Enhanced Oil Recovery from Oil-Wet Carbonate Rock by Spontaneous Imbibition of Aqueous Surfactant Solutions

DAG CHUN STANDNES

URN:NBN:no-1285

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Dedicated to my wife Gyoung-yei and our wonderful daughter Ida Lilly

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Department for Petroleum Technology, Stavanger, September 17th 2001.

Dag Chun Standnes

List of papers

This dissertation consists of 8 scientific papers. Paper I and II have been published in Journal of Petroleum Science and Engineering, whereas paper III-VIII are submitted and they are currently under referee in the same journal. A brief description of the content in each paper is described in Section **1.5. Project description**.

Papers:

I **Wettability alteration in chalk 1. Preparation of core material and oil properties.**
D. C. Standnes and T. Austad
Journal of Petroleum Science and Engineering, 28, (2000), pp. 111-121.

II **Wettability alteration in chalk 2. Mechanism for wettability alteration from oil-wet to water-wet using surfactants.**
D. C. Standnes and T. Austad
Journal of Petroleum Science and Engineering, 28, (2000), pp. 123-143.

III **Wettability alteration in chalk 3. Interaction between cationic surfactant and carboxylates as a key factor in wettability alteration from oil-wet to water-wet conditions.**
D. C. Standnes and T. Austad
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IV **Wettability alteration in carbonate 4. An evaluation of spontaneous imbibition of water into oil-wet carbonate reservoir cores using a non-ionic and a cationic surfactant.**
D. C. Standnes, L. A. D. Nogaret, H. L. Chen and T. Austad
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V **Wettability alteration in chalk 5. Spontaneous imbibition of aqueous surfactant solution into oil-wet chalk: capillary- vs. gravity dominated fluid flow.**
D. C. Standnes and T. Austad
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VI **Wettability alteration in chalk 6. Non-toxic and low-cost amines as wettability alteration chemicals in carbonates.**

D. C. Standnes and T. Austad

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VII **Wettability alteration in chalk 7. Low-cost ammonium-surfactants based on bio derivates from the coconut palm as active chemicals to change the wettability form oil-wet to water-wet conditions.**

D. C. Standnes and T. Austad

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VIII **Wettability alteration in chalk 8. Thermally induced spontaneous imbibition of water into oil-wet chalk at elevated temperature.**

D. C. Standnes, E. J. Høgnesen and T. Austad

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Symbols and abbreviations

API	American Petroleum Institute
AN	Acid Number, (mg KOH/g oil)
AR	Aspect Ratio. Pore body- to pore throat diameter, (meter/meter)
ASTM	American Society for Testing and Materials
BET	Braunauer-Emmett-Teller
BN	Base Number, (mg KOH/g oil)
C	Dimensionless constant for capillary tube model, (= 0.4)
CMC	Critical Micelle Concentration, (wt.%, M)
COBR	Crude Oil/Brine/Rock
C_nTAB	Surfactant of the type, alkylTrimethylAmmonium Bromide, n = 8, .., 18
C_nTAC	Surfactant of the type, alkylTrimethylAmmonium Chloride, n = 12, .,18
$c_{oilphase}$	Total concentration of the surfactant in the oil phase, (mole/l)
$c_{waterphase}$	Total concentration of the surfactant in the water phase, (mole/l)
DDDC	Dual-Drop-Dual-Crystal
D_{body}	Diameter of pore body, (m)
D_{throat}	Diameter of pore throat, (m)
EA	Ethoxylated Alcohol
EO	EthOxy-group ($-CH_2CH_2-O-$)
EOR	Enhanced Oil Recovery
E_m	Microscopic Displacement Efficiency, (fraction)
F_c	Oil-water IFT interpreted as force per unit length, (N/m)
$f(\theta)$	Wettability factor, (-)
G-AB	API Gravity-Acid Number and Base Number
g	Acceleration due to gravity, (= 9.8 m/s^2)
H	Height of the liquid column/Height of the core material, (m)
HPLC	High Performance Liquid Chromatography
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectrometry
IFT	InterFacial Tension, (N/m)
IOR	Improved Oil Recovery
I_{A-H}	Amott-Harvey index, (-)
I_o	Amott index to oil, (-)
I_w	Amott index to water, (-)

