted-bitumen emulsion (or water-in-DB emuslion):

An emulsion that is made up by dispersing water into a solution of de-asphalted bitumen and hex-tol.

- IFT:

Interfacial tension.

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Table 1-1. Boiling ranges and uses of petroleum cuts (reproduced from [Gray, 1994])

Cut	Boiling Point Range (°C)	Use
Light Naphtha	1-150	Gasoline, solvent
Gasoline	1-180	Gasoline
Heavy Naphtha	150-205	Reformed for gasoline
Kerosene	205-260	Jet fuel, solvent
Stove Oil	205-290	Fuel, solvent
Light Gas Oil	260-315	Diesel Fuel
Heavy Gas Oil	315-425	Catalytic or hydrocracker feed
Lubricating Oil	> 400	Lubricating oil
Vacuum Gas Oil	425-600	Catalytic or hydrocracker feed
Residuum	> 600	Asphalt, coker or hydrocracker feed

Table 1-2. Composition of different feedstocks

(reproduced from [Speight, 1996])

Substance	Asphaltenes (%)	Resins (%)	Oils (%)
Petroleum	< 0.1 - 12	3-22	67-97
Heavy oil/bitumen	11-45	14-39	24-64
Residue	11-29	29-39	32-49

Table 1-3. Properties of Alberta Bitumens

(reproduced from [Strausz, 1989])

Composition (wt%)		Solubility Class (wt%)	
Carbon	81-84	Asphaltenes	16-22
Hydrogen	10-11	Resins	29-49
Nitrogen	0.3-0.6	Saturates	15-21
Oxygen	0.8-1.6	Aromatics	18-32
Sulfur	4.6-5.6		
Nickel	60-100 (mg/kg)		
Vanadium	160-300 (mg/kg)		
Ash	0.5-1.0		

H/C Atomic Ratio	1.46-1.50
Molar Mass	490-620 g/mol
Density	0.97-1.02 g/cm^3
Viscosity	10^4-10^6 mPa·s @ 15°C
Heat of Combustion	41.0-42.6 MJ/kg

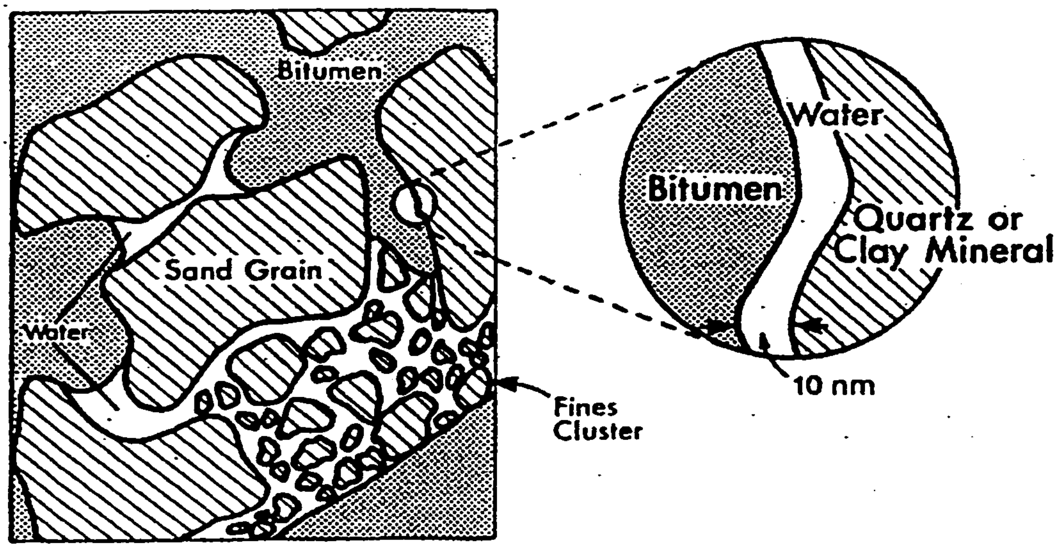

Figure 1-1. Schematic structure of the water-wet Athabasca oil sand (reproduced from [Takamura, 1982])

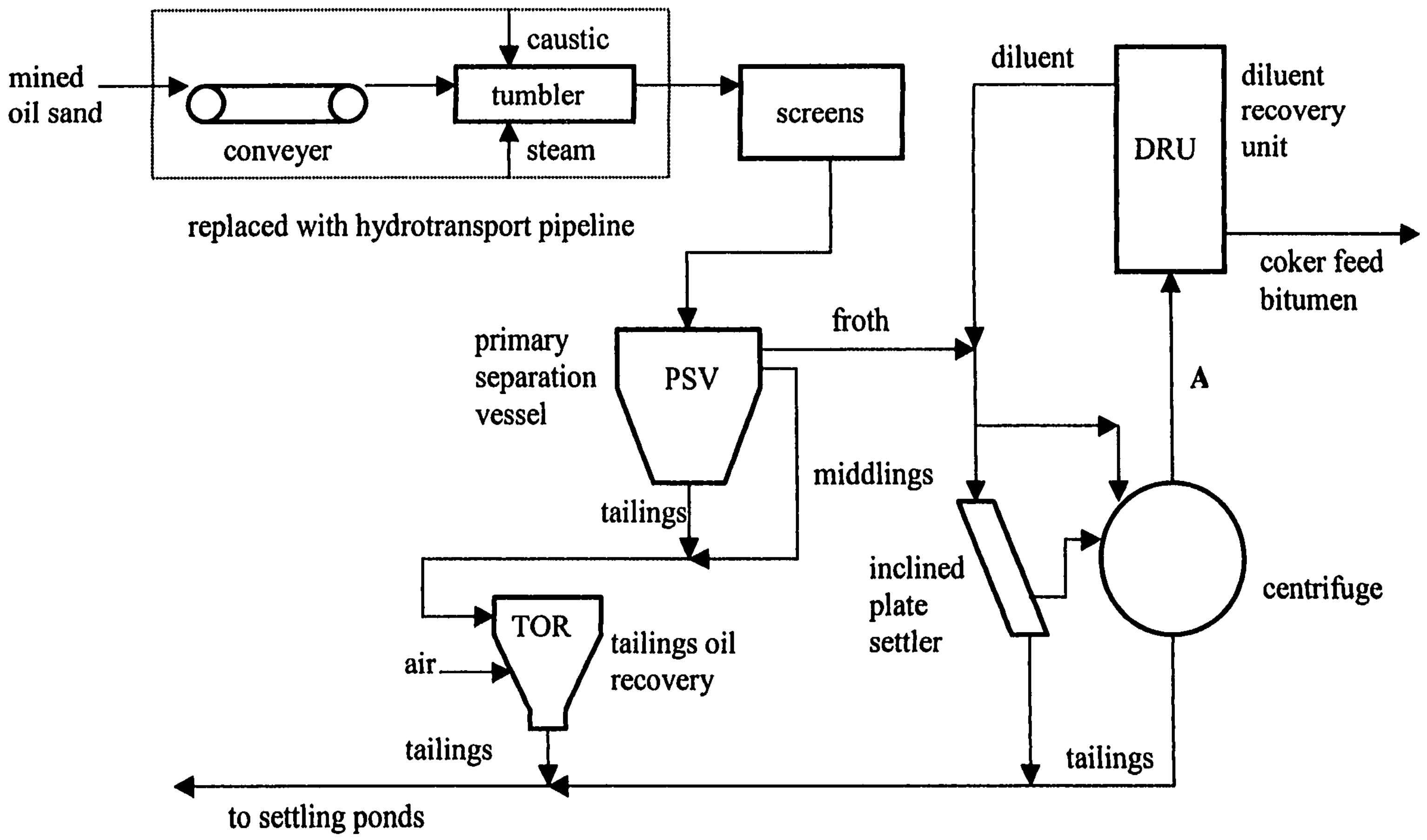

Figure 1-2. Schematic of a typical bitumen extraction plant
(reproduced from [Yarranton, 1997])

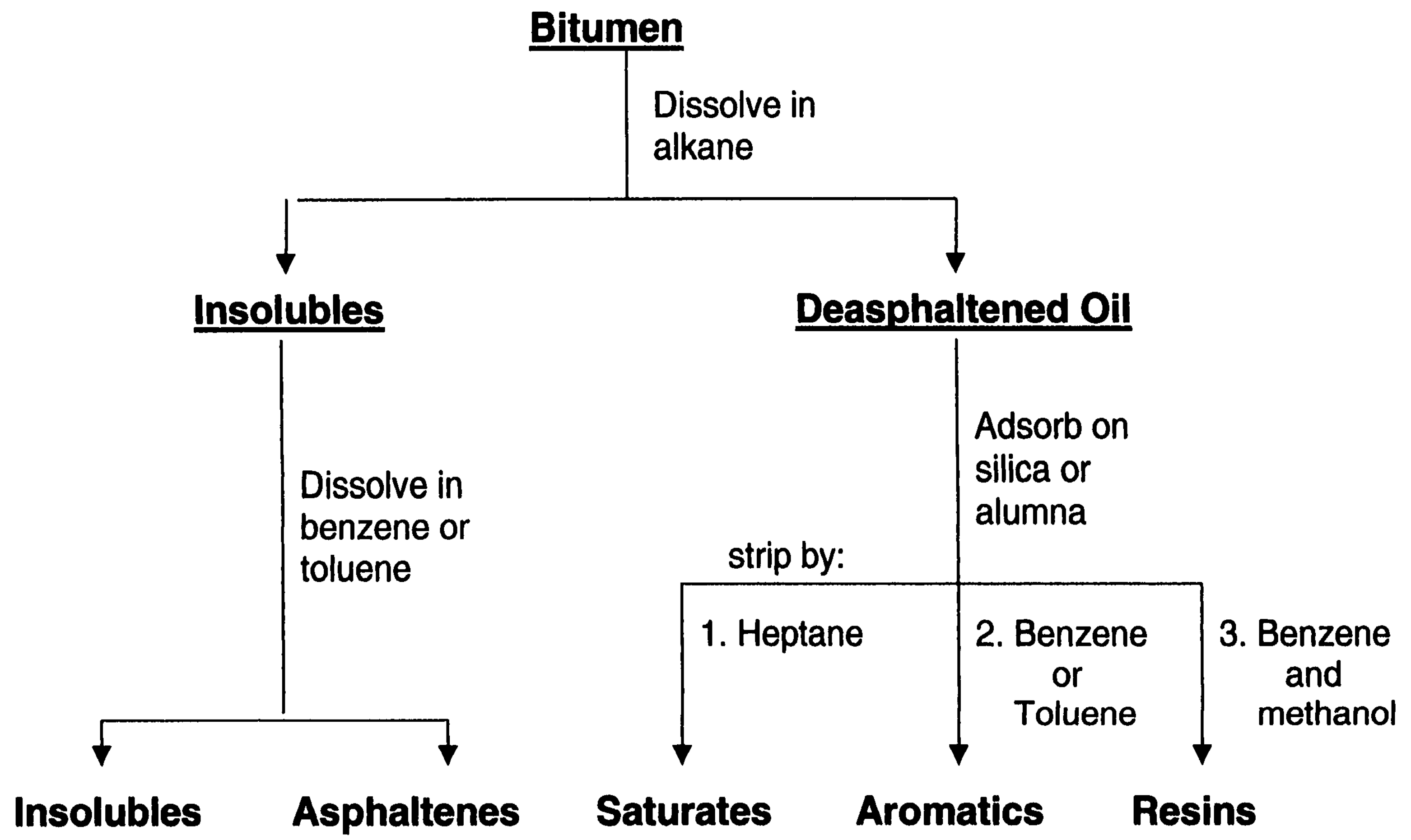

Figure 1-3. Simplified solubility classes of petroleum (adapted from [Speight, 1996])

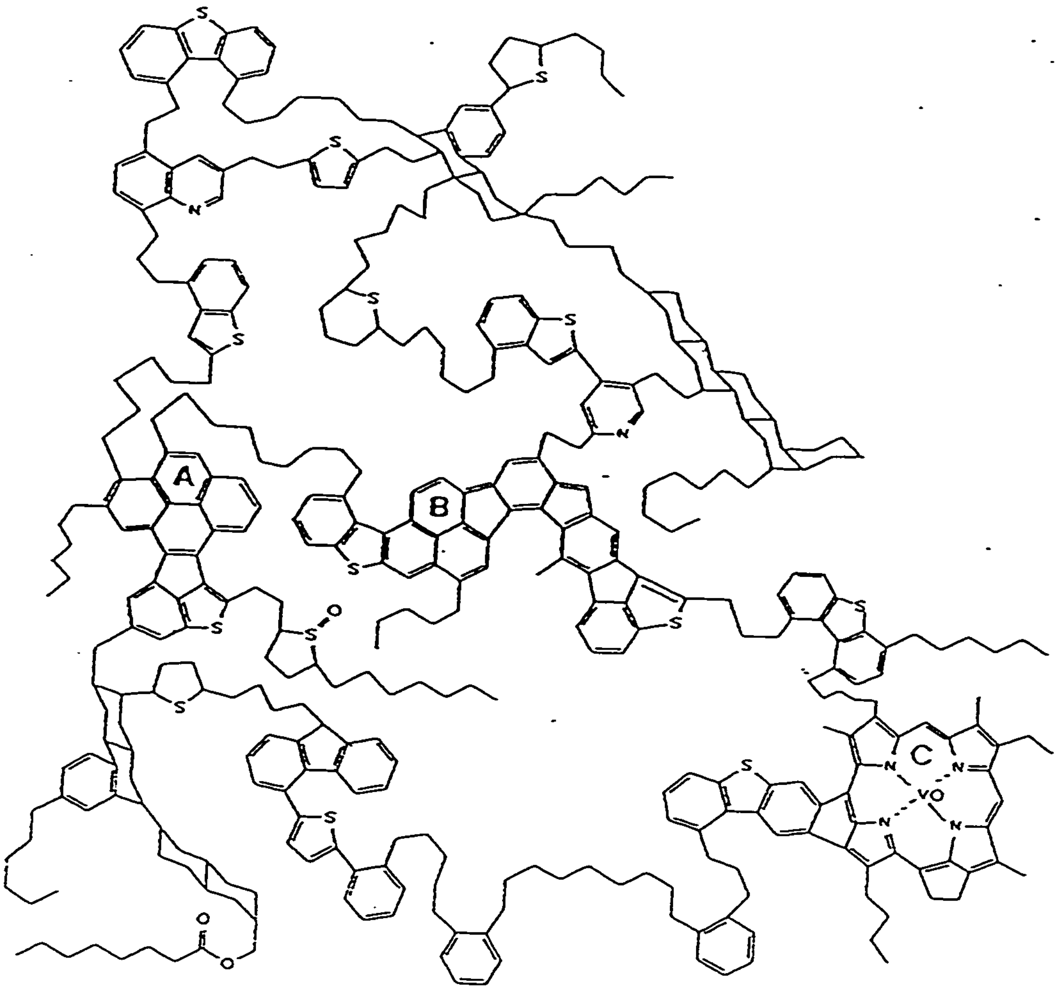

Figure 1-4. A hypothetical structure of an asphaltene molecule [Strausz *et al.*, 1992]

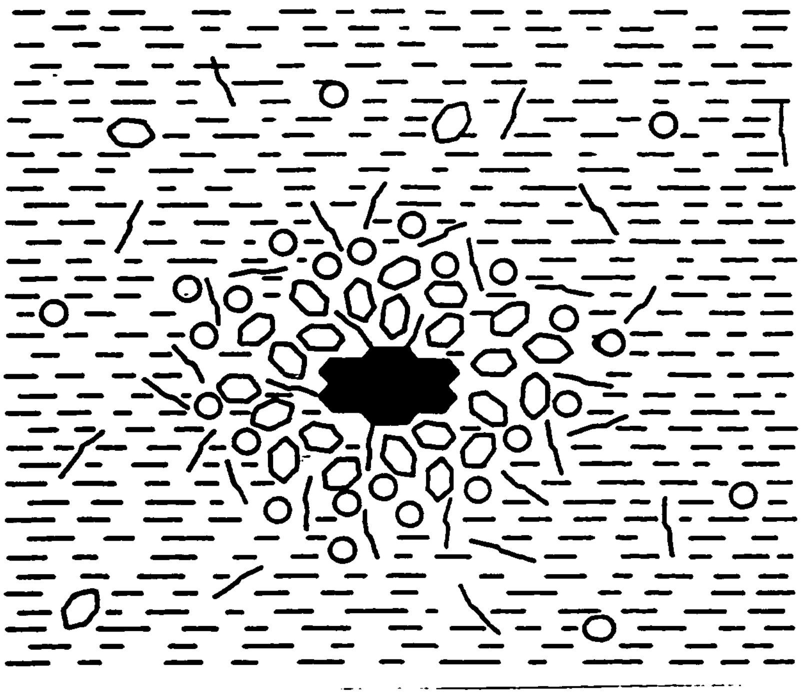

Figure 1-5. An early model of the physical structure of petroleum showed the asphaltenes dispersed and peptized by resin species [Speight, 1996]

CHAPTER 2.

MATERIALS AND MEASUREMENTS

2.1 Materials

Bitumen used in this study is Syncrude coker-feed bitumen that has been treated to remove most of the water and fine solids and is ready for upgrading. The solvents used throughout this work were HPLC grade hexane and Certified A.C.S grade toluene purchased from Fisher Scientific. All water used was de-ionized ultra-filtered water, which was also purchased from Fisher Scientific.

Asphaltene-solids (that is asphaltene with solids) were extracted from the bitumen by hexane at an approximately 40:1 volume ratio of hexane:bitumen. The details of the procedure are as follows.

1. Bitumen was dissolved in hexane with a concentration of 1 g of bitumen to 40 ml of hexane at 22°C. According to literature [Strausz, 1989], the density of Alberta bitumen is 0.97 – 1.02 g/cm^3. Therefore the volume ratio of hexane:bitumen was about 40:1. Usually, 1000 ml of hexane was added to 25 g of bitumen. The bitumen/hexane mixture was stirred using an electric mixer (purchased from Universal Electric Co., model AB2R066N#) at 175 rpm for 4 hours. Then, the solution was allowed to stand overnight in order to allow the asphaltenes and their associated solids to precipitate.

