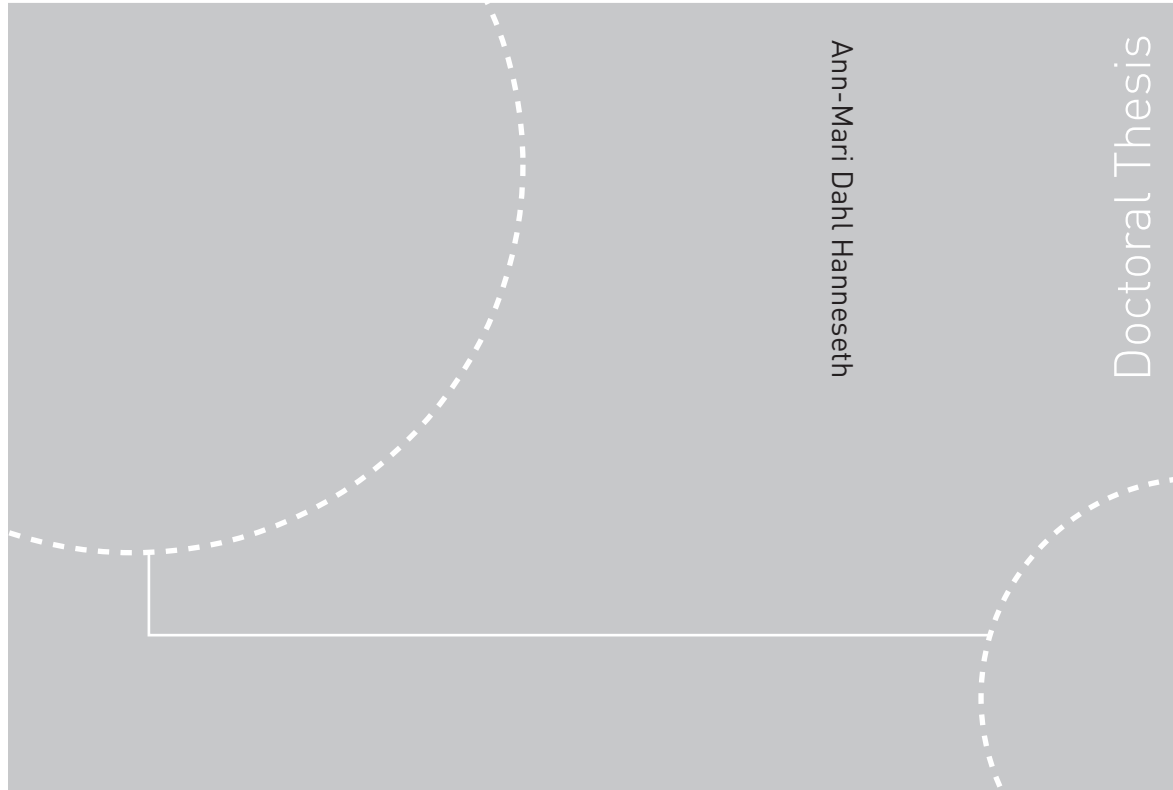


Doctoral theses at NTNU, 2009:25

Ann-Mari Dahl Hanneseth
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Naphthenic Acids at w/o Interfaces**
Reactivity, Inhibition and Emulsion Formation



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PREFACE

This thesis is submitted for fulfilment of the PhD degree at the Norwegian University of Science and Technology. The work has been performed at the Ugelstad Laboratory at the Department of Chemical Engineering and has resulted in five papers. Professor Johan Sjöblom has been supervising this work.

I received my BSc in Chemical Engineering in June 2002 at Sør-Trøndelag University College. I was introduced to the world of surface and colloid chemistry by Johan Sjöblom as a summer student at Statoil in 2002, two years later in 2004 I received my MSc at the Norwegian University of Science and Technology (Ugelstad Laboratory) in the field of surface and colloid chemistry on the subject of naphthenates. In 2004 I joined the joint industrial program (JIP) “Chemistry and Physico-Chemical Behaviour of “ARN” Naphthenic Acids and Corresponding Metal Naphthenates” financed by petroleum companies (BP, Chevron, Saudi Aramco, Shell, StatoilHydro (Statoil), Talisman, Total) and chemical vendors (Akzo Nobel, Baker Petrolite, ChampionTechnologies, Clariant). After a first year as a department engineer, I was accepted for a PhD grant in the subject of naphthenic acids through the VISTA program, financially supported by Statoil and The Norwegian Academy of Science and Letters.

During the years I have been involved in the JIP I have attended, followed up and presented on meetings twice a year, both domestic and abroad, including contributions at international conferences.

ACKNOWLEDGEMENTS

First, I would like to express my gratitude to my supervisor, Professor Johan Sjöblom, for the opportunity carry out my PhD degree at Ugelstad Laboratory, for his excellent supervision, research facilities and means available at the laboratory.

I would like to thank my colleagues at the Ugelstad Laboratory. Special thanks go Cecilie, Helene, Caty, Bodhild, Erland and Øystein.

Anne, my best friend. We both finally made it (I hope☺)! These years have been the best and worst of my life, without you by my side every single day it would have been more of the worst part. It is not the same not seeing your every morning (thank god or SH for free cell phones). But at least now we are able to focus on our work ☺ You mean the world to me!

I will also acknowledge my former teacher Siss Aukan for once saying to me “Ann-Mari you can become what ever you set you mind upon being”, your were right!

Stian, for all your support and for being a great father for Tuva. To my lovely daughter Tuva, I'm sorry I have not been around as much as I should, this work I dedicate to you!!

Statoil ASA and The Norwegian Academy of Science and Letters are acknowledge for the financial support trough the VISTA program. Acknowledgements are also extended to the JIP consortium consisting of AkzoNobel, BakerPetrolite, BP, Champion Technologies, Chevron, Clariant, SaudiAramco, Shell, Statoil/StatoilHydro, Talisman and Total. Particularly, Andrew Shepherd (Shell) for his interest and inputs regarding my work.

Katharina, all my friends, and family who have supported me with every means possible.

And last but not least, Kjetil, thank you for being so enthusiastic and optimistic, for supporting and backing me up, and for being...You are one of a kind and I love you!

“You complete me”

ABSTRACT

Deposition of naphthenate has become an increasing problem in crude oil production¹ and a large number of fields are experiencing this problem, among others in the North Sea and West Africa. Naphthenate accumulates mainly in topside separators and de-salters, but also in tubing and pipelines which can lead to severe flow assurance problems. It is formed as a consequence of pressure drop which leads to release of CO₂ and an increased pH in the co-produced water. When the pH increases the acid groups dissociate and react with metal ions in the water phase to form the corresponding naphthenate. Since the naphthenic acids and their naphthenates are amphiphilic molecules they accumulate at the interface between the oil and water phase, which in turn makes them able to stabilise emulsions. The increased focus on the naphthenate problem led to the discovery of the ARN acids, which now are believed to cause the calcium naphthenate problem. The reason is its high interfacial activity and its ability to form a cross linked network when reacting with Ca²⁺. Monoacids instead react with calcium in a 2:1 ratio and form complexes dispersed either in the oil phase or the water phase, depending on the acidity of the acid. The molecular structure of the ARN acids has been extensively studied and is found to be four-branched, aliphatic molecules with one terminal carboxylic group attached to each branch. The aliphatic chain contains several five-membered, saturated rings.

This family of fatty acids is a new discovery and has not been much studied before. Therefore a fundamental chemical approach with regard to the physico-chemical properties, interfacial activity and reactivity, and film-forming properties is of great importance and the key for understanding and solving the problem with naphthenate deposition.

This work was developed within the aims of the project “Chemistry and Physico-Chemical Behaviour of ARN Naphthenic Acids and Corresponding Metal Naphthenates”

Publication I focus on the isolation and characterization of the ARN acid, different experimental techniques have been used to clarify the structure and the acids interfacial properties. In publication II and IV different methods and experimental techniques have been utilized to develop methods to screen inhibitor, in publication II model system with monoacid

have been studied while in publication IV this system have been further developed and different systems consisting of monoacid and tetraacids have been studied.

In publication III the C₈₀ naphthenic acid has been studied with regards to its thermal, interfacial and structural properties. And Publication V has been devoted to emulsions stabilized by C₈₀ naphthenic acids and stearic acid.

LIST OF PUBLICATIONS

Publication I

Brandal, Ø., Hanneseth, A-M., Hemmingsen, P.V., Sjöblom, J., Kim, J., Rodgers, R.P., and Marshall, A.G.: Isolation and Characterization of Naphthenic Acids from Metal Naphthenate Deposits. Molecular Properties at Oil-Water and Air-Water Interfaces, *J Dispersion Sci Technol*, 27, 295-305, 2006

Publication II

Hanneseth, A-M., Brandal, Ø., and Sjöblom, J.: Formation, Growth, and Inhibition of Calcium Naphthenate Particles in Oil-Water Systems as Monitored by means of Near Infrared Spectroscopy, *J Dispersion Sci Technol*, 27, 185-192, 2006

Publication III

Magnusson, H., Hanneseth, A-M. D., Sjöblom, J., Characterization of C80 Naphthenic Acid and its Calcium Naphthenate, *Journal of Dispersion Science and Technology*, 29(3), 2008

Publication IV

Nordgård, E.L, Hanneseth, A-M.D., E.L., and Sjöblom, J., Inhibition of Calcium Naphthenate. Experimental Methods to Study the Effect of Commercially Available Naphthenate Inhibitors (JDST)

Publication V

Hanneseth, A-M.D., Selsbak, C.M., and Sjöblom, J., Behaviour and stability of naphthenic acid/naphthenate stabilized emulsions. Combination of C80-tetraacid and Stearic Acid (JDST)

Additional Publications

Brandal, Ø., Hanneseth, A-M., and Sjöblom, J.: Interactions Between Synthetic and Indigenous Naphthenic Acids and Divalent Cations across Oil-Water Interfaces. Effects of Addition of Oil-Soluble Non-Ionic Surfactants, *Colloid Polym Sci*, 284, 124-133, 2005

Glomm, W.R., Halskau, Ø., Hanneseth, A-M.D., Volden, S.,
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Correlated to Their Native Fold, Stability and pI. *J. Phys. Chem. B*, 2007

Nordgård, E.L., Magnusson, H., Hanneseth, A-M. D., Sjöblom, J.: Model Compounds for C80 Isoprenoid Tetraacids. Part II: Interfacial Reactions and Physicochemical Properties and Comparison with Indigenous Tetraacids. To be submitted to *Colloids & Surfaces A*.

Conferences and Seminars

Sjöblom, J., Brandal, Ø., Hanneseth, A-M. D., Mediaas, H., The Importance of Naphthenic Acid Structure for Stabilization of Emulsions and Precipitation of Ca-Naphthenate, SPE 4th International Symposium on Oilfield Scale, Aberdeen, 2006 (oral presentation)

Brandal, Ø., Hanneseth, A-M. D., Hemmingsen, P.V., and Sjöblom, J., Interfacial Behaviour of C80 Tetrameric Naphthenic Acids Responsible for Naphthenate Deposition in Crude Oil Processing, , 7th International Conference on Petroleum Phase Behavior and Fouling, North Carolina, 2006 (oral presentation)

Hanneseth, A-M. D., Selsbak, C., Sjöblom J. Naphthenate and Naphthenic Acid stabilised emulsions, 8th International Conference on Petroleum Phase Behavior and Fouling, Pau, 2007 (oral presentation)

Magnusson, H., Hanneseth, A-M. D., Sjöblom, J., Characterization of C80 Naphthenic Acid and its Calcium Naphthenate, 8th International Conference on Petroleum Phase Behavior and Fouling, Pau, 2007 (oral presentation)

Sjöblom, J., Hanneseth, A-M. D., Nordgård, E.L., and Simon, S., Setting the scene: The current understanding and role of different naphthenates (Ca, Na, Ba, Sr), SPE Applied Technology Workshop Managing Naphthenates and Soap Emulsions, Pau , 10 – 13 March 2008 (Oral presentation)

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1

2 PETROLEUM

The use of petroleum and its derivatives was practiced as early as 4000 BC in the Tigris-Euphrat valley, where bitumen and asphalt were used in construction and in ornamental work. The modern petroleum industry began in the later years of the 1800. Seneca Oil Company with Edwin L. Drake as technical chef was the first company to start drilling for oil, and in 1859 they discovered oil at 23 metres depth in Titusville, Pennsylvania. This was the start of the oil fever and the world's first "oil city", Pithole City, where established close by.[1] The Norwegian petroleum industry began on the day before Christmas Eve 1969 when a message was wired to the Norwegian authorities. Oil had been found at the Ekofisk field in the North Sea. A joint exploration agreement between Hydro, Elf and 6 other French companies together with Phillips led to the beginning of the Norwegian oil era.[2]

2.1 Introduction

Petroleum is perhaps the most important raw material consumed in modern society. Petroleum is a mixture of gaseous, liquid and solid hydrocarbon compounds that occur in sedimentary rock deposits throughout the world and also contains small quantities of nitrogen-, oxygen-, and sulphur containing compounds as well as trace amount of metallic constituents [3] or as defined by American Society of Testing and Materials, a natural occurring mixture of hydrocarbons, generally in a liquid state, which may also include compounds of sulphur, nitrogen, oxygen, metals and other elements.

Petroleum is a necessity in the world's industrial production, and the greater part of the industrial power demands are covered by oil and gas. In addition petroleum/petroleum products participate as an intermediate or end product in a large number of industries such as food production, clothing, homes, and construction, health, hygienic and personal effects and also in transportation and communications. Some examples of products derivate from petroleum are fertilizer, textiles, paint, detergents and synthetic polymers and plastics for components used in production of vehicles.

2.2 Origin, Occurrence and Composition

Two theories have been postulated for the origin of carbon fuels, the abiogenic theory and the biogenic theory. Per today the biogenic theory is the valid one. According to this theory, less than 20% of the petroleum is produced from living organisms and the remaining part is produced by various processes that convert other organic materials (small plankton organisms, marine animals and terrestrial plants) to hydrocarbons as a part of maturation processes generally referred to as diagenesis, catagenesis and matagenesis, which are a combination of bacteriological action and low-temperature reactions.

Over many centuries this organic material mixed with mud, has been buried under sedimentary layers of material (diagenesis). This results in high levels of heat and pressure which cause the remains to metamorphose, first into a waxy material known as kerogen and than further into liquids and gaseous hydrocarbons (catagenesis). These hydrocarbons migrate through adjacent rock layers until they become trapped underground in porous rocks called reservoirs, forming an oil field from which the liquid can be extracted by drilling and pumping.[1]

Most of the crude oil is today produced from underground reservoirs, however surface seepage of crude oil and natural gas are common in many regions. Figure 1.1 shows the worlds oil producing countries and figure 1.2 shows the world reserve.