K	Partitioning coefficient, (-)
k	Absolute permeability, (m^2)
L_C^2	Characteristic length, (m)
L_H	Vertical height of core sample, (m)
MDE	Microscopic Displacement Efficiency, (fraction, %)
NMR	Nuclear Magnetic Resonance
NSO	Nitrogen-Sulphur-Oxygen
N_B^{-1}	Inverse Bond number, (-)
$n_{oilphase}$	Total number of surfactants in the oil phase, (mole)
$n_{waterphase}$	Total number of surfactants in the water phase, (mole)
OOIP	Original Oil In Place, (m^3)
P.A.	Pro Analysis
Ph	Phenyl-group ($-C_6H_5$)
PV	Pore Volume, (m^3)
pH	$-\log\{[H^+]\}$
P #	Paper #
P_c	Capillary pressure (defined as $p_o - p_w$), (Pa)
p_o	Pressure in the oil phase, (Pa)
p_w	Pressure in the water phase, (Pa)
Q_{aq}^+	Cation in the water phase
Q_0	Cumulative oil production, (m^3)
Q_∞	Cumulative oil production after infinite time, (m^3)
QX_{org}	Ion-pair/catanionic in the organic phase
R-	Alkyl group
R	Oil recovery, (% OOIP)
R	Tube radius, (m)
RDI	Relative Displacement Index
$R_{1,} R_2$	Radii of curvature of the oil-water interface measured perpendicular to each other, (m)
S #	Section #
SDS	Sodium DodecylSulfate
SEM	Scanning Electron Microscope
SI	Spontaneous Imbibition
SS #	SubSection #

S_{oi}	Initial oil saturation, (%, fraction)
S_{or}	Water saturation after forces water imbibition, (%, fraction)
S_{os}	Water saturation after spontaneous uptake of oil, (%, fraction)
S_{wi}	Initial water saturation, (%, fraction)
S_{wr}	Water saturation after forces uptake of oil, (%, fraction)
S_{ws}	Water saturation after spontaneous imbibition of water, (%, fraction)
TDS	Total Dissolved Solid, (g dissolved solid/l water)
t	Imbibition time, (s)
t_D	Dimensionless imbibition time, (-)
$t_D(c + g)$	Dimensionless time including capillary- and gravity forces, (-)
UR	Ultimate Recovery, (% or fraction of OOIP)
USBM	United States Bureau of Mines
W_R	Wettability index based on pseudo work of imbibition, (-)
X_{aq}^-	Negative counter ion in the water phase
# X	# Times magnification
II(-)	Oil-in-water microemulsion with excess oil phase
II(+)	Water-in-oil microemulsion with excess water phase
III	Bicontinuous middle phase microemulsion with excess oil and water

Greek letters

ΔG	Change in Gibbs free energy, (J)
ΔP_g	Pressure difference between oil and water due to gravity, (Pa)
$\Delta\rho$	Density difference between oil and water, (kg/m^3)
ϕ	Porosity, (%, fraction)
μ_o	Oil viscosity, (Pa·s)
μ_w	Water viscosity, (Pa·s)
θ, θ_A	Advancing contact angle measured through the water phase, (degree)
θ_R	Receding contact angle measured through the water phase, (degree)
σ_{os}	Oil-solid IFT, (N/m)
σ_{ow}	Oil-water IFT, (N/m)
σ_{ws}	Water-solid IFT, (N/m)

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Papers

Part 1 Introduction

Chapter 1. Introduction and background

1.1. Enhanced oil recovery

Normally, only 5-30 % of original oil-in-place (OOIP) can be produced by the native pressure energy stored in the reservoir (Castor *et al.*, 1981; Farouq-Ali and Stahl, 1970). This phase of the oil production cycle is called the ***primary production period***. As the reservoir pressure falls towards the bubble point of the oil, great advantage can usually be taken by maintaining the reservoir pressure above the bubble point hindering the liberation of high mobility gas in the reservoir. ***Injection of water*** into the reservoir is the usual way to maintain the reservoir pressure during production. The method can be a supplement to reservoirs having natural water-drive or an expanding gas cap. The injected water will fulfill two missions when being injected,