2. The bitumen/hexane solution was filtered with one layer of filter paper under vacuum to separate the asphaltene-solids from the de-asphalted bitumen/hexane solution. The pore size of the filter paper was 0.22 μm.
3. The asphaltene-solids obtained in step 2 were again mixed with some hexane. The amount of the hexane used in this step was 6 ml hexane per 1 g of the original bitumen. For example, if 25 g of bitumen were dissolved in hexane in the first step, 150 ml hexane would be needed to wash asphaltene-solids in this step. This asphaltene-solids/hexane mixture was then allowed to stand for another 4 hours and was filtered again with a 0.22 μm filter paper. Thus the remaining components of bitumen (de-asphalted bitumen) attached to the precipitated asphaltene were washed away by the hexane.
4. The asphaltene-solids collected from the filtration steps were dried at ambient conditions until there was no further change in weight.
5. The supernatant from step 2 and step 3 was transferred to a container to evaporate the hexane by vacuum until the concentration of de-asphalted bitumen in hexane reached 5 ml hexane to 1 g de-asphalted bitumen. By knowing that asphaltene-solids make up approximately 16% of bitumen, asphaltene-solids' density is 1220 kg/m^3 and bitumen density is 1016 kg/m^3 (see section 2.2), the amount of the de-asphalted bitumen in a given amount of the original bitumen can be calculated. Therefore the concentration of de-asphalted bitumen in hexane can be easily controlled. The concentrated de-asphalted bitumen/hexane solution was kept in a sealed bottle for later use.

The recovered dried asphaltene-solids were weighed and found to make up 15.7% to 16.2% of the original bitumen. Since solids were filtered off from the supernatant, the de-asphalted bitumen obtained in step 5 was considered to be solids-free.

When it was necessary to use de-asphalted-bitumen-solids (DB-solids), the solids were added to the de-asphalted bitumen using the following procedure.

1. 25 g of bitumen was dissolved in toluene with a ratio of 40 ml toluene to 1 g bitumen. The bitumen/toluene mixture was stirred using an electric mixer at 175 rpm for 1 hour. Then the solution was heated at 80 °C for 12 hours.
2. When the heated solution was cooled down to room temperature (22 °C), it was filtered with 0.22 μm filter paper under vacuum. It was essential to change the filter paper for every 50 ml of the mixture filtered, otherwise the filtration would proceed extremely slowly because the fine solids accumulating on the filter paper provided increased resistance to filtration.
3. The used filter papers with solid "cakes" on them were soaked in toluene with a ratio of 6 ml toluene to 1 g of the original bitumen. The solids/toluene suspension was ultrasonified in an ultrasonic cleaner (FS20, purchased from Fisher Scientific) for 5 minutes to remove all the solids from the filter papers and dissolve the small amount of bitumen that remained on the solids into the toluene.
4. The solids/toluene suspension was then filtered with 0.22 μm filter paper.
5. Another wash as in step 3 was conducted to remove the remaining solids from the filter papers. The filter papers were washed and ultrasonified in toluene one more

time and the solids/toluene suspension from each washing step was collected.

6. The collected solids/toluene suspension was poured into the DB/hexane solution and the new suspension was ultrasonified for several minutes. The time that was used for the ultrasonification was about 5 minutes per 150 ml mixture because it was observed by using a microscope that, the solids could be dispersed quite well in a DB/hex-tol solution in that way.

All the supernatant fractions from each filtration step, which were solids-free bitumen, were collected for later use.

2.2 Density Measurements

Densities were measured with an Anton Paar DMA 45 density meter calibrated with deionized water and air at 22°C. The standard specific volumes of the two substances that were used in the calibration are 1.002×10^{-3} m^3/kg for water and 0.847 m^3/kg for air at 22°C and 1 atm.[Liley *et al.*, 1984]. The densities of de-asphalted bitumen and asphaltene-solids were measured. The density of bitumen can therefore be calculated. The accuracy of the densities measured with this instrument is ±0.03 kg/m^3. All measurements were made at 22°C.

According to the design of this density meter, densities are calculated from the density meter readings as follows [DMA 02C Instruction Manual]:

$$\rho = \frac{R^2 - B}{A} \tag{2-1}$$

where ρ is the density of the measured substance (g/cm^3), R is the meter reading (non-dimensional), A and B are coefficients that are to be determined from calibration with two pure substances that are air and water in this work. From Equation (2-1), the calibration equations for A and B are obtained as:

$$A = \frac{R_1^2 - R_2^2}{\rho_2 - \rho_1} \tag{2-2}$$

and

$$B = R_1^2 - A\rho_1 \tag{2-3}$$

where the subscripts 1 and 2 denote air and water used for the calibration.

The principal of measuring and calculating the densities of de-asphalted bitumen and asphaltene will be explained by taking de-asphalted bitumen as an example. The density of de-asphalted bitumen was calculated by measuring the specific volume of DB/hexane mixture with de-asphalted bitumen mass fractions ranging from 0% to 2%. At low concentrations, regular solution behavior can be assumed. Therefore, the de-asphalted bitumen density can be determined indirectly from the DB/hexane mixture specific volume and DB mass fraction in the mixture that is:

$$\frac{1}{\rho_m} = \frac{1}{\rho_h} + \left(\frac{1}{\rho_{db}} - \frac{1}{\rho_h}\right) x_{db} \tag{2-4}$$

Where ρ_m, ρ_h and ρ_{db} are the densities (kg/m^3) of the mixture, hexane and DB, respectively, x_{db} is DB mass fraction in DB/hexane solution. Rearranging Equation (2-4), we get

$$\frac{1}{\rho_{db}}=(\frac{1}{\rho_m}-\frac{1}{\rho_h})\frac{1}{x_{db}}+\frac{1}{\rho_h} \tag{2-5}$$

Therefore,

$$\rho_{db}=\frac{1}{S+I} \tag{2-6}$$

where

$$S=(\frac{1}{\rho_m}-\frac{1}{\rho_h})\frac{1}{x_{db}} \tag{2-7}$$

$$I=\frac{1}{\rho_h} \tag{2-8}$$

and

$$\frac{1}{\rho_m}=S\cdot x_{db}+I \tag{2-9}$$

where S and I are the slope and intercept of the inverse mixture density plot. Hence DB density can be calculated by obtaining a plot of the specific volume of the mixture versus DB mass fraction in hexane. Similarly, the density of asphaltene-solids was calculated by measuring the specific volume of asphaltene-solids/toluene mixture with the asphaltene-solids mass fraction ranging from 0% to 1%.

All the specific volume measurements were performed after the solute (DB or asphaltene-solids) had been mixed with the solvent overnight. The asphaltene-solids and toluene must be mixed with an electric mixer to allow the asphaltenes to dissolve in toluene. Figure 2-1 shows a specific volume plot for the de-asphalted bitumen/hexane solution. The average density of de-asphalted bitumen calculated is

977 kg/m^3. Figure 2-2 shows a specific volume plot of asphaltene-solids/toluene mixture. The asphaltene-solids density was found to be 1220 kg/m^3 which is within the range of the literature data (1200 kg/m^3 to 1240 kg/m^3) [Yarranton, 1997]. The error of the density measurement is within ±0.4 kg/m^3, which mainly arises from the error in the mass fraction of the solute.

Assuming that asphaltene-solids make up 16% of bitumen and that the asphaltene-solids/toluene is an ideal mixture, the density of bitumen can be calculated to be

$$1220 \times 16\% + 977 \times 84\% = 1016 \text{ kg/m}^3$$

According to literature data, densities of Alberta bitumens are between 970 and 1020 kg/m^3 [Strausz, 1989].

2.3 Interfacial Tension Measurements

2.3.1 Spinning Drop Tensiometer

A Jefri spinning drop tensiometer (Model: IFT-ARC-DBR-150-Spin) on loan from the Alberta Research Council was first used for interfacial tension measurements. The rotational speed of this tensiometer ranges from 0 to 19,500 rpm. The systems to be measured can be heated up to 204 °C when it is required.

During the measurement of the interfacial tension of two liquid phases, a droplet of the lighter fluid is immersed in the heavier fluid that spins in a spinning glass tube. The lighter (low density) phase tends to migrate to the axis of rotation due to centrifugal force. The balance of this force with the interfacial force determines the extent of deformation of the droplet. When the ratio of L/D > 4 (where L is the length and D is the diameter of the droplet), the expression for the calculation of interfacial tension is of the form [Princen *et al.*, 1967]:

$$\gamma = \tfrac{1}{4}\Delta\rho\,\omega^2 r^3 \times 10^3 \qquad (2\text{-}10)$$

where γ (mN/m) is the interfacial tension, $\Delta\rho$ (kg/m^3) is the density difference between the droplet and the surrounding fluid, ω (rad/s) is the rotational speed, and r (m) is the radius of the droplet at its center.

The reading of the drop diameter was not the actual diameter of the droplet because of the refractive index of the heavier fluid phase and the glass tube containing the fluids. Thus the tensiometer was calibrated by measuring the diameter of a copper wire with a known diameter of 1.05 mm immersed in the heavier fluid phase in the glass tube.

The surface tension of air-water measured with this tensiometer is shown in Figure 2-3. It can be seen from this figure that the surface tension varied from 68.2 to 73.6 mN/m. The error of this measurement is mainly due to the inaccurate diameter reading of the droplet. During the experiments, the diameters of the droplet were read by naked eye through a microscope. Since this instrument was not well maintained, some of its parts such as bearings were not in a perfect running condition and therefore caused vibration of the liquid system during the spinning. As well, the scale in the microscope was only divided into 10 units which was not sufficient for accurate readings. Hence the reading error of the drop diameter could be up to ± 0.1 unit which introduced significant error in the calculated surface tension. For a 70 mN/m interface, ± 0.1 unit reading error can cause a deviation of ± 2.5 mN/m from the true interfacial tension value. The higher the rotational speed of the system was, the higher the error was.

2.3.2 Platinum Ring Tensiometer

As a comparison, a Fisher deNouy platinum ring tensiometer was also used to measure the interfacial tensions of organic solutions in contact with de-ionized water. The accuracy of the tensiometer is ± 0.5 mN/m. All measurements were taken at 22 °C. Each interfacial tension value reported is an average of two repeated measurements.

Figure 2-4 illustrates the principle of a ring tensiometer. When the ring is pulled through an interface, there are three forces exerting on it. The upward pulling force W_{tot} equals the sum of two downward forces, the interfacial force ($4\pi R\gamma$) and the weight of the ring itself and the small amount of the liquid attached to the ring W_{ring}. The interfacial force is the interfacial tension multiplied by twice the periphery of the ring. By measuring the pulling force W_{tot} and the weight W_{ring}, interfacial tension γ can be calculated.

The apparatus is shown schematically in Figure 2-5. The platinum ring (1), with known perimeter and wire diameter, is suspended on a lever that is balanced by a balancing force at the other end. The balancing force shown on the dial reflects the downward force imposed by the interfacial tension. The organic mixture and water are placed in a beaker (4), which is mostly covered by a piece of Parafilm (laboratory film) to minimize the evaporation of the solvent. The platform (6) carrying the beaker may be moved up and down by means of the screw (10) to change the vertical position of the interface. During the measurement, the ring that was originally submerged in the lower phase is pulled through the interface. The maximum balancing force required to keep the lever horizontal during the process reflects the interfacial tension. This final reading from the instrument needs to be corrected for the weight of the raised liquid to obtain the correct interfacial tension.

Before each measurement, the platinum ring was rinsed in toluene and was placed on a flame before use to remove surface contaminants. Then the surface tension of the water was checked. For each measurement, the ring was placed in the water, the organic solution was added drop by drop to the water surface and the two-phase system was left to equilibrate for the desired length of time before the ring was pulled through the interface. All measurements were corrected for the densities of the organic solutions by an equation based on the Harkins and Jordan tables [Harkins and Jordan, 1930],

$$\frac{\gamma}{\gamma_m} = 0.7250 + \left(\frac{0.01452\,\gamma_m}{p_r^2 \Delta\rho} + 0.04534 - \frac{1.679}{\xi_r} \right)^{1/2} \tag{2-11}$$

where γ_m and γ (mN/m) are the measured and corrected interfacial tensions, respectively. The symbol p_r (cm) refers to the circumference of the platinum ring, ξ_r is the ratio of the radius of the ring to the radius of the wire and $\Delta\rho$ (g/cm^3) is the density difference between the two phases. In our case, p_r is 5.915 cm and ξ_r is 52.987.

Surface tensions and interfacial tensions for several systems in contact with water were compared with literature values as shown in Table 2-1. The corrected values are generally 2 - 3 mN/m below published values for similar substances. The reason for the discrepancy is not clear but it may arise from errors in the correction factor equation, impurities in the solvent, air and water or from the technique of the experimenter. Some previous researchers noticed that different values could be obtained from the same system with different operators [Yarranton, 1997].

In complex systems containing surface active species, interfacial tension changes with time as some diffusion of the active species takes place between the two phases after contact. In multi-component systems, the composition at the interface changes until equilibrium is reached. To determine how long the systems of interest take to reach equilibrium, interfacial tensions were measured for solutions of toluene, hexane and de-asphalted bitumen in contact with water after the systems were left to equilibrate for various times. From Figure 2-6 one can observe that in the first hour, the interfacial tensions decreased about 2.5-3 mN/m and were 3% to 6% higher than the equilibrium values. The interfacial tension values in the second hour were almost the same as the equilibrium values. No matter what the concentration of de-asphalted bitumen was, the systems generally needed two hours to attain equilibrium for interfacial tension measurements.

Similar time dependent behavior was observed by other researchers in their interfacial tension measurements of asphaltene/toluene solutions over NaOH solutions as shown in Figure 2-7 [Sheu *et al.*, 1992]. The interfacial tensions decreased to within 5-15% of the equilibrium value after 1 hour and to within 1% after 2 hours.

Since hexane and toluene are highly volatile solvents, the loss of the solvents during the two hours of interface equilibrating should be considered with care. Firstly, a piece of Parafilm was used to cover the beaker containing the two measured phases. In this way, the evaporation of solvents could be reduced to 0.2 g/hr per 15ml solution of hex-tol and de-asphalted bitumen with a surface area of 12.6 cm^2 based on the inside diameter of the container. Secondly, the loss of the solvent was considered while correcting the concentration of de-asphalted bitumen in the solvent for the calculation of interfacial tensions.

Experimentally, the platinum ring method of measuring interfacial tension is quite reliable though its accuracy is only ± 0.5 mN/m. During a measurement, the ring should be kept horizontal and care must be taken to avoid any disturbance of the surface as the critical point of detachment is approached. Additional details are given by Gaonkar and Neuman [Gaonkar and Neuman, 1984].

After comparing the results from the Jefri spinning drop tensiometer with the deNouy tensiometer, the deNouy tensiometer was chosen to perform all the remaining interfacial tension measurements because of it lower error and high repeatability.

2.4 References

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Table 2-1. Surface and interfacial tension measurements of various systems

System	Interfacial Tension (mN/m)			
	Present work (22°C)		H. Yarraton's[a] (22°C)	Literature (20°C)
	Raw Data	Corrected		
Water/air	75.3	70.53	70.12	72.75[b] 72.45[c] at 22 °C
Toluene/air	30.8	27.64	27.22	-
Hexane/air	20.6	18.30	19.12	18.1[d]
Toluene/water	32.55	34.47	34.77	35.8[e]
Hexane/water	48.5	48.18	47.83	50.1[e]

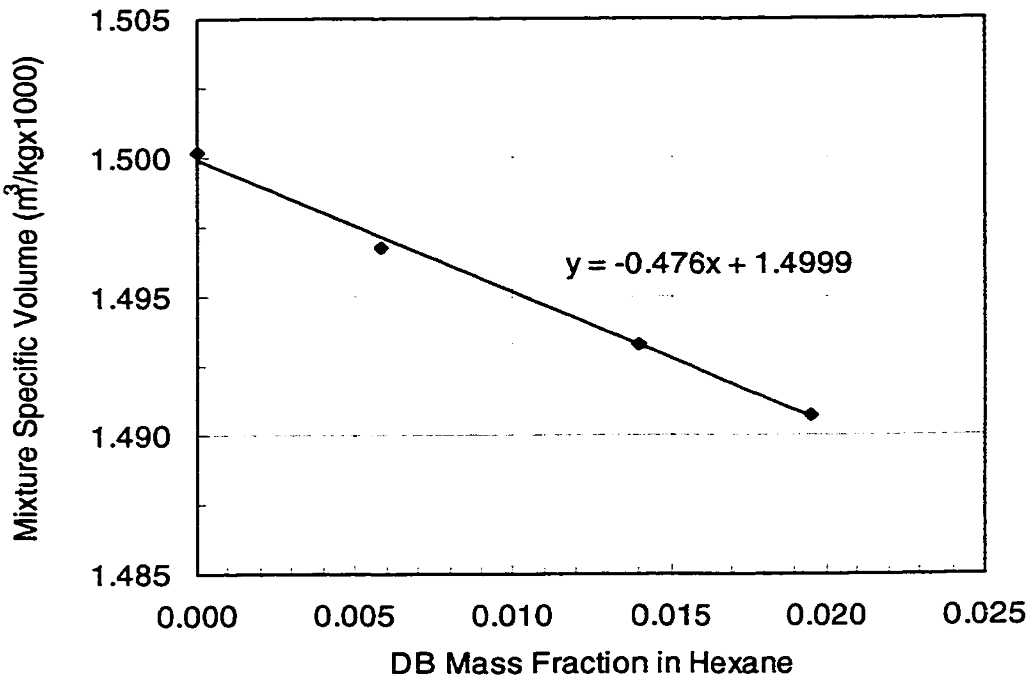
a – [Yarranton, 1997]

b – [Adamson, 1990]

c – [Weast, 1987-1988]

