Asphaltene Aggregation and Fouling Behavior

by

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To my parents, my brother and my beloved aunts

for their endless support during my studies far away from home

and

To my dear aunt Roya and my lovely grandma Maahiyaan who are no longer with us and I did not even have a chance to say goodbye to them
Abstract

This thesis explored the properties of asphaltene nano-aggregates in crude oil and toluene based solutions and fouling at process furnace temperatures, and the links between these two phenomena. The link between stability of asphaltenes at ambient conditions and fouling at the conditions of a delayed coker furnace, at over 450°C, was examined by blending crude oil with an aliphatic diluent in different ratios. The stability of the blends were measured using a S-value analyzer, then fouling rates were measured on electrically heated stainless steel 316 wires in an autoclave reactor. The less stable the blend, the greater the rate and extent of fouling. The most severe fouling occurred with the unstable asphaltenes. SEM imaging of the foulant illustrates very different textures, with the structure becoming more porous with lower stability. Under cross-polarized light, the coke shows the presence of mesophase in the foulant layer. These data suggest a correlation between the fouling rate at high temperature furnace conditions and the stability index of the crude oil. Three organic polysulfides were introduced to the crude oil to examine their effect on fouling. The polysulfides are able to reduce coking and carbon monoxide generation in steam crackers. The fouling results demonstrated that polysulfide with more sulfur content increased the amount of corrosion-fouling of the wire.

Various additives, solvents, ultrasound, and heat were employed to attempt to completely disaggregate the asphaltene nano-aggregates in solution at room temperature. The primary analytical technique used to monitor the nano-
The aggregation state of the asphaltenes in solution was the UV-visible spectroscopy. The results indicate that stronger solvents, such as pyridine and quinoline, combined with ionic liquids yield a slight reduction in the apparent absorbance at longer wavelengths, indicative of a decrease in the nano-aggregate size although the magnitude of the decrease is not significant. Analysis of the spectra of the whole asphaltene samples in toluene indicates that the absorbance of visible light with wavelengths > 600 nm follows a $\lambda^{-4}$ dependence. This functional dependence is consistent with Rayleigh scattering. Rayleigh scattering provides strong evidence that the apparent absorption of visible light by asphaltenes from 600-800 nm is not a molecular absorption phenomenon but rather a scattering mechanism. Rayleigh scattering equations were combined with experimental visible spectra to estimate the average nanoaggregate sizes, which were in a very good agreement with the sizes reported in the literature.

The occlusion of two polynuclear aromatic hydrocarbons (PAHs) (pyrene and phenanthrene) in asphaltene precipitates was tested by adding PAHs to the asphaltene in toluene solutions, precipitating by n-pentane and determining the amount of PAHs in precipitates using simulated distillation instrument. Pyrene and phenanthrene, which are normally soluble in the toluene-n-pentane solutions, were detected in the asphaltene precipitates at up to 6 wt% concentration. Trapping of PAHs outside of the nanoaggregates during precipitation gave 7-14 times less of the PAHs in the solid precipitate. This study shows that asphaltene aggregates can interact significantly with PAHs. The results are consistent with the presence open porous asphaltene nanoaggregates in solutions such as toluene.
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List of Symbols

Abbreviations

FF  Fouling factor
S_{BN}  Solubility blending number
I_N  Insolubility number
PAHs  Polynuclear aromatic hydrocarbon
C5  Precipitated asphaltenes with n-pentane
C7  Precipitated asphaltenes with n-heptane
IL  Ionic liquid
FR  Flocculation ratio
CMC  Critical micellar concentration
RICO  Ruthenium ion catalyzed oxidation
VPO  Vapor pressure osmometry
MS  Mass spectrometry
FD  Fluorescence depolarization

Symbols

R_f  Thermal resistance (m^2K/W)
$U_0$ Clean overall heat transfer coefficient ($\text{W/m}^2\text{K}$)

$U_f$ Fouled overall heat transfer coefficient ($\text{W/m}^2\text{K}$)

$T_w$ Wall temperature (°C)

$T_b$ Bulk temperature (°C)

$\delta$ Solubility parameter (MPa $^{1/2}$)

$V$ Molar volume ($\text{m}^3$/mol)

$\Delta H^v$ Molar enthalpy of vaporization (kJ/mol)

$\Delta U^v$ Internal energy of vaporization (kJ/mol)

$V_T$, $V_H$, $V_{oil}$ Volume fraction of toluene, heptanes and oil

$\rho_f$ Deposit density ($\text{kg/m}^3$)

$k$ Deposit thermal conductivity (W/mK)

$x$ Deposit thickness (m)

$m$ mass of deposit per unit area (kg/m$^2$)

$Q_C$ Heat transferred to the clean wire (W)

$Q_f$ Heat transferred to the fouled wire (W)

$A$ Heat transfer area ($\text{m}^2$)

$T_{wire, c}$ Temperature of clean wire (°C)

$T_{wire, f}$ Temperature of fouled wire (°C)

$C$ Molar concentration (mol/L)

$N_A$ Avogadro’s number

$a_{C,A}$ Absorption cross section (mm$^2$)

$a_{C,S}$ Scattering cross section (mm$^2$)

$n_s$ Refractive index of solvent
\( n_p \)  
Refractive index of particles

MW  
Mass average molecular weight \((g/mol)\)

\( W_A \)  
Mass concentration of analyte \((g/L)\)

\( \lambda \)  
Wavelength (nm)

\( d \)  
Diameter (nm)

\( r \)  
Radius of analyte molecules and/or particles (nm)

\( I_0 \)  
Incident radiation intensity

\( I \)  
Transmitted radiation intensity

\( A \)  
Absorbance

\( Da \)  
Dalton

\( \varepsilon \)  
Total extinction coefficient \((L/mol.mm)\)

\( b \)  
Path length (mm)

\( S \)  
State of peptization of asphaltenes

\( S_a \)  
Solvency requirements of peptized asphaltenes

\( S_o \)  
Peptizing power of oil medium

\( m \)  
A number in a power law relationship
1 INTRODUCTION

Petroleum is a fundamental source of energy for the whole world and will probably remain so for many decades in future. Due to the global decline of conventional oil supply, oil industries and governments are investing in unconventional oil sources such as heavy oils and bitumen to supply the increasing demand for fuels. Alberta’s oil reserves play an important role in the Canadian and world economy since the Alberta’s oil sands after Saudi Arabia and Venezuela is the largest proven crude oil reserve. Most of the oil sands of Alberta are located in three major deposits in Athabasca, Cold Lake and Peace River. Employing the available technologies, there are over 170 billion barrels of recoverable oil in the northern Alberta. Every year new projects are being added to increase the production which was 1.31 million barrels per day in 2008, to 3 million barrels per day in 2018.

Oil sand is a naturally occurring mixture of sand, water, clay or other minerals and bitumen. Bitumen is a heavy and extremely viscous oil, which makes the extraction, transportation and refining difficult and challenging. Upgrading of heavy oil and bitumen is a series of physical and chemical processes that transform bitumen into synthetic crude oil. This treatment adds a huge value to the raw resource and it is a necessary part in oil sands development before the bitumen can be used by conventional refineries. The chemistry of the upgrading processes is very complex and can result in producing unexpected insoluble material in addition to the favorable lower boiling products. One of the major
problems that upgrading development has confronted and is struggling with is the fouling issue. Fouling is the unwanted deposit of insoluble material on heat transfer surfaces, which can reduce unit reliability and increase maintenance, operating and energy costs. The asphaltene fraction, which is by definition a solubility class of crude oil and has low hydrogen to carbon ratio and high heteroatom content, has a high tendency to form coke and foulant during thermal upgrading processes. Asphaltene instability in the crude oil which causes the precipitation of asphaltene, is a major contributor to fouling. The delayed coking process is a favored technology for upgrading the heavy fractions of bitumen but fouling in furnace tubes that preheat the feed which is the major focus of the present study, results in significant cost penalties due to increased fuel consumption, and time for shut-down that is often required for cleaning. The deposits have been shown to be mainly carbonaceous and usually derived from asphaltenes in the feed. Iron sulfide also is a major component in some foulants. To date the mitigation methods used for furnace tubes fouling consist of physical and chemical methods. Online spalling is one of the physical methods in which the steam is injected to the tubes to break the deposits, which then goes to the coke drum. The main problem is in controlling the velocity and speed of spalling off the coke. If the steam velocity is too high it can erode the metals and also too fast spalling can plug the tube outlet. The other physical method which is commonly used is pigging in which water is utilized to push pigs through the tubes and clean the deposits attached to the tube surface. This method gives a very clean tube at the end but takes several days because the tubes should be cool
Antifoulants are chemical additives which are used to stop or reduce the chemical (or physical) processes leading to formation of foulants or attachment of the foulant particles to the surface. For high temperature units where coke formation is the main cause of fouling some kind of surfactant molecules including sulfonates, phosphorus and organic phosphates, aluminum, organic amines and boron is used as the additive. These kinds of additives are very surface active and prevent the coke formation on surfaces. Since the asphaltene is stable in the oil phase no fouling will occur. Therefore keeping the asphaltene stable in the oil phase using dispersants would reduce its deposition tendency and may help to prevent fouling. Although there are some methods to reduced fouling but because of the complex nature of the crude oils, the knowledge for predicting the model to find the effective mitigation methods is still inadequate.

1.1 Research objectives

The onset of asphaltene flocculation is a good predictor of fouling in heat exchangers at relatively low temperatures (i.e. below 350 °C). In this study, our objective was to examine the effect of asphaltene stability at room temperature on subsequent fouling at delayed coking process furnace conditions, with surface temperatures over 450 °C. A modified autoclave reactor was used to simulate plant conditions with controlled temperature and pressure. A series of blended feeds utilized to develop a quantitative relationship between asphaltene stability and fouling. Another goal was to investigate the change in the coke texture as the
result of change in asphaltene stability. Role of three kinds of additives which were mainly contain polysulfides on the foulant formation under the coker furnace conditions was another target. Since the asphaltene precipitation is definitely a major reason for fouling, complete disaggregation of asphaltenes could eliminate or suppress many subsequent drawbacks, including fouling. Consequently, our next objective was to disaggregate asphaltene completely in toluene-based solutions at room temperature using effective dispersants which are used to prevent asphaltene floculation, in combination with solvents, heat and ultrasound.

Our last objective was to investigate the occlusion of polynuclear aromatic hydrocarbons (PAHs) within asphaltene nanoaggregates and thereby their contribution to asphaltene deposition, even though these compounds are fully soluble. The aim was tested by dissolving pyrene and phenanthrene in toluene solutions of asphaltene, adding n-pentane to give precipitation, then analyzing the precipitates for the presence of the PAH compounds.

1.2 Thesis outline

The current chapter gives an overall introduction and main objectives of the work done toward this thesis. The next chapter is the literature background, which serves a short overview of asphaltenes, asphaltene aggregation, fouling and coke formation. The delayed coking process and the fouling in delayed coker furnace tubes will be briefly reviewed. In Chapter 3 the focus is on the effect of asphaltene stability on fouling at delayed coking process furnace conditions as
well as the change in coke texture as the result of stability change. We studied the
effect of polysulfides additives on the fouling at process furnace conditions in
Chapter 4. Chapter 5 reports the attempts to disaggregate asphaltenes in nano-
scale in toluene based solutions. It also presents the result of the interactions of
nanoaggregates with UV-visible radiation, as a tool to probe aggregation. The
intent of Chapter 6 is to study the occlusion of PAHs within asphaltenene
aggregates. Pyrene and phenanthrene were chosen as the PAHs and their
interaction with asphaltenene nanoaggregates in toluene solutions is reported.
Finally Chapter 7, the last chapter of the thesis, includes the overall synthesis of
the previous chapters. The major conclusions and recommendations are also
summarized.

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2 LITERATURE BACKGROUND

This chapter deals with a brief overview of asphaltenes and their aggregation, fouling of heat transfer surfaces, stability of asphaltenes and coke formation and their impact on fouling especially fouling in the condition of delayed coker furnace tubes which is the main target of the present study. The asphaltenes have a high propensity to create coke which is an essential part of foulant formed in moderate temperatures (between 350 °C-600 °C). Also asphaltene instability in the crude oil and blends causes asphaltene precipitation and results in foulant and coke formation. So we start here with asphaltenes which has the essential contribution to fouling.

2.1 Asphaltenes

Asphaltene is considered as the heaviest and most polar component of crude oil and is defined as a solubility class which is insoluble in light aliphatic solvents such as n-pentane or n-heptane, and soluble in aromatic solvents like toluene \(^1\). When different solvents are used for asphaltene precipitation, the yield and properties of the precipitated asphaltenes could be different \(^2\). As an example, the molar mass of the asphaltenes precipitated by n-heptane is higher than asphaltenes which is precipitated by n-pentane and the yield of precipitated asphaltenes has the reverse trend for the aforesaid solvents \(^3\). Thus the precipitated asphaltenes are usually labeled and identified by the precipitating solvent; \(C_5\) asphaltenes or \(C_7\) asphaltenes for instance. As a solubility class, asphaltenes
contain a wide range of molecular chemistries; therefore, they are chemically heterogeneous. The most basic properties of any chemical compound are its elemental constituents. Fortunately there is no controversy among researchers in this regard. This fraction of crude oil contains a high amount of carbon and low hydrogen content, and is rich in heteroatoms such as sulfur, nitrogen, oxygen, nickel and vanadium. The CHNSO elemental composition values (%w/w) for asphaltenes from Alberta heavy oils and bitumen fall in the range of 80.06-86.61% C, 6.93-8.45% H, 3.47-8.21% S, 0.94-2.82% N and 0.44-2.61% O. Asphaltenes usually exhibit atomic H/C ratio between 1.0-1.3. This low H/C ratio indicates the highly aromatic nature of asphaltenes. The second most important attribute of asphaltenes that has received much attention in the literature and is the subject of a significant controversy is their molecular weight. Some common experimental techniques used for molecular weight determination are vapor pressure osmometry (VPO), mass spectrometry (MS) and fluorescence depolarization (FD). But there is little agreement between the results obtained using these techniques. The results reported to be in the range of 400-10000 Da. Even for a single technique like VPO, different molecular weights are observed at different temperatures, solvents and asphaltene concentrations. Asphaltenes tend to aggregate in solution even at very low concentrations in aromatic solvents. This well-known property of asphaltenes, which will be discussed later is known to affect the VPO measurements. The inconsistencies and ambiguities arising from the application of these techniques speak to the very complex nature of asphaltenes.
The molecular structure of asphaltenes also is a subject of significant debate. The two main sides of debate suggested two configurations for asphaltene molecular structures; The “continental” or “hand” or “island” configuration\textsuperscript{13, 14} in which an aromatic core with 6-8 fused aromatic rings is surrounded by alkyl chains and the “archipelago” configuration which composed of several smaller aromatic (fused ring) regions that are interconnected by alkyl chains\textsuperscript{15, 16}. Island model is supported by either fluorescence spectroscopy\textsuperscript{13} which can’t be utilized to determine most probable structures in a complex component mixture, or mass spectrometry without proper calibration by suitable reference compounds\textsuperscript{17}. Supports for the archipelago structure are growing in the literature. Using the ruthenium-ion-catalyzed oxidation (RICO) in which the aromatic carbons are removed as CO\textsubscript{2} and intact saturated carbon are left showed the significance of bridges and alkyl chains in the asphaltenes\textsuperscript{16, 18}. Moreover the detection of sulfide and ether bridges\textsuperscript{15, 19}, the characterization of alkyl bridges between aromatic groups\textsuperscript{20} and quantitative evidence for the presence of bridged structures in the asphaltenes by cracking of thin film at 500°C\textsuperscript{21} along with the behavior of asphaltenes during processing\textsuperscript{22} all supports archipelago model to be the dominant structure.

\textbf{2.2 Asphaltene self-association}

As mentioned earlier, one well-documented property of asphaltenes is their propensity for aggregation. Asphaltenes self-associate into nano-scale aggregates. Under increasingly poor solvent conditions, larger-scale flocs and
precipitates are formed. For a long time, it was believed that asphaltenes have a critical micellar concentration (CMC) behavior, similar to surfactants because of several similarities between these two such as stabilization in-oil-water emulsion. The self-associating behavior of asphaltenes was thought to initiate above CMC. Self-association of asphaltenes has been understood to be the first step in the formation of small aggregates. However, the concept of considering CMC as a characteristic for asphaltenes has been questioned by many authors. Anderson et al. used isothermal titration calorimetry to show that the titration of asphaltenes with toluene does not fit the behavior of a micelle-like system and stated that using this concept for asphaltene aggregation is inappropriate.

The nature of forces and the cause and mechanism of aggregate formation is a subject of significant debate in the literature. As discussed above, different structures of asphaltene molecules have been proposed. These structures lead to different points of view of the self-association mechanism of asphaltenes. First, Yen et al. proposed that asphaltene aggregation take place by forming stacks of condensed aromatic cores and therefore the main associative force was suggested to be π–π stacking. The “continental” configuration of asphaltenes implied that that π–π stacking would be the dominant force. This model does not predict many properties reported for asphaltenes in the literature such as the existence of substantial microporous structural units which enable asphaltenes to adsorb and occlude other molecular species in the oil reservoirs, adhesion of asphaltenes to the surfaces and the mechanical properties of asphaltenes. Recently, Gray et al proposed a new model for aggregation of asphaltenes...
which attempts to reconcile the various properties and reactions of this petroleum class. They suggested that the \( \pi-\pi \) stacking is only a contributing factor rather than the dominant one and other factors are participating in the aggregation of asphaltenes as well. The model best fit with the archipelago configuration that has multiple functional groups. Figure 2.1 shows the molecular depiction of a representative asphaltene aggregate proposed by Gray et. al. As shown in Figure 2.1 there are numbers of forces that acts simultaneously to form asphaltene aggregates such as acid-base interaction and hydrogen bonding shown in blue, metal coordination shown in red, hydrogen pocket shown in orange and \( \pi-\pi \) stacking which is shown in green.
Figure 2.1 Molecular schematic representation of a supramolecular assembly in a representative asphaltene aggregate. Associations between molecules are color-coded in: acid-base interactions and hydrogen bonding (blue), metal coordination complex (red), a hydrophobic pocket (orange), π-π stacking (face-to-face dark green; within a clathrate containing toluene, light green). (Reprinted with permission from Gray M.R., Tykwinski R.R., Stryker J.M., Tan X. Supramolecular assembly model for aggregation of petroleum asphaltenes (2011) Energy and Fuels, 25 (7), pp. 3125-3134. Copyright 2012 American Chemical Society)
2.3 Fouling of heat exchanger equipment

The accumulation of unwanted solid or semi-solid materials on heat transfer surfaces is called fouling. The foulants are either already present in the process fluid or are built-up from precursors by chemical or physical processes, therefore fouling is a very complex phenomenon involving momentum, heat and mass transfer that may be accompanied by phase change and chemical reactions. In the petroleum industry, these unwanted materials may be asphaltenes, coke, wax emulsions or inorganic solids. The economic loss due to the fouling is one of the major problems of the industries dealing with heat transfer equipment. Fouling increases capital expenditures due to oversizing, increases energy input both for direct heating and for pumping due to increase in pressure drop, and increases maintenance cost to remove the deposits or to add fouling inhibitors. Increased maintenance also reduces production from the affected units.