- Maintain the reservoir pressure above the bubble point ensuring that no gas is liberated in the reservoir and thereby maintain high relative permeability for oil
- Push the oil in front of the water towards the production well

The waterflooding method discovered nearly by accident in 1870 (Schumacher, 1978), will usually increase the oil production to a total recovery of 40-60 % of OOIP. This stage of the oil production process is called the ***secondary production period***. During the waterflooding period, oil is produced at a steady increasing water-oil ratio at the production wells. When the water-oil ratio has become to high, oil cannot be produced in a cost effective way any more and the field has reached the economical limit. At this point there is still about 40-60 % of OOIP left in the reservoir, mainly because of unfavorable wettability conditions, heterogeneous rock properties (fractures, layers with large permeability contrasts, impermeable layers) and capillary trapped- and bypassed oil. It is this residual oil left in the reservoir after the secondary oil production stage, which is the target for enhanced oil recovery (EOR) processes. Since EOR processes are following the period of secondary recovery processes, they are sometimes called ***tertiary oil recovery methods***. The purpose of initiating tertiary oil recovery processes is therefore to extend the lifetime of oil reservoirs producing by support of waterflooding or other conventional methods, which are approaching the economical limit. Bavière (1991) defined EOR in the following way**, *"EOR consists of methods aimed at increasing ultimate oil recovery by injecting appropriate agents not***

normally present in the reservoir, such as chemicals, solvents, oxidizers and heat carriers in order to induce new mechanisms for displacing oil". This definition excludes water- and gas injection, which are using mechanical energy to maintain the pressure. Infill drilling, well stimulations and enhanced drilling techniques like horizontal drilling are also outside the range of this definition. It also differ from the definition of improved oil recovery (IOR) methods given by the Norwegian Petroleum Directorate (1993) which reads, ***"Actual measures resulting in an increased oil recovery factor from a reservoir as compared with the excepted value at a certain reference point in time"***. This definition is much wider and includes all optimize techniques used to increase the oil production, which were not planned at the start of production. Conventional methods like water- and gas injection are therefore included, as well as different EOR projects at a later production stage. It should also be mentioned that it is highly recommended to initiate EOR processes at least from a technical point of view, at an earlier stage than right after the secondary oil recovery period has come to an end. However, the additional expenses attributed to tertiary oil recovery processes in relationship to the expected additional recoverable oil will decide the initiation for any EOR project in practical life (Chaumet and Cottin, 1991).

A distinction will be drawn in this thesis between test temperatures below and above 70 °C, respectively. Temperatures equal to or below 70 °C will be referred to as low-temperature tests, whereas tests performed above 70 °C will be referred to as high-temperature tests. Low-temperature imbibition tests conducted using brine, as the imbibing fluid, will be regarded as the baseline and equal to the oil production level after the secondary oil recovery period. Any incremental oil production exceeding that from brine imbibition in this temperature range can therefore be attributed to the applied EOR method. High-temperature tests were conducted using pure brine as the imbibing phase. In this case, the EOR will be discussed related to induced physico-chemical changes in the crude oil/brine/rock (COBR) system due to supply of thermal energy.