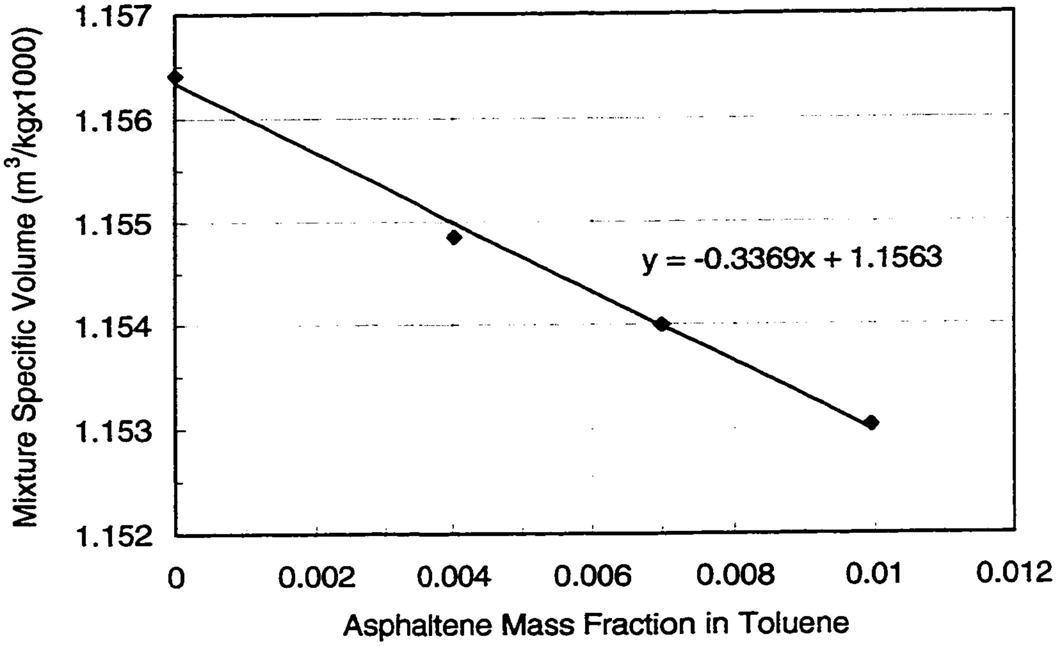
d – [Ross and Patterson, 1979]

e – [Li and Fu, 1992]



$$\rho_{DB} = 1/(-0.476+1.4999)\times 1000 = 977\ (kg/m^3)$$

Figure 2-1. Dependence of DB/hexane mixture specific volume on DB mass fraction



$$\rho_{Asphaltene} = 1 / (-0.3369 + 1.1563) \times 1000 = 1220\ (kg/m^3)$$

Figure 2-2. Dependence of asphaltene-solids/toluene mixture specific volume on asphaltene-solids mass fraction

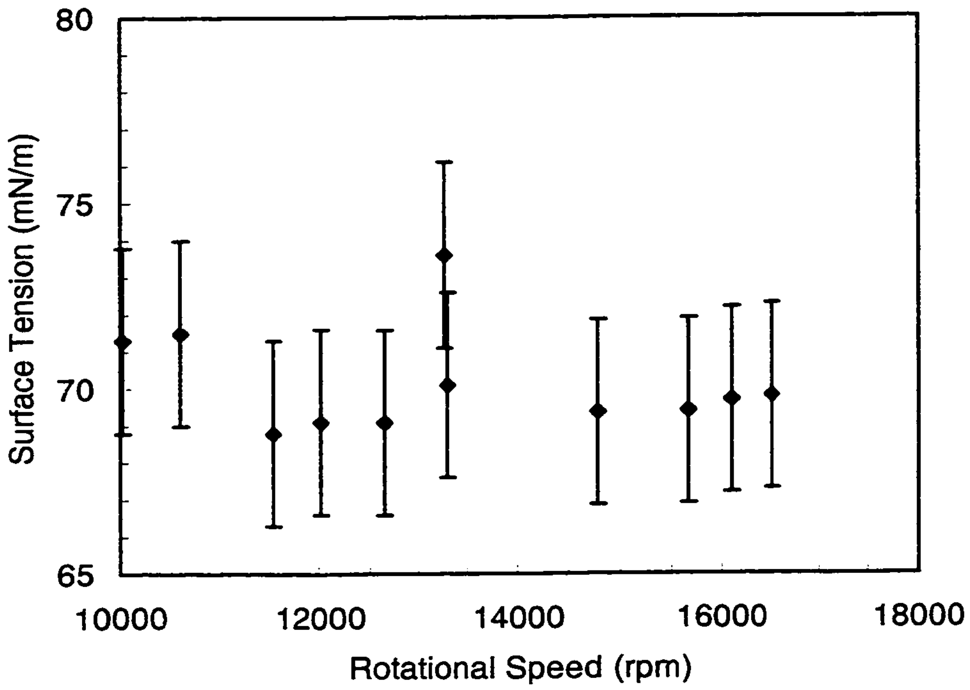
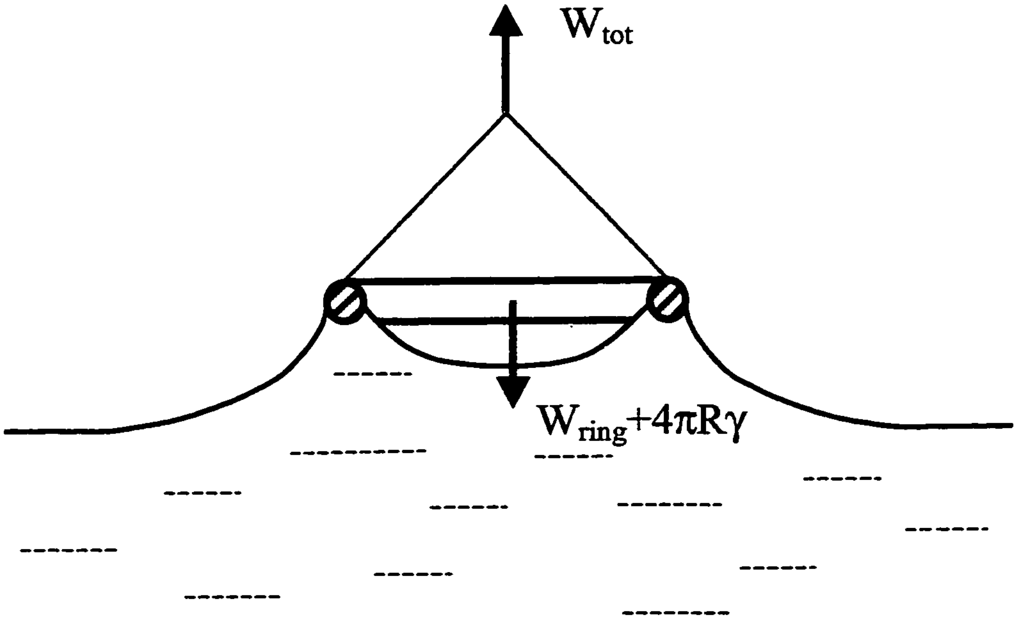
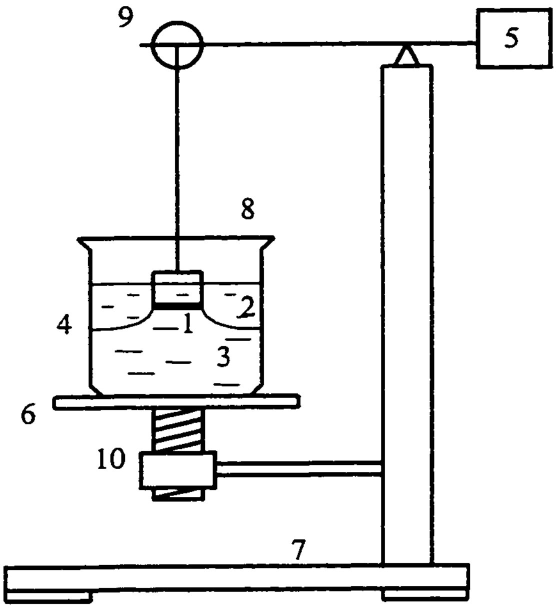


Figure 2-3. Surface tension of water measured using a Jefri spinning drop tensiometer



$$W_{tot} = W_{ring} + 4\pi R\gamma$$

Figure 2-4. Principle of a ring tensiometer



1. Platinum ring
2. Upper liquid phase
3. Lower liquid phase
4. Beaker
5. Balance & dial
6. Movable platform
7. Support
8. Lid
9. Lever indicator
10. Screw

Figure 2-5. Schematic of a deNouy ring tensiometer

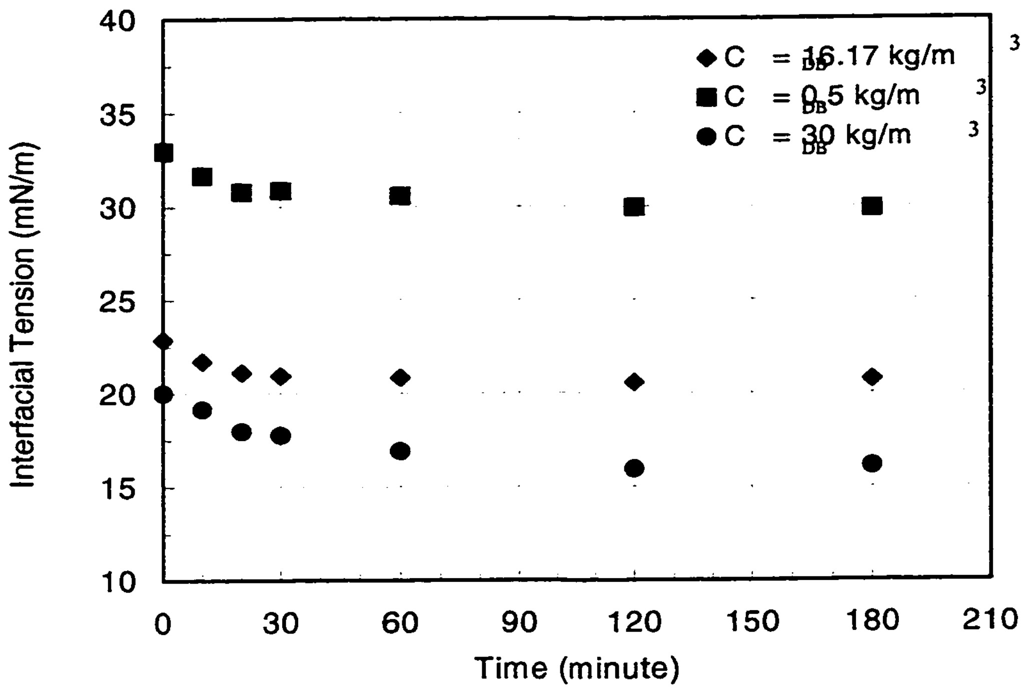


Figure 2-6. Time dependence of the interfacial tension of

de-asphalted bitumen/hex-tol over water

(C_{DB} = Mass of solute/Volume of solvent)

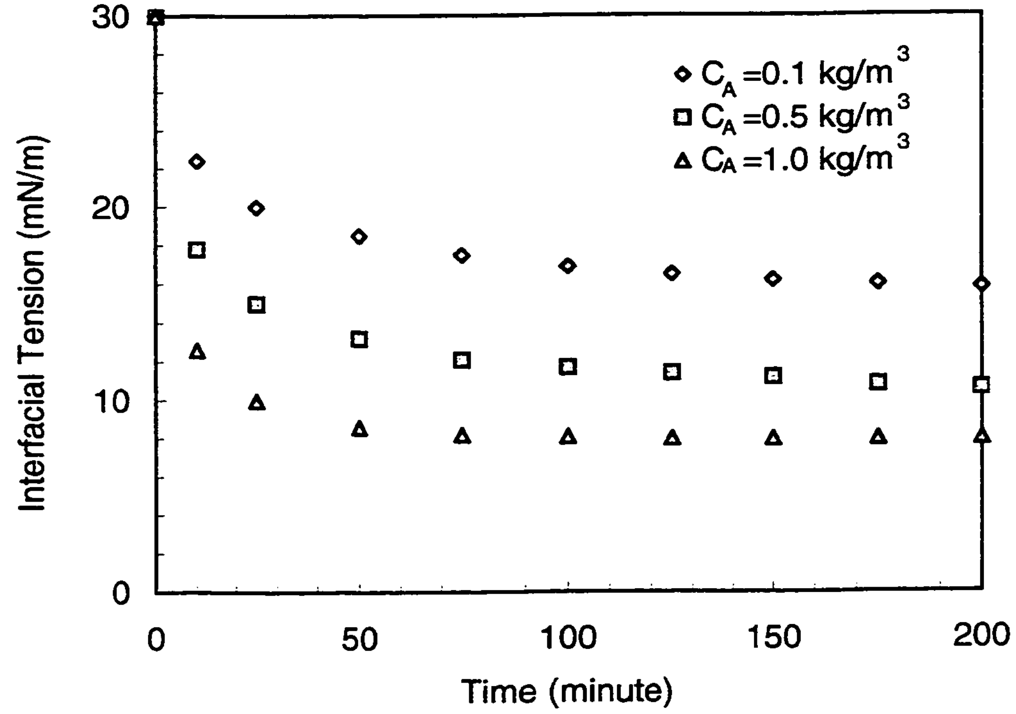


Figure 2-7. Dynamic interfacial tensions of asphaltene/toluene against NaOH

(reproduced from [Sheu, 1992])

(C_A = Mass of solute/Volume of solvent)

CHAPTER 3.

INTERFACIAL TENSION OF THE MAIN BITUMEN COMPONENTS IN CONTACT WITH WATER

3.1 Introduction

A study of interfacial tension is the first step in understanding the behavior of a water/bitumen interface. It is well known that surface-active substances, e.g. surfactants, affect interfacial behavior. By using a spinning drop tensiometer, Pasquarelli and Wasan [1981] measured the interfacial tensions between a crude oil and alkaline brine solutions. They concluded that asphaltic material greatly contributed to surface activity. Mackay *et al.* [1973] suggested that the emulsifying agent responsible for the formation of water-in-crude-oil emulsions was an asphaltic-type substance. However, Mohammed *et al.* [1993] measured the interfacial tensions of diluted asphaltenes and resins with water with a hydrophobic Wilhelmy plate and no clear conclusion could be obtained.

In this chapter, measurements of interfacial tension of diluted asphaltene-solids, de-asphalted bitumen and whole Athabasca bitumen in contact with de-ionized water are reported. A series of tests at different concentrations in solvent was conducted and surface-active components were found in de-asphalted bitumen. A rough estimation of the average molar mass of the surface active molecules in de-asphalted bitumen was made from the interfacial tension measurements.

The solvents used to dilute the aforementioned materials were hexane and toluene. For convenience the solvent is called hex-tol in this thesis. The whole bitumen or the asphaltene-solids was dissolved in a certain amount of toluene and was stirred by an electric mixer at 175 rpm for 30 minutes. Then hexane was added to the solution. The added material/hex-tol solution was stirred with a glass rod slowly for 2 minutes to allow thorough mixing. After the solution was allowed to stand overnight, it was ready for interfacial tension measurements.

The preparation of the diluted de-asphalted bitumen was the same as the aforementioned procedure except that the de-asphalted bitumen was already diluted with hexane before it was mixed with toluene. This was due to the way that de-asphalted bitumen was separated from the whole bitumen (refer to Chapter 2).

3.2 Theory

At constant temperature, for an interface of water in contact with a dilute solution of one type of surface active molecules and a type of solvent, the dividing surface may be placed at a position such that there is no adsorption of solvent molecules [Lupis, 1983]. Given the aforementioned assumptions, the following thermodynamic relation holds [Perry and Green, 1984],

$$\frac{d\gamma}{d\ln x} = -RT\Gamma = -\frac{RT}{A} \tag{3-1}$$

$$x = \frac{N}{N + N_{solvent}} \tag{3-2}$$

where γ (N/m) is the interfacial tension, x (mol/mol) is the mole fraction of the surface active molecules in the bulk solution, R (J/mol·K) is the universal gas constant, T (K) is the temperature at which the interfacial tension is measured, Γ (mol/m^2) is the relative surface excess or relative adsorption of the surface-active molecules with respect to the solvent molecules [Lupis, 1983], A (m^2/mol) is the molar surface area of the surface-active molecules. Here N (mol) is the number of moles of the surface active component and $N_{solvent}$ is the number of moles of the solvent molecules in the solution. The unit "mol" refers to gmol throughout the thesis.

For a dilute solution, one can write,

$$\begin{aligned} x &\cong \frac{N}{N_{solvent}} \\ &= C \cdot \frac{M_{solvent}}{M} \cdot \mathrm{v}_{solvent} \\ &= C \cdot \text{constant} \end{aligned} \tag{3-3}$$

and

$$d \ln x = \frac{dx}{x} \cong \frac{dC}{C} = d \ln C \tag{3-4}$$

where C (kg/m^3) is the concentration of a surface active species in the solution on a solute-free basis, M (g/mol) is the molar mass and v (m^3/kg) is the specific volume. Consequently, for a dilute solution, Equation (3-1) can be re-written as

$$\frac{d\gamma}{d \ln C} = -RT\Gamma = -\frac{RT}{A} \tag{3-5}$$

where

$$A = -\frac{RT}{\left(\frac{d\gamma}{d\ln C}\right)} \qquad (m^2/mol) \qquad (3\text{-}6)$$

From Equation (3-5), one can note that the rate of the change of γ with $\ln C$ is proportional to Γ, the relative number of surface active molecules adsorbed on an unit area of the interface. If γ is plotted versus $\ln C$, the local slope of the γ - $\ln C$ curve is proportional to the number of adsorbed molecules on the interface. The steeper the γ - $\ln C$ curve is, the more molecules are adsorbed on the interface. When the interface becomes saturated with the molecules, Γ will not change with C and therefore the γ versus $\ln C$ curve becomes a straight line.

When the interface is saturated with surface-active molecules, the term A in Equation (3-5) and (3-6) can be assumed to be approximately the molar cross-sectional area of the adsorbed surface active molecules on the interface. The cross-sectional area of such a molecule may be found from

$$a = A / N_a \qquad (m^2 / molecule) \qquad (3\text{-}7)$$

where N_a is Avogadro's number that is given by 6.022×10^{23} (molecules/mol). The molar mass of the molecules can be estimated by using a in the saturation state. But first of all, a molecular geometry of the molecules must be assumed in order to calculate the molar volume from a. Although the molecular geometry is unknown, it can be approximated as spherical or cylindrical [Yarranton and Masliyah, 1996]. Due to the limited information of the complicated species of bitumen molecules and also for simplicity, the spherical geometry is used in this work. If the centers of all suface active molecules stay on the interface or in other words, if a is the largest cross-sectional area of a spherical adsorbed molecule, then the diameter of the molecules is given by:

$$\begin{aligned} d &= \left(\frac{4}{\pi}a\right)^{1/2} \\ &= \left(-\frac{4}{\pi}\frac{1}{N_a}\frac{RT}{(d\gamma / d\ln C)}\right)^{1/2} \qquad (m) \end{aligned} \tag{3-8}$$

Hence the molar mass of the adsorbed surface-active molecules is:

$$M = 1000 \cdot \rho \cdot (\frac{1}{6}\pi d^3)N_a \qquad (g / mol) \tag{3-9}$$

where ρ (kg/m^3) is the density of the molecules.