Many types of fouling may occur in heat transfer equipment, but they are generally classified into six categories; particulate, reaction, corrosion, precipitation, biological and solidification fouling. Particulate fouling is defined as accumulation of suspended particles in the liquid or gaseous process streams onto the heat transfer surfaces. In reaction fouling, the deposit formation occurs by chemical reactions at the heat transfer surfaces in which the surface material itself is not a reactant. Cracking, polymerization and coking are common examples of reaction fouling. Temperature is the most important factor in this type of fouling. Corrosion fouling is due to the accumulation of corrosion product on the heat transfer surfaces. In this type of fouling process the heat transfer
surface material itself react to produce the corrosion products. Corrosion is the deterioration of material (usually metal) by reaction with its surroundings because of water, impurities in the fluid or the presence of H$_2$S and CO$_2$ in the produced fluid for instance $^{36}$. Precipitation fouling includes the crystallization of the dissolved substances of solutions, and this mechanism includes scaling in boilers. Biological fouling is the attachment of living materials (micro- or macroorganisms like bacteria, molluscs, etc.) to the heat transfer surface. Solidification fouling (or freezing fouling) is the freezing of high-melting components from a multi-component solution on subcooled heat transfer surfaces $^{37}$.

In many cases, the structure and composition of deposits can change with time. This time-dependent change is called aging. After accumulation of the deposits on the surface, the chemical structure can be changed with time by reactions, such as polymerization $^{38}$. This process is especially important at constant heat flux, because the skin temperature of the heat exchanger or furnace tube increases with time.

The most common causes of fouling in petroleum refining processes are incompatible and insoluble asphaltenes, inorganics, coke formation, polymerization of olefins after thermal conversion, and oil-water emulsions $^{34}$. Murphy and Campbell $^{39}$ listed the causes of fouling in refineries under seven classifications, comprising inorganic salts, sediments, filterable solids, corrosion products, oxidative polymerization, asphaltene precipitation, and coke formation from chemical reactions. Srinivasan and Watkinson $^{40}$ added iron sulfide
formation to the above list, although they stated that presence of iron is normally attributed to products of upstream corrosion processes.

### 2.4 Parameters that influence fouling

Many variables have an effect on fouling, such as properties of the fluid and its tendency for fouling, the nature of the species dissolved or entrained in the fluid, surface and fluid temperature, velocity and hydrodynamic effects, surface composition, and surface roughness and defects. Ash particles and volatile inorganics such as sodium sulfate favor fouling, and some elements like vanadium, nickel and iron may catalyze fouling processes. Temperature alone is often not a very good parameter to correlate fouling rates. For instance, in asphaltene precipitation, which is one of the main causes of fouling in refining, as temperature increases the solubility of asphaltene increases, giving reduced fouling of heat exchangers. On the other hand, increasing the bulk temperature increases the fouling rate due to reactions of corrosion products or formation of gum particles.

Hydrodynamic effects like shear stress at the heated surface and velocity also affect fouling. Higher shear stresses help to propel deposits and reduce fouling, however, the effect of bulk velocity depends on the controlling mechanism. If mass transfer of foulants and products to the wall is the controlling mechanisms, increasing the bulk velocity can increase fouling. But if chemical reaction in the thermal boundary layer or wall or sticking of deposits to the surface is controlling, then increasing the bulk velocity will decrease fouling. The
reason is that higher velocities cause better thermal performance and suspended particles in the fluid can deposit on the wall better in lower velocities and where the velocity quickly changes.\textsuperscript{43}

Selection of material for heat exchange surfaces is important for naphthenic acid corrosion and fouling. Most process equipment is made from carbon steel, which is not very expensive but it is subject to corrosion for reactions especially in temperatures above $230^\circ\text{C}$.\textsuperscript{35} 5Cr 5 Mo steels are more resistant at higher temperature. Aluminized steels, the alloys Inconel 600 and Incoloy 800, ferritic and martensitic stainless steel are also good materials. Austenitic stainless steels containing molybdenum are the most resistance materials.\textsuperscript{44-45} Corrosion resistant materials such as stainless steel, nickel alloys, and titanium are more expensive. If the tubes are made up of glass, Teflon or graphite they can resist fouling, but these materials are limited in temperature range and thermal conductivity. Besides, using plastics, glass and some polymers for surface treatment can help to minimize the deposits on the surfaces. Suspended solids may cause particulate fouling therefore sometimes it is better to filter the process fluid before it enters the system.\textsuperscript{35} Also increasing surface roughness can increase fouling, because roughness of surface can promote nucleation, adsorption of the suspended fluid particles on the surface and/or surface chemistry activity.\textsuperscript{41}

\section*{2.5 Measurement of fouling resistance}
Figure 2.2 shows the temperature profile of hot heat transfer surfaces before and after fouling. The figure clearly illustrates the wall temperature increase due to the fouling. The process of fouling on heat transfer surfaces can be treated by adding an additional thermal resistance, $R_f$, to the surface resistance itself as illustrated in Figure 2.3. It shows the thermal resistances where one side of the wall is subjected to a constant heat flux and the fluid is flowing on the other side. For the clean condition we have:

$$\frac{1}{U_0} = R_w + R_1 \quad (2.1)$$

$$\dot{q} = U_0(T_{w0} - T_{b0}) \quad (2.2)$$

Where $T_{w0}$ is clean wall temperature, $T_{b0}$ is the bulk temperature, $U_0$ is the clean overall heat transfer coefficient and $\dot{q}$ is the heat flux.
Figure 2.3 Heat transfer resistances through a wall (a) without, (b) with fouling deposit.

As the deposit attaches and forms on the surface, the thermal resistance caused by deposit formation and the surface temperature increase. For the fouled condition at a constant heat flux $\dot{q}$, the governing equations are as follows:

$$\frac{1}{U} = R_w + R_f + R_1$$  \hspace{1cm} (2.3)

$$\dot{q} = U(T_w - T_b)$$  \hspace{1cm} (2.4)

Where $T_w$ is wall temperature after fouling formation, $T_b$ is the bulk temperature, $U$ is the fouled overall heat transfer coefficient and $\dot{q}$ is the heat flux.

The fouling resistance, $R_f$, changes with time and can be calculated as follows:

$$R_f = \frac{1}{U} - \frac{1}{U_0}$$  \hspace{1cm} (2.5)
\[
R_f = \frac{(T_{w} - T_B)}{q} - \frac{(T_{w} - T_B)_0}{q} \quad (2.6)
\]

\[
R_f = \frac{T_w - T_{w0}}{q} \quad (2.7)
\]

The thermal fouling resistance reflects the decrease in heat transfer coefficient with time and is calculated from the increase in surface temperature at constant heat flux. In laboratory systems for measurement of fouling, fouling is commonly induced by electric heating of an element or wire immersed in a liquid. The skin temperature of the heated element or wire is commonly determined directly from the resistance using a calibration curve, and the heat input is given by the electric power applied. By measuring both resistance and power consumption continuously, these probes can provide direct measurement of \(R_f\) versus time for the cases of constant heat flux, constant skin temperature, or for other trajectories \(^{46-48}\).

### 2.6 Solubility and incompatibility of asphaltenes

The most accepted empirical thermodynamic approach to describe asphaltene stability is the solubility parameter. The concept of solubility parameter was developed by Hildebrand and co-workers \(^{49-51}\) for regular solutions and is a measure of the solvent power or the energy of the solution to overcome the association forces of the solute \(^{52}\) and can be defined as the square root of cohesive energy density as follows:

\[
\delta = \left(\frac{\Delta H^v}{V}\right)^{1/2} = \left(\frac{\Delta H^v - RT}{V}\right)^{1/2} \quad (2.8)
\]
Where $\Delta U^\text{v}$ is the internal energy of vaporization (kJ/mol), $\Delta H^\text{v}$ is the molar enthalpy of vaporization (kJ/mol) at temperature T, R is the ideal gas constant and $V$ is the molar volume (m$^3$/mol). “Hildebrand defined a regular solution as the mixture in which components mix with no excess entropy provided and there is no volume change on mixing” 53. In these solutions no specific interactions take place and are characterized by random orientation and distribution of molecules. These solutions are often highly non-polar. The Equation (2.8) shows that solvents with enough energy of solution to overcome the association forces between the asphaltene aggregates are capable of dissolving asphaltenes. The most widely used solvent for the precipitation of asphaltenes is n-heptane. Propane and n-pentane are also common, especially for industrial scale applications. The solvents with lower solubility parameters will cause more asphaltenes to precipitate, i.e. propane ($\delta = 13.1 \text{ MPa}^{0.5}$) can separate more asphaltenes than n-pentane ($\delta = 14.4 \text{ MPa}^{0.5}$) and n-pentane precipitates more than n-heptane ($\delta = 15.3 \text{ MPa}^{0.5}$). Solubility parameters of asphaltenes can be estimated by various methods such as spot tests and flocculation titration threshold. The condition which is important in asphaltene precipitation problems is the point where asphaltene begins to precipitate. This point which is called onset of asphaltene precipitation or flocculation is defined as the minimum amount of precipitant necessary to induce the precipitation of solids.

Fouling due to asphaltene stability was classified into three modes by Wiehe: self-incompatible, incompatible on blending, and nearly incompatible. Self-incompatible oils are those that contain insoluble asphaltene without
blending oils. Thermal conversion of petroleum residus such as visbreaking can produce heavy oil byproduct that has the sediments of insoluble asphaltene which can cause fouling \(^ {54}\). Blending of crude oils, especially with different origins, may give incompatibility and start to precipitate asphaltene. This precipitation can cause fouling and coking in preheat trains. The proportion and the order of blending oils are important in compatibility of blending. Wiehe \(^ {55}\) pointed out that the solubility parameter of a liquid mixture is the volumetric average solubility of its constituents.

\[
\delta_f = \frac{V_T \delta_T + V_H \delta_H + V_{oil} \delta_{oil}}{V_T + V_H + V_{oil}}
\]  
\[
(2.9)
\]

Where \(\delta_f\) is flocculation solubility parameter, \(\delta_{oil}\) is the solubility parameter of oil, \(\delta_T\) is toluene solubility parameter, \(\delta_H\) is n-alkane solubility parameter and \(V_T\), \(V_H\), \(V_{oil}\) are volume fraction of toluene, n-alkane and oil respectively at the point where the precipitation of asphaltene is first observed. If the solubility parameter of oil is greater than flocculation solubility parameter then asphaltene is soluble in oil and does not precipitate.

Before defining nearly incompatible oils two parameters should be defined; the solubility blending number \((S_{BN})\) and the insolubility number \((I_N)\). They are defined as follows \(^ {56}\):

\[
S_{BN} = 100 \left( \frac{\delta_{oil} - \delta_H}{\delta_f - \delta_H} \right)
\]  
\[
(2.10)
\]

\[
I_N = 100 \left( \frac{\delta_f - \delta_H}{\delta_f - \delta_H} \right)
\]  
\[
(2.11)
\]
The ratio of solubility blending number of a mixture of crude oils to the maximum insolubility number in the mixture can be a measure of distance from incompatibility. When this ratio is equal to one or less than one, incompatibility is anticipated. Nearly incompatible oils are those $S_{BN}/I_N$ is between 1.0 and 1.4 and can cause fouling on heated metal surfaces by asphaltenes\textsuperscript{56}.

2.7 Coke formation

Coke is commonly defined as the toluene insoluble carbonaceous solid that is formed during thermal reaction of carbon-rich materials\textsuperscript{1}. Coke is generally believed to form as a result of reactions such as cracking, polymerization and condensation. Phase behavior also plays an important role in the formation of coke\textsuperscript{57}. Asphaltenes have the highest propensity to contribute to coke formation upon exposure to high temperatures. Coke can form on surfaces or in the fluid phase. When crude oil blending or phase change made asphaltenes precipitate, this insoluble component could be one of the main precursors or products of fouling. One of the problems of coke formation is that the process is irreversible. Holding the oil above 350°C for enough time in the delayed coker furnace tubes, visbreakers and distillation units forms thermal coke. For oils containing insoluble asphaltenes, this temperature can be even lower. Coking in delayed or fluid coking reactors is expected but in the furnace tubes, heaters and process vessels, coking causes fouling which is absolutely unwanted. Wiehe\textsuperscript{34, 58} in an attempt to describe the thermal cracking of petroleum residua, linked phase behavior and coking and suggested that coke forms because of the formation of a separated liquid phase, leading to mesophase coke formation. In this model,
asphaltenes are composed of polynuclear aromatic cores with pendant groups connected to the cores and cracking causes the cores to lose hydrogen-rich pendant groups. Once the concentration of the cores exceeded their solubility limit in the remaining media, these cracked cores formed a separate liquid phase, followed by rapid cross-linking reactions that eventually recombine them to form insoluble coke. Wiehe’s kinetic model which he developed base on this pendant-core model can successfully explain some phenomena occurring in the heavy oil coking. Wiehe’s model was continued and modified by Rahmani et. al. They incorporated the hydrogen donating ability of the solvent and the hydrogen accepting ability of the asphaltenes in the model which both play a key role in coke yield determination. Their model was in a good agreement with coke formation from asphaltenes data in different solvents. While Wiehe focused only on aromaticity as the driving force for phase separation, Alshareef et al., showed that oligomerizarion is a second driving force, and any combination of these two main forces may also drive components across the phase boundary proposed by Wiehe.

It is important to note that toluene-insoluble material is not all mesophase, and hence coke formation may or may not require the unique ordered structure of mesophase materials. Carbonaceous mesophase is an intermediate phase that can form during the cracking of heavy oil and is defined by its optical properties rather than its solubility. This liquid crystalline material is a subset of coke phase which is distinguished by its anisotropy. Various methods used for studying the formation of mesophase, but polarized-light microscopy is generally
the most useful method, because carbonaceous mesophase was discovered and defined by its optical anisotropy \(^\text{62, 64}\). Temperature, residence time, heating rate, gas flow rate and stirring rate play important role in mesophase formation process \(^\text{65}\). Once mesophase spheres begin to form, they can coalesce to form larger mesophase domains. These larger domains deposit as coke on the interior surfaces of process equipment.

### 2.8 Delayed coking process

Delayed coking is a semi batch thermal cracking process used to upgrade and convert the heavy petroleum fractions, normally vacuum residue, into more valuable light liquid products, gas and solid coke which is enriched of sulfur, nitrogen and metals relative to the feed, as the byproducts, which are less valuable. The first delayed coking unit was built in 1930, and it has become one of the most widely used technologies for conversion of vacuum residues to distillate products \(^\text{66}\). The process feed is heated to circa 500°C by the coker furnace in the pressure of around 4 bars (60 psig) and then moved to the coke drum as fast as possible to minimize the amount of coke formation in furnace tubes. The feed stream is switched between two drums. The coke solids form in the coke drum gradually while the other drum is being steam-stripped, cooled, decoked, pressure checked and warm up. As the first drum fills up feed is switched to another one and the coke in the first drum is removed. The typical switching time in bitumen processing is about 12-14 hours \(^\text{67}\). The overhead
vapors from the coke drums flow to a fractionator, usually called a combination tower. This fractionator tower has a reservoir in the bottom where the fresh feed is combined with condensed product vapors (recycle) to make up the feed to the coker heater. The yield of products from delayed coking depends on the feed composition, especially carbon residue content (measured as MCR or CCR) of the feed. Coking processes are very useful for mineral solids and metals rejection.

A fired heater with horizontal tubes is used in the process to reach thermal cracking temperature of 485 to 505°C. The tubes are typically manufactured from chromium steels. With short residence time in the furnace tubes, coking of the feed material is thereby “delayed” until it reaches large coking drums downstream of the heater. Three physical structures of petroleum coke: shot, sponge, or needle coke can be produced by delayed coking. Shot coke production needs high concentrations of asphaltene in the feedstock, dynamic (velocity and/or turbulence) in the coke drum and high coke drum temperature. Sponge coke is produced with a low to moderate asphaltene concentration and if it meets strict property specifications it is considered anode grade sponge coke suitable for making carbon anode for aluminum industry. Needle coke is produced from asphaltene free feedstock used in graphite electrode manufacturing.

2.9 Fouling of delayed coker furnaces

Little studies have appeared in the literature on the fouling in the coker furnace conditions. Researchers suggested that for the temperatures of furnace inlet, iron sulfide formation and coke formation are the two dominant
reactions happened in fouling. Albright 70 proposed a coke formation theory in which the asphaltene dehydrogenated at the hot surfaces and resulted coke formation and growth on the wall to form thick deposit. The degree of asphaltene instability had a direct relation to fouling rate. Once the molecules of asphaltene were destabilized, the carbon rich core was available for surface chemical reactions like coke formation, polymerization and deposition. At high temperatures like the furnace outlet, carbon-carbon bonds are broken and free radicals of carbon which are very reactive are produced and probably react with surface species such as iron or hydrocarbons. Parker and McFarlane 69 studied the foulant of Suncor furnace tubes removed by pigging, and reported that the main components of foulant are carbon, sulfur and iron. They proposed that the iron sulfide may be produced via decomposition of oil soluble iron species at furnace temperature (350-500°C) and reaction with sulfur compounds. They also observed that going from the center of the tube to the wall, the amount of iron and sulfur increased and the carbon, hydrogen, silicon, aluminum and calcium content decreased. The presence of aluminum, calcium and silicon proved the presence of clay minerals in deposits. Fe/S ratio in the foulant was reported to be close to 1:1 which was corresponded to the pyrrhotite structure. Petrographic examination of the coke indicated that near the bulk, the coke had a porous and open structure and clay particles were entrapped.

Panchal 71 proposed that oil soluble iron salts decompose and then react with sulfur compounds present in the fluid. Gentzis et al 72 stated that the fouling layer formed at skin temperature as high as 630°C, adjacent to the furnace wall,
consisted of a continuous film of iron sulfide, while the iron sulfide observed in the bulk of the foulant material was particulates. This result shows that sulfide precursors may have a tendency to fully wet the steel surfaces and to have a strong chemical interaction with the wall. Lemke and Stephenson \textsuperscript{73} examined the composition of more than 20 foulants from 14 delayed coker and visbreakers. Loss on ignition (LOI) test (which is a test to analyze minerals consists of heating the sample strongly (igniting) and let the volatile substance escape until the mass of the sample stops changing) was used to determine the involvement of organic compounds to foulant formation. It showed that the deposits are mainly organic. 10% wt of the deposits was inorganic. Hydrogen, carbon, nitrogen and sulfur are the main elements in deposits. Fe, Mo, Ca, Na and V are the inorganic elements. The elemental analysis comparison between the feeds and foulants has been shown that the deposits have less hydrogen than the feed while the amount of carbon was nearly unchanged. The amount of sulfur in the foulant increased with increasing amounts of sulfur in the feed. It is also observed that in heater deposits, the sulfur concentration depended on the location of the deposit in the heater. The other point the authors recognized was that flocculation and precipitation of a subgroup of asphaltenes was the main contributor to coke in the deposits.

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3 EFFECT OF ASPHALTENE STABILITY ON FOULING AT DELAYED COKING PROCESS FURNACE CONDITIONS

3.1 Introduction

The delayed coking process is a favored technology for upgrading the vacuum residue fractions of petroleum and bitumen, fractions with boiling points over 524°C. The first stage of this process is to pass liquid feed through a fired furnace. In the furnace tubes, the liquid feed is heated from 350°C to circa 500°C, with a furnace tube wall temperature of approximately 550°C. Under these conditions, the interior of the tubes accumulates thermal coke material, which requires a gradual increase in furnace operating temperature with time. Energy efficiency and productivity are two major issues in any petroleum refinery, and so fouling results in significant cost penalties due to increased fuel consumption, and eventually the time for shut-down for cleaning. Most prior studies of fouling have dealt with fouling of heat exchangers at temperatures below 350°C and steam cracking furnaces operation at temperatures over 800°C. More work needs to be done on the fouling of heat transfer surfaces at intermediate temperatures, where liquid phase and reactive species are both present.