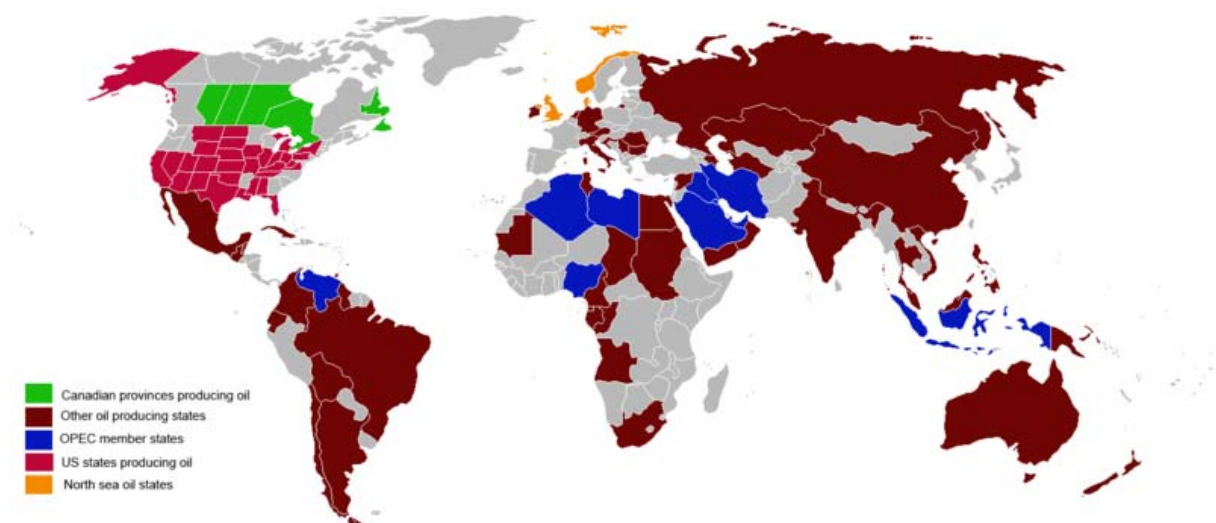


Figure 1.1 The worlds oil producing countries [4]

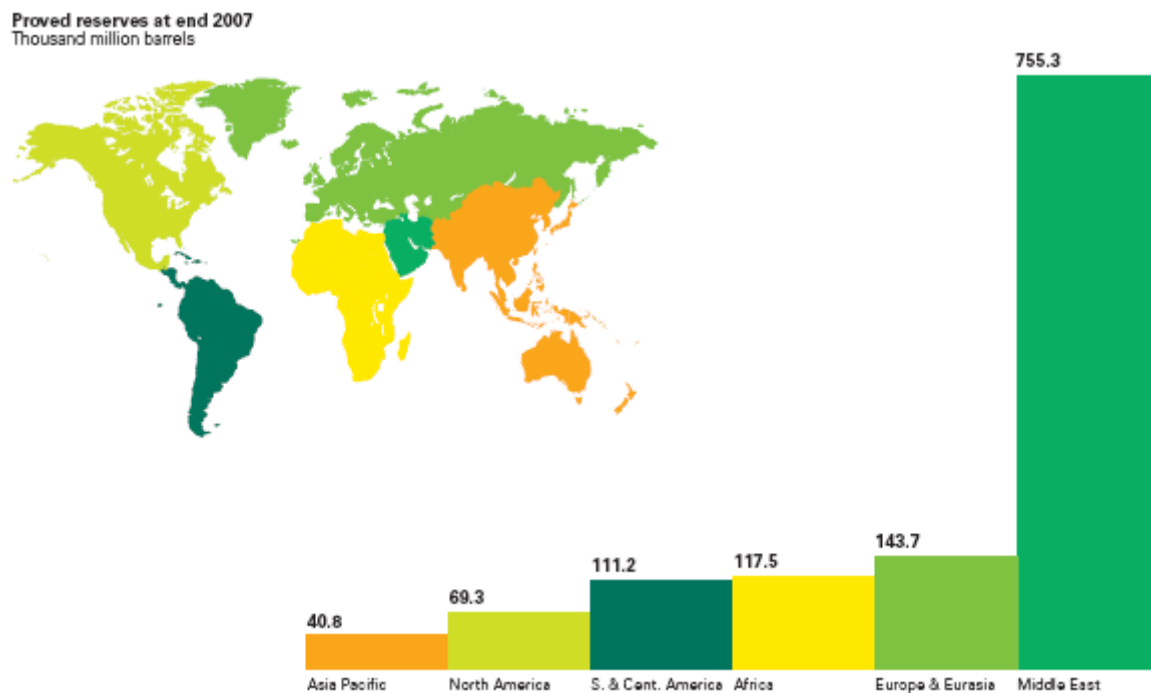


Figure 1.2 World reserves at end of 2007[5]

The elemental composition of crude oil is listed in table 1.1. Since petroleum is a mixture of a wide range of different compounds that varies from field to field and even from well to well in the same field, chemical characterisation of the different crude oils on a molecular level is not possible and also meaningless. Therefore compositional characterisations by fractionation into chemical families are of more importance. SARA fractionation, as described by Aske et al.[6] is one way to characterise crude oils. Figure 1.3 shows a schematic overview of this method. This method is a group type analysis which separates the crude oil into four main classes, saturates (S), aromatics (A), resins (R) and asphaltenes (A), based on differences in solubility and polarity. Saturates are the non-polar compounds containing no double bonds and includes both alkanes and the cycloalkanes. Aromatics consist of all compounds that have one or more benzene ring. Resins comprise polar molecules, often containing heteroatoms. Naphthenic acid is part of this fraction. The fourth group asphaltenes are polar molecules that can be regarded as similar to the resins, but of higher molecular weight, typically 500-1500 g/mole.[7]

Table 1.1 Elemental composition of petroleum[1]

Element	Composition range, wt%
Carbon	84-87
Hydrogen	11-14
Sulphur	<0.1-8
Oxygen	<0.1-1.8
Nitrogen	<0.1-1.6

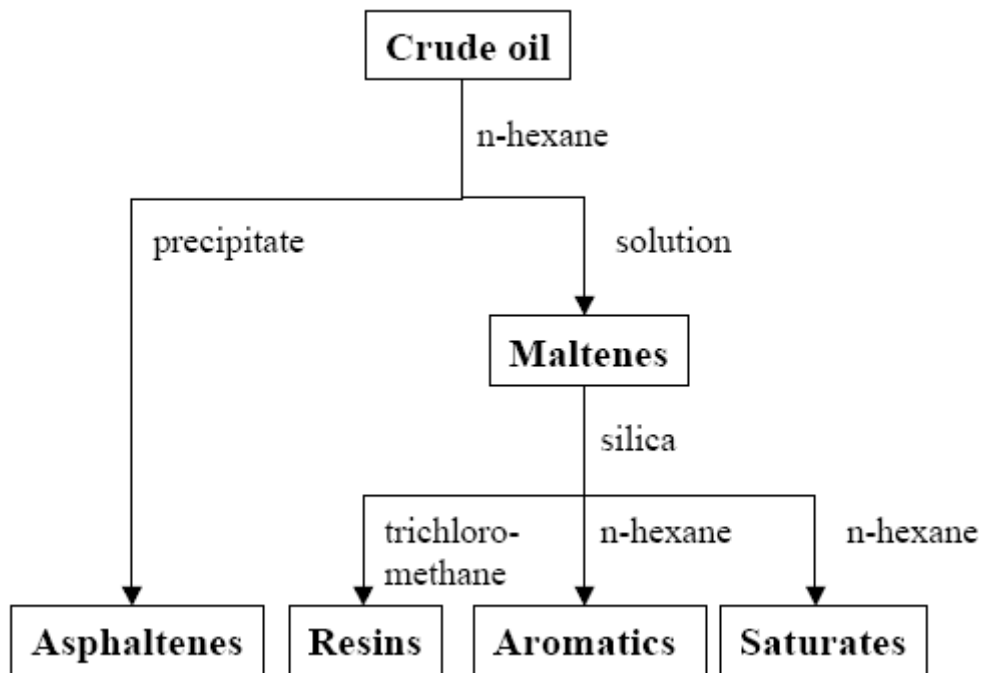


Figure 1.3 SARA-separation scheme as described by Aske et al.[6]

2.3 Petroleum Processing

Recovery of crude oil is mainly divided into three phases, primary, secondary and enhanced oil recovery. What differs these three phases is the need for chemical, thermal or physical methods in order to maintain a sufficient recovery.

Primary recovery is dependent on the natural driving energy of the reservoir to the well bore, by rock and liquid expansion, depletion, gas cap, water gravity drainage or combinations of these, without any external injections or addition of chemicals.

Secondary recovery is the additional recovery promoted by injection of water or gas to maintain the depleted reservoir pressure and force the crude oil from the injection well towards the producing well.

In enhanced oil recovery (EOR) different methods used to recover residual oil from the reservoir after both primary and secondary recovery methods have been exploited to their economical limits. [1]

EOR methods include:

- Polymer flooding
- Surfactant flooding
- Alkaline flooding
- Miscible fluid displacement
- Steam drive injections
- Cyclic steam injections
- In-situ combustion, etc.

Most crude oil need pre-treatment before transportation to the refinery since the crude oils seldom are pure. During production water, gas and even sand is co-produced. Separation needs to be preformed before transportation. This is normally performed at the installation. An example of a liquid treatment system is shown in figure 1.4. This is necessary to meet the basic sediment and water (BS&W) demands for transportation which at the moment have an upper limit of 0.5%.

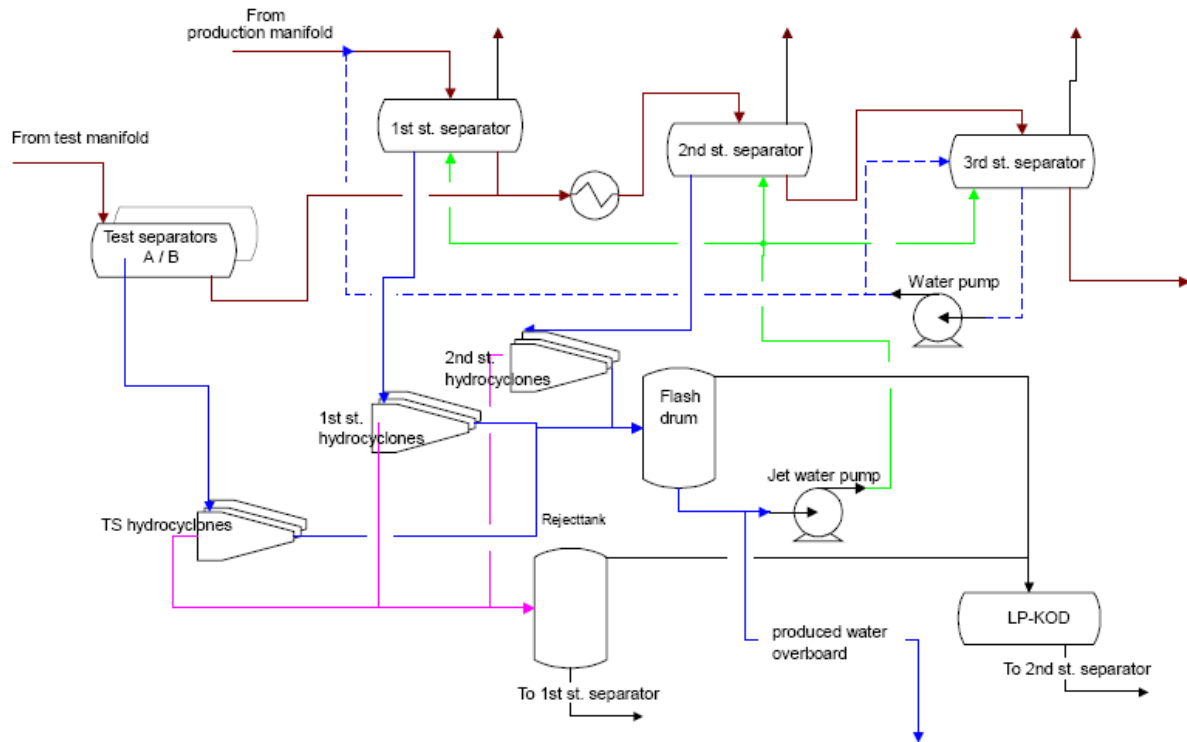


Figure 1.4 An example of a liquid treatment system on an off shore installation [8]

Transportation of crude oil from the producing field to the refinery normally takes place through pipelines or by tankers, but crude oil can also be transported by cars and trains.

Oil refineries are complex plants and include both physical processes such as distillation and extraction and chemical processes which many are catalytic. After desalting and dehydration, the crude oil is separated into fractions by distillation. These fractions are not directly applicable so several processes are carried out in order to produce the required products. [9] Figure 1.5 shows an overview of the different processes included in and product outcome from a typical refinery.

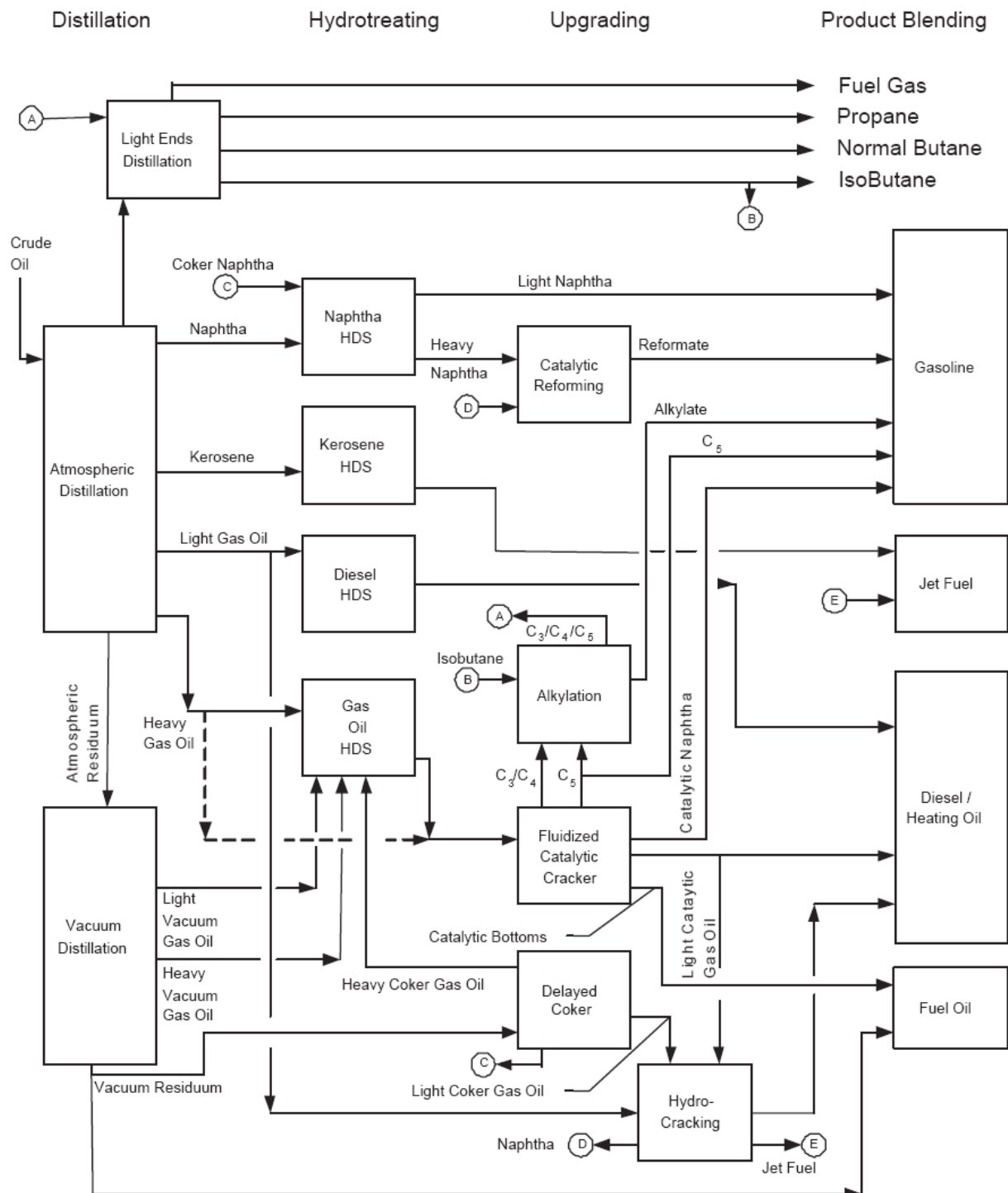


Figure 1.5 Refinery flow scheme [10]

For refineries different crude oil properties are important.

- API gravity- is one expression of the relative mass of crude oil and is defined as,

$$^{\circ}API = \frac{141.5}{SG} - 131.5 \quad (1.1)$$

Where SP is the specific gravity of the crude, which is gained by dividing the density of the crude by the density of water. Low API gravity indicates a heavy crude oil while high API gravity indicates a lighter crude oil.

Other variables of importance for the crude oil quality is

- Salt content
- Sulfur content
- Pour point
- Ash Content

Also naphthenic acids in crude oil can be an issue for refineries. Figure 1.6 gives a simplified overview of the different problems related to naphthenic acids, calcium naphthenate and sodium naphthenate in refining process. These problems will be further described in the next chapter.