When Equations (3-5) to (3-9) are applied to a multi-component solution, they give an "average" molar mass. This "average" molar mass is only a rough estimate due to several simplifications made. One simplification is that all kinds of molecules in a complex material were treated as one kind of molecule that has the average physical and chemical properties of all the actual molecules. And it is assumed that the adsorbing molecules have the same characteristics as the average characteristics in the bulk. Hence the molar concentration and the density used in the calculation are a bulk concentration and a bulk density of all the species. The other simplification was to assume that the molecules have spherical geometry. Because the organic molecules are very complicated in structure, they are normally not spherical. The shape of the molecules needs to be determined in further work.

3.3 Interfacial Tension Measurements

The interfacial tension values reported in this chapter were measured with a deNouy platinum ring tensiometer as was described in Chapter 2.

3.4 Results and Discussions

3.4.1 Interfacial Tension of the De-asphalted Bitumen-water System

Figure 3-1 shows a typical γ - lnC_{DB} plot of diluted DB (de-asphalted bitumen) in contact with water. The solvent used was hex-tol (hexane and toluene with 50% toluene by volume). As can be seen in the figure, with increasing de-asphalted bitumen concentration in hex-tol, the interfacial tension decreases and the absolute value of the slope of the curve becomes higher. From the data in Figure 3-1 and the relationship given in Equation (3-5), the number of DB molecules adsorbed on the interface, Γ_{DB}, was plotted versus C_{DB} in Figure 3-2 from which it can be seen that more molecules adsorb on the interface as the de-asphalted bitumen concentration increases. From Figure 3-1, one can assume that there are surface-active molecules in de-asphalted bitumen. When C_{DB} reaches about 100 kg/m^3, the interfacial tension may be level off. However, it is difficult to conclude from the limited number of data points. This region is possibly the critical micelle concentration (cmc) above which interfacial tension doesn't change with solute concentration due to the formation of the micelles. The presence of a critical micelle concentration could be another piece of evidence of the presence of surfactants in de-asphalted bitumen. In order to obtain a clear understanding of what is happening at this point where the surface tension levels off, future work is needed.

In Figure 3-1, the γ - lnC_{DB} curve is close to linear when C_{DB} is between 10 and 100 kg/m^3 and in Figure 3-2 the Γ_{DB} is relatively constant when C_{DB} is in the same region. This means that the interface is saturated with the surface-active molecules contained in DB at those concentrations. By measuring the slope of the linear portion of the γ - lnC_{DB} curve or directly using an average Γ_{DB} value of the saturation region, an approximate "average" molar mass of DB molecules can be calculated using Equations (3-8) and (3-9). The results for the molar masses will be discussed later in this chapter.

Data for interfacial tensions of diluted DB with water are shown in Figure 3-3. De-asphalted bitumen was diluted with hexane and toluene having various ratios. In general, the DB molecules, or some of them, are surface-active for all different compositions of diluent studied. However, the adsorption processes were somehow affected by the diluent composition. When DB is diluted with hex-tol (3:1), the diluted DB/water interface became saturated at a relatively low concentration of about 0.01 kg/m^3. However, when DB was diluted with hex-tol (9:1), the surface-active molecules in DB kept adsorbing on the interface until C_{DB} reaches a value of about 10 kg/m^3.

On the other hand, it was found (see Figure 3-3) that the location of the constant surface tension region was not strongly dependent on the diluent composition.

Assuming that all de-asphalted bitumen molecules are surface-active or that the surface active molecules have the same average chemical characteristics of the bulk, the "average" molar masses of DB molecules were calculated with Equations (3-8) and (3-9) using the slope of the γ - $\ln C_{DB}$ curves at the interface saturation states, shown in Figure 3-4. The calculation results are listed in Table 3-1. The "average" molar masses of de-asphalted bitumen molecules, listed in Table 3-1, range between 229 g/mol and 800 g/mol. It seems that toluene-rich-diluents give smaller DB molar masses and hexane-rich-diluents give larger molar masses. This phenomenon doesn't definitely reflect the real situation because of the assumptions made in the calculations. The first assumption was treating all kinds of molecules in DB as one kind of molecules that has the average behavior of the real molecules. The second assumption was that all de-asphalted bitumen molecules are surface active, which may not be true. Hence, the bulk concentration and bulk density of all DB molecules, which were larger than the concentration of the surface-active species, were used as the concentration and density of the surface-active species. However, from Equation (3-8) and (3-9) one can note that a larger concentration C_{DB} would make our estimation an upper limit for the molar mass of DB. Consequently, the surface-active DB molecules would be expected to be smaller than the data listed in Table 3-1. Thirdly, it was assumed that the DB molecules were spherical. In fact, DB molecules can not be absolutely spherical due to their complex molecular structures.

It is, however, meaningful to compare the "average" molar mass of de-asphalted bitumen with that obtained in a similar manner for asphaltenes. The molar masses of asphaltenes in Table 3-1, in diluents with different toluene content, range from 2997 g/mol to 5454 g/mol. These are much higher than the "average" molar masses of DB molecules. The asphaltene molar masses listed in Table 3-1 were obtained in a similar way to the present work except that the asphaltene molecules were assumed to be cylindrical [Yarranton and Masliyah, 1996]. This comparison presents a qualitative perspective of the size of the de-asphalted bitumen molecules. Since asphaltene bulk concentration was correct and our assumption on bulk concentration leads to an upper limit on DB size, we can indeed conclude the surface active DB molecules are smaller than asphaltene molecules.

3.4.2 Comparison of the Interfacial Tensions of Bitumen, DB and Asphaltene-Solids in Contact with Water

As a comparison to de-asphalted bitumen, the interfacial tensions of diluted whole bitumen and asphaltene-solids, respectively, in contact with water were measured in the same manner. The results are shown in Figure 3-5. The three curves are plotted with the abscissa being the "original bitumen concentration" instead of the absolute concentration of each specimen in the diluent. The original bitumen concentration is the concentration of the whole bitumen that is needed to extract the necessary amount of asphaltene-solids or DB used in the interfacial tension measurement. For example, if the abscissa of a point on the asphaltene-solids curve is 10 kg/m^3, the true asphaltene-solids concentration in hex-tol is 10 kg/m^3 × 16% = 1.6 kg/m^3, assuming that the asphaltene-solids make up 16% of the original whole bitumen. Thus, the 10 kg/m^3 is the original bitumen concentration when de-asphalted bitumen molecules haven't been removed. The bitumen curve in Figure 3-5 is plotted using the true absolute bitumen concentration since nothing was taken out from the original bitumen.

From Figure 3-5, we can observe the interfacial tension difference among the three materials. Asphaltene-solids has the highest interfacial tension with water, while de-asphalted bitumen has the lowest interfacial tension with water. When C_B (original bitumen concentration) is above the value of 0.2 kg/m^3, the drop in the interfacial tension of asphaltene-solids is smaller than that of the de-asphalted bitumen. Therefore, the de-asphalted bitumen contains species that are more surface-active than asphaltene-solids. The interfacial tension of the whole bitumen, which contains both asphaltene-solids and de-asphalted bitumen, is between that of asphaltene-solids and de-asphalted bitumen. Hence, both large asphaltene molecules and smaller molecules present in de-asphalted bitumen cover the water/bitumen interface.

3.5 Conclusions

Interfacial tension measurement results show that de-asphalted bitumen has surface-active components. By comparing with asphaltene-solids, it was found that the surface activity of de-asphalted bitumen is higher than that of asphaltene-solids.

The "average" molar mass of DB molecules was roughly estimated using the measured interfacial tension and a thermodynamic relationship. The "average" molar mass of DB was found to be much smaller than that of asphaltenes.

The interfacial tension of bitumen is between that of asphaltene-solids and de-asphalted bitumen. Consequently, the water/bitumen interface is covered not only by asphaltene molecules and solids but also by other smaller molecules contained in bitumen.

3.6 References

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Table 3-1. Molar mass comparison of de-asphalted bitumen and asphaltene molecules

Items	Density	$d\, lnC_{solute} / d\gamma$	Molecular cross-sectional area	Molar mass of solute
	kg/m^3	-	*(nm)*^{2}	*g/mol*
Present work (solute is de-asphalted bitumen)				
90% Toluene	1014	-0.1542	0.63	*229*
75% Toluene	1014	-0.1251	0.51	*167*
50% Toluene	1014	-0.2473	1.01	*464*
25% Toluene	1014	-0.3555	1.45	*800*
Literature (solute is asphaltenes) [Yarranton, 1997]				
100% Toluene	1162	-1.1670	4.75	*5454*
50% Toluene	1159	-1.0948	4.46	*4943*
40% Toluene	1152	-1.0896	4.44	*4878*
25% Toluene	1129	-0.8720	3.55	*3423*
20% Toluene	1123	-0.8008	3.26	*2997*

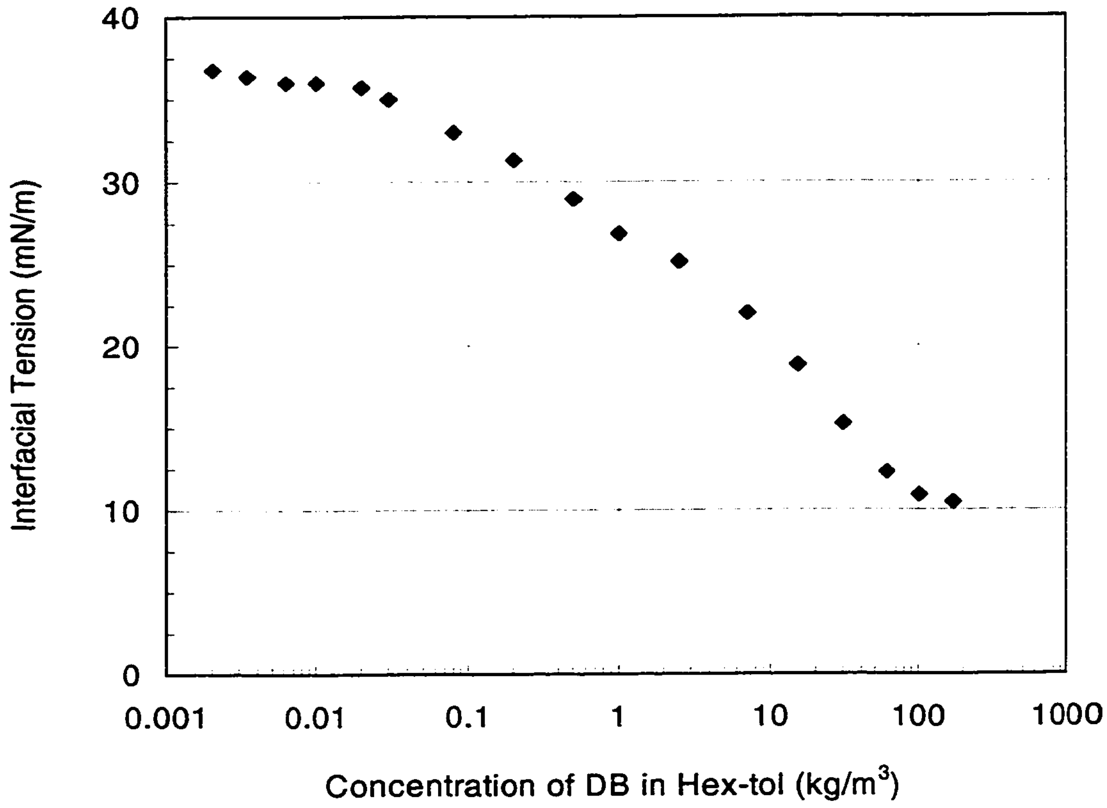

Figure 3-1. Interfacial tension of hex-tol diluted de-asphalted bitumen over water versus DB concentration

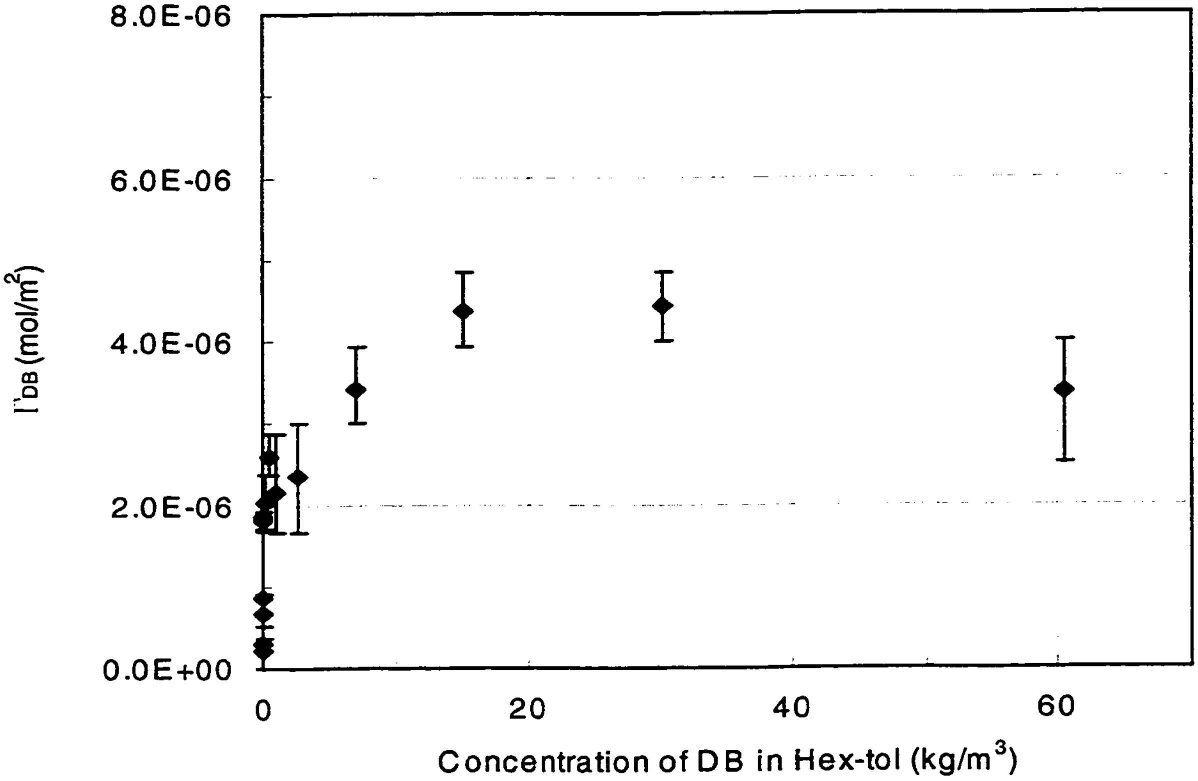

Figure 3-2. Molar surface coverage of de-asphalted bitumen molecules on the DB/water interface

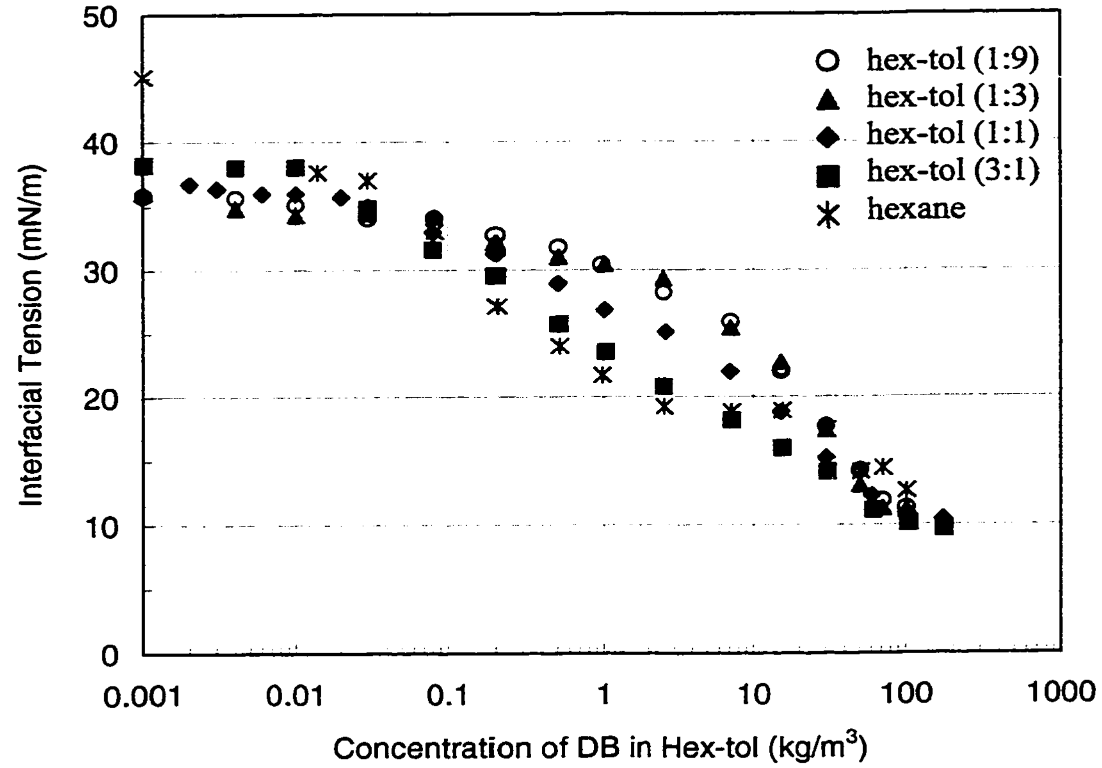

Figure 3-3. Interfacial tensions of de-asphalted bitumen over water with different hexane/toluene ratios of the solvent

