The Investigation of Asphaltene-Naphthenic Acid and Asphaltene-Surface Interactions

David Tristan Heaps
University of Southern Mississippi

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THE INVESTIGATION OF ASPHALTENE-NAPHTHENIC ACID
AND ASPHALTENE-SURFACE INTERACTIONS

by

David Tristan Heaps

Abstract of a Dissertation
Submitted to the Graduate School
Of the University of Southern Mississippi
In Partial Fulfillment of the Requirements
For the Degree of Doctor of Philosophy

December 2011
ABSTRACT

THE INVESTIGATION OF ASPHALTENE-NAPHTHENIC ACID AND ASPHALTENE-SURFACE INTERACTIONS

by David Tristan Heaps

December 2011

Asphaltenes represent a ubiquitous problem in the oil industry due to their adverse effects on recovery, production, and processing equipment. These problems have affected oil companies throughout the world, resulting in significant financial losses. In order to expand the existing body of knowledge related to asphaltenes, we have examined how the presence of naphthenic acids contributes to the particle aggregation and sedimentation behavior of asphaltene suspensions as well as how the physics and chemistry of a substrate affect asphaltene adsorption/deposition.

The flocculation of asphaltenes in the presence of naphthenic acids was investigated using dynamic light scattering (DLS), near-infrared spectroscopy (NIR), and molecular modeling calculations. In these studies the flocculation of asphaltenes was monitored as function of added precipitant to model asphaltene solutions alone and in the presence of select naphthenic acids. A delay in the onset of flocculation was observed in naphthenic acid-containing samples by DLS and NIR, showing good agreement among the two light-scattering techniques. Additionally, molecular modeling calculations supported the experimental results and allowed for the determination of specific structure property relationships among constituents.
A quartz crystal microbalance with dissipation measurements (QCM-D) was implemented in order to probe how the physics and chemistry of a substrate affected the adhesion of asphaltene particles. In this work SiO$_2$-coated QCM-D sensor crystals were chemically modified with different organosilane compounds, and the degree of asphaltene adsorption on these surfaces was examined. The derivatized sensor surfaces were characterized with solvent contact angle measurements and surface energy calculations using well-established methods. Contact angle measurements showed that the derivatized surfaces varied in their degree of hydrophilicity and supported surface functionalization. Additionally, surface energy calculations varied over a wide range of values. The QCM-D experiments revealed that all of the surfaces adsorb asphaltenes roughly to the same extent with the exception of the amine derivatized surface. In the case of the amine surface, a greater asphaltene mass was adsorbed and a distinctly different adsorption profile was observed compared to the other surfaces investigated. It is believed that there is a possible reaction taking place between the primary amine on the sensor surface and an activated carbonyl group on the asphaltene molecule. Dissipation shifts were small throughout all of the QCM-D experiments suggestive of a rigidly attached layer of asphaltenes on the substrate. Maximum rates of asphaltene adsorption were calculated on each surface; however, rates were similar among the surfaces studied with the exception of the carboxylic acid derivatized surface. The carboxylic acid derivatized surface adsorbed asphaltenes at a greater rate which was expected due to the findings from the first phase of this research effort describing the strong interactions between asphaltenes and organic acids. Plots of the adsorbed asphaltene mass versus the
calculated surface energy for each surface by each method were generated; however, the plots did not reveal a correlation between the surface energy and mass of asphaltenes adsorbed.
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A Dissertation
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Approved:

Janice Paige Buchanan
Director

James Wynne

Douglas Masterson

Wujian Miao

Sarah Morgan

Susan A. Siltanen
Dean of the Graduate School

December 2011
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# TABLE OF CONTENTS

ABSTRACT........................................................................................................................................... ii

ACKNOWLEDGMENTS..................................................................................................................... v

LIST OF TABLES.......................................................................................................................... vii

LIST OF ILLUSTRATIONS.......................................................................................................... viii

CHAPTER

I. BACKGROUND AND SIGNIFICANCE.................................................................................... 1

II. INVESTIGATION OF THE PRECIPITATION BEHAVIOR OF ASPHALTENES IN THE PRESENCE OF NAPHTHENIC ACIDS USING LIGHT SCATTERING AND MOLECULAR MODELING TECHNIQUES................................................................................. 10

Abstract
Introduction
Materials and Methods
Results and Discussion
Conclusions

III. THE INVESTIGATION OF ASPHALTENE ADSORPTION ON SURFACES USING THE QUARTZ CRYSTAL MICROBALANCE WITH DISSIPATION (QCM-D) TECHNIQUE................................................................. 41

Abstract
Introduction
Materials and Methods
Results and Discussion
Conclusions

IV. SUMMING IT ALL UP.......................................................................................................... 100

Summary of Conclusions

BIBLIOGRAPHY.......................................................................................................................... 106
LIST OF TABLES

Table

1. Interaction Energy Values Calculated Between 5β-Cholanic Acid (isomer-2) and Asphaltene........................................................................................................34
2. Interaction Energy Values Calculated Between Methyl Abietate and Asphaltene........................................................................................................35
3. Interaction Energy Values Calculated Between Reduced Methyl Abietate and Asphaltene..........................................................................................36
4. Interaction Energy Values Calculated Between 5β-Cholanic Acid (isomer-1) and Asphaltene....................................................................................37
5. Interaction Energy Values Calculated Between 5β-Cholanic Acid-3-one and Asphaltene.........................................................................................38
6. Average Interaction Energy Values Calculated Between the Various Naphthenic Acids and Asphaltenes....................................................................39
7. Contact Angle Measurements of Water on the SiO$_2$, TiO$_x$, Al$_2$O$_3$, and FeO$_x$ Surfaces........................................................................................................56
8. Relative Absorbance at 2924 cm$^{-1}$ for Asphaltene Coated Particles........63
9. Contact Angle Measurements of Water on the Derivatized Surfaces........77
10. The Calculated Surface Energy Values for Each Surface by the Zisman, Geometric Mean, and Acid-Base Methods..............................................82
11. The Calculated Adsorbed Masses for 50 and 100 ppm Asphaltene Samples on the SiO$_2$ and Methyl Surfaces.................................................................89
12. Summary of Adsorbed Mass, Maximum Rate of Adsorption, and Dissipation Shifts for All Surfaces Examined...........................................................92
13. Asphaltene Mass Desorbed From Each Surface After 30 Minutes of Rinsing with Toluene.......................................................................................98
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>SARA Solvent Fractionation Procedure for Crude Oils</td>
<td>2</td>
</tr>
<tr>
<td>2.</td>
<td>The “Long Diagram” Showing That N-Heptane and N-Pentane Separated Asphaltenes are the Highest Molecular Weight, Most Polar, and Most Aromatic Species of Crude Oil</td>
<td>4</td>
</tr>
<tr>
<td>3.</td>
<td>Proposed Structure of an Asphaltenne</td>
<td>5</td>
</tr>
<tr>
<td>4.</td>
<td>Pipeline Blockage Resulting from Asphaltenne Deposition: The “Cholesterol of Petroleum”</td>
<td>7</td>
</tr>
<tr>
<td>5.</td>
<td>Examples of Naphthenic Acid Structures</td>
<td>8</td>
</tr>
<tr>
<td>6.</td>
<td>Naphthenic acid structures: 4-(10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoic acid (5β-cholanic acid), 4-(10,13-dimethyl-3-oxohexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoic acid (5β-cholanic acid-3-one), methyl 7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,4b,5,6,10,10a-decahydrophenanthrene-1-carboxylate (methyl abietate), methyl 7-isopropyl-1,4a-dimethyltetradecahydrophenanthrene-1-carboxylate (hydrogenated methyl abietate)</td>
<td>15</td>
</tr>
<tr>
<td>7.</td>
<td>Schematic Showing How the Interaction Energy is Calculated Between Asphaltenes and Naphthenic Acids</td>
<td>20</td>
</tr>
<tr>
<td>8.</td>
<td>TEM Image of Shell Asphaltenes and Plot of Asphaltenene Particles Size by Dynamic Light Scattering; Average Particle Size by DLS and TEM Were 9 ± 2 nm and 10 ± 2 nm</td>
<td>22</td>
</tr>
<tr>
<td>9.</td>
<td>Plot of the Absolute Value of the Interaction Energy Versus the Rotation Angle for an Asphaltenene Dimer and the Structure Corresponding to the Most Favorable Interaction Energy at 135°</td>
<td>23</td>
</tr>
<tr>
<td>10.</td>
<td>DLS Particle Size as a Function of Volume% of N-Heptane Precipitant Added to Toluene Dispersions of Asphaltenes in the Presence of Select Naphthenic Acids</td>
<td>24</td>
</tr>
<tr>
<td>11.</td>
<td>DLS Particle Size as a Function of Volume% of N-Heptane Precipitant Added Fit to Non-Linear Equation, y = a +be^x; Correlation Coefficients Ranged from 0.86 to 0.98</td>
<td>25</td>
</tr>
</tbody>
</table>
12. DLS Particle Size as a Function of Volume% of N-Heptane Precipitant Added to Toluene Dispersions of Hydrogenated Methyl Abietate, Showing the Average Reproducibility Among Experiments

13. NIR Absorbance Spectrum of Asphaltene Suspension in Toluene

14. NIR Transmission Values as a Function of Volume% of N-Heptane Precipitant Added to Toluene Dispersions of Asphaltenes in the Presence of Select Naphthenic Acids

15. Molecular Modeling Results Describing Minimized Interaction Geometries Between Asphaltenes and Naphthenic Acids (a) 5β-Cholanic Acid, Interaction Distance is 3.99 Å; (b) Methyl Abietate, 4.10 Å; (c) Hydrogenated Methyl Abietate, 4.58 Å; (d) 5β-Cholanic Acid-3-One

16. Sites for Hydrogen Bonding for Naphthenic Acids on the Asphaltene Molecule

17. Naphthenic Acid Structures Used in the Molecular Modeling Calculations

18. Image of the VCA Optima from AST Products

19. Organosilanes Utilized in Surface Derivatization Reactions. (a) 3-aminopropyltrimethoxysilane, (b) benzylidimethylchlorosilane, (c) trimethylechlorosilane, (d) triethoxysilylpropyl succinic anhydride, and (e) heptadecafluoro-1,1,2,2-tetrahydrodecyldimethylchlorosilane

20. Reaction Schemes for the Functionalization of SiO$_2$-Coated QCM Sensor Crystals with Chlorosilanes (a-c), 3-aminopropyltrimethoxysilane (d), and triethoxysilylpropyl succinic anhydride (e)

21. Young’s Relation. The Contact Angle of a Liquid Drop on a Solid Surface Under the Influence of the Solid-Vapor Interfacial Tension ($\gamma_{sv}$), Solid-Liquid Interfacial Tension ($\gamma_{sl}$), and the Liquid-Vapor Interfacial Tension ($\gamma_{lv}$)

22. Representative Zisman Plot for the Fluoro Surface. The Calculated Surface Energy was Found to be -1.21 dyne/cm

23. A Representative QCM-D Experiment Plot for 50 ppm Asphaltene Sample on the Methyl Derivatized Surface

24. A QCM-D Experiment Conducted Using a 100 ppm Asphaltene Sample in Toluene on the Acid Modified SiO$_2$ Surface. Figure Shows the Points Where the Frequency Values were Recorded for Calculations Surface
25. A Representative QCM-D Experiment Using a 100 ppm Asphaltene Sample in Toluene on the Amine Derivatized Surface. Frequency is Plotted on the Left (Y1) Axis, Dissipation is Plotted on the Right (Y2) Axis, and Time (sec) is Plotted on the X-Axis..............................................................................................................88

26. An Example of a Derivative Plot Generated From the QCM-D Experiment Using a 100 ppm Asphaltene Sample in Toluene on the Acid Derivatized Surface........90

27. Plots of the Adsorbed Asphaltene Mass on Each Surface Versus Surface Energy Calculated for Each Surface by (a) Zisman Method, (b) Geometric Mean Method, and (c) Acid-Base Method..............................................................................................................94

28. Plots of the Adsorbed Asphaltene Mass on Each Surface Except for the Amine Surface Versus Surface Energy Calculated by (a) Zisman Method, (b) Geometric Mean Method, and (c) Acid-Base Method............................................................96
CHAPTER I
BACKGROUND AND SIGNIFICANCE

Petroleum exists as an expansive collection of hydrocarbon compounds that are present as liquids, gasses, and solids, along with others that contain different amounts of nitrogen, oxygen, sulfur, as well as trace amounts of iron, nickel, and vanadium.\(^1\)

Petroleum is found all over the world in porous and permeable sedimentary rock deposits through the earth’s crust.\(^1\) Crude petroleum has little value, but refined petroleum provides liquid fuels, solvents, lubricants, and many other valuable products.\(^1\)

Additionally, crude oil consists primarily as an assortment of compounds that have different boiling temperatures, which can be separated into different fractions via distillation.\(^1\) From this definition, it is obvious that the term petroleum or crude oil includes an extensive variety of materials which differ in volatility, specific gravity, and viscosity.\(^1\) The compounds that contain metals generally reside in highly viscous crude oils in very small amounts (ppm range), and the presence of these metal compounds can have adverse effects on the processing and production of these crude oils.\(^1\)

Due to the fact that crude oil composition can fluctuate with the location, age, and depth of the field, it is important to classify crude oils based on their physical composition.\(^1\) One of the main techniques utilized in determining the physical composition of petroleum is elemental analysis. Although the molecular composition of petroleum varies from source to source, the amount of elements present is somewhat constant: carbon 83-87\%, hydrogen 10-14\%, nitrogen 0.1-2\%, oxygen 0.05-1.5\%, sulfur 0.05-6\%, metals <1000ppm.\(^1\) Another technique used to characterize the physical composition of petroleum is solvent fractionation. Solvents induce separation between
the constituents of crude oil based on differences in their molecular weight, aromatic nature, and polarity. One of the main solvent fractionation methods involves the separation of crude oil into four basic fractions: saturates, aromatics, resins, and asphaltenes (SARA). In this procedure the asphaltene fraction is precipitated from crude oil with n-heptane, the resin fraction is precipitated with acetone, and the saturates fraction is precipitated with dimethylformamide. This procedure is summarized in Figure 1. After all compounds have been isolated, many techniques can be used to further characterize the physical composition of these fractions. Some of these techniques include $^1$H Nuclear Magnetic Resonance (NMR), Infrared Spectroscopy (IR), and Mass Spectrometry (MS).

![Figure 1. SARA solvent fractionation procedure for crude oil.](image)

Petroleum is the most frequently used source of liquid fuels. However, due to the depletion of earth’s non-renewable petroleum resources, there is an increasing demand for new sources of liquid fuels. In order to compensate, petroleum refineries are
producing light oil fractions from increasingly heavy crude oils. These heavy crude oils are different from conventional petroleum, in that, they are much more viscous making recovery operations very difficult. Additionally, these heavy crude oils generally consist of various high molecular weight species which are present as solid particles suspended in the crude oil and may precipitate within the pipeline walls and form sediments. The sediments have the potential to cause pipeline blockages, which lead to substantial economic loss to oil production operations. Of these compounds, asphaltenes and naphthenic acids are credited as the main contributors to the sedimentation and corrosion in oil production equipment.

Asphaltenes constitute a group of complex molecules that exist in crude oil along with other materials, such as resins, mercaptans, paraffin/waxes, aromatic hydrocarbons, and organometallic compounds. They are the heaviest, most polar, most aromatic fraction of crude oil, and therefore are also the non-volatile, highest molecular weight fraction of crude oil. This is illustrated in Figure 2, which is known as a “Long diagram”.
Figure 2. The “Long diagram” showing that n-heptane and n-pentane separated asphaltenes are the highest molecular weight, most polar, and most aromatic species of crude oil.\textsuperscript{6}

Due to their complex nature, asphaltenes cannot be defined by a molecular structure\textsuperscript{7} or grouped into a specific class of compounds\textsuperscript{8}, although in general they are accepted as basic components of crude. Asphaltenes are defined and isolated on the basis of their solubility behavior. They are the oil fraction that is not soluble in low-boiling point, aliphatic solvents like n-heptane and soluble in aromatic solvents such as toluene.\textsuperscript{1} Since the structure and properties of asphaltenes mainly depend on the source of the crude oil, it is very difficult to identify the exact structure of asphaltenes.\textsuperscript{9,10} Nonetheless, several proposed structures exist, one of which can be seen in Figure 3.
Researchers all seem to agree that asphaltenes exist as a core of stacked, polyaromatic rings connected at their periphery by aliphatic and naphthenic ring systems. The core of stacked aromatic rings also contain oxygen, nitrogen, and sulfur atoms, as well as metal complexes of nickel and vanadium. Additionally, asphaltenes primarily consist of carbon and hydrogen with a ratio of 1:1.1 and approximately 40% of the carbon exists in aromatic systems. Furthermore, approximately 90% of the hydrogen exists substituted on saturated carbons as methyl and methylene groups. The asphaltene molecules also possess oxygen (0.5-7%), nitrogen (2-5%), and sulfur (0.3-10.3%) heteroatoms in different weight percents. Due to the presence of these nitrogen, oxygen, and sulfur heteroatoms, asphaltenes are considered the basic organic components of crude oils.