Many factors can influence fouling, including surface and bulk temperature, velocity, crude type and crude oil blending. Flocculation and precipitation of asphaltenes can lead to deposition onto the walls of heat exchangers or furnace tubes and, ultimately, to the formation of coke.
Understanding of the effect of stability of asphaltene in the feed can be a guide for strategies to mitigate fouling. Considerable research $^{11-17}$ has been conducted to the issue of solubility of asphaltenes in petroleum liquids in order to avoid conditions for precipitation, but these studies were done at low temperatures.

Wiehe and Kennedy $^{18}$ used a solubility-parameter based model to systematically investigate the blends of two crude oils, and used these results to define ranges of incompatibility and fouling. Hong and Watkinson $^{14}$ studied asphaltene precipitation and fouling from blends of Athabasca and Cold Lake heavy oil with different diluents containing from 0.6 to 25% aromatics. In their fouling tests, surface temperature was in the range of 230-310˚C. The amount of asphaltene precipitated in isothermal (85˚C) batch experiments was also determined. They showed that asphaltene precipitation and fouling were negligible when the two oils were blended with the most aromatic diluents. For the tested mixtures in the case of unstable blends, solubility parameter of the oil mixtures or more precisely the difference between the solubility parameter and flocculation solubility parameter for the mixtures $(\delta_{\text{mix}}-\delta_{\text{f}})$ was a good predictive factor for the tendency to foul heat exchangers. Asomaning and Watkinson $^{15}$ found that fouling due to asphaltenes was higher with n-alkane diluents. They proposed an instability index on the basis of crude oil composition to correlate the fouling. They concluded that higher asphaltene content in solution does not necessarily mean increase in fouling; rather it is the incompatibility which drives fouling by asphaltenes. Similarly, Van den Berg et al. $^{16}$ suggested that instability of asphaltenes in the oil mixtures drives fouling. Much of this work was driven by
observations that blends of crude oils can cause more severe fouling than crude oil on its own.

As a special case, Eaton and Lux $^{19}$ designed a fouling test apparatus to simulate a small section of a heat exchanger tube. They investigated the effect of air, bath and surface temperature, acids, resin, and asphaltene solubility on the fouling tendency. They stated that the feedstocks which contain asphaltene produced much more fouling, compared to asphaltene free feedstocks. When they mixed 5% of vacuum residue material with different ratios of a paraffinic oil and xylene, they found that asphaltene solubility has a significant effect on fouling rate. When asphaltenes were completely soluble in solution, no fouling occurred.

Many researchers $^{20-27}$ modeled the fouling phenomenon based on deposition in models for heat exchanger tubes. The most widely used model was proposed by Ebert and Panchal $^{28}$, where the rate of fouling by crude oil is as follows:

$$\frac{dR_f}{dt} = \alpha Re^\beta \exp\left(\frac{E}{RT_f}\right) - \gamma \tau_w$$  \hspace{1cm} (3.1)

Where $R_f$ is the fouling resistance, $Re$ is the Reynolds number of the fluid, $T_f$ is the film temperature and $\tau_w$ is the wall shear stress. The activation energy, $E$, and empirical parameters $\alpha$, $\beta$ and $\gamma$ are adjustable parameters. The model suggests that the fouling rate is controlled by two competing mechanisms. The first term in Equation (3.1) relates to the chemical reaction and film temperature which promote fouling, and the second term shows that tube wall shear stress or fluid velocity help in removing fouling material. At the point where these two
mechanisms are balanced, the net fouling rate is zero and no significant fouling occurs. Later this model was extended by Polley et al.\textsuperscript{29} as follows:

\[ \frac{dR_f}{dt} = \alpha R \cdot Re^{-0.8} Pr^{-0.33} \exp \left( - \frac{E}{RT_w} \right) - \gamma' Re^{0.8} \]  \hspace{1cm} (3.2)

Where $Pr$ is the Prandtl number of the fluid. For the case where the fluid properties and velocity field are constant, and the composition is variable, these models suggest that the rate of fouling will be dominated by chemical rate effects which are not explicitly defined.

In this study, our objective was to examine the effect of asphaltene stability at room temperature on subsequent fouling of stainless steel 316 at delayed coking process furnace conditions, with surface temperatures over 450°C. At lower temperatures in heat exchangers, the onset of asphaltene precipitation is the exact predictor of fouling. Our hypothesis was that the extent of fouling at high temperature would increase as the stability of the asphaltene was reduced, not just after the onset of asphaltene precipitation, and that a systematic series of blended feeds could be used to develop a quantitative relationship. The change in the coke texture as the result of change in asphaltene stability and fouling propensity was also investigated.

### 3.2 Materials and Methods

The crude oil sample used was the atmospheric bottoms fraction (nominally 400°C+) from a Midwestern U.S. refinery (provided courtesy of ConocoPhillips). The density of the crude oil was 969 kg/m\(^3\) (14.5 API). The diluent was a hydrotreated lube oil base stock with almost no aromatic, sulfur and
nitrogen content and density of 870 kg/m$^3$ (Paraflex HT100, PetroCanada Ltd, Mississauga, ON) which is recognized as a non-fouling oil based on previous studies $^{30, 31}$. Table 3.1 shows the main properties of the crude oil. The elemental analysis was done using a Carlo Erba EA 1108 elemental analyzer. The total acid number of the oil was determined using a Metrohm TIAMO 1.3 titration analyzer with KOH solution based on the ASTM D664-09a standard method. Thermogravimetric analysis (TGA) for pyrolysis residue and ash content was conducted using a Thermo Cahn TherMax 300 TGA analyzer by heating first in Ar to 500$^\circ$C, then by combustion of residual carbon in air. The former measure approximates the microcarbon residue content. The density of the oil was determined at 15 $^\circ$C using Anton Paar DMA 5000 M density meter. C$_5$ asphaltene was separated by blending oil with pentane in the ratio of 40:1 (solvent to oil), and mixing overnight. The asphaltene precipitate was recovered by filtration on a 0.22 µm filter paper. Metal content was measured using ICP-MS technique.
Table 3.1 Composition properties of the crude oil

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>N (wt %)</td>
<td>0.4</td>
</tr>
<tr>
<td>C (wt %)</td>
<td>84.3</td>
</tr>
<tr>
<td>H (wt %)</td>
<td>10.1</td>
</tr>
<tr>
<td>S (wt %)</td>
<td>3.4</td>
</tr>
<tr>
<td>C₅ asphaltene content (wt %)</td>
<td>8.5</td>
</tr>
<tr>
<td>TGA residue content (wt %)</td>
<td>6.5</td>
</tr>
<tr>
<td>Ash content (wt %)</td>
<td>0.02</td>
</tr>
<tr>
<td>Total acid number (mg KOH/g oil)</td>
<td>0.46±0.06</td>
</tr>
<tr>
<td>Fe (ppmw)</td>
<td>88</td>
</tr>
<tr>
<td>Ni (ppmw)</td>
<td>32</td>
</tr>
<tr>
<td>V (ppmw)</td>
<td>68</td>
</tr>
</tbody>
</table>

A series of blends of the crude oil with the diluent were prepared, up to 57 volume % diluent. The crude oil was heated to 70 °C, and then mixed with the diluent by shaking for 30 min. The stability of each blend was determined using a fuel stability analyzer (S-value Analyzer, DPC SA, Rofa France) based on ASTM
The oil was diluted with toluene, heated on a magnetic hot plate for boiling under reflux at 175 °C and 70 rpm for 45 minutes and then cooled mixture automatically titrated with n-heptane at the rate of 1 cm³/min. During the flocculation the light signal changes drift direction and this inflexion shows the phenomenon of flocculation we are looking for. The n-heptane volumes for each toluene diluted sample at the onset then extrapolated to determine the amount of n-heptane required for asphaltene precipitation from the oil sample without toluene.

The fouling test apparatus (Figure 3.1) is a 2L stirred pressure batch autoclave reactor (Parr Instrument Company, Moline, IL, USA) equipped with probes to measure fouling. The oil inside the vessel was heated to 250 (± 5) °C and then was kept constant based on the reading of a thermocouple in a thermowell. The autoclave had two probes, each with a wire for fouling measurements, inserted through the head of the reactor. The 316 stainless steel wires were purchased from California Fine Wire Company. The diameter of the wires was 0.2 mm. The wires were heated independently above the bath temperature by passing a constant electrical current of 5 A. The resistance of the wires was used to estimate the temperature; the resistance as a function of temperature was independently determined outside the autoclave in a tubular furnace. Based on this calibration, the temperature of the wire and rate of the heat transfer to the liquid can be calculated by knowing the wire resistance at any time.
The pressure vessel was gently mixed by a rotating cylinder within the autoclave, operating at 300 RPM. Before each experiment the probes were cleaned with methanol, xylene and acetone. The test mixture was kept in an air-free container to avoid any possible oxidation reactions. The sample was added to the autoclave and the reactor was purged with nitrogen for about 10 minutes and pressurized to 8.84 atm. Each fouling experiment had a duration of 4.2 hours. After the reactor had cooled, the probes were removed from the reactor and wires were rinsed with xylene in a Vortexer for about 30 seconds, and then with acetone and isopropyl alcohol, then dried with a jet of compressed air.

The fouled wires were mounted in epoxy resin to examine the cross section of the foulant layer and its thickness. For this purpose the wires were cut in the middle and were held with small clips vertically and put in small plastic cups. The epoxy resin was mixed with a fine nickel powder (purchased from Buehler
Canada) at a mass ratio of 1 to 1 to make the sample conductive for SEM imaging. The SEM used was a Hitachi S-2700 equipped with a PGT (Princeton Gamma-Tech) IMIX digital imaging system and PGT PRISM IG (Intrinsic Germanium) detector for EDX analysis. After hardening, the sample was ground with silicon carbide papers from 320 to 4000 grit. For optical microscopy, small flakes of foulant layer which covers the fouled wire were broken and mounted in epoxy, but without nickel powder. The samples were examined under cross-polarized filters to detect mesophase (Zeiss Axio observer.D1m polarized light microscope).

3.3 Results and discussion

3.3.1 Stability of oil blends

The S-value standard test method (ASTM D7157-05) quantifies asphaltene stability in terms of three parameters; $S$, $S_\theta$ and $S_a$. $S$ is the state of peptization of the asphaltene which is defined as $S=1+X_{\text{min}}$, where $X_{\text{min}}$ is the minimum volume (in mL) of paraffinic solvent (n-heptane in this case) that must be added to 1 gram of oil to cause flocculation of asphaltene. $S_\theta$ indicates the intrinsic stability of the oil phase, and $S_a$ is the solvency requirements of the peptized asphaltene, where $S_a=1-S_\theta/S$. The most common empirical thermodynamic approach to describe asphaltene stability is the solubility parameter. The concept of solubility parameter was developed by Scatchard and Hildebrand \textsuperscript{34} for regular solutions, and defined as the square root of cohesive energy density. In apolar solvents, solubility of a solute is maximal when the
solubility parameter of the solute is equal to that of the solvent. The measured $S$-value parameters were converted into solubility parameter using these two equations:

$$\delta_{oil} = S_o (\delta_T - \delta_H) + \delta_H$$  \hspace{1cm} (3.3)

$$\delta_f = (1 - S_a) (\delta_T - \delta_H) + \delta_H$$  \hspace{1cm} (3.4)

where $\delta_T$ and $\delta_H$ are equal to 18.23 MPa$^{1/2}$ and 15.3 MPa$^{1/2}$ respectively. The data of Figure 3.2 show the solubility parameter and flocculation onset point solubility parameter of blends of the crude oil with the diluent. As expected, the data show that adding more diluent reduces the difference between the solubility parameter of the liquid phase and the solubility parameter for the onset of flocculation. The blend with the highest ratio of diluent ($v_{diluent} = 57\%$) was at the flocculation point where the asphaltenes begin to precipitate.
Figure 3.2 Solubility parameters and flocculation solubility parameters for crude oil when it is diluted with diluent in different ratios. Dashed line shows the linear regression for solubility parameter of oil blends. The solid horizontal line ($\delta=16.1$ MPa$^{1/2}$) shows the flocculation solubility parameter of the oil.

The solubility parameter of the diluent cannot be determined directly with the S-value method, therefore Equation (3.5) which determines the solubility parameter of the crude oil-diluent blend by the sum of the component parameters is utilized:

$$\delta_{mix} = \sum_{i=1}^{n} v_i \delta_i$$  \hspace{1cm} (3.5)

In the above equation $v_i$ is the volume fraction and $\delta_i$ is the solubility parameter of each component of the blends. The solubility parameter of the crude oil is equal to
17.7 MPa$^{1/2}$ and from Equation (3.5) the solubility parameter of the diluent is equal to 14.7 MPa$^{1/2}$.

### 3.3.2 Temperature and fouling factor comparison for oil blends

The data of Figure 3.3 show the wire temperature as a function of time during the fouling experiment with each blend. The mean initial temperature was 550 °C with a standard deviation of 31°C for this series of experiments. The current was constant at 5 A in every case, with the same length of wire in the same environment, therefore, the variability was due to the calibration of temperature versus resistance for the different wires. The temperature at the end of the experiments ranges from 669 °C to 885 °C from the base oil case to the case in which the volume fraction of diluent in the bath oil was 0.57. The temperature of the wires was observed to increase with time in all cases. The change of temperature from during the 4.2 h experiments increased from 167 to 330 °C for volume fraction of diluents from 0 to 0.57. The data of Figure 3.3 also show the standard error for repeated experiments, each with two probes in these five cases, at a given time for comparison (7991 s). The standard error ranged from 12 to 29°C.
Figure 3.3 Wire temperature versus time during fouling experiment with different blends. The legend numbers show the volume fraction of the diluent. The error bars show the standard error of temperature from repeated experiments with two probes (n=4) at t=7991 s

The fouling factor, due to the resistance of the coke layer on the surface of the wires, was determined as follows:\textsuperscript{35}:

\[ FF = \frac{1}{U_f} - \frac{1}{U_c} \tag{3.6} \]

Where \( U_f \) is the overall heat transfer coefficient of the fouled wire at time \( t \), and \( U_c \) is the overall heat transfer coefficient of the clean wire, i.e. at \( t=0 \). If we
assume that heat transfer area remains constant, then the heat transfer coefficients can be expressed in terms of the heat transferred and the temperature difference,

\[
FF = A\left[\frac{(\text{T}_\text{wire,f} - \text{T}_\text{bath})}{Q_f} - \frac{(\text{T}_\text{wire,c} - \text{T}_\text{bath})}{Q_c}\right]
\]  

(3.7)

where \(Q_c\) is the heat transferred from the clean wire at time \(t=0\) (\(Q_c=IV(t=0)\)) and \(Q_f\) is the heat transferred from the fouled wire at time \(t\) (\(Q_f=IV(t)\)). During the constant current tests, the voltage on the stainless steel wires for the unstable blend case as an example, changes from 9.3 to 9.9 V.

When the fouling was more severe, the heat transfer area changed with time due to the deposition of coke. For this reason Equation (3.7) cannot be used for the entire duration of the experiment. Consequently, we divided the calculation of the fouling factor into two parts; one for initial times and the other one for the end of the experiments. We assumed that the cross section of the fouled wire was constant during the first 1000 second of heating. Figure 3.4 shows the fouling factor calculated using Equation (3.7) for different volume fractions of diluents in short times. The figure illustrates the increasing of fouling factor due to the increasing diluent volume, giving less and less stable asphaltenes. The data for each ratio are the mean calculated from replicate experiments with two probes. As mentioned earlier, the diluent oil used in this study gave no fouling in previous experiments \(^{30, 31}\); therefore the increase in fouling with the amount of diluents was due only to the crude oil components. In case of 0.27 one of the probes showed strange trend and was deleted from mean
calculation. For the remained three probes, the mean of first 400 was slightly above the usual trend but after 400 seconds it came back to the normal.

Figure 3.4 Fouling factor comparison for different oil blends during first 1000 seconds. The legend indicates the volume fraction of diluents. We assume that cross section area of the wire remains constant during the initial period. The means calculated from replicate experiments with two probes (n=4)

At the end of each experiment, the actual measured diameter of the fouled wire was used to calculate the actual fouling factor. The lower graph in Figure 3.5 shows the trend of the end point fouling factor with volume fraction of diluent. The end point fouling factor and diluent volume fraction gave a linear relationship, with FF=11.4v+0.34.
Figure 3.5 Initial and final fouling factor as a function of diluent volume fraction. The upper graph shows the slope of fouling factor at time=0 and the lower graph show the fouling factor at the end of the experiments versus the volume fraction of diluent. The error bars shows the standard error from replicate experiments with two probes (n=4).
The upper graph of Figure 3.5 shows the slope of fouling factors at \( t=0 \), also showing a relatively linear relationship between fouling factor and diluents volume fraction. These results confirm that even at these high temperatures that are hundreds of degrees above the conditions used to measure S-value, the asphaltene stability is an important factor in fouling propensity of a crude oil blend.