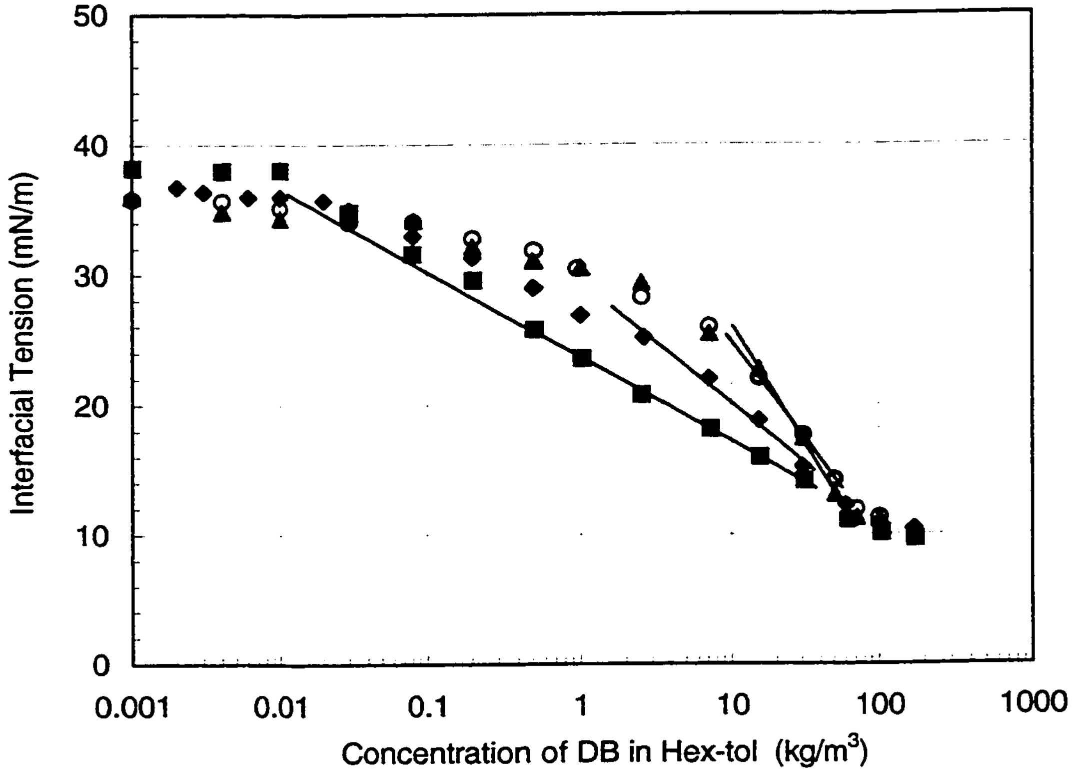

Figure 3-4. Slopes at the interface saturation states of the DB/water interface

○ hex-tol (1:9): y = -6.484 ln(x) + 39.745
▲ hex-tol (1:3): y = -7.9971 ln(x) + 44.566
◆ hex-tol (1:1): y = -4.0433 ln(x) + 29.439
■ hex-tol (3:1): y = -2.8134 ln(x) + 23.701

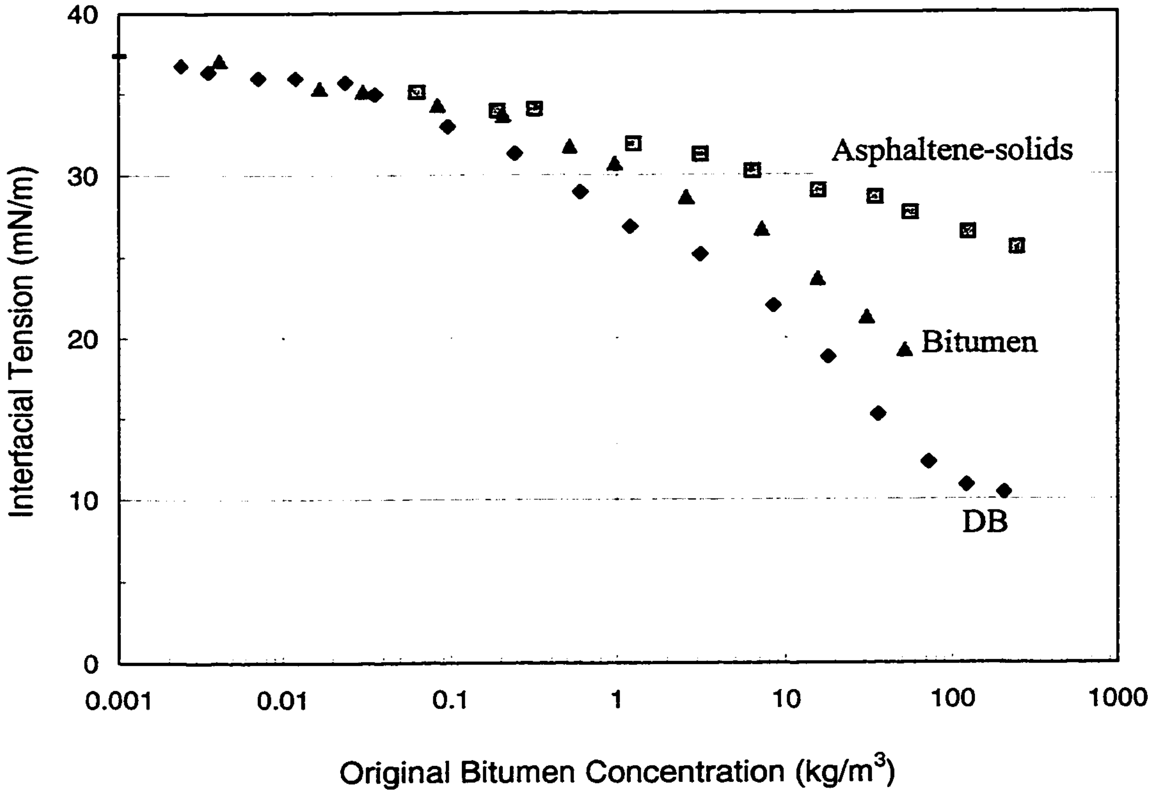

Figure 3-5. Comparison of the interfacial tensions of hex-tol diluted bitumen, DB and asphaltene-solids in contact with water

CHAPTER 4.

ROLES OF VARIOUS BITUMEN COMPONENTS IN STABILIZING WATER-IN-BITUMEN EMULSIONS

4.1 Introduction

Water-in-crude-oil emulsions in the oil processing industries are considered to be harmful for a variety of reasons. The emulsified water formed in the bitumen extraction process eventually brings chlorides into coker feed bitumen. The chlorides can cause corrosion when they contact downstream hot metal processing facilities. As well, water-in-crude-oil emulsions formed in oceanic oil spills can make clean up more difficult and therefore lead to environmental damage [Mackay *et al.*, 1973]. Usually water-in-oil emulsions are very stable and the water in such emulsions is difficult to remove. Therefore it is of great interest to the oil industry to understand how emulsions are stabilized in order to allow the development of de-emulsification methods [Yarranton, 1997, Mohammed *et al.*, 1993].

Research was carried out on different aspects of the stability of water-in-crude-oil emulsions. Some researchers have ascribed the stability of water-in-crude-oil emulsions to the rheological characteristics of the interface [Mohammed *et al.*, 1993]. Reisberg and Doscher [1956] have obtained values for the equilibrium interfacial tension to be in the range of 27.5 to 34 mN/m for different crude-oil/water systems. By using a Langmuir trough to study interfacial film behavior at the crude-oil-water interface for Kuwait, Iranian Heavy, Ninian and Forties crudes, Jones *et al.* [1978] distinguished three types of film and film behavior. They indicated that the dynamics of the film relaxation process dictate the extent of the barrier to emulsion stability. In short, such studies of water-in-crude-oil emulsions were conducted from a microscopic point of view.

Macroscopically, Yarranton [1997] studied the stability of asphaltene-stabilized water-in-hex-tol emulsions by measuring the water drop size distributions over time. He concluded that only soluble, surface active asphaltenes stabilized the emulsions and that the emulsions appear to destabilize through a form of Ostwald ripening.

According to the aforementioned studies, asphaltenes are commonly regarded as the agent responsible for stabilizing water-in-crude-oil emulsions. However, it was not clearly known how asphaltenes stabilize a water-oil interface in the presence of resins and other smaller molecules contained in bitumen. As well, it was not known whether or not resins enhance the stability of the emulsions. In short, the connection between interfacial tension values and emulsion stability was not clear.

Focused on these questions, in the present work the stability of water-in-bitumen emulsions was studied experimentally at a macroscopic scale. In order to investigate roles of different bitumen components in stabilizing water-in-bitumen emulsions, a series of emulsions were prepared, the stabilities of which were compared.

Precisely, in order to study the role of component "*i*" in bitumen, the stability of two emulsions are compared: one emulsion is a water-in-bitumen emulsion, the other one is a water-in-"*i*"-free-bitumen emulsion. The design of the emulsion experiments is illustrated in Table 4-1. The three components that were studied are de-asphalted bitumen, asphaltenes and solids. They are given in the top row of Table 4-1 while possible compositions of the emulsions are given in the first column of Table 4-1. (Water and hex-tol are included in all emulsions and have been left off the table). The symbols A,B,C,D,E in the second row of the table represent 5 emulsions used in the experiments. Take DB as an example. In order to examine the role of DB in stabilizing water-in-bitumen emulsions, two emulsions, represented by A and B in Table 4-1, were compared. Emulsion A was prepared by emulsifying water into hex-tol diluted whole bitumen in which DB, asphaltenes and solids were all present. In emulsion B, DB was removed from the whole bitumen before water was emulsified in the bitumen. Hence emulsion B was actually prepared by dispersing water into hex-tol diluted DB-free bitumen, which consisted only of asphaltenes and solids. The difference of the stability of the two emulsions could be used as a measure of the role of de-asphalted bitumen. Similarly, the roles of asphaltenes and solids in stabilizing water-in-bitumen emulsions were investigated by comparing the stability of the emulsions listed in Table 4-1.

4.2 Experiment

4.2.1 Preparation of the Organic Solutions for the Emulsions

During the recovery of bitumen from oil sands, hot water is used to recover bitumen from sand grains (refer to Figure 1-2). In order to remove the water from bitumen froth produced during the bitumen extraction process, bitumen froth is diluted with naphtha in order to reduce the hydrocarbon phase viscosity. Presently, heptane and hexane are also suggested to be used as substitutes for naphtha as part of an overall strategy for salt reduction [Shelfantook *et al.*, 1996]. To simulate the industrial situation of naphtha usage, and also to simplify the study, hexane and toluene with a 1:1 volume ratio were used in this work as the diluent. "Hex-tol" in the following is an abbreviation of "hexane and toluene".

The first step in making the above-mentioned emulsions is to prepare the organic solution in which water is to be emulsified. Specifically, the organic phase consists of diluted bitumen or bitumen components, including de-asphalted bitumen, asphaltenes and solids.

In order to make the emulsions comparable, when diluting bitumen or the various compositions of bitumen components, the original bitumen concentrations in hex-tol for each organic solution are kept the same, that is 30 kg/m^3. The "original bitumen concentration" is the concentration corresponding to the amount of whole bitumen that was originally used to extract the certain amount of the bitumen components that were used to prepare the solution. For example, the diluted DB-free-bitumen solution is prepared by dissolving the asphaltene-solids extracted from whole bitumen in hex-tol. Since the original bitumen concentration is set as 30 kg/m^3, the actual asphaltene-solids concentration in hex-tol is 30 kg/m^3 × 16% = 4.8 kg/m^3, assuming asphaltene-solids make up approximately 16% of whole bitumen. This diluted asphaltene-solids solution is equivalent to the one prepared by taking out all DB molecules from a 30 kg/m^3 diluted whole bitumen solution.

After the amount of the solute and the solvent needed were calculated, one or more of the three main bitumen components was mixed with hex-tol using the same procedure described in Chapter 3. After the organic solution was allowed to stand overnight, it was ready for making water emulsions.

4.2.2 Preparation of the Emulsions

The procedure for preparing an emulsion was strictly controlled. As is shown in Figure 4-1, after the organic solution was ready to use, 400 ml of solution was placed in a 1-liter beaker. Then 40 ml of de-ionized water was poured slowly into the organic solution. The water was emulsified with a homogenizer for 5 minutes. The homogenizer is a 1L-1998 model, purchased from Greeco Company. The input voltage of the homogenizer was set at 36 volts, which gave approximately 2350 rpm.

Immediately after the emulsion was prepared, the emulsion was transferred into a 500 ml graduated cylinder. Because the organic solution was not very viscous due to the presence of the diluent, water drops started to settle to the bottom of the cylinder within several minutes. If the emulsion was not stable, some free water would appear at the very bottom of the cylinder after a period of time. The less stable the emulsion is, the more the free water appears at the bottom of the cylinder. Hence, by comparing the volume of free water after 48 hours, the stability of the emulsions could be compared. The reading of free-water volume may vary within ±2.5 ml for different samples.

In some cases, if the two emulsions to be compared were very stable with no free water appearing, it would not be possible to quantify the stability difference between them. In that case, the stability of the 1st-stop emulsions was further compared. A 1st-stop emulsion is an emulsion prepared by emulsifying 40 ml of water into 400 ml of the organic supernatant in the original emulsion that was prepared with the "fresh" organic solution. Similarly, a 2nd-stop emulsion was prepared from 40 ml water and 400 ml of the organic supernatant originating from the 1st-stop emulsion. Since the surface-active molecules tend to adsorb at the interface, the number of surface-active molecules in the supernatant of an emulsion is less than that in the original organic solution used to prepare the emulsion. Therefore, the various emulsions, in order of high stability to low stability, are the original emulsion, the 1st-stop emulsion and the 2nd-stop emulsion.

While the volumes of the settled emulsion were recorded with time, microscopic photographs of the water droplets in the settled emulsions were taken at 30 and 60 minutes after the emulsions were prepared. Because the water droplet size distribution varies with the height of the settled emulsion layer, the location of the sampling point of the emulsion could introduce some variability into the estimation of the average size of the water droplet [Yarranton, 1997]. The droplets at the very top layer of the settled emulsion appear to grow more slowly [Yarranton, 1997]. In order to minimize this variance, all the samples used for taking the photographs were drawn from approximately the center of the settled emulsion.

4.3 Results and Discussions

4.3.1 Role of DB in Stabilizing Water-in-Bitumen Emulsions

As was illustrated in Table 4-1, in order to investigate the role of de-asphalted bitumen in stabilizing water-in-bitumen emulsions, the stability of two emulsions were compared. One emulsion was prepared with the whole bitumen while the other emulsion was prepared with asphaltene-solids extracted from the whole bitumen. By comparing the stability of the two emulsions, prepared with and without DB, the role of DB can be investigated.

Figure 4-2 shows the volume of the settled emulsion and the free water after the emulsions were allowed to settle for 48 hours. For the two original emulsions, both the water-in-bitumen and the water-in-asphaltene-solids emulsions were very stable as no free water layer was evident after 48 hours. In order to quantify the stability difference between the two original emulsions, 1st-stop emulsions were prepared with the supernatant of the original respective emulsions. As shown in Figure 4-2, after 48 hours of settling, it was observed that the 1st-stop emulsion prepared with bitumen yielded about 14 ml of free water, but the one prepared with asphaltene-solids was still very stable without any free water. After the 2nd-stop emulsions were allowed to stand for 48 hours, the 2nd-stop bitumen emulsion was not stable at all. All water drops disappeared and only free water and organic solution existed in the system. However, the 2nd-stop water-in-asphaltene-solids emulsion was still very stable, with no free water appearing. Therefore, one can conclude that the water-in-bitumen emulsion is less stable than the water-in-asphaltene-solids emulsion. In other words, when de-asphalted bitumen molecules are removed from bitumen, the stability of the water-in-bitumen emulsion increases. The presence of DB molecules decreases the stability of water-in-asphaltene-solids emulsions.

Reports from previous studies show that the principal source of stability of water-in-oil emulsions arises from the formation of a condensed and viscous interfacial film [Blair, 1960]. Such films present a barrier to flocculation and coagulation of the dispersed water droplets. Through a series of experiments, it was found out that the film, which encapsulates each droplet, is mainly composed of asphaltenic type substance [Mackay, 1973]. Based on these previous findings, there are two possible explanations to the phenomenon observed in the present work. One explanation is that the smaller and less aromatic molecules in de-asphalted bitumen dissociate the larger asphaltene agglomerates into smaller ones and hence decrease their ability of forming a strong interface film. Another possible explanation is that the de-asphalted bitumen molecules present on the water/bitumen interface can separate asphaltene molecules from each other and hence weaken the attraction force between the asphaltene molecules greatly. In both situations, the mechanical strength of the asphaltenic film would be decreased and the stability of water-in-bitumen emulsions would be expected to be less than that of water-in-asphaltene-solids emulsions.

During the experiments, it was noticed that the colors of the settled emulsions were different. In the water-in-asphaltene-solids emulsion, the settled emulsion was dark brown. In the water-in-bitumen emulsion, it was medium brown. Unfortunately, no useful information about the colors was obtained from the optical micrographs.

4.3.2 Roles of Asphaltenes and Solids

As shown in Table 4-1, two pairs of emulsions were prepared to observe the role of asphaltenes in stabilizing water-in-bitumen emulsions. The first pair of emulsions includes a water-in-bitumen emulsion and a water-in-DB-solids emulsion. The latter emulsion can also be thought of as an emulsion prepared with asphaltene-free-bitumen. By comparing the stability of such a pair of emulsions, the role of asphaltenes can be investigated. To remove any possible effects of the solids contained in the emulsions, a second pair of emulsions, prepared with solids-free-bitumen and DB, respectively, was compared.

Figure 4-3 shows the results of stability tests for two pairs of the emulsions. For the first pair of emulsions, the water-in-bitumen emulsion was very stable as was mentioned earlier. The emulsion prepared with DB-solids, which was actually asphaltene-free-bitumen, was less stable than the water-in-bitumen emulsion where more than 25 ml of free water appeared in 48 hours after the emulsion was prepared. Hence, the stability of the water-in-bitumen emulsion decreases when asphaltenes are removed from the bitumen. Asphaltenes act as stabilizers for water-in-bitumen emulsions.

From Figure 4-3, one can obtain the same conclusion from the second pair of emulsions, in which solids have been removed from both emulsions. The emulsion prepared with only de-asphalted bitumen was not stable at all. It produced a free water phase and an organic phase with no emulsion present after 48 hours. However, for the emulsion made with DB and asphaltenes, i.e. solids-free-bitumen, about 20 ml of settled emulsion remained in addition to the 20 ml of free water. Therefore, the presence of the solids doesn't affect the interfacial adsorption properties of the asphaltenes. Asphaltenes alone can stabilize the water/bitumen interface fairly effectively.

The role of the solids in stabilizing water-in-bitumen emulsions was also studied. The results are shown in Figure 4-4. The first pair of emulsions was prepared with bitumen and solids-free-bitumen filtered with 0.22 μm filter paper. It is clear that the water-in-solids-free-bitumen emulsion was less stable than that prepared with bitumen. In the second pair of emulsions in Figure 4-4, asphaltenes were removed from the organic phase prior to emulsion preparation. Therefore, the possible effect of the asphaltenes on the interfacial behavior of the solids was avoided. From Figure 4-4, it can be seen that no matter whether or not asphaltenes are present in the systems, solids act as a stabilizer for the water-in-bitumen emulsion. The stability of water-in-bitumen emulsions decreases if solids are removed from the bitumen.