<p>Na Nap</p> <p>Ca Nap</p> <p>↑</p> <p>↓</p> <p>Nap Ac</p>		Soaps into the Kerox	
		Fouling	Fouling Catalytic poisoning
	Environmental Issues LT Corrosion	HT Corrosion Environmental Issues Emulsion into the desalter	HT Corrosion
	Low MW	Medium MW	High MW

Figure 1.6 Naphthenic acid related problems in crude oil refining [11]

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3 ACIDIC CRUDE OILS

3.1 Introduction

Crude oils with high amounts of naphthenic acids are found in several fields around the world, like Angola, Congo, Nigeria, North Sea and Venezuela. They all share the same characteristics with high TAN value, low levels of paraffinic components and usually higher densities than non-acidic crudes. Several problems are related to such crudes. One of them is organic scale, often a mixture of calcium soaps associated with other minerals such a calcium carbonate, clays and iron carbonate. In the following text this type of scale is called calcium naphthenate. Table 2.1 shows examples of fields that are/have been experiencing these types of problems.[1, 2] It has been discovered that calcium naphthenate deposits mainly consist of the calcium salts of one tetraprotic acid, identified and named ARN by Statoil and ConocoPhillips[3, 4]. From here on, this family of acids will be called C₈₀-naphthenic acids.

Table 2.1 Fields experiencing naphthenate problems

Oil Field	Location
Afia	Nigeria
Attaka	Indonesia
Blake	Great Britain
Heidrun	Norway
Kuito	Angola
EDC	China
Kita	Cameroon
Asoma	Cameroon

In addition to calcium naphthenate deposits that are caused by the C₈₀-naphthenic acids, other high TAN crude oils lead to tremendous problems with sludge-like emulsion. This problem is not caused by C₈₀-naphthenic acids but rather monoacids with lower molecular weight (~200 to 400 g/mole) that react with sodium instead of calcium. As previously mentioned there is another major problem related to processing of acidic crudes. Refineries are concerned by the

potential corrosion problem caused by acidic crudes at high temperatures. For this reason the acidic crudes are downgraded on the basis of their TAN value. [5]

3.2 Naphthenic Acids

The term “naphthenic acid” is commonly used to account for all carboxylic acids present in crude oil, including acyclic acids, even though it is not entirely correct; the more correct description is that carboxylic acids include naphthenic acids.

Naphthenic acids comprise a complex mixture of alkyl-substituted acyclic and cycloaliphatic carboxylic acids, with the general chemical formula $C_nH_{2n+Z}O_2$, where n indicates the carbon number and Z specifies a homologous series. Z equal to zero for saturated, acyclic acids and increase to two in monocyclic naphthenic acids etc. Figure 2.1 shows examples of typical naphthenic acid structures. [6, 7]

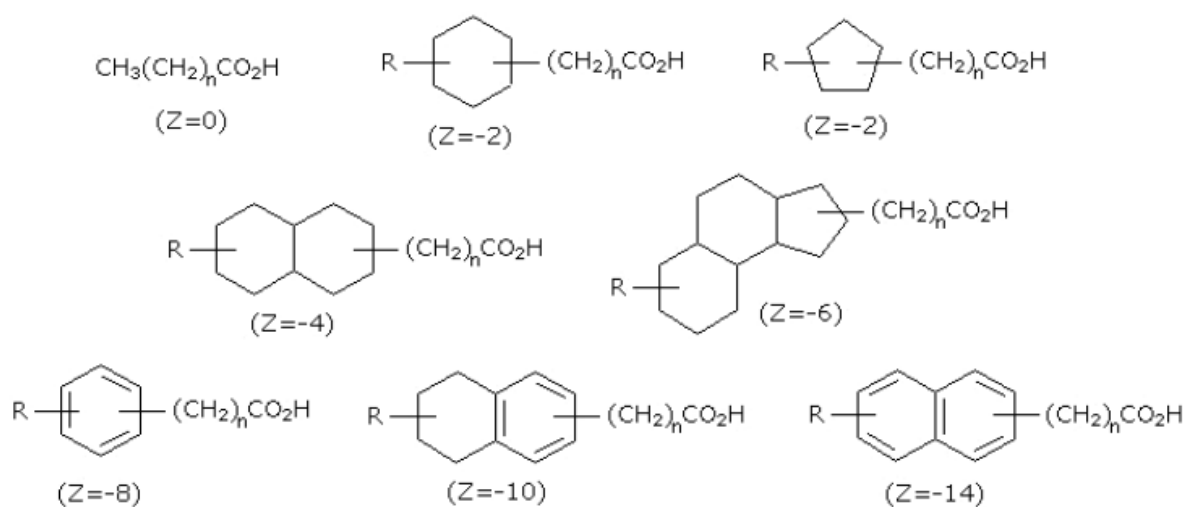


Figure 2.1 Example of typical naphthenic acids

Naphthenic acids are non-volatile, chemically stable, and act as surfactants with dissociation constants in the range 10^{-5} to 10^{-6} [7]. Naphthenic acids are natural components of petroleum in a range from a few ppm up to 3 wt%, and are predominantly found in immature heavy crude oils [7, 8]. The deposit has either not undergone sufficient catagenesis or it has been biodegraded by bacteria [9-11]. However, the naphthenic acid fractions of petroleum do not

solely comprise cyclic or acyclic alkanolic acids with the general formula $C_nH_{2n+2}O_2$. For example, UV and IRE analyses showed the presence of pyrroles, thiophenes, and phenols in naphthenic acids purified from a California crude oil [12]. Because of the complexity of these naphthenic acids mixtures, the separation, quantification, and identification of individual compounds has not been achieved.

Analytical methods have been developed to measure the total naphthenic acids concentrations in oil or water. Total acid number (TAN) is the measurement of the acidity of different crude oils. The TAN value is the number of milligram of KOH required to neutralize the acidity of one gram of crude oil. Several analytical techniques have been utilized to qualitatively characterize naphthenic acids extracted from crude oils, including various mass spectrometry (MS) methods [13-17], gas chromatography-mass spectrometry (GC-MS) [18-20], and these methods combined with Fourier transform infrared (FT-IRE) and/or nuclear magnetic resonance (NMR) spectroscopy [20-22].

As previously mentioned several problems are related to crude oil containing high amounts of naphthenic acids, such as formation of tight emulsion, calcium naphthenate deposition, and corrosion in during transportation and refining. Also, generation of high calcium content in crude oils due to the oil soluble calcium salts of low molecular weight naphthenic monoacids are problems related to crude oil quality. In addition several problems related to environmental aspects due to the toxicity of the water-soluble naphthenic acids and their salts leads to challenges in the waste water treatment and disposal. The problems related to emulsion/sludge formation and calcium naphthenate deposition will be thoroughly described in later subchapters.

3.2.1 Naphthenic Acids in Oil/Water Bulk Systems

Several equilibriums are involved in naphthenic acids/oil/water systems. Since naphthenic acids are amphiphilic molecules, a molecule that has a hydrophilic and a hydrophobic part, the naphthenic acids may be distributed between the oil and the water phase. This distribution depends strongly upon conditions like pH and salinity of the aqueous phase. Partitioning of naphthenic acid monomers between oil (O) and water (W) may be described by the equilibrium in equation 2.1,



where the corresponding partitioning coefficient $K_{w/o}$ is given by

$$K_{w/o} = \frac{[RCOOH]_w}{[RCOOH]_o} \quad (2.2)$$

The degree of partitioning will depend on the relative solubility of the molecules. Hence, naphthenic acids with a large hydrocarbon moiety will exhibit lower partition coefficients than compounds with smaller hydrophobic parts. The distribution of acid between the oil and the water phase will also be affected by the pH. Increasing the pH, will leads to dissociation of the acids groups and the monomers will become more water-soluble. Reinsel et al. [23] investigated the effects of pH, temperature, and organic acid concentration on the partition coefficients for short chain organic acids in a crude oil/water system. At pH 5-7, more than 85% of the acids were dissolved in the aqueous phase. Moreover, they found an approximately linear descending relation between the partition coefficient and the number of carbon atoms in the hydrocarbon moiety. A similar relation was also reported by Havre et al.[24] from a partitioning study of a series of synthetic naphthenic acids in oil-water systems under different experimental conditions. Kocherginsky and Grishchenko [25] measured the transfer rate of long chain fatty acids from octane into aqueous solution through a flat porous membrane. At pH 4, they found that the transfer rate was inversely proportional to $K_{o/w}$. By increasing the pH to 12, a 20-fold increase of the rate was observed in the case of octanoic acid, and a 1000 fold in the case of oleic acid.

3.2.2 Interfacial Behaviour Theory

A fundamental feature of amphiphilic molecules is their ability to adsorb onto interfaces and stabilize colloidal structures. For two immiscible liquids in contact, the molecules in the bulk phase are symmetrically surrounded by other molecules so that the molecular interactions in all directions are identical and the sum of all interacting forces is zero. At the interface, however, the molecules are affected by interactions between the two phases, causing a net force towards the respective bulk phases. The molecules at the interface are thus forced

towards the bulk phases, which in turn cause a minimizing of interfacial area. The interfacial tension (IFT) is a commonly used parameter to measure the cohesive energy existing at a given interface, and can be correlated to the interfacial energy and the corresponding interfacial area by equation 2.3,

$$\gamma = \left(\frac{dG}{dA} \right)_{p,T} \quad (2.3)$$

where γ is the IFT, G is the interfacial Gibbs free energy, and A is the interfacial area at constant pressure p and temperature T . Hence, any factor which lowers G , like introducing interfacially active compounds, will also cause a lowering of the IFT. When an interface between acidic oil and water is freshly formed, the IFT is very close to that of the pure solvent. The interfacially active acid monomers will immediately start to diffuse from the oil bulk towards the interface [26]. As they accumulate at the interface, the IFT will decay until the equilibrium tension value is reached. After that point, since the adsorption of surfactants is a dynamic phenomenon, the flux of adsorption will be equal to the flux of desorption, according to equation 2.4,

$$\frac{d\Gamma_{eq}}{dt} = j_{ads} - j_{des} = 0 \quad (2.4)$$

where Γ_{eq} is the interfacial concentration of surfactants at equilibrium, t is the time and j_{ads} and j_{des} the fluxes of adsorption and desorption, respectively. The period of time dt during which the equilibrium is obtained may range from milliseconds to hours depending on the surfactant type and concentration [27]. Equilibration of acid monomers at the interface involves relaxation processes where the IFT normally decays exponentially with time, according to equation 2.5 [28]:

$$\gamma = \gamma_{eq} + (\gamma_0 - \gamma_{eq}) e^{-kt} \quad (2.5)$$

The term γ_{eq} represents the interfacial tension at equilibrium, γ_0 is the interfacial tension extrapolated to $t \rightarrow 0$, t is the time and $k^{-1} = \tau$ is the relaxation time of the process. The relaxation period is assumed to include processes like reorientation of the molecules in the

adsorption layer and solvation/desolvation of the adsorbed species. At equilibrium, the interfacial concentration of monomers is also linked to the concentrations in the bulk media as illustrated by the following relations,



where HA and A^- represent naphthenic acids in undissociated and dissociated states, and the subscripts O , int , and W indicate oil bulk, o/w interface, and water bulk, respectively. Due to their tendency to accumulate at water/oil interfaces, the naphthenic acids may contribute to stabilization of crude oil emulsions [29, 30]. The interfacial affinity is dependent on conditions like molecular structure, hydrophilic-lipophilic balance, concentrations, and the pH and the salinity of the aqueous media. The fact that the IFT decreases at increased pH may also be benefited from, like in EOR, where alkaline solutions are injected into reservoirs in order to lower capillary forces and hence mobilize residual oil.[31-33] For very low tensions, several authors [31, 34] have reported that the IFT goes through an ultralow minimum at a specific pH value before a steep increase is observed. For acidic model and crude oil-water systems, Rudin and Wasan [35, 36] ascribed this effect to a simultaneous adsorption of ionized and unionized acids, causing an optimum packing of surfactants at the interface. Similar explanations were also given by Touhami et al. [37].

3.3 C₈₀-naphthenic Acids Responsible for Calcium Naphthenate Deposition

The so called ARN acid (C₈₀-naphthenic acids), was discovered by ConocoPhillips and Statoil and is now believed to be responsible for calcium naphthenate deposition [3, 4]. Baugh et al. isolated acid from a calcium naphthenate deposit from the Heidrun field by use of the Acid IER method developed by Mediaas et al.[38]. This acid fraction was analysed by ¹³C NMR, potentiometric titrations, LCMS, and VPO. The NMR result showed a sharp, baseline resolved, aliphatic signals and on sharp carboxylic acid signal. This represented a small family of related structures different from normal naphthenic acids. LCMS measurements were also performed and the molecular weight of this acid fraction was determined to be in the range 1227-1235 amu. The range of mole weights indicated that this was not one particular acid but a family of acid with a varying degree of unsaturation in the hydrocarbon

skeleton. In addition the same analysis was performed on several deposits offshore Norway, Great Britain and West Africa with the same finding. Analysis of the acid by high resolution mass spectrometry confirms the molecular formula of the most pronounced isomer as $C_{80}H_{142}O_8$. Further mass spectral analysis of the methyl and benzyl esters confirmed the presence of four carboxylic groups. [3, 4]

In paper one we report on acids isolated from a West African deposit which were characterized by electrospray ionisation Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) in negative mode. The main peak located at m/z 1230.0627 was consistent with the ion $[C_{80}H_{141}O_8]^-$, *i.e.* the parent compound being $C_{80}H_{142}O_8$. [39]

The molecular formula of this family of acids has also been extensively studied by Lutnaes *et al.* [40] They are four-branched, aliphatic molecules with one terminal carboxylic group attached to each branch. The aliphatic chain contains 4-8 five-membered saturated rings. An example of this structure is shown in figure 2.2. Figure 2.3 shows the different conformations of the C_{80} -naphthenic acids.

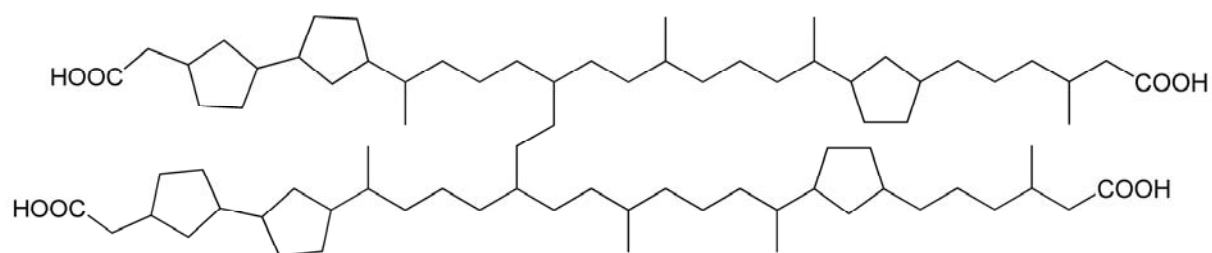


Figure 2.2 Example of C_{80} -naphthenic acids structure

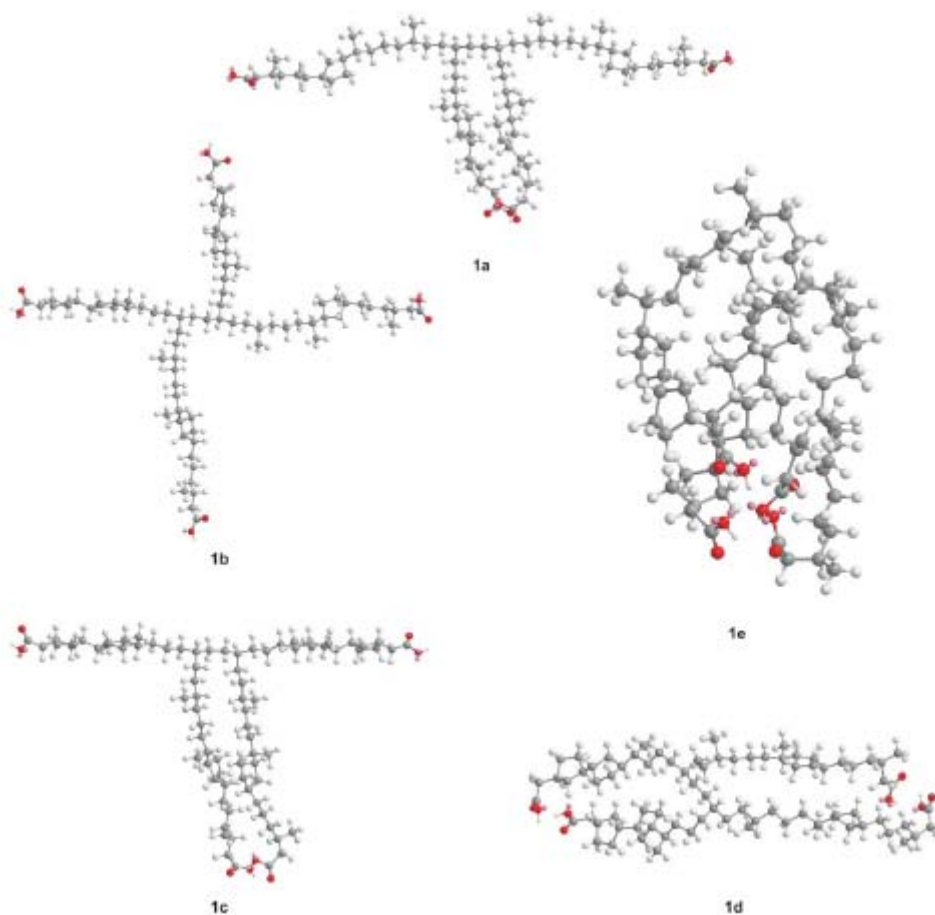


Figure 2.3 Conformations of the C₈₀-naphthenic acids responsible for naphthenate deposition problems according to Lutnaes et al.[40]

Also, methyl-substituted C₈₁-naphthenic acids and C₈₂-naphthenic acids analogues containing 7 and 8 five-membered rings have been reported on.[41, 42]

Detection of the C₈₀-naphthenic acids in crude oil is not an easy task since the acid only exists in ppm level. To be able to detect it is necessary to consecrate the acid fraction. Methods such as High Temperature Gas Chromatography (HTGC) [41], Liquid Chromatography Mass Spectrometry (LCMS) [3] have been utilized to detect and analyse this acid. At the Ugelstad Laboratory a method to determine quantitatively the content of the C₈₀-naphthenic acids in calcium naphthenate deposits have been developed [43]. The method consists of four steps. Molecules present in the deposit are first dissolved in a mixture of toluene and 2-butanol after an acidic treatment. All acid molecules are then selectively extracted and concentrated by a Solid-Phase Extraction (SPE) method. After derivatization of acids into their naphthacyl esters to increase the sensitivity of the detection, C₈₀-naphthenic acids is separated and detected by reversed-phase HPLC with UV detection.

