Formation of Calcium Naphthenate in Water/Oil Systems, Naphthenic Acid Chemistry and Emulsion Stability

by

Trond Erik Havre

Thesis Submitted in Partial Fulfilment of the Requirements for the Degree of

DOKTOR INGENIØR

Department of Chemical Engineering
Norwegian University of Science and Technology
Trondheim, October 2002
Preface

This thesis is submitted in partial fulfilment of the requirements for the degree of dr.ing. at the Norwegian University of Science and Technology. It consists of six papers that are based on work performed at Statoil R&D Centre from January 2000 to October 2002. In addition, some of the experiments were performed at the University of Bergen in February 2001.

I finished my sivilingeniør degree, at the Department of Chemical Engineering, NTNU, in December 1999. In January 2000, I joined the research programme FLUCHA II (Fluid Characterisation at Elevated Temperatures and Pressures). The programme is supervised by Professor Johan Sjöblom, and is a joint event between Statoil R&D Centre and Ugelstad Laboratory, Department of Chemical Engineering at NTNU in Trondheim. FLUCHA II is financed by The Research Council of Norway, Statoil, Norsk Hydro, TotalFinaElf and ABB. The sponsors have acted as a reference group by evaluating the programme progress twice a year. The project has involved three doctoral students and one post doc.

Parts of the work contained in this thesis were presented at the 2nd International Conference of Petroleum and Gas Phase Behaviour and Fouling in Copenhagen, Denmark in August 2000 and at the 3rd International Conference on Petroleum Phase Behavior and Fouling in New Orleans, USA in March 2002.
Acknowledgements

I would like to express my gratitude to:

Professor Johan Sjöblom for accepting me into the FLUCHA-group, for excellent supervision during my doctoral work and for frequently organizing the famous FLUCHA social events.

Dr. Jens Emil Vindstad and the Naphthenate Group at Statoil R&D Centre for introducing me to the world of naphthenates, for valuable discussion during the regular naphthenate meetings, and for giving me the opportunity to visit the Heidrun Platform in October 2001.

Dr. Narve Aske, Dr. Inge Harald Auflem and the rest of my FLUCHA-colleagues for providing a good and friendly working environment.

Statoil R&D Centre for providing office and laboratory facilities and the Statoil employees for their helpfulness and kindness.

The Research Council of Norway, ABB, Norsk Hydro, Statoil and TotalFinaElf for their financial support through the FLUCHA II project.
Abstract

In recent years the production of crude oils with high amounts of naphthenic acids has increased. Certain problems are related to this type of crude oils and a better understanding of the chemistry of the naphthenic acids is therefore of interest.

Synthetic model naphthenic acids, as well as commercial mixtures and crude oil naphthenic acids have been utilized to study the chemistry of naphthenic acids. Partitioning of naphthenic acids between oil and water and the dissociation equilibria in water have been studied in addition to their interfacial tension and micellisation behaviour.

A method for studying the precipitation of calcium naphthenate particles by means of near infrared spectroscopy was presented. It was shown that the method gives information about the induction period and about the rate of reaction for particle growth. Solubility products can also be estimated.

Near infrared spectroscopy were also utilized to study the ability of naphthenic acids and other amphiphiles to disintegrate asphaltene particles. It was shown that the structure of the naphthenic acids is important and that a commercial mixture of different surfactants had the best disintegration effect. The technique is applicable for screening the efficiency of various additives as disaggregation chemicals.

Emulsion stability was studied by means of Langmuir technique, critical electric field and bottle tests. The Langmuir study showed that the presence of Ca\(^{2+}\)-ions at elevated pH gave rise to stable naphthenate monolayers. Oil/water emulsions stabilized with different carboxylic acids were investigated at different pH-levels and water-contents. It was demonstrated that water/oil emulsions could be stabilized by a combination of multilayer (D-phase) and asphaltene particles. Critical electric field was used to determine the emulsion stability of these systems and it was shown that a combination of 60% asphaltene particles and 40% D-phase gave the stablest w/o-emulsions. This investigation verifies the importance of D-phase stabilization in combination with asphaltene particles in systems with acidic heavy crude oil (including bitumen) and water.
List of Papers


Additional publications


## Contents

Preface ...................................................................................................................... I
Acknowledgements..................................................................................................... II
Abstract................................................................................................................... III
List of Papers............................................................................................................ IV
Contents.................................................................................................................. VI

1  Introduction........................................................................................................ 1

2  Naphthenic Acid Chemistry ...................................................................................2
   2.1  Origin and Structure....................................................................................2
   2.2  Equilibria in water/oil/naphthenic acid systems ...............................................3
   2.3  Interfacial Activity of Naphthenic Acids...........................................................6
   2.4  Micelle formation ........................................................................................7
   2.5  Phase Equilibria ........................................................................................9

3  Crude Oil Composition and State ......................................................................... 12
   3.1  Composition............................................................................................. 12
   3.2  Structure................................................................................................. 14

4  Emulsions......................................................................................................... 16

5  Formation of Calcium Naphthenate ...................................................................... 19
   5.1  Mechanism and Inhibition .......................................................................... 19
   5.2  Crystallization Theory ................................................................................ 21

6  Techniques....................................................................................................... 24
   6.1  Langmuir Films......................................................................................... 24
   6.2  Near Infrared Spectroscopy ........................................................................ 27
   6.3  Critical Electric Field .................................................................................. 29
   6.4  LC/MS..................................................................................................... 31

7  Main Results ..................................................................................................... 33
   Paper I........................................................................................................... 34
   Paper II ......................................................................................................... 38
   Paper III ......................................................................................................... 41
   Paper IV......................................................................................................... 45
   Paper V.......................................................................................................... 50

8  Concluding Remarks .......................................................................................... 56

References ............................................................................................................... 57

Paper I-VI are enclosed and separated by grey sheets.
1 Introduction

In recent years there has been an increase in the production of acidic crude oils with high amounts of naphthenic acids [1, 2]. Certain problems are related to this type of crudes and a better understanding of the chemistry of the naphthenic acids is therefore of great interest.

The corrosive properties of naphthenic acids have been known for a long time. The mechanism of this process takes place in an oil environment and is not clarified in detail [3-6]. Because the naphthenic acids and their soaps are surface/interfacially active they will accumulate at w/o interfaces and stabilize colloidal structures [7-9]. The worst scenario from an operational point of view is the stabilization of water-in-oil emulsions, which can cause problems in the separation process [10]. The naphthenic acids can affect the emulsion stability directly or through interactions with other crude oil components. Due to the hydrophilic acid group, the lower molecular weight naphthenic acids have a high water solubility compared to other crude oil components. The presence of naphthenic acids in the wastewater can cause significant environmental problems [11].

Under certain conditions, the naphthenic acids will form metallic soaps with metal ions in the produced water. These metallic soaps, mainly calcium naphthenates, are neither soluble in water nor oil, and due to their density they will accumulate at the oil-water interface in separators. They may also precipitate in other parts of the process. The formation of naphthenate deposit will cause operational problems with shutdown periods, during which thorough cleaning must take place.

With this background, it is evident that a better understanding of the chemistry of naphthenic acids is needed. Although the corresponding paraffinic fatty acids are very well characterized with regard to association and micellization in water, phase equilibrium, formation of lyotropic liquid crystals and microemulsions, monomolecular film properties, etc. [12-24], little information is available for naphthenic acids.

This thesis focuses on the basic chemistry of naphthenic acids, their impact on emulsion stability and naphthenate formation.
2 Naphthenic Acid Chemistry

2.1 Origin and Structure

Naphthenic acids are classified as carboxylic monoacids of the general formula RCOOH, where R represents any cycloaliphatic structure. Generally, the term “naphthenic acid” is used to account for all carboxylic acids present in crude oil, including acyclic and aromatic acids. Nearly all crude oils contain some naphthenic acids. Heavy crudes from geologically young formations have the highest acid content while paraffinic crudes usually have low acid content [25]. Naphthenic acids are known to be produced during the in-reservoir biodegradation of petroleum hydrocarbons [26], and they are considered to be a class of biological markers, closely linked to the maturity and the biodegradation level of the oil fields [2].

The naphthenic acids are complicated mixtures. Many different methods and analytical techniques have been used for analyzing these acids [9, 27-32]. An overview shows them to be C\textsubscript{10}-C\textsubscript{50} compounds with 0-6 fused saturated rings and with the carboxylic acid group apparently attached to a ring with a short side chain [33]. The distribution of carbon number and ring content varies with crude oil source and distillate fraction. Naphthenic acids with similar total acid number (TAN) and average molecular weight can have significantly different profiles [34]. Examples of structures of naphthenic acids that may be found in crude oils are given in Figure 2.1.

![Figure 2.1 Examples of structures of naphthenic acids that may be found in crude oils.](image-url)
Roussis and Lawlor [35] have published the distribution of naphthenic acids in a crude oil from the Norwegian continental shelf. This is reproduced in Figure 2.2. $z=0$ corresponds to fully saturated (aliphatic) acid, $z=-2$ to one-ring naphthenic acids, $z=-4$ to two-ring naphthenic acids etc.

![Figure 2.2](image.png)

Figure 2.2 Molar amount of naphthenic acids with different number of carbons for a crude oil from the Norwegian continental shelf. $z=0$ indicates no ring, $z=-2$ one ring, $z=-4$ two rings etc. [35].

### 2.2 Equilibria in water/oil/naphthenic acid systems

In a system that consists of naphthenic acids in combination with a water phase and an oil phase, several equilibria will be involved. The two terms believed to be most important at low pH is the partitioning of undissociated acid between the phases and the dissociation of carboxylic acid in the water phase. At higher pH formation of micelles in the water phase and reversed micelles in the oil phase is believed to be of importance. Other equilibria involved in the system are dimerisation in both water and oil and formation of different metal soaps. As a consequence of the amphiphilic nature of the carboxylic acid, they will prefer the oil-water interface. Hence, equilibria of adsorption and desorption at the interface are established.

The monomeric form of the naphthenic acids will be distributed between the hydrocarbon and the water phase according to Equation 1, where $HA_o$ and $HA_w$ represent undissociated naphthenic acid in the oil and water phase, respectively.
\[ \text{HA}_o \rightleftharpoons \text{HA}_w \] (2.1)

This equilibrium can be described in terms of a partition coefficient, given by Equation 2.2.

\[ K_{wo} = \frac{[\text{HA}]_w}{[\text{HA}]_o} \] (2.2)

The acid will dissociate in the water phase according to Equation 2.3, with equilibrium constant given in Equation 2.4.

\[ \text{HA}_w \rightleftharpoons \text{A}_w^- + \text{H}^+ \] (2.3)

\[ K_a = \frac{[\text{A}_w^-] \cdot [\text{H}^+]}{[\text{HA}]_w} \] (2.4)

Dimerization of carboxylic acids has been the subject for several studies. Goodman [36] found that fatty acids of chain length 14C and below had monomer-dimer equilibrium in the oil phase (n-heptane) and no association in the aqueous phase. The relative amount of dimers in aqueous solution tends to increase with an increase in alkyl chain length according to Suzuki [37]. Takeda et al. [38] found that the dimerization in the hydrocarbon phase increased with increasing concentration. Somasundaran et al. [39] determined the dimerization constant of oleate in aqueous solution of 6E-3 (mol dm\(^{-3}\))\(^{-1}\) at pH=11.4. Mukerjee [40] studied association of long chain fatty acid anions in water. It was found that the association involves only two anions. The formation of trimers and higher is negligible. The dimerisation increases progressively with increasing chain length up to palmitate (C16). However, stearate, oleate and linoleate have dimerisation constants at the same order as palmitate. Mukerjee also concluded that dimerisation of undissociated acid is less significant than dimerisation of dissociated acid.