In Figure 4-4, one can also observe that the stability of water-in-bitumen emulsions is very high when both asphaltenes and solids are present. If either of them is removed from bitumen, the water-in-bitumen emulsion will be less stable. By comparing the second and third bars of Figure 4-4, the strength of the two kinds of stabilizers: asphaltenes and solids can be compared. The second bar is for a water-in-solids-free-bitumen emulsion. The third bar is for a water-in-DB-solids emulsion—the emulsion prepared with asphaltenes-free-bitumen. Both emulsions yielded some free water in 48 hours. Although the solids-free-bitumen emulsion seemed to be more stable than the DB-solids emulsion, the difference between them, which was about 4ml of free water, was within the experimental error. Hence, as far as we can conclude from these experimental results, solids and asphaltenes are both effective stabilizers for water-in-bitumen emulsions, and they reinforce each other in their stabilization effectiveness.

It was also found that the role which solids played in stabilizing water-in-bitumen emulsions was dependant upon the size of the solids. Figure 4-5 shows emulsion stability tests conducted with whole bitumen and two solids-free-bitumen emulsions. The solids were filtered from the whole bitumen using 8 μm and 0.22 μm filter paper respectively. Figure 4-6 shows SEM micrographs of the solids filtered using these two sizes of filter papers. Solids captured by the 8 μm filter paper made up 0.6 wt.% of the whole bitumen while 0.22 μm filter paper could capture solids that made up about 1 wt.% of the whole bitumen. Most solids captured by the 8 μm filter paper were larger than 0.5 μm. The size distribution of the solids captured by the 0.22 μm filter paper was very wide with much more solids smaller than 0.5 μm. The emulsion prepared with the

8μm-filtered-bitumen was very stable without any occurrence of free water in 48 hours. However, the emulsion prepared with the 0.22μm-filtered-bitumen, as described previously, was not quite stable with approximately 20 ml of free water coming out in 48 hours. Therefore, not all the solids are equally effective in stabilizing water-in-bitumen emulsions. According to these experiments, one can conclude that fine solids, which would be removed with 0.22 μm filter paper and would not be removed with 8 μm filter paper, stabilize the water/bitumen interface effectively.

4.3.3 Water Droplet Size and Settling

Microscopic photographs were taken for every emulsion type at 30 and 60 minutes after the emulsions were prepared. Figures 4-7, 4-8 and 4-9 show the most representative photographs. It is clear that within one hour after the emulsions were prepared, water drop sizes did not change much with time. This agrees with Yarranton's observation for asphaltene emulsions that "no evidence of coalescence was observed more than 5 minutes after blending, while the effects of Ostwald ripening are not apparent for at least 24 hours" [1997].

It is interesting to consider the Sauter mean diameters of the emulsion droplets. The Sauter mean diameter is inversely related to the surface area of an emulsion [Yarranton, 1997]. The exact relationship for the Sauter mean diameter is given by Equation (4-1),

$$d_{32} = \frac{6V_w}{A_w} = \frac{\pi N \sum \hat{F}_i d_i^3}{\pi N \sum \hat{F}_i d_i^2} \tag{4-1}$$

where V_w (m^3) is the volume of the dispersed water phase, A_w (m^2) is the total surface area of the water droplets, $\hat{F}_i$ is the drop number frequency, N is the total number of water drops and d_i (m) is the diameter of drop i. The Sauter mean diameter is a useful parameter for analyzing the stability and conditions of an emulsion because it is a measure of the stabilized interfacial area in an emulsion.

The Sauter mean diameters can be calculated from the microscopic photographs of the emulsions. By comparing several photographs taken at 30 minutes after the emulsification step was conducted, the clearest and representative photograph was selected to perform the drop size measurement. Also, in order to reduce workload, a rectangular area of about 300 × 225 μm of each photograph was defined and the diameters of water drops, d_i, within this area were measured by a ruler. Thus $\hat{F}_i$ and the Sauter mean diameters could be calculated accordingly from approximately 150 droplets. The error of this calculation was found to be within ± 2μm by comparing the results obtained from different measurement regions on one or more photographs.

Table 4-2 lists the Sauter mean diameters of the water drops in the various settled emulsions. The size of the water droplets seems to be related to the stability of the emulsions. While the water-in-asphaltene-solids emulsion is the most stable emulsion, its droplet Sauter mean diameter is the largest at 24 μm. The water-in-de-asphalted-bitumen emulsion had the smallest water droplets with a Sauter mean diameter of 19 μm.

Figure 4-10 shows the settling process of the water droplets with time for the three emulsions. In the first 30 minutes after the emulsions were prepared, the water-in-asphaltene-solids emulsion had the largest volume of settled emulsion, which was approximately 63 ml, with the water droplets packing loosely at the bottom of the cylinder. However, at the same time, the water-in-bitumen emulsion obtained only about 41ml of settled emulsion.

4.4 Conclusions

Asphaltenes and solids are found to be the main stabilizers of water-in-bitumen emulsions. The two components can stabilize water-in-bitumen emulsions independently. Without them, the stability of water-in-bitumen emulsions is greatly decreased.

Emulsion stability tests showed that de-asphalted bitumen molecules do not stabilize the water/bitumen interface. The presence of small molecules like resins and aromatics in bitumen weakens the stability of water-in-bitumen emulsions.

Microscopic photographs of the emulsions showed that with the same emulsification operation procedure, the water drop size varies little for the different emulsions. Generally, the more stable the emulsion is, the larger the water droplets in the emulsion are.

It was also noticed that fine solids removed with 0.22 μm filter but not with 8μm filter play the key role in emulsion stabilization.

4.5 References

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Table 4-1. Design of the emulsion stability tests

Role of / Composition of Emulsion	DB		Asphaltenes				Solids			
	A	B	A	C	D	E	A	D	C	E
DB	○	■	○	○	○	○	○	○	○	○
Asphaltenes	○	○	○	■	○	■	○	○	■	■
Solids	○	○	○	○	■	■	○	■	○	■

■ : Not present in the emulsion

○ : Present in the emulsion

Table 4-2. Sauter mean diameters of the water droplets in the emulsions

Emulsions	Sauter mean diameter (μm)
Water-in-Bitumen	21 ±2
Water-in-Asphaltene-solids	24 ±2
Water-in-De-asphalted Bitumen	19 ±2

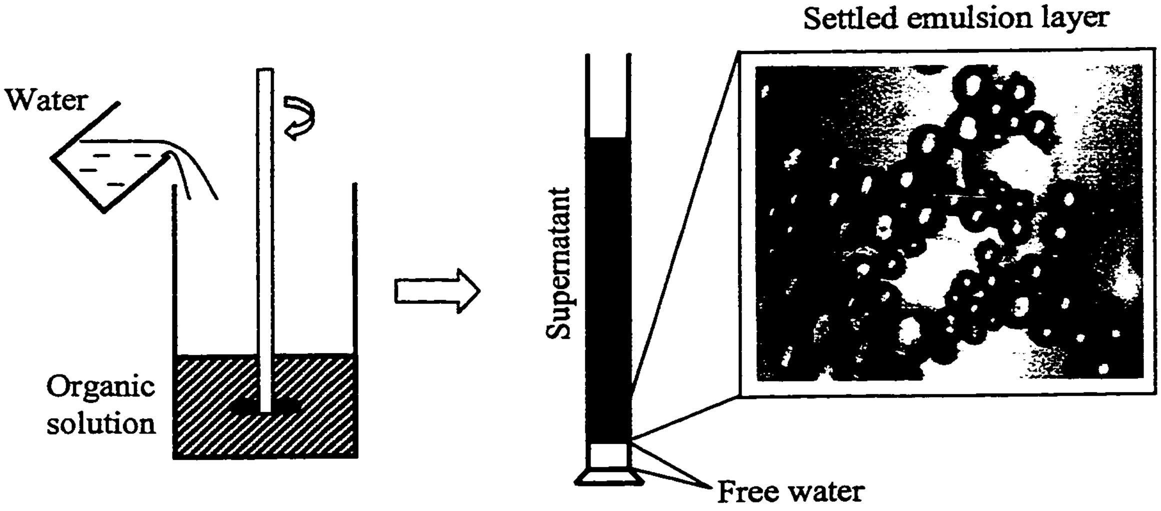


Figure 4-1. Preparation of an emulsion

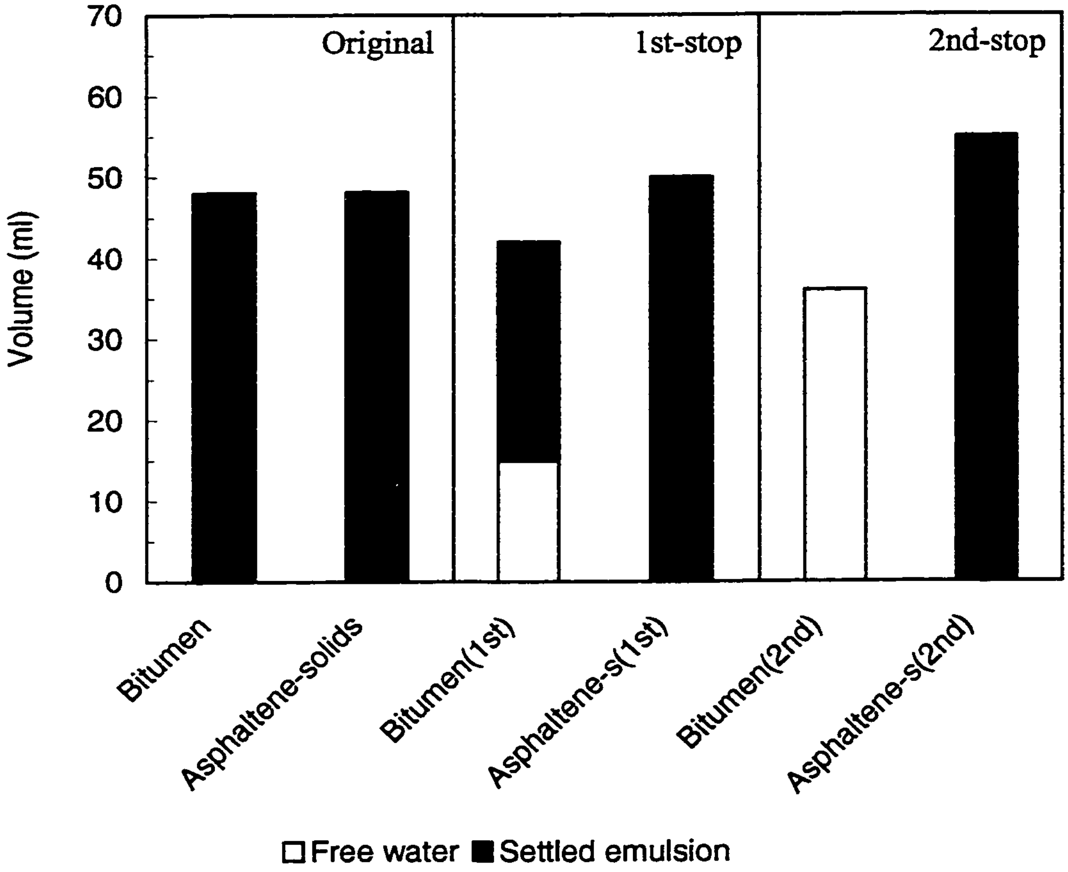


Figure 4-2. Role of de-asphalted bitumen in stabilizing water-in-bitumen emulsions

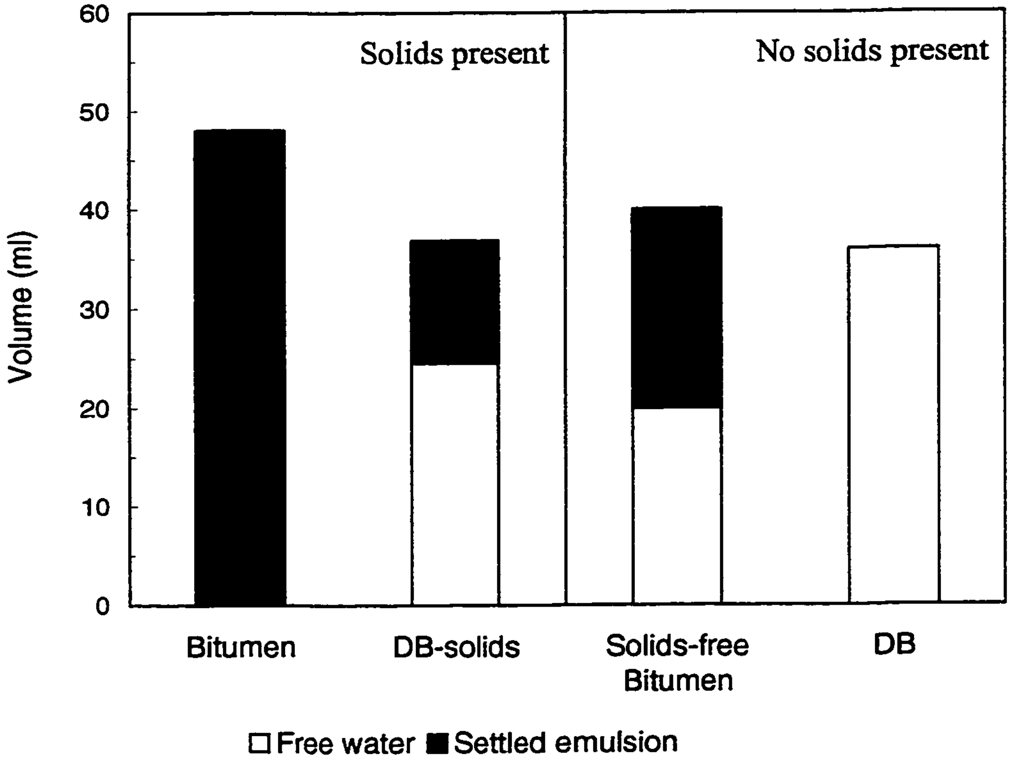


Figure 4-3. Role of asphaltenes in stabilizing water-in-bitumen emulsions

(Solids were removed with 0.22 μm filter paper.)

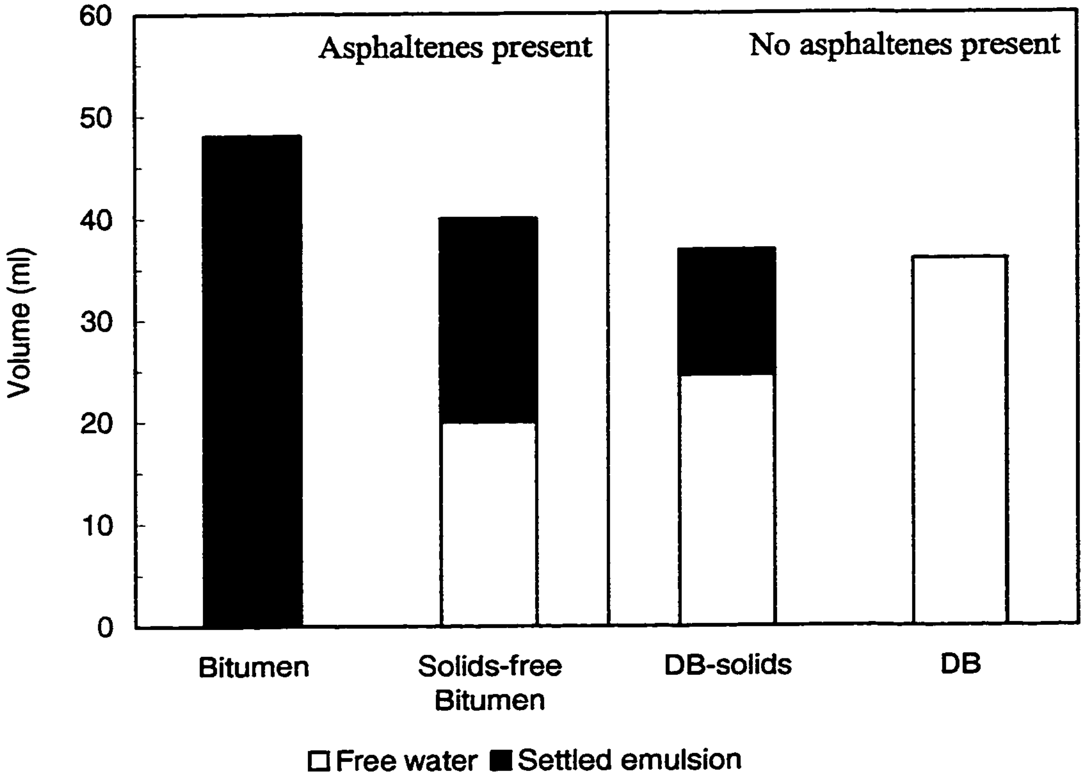


Figure 4-4. Role of solids in stabilizing water-in-bitumen emulsions

(Solids were removed with 0.22 μm filter paper.)