1.2. Classification of enhanced oil recovery methods

The most frequently applied EOR methods can be divided into three big families, which according to Marle (1991) consist of the following methods: ***chemical-, miscible- and thermal methods***. **Figure 1-1** shows from left to right the scale (field scale contrary to pore scale) by which each EOR method is acting, the effect on the physical parameters involved and the actual name of the corresponding EOR method. Each method is aimed to either:

- Increase the sweep efficiency, i.e., increase the area swept by the injected water, or

- Act on the pore scale level by increasing the microscopic displacement efficiency (MDE) in areas previously swept by water, hence reducing the residual oil saturation

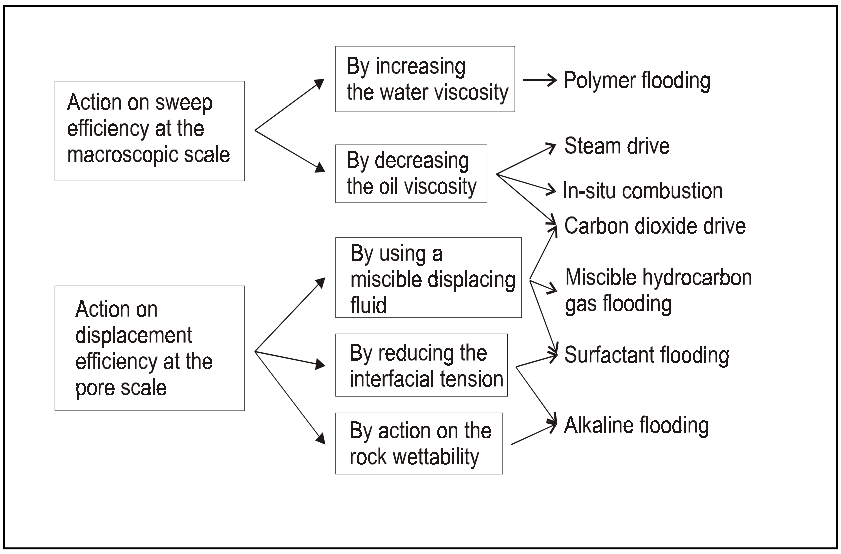


Figure 1-1. The 3 main types (chemical, miscible and thermal) of EOR methods are acting on the sweep efficiency on the macroscopic scale or on the displacement efficiency at the pore scale. Redrawn after Marle (1991).

Of course, some of the methods can improve both the sweep efficiency at the macroscopic scale and the displacement efficiency at the pore scale at the same time.

A chemical EOR method is the subject in this thesis, and it is therefore interesting to note that chemical methods have been used both to increase the macroscopic sweep efficiency and the MDE on the pore scale level. Polymer-gel treatment and polymer flooding have been used to shut-off high-permeability zones in the reservoir (Lund *et al.*, 1995; Seright and Liang, 1994; Sydansk and Southwell, 1998) and to increase the swept areas in the reservoirs due to increased water viscosity (Chauveteau and Sorbie, 1991; Clampitt and Reid, 1975; Sorbie, 1991; Szabo, 1975), respectively. Both methods are used with the purpose of increasing the macroscopic sweep efficiency. Alkaline- (Jennings *et al.*, 1974; Raimondi *et al.*, 1976) and surfactant flooding (Adams and Schievelbein, 1987; Ashayer *et al.*, 2000; Austad and Milter, 1997; Boneau and Clampitt, 1977; Chen *et al.*, 2000; Danielson *et al.*, 1976; Ely, 1972; Foster, 1973; French *et al.*, 1973; Inks and Lahring, 1968; Knight and Baer, 1973; Michels *et al.*, 1996; Olsen *et al.*, 1990; Pope and Bavière, 1991; Pursley *et al.*, 1973; Wellington and Richardson, 1997) are two other chemical methods which are mainly acting by decreasing the oil-water interfacial tension (IFT). In some cases, alkaline flooding is assumed to induce wettability alteration of the reservoir rock, which under certain circumstances can benefit oil recovery (Arteaga-Cardona et al., 1996; Cooke *et al.*, 1974; Emery *et al.*, 1970; Johnson, Jr., 1976; Leach *et al.*, 1962). Decreasing the residual oil saturation on pore scale level by remobilizing oil in previously waterflooded zones is the main purpose of these two methods.