Other equilibria will also exist and influence the system. Formation of metal soaps can be of importance if divalent metal ions are present in the aqueous phase. In addition,
The formation of micelles and reverse micelles can occur at higher pH. The micellisation can be treated as a pseudophase phenomenon, i.e.

\[ nM \rightleftharpoons M_n \tag{2.5} \]

where \( M \) is a monomeric fatty acid or carboxylate molecule. The corresponding equilibrium constant is given by:

\[ K_{mic} = \frac{[M_n]}{[M]^n} \tag{2.6} \]

The micellisation must be accounted for when the total concentration exceeds the critical micelle concentration. Figure 2.3 shows how the complexity of the system increases when going from a system involving only monomer equilibria, at low pH, to a system, at higher pH, with micellisation involved.

![Equilibria in water/oil/naphthenic acid systems](image)

According to Leo et al. [41] association becomes significant even at low concentration with long chain fatty acids. Even though one works with concentration below the critical micelle concentration (CMC), association in the water phase cannot be completely eliminated. Formation of micelles is described in detail in Chapter 2.4 (page 7).
2.3 Interfacial Activity of Naphthenic Acids

In addition to the equilibria discussed earlier, equilibria involving adsorption and desorption of amphiphiles at the oil/water interface will be established. The presence of amphiphilic carboxylic acids in a water/hydrocarbon system will lower the interfacial tension. The dissociated and associated form of the acid molecules will have different interfacial properties. Several studies have been performed in assessing the pH dependence on interfacial tension in oil/water/carboxylic acid-systems [42-50]. The interfacial activity for surfactants in crude oil has also been studied by several authors [8, 10, 51, 52]. Generally, a marked decrease in interfacial tension as the pH of the water phase increases has been observed. The interfacial tension will continue to decrease after complete ionization. Danielli [44] have explained this by use of the Donnan equilibrium.

Rudin and Wasan [47, 48] studied the mechanism for lowering of interfacial tension in alkali and acidic oil systems. They related the lowering of interfacial tension to dissociation of acid molecules, and they also considered the presence of unionized acids at the interface. They argue that the interfacial tension vs. pH goes through an ultra low minimum due to simultaneous adsorption of ionized and unionized acids. They also consider how formation of micelles influenced the amount of surfactants at the interface.

The fact that interfacial tension decreases at high pH for acidic crude oils is used in enhanced oil recovery. Alkaline solutions can be injected into the reservoir in order to lower capillary forces and thereby facilitate oil recovery [48].

The bulk concentration of surface-active species is in equilibrium with the concentration at the oil/water interface according to Equation 8 and 9.

\[
A_w^- \rightleftharpoons A_{\text{int}}^- \quad (2.7)
\]

\[
HA_o \rightleftharpoons HA_{\text{int}} \rightleftharpoons HA_w \quad (2.8)
\]

where \(A_{\text{int}}^-\) and \(HA_{\text{int}}\) are the concentration of ionised and unionised naphthenic acid at the interface.

The pH at the interface, \(pH_{\text{int}}\), can be related to the bulk phase \(pH_{\text{bulk}}\), by assuming a Boltzmann distribution of the counterions in the electrical double-layer, i.e.
\[ \text{pH}_{\text{int}} = \text{pH}_{\text{bulk}} + \frac{e \psi}{2.3kT} \]  

(2.9)

where \( e \) is the electronic charge, \( \psi \) is the surface potential, \( k \) is the Boltzmann constant, and \( T \) is the temperature [45]. Hence, for a given bulk pH the interfacial pH will be lower and the fraction of dissociated acid at the interface will therefore be lower than the fraction of dissociated acid in the bulk phases.

The concentration of the surfactants at the interface is related to the bulk concentration if the effect of the counterions in the electrical double layer is accounted for. Hence, the total amount of the different acid forms in the bulk phases will govern the amount of each form at the oil/water interface. The interfacial concentration is related to the interfacial tension, since the dissociated acids are more interfacially active than the undissociated form.

### 2.4 Micelle formation

Naphthenic acids and naphthenates are amphiphilic molecules, were the carboxylic acid group represents the hydrophilic part and the carbon moiety represents the hydrophobic part. Molecules of this nature may form micelles in the water phase. The micelles are aggregates of molecules where the oil-soluble, hydrophobic part of the molecules are directed into the centre of the micelles, while the water-soluble, hydrophilic part is directed towards the water phase. The aggregation process is driven by an increase in entropy [53]. When a hydrocarbon chain is put in contact with water, the water molecules close to the chain will order themselves leading to reduced entropy compared to bulk water. The entropy will increase if the hydrocarbon chains are removed from contact with the water into the micelles.

A crucial parameter for surfactant association and for the formation of different kind of structures is the molecular packing parameter, MPP, defined by Equation (2.10) [17].

\[ \text{MPP} = \frac{V}{a \cdot l} \]  

(2.10)
Here, \( V \) is the volume of the surfactant, \( a \) is the head-group area (topological) and \( l \) is the length of the almost extended hydrocarbon chain. Restrictions with regard to geometries of aggregates will occur depending on the topology of the area of the end group and volume of the hydrocarbon chain. Possible aggregate shapes expected for different values of MPP are shown in Figure 2.4 [17].

\[
\frac{v}{al} \begin{cases} < \frac{1}{3} & \frac{1}{2} \cdot \frac{1}{3} \\ \frac{1}{2} - l & > 1 \end{cases}
\]

**Figure 2.4** Schematic diagram of possible aggregate shapes expected for different geometries of the surfactant molecule according to MPP=\(v/\text{al}\) criteria [17].

When \( \text{MPP} \leq 1/3 \) spherical aggregates with a large area will form. When the value of MPP is between 1/3 and 1/2, rod-shaped aggregates are most probable, while lamellar structures are formed for \( 1/2 \leq \text{MPP} \leq 1 \). For MPP>1 reverse structures with the hydrocarbon chain directed outwards occur.

For charged surfactants, the tendency will be to form spherical micelles, due to a strong electrostatic repulsion between the head-groups. In a system consisting of a naphthenic acid, RH and a naphthenic salt, RNa, the ratio, RH/RNa, will determine the geometry formed. Normally by varying RH/RNa (in water), at high enough pH, one will have micelles, liquid crystals and reversed structures [54].

The formation of micelles occurs when the concentration of the micelle-forming species is above a certain concentration known as the critical micelle concentration (CMC). The CMC is often determined by measuring the surface tension at different concentration of surfactant. Upon addition of surfactant to a water solution, the surface tension decreases until CMC is reached. Above this concentration, surfactants that are added will form
micelles and the concentration of monomeric surfactant will remain practically constant, resulting in a constant surface tension. CMC can also be determined by measuring other physiochemical properties that changes over the CMC; such as electric conductivity, refractive index, x-ray diffraction or viscosity [55].

The CMC-value gives a first basis in understanding the intermolecular interactions in aqueous solutions of surfactants. For paraffinic fatty acid salts with sufficiently long alkyl chains a distinct CMC is normally observed. At the same time the paraffinic alkyl chains do not have any severe packing constraint. On the other hand pharmaceutical surfactants with condensed ring structures are known to have a step-wise association in water and a weak CMC is resulting. These molecules have restrictions in their packing, and ordinary spherical micellar structures do not emerge. The difference in the molecular packing is also reflected in the aggregation numbers. For the paraffinic fatty acid salts the micelles can contain up to 100 monomers, which is considerably higher than for the monomers with large condensed ring structures. The logarithm of CMC often varies linearly with the size of the hydrophobic part of surfactants [17, 56]. In an aqueous solution of carboxylic acids, there will be mixed micelles composed of ionised and unionised acid molecules. The pH will determine the amount of the different forms. Theander and Pugh [57] showed that the CMC increases with pH over the pH range 7-12 in a solution of sodium oleate.

2.5 Phase Equilibria

As the concentration of “naphthenic acid / naphthenates” increases beyond the CMC, eventually, different types of liquid crystalline phases will result. Per today, no detailed and complete phase equilibria of a “sodium naphthenate / naphthenic acid / water / oil” system have been published. Horváth-Szabó and co-workers have published qualitative phase equilibria of sodium naphthenates in aqueous solution [54] and “sodium naphthenates / toluene / water” systems [58]. One of the most important findings of these investigations is that liquid crystals can be present over a large range of compositions in sodium naphthenate / water / toluene mixtures. The effect on the phase equilibria on adding heptane to a “sodium naphthenate / toluene / water”-systems have also been studied [59] in addition to the presence of sodium naphthenate liquid crystals at oil/water interfaces [60].

It is our opinion that the phase equilibria in the system water/sodium hexadecanoate (NaC16)/hexadecanoic acid (HC16) at 70°C is representative also for naphthenic acid
based systems. The phase diagram of this system has been published by Skurtveit et al. [16] and is given in Figure 2.5.

![Figure 2.5 Phase equilibria in the system water/hexadecanoic acid (HC16)/sodium hexadecanoate (NaC16) at 70°C. The diagram is expressed in weight percent [16].](image)

In this system, existence of 4 or 5 isotropic phases can be observed. These are a micellar L1-phase (with ordinary micelles), a hexagonal liquid crystalline E-phase (with long rods in an aqueous environment), a lamellar liquid crystalline D-phase (with a bilayer structure) and a reversed solution phase L2 (with reversed micelles). It is questionable if a F-phase with a reverse hexagonal structure exists.

The importance of phase equilibria in water/oil/stabilizer systems were first linked with emulsion stability by Professor Friberg. He documented the importance of the existence of a lamellar liquid crystal (D-phase) and a corresponding increase in emulsion stability [61-64]. The basic idea is to cover the emulsion droplets with a multiple layer of surfactant/water to enhance the rigidity of the interfacial w/o-layer. In this way a barrier against coalescence is built up.

The importance of the stabilization of water/oil emulsions, due to the D-phase has been documented for the phase diagram in Figure 2.5 [16]. It is noticeable that an upper limit
of phase equilibria including the D-phase, seems to be $\text{HC16}/\text{NaC16} \approx 85/15$, and a lower limit is $\text{HC16}/\text{NaC16} \approx 15/85$. Hence, it can be claimed that in an equivalent naphthenic acid-based system, a D-phase can exist for ratios of naphthenic acid to sodium naphthenate $\sim 0.1$ to $6$. It is sufficient to have only $10\%$ of a naphthenate salt to obtain the D-phase.