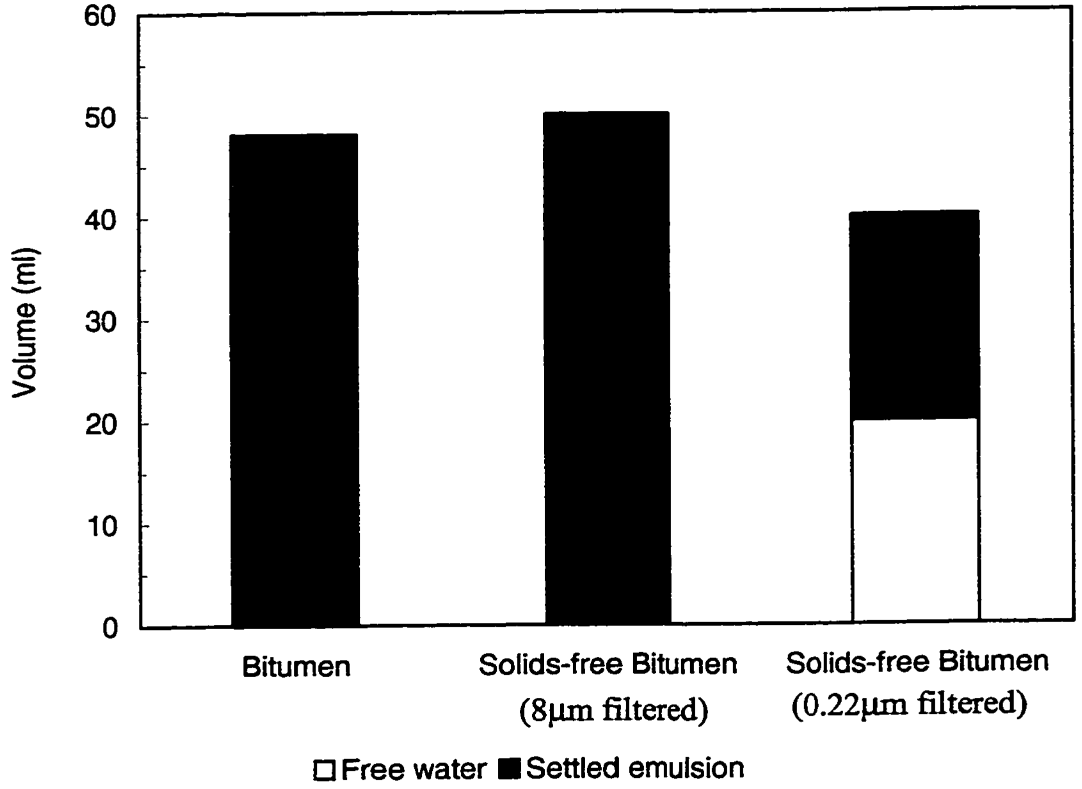
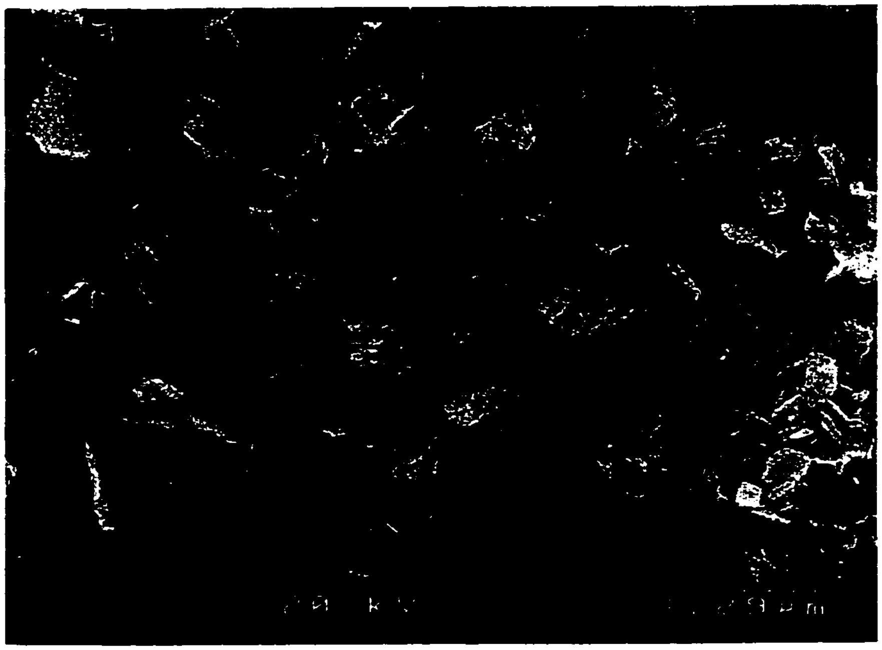


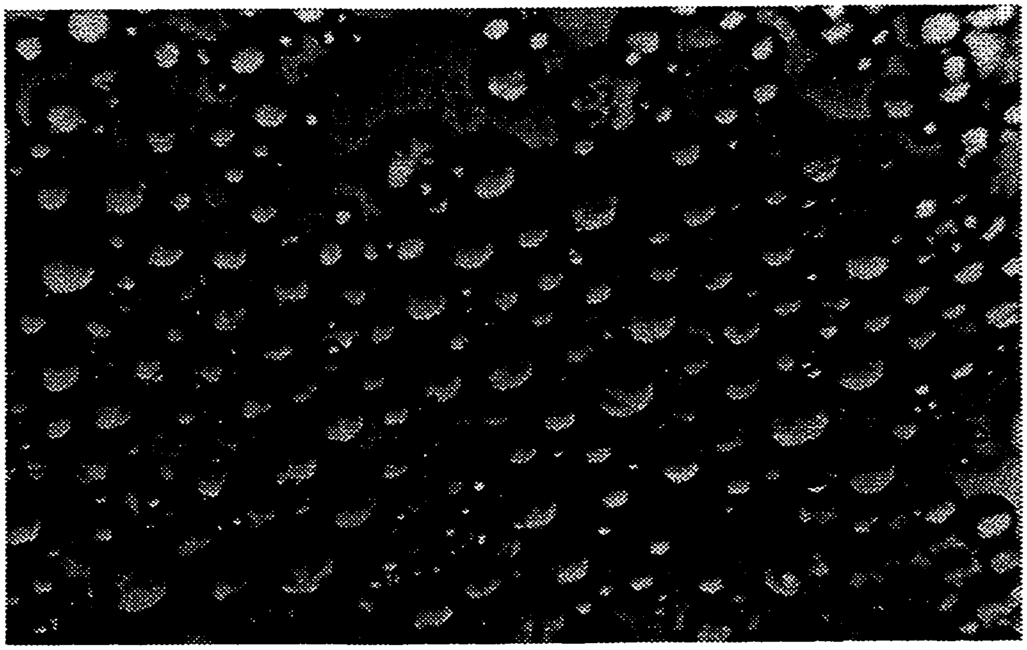
Figure 4-5. Effect of solid size on water-in-bitumen emulsion stability

0.22 μm filter paper

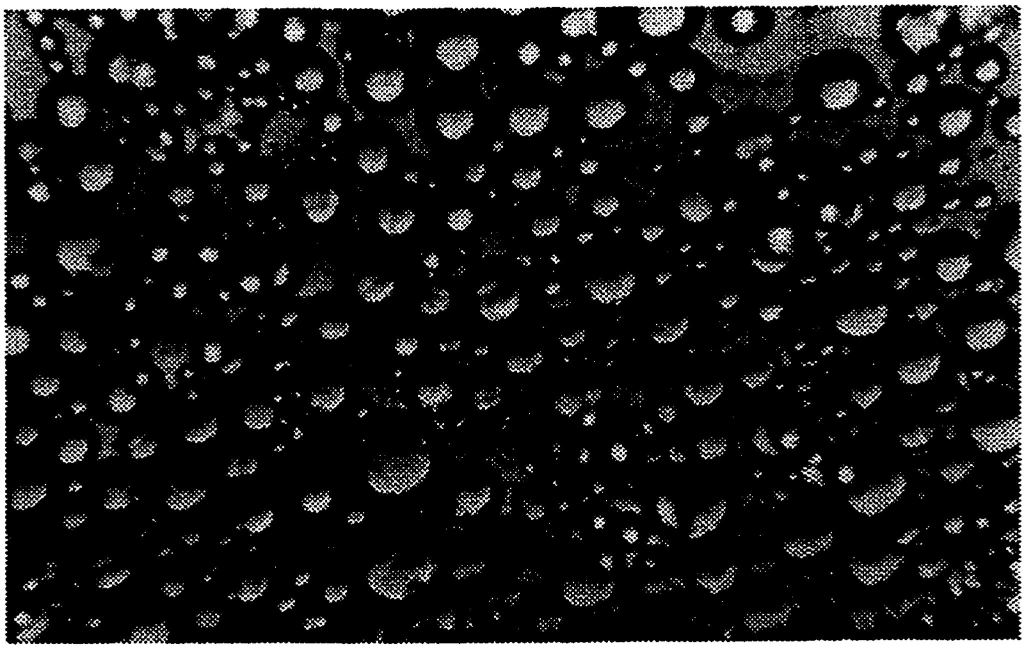


8 μm filter paper

Figure 4-6. SEM micrographs of solids captured by 0.22 μm and 8 μm filter papers

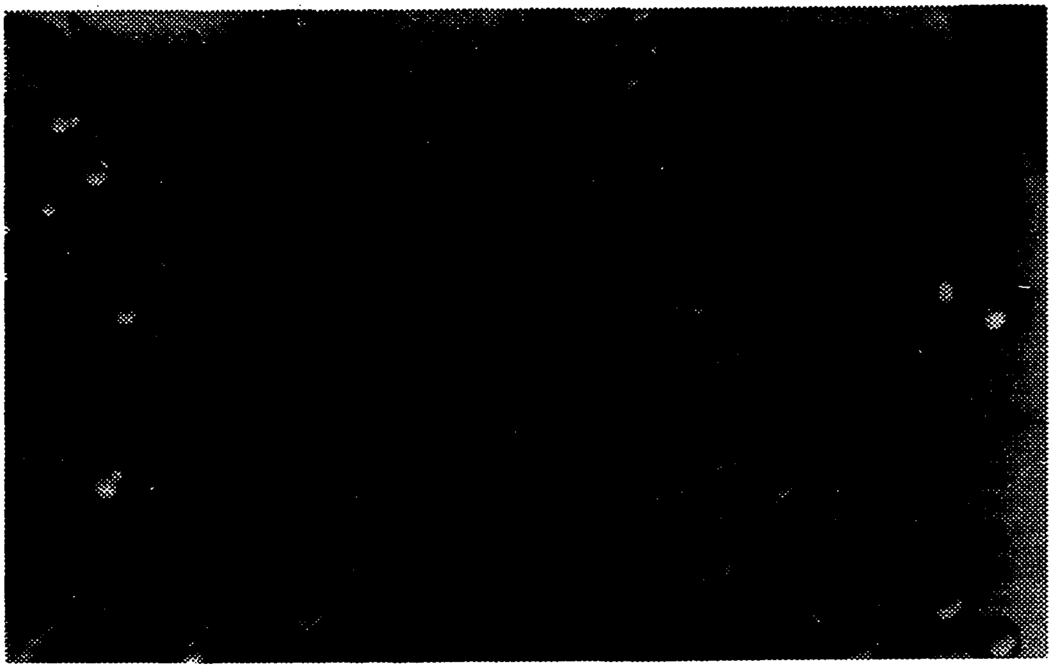


(a) at 30 min.

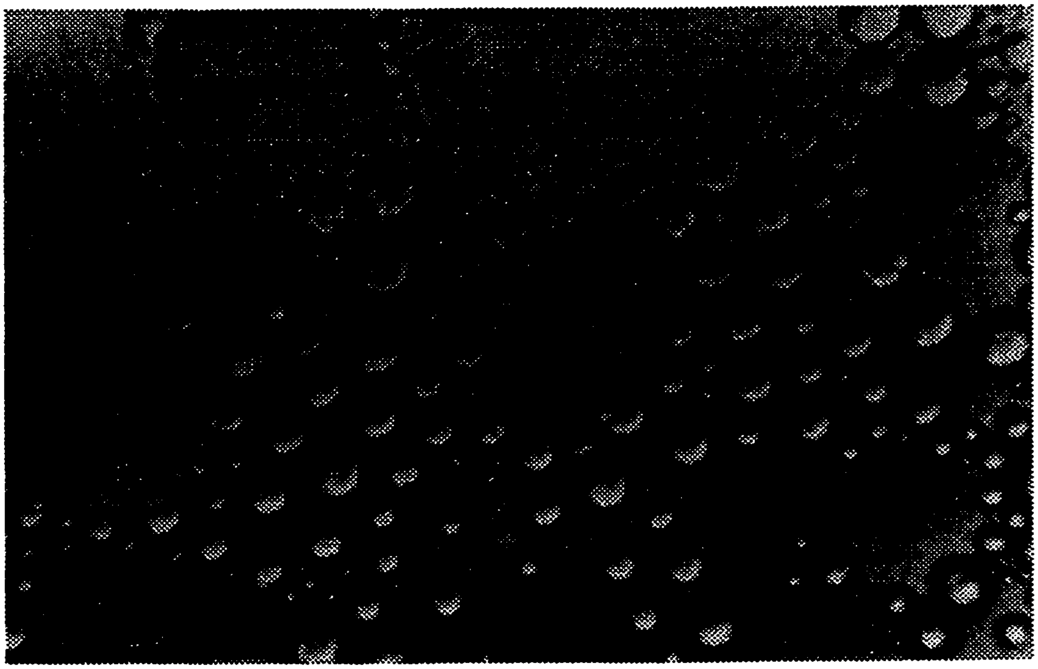


(b) at 60 min.

Figure 4-7. Microscopic photographs of the emulsions prepared with asphaltene-solids

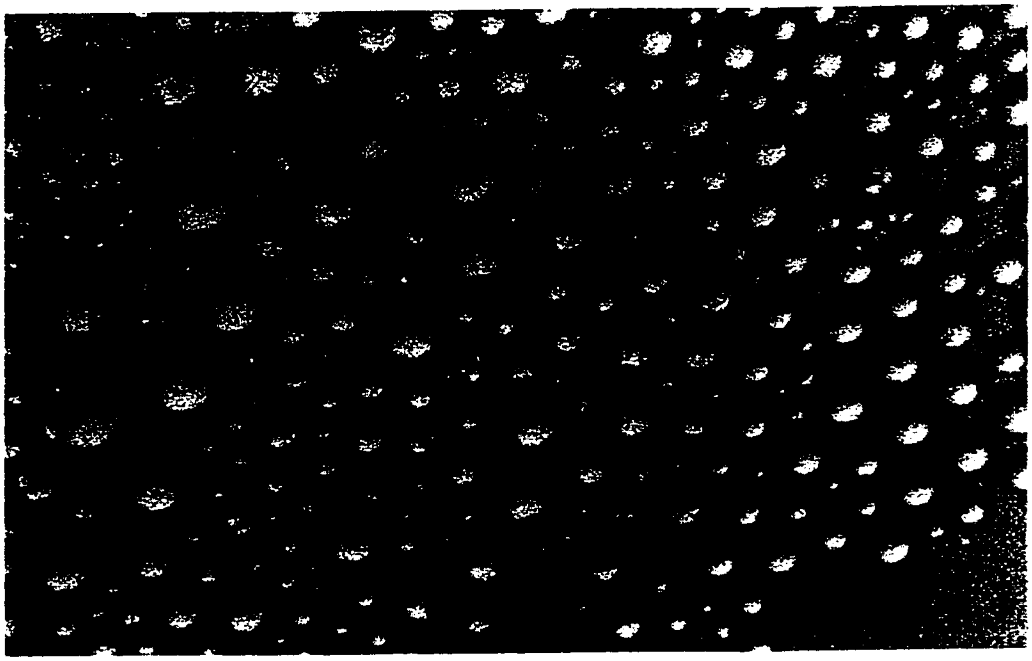


(a) at 30 min.

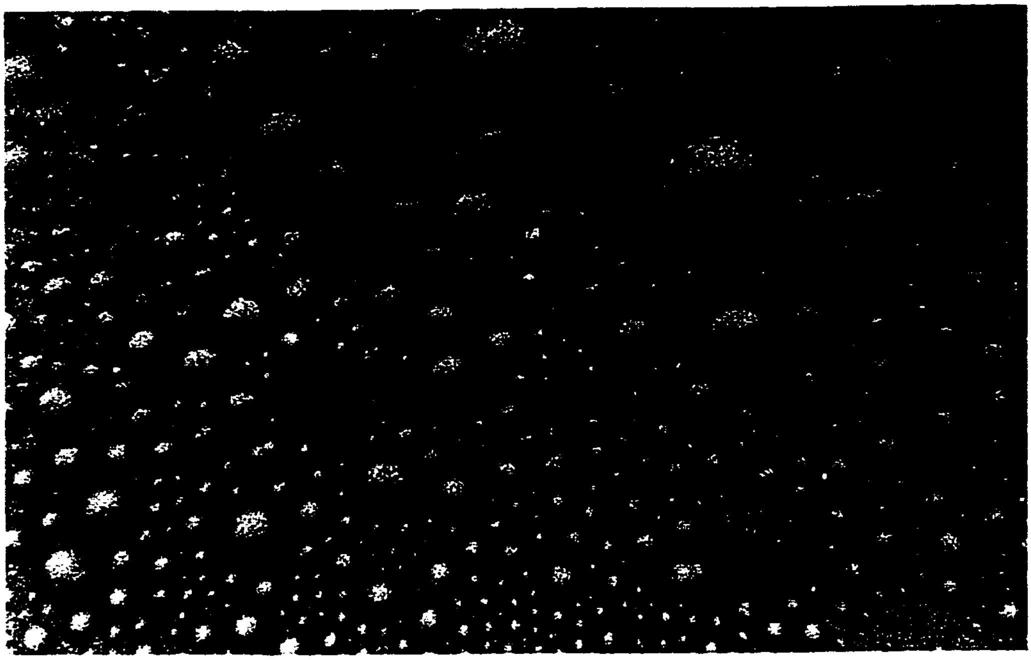


(b) at 60 min.

Figure 4-8. Microscopic photographs of emulsions prepared with bitumen



(a) at 30 min.



(b) at 60 min.

Figure 4-9. Microscopic photographs of emulsions prepared with de-asphalted bitumen

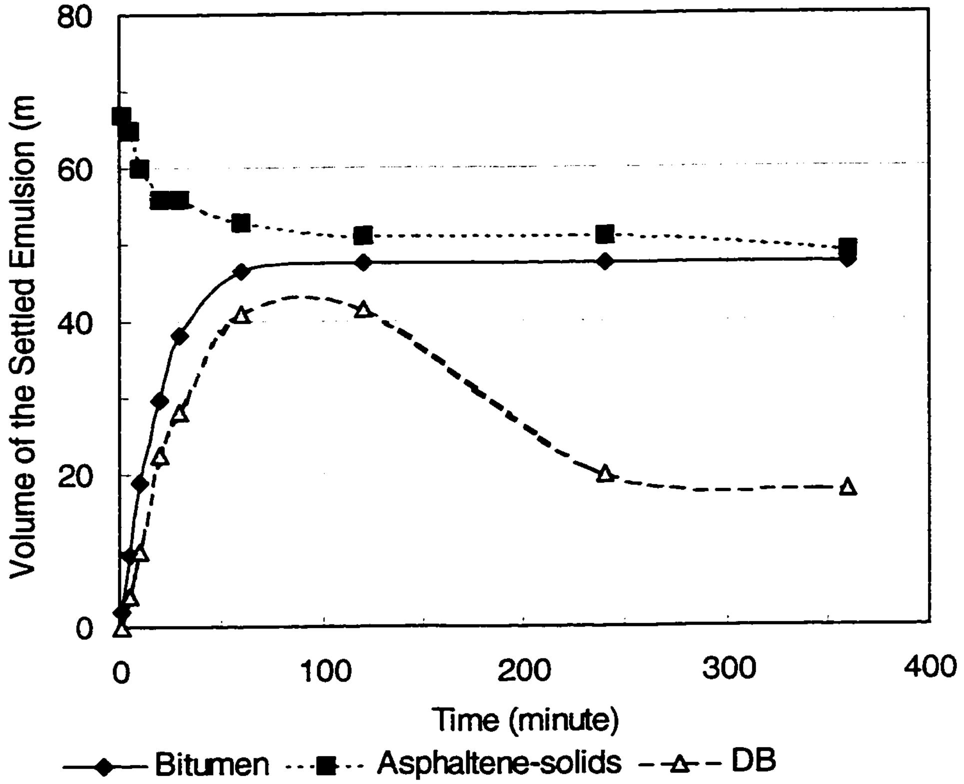


Figure 4-10. Settling process of the emulsions

CHAPTER 5.