EOR induced by a wettability alteration of the rock material is the subject in this thesis. The number of articles treating this subject is more scattered, but Downs and Hoover (1989) reported promising results from a pilot test in the Torrance field. The wettability alteration concept has also been tested in the laboratory by performing tests on sandstone cores (Alveskog *et al.*, 1998; Michaels and Timmins, 1960; Wagner and Leach, 1959), carbonate cores (Austad and Milter, 1997; Austad *et al.*, 1998; Chen *et al.*, 2000; Spinler *et al.*, 2000b) and model systems (Morris and Wieland, 1963), respectively.

1.3. Fractured reservoirs

Naturally fractured carbonate reservoirs consist of a specially challenging group of reservoirs to produce. The problem arises because the injected water is likely to follow the fracture system to the production well, bypassing most of the oil residing in the matrix blocks. It was the production from the highly fractured Spraberry field in west Texas in the early 1950s (Brownscombe and Dyes, 1952), which turned the attention towards the mechanism referred to as spontaneous imbibition (SI) of water into the matrix blocks as an efficient way to increase oil recovery from fractured reservoirs. Water will imbibe spontaneously into the matrix blocks and expel the oil to the fracture system, if the reservoir rock is water-wet. This mechanism is currently regarded as the most important contributor to increase the displacement efficiency in fractured reservoirs. However, the method will not work efficiently as long as the reservoir rock is oil-wet due to negative capillary pressure and absence of SI of water.

The EOR method described in this thesis is aimed to enhance oil recovery from fractured oil-wet reservoirs. The types of reservoirs under consideration are illustrated in **Figure 1-2**. It should be mentioned that most of the produced oil worldwide has its origin from fractured oil reservoirs (Torsæter and Silseth, 1985). Two comprehensive evaluations of the wetting state for different reservoirs from all over the world also indicate that most carbonate reservoirs seem to be neutral to oil-wet (Chilingar and Yen, 1983; Treiber *et al.*, 1972). The EOR potential for reservoirs suffering from low displacement efficiency due to fractures and unfavorable wettability conditions is therefore very high.

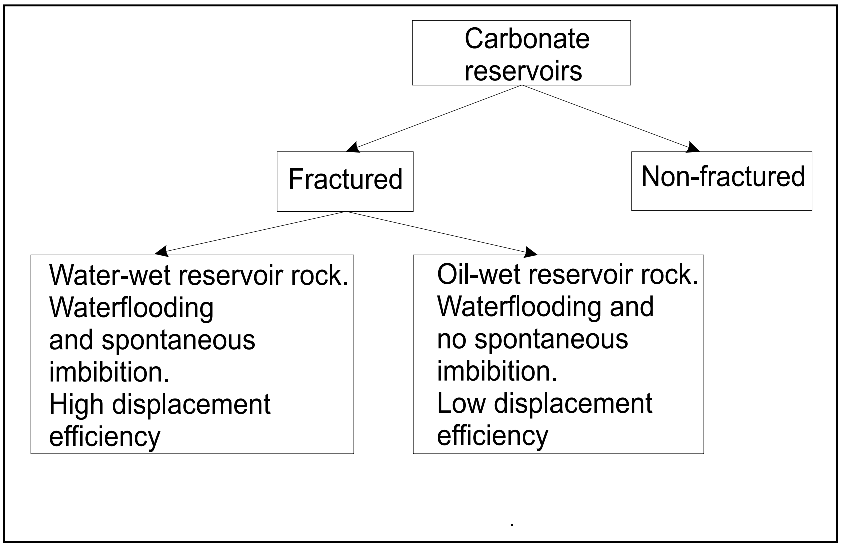


Figure 1-2. The purpose of the method treated in this thesis is to increase the oil recovery from fractured, oil-wet carbonate reservoirs.

The process referred to as SI is a central concept in this thesis, and it is important to note that the concept will be used when referring to an ***increase in water saturation*** in the porous medium, where the term water also includes brine and aqueous surfactant solutions. Sometimes imbibition is used when referring to an increase in wetting phase saturation. This definition has only a clear meaning when talking about strongly wetted systems (Buckley, 1996). Some mixed-wet cores will imbibe both water and oil spontaneously and it will be arbitrary which phase is chosen as the wetting one. If the porous medium is oil-wet, oil will spontaneously flow into the medium, thus decreasing the water saturation. This process will here be referred to as ***spontaneous uptake of oil***.