Asphaltenes are a major concern for the oil and gas industry because of their adverse effects on production, storage, and refining equipment. These problems have
affected oil companies around the world, resulting in large economic losses.\textsuperscript{22-24}

Asphaltene molecules/aggregates tend to associate and precipitate from suspension as a result of many factors such as a change in the temperature, pressure, composition, etc. Asphaltenes are responsible for the heavy organic deposits that form in oil reservoirs, oil wells, pipelines, and in the equipment used for production and processing. In fact, Kokal and Sayegh\textsuperscript{11,25} referred to asphaltenes as the “cholesterol of petroleum”, because their deposition on pipeline surfaces reduces crude oil flow. An example of the arterial blockage due to asphaltene deposition can be seen in Figure 4. Once formed, the deposit slowly thickens, further reducing oil flow, and results in substantial loss in revenue.\textsuperscript{11} Remediating these deposits is a very costly process, for example, it is estimated that removing a deposit can cost anywhere from $0.5 MM U.S. for land operations up to $3 MM U.S. for offshore operations.\textsuperscript{11} In addition, the average production in a day for an oil operation is around 40 MBOD (thousand barrels of oil per day), which translates to approximately $1.2 MM U.S. in lost production per day.\textsuperscript{11}
It is well known that several types of carboxylic acids are present in crude oils. These organic acids are referred to by the collective term naphthenic acids. Found mainly in immature, heavy crude oils, these compounds are believed to be the products of microorganism biodegradation. Naphthenic acids are known to exist in crude oil as a mixture of alkyl-substituted cycloaliphatic and acyclic carboxylic acids, with a broad range of molecular weights and structures. Naphthenic acids are considered to be part of the resin fraction of crude oil and may act as surfactants to stabilize asphaltenes. Some of the structures that constitute this fraction can be seen in Figure 5. Understanding the role that naphthenic acids/resins play in peptizing asphaltenes is vital to remediating the problems experienced while recovering, processing, and refining today’s heavy crudes.
Figure 5. Examples of naphthenic acid structures.$^{28}$

Much of the published literature focuses on the colloidal stability of asphaltenes with respect to the stabilizing effects of resins. However, to date, investigations of the interactions between asphaltenes and naphthenic acids have been scarcely studied.$^{29-31}$ Of those investigations there has been no evidence provided of the type or extent of interactions which have been correlated to structure property relationships. Therefore, the available literature has shown that interactions do exist between naphthenic acids and asphaltenes. However, there is minimal evidence to characterize the extent of
interactions or what the short and long term affects the presence of naphthenic acids have on asphaltene dispersions. The motivation behind this work is to identify the role of the various functional groups responsible for the interactions between naphthenic acids and asphaltenes and to determine characteristics of a surface coating for the inner surfaces of pipelines which can deter asphaltene deposition.
CHAPTER II

INVESTIGATION OF THE PRECIPITATION BEHAVIOR OF ASPHALTENES IN THE PRESENCE OF NAPHTHENIC ACIDS USING LIGHT SCATTERING AND MOLECULAR MODELING TECHNIQUES

Abstract

A delay in the onset of flocculation was observed for asphaltenes in the presence of several naphthenic acids: methyl abietate, hydrogenated methyl abietate, 5β-cholanic acid and 5β-cholanic acid-3-one. This flocculation behavior was monitored as a function of added precipitant (n-heptane) to solutions of suspended asphaltenes and naphthenic acids in model solutions of toluene:n-heptane, using a combination of dynamic light scattering (DLS) and near-infrared spectroscopic (NIR) techniques. DLS and NIR show very good correlation in indentifying the onsets of flocculation, which varied among the series of naphthenic acids. Specific interaction energies and equilibrium intermolecular distances of asphaltenes and naphthenic acids were calculated using molecular mechanics. The results from molecular mechanics calculations support the experimental results of the titrations, and structure property relationships were defined.

Structure/property relationships were established for naphthenic acids, defining the relative contributions and importance of various functional groups: C=C, C=O, COOR, and COOH. The additive effects of naphthenic acids, defined by an increase in precipitation onset, increased in the order of 5β-cholanic acid-3-one < hydrogenated methyl abietate < methyl abietate < 5β-cholanic acid, with experiments containing 5β-cholanic acid-3-one revealing unexpected and interesting results.
Introduction

Although several studies exist on the self-association and aggregation behavior of asphaltenes, the interaction of asphaltenes and naphthenic acids, the acidic and basic components of crude samples, are largely overlooked. In an earlier study, Gonzalez and Middea\textsuperscript{32} described the effects of adding different peptizing agents to organic dispersions of asphaltenes in heptane and toluene. The authors determined the effectiveness of the peptizing agents at dispersing asphaltenes by adding different concentrations of amphiphiles to dispersions of asphaltenes in heptane. After allowing the solutions to equilibrate, the samples were centrifuged, and UV/VIS absorbance values were measured at 400 nm, from which the remaining soluble concentration of asphaltenes was calculated. The effectiveness of the amphiphiles at dispersing the asphaltenes was correlated to the amount of asphaltenes remaining in the heptane, which is an asphaltene nonsolvent. From the results the authors were able to conclude that nonyl phenol was the most effective peptizing agent. The effectiveness of nonyl phenol at preventing asphaltene precipitation was also studied by adding heptane to dispersions of asphaltenes in toluene containing different concentrations of nonyl phenol. The effectiveness was determined in the same manner as the peptization tests. In these experiments it was found that without additive present asphaltene precipitation occurred at 40 volume % of heptane; however, when nonyl phenol was present at 0.5 volume % precipitation did not occur until 60%. Also, when the concentration of nonyl phenol was increased to 1.0 volume % no precipitation was observed. From these results the authors proposed that the ability of the peptizing agent to stabilize asphaltenes arose from the interactions between the polar groups of the peptizing agent and the polar groups on the asphaltene
molecule. In addition to these dipole-dipole interactions, the presence of π electrons and hydrogen bonding are discussed as contributors to the stabilization of asphaltene suspensions. Another study of importance was conducted by Chang and Fogler, who reported on the stabilizing effects of alkyl benzene derivatives on asphaltenes. In this work the authors examine how changes in chemical structure lead to differences in the amphiphile’s ability to produce stabilized asphaltenes, as well as, the strength of the asphaltene-amphiphile interaction using UV-Vis and FTIR spectroscopy. In the studies that examined how chemical structure influenced the ability of the amphiphiles to stabilize asphaltenes, samples were prepared by mixing solutions of asphaltenes, amphiphiles, and alkane solvents at different concentrations. After the solutions reached equilibrium, they were filtered, and asphaltene concentrations were determined from UV-Vis absorbance readings. The results of these experiments show that p-dodecylbenzenesulfonic acid (DBSA), the most polar of the amphiphiles investigated, was the most effective stabilizer. Investigating the strength of the asphaltene-amphiphile interaction was accomplished by measuring the adsorption of amphiphiles from alkane solutions to asphaltene surfaces. After mixing solutions of asphaltenes and amphiphiles and equilibrating, the samples were centrifuged. Then, the concentrations of the amphiphiles in the supernatant were measured via FTIR. Infrared adsorption peaks specific to the amphiphiles were used to quantify the amount of amphiphiles remaining in the supernatant. Therefore, the strength of the asphaltene-amphiphile interaction was correlated to a decrease in the peak intensities resulting from the disappearance of amphiphiles from solution and their inferred adsorption onto asphaltenes and asphaltene aggregates. The same trend was observed here as in the previous study, with DBSA
having the highest adsorption on asphaltene surfaces. The authors indicate that the polarity of the amphiphile’s head group and the alkyl tail length are the controlling factors that dictate the effectiveness of the amphiphiles in dispersing asphaltenes. Auflem et al.\textsuperscript{29} studied the dispersive effects of several naphthenic acids on asphaltenes as a function of time and amphiphile concentration using Near-IR spectroscopy (NIR). The researchers in this study monitored the dissolution of asphaltene aggregates by monitoring asphaltene adsorption spectra in the wavelength region of 1100–2200 nm. In particular, the researchers monitored the transmittance values at 1600 nm of asphaltene dispersions containing various concentrations of additives. The transmittance values were then converted into optical density and were plotted as a function of time. The efficiency of the additives to solubilize asphaltenes was based on the idea that as the aggregates are dissolved there is a subsequent decrease in light scattered from the sample and therefore a decrease in the optical density. This study was based on earlier assumptions that naphthenic acids and asphaltenes would associate through hydrogen bonding, acid-base, and charge transfer interactions, which was supported by the observation that decahydro-1-naphthalenepentanoic acid was the most efficient in stabilizing the asphaltenes.

The work of Ostuland et al.,\textsuperscript{30} using the Pulsed Field Gradient Spin Echo (PFG-SE) NMR technique to examine samples of asphaltenes after addition of a naphthenic acid, suggests that asphaltenes and naphthenic acids do associate and that this association is influenced by asphaltene concentration and asphaltene type. In a two-part study by Varadaraj and Brons,\textsuperscript{35,36} concerning the oil-water interfacial properties of extracted crude oil asphaltenes, much of the interaction at the interface was contributed to the
presence of surface-active naphthenic acids that were coincidently extracted with the asphaltenes. A strong acid-base interaction was found to exist between the nitrogen-containing asphaltenes and the acid-containing naphthenic acids, which produced complexes dominating the chemistry of the interfacial region.

Our research interests lie in understanding how the presence of naphthenic acids may contribute to the particle aggregation and sedimentation behavior of asphaltene suspensions. In this effort, the aggregation and sedimentation behavior of asphaltenes in the presence of select naphthenic acids – methyl abiate, hydrogenated methyl abiate, 5β-cholic acid and 5β-cholic acid-3-one, (Figure 6) – are investigated using dynamic light scattering (DLS), near-infrared spectroscopy (NIR), and molecular mechanics. Aggregation behavior of asphaltenes is monitored as a function of added precipitant (n-heptane) to solutions of suspended asphaltenes and naphthenic acids in model solutions of toluene:n-heptane, and onsets of flocculation are determined. Flocculation onset values have been determined using DLS and NIR techniques; however, there is limited information on the correlation of these two techniques. Our group’s efforts have focused on the study of specific interactions among asphaltenes and naphthenic acids using experimentation, supported by molecular modeling.
Figure 6. Naphthenic acid structures: 4-(10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoic acid (5β-cholanic acid), 4-(10,13-dimethyl-3-oxohexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoic acid (5β-cholanic acid-3-one), methyl 7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,4b,5,6,10,10a-decahydrophenanthrene-1-carboxylate (methyl abietate), methyl 7-isopropyl-1,4a-dimethyltetradecahydrophenanthrene-1-carboxylate (hydrogenated methyl abietate).

Materials and Methods

Materials

Crude oil was generously provided by Shell Oil and was the product of a Gulf of Mexico reservoir. N-heptane (HPLC grade, 99%) was purchased from Fisher and used as received. Toluene (HPLC grade, 99%) was purchased from Sigma-Aldrich and used as received. Methyl abietate was purchased from Sigma-Aldrich Library of Rare Chemicals and used as received. 5β-cholanic acid and 5β-cholanic acid-3-one were purchased from Sigma-Aldrich and used as received. Anhydrous ethanol (99.5%, 200 proof) was purchased from Sigma-Aldrich and used as received. Palladium 10 wt% on activated
carbon was purchased from Sigma-Aldrich and used as received. Dichloromethane (HPLC grade, 99%) was purchased from Sigma-Aldrich and used as received.

**Asphaltene isolation**

Asphaltenes were isolated from crude oil samples provided by Shell using a modified n-heptane method. A solution of 1:1 Shell crude oil:toluene was prepared and sonicated for 10 minutes. N-heptane was added to this solution in a 40:1 ratio, and the sample was sonicated for 30 minutes followed by gentle stirring for 24 hours in the dark. Precipitated asphaltenes were collected via reduced pressure filtration using a 0.2 µm PTFE membrane filter. The collected asphaltenes were then washed three times with ~400 mL, 60°C n-heptane. Lastly, residual solvents were removed under reduced pressure in a room temperature vacuum oven for 24 hours prior to sample use. Isolated asphaltene samples were characterized using gel permeation chromatography (GPC) and were found to possess average molecular weights ranging from 500-1000 g/mol. Elemental analysis gave C% 82.52, H% 7.07, N% 1.28, O% 2.00, and S% 1.81.

**Transmission electron microscopy (TEM) of asphaltenes**

TEM micrographs were taken on a Zeiss High-Resolution Electron Microscope EM 10C/CR operated at 50 kV at a magnification of 140k. Ted Pella Inc. carbon type-B, 200 mesh copper grids were used for TEM sampling. TEM grids were prepared further diluting a 0.25 wt % asphaltene sample in toluene and allowing one drop to evaporate from the grid surface.

**Asphaltene onset of flocculation determination via DLS**

A 12.5 mg sample of asphaltenes was suspended in a solution of 60:40 toluene:n-heptane in the presence of 125 mg of naphthenic acid. Solutions were prepared for each
naphthenic acid. Subsequent titrations were performed on asphaltene solutions of 45:55 toluene:n-heptane due to the fact that no change in particle size was detected up to 55 vol% n-heptane. Hydrogenated methyl abietate was prepared from methyl abietate by a modified hydrogenation procedure from Mori, A. et al.\textsuperscript{37} Samples were titrated with n-heptane over a period of 8.3 min to introduce 0.5 mL. The temperature was held constant at 24°C by a circulating chiller. After adding n-heptane, the solutions were stirred in the dark for 30 min and then allowed to sit for 5 min before measurement. Particle size measurements were conducted utilizing the Dynamic Light Scattering technique. The instrumentation used was a Microtrac Nanotrac Ultra equipped with an external probe. Particle size ranges are calculated using the power spectrum generated from Doppler shifted frequencies of scattered light from suspended particles under Brownian motion. Each data point is the computer average of 3 scans, and then 3 data points are collected for each sample (equals to 9 actual interrogations of the sample). The particles were treated as absorbing and irregular shaped. The refractive index used for toluene was 1.50 with a density of 0.590 at 20°C and 0.526 at 30°C. Measurement capabilities extend from 0.8 – 6500 nm, using a 780 nm laser diode and an interrogation angle of 180°.

Experiments were performed in triplicate.

\textit{Asphaltene onset of flocculation determination via NIR}

The procedure for these experiments was adopted from Auflem et al.\textsuperscript{29} and modified. Asphaltene/naphthenic acid suspensions were prepared as previously described and the titration with n-heptane was conducted in the same manner as in the DLS experiments. Before beginning the titration series, a NIR spectrum was collected from 1100 nm to 2200 nm on a 45:55 n-heptane:toluene solution of asphaltene:naphthenic acid
in order to find a wavelength where absorption from the hydrocarbon components was minimal and to determine an initial transmittance value. After each addition cycle in the titration, transmittance values were recorded at 1600 nm. Transmittance values were plotted as a function of added precipitant volume percentage in order to determine the onset of flocculation. A Varian Carey 500 UV-Vis-NIR spectrophotometer was used with a 1 mm path length quartz cuvette.

*Calculation of asphaltene/naphthenic acid interaction energies*

Asphaltene/naphthenic acid interaction energies were calculated using a molecular mechanics program Discover (Accelrys Materials Studio). Interfacial binding characteristics of asphaltenes and their interactions with naphthenic acids were investigated using molecular mechanics and molecular dynamics simulations using the CVFF forcefield. A representative structure of asphaltenes was obtained from published sources.\textsuperscript{11,38} An atom based summation method was used with a non-bonded interactions cutoff set to 15.5 Å, accompanied by a spline width of 5.0 Å and a buffer width of 2.0 Å. The models were first minimized using the steepest descent convergence method, followed by a conjugate gradient method, and Newton methods until the convergence reaches $1.0 \times 10^{-5}$ kcal/mol/Å. The optimized structure for asphaltene was obtained through a series of minimizations originating from multiple starting point geometries. The five lowest energy conformations were selected followed by additional minimization using molecular dynamics to produce a preferred structure. For the construction of the representative asphaltene dimer, a docking process was used. As the spatial disposition between the two asphaltene molecules involved was changed, a new interaction energy
was calculated. The absolute value of the interaction energies were plotted against rotation angle, therefore stronger interactions are represented by larger values.

The interaction between the asphaltene and a naphthenic acid molecule comes from the electrostatic and van der Waals forces in the molecular system. Generally, the interaction energy is estimated from the energy difference ($\Delta E$) between the total energy of the composite and the sum of the energies of individual molecules as shown in Equation 1.

$$E_{\text{int}} = \Delta E = E_{\text{(total)}} - \left( E_{\text{(asphaltene)}} + E_{\text{(naphthenic acid)}} \right)$$

$E_{\text{(total)}}$ is the total energy of the composite, $E_{\text{(asphaltene)}}$ is the energy of the asphaltene without the naphthenic acid, and $E_{\text{(naphthenic acid)}}$ is the energy of the naphthenic acid without the asphaltene. In other words the interaction energy can be calculated as the difference between the minimum energy and the energy at the infinite separation of the asphaltene and naphthenic acid. Since the asphaltene surface is discontinuous and contains different functional groups, interaction energies were calculated at more than one location on the asphaltene surface. In this approach, multiple starting point orientations (> 15) were considered for each calculation, to reduce the probability of finding a false minimized relative orientation. Therefore, five interaction energy values were selected for each naphthenic acid, Figure 7.39 These calculations were conducted by Dr. Praveen Madasu.
Figure 7. Schematic showing how the interaction energy is calculated for asphaltenes and naphthenic acids. \(^{39}\)

In addition to the molecular mechanics calculations to determine interaction energies and the corresponding minimized energy geometries, density functional theory calculations \(^{40,41}\) were performed by Dr. David Magers on the four naphthenic acids considered in this study to estimate their dipole moments. The functional employed is the B3LYP hybrid functional comprising Becke’s three parameter functional \(^{42}\) using the LYP correlation functional of Lee, Yang, and Parr. \(^{43}\) The basis set used is the augmented correlation consistent basis set aug-cc-pVTZ created by Dunning and co-workers. \(^{44,45}\) Before it is augmented, this basis set uses a triple-\(\zeta\) description for valence electrons and a single-\(\zeta\) description for core electrons. Its polarization functions consist of two \(d\) and one \(f\) function for each carbon and oxygen, and two \(p\) and one \(d\) function for each hydrogen. When augmented, diffuse \(s, p, d,\) and \(f\) functions are added to every non-hydrogen atom, and diffuse \(s, p,\) and \(d\) functions are added to each hydrogen. For calculations on 5\(\beta\)-cholanic acid-3-one, the largest naphthenic acid considered here, this
basis set results in 1,342 functions. All density functional theory calculations were performed using the Gaussian09 program package.46

Hydrogenation of methyl abietate

A 316 mg sample of methyl abietate was dissolved in 3 mL of anhydrous ethanol and charged to a 2-neck, round-bottom flask equipped with a condenser. While stirring, 31.6 mg of palladium 10 wt % on activated carbon was added to the flask, followed by a series of three vacuum evacuations backfilling with hydrogen. A positive pressure of hydrogen was maintained via a hydrogen balloon. The reaction mixture was maintained at reflux for 5 days, after which the catalyst was removed by filtration on a PTFE membrane. Conversion of starting material was monitored by 1H NMR, as the disappearance of vinylic hydrogens between 5 and 6 ppm. Product was isolated on a silica column, using dichloromethane as the eluting solvent. Fractions containing product were identified by TLC, combined, and concentrated to yield 81 mg (26 % isolated yield) of hydrogenated product.