CONCLUSIONS

In Chapter 1, the objectives of this thesis were set. They were to:

1. Measure the interfacial tension of water in contact with hex-tol diluted asphaltenes, de-asphalted bitumen and bitumen respectively;
2. Compare the surface activities of the above three systems by analyzing the interfacial tension measurement results;
3. Examine the stability of water-in-bitumen, water-in-asphaltene and water-in-de-asphalted bitumen emulsions;
4. Investigate the role of de-asphalted bitumen, as well as asphaltenes and solids, in stabilizing the water/bitumen interface.

The conclusions obtained for each objective will be explained accordingly in the following.

5.1 Interfacial Tension Study of De-asphalted Bitumen

The stabilization of water-in-bitumen emulsions is directly related to properties of the diluted bitumen/water interface and adsorption at that interface. Although the surface-active behavior of asphaltenes has been studied extensively, very little research was done on the components of bitumen other than the asphaltenes. Present work shows that there are surface-active components present in de-asphalted bitumen.

The change of interfacial tension was used to study the properties of adsorbing molecules at the interface between water and de-asphalted bitumen diluted with hexane and toluene. The de-asphalted bitumen was obtained from Syncrude coker feed bitumen by precipitating out the asphaltene-solids using an excess amount of hexane. The interfacial tension measurements were made using a de-Nouy platinum ring tensiometer at 22°C.

Interfacial tension measurement results indicated that de-asphalted bitumen contained surface-active components that can lower the interfacial tension of the diluted DB/water interface. At relatively high DB concentrations in hex-tol, the interfacial tension of DB and water did not decrease with further increase in DB concentration. This region of high concentration suggests that a critical micelle concentration may have been reached.

The average molar masses of de-asphalted bitumen molecules were estimated roughly by using the measured interfacial tension and thermodynamic relations. The average molar masses of DB were found to be much smaller than those of asphaltenes. Because of several assumptions made for this estimation (refer to Chapter 3), only a qualitative conclusion could be drawn.

The interfacial tension of diluted de-asphalted bitumen in contact with water was compared with that of diluted asphaltene-solids and bitumen, respectively, in contact with water. It was found that the surface activity of de-asphalted bitumen is higher than that of the other two substances. Among the three species, asphaltene-solids showed the least surface activity. The interfacial tension and the surface activity of bitumen are between that of asphaltene-solids and de-asphalted bitumen. Therefore, the water-bitumen interface is covered not only by asphaltene molecules and solids but also by other smaller molecules.

5.2 Emulsion Stability Investigation

The stability of emulsions prepared with various bitumen components was studied by observing the amount of free water appearing from the emulsions in 48 hours. Although de-asphalted bitumen is more surface-active than asphaltene-solids and bitumen in terms of reducing interfacial tension, de-asphalted bitumen doesn't stabilize water-in-bitumen emulsions. The presence of the small molecules such as resins and aromatics in bitumen weakens the stability of water-in-bitumen emulsions.

Asphaltenes and solids were found to be the main stabilizers of water-in-bitumen emulsions. The two substances can stabilize water-in-bitumen emulsions independently. When both asphaltenes and solids are present in water-in-bitumen emulsions, the emulsions show the highest stability. Without them, the stability of water-in-bitumen emulsions is greatly decreased.

The Sauter mean diameters of the water droplets of each emulsion were calculated from their microscopic photographs. It was shown that with the same emulsification operation procedure, the water drop sizes varied little with the different emulsions.

It was also noticed that solids larger than 8 μm do not affect the water-in-bitumen emulsion stability as effectively as smaller solids. Solids that can be removed by 0.22 μm filter paper showed a strong ability to stabilize water-in-bitumen emulsions.

One of the major conclusions from the present study is that interfacial tension is not necessarily related to the stability of emulsions. It was shown that although de-asphalted bitumen lowers the interfacial tension more than asphaltene-solids do, it does not stabilize water-in-bitumen emulsions.

CHAPTER 6.

RECOMMENDATIONS FOR FUTURE WORK

6.1 Recommendations for Future Work

Having concluded this work, there is some work that may be done in the future to complete the study of water-in-bitumen emulsions.

The interfacial tension measurement results indicated that the de-asphalted bitumen contained surface-active components that can lower the interfacial tension of DB and water. At relatively high DB concentrations in the solvent, the interfacial tension of DB and water did not drop with increase in the DB concentration. This region of DB concentration suggests that a critical micelle concentration may have been reached. Future experiments to elucidate what happens in this situation will be a necessary complement to understanding the structure of the diluted bitumen/water interface. Moreover, experimental research is needed in the future to find out molecular information about the surface-active species in de-asphalted bitumen. This could be performed by separating DB into more fractions such as resins, aromatics and saturates and studying the interfacial behavior of these fractions separately.

A perception of the size difference of surface-active DB molecules and asphaltenes was given through a rough estimation in this work. In order to improve the accuracy of this estimation, further work may be done in two areas. One area is to find out the surface-active fractions in de-asphalted bitumen instead of assuming all DB molecules are surface-active. Based on this knowledge, the other area will be to use the cylindrical geometry of the surface-active molecules in DB in making the molar mass estimation. The height of the molecule cylinders can be obtained by referring to another method such as vapor pressure osmometry [Yarranton and Masliyah, 1996].

The study of the stability of emulsions prepared with water and various bitumen components showed that the presence of small molecules in de-asphalted bitumen such as resins and aromatics weakens the stability of water-in-bitumen emulsions. Further experimental work at the microscopic scale will be helpful in understanding the structure of the water/oil interface and the relationship of the DB molecules and asphaltenes and solids.

It was also noticed that solids larger than 8 μm do not affect water-in-bitumen emulsion stability. Solids that can be removed by 0.22 μm play an important role in water-in-bitumen emulsions stabilization. Further experiments can be done to find out the largest solids size that the emulsion can be stabilized with.

6.2 References

Yarranton, H.W. and J.H. Masliyah, 1996, "Molar mass distribution and solubility modeling of asphaltenes", AIChE, Vol. **42**, No. 12, 3533.

APPENDIX A.

RAW DATA FOR THE FIGURES IN THE THESIS

Figure 2-1. Dependence of DB/hexane mixture specific volume on DB mass fraction

Mass fraction of DB in DB/hexane	0.0195	0.0140	0.00596	0
Instrument reading	5.1390	5.1375	5.1355	5.1335
Density (kg/m^3)	670.800	669.651	668.12	666.582
Specific volume (m^3/kg × 1000)	1.491	1.493	1.497	1.500

Figure 2-2. Dependence of asphaltene-solids/toluene mixture specific volume on asphaltene-solids mass fraction

Mass fraction of asphaltenes in asphaltenes/toluene	0.00403	0.006995	0.00995	0
Instrument reading	5.3871	5.3879	5.3888	5.3857
Density (kg/m^3)	865.910	866.552	867.28	864.741
Specific volume (m^3/kg × 1000)	1.155	1.154	1.153	1.156

Figure 2-3. Surface tension of water measured using a Jefri spinning drop tensiometer

rpm	Measured diameter of the air bubble (instrument reading)	IFT (mN/m)
13260	7.18	73.6
14780	6.54	69.4
16100	6.20	69.7
15670	6.30	69.4
8540	9.37	67.8
9460	8.76	68.2
10020	8.56	71.3
10590	8.26	71.5
11530	7.70	68.8
12020	7.50	69.1
12650	7.25	69.1
13290	7.05	70.1
16510	6.10	69.8

Figure 2-6. Time dependence of the interfacial tension of

de-asphalted bitumen/hex-tol over water

Time (min)	Interfacial Tension (mN/m)					
	C_{DB} = 0.5 kg/m^3		C_{DB} = 16.17 kg/m^3		C_{DB} = 30 kg/m^3	
	Raw Data	Corrected	Raw Data	Corrected	Raw Data	Corrected
0	33.30	33.0	23.85	22.9	21.10	20.0
10	32.10	31.7	22.70	21.7	20.25	19.1
20	31.30	30.8	22.10	21.1	19.10	18.0
30	31.35	30.9	21.90	20.9	18.90	17.8
60	31.10	30.6	21.70	20.8	18.05	16.9
120	30.45	30.0	21.25	20.6	17.10	15.9
180	30.35	29.9	21.30	20.7	17.25	16.1

Figure 3-1. Interfacial tension of hex-tol diluted de-asphalted bitumen over water versus DB concentration

DB concentration (kg/m^3)	Interfacial tension (mN/m)		
	Raw Data		Corrected
0.03	35.10	35.10	35.0
0.08	33.35	33.20	33.0
0.201	31.85	31.65	31.3
0.504	29.65	29.55	29.0
1.009	27.65	27.60	26.9
2.522	26.25	26.80	25.2
7.062	23.10	22.90	22.0
15.132	19.90	19.90	18.8
30.265	16.35	16.35	15.2
60.529	13.35	13.35	12.3
0.002	36.75	36.65	36.8
0.003	36.30	36.40	36.4
0.006	36.10	35.90	36.0
0.010	36.05	35.95	36.0
0.020	35.75	35.75	35.7
101.667	11.90	11.90	10.9
171.803	11.40	11.40	10.5

Figure 3-2. Molar surface coverage of de-asphalted bitumen molecules on DB/water interface

DB concentration (kg/m^3)	Γ_{DB} (mol/m^2)
0.002	0.000667
0.003	0.000667
0.006	0.000304
0.010	0.000211
0.020	0.000855
0.030	0.001855
0.080	0.001816
0.201	0.002040
0.504	0.002589
1.009	0.002170
2.630	0.002350
7.062	0.003412
15.132	0.004367
30.265	0.004422
60.529	0.003362

Figure 3-3. Interfacial tensions of de-asphalted bitumen over water with different hexane/toluene ratios of the solvent

DB concentration (kg/m^3)	Interfacial Tension (mN/m)		
	Raw Data		Corrected
	Solvent: Hexane		
0.001	45.75	45.65	45.1
0.004	44.20	44.20	43.5
0.014	38.65	38.90	37.6
0.030	38.25	38.15	37.0
0.082	34.25	34.60	33.0
0.205	28.70	28.85	27.2
0.517	25.60	25.70	24.0
0.966	23.40	23.35	21.7
2.542	21.10	20.60	19.2
7.110	20.15	20.75	18.8
15.243	20.75	20.35	18.9
30.441	19.75	18.25	17.4
50.673	16.00	15.25	14.2
70.837	15.75	16.10	14.4
100.908	14.20	13.90	12.7

Figure 3-3. (continued)

DB concentration (kg/m^3)	Interfacial Tension (mN/m)		
	Raw Data		Corrected
	Solvent: Hex-tol (3:1)		
0.001	38.70	38.60	38.1
0.004	38.55	38.60	38.1
0.010	38.60	38.60	38.1
0.030	35.60	35.60	34.8
0.080	32.55	32.60	31.6
0.203	30.70	30.65	29.6
0.512	27.10	27.05	25.8
1.033	24.90	24.90	23.6
2.540	22.75	21.65	20.8
7.229	19.55	19.55	18.2
15.490	17.40	17.35	16.0
30.981	15.50	15.45	14.1
61.961	12.20	12.30	11.3
104.449	11.35	11.25	10.1
175.106	10.80	10.75	9.6

Figure 3-3. (continued)

DB concentration (kg/m^3)	Interfacial Tension (mN/m)		
	Raw Data		Corrected
	Solvent: Hex-tol (1:1)		
0.002	36.75	36.65	36.8
0.003	36.30	36.40	36.4
0.006	36.10	35.90	36.0
0.010	36.05	35.95	36.0
0.020	35.75	35.75	35.7
0.030	35.10	35.10	35.0
0.080	33.35	33.20	33.0
0.201	31.85	31.65	31.3
0.504	29.65	29.55	29.0
1.009	27.65	27.60	26.9
2.522	26.25	26.80	25.2
7.062	23.10	22.90	22.0
15.132	19.90	19.90	18.8
30.265	16.35	16.35	15.2
60.529	13.35	13.35	12.3
101.667	11.90	11.90	10.9
171.803	11.40	11.40	10.5

Figure 3-3. (continued)

DB concentration (kg/m^3)	Interfacial Tension (mN/m)		
	Raw Data		Corrected
	Solvent: Hex-tol (1:3)		
0.001	35.20	35.15	36.1
0.004	34.05	34.05	34.8
0.010	33.70	33.65	34.4
0.030	33.85	33.75	34.5
0.081	33.50	33.40	34.1
0.202	31.80	31.75	32.2
0.505	30.70	30.80	31.0
1.011	30.30	30.25	30.5
2.537	29.25	29.35	29.4
7.105	25.80	25.75	25.5
15.224	23.30	23.25	22.8
30.373	18.30	18.25	17.5
50.622	14.75	13.35	13.2
71.314	12.30	12.25	11.4
101.877	12.15	12.15	11.3

Figure 3-3. (continued)

DB concentration (kg/m^3)	Interfacial Tension (mN/m)		
	Raw Data		Corrected
	Solvent: Hex-tol (1:9)		
0.001	34.25	34.25	35.8
0.004	34.00	34.10	35.6
0.010	33.70	33.70	35.1
0.030	32.85	32.75	34.1
0.081	32.75	32.75	34.1
0.202	31.70	31.70	32.8
0.507	30.80	30.90	31.8
0.966	29.75	29.65	30.5
2.543	27.85	27.75	28.3
7.121	25.75	25.75	26.0
15.260	22.35	22.25	22.2
30.432	18.30	18.25	17.8
50.720	15.00	15.05	14.4
71.008	12.85	12.75	12.1
101.440	12.10	12.20	11.5

Figure 3-5. Comparison of the interfacial tensions of hex-tol diluted bitumen, DB and asphaltene-solids in contact with water

Equivlent Bitumen concentration (kg/m^3)	Solute Concentration (kg/m^3)	Interfacial Tension (mN/m)		
		Raw Data		Corrected
Asphaltene				
1.258	0.201	32.30	32.25	31.9
0.189	0.030	34.10	34.30	34.0
0.317	0.051	34.35	34.25	34.1
0.063	0.010	35.35	35.00	35.1
3.144	0.503	31.75	31.65	31.3
6.337	1.014	30.75	30.70	30.2
15.696	2.511	29.60	29.70	29.0
34.725	5.556	29.30	29.25	28.7
56.204	8.993	28.45	28.35	27.7
123.783	19.805	27.20	27.25	26.5
246.235	39.398	26.25	26.25	25.6
Bitumen				
0.030	0.030	35.20	35.15	35.1
0.083	0.083	34.10	34.50	34.1
0.204	0.204	33.80	34.00	33.7
0.519	0.519	31.65	31.85	31.3
0.976	0.976	30.75	30.65	30.2
2.597	2.597	28.70	28.70	28.0
7.189	7.189	26.75	26.65	25.9
15.404	15.404	23.60	23.70	22.7
30.808	30.808	21.15	21.30	20.2
51.946	51.946	20.35	20.25	19.3
0.017	0.017	35.40	35.35	35.3
0.004	0.004	37.20	36.90	37.2

Figure 3-5. (continued)

Equivlent Bitumen concentration (kg/m^3)	Solute Concentration (kg/m^3)	Interfacial Tension (mN/m)		
		Raw Data		Corrected
72.725	72.725	11.75	11.75	10.7
103.893	103.893	11.25	11.00	10.2
De-asphalted bitumen				
0.002	0.002	36.75	36.65	36.8
0.004	0.003	36.30	36.40	36.4
0.007	0.006	36.10	35.90	36.0
0.012	0.010	36.05	35.95	36.0
0.024	0.020	35.75	35.75	35.7
0.036	0.030	35.10	35.10	35.0
0.095	0.080	33.35	33.20	33.0
0.239	0.201	31.85	31.65	31.3
0.600	0.504	29.65	29.55	29.0
1.201	1.009	27.65	27.60	26.9
3.131	2.630	26.25	26.80	25.2
8.407	7.062	23.10	22.90	22.0
18.014	15.132	19.90	19.90	18.8
36.030	30.265	16.35	16.35	15.2
72.058	60.529	13.35	13.35	12.3
121.032	101.667	11.90	11.90	10.9
204.527	171.803	11.40	11.40	10.5

Figure 4-2. Role of de-asphalted bitumen in stabilizing water-in-bitumen emulsions

Emulsion	Settled emulsion ml	Free water ml
Bitumen	48	0
Asphaltene-solids	48	0
Bitumen(1st)	27	15
Asphaltene-s(1st)	50	0
Bitumen(2nd)	0	36
Asphaltene-s(2nd)	55	0

Figure 4-3. Role of asphaltenes in stabilizing water-in-bitumen emulsions

Emulsion	Settled emulsion ml	Free water ml
Bitumen	48	0
DB-solids	12	25
Bitumen-solidfree	20	20
DB	0	36

Figure 4-4. Role of solids in stabilizing water-in-bitumen emulsions

Emulsion	Settled emulsion ml	Free water ml
Bitumen	48	0
Bitumen-solidfree	20	20
DB-solids	12	25
DB	0	36

Figure 4-5. Effect of solid size in water-in-bitumen emulsion stability

Emulsion	Settled emulsion ml	Free water ml
Bitumen	48	0
Bitumen-solidfree (8 μm)	50	0
Bitumen-solidfree (0.22 μm)	20	20

Figure 4-10. Settling process of the emulsions

	Time (min)	Settled emulsion (ml)
Bitumen	1	2
	5	11
	10	21
	20	33
	30	42
	60	52
	120	53
	240	53
	360	53
Asphaltene-solids	1	76
	5	74
	10	0
	20	64
	30	64
	60	60
	120	58
	240	58
	360	56
DB	1	0
	5	4
	10	10
	20	22.5
	30	28
	60	41
	120	41.5
	240	20
	360	10