In order to find the best additives for emulsion breaking in the oil industry, a detailed understanding of the mechanism responsible for the formation of kinetically stable emulsions is an advantage. It is evident that the investigation of the phase behaviour, beyond its theoretical importance, can support the development of efficient separation methodologies, if the phase diagram is mapped together with the emulsion stability. Phase behaviour investigations, in certain cases, can help eliminate the need for emulsion breakers in industrial processes since a small change in the composition can lead to a dramatic change in the separation efficiency [59].

Phase diagrams usually represent equilibrium systems, while in industrial processes the components are usually in a non-equilibrium state. Studies of non-equilibria systems can be useful for industrial purposes. However, an understanding of the equilibria system is necessary as a starting point for understanding the non-equilibria phase behaviour [59].
3 Crude Oil Composition and State

3.1 Composition

Crude oil is a complex mixture of gaseous, liquid and solid hydrocarbons with small quantities of organic compounds containing sulphur, oxygen, nitrogen, and trace amounts of metallic constituents [65]. The hydrocarbons in a light distillate of petroleum can be divided into three types: alkanes (paraffins), cycloalkanes (naphthenes) and aromatics. Heteroatoms tend to concentrate in the higher molecular weight proportion of the crude oil. The crude oil composition may vary widely from one oil field to another. Due to the large number of isomers, a determination of the molecular composition of crude oil is not possible. Hence, analysis of crude oil properties and structure is done on fractions, consisting of large number of different molecule structures. Four fractions, defined by polarity and solubility, are readily used. These fractions are known as the SARA-fractions, i.e. saturates, aromatics, resins and asphaltenes.

Asphaltenes are defined by solubility characteristics, i.e. they are insoluble in \( n \)-heptane or \( n \)-pentane and are soluble in toluene [65]. They are generally composed of polyaromatic nuclei carrying aliphatic chains and rings and a number of heteroatoms, including sulphur, oxygen, nitrogen and metals such as vanadium, nickel and iron. These heteroelements account for a variety of polar groups, such as aldehyde, carbonyl, carboxylic acid, amine and amide [66-68]. The average molecular weight of asphaltene molecules is difficult to measure due to their tendency to self-aggregate. However, molecular weights in the range 500-2000 g mole\(^{-1}\) are believed to be reasonable [69]. Figure 3.1 shows the structure of a hypothetical asphaltene monomer molecule [70]. The sizes of asphaltene monomers have been reported to be in the range 12-24 Å [65, 71].
Saturates account for the alkanes (paraffins) and cycloalkanes (naphthenes) in the crude oil and are generally the lightest fraction of crude oil. Wax is a sub-class of the saturates, consisting primarily of straight-chain alkanes, mainly ranging from C\textsubscript{20} to C\textsubscript{30}. Wax precipitates as a particulate solid at low temperatures, and is known to affect emulsion stability properties of crude oil systems [69].

The aromatic fraction contains molecules with aromatic or condensed aromatic rings. Representatives of which are benzene, naphthalene, phenanthrene as well as higher condensed ring systems and their derivates. Polar, higher molecular weight aromatics may fall in the resin or asphaltene fraction [65].

Resins are readily defined as soluble in \textit{n}-heptane or \textit{n}-pentane but insoluble in liquid propane [65]. They contain various polar groups, often containing heteroatoms such as nitrogen, oxygen and sulphur. Since resins are defined by solubility, overlap to the aromatic fraction will occur. The resins are similar to the asphaltenes but have a higher H/C ratio, indicating less aromaticity and they generally have a lower molar mass. Naphthenic acids are a part of the resin fraction. The naphthenic acids have been described in detail in Chapter 2 (page 2).

Crude oil can be fractionated into the SARA-fractions by first precipitating the asphaltenes in \textit{n}-pentane. The remaining fractions can then be separated by their polarity with high pressure liquid chromatography (HPLC) as described by Aske \textit{et al.} [72].
3.2 Structure

The structure of crude oil is closely related to the state of the asphaltene fraction, i.e. the form in which the asphaltene molecules exist in the hydrocarbon solution. Asphaltenes exist in a monomeric form in aromatic solvents in dilute concentration. However, in most hydrocarbon solutions the asphaltenes tend to self-associate into particles or micelles. The asphaltene monomers are believed to be held together by charge transfer, hydrogen bonds and van der Waal forces [65].

Pressure, temperature, aromaticity and polarity of the asphaltenes and the surrounding solution are all parameters that will affect the aggregation of asphaltenes and thus the state of the crude oil.

Resins are essential in dissolving the asphaltenes in the crude oil. They are thought to attach to the asphaltene aggregates with their polar groups and stretch their aliphatic groups outward, thereby stabilizing the asphaltenes against aggregation. This is illustrated in Figure 3.2 [73].

![Figure 3.2 Stabilization of asphaltene aggregates by interactions with resins [73].](image)

Other amphiphiles can also disintegrate asphaltene particles in the same way as resins. Gonzalez and Middea [74] studied the peptization of asphaltenes in aliphatic solvents by various oil-soluble amphiphiles. They showed that the effectiveness of amphiphiles on
asphaltene stabilization was influenced by the interactions between the polar headgroups of the amphiphiles and polar groups on the asphaltene molecules. However, their results also indicated that other interactions could be of importance. For example, the π-electrons of the aromatic portions of the asphaltenes may act as electron donors for hydrogen bonds with hydroxyl groups of the amphiphiles. In 1994, Chang and Fogler [75, 76] discussed the stabilization of asphaltenes in aliphatic solvents using alkylbenzene-derived amphiphiles. The results supported earlier suggestions of a hydrogen-bonding effect or possible acid–base interactions between the amphiphile headgroups and polar groups on the asphaltenes, and also showed that the length of the alkyl tail of the amphiphiles was of significance. They also found that in some cases the asphaltenes and the amphiphiles (p-dodecylbenzenesulfonic acid) could associate into large electronic conjugated complexes. It has been shown by Östlund et al. [77] that the effectiveness of naphthenic acids to disperse asphaltenes depends on the type of asphaltenes.

In Paper II [78] the disintegration of asphaltene aggregates by various amphiphiles was studied by means of near infrared spectroscopy.
4 Emulsions

The concept of emulsions has been defined by IUPAC as a dispersion of droplets of one liquid in another one with which it is incompletely miscible. In emulsions the droplets often exceed the usual limits for colloids in size [79].

Emulsions of oil-droplets in a continuous water-phase are termed oil-in-water emulsions (o/w), while emulsions made up of droplets of water in a continuous oil-phase are termed water-in-oil emulsion (w/o). In petroleum industry, emulsions of the latter type are most common. In addition to the usual emulsion types, multiple emulsions of for instance oil droplets dispersed in water droplets that in turn are dispersed in a continuous oil phase (o/w/o) can occur. The size of the water droplets in a crude oil emulsion can be up to 100 µm, which is large compared to the common definition of the upper limit of colloidal size (1 µm) [80]. The emulsion formation is a result of the co-production of water from the oil reservoir. During processing, pressure gradients over chokes and valves introduce sufficiently high mechanical energy input to disperse water as droplets in the oil phase [81]. An efficient separation of water-in-crude oil emulsions is of importance in order to reduce processing costs and increase the quality of the crude oil. Emulsions of the o/w type can exist in the produced water, causing environmental problems.

All emulsions, except microemulsions are thermodynamically unstable. The presence of different types of stabilizers can however make an emulsion stable for a considerably long time. Components that can work as stabilizers in petroleum industry are asphaltenes, resinous substances, naphthenic acids, finely divided carbonate scale, silica, clays, metal sulphates, metal sulphides and chemical additives [80]. These components stabilize emulsions by adsorbing at the o/w interface creating a steric or electrostatic repulsion between droplets that hinders coalescence.

Asphaltenes are known to be the dominant contributor in stabilizing water in crude oil emulsions [82]. The primary mechanism of stabilization is through the formation of a cross-linked three-dimensional network with high mechanical rigidity at the oil water interfaces. This film also consists of resins. Ese et al. [83] used atomic force microscopy images in addition to Langmuir studies to explain the interactions of asphaltenes and resins at an oil/water interface. The interactions between asphaltenes and resins and its importance for emulsion stabilization have also been studied by others [73, 84]. The asphaltenes are believed to accumulate at the oil/water interface as illustrated in Figure 4.1 [85].
The interactions between the different crude oil components will be crucial for the formation of stable emulsions. In Paper II [78] it is described how naphthenic acids and other amphiphilic molecules can disperse the asphaltenes into the solution and hinder them from stabilizing emulsions.

Naphthenic acids are surface active and will influence the stability of crude oil emulsions [1, 10, 51]. Alkali soaps were among the first compounds used to stabilize emulsions [86]. The pH together with the solubility will be sensitive variables for the ability of naphthenic acid monomers to stabilize emulsions [87]. As the pH of the water phase increases, the acids become ionized and can thus stabilize oil in water emulsions by an electrostatic repulsion between droplets.

Emulsions can be stabilized by formation of a stable monolayer of surfactants that sterically hinders coalescence. The Langmuir technique can be used to study the ability of surfactants to form such a monolayer. This technique is described in Chapter 6.1 (page 24). In Paper I [88] this technique was employed in order to study monolayers of naphthenic acids and naphthenates.

The presence of a surfactant multilayer (D-phase) can be efficient in stabilizing droplets and hinder coalescence through a sterical mechanism. The phase behaviour of naphthenic acids/naphthenates is described in Chapter 2.5 (page 9). In Paper III [89],

\[ \text{Figure 4.1 Accumulation of asphaltene aggregates at the oil/water interface [85].} \]
we showed that a multilayer (D-phase) of carboxylic acids/carboxylates together with asphaltene particles can stabilize emulsions in a combined mechanism.

The break-up of emulsions basically involves three mechanisms; i.e. flocculation, sedimentation (or creaming) and coalescence. Sedimentation is favoured by large droplet sizes, high differences in density and low viscosity of the continuous phase. While coalescence is the complete association of two bubbles into one, flocculation is a reversible formation of droplet clusters with virtually no change in the total oil/water interface area. Formation of flocculates will increase the sedimentation rate and eventually, coalescence will occur. The mechanisms are illustrated in Figure 4.2.

Figure 4.2 Emulsion separation by flocculation, sedimentation, and coalescence.
5 Formation of Calcium Naphthenate

Under certain conditions, the naphthenic acids present in acidic crude oil will precipitate with Ca$^{2+}$-ions that are present in the co-produced water and form calcium naphthenate and, to a lesser extent, other metal naphthenates. This precipitation accumulates predominantly in oil/water separators and de-salters, but naphthenates can also deposit in the tube and pipelines. Calcium naphthenate deposit from an oil/water separator are shown in Figure 5.1.

Figure 5.1 Calcium naphthenate deposit (right picture) collected from an o/w-separator. The outlet of the separator (left picture) is located at the o/w-interface. [Pictures, by courtesy of Statoil ASA]

The literature have been lacking on information about the formation of calcium naphthenate in crude oil production facilities. However, recently several reports regarding the subject have been published [1, 2, 90-92].

