

Role of Naphthenic Acids in Stabilizing Water-in-Diluted Model Oil Emulsions

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The need for alkaline conditions in oil sands processing is, in part, to produce natural surfactants from bitumen. Previous studies have shown that the produced surfactants are primarily carboxylic salts of naphthenic acids with the possibility of sulfonic salts as well. The role of these natural surfactants, particularly those in the naphthenate class, is to provide a physicochemical basis for several subprocesses in bitumen extraction. In this study, it was found that the content of indigenous naphthenic acids in bitumen can destabilize, to some extent, the water-in-oil emulsion by lowering the interfacial tension, reducing the rigidity and promoting the coalescence of water droplets.

1. Introduction

Emulsions are colloidal systems in which at least one liquid is dispersed as drops throughout an immiscible liquid. The dispersed droplets can have diameters ranging on the order of 1–10 μm .^{1,2} The improved understanding of emulsions has significantly contributed to the development of construction materials, biomedical, pharmaceutical, food, petrochemical, petroleum, and environmental and health industries.¹ Controlling the stability of emulsions is very important for commercial products and processes. For example, cosmetics and dairy products must be in the form of stable emulsions to ensure its quality and shelf life. Microencapsulated drug delivery systems need to be stable everywhere except at the target organ where the microemulsion is designed to become unstable and release the drug. However, the stability of the emulsions in petroleum production needs to be low to allow successful phase separation and dewatering/desalting.

Stable water-in-oil emulsions have been a major concern in the oil sands industry because the chlorides in the emulsified water droplets can adversely affect downstream bitumen upgrading to sweet crude oil. Extensive studies have been carried out to understand the role of bitumen components, e.g., suspended fine solids, asphaltenes, resins, and other naturally occurring surfactants^{3–8} on emulsion stability. Asphaltenes, the highest molecular weight components of bitumen, are soluble in light aromatic hydrocarbons (i.e., toluene and benzene) but insoluble in paraffinic solvents (i.e., heptane, pentane and hexane). Asphaltenes are adsorbed slowly and irreversibly at the diluted bitumen–water interface to form rigid/elastic films that resist the deformation of the interface.^{9,10} The stability of water-in-oil emulsions is believed to originate from a steric asphaltene-rich interface at the emulsified water droplet surface. A fluid interface has been observed in more concentrated bitumen solutions due to the competitive adsorption between asphaltenes and maltenes (i.e., deasphalted bitumen) in bitumen.¹¹

In conventional bitumen extraction, sodium hydroxide (e.g., increasing the aqueous solution pH) is used as a process aid to release (saponify) natural surfactants from the bitumen to the aqueous phase. Previous studies have shown that the surfactants released from the bitumen were mainly carboxylic salts of naphthenic acids along with a lower amount of sulfonic acids.^{12–14} Naphthenic acids (NAs) are a complex mixture of cyclic carboxylic acids that may contain aliphatic side chains.¹⁵ The molecular weight of these surfactants ranges from about 166 to 450 g/mol.¹⁶ Most of the indigenous naphthenic acids (~90%) in Athabasca bitumen are C₂₁–C₂₄ tricyclic terpenoid acids.^{17–19} Under alkaline conditions of bitumen extraction with NaOH addition, the naphthenic acids are easily converted to sodium naphthenates (NaNs). It has been reported that these NaNs remain largely soluble in the maltenes when asphaltenes are precipitated with *n*-pentane.²⁰ The presence of NaNs has been known to “soften” the interface of the emulsified water droplets in 0.1 wt % naphtha diluted bitumen emulsion.²¹ Concentrated surfactant solutions can form mesomorphic phases, such as the liquid crystalline phase.²² The multilayered structure of this phase at the oil–water interface can increase the stability of water in hydrocarbon emulsions. The liquid crystalline NaNs have been observed as thick, viscous layers at oil–water interfaces. However, the phase equilibria of NaNs in the NaN–toluene–water system showed that it is hard to form such a liquid crystalline phase in industrial processing conditions.²³ The role of the indigenous NAs on emulsion stability remains unclear. Understanding these issues is our primary focus of this work.

In this study, a protocol is established to extract the indigenous NAs from maltenes. The interfacial properties of the extracted indigenous NAs at an oil/water interface were measured by the Langmuir trough technique. The micropipet technique was employed to study mechanical aspects of water-in-diluted oil emulsions due to its unique opportunity to keep the real surface area-to-volume ratio of practical emulsion systems. This technique makes it possible to visualize in situ interactions of water droplets in diluted oil emulsions.

2. Experimental Materials and Methods

2.1. Materials. “Atmospheric-topped” bitumen (coker feed bitumen) supplied by Syncrude Canada Ltd. was used in this

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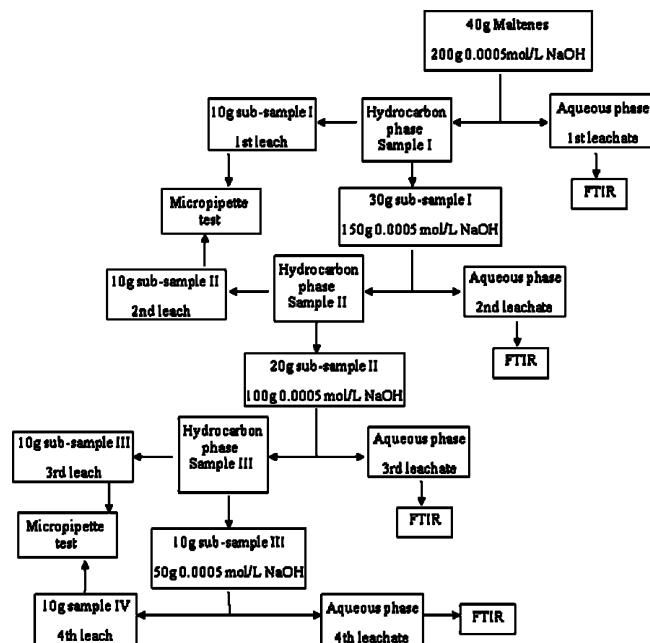


Figure 1. Procedure for extraction of naphthenic acids from maltenes using caustic soda.

study. Deionized water was produced from a Millipore Milli-Q water system equipped with a $0.22\ \mu\text{m}$ filter. Spectral grade methylene chloride was purchased from Fisher Scientific. Heptol, a mixture of *n*-heptane and toluene (both of optima grade) at a volume ratio of 4:1, was used as a model oil. All the other solvents were HPLC grade products purchased from Fisher Scientific. The commercial sodium naphthenates (NaNs) were purchased from Acros Organics/Fisher Scientific and used as received. Sodium hydroxide (solid) was also purchased from Fisher Scientific and used as received. The standard naphthenic acid was from Fluka.