Results and discussion

In crude oil asphaltene molecules/aggregates tend to associate and precipitate during recovery operations. Thermodynamic driving forces for this strong self-association stem from the combination of van der Waals forces between aromatic rings, dipole-dipole interactions among polar functional groups, hydrogen bonding, and charge transfer interactions. TEM image and DLS results obtained on asphaltene suspensions in 100% toluene are provided in Figure 8, showing that in 100% toluene very little agglomeration producing large particles is observed.
Figure 8. TEM image (insert) of Shell asphaltenes and plot of asphaltene particle size by dynamic light scattering; average particle size by DLS and TEM were 9 ± 2 nm and 10 ± 2 nm.

In order to achieve a better understanding of the type and extent of association in asphaltene aggregates, interaction energies of an asphaltene dimer were calculated using molecular mechanics. In Figure 9(a), the most favorable interaction occurs when one of the asphaltene molecules of the dimer is rotated 135° with respect to the other asphaltene molecule. The absolute value for the calculated interaction energy at this rotation angle is approximately 83 kcal/mol. Figure 9(b) illustrates the asphaltene dimer in its most stable configuration. One can see from the molecular mechanics calculations that there is a strong association between asphaltene molecules, which must be disrupted to deter aggregation and precipitation.
Figure 9. (a) Plot of the absolute value of the interaction energy versus rotation angle for an asphaltene dimer and the (b) structure corresponding to the most favorable interaction energy at 135°.

From the onsets of flocculation determined by DLS, Figure 10, asphaltene suspensions tend to dramatically increase in average particle size, flocculate and precipitate at ~65% of added precipitant. However, in the presence of select naphthenic acids, flocculation may be delayed to a larger volume percent of precipitant ~71%. The data gathered from the DLS experiments was fit to the best fit polynomial of $y = a + be^x$ in order to get a better representation of the onset determinations, Figure 11. The correlation coefficients of these fits showed good agreement. Precipitation experiments were performed in triplicate, with excellent reproducibility, as demonstrated in Figure 12. Determining flocculation onsets using DLS has been reported in the literature and often criticized due to the fact that asphaltene suspensions typically absorb at laser interrogation wavelengths. A new heterodyne instrument configuration allows for samples containing absorbing, non-spherical particles at higher concentrations to be
investigated. For non-spherical particles, particle orientation presented to the incident light is constantly changing, and the refraction pattern is a composite of these many orientations. Our group has successfully correlated measured DLS particle sizes of irregular-shaped, high index of refraction (RI) particles, such as iron oxide, to particle sizes measured by TEM analysis.

*Figure 10.* DLS particle size as a functional of volume% of n-heptane precipitant added to toluene dispersions of asphaltenes in the presence of select naphthenic acids.
Figure 11. DLS particle size as a functional of volume% of n-heptane precipitant added fit to non-linear equation, \( y = a + be^x \); correlation coefficients ranged from 0.86 to 0.98.
Figure 12. DLS particle size as a functional of volume% of n-heptane precipitant added to toluene dispersions of hydrogenated methyl abietate, showing average reproducibility among experiments.

Precipitation onsets were also determined using the more commonly reported NIR technique, which detects the increase of light scattering due to the onset of precipitation at NIR wavelengths. This technique has historically been performed at NIR wavelengths due to the absorption characteristics of asphaltenes over visible wavelengths. It was observed that at 1600 nm there is minimal absorbance from these components; therefore, transmittance at this wavelength was chosen as the observable during the titrations, Figure 13. %T was then plotted versus concentration of precipitant (vol %) for asphaltenes alone and in the presence of naphthenic acids, Figure 14. Comparable to DLS techniques, the data gathered by NIR titrations also shows an additive effect when naphthenic acids are present. Thus, these two techniques show a very good correlation in detecting the onset of flocculation for asphaltene and asphaltene/naphthenic acid
suspensions. One area of curiosity was to determine if the degree of onset delay could be correlated to the structure and the specific interactions among asphaltenes and naphthenic acids using molecular modeling techniques.

Figure 13. NIR absorbance spectrum for asphaltene suspensions in toluene.
Figure 14. NIR transmission values as a function of volume% of n-heptane precipitant added to toluene dispersions of asphaltenes in the presence of select naphthenic acids.

Molecular modeling results supported the interesting trend revealed in the experimental onset values determined using DLS and NIR techniques, and minimized energy geometries are provided in Figure 15 (a-d). From the molecular mechanics calculations of asphaltene with methyl abietate and hydrogenated methyl abietate, minimized interaction distances of 4.10 and 4.57 Å were obtained and overall interaction energies of −32.5 and -29.6 kcal/mol. This data shows that the presence of the π system in methyl abietate offers more extensive interaction with the asphaltene than when the π system is absent (hydrogenated methyl abietate). Thus, the onset of flocculation for asphaltene in the presence of methyl abietate is delayed to a greater extent than with hydrogenated methyl abietate, which exhibits a less favorable interaction. In both DLS and NIR onsets, 5β-cholanic acid presents the largest additive effect, suggesting a strong
association between acidic and basic groups. Additionally, these findings are supported by molecular modeling through a closer association distance of 3.99 Å and interaction energy of -34.7 kcal/mol for 5β-cholanic acid. In all preferred geometries where an additive effect is observed, the asphaltene adopts a cup-like orientation, with the naphthenic acid residing in the well of the cup. However, minimized geometries obtained for 5β-cholanic acid-3-one with the model asphaltene indicates an alternative preferred configuration, and one that does not lead to a delayed precipitation onset.

Finally, with the exception of the ketone, the dipole moments for the naphthenic acids determined with density functional theory also follow the same trend revealed in the experimental onset values. The larger the dipole of the naphthenic acid, the longer the onset of flocculation is delayed. At the B3LYP/aug-cc-pVTZ level, the dipole moments for the minimum energy conformation of 5β-cholanic acid, methyl abietate, and hydrogenated methyl abietate are 2.07, 1.49, and 1.32 Debye, respectively. It should also be pointed out that the second lowest conformation of methyl abietate, which lies only 1.67 kcal/mol above the minimum energy conformation at this level, has a dipole moment of 1.79 Debye. Thus, the difference in dipole moments for these three systems is not trivial and could help explain the differences in interaction energies with the asphaltene discussed above. However, the dipole moment of the ketone, 5β-cholanic acid-3-one, breaks this trend. The dipole moment of its minimum energy conformation computed at the B3LYP/aug-cc-pVTZ level is 2.68 Debye, and the dipole moment of the second lowest energy conformation, which lies only 1.33 kcal/mol above the minimum energy conformation, is 3.50 Debye. Though, as shown above, the ketone appears to interact in a different way with the asphaltene than the other three naphthenic acids.
considered here. Perhaps, its much larger dipole moment leads, at least in part, to this difference.
Figure 15. Molecular modeling results describing minimized interaction geometries between asphaltenes and naphthenic acids (a) 5β-cholanic acid, interaction distance is 3.99 Å; (b) methyl abietate, 4.10 Å; (c) hydrogenated methyl abietate, 4.57 Å; and (d) 5β-cholanic acid-3-one.
Dr. Praveen Madasu conducted a series of molecular modeling calculations in order to further identify a number of structure property relationships, including the relative effects of hydrogen bonding and van der Waals interactions existing between asphaltenes and naphthenic acids.

Since naphthenic acids possess carboxylic acid functional groups they are capable of forming hydrogen bonds with the electronegative heteroatoms present on the asphaltene molecular structure. However, the differences in the various naphthenic acid molecular structures, influences the naphthenic acids to favor interaction with certain electronegative atoms on the asphaltene molecule. Figure 16 illustrates the functional groups present on the asphaltene molecule.

![Figure 16](image)

*Figure 16. Sites for hydrogen bonding for naphthenic acids on asphaltene molecule.*

The naphthenic acid structures used in the molecular modeling calculations are shown in Figure 17.
Five interaction energy values, which have been calculated for each naphthenic acid implemented in this study, (Figure 17) are tabulated in Tables 1 to 5. The contributions from hydrogen bonding, dipole (electrostatic interactions), and van der Waals interactions to the total interaction energy were examined.\textsuperscript{39}
Table 1

*Interaction energy values calculated between 5β-cholanic acid (isomer-2) and asphaltene.*

<table>
<thead>
<tr>
<th>Functional Group</th>
<th>5β-cholanic acid (isomer-2)</th>
<th>Interaction energy (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S=O</td>
<td>interaction Energy</td>
<td>-42.06</td>
</tr>
<tr>
<td></td>
<td>van der Walls</td>
<td>-36.18</td>
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<tr>
<td></td>
<td>electrostatic</td>
<td>-7.26</td>
</tr>
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<td>interaction energy</td>
<td>-36.22</td>
</tr>
<tr>
<td></td>
<td>van der Waals</td>
<td>-30.15</td>
</tr>
<tr>
<td></td>
<td>electrostatic</td>
<td>-5.76</td>
</tr>
<tr>
<td>N2</td>
<td>interaction energy</td>
<td>-33.34</td>
</tr>
<tr>
<td></td>
<td>van der Waals</td>
<td>-29.74</td>
</tr>
<tr>
<td></td>
<td>electrostatic</td>
<td>-3.86</td>
</tr>
<tr>
<td>S</td>
<td>interaction energy</td>
<td>-34.31</td>
</tr>
<tr>
<td></td>
<td>van der Waals</td>
<td>-31.94</td>
</tr>
<tr>
<td></td>
<td>electrostatic</td>
<td>-5.23</td>
</tr>
<tr>
<td>N1</td>
<td>interaction energy</td>
<td>-31.36</td>
</tr>
<tr>
<td></td>
<td>van der Waals</td>
<td>-33.32</td>
</tr>
<tr>
<td></td>
<td>electrostatic</td>
<td>-1.73</td>
</tr>
</tbody>
</table>

The interaction energies between the asphaltene and 5β-cholanic acid were calculated at various locations on the surface and can be seen in Table 1. These five interactions energy values were calculated when the carboxylic acid of 5β-cholanic acid formed hydrogen bonds with the electronegative atoms present on the asphaltene molecule. The greatest interaction energy was achieved when the carboxylic acid of 5β-cholanic acid formed a hydrogen bond with the –S=O functional group of the asphaltene. Additionally, the electrostatic component of the interaction energy (-7.26 kcal/mol) is primarily due to this hydrogen bonding.
Table 2

Interaction energy values calculated between methyl abietate and asphaltene.\(^{39}\)

<table>
<thead>
<tr>
<th>Orientation</th>
<th>Methyl abietate interaction energy (kcal/mol)</th>
<th>asphaltene interaction energy (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orientation-1</td>
<td>Interaction Energy</td>
<td>-34.35</td>
</tr>
<tr>
<td></td>
<td>van der Waals</td>
<td>-34.17</td>
</tr>
<tr>
<td>Orientation-2</td>
<td>COOH of interaction energy</td>
<td>-31.62</td>
</tr>
<tr>
<td></td>
<td>electrostatic</td>
<td>-3.85</td>
</tr>
<tr>
<td>Orientation-3</td>
<td>Interaction energy</td>
<td>-33.17</td>
</tr>
<tr>
<td></td>
<td>van der Waals</td>
<td>-34.45</td>
</tr>
<tr>
<td>Orientation-4</td>
<td>Interaction energy</td>
<td>-33.17</td>
</tr>
<tr>
<td></td>
<td>electrostatic</td>
<td>0.01</td>
</tr>
</tbody>
</table>

The molecular structure of methyl abietate contains one hydrogen bond acceptor functional group (-COOCH\(_3\)) but does not contain a hydrogen bond donor functional group.\(^{39}\) The model asphaltene used in these calculations has one hydrogen bond donor functional group in the carboxylic acid (-COOH).\(^{39}\) In all of the interaction energies calculated for methyl abietate (Table 2) the electrostatic contribution to the total interaction energy is quite small except when the carboxylic acid of the asphaltene forms a hydrogen bond with the ester of methyl abietate (-3.85 kcal/mol).\(^{39}\)
Reduced methyl abietate is generated from the reduction of the conjugated double bonds in methyl abietate. The calculated interaction energy values between the asphaltene molecule and reduced methyl abietate are relatively low due to the absence of the double bonds (Table 3). The lack of these double bonds lowers the van der Waals interaction (low π-π interactions) and consequently decreases the overall interaction energy. Reduced methyl abietate possesses one hydrogen bond acceptor functional group (\(-\text{COOCH}_3\)) and does not possess a hydrogen bond donor functional group. Again, asphaltene contains one hydrogen bond donor functional group (\(-\text{COOH}\)). The electrostatic contribution to the total interaction energy is quite small except when the
carboxylic acid of the asphaltene formed a hydrogen bond with the ester of reduced methyl abietate (−4.13 kcal/mol).39

Table 4

Interaction energy values calculated between 5β-cholanic acid (isomer-1) and asphaltene.39

<table>
<thead>
<tr>
<th>Functional Group</th>
<th>5β-cholanic acid (isomer-1)</th>
<th>Interaction energy (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S=O</td>
<td>interaction Energy</td>
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</tr>
<tr>
<td></td>
<td>van der Walls</td>
<td>-29.49</td>
</tr>
<tr>
<td></td>
<td>electrostatic</td>
<td>-6.11</td>
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<tr>
<td>COOH</td>
<td>interaction energy</td>
<td>-32.07</td>
</tr>
<tr>
<td></td>
<td>van der Waals</td>
<td>-27.99</td>
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<tr>
<td></td>
<td>electrostatic</td>
<td>-6.40</td>
</tr>
<tr>
<td>N2</td>
<td>interaction energy</td>
<td>-36.65</td>
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<td></td>
<td>van der Waals</td>
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</tr>
<tr>
<td></td>
<td>electrostatic</td>
<td>-3.09</td>
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<td>S</td>
<td>interaction energy</td>
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</tr>
<tr>
<td></td>
<td>van der Waals</td>
<td>-32.44</td>
</tr>
<tr>
<td></td>
<td>electrostatic</td>
<td>-1.51</td>
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<tr>
<td>N1</td>
<td>interaction energy</td>
<td>-33.59</td>
</tr>
<tr>
<td></td>
<td>van der Waals</td>
<td>-29.03</td>
</tr>
<tr>
<td></td>
<td>electrostatic</td>
<td>-6.32</td>
</tr>
</tbody>
</table>

5β-cholanic acid has the greatest interaction energy when it forms a fairly weak hydrogen bond with N2, and the van der Waals contribution to the total interaction energy is highest for this arrangement (Table 4).39 Additionally, 5β-cholanic acid formed hydrogen bonds with −COOH, N1, and −S=O groups.39 The interaction energy is greatest when the sum of the electrostatic and van der Waals interactions is largest.39
Interaction energy values calculated between 5\(\beta\)-cholanic acid-3-one and asphaltene.\(^{39}\)

<table>
<thead>
<tr>
<th>Functional Group</th>
<th>5(\beta)-cholanic acid-3-one</th>
<th>Interaction energy (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S=O</td>
<td>interaction energy</td>
<td>-32.46</td>
</tr>
<tr>
<td></td>
<td>van der Waals</td>
<td>-32.10</td>
</tr>
<tr>
<td></td>
<td>electrostatic</td>
<td>-5.28</td>
</tr>
<tr>
<td>COOH</td>
<td>interaction energy</td>
<td>-38.92</td>
</tr>
<tr>
<td></td>
<td>van der Waals</td>
<td>-28.31</td>
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<tr>
<td></td>
<td>electrostatic</td>
<td>-10.07</td>
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<tr>
<td>N2</td>
<td>interaction energy</td>
<td>-34.64</td>
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<td></td>
<td>van der Waals</td>
<td>-34.06</td>
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<td>-0.49</td>
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<tr>
<td>S</td>
<td>interaction energy</td>
<td>-32.33</td>
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<tr>
<td></td>
<td>van der Waals</td>
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<td>electrostatic</td>
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<td>N1</td>
<td>interaction energy</td>
<td>-30.95</td>
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<td>van der Waals</td>
<td>-31.81</td>
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<tr>
<td></td>
<td>electrostatic</td>
<td>-1.95</td>
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</table>

The molecular structure of 5\(\beta\)-cholanic acid-3-one possesses one hydrogen bond donor functional group (-COOH) and contains two hydrogen bond acceptor functional groups (-COOH, -C=O).\(^{39}\) However, two concurrent hydrogen bonds are not achievable in most of the arrangements due to the length of its structure.\(^{39}\) 5\(\beta\)-cholanic acid-3-one showed the greatest interaction energy when it formed hydrogen bonds with the carboxylic acid of the asphaltene molecule (-38.92 kcal/mol) (Table 5). In addition, this arrangement had the highest electrostatic interaction (-10.07 kcal/mol).\(^{39}\)

The average interaction energy values between the model asphaltene molecule and the various naphthenic acids are summarized in Table 6.\(^{39}\) The electrostatic component of the interaction energy indicates hydrogen bonding [i.e. typical values: O—
H...N (6.9 kcal/mol), O—H...:O (5.0 kcal/mol), N—H...:N (3.1 kcal/mol), N—H...:O (1.9 kcal/mol). In some cases, the carboxylic acid of the naphthenic acids was unable to form a hydrogen bond with the asphaltene because of geometric constraints. In these cases the polar constituents of the naphthenic acids interacted with the polar constituents of the asphaltene. This is the explanation for the greater contribution of the electrostatic interactions to the total interaction energy. It is obvious from the interaction energy values that numerous naphthenic acid molecules are required to disperse asphaltenes.