1.4. Background and the purpose of the thesis

The main theme in this thesis is an ***experimental investigation of SI of aqueous cationic surfactant solution into oil-wet carbonate*** (chalk- and dolomite cores). The static imbibition process is believed to represent the matrix flow of oil and water in a fractured reservoir (Yang and Wadleigh, 2000).

Austad and Milter (1997) observed that aqueous solution of C_{12}-$N(CH_3)_3Br$ (C12TAB) was able to imbibe spontaneously into nearly oil-wet chalk material. The chemical mechanism for the process was, however, not understood at that time. This project was therefore initiated with the two following main purposes:

- ***Put forward a hypothesis for the chemical mechanism underlying the SI of C12TAB solutions into oil-wet chalk material based on experimental data***
- ***Perform screening tests of low-cost commercial available surfactants for their ability to displace oil by SI of water into oil-wet carbonate rock material***

It is essential for optimal use of the surfactant in field application to have detailed knowledge about the mechanism underlying the SI process. Knowing the chemical mechanism behind the SI process will also makes it easier to suggest other cheaper chemicals having similar properties as the expensive pure C12TAB. When the mechanism is established, further investigations with the aim of practical application of the method in the field can take place. These investigations include for example SI tests on real reservoir cores, tests for surfactant phase behavior at different temperatures and concentrations, simulation of the SI process with history match and predictions of field production, an estimation of loss of surfactants due to adsorption onto the rock material, screening of cheap commercial surfactants and optimize of the system for field application. Some of the topics mentioned are included in the enclosed papers. The thesis also contains some preliminary experimental results and suggestion of possible mechanisms for EOR from oil-wet carbonate rock induced by supply of thermal energy.

1.5. Project description

In the limit of real reservoir core material, oil-wet chalk cores had to be established from originally strongly water-wet outcrop material from Stevns Klint, Denmark. It is well known that crude oils contain certain surface-active components, which have the ability to alter the wettability of strongly water-wet material towards oil-wet condition. Crude oil was therefore used to ***alter the wettability of the chalk material from strongly water-wet to oil-wet*** to mimic the adsorbed material on the mineral surface in a real reservoir as close as possible. The oil-wetness of the cores after restoration was evaluated by the SI method. No SI of water indicates that the core material was oil-wet (Anderson, 1986b). However, altering the wettability of the chalk material to oil-wet was not an easy task, and 6 different crude oils had to be tested before the chalk material became oil-wet. In addition, some problems appeared when trying to establish a uniform wettability inside the core material during the core preparation procedure. The results from this work are described in Paper I. **Figure 1-3** shows a total overview of the experimental project plan.