3.4 Acidic Crude Oil Related Problems

All crude oils normally contain naphthenic acids. The majority has small amounts that do not lead to problems, but in some crudes they can become a nuisance if they come in contact with the produced water. Depending on the type and amount of naphthenic acids it can lead to several types of problems:

- Very tight and strong emulsions formed by salts of the more aliphatic organic acids in the crude. In the worst case, this type of emulsion behaves like sludge.
- The larger quantities of organic acids in oilfield produced waters, formed by the water soluble salts of very low molecular weight naphthenic acids cause significant oil in water problems.
- The oil soluble calcium salts of the low molecular weight naphthenic monoacids generate high calcium content in crude
- Sticky deposits formed by the polymeric salts of calcium and/or iron with ARN
- Naphthenic acid corrosion of process equipment
- Toxicity and waste water related problems

In this thesis the sodium emulsion soap and the calcium naphthenate problems will be further elucidated.

3.4.1 Sodium emulsion soaps

Sodium emulsion soaps are usually formed from the lighter oil types with a typical °API ranging from 32-41, and these oils can have a variable content of organic acids. They have usually low TAN value, low sulphur, asphaltene and resin content and typical high to moderate wax content. They are non-biodegraded to slightly biodegraded. The oil contains significant fatty carboxylic acids ranging from C₂₀-C₃₇ that are involved in soap formation and minor amounts C₈₀-naphthenic acids can be present but are not involved in creating soaps. The water phase normally has very high bicarbonate content and high volatile fatty acid content and low salinity. These linear fatty acids mostly react to form salts of monovalent cations like sodium and potassium, but also rare occurrence with calcium iron and magnesium is seen.

Soap formation can be a self-scaling effect, the result is highly viscous emulsions predominantly formed by monovalent ions, e.g. sodium. It typically occurs as soap stabilized emulsions in wells and accumulates at interfaces of separation vessels. It remains soft when cooled and exposed to air, and often show a layer formation tendency. This sludge formation can have severe consequences for production facilities. The precipitation of soap can occur both down hole and topside dependent on where the fluids reach their saturation pressure. There is also possibility of near-wellbore skin damage due to soaps. The sodium soap is a dominant emulsifying agent and can entrain other solids and water drops. It also effects the dehydration efficiency and export oil BS&W contents, while well fluids can become very viscous. It reduces the residence time and form a barrier against water drop coalescence and efficient water dehydration. Unlike calcium naphthenate however, sodium soaps do not stick to external surfaces or to exotic metals.

The removal of this sludge requires careful considerations, since the viscous sludge can contain heavy metals, and have a high content of naturally occurring radioactive materials (NORM) also, naphthenic acids/naphthenates are toxic in their own right. The water quality can be affected and water discharge issues can be raised due to oil-wet soap particles suspended in offshore produced water.[44]

3.4.2 Calcium Naphthenate

Vinstad et.al.[45] were the first to report on the calcium naphthenate issue in 2003. During a maintenance and inspection shut-down in 1996 just after water breakthrough a solid black deposit were found in the 1st and 2nd stage separators. Analysis showed that this was calcium salts of naphthenic acids. At this moment no operational problems were related to this. But as time went on the problem accelerated, and became a problem in virtually all parts of the liquid system at the Heidrun platform. In addition to the separator train, naphthenate were found in the produced water system, closed drain and low pressure flare KO drum, and in the sand cleaning system, figure 2.5 and 2.6. By end of 1997 it was generally acknowledge as the most serious threat against continuous oil production.

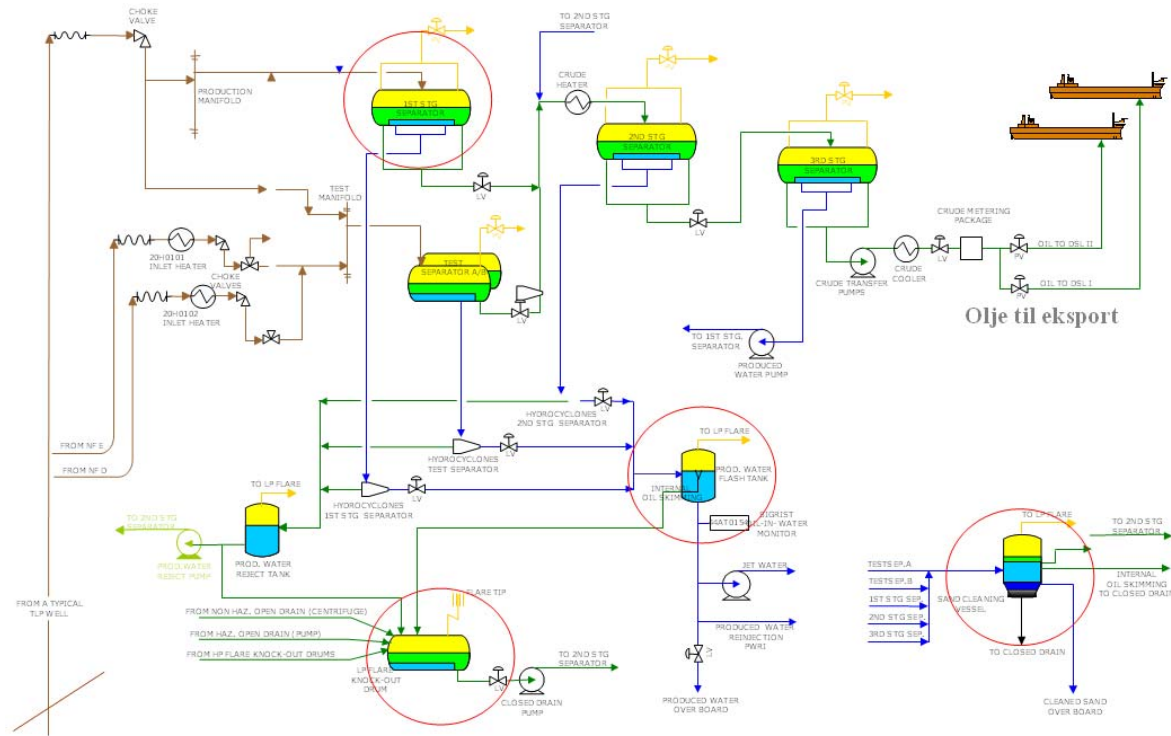


Figure 2.4 Liquid treatment system at the Heidrun platform, problem areas are highlighted. [46]



Figure 2.5 Naphthenate deposit in separator (left)[46] and in process heater (right)[47]

The problem arise from pressure drops and degassing of carbon dioxide during the transportation of the fluids from the reservoir to the topside facilities, leading to dissociation of naphthenic acid at the interface between the crude and the co-produced water to form naphthenate. The calcium naphthenate is soluble in neither oil nor water. Hence, it accumulates at the interface. Since the C_{80} -naphthenic acids, which is believed to be responsible for the naphthenate problem, is a four-protic acid it will in reaction with divalent cations as calcium lead to formation of a continuous network, as seen in figure 2.6. The

picture illustrates the difference between calcium naphthenate formed with C₈₀-naphthenic acids and monoacids. As seen in the picture in figure 2.6, monoacids will form particles at the interface, which will disperse either in the oil or the water phase dependent on the solubility of the product (left vial). While C₈₀-naphthenic acids form a continuous sticky network at the interface, insoluble both in water and oil. This network will function as glue and will under real production conditions bind up sand, scale and other crude oil components and precipitate in process equipments, in addition due to its stickiness also fasten to internals of process equipments.



Figure 2.6 Calcium naphthenate of C₈₀ naphthenic acids (left) and of p-(n-dodecyl) benzoic acid (right).

3.5 Isolation of acid from deposits: The Acid IER Method

The Acid IER Method is a method for selective isolation of carboxylic acids from crude oil and other organic solvents and the method can also be used on solids and non-organic solvents. The selectivity of the method is reported to be >98mol%, verified by use of two model acids.

The method utilizes a QAE Sephadex A-25 ion exchange resin (IER) which is sugar based (poly-1, 6-glucose). This is a resin with diethyl-(2-hydroxy-propyl)aminoethyl as the ion exchange group. It is a potent ion exchanger and the fact that it is hydrophilic makes it selective towards carboxylic acids.

The method is a time-consuming process where the deposit first is thoroughly cleaned, followed by acid treatment with 1M HCl and toluene to dissolve the acid in the organic solvent. The Acid-IER needs pre treatment by Na_2CO_3 before use to exchange Cl^- with HCO_3^- . Finally, IER is directly applied to the toluene phase and the acid is extracted. The method is thoroughly described by Mediaas et al.[38]

3.6 Inhibition of Calcium Naphthenate

There are several ways to deal with the naphthenate problem. The first and most well known method is to treat the fields with a strong acid like acetic acid. By injection of acid, the pH is decreased and the acid exists in its undissociated form. The interfacial tension increase and the reaction with metal ions are suppressed, also leading to decrease in the stability of naphthenic acid stabilized emulsions. A drawback with this method is increased corrosion of process equipment and the high amount of acid needed to decrease the pH to the desired level to prevent acid dissociation at the interface. The second method is sequestering. In this method chemicals are added with the purpose of complexing divalent cations and remove them from the water phase, in that way prevent reaction with TA. Since the concentration of ions in the produced water can be quite high large volumes of chemicals are needed. Neutralization of the naphthenic acids in the oil phase with organic bases is a third method, but this method also requires addition of large volumes of chemicals if the crude oil is of high TAN values.

The ideal method to deal with the problem is to block the reaction between the acid species and calcium with inhibitors/chemical additives. Chemical vendors are constantly developing new surfactant blends for treating naphthenate and emulsion problems related to naphthenate/naphthenic acids. These chemicals consist of different surfactant blends, and use the mechanism of interfacial crowding to inhibit salt formation. These surfactants are in some cases more interfacially active than the C_{80} -naphthenic acid molecules and therefore accumulate at the interface to a larger extent than TA. Therefore, they inhibit the reaction between acids and counter ions. This method either alone or in combination with acid treatment is believed to be the most effective and cause lower problems at low dosages than acid treatment alone.[48, 49]

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4 EMULSIONS AND EMULSION STABILITY

4.1 Emulsions

The IUPAC definition of an emulsion is “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”. [1]

There are two main types of emulsion, oil-in-water (O/W) and water-in-oil (W/O), defined by the continuous phase. In addition to these usual emulsion types multiple emulsions can occur. In the petroleum industry water-in-crude oil emulsions is most commonly seen. The size of the water droplets can be up to 100 μ m which is quit large compared to the common definition of the upper limit for colloidal size which is 1 μ m.

All emulsions are thermodynamically unstable, meaning that it will always break in to two separate equilibrium phases with time. Emulsions can however be kinetically stabilized if the coalescence rate is reduced. The driving force for coalescence of two immiscible phases is the energy stored in the O/W interface. The interfacial tension γ_{AB} between the two phases A and B can expressed from the surface tension $\gamma_{A/B}$ and the dispersion energies γ_{AB}^d [2]

$$\gamma_{AB} = \gamma_A + \gamma_B - 2\sqrt{\gamma_A^d \gamma_B^d} \quad (3.1)$$

The amount of energy stored at the O/W interface depends on the interfacial tension and the interfacial area. The interfacial tension between two immiscible liquids is high, and the two phases will separate within short time. Addition of surfactants will reduce the interfacial tension significantly since the surfactant molecules will orient themselves at the interface with the hydrocarbon tail in the oil phase and the hydrophilic head group in the aqueous phase. The presence of surfactant reduces the work needed to emulsify water and oil and the energy gain upon coalescence. Emulsions can be stabilized electrostatically, sterically, by particles or by lamellar liquid crystals.

In the petroleum industry typical stabilizers of emulsions are asphaltenes, resins, naphthenic acids, finely divided carbonate scale, silica, clays, metal sulphates, and chemical additives. [3]

Electrostatically stabilized emulsions reduce the coalescence rate due to electrostatic repulsion between oil droplets with equal surface charge. This situation occurs when an ionic surfactant is the stabilizing agent. [4]

Sterically stabilized emulsions have a reduced coalescence rate due to the presence of adsorbed surfactants or polymers that are protruding into the aqueous phase. This forms a physical barrier towards coalescence. In addition to the physical repulsion, solvated surfactants or polymer chains give rise to an osmotic pressure if the droplets are pushed together.

Fine particles can stabilize an emulsion if both oil and water wet the particle surface. If the contact angle is around 90° the particle will penetrate equally into the oil- and the water phase and stabilization is optimal. Coalescence is then prevented since the droplets do not come in direct contact upon collision.

Lamellar liquid crystalline phase can also form a barrier against coalescence. In order to understand such a mechanism, phase equilibria of water/oil/surfactant systems are of importance.[5-8]

4.2 Destabilization of Electrostatically Stabilized Emulsions

With regards to naphthenic acids above pK_a , is it usually the electrostatic stabilization mechanism of oil or water droplets that are of interest. But also scenarios with particle stabilized emulsions or emulsions stabilized by lamellar liquid crystals can occur.

In this section destabilisation of electrostatically stabilized emulsions will be described.

A collision between two droplets will result in either coalescence or an intermediate step of flocculation. The processes taking place during destabilization of emulsions are shown in figure 3.1.