Table 6

*Average interaction energy values calculated between the various naphthenic acids and asphaltene.*

<table>
<thead>
<tr>
<th>Naphthenic Acid</th>
<th>S=O/Orient 1</th>
<th>COOH/Orient 2</th>
<th>N2/Orient 3</th>
<th>S/Orient 4</th>
<th>N1/Orient 5</th>
<th>Avg IE</th>
</tr>
</thead>
<tbody>
<tr>
<td>5β-Cholanic Acid (isomer-2)</td>
<td>-42.06</td>
<td>-36.22</td>
<td>-33.34</td>
<td>-34.31</td>
<td>-31.36</td>
<td>-35.46</td>
</tr>
<tr>
<td>5β-Cholanic acid (isomer-1)</td>
<td>-35.51</td>
<td>-32.07</td>
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<tr>
<td>Reduced methyl abietate</td>
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<td>-29.22</td>
<td>-29.05</td>
<td>-28.44</td>
<td>-29.63</td>
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<tr>
<td>5β-Cholanic acid-3-one</td>
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<td>-38.92</td>
<td>-34.64</td>
<td>-34.64</td>
<td>-30.95</td>
<td>-34.32</td>
</tr>
</tbody>
</table>
Conclusions

In conclusion, a goal of this study was to investigate the effects of select naphthenic acids on the sedimentation and aggregation behavior of asphaltenes in model solutions, representing acidic and basic components of crude oil. Four different naphthenic acids were employed - methyl abietate, hydrogenated methyl abietate, 5β-cholanic acid, and 5β-cholanic acid-3-one – having a range of molecular functionality and varied resulting intermolecular forces. The effects on the sedimentation behavior and aggregation were monitored by DLS and NIR light scattering methods and supported by molecular modeling results. Although a number of light scattering papers exist related to the interactions of asphaltenes with various polar species, detailed studies correlating these techniques are rare. DLS and NIR show very good agreement in identifying the onsets of flocculation. Molecular mechanics calculations support the experimental results of the titrations, and structure property relationships were defined.
CHAPTER III
THE INVESTIGATION OF ASPHALTENE ADSORPTION ON SURFACES USING THE QUARTZ CRYSTAL MICROBALANCE WITH DISSIPATION (QCM-D) TECHNIQUE

Abstract

This chapter details progress towards identifying how surfaces of different energy and functionality affect the adsorption of asphaltenes from model crude oil solutions. SiO$_2$-coated quartz crystal microbalance (QCM) sensors were chemically modified with select organosilane compounds and the extent of asphaltene adsorption on these derivatized surfaces was determined. In the QCM experiments, the oscillation frequency and dissipation response of a quartz crystal is continuously monitored while solutions of asphaltenes flow over the sensor surfaces. In addition, the derivatized sensor surfaces were characterized using contact angle measurements and surface energy calculations. The current published literature regarding the adsorption/deposition of asphaltenes on metal surfaces involves the use of a variety of analytical techniques such as UV-Vis spectroscopy and QCM to probe the adsorption/deposition of asphaltenes onto metal surfaces and asphaltene-metal interactions. The focus of our research differs in that we investigate how the surface energy and surface functionality of a substrate affects the adhesion of asphaltene particles under flow conditions. SiO$_2$-coated QCM sensors were successfully derivatized. The derivatized surfaces were characterized by contact angle measurements of water and surface energy calculations were performed by three methods. Contact angle measurements proved that the derivatized surfaces had a varying degree of hydrophilicity which was consistent with the functional groups employed in the
derivatizations reactions. QCM-D experiments demonstrated that all of the surfaces adsorb asphaltenes roughly to the same extent with the exception of the amine surface. The dissipation shifts were small lending credibility to the calculated adsorbed masses on the surfaces and supporting the qualitative description of the adsorbed asphaltenes layer as rigid. The calculated maximum adsorption rates were very similar for all surfaces with the exception of the acid surface. Plots of adsorbed mass for each surface versus the surface energy calculated by each method did not reveal a correlation between surface energy and asphaltenes adsorbed mass.

Introduction

Pipeline blockage due to the deposition of heavy organics from petroleum fluids is a ubiquitous problem in the oil industry. Asphaltenes aggregates have a tendency to precipitate from crude oil and eventually deposit on the inner surfaces of recovery, production, and processing equipment. These deposits slowly thicken over time and ultimately bring production operations to a halt. Acevedo et al.\textsuperscript{47} analyzed the chemical composition of deposits formed on the pipeline walls of production tubing and found that the deposits consisted of large amounts of asphaltenes and resins. To date, the process of asphaltenes deposition onto surfaces is not well-known; however, Yarranton et al.\textsuperscript{48} provided some of the steps that are likely to occur in this process. These researchers suggested that the mechanism of deposition begins with the precipitation of asphaltenes due to changes in the pressure, temperature, and/or composition of the crude oil as a result of the recovery operations. Next, flocculation of the precipitated particles takes place followed by adhesion of the flocculated particles to surfaces. Yarranton and co-workers\textsuperscript{48} also explain that asphaltenes can adsorb onto surfaces before precipitation and
that these adsorbed particles can act as a site for flocculated asphaltenes to adhere. Dos Santos and co-workers\textsuperscript{49} showed that asphaltenes and naphthenic acids play important roles in altering the oil wettability of metal surfaces. These researchers pointed out that the contributions to the wetting of the metal surfaces arise from the dispersion forces associated with the aromatic nature of the asphaltenes and the acid-base interactions of naphthenic acids. In order to achieve a better understanding of asphaltene deposition researchers have investigated the chemical composition of adsorbed asphaltenes on metal surfaces using X-ray photoelectron spectroscopy (XPS)\textsuperscript{50,51} and time-of-flight secondary ion mass spectroscopy (ToF-SIMS).\textsuperscript{51} Abdallah and Taylor\textsuperscript{50} examined the chemical composition of adsorbed asphaltenes on a stainless steel surface utilizing the XPS technique. The purpose of this research was to develop a procedure for generating reproducible asphaltene films on stainless steel and to investigate the chemical composition of the adsorbed asphaltene films. In this study asphaltene deposits were generated by using a special, cylindrical adsorption apparatus. The adsorption process involved immersing circular, stainless steel discs vertically in asphaltene solutions in the adsorption apparatus. Then, the asphaltene solution was sealed in the oxygen-free environment for 3 days. After 3 days, the asphaltene solutions were removed and the solvent was evaporated from the discs. Asphaltene films were prepared on the stainless steel surfaces for XPS analysis in dichloromethane and toluene at a concentration of $1 \times 10^{-04}$ g cc$^{-1}$. The survey spectra collected on both of the asphaltene films showed Si 2p/2s, S 2p/2s, C 1s, O 1s, N 1s, Cr 2p peaks, Fe 2p photoemission features, and O and C Auger features. Upon further analysis of the C 1s, N 1s, O 1s, and S 2p photoemission peaks, carboxylic, pyrrolic, pyridinic, thiophenic, and sulfite functional groups were
identified on both of the adsorbed asphaltene layers. Therefore, these authors concluded that the aforementioned functional groups were present on the adsorbed asphaltene molecule.

Another important study conducted by Abdallah and Taylor\textsuperscript{51} involved characterizing adsorbed asphaltenes from four different origins on a stainless steel surface using XPS and ToF-SIMS. The objective of this research was to characterize adsorbed asphaltenes in order identify the bonds that were formed with the surface and to determine the functional groups responsible for surface interaction. ToF-SIMS was implemented in this study in order to complement the XPS analysis of the adsorbed asphaltene film. The asphaltene layer on the stainless steel surface was generated in the same manner as in the previous study\textsuperscript{50} with the exception that only toluene solutions were used and the concentration of these solutions were $5 \times 10^{-4}$ g cm\textsuperscript{-3}. The survey spectra from the XPS analysis of all the adsorbed asphaltene films confirmed the presence of C, O, N, S, elements. Results from the XPS analysis revealed that nitrogen was present on the asphaltene film in the form of pyrrolic and pyridinic heterocyclic compounds, where as sulfur was found to be present as thiophenic and sulfite groups. Also, carbon was determined to be present in the form of C-H or C-C bond and as C-O bonds. When the spectra for each type of asphaltene were compared it was found that the atomic concentrations of specific elements, such as O, N, S, and C, varied from sample to sample. These researchers contributed the differences observed in the atomic concentrations of specific elements in asphaltenes to the origins of the sample. The ToF-SIMS analysis revealed heteroatom-containing negative ions of O\textsuperscript{−} (m/z = 16), OH\textsuperscript{−} (m/z = 17), N\textsuperscript{−} (m/z = 14), CN\textsuperscript{−} (m/z = 26), S\textsuperscript{−} (m/z = 32), SO\textsuperscript{−} (m/z = 48), and SiO\textsubscript{2}\textsuperscript{−} (m/z = 60)
which supported the XPS analysis. In summary, these researchers were able to identify the aforementioned functional groups on the adsorbed asphaltenes and C-O bonds on the surface which were supported by the ToF-SIMS analysis. Additionally, the results from this study confirmed the results of the previous study published by Abdallah and Taylor.\textsuperscript{50}

The kinetics and thermodynamics of asphaltene adsorption onto metal surfaces has been examined using spectroscopic techniques such as ultraviolet-visible (UV-Vis)\textsuperscript{52} and near-infrared (NIR) spectroscopy\textsuperscript{53}, Raman microscopy\textsuperscript{53}, and the quartz crystal microbalance with dissipation monitoring (QCM-D).\textsuperscript{58,59} Nassar\textsuperscript{52} investigated the kinetics and thermodynamics of asphaltene adsorption from model crude oil solutions onto alumina nanoparticles using UV-Vis spectroscopy. This study was based on the idea that the alumina particles would adsorb large amounts of asphaltenes from heavy crude oils, thereby removing the asphaltenes and making the crude much easier to recover. In these experiments asphaltene adsorption was achieved by adding alumina nanoparticles to solutions of asphaltenes in toluene and shaking them at 300 rpm at a given temperature until equilibrium was achieved. The nanoparticles were then separated from the solution by centrifugation. After separating the asphaltene-containing nanoparticles, the supernatant was analyzed by UV-Vis to determine the concentration of asphaltenes remaining in solution. In the adsorption kinetic studies asphaltene solutions of 100, 500, and 1000 ppm were employed. By plotting the adsorbed amount of asphaltenes as a function of time it was found that the adsorption reached equilibrium in less than 2 hours. The data was evaluated using Lagergren’s pseudo-first-order and pseudo-second-order kinetic models and found to correlate very well with the pseudo-
second-order model. The effect of temperature on the adsorption of asphaltenes was also investigated in this study. To evaluate the temperature effects on asphaltene adsorption, experiments were conducted in the temperature range of 298-328 K, and the results revealed that asphaltene adsorption decreased as the temperature increased. Nassar suggested that this observation supported the idea that asphaltene adsorption onto the nanoparticles was an exothermic process. Adsorption isotherms were collected at different temperatures to determine the saturation adsorption and equilibrium isotherm constants of asphaltene adsorption. Langmuir type I isotherms were observed for each temperature in these studies which suggested that the alumina surface was covered with a monolayer of asphaltenes. Additionally, these studies utilized thermodynamic parameters to describe the degree of asphaltene adsorption with respect to temperature. The Gibbs free energy of adsorption, enthalpy of adsorption, and entropy of adsorption at different temperatures were obtained using the Gibbs (Equation 2) and van’t Hoff (Equation 3) equations.

\[
\Delta G_{ads}^0 = -RT \ln K
\]

Equation 2:

\[
\ln(K) = -\frac{\Delta H_{ads}^0}{RT} + \frac{\Delta S_{ads}^0}{R}
\]

Equation 3:

Researchers found that the adsorption process was spontaneous and thermodynamically favored due to a negative value calculated for the Gibbs free energy of adsorption. The enthalpy and entropy of adsorption were calculated from the slope and y-intercept of a plot of the van’t Hoff equation of ln (K) versus 1/T. Negative values for the enthalpy of adsorption were calculated which provided further evidence that the interaction between the asphaltenes and nanoparticles was exothermic. Calculated values for the entropy of
adsorption were positive, and this finding suggested that the adsorption of asphaltenes resulted in an increased randomness at the solid-liquid interface.

Recently, Balabin et al.,\textsuperscript{53} examined the kinetics and thermodynamics of asphaltene adsorption onto an iron surface using NIR spectroscopy and Raman microscopy. The focus of this research was to investigate asphaltene adsorption behavior using thermodynamic and kinetic analyses to develop an understanding of the asphaltene-metal interactions that contribute to the deposition process. In this study asphaltene films were created by immersing iron sheets and iron foil in asphaltene solutions. The substrates were then removed at various times from 5 to 1200 minutes and the remaining solution was analyzed via NIR in the region of 1111–769 nm. Asphaltene adsorption kinetics was determined from the concentrations of asphaltene solutions before and after the iron substrates were exposed to asphaltene solutions. Additionally, a partial least-squares regression analysis was implemented to interpret the NIR data. Plots of adsorbed mass density (mg m\textsuperscript{-2}) versus time (minutes) were generated from the data gathered during the NIR kinetics analysis of asphaltene adsorption kinetics. These plots, which were created for two asphaltene solutions at different concentrations, illustrated that the asphaltenes achieved a stationary mass density in 200-700 minutes. A concentration dependence on the adsorption kinetics was also observed from these plots; higher asphaltene concentrations lead to a faster saturation adsorption. Adsorption isotherms were also derived from the NIR data by plotting the adsorbed mass density values versus concentration. A value of 4.90 mg m\textsuperscript{-2} was calculated for the maximum adsorbed mass density, and a value of 0.084 L mg\textsuperscript{-1} was calculated for the asphaltene adsorption constant from the adsorption isotherms. Additionally, these researchers utilized a first-order
Langmuir adsorption model to calculate the rate constant for asphaltene adsorption from the NIR data. The calculated first-order rate constant for asphaltene adsorption was found to be $4.95 \times 10^6 \text{ L mg}^{-1} \text{ min}^{-1}$. Another observation resulting from these studies was that the adsorbed mass density came to a maximum value when asphaltene concentrations between 250-350 mg L$^{-1}$ were employed in the adsorption studies. The authors concluded that the adsorption was occurring from partially aggregated molecules and not from single asphaltene molecules. The Gibbs free energy for asphaltene adsorption was also calculated from the NIR data and this value was determined to be $-34.3 \text{ kJ mol}^{-1}$. Raman microscopy data was collected on the adsorbed asphaltenes in order to validate the kinetic and thermodynamic values calculated from the NIR data. The amount of adsorbed asphaltenes was calculated from the Raman bands under the 1000-1800 cm$^{-1}$ spectral region. The results obtained from these experiments supported the NIR calculations due to the fact that virtually identical kinetic curves and adsorption isotherms were produced. Additionally, the Gibbs free energy of adsorption calculated by the Raman microscopy analysis was found to be in very good agreement with the value calculated by the NIR analysis.

Yarronton et al.$^{48}$ investigated the adsorption of asphaltenes on stainless steel, iron, and aluminum powders using UV-Vis spectroscopy. The aim of this research was to examine the influence of the environmental conditions surrounding asphaltenes and how metal type influenced asphaltene adsorption. Asphaltene adsorption was achieved by adding the metal powders to separate asphaltene solutions and placing them on a roller for 72 hours. The suspended metal particles were then removed from the solutions by centrifugation. Asphaltene adsorption was quantified in these experiments by measuring
the concentration of the asphaltene solutions prior to and following the introduction of the metal powders. These authors suggested that asphaltene adsorption on metals could be influenced by the type of metal surface, the type of asphaltenes, the existence of resins, temperature, and the surrounding medium. As a result, each of these factors was investigated. To determine the effects of the metal and asphaltene type on asphaltene adsorption, two different asphaltenes were allowed to adsorb onto stainless steel, iron, and aluminum powders. Results from this investigation demonstrated that asphaltene adsorption was highest on stainless steel and lowest on aluminum. Adsorption isotherms were generated from these studies by plotting the saturation adsorption on each of the metals versus the asphaltene concentrations for the two types of asphaltenes. The adsorption isotherms revealed Langmuir (type I) isotherms which indicated to the authors that the asphaltenes adsorbed as a monolayer on the metal surfaces and that the surfaces were saturated with asphaltenes. However, the saturation adsorptions on the metals were found to have coverage of only 5 to 30% of the surfaces which led to the conclusion that asphaltene adsorption on the metals was limited by the number of adsorption sites. It was also found that one type of asphaltene adsorbed up to 35% more than the other in all of the examinations. Enhanced adsorption was hypothesized to be the result of differences in their molar masses and/or differences in their chemical structure. As a result of these experiments, the authors concluded that asphaltene adsorption was influenced by asphaltene surface charge and the surface properties of the metals. The effect of resins on asphaltene adsorption was also examined. These experiments were conducted by monitoring the adsorption of asphaltenes from solutions containing various concentrations of previously separated resins. A trend of decreased saturation adsorption
with increased resin content was observed in these adsorption experiments. It was deduced that the decreased saturation adsorption was either due to resins decreasing the degree of self-association among the asphaltenes or the smaller resins were able to access more of the surface than the larger asphaltenes due to the surface morphology of the metals. The effect of temperature on asphaltene adsorption was investigated by monitoring asphaltene adsorption onto stainless steel powder at temperatures of 22°C, 40°C, and 60°C. A decrease in the saturation adsorption at 60°C was observed which was attributed to the decrease in aggregate size with increasing temperature. Lastly, the influence of the composition of the liquid medium on asphaltene adsorption was examined. This was accomplished by dissolving asphaltenes in solutions with n-heptane:toluene ratios of 0:100, 25:75, 35:65, and 45:55 and measuring the adsorption onto stainless steel. Asphaltene adsorption was seen to increase as the ratio of heptane:toluene increased. These results were attributed to the fact that n-heptane is a poor solvent for asphaltenes. It was assumed that the degree of asphaltene self-association increased as a result of the increased amount of n-heptane which, in turn, led to the formation of larger particles on the surface causing a higher mass saturation adsorption.