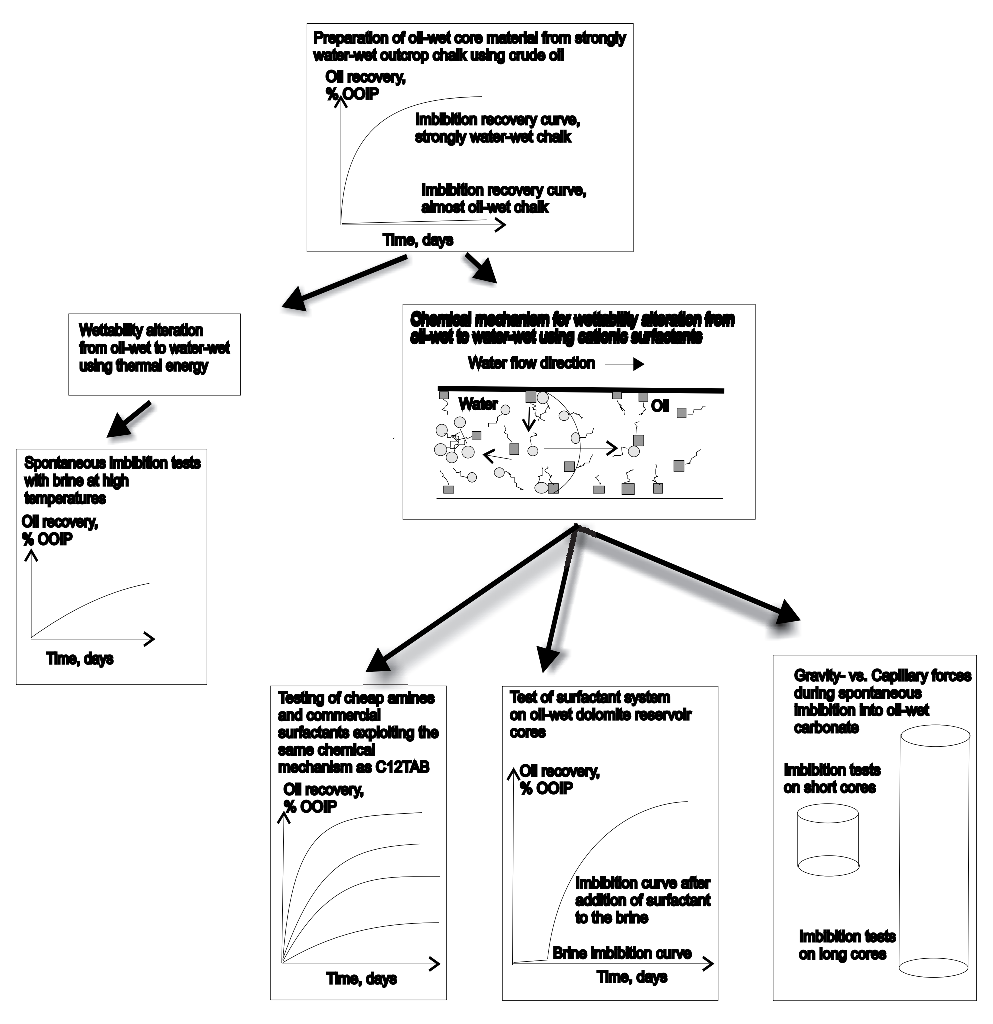


Figure 1-3. Overview of the experimental project plan.

Paper II contains results from SI tests, and a mechanism is suggested for SI of cationic surfactant solution into oil-wet chalk material. Further investigations using model systems supported the suggested mechanism, and the results are discussed in Paper III. The C12TAB surfactant was tested and compared with a non-ionic surfactant, ethoxylated alcohol (EA), for their ability to produce oil by SI on restored oil-wet dolomite reservoir cores from a field in west Texas. The response and behavior of the surfactant systems to the reservoir cores and the outcome of the comparison between the two surfactants are described in Paper IV. The relative influence of capillary- and gravity forces during SI into low-permeability oil-wet chalk was the subject in Paper V. To increase the influence of gravity forces, the SI tests were performed using long oil-wet composite chalk cores. Paper VI and Paper VII contains results from SI tests on oil-wet chalk- and dolomite cores using cationic primary amine solutions and commercial available cationic surfactants based on derivates from the coconut palm, respectively. The coconut products contained mixtures of alkyltrimethylammonium chloride with the alkyl chain ranging from C_{12} to C_{18}.

The first purpose regarding the fundamental aspects related to the chemical mechanism underlying the SI process is covered by Paper II and III, whereas Paper IV-VII are more related to impact of capillary- and gravity forces dictating the type of fluid flow, and the challenge of finding cheaper chemicals for field application. Preliminary experiments to alter the wettability of oil-wet chalk at increasing temperature was also performed, and a possible mechanism is suggested based on the present experimental data and reported data in the literature. This is discussed in Paper VIII.

1.6. Organization of the thesis

This thesis is organized into 5 Parts, **Figure 1-4**. Each part is subdivided into Chapters, Sections and Subsections. References to Papers, Sections and Subsections will be given as P #, S # and SS #, respectively.