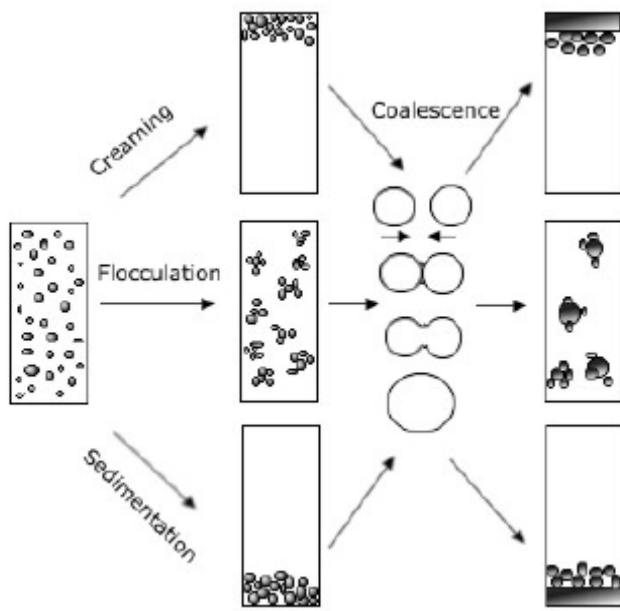


Figure 3.1 Processes taking place in an emulsion leading to emulsion breakdown and separation.[9]

A high kinetic energy is needed for a collision between charged oil droplets to give coalescence. The importance of surface charge for colloidal stability in aqueous solutions has been investigated by several authors with the intention of to give a good description of the system. A model for the potential gradient outside a planar charged surface was first proposed by Gouy in 1910, and further developed by Chapman in 1913. This theory take into account that charged surfaces will attract opposite charged counter-ions. In 1924, Stern corrected the model by introducing a surface concentration limitation of the counter ions. This model accounts for the fact that the counter ions have a certain size and therefore occupy some space. A schematic illustration of the variation of potential with distance from the charged wall in the presence of a Stern layer is presented in figure 3.2. In the model, the innermost layer of ions is assumed to be adsorbed at the charged surface and the plane through these ions is referred to as the Stern surface. Outside this surface is the diffuse layer, which is basically the same as presented in the Gouy-Chapman model, starting from the zeta potential ζ at a distance δ from the charged surface.

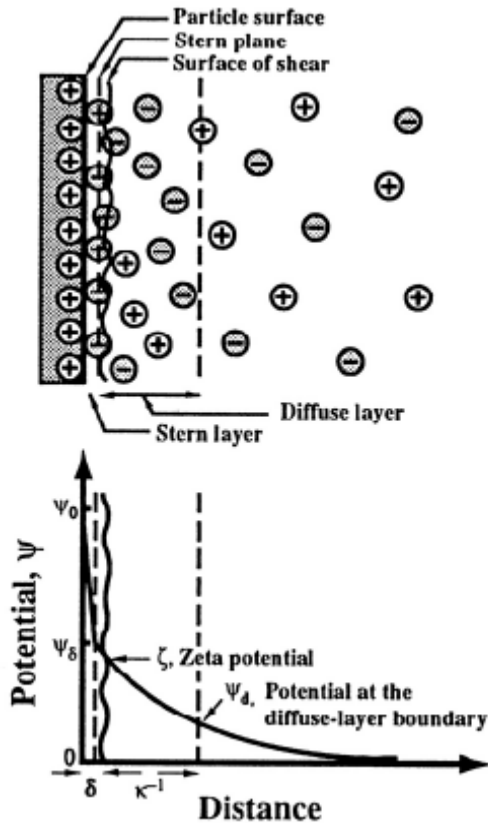


Figure 3.2 Sketch of how the potential vary through the electric double layer. [10]

Despite difficulties in quantitatively applying the mathematical expressions for the double layer on real systems, the theory is fundamental for the understanding of colloidal stability. Upon additions of counter-ions the double layer is compressed. Hence, adding an electrolyte will reduce the repulsion between the oil droplets, and increases the probability that a droplet collision leads to coalescence. At high ionic strength the electrostatic repulsion is eliminated and the oil droplets may flocculate. Under such conditions the coalescence is limited by the film rupturing rate. A detailed treatment of this subject in terms of the characteristic times for flocculation, coagulation and film-rupture has been given elsewhere[3]. Adding a substance such as an alcohol, which is soluble in both phases, is known to increase the coalescence rate [11].

At low ionic strength an electrostatic stabilized emulsion is fairly stable since the coalescence rate is slow. Still, if the oil components are slightly water soluble, a degradation of a stable emulsion may occur, where the larger oil droplets grows on the expense of the smaller droplets. This phenomenon is called Ostwald ripening [12].

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5 CHARACTERIZATION TECHNIQUES

In this section only experimental techniques used by the author are described. For detailed knowledge of the other methods used in the articles present in this thesis, description and references are given there.

5.1 Pendant Drop Technique

The pendant drop method was utilized in paper I, II, III and IV.

The technique most suitable for measurements of dynamic interfacial tension (IFT) is the pendant drop technique. This technique has a number of advantages compared to other techniques developed to determine the surface and interfacial tension. First, it is highly accurate the error margin is $\pm 0.15\%$ or less [1] Secondly, the measurements are performed rapidly and successive measurements can be performed without disturbing the interface, since no direct contact occurs. Figure 3.1 show a schematic overview of the CAM 200 pendant drop equipment (KSV Ltd.) used in this thesis.

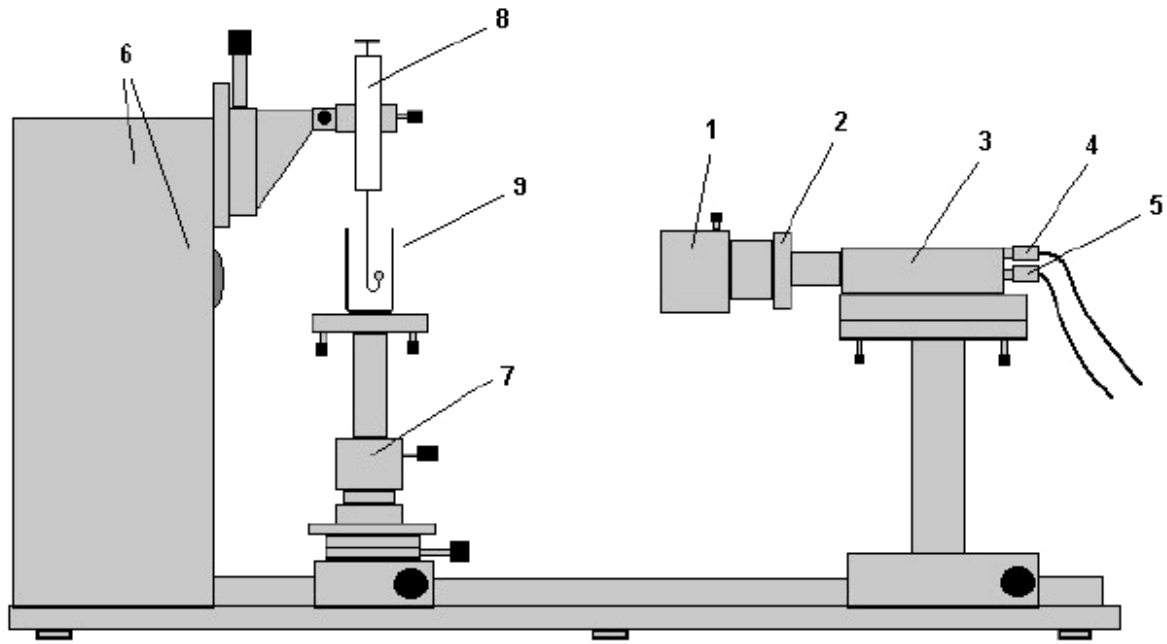


Figure 3.1. Cam200 equipment (KSV Ltd.) The setup includes (1) camera lens zoom, (2) lens aperture adjustments, (3) CCD camera, (4) light synchronizing cable, (5) video out cable, (6) light source and interface unit, (7) stage for sample, (8) syringe with a pendant drop, and (9) transparent liquid chamber.

The pendant drop method is used in combination with axisymmetric drop shape analysis (ADAS). The theory behind the mathematical consideration has frequently been given in the literature [1-4]

A relation between the drop shape and the interfacial tension is given by the classical Young-Laplace equation:

$$\Delta P = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad (3.1)$$

Where ΔP is the pressure difference across the drop interface, γ is the interfacial tension. The radii of curvature, R_1 and R_2 , are determined from geometrical considerations/correlations whereas the density difference between the two phases, is measured with an independent method. A detailed explanation to the geometrical correlations can be found in Sjöblom et. al. [5]. Several additional methods to measure surface and interfacial tension are also available, such as the Wilhelmy plate method, different kinds of ring and rotating drop tensiometry, techniques based on capillary rise, method of drop counting among others.

5.1.1 Interfacial Dilational Rheology

The instrumentation used in the oscillating drop experiments, in paper III, was a modified pendant drop instrument (Cam200, KSV Ltd.) with a piezoelectric actuator (Physik Instrument PI-840.6) mechanically connected to the syringe (SGE gastight, 25 ml) and to a signal generator (Agilent 33250A). Due to the $\pm 4V$ limit of the signal generator a built in, home-made amplifier from a radio tube were used to provide the piezoelectric positioner with voltage up to 100V. A more detailed description of the instrumentation is given elsewhere.[6, 7]

The experiments were performed as described above for the interfacial tension-experiments. The drop was oscillated continuously at a frequency of 0.1 Hz.

The surface dilational modulus (E^*) is defined as

$$E^* = \frac{d\gamma}{d \ln(A)} \quad (3.2)$$

E^* can be written as the sum of the storage modulus (E') and loss modulus (E'')

$$E^* = E' + i\omega E'' \quad (3.3)$$

E' is equal to the pure elastic contribution while E'' is proportional to the viscous contribution to E^* .

The rheological parameters were calculated from the interfacial tension and area wave using Fast-Fourier-Transformations (FFT, 512-point), thoroughly described by Hannisdal et al[6]. Theory regarding the oscillating pendant drop method is described thoroughly by several authors [8-10].

5.2 Langmuir and Langmuir-Blodgett

The Langmuir technique, utilized in paper I, gives information about the monolayer properties of surface active molecules, and was developed by Langmuir in 1920 [11]. The instrument is used to measure physico-chemical properties of monolayers of water insoluble amphiphiles adsorbed onto air/water or oil/water interfaces under different experimental conditions. By using this method information about molecular area, intermolecular interactions, and film resistance against mechanical rupture can be gained.

The instrument consists of a rectangular trough with movable barriers and a device for measuring the surface tension. The surface pressure is normally measured by means of the Wilhelmy plate method [12]. The experimental setup is shown in figure 3.2.

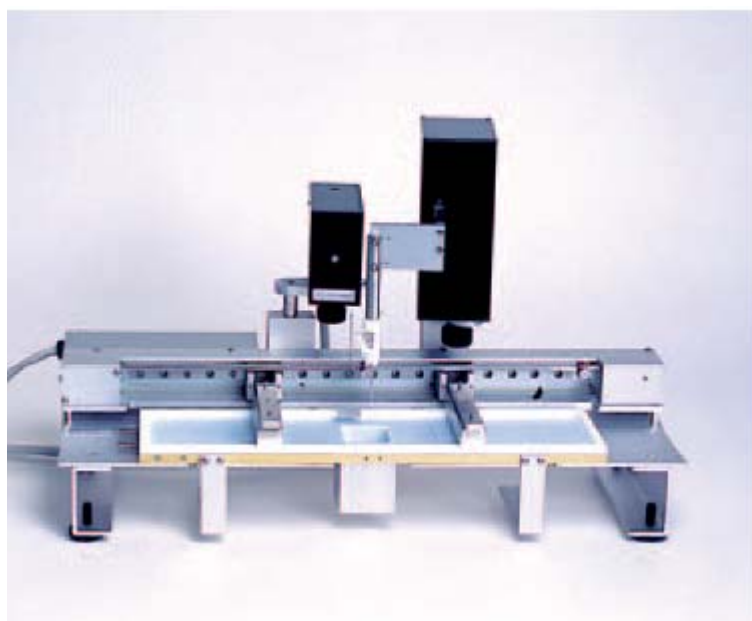


Figure 3.2. Langmuir Minitrough (KSV Ltd.)[13]

A measurement on the Langmuir is carried out by placing the barriers at the edge of the trough. The liquid phase is then poured in to the trough up to the rim. Then the Wilhelmy plate partially immersed in the water phase and attached to the balance. The monolayer is formed by spreading the amphiphile on the water surface. The amphiphiles are normally not easily spread by them selves so an appropriate spreading solvent is used 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 solvent also needs to evaporate quickly. The application of the spreading solvent to the surface is usually accomplished by allowing small drops to fall from a syringe a few millimetres above the surface. After the solvent evaporation, the barriers are put in motion at a given speed. This will lead to a compression of the monomolecular film at the interface. The molecules will start to interact and cause an increase in the surface pressure Π , according to equation 3.4.

$$\Pi = \gamma_0 - \gamma \quad (3.4)$$

where γ_0 and γ is the surface tension in absence and in presence of a monolayer, respectively. Hence, by plotting Π versus molecular area, the properties of and the interaction in the film as the area gradually becomes smaller can be followed. An example of surface pressure versus molecular area isotherm is shown in figure 3.5.

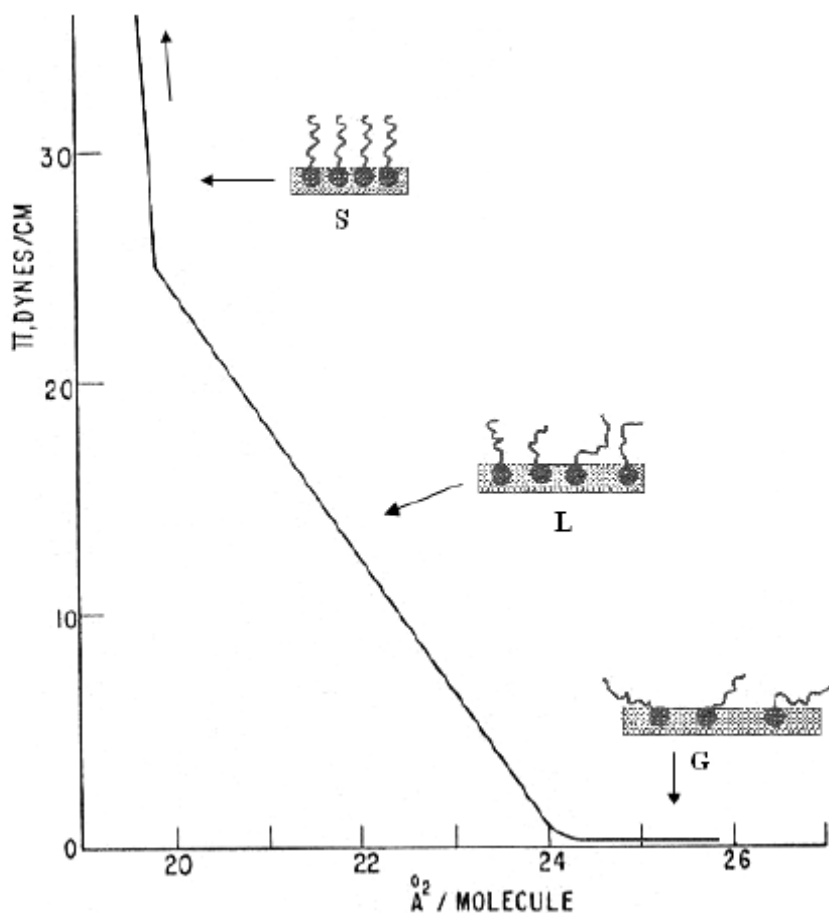


Figure 3.5. Example of surface pressure-area isotherm for stearic acid onto acidic aqueous surface

As the barriers reduce the surface area, the molecules start to interact by the hydrocarbon chain or by electrostatic forces and an increase in the surface pressure occurs. In the beginning the area per molecule is large and molecular-molecular interactions are only weak. This state is normally referred to as gaseous (G). By further compression, the film goes through a liquid state, expanded or condensed, depending on the compressibility of the monolayer. If the molecules are able to adhere strongly to each other through van der Waals forces, the liquid phase might be followed by a solid state. To attain a solid state, the film forming material has to comprise a very regular structure. At a specific point, the resistance of the monolayer will reach its maximum and a film collapse occurs. This point is observed as a sharp break in the isotherm. The presence of the different phases is strongly dependent on the molecular structure of the surfactant molecule.

5.3 Near Infrared Spectroscopy

Applications of near infrared (NIR) spectroscopy in the oil industry are numerous, and can be divided into two groups, for prediction of physicochemical properties and for studies of the degree of aggregation and/or aggregation size. The method has four major advantages; efficiency, simplicity, multiplicity of analysis from a single spectrum, and the non-consumption of the sample. In paper II this technique has been used to study the particle formation growth in an oil water system.