5.1 Mechanism and Inhibition

When the crude oil is being processed offshore the pressure decreases. This leads to degassing of carbon dioxide from the formation water and hence an increase in pH. When the pH of the water increases, the concentration of dissociated acid also increases, which in turn favours the formation of calcium naphthenate. Calcium naphthenate is neither soluble in water nor oil. Having a density lower than water and higher than the oil phase, accumulation of voluminous particles at the oil/water interface in separators may result. This will lead to costly shutdown periods in which thorough cleaning must take place.
Addition of acid will keep the pH low and thereby avoid naphthenate formation. However, such addition is costly, it will increase corrosion problems and it is environmentally unfavourable. Use of special additives, such as demulsifiers or dispersants, have given encouraging results, but an additive which works well with one crude can be inefficient with another [2]. Naphthenates are often found to co-precipitate with scale. Goldszal et al. [1] have studied the inhibition of naphthenate and scale in deep-offshore fields. They found that if naphthenates are present at the oil water interface, small amounts of minerals (~5wt%) can induce precipitation. To inhibit naphthenate formation it is necessary to destabilize or prevent emulsions from being formed, disperse the naphthenates to avoid accumulation, and to prevent formation of scale. Some additives where found to be efficient in terms of demulsification and naphthenate deposit prevention. Poggesi et al. [91] have reported on multifunctional chemicals that have proved useful as inhibitors for naphthenate formation.

Gallup et al. [90] reported on the formation of “metallic soap sludge” in an Indonesian field. The greenish-brown sludge accumulates in onshore oil storage tanks. The sludge consists of metallic soaps with bicarbonate complexation, closely related to naphthenate deposits.

The deposition of insoluble metal soaps can also be a problem in paper industry. Deposits that can be formed as multivalent metal ions react with fatty or resin acids at pH>6 [93, 94]. Stenius and co-workers [95-100] have studied the phase behaviour and micellisation of sodium abietate and oleate as model compounds for resins and fatty acid soaps, respectively.

For calcium naphthenate to precipitate it is expected that the naphthenic acids must be present in the Ca\(^{2+}\)-containing water phase at its dissociated form. The concentration of the dissociated acid and the solubility of the corresponding calcium soap are thus interesting parameters for an understanding of when naphthenate deposits are formed. In Paper IV [101], pK\(_a\) and partitioning constants for several naphthenic acids were determined. Solubility products for some carboxylic acids were estimated in Paper V [102]. In addition to information about the different equilibria in water/oil/naphthenic acid systems, knowledge of the kinetics of precipitation and accumulation is necessary. A method for studying the formation and growth of calcium naphthenate particles were presented in Paper V. The total oil/water interfacial area as well as the agitation during production may be important variables for naphthenate deposit to form.
5.2 Crystallization Theory

The theory for crystallization is described by Mullin [103]. A brief description is given below.

The first step in a crystallization process is the nucleation. While secondary crystallization is induced by already present crystals, primary crystallization occurs either spontaneous (homogeneous) or is induced by foreign particles (heterogeneous).

A period of time elapses between the achievement of supersaturation and the appearance of crystals. This time lag, generally referred to as an “induction period”, is influenced by the supersaturation, state of agitation, presence of impurities viscosity etc. The induction period, \( t_{\text{ind}} \), can be considered as made up of several parts defined by Equation 5.1.

\[
t_{\text{ind}} = t_r + t_n + t_g
\]  
(5.1)

Where \( t_r \) is the “relaxation time” required for the system to achieve a quasi-steady-state distribution of molecular clusters, \( t_n \) is the time necessary to form a stable nucleus and \( t_g \) is the time needed for the particle to grow to a detectable size. The nucleation time depends mainly on temperature, supersaturation and the interfacial tension between the solution and the solid formed.

The rate of nucleation, \( J \), i.e. the number of nuclei formed per unit time per unit volume, can be expressed as:

\[
J = A \cdot \exp \left( \frac{16\pi \gamma^3 v^2}{3k^3 T^2 (\ln S)^2} \right)
\]  
(5.2)

where \( A \) is a constant, \( r \) is the particle radius, \( \gamma \) is the interfacial tension, \( v \) is the molecular volume, \( k \) is the Boltzmann constant, \( T \) is the temperature and \( S \) is the supersaturation. For systems involving sparingly soluble salts, the supersaturation, \( S \), can be defined as the ratio of the ion concentration product, \( Q \), to the solubility product, \( K_{\text{sp}} \). For a calcium naphthenate system this will be according to Equation 5.3.

\[
S = \frac{[Ca^{2+}]_e \cdot [A^-]_e}{[Ca^{2+}]_{eq} \cdot [A^-]_{eq}} = \frac{Q}{K_{\text{sp}}}
\]  
(5.3)
were \([\text{Ca}^{2+}]\) and \([\text{A}^-]\) are the actual concentration of calcium ions and dissociated acid respectively. \([\text{Ca}^{2+}]_{\text{eq}}\) and \([\text{A}^-]_{\text{eq}}\) are the concentrations in an aqueous solution in equilibrium with the solid salt.

The induction period cannot be regarded as a fundamental property since it is affected by many external parameters. By assuming that it is inverse proportional to the rate of nucleation, information about the nucleation process can be extracted. The induction period will then depend on the supersaturation according to Equation 5.4.

\[
\log t_{\text{ind}} \propto \frac{\gamma^3}{T^3 (\log S)^2}
\]  

Hence, a plot of \(\log t_{\text{ind}}\) versus \((\log S)^{-2}\) will give a straight line with a slope dependent on the temperature and the interfacial tension.

The induction period is followed by a period where the particles grow. In order to understand the kinetics of this process, several different mechanisms are proposed. The surface energy theories claim that the shape the growing crystals assume is the one with a minimum surface area. The diffusion theories presume that matter is deposited at the surface due to the concentration gradient between the bulk solution and at the surface. Adsorption layer theories assume that the crystals grow by a layer-by-layer adsorption process.

Burton, Cabrera end Frank have proposed a relationship between the growth rate and the supersaturation, i.e. the BCF-relationship, given by Equation 5.5.

\[
R = A(S-1)^2 \tanh\left(\frac{B}{S-1}\right)
\]  

were \(R\) is the rate of crystallization, \(S\) is the supersaturation and \(A\) and \(B\) are complex temperature dependent constants. At low supersaturations the rate of reaction is proportional with \((S-1)^2\), while at high supersaturations it is proportional with \((S-1)\). Other models end up with a similar result. Due to the complexity of the crystallization processes, empirical models as given in Equation 5.6, are readily used \[104\].

\[
R = k(S-1)^n
\]
were $k$ is a constant and $n$ is the effective order of crystallization.

Agglomeration of particles can occur in a crystallization process. The rate of agglomeration will depend on the number of particles, the stirring speed and the ability of the particles to be stable towards agglomeration upon collision. For calcium naphthenate particles to be stable against agglomeration, the ratio of acid to calcium may be of importance. Precipitation phenomena of calcium oleate in aqueous solution have been studied by Matijević et al. [105]. It was shown that a ratio of oleate ions to Ca$^{2+}$ of 2:1 gave solutions with the highest turbidity. Excess of any of the two ions led to formation of small particles that were stable towards agglomeration due to electrostatic stabilization. Small particles will contribute less to the turbidity. Precipitation phenomena of colloidal laureate soap particles with different cations were studied by Young et al. [106]. They came to the same conclusion regarding particles of calcium and copper laureate. For thallium and lanthanum laureate the systems were influenced by formation of complex ions. With this background, it is likely that agglomeration of particles will be most prominent in systems were the ratio of Ca$^{2+}$ to dissociated acid is 1:2. However, high electrolyte concentration in the water will decrease the particles ability to be electrostatically stabilized towards agglomeration.

Ostwald ripening will also influence the particle sizes. Ostwald ripening is the process in which small particles dissolves and the solute deposit subsequently on the larger particles. The driving force of this process is the lowering of the total surface energy.
6 Techniques

Different analytical techniques have been utilized in this doctoral work. An outline of the most important ones are given in this chapter.

6.1 Langmuir Films

A central property for emulsion stabilization is the formation of a w/o film that is stable against coalescence. Film formation of naphthenic acids can be studied by the Langmuir technique. The technique is used in order to characterize monolayer properties of surface-active materials. The objective is to get information about how the molecules pack in a monolayer, i.e. how much area each molecule requires and how the molecules interact with each other. A stable monolayer indicates the ability of the surfactant to stabilize emulsions. Børve [107] found a strong correlation between the ability of different crude oil fractions to stabilize w/o emulsions, and the properties of the films formed by the different fractions at the air/water interface.

In order to perform a Langmuir experiment the amphiphilic molecules must be spread on a water surface. Since many film-forming substances do not spread well by themselves, it is normal to use a spreading solvent. This spreading solvent must have the ability to disperse the film-forming molecules so that they are in a monomeric form at the water surface. For this to happen, the spreading coefficient of the solvent on the bulk phase must be positive. The spreading solvent must evaporate completely within a reasonably short time (15 minutes), and it must have sufficient solvency power so that the volume of solvent needed to produce a film does not become too large. The application of the spreading-solvent to the surface is usually accomplished by allowing small drops to fall from a syringe, held a few millimeters above the surface [108].

The Langmuir instrumentation consists of a shallow rectangular trough in which a liquid sub-phase is added until a meniscus appears above the rim. Two moving barriers are placed at the edges of the through. The monolayer is deposited between the barriers and by moving the barriers the area of the water-air surface is changed.

When the available area for the monolayer is large the distance between adjacent molecules is large and their interactions are weak. The monolayer can then be regarded as a two-dimensional gas. Under these conditions the monolayer has little effect on the surface tension of water. If the available surface area of the monolayer is reduced by a
barrier system, the molecules start to exert a repulsive effect on each other. This two-dimensional analogue of a pressure is called surface pressure, $\Pi$, and is given by Equation 6.1.

$$\Pi = \gamma - \gamma_0$$  \hspace{1cm} (6.1)

where $\gamma$ is the surface tension in absence of a monolayer and $\gamma_0$ the surface tension with the monolayer present. The surface pressure is measured with a Wilhelmy plate partially immersed in the water sub-phase. The Wilhelmy plate is hanging on a balance and the surface pressure is calculated from the force that works on the plate due to surface tension [109].

An important indicator of the monolayer properties of an amphiphilic material is given by measuring the surface pressure as a function of the area of water surface available to each molecule. This is carried out at constant temperature and is known as a surface pressure - area isotherm. Usually an isotherm is recorded by compressing the film (reducing the area with the barriers) at a constant rate while continuously monitoring the surface pressure [109]. An example of such isotherm is shown in Figure 6.1 [110]. The diagram is not intended to represent that observed for any particular substance, but shows most of the features observed for long chain compounds.