### 3.3.3 Structure and thickness of foulant for different blends

Stephenson et al.\(^{33}\) suggested a mechanism for fouling process on stainless steel 316 and pure iron at the temperature range of the present study. They proposed a synergy between fouling and corrosion in which iron from the wire reacts with the sulfur from the oil (likely as \( \text{H}_2\text{S} \)) to form an iron sulfide layer with the pyrrhotite \( \text{Fe}_{(1-x)}\text{S} \) structure. The coke layer then forms on top of the iron sulfide layer. In the case of stainless steel 316, a highly adherent chromia layer was observed on the wire which protected the underlying steel wire from more corrosion reactions. Figure 3.6 shows the SEM micrographs of the stainless steel 316 wires fouled in different ratios of crude oil and the diluent after 4.2 hours of experiment. A fouled wire which was immersed in the bath oil with the volume fraction of diluent equal to 0.23 during the experiment, selected to show the iron sulfide, coke, wire and nickel-epoxy on cross section of the fouled wires after mounting in nickel-epoxy and grinding (Figure 3.6a). The iron sulfide is observed close to the surface of the wire and projects domains radially into the foulant layer. The coke is the thick dark brittle layer formed on top of iron sulfide. The rest of the surrounding medium is nickel-epoxy.
Figure 3.6 SEM micrographs of SS-316 fouled wire cross section after 4.2 fouling experiment at 5A constant current when the volume fraction of diluent in the bath oil was (a) 0.23 (b) 0.57.
For the fouled wires the coke thickness was increased with an increase in the volume fraction of diluent. Figure 3.6b shows the cross section of the fouled wire for the unstable case which had the largest coke thickness. The cross-section images suggested that the iron sulfide layer may have increased with increasing diluent volume fraction, presumably because of more H$_2$S formation. To confirm this statement, elemental analysis of the foulants in different volume fractions of diluent was conducted. Table 3.2 lists the results. However, to conclude on iron sulfide increase or decrease, absolute weight of deposit is required. As Stephenson $^{33}$ proposed, the wire itself reacts in corrosion reactions; therefore the mass of foulant cannot simply be calculated by subtraction of end and beginning mass of the fouled and clean wire. For this reason, the foulant was removed from each wire and weighed, to give the total mass. The results in Table 3.3 which show the approximate absolute weight of iron per area of the wire indicate that the amount of iron sulfide increased with decreasing in stability. As a special example, base oil foulant and unstable blend was compared. In the base oil case, the thin foulant layer contains a high concentration of iron sulfide, with approximately 100-78.1 = 21.9 wt% iron. In contrast, the thick deposit at $v_{diluent} = 0.57$ is dominated by carbon-rich coke material, giving a much lower weight percent of iron. However, the total mass shows that the absolute iron sulfide increased significantly comparing to base oil case. The hydrogen to carbon ratio for the unstable case ($v_{diluent} = 0.57$) is lower than in the base oil case, due to the exposure to higher temperatures which would drive evolution of light ends and loss of hydrogen.
Table 3.2 Elemental analysis of foulant (wt %)

<table>
<thead>
<tr>
<th>Element</th>
<th>$v_{\text{diluent}}=0$</th>
<th>$v_{\text{diluent}}=0.23$</th>
<th>$v_{\text{diluent}}=0.27$</th>
<th>$v_{\text{diluent}}=0.41$</th>
<th>$v_{\text{diluent}}=0.57$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base crude oil (wt %)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrogen</td>
<td>1.3</td>
<td>1.4</td>
<td>1.31</td>
<td>1.6</td>
<td>1.8</td>
</tr>
<tr>
<td>Carbon</td>
<td>61.4</td>
<td>62.7</td>
<td>54.6</td>
<td>69.2</td>
<td>83.4</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>1.7</td>
<td>1.8</td>
<td>1.8</td>
<td>2.0</td>
<td>2.2</td>
</tr>
<tr>
<td>Sulfur</td>
<td>13.7</td>
<td>14.0</td>
<td>15.5</td>
<td>11.3</td>
<td>8.1</td>
</tr>
<tr>
<td>Total</td>
<td>78.1</td>
<td>79.9</td>
<td>73.2</td>
<td>84.1</td>
<td>95.5</td>
</tr>
</tbody>
</table>

Table 3.3 Approximate iron content in foulant iron sulfide

<table>
<thead>
<tr>
<th>$v_{\text{diluent}}$</th>
<th>Fe[wt%]$^{1}$</th>
<th>Mass of foulant per area of wire (g/m$^2$)</th>
<th>Mass of iron per area of wire (g/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>21.9</td>
<td>9.0</td>
<td>2.0</td>
</tr>
<tr>
<td>0.23</td>
<td>20.1</td>
<td>29.0</td>
<td>5.8</td>
</tr>
<tr>
<td>0.27</td>
<td>26.8</td>
<td>28.8</td>
<td>7.7</td>
</tr>
<tr>
<td>0.41</td>
<td>15.9</td>
<td>60.5</td>
<td>9.6</td>
</tr>
<tr>
<td>0.57</td>
<td>4.5</td>
<td>520.3</td>
<td>23.4</td>
</tr>
</tbody>
</table>

1- Calculated from Table 3.2 as 100-sum of elemental masses

Figure 3.7 shows the plan view of the coke texture for three selected fouled wires after 4.2 hours of experiment. As the ratio of the diluent increases,
the outer layer of the foulant becomes more and more porous. This porosity can be explained by the gas evolution from corrosion of the wire surface and by evolution of vapor-phase components from the prolonged heating and reaction of the coke layer. The coke formation was consistent with condensation and polymerization reactions in a new phase that formed by asphaltene deposition on the wire\textsuperscript{36}. The concentration of the asphaltenes was actually lower in the blends than the crude oil itself, since this component was not present in the diluents; therefore, the reduction in the stability of the asphaltenes is much more important than their concentration.

(a)
Figure 3.7 SEM micrographs of SS-316 fouled wire (plan view) after 4.2 h fouling experiment at constant 5A current when the volume fraction of diluent in the bath oil was (a) 0, (b) 0.41 and (c) 0.57
Since coke formation may or may not require the unique ordered structure of mesophase materials the coke flakes were examined under the cross-polarized light in the base oil case (no diluent added) the most unstable case \( (v_{\text{diluent}} = 0.57) \) to determine whether mesophase was formed. The carbonaceous mesophase is a liquid crystalline coke phase which appears as bright domains under crossed polarized light, whereas amorphous or isotropic material is dark. During the cracking of oil, thermal decomposition and polymerization reactions lead to the formation of polycondensed aromatic hydrocarbons. The mesophase spherule is formed by the accumulation of these oriented polycondensed aromatic hydrocarbons in layers. Figure 3.8 shows the bright mesophase in these two cases. In the left figure there is definitely some mesophase in the sample, but clearly the fraction of the total area is quite small. In the right figure for the unstable case, the bright domains are much more extensive and more developed. The likely reason is the temperature that the foulant experienced in the two cases. The time of the experiment is the same for both, but the temperature difference from the beginning to the end for the unstable case (330 \(^{\circ}\)C) is much more than base oil case (167 \(^{\circ}\)C). As the temperature increased with time, the size of mesophase spherules would gradually increase, driven by the higher temperatures in the thick foulant layer with \( v_{\text{diluent}} = 0.57 \).
Figure 3.8 (left) polished section of flakes of foulant in base oil case ($v_{\text{diluent}} = 0$) under polarized light $^{34}$; the bright mesophase can be observed inside the red circles. (Right) polished flakes in unstable blend case ($v_{\text{diluent}} = 0.57$); all the bright sections show mesophase.

The final texture of a coke material can be influenced by many factors such as temperature of deposition, gas pressure, H: C ratio of the feed and geometry of the substrate $^{38}$. As the figures illustrate, the coke thickness is increased by increasing the volume fraction of diluent. In the case of the unstable blend the coke thickness was largest, the porous texture was most pronounced, and mesophase content was significant. Parker and McFarlane $^{39}$, in an investigation on foulant of furnace tubes removed by pigging, stated that the hydrogen to carbon ratio of the coke nearest the wall was less than the loose carbonaceous material nearer to the bulk fluid. The change in coke texture from the wall to the bulk was likely due to both temperature gradients from the wall to the bulk and the aging of the older deposits near the wall to forming a more
structured material. From the cross sectional pictures, especially in the unstable case in Figure 3.6b, the porous structure is more evident near the bulk of the fluid and denser material is observed near the wire surface.

3.3.4 Fouling, stability (solubility) and coke thickness relation

The micrographs show in Figures 3.6 help to determine quantitatively the coke thickness (more precisely the foulant thickness).

Figure 3.9 End point coke thickness when the fouling oil is diluted with different ratios of diluents, after 4.2 h of deposition. The error bars show the standard error from repeated experiments for two probes (n=4).
Since the wires do not foul evenly, the cross sections are not perfect circles. By averaging the thickness in several places, the average coke thickness for each case was determined. Figure 3.9 shows the end point average coke thickness (µm) of the fouled wires in terms of the volume fraction of diluent. The figure shows that as the volume fraction of diluent increases the coke thickness increases monotonically.

In the present study at high temperatures, a measurable amount of fouling occurred in all cases over the course of a four-hour experiment, and there was a correlation between the solubility parameter and the rate of fouling prior to the onset of instability. As mentioned earlier Wiehe\textsuperscript{10} suggested that if compatible oils are mixed together, and the order and proportions of blending chosen carefully then there should be no significant fouling. Similarly, Stark and Asomaning\textsuperscript{40} stated that if the oil blend is compatible then the blend has minimal fouling potential. Hong and Watkinson\textsuperscript{14} gave the same advice, but they observed some precipitation of asphaltenes and fouling even when the mixtures were stable. They suggested that such fouling was due to the non-asphaltene solids such as clay in the oil. These approaches to fouling, largely based on lower-temperature conditions, are inconsistent with our data for behavior at the thermal cracking conditions of a furnace for delayed coking. The data of Figures 3.5 and 3.9 indicate that the onset of asphaltene precipitation was not the only point where significant fouling occurred. The fouling started in the base oil case and as the stability of the blends decreased the fouling progressively became worse; i.e. a linear dependence of fouling and $\delta_{\text{mix}}-\delta_f$ can be seen. Under these more extreme
conditions of surface temperature, there is no threshold, and the mitigation strategies Wiehe proposed are less effective.

The end point coke thickness enabled us to calculate the actual fouling factor for the end of the experiments. Figure 3.10 shows this endpoint fouling factor in terms of coke thickness. The figure shows that the actual end point fouling factor and the average coke thickness have a roughly linear relationship.

Figure 3.10 Relationship between fouling factor and coke thickness when the fouling oil was diluted with different ratios of diluent. The error bars in the x and y directions shows the coke thickness of the fouled wires and the end point fouling factor standard error from repeated experiments for two probes (n=4) successively.
The models for fouling based on Ebert and Panchal in Equations (3.1) and (3.2) are inadequate for the present case because they include only fluid mechanic and reaction terms, making no allowance for the role of asphaltene stability. Modeling of thermal fouling resistance (fouling factor) can be considered at short times when the heat transfer area is known. We know that the following differential relationship will apply:

$$dR_f = \frac{dx}{k_f} = \frac{dm}{\rho_f k_f}$$

(3.8)

Where $R_f$ is thermal fouling resistance (fouling factor), $m$ is the mass of deposit per unit heat transfer surface, $x$ is the deposit thickness, $k_f$ deposit thermal conductivity and $\rho_f$ is the deposit density. The density of the coke which is used in Equation (3.8) is hard to determine, because the coke is porous and the porosity changes from case to case. Even for the base oil, where the foulant has the least porosity, a high concentration of iron sulfide gives a large error in the determination of coke density. The current experiments show coupling of corrosion and coke formation, which makes providing a good model for the transport phenomena and thermal fouling impossible.

### 3.4 Conclusions

The results show that the stability of asphaltene in the oil blends which was determined using S-value method plays an important and completely relevant role in the fouling of stainless steel wires fouled in furnace tubes conditions. As
the stability decreases the fouling factor which shows the resistance of the foulant, increases. As the fouling factor increase the thickness of the coke also increases linearly. The coke texture changes from base oil case to the unstable case, becoming more porous when the stability of the blends reduced. Mesophase coke is present in the foulant structure, but very little is visible in base oil case compared to the considerable amount in the unstable blend.

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4 POLYSULFIDE ACCELERATED CORROSION–FOULING OF HEATED STAINLESS STEEL SUBMERGED IN CRUDE OIL

4.1 Introduction

Heated metal surfaces employed in high-temperature refinery units, such as process furnaces, tend to accumulate thick thermally insulating foulant layers largely composed of metallic sulfides and carbonaceous coke. Such fouling is a major industrial problem that results in hundreds of millions of dollars in additional operating costs. Deposits accumulate on the interior of the furnace tubes, requiring a gradual increase in furnace temperature and thus fuel consumption to run the unit, causing a concomitant increase in greenhouse gas emissions and cost. Such fouling is experienced in several related industrial processes, where the buildup of a thick thermally insulating buildup occurs progressively degrading thermal efficiency.

High-rate “catastrophic” fouling brought on by large-scale asphaltene flocculation in incompatible oil mixtures, nearly incompatible oil mixtures, and self-incompatible oils have been discussed in literature by Wiehe and coworkers. The asphaltene is a well-known potential cause of foulant build up, though its true role is still under extensive debate. In regards to low rate steady state or “chronic” fouling, progressively more evidence points to a corrosion mechanisms that may both initiate the fouling reaction and occur in parallel to provide a
synergistic effect. For the case of crude oil fouling in the temperature range of 350–500°C it has been observed that the amount of iron and sulfur within the foulant layer increased significantly with the proximity to the furnace walls. Falkler and Stark proposed that this enrichment may be caused by the trapping of solid particles from oil in a viscous layer on the furnace tubes, resulting in the accumulation of inorganic material over time. The iron sulfide may be introduced through pre-existing sulfide impurities or corrosion products in the oil that were carried from upstream operations and deposited onto the heat transfer surfaces.

An alternate source for iron sulfides is the metal of the heat transfer surface itself. Eaton and Williams proposed a fouling scenario based on a two-stage coking process: First the coke forms on a metal surface, subsequently becoming either oxidized, sulfided or inhibited. Eaton and coworkers previously demonstrated that hydrochloric acid and subsequent application of neutralizers determine the formation of iron sulfide with consequent fouling, and that fouling decreases with increasing Cr content of the metal. Other authors proposed that fouling is accompanied by corrosion of the metal surface in the presence of naphthenic acid and hydrogen sulfide. Iron sulfide deposition has been shown to be an integral part of fouling in sour Canadian crudes in the surface skin temperature range of 300–380°C. At low temperatures (100°C) fouling of hydrotreater feed filters is known to be accelerated by the corrosion reaction between naphthenic acid and the steel piping. A comprehensive review on fouling concluded that while the influence of oil composition is relatively well
characterized, much less is known regarding the actual mechanisms that lead to the fouling deposits. Stephenson et al. recently conclusively demonstrated that fouling by liquid crude oil at high surface temperatures, in excess of 500°C is in fact a corrosion-catalyzed process. The authors demonstrated the role of H₂S-based corrosion in catalyzing fouling reactions in stainless steel, nickel-based alloys, and in iron. In particular, there was a synergy between the measured macroscopic fouling and the underlying microscopic corrosion, where the iron from the wire migrated and reacted with the sulfur in the oil to build up a thick sulfide layer.

At temperatures over 350°C, hydrogen sulfide forms from the thermal reactions of the aliphatic sulfur compounds in heavy crude oil fractions. In contrast, the majority of the sulfur in the crude oil is in the thermally stable thiophene form. In order to study the coupling between sulfur species, fouling and corrosion, one approach is to add selected sulfur species to a crude oil. Hydrogen sulfide could be added directly to the reactor headspace, but this approach requires specialized facilities for safe handling of the gas mixtures. Aliphatic sulfides are available, but their molecular weight is too low to remain in the liquid phase at high temperature. Polysulfide compounds with the general formula of R-Sₓ-R are used commercially for cross-linking or vulcanizing rubber, and as sulfiding agents in some corrosion and fouling applications. Polysulfides begin to decompose at temperatures over 150°C, depending on the structure. The products of decomposition include elemental sulfur and reactive sulfur fragments that can react with alkenes from thermals cracking reactions. Further
reaction will generate hydrogen sulfide gas in situ, in the vicinity of the heated metal surfaces. Our hypothesis in this study is that the addition of reactive polysulfide will give rise to an increase in corrosion-fouling due to the generation of hydrogen sulfide gas.

4.2 Experimental procedure

The crude oil sample used was the atmospheric bottoms fraction (nominally 400°C+) from a Midwestern U.S. refinery (provided courtesy of ConocoPhillips) containing 0.4 wt% nitrogen and 3.4 wt% sulfur. The asphaltene content of the oil was 8.5 wt%, the MCR content was 6.5 wt%, the ash content was 0.02 wt%. Three organic polysulfide additives were provided by Champion Technologies, Texas, USA. Additive A contained polysulfide with short alkyl chains, while additives B and C had C₈ terminal groups (C₈H₁₇-Sₓ-C₈H₁₇).

The CHNS analysis of the three organic polysulfides was done using a Carlo Erba EA 1108 elemental analyzer. The simulated distillation (SimDis.) analyzer was a Varian 450-GC gas chromatograph according to method ASTM D5307. The column had inside diameter of 0.53 mm, outside diameter of 0.8 mm, and a film thickness of 0.09 μm with a maximum allowable operating temperature of 450°C (Capillary column WCOT Ultimetal with Reference number of CP7569, Agilent Technologies, New Castle, De, USA). The temperature profile consisted of an isothermal stage of 1 min at 35 °C followed by ramping up to 400 at 20 °C/min with a total heating time of 45 min. Samples of additives were injected as 1% by weight solutions in carbon disulfide (CS₂). Additives were also analyzed.
by a Thermo Scientific Trace GC Ultra gas chromatography–flame ionization detector (GC–FID), with identification of the corresponding peaks achieved by using a DSQII mass spectrometer (both from Thermo Electron Corporation, Waltham, MA). The GC oven is typically set at 100 °C for 1 min followed by a continuous ramping at 10 °C/min to a final temperature up to 300 °C. The injector inlet temperature was 200 °C. Helium was used as the carrier gas at 2 mL/min in a split mode in the GC–FID and splitless in GC-MS. The columns were TR5–MS of 15 m × 0.25 mm ID × 0.25 µm film thickness.

The fouling test apparatus is a 2L stirred pressure autoclave reactor described in Chapter 3. A concentration of 0.1 wt% (1000 ppmw or 1 g/kg) of each additive separately added to the oil inside the vessel, mixed and heated to 250 (± 5) °C. The SEM instrument used was a Hitachi S-3000N with an Oxford INCA EDX system.

4.3 Results

4.3.1 Characterization of polysulfide additives

Because commercial polysulfides are mixtures of polysulfides of different molar masses in a mineral oil solution, the additives were characterized by chemical analysis. Table 4.1 shows the CHNS elemental analysis of the three additive mixtures named A, B and C.
Table 4.1 Elemental analysis of polysulfide mixtures

<table>
<thead>
<tr>
<th>Additive</th>
<th>N[wt %]</th>
<th>C[wt %]</th>
<th>H[wt %]</th>
<th>S[wt %]</th>
<th>Sum</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.5</td>
<td>72.1</td>
<td>11.0</td>
<td>10.5</td>
<td>94.1</td>
</tr>
<tr>
<td>B</td>
<td>0.7</td>
<td>53.7</td>
<td>9.0</td>
<td>37.1</td>
<td>100.5</td>
</tr>
<tr>
<td>C</td>
<td>1.3</td>
<td>52.3</td>
<td>8.8</td>
<td>36.7</td>
<td>99.1</td>
</tr>
</tbody>
</table>

To confirm the approximate structure of the additives, GC-MS and simulated distillation measurements were conducted. Figure 4.1 shows the results of simulated distillation analysis. Since the mineral oil in additive A is too high-boiling for GC-MS measurement, only additive B and C were analyzed. Figure 4.2 shows the GC-MS results. The GC-MS results gave two major peaks for both B and C, the first with a mass spectrum consistent with elemental sulfur (the cyclic octaatomic allotrope of sulfur (S₈)) and the second with bis (1, 1, 3, 3-tetramethylbutyl) disulfide, with the formula of C₁₆H₃₄S₂, based on the NIST library. These results are consistent with decomposition of the polysulfides to disulfides and elemental sulfur in the injection port of the GC at a temperature of 200°C. Consequently, the approximate structure of additives B and C is C₈H₁₇-Sₓ-C₈H₁₇. The data of Table 4.1 show the simulated distillation results for the additives, which detected polysulfides and their fragments, and the mineral oils or non-sulfur components that are used as a carrier liquid. Samples B and C contained relatively light carrier oils, with end points of 390°C (C24) and 440°C (C28), respectively. Sample A showed an end point of 730°C (>C62), indicating a much higher boiling mixture.
(a) Additive A
(b) Additive B
Figure 4.1 Simulated distillation measurements for Additive A, B and C

Table 4.2 Chemical composition of polysulfide mixtures

<table>
<thead>
<tr>
<th>Additive</th>
<th>Mineral oil [wt %]</th>
<th>Maximum Elution T [°C]</th>
<th>Average Chemical Formula</th>
<th>Mean mol of S per mol of polysulfide</th>
<th>Mol of C/Mole of S</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>18.9</td>
<td>730</td>
<td>N/A</td>
<td>N/A</td>
<td>14.0</td>
</tr>
<tr>
<td>B</td>
<td>11.5</td>
<td>390</td>
<td>C_{16}H_{34}S_{5}</td>
<td>5.2</td>
<td>3.2</td>
</tr>
<tr>
<td>C</td>
<td>11.4</td>
<td>440</td>
<td>C_{16}H_{34}S_{5}</td>
<td>5.2</td>
<td>3.1</td>
</tr>
</tbody>
</table>
The overall elemental analysis of additives B and C indicate that a polysulfide with 16 carbons in the terminal alkyl groups per mol must have a minimum of at least four sulfurs on average (i.e. \( x > 4 \)). The mass of mineral oil was subtracted from the total mixture, based on the simulated distillation data, to give the mass of the mixture of polysulfide compounds alone. The sulfur/carbon ratio after subtraction of the carbon in the mineral-oil indicates \( x = 5.2 \) for B and C. The mineral oil was assumed to have a chemical composition of 85.66 wt% carbon, 13.73 wt% hydrogen and zero sulfur and nitrogen as reported by Hong and Watkinson for similar materials\(^2\). Although the chemical formula for A cannot be determined, the mol ratio of C/S can be obtained using elemental analysis of mineral oil and polysulfide mixtures. This ratio is 14 for additive A and 3 for additives B and C, therefore, B and C have much more sulfur in one mole of polysulfide than A. The commercial polysulfides often contain 4-6 sulfur atoms per mol on average (i.e. \( x = 4-6 \)), consistent with the above estimate\(^{26}\). Based on the literature information and our estimates, polysulfides B and C should have in the range of 3-9 sulfur atoms per mol and an average value of 5.2.
(a) Full scan GC-MS result for Additive B
4.3.2 Fouling of the wires with and without additives

The micrographs of Figure 4.3 show the cross sections of the SS316 fouled wire for the base crude oil and with the addition of each of the three polysulfides. Iron sulfide and coke are demarcated in the images. As the figure illustrates the coke thickness for the base oil and additive A were much thinner than with the other two additives. Table 4.3 shows the elemental analysis of the
foulant of base oil and with the 0.1 wt % polysulfide addition. As the iron and sulfur wt% shows, for additives B and C the amount of iron and sulfur is more than A, which is the result of more iron sulfide formation.