2.2. Separation of Asphaltenes and Maltenes. Asphaltenes and maltenes were separated by solvent extraction from the bitumen sample. Initially, 1 g of bitumen was completely dissolved in 1 mL of toluene, and 40 mL of *n*-pentane was then added to the mixture to precipitate the asphaltenes. The precipitated asphaltenes were filtered, repeatedly washed with *n*-pentane until the supernatant become colorless, and then dried in a vacuum oven at $110\ ^\circ\text{C}$ for 4 h to obtain dry powder for future use. The pentane soluble fraction of bitumen, known as maltenes, consists of saturates, aromatics, and resins. The residue pentane and toluene in maltenes were removed by a Laborota 4002 rotary evaporator. Quantitative analysis of bitumen was completed using Syncrude Analytical Method 5.1.²⁴ The bitumen used in the present study was found to contain $\sim 20\ \text{wt}\%$ asphaltenes.

2.3. Extraction of Indigenous Naphthenic Acids (NAs) from Maltenes. Photoacoustic spectroscopy–Fourier transform infrared (PAS–FTIR) analysis shows that NAs remain largely soluble in the maltenes when asphaltenes are precipitated with *n*-pentane.²⁰ A protocol (Figure 1) was established to extract different amounts of NAs from maltenes by incremental addition of sodium hydroxide aqueous solutions. The concentration of sodium hydroxide was selected to ensure that only NAs will be extracted, which was confirmed by the FTIR analysis to be discussed later. A sodium hydroxide stock solution of $0.0005\ \text{mol/L}$ was added to the maltenes at a fixed mass ratio of 5:1 in each step. The mixture was stirred for 30 min at $70\text{--}80\ ^\circ\text{C}$ and then left for 1 h to allow phase separation (aqueous phase and

hydrocarbon phase). A subsample of 10 g was taken from the hydrocarbon phase in each step with the remaining hydrocarbon phase being used in the subsequent NAs extraction. The 10 g subsample taken was diluted with toluene and centrifuged to remove the trapped aqueous phase. The toluene in the organic phase of the diluted subsample was removed by a Laborota 4002 rotary evaporator. The remaining organic phase (maltene after first NAs extraction) was used for the micropipet test. The above procedure was repeated for the subsequent second, third, and fourth NA extractions. The aqueous leachate from each step was sent for quantitative NAs analysis using FTIR method to determine the amount of NAs extracted in each step.

2.4. Emulsion Preparation. Heptol, a mixture of *n*-heptane and toluene at a volume ratio of 4:1, was used as the model oil. The preparation of water-in-oil emulsions was described in our previous study.¹¹ Briefly, $100\ \mu\text{L}$ of aqueous (deionized water) phase was introduced into 10 mL of the continuous model oil phase. The emulsion was formed by agitating the mixture in a water-bath sonicator (Fisher Scientific, model No. F56) at $\sim 60\ ^\circ\text{C}$ for $7\text{--}10\ \text{s}$.²¹ The emulsions formed were aged for $10\text{--}20\ \text{min}$ to reach the equilibrium state prior to being used in subsequent analysis. Deionized water instead of plant process water was used in this study to avoid potential unknown complications of electrolytes in the plant process water on interpretation of the results. It should be cautioned that the presence of electrolytes in the plant process water may affect the interfacial behavior of naphthenates.

2.5. Experimental Setup and Methods. 2.5.1. Micropipet Technique. The micropipet technique makes it possible to study the in situ behavior of emulsions at surface area-to-volume ratios of water droplets that are representative of commercially encountered emulsions. Two micropipets, with an inside diameter ranging from $5\text{ to }10\ \mu\text{m}$ at the tip, were mounted on a micromanipulator (Narishige, Tokyo; model MHW-3) to ensure the continuous movement of the micropipets at micrometer resolution in the studied emulsions. The important parameters in evaluating emulsion stability, including interfacial tension (based on maximum bubble pressure method), crumpling ratio and the probability of droplet coalescence, were measured using this technique. A detailed description of the experimental setup and procedures can be found in a previous study.⁹

2.5.2. Fourier Transform Infrared Spectroscopy. Naphthenic acids (NAs) have characteristic absorbance bands at 1740 and $1703\ \text{cm}^{-1}$ and can therefore be quantified by FTIR.²⁵ In the liquid or solid state, most carboxylic acids exist as a dimer due to the hydrogen bond between neighboring $-\text{COOH}$ groups. The dimer gives rise to a single sharp intense $\text{C}=\text{O}$ stretch band at $1703\ \text{cm}^{-1}$. In diluted solutions, an equilibrium exists between monomers and dimers. The monomer $\text{C}=\text{O}$ stretch band is at $1740\ \text{cm}^{-1}$. In this study, FTIR spectroscopy was used to determine naphthenic acid content in the aqueous leachate from each step (Figure 1). The aqueous samples were thoroughly mixed with spectral grade methylene chloride, loaded into the sample cell, and then analyzed against a methylene chloride background. FTIR spectra were acquired using a Thermo-Nicolet FTIR spectrometer (8700) and a variable path length KBr liquid cell (Thermo Instrument Inc.). The spectra over a wavenumber range of $400\text{--}7400\ \text{cm}^{-1}$ were acquired at a resolution of $4\ \text{cm}^{-1}$. The instrument was operated at interferometer mirror velocity of $0.6329\ \text{cm/s}$, 128 scans per run, and data spacing of $1.928\ \text{cm}^{-1}$.