![Figure 6.1 Surface pressure–area isotherm for a hypothetical long chain organic compound](image)

Figure 6.1 Surface pressure–area isotherm for a hypothetical long chain organic compound [110].
When the monolayer is compressed it can pass through several different phases, which are identified as discontinuities in the isotherm [110]. At first, when the molecules are far apart, little or no interactions exist between the molecules and the monolayer is in a gaseous state (G). As the available area is reduced, the monolayer can undergo a phase transition to the liquid-expanded state (E). In this state the molecules start to interact with each other. The hydrocarbon chains are in a random rather than in a regular orientation. Upon further compression, condensed phases (C) may appear. There may be more than one of these and the emergence of each condensed phase can be accompanied by constant pressure regions in the surface pressure-area plot. In the condensed phase, the molecules are closely packed and are oriented with the hydrocarbon chain pointing away from the water surface. If the monolayer is further compressed, a collapse of the condense monolayer into a multilayer will eventually take place as illustrated in Figure 6.2 [110].

The phase behaviour of the monolayer is mainly determined by the physical and chemical properties of the amphiphile, the subphase temperature and the subphase composition. For example, various monolayer states exist depending on the length and structure of the hydrocarbon chain length and the magnitude of other cohesive and repulsive forces existing between head groups. An increase in the chain length increases the attraction between molecules. On the other hand, if an ionisable amphiphile is used, the ionisation of the head groups induces repulsive forces between the molecules [110].
6 Techniques

In order to investigate the stability of the monolayers, the area loss at constant surface pressure can be measured. This is done by compressing the film to a surface pressure of for example 10 mN m\(^{-1}\). The area of the monolayer is changed in order to keep the surface pressure at this value. The results are normally presented as a plot of \(A/A_0\) versus time \(t\), where \(A_0\) is the area of the monolayer after compression to constant surface pressure and \(A\) is the area of the monolayer at time \(t\). If the monolayer is stable, the area, \(A\), will remain about constant. Rearrangement of the molecules, dissolution of the film into the sub-phase or evaporation will lead to a decrease in the area. Higher surface pressure leads to faster area loss [108].

6.2 Near Infrared Spectroscopy

Over the last 30 years near infrared spectroscopy (NIR) has been increasingly used as an analytical tool, particularly by the food and agricultural industries, but also by textile, polymer and petroleum industry. The increasing popularity is due to four principal advantages of the method; efficiency, simplicity, multiplicity of analysis from a single spectrum, and the non-consumption of the samples. The rapid development of advanced and user-friendly software for multivariate analysis further enhance the usability of NIR [69]. Optical fibers can be used to carry the light from the light source to the point of measurement and back to the light detector. This makes NIR applicable in many processes, for example in high-pressure environments [111].

When light is sent through a chemical sample not all light will be transmitted. This can be accounted for by two distinct mechanisms; electronic absorption by the different molecules and scattering from particles or aggregates. Due to the light scattering, the near infrared spectra will display a baseline elevation that is dependent on the size and number of the particles. Hence, by monitoring the baseline elevation, the growth of particles can be followed. In this doctoral thesis, NIR have been utilized to measure disintegration of asphaltenes in Paper II [78] and the growth of calcium naphthenate particles in Paper V [102].

Light scattering in the near-infrared region is described in detail by Mullins [112] and Kerker [113]; a brief description is given below.

The light scattering can be divided into two groups: wavelength-independent scattering, where the size of the particles is large compared to the wavelength of the light, and wavelength-dependent scattering, where the particles are of comparable sizes to or smaller than the wavelength of the light. The latter group contains the case of \(r/\lambda \leq 0.05\),
where $\lambda$ is the wavelength of light and $r$ the particle radius. At this, so-called Rayleigh condition, the particle is so small that the electromagnetic field it experiences is uniform over the particle. By also assuming that the particles are slightly lossy and dielectric, an expression for the scattering cross section of a particle is given by Equation 6.2.

$$
\sigma_{sc} = \frac{2 \pi^5}{3} \frac{r^6}{\lambda^2} \left( \frac{n^2 - 1}{n^2 + 2} \right)^2
$$

(6.2)

where $r$ is the particle radius, $\lambda$ the wavelength of the incident light and $n$ is the ratio of the discrete phase to the continuous phase index of refraction. In the absence of multiple scattering, and in the Rayleigh limit ($r/\lambda \leq 0.05$), fewer, but larger spheres are much more efficient scatterers than the same mass of smaller particles.

Within the Rayleigh limit, the light extinction can be considered a sum of the absorbance and scattering contribution, represented by the particle cross-sections.

$$
\sigma_{tot} = \sigma_{sc} + \sigma_{abs}
$$

(6.3)

where $\sigma_{tot}$, $\sigma_{sc}$ and $\sigma_{abs}$ are the total, scattering and absorption cross sections, respectively. The absorption cross section scales with $r^3$, while the scattering cross section scales with $r^6$. Hence, the change in the total cross section as a result of particle growth will be governed by the scattering contribution.

The optical density, OD, is given by:

$$
OD = \log \left( \frac{I_0}{I} \right) = 0.434N\sigma_{tot}
$$

(6.4)

where $I$ and $I_0$ are the intensities of the transmitted and incident light respectively and $N$ is the number of particles in the total cross section $\sigma_{tot}$.

The measured optical density is thus a combination of absorption and scattering contributions. The effect of multiple scattering is not accounted for in this equation. Absence of multiple scattering implies that radiation scattered by a single particle proceeds directly to the detector without any further scattering encounters. In case of multiple scattering, the scattering and absorption cannot be treated separately.
Conditions for single scattering can usually be attained by working with dilute systems and with small volumes.

Figure 6.3 demonstrates the effect of particle size on NIR spectra. The spectra are taken at different time during growth of calcium naphthenate particles in water. The increasing optical density due to increasing particle size is clearly seen for wavelengths were the absorption from the surrounding media is low, for example around 1280 nm.

Several authors report on the use of NIR for determination of particle sizes, often in combination with multivariate analysis [114-117].

### 6.3 Critical Electric Field

Electrocoalescence is commonly used for demulsification in the petroleum industry. Water is separated from the emulsion by applying a electric field of 1-10 kV/cm to cause flocculation and coalescence of water droplets in a continuous oil phase [118]. This
principle can be applied to evaluate the different levels of emulsion stability in different systems.

In the critical electric field technique, an increasing electric field is applied to an emulsion and the current that passes through the sample is continuously measured. When the voltage is increased (but below the critical value) the droplets undergo a flocculation and as a result “a bridge of droplets” is formed between the electrodes. $E_{\text{crit}}$ is defined as the electric field necessary to achieve a sudden increase in the current. This increase is due to breakdown of the emulsion droplets and a formation of a continuous water-channel between the electrodes. Figure 6.4 [69] demonstrates the effect on the water droplets when the electric field is increased over an emulsion.

![Figure 6.4 Emulsion droplets in an increasing electric field [69].](image)

The mechanism behind the breakdown is believed to be an ion-transport between the aqueous droplets over the protecting membrane. Hence the critical electric field will reflect the resistance towards coalescence of the interfacial structures.

In Paper III [89], an electric field cell was used for the determination of emulsion stability. The method is similar to the one employed by Aske et al. [119] and Kallevik et al. [120]. The cell for determining the critical electric field is depicted schematically in Figure 6.5. It consists of a Teflon plate with a hole in the centre ($r = 5 \text{ mm}$), and a brass plate on each side. The distance between the plates is 0.5 mm, and the upper brass plate has holes for sample injection. The system is held together with isolating Plexiglas plates. The brass plates are connected to a computer-controlled power supply (Agilent Model 6634B) that can deliver a maximum of 100 V DC. The cell can be placed in a heating
Techniques

cabinet if elevated temperatures are desired. The emulsion samples are injected into the cell and the power supply is starting at 0 V and increased by steps of for example 1V every other second, corresponding to an increase in the electric field of 0.01 kV cm\(^{-1}\) s\(^{-1}\). The electric field required to break the emulsions, \(E_{\text{critical}}\) is recorded when a sudden increase in the current through the sample is seen.

![Electric field cell for emulsion stability measurements.](image)

6.4 LC/MS

Liquid chromatography/mass spectrometry (LC/MS) has been used to determine the concentration of naphthenic acid in an aqueous phase in Paper IV [101]. The samples go through a LC column were the molecules are separated on the basis of their polarity. A mass spectrometer is then utilized to determine the ratio of mass to charge (m/z) for the various naphthenic acid species.

Liquid chromatography is a fundamental separation technique in the life sciences and related fields of chemistry. Unlike gas chromatography, which is unsuitable for non-volatile and thermally fragile molecules, liquid chromatography can safely separate a wide range of organic compounds, from small-molecule drug metabolites to peptides and proteins [121].

After the LC separation, a mass spectrometer is used as detector. In addition to signal strength, they generate mass spectral data that can provide valuable information about the molecular weight, structure, identity, quantity, and purity of a sample. Mass spectrometers work by ionising molecules and then sorting and identifying the ions.
according to their mass-to-charge (m/z) ratios. Two key components in this process are the ion source, which generates the ions, and the mass analyser, which sorts the ions. Different types of ion sources and mass analysers are used for different analyses [121].

LC/MS was used to determine the concentration of different carboxylic acids in water in Paper IV. The advantages of the method are that the analysis can be performed directly on water and that the sample consumption is small. The latter is important due to use of costly special synthesized naphthenic acids.
7 Main Results

This chapter summarises the main results from the papers presented in this thesis.

In Paper I we report on a Langmuir study of naphthenic acids at different pH-levels and electrolyte concentrations. The formation of stable films was seen when cations were present in the bulk phase at elevated pH. In Paper II the interactions between asphaltenes and various surfactants, including synthetic and natural naphthenic acids were studied. The ability of the different amphiphiles to disintegrate asphaltene particles in model heptane-toluene mixtures was documented with the use of near infrared spectroscopy. Emulsion stabilization was the topic of Paper III. Stabilization of emulsions by combined surfactant multilayer (D-phase) and asphaltene particles was reported. In addition, the ability of carboxylic acids to stabilize water-continuous emulsions at different pH-levels and water-cuts was investigated. In Paper IV the oil/water-partitioning and interfacial behaviour of naphthenic acids were investigated. Near infrared spectroscopy was presented as a tool for studying the formation and growth of calcium naphthenate particles in Paper V.

Paper VI is a review article about the stabilization mechanism of crude oil emulsions. Crude oil components that are important for the emulsion stability are described. Techniques for describing these components as well as oil/water interfaces, for pressures ranging from ambient to high, are presented along with recent results.
Paper I

A central property for emulsion stabilization is the formation of a w/o film that is stable towards coalescence. Film formation of naphthenic acids can be studied by Langmuir technique. The technique, described in Chapter 6.1 (page 24), is used in order to characterize monolayer properties of surface-active materials. The objective is to get information about how the molecules pack in a monolayer, i.e. how much area each molecule requires and how the molecules interact with each other. The stability of the monolayer and how the pH and electrolyte concentration affect this stability can also be discovered. A stable monolayer indicates the ability of the surfactant to stabilize emulsion droplets towards coalescence.