The NIR spectroscopic region extends from 780-2500 nm. When a liquid sample is exposed to light, the light is transmitted through the liquid, absorbed by the different molecules, and/or scattered by particles or aggregates existing in the solution. One of the main advantages using NIR spectroscopy in colloidal system is the ability to gain information about the physical state of particles in solutions. Due to scattering, the NIR spectra will display a baseline elevation depending on the size and the number of particles. This phenomenon has frequently been used to qualitatively study aggregation or disintegration of crude oil fractions [14, 15], or to estimate the sizes of different kinds of particles [16-19].

Light scattering in the NIR region is described in detail by Mullins[20] and Kerker[21]. A brief description is given below.

For slightly lossy dielectric particles in the Rayleigh limit $r/\lambda \leq 0.05$, where r is the particle radius and λ is the wavelength of the incident light, the light extinction can be considered as a sum of the scattering and the absorbance:

$$\sigma_{tot} = \sigma_{sc} + \sigma_{abs} \quad (3.4)$$

where σ_{tot} , σ_{sc} , and σ_{abs} are the total, scattering, and absorption cross-sections, respectively. The absorption cross-section scales with the third power of the radius (r^3). The scattering cross-section, on the other hand, scales with r^6 , according to equation 2:

$$\sigma_{sc} = \frac{2^7 \pi^5 r^6}{3 \lambda^4} \left(\frac{n^2 - 1}{n^2 + 2} \right)^2 \quad (3.5)$$

where n is the ratio of the discrete phase to the continuous phase index of refraction. Hence, the particle size is very important for determining the magnitude of the particle scattering. The light intensities and the number of particles N in a given total cross-section may be related to optical density OD by the following equation:

$$OD = \log\left(\frac{I_0}{I}\right) = 0.434 N \sigma_{tot} \quad (3.6)$$

where I and I_0 are the intensities of the transmitted and the incident light, respectively. The effect of multiple scattering is not accounted for in this equation. In the case of multiple scattering, the scattering and the absorption cannot be treated separately.

5.4 Thermal Analysis

5.4.1 Thermogravimetric Analysis

In thermogravimetric analysis (TGA) a sensitive balance is used to follow the weight change of the sample as a function of temperature. Typical applications include the assessment of thermal stability and decomposition temperature, extent of cure in condensation polymers,

composition and some information on sequence distribution in copolymers, and composition of filled polymers among others.

In paper III TGA was used to monitor the decomposition of both C₈₀-naphthenic acids and calcium soaps of C₈₀-naphthenic acids. The measurements was performed on a TGA100Q (TA instruments) in both helium and air. The samples were heated at 7 °C/minute to 600 °C and kept at that temperature for 20 minutes to ensure complete degradation. The decomposition temperatures were defined as the peak values of the first derivative of the TG trace.

5.4.2 Differential Scanning Calorimetry

In Differential Scanning Calorimetry (DSC) an average-temperature circuit measure and controls the temperature of the sample and a reference to conform to a predetermined time-temperature program. This temperature is plotted on one axis of an x-y recorder. At the same time, a temperature-difference circuit compares the temperatures of the sample and reference holder and proportions power to the heater in each holder so that the temperature remains equal. When the sample undergoes a thermal transition, the power to the two heaters is adjusted to maintain the temperature and a signal proportional to the power differences in plotted on the second axis of the recorder. The area under this curve is a direct measure of the heat of transition.

In paper III DSC was used to detect the transitions in both C₈₀-naphthenic acids and calcium soaps of C₈₀-naphthenic acids. DSC was performed on a DSC300Q (TA instruments) in nitrogen atmosphere. All samples were first heated to the maximum temperature of the cycle, 300 °C for the C₈₀-naphthenic acids and 350 °C for its calcium soap, in order to obtain a comparable thermal history and to evaporate lower-boiling impurities. The sample was heated at 5 °C/minute to the maximum temperature, kept isothermal for 5 minutes, cooled at the same rate to -50 °C and kept isothermal for another 5 minutes.

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6 MAIN RESULTS

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

6.1 Publication I

In publication I naphthenic acids from a West African metal naphthenate deposit were isolated and characterized by infrared (IR) spectroscopy, nuclear magnetic resonance (NMR) and Fourier transform-ion cyclotron resonance mass spectrometry (FT-ICR MS)

The result showed that the acid fraction in the deposit was dominated by a narrow group of 4-protic naphthenic acids with a molecular weight around 1230 g/mole. The determined mass 1230.0627 Da, identifies a compound with the elemental composition of $C_{80}H_{142}O_8$. The compound has 6 saturated rings, and this finding is consistent with the findings from other fields. Figure 5.1 shows results from the characterization of the isolated acid fraction

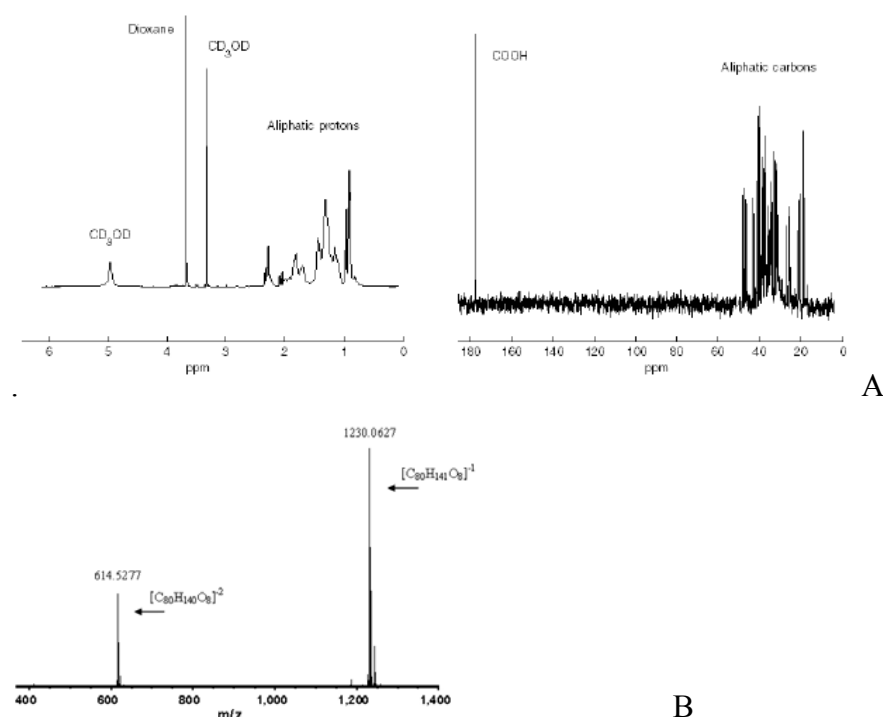


Figure 5.1 1H (left) and ^{13}C (right) NMR spectra of the naphthenic acid sample (A) and ESI FT-ICR MS spectrum of the naphthenic acid sample (B)

The second part of the study focused on the interfacial behaviour of the isolated C₈₀-naphthenic acids. Measurements of o/w interfacial activity were carried out using the CAM200 pendant drop equipment while monolayer properties at different conditions were investigated by means of the Langmuir technique.

In oil water systems the C₈₀ naphthenic acids become highly interfacially active under conditions of high pH in the aqueous phase. By increasing the pH from 5.6 to 9 the interfacial tension is lowered by several units as seen in figure 5.2. The increasing interfacial activity is due to a higher degree of dissociation at the interface. At pH 9.0 and at concentrations of only 0.0050-0.010 mM of acid, the interfacial tension is found to be about 40 mN/m lower than the value of the pure toluene/hexadecane (1:9 vol.) – water interface. The rate of the decrease in interfacial tension is also concentration dependent within this concentration range, and a welldefined value of the interfacial tension is attained at long observation times. The naphthenic acids acquired from the deposit sample are much more interfacially active than naphthenic acids extracted from crude oil. This property is likely one of the reasons why the C₈₀ naphthenic acids are found to dominate in naphthenate deposits.

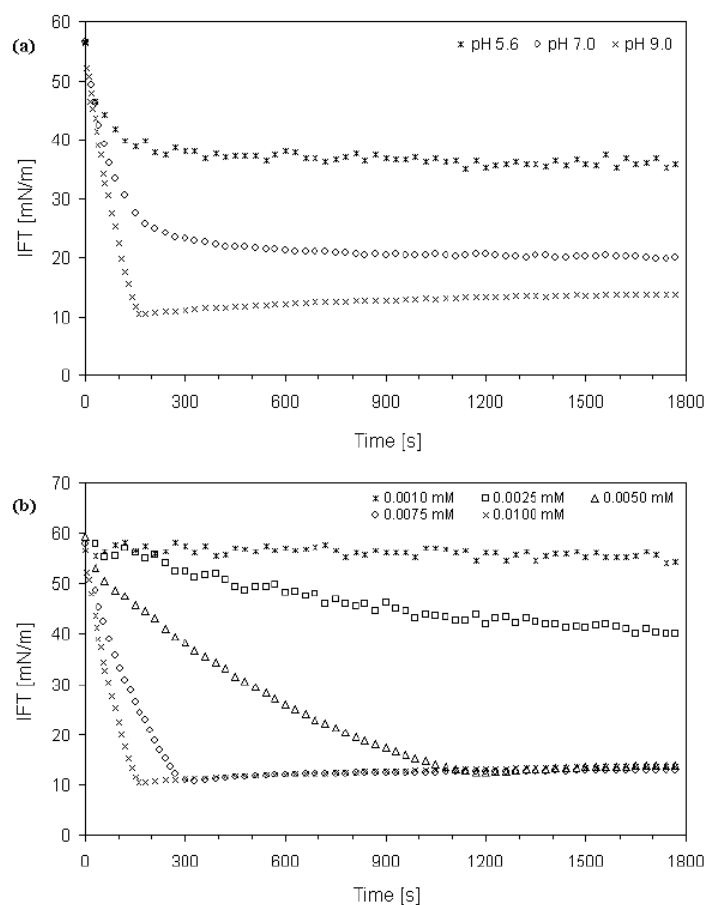


Figure 5.2: Dynamic IFT for an o/w interface of the C₈₀-naphthenic acids as a function of (a) pH (0.010mM acid), and (b) concentration (pH 9.0).

In general, the C₈₀ naphthenic acids form relatively unstable Langmuir monolayers. The stability decreases further with increasing pH as more monomers become dissociated and dissolve into the aqueous phase. By adding calcium ions into the sub phase at high pH, the films become less soluble due to formation of calcium naphthenate at the surface. In the non-interacting region, the undissociated naphthenic acids have a molecular area of about 160 Å²/molecule. The high area reflects an extensive molecular structure comprising four carboxylic head groups, which are likely to be separated by hydrocarbon chains. The results are shown in figure 5.3.

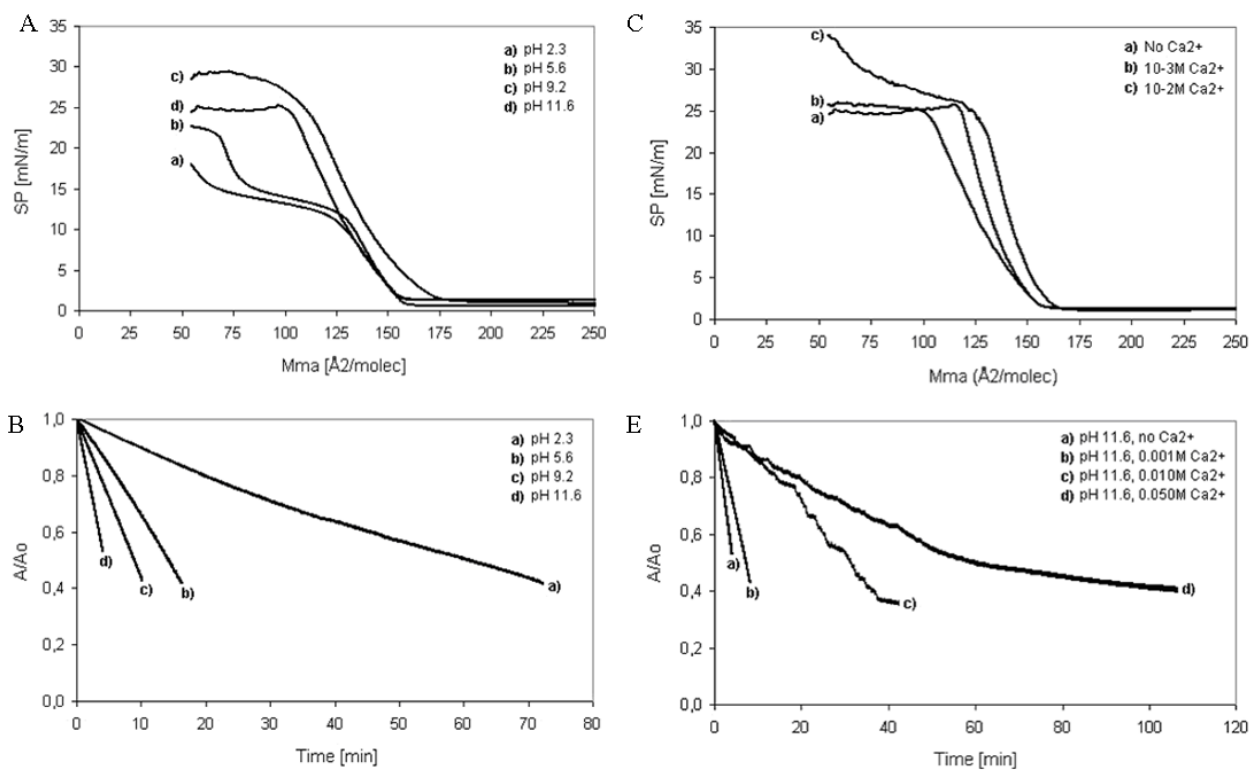


Figure 5.3 Langmuir monolayers of the C80 naphthenic acids at different pH levels, (A) compression isotherms, and (B) stability isotherms at constant surface pressure of 10 mN/m, and with Ca²⁺ at pH 11.6, (C) compression isotherms, and (D) stability isotherms at constant surface pressure of 10 mN/m.

6.2 Publication II

In publication II a new experimental setup based on near infrared (NIR) spectroscopy for online studies of formation, growth, and inhibition of calcium naphthenate particles in o/w systems was reported. The aim of the work was to investigate how particle formation and growth depended on different conditions such as the naphthenic acid structure, the concentrations of reactants, and the pH of the aqueous phase. Moreover, different oil-soluble surfactants, which are basis compounds for metal naphthenate inhibitors, were added in order to study their effect on the particle formation. A sketch of the experimental setup is shown in figure 5.4.

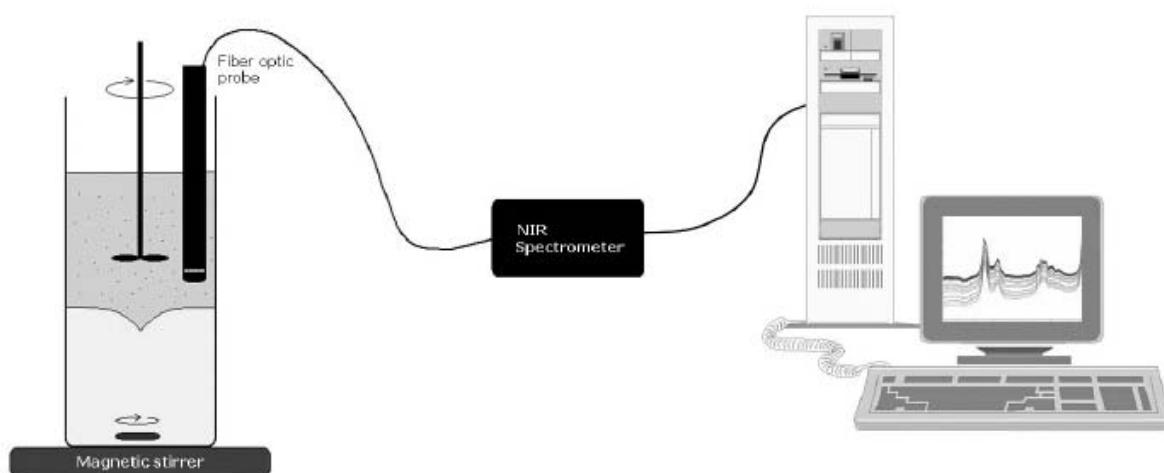


Figure 5.4 A sketch of the experimental setup used in the NIR spectroscopic study.