2.5.3. Langmuir Trough. The monolayer behavior of three samples at Heptol–water interfaces was characterized using a commercial Langmuir interfacial trough (KSV instruments,

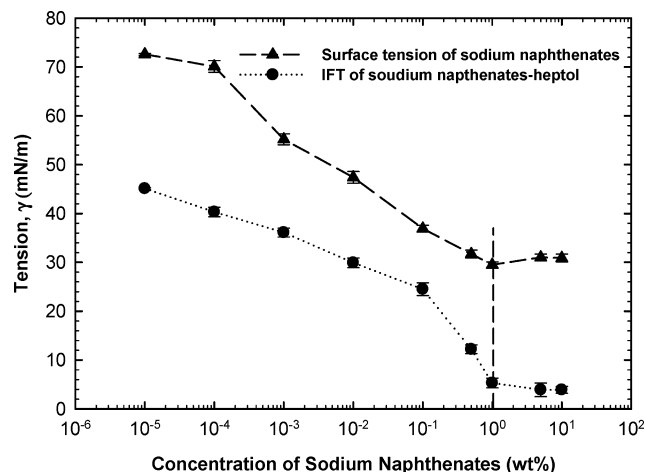


Figure 2. Surface tension of aqueous sodium naphthenates solutions (solid triangles) and interfacial tension (IFT) of aqueous sodium naphthenates solutions in contact with Heptol (solid circles). Both surface tension and interfacial tension tend to level off at a sodium naphthenate concentration of 1.0 wt % (apparent critical micelle concentration).

Finland). The Langmuir interfacial trough consists of three main parts: (1) a lower compartment built with hydrophobic and inert PTEE to avoid subphase contamination; (2) a pair of coupled, movable barriers to control the surface area; and (3) a microbalance sensor to measure the surface pressure. A detailed description of this technique can be found elsewhere.²⁶ The interfacial pressure was measured using the Wilhelmy plate made of a strip filter paper. A standard procedure²⁷ was used to obtain interfacial pressure–area (π – A) isotherms. The trough was initially filled with 120 mL of Milli-Q water as the subphase. A given volume of samples (25 μ L of 1 mg/mL asphaltene-in-toluene, 25 μ L of 0.1 wt % commercial sodium naphthenates, or 50 μ L of the mixture of the two at a volume ratio of 1:1) was spread dropwise and evenly on the water subphase using a Hamilton Microliter Syringe (Sigma-Aldrich). The top phase was formed by carefully introducing 100 mL of Heptol (optima grade) on the interface using a glass rod. All the solvents used in this study were presaturated with water in a closed container for 24 h to avoid any dissolution of water in the top oil phase during the tests. The whole system was aged for 3 h before the pressure–area (π – A) isotherm measurement. The isotherms were obtained by compressing the barriers at a fixed compression rate of 5 mm/min, suitable for the current system. After the compression, the top phase was carefully collected, spread on a clean subphase, and compressed again to make sure that no surface materials migrated during the first compression. All the measurements were conducted at room temperature. To ensure reliability of the results, measurements were repeated at least three times.

3. Results and Discussion

3.1. Surface/Interfacial Tension of Commercial NaNs. In early studies, lamellar liquid crystals and micelles were observed to form in the aqueous NaN solutions. The surface tension isotherms of these systems in (Figure 2) show that the surface tension decreases with increasing NaN concentration and levels off at around 31 mN/m at a NaN concentration of 1.0 wt %. This NaN concentration is referred to as the apparent critical micelle concentration (apparent CMC), analogous to the critical micelle concentration of classical surfactants. The difference in the apparent CMC value of 1.0 wt % obtained in this study

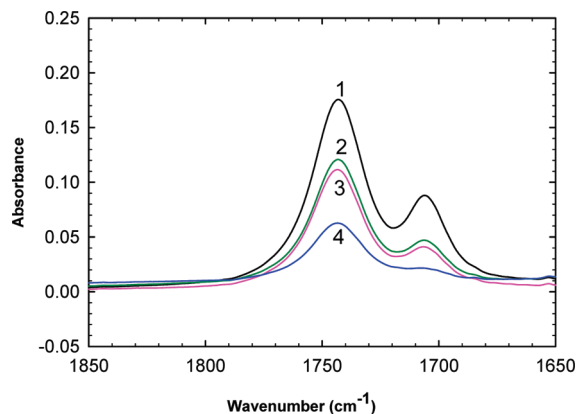


Figure 3. FTIR spectra of the indigenous NAs in the leachates extracted from maltenes. NAs have characteristic absorbance bands at 1740 and 1703 cm^{-1} and therefore can be quantified by FTIR. The number in the figure represents the number of extraction by which the leachate was obtained.

from the reported value of 0.1 wt % with a corresponding level-off surface tension of 26.8 mN/m²⁸ is attributed to the source and extraction methods of naphthenates, which also depends on the solvent ratio used in the extraction. The interfacial tension isotherm of a NaN aqueous solution in contact with Heptol indicates a similar interfacial behavior of NaNs to classical surfactants, exhibiting an apparent CMC at about 1.0 wt % of NaNs, beyond which the interfacial tension levels off at around 3 mN/m. It is not surprising that the apparent CMC obtained from the interfacial tension isotherms is the same as that obtained from the surface tension isotherm. The surface activity of naphthenic acids in bitumen from oil sands was recently evaluated using the concept of the hydrophilic–lipophilic balance.²⁹ A previous study²¹ showed that the addition of NaNs at low concentrations (10^{-5} to 0.01 wt %) had little or no effect on interfacial properties of diluted bitumen in which an ample amount of naturally occurring surface active components are present; however, the added NaN dominated the interfacial behavior of the model oil–water interface at a NaN concentration higher than its apparent CMC of 1.0 wt %. In our study, the 0.1 wt % NaN concentration was used to investigate its influence on interfacial behavior of a diluted asphaltene system.

3.2. NA Concentration in Serial Leaching of Maltenes. The indigenous NAs were extracted from maltenes by incremental addition of 0.0005 mol/L sodium hydroxide aqueous solutions, as described above. The concentrations of the NAs extracted by the sodium hydroxide aqueous phase were quantified by FTIR with the absorbance bands at 1740 and 1703 cm^{-1} (Figure 3).

Figure 4 shows the quantitative relationship between the caustic addition and the cumulative amount of NAs extracted from maltenes. The amount of NAs extracted increases with increasing NaOH addition. The surface properties of maltenes after the extraction of different amounts of NAs were measured to understand the influence of NAs on emulsion stability.