In Paper I, Fluka naphthenic acid (a commercial mixture), 5β(H)-cholanoic acid (1) and 1-naphthalenepentanoic acid, decahydro- (9CI) (2) (Chiron AS) have been used in a Langmuir study [88].

1-naphthalenepentanoic acid, decahydro- (2) rapidly dissolves into the bulk phase and, hence, no stable films are formed. Acidifying the subphase or addition of cations does not influence this situation.

5β(H)-cholanoic acid (1) and Fluka naphthenic acid form stable films when cations are present in the aqueous sub phase. The stability isotherm for 5β(H)-cholanoic acid is given in Figure 7.1. The results are expressed as \( A/A_0 \) versus time, \( t \), where \( A_0 \) is the area of the monolayer after compression to constant surface pressure (10 mN/m) and \( A \) is the area of the monolayer at time \( t \). At lower pH, the addition of metal ions will have less effect since the naphthenic acid is not protolyzed and naphthenates will not be formed. The divalent calcium ions have a more stabilizing effect on the film than the sodium ions.

Scheme 7.1: Naphthenic acids used in Langmuir study.
Figure 7.1 Stability isotherms (surface pressure of 10 mN/m) for 5β(H)-cholanoic acid at a pH 5.6, [Ca²⁺]=0.01 M, b pH 7.0, [Na⁺]=0.1 M, c pH 3.1, [Na⁺]=0.1 M and d pH 5.6, pure water.

Pressure-area isotherms for different pH values, at a fixed sodium ion concentration of 0.1 M, are given in Figure 7.2. As the pH increases, the film tends to tolerate a higher pressure before collapse. This is an indication of more stable films due to naphthenate formation. The figure shows that the pressure increase sets in at different areas per molecule at the different pH values. At pH 3.0 the film properties are dominated by the fact that this film has a low long-term stability (Figure 7.1, curve c). The reason for this is that the molecules are in an undissociated form and will not be stabilized by Na⁺ ions.

Figure 7.2 Pressure–area isotherms for 5β(H)-cholanoic acid at [Na⁺]=0.1 and pH 11.1, 7.0, 5.6 and 3.0.
Joos [122, 123] has suggested that the collapse pressure, $\pi_{c,m}$, of a mixed miscible monolayer may be evaluated from the collapse pressures, $\pi_{c,1}$ and $\pi_{c,2}$, of the separate components according to Equation 7.1.

$$X_1 \exp \left( \frac{(\pi_{c,m} - \pi_{c,1})\omega_1}{kT} \right) + X_2 \exp \left( \frac{(\pi_{c,m} - \pi_{c,2})\omega_2}{kT} \right) = 1$$  \hspace{1cm} (7.1)

$X_1$ and $X_2$ are the mole fractions in the monolayer of component 1 and 2 respectively and $\omega_1$ and $\omega_2$ are their partial molecular area. The activity coefficients are neglected, and it is assumed that equilibrium exist between the molecules in the monolayer and in the collapsed phase. The acidity constant, $K_a^s$, in the monolayer can be defined according to Equation 6.2.

$$K_a^s = \frac{X_{ZH}}{X_{ZNa} [H^+]}$$  \hspace{1cm} (7.2)

Here $X_{ZH}$ and $X_{ZNa}$ represent the mole fractions in the monolayer of naphthenic acid and sodium naphthenate, respectively. $[H^+]$ refers to the bulk concentration of H$^+$ ions. Due to the electrical double layer, the concentration of H$^+$ at the surface will be higher than in the bulk. The p$K_a^s$-value will thus be higher than an ordinary p$K_a$.

If it is assumed that the partial molecular area of the undissociated and the soap form of the acid is the same ($\omega_{ZH} = \omega_{ZNa} = \omega$), Equations 7.1 and 7.2 can be rewritten as

$$\pi_{c,m} = -\frac{kT}{\omega} \ln \left[ \frac{[H^+]}{K_a^s + [H^+]} \exp \left( \frac{-\pi_{c,ZNa}\omega}{kT} \right) + \frac{K_a^s}{K_a^s + [H^+]} \exp \left( \frac{-\pi_{c,ZNa}\omega}{kT} \right) \right]$$  \hspace{1cm} (7.3)

This equation gives the collapse pressure of the monolayer as a function of the H$^+$ concentration or the pH of the bulk phase, provided the collapse pressures of the acid form and the soap form are known. It is seen that the surface dissociation constant, $K_a^s$, can be evaluated from such experiments.

A plot of a curve according to Equation 7.3 and the experimental points from Figure 7.2 are shown in Figure 7.3. The fitting of the theoretical curve to the experimental values gives a p$K_a^s$ of 5.65 for 5β(H)-cholanoic acid. The barrier speed and the composition of the subphase will probably influence the determination of p$K_a^s$. 

---

7 Main Results
Figure 7.3  Collapse pressure of a 5β(H)-cholanoic acid monolayer as a function of pH. 
*Points:* experiment; *full line:* calculated according to Equation 7.3. $\omega=46\AA^2$, \( T=293\,\text{K} \), \( \text{pK}_a^+=5.65 \), \( \pi_{c,\text{ZH}}=15 \), \( \pi_{c,\text{ZNA}}=32.5 \).

Critical micelle concentrations (CMC) were determined for some naphthenic acids in Paper I. CMC-values of additional naphthenic acids were reported in Paper III [89]. The main results from both these studies are given in the description of Paper III, page 41.
Paper II

Asphaltenes are known to be the dominant contributor in stabilizing water in crude oil emulsions [82]. How the asphaltenes interacts with other crude oil components are thus of great interest.

In Paper II, the dispersive effects of naphthenic acids and other amphiphilic molecules on asphaltenes in model heptane-toluene mixtures were studied. Near infrared spectroscopy (NIR) was used to follow the disintegration of the asphaltene aggregates as a function of time and chemical additive concentration. The use of NIR as a method to study particle sizes is described in Chapter 6.2 (page 27).

Different chemicals with different functional groups were employed in the experiments. The structures of the naphthenic acids are given in Scheme 7.2. In addition to these acids, two commercial blends, Fluka and Crude Naphthenic Acid (CNA), as well as acids extracted from a crude oil, were used. Fatty alcohols, fatty amines and a commercial inhibitor, designed to inhibit asphaltene precipitation, were also used in the study.

![Scheme 7.2: Structures of naphthenic acids used in asphaltene disintegration study.](image)

The experiments were performed by continuously measuring the change in scattering at a wavelength of 1600 nm, upon addition of various chemicals, in a solution of asphaltenes in heptane/toluene (70/30 by volume). At this aromatic/paraffinic ratio, the asphaltenes is expected to form rather large aggregates. Hence, any effect on the size ought to be easily detected.

In Figure 7.4, the effect of different concentrations of a polydisperse naphthenic acid on the aggregate sizes is shown. The results indicate a clear decrease in scattering as a function of time after the acid was introduced, i.e. the aggregate sizes decrease. Faster disaggregation is seen as the concentration of added naphthenic acid is increased.
Figure 7.4 NIR scattering measurements at 1600 nm for 0.125 wt% asphaltenes in a 70/30 by volume \textit{n}-heptane/toluene mixture with crude naphthenic acid (CNA) added in various concentrations.

The relative optical density versus time for toluene/\textit{n}-heptane/asphaltene mixtures with various naphthenic acids are plotted in Figure 7.5.

Figure 7.5 NIR scattering measurements at 1600 nm for 0.125 wt% asphaltenes in a 70/30 \textit{n}-heptane/toluene mixture with 1.25 wt\% of various naphthenic acids added.
The commercial Fluka naphthenic acid and the naphthenic acid extracted from a North Sea crude seem to affect the state of the asphaltenes only to a minor extent. CNA is most efficient of these polydisperse naphthenic acids. A comparison between 2C4, C42 and CHOL (Scheme 7.2) shows these species to be somewhat more efficient than the previous group. Especially, the 2C4 molecule has a very efficient breakdown to start with and also attains a low final value. It is interesting to see that the molecular structure affects the results to this extent.

The other amphiphiles showed a varying effect on the disintegration of the asphaltenes. In all cases the most efficient treatment was obtained by Inhibitor A, the commercial mixture.

Alkylbenzenesulfonic acid was shown to associate with the asphaltenes and create aggregates of increased sizes. This is in accordance with the results obtained by Chang and Fogler [75] in a UV/Vis spectroscopic study. They suggested that asphaltenes and dodecylbenzenesulfonic acid could associate into large electronic conjugated complexes.

The conclusions of this paper are that NIR spectroscopy is a powerful method for following the disintegration of asphaltene aggregates upon addition of chemicals. The NIR technique, which is very fast and accurate, is hence a good choice for the initial screening of large numbers of chemicals for asphaltene inhibition. The results show that additives that are efficient in replacing hydrogen bonds, possess dispersive power and can serve as inhibitors.
**Paper III**

Emulsions constitute a major problem in crude oil production offshore. In this paper the CMC-values of some naphthenic acids were obtained and the influence of different carboxylic acids on emulsion stability were investigated. It was shown that water-in-oil emulsions can be stabilized by a combined mechanism of multilayer and asphaltene particle stabilization.

**Critical micelle concentration at high pH**

The theory behind micellisation is described in Chapter 2.4, page 7. Critical micelle concentrations (CMC) were determined for some naphthenic acids in Paper I [88] and additional CMC-values were reported in this paper. The determined CMC-values and the area/molecule at the water surface are given in Table 7.1.

<table>
<thead>
<tr>
<th>Carboxylic acid</th>
<th>pH</th>
<th>CMC</th>
<th>Area/molecule</th>
</tr>
</thead>
<tbody>
<tr>
<td>[C7a1] 4-heptylbenzoic acid</td>
<td>11.5</td>
<td>1.7E-2</td>
<td>31</td>
</tr>
<tr>
<td>[C51] trans-4-n-pentylcyclohexanecarboxylic acid</td>
<td>11.5</td>
<td>6.7E-2</td>
<td>35</td>
</tr>
<tr>
<td>[2C4] 1-naphthalenepentanoic acid, decahydro-</td>
<td>11.0</td>
<td>2E-4</td>
<td>52</td>
</tr>
<tr>
<td>[CNA] CNA 160-170 Corn van der Locke</td>
<td>11.3</td>
<td>2.7E-4</td>
<td>71</td>
</tr>
<tr>
<td>[Fluka] Fluka Naphthenic Acid</td>
<td>11.3</td>
<td>8E-4</td>
<td>61</td>
</tr>
</tbody>
</table>

CMC-values for the sodium n-alkanoates were collected from Mukerjee and Mysels [55] and compared with CMC-values for the naphthenates. Figure 7.6 shows the molecular weight (of the acidic forms) versus log[CMC]. It should be noted that the values from Mukerjee and Mystels [55] are for pure aqueous solution while the other are for pH>11. It is well known that the logarithm of CMC often vary linearly with the size of the hydrophobic part of surfactants [17, 56].
The naphthenates from the commercial mixtures of naphthenic acids (CNA and Fluka) and 2C4 have lower CMC-values than straight chain carboxylates with similar molecular weight. Characteristic for the structures of C51 and C7a1 is that they have the acid group connected directly to a condensed and an aromatic ring respectively. These two acids have CMCs that are higher than corresponding n-alkanoates.