Figures 5.5-5.7 show plots of square root of OD vs. time for naphthenate solutions consisting of particles of a single naphthenic acid obtained at different acid concentrations and particles of different naphthenic acid structures obtained at pH 9.0 respectively. As clearly indicated in figure 5.5, the OD increases more rapidly the higher the concentration of naphthenic acid since more particles are formed at the interface. As shown in figure 5.6, the naphthenic acids with aromatic rings are also forming particles at a higher rate and with a larger volume than the acid with condensed ring. The reason for this is the higher interfacial affinity which causes a higher density of acid monomers at the o/w interface. Due to the aromatic rings and the π -

bonds between them, the acid monomers will pack more densely at the interface than the acid with condensed ring, favouring interfacial formation of 2:1 complexes of acid and Ca^{2+} . Monomers with two aromatic rings will pack even denser than monomers with only one ring, causing a higher reaction rate as demonstrated by comparing the slopes of the ascending curves at the beginning of the experiments.

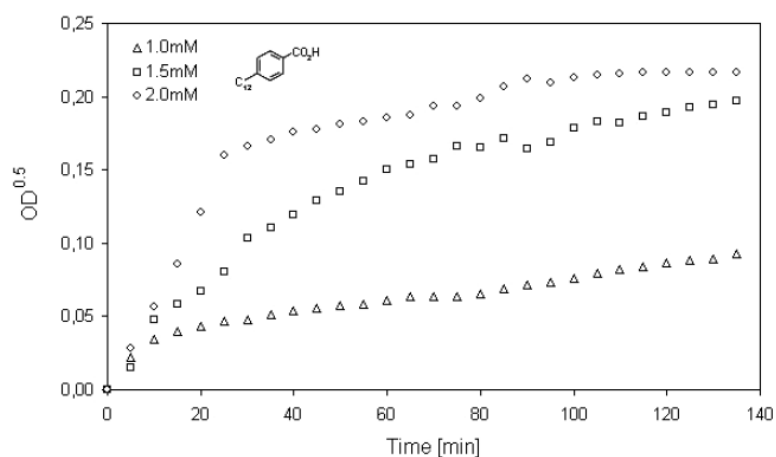


Figure 5.5 Square root of OD vs. time for naphthenate solutions containing particles of the aromatic single-ring naphthenic acid, obtained at different acid concentrations. The concentration of Ca^{2+} is twice the concentration of acid.

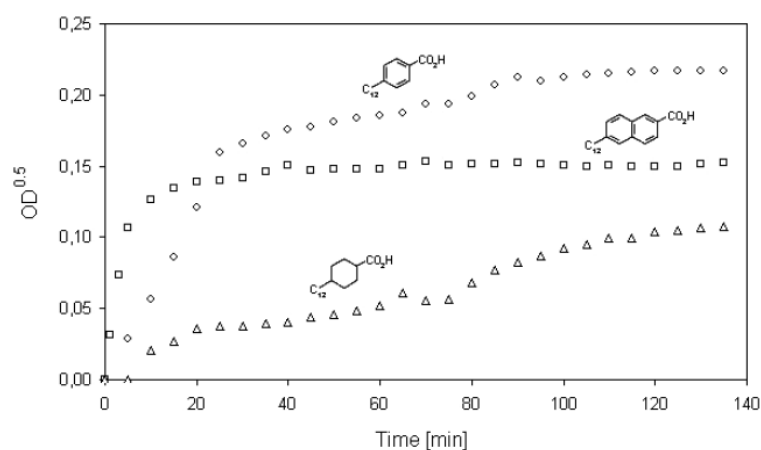


Figure 5.6 Square root of OD vs. time for naphthenate solutions containing particles of different naphthenic acid structures. The concentrations of acid and Ca^{2+} are 2mM and 4mM, respectively.

Figure 5.7 shows plots of square root of OD vs. time for naphthenate solutions containing particles of the aromatic single-ring naphthenic acid (2mM) in addition of 50ppm of three different oil-soluble surfactants (A-C). As indicated, addition of all the surfactants causes a lowering of the OD as compared to the system without additives. Surfactant A, which,

according to figure 5.8 is more interfacially active than C, also causes a lower particle volume. However, the most interesting observation is that surfactant B, which is highly water soluble compared to A and C, causes a lower OD than the more interfacially active A. Due to the low o/w interfacial affinity, it is unlikely that the mechanism is interfacial dilution of the acid monomers. To verify the partitioning of B into water, the surface tension (ST) of bulk water was measured for two different systems at different times; (1) water pH 9.0 in contact with oil (1:1 vol.) containing 50ppm of B, and (2) water pH 9.0 in contact with oil (1:1 vol.) containing 2mM of naphthenic acid and 50ppm of B upon addition of Ca^{2+} . The ST of the aqueous phase of system (1) was found to descend with time, indicating dissolution of B into water. For system (2), on the other hand, the ST of the water phase remained constant at the value of pure water ($\sim 72\text{mN/m}$). Hence, surfactant B do not partition into the aqueous solution when naphthenate particles are present in the oil phase. Possible reasons for the lower OD in presence of B are interactions between the particles and the reactants, i.e. between B and the naphthenic acid and/or Ca^{2+} , or interactions between B and the particles, causing disintegrating into smaller aggregates. The assumption about smaller particles was further supported by measuring the particle size of systems both in presence and in absence of B.

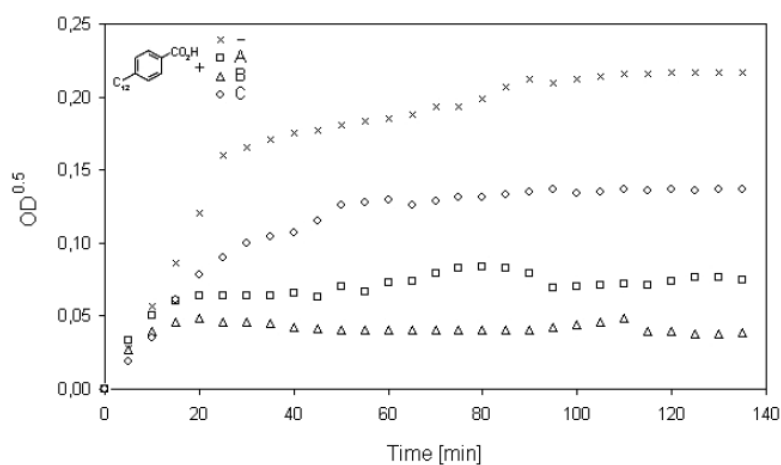


Figure 5.7 Square root of OD vs. time for naphthenate solutions in addition of different surfactants.

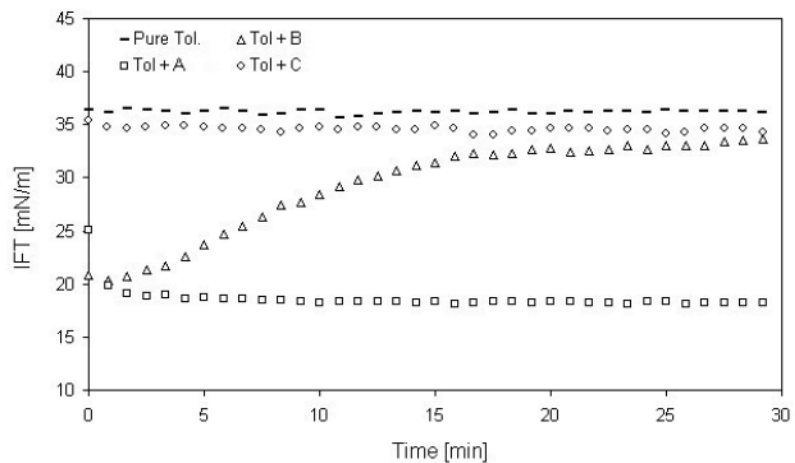


Figure 5.8 Dynamic interfacial tensions for toluene-water (pH 9.0) in presence of 50ppm of the different surfactants in the toluene phase.

6.3 Publication III

C₈₀ naphthenic acids isolated from a North Sea deposit and its calcium naphthenate have been characterised with respect to its thermal properties and surface activity. Langmuir-Blodgett films from the two systems have been deposited and analysed by microscopy. Table 5.1 shows the results from the thermal analysis.

Table 5.1 Thermal properties of the C₈₀-naphthenic acids and its calcium naphthenate

Sample	C₈₀-naphthenic acids	TA Calcium Naphthenate
Decomposition (He)	463 °C	463 °C
Decomposition (air)	393 °C	459 °C
Purity	94 %	97 %
T_g (2nd cooling)	-15 °C	-19 °C, 73 °C
T_g (2nd heating)	-11 °C	-30 °C, 82 °C
Residual	>1%	12,5 %
Ca²⁺ /acid group	-	0,7

C₈₀ naphthenic acids as well as its calcium naphthenate show considerable surface activity and both form stable, elastic films at the oil-water interface. Both materials tend to form polymer-like networks in the bulk and at oil/water- and air/water interfaces. For C₈₀ naphthenic acids, the network is formed by intermolecular hydrogen bonds between the acid groups. At ambient temperature, the polytetraacid is above its glass transition and very flexible. The polynaphthenate on the other hand is well below its glass transition temperature of 73 °C at room temperature and very stiff.

Dilational rheology experiments showed that the storage modulus was larger than the loss modulus for both systems, which suggests a strong interaction between the molecules and a “solid like” film. The storage modulus was nearly three times higher for the calcium naphthenate film than for the tetra acid film. The result is shown in figure 5.9. The naphthenate film was in fact stable enough to be studied visually in magnification.

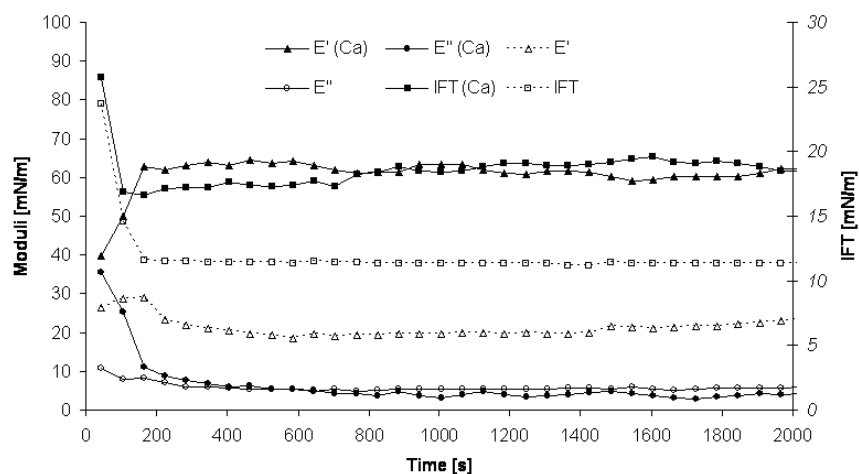


Figure 5.9 IFT, Storage modulus (E') and the loss modulus (E'') for C_{80} naphthenic acids with and without calcium ions present in the aqueous phase, measured by oscillation pendant drop

Microscopic analysis of films from both compounds formed at the air/water interface in part support the results obtained by the interfacial rheology techniques and thermal analysis. The calcium naphthenate forms a “plastic-like” film on the substrate, very similar in appearance to the film surrounding the oil drop in the “oscillating drop”-experiments at equilibrium, as seen in figure 5.5. C_{80} naphthenic acids, on the other hand, show a tendency to crystallise during compression at low interfacial pressures. As the interfacial pressure increases, the crystals are squeezed and form diagonal lines on the film. The orientation at the air-water interface in combination with slow compression of the film appears to promote crystallisation though the tetra acid does not crystallise under bulk conditions.



Figure 5.10 Contracted oil drops covered with C_{80} naphthenic acids (left) and calcium naphthenate (right)

6.4 Publication IV

Reliable and simple methods to study the effect of different types of inhibitor blends are important. In paper five different methods have been developed for the screening of naphthenate inhibitors. One method is based on interfacial activity of systems with naphthenic acids, inhibitors and calcium which can give indication of reaction mechanisms at interfaces of the inhibitors. Figure 5.11 shows the results from measurements of the interfacial tension of the different compounds.

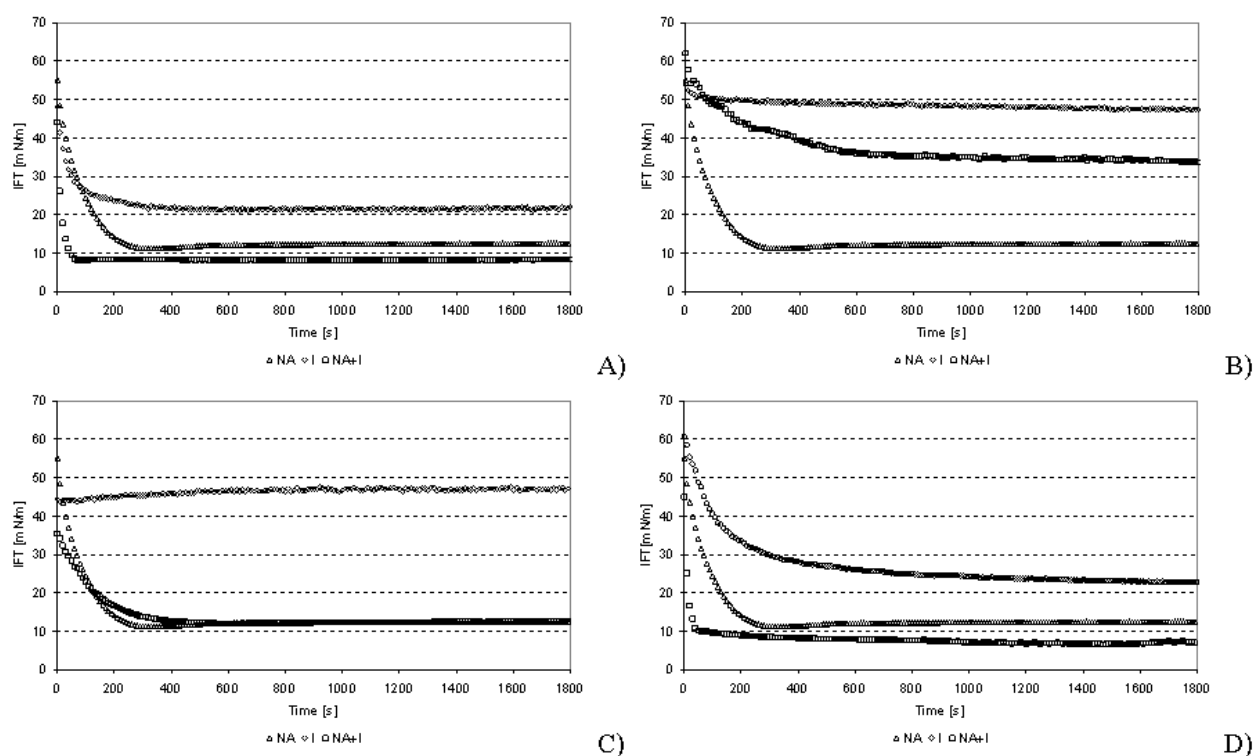


Figure 5.12 Interfacial activity for the systems C_{80} -naphthenic acids, Inhibitor, and C_{80} -naphthenic acids and Inhibitor, A) Inhibitor A, B) Inhibitor B, C) Inhibitor C and D) Inhibitor D

The second method is based on gravimetric determination of interfacial layer in a two phase system and gives a thermodynamic approach to naphthenate formation. This method gives information about the long term effect of the different inhibitors, the result is shown in figure 5.13.