Figure 4.3 Micrographs of cross sections of wires fouled with base oil and with additives.
To have an accurate comparison total weight of the foulants also needed. In the mechanism of iron sulfide formation on fouling under the conditions of the current work Stephenson \(^{18}\) proposed that iron from the wire reacts with \(\text{H}_2\text{S}\) of the feed to form iron sulfide, therefore, the change in the mass of wire before and after the fouling is not a direct measure of the total foulant mass. For this reason, the foulant was removed from each wire and weighed, to give the total mass. The results listed in Table 4.4. If we assume that 100-sum of elemental weight percent tabulated in Table 4.3 is mainly iron, then the results show that both more coke and iron sulfide formed when the sulfur content in the additives increased. In other words, additive B and C caused both more coke and iron sulfide formation than A. As the micrograph and elemental analysis showed, additive A can reduce the extent of fouling and can give less increase in foulant formation than B and C.

<table>
<thead>
<tr>
<th>Additive foulant</th>
<th>N [wt%]</th>
<th>C [wt%]</th>
<th>H [wt%]</th>
<th>S [wt%]</th>
<th>Sum</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>1.3</td>
<td>61.4</td>
<td>1.7</td>
<td>13.7</td>
<td>78.1</td>
</tr>
<tr>
<td>A</td>
<td>1.5</td>
<td>71.9</td>
<td>2.2</td>
<td>10.4</td>
<td>85.7</td>
</tr>
<tr>
<td>B</td>
<td>1.4</td>
<td>65.9</td>
<td>1.7</td>
<td>12.8</td>
<td>81.8</td>
</tr>
<tr>
<td>C</td>
<td>1.2</td>
<td>64.7</td>
<td>1.6</td>
<td>13.1</td>
<td>80.6</td>
</tr>
</tbody>
</table>
4.3.3 Fouling factor with additives and its relation with coke thickness

The experimental approach to fouling was to measure the change in electrical resistance in the wire as a function of time with constant current passing through the wire. This allowed us to monitor the resistance to heat transfer with time. The fouling factor (FF), which shows the increasing thermal resistance of the deposits on the surface of the wires, is determined and described in Chapter 3, as follows:

As Figure 4.3 illustrates, the cross section of the wires did not remain constant. The actual diameter of the wires plus surface deposits increased over the course of the experiment, especially with additives B and C in comparison to the base oil. Therefore, Equation (4.2) can be used rigorously only when the area for heat transfer is known, which is for short times when area is approximated by the area of the wire, and at the end of the experiment when the area of the fouled wire

\[ FF = \frac{R(t)}{R_0} \cdot 100 \]

where \( R(t) \) is the resistance at time \( t \), \( R_0 \) is the initial resistance, and \( FF \) is the fouling factor.
can be measured. Figure 4.4 shows the apparent fouling factor of the 316SS wires with the oil with and without additives A to C in the first 1000 seconds.

Figure 4.4 Fouling factor at short times with and without additives. The data points are the averages from two repeated experiments

The results show that addition of additive B and C increased the amount of fouling factor dramatically.

Knowing the actual diameter of the fouled wire in the end of each experiment, the actual end point fouling factor can be determined using Equation 3.7. Figure 4.5 shows the coke thickness and the end point fouling factor of the oil on SS316 wire with and without addition of polysulfides. As expected, the figure shows that addition of B and C increases both the coke thickness of the foulant and fouling factor comparing to base oil. In contrast, the addition of A does not
show any distinct difference in coke thickness and fouling factor in comparison to base oil. The data also show that the fouling factor was not a simple function of the thickness of the fouling layer.

![Figure 4.5 Relationship between end point fouling factor and coke thickness at the end of the experiments](image)

4.4 Discussion

In these experiments, the addition of polysulfides increased the local concentration of reactive sulfur species at the surface of the wire. In the base oil, the total sulfur concentration was 3.4%, of which on the order of 40% would be in the more reactive alkyl sulfides, or 1.3 wt% 27. Only a fraction of this material
would react at the surface of the heated wire to generate hydrogen sulfide, so that a much lower fraction would be active. Based on the elemental composition, the experiments with additives added 100 ppm (additive A) to 370 ppm (Additive B) to the reactive species already in the oil. Within the alkyl sulfur species, the thermal stability decreases with the number of sulfur atoms, from sulfides to disulfides to polysulfides. For one special case, Pickering et al. showed that trisulfide thermal decomposition is much slower than tetrasulfide. Rama Rao and Radhakrishnan reported that the dissociation energy for higher polysulfides is much lower than disulfide linkage. The dissociation energy of sulfur-sulfur bonds in various aliphatic disulfide compounds is in the order of 65 to 75 kcal/mol, while the dissociation energy of polysulfides is estimated to be about 35 kcal/mol. This energy is much less than C-S bond which is about 77 kcal/mol. From the carbon to sulfur ratio of the three additives listed in Table 4.2, for the same number of carbon in a chemical formula for three additives, additive A which has less sulfur should have shorter sulfur chain than B and C and it will be more stable thermally comparing to B and C in the bath oil.

The decomposition of dimethyl tetrasulfide proves an example for the thermal decomposition of polysulfides. Abrahams found that the central bond in a tetrasulfide is longer that the other two sulfide-sulfide bonds, and thus presumably weaker. The tetra-sulfide decomposes into a mixture of alkyl polysulfides containing 3 to 6 or more sulfurs, which suggests that, both breakage and addition reactions can occur depending on the composition of the reacting mixture. These addition reactions allow for the elimination of $S_8$ as observed in
our GC-MS analysis, regardless of the number of sulfur atoms in the starting compound. At high temperatures, thermal cracking of crude oil produces olefins, and the addition of elemental sulfur initiates free radicals and accelerates reactions\(^{38,39}\). For example, during the formation of coke from asphaltene above 350 °C, the condensation between aromatic and aliphatic moieties of asphaltenes was obviously promoted by elemental sulfur addition, which in turn converted to H\(_2\)S, and produced coke with good properties \(^{38}\). Chang et al. \(^{39}\) observed that elemental sulfur promoted the condensation reactions of asphaltene, which resulted in the formation of coke. In addition, elemental sulfur promoted the decomposition of residue which resulted in an increase in yield in the middle distillate range. Addition of small amounts of elemental sulfur to vacuum residue can abstract hydrogen from hydrocarbon molecules and form both free radicals and hydrogen sulfide. Similar to the asphaltenes, reaction of thiols in the presence of elemental sulfur gives high reactivity and crosslinking with the release of H\(_2\)S \(^{40}\).

Based on the above information, we propose a simplified mechanism for the interactions of polysulfides with the crude oil and the metal surface. The decomposition of the polysulfides will give rise to a mixture of free radical and sulfur species which we do not attempt to represent here \(^{41,42}\).

\[
\text{Reactive VR} \rightarrow \text{fragments} + \text{olefins} \quad (4.1)
\]

\[
\text{Alkyl polysulfide} + \text{olefins} \rightarrow \text{Cross-linked olefins} \quad (4.2)
\]

\[
\text{Alkyl polysulfides} \rightarrow \text{Polysulfide fragments} \quad (4.3)
\]

\[
\text{Polysulfide fragments} + \text{VR} \rightarrow \text{H}_2\text{S} + \text{reactive VR} \quad (4.4)
\]
Fe(s) + H₂S→Fe_{(1-\gamma)}S (s) +H₂  \hspace{1cm} (4.5)

The three interactions between added polysulfides and fouling processes are formation of cross-linked species, activating the vacuum residue (VR) to give reactive intermediates, and the formation of hydrogen sulfide and FeS. In the absence of polysulfide, cracking of the VR, formation of H₂S, and formation of FeS will all occur, but at a lower rate. The crude oil contained 3.4% sulfur, of which on the order of 10% could form hydrogen sulfide under very severe thermal cracking conditions \(^{43}\). By adding 0.1 wt% of polysulfide, additive A would increase this potential by at least 3%, and additives B and C would give an increase of at least 11%, assuming that all of the sulfur in the additives is reactive. At the same time, iron sulfide formation would increase with the additives due to the localized increase in the H₂S formation which was caused by addition of additives. We cannot comment on the possible role of iron sulfide in accelerating formation of the coke fouling layer, because organic-phase reactions could account for this change. Direct addition of hydrogen sulfide gas would be required to evaluate the hypothesis that formation of iron sulfide accelerates coke formation independent of other factors.

The results showed that additive A gave some inhibition relative to B and C. Polysulfides are one type of effective inhibitors to resist naphthenic acid corrosion. They also act as sulfiding agents that decompose to form sulfidic surfaces inside the surfaces of the steam crackers and reduce coke formation. They probably make a coating layer on the surface of wall and protect the metal
or alloy of the wall from more corrosion. Here, additive A may produce a protective coating layer on stainless steel surface to prevent more corrosion. Additive B and C may also create this protective layer on the wire initially but because of their higher sulfur content they produce much more hydrogen sulfide which favored corrosion comparing to A and this cause the formation of severe fouling.

4.5 Conclusions

Fouling of SS316 wire in an crude oil bath at temperatures above 450 °C with and without the presence of 0.1 wt % three polysulfide additives were examined. Additives with higher sulfur content produced more coke and iron sulfide comparing to the base oil fouling. Additive A which had less sulfur content comparing to B and C, gave less increase in foulant formation than base oil.

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5 DISPERSION OF ASPHALTENE NANOAGGREGATES AND
THE ROLE OF RAYLEIGH SCATTERING IN THE
ABSORPTION OF VISIBLE ELECTROMAGNETIC
RADIATION BY THESE NANOAGGREGATES¹

5.1 Introduction

Asphaltenes components associate with each other even at very low concentrations ¹, ⁸. The self-association of asphaltenes can be observed using various methods including vapor pressure osmometry ², ⁶, ⁹, ¹⁰, small angle X-ray and neutron scattering (SAXS and SANS) ¹¹-¹⁵, and fluorescence ⁹. All of these methods give indirect information that must be interpreted in terms of models. Because of this associative behavior, measurements of the average molar mass of asphaltene molecules are laden with uncertainty ² since the apparent molecular weight is dependent on the concentration, temperature, and the nature of the solvent ¹³, ¹⁶-¹⁹. Although the size of these colloidal structures in solution will vary with the experimental conditions, most techniques place the size somewhere in the range of 2-20 nm in toluene solution ⁵, ¹³, ¹⁵, ²⁰-²⁵. Consequently, these structures are most commonly described as “nano-aggregates” ²⁶, ²⁷. In the past, the primary force leading to asphaltene association was thought to be π-π stacking

¹ This chapter is a collaboration with Greg Dechaine and includes significant data from his thesis
in which large aromatic cores form a stack with extended aliphatic side chains protruding out from the stack. Recently Gray et al. suggested a new model for asphaltene nano-aggregation in which \( \pi-\pi \) stacking is only one of many contributing factors driving the nano-aggregation. Other associative forces such as acid-base interaction, hydrogen bonding, metal coordination, and hydrophobic pockets are likely to act simultaneously with \( \pi-\pi \) forces to drive asphaltene nano-aggregation. This model reconciles the various properties and reactions of asphaltenes better than \( \pi-\pi \) stacking alone. When the asphaltenes become unstable in solution, the nano-aggregates undergo coagulation or flocculation to form macroscopic solids which then precipitate from solution. For convenience, we will refer to this precipitated material with length scales of over 1 micron as precipitate. This length scale corresponds to detection by optical methods such as microscopy. Several different ideas have been proposed for the physical state of asphaltene precipitates, including flocculated colloidal particles, and coagulated material below its glass transition temperature. Modeling of the precipitation process has commonly treated the asphaltene precipitate as a liquid phase.

The effects of temperature, pressure, concentration, and solvent on the nano-aggregation of asphaltenes in solution have been investigated extensively. An increase in temperature results in a continuous decrease in the degree of nano-aggregation for a wide range of asphaltenes and solvents. The disaggregation starts at ambient temperatures and extends to temperatures on the order of 290 °C. At elevated temperatures in excess of 350°C, thermal cracking reactions emerge and analysis of disaggregation beyond this point is no longer
feasible. Espinat et al. 39 suggested the existence of a range of interactions between nano-aggregates such that the weakest interactions break at low temperatures and the strongest persist to high temperatures. Although elevated temperatures are shown to decrease the nano-aggregate size, the complete dissociation of asphaltene nano-aggregates cannot be achieved even at the highest possible temperatures 39. Concentration also has strong effect on nano-aggregate size. Dilute mixtures of asphaltenes in toluene, for instance, have much smaller nano-aggregates compared to more concentrated mixtures 40. The apparent average molar mass of asphaltenes was found to increase with asphaltene concentration up to a plateau at concentrations between 10-20 kg/m^3 6, 7. This limiting value decreases as the polarity of the solvent and the temperature increase. According to Yarranton et al. 6 this limiting apparent molar mass is higher for C_7-asphaltenes compared to C_5-asphaltenes, due to changes in the distribution of sizes of nano-aggregates with different components in the heavy oil solution. Espinat el al. 41 found that the average molecular weight of asphaltenes is much larger in benzene than in pyridine. On the effect of pressure, they reported elsewhere 39 that even for very different temperature ranges a variation of 100 bar had a minor effect on asphaltene nano-aggregation in toluene.

One method for controlling the precipitation of asphaltenes is the addition of dispersants capable of stabilizing the colloidal suspension of asphaltene nano-aggregates. Such chemical additives generally adsorb on the surface of nano-aggregates and prevent the formation of precipitate 42. These dispersants can also lead to a larger proportion of asphaltene nano-aggregates of smaller sizes 43. Some
polar components in crude oils can perform the same function. Amphiphiles are frequently used to suppress asphaltene precipitation, and asphaltenes themselves are surface active amphiphiles. This surface activity could be due to both nano-aggregates and the molecular species. The activity of the amphiphiles is related to the maximum amount of amphiphile adsorbed on the asphaltene surface. The strength of the asphaltene-amphiphile interactions plays an important role in asphaltene stabilization in the crude oil. Studies on the asphaltene stabilization in aliphatic solvents showed that the effectiveness of the amphiphiles is influenced by their polar head groups which interact with the polar group of asphaltenes, the length of the alkyl tail on the amphiphiles which promotes a steric-stabilization layer, and other interactions such as hydrogen bonding and acid base interactions. Chang and Fogler used different alkyl-benzene-derived amphiphiles, while Wiehe used a sulfonic acid group as the polar head attached to a two ring aromatic structure and a branched tail of at least 30 carbons. n-Alkylbenzenesulfonic acid, naphthenic acids, fatty alcohols, and fatty amines have been reported to be good dispersant options. Manek and Sawhney used alkylsubstituted phenol-polyethylene-polyamine-formaldehyde resins as asphaltene dispersants. Miller and co-workers utilized ethercarboxylic acids, mixtures of alkylphenol-formaldehyde resins with oxalkylated amines, and mixtures of phosphoric ester with carboxylic acids as asphaltene dispersants. Nonylphenol has also been reported as a good dispersant of asphaltenes in n-heptane. All of these components can disperse asphaltenes to prevent
precipitation, but their ability to suppress the molecular association to form nano-aggregates has not been evaluated.

The main objectives of the work in this chapter is to attempt to disaggregate the asphaltene nano-aggregates at room temperature using different combinations of additives, solvents, ultrasound, and heat. The solutions of a sample of whole crude oil and a sample of precipitated asphaltene as an asphaltene rich source were used. The combination of these two samples allowed to investigate the interactions of crude oil medium such as resin with asphaltene nano-aggregate in the presence of the treating effect and its comparison with asphaltene rich samples that does not have this surrounding medium. The ability of the dispersants to suppress precipitation was confirmed by analyzing the S-value of selected samples. The success in achieving this goal was evaluated by Rayleigh scattering of visible radiation and by acoustic measurements of particle size.

5.2 Experimental procedure

5.2.1 Materials

Spectraanalyzed HPLC grade toluene was used as received from Fisher Scientific. Spectrophotometric grade Pyridine (99.0% purity) was used as received from Acros organics and quinoline was used as received (≥97% purity) from Sigma-Aldrich. The chemicals used as dispersants were C_{14}C_{16}dimethyl naphthalene sulfonic acid from Oil Chem. Technologies, Inc. (labeled as #1), dinonylnaphthalene sulfonic acid (CAS #25322-17-21) with ethylene glycol butyl
ether solvent (CAS #111-76-2) from King Industries, Inc. (labeled as #2), alkylaromatic sulfonic acid (CAS # is a trade secret) with aromatic hydrocarbon (CAS #64742-94-5) form King Industries, Inc. (labeled as #3), nonyl phenyl 4 mole ethoxylate (IGE PAL Co-430, #7322771) from Stepan Canada Inc. (labeled as #4), and nonylphenol supplied from Sigma-Aldrich (labeled as #5). The ionic liquids used were 1-butyl-3-methylimidazolium tetrafluoroborate (BMIMBF4, labeled as IL1), 1-Butyl-3-methylimidazolium hexafluorophosphate (BMIM-PF6, labeled as IL2), and 1-Butyl-3-methylimidazolium hydrogen sulfate (BMIM-HSO4, labeled as IL3), all supplied by Sigma-Aldrich.

The crude oil sample used was the atmospheric bottoms fraction (nominally 400 °C+) from a Midwestern U.S. refinery (provided courtesy of ConocoPhillips). The asphaltenes used in this study were precipitated from an Athabasca bitumen produced by steam-assisted gravity drainage using n-pentane in an industrial pilot plant. This material had low concentration of mineral solids and is labeled as C5 industrial asphaltenes. The other asphaltene samples used were the same as those used in the membrane diffusion studies of Dechaine and Gray23 and as such the details will not be reiterated herein. All of those asphaltene samples are n-heptane insoluble asphaltenes.