3.3. Interfacial Pressure–Area (π – A) Isotherms. Interfacial pressure (π) is defined as

$$\pi = \gamma_0 - \gamma \quad (1)$$

where γ_0 is the interfacial tension after the aging process at the original trough area (i.e., no barrier compression) and γ is the interfacial tension at a given extent of compression of the trough area. The observed interfacial pressures are due to the interac-

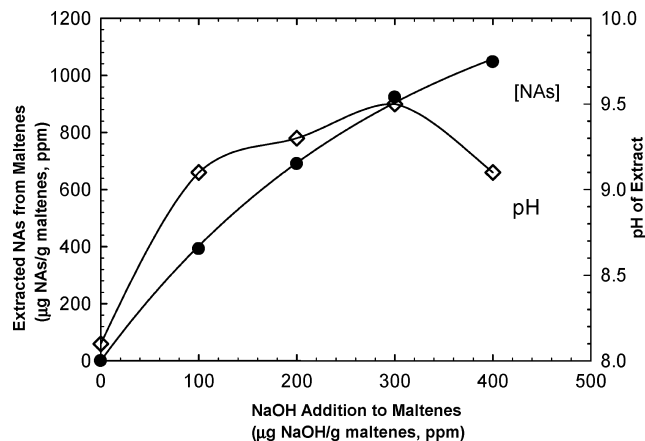


Figure 4. Quantitative relationship between caustic addition and the cumulative amount of NAs extracted from maltenes.

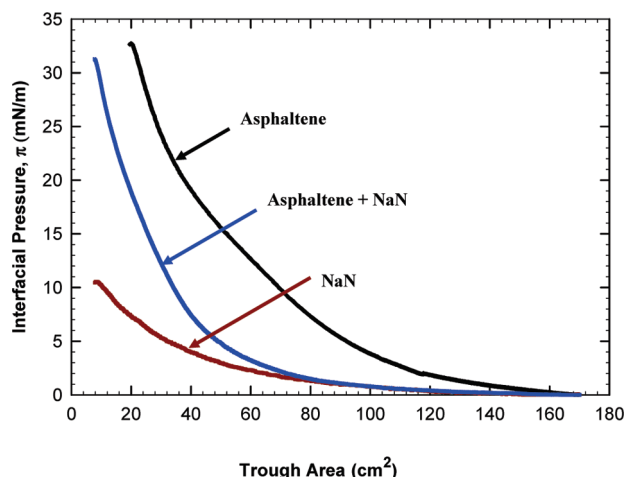


Figure 5. Interfacial pressure–area isotherms for asphaltene (25 μL) at the Heptol–water interface, sodium naphthenates (NaN, 25 μL) at the Heptol–water interface, and a mixture of asphaltene and NaN (50 μL , volume ratio 1:1) at the Heptol–water interface.

tions of the surface active materials (asphaltenes or sodium naphthenates) residing at Heptol–aqueous interfaces. The interfacial behavior of asphaltenes-in-toluene, NaNs in toluene (0.1 wt %), or the mixture of the two at a volume ratio of 1:1 is shown in Figure 5. At a constant compressed trough area, a higher interfacial pressure indicates a more stable interfacial film due to the interactions of adsorbed surface active materials.

Clearly, the adsorption of asphaltenes at the interface tends to form the most rigid interfacial film, indicating a strong resistance or barrier to coalescence. However, the adsorption of NaNs at the interface shows little resistance to the compression. The behavior of the mixture does not show additive nature. It appears that the presence of NaNs hindered asphaltene adsorption. Such a behavior is similar to the effect of the chemical demulsifiers in a water-in-oil emulsion.³⁰ This finding indicates that NaNs can partially displace asphaltenes adsorbed at the water–oil interface to reduce the rigidity of the interface. Such performance tends to destabilize the emulsion and eventually leads to demulsification.

3.4. Influence of NaNs on the Stability of Water-in-Asphaltenes Emulsions. While the interfacial pressure isotherm provides valuable information to qualitatively understand the stability of the water-in-oil emulsions, it is inadequate to quantitatively assess the emulsion stability. To further understand the role of NaNs in emulsion stabilization as encountered in oil sands industry, water-in-oil emulsions were prepared in

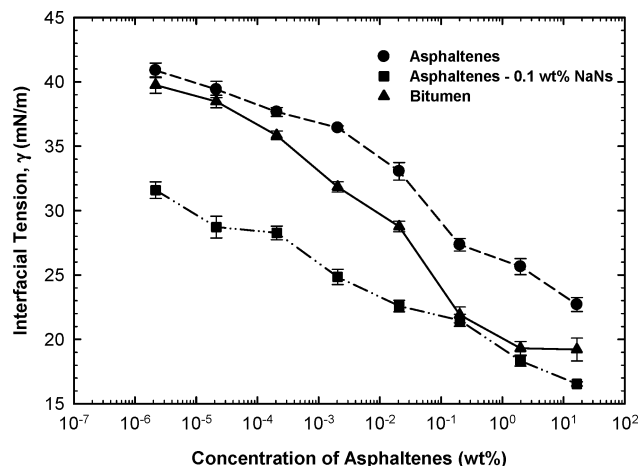


Figure 6. Comparison of interfacial isotherms for diluted bitumen–Heptol (solid triangles), diluted asphaltene–Heptol (solid circles), and asphaltene–Heptol–0.1 wt % NaNs (solid squares).

Heptol containing bitumen, asphaltenes, and the mixture of asphaltenes and 0.1 wt % commercial NaNs in Heptol, which is referred to as the model oil. The interfacial tension, crumpling ratio, and the probability of droplet coalescence were measured using the prepared emulsions. In an attempt to make the results comparable, a concentration of asphaltenes equivalent to that found in the original bitumen was used in the model oil.

3.4.1. Interfacial Tension Isotherm. The interfacial tensions of water droplets in the three different model oils were evaluated by the maximum bubble pressure method. A water droplet was aged in an oil solution at a micropipet tip for 3 min to enable the system to reach an equilibrium state. Data points in Figure 6 represent the average of measurements using 20 or more water droplets with the standard deviation shown as the error bars.