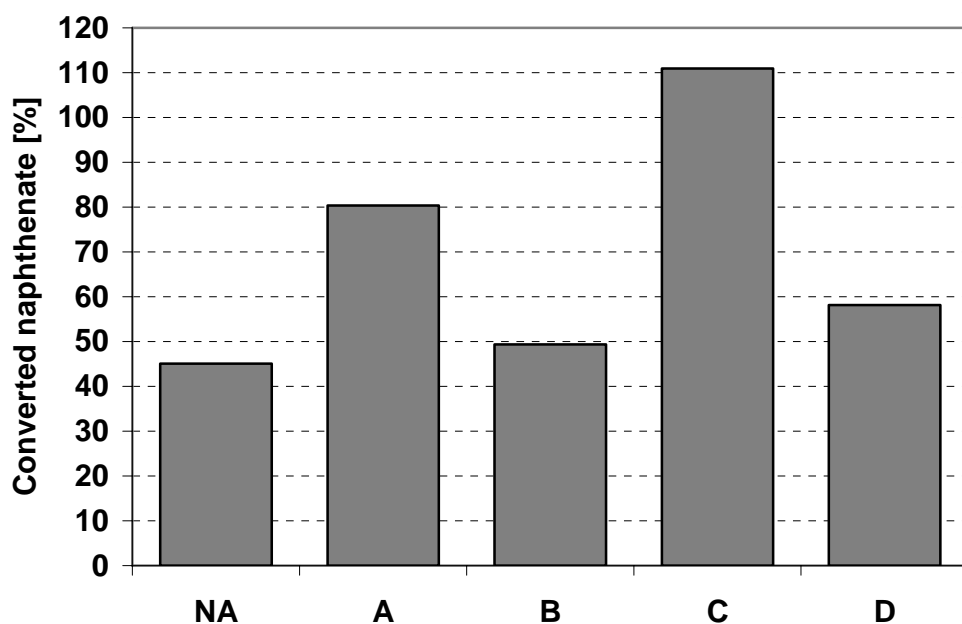
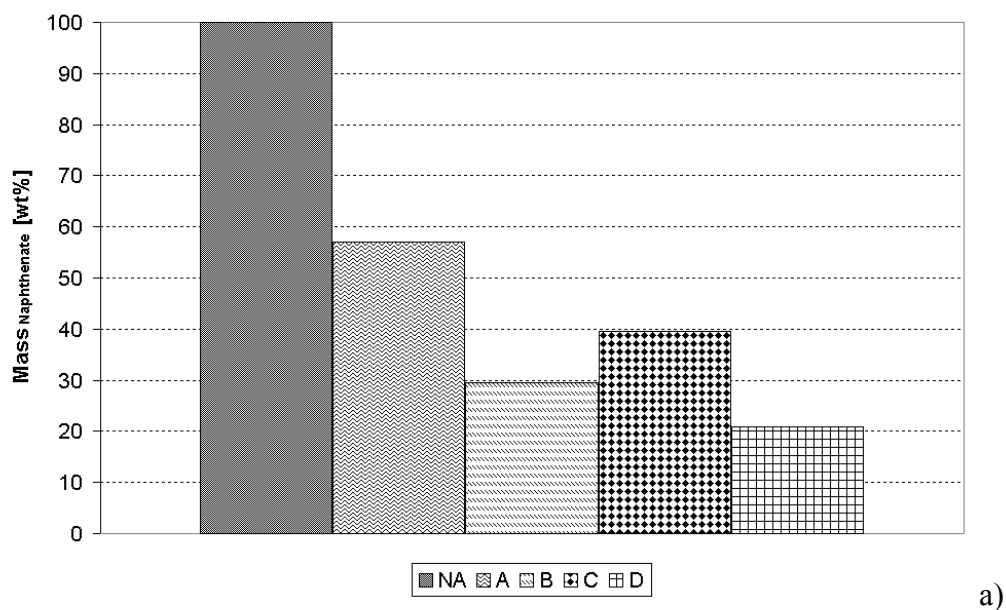
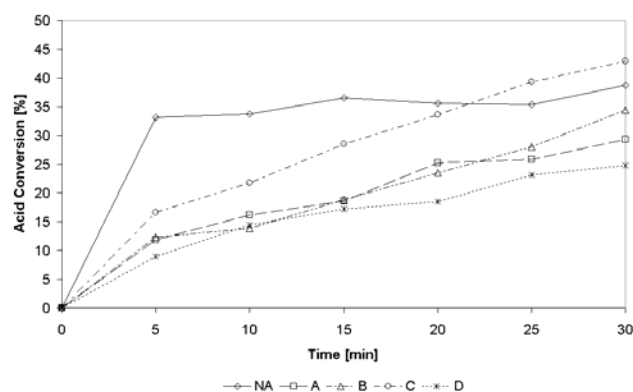
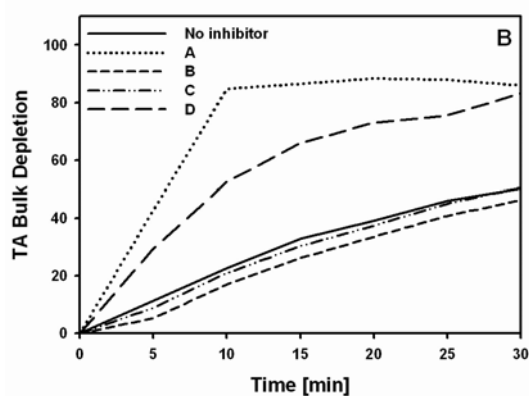


Figure 5.13 Conversion of tetraacid to its naphthenate film in a two-phase system at a) $C_{TA} = 0.2 \text{ mM}$, $C_I = 20\text{ppm}$ and $C_{MA} = 1.6 \text{ mM}$ and b) $C_{TA} = 1.0 \text{ mM}$ og $C_I = 1000\text{ppm}$. The two phases were in contact for 2 hours.

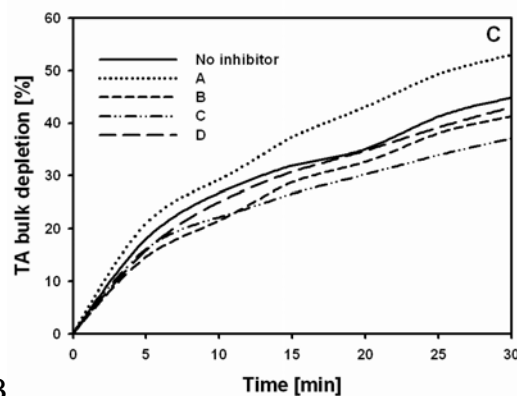
The third method utilises a UV-active model tetraacid to directly determine the depletion in bulk phase concentration during a two-phase reaction. The results indicate that inhibitors may not be acting through one single mechanism. Depending on the total system different mechanisms may vary in efficiency and there could be a combination of several mechanisms as seen in figure 5.14.



A



B



C

Figure 5.14 Conversion of a synthetic tetraacid, BP10, to its calcium naphthenate as a function of time with (A) $C_{TA} = 0.2 \text{ mM}$ og $C_I = 500\text{ppm}$,chloroform as oil phase and water phase at pH9, (B) $C_{TA} = 1.0 \text{ mM}$, $C_I = 1000\text{ppm}$, toluene as oil phase and water phase at pH9, and (C) $C_{TA} = 1.0 \text{ mM}$, $C_I = 1000\text{ppm}$, toluene as oil phase and water phase at pH 7.5

Each of these methods has their advantages and limitations, but together these methods can give a high degree of information concerning the choice of inhibitor. Their interfacial activity profile is of great importance to reveal the mechanism and a gravimetric determination of the interfacial layer gives information about the long term effect of the inhibitor. Using synthesised model compounds with UV-activity opens up for kinetic studies with direct characterization of the bulk concentration at any given time during a two-phase reaction. The studies show that inhibitors influences the naphthenate formation by various mechanisms, both at the interface and in bulk, and the inhibitor of choice is dependent on the concentration, pH and temperature. Naphthenate formation, assumed to be an interfacial phenomenon, is also greatly affected by the available reaction area in the system.

6.5 Publication V

In this publication the emulsion forming properties of C₈₀ naphthenic acids have been studied and compared to stearic acid stabilized emulsions. Emulsions containing stearic acid (4mM) and C₈₀-tetraacid (0.6mM/0.06mM) at water cuts ranging from 10-90 vol%, pH from 4-11 were prepared. Under this condition C₈₀ naphthenic acids form only oil-in-water emulsions, independent on the presents of stearic acid and the ratio between stearic acid and C₈₀ naphthenic acids.

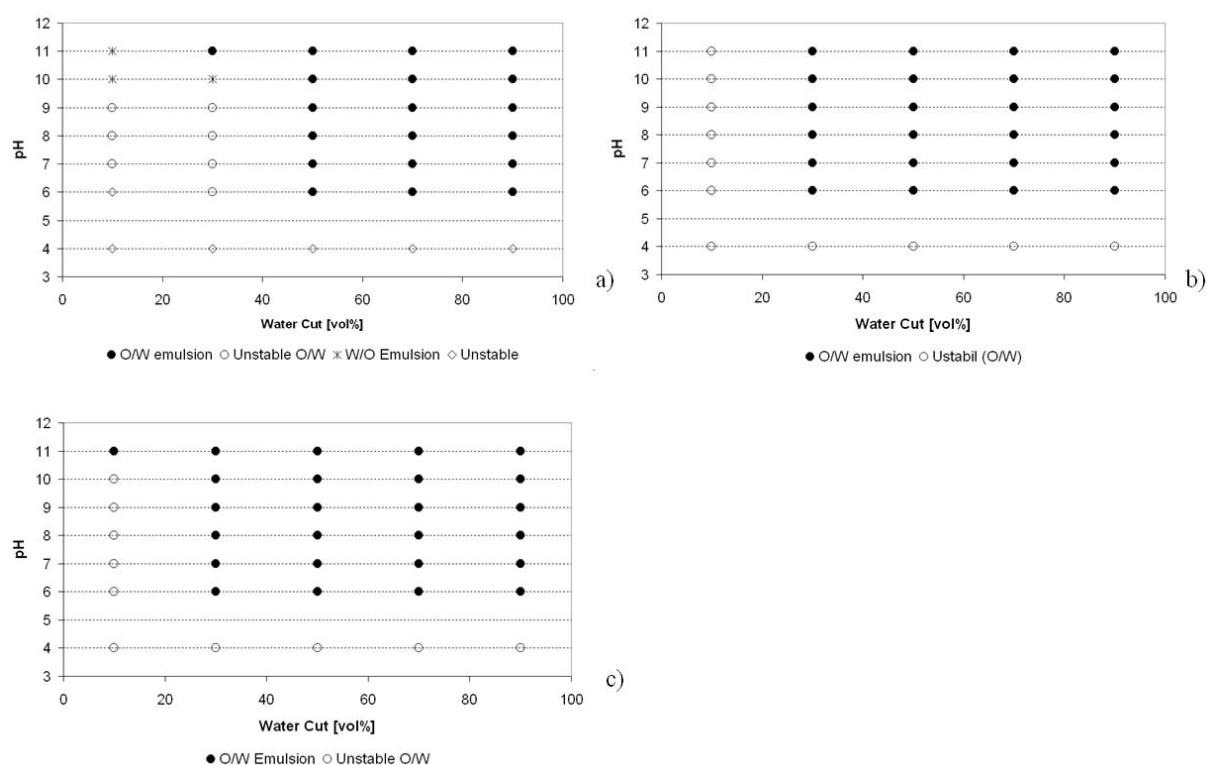


Figure 5.5.1 Type of emulsion formed a) stearic acid, b) C₈₀ naphthenic acid, and c) stearic acid and C₈₀ naphthenic acid.

In addition the interfacial properties of the same systems have been studied. The interfacial tension measurements showed at high pH a dominating presents of C₈₀ naphthenic acids at the interface, independent on the concentration of C₈₀ naphthenic acids. Compared to stearic acid it has an extremely high interfacial activity and affinity to the interface, and dominates in competition with other interfacially active molecules.

The values of the zeta-potential showed that all emulsions at high pH were electrostatically stabilized.

The highest stability is seen at intermediate water cuts. And most stable emulsions were formed when both stearic acid and C₈₀ naphthenic acids were used as emulsifiers..

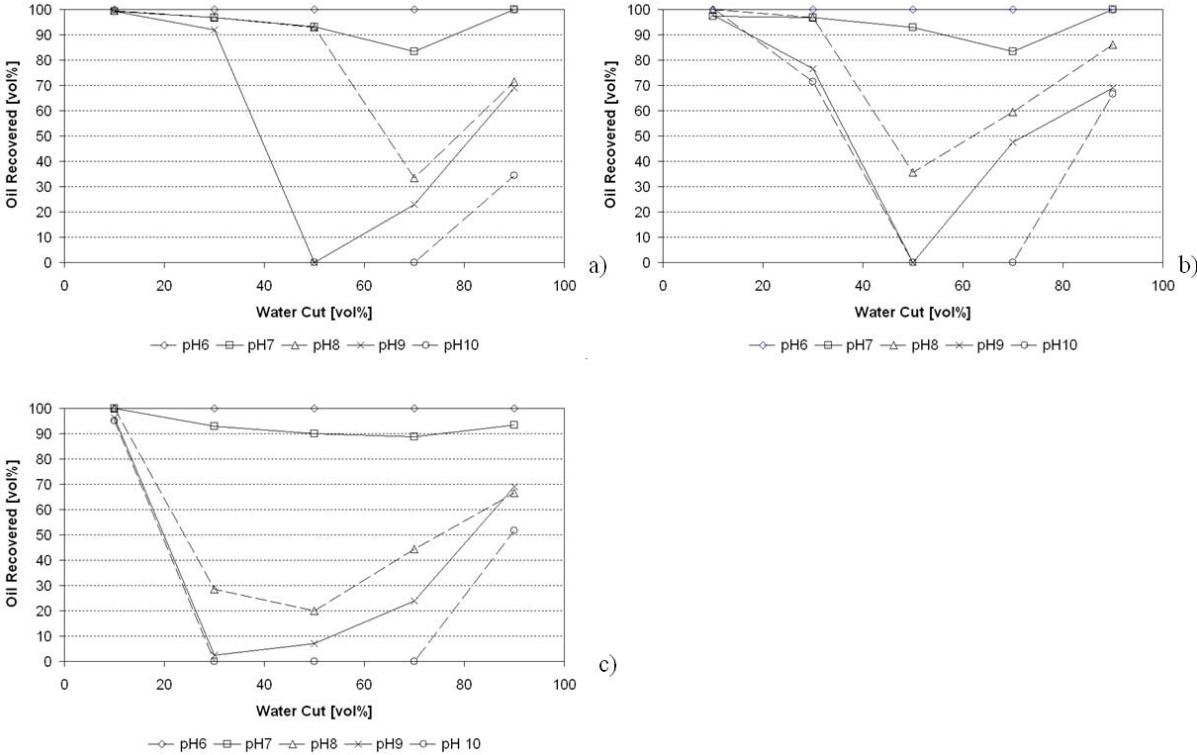


Figure 5.5.2 Emulsion stability a) stearic acid, b) C₈₀ naphthenic acid and c) stearic acid and C₈₀ naphthenic acid.

7 MAIN CONCLUSIONS

This chapter summarise the publications present in this thesis.

In publication I acid was isolated form a West-African deposit and a narrow group of 4-protic naphthenic acids with molecular weight around 1230 g/mol were found to be the dominating specie of the deposit acid fraction. The determined mass, 1230.0627 Da, identifies a compound with the elemental composition $C_{80}H_{142}O_8$. The interfacial properties were also studied in this publication and the acid were found to become highly o/w interfacially active when increasing the pH of the aqueous phase. The increased interfacial activity is due to a higher degree of dissociation at the interface. This property is likely one of the reasons why the C_{80} naphthenic acids are found to dominate in naphthenate deposits.

In general, the C_{80} naphthenic acids form relatively unstable Langmuir monolayers. The stability decreases further with increasing pH. On addition of calcium ions into the subphase at high pH, the films become less soluble due to formation of calcium naphthenate at the water surface. In the noninteracting region, the undissociated naphthenic acids have a molecular area of $160 \text{ \AA}^2/\text{molecule}$. The high area reflects an extended molecular structure comprising four carboxylic head groups, which are likely to be separated by hydrocarbon chains.

Publications II and IV were dedicated to developing easy methods for screening of inhibitors, and it was concluded that a number of methods are necessary to utilize for screening of inhibitors.

Publication III were dedicated to the polymeric network formation of the C_{80} naphthenic acids, both the acid and the metal naphthenate were studied with regards to its thermal properties and elastic behaviour.

Publication V was dedicated to emulsions. In this publication, C_{80} naphthenic acids were studied with regards to its ability to form emulsions and the stability of these emulsions. It were concluded that the acid under these experimental conditions only were able to form O/W emulsions. At high pH these emulsion were of high stability due to the electrostatic repulsions between the droplets.

Publications I –V are not included due to copyright