5.2.2 Heating experiments

To investigate the effect of heat on the nano-aggregation, small tubular stainless steel batch reactors with an internal volume of 15 mL, referred to as
microreactors, were used. These microreactors were loaded to ≈1/2 of their volume with sample. This reactor consists of a 19.05 mm (3/4”) OD by 76 mm (3”) long stainless steel tube fitted with a Swagelok cap at the bottom and a reducing union at the top. The reducing union was attached to a high temperature needle valve by a 1/8” OD by 17.1cm (6 ¼”) long stainless steel tube which was also connected and capped with Swagelok fittings. The needle valve was connected to a nitrogen cylinder to perform the nitrogen purging step. The reactor was loaded with the mixtures of solvents and C₅ industrial asphaltenes or crude oil, leak tested at 2.76 MPa, purged with nitrogen at least three times for two minutes at 0.55 MPa, and immersed in a heated fluidized sand bath (Tecam Fluidized Sand Bath Model No. SBS-4) at 200 °C. The set point temperature of the sand bath and the actual temperature of the solutions inside the microreactor differed by less than 3 °C. The microreactor was shaken continuously by a rotary motor for one hour at 200 °C then kept untouched out of the sand bath for cooling for 20 minutes and finally quenched to room temperature.

5.2.3 Preparation of analyte solutions

One liter stock solutions of C₅ industrial asphaltenes and of the crude oil in toluene, pyridine, and quinoline with a concentration of 1 g/L were prepared in advance and used for all of the dispersion studies. For each test, 100 mL of stock solution was transferred to a 100 mL volumetric flask to which different concentrations of the five dispersants (0.01 g/L to 1 g/L), as well as 3 g/L of the three ionic liquids were added. The mixtures were then sonicated for 30 minutes
using a Fisher Scientific model FS30 sonicator, heated for 1 hour at 200°C (in the case of the addition of dispersants) and cooled down to ambient temperature at which point the samples were ready for UV-visible spectroscopy measurements using 10mm cuvettes. In the case of the other asphaltenes, high concentration stock solutions of asphaltenes in toluene (10 g/L or 2 g/L) were prepared by weighing out the solid asphaltenes on a micro balance (±0.001 mg) and carefully transferring them to a class A 100 mL volumetric flask. The flask was filled to the base of the neck with toluene and sonicated for at least 1 hour to accelerate dissolution. Afterwards, the flask was allowed to cool, topped to the mark, and the final weight recorded to ±0.0001g. The stock solutions were then serially diluted to yield solutions with varying concentrations of asphaltenes ranging from 30 mg/L to 10 g/L, spanning 3 orders of magnitude in concentration. The concentrations of these solutions were quantified both volumetrically (using volumetric flasks) and gravimetrically, and the mean of these two values represents the final reported concentration of the solution. The solutions synthesized in this manner were scanned in triplicate using the different sized cuvettes as noted, and the data points presented in this work represent the mean of the three scans.

5.2.4 S-value measurements

The stability of the crude oil without and with the addition of the five selected dispersants was determined using a fuel stability analyzer (S-value Analyzer, DPC SA, Rofa France) based on ASTM D7157-05. The oil was diluted
with toluene and refluxed at 175 °C and 70 rpm for 45 minutes. The resulting mixture was then cooled and automatically titrated with n-heptane at a rate of 1 cm³/min. During the flocculation process, the light signal changes drift direction, and it is the location of this inflection that indicates the onset of flocculation. The n-heptane volumes for each toluene diluted sample at the onset of flocculation are then extrapolated to determine the amount of n-heptane required for asphaltene precipitation from the oil sample without toluene. This n-heptane value is then used for calculating the S-value parameters: S, Sₐ, and Sₒ. The instrument calculated the stability parameters using the following equations:

\[ S_a = 1 - FR_{max} \]  \hspace{1cm} (5.1)

\[ S_o = (FR_{max})(1 + X_{min}) \]  \hspace{1cm} (5.2)

\[ S = 1 + X_{min} \]  \hspace{1cm} (5.3)

Where \( X_{min} \) is the minimum volume (in mL) of paraffinic solvent (n-heptane in this case) that must be added to 1 gram of oil to cause flocculation of asphaltenes and \( FR \) (flocculation ratio) is defined as follows:

\[ FR = \frac{V_{arom}}{V_{arom} + V_{para}} \]  \hspace{1cm} (5.4)

In which \( V_{arom} \) and \( V_{para} \) are the volume of toluene in the mixture (mL) and the volume of n-heptane in the mixture at the inflection point (mL) respectively.

\( FR_{max} \) is the flocculation ratio at the point where oil to solution ratio (g/mL) is equal to zero.
5.2.5 UV-visible spectroscopy measurements

Two models of UV-visible spectrophotometer were used for the UV-visible spectroscopy measurements. An SI-Photonics (Tucson, AZ.) model 440 spectrophotometer, using a combination of a deuterium light source for wavelengths of 200-460 nm and a tungsten source for wavelengths from 460-950 nm, was used for all measurements related to assessment of Rayleigh scattering for asphaltenes. The spectrophotometer has a spectral bandwidth of 1.118 nm, which is as an inherent property of the CCD array detector installed in the instrument. Both 10.00±0.01 mm and 1.00±0.01 mm pathlength quartz cuvettes (Hellma Canada limited, Concord, Ontario) were used along with an SI-Photonics fiber optic cuvette holder. A Varian Cary 50 UV-Vis (Agilent Technologies, Santa Clara, CA) was used for all of the measurements related to the effect of dispersants, ionic liquids, heat, and sonication on asphaltene nano-aggregation except for quinoline experiments where the SI-Photonics (Tucson, AZ.) model 440 spectrophotometer was utilized. A 10.00±0.01 mm pathlength quartz cuvettes (Hellma Canada limited, Concord, Ontario) were used with this instrument. All spectra were collected at ambient conditions.

5.2.6 Acoustic spectroscopy measurements

A DT-1200 (Dispersion Technology, Inc. NY) acoustic spectrometer was used to measure the size distribution of the asphaltene nano-aggregates in toluene
solution and to investigate the heating and dispersant addition effects on asphaltene nano-aggregate size. This instrument yields a relationship between measured macroscopic acoustic properties, such as the speed of sound, attenuation, acoustic impedance, angular dependence of the scattered sound, etc., and the particle size distribution. The measuring chamber of the DT-1200 contains both acoustic and electroacoustic sensors. Therefore the instrument is capable of simultaneously measuring attenuation spectra for particle size distribution as well as colloid vibration current for zeta potential. The concentration of the solute (or dispersed phase) in the solution must be at least 1 wt % in order for the instrument to operate properly. The samples were transferred to the instrument chamber and stirred during the experiment to keep the solution homogenous. The size distribution, bimodal, and unimodal data were then reported by the DT1200 software.

5.3 Rayleigh scattering theory

The primary analytical technique used in this work is UV-Visible spectroscopy, illustrated schematically in Figure 5.1. The sample is irradiated with a beam of electromagnetic radiation having wavelengths from 200 nm up to 1000 nm (200-400 nm is the UV region and 400-1000 nm is the visible region). Radiation with these wavelengths, or more accurately with these energy levels, is capable of interacting with molecules in solution by promoting an electron from the ground state to an excited state. The electrons that are susceptible to being promoted in this fashion are generally bonding electrons (e.g. π electrons) that are
unique to the molecule and therefore this form of spectroscopy is also referred to as molecular absorption spectroscopy\(^57, 58\). At the same time, the incident radiation can be scattered by particles or droplets in the solution, depending on their size and the wavelength of the light.

The detector is located in a straight line with the incident beam and therefore only radiation which passes through the entire length of the sample cell without interacting with the analyte(s) will be detected. Radiation which is either absorbed or scattered by the sample will not reach the detector and is said to have been attenuated. This phenomenon is also referred to as “extinction” of the incident beam. In this configuration, UV-Visible spectroscopy cannot differentiate between molecular absorption and scattering since the detector is only measuring the radiation which has not been attenuated by the particles. The same apparatus can be used for true solutions, for particle suspensions such as bacterial cells, and mixtures of the two.
Figure 5.1 Schematic of a UV-Visible spectroscopic experiment illustrating extinction of radiation by a collection of molecules and/or particles. $I_0 =$ the incident radiation intensity, $I =$ the transmitted radiation intensity, $I_S =$ the intensity of the light scattered by the solution, $I_A =$ the intensity of the light absorbed by the analyte molecules in solution.

If we let $I_0$ be the baseline intensity of the radiation through the solvent without any particles present, and $I$ the intensity of light transmitted through the analyte solution, then the amount of the incident radiation that does not reach the detector is given quantitatively by the dimensionless absorbance, $A$, and is given mathematically by Beer’s law$^{57,58}$.

$$A = - \log_{10} \left( \frac{I}{I_0} \right) = \varepsilon b C$$

(5.5)

where $\varepsilon$ is the total extinction coefficient (L/(mol·mm)), $b$ is the path length (mm), and $C$ is the molar concentration of analyte (mol/L). As mentioned above, since the detector in UV-Visible spectroscopy is along the same path as the incident
radiation, the measured absorbance is the sum of both scattering and molecular absorption phenomena. Therefore, absorbance can also be referred to as the total attenuation or total extinction. The total extinction coefficient, $\varepsilon$, is therefore given by:

$$\varepsilon = \frac{N_A}{2.303} (a_{C,A} + a_{C,S})$$  \hspace{1cm} (5.6)

where $N_A$ is Avogadro’s number ($6.0221367 \times 10^{23}$ mol$^{-1}$), $a_{C,A}$ is the absorption cross-section (mm$^2$), and $a_{C,S}$ is the scattering cross-section (mm$^2$). Note that the scattering cross sections do not refer to the geometrical cross sectional area of the particle but rather a hypothetical area indicative of the probability that an incident wave will be attenuated by either absorption or scattering. When the radius of the analyte molecules ($r$) and/or particles are significantly smaller than the wavelength ($\lambda$) of the incident radiation ($r < 0.1\lambda$), Rayleigh scattering can occur with the following scattering cross-section:

$$a_{C,S-Rayleigh} = \frac{128\pi^2 n_s^2}{3} \left[ \frac{(n_p/n_s)^2 - 1}{(n_p/n_s)^2 + 2} \right]^2 r^6 \frac{\lambda^4}{\lambda^4}$$  \hspace{1cm} (5.7)

where $a_{C,S-Rayleigh}$ is the Rayleigh scattering cross section for a spherical particle of radius $r$, and $n_s$ and $n_p$ are the refractive indices of the solvent and particle, respectively. If the measured extinction is assumed to be a function of scattering only (i.e. $a_{C,A} = 0$), then Equations (5.5)-(5.7) give:

$$A = bC \xi \frac{r^6}{\lambda^4}$$  \hspace{1cm} (5.8)

$$\xi = \frac{128\pi^2 n_s^2 N_A}{6.909} \left[ \frac{(n_p/n_s)^2 - 1}{(n_p/n_s)^2 + 2} \right]^2 \text{=constant}$$  \hspace{1cm} (5.9)

Equations (5.8) and (5.9) indicate that if Rayleigh scattering is responsible for the
measured extinction, then the measured absorbance, \( A \), would vary linearly with the inverse 4\(^{\text{th}}\) power of the wavelength (\( \lambda^{-4} \)). In contrast, if the observed extinction were due to molecular absorption then the measured absorbance would vary linearly with \( 1/\lambda^{-59} \). If the absorption, \( A \), is plotted as a function of \( \lambda^{-4} \), and a straight line is obtained, then the slope of that line can be related to the mean radius of the spherical scatterer, \( r \), using Equations (5.10) and (5.11):

\[
\text{slope} = b C \xi r^6 \\
\]  
\[ r = \left[ \frac{\text{slope} \times M_w}{b w_A} \right]^{\frac{1}{6}} \]  

(5.10) \hspace{2cm} (5.11)

where \( M_w \) is the mass-average molecular weight of the scatterer and \( w_A \) is the mass concentration of the analyte. Equation (5.11) is written in terms of the mass concentration, \( w_A \), since, as mentioned earlier in the introduction and will be also discussed later, the molecular weight of asphaltenes is not known with any certainty and therefore solutions of asphaltenes can only be prepared by mass.

### 5.4 Results and discussion

#### 5.4.1 Interaction of Asphaltene nano-aggregates with UV-visible radiation: The Rayleigh scattering effect

In a recent publication, Dechaine and Gray\(^ {23} \) observed that ultrafiltration membranes with pore sizes <5 nm were able to retain a large portion of the total
asphaltenes in toluene solution. Although asphaltenes in solution absorb radiation across the entire UV-Visible spectrum, the permeate from the aforementioned filtration process displayed no absorbance in the visible (\( \lambda > 550 \text{ nm} \)) range. The fact that the absorbance in the visible region was eliminated by a filtration process indicates that this absorbance is likely linked to asphaltenes nano-aggregates, since these species are retained by the membrane if the pores are smaller than the size of the nano-aggregates. Therefore, it is plausible that the interactions of visible light with asphaltenes are affected by a scattering (i.e. size dependent) mechanism, and if so, nano-aggregate size, or more importantly disaggregation phenomena, can be monitored by the UV-visible spectroscopy.

Figure 5.2 shows some representative UV-Visible spectra of Athabasca C\(_7\) asphaltenes in toluene. Several other C\(_7\) asphaltene samples were also examined as part of this study (Venezuelan, Safaniya, and partially demetallated Athabasca, see the paper of Dechaine and Gray\(^{23}\) for details regarding these samples) and their spectra exhibited the same characteristic sloping tail seen in Figure 5.2 and as such are not shown. The small hump evident at 408 nm of some of these spectra is evidence of vanadyl porphyrins present in the asphaltenes\(^{23,60}\), which represents a contribution from molecular absorption as in Equation (5.6).
Figure 5.2 Raw spectra of Athabasca C₇ asphaltenes in toluene at 20 ± 2 °C. The concentrations indicated are all in g/L.²

All the spectra from Figure 5.2 were converted to the Rayleigh scattering form given by Equations (5.8) and (5.9), and the results are shown in Figure 5.3. For the sake of clarity, only a small sampling of the spectra collected are shown, although this analysis was completed for all spectra collected.
Figure 5.3 Rayleigh scattering curves for Athabasca C₇ asphaltenes in toluene. All the concentrations above each scattering curve are in g/L. ⁶¹
All of the modified spectra shown in Figure 5.3 are linear within the range of wavelength from 600 to 950 nm, with a coefficient of determination \( R^2 \) in excess of 0.996 for least squares regression fits of the data. The fact that these curves are highly linear suggests that the primary mechanism for the observed extinction in the visible region is indeed Rayleigh scattering. If absorption was significant in this region, it would be expected that the coefficient for \( \lambda \) would be somewhere between 1 (absorption) and 4 (Rayleigh scattering). In fact, Owen \(^{62}\) states that for complex chemical systems, the effective exponent can vary between 2 to 4. However, none of the spectra in Figure 5.3 show any signs of significant deviations from linearity indicating limited molecular absorption in this region of the UV-visible spectrum.

This analysis agrees with the observations of Dechaine and Gray \(^{23}\) that the spectra of asphaltenes that permeate through ultrafiltration membranes with pore sizes of < 5 nm have no absorbance in the visible region. As indicated by Equation (5.8), the absorbance due to scattering is directly proportional to \( r^6 \) and hence the magnitude of the scattering extinction will increase dramatically with the size of the solute. By retaining the large nano-aggregated asphaltene species, the scattering effect is effectively eliminated and as such there is no absorbance observed beyond 600 nm.

This analysis can be extended further using the slope of each spectrum in Figure 5.3 with Equation (5.11) to estimate the approximate size of the scatterers in the solution. First of all, Equation (5.11) requires an estimate for the average molecular weight of the scattering particles. Unfortunately, the average molecular
weight of asphaltenes in solution is not a constant value. For the purpose of this analysis, the step-wise polymerization model of Agrawala and Yarranton\(^7\) was used to estimate the average molecular weight of the asphaltenes in toluene solution as a function of the concentration. The parameters given by Agrawala and Yarranton were linearly extrapolated down to 25 °C for estimating the molecular weight distribution of each asphaltene solution (see Dechaine and Gray\(^{23}\) for examples of the molecular weight distributions obtained with this model).

The base model of Agrawala and Yarranton is based on vapor pressure osmometry data and as such it yields a number-average molecular weight (\(M_n\)) while scattering measurements are known to be a function of the mass-average molecular weight (\(M_w\))\(^{63}\). Therefore the values from Agrawala and Yarranton’s model were corrected to a mass-average basis by calculating the actual molecular weight distribution and calculating the mass average molecular weight using the following equation\(^{63}\):

\[
M_w = \sum_i w_i M_i 
\]

\(\text{(5.12)}\)

Where \(w_i\) is the weight fraction of molecules with molar mass \(M_i\). Equation 5.5 must be solved for \(\xi\), which requires values of the refractive indices of both the solvent and the scattering particle. The refractive index for toluene is \(n_{\text{Toluene}} = 1.494\)\(^{64}\) at 25 °C. The refractive index of the asphaltene particles, on the other hand, is a little more difficult to obtain. Asphaltenes at ambient conditions are opaque solids and therefore their refractive index cannot be measured directly.

Several investigators have used extrapolation of dilute solution data to estimate
the refractive index of asphaltenes to be $n_{\text{Asphaltenes}} \approx 1.7^{65, 66}$. These values combined with Equation (5.9) give a value of $\xi = 1.36 \times 10^{26}$, which is a constant for each combination of scatterer and solvent (asphaltenes in toluene in this case).

![Graph showing mean diameter of nano-aggregated C\textsubscript{7} asphaltene particles in toluene solution as a function of concentration at 20 ± 2 °C.](image)

Figure 5.4 Mean diameter of the nano-aggregated C\textsubscript{7} asphaltene particles in toluene solution as a function of concentration at 20 ± 2 °C\textsuperscript{61}.

The above molecular weight and refractive index information, as well as the slopes of the least squares regression for each linear Rayleigh scattering curve (Figure 5.3) were then combined with Equation (5.11) to determine a mean radius (or diameter, $d = 2r$) for the scatterers in each solution. The results of this analysis are summarized in Figure 5.4. According to this relatively simple analysis, the sizes of the asphaltene nano-aggregates for different asphaltenes for concentrations from 30 mg/L to 10 g/L at 20 ± 2 °C ranges between 5-8 nm.
These data are in very good agreement with the 5-9 nm size range obtained using membrane diffusion measurements\textsuperscript{23}.

This scattering analysis is in stark contrast to the analysis of Ruiz-Morales \textit{et al.}\textsuperscript{67, 68} who explained the absorbance in the visible region (> 600 nm) using molecular orbital calculations. They proposed that the absorbance in the visible region is due to large fused-ring systems with 4-10 fused rings per molecule. However, a large part of this explanation relies on the claim that the absorbance in this region is linear when plotted as a function of 1/\(\lambda\). Closer examination of their measured absorbances indicates that their data are clearly not linear in this region. As well, their analysis does not take into account the effects of association on the absorption of the asphaltene systems, which as the preceding results indicate clearly occurs for these systems. Evdokimov \textit{et al.}\textsuperscript{69-72} have studied the optical absorption behavior of crude oils and asphaltenes in depth. They observed a power law relationship of \(A \propto \lambda^{-m}\) with \(m\) ranging between 3.14 and 4.33\textsuperscript{69} which fits with the trends observed in this work. In fact, their analysis included some of the same data used by Ruiz-Morales \textit{et al.}\textsuperscript{67, 68} noted above. The varying value of \(m\) is indicative of a heterogeneous chemical system, although the fact that the observed exponents are centered on a value of 4 suggests that Rayleigh scattering is the dominant mechanism. Further scattering measurements which were performed\textsuperscript{70} to study the effect of asphaltene concentration on intensity of a laser light scattered at 90° (\(\lambda=633\) nm), supported the contention that Rayleigh scattering was occurring within similar concentration ranges and wavelengths as used in this work.
The agreement of the Rayleigh scattering analysis with other independent, physical size measurement techniques gives credibility to the notion that the absorbance in the visible region can be used as a simple and robust indicator of the nano-aggregation state (i.e. size) of asphaltenes in solution. Inverting this argument, since a number of different methods indicate formation of asphaltene nano-aggregates in the size range of 2-20 nm, even at astonishingly low concentrations, physics dictates that Rayleigh scattering must be expected for visible light in asphaltene solutions. As such, this technique will now be applied to assess the impact and efficacy of various treatments (additives, sonication, and heat) on the nano-aggregation of asphaltenes in solution.