Wang et al. studied asphaltene deposition under flowing conditions using an apparatus equipped with stainless steel capillary tubing. The focus of this study was to examine how deposits formed from solutions in which asphaltenes have limited solubility. The different factors investigated were the effect of the degree of asphaltene instability and the effect of precipitant molar volume on asphaltene deposition. Deposition experiments were conducted from supersaturated mixtures of stock tank oils
and n-alkanes while pressure drops across the tubing were used to determine the quantity and distribution of the deposits. In order to examine how the degree of asphaltene instability affected asphaltene deposition, asphaltenes were destabilized in the stock tank oils by adding n-alkane precipitants. These solutions were then pumped though the capillary tubing of the deposition test apparatus. Two levels of asphaltene instability were examined: (1) near-onset mixtures and (2) 50:50 mixtures of stock tank oils:n-alkanes. The researchers observed evenly distributed deposits along the length of the capillary tubing and found different rates of deposition for both of the mixtures. Here, larger deposition rates occurred for the mixtures having a greater degree of supersaturation. The effect of precipitant molar volume on asphaltene deposition was examined by mixing n-pentane, n-decane, and n-pentadecane with the stock tank oils to the levels of supersaturation mentioned above. Increased rates of deposition and an increased amount of deposited material were observed as the precipitant molar volume increased. Conclusions were not drawn from the latter observation because it is well known that smaller amounts of asphaltenes are precipitated with larger molecular weight precipitants.

The QCM-D technique has been used to investigate the adsorption/deposition of asphaltenes on metal surfaces under static and dynamic conditions. Ekholm et al. investigated the adsorption of extracted asphaltenes and resins onto a gold surface using QCM-D. This study focused on the adsorption and desorption of redissolved resins and asphaltenes in heptane, a 50:50 mixture of heptane:toluene, and in pure toluene. Resins and asphaltenes were studied individually as well as in the presence of one another. Adsorption studies were conducted on crude oil samples mixed with a 50:50 mixture of
heptane:toluene in order to compare the results with those of the redissolved samples. The experiments involving redispersed resins in heptane were performed on samples with concentrations ranging from 100 to 5000 ppm. During these experiments the amount of resins adsorbed increased as the concentration was increased. Another observation made during the resin adsorption experiments was that the frequency response stabilized very quickly. This result led the authors to believe that the resins were adsorbing onto the gold surface rather than depositing. Additionally, the only significant increase in the dissipation factor was observed for the 5000 ppm sample. Although the increase in the dissipation factor was small for the lower concentrated samples, the researchers hypothesized that the resins adsorbed as a rigidly attached monolayer and as single molecules instead of aggregates. In subsequent examinations, resins were redissolved in a mixture of 50:50 heptane:toluene at concentrations between 25 and 2500 ppm and at concentrations between 100 and 5000 ppm in pure toluene. Results from these studies revealed that very little adsorption occurred from the 50:50 mixture and that no significant adsorption of resins occurred from the toluene. Therefore, as the toluene content increased the amount of adsorbed resins decreased. The authors attributed this phenomenon to the increased solubility of the resins in toluene, and speculated that resin solubility was the main influence on the extent of adsorption.

Asphaltene adsorptions experiments were conducted utilizing the same solvents and solvent mixtures that were used in the resin adsorption experiments. However, the researchers were unable to obtain any results from the adsorption experiments conducted in heptane due to the poor solubility of asphaltenes in this solvent. The adsorption studies of asphaltenes in 50:50 heptane:toluene were examined using concentrations
ranging between 25 and 1000 ppm. A substantial frequency and dissipation shift occurred when the 50 ppm sample was measured. Additionally, the signal stabilized after only a few minutes and this was believed to be a result of the asphaltenes adsorbing as small aggregates. When asphaltene samples of higher concentrations were measured, no significant change in the frequency or dissipation occurred. After all of the asphaltene samples had been injected, the measurement chamber was rinsed with toluene. A small change in the dissipation factor was noticed upon rinsing the measurement chamber, leading the authors to the conclusion that the asphaltenes adsorbed as a rigid layer.

Adsorption studies of asphaltenes in toluene were conducted using a concentration range of 50 to 10,000 ppm. Again, the frequency and dissipation signals stabilized quickly which suggested that the adsorption of asphaltenes was occurring instead of the deposition of aggregates. Asphaltene adsorption was observed to increase as the concentration increased, but the adsorbed amount did not level off as the higher concentrations were injected, as it did in the 50:50 mixtures. This was speculated to be a result of asphaltenes adsorbing as multilayers from toluene. Additional investigations of this study involved monitoring the adsorption of two different mixtures of asphaltenes and resins redissolved in a 50:50 mixture of heptane:toluene. One mixture contained 290 ppm asphaltenes and 1380 ppm resins, and the second mixture contained 1450 ppm asphaltenes and 6900 ppm resins. These experiments were conducted by injecting the first mixture two times into the measurement chamber followed by the injection of the second mixture two times and then the surface was washed with 50:50 heptane:toluene. The results from this study showed an adsorbed mass of 6.8 mg/m², which was greater than the adsorbed masses observed for the pure samples of the two fractions. This result
led the authors to believe that mixed aggregates were being adsorbed on the surface. In addition, the researchers observed a small dissipation shift during these experiments, meaning the adsorption resulted in a rigidly attached layer on the surface. Upon rinsing the measurement chamber the adsorbed amount decreased slightly and the dissipation factor substantially decreased. This significant decrease in the dissipation factor was believed to be the result of an extremely compact layer remaining on the surface. The final investigation of this study examined the adsorption of crude oil diluted with a 50:50 mixture of heptane:toluene at concentrations of 10,000 and 50,000 ppm. These experiments were carried out by injecting the 10,000 ppm sample into the measurement chamber and replacing it three times. The frequency shift observed for this sample was -70 Hz and related to an adsorbed amount of 4.2 mg/m². A 50,000 ppm sample was injected in the same manner as the 10,000 ppm sample. A frequency shift of -150 Hz was observed, corresponding to an adsorbed amount of 8.9 mg/m². Also, a dissipation shift of +11 was observed which revealed to the authors that the surface layer was much more loosely bound to the surface due to the increased adsorption. Furthermore, the adsorbed amount and the dissipation shift for the 50,000 ppm sample were much greater than the values observed for the mixtures of the redissolved resins and asphaltene samples. These results demonstrated that the aggregates adsorbed from the crude oil were much larger and more loosely packed. Additionally, the adsorption process for asphaltenes in crude oil was distinctly different compared to that from the model solution, in that, the frequency and dissipation shifts were much larger. This observation was believed to be due to the presence of other constituents existing in crude oil.
Hannisdal and co-workers\textsuperscript{56} performed preliminary studies on the adsorption of asphaltenes and resins from toluene solutions onto silica using the QCM-D technique. In these experiments, 1.0 wt\% solutions of asphaltenes and resins in toluene were examined separately. In the asphaltene adsorption experiments, the frequency rapidly decreased while the dissipation significantly increased upon introduction of the sample. This suggested that the asphaltenes were adsorbing very quickly to the silica surface. Upon replacing the asphaltene solution with a duplicate solution at 15 minutes, no considerable response was identified in the frequency or dissipation signals. The lack of a response from the frequency and dissipation signals when a second solution was introduced into the measurement chamber implied that the surface was already saturated with asphaltenes. As the surface was rinsed with toluene the frequency increased and the dissipation factor decreased. The authors explained that this was due to the weakly bound asphaltenes being removed from the surface. It was also noticed that the majority of the asphaltenes were retained on the surface and that the remaining asphaltene film was rigid. Resin adsorption experiments were conducted in the same manner as the asphaltene adsorption experiments. From these experiments, resin adsorption behavior was found to be completely different than the asphaltene adsorption behavior. The researchers observed much smaller frequency shifts from the resin adsorption and determined that much less mass remained on the surface after the toluene rinse. These researchers claimed that there was not enough information to draw any conclusions about the adsorbed resin layer properties due to the weak signal responses encountered in these experiments.
Dudasova et al.\textsuperscript{57} utilized the QCM-D technique to study the adsorption and desorption of asphaltenes onto different hydrophilic surfaces in solutions of 50:50 heptane:toluene and toluene at concentrations of 0.1 and 0.01 g L\textsuperscript{-1}. The hydrophilic surfaces used in this study were SiO\textsubscript{2} (silica), Al\textsubscript{2}O\textsubscript{3} (alumina), TiO\textsubscript{x} (titanium) and FeO\textsubscript{x} (iron oxide). These surfaces were analyzed via contact angle measurements with water in order to determine their degree of hydrophilicity. The contact angle measurements are shown below in Table 7.

Table 7

<table>
<thead>
<tr>
<th>Surface</th>
<th>Contact Angle (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO\textsubscript{2}</td>
<td>8° ± 2°</td>
</tr>
<tr>
<td>TiO\textsubscript{x}</td>
<td>55° ± 2°</td>
</tr>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3}</td>
<td>62° ± 3°</td>
</tr>
<tr>
<td>FeO\textsubscript{x}</td>
<td>70° ± 2°</td>
</tr>
</tbody>
</table>

Pure solvents and samples were introduced into the measurement chamber by injecting them via a syringe into a temperature loop. Data collection began by first injecting pure solvent into the measurement chamber and exposing it to the sensor surface until a stable baseline was obtained, asphaltene solutions of increasing concentration were then injected. Each sample was exposed to the sensor surface for 30 minutes. Once the highest concentration was injected and exposed to the sensor surface for 30 minutes, the sensor was rinsed with pure solvent to remove any residual asphaltenes. The frequency and dissipation response were monitored throughout this procedure and the mass of
adsorbed asphaltenes was calculated using the Sauerbrey equation (Equation 9).

Frequency shifts in these experiments corresponded to adsorbed amounts of asphaltenes on the various surfaces to be 1.5 to 9.8 mg m\(^{-2}\) from the heptane:toluene solution and 1.7 to 9.1 mg m\(^{-2}\) from the toluene solution. The dissipation shifts were small which indicated that the adsorbed asphaltenes formed a rigidly attached layer and that asphaltene aggregates were present on the surface. After analyzing samples of asphaltenes redispersed in heptane:toluene and toluene on the different sensor surfaces, the adsorbed amount of asphaltenes on the sensor surfaces was plotted as a function of asphaltene concentration. A correlation between the degree of hydrophilicity and the adsorbed amount of asphaltenes was expected. This trend was not observed, but the data did reveal that the most hydrophilic surface, silica, adsorbed the largest amount of asphaltenes from the heptane:toluene solution. Unfortunately, no association between the adsorbed amounts and chemical composition or surface wettability was observed. Additionally, no significant asphaltene desorption was found to occur over the course of these experiments. Conversely, a trend was found between asphaltene size and the adsorbed amount, in that, the larger the asphaltene size the higher the amount adsorbed.

Xie and Karan\(^5\)\(^8\) examined the kinetics and thermodynamics of asphaltene adsorption on a gold surface from model solutions of heptane:toluene and pentane:toluene using a research QCM equipped with a flow cell. These adsorption experiments were accomplished by first allowing the sensor crystal to equilibrate in air and then in a blank solvent as it flowed through the measurement chamber by means of a peristaltic pump. The asphaltene samples were flowed through the measurement chamber and the frequency response was monitored continuously throughout the course
of the experiments. As in other studies utilizing the QCM technique, the change in frequency was attributed to asphaltene adsorption on the crystal surface. The first investigation of this study was to determine how concentration affected asphaltene adsorption kinetics. Solutions of asphaltenes were prepared in 50:50 hepane:toluene at concentrations between 10-200 ppm and the adsorption kinetics were evaluated by plotting the adsorbed amount of asphaltenes as a function of time for the various concentrations. From this plot it was observed that as the asphaltene concentration increased the initial rate and the amount of asphaltenes ultimately adsorbed also increased. These researchers also noticed that the lower asphaltene concentrations reached a stationary value after 700 minutes, whereas the higher concentrations did not.

In order to determine if the rate of asphaltene adsorption was controlled by the kinetics of adsorption or by diffusion, an adsorption experiment was conducted at three different flow rates. The initial rate of adsorption was independent of flow rates; however, after long periods of time flow rates did affect the rate of adsorption. Because the initial rates of adsorption were independent of flow rate, the researchers were able to perform an asymptotic analysis of the initial adsorption rates. This was done to further investigate if the initial adsorption process was controlled by kinetics or diffusion. It was concluded from the asymptotic analysis that asphaltene adsorption was limited by the diffusion of asphaltenes from the solution to the sensor surface. A thermodynamic framework was developed to describe asphaltene-metal interactions in terms of the Lifshitz-van der Waals and acid-base free energy interactions. The thermodynamic framework accounted for the different types of interactions between the asphaltene and metal surface in the
presence of a solvent. Here, the total free energy of interaction was written as a summation of various interactions (Equation 4):

Equation 4:

\[ \Delta G_{132}^{\text{tot}} = \Delta G_{132}^{LW} + \Delta G_{132}^{AB} + \Delta G_{132}^{EL} + \ldots \]

where \( \Delta G_{132}^{LW} \) includes London dispersion, Keesom, and Debye components of the van der Waals interactions, \( \Delta G_{132}^{AB} \) interactions correspond to the acid-base interactions, and the third term, \( \Delta G_{132}^{EL} \), represents the electrostatic interactions. The Lifshitz-van der Waals and acid-base interactions can be calculated from Equations 5 and 6 if the surface tension components are identified for the asphaltene, the metal surface, and the solvent.\(^{58}\)

Equation 5:

Equation 6:

Equation 4 was simplified by assuming that there was no electrical charge or ions in the system, therefore, the electrostatic term was ignored and was written as Equation 7.

Equation 7:
In order to calculate the free energy of adsorption, the surface tension components were acquired by measuring the contract angles of water, glycerol, and diiodomethane on a gold surface and on an asphaltene coated surface. The free energy values for asphaltene adsorption from toluene solutions onto gold, stainless steel, and aluminum were calculated using their thermodynamic framework in order to predict asphaltene-metal interactions. The calculated free energy values were: -0.957 mJ m$^{-2}$ for gold, -0.361 mJ m$^{-2}$ for stainless steel, and -0.059 mJ m$^{-2}$ for aluminum. The authors proposed that the calculated adsorption free energy values predicted the adsorbed amount of asphaltenes on the metal surfaces. Therefore, based on the calculated Gibbs free energy of adsorption, gold would adsorb the most and aluminum would adsorb the least amount of asphaltenes. This trend was confirmed by Yarranton et al.$^{48}$

Recently Karan et al.$^{59}$ investigated asphaltene-metal interactions by studying asphaltene adsorption onto a gold surface using QCM and X-ray photoelectron spectroscopy (XPS). Asphaltene adsorption was examined from toluene solutions at concentrations between 50 and 1500 ppm using a QCM equipped with a flow cell. The experimental conditions for the QCM studies were identical to those of Xie and Karan.$^{58}$ Asphaltene adsorption kinetics showed a fast initial adsorption rate. The adsorbed amounts of asphaltenes increased with concentration and ranged from approximately 2.1 to 8.9 mg m$^{-2}$. An asymptotic analysis was performed on the QCM data by plotting the adsorbed masses as a function of time and square root of time. This analysis revealed a linear trend which indicated that the initial adsorption rates were diffusion controlled. In addition, it was found that at longer times the data followed first-order kinetics. An adsorption isotherm was generated by plotting the equilibrium mass adsorbed versus the
asphaltene concentration. The plot was observed to fit very well with the Langmuir (type I) isotherm model which indicated that the asphaltenes adsorbed as a monolayer. The chemical characterization of adsorbed asphaltenes on gold surfaces via XPS was also conducted. In these experiments asphaltenes were accumulated on gold surfaces by two different methods: (1) asphaltenes were adsorbed onto the surface and (2) bulk asphaltenes were coated onto the surface. The first method (1) entailed immersing the gold substrates in an asphaltene solution of known concentration for 2 days. After the two day period the substrates were removed from the solution and blown dry with an N$_2$ stream. The second method (2) involved immersing the substrate in a viscous slurry of asphaltenes in dried toluene. This step was followed by drying the sample with an N$_2$ stream and storing it in a nitrogen filled container. The XPS analysis of these two samples allowed for the spectra of the bulk asphaltene to be compared to that of the asphaltene adsorbed from solution. The difference in the spectra (e.g. the presence or absence of a functional group in the bulk asphaltene in comparison to the adsorbed asphaltene) could reveal the role of those groups in asphaltene-metal interactions. The survey spectra from the XPS analysis revealed the presence Au, C, S, N, and O in both samples. Additionally, it was found that carboxylic, thiophenic, sulfide, sulfoxide, pyridinic, and pyrrolic functional groups were present for both the adsorbed and bulk asphaltenes. The free energy of asphaltene adsorption was also calculated using the following equation (Equation 8):

Equation 8:

$$\Delta G_{ads} = -RT \ln K$$

here, R is the universal gas constant (0.008314 kJ/mol K), T is the temperature in Kelvin, K is the adsorption equilibrium constant, and $\Delta G_{ads}$ is the free energy of adsorption.
(kJ/mol). The free energy of adsorption was calculated from the data generated from both the QCM and XPS based on the assumption that the asphaltene molecular weight was in the range of 750 – 5000 g/mol. The free energy of adsorption was calculated to be -27 kJ/mol when the assumed asphaltene molecular weight was 750 g/mol, while a value of -32 kJ/mol was calculated when the assumed asphaltene molecular weight was 5000 g/mol.