The decrease of interfacial tension with increasing crude oil concentration is attributed to the adsorption of surface active materials at the oil–water interface. If the bitumen concentration in the Heptol-diluted bitumen is X wt %, the concentration of the pure asphaltenes in Heptol will be $0.2X$ wt %, where asphaltenes constitute 20 wt % of the bitumen. At the same equivalent asphaltene concentration, the interfacial tension of bitumen system is lower than that of the asphaltene system due to competitive adsorption of nonasphaltenic bitumen components, such as NAs. To illustrate the role of naphthenic acids in controlling the interfacial behavior of water in naphtha-diluted bitumen emulsions, the interfacial tension was measured by adding NaNs to asphaltene in naphtha solutions. For a given asphaltene concentration, a significant reduction in interfacial tension was observed when NaNs were added to asphaltene in naphtha solutions. It appears that the added NaNs competitively adsorbed at oil–water interfaces, which limited the irreversible adsorption of asphaltenic molecules at the interfaces.

The Gibbs adsorption principles can be employed to evaluate the coverage (Γ , number of adsorbed molecules per unit area) of surface active components at the oil–water interface,

$$-d\gamma = kT \Gamma d \ln C \quad (2)$$

where γ is the oil/water interfacial tension, k is the Boltzmann constant ($k = R/N_A$, where R is the universal gas constant and N_A is the Avogadro number), T is temperature, and C is the concentration of the adsorbates. The “apparent” surface coverage (Γ) of an “equivalent” surface active species can be evaluated from eq 2. In this case, a complex molecular mixture is lumped

TABLE 1: Estimation of Average Surface Area Occupied by Surface Active Species

interface	effective molecule cross section area (nm ²)
diluted bitumen (10 ⁻³ to 1 wt %)-water	2.97
diluted asphaltene (10 ⁻³ to 1 wt %)-water	3.12
air-NaN solution	0.97
Heptol-NaN solution (0.1–1 wt %)	0.51

into an equivalent single molecular species of the same average molar mass. The slope of the linear regime (Figures 2 and 6) reflects the surface activity of the adsorbates: the steeper the slope, the greater the apparent surface coverage of surfactants, which indicates more surface active adsorbates. The effective molecular cross section area (the area per “site”) of the equivalent molecular species³¹ is given by the reciprocal of Γ (Table 1). The similar values of apparent surface coverage for diluted bitumen and asphaltenes suggest that large asphaltene molecules dominate the interface.

3.4.2. Quantitative Characterization of Skin Formation. It is well documented that the steric layer (skin) at the oil–water interface is the key contributor to emulsion stability.^{32–34} This skin formation has been largely attributed to irreversible adsorption of surface active asphaltenic molecules at the oil–water interface. The incompressible nature of these irreversibly adsorbed molecules results in out-of-plane deflections¹¹ when they are drawn together with a reduction in surface area of the water droplets. Droplet volume extraction experiment⁹ aims to quantify the skin formation by introducing a physical parameter of crumpling ratio (CR),

$$CR = \frac{A_f}{A_i} = \frac{\pi R_f^2}{\pi R_i^2} = \frac{R_f^2}{R_i^2} \quad (3)$$

where A_i is the initial projected area of the water droplet and A_f is the projected area of water droplet right at the point where crumpling was first observed. The crumpling ratio of water droplets in bitumen, asphaltenes, and asphaltenes–NaNs in naphtha solutions was measured as a function of bulk concentration of individual components. A high CR as defined in eq 3 represents a more stable interface. The results are shown in Figure 7. Each data point in Figure 7 is an average of measurements with 35 or more water droplets, and the error bar represents the standard deviation of the measurements. Crumpling was not observed at very low bitumen or asphaltene concentrations (less than 10⁻⁴ wt %) due to very little or no irreversible adsorption of surface active materials. Between 10⁻⁵ and 10⁻⁴ wt % of bitumen concentration, a sharp increase in CR was observed, indicating the formation of irreversibly adsorbed interfacial films. At higher bitumen concentrations, the CR decreases with further increasing of bitumen concentration, possibly because of the competitive adsorption between asphaltenes and surfactants in maltenes. Compared with asphaltenes, the surface active components in maltenes are shown to be easier to adsorb at the oil–water droplet interface due to favorable partitioning, depleting the space available for asphaltenes. In the case of asphaltenes, the CR increases steadily with increasing asphaltene concentrations, which means increasing irreversible adsorption. It is anticipated that increasing asphaltene

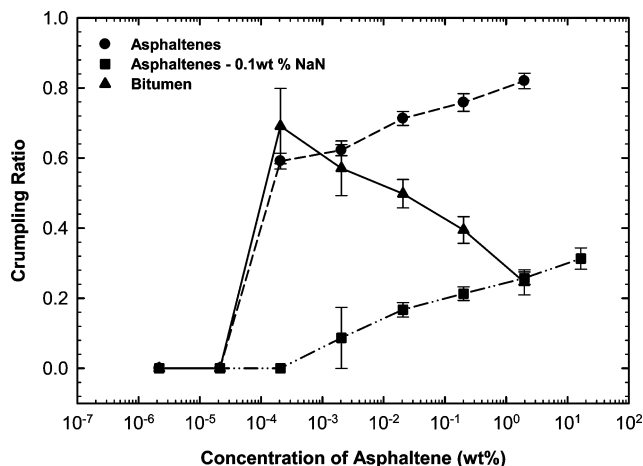


Figure 7. Comparison of crumpling ratio for diluted bitumen–Heptol (solid triangles), diluted asphaltene–Heptol (solid circles), and asphaltene–Heptol–0.1 wt % NaN (solid squares) systems.

concentration in Heptol would force more asphaltenes to move to the oil–water interface, leading to a more rigid interface and hence higher CR, although more difficult as the interface approaches its saturation. It is interesting to note that the sharp increase in CR occurred at 10⁻⁵ wt % concentration for both asphaltene and bitumen, indicating that asphaltene dominates the oil–water interfacial behavior of low bitumen concentration. However, with the addition of NaNs in the asphaltene system, the crumpling ratio drastically drops from 0.6 to ~0 at 10⁻⁴ wt % equivalent asphaltene concentration. This, in combination with the interfacial tension isotherm and surface coverage data, demonstrates that NaNs can hinder the development of a rigid interface, perhaps by fast adsorption–desorption kinetics (reaching equilibrium state). Meanwhile, at a fixed NaN concentration of 0.1 wt %, increasing asphaltene content in the system slightly increases the CR (0–0.3). This is because at high asphaltene concentration there are more asphaltenic molecules to compete for irreversible adsorption at the interfaces.