5.4.2 Disaggregation

5.4.2.1 Effect of dispersants on crude oil stability

The five dispersants listed in Table 5.1 were added to the crude oil at a ratio of 1 wt % and the stability of the resulting mixtures was measured with the S-value instrument. Figure 5.5 shows the stability results for the current crude oil sample. A comparison of the S-values shows that additives #2 to #5 increased the stability of oil. The intrinsic stability of the crude oil medium (S_o) increased with additives #4 and #5 relative to the others, and the solvency requirements (S_a) for all the cases were constant. Some investigators presented the effect of addition of dispersants on onset of asphaltene precipitation in terms of mL n-heptane/g oil which is equal to X_{min} for S-value calculations. Since S=1+X_{min}, the changes in S
in equal to the changes in $X_{\text{min}}$. Mohamadshahi and Nazar\textsuperscript{73} reported the effect of some vegetable oil types, benzyl alcohol and 4-dodecylresorcinol on the onset of asphaltene precipitation and they listed all of the additives to be effective dispersants. For all the cases except 4-dodecylresorcinol, which shows a very significant onset displacement (i.e. 0.5-0.7 mL/g), for 1 wt % of dispersants the mL n-heptane/g oil changed from 0.2 to 0.4 mL/g. Results from Oh and Deo\textsuperscript{74} also showed that the addition of 1wt % of a series of organic compounds as additives changed the onset about 0.1-0.2 mL/g. Even Andersen\textsuperscript{75} investigated the effect of 50, 100 and 500 ppm of an inhibitor on the flocculation titration and saw no apparent meaningful change in onset while the inhibitor was used successfully for treating the oil in its reservoir from asphaltene precipitation. He concluded that either the significant interactions of asphaltene or the inhibitor did no longer exist in ambient conditions or the dispersant was operative to disperse the asphaltene from more flocculation instead of keeping it from precipitation. These comparisons indicated that with the exception of additive #1, the current proposed additives which increased the onset from 0.1-0.4 mg/L could be candidates to disaggregate the asphaltene nano-aggregates present in toluene solutions.
Table 5.1 List of the dispersants tested in this work

<table>
<thead>
<tr>
<th>Dispersant name</th>
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<tbody>
<tr>
<td># 1 $\text{C}<em>{14}\text{C}</em>{16}$ dimethyl naphthalene sulfonic acid</td>
</tr>
<tr>
<td># 2 Dinonylnaphthalene Sulfonic acid</td>
</tr>
<tr>
<td>(Ethylene Glycol Butyl Ether solvent)</td>
</tr>
<tr>
<td># 3 Alkylaromatic Sulfonic Acid</td>
</tr>
<tr>
<td># 4 Nonyl phenyl 4 mole ethoxylate</td>
</tr>
<tr>
<td># 5 Nonylphenol</td>
</tr>
</tbody>
</table>

Figure 5.5 Comparison of the stability of the crude oil sample with and without the addition of 1wt% selected additive.
5.4.2.2 Effect of sonication

Samples of different concentrations of the crude oil in toluene were prepared and sonicated for 30 minutes and the visible absorbance of these samples was measured using the Cary 50 UV-visible spectrometer. The effect of sonication on the absorbance of these samples is shown in Figure 5.6. The absorbance at a wavelength of 600 nm was chosen to illustrate the trend, although any wavelength in the visible region ($\lambda > 550$ nm) would yield the same result(s). The figure clearly indicates that sonication had no effect on the absorbance of the solutions.

Figure 5.6 Effect of 30 minutes sonication of crude oil in toluene at different concentrations. The absorbance was measured at a wavelength of 600 nm.
5.4.2.3 Effect of dispersants and sonication combined

The dispersants (Table 5.1) were first dissolved in toluene at different concentrations and the background absorbance of the additives in toluene was measured by UV-visible. These dispersant-toluene solutions were then added to the asphaltenes (all references to asphaltenes in Section 5.4.2 are C5 industrial asphaltene, see Section 5.2.1 for details) and crude oil solutions. In all cases, for low concentrations up to 1 g/L, the absorbance due to the additive was negligible. Even at higher concentrations (e.g. 1 wt %), the absorbance in the range of 550-800 nm was less than 0.2. Additives are used in the petroleum industry at relatively low concentrations (circa 0.5 wt %) and increasing the amount of additive beyond this point does not improve their efficiency appreciably. Here, different concentrations of dispersants ranging from 0.01 g/L to 1 g/L were examined. The concentration of 0.01 g/L was chosen for the dispersants because the increase in concentration of dispersants increases the absorbance of asphaltene and crude oil solutions in toluene distinctly. Figure 5.7 is an example of how the addition of dispersants affects the absorbance of the solution. One of the middle dispersants concentrations (0.1 g/L) was selected to show the trend. The solid curve shows the absorbance of a 1 g/L asphaltene solution in toluene with no dispersant added. In the case of dispersants #1 to #3, the dispersant resulted in an increase in the absorption of the solution, indicating an increase in the size of the nano-aggregates. The size increase calculation based on Rayleigh scattering equation will be explained later in Section 5.4.2.9 the absorption of dispersants on their own in toluene solution is negligible comparing to absorption increase
shown in Figure 5.7. For additive concentrations of 0.1 wt % in toluene the increase in absorbance comparing to toluene as the blank was less than 0.001 for all cases except dispersant #1 with absorption increase of only 0.006 at 700 nm. While the absorbance increase of asphaltene in toluene solutions in the presence of dispersants #1 to #3 was from 0.25 to 0.15 at 700 nm as shown in Figure 5.7. Chang et al. 48 observed by small angle X-ray scattering that asphaltene-nonylphenol precipitates are slightly larger than asphaltene precipitates alone. The same result is observed here for dispersants #1-5 (Figure 5.8). The addition of dispersants including nonylphenol to the nanoaggregate of asphaltenes increased the absorbance, indicative of an increase in the size of the nano-aggregates.

Figure 5.7 Absorbance of 1 g/L asphaltenes in toluene after 30 min sonication and addition of 0.1 g/L of dispersants #1-3.
Addition of the dispersants at different concentrations ranging from 0.01 g/L to 1 g/L followed by 30 minutes of sonication are not shown here since for both the C₅ industrial asphaltenes and the crude oil sample the results are the same.

![Absorbance at 700 nm](image)

Figure 5.8 Absorbance of asphaltenes in toluene (1 g/L) at 700 nm with the addition of the selected additives followed by 30 min of sonication. The concentrations of additives were 0.01 g/L for additives #1-3 and 0.02 g/L for additive #4 and #5. The error bar shows the standard deviation of 5 replicates for the solution of asphaltene in toluene (1 g/L) without any additives.

Figure 5.8 shows the absorbance at 700 nm of 1 g/L asphaltenes in toluene with and without the addition of the dispersants, followed by 30 minutes of sonication. The results show that the addition of the dispersants does not decrease
the absorbance of the asphaltene solutions, which in turn implies that they do not reduce the size of the nano-aggregates. The results for the crude oil in toluene are shown in Figure 5.9 at 1 g/L with and without the addition of the dispersants.

![Absorbance at 700 nm](image)

Figure 5.9 Absorbance of the crude oil in toluene (1 g/L) at 700 nm with and without the addition of the dispersants followed by 30 min of sonication. The concentrations of additives were 0.01 g/L. The error bar shows the standard deviation of 5 replicates for the solution of the crude oil in toluene (1 g/L) without any additives.

As the figure shows, similar to asphaltene in toluene results (Figure 5.8), the addition of the dispersants does not decrease the absorbance of the crude oil solutions, which means that they do not reduce the size of the nano-aggregates.
5.4.2.4 Effect of sonication, dispersants, and heat

Figures 5.10 and 5.11 show the effect of 30 minutes of sonication, 0.01 g/L of dispersant, and 1 hour of heating at 200 °C for the asphaltene and crude oil solutions in toluene, respectively. The results for both asphaltenes and the crude oil show that these combined treating effects (sonication, dispersants and heating) do not decrease the absorbance of the solutions but rather led to an increase in each case. While the addition of dispersants had very little effect on the absorbance (previous section), the addition of heat to the treating factors did lead to a distinct increase in the absorbance.

![Figure 5.10 Absorbance of asphaltenes in toluene (1 g/L) at 700 nm with addition of the additives, followed by 30 min of sonication, and heating at 200 °C for 1 hour. The concentrations of additives were 0.01 g/L for additives #1-3 and 0.02 g/L for additive #4 and #5. The error bar shows the standard deviation of 5]
replicates for the solution of asphaltenes in toluene (1 g/L) without any additives.

Figure 5.11 Absorbance of the crude oil in toluene (1 g/L) at 700 nm with the addition of the additives, followed by 30 min of sonication and 200 °C heating for 1 hour. The concentrations of additives were 0.01 g/L. The error bar shows the standard deviation of 5 replicates for the absorbance of the crude oil in toluene (1 g/L) without any additives.

5.4.2.5 Acoustic spectroscopy results

To prove that the change in absorbance of the samples has a direct relationship with the change in the nano-aggregate size, particle size measurements were performed on four selected samples using an acoustic
spectrometer and the results are shown in Figure 5.12. The measurements were done on a 1 wt % asphaltene in toluene solution with and without the addition of dispersants #1 and #2, and with heating without any dispersant addition to 200 °C for one hour. The acoustic technique needs at least 120 mL of sample, therefore for these experiments the heating was done in a 500 mL stirred pressure batch autoclave reactor (Parr Instrument Company, Moline, IL, USA) rather than in the microreactors. The sizes in Figure 5.12 determined from the acoustic spectroscopy measurements are consistent with the analysis of the UV-visible results based on Rayleigh scattering. The addition of dispersants #1 and #2 increased the nano-aggregate size, as did the heating process. These results confirm that UV-visible spectroscopy can be used to monitor changes in asphaltene nano-aggregation.
Figure 5.12 Asphaltene nano-aggregate size(s) measured with an acoustic and electroacoustic spectrometer (DT1200) for a 1 wt % C5 industrial asphaltene solution in toluene with either: 1 g/L of additive #1 or #2, or heating to 200°C for one hour.

5.4.2.6 Effect of heating severity

One possible explanation for the increased absorbance following the heat treatment is due to toluene evaporation and subsequent concentration of the asphaltenes in the remaining solution. The evaporation of a portion of the toluene during the purging and quenching process is expected. By measuring the weight of the solution before and after heating, and assuming that the asphaltene are non-volatile at 200°C, the concentration of asphaltenes in toluene following the heat treatment can be estimated. In all cases the change in concentration due to
evaporation combined with the calibration curve of asphaltene absorbance cannot account for the increase in the absorbance shown in Figures 5.10 and 5.11.

To verify that the concentration changes due to evaporation are not responsible for the increased absorbance due to heating, a 1 g/L solution of asphaltenes in toluene was heated to 120 °C, 140 °C, 160 °C, 180 °C and 200°C for one hour and cooled to room temperature. The concentrations of the samples before and after this treatment are summarized in Table 5.2, and the absorbance at 700 nm for each solution following heat treatment is shown in Figure 5.13. As the results in Table 5.2 show, the final concentration of the samples is not a function of temperature. Figure 5.13 shows that by increasing the temperature from ambient to 120 °C, 140 °C, 160 °C, 180 °C and 200°C, the absorbance of the solutions increased progressively. To determine if the heating effect can be eliminated by heating over longer periods of time, a 1 g/L sample of asphaltenes in toluene was heated at 200 °C for 7 days, and the absorbance of the cooled sample is shown in Figure 5.14. Evidently heating the sample for extended periods of time does not eliminate the heating effect. The reason of the heating effect could be the strength reduction of the solvent with temperature reduction or acceleration in the nano-aggregation process during cooling. Swelling phenomenon in which some toluene molecules trapped in asphaltene nano-aggregates during cooling, and they did not have the chance to escape from the nano-aggregates could also be another reason.
Figure 5.13 Absorbance of asphaltene in toluene (1g/L), without heating and with heating to 120°C, 140°C, 160°C, 180°C and 200°C and cooling to room temperature.

Table 5.2 Concentration of asphaltene solutions in toluene before and after heating to different temperatures

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial concentration (g/L)</th>
<th>Final concentration (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Asphaltene in toluene heating to 120 °C</td>
<td>1.00</td>
<td>1.029</td>
</tr>
<tr>
<td>Asphaltene in toluene heating to 140 °C</td>
<td>1.00</td>
<td>1.029</td>
</tr>
<tr>
<td>Asphaltene in toluene heating to 160 °C</td>
<td>1.00</td>
<td>1.023</td>
</tr>
<tr>
<td>Asphaltene in toluene heating to 180 °C</td>
<td>1.00</td>
<td>1.029</td>
</tr>
<tr>
<td>Asphaltene in toluene heating to 200 °C</td>
<td>1.00</td>
<td>1.028</td>
</tr>
</tbody>
</table>
Figure 5.14 Absorbance of asphaltene solution in toluene (1g/L) when heated for 7 days in 200 °C and cooled to room temperature.

5.4.2.7 Effect of ionic liquids

Table 5.3 shows the list of ionic liquids used as additives to the 1 g/L asphaltene solutions in pyridine. Recent studies have shown\(^{78-80}\) that ionic liquids work well for separating bitumen and oil from sand at ambient temperatures. 1-butyl-3-methylimidazolium chloride is also reported\(^{81, 82}\) to be able to fragment, disperse, and partially dissolve coal. Therefore ionic liquids could be reasonable choices as dispersants for asphaltene nano-aggregates. Pyridine was selected as the solvent since ionic liquids are fully miscible in pyridine but immiscible in
toluene. The mass ratio of the ionic liquids to asphaltenes was set at 3:1 which was selected based on the effective mass ratios of ionic liquids reported in the literature. The higher mass ratios also examined but had no better effect. Figure 5.15 shows the absorbance of the asphaltene + ionic liquids solutions in pyridine at 700 nm. As Figure 5.15 shows, the addition of IL1 reduced the absorbance very little (less than 3%) while the other two ionic liquids had little or no effect on the absorbance.

### Table 5.3 List of ionic liquids

<table>
<thead>
<tr>
<th>Name of the ionic liquid</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>IL1</strong></td>
<td>1-butyl-3-methylimidazolium tetrafluoroborate (BMIMBF4)</td>
</tr>
<tr>
<td><strong>IL2</strong></td>
<td>1-Butyl-3-methylimidazolium hexafluorophosphate (BMIM-PF6)</td>
</tr>
<tr>
<td><strong>IL3</strong></td>
<td>1-Butyl-3-methylimidazolium hydrogen sulfate (BMIM-HSO₄)</td>
</tr>
</tbody>
</table>
5.4.2.8 Effect of solvent and combination of additives

To test the effect of the solvent on the nano-aggregation phenomenon, quinoline, which is considered a stronger asphaltene solvent than toluene, was tested along with the dispersants from Section 5.4.2.1 both individually and as a mixture (#3, #4 and #5), all at concentrations of 1 g/L followed by heating at 200 °C for 1 hour and quenched to room temperature. The absorbance of the resulting solutions is shown in Figure 5.16. The results indicated that addition of the mixture of the dispersants decreased the absorbance very little (less than 2.5%), and in case of the individual dispersants had no appreciable effect. As was the
case for toluene, heating led to a significant increase in the absorbance with the quinoline solvent.

Figure 5.16 Absorbance of asphaltene solution in quinoline (1 g/L) at 700 nm when 1 g/L of dispersant #4, #5, and mixture of dispersants #3, #4, and #5 were added to the solution and heated at 200 °C for 1 hour.

5.4.2.9 Rayleigh scattering analysis of treatments

Similar to Rayleigh scattering effect and nano-aggregate size measurement described in Section 5.4.1, Figure 5.17 shows the Rayleigh scattering curves for C₅ industrial asphaltenes in toluene without and with addition of the five dispersants, heat and sonication. Rayleigh scattering curves for 1 g/L of C₅ industrial asphaltenes in toluene when heated from room temperature to 120°C,
140°C, 160°C and 180°C and 200 °C and cooled to room temperature also shown in this figure. All of the modified spectra shown in Figure 5.17 are linear within the region examined, with a coefficient of determination (R^2) in excess of 0.994 for least squares regression fits of the data. Addition of dispersants #1-5 increased the absorbance (Figure 5.8) and the slope of Rayleigh scattering curve as shown in Figure 5.17. From Equation (5.10) and (5.11), addition of slope resulted in increase in size. Here molecular weight assumed to remain constant and shape of molecules assumed to be sphere. Although the scattering could be altered if the shape of the particles changes, but it is outside the scope of Equations 5.10 and 5.11 that shape assume to spheres.

Figures 5.18 and 5.19 show the nano-aggregate size mean diameter results based on Rayleigh scattering equation. These data are also in very good agreement with the 5-9 nm size range obtained using membrane diffusion measurements\textsuperscript{23}. Because of the lack of information on asphaltene molecular weight in pyridine and quinoline in the literature, the size of the nano-aggregates for those cases could not be estimated.
Figure 5.17 (a) to (e) Rayleigh scattering curves for C$_5$ industrial asphaltenes in toluene without and with addition of the five dispersants, heat and sonication. The concentrations of additives were 0.01 g/L for additives #1-3 and 0.02 g/L for additive #4 and 5. (f) shows the Rayleigh scattering curves for 1 g/L of C$_5$ industrial asphaltenes in toluene when heated from room temperature to 120°C, 140°C, 160°C and 180°C and 200 °C and cooled to room temperature.
Figure 5.18 Mean diameter of the nano-aggregated C5 industrial asphaltene particles in toluene solution (1 g/L) with the addition of the five selected dispersants, 30 min sonication and heating to 200 °C. The concentrations of additives were 0.01 g/L for additives #1-3 and 0.02 g/L for additive #4 and 5.

Since the apparent molecular weight of C₅ and C₇ asphaltene at low concentrations circa 1 g/L, which was used for these series of experiments, does not differ very much, the mass average molecular weight of C₇ asphaltenes was used for size determination. One point that should be taken into consideration is the effect of heating and cooling on molecular weight of asphaltenes. The size and molecular weight usually have a direct and simultaneous relation on a particle in which larger particles usually have more molecular weights. From the Rayleigh scattering slopes which increased as shown in Figure 5.17, it is hard to tell that if this increase is only the effect of size increase or both size and molecular weight increase. However from Equation 5.11 we know that size has a relation with 6th
root of molecular weight. Therefore even if the molecular weight has changed 10%
it affects the size calculation only 1%. For Figures 5.18 and 5.19 it was
assumed that the molecular weight of asphaltene did not change with heating and
cooling back to the ambient temperature and from the above discussion this
assumption should be a reasonable one.