The CMC-measurements reveal that the naphthenic acid salts behave as micelle-forming surfactants at appropriate pH values.

The area per molecule given in Table 7.1 reveals that the naphthenic acids tested occupy between 31-71 Å²/molecule. Ovalles et al. [52] have reported values for the area per molecule for naturally occurring naphthenic acids at an interface between water and toluene, finding 113–152 Å²/molecule for different fractions. For these systems (at full dissociation) a strong electrostatic repulsion is dominant, which is explaining the large area demands at high pH. In a system consisting of a naphthenic acid, RH and a naphthenic salt, RNa, the ratio, RNa/RH, will determine what kind of structure to occur. Normally by varying RNa/RH (in water), at high enough pH, one will have micelles, liquid crystals and reversed structures [54]. For emulsion stabilization, the occurrence of a lamellar liquid crystalline D-phase will be crucial.
Oil in Water Emulsions
The emulsion stability of systems containing paraffinic, aromatic or naphthenic acid (~1wt%), water and heptane/toluene were investigated at different pH-levels. High pH (around 11) gave rise to o/w emulsions that were stable for several days. The drop size distribution of these emulsions was narrow with drop sizes in the range 9-24 nm. A decrease in pH reduced the emulsion stability significantly. High molecular weight acids seem to have a slightly better stabilizing effect on the emulsions.

Combined D-phase and Asphaltene Particle Stabilization
It is our opinion that the phase equilibria in the system water/sodium hexadecanoate (NaC16)/hexadecanoic acid (HC16) at 70°C is representative also for naphthenic acid based systems. This diagram is given and explained in Chapter 2.5, page 9. In this diagram, the importance of the stabilization of water/oil emulsions, due to the D-phase has been documented [16].

In order to evaluate the different levels of emulsion stability in different systems, the critical electric field technique can be applied. This technique is explained in Chapter 6.3, page 29. The critical electric field will reflect the resistance towards coalescence of the interfacial structures and thus serve as a parameter for emulsion stability.

The competition between D-phase stabilization and asphaltene-particle stabilization of water/oil emulsions was investigated using the following experiments. A hexadecanoic acid / sodium hexadecanoate D-phase was prepared based on the equilibria in Figure 2.5 (page 10). A dichloromethane solution, containing dissolved asphaltenes, was mixed with the D-phase and the solvent was evaporated. After 24 hours there was clear evidence of asphaltene particles present in the D-phase. This D-phase, modified with different amount of asphaltenes, was used to stabilize w/o-emulsions at 70°C. The emulsions were prepared from 55.7 wt% n-decane, 32.7 wt% 0.5M NaCl and 11.7 wt% asphaltene modified D-phase. In order to measure the emulsion stability, the $E_{\text{critical}}$ was determined. The result is shown in Figure 7.7.
Figure 7.7 Emulsion stability, represented by the critical electric field, $E_{\text{crit}}$, as a function of different asphaltene fractions of the modified D-phase (by weight).

Obviously, the addition of asphaltene particles can enhance the w/o-emulsion stability from the case with just a D-phase present. However, too high amount of asphaltene particles will give a destabilization. A ratio of 0.6, i.e. 60 wt% particles and 40 wt% D-phase seems to be optimal. The mechanism is most likely that these nano-particles are dispersed in the surfactant multilayer of the D-phase, giving further protection towards coalescence. The experiment in Figure 7.7 is very important in visualizing different mechanisms behind emulsion stability in crude oils with high amounts of asphaltenes and naphthenic acids. Representatives to these are heavy crudes, and bitumens.
An understanding of the equilibria involved in a water/oil/naphthenic acid system is important in order to understand the different problems naphthenic acids causes in crude oil production. In Paper IV the dissociation and partitioning equilibria, in addition the interfacially behaviour of the naphthenic acids at different pH have been studied. Equilibria in water/oil/naphthenic acid systems are described in Chapter 2.2 (page 3).

A crude oil from the Norwegian continental shelf, with an acid content of 2 wt%, was used to study the partitioning and acidic constants of the naphthenic acids. The crude oil samples were mixed with an equal amount of water with different pH-values. The samples was agitated for at least 24 hours, separated and the concentrations of the naphthenic acids in the water phase were determined with GC/MS. The naphthenic acids in the crude oil used, were extracted by an ion exchange method [124] and then analyzed by GC/MS. With this technique it was possible to determine the content of some of the naphthenic acid structures defined by size and number of double bound equivalents. It was assumed that each double bound equivalent corresponded to one ring rather than one double bond since the olefins are unstable and, consequently, not present in crude oils [27].

The total concentration of naphthenic acid in the water phase can be expressed as a function of the total concentration of acid, pH, the partitioning constant, $K_{wo}$ and the acidic constant, $K_a$. By fitting this expression to experimental determined points (concentration of acid in water at different pH), the equilibria constants can be determined. $pK_a$-values for C10-C16 naphthenic acids with one, two, or three saturated rings were determined to $4.9\pm0.1$ at 25°C. Water-soluble paraffinic carboxylic acids have $pK_a$-values ranging from 4.8 to 4.9 [125]. Cyclohexanecarboxylic acid are reported to have $pK_a=4.91$ [126]. Hence, the crude oil naphthenic acids have $pK_a$-values in the same order as the water-soluble aliphatic acids.

The partitioning constants for the crude oil naphthenic acids are shown in Figure 7.8. The logarithm of the determined partition coefficients varies linearly versus the number of methyl groups in the naphthenic acid molecules. This is in accordance with findings of Reinsel et al. [127] who have studied the partitioning of acetic, propionic and butyric acids between crude oil and water. The naphthenic acids with three rings are apparently more hydrophilic than acids with one or two rings.
Different synthetic or commercially available carboxylic acids were added to a mixture of \( n\)-heptane and toluene (50:50 by volume). Water with different pH was added. The mixtures were stirred for 24 hours, separated by centrifugation and the naphthenic acid content in the water phase was analyzed by LC/MS. At higher pH the collected water samples were diluted prior to LC/MS analysis. The experimentally determined concentrations of the different acids in water at different pH were fitted to the theoretical expression in the same way as for the crude oil naphthenic acids. Figure 7.9 gives the experimental points and the fitted model-line for C41a1. For C41a1, the model gives a good fit to the experimental points.

---

Figure 7.8 Partitioning constants, \( K_{wo} \), for naphthenic acids with one, two and three rings and different numbers of methyl groups.

Figure 7.9 pH versus total concentration of C41a1 in the water phase. The theoretical model (line) is fitted to the experimental points.
C42, C7a1 and C51 were investigated at a higher acid concentration than C41a1. For these acids, the experimental determined points at pH 2, 6 and 7 were used. The model could not describe the concentrations at pH 9 and 11. It is believed that the reason for the deviation between the model and the experimental points at high pH is the formation of micelles and reversed micelles. These processes will enhance the complexity of the system, and a detailed investigation is needed in order to map all the equilibria. Partitioning experiments were performed at pH 9 with variable total acid concentration. The results from this study showed that the relative deviation from the model decreased with decreasing total acid concentration. This indicates that in dilute solutions, it is sufficient to account for the dissociation and partitioning of undissociated acid monomers in order to get a good description of the system, also at higher pH. The values for $K_{wo}$ and $pK_a$ for the carboxylic acids are given in Table 7.2.

<table>
<thead>
<tr>
<th>Shortname</th>
<th>Structure</th>
<th>Concentration [mol dm$^{-3}$ water]</th>
<th>$pK_a$</th>
<th>$K_{wo}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[C42]</td>
<td>![Structure Image]</td>
<td>3.0E-2</td>
<td>4.9</td>
<td>3.0E-5</td>
</tr>
<tr>
<td>[C41a1]</td>
<td>![Structure Image]</td>
<td>3.3E-3</td>
<td>3.4</td>
<td>1.5E-4</td>
</tr>
<tr>
<td>[C7a1]</td>
<td>![Structure Image]</td>
<td>3.3E-2</td>
<td>5.0</td>
<td>1.2E-4</td>
</tr>
<tr>
<td>[C51]</td>
<td>![Structure Image]</td>
<td>3.3E-2</td>
<td>5.1</td>
<td>8.0E-5</td>
</tr>
</tbody>
</table>

The $K_{wo}$-values are of the same order as the crude oil naphthenic acid for C42 and C7a1. For C41a1 the determined value of $K_{wo}$ (1.5E-4) is higher than determined for crude oil naphthenic acids with two rings (2.3E-5). This is reasonable since the aromatic ring causes the molecule to be more hydrophilic. The $K_{wo}$-value for C51 is lower than for crude oil acids with the same number of carbon atoms. This may be explained by the fact that the structure of C51 differs from the crude oil naphthenic acids in that the acid group is attached directly to the ring. Analyses of crude oil naphthenic acids have indicated that the carboxylic acid group generally is attached to a ring with a short side.
Main Results

The $pK_a$ for the acids C41a1 and C7a1 was determined as 3.4 and 5.0, respectively. For C7a1, being an aromatic acid, a value of 5.0 is unexpectedly high and probably not a correct $pK_a$-value. The reason for this high value might be that other equilibria are of importance also at lower pH values for this acid. The saturated C51 and C42 have $pK_a$-values in the same order as the crude oil naphthenic acids.

**Interfacial activity of naphthenic acids**

The interfacial tension between water and different hydrocarbon phases were investigated for several different naphthenic acids. Interfacial tension between heptane/toluene (50:50 by volume), containing 5.3E-5M of different naphthenic acids, and water are plotted as a function of pH in Figure 7.10. The volume of water was equal to the volume of hydrocarbon phase.

At low pH the molecules at the oil/water interface will be unionized giving rise to a interfacial tension, $\gamma_1$. At high pH the interface will consist of dissociated acid molecules and it is seen from Figure 7.10 that the interfacial tension approach a value close to 0 for full dissociation. If it is assumed that the lowering of interfacial tension is directly related to ionization, the amounts of dissociated and undissociated acid at the interface are equal when the interfacial tension is equal to $\frac{1}{2}\gamma_1$. For C42 this occurs at pH=10.4. It is assumed that the presence of 10% C41a1 do not cause a significant different interfacial

\[\text{Figure 7.10 Interfacial tension between heptane/toluene, containing 5.3E-5M of different naphthenic acids, and water as a function of pH. Structures for C42 and C41a1 are given in Table 7.2.}\]
behaviour than if 100% was 2C4. Micellisation will most likely not occur in this dilute system (5.3E-5 mol acid / dm³ water) and it can be shown that the concentration of ionised and unionised C42 will be equal in the bulk phases at pH=pKₐ+pKₜₒ=9.4. Hence, in order to have equal amounts of the two acid forms at the interface, the concentration of dissociated acid must dominate over the concentration of undissociated acid in the bulk phases. This fact can be explained in term of the electrical double-layer. The pH close to the oil/water interface will be less than the bulk pH.