3.4.3. Droplet–Droplet Interaction. Water droplet interactions are measured to understand the demulsification potential of NAs by flocculation or coalescence. As two water droplets are pressed against each other by a micropipet, the direct contact of the droplets allows for the drainage of the intervening liquid sandwiched in the planar region between the droplets by mechanical forces. It should be noted that the applied force in these experiments was sufficient to deform the droplets,³⁵ as visually confirmed. If the droplets do not flocculate, they can be easily separated when the applied force is removed. The statistic nature of the droplet coalescence is represented by the probability of coalescence, ϕ . In the present study, on average three sets of interaction experiments for a minimum of 50 water droplet pairs are tried for every data point with the precision being given by standard deviation. As can be seen from Figure 8, the probability of coalescence for all three systems at very low concentrations of surface active components (10⁻⁶ to 10⁻⁴ wt %) is 1, indicating the absence of irreversibly adsorbed asphaltenic films to prevent coalescence.⁹ At intermediate concentrations (10⁻⁴ to 0.1 wt %), a sharp decrease in the coalescence probability was observed for all the three systems due to buildup of irreversibly adsorbed asphaltenic films. At an equivalent concentration of bitumen above 0.01 wt %, the probability of coalescence reduced to zero; i.e., no droplet coalescence was observed regardless of compositions of oil systems. However, the addition of NaNs to the asphaltene system greatly increases the probability of coalescence in the

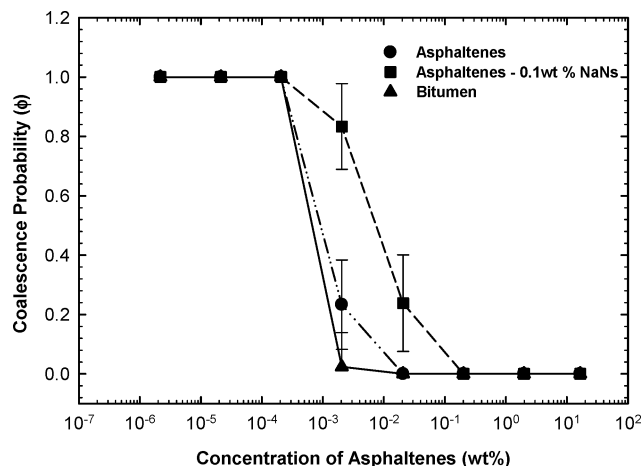


Figure 8. Coalescence probability of emulsified water droplets for diluted bitumen–Heptol (solid triangles), diluted asphaltene–Heptol (solid circles), and asphaltene–Heptol–0.1 wt % NaNs (solid squares) systems.

intermediate asphaltene concentration (10^{-4} to 0.1 wt %) region. The presence of NaNs makes the interface more fluid by winning the competitive adsorption with asphaltenes. To better understand the influence of NaNs in asphaltenes on stabilization of water-in diluted bitumen emulsions, Table 2 shows the qualitative description of the skin formation at the interface and droplets interactions in different systems. In the case of NaNs in Heptol, there was no skin formation at the water droplet surfaces and, therefore, spontaneous coalescence is observed for all the trails of droplet interactions. Regarding the asphaltene in Heptol with added NaNs, the results depend on the asphaltene concentration of the oil phase. In the highly diluted asphaltene region (10^{-6} to 10^{-4} wt %), coalescence is often observed, which is attributed to the absence of irreversibly adsorbed asphaltenic films. This finding agrees well with the absence of skin formation at oil–water interfaces. With increasing concentration of asphaltenes in the oil phase (10^{-4} to 0.1 wt %), sporadic coalescence is observed, due to a limited rigid skin formation. However, flocculation (Figure 9) is often observed in this regime. At high asphaltene concentrations of 0.1–10 wt %, the presence of a large amount of asphaltenes eventually dominates the interface, leading to the absence of coalescence.

3.5. Influence of Indigenous NAs on the Stability of Water in Naphtha-Diluted Maltene Emulsions. Since most of the indigenous NAs remain in the soluble maltene fraction, a protocol (Figure 1) was established to remove different amounts of naturally occurring NAs from the maltene fraction to identify their influences on the emulsion stability. Our previous study showed that the adsorption of maltenes on water droplets might contribute, to some extent, to a reduced emulsion stability without skin formation, provided that its concentration is sufficiently high.¹¹ Consequently, three maltene-in-Heptol solutions (0.85, 7, and 45 wt %) were used to create bulk samples for the extraction of naturally occurring NAs. On the basis of the proposed protocol, the indigenous NAs in the bulk solution are divided into two parts, the extracted and unextracted fractions under a given pH condition. Apparently, the higher the concentration of maltene in Heptol, the more the unextracted indigenous NAs remaining in the bulk solution for the same amount of sodium hydroxide addition. With this approach, emulsions containing different amounts of indigenous NAs are prepared for the microscale measurements. The interfacial tension, crumpling ratio, and probability of coalescence of these

emulsions were evaluated to understand the influence of naturally occurring NAs on the emulsion stability.

For the purpose of comparison, a blank emulsion was created by introducing the extracted indigenous NAs into pure Heptol. Regardless of the concentration of the indigenous NAs, no skin formation was observed when the volume contraction tests were performed. Also, coalescence was always observed in such systems.

3.5.1. Interfacial Tension Isotherms. The effect of indigenous NAs in the model oil phase on the interfacial tension was evaluated as a function of extracted NAs from maltene system. Data points in Figure 10 represent the average of measurements using 20 or more of emulsified water droplets with the standard deviation being shown as the error bars. It is clear that, at the same concentration of maltene in Heptol, the interfacial tension decreases with the decreasing amount of NAs extracted (removed) from the maltenes, although to a reduced extent as the droplet surface approaches its saturation. This observation can be explained by the preferential adsorption of NAs at the water droplet surface as compared with other naturally occurring components in the maltenes. Alternatively, the presence of NAs may displace or interact with other naturally occurring components to make them less available at the oil–water interface. For the same amount of NAs extracted from the maltenes, the higher the concentration of maltene in Heptol, the more the unextracted NAs will remain in the emulsion, leading to a lower interfacial tension. The similarity in slopes of interfacial tension isotherms in Figure 10 suggests the competitive adsorption among NAs and other naturally occurring components and a complex interaction of these species at the interfaces.