Figure 5.19 Mean diameter of the nano-aggregated C5 industrial asphaltene
particles in toluene solution (1 g/L) when heated from room temperature to
120°C, 140°C, 160°C and 180°C and 200 °C and cooled to room temperature

5.5 Conclusions

The visible spectra of asphaltene samples in toluene solution for
wavelengths > 600 nm follow a λ⁻⁴ dependence regardless of concentration or
geographical origin. This functional dependence is consistent with Rayleigh scattering rather than a mixture of chromophores. The fact that the “chromophores” above 600 nm have sizes > 5 nm and can be filtered out, and the fact that the “absorbance” follows the classical $\lambda^{-4}$ dependence for Rayleigh scattering provide strong evidence that the apparent absorption of visible light by asphaltenes from 600-850 nm is a scattering mechanism. This sensitivity of visible absorbance to nano-aggregation and size for asphaltenes was exploited to monitor the effects of various treatments (additives, sonication, and temperature) on the nano-aggregation state of asphaltenes in solution. Asphaltenes could not be disaggregated completely by any of the additives tested, nor by sonication and heating for 1 hour at 200 °C.

5.6 References


26) Andreatta G., Goncalves C.C., Buffin G., Bostrom N., Quintella C.M., Arteaga-Larios F., Perez E., Mullins O.C. Nanoaggregates and structure-


54) Miller D., Vollmer A., Feustel M., Klug P. Synergistic mixtures of phosphoric esters with carboxylic acids or carboxylic acid derivatives as asphaltene dispersants, U.S. Patent 6,204,420, 2001


64) Design Institute for Physical Properties, 2008


6 OCCLUSION OF POLYAROMATIC COMPOUNDS IN ASPHALTENE PRECIPITATES SUGGESTS POROUS NANOAGGREGATES

6.1 Introduction

The mechanisms of aggregate formation are the subject of much speculation and ongoing research. Recently Gray et al. \(^1\) proposed a new model for aggregation of asphaltenes which attempts to reconcile the various properties and reactions of this petroleum class. The implication of this supramolecular assembly of complex molecules is that the dispersed nanoaggregates of asphaltenes in solution are porous structures, consistent with data from NMR spectroscopic diffusion measurements and neutron scattering data \(^2-4\). A further implication of the research on supramolecular assembly of defined compounds is that occlusion of components which are otherwise soluble will occur within the aggregated structure. In this context, occlusion means physical entrapment by whatever mechanism within the non-covalent matrix of asphaltene nanoaggregates. Liao et al. \(^5\) suggested that occlusion was responsible for the survival of otherwise unstable biomarker compounds, while Strausz et al. \(^6\) showed that sequential reprecipitation of asphaltenes gives the release of large amount of materials which are soluble in the precipitant. Liao et al. \(^7\) reported the detection of some saturated hydrocarbons occluded inside asphaltene aggregates. Unsaturated alkenes and some unusual biomarkers were also detected inside
asphaltene aggregates. Some asphaltene aggregates appear to be stable at up to 300°C, so these biomarkers are shielded and preserved over geological time. Finally, occlusion may contribute to the long-term stability of free radicals in asphaltenes. Radicals are extremely reactive species, therefore survival of these radicals in asphaltenes led to suggestions that trapping of such species in asphaltene aggregates is due to a type of host-guest complex which isolates radicals from the environment.

Trapping of compounds by asphaltene aggregates is an interesting phenomenon which is relevant to properties such as swelling and solvent trapping, and which has significance in the analysis of asphaltene deposits and interfacial material, where the structure-forming components, or “hosts”, and the occluded components, or “guests”, may be difficult to distinguish by conventional analytical approaches. The idea of host-guest complex can be extended to any component that is able to play the guest role. Our hypothesis is that polynuclear aromatic hydrocarbons (PAHs) can be occluded within asphaltene nanoaggregates and thereby contribute to asphaltene deposition even though these compounds are fully soluble. This hypothesis was tested by dissolving pyrene and phenanthrene in toluene solutions of asphaltene, adding n-pentane to give precipitation, then analyzing the precipitates for the presence of the PAH compounds.
6.2 Experimental section

Materials: The asphaltene used in these experiments was obtained from an industrial deasphalting unit operating with n-pentane on a feed of Athabasca bitumen from steam-assisted gravity drainage production. Called “industrial C5-asphaltene”, this material contained about 28 wt% pentane soluble materials based on the standard method of dissolution then precipitation in 40:1 solvent \(^{13}\). The asphaltene used for these experiments was prepared by washing the industrial C5-asphaltenes with extra n-pentane to remove the pentane soluble fraction and then filtered by 0.22µm membrane filter paper (Millipore) and dried at room temperature overnight. The two polyaromatic hydrocarbons used were pyrene (Sigma-Aldrich 98%) and phenanthrene (Sigma-Aldrich, >96% HPLC grade) and the solvents were toluene and n-pentane (HPLC grade) obtained from Fisher (Mississauga ON).

Precipitation of asphaltenes and PAHs: In all cases, a 0.1 g/mL solution of asphaltene, PAH, or PAH + asphaltene was prepared in toluene solution. Precipitation was by the addition of n-pentane to achieve the desired final solvent ratios. After vacuum filtration and overnight air-drying the weight of the precipitated asphaltene was determined.

Simulated distillation measurements: The precipitates were analyzed by simulated distillation (SimDis) using a Varian 450-GC gas chromatograph according to method ASTM D5307. The column had inside diameter of 0.53 mm, outside diameter of 0.8 mm, and a film thickness of 0.09 µm with a maximum allowable operating temperature of 450°C (Capillary column WCOT Ultimetal...
with Reference number of CP7569, Agilent Technologies, New Castle, De, USA). The temperature profile consisted of an isothermal stage of 1 min at 35 °C followed by ramping up to 400 at 20 °C/min with a total heating time of 45 min. Calibration was with mixtures of pyrene and phenanthrene dissolved in carbon disulfide. The SimDis method is the only gas chromatographic technique which allows us to analyze asphaltenes without plugging the analytical columns. Asphaltene does not show any sharp peaks in the detector, but rather gives a very broad peak due to thousands of components eluting at high temperature. Consequently, pure compounds such as pyrene and phenanthrene are readily observed as a distinct sharp peak against the asphaltene background.

The asphaltene precipitates were sampled for SimDis analysis in two ways. In the first method, the entire filter cake (about 2 g) was mixed with CS$_2$ and diluted to give a 1 wt% mixture and then analyzed by SimDis. In the second method, each precipitate was subsampled at different locations on the filter paper, removing 18 mg each time to be mixed with CS$_2$ to make a 1 wt% mixture for injection into the gas chromatograph.

6.3 Results and discussion

Selection of n-pentane ratio: In order to determine how much n-pentane is needed for asphaltene precipitation, a 0.1 g/mL solution of asphaltene in toluene was prepared and then precipitated with n-pentane at increasing solvent ratios. After vacuum filtration and overnight air-drying, the weight of the precipitated
asphaltene was compared to the initial weight of the asphaltene. The data of Figure 6.1 show the mass of asphaltene precipitated in different n-pentane ratios. n-Pentane ratios above 4 gave much less sensitivity of the mass precipitated to the volume of solvent, therefore, we selected a ratio equal to 5 for subsequent experiments. At this mass ratio the amount of asphaltene precipitated was highly repeatable at 68.4 ± 1.3 wt% of the initial mass, but the aromatic compounds pyrene and phenanthrene were fully soluble.

![Figure 6.1 Asphaltene precipitation weight percent in different n-pentane ratios.](image)

Figure 6.1 Asphaltene precipitation weight percent in different n-pentane ratios. The mass of mixture in the calculation of the horizontal axis was the initial mass of asphaltene plus toluene

*Solubility of pyrene and phenanthrene in solvent blend:* A relatively low ratio of n-pentane to sample was selected to ensure that the added PAH compounds did not exceed their solubility limits. As a test, 3 g of pyrene and 3 g
of phenanthrene (separately) were mixed with 30 ml toluene, and then 5 times this mass of n-pentane was added to the mixtures, followed by vacuum filtration using 0.22 µm filter paper. After overnight air drying, the filter paper was weighted and no change in mass due to precipitate was detected. We concluded that both pyrene and phenanthrene were quite soluble in this toluene-n-pentane mixture.

Design of occlusion experiments: Our hypothesis was that the PAH compounds would penetrate the asphaltene nanoaggregates (Figure 6.2a, Type A mechanism). In this case, intra-aggregate PAH would then become trapped upon the addition of n-pentane and be detected in the precipitate. This hypothesis was tested by mixing 3 g of PAHs and 3 g of asphaltene with 30 ml of toluene in an Erlenmeyer flask, which was sealed and stirred for 2 days. The mixture then was precipitated by 5 times of weight n-pentane and vacuum filtered with 0.22µm filter paper, by the normal method described above.
An alternate mechanism for the PAHs to appear in the filter cake would be trapping between the nanoaggregates during the precipitation step, or adsorption on their exterior surfaces, which would lead to the detection of some PAH in the filter cake (Figure 6.2b). As a control experiment for this extra-aggregate precipitation mechanism, two solutions were prepared. In solution 1, 3 g of PAHs and 30 ml of toluene was mixed with 5 masses by weight n-pentane. In solution 2, 3 g of asphaltenes was mixed with 30 ml of toluene. Both solution 1 and solution 2 were uniform solutions, with the PAHs dissolved in solution 1 and the asphaltenes fully dispersed in solution 2. Then solution 2 was poured into solution 1 and stirred overnight. The mixture of the two solutions was then precipitated by adding a further 5 masses of n-pentane and filtered and dried for analysis.

*Analysis of PAHs in asphaltene precipitates*: The concentration of PAHs in the precipitated asphaltenes is shown in Figure 6.3, for the analysis of the total precipitated sample. The amount of PAH occluded was not large; 6 wt% of the precipitate was pyrene, and in the presence of phenanthrene only 0.6 wt% of the precipitate mass the occluded material, but these amounts were readily detected by SimDis. The fractions of total aromatic compounds occluded in the asphaltene is 3.9% of the 3 g of pyrene and 0.38% of the 3 g phenanthrene that were present in the total mixture in each experiment. Both PAHs were occluded much more by

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Figure 6.2 (a) Type A: Intraggregate occlusion of PAHs in asphaltenes in a toluene solution, with gray color representing asphaltenes and black indicating PAHs. (b) Type B: Extra-aggregate trapping and adsorption of PAHs during precipitation.
the intra-aggregate mechanism (Type A) than by extra-aggregate trapping and adsorption (Type B) during the precipitation step, by a factor of 14 for pyrene and 7 for phenanthrene.

Figure 6.3 Overall concentration of pyrene and phenanthrene occluded in asphaltene precipitates by intraaggregate mechanism (Type A) and extraaggregate trapping (Type B). In case of pyrene the error bars calculated from repeated experiments for Type A and 3 repeated experiments for Type B. For phenanthrene (Type A and B) the error bars calculated from three different subsampling of the same sample.

These data support the hypothesis that the asphaltene nanoaggregates in solution are porous and can be penetrated by aromatic compounds such as pyrene and phenanthrene. The more extensive occlusion of pyrene than phenanthrene suggests a chemical dependence with the interior of the asphaltene aggregates,
since simply filling a pore or fractal structure without any chemical interaction
would not give a higher selectivity for the larger molecule. These experimental
results are consistent with the model proposed by Gray et al. ¹ for the structure of
asphaltene nanoaggregates. The recruitment of aromatic compounds in aggregated
structures in binary donor-acceptor solutions was reported by Rizkov et al. ¹⁴, who
observed ratios as high as 15 mol of aromatic compound per mol of acceptor.

Figure 6.4 Small subsamples of precipitates showed extreme variability in local
concentration for both pyrene and phenanthrene (Phen.). The data are for 18 mg
subsamples of Type A precipitate. Note that the mean values in Figure 6.3 were
determined by analyzing the entire mass of precipitate, not from averaging of
subsample data presented in this figure.
Surprising variability in the measured concentrations was observed when small 18 mg subsamples of the precipitates were analyzed by simulated distillation. As the data of Figure 6.4 show, the pyrene and phenanthrene occlusion is not evenly distributed in asphaltene precipitates; instead the aromatic compounds are heterogeneously dispersed and trapped in the asphaltene precipitates. One explanation for this variability would be preferential co-precipitation of nanoaggregates of a particular type; in this case the nanoaggregates that contain the highest or lowest concentration of the PAHs appear to precipitate together. The presence of a highly heterogeneous population of nanoaggregates was suggested by Gray et al. ¹

These results also underscore the inherent failure of asphaltene precipitation to give conventional chemical separations based on chemical structure and solubility. Pyrene is clearly a simple aromatic compound, and based on its structure and solubility it should not precipitate in the n-pentane-toluene solutions used in this study. Rather, it should appear in the “aromatics” fraction of a saturates-aromatics-resins-asphaltenes (SARA) classification. While these data do not contradict the use of SARA data to develop empirical correlations, they clearly show that the components in asphaltene precipitates can appear as much because of physical interactions with other asphaltene components, i.e. matrix effects, as on intrinsic molecular structure or each component.
6.4 Conclusions

The experiments showed that the polynuclear aromatic hydrocarbons pyrene and phenanthrene were significantly occluded within asphaltene nanoaggregates, with concentrations 7-14 times higher than the trapping and adsorption on the outside of nanoaggregates during precipitation. These results are consistent with the presence of porous nanoaggregates, and possibly the formation of host-guest complexes.

6.5 References


7 SYNTHESIS, CONCLUSIONS AND RECOMMENDATIONS

7.1 General discussion and practical implication

Chapter 3 presented a new insight into the relationship between fouling and stability at temperatures of 450-600°C. Since most of the studies presented in the literature were done on lower-temperature fouling, the onset of asphaltene precipitation was the only point that was taken into consideration for fouling of crude oil blends. The results of Chapter 3 showed that fouling at moderate temperatures, which has coke formation as an inevitable part, will occur in any stability of asphaltene, even far from onset of flocculation. These results suggest that in process furnaces in refineries, the stability of asphaltene in the blend is very important, not just the onset of precipitation. If the blend of crude oils needed to pass through the furnace tube, or anywhere in the refinery with the same temperature as coker furnace tubes, the stability of blend should be maximized to have less coke formation and fouling. The data of Chapter 3 also showed that the coupling between corrosion and fouling was important, so that the deposition of coke form progressively less stable blends was accompanied by the release of more metal from the heat transfer surface. The coupling between the two processes was likely the thermal generation of hydrogen sulfide. The application of three commercial polysulfide used for fouling suppression was discussed in Chapter 4, in order to probe the role of sulfur compounds. The results showed and that the polysulfides with high sulfur content did enhance the
corrosion and fouling of the heat transfer surface, giving more release of metal into the fouling layer. Unfortunately, these organic polysulfides can also accelerate coke formation, which in turn would generate more hydrogen sulfide, so a clear definition of the mechanism was not achieved. Studies with direct addition of hydrogen sulfide would be necessary to fully define the coupling between metal corrosion and deposition of the asphaltenes.

The main precursor for coke formation at 450-600°C is asphaltenes. Therefore in Chapter 5 the attempt was to try disaggregating asphaltene completely, as a potential strategy to prevent coke formation. Unfortunately, this strategy was not successful. Given the importance of stability that was observed in Chapter 3, we cannot rule out the possibility that additives could be highly beneficial in suppressing fouling, by preventing the interaction of the asphaltene nano-aggregates with the metal of the heat transfer surface.

One of the properties of asphaltene that is a result of their nanoaggregation is porosity and the capability to occlude materials. This property checked for polynuclear aromatics (PAHs) in Chapter 6 and it was proved that PAHs can be entrapped in asphaltenes aggregates. The results confirmed the porosity of asphaltene aggregates and is consistent with the recent nanoaggregation model proposed by Gray et. al.¹ Having more evidence for any nanoaggregate model can help to understand the asphaltenes better, and can give tools for breaking the forces both within and between nano-aggregates to enable better control of the behavior of asphaltenes in heavy crude oils and bitumens.
7.2 Conclusions

1- The stability of asphaltenes in the oil blends controlled the fouling of 316 stainless steel wires at coker furnace conditions. The stability of asphaltenes, which was determined at room temperature with a S-value analyzer, decreased with the addition of paraffinic solvent to reach the onset of asphaltene precipitation. As the stability decreased the fouling factor and coke thickness increased. The coke texture changed from base oil case to the unstable case, becoming more porous when the stability of the blends reduced. Mesophase coke was present in the foulant structure, but very little was visible in the base oil case compared to the considerable amount in the unstable blend.

2- Fouling of 316 stainless steel wires at coker furnace conditions with and without the presence of 0.1 wt % of three polysulfide additives were examined. Additives with higher sulfur content produced more coke and iron sulfide comparing to the base oil fouling.

3- The visible spectra of asphaltene samples in toluene solution for wavelengths > 600 nm follow a $\lambda^{-4}$ dependence consistent with Rayleigh scattering. This fact provides evidence that the apparent absorption of visible light by asphaltenes from 600-800 nm is subject to a scattering mechanism. This sensitivity of absorbance of visible light to nano-aggregation and size for asphaltenes was employed to monitor the effects of various treatments (additives, sonication, and temperature) on the nano-aggregation state of asphaltenes in solution. The results indicate that asphaltenes could not be disaggregated completely by any of the additives tested, nor by sonication and heating for 1 hour.
at 200 °C. The nano-aggregate size was reduced very little when stronger solvents such as pyridine and quinoline were combined with ionic liquids.

4- The occlusion results showed that the polynuclear aromatic hydrocarbons pyrene and phenanthrene were significantly occluded within asphaltene nanoaggregates, with concentrations 7-14 times higher than the trapping and adsorption on the outside of nanoaggregates during precipitation. These results are consistent with the presence of porous nanoaggregates, and possibly the formation of host-guest complexes.

7.3 Recommendations for future work

1- Determination of the stability of oil blends at high temperatures (same temperature as coker furnace tubes) is recommended to confirm the room temperature stability relation with fouling. Designing an experiment for finding the actual data rather than extrapolation of the low temperature results can give a much accurate outcome.

2- The iron sulfide formation is coupled with coke formation in fouling phenomenon at furnace tube temperatures. Effect of iron sulfide in accelerating coke fouling layer formation independent of other factors is not well understood because organic-phase reactions could also account for that. Direct addition of hydrogen sulfide would help to evaluate this effect.
3- Effect of heating and cooling back to the same temperature of asphaltene solutions in toluene on visible-light absorbance of asphaltene needs more investigation. Is there a real hysteresis, due to the effect of solvent swelling at high temperatures and trapping the molecules on the asphaltenes nanoaggregates?

4- The occlusion of other PAHs in asphaltene aggregates, the effect of size of PAHs on entrapment percentage, and the role of time and concentration of solvents should be studied. Also different asphaltenes from different origins can be tested to investigate if there is any possibility to assign any average porosity number to different asphaltenes. In addition, the properties of asphaltenes (such as solubility and absorption) which contain entrapped PAHs can be compared to the pure asphaltenes.

5- The occlusion of pyrene much more than phenanthrene in asphaltene nano-aggregates suggested chemical selectivity. This type of experiment can be expended to other probe compounds to better understand the factors that stabilize the nano-aggregates in the crude oil.

7.4 Reference

APPENDIX A: UNSTABLE BLEND UNDER THE OPTICAL MICROSCOPE

The unstable blend of the crude oil and the diluent described in chapter 3 ($v_{\text{diluent}}=0.57$), was observed under the optical microscope after 15 minutes (Figure A.1) and 70 hours (Figure A.2). The asphaltene precipitates (the dark dots in Figure A.1) were observed throughout the entire oil medium and during the time these dots flocculated more and convert to the bigger agglomerates shown in Figure A.2.

Figure A.1 Unstable blend ($v_{\text{diluent}}=0.57$) under the optical microscope after 15 minutes
Figure A.2 Unstable blend ($v_{\text{diluent}}=0.57$) under the optical microscope after 70 hours