To date, investigations of asphaltene adsorption onto chemically modified surfaces has been scarcely studied. Hannisdal et al. investigated the adsorption of asphaltenes onto chemically modified silica particles of various wettabilities. These investigations were designed to determine the capacity of silica particles to stabilize water-in-oil and oil-in-water asphaltene emulsions. However, the investigations pertaining to the adsorption of asphaltenes on silica and chemically modified silica particle surfaces did provide valuable information regarding asphaltene adsorption onto surfaces of different wettabilities. Asphaltenes were coated on unmodified and chemically modified silica particles by immersing them in 1.0 wt% asphaltenes solutions in toluene for 24 hours. The coated particles were then centrifuged and washed with toluene to remove any excess asphaltenes. In this study, the modified silica particles were derivatized with 3-methacryl-oxypropyl-trimethoxysilane (Aerosil® 7200), polydimethysiloxane (Aerosil® 202), and dimethyldichlorosilane (Aerosil® 972). Aerosil® 200 designated the unmodified silica. Aerosil® 200 and 7200 were hydrophilic and Aerosil® 202 and 972 were hydrophobic in nature. Upon visual inspection of the particles that had been exposed to the asphaltene solutions for 24 hours, these researchers determined that the hydrophilic particles appeared darker in color than the hydrophobic
particles. In order to support these observations a near-infrared spectroscopy analysis was conducted on the asphaltene coated particles by monitoring the relative absorbance of the coated particles at 2924 cm$^{-1}$. The asymmetric stretching vibration from the methylene groups at 2924 cm$^{-1}$ served as a measure of the hydrocarbon content on the coated surfaces. The absorbance for each asphaltene coated particle is shown in Table 8.

Table 8

(relative absorbance at 2924 cm$^{-1}$ for asphaltene coated particles)

<table>
<thead>
<tr>
<th>Silica Particle</th>
<th>Absorbance at 2924 cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerosil® 200</td>
<td>0.122</td>
</tr>
<tr>
<td>Aerosil® 7200</td>
<td>0.104</td>
</tr>
<tr>
<td>Aerosil® 972</td>
<td>0.057</td>
</tr>
<tr>
<td>Aerosil® 202</td>
<td>0.036</td>
</tr>
</tbody>
</table>

These results confirmed the observations made during the visual inspection of the particles.

Turgman-Cohen et al.$^{60}$ examined asphaltene adsorption onto silica surfaces modified with self-assembled monolayers (SAMs) of mixed aromatic and aliphatic trichlorosilanes. The main focus of this study was to investigate how varying the content and packing densities of the SAMs affected the tendency for asphaltenes to adhere to the substrate surface. The organosilanes used in these investigations were n-butyltrichlorosilane (BTS), n-octadecyltrichlorosilane (ODTS), n-phenyltrichlorosilane (PTS), and n-phenethyltrichlorosilane (PETS). Mixed SAMs of phenyl and alkyl-based organosilanes were formed from mixtures of PTS:BTS, PTS:ODTS, PETS:BTS, and
PETS:ODTS by immersing the silicon substrates into solutions of trichlorosilanes for 16 hours. The modified substrates were removed from the solutions, rinsed with toluene and absolute ethanol, and dried with an N₂ stream. Each sample was replicated to determine the properties of the SAMs before and after exposure to the asphaltenes and to verify the reproducibility of the experiments. These mixed SAMs were characterized by contact angle measurements, spectroscopic ellipsometry, and near edge X-ray absorption fine structure (NEXAFS) spectroscopy to evaluate their hydrophobicity, film thickness, and molecular composition. Adsorbed asphaltene molecular structure and the extent of asphaltene adsorption were evaluated using NEXAFS and ellipsometry. Asphaltene adsorption was achieved by immersing the derivatized substrates in asphaltene solutions of 0.5 wt% for 12 hours. These samples were removed from the asphaltene solution, rinsed, and sonicated in toluene for 5 minutes to remove residual asphaltenes. The adsorption of asphaltenes onto the various modified silica substrate surfaces was monitored by changes in the positions and intensities of the different NEXAFS peaks and the degree of the edge-jump in the NEXAFS spectra. To determine the effect of aromaticity and thickness of the SAMs on asphaltene adsorption, these researchers first examined NEXAFS spectra of mixed SAMs of PTS:ODTS before and after being exposed to the asphaltene solutions. In these studies, the PTS:ODTS content of the SAMs was varied from 100:0, 85:15, 15:85, 7.5:92.5, and 0:100. The spectra revealed that very little asphaltenes adsorbed onto the ODTS surface, however as the aromatic content increased in the SAMs (PTS > 15%) asphaltene adsorption increased. In order to further investigate the effects of aromaticity and thickness of the SAMs on asphaltene adsorption, the researchers plotted the 1s to π⁎ C=C peak area before and after asphaltene
adsorption as a function of the aromatic fraction for all of the mixed SAMs. Difficulties in measuring the degree of asphaltene adsorption of the SAMs were experienced due to the probing depth of the partial electron yield (PYE) detector used in the NEXAFS instrument. To circumvent this problem, the asphaltene thickness on the SAMs was plotted as a function of the aromatic fraction in the SAMs. The thickness of the adsorbed asphaltene layer increased with increasing aromatic character for the ODTS-based SAMs. However, the thickness of the asphaltene layer decreased with increasing aromatic content for the BTS-based SAMs. When the authors analyzed the thickness of the two SAMs they found that the ODTS-based SAMs were thicker than that of the BTS-based SAMs. Based on this observation the authors suggested that the extent of asphaltene adsorption depended mainly on the thickness of the SAM and not on its aromaticity. To further investigate how the SAM film thickness affected asphaltene adsorption, the thickness of the asphaltene layer was plotted as a function of the SAM thickness for all of the mixed SAMs. The plots revealed that the thickness of the asphaltene layer decreased as the SAM thickness increased. Additionally, the researchers divided the data into three groups based on the major component making up the SAM. It was shown that the BTS-rich SAMs were the thinnest of the SAMs and adsorbed the largest amounts of asphaltenes, followed by the aromatic-rich SAMs, PTS and PETS. These SAMs were of intermediate thickness compared to the BTS-rich and ODTS-rich SAMs. They exhibited the same order of thickness and adsorbed similar amounts of asphaltenes. The third group consisted of the ODTS-rich SAMS. ODTS-rich SAMs showed the smallest amount of asphaltene adsorption and were the thickest, and most hydrophobic. The authors proposed that the interactions influencing asphaltene adsorption onto the SAMs
are the interactions of the asphaltenes with the substrate and not the interactions with the tail groups of the SAMs. The authors further explained that defects in the SAM layers act as possible sites for interactions with asphaltene polar groups. The role of defects in thicker SAM films is reduced due to shielding effects from long alkane moieties whereas, in thin SAM films there are no long chemical moieties present to shield the interactions at the sites which results in larger amounts of adsorbed asphaltenes.

As summarized in the review of prior work, it is evident that asphaltenes adsorb differently onto different surfaces. This project can improve the existing body of knowledge in this field in that our focus is to investigate how a substrate’s surface energy and functionality affects the adsorption of asphaltenes. The QCM-D technique has been implemented in order to examine these surface effects on asphaltene adsorption. QCM-D is an advantageous technique for this study, because it can identify surface interactions through subtle changes in resonant frequency of a quartz crystal in solution regardless of the solution’s transparency. The chemically modified surfaces utilized in this study have been characterized by surface energy calculations using three separate methods which employ different levels of theory. These calculations were obtained by measuring the contact angle of well characterized liquids on the substrate surfaces. The adsorbed asphaltene mass on each surface was plotted as function of the surface energy to determine the relationship between asphaltene adsorption and a substrate’s surface energy.

*Materials and Methods*

*Materials*
Crude oil was graciously provided by Shell Oil and was a product of a Gulf of Mexico reservoir. N-heptane (HPLC grade, 99%) was used as received from Fisher. Toluene (HPLC grade, 99%) purchased from Sigma-Aldrich was distilled over CaH₂ under a positive pressure of N₂. Hellmanex® III was purchased from Hellma Analytics and used as received. Dichloromethane (HPLC grade, 99%) purchased from Sigma-Aldrich was distilled over CaH₂ under a positive pressure of N₂. Trimethylchlorosilane was purchased from Sigma-Aldrich and used as received. Benzyldimethylsilane, heptadecafluoro-1,1,2,2-tetrahydrodecyldimethylchlorosilane, 3-aminopropyltrimethoxysilane, and triethoxysilylpropyl succinic anhydride were purchased from Gelest, Inc. and used as received. N,N-dimethylformamide (DMF, HPLC grade, 99%), purified water, and 2-ethoxyethanol (99%) were purchased from Fluka and used as received. 2-furaldehyde (99%), formamide (99%), methylene iodide (99%), o-xylene (99%), ethylene glycol (99%), 1-bromonaphthalene (99%), dimethylsulfoxide (DMSO, 99%), and glycerol (99%) were purchased from Sigma-Aldrich and used as received.

Asphaltene isolation

Asphaltenes were isolated via precipitation from crude oil samples provided by Shell using a method modified from ASTM D-3279, which uses n-heptane as the precipitating solvent. In this method, a solution of 1:1 Shell crude oil:toluene was prepared and sonicated for 10 min. N-heptane was added to this solution in a 40:1 ratio, and the sample was sonicated for 30 min followed by gentle stirring for an additional 24 hours in the dark. Asphaltene precipitates were then collected via reduced pressure filtration using a 0.2 µm PTFE membrane filter. The collected asphaltenes were washed
three times with ~400 mL, 60°C n-heptane. Lastly, residual solvent was removed under reduced pressure at room temperature in a vacuum oven for 24 hours prior to sample use.

Cleaning and functionalization of SiO₂-coated quartz crystal microbalance (QCM) sensors

SiO₂-coated sensor crystals (purchased from QSense, Inc.) were cleaned and immediately functionalized using select organosilane compounds using the following general procedures. Cleaning of the sensors was accomplished by immersing the QCM sensor crystals in a 2% solution of Hellmanex® III in deionized (DI) water for 2 hours. The sensors were then rinsed with ~300 mL of DI water and blown dry in a N₂ stream. The sensor crystals were used immediately after cleaning.

SiO₂-coated sensors were characterized using water contact angle measurements obtained with a VCA Optima (AST Products, Inc.) (Figure 18) instrument before and after chemical modification. A change in contact angle after functionalization was considered indicative of a change in surface functionality.

Figure 18. Image of the VAC Optima from AST Products.

Static contact angles were determined after releasing a 10 µL drop of purified water on the surface at 3 different locations. The reported contact angle is the average of three replicates of the mean value of the left and right contact angles. Derivatized sensors were
characterized immediately after functionalization, following a 1 hour RT vacuum oven drying, or, in the case of the bare SiO$_2$ sensor, after cleaning and 1 hour drying. Multiple (≥3) sensor disks were prepared of each derivatized surface. Functionalization procedures are detailed as follows:

*Functionalization of SiO$_2$-coated QCM sensor crystals with chlorosilanes*

In a general procedure, SiO$_2$-coated QCM sensor crystals were derivatized with 3 chlorosilanes - trimethylchlorosilane, benzyldimethlychlorosilane, and heptadecafluoro-1,1,2,2-tetrahydrodecyldimethylchlorosilane - by immersing the crystal in a 5% (v/v) solution of the chlorosilane in distilled dichloromethane for 1 hour while stirring on an orbital shaker. The sensors were removed from the reaction solution and rinsed by immersing them in 100 mL dry dichloromethane for 20 min. After rinsing, the crystals were dried in an N$_2$ stream and placed under vacuum for 12 hours to remove remaining solvent. Surfaces will be identified according to the significant functional group component, for example methyl, benzyl, and fluoro.

*Functionalization of SiO$_2$-coated QCM sensor crystals with 3-aminopropyltrimethoxysilane*

SiO$_2$-coated QCM sensors were functionalized with 3-aminopropyltrimethoxysilane in dry toluene according to two separate procedures. In the first procedure, pre-cleaned sensors were placed on a spin coater and 30 µL of 1.0% (v/v) of 3-aminopropyltrimethoxysilane solution in toluene was pipetted onto the sensor surface. The sensors were then spun at rate of 4000 rpm for 30 seconds. The sensor was removed from the spin coater and placed in an oven at 50°C for 12 hours. Lastly, the sensors were removed from the oven and further dried in a vacuum oven for 12 hours.
Several experiments were conducted in order to optimize the procedure by varying the concentration, spin rates, and volume pipette onto the sensor surface. The second procedure involved immersing pre-cleaned sensors in a 1% (v/v) solution of aminosilane in toluene for 4 minutes at 60°C. After four minutes the sensors were removed from the solution and rinsed 5 times with toluene. Following removal from the rinsing solution the sensors were dried under an N₂ stream and placed under vacuum for 12 hours. These surfaces will be referred to as the amine surface.

**Functionalization of SiO₂-coated QCM sensor crystals with triethoxysilylpropyl succinic anhydride**

SiO₂-coated QCM sensor crystals were modified with triethoxysilylpropyl succinic anhydride in toluene in order to impart carboxylic acid functionality to the sensor surface. Functionalization of these sensors was accomplished by immersing pre-cleaned sensors in 10% (v/v) solution of triethoxysilylpropyl succinic anhydride in toluene for 16 hours. The sensors were removed from the reaction solution and washed serially for 20 minutes in 100 mL of toluene and 100 mL of N,N-dimethylformamide. The sensors were then dried via N₂ stream and placed under vacuum for 12 hours. This surface will be referred to as the acid surface.

**QCM-D instrument set-up**

QCM-D experiments were conducted using a Q-Sense E4 equipped with a single flow module. The sensor crystals used were 14 mm diameter, AT-cut, SiO₂ coated (50 nm) quartz with a fundamental frequency of 5 MHz (purchased from Q-Sense). The sensor crystal was mounted on a Peltier element that gives accurate temperature control of ± 0.02°C in the measurement chamber. All solutions used in these experiments were
filtered through a 0.2 µm PTFE membrane filter and degasser assembly. Samples and solvents were stored in a temperature controlled room and the experimental temperatures were set to match the surrounding room temperature. Solvent and liquid samples were circulated through the measurement chamber using a peristaltic pump operating at a flow rate of 1.0 µL/min. Before beginning the experiments the entire measurement chamber was disassembled and all parts were cleaned by immersing them in methanol and sonicating for 30 minutes. The measurement chamber components were immersed in toluene and sonicated for an additional 30 minutes. Lastly, individual components were dried beneath an N₂ stream and reassembled with new o-rings and flow channel gasket.

The flow module was equipped with Teflon tubing (ID 0.75mm) and connected to the peristaltic pump tubing which consisted of viton (ID 0.75mm).

QCM-D adsorption experiments using SiO₂-coated sensor crystals

Prior to all experiments the SiO₂-coated sensor crystals were cleaned using 2% Hellmanex® III in water for 120 minutes, rinsed with DI water, and then dried via an N₂ stream. Chemically modified sensor crystals were used immediately upon removal from vacuum following the functionalization procedure. Solutions of asphaltenes were prepared by dissolving the appropriate amount of asphaltenes in toluene to make solutions of 50 and 100 ppm. The asphaltene samples were sonicated for 10 minutes to ensure all aggregates were dissolved and were allowed to equilibrate for 24 hours in the dark prior to analysis. The temperature of the flow cell was set to the surrounding room temperature which was 22±2°C and solvent was allowed to flow through the measurement chamber for 1 hour to allow the instrument to stabilize before experimental runs were conducted. Pure solvent was allowed to flow through the measurement
chamber for 10-15 minutes to achieve a stable baseline reading. For all experiments the solvent baseline was considered stable when the variation of the signal was less than $\pm 2$ Hz. Asphaltene samples were introduced via a peristaltic pump and were allowed to flow through the measurement chamber over the sensor surface until the frequency response leveled off. The sensor surface was then rinsed with pure toluene to remove all asphaltenes from the surface or until the frequency response reached a plateau. The frequency response was monitored continuously throughout the experiments and the frequency shift was attributed to the adsorption or desorption of asphaltenes on the sensor surface. Solvent and asphaltene samples were introduced into the measurement chamber by stopping the peristaltic pump, moving the Teflon tubing from the solvent container to the sample container, and restarting the pump. This methodology was utilized for all the experiments. For all experimental measurements the third overtone ($n = 3$) of the fundamental frequency and dissipation was used due to its higher sensitivity and low signal-to-noise ratio. The mass of the adsorbed layer was calculated at the end of each adsorption and rinse cycle for every surface using the Sauerbrey equation (Equation 9). Reproducibility studies were conducted by repeating the aforementioned process several times.

Results and Discussion

Investigations of asphaltene adsorption on select surfaces were conducted using the dissipative quartz crystal microbalance technique (QCM-D). The QCM-D is a highly sensitive piezoelectric microbalance that consists of a thin, AT-cut quartz crystal disk that has metal electrodes deposited on each side. The quartz crystal is made to oscillate at its resonant frequency ($f$) when an AC voltage is applied across the electrodes on either
side of the quartz disk. QCM-D measures changes in the resonance frequency (f) and dissipation (D) due to mass adsorption on the sensor crystal surface. As mass is adsorbed or removed from the active electrode surface the oscillation frequency of the crystal will change proportionally to the amount of mass adsorbed or removed. The linear relationship between the change in mass ($\Delta m$) on the active electrode surface and the corresponding frequency shift ($\Delta f$) is demonstrated by the Sauerbrey relation (Equation 9).