3.5.2. Quantitative Characterization of “Skin Formation”. It has been demonstrated that maltenes alone do not contribute to the formation of the rigid interfacial film, known as skin at the water droplet surface. This can be explained by the fast-reversible adsorption kinetics of some indigenous components in maltenes. Figure 11 shows the trend of skin formation as a function of the removal of natural NAs from maltenes. Each data point is an average of measurements with 35 or more water droplets, and the error bar represents the standard deviation of the measurements. At a higher concentration of maltene in Heptol (45 and 7.5 wt %), the CR remains zero (i.e., no skin formation) regardless of the amount of NAs extracted (removed) from maltenes. This observation suggests the reversible adsorption of remaining surface active components in maltenes at the oil–water interface, most likely due to the presence of abundant naturally occurring NAs remained in the maltenes. However, at a low concentration (0.85 wt %) of maltene in Heptol, the CR increases with increasing the amount of NAs extracted from maltenes. In this case, there is a decreasing amount of naturally occurring NAs in the system after a progressive extraction (removal) of NAs from the maltenes. Since there is no clear formation of skins in the Heptol system containing the indigenous NAs, the observed increase in CR with the increasing amount of NAs extracted from the maltenes indicates that the adsorption of certain surface active components in maltenes, other than NAs, can cause the skin formation. It should be noted that the contraction ($0 < CR < 0.14$) in this system is much smaller compared to the case of asphaltenes ($1 > CR > 0.2$).

3.5.3. Droplet–Droplet Interactions. Droplet contact is prerequisite for droplet coalescence, a means of emulsion destabilization. In the present study, an average of three sets of droplet interaction experiments for a minimum of 50 water droplet pairs are tried for every data point with the standard

TABLE 2: Qualitative Description of the Skin Formation at the Interface and Droplet Interactions in the Presence of NaN

sodium naphthenates	oil phase	skin formation	droplet–droplet interaction
0.1–10 wt %	pure Heptol	no	coalescence
0.1 wt %	10^{-6} to 10^{-4} wt% diluted asphaltenes	no	coalescence
0.1 wt %	10^{-4} to 0.1 wt % diluted asphaltenes	limited	coalescence and flocculation
0.1 wt %	0.1–10 wt % diluted asphaltenes	yes	no coalescence but some flocculation

deviation shown by the error bars. For a given concentration of maltene in Heptol, the probability of coalescence decreases with the increasing amount of NAs extracted from maltenes (Figure 12), suggesting an increase in emulsion stability. This finding indicates that the adsorption of an increasing amount of NAs at the droplet surfaces with a reducing amount of NA removal from maltenes can gradually remove the barrier for coalescence. The interfacial tension profiles for 45 and 7.5 wt % maltene in Heptol solutions are nearly identical. This observation is attributed to the adsorption of other natural surfactants in maltenes, which are in excess quantity at high maltene concentrations. Only the interfacial behavior of the 45 wt % maltene in Heptol solution is considered in the following discussions. It is perhaps surprising that the 45 wt % maltene in Heptol solution can still contribute to emulsion stability, even without skin formation. Recall that neither skin formation nor the barrier to coalescence is caused by the presence of

indigenous NAs. This phenomenon has two implications. It shows that the adsorption of the other surface active natural components in maltene at the oil–water interface can be partially masked by the presence of a high concentration of NAs (as confirmed by high crumpling ratio). Furthermore, the adsorption of these natural surface active components will provide a barrier for coalescence at high maltene concentrations. However, all the interactions still lead to flocculation even though the coalescence was not observed, as shown in Figure 13. Moreover, the less the NAs are extracted from maltenes, the stronger the flocculation. It appears that the adsorption of NAs tends to “soften” the droplet surface and promote the flocculation and coalescence of water droplets.

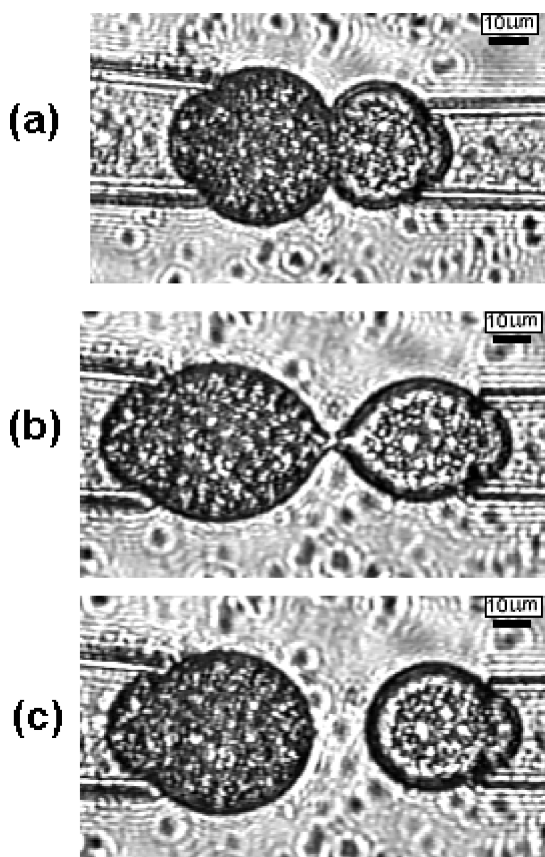


Figure 9. Sequential micrographs of visualization (a–b–c) describing flocculation of emulsified water droplets in 0.1 wt % NaNs and 0.1 wt % asphaltene in Heptol solutions. (a) One droplet is directed toward another static droplet to enable a “head-on” contact, and external force is applied to cause noticeable deformation of the contacting region for a sufficient time (allowing for the film drainage between the droplets to reach equilibrium shape of droplets). (b) The droplets show a sign of flocculation and deformation when the external force is reversed from compression to stretching. (c) The droplets return to its original state after the detachment from the flocculation state.