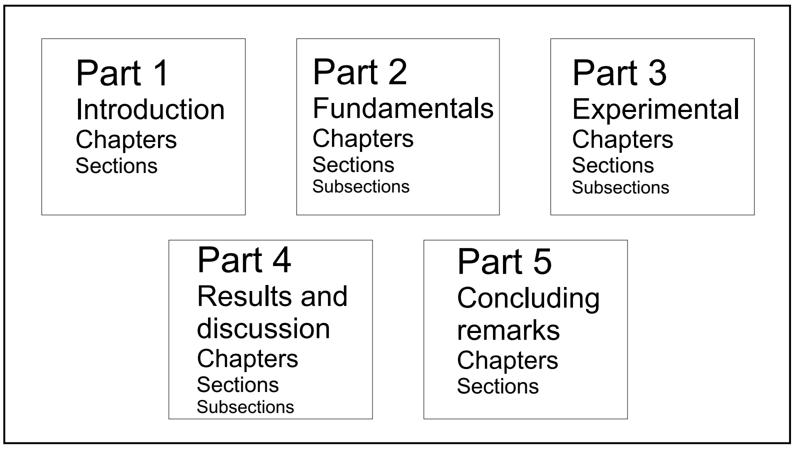


Figure 1-4. Organization of the thesis in Parts, Chapters, Sections and Subsections.

Part 1 contains the introduction presenting the background, the topic and the purpose of the work. Part 2 contains general fundamental aspects related to wettability, residual oil saturations, the SI process, flow of oil and water in porous media and characteristic properties of surfactants. Part 3 describes equipment, techniques and procedures used during the experimental work. The porous media are characterized and fluid properties are described together with information about the surfactants used in the SI tests. Part 4 presents the main results from the papers emphasizing the connection between each paper and the development of the project. Part 5 contains the conclusions drawn from the work, together with recommendations for future studies. The papers, which this thesis is based on, are located at the very back after the References.

Part 2 Fundamentals

This part of the thesis will describe general principles and fundamental concepts related to wettability, fluid flow and residual oil saturation in porous media. Surfactants and their most important properties will also be presented. The treatment is tailored to cover the methods and phenomena pertinent for the experimental work.

Chapter 2. Wettability

2.1. Definition of wettability and different types of wettability in porous media

Wettability can be defined thermodynamically as, ***"the tendency of one fluid to spread on or adhere to a solid surface in the presence of other immiscible fluids"***, (Anderson, 1986a). The fluid with the highest affinity for the solid surface is called the wetting phase, whereas the other is called the non-wetting. There exist an angle, the so-called contact angle, for a system consisting of two pure immiscible fluids placed on a smooth homogeneous surface. The contact angle is described by Young's equation (Young, 1805), which can be regarded as a mechanical force balance (Hiemenz and Rajagopalan, 1997; Morrow, 1970) for the interfacial/surface tensions involved, **Figure 2-1**:

$$\sigma_{os} = \sigma_{ws} + \sigma_{ow} \cdot \cos\theta \qquad [2\text{-}1]$$

where,

σ_{os}: Oil-solid IFT, (N/m)
σ_{ow}: Oil-water IFT, (N/m)
σ_{ws}: Water-solid IFT, (N/m)
θ: Contact angle, (degree)

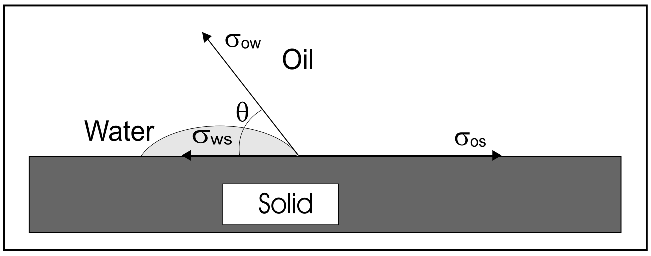


Figure 2-1. Force balance at the oil-water-solid contact line defining the contact angle θ.

Water will be taken as the reference fluid phase and oil as the non-reference fluid phase in this thesis. θ will therefore always be measured through the water phase independent of whether water is the wetting phase or not. The