Equation 9:
$$\Delta m = -\frac{C \times \Delta f}{n}$$

Here, C is a constant for a 5 MHz quartz crystal and is 17.7 ng Hz$^{-1}$ cm$^{-2}$, $\Delta f$ is the change in frequency in Hz, and $n$ is the overtone number and equals 1, 3, 5, 7, or 9. The larger overtone numbers ($n > 1$) are more sensitive to the area close to the sensor surface compared to the fundamental frequency ($n = 1$). The Sauerbrey relation is valid if the mass added is (1) rigid, (2) small compared to the mass of the crystal, and (3) evenly distributed over the sensor crystal surface. If the film adsorbed on the sensor surface is not rigid but soft, the Sauerbrey relation is no longer valid and will underestimate the mass on the surface. This is because a soft film will not completely couple to the oscillation of the crystal, causing the crystal’s oscillation to be dampened. Thus, the dissipation factor (D) of the crystal oscillation is a measure of the softness of the film and is proportional to the power dissipated in the system. The dissipation factor, D, is defined by Equation 10.

Equation 10:
$$D = \frac{E_{\text{dissipated}}}{2\pi E_{\text{stored}}}$$
Where, $E_{\text{dissipated}}$ is the energy dissipated during one period of oscillation, and $E_{\text{stored}}$ is the energy stored in the oscillating system. Therefore, the measured change in $D$ is the sum of all the contributions that dissipate energy from the oscillating system such as viscous and frictional losses. When performing QCM-D experiments in liquids the change in dissipation is given by the Equation 11.

$$
\Delta D = \frac{1}{\rho_q t_q} \sqrt{\frac{\rho_1 \eta_1}{2\pi f}}
$$

Equation 11:
Where $\rho_1$ and $\eta_1$ are the density and viscosity of the liquid, $t_q$ and $\rho_q$ are the thickness and density of the quartz disk, and $\pi$ and $f$ have their usual designations.

SiO$_2$-coated QCM sensor crystals were derivatized with various organosilane compounds in order to investigate how surface functionality and surface energy affected the adhesion of asphaltene particles. The organosilanes selected for surface derivatizations were chosen so that asphaltene adsorption, or a lack thereof, could be attributed to specific molecular interactions between the derivatized surface and the asphaltenes themselves. Another objective of this research was to identify possible substrate surface treatments capable of deterring asphaltene adsorption which could be applied to oil field operations. The compounds used to derivatize the SiO$_2$-coated QCM sensor surfaces can be seen in Figure 19 below.
Figure 19. Organosilanes utilized in the surface derivatization reactions. (a) 3-aminopropyltrimethoxysilane, (b) benzyldimethylchlorosilane, (c) trimethylchlorosilane, (d) triethoxysilylpropyl succinic anhydride, and (e) heptadecafluoro-1,1,2,2-tetrahydrodecyltrimethylchlorosilane.

Figure 20 shows the reaction schemes for the functionalization of SiO$_2$-coated QCM sensor crystals with chlorosilanes (a-c), 3-aminopropyltrimethoxysilane (d), and triethoxysilylpropyl succinic anhydride (e).
Figure 20. Reaction scheme for the functionalization of SiO\textsubscript{2}-coated QCM sensor crystals with chlorosilanes (a-c), 3-aminopropyltrimethoxysilane (d), and triethoxysilylpropy succinic anhydride (e).

Functionalized surfaces were characterized with water contact angle measurements to confirm that the surface had been modified. Contact angle measurements on unmodified cleaned SiO\textsubscript{2} surfaces resulted in the water droplet completely wetting the surface rendering the contact angle undetectable. Therefore, any change in the water contact angle on the surfaces provides evidence that the surfaces
were functionalized. Table 9 shows the water contact angle measurements on the various surface utilized in this study. All of the surfaces did vary in their hydrophilicity/hydrophobicity, with contact angles ranging from 0° to 99°. Additionally, the measured contact angle values showed a very small amount of variability.

Table 9

*Contact angles of water on the derivatized surfaces.*

<table>
<thead>
<tr>
<th>Surface</th>
<th>Average Contact Angle (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzyl</td>
<td>64°±1°</td>
</tr>
<tr>
<td>Methyl</td>
<td>60°±1°</td>
</tr>
<tr>
<td>Acid</td>
<td>35°±2°</td>
</tr>
<tr>
<td>Fluoro</td>
<td>99°±1°</td>
</tr>
<tr>
<td>Amine</td>
<td>37°±2°</td>
</tr>
<tr>
<td>SiO₂</td>
<td>0°</td>
</tr>
</tbody>
</table>

SiO₂-coated sensor surface was derivatized with the amine compound by two different methods. Different methods were utilized for functionalizing the sensor surfaces because a very different adsorption profile was observed for the amine derivatized sensor during the initial QCM-D experiments. Using sensors prepared by different methods gives confidence that the observed adsorption characteristics are not due to variability in sensor derivatization methods. Upon functionalizing another sensor by a known procedure⁶², a virtually identical adsorption profile was observed. Upon characterizing the sensor with contact angle measurements and surface energy calculations nearly identical results were found for both of the surfaces. Therefore, the
contact angle measurements, surface energy calculations, and the QCM-D experiments for both methods have been combined in all of the results discussed within this text.

The idea to estimate a solid’s surface tension $\gamma_{sv}$, from liquid contact angle measurements began with Young’s relation.\textsuperscript{67,68} In Young’s relation, the contact angle of a liquid drop on a solid surface is described by the equilibrium of the liquid under the influence of three interfacial tensions; the solid-vapor interfacial tension ($\gamma_{sv}$), the solid-liquid interfacial tension ($\gamma_{sl}$), and the liquid-vapor interfacial tension ($\gamma_{lv}$).\textsuperscript{68} A schematic of Young’s relation is shown in Figure 21. Young’s relationship related contact angle to the three interfacial tensions in Equation 12.

![Figure 21. Young’s relation. The contact angle of a liquid drop on a solid surface under the influence of the solid-vapor interfacial tension ($\gamma_{sv}$), solid-liquid interfacial tension ($\gamma_{sl}$), and the liquid-vapor interfacial tension ($\gamma_{lv}$).](image)

Equation 12:

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta$$

Where, $\gamma_{sv}$, $\gamma_{sl}$, and $\gamma_{lv}$ are the solid-vapor, solid-liquid, and liquid-vapor interfacial tensions, and $\theta$ is the measured contact angle. In this equation, the contact angle ($\theta$) and the liquid-vapor interfacial tension ($\gamma_{lv}$) are measurable but the other two quantities are unknown.\textsuperscript{68,69} Therefore, the surface tension of a solid cannot be determined easily from
this equation and, consequently, additional relationships are required.\textsuperscript{69} Establishing these relationships has been the motivation of many researchers, however only the attempts of Zisman\textsuperscript{70}, Owens-Wendt-Kaelble\textsuperscript{71}, and van Oss\textsuperscript{72} are within the scope of this text. These models generate a relation between the contact angle and the liquid’s surface tension by combining Young’s equation with some expression for the solid-liquid interfacial tension ($\gamma_{sl}$).\textsuperscript{73} This relation can then be used to calculate the surface energy of the solid.\textsuperscript{73}

One of the first methods utilized for determining a solid’s surface tension from contact angle measurements was developed by Zisman.\textsuperscript{70} In this method, contact angles are measured on a solid surface using at least three liquids of different surface tensions ($\gamma_l$). The critical surface tension of the solid is determined by plotting $\cos \theta$ versus the surface tensions ($\gamma_l$) of the test liquids and extrapolating to $\cos \theta = 1$.\textsuperscript{69} The extrapolated value ($\gamma_l$) corresponds to the critical surface tension of the solid.\textsuperscript{73} According to this method the critical surface tension is defined as equal to the surface tension of the liquid with the highest surface energy that completely wet the solid surface.

A second method utilized to approximate the surface energy of the derivatized sensor surfaces was the geometric mean method, also known as the Owens-Wendt-Kaelble approach.\textsuperscript{71} In this method the overall surface tension is defined as the sum of two components (Equation 13).\textsuperscript{68}

\textbf{Equation 13:}  
\[ \gamma = \gamma^d + \gamma^h \]

Where $\gamma^d$ represents the surface tension component due to dispersive forces which result from London forces, and $\gamma^h$ represents the surface tension component due to hydrogen bonding and dipole-dipole interactions.\textsuperscript{68} Thus, the contributions to the individual
Surface tension components are based on specific intermolecular forces existing between the liquid and solid surface and their contributions are combined by a geometric mean. When the expression for geometric mean surface energy is combined with Young’s equation the resulting relationship is obtained (Equation 14):

\[
(1 + \cos \theta_i)\gamma_i = 2\left(\sqrt{\gamma_i^d \gamma_s^d} + \sqrt{\gamma_i^p \gamma_s^p}\right)
\]

Equation 14:

Where \(\gamma_i\) is the surface tension of test liquid, \(\theta_i\) is the contact angle of test liquid, \(\gamma_i^d\) and \(\gamma_i^p\) are the dispersive and polar components of the liquid surface tension, and \(\gamma_s^d\) and \(\gamma_s^p\) are the dispersive and polar components of the solid surface tension. In this expression \(\gamma_i^d\) and \(\gamma_i^p\) are known values, \(\theta_i\) is measured; therefore, the polar \((\gamma_s^p)\) and dispersive \((\gamma_s^d)\) surface energy components of the substrates can be calculated. This method requires the contact angle measurements of two well-characterized liquids in order to calculate the surface energy by this approach. Methylene iodide and water were used for the contact angle measurements to calculate the surface energy of the derivatized SiO\(_2\) surfaces.

The final method used for estimating the surface energy of the derivatized SiO\(_2\) sensor surfaces was the acid-base theory developed by van Oss. This method also uses a geometric mean to combine the contributions of the surface tension components; however, the total surface energy is expressed as the sum of the Lifshitz-van der Waals, acid, and base components. In this method the total surface tension is expressed in Equation 15.
Equation 15:

\[ \gamma_i = \gamma_i^{LW} + 2\sqrt{\gamma_i^+ \gamma_i^-} \]

Here, \( \gamma_i^{LW} \) is the Lifshitz-van der Waals surface tension component, \( \gamma_i^+ \) represents the electron acceptor, or Lewis acid, interactions of the surface tension component, and \( \gamma_i^- \) represents the electron donor, or Lewis base, interactions of the surface tension component. In addition, \( i \) denotes either the solid or liquid phase. When the expression for the acid-base theory is combined with Young’s equation it produces the following relationship (Equation 16):^68

\[ (1 + \cos \theta_i) \gamma_i = 2 \left( \sqrt{\gamma_i^{LW} \gamma_2^{LW}} + \sqrt{\gamma_i^+ \gamma_2^+} + \sqrt{\gamma_i^- \gamma_2^-} \right) \]

Equation 16:

In this expression \( \gamma_i^{LW} \) and \( \gamma_2^{LW} \) represent the Lifshitz-van der Waals interactions for the liquid and the solid, \( \gamma_i^+ \) and \( \gamma_2^+ \) represent the acid-base interactions of the solid, and \( \gamma_i^- \) and \( \gamma_2^- \) represent the acid-base interactions of the liquid. To calculate surface energy by this method contact angle measurements have to be acquired for at least three different, well characterized liquids in order to solve for the three unknowns in the equation above. Additionally, van Oss emphasized that the best results would be achieved when contact angle measurements were measured using methylene iodide, glycerol, and water.\(^74\) These liquids were used for the contact angle measurements in order to calculate the surface energy by the acid-base theory.

Modified SiO\(_2\)-coated QCM sensor surfaces were characterized by surface energy calculations using three different levels of theory. The methods used in the surface energy calculations were Zisman’s method\(^70\), the geometric mean method using the
Owens-Wendt-Kaelble approach\textsuperscript{71}, and the acid-base method according to van Oss.\textsuperscript{72}

The calculated surface energy values for the various surface can be seen in Table 10. Although each of these methods produced differing results, the surface energy of the modified surfaces did vary over a wide range of values for each method. This observation coupled with the contact angle measurements of water verified that the surfaces were derivatized.

Table 10

*The calculated surface energy values for each surface by the Zisman, geometric mean, and acid-base methods.* *Where available, literature values\textsuperscript{75} for similar surfaces are provided in parenthesis.*

<table>
<thead>
<tr>
<th>Surface</th>
<th>Surface Energy via Zisman’s Method (dyne/cm)</th>
<th>Surface Energy via the Geometric Mean Method (dyne/cm)</th>
<th>Surface Energy via the Acid-Base Theory (dyne/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl</td>
<td>18.1</td>
<td>42.7</td>
<td>37.9</td>
</tr>
<tr>
<td>Benzyl</td>
<td>27.1</td>
<td>44.5</td>
<td>44.2</td>
</tr>
<tr>
<td></td>
<td>(26.2)</td>
<td>(35.8)</td>
<td></td>
</tr>
<tr>
<td>Amine</td>
<td>27.8</td>
<td>68.3</td>
<td>51.7</td>
</tr>
<tr>
<td></td>
<td>(25.1)</td>
<td>(45.3)</td>
<td></td>
</tr>
<tr>
<td>Acid</td>
<td>28.1</td>
<td>61.5</td>
<td>58.1</td>
</tr>
<tr>
<td>Fluoro</td>
<td>-1.2</td>
<td>19.7</td>
<td>18.9</td>
</tr>
<tr>
<td></td>
<td>(-1.3)</td>
<td>(13.5)</td>
<td></td>
</tr>
<tr>
<td>SiO\textsubscript{2}</td>
<td>(143.5)</td>
<td>(77.3)</td>
<td></td>
</tr>
</tbody>
</table>
A reasonable comparison could be made to published literature values for similar substituted surfaces where available. From Table 10 it is evident that the surface energy values calculated for the benzyl, amine, and fluoro surfaces were all in good agreement with the literature values determined by Zisman’s method, whereas those calculated by the geometric mean method showed a larger deviation from the published values.

Although a critical surface tension of 143.5 dyne/cm was calculated by Janssen and co-workers for a SiO$_2$ surface by Zisman’s method, these authors surmised that this value is not comparable to the values calculated by more accurate methods such as the geometric mean method. Therefore, since the surface energy of the SiO$_2$ surface used in our study could not be measured via contact angle measurements, a literature value of 77.3 dyne/cm was used. Additionally, Table 10 shows that a negative critical surface tension was calculated for the fluorinated surface by Zisman’s method. A negative surface energy for the same derivatized surface was also obtained by Jannsen et al. Janssen et al. expressed that a linear relationship existing between cos $\theta$ and the test liquid’s surface tension ($\gamma_l$) could only be applied to purely disperse liquid-solid systems. Therefore, implementing the Zisman method for determining the surface energy of a solid may be inaccurate. The Zisman method has been established as an estimation of surface energy, thus additional, more accurate methods were implemented in this study.

Figure 22 shows a representative Zisman plot for the fluorinated surface.
Figure 22. Representative Zisman plot for the fluoro surface. The calculated surface energy was found to be -1.21 dyne/cm.

Figure 23 provides a representative QCM-D experiment plot - 50 ppm asphaltene sample on a methyl derivatized surface - where the 3rd overtone of the fundamental frequency (f) is plotted as a function of time (sec). In a typical QCM-D experiment, data collection begins by flowing pure solvent through the measurement chamber, while monitoring the frequency response until a stable baseline is obtained. After approximately 10 minutes, an asphaltene sample in toluene is introduced into the measurement chamber. The asphaltenes were observed to foul the sensor surface through a fast reduction in the frequency response, and the experiment continues until the frequency value plateaus. This period is referred to as the foul. Following the foul, pure toluene is introduced into the measurement chamber to clean the sensor crystal, referred
to as the rinse. In all experiments, asphaltenes were never completely rinsed from the crystal surface, as demonstrated by the observation that the frequency response never returns close to its original value.

Figure 23. A representative QCM-D experiment plot for a 50 ppm asphaltene sample on a methyl derivatized surface.

The mass of adsorbed asphaltenes was calculated for each surface using the Sauerbrey equation (Equation 9). The change in frequency (Δf) was determined by recording the frequency (Hz) before an asphaltene sample was introduced to the sample chamber and the plateau region at the end of the adsorption cycle. Figure 24 depicts the points where the frequency values were recorded. Figure 24 shows the point before the asphaltene sample was introduced corresponded to a value of -0.313 Hz and the point at the end of the adsorption cycle corresponded to a value of -29.45 Hz.
Figure 24. The QCM-D experiment conducted using a 100 ppm asphaltene sample in toluene on the acid modified SiO$_2$ surface. Figure shows the points where the frequency values were recorded for calculations.

The mass of adsorbed asphaltenes was calculated by inserting the frequency values and constants into the Sauerbrey equation (Equation 9) and solving for $\Delta m$. Once the adsorbed mass was calculated, the 171.91 ng cm$^{-2}$ adsorbed mass value was converted into 1.7191 mg m$^{-2}$ or 1.72 mg m$^{-2}$, which is a more common unit for representation.

$$\Delta m = -\frac{(17.7 \text{ ng Hz}^{-1} \text{ cm}^{-2}) \times (-29.45 \text{ Hz} - (-0.313 \text{ Hz})}{3}$$

$$= 171.91 \text{ ng cm}^{-2}$$

$$= 1.72 \text{ mg m}^{-2}$$
Figure 25 depicts a representative QCM-D experiment using a 100 ppm asphaltene sample in toluene on the amine modified surface. The frequency is plotted on the left (Y1) axis (blue line), dissipation is plotted on the right (Y2) axis (gold line), and time is on the x-axis. Here, the dissipation shifted from a value of ~0 to 0.58 when the asphaltene sample was introduced into the measurement chamber and continued to decrease during the adsorption cycle to a value of 0.38. Therefore, the largest shift in dissipation was 0.58. The dissipation shift was small (< 1) in all experiments, supporting previously published results by other researchers that asphaltenes adsorb as a rigidly attached layer and that the Sauerbrey equation (Equation 9) is appropriately applied. Additionally, the adsorption profile for the amino derivative behaved very differently when compared to the other surfaces investigated. This observation leads to an interesting discussion regarding the interpretation of data concerning this sensor.
Figure 25. A representative QCM-D experiment using a 100 ppm asphaltene sample in toluene on the amine derivatized surface. Frequency is plotted on the left (Y1) axis, dissipation is plotted on the right (Y2) axis, and time (sec) is plotted on the x-axis.