The reduction in interfacial tension sets in at a lower pH for the crude oil naphthenic acid. This is believed to be due to the presence of low molecular weight naphthenic acid that dissociates at the interface at lower pH.
**Paper V**

In Paper V, near infrared spectroscopy (NIR) was introduced as a method to study the formation of calcium naphthenate particles at elevated pH.

Naphthenic or fatty acids were dissolved in water at high pH (11.2-11.5). Upon addition of Ca\(^{2+}\)-solution the nucleation period and particle growth was monitored. The near infrared spectra experience a baseline elevation due to the formation and growth of calcium naphthenate particles. The use of NIR to detect particles sizes is explained in Chapter 6.2 (page 27).

Figure 7.11 shows the square root of the optical density (OD) at 1280 nm vs. time for experiments with a naphthenic acid labelled 1a1C4. The structure of 1a1C4 is given in the same figure.

![Figure 7.11](image)

**Figure 7.11** (Optical density)\(^{0.5}\) at 1280 nm vs. time for different concentration of Ca\(^{2+}\) and 1a1C4.

The reason for plotting the square root of OD is that OD depends on radius\(^6\) or volume\(^2\) of the particles. Hence, change in the square root of OD can serve as a measurement of change in the total volume of precipitate. The square root of OD is directly proportional to the particle volume in systems consisting of a constant number of monodisperse particles. In the systems investigated, with polydisperse particles, the larger particles will govern the resulting OD since they contribute much more to OD than the small particles.
The number of particles is also unknown. Nevertheless, the curves give a good qualitative description of the calcium naphthenate formation.

**Induction period**

The induction period is the period where nucleation and growth of nuclei to a detectable size occurs. By assuming that the induction period is inverse proportional to the rate of nucleation, information about the nucleation process can be extracted. The induction period will then depend on the supersaturation according to Equation 7.4.

\[
\log t_{ind} \propto \frac{\gamma^3}{T^3 (\log S)^2}
\]  

(7.4)

In Figure 7.12, the logarithm of the induction period for systems consisting of 1a1C4 is plotted versus (log S)\(^{-2}\).

![Figure 7.12 The logarithm of the induction period as a function of (log S)\(^{-2}\) for 1a1C4.](image)

For ideal homogeneous nucleation, the plot would give a straight line according to Equation 7.4. At high supersaturations (to the left in the figure) \(\log t_{ind}\) depends linearly on (log S)\(^{-2}\). A sudden decrease in the slope of the curve is then seen when approaching lower levels of supersaturation. This indicates a change in the interfacial tension between the solid and the water. The change in the curve at (log S)\(^{-2}\) ~ 10 is most likely due to a transition from heterogeneous to homogeneous nucleation. At high supersaturation, the
nucleation is homogeneous and at lower supersaturation the nucleation becomes heterogeneous. The reason for this is that the concentration of impurities, leading to heterogeneous nucleation, will be constant in the system independently of the supersaturation. Since the rate of homogeneous nucleation is lower for lower supersaturations, the heterogeneous nucleation process will dominate.

The NIR-technique presented here can measure induction periods when it lasts for a certain time. When the induction period is less than about 5 seconds, difficulties arise. The mixing time of the solutions with the reactants can in this case be comparable with or exceed the measured induction period. In the experiments performed here, 10-20 seconds were allowed for the addition of calcium to the solution with carboxylic acid. In this case, if the induction period is determined to a value under 30s, the uncertainty will be large. If the Ca$^{2+}$-solution is added too fast, there is a chance that high local concentration of Ca$^{2+}$ can initiate the precipitation.

**Growth period**

For all the systems investigated, higher concentration of acid and calcium ions led to an increase in the slope of the OD versus time curves after the induction period, representing an increase in the rate of reaction. In Figure 7.13, the slope of OD$^{0.5}$ versus time, representing the rate of crystallization, is plotted as a function of $(S-1)^2$ for 1a1C4. $S$ is the supersaturation defined by Equation 5.3 (page 21).

![Figure 7.13](image)

**Figure 7.13** $d(OD^{0.5})/dt$ versus $(S-1)^2$ for 1a1C4.
A linear relationship is seen for the lower supersaturations. The slope of the curve increases for higher supersaturations. The increase in the slope occurs at the same supersaturation level ($S \sim 1.4$) as were the dependence of $\log t_{\text{ind}}$ versus $(\log S)^{-2}$ changes in Figure 7.12. It was suggested that a transition from heterogeneous to homogeneous nucleation occurred at $S \sim 1.4$. If the nucleation process is heterogeneous the number of nucleus will be considerably lower than if homogeneous nucleation occurs.

For the other carboxylic acids tested (Table 7.3), $\frac{d \text{OD}^{0.5}}{dt}$ depended on $(S-1)^n$, were $n$ is in the range 0.2-0.5. This means that the change in $\frac{d \text{OD}^{0.5}}{dt}$ at higher levels of supersaturation was less than for lower levels of supersaturation. This is the opposite of what was found for the naphthenic acid, labelled 1a1C4 (Figure 7.13).

Independently of whether a transition from heterogeneous to homogeneous nucleation occurs, the number of particles is expected to be higher for higher levels of supersaturations. The reason for this is that supersaturation affects the nucleation rate more than the growth rate [128]. This fact can affect the resulting $\frac{d \text{OD}^{0.5}}{dt}$ in different ways.

The sizes of the particles are more important than the number for the response in OD. For a given value of $\frac{d \text{OD}^{0.5}}{dt}$, the actual crystallization rate will be higher for systems with a large number of small particles than for a system consisting of a less number of large particles. It is therefore expected that when going from a system were the number of particles are low, to a system with a large number of particles, the dependency of $\frac{d \text{OD}^{0.5}}{dt}$ on $(S-1)$ would decrease. Evidence for the formation of smaller particles at high supersaturation can be found by studying Figure 7.11. The curve with the highest supersaturation (to the left) reaches a final OD lower than expected. The final value increases with supersaturation for the other experiments. This indicates that even if the experiment with highest supersaturation yield the highest amount of solid material, the particles are small and therefore their scattering efficiency is bad.

The presence of a large number of small particles, rather than a small number of large particles can also lead to an increased effect in $\frac{d \text{OD}^{0.5}}{dt}$. The rate of agglomeration will obviously depend on the number of particles. When particles agglomerate, OD will increase even though the volume of precipitated material remains constant. Ostwald ripening may also be of importance. Ostwald ripening is the process in which small particles dissolve and the solute deposits subsequently on the larger particles. The driving force of this process is the lowering of the total surface energy. The total surface area increases with decreasing number of particles. It is expected that this will increase
the rate of crystallization for the smaller particles. In all cases, the results may be influenced by the fact that the largest particles will govern the resulting OD. Different influence of the mechanisms may explain the different behaviour of dOD^{0.5}/dt versus supersaturation for 1a1C4 and the other acids.

The particles tendency to agglomerate upon collision may be affected by the ratio of Ca^{2+} to naphthenic acid. An excess of one of the component may lead to an electrostatically stabilization that it sufficient to prevent the particles from agglomeration. However, this mechanism was not prominent enough to explain the results obtained in this study.

**Estimation of solubility products**

As the amount of Ca^{2+} and carboxylic acid is decreased, the response on the NIR-measurements will eventually become zero. The concentration at which this happens can be used to estimate the solubility products, $K_{sp}$, for the different calcium soaps. The solubility products were found by extrapolating a curve of dOD^{0.5}/dt versus the ion concentration product to dOD^{0.5}/dt=0. The $K_{sp}$-values are given in Table 7.3 and are plotted versus the molecular weight of the acidic form in Figure 7.14.

**Table 7.3** Solubility products for the calcium salt of different carboxylic acids. (Detailed information of the acids is given in Table 1)

<table>
<thead>
<tr>
<th>Shortname</th>
<th>Chemical structure</th>
<th>$K_{sp}$ [mol^3 dm^{-3}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[a1C4]</td>
<td><img src="image" alt="Chemical structure" /></td>
<td>6.1E-8</td>
</tr>
<tr>
<td>[1a1C4]</td>
<td><img src="image" alt="Chemical structure" /></td>
<td>2.8E-8</td>
</tr>
<tr>
<td>[C51]</td>
<td><img src="image" alt="Chemical structure" /></td>
<td>2.2E-9</td>
</tr>
<tr>
<td>[C7a1]</td>
<td><img src="image" alt="Chemical structure" /></td>
<td>1.2E-10</td>
</tr>
<tr>
<td>[C16]</td>
<td>CH_3(CH_2)_14COOH</td>
<td>6.4E-13</td>
</tr>
</tbody>
</table>
A method for studying the precipitation of calcium naphthenate in an aqueous phase was presented in Paper V. It is shown that the induction period can be determined. Information about the rate of reaction for particle growth can be obtained. However its qualitative value is uncertain. This is because the number of particles and the total amount of precipitate is not known at a given time. In addition the larger particles will govern the resulting scattering contribution. The rate of nucleation versus the rate of growth, agglomeration, particles sizes and Ostwald ripening will influence the results. Solubility products can also be estimated. Although the method has some quantitative limitations, it is obvious that it has a qualitative advantage, for example to study the efficiency of different calcium naphthenate inhibitors.
8 Concluding Remarks

The main focus of this thesis has been to increase the understanding of acidic crudes, formation of calcium naphthenate deposits and the emulsion behaviour in these systems.

The equilibria involved in a water/oil/naphthenic acid system have been investigated and it was found that the naphthenic acids in crude oil have $pK_a$-values around 4.9. Naphthenic acids tend to form micelles at higher pH. Due to the many equilibria involved in a water/oil/naphthenic acid system, especially at high pH, the results from this study only gives a first basic in understanding the chemistry. A more in-detail study of the different equilibria involved is of great interest for further work.

The results obtained in this doctoral work clearly indicate that the naphthenic acids are of importance in the formation of undesirable emulsions in crude oil production offshore. The naphthenic acids will stabilize water-continuous emulsions electrostatically at higher pH. It was shown that a multilayer of carboxylic acids can stabilize w/o emulsions in a combined mechanism with asphaltenes. A combination of 60% asphaltene particles and 40% D-phase gave the most stable w/o-emulsions. This investigation verifies the importance of D-phase stabilization in combination with asphaltene particles in systems with acidic heavy crude oil (including bitumen) and water. Stable monolayers of calcium naphthenate are formed when the pH is sufficiently high. This monolayer can stabilize water droplets against coalescence. Since asphaltenes are the dominant contributor to emulsion stability in crude oil systems, the ability of the naphthenic acids to disintegrate asphaltenes in solution will be important for the emulsion stability. The disintegration effect of several different naphthenic acids and other amphiphiles were investigated.

The formation of calcium naphthenates in crude oil equipment is a potential threat to offshore production of acidic crudes. The ability to know at which conditions formation of naphthenate deposits can occur is of great importance in order to avoid costly shutdown periods. It is shown that near infrared spectroscopy can be used as a method to get a first basic description of the formation mechanism. The method can also be used to estimate solubility products.
References


References


References