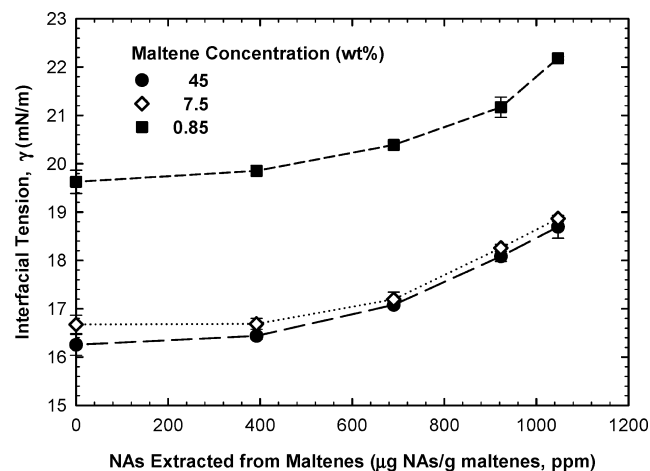


Figure 10. Interfacial tension of maltene in Heptol solutions in contact with water as a function of NAs extracted (removed) from the original maltenes. The maltenes after NA extraction are diluted in Heptol to create three concentrations: 45 wt % (solid circles), 7.5 wt % (open diamonds), and 0.85 wt % (solid squares).

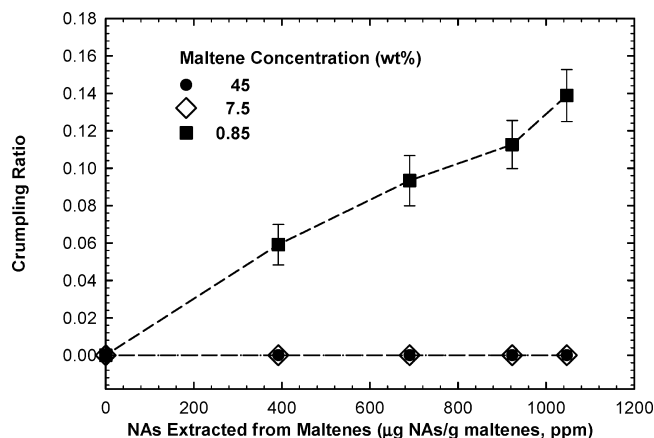


Figure 11. Crumpling ratio of water droplets emulsified in maltene in Heptol solutions as a function of NAs extracted (removed) from the original maltenes. The maltenes after NA extraction are diluted in Heptol to create three concentrations: 45 wt % (solid circles), 7.5 wt % (open diamonds), and 0.85 wt % (solid squares).

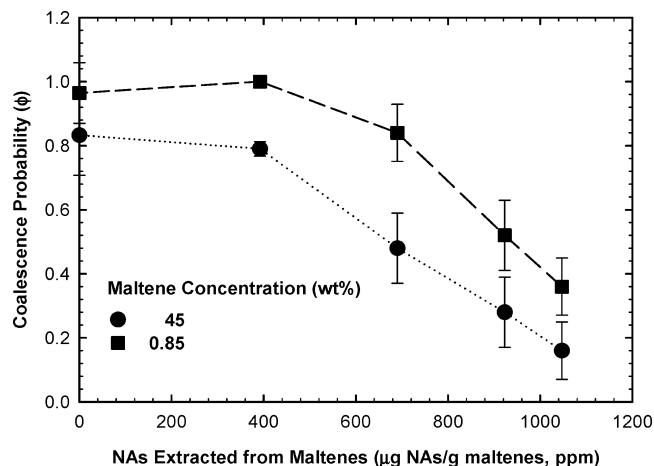


Figure 12. Probability of water droplet coalescence in maltene in Heptol solutions as a function of NAs extracted (removed) from the original maltenes. The maltenes after NA extraction are diluted in Heptol to create two concentrations: 45 wt % (solid circles) and 0.85 wt % (solid squares).

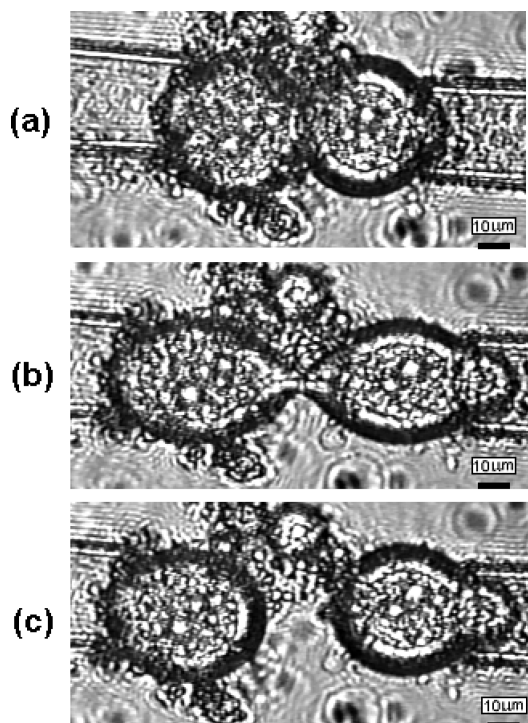


Figure 13. Sequential micrographs of visualization (a–b–c) describing flocculation of emulsified water droplets in 0.85 wt % maltene in Heptol after extraction of 690 ppm NAs from the original maltenes. (a) One droplet is directed toward another static droplet to enable a “head-on” contact and external force is applied to cause noticeable deformation of the contacting region for 2 min, a sufficient period allowing the film between the droplets to drain and reach equilibrium shape of droplets. (b) The droplets show a sign of flocculation and deformation when the external force is reversed from compression to stretching. (c) The droplets return to its original state after the detachment from the flocculation state.

4. Conclusions

In conventional bitumen extraction processes, a natural surfactant group, naphthenic acids (NAs) is released through the addition of sodium hydroxide. The level of NAs remaining in the bitumen or maltenes varies with caustic addition (sodium hydroxide) and the source and properties of oil sands ores.

The current investigation demonstrated that the level of NAs could affect the surface properties of water droplets in bitumen or its components (asphaltenes and maltenes) in Heptol solutions. NAs are capable of reducing the interfacial tension, soften rigid asphaltenic films, and promote the coalescence of water droplets, all of which would lead to destabilization of water-in-diluted bitumen emulsions. Such an observation would indicate that there may be a critical level of NAs to allow for minimum rag layer (rejected interfacial material from water drops) development in the commercial bitumen production processes. Possibly, a marker can be found to optimize bitumen recovery and efficiency of naphthenic bitumen froth treatment based on the relationship between caustic addition and the content of NAs released from the oil sands during processing.

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