The first series of QCM-D experiments were selected to determine the concentration influence of the asphaltene solution on the absorbed mass detected by the sensor. Two asphaltene concentrations were prepared at 50 and 100 ppm, and these concentration values were selected based on their use in reference studies. The adsorbed mass was determined from 50 and 100 ppm asphaltene solutions on the unmodified and methyl modified surfaces. Concentration results are provided in Table 11. Remarkably, the calculated masses of adsorbed asphaltenes on the two different surfaces did not increase as the asphaltene concentration increased. Therefore, it was concluded that asphaltene adsorption was not concentration dependant, at least at these concentrations. Due to this finding, the subsequent QCM-D experiments were conducted with 100 ppm
asphaltene solutions. These experiments were repeated multiple times to ensure reproducibility.

Table 11

*The calculated adsorbed masses for 50 and 100 ppm asphaltene samples on the SiO$_2$ and methyl surfaces.*

<table>
<thead>
<tr>
<th>Sample I.D.</th>
<th>Adsorbed Mass (mg/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 ppm</td>
<td></td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>1.42 ± 0.16</td>
</tr>
<tr>
<td>Average of 3 Runs</td>
<td></td>
</tr>
<tr>
<td>100 ppm</td>
<td></td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>1.37 ± 0.11</td>
</tr>
<tr>
<td>Average of 3 runs</td>
<td></td>
</tr>
<tr>
<td>50 ppm</td>
<td></td>
</tr>
<tr>
<td>Methyl</td>
<td>1.67 ± 0.17</td>
</tr>
<tr>
<td>Average of 3 Runs</td>
<td></td>
</tr>
<tr>
<td>100 ppm</td>
<td></td>
</tr>
<tr>
<td>Methyl</td>
<td>1.63 ± 0.16</td>
</tr>
<tr>
<td>Average of 3 Runs</td>
<td></td>
</tr>
</tbody>
</table>

To probe how the surface energy and functionality contribute to asphaltene adsorption, derivative plots were generated from the frequency response during the foul cycle with respect to time. Figure 26 is an example of the derivative plot which was created for the QCM-D experiment of a 100 ppm asphaltene sample on the acid modified
surface. Here, the maximum rate of adsorption was extracted by obtaining the value at the peak of the derivative plot. For this surface it was found that the asphaltenes adsorbed a maximum rate of 0.45 Hz/sec/sec. All surfaces were analyzed in a similar fashion, and the maximum rates are included along with the adsorbed mass of the foul in Table 12.

![Derivative plot](image)

**Figure 26.** An example of a derivative plot generated for the QCM-D experiments using a 100 ppm asphaltene sample in toluene on the acid derivatized surface.

Table 12 summarizes the calculated adsorbed mass, the dissipation shift, and the maximum rate of adsorption for the surfaces examined in this study. The general conclusions are that (1) all surfaces foul and foul quickly; (2) all surfaces foul to roughly the same extent, as determined by the absorbed mass; (3) all surfaces foul at approximately the same rate, as determined by the derivative plots; and (4) changes in dissipation values are small, supporting the description of the asphaltene film as rigid.
Several of these general findings were unexpected. In the context of the prior work performed by our group, detailing the specific interactions between asphaltenes and additives in precipitation studies, one expects the surface functionality to influence the amount of adsorbed mass. There are two possible scenarios, all surfaces are roughly equal to asphaltene adsorption, or alternatively, concentrations of reagents involved in this study are too high and the sensor becomes quickly saturated so no difference among samples is detected. The second explanation may be probed further, if a much lower concentration study produces suggestive results.
Table 12

Summary of the adsorbed mass, maximum rate of adsorption, and dissipation shifts for all surfaces examined.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Adsorbed Mass (mg/m²)</th>
<th>Maximum Rate of Adsorption (Hz/sec/sec)</th>
<th>∆D (n x 10⁻⁶)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl</td>
<td>1.63 ± 0.16</td>
<td>-0.19</td>
<td>0.64</td>
</tr>
<tr>
<td>Amino</td>
<td>2.26 ± 0.11</td>
<td>-0.23</td>
<td>0.59</td>
</tr>
<tr>
<td>Acid</td>
<td>1.72 ± 0.11</td>
<td>-0.45</td>
<td>0.79</td>
</tr>
<tr>
<td>Fluoro</td>
<td>1.36 ± 0.23</td>
<td>-0.32</td>
<td>0.36</td>
</tr>
<tr>
<td>Benzyl</td>
<td>1.55 ± 0.12</td>
<td>-0.14</td>
<td>0.43</td>
</tr>
<tr>
<td>SiO₂</td>
<td>1.37 ± 0.11</td>
<td>-0.15</td>
<td>0.45</td>
</tr>
</tbody>
</table>

The adsorption profile for the amine surface was unlike the adsorption profiles observed for the other surfaces investigated. This phenomenon is not fully understood; however, there may be a chemical reaction taking place with the asphaltenes instead of a solely physical adsorption event. Perhaps residual active carbonyl-containing functional groups such as an activated carboxylic acid or ester (RC=OOR) on the periphery of the
asphaltene molecule are undergoing a reaction with the primary amine on the sensor surface to form an amide linkage. The amine surface statistically absorbed the most mass.

Another difference noticed in the asphaltene adsorption behavior was seen among the maximum rates of adsorption exhibited by the various surfaces. The surface derivatized with the dicarboxylic acid adsorbs asphaltenes at the fastest rate. This behavior can be rationalized in the context of our prior work. Asphaltenes are shown to interact quite strongly with the naphthenic acids present in crude oils, so it not surprising that the asphaltenes, considered the basic components of crude oil, would have the fastest absorption rate on an acidic surface.

Plots of the adsorbed mass versus surface energy were generated from Table 12 and calculated surface energies (Table 10) to provide a graphical illustration of the data for discussion. Error bars are included on data points to reflect the standard deviation from run to run, determined by running multiple experiments. Six total plots are provided, three of these include the amine surface data Figure 27(a-c) and three do not Figure 28(a-c). The mass adsorbed for each surface was plotted against the surface energy of each surface calculated by the three methods employed: Zisman, geometric mean and acid-base models. No apparent trend was observed with respect to surface energy and the rate or extent of adsorption of asphaltenes. This becomes more obvious when the amine data points are removed as in Figure 28 (a-c). A linear relationship with slope=0 appears to exist. The fact that the amine data points fall outside of this correlation is further evidence for a differing mechanism of interaction in this system.
Figure 27. Plots of the adsorbed mass on each surface versus surface energy calculated for each surface by (a) Zisman method, (b) geometric mean method, and (c) acid-base method.
Figure 28. Plots of adsorbed mass on each surface except for the amine surface versus surface energy calculated by (a) Zisman method, (b) geometric mean method, and (c) acid-base method.

Since a correlation could be established between surface energy and the adsorbed mass during the foul, the rinse portion of the experiment was examined more closely to see if any differences could be established among the surface series. Table 13 lists the asphaltene mass desorbed from each surface after 30 minutes of rinsing with toluene. The calculated values shown in Table 13 demonstrate that small amounts of asphaltenes do desorb from the surface, although again there appears to be no observable trend with surface energy. The data from 30 minutes into the rinse cycle is provided as a representative set, although this trend held at all times evaluated.
Table 13

Asphaltene mass desorbed from each surface after 30 minutes of rinsing with toluene.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Mass Desorbed After 30 mins (mg m⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl</td>
<td>0.178 ± 0.065</td>
</tr>
<tr>
<td>Benzyl</td>
<td>0.184 ± 0.054</td>
</tr>
<tr>
<td>Amine</td>
<td>0.105 ± 0.038</td>
</tr>
<tr>
<td>Acid</td>
<td>0.128 ± 0.047</td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.222 ± 0.036</td>
</tr>
<tr>
<td>Fluoro</td>
<td>0.172 ± 0.043</td>
</tr>
</tbody>
</table>

Conclusions

To conclude, SiO₂-coated QCM sensor crystals were successfully derivatized by the methods employed. The surfaces were characterized by contact angle measurements and subsequent surface energy calculations were performed by 3 methods, increasing in complexity of the theoretical treatment used in calculation. Contact angle measurements supported the preparation of a series of surfaces having a wide variation in the degree of hydrophilicity consistent with the functional groups employed in the derivatization experiments. The QCM-D experiments demonstrated that all of the surfaces adsorb asphaltenes roughly to the same extent with the exception of the amine surface. Perhaps the asphaltene samples used in these experiments were overly concentrated, or the QCM-D technique may not be the best technique for determining the effect of surface energy and surface functionality on asphaltene adsorption. Additionally, dissipation shifts were
small lending credibility to the calculated adsorbed masses on the surfaces and supporting a qualitative description of the adsorbed asphaltene layer as rigid. Maximum rates of adsorption were calculated from derivative plots of the frequency with respect to time. The calculated maximum adsorption rates were very similar for all surfaces with the exception of the acid surface, which is an obvious extension of the results from the first phase of this research effort describing the strong interactions among asphaltenes and organic acids. Plots of the adsorbed mass for each surface versus the surface energy calculated by each method were generated in order to identify a correlation between surface energy and the adsorbed mass of asphaltenes. These plots did not reveal a correlation between surface energy and asphaltene adsorbed mass. In an attempt to further identify a trend between the surface energy and asphaltene adsorption the amine surface was omitted from these plots and a linear regression analysis was performed on the data. This analysis also did not produce the anticipated result of a correlation existing between the adsorbed amount of asphaltenes and the surface energy of the substrate.
CHAPTER IV
SUMMING IT ALL UP

Summary of Conclusions

The goals of this research project were to (1) determine how the presence of naphthenic acids contributed to the particle aggregation and sedimentation behavior of asphaltenes in model crude oil suspension and (2) understand how the physics and chemistry of a substrate surface affected the adhesion of asphaltene particles and how asphaltene deposition may be controlled through substrate surface modification. The specific research tasks derived from these goals were (1) isolate and characterize Shell asphaltenes, (2) perform asphaltene and asphaltene-naphthenic acid aggregations studies using near-infrared spectroscopy (NIR) and dynamic light scattering (DLS) to determine the onsets of precipitation and correlate these results with molecular modeling calculations, and (3) directly measure asphaltene-surface interactions using the quartz crystal microbalance with dissipation measurements (QCM-D) technique. The conclusions drawn from each of these specific research efforts are discussed.

Asphaltenes were isolated from Shell crude oil samples via a modified n-heptane method. Isolated asphaltenes were then characterized by elemental analysis, TEM, DLS, and GPC. The elemental analysis results showed the presence of C (82.52%), H (7.07%), N (1.28%), O (2.00%), and S (1.81%). TEM and DLS were conducted in order to determine the average particle size of the asphaltenes in toluene. The average particle size was determined to be $9 \pm 2$ nm by DLS and $10 \pm 2$ nm by TEM. GPC was conducted in order to get an idea of the asphaltene molecular weight and the results suggested a molecular weight between 500 – 1000 g/mol.
Before the precipitation studies were conducted, Dr. Praveen Madasu performed molecular mechanics calculations on an asphaltene dimer in order to achieve a better understanding of the type and extent of the association in asphaltene aggregates. From these calculations it was found that the interaction energy between the asphaltene molecules of the dimer was approximately -83 kcal/mol. This result suggested that there is a strong association between asphaltene molecules. Subsequently, asphaltene aggregation studies were conducted on asphaltene suspensions alone and in the presence of select naphthenic acids. Four different naphthenic acids were employed in these studies – methyl abietate, hydrogenated methyl abietate, 5β-cholanic acid, and 5β-cholanic acid-3-one. From the onsets of flocculation determined by DLS, asphaltene suspensions precipitated at ~65 % of added precipitant. However, in the presence of the naphthenic acids, flocculation was delayed to a larger volume percent of precipitant to ~71 % with 5β-cholanic acid delaying the onset the most. The data generated from the DLS experiments was fit to a polynomial of y = a + be^x in order to obtain a better representation of the onsets. These fits showed the same trend observed in the experiments and had very good agreement, with correlation coefficients ranging from 0.86 to 0.98. Precipitation onsets were also determined using the NIR technique. A NIR spectrum of asphaltenes in toluene was collected before beginning the experiments to determine where the absorbance from hydrocarbon components in the mixture was minimal and to obtain an initial transmittance value. It was observed that absorbance from the hydrocarbon components in the mixture was smallest at 1600 nm. Therefore, transmittance at this wavelength was chosen as the observable during the onset determinations. From these experiments asphaltene precipitation was observed to occur
at ~65 % of added precipitant and the same trend was observed as in the DLS experiments when naphthenic acids were present in the suspensions. Thus, these two techniques showed a very good correlation in detecting the onset of flocculation for asphaltene and asphaltene/naphthenic acid suspensions.

Molecular mechanics calculations were conducted in order to determine the interaction energy between the naphthenic acids and a model asphaltene molecule. The results from these investigations supported the experimental studies using DLS and NIR techniques. It was observed that methyl abietate and hydrogenated methyl abietate had minimized interaction distances of 4.10 and 4.57 Å and overall interaction energies of -32.5 and -29.6 kcal/mol. This data revealed that the presence of the π system in methyl abietate offered more extensive interaction with the asphaltene than when the π system was absent (hydrogenated methyl abietate). 5β-cholanic acid had a minimized interaction distance of 3.99 Å and an overall interaction energy of -34.7 kcal/mol. Again, 5β-cholanic acid presented the largest additive effect in the precipitation experiments, which suggested a strong association between acidic and basic functional groups. In all of the preferred geometries where and additive effect was observed, the asphaltene adopts a cup-like orientation, with the naphthenic acid residing in the well of the cup. However, the minimized geometries obtained for 5β-cholanic acid-3-one showed an alternative preferred configuration, which did not lead to a delayed precipitation onset.

Dipole moments of the naphthenic acids were calculated by Dr. David Magers in order to identify how dipole-dipole interactions influenced the extent of interaction with the asphaltene. The results from these calculations showed that the dipole moments from the minimum energy conformations of 5β-cholanic acid, methyl abietate, hydrogenated
methyl abietate, and 5β-cholanic acid-3-one were 2.07, 1.49, 1.32, and 2.68. Therefore, with the exception of the ketone, the dipole moments for the naphthenic acids followed the same trend observed in the experimental onset values. Meaning, the larger the dipole of the naphthenic acid, the longer the onset of flocculation was delayed. Based on these results it is believed that 5β-cholanic acid-3-one would rather interact with another 5β-cholanic acid-3-one molecule and dimerize rather than interact with the asphaltene.

Molecular mechanics calculations were conducted a second time in order to further identify a number of structure property relationships, including the relative effects of hydrogen bonding and van der Waals interactions existing between asphaltenes and naphthenic acids. The results from these calculations demonstrated that the molecular structure of the naphthenic acids influenced the type and extent of interaction with various electronegative atoms on the asphaltene molecule. It was found that the most favorable interaction existing between the asphaltene and the naphthenic acids occurred when hydrogen bonds were formed between the heteroatoms of the asphaltene and the carboxylic acids and esters of the naphthenic acids. Additionally, the van der Waals component of the interaction energy was highest when hydrogen bonding occurred between methyl abietate and the asphaltene. The interaction energy was relatively low between the asphaltene and the reduced methyl abietate due to the absence of the π systems. 5β-cholanic acid-3-one was unable to form two simultaneous hydrogen bonds with the asphaltene even though its structure contains two hydrogen bond acceptor functional groups (-COOH, -C=O). This was due to geometric constraints arising from the length of the 5β-cholanic acid-3-one molecular structure.
SiO$_2$-coated QCM sensor crystals were derivatized with select organosilane compounds in order to investigate how surface functionality and surface energy affected the adhesion of asphaltene particles. The organosilanes selected for surface derivatizations were chosen so that asphaltene adsorption, or lack thereof, could be attributed to specific molecular interactions between the derivatized surface and the asphaltenes themselves. Another important aspect of this research was to identify possible substrate surface treatments capable of deterring asphaltene adsorption. The derivatized SiO$_2$-coated QCM sensor surfaces were characterized by contact angle measurements and subsequent surface energy calculations by 3 methods. Contact angle measurements supported that the surfaces were derivatized and that the surfaces did vary in their degree of hydrophilicity. Surface energy calculations showed that the surfaces did vary widely in their surface energy by each of the methods employed. The QCM-D experiments revealed that there was no concentration dependence on asphaltene adsorption and that all of the surfaces adsorbed asphaltenes more or less to the same extent with the exception of the amine surface. A very different adsorption profile was observed for the amine surface which suggested that there may be a reaction taking place between the primary amine on the surface and the residual activated carbonyl-containing functional groups on the periphery of the asphaltene molecule. Maximum rates of adsorption were calculated from derivative plots which were generated from the frequency shifts during the fouling cycle of the QCM-D experiments. The results from these calculations revealed that all of the surfaces foul at similar rates with the exception of the acid surface. This was expected because the results from the first phase of this research demonstrated that asphaltenes do interact quite strongly with organic acids. In
order to identify a correlation between the adsorbed asphaltene mass and surface energy of the substrate, plots of the adsorbed mass for each surface were plotted versus the surface energy calculated by each method. These plots did not reveal a correlation between the surface energy and the asphaltene adsorbed mass. In an attempt to further identify a trend between the surface energy and asphaltene adsorption the amine surface was omitted from these plots and a linear regression analysis was performed on the data. Once again, this analysis did not provide a correlation between the adsorbed asphaltene mass and the surface energy of the substrate. Since a correlation was not observed from these plots, the rinse portion of the experiments were examined to further probe any differences among these surfaces with respect to surface energy. This was done by calculating the amount of asphaltenes desorbed from the surfaces at various times while rinsing with toluene. These calculations revealed that small amounts of asphaltenes did desorb from the surface, however no observable trend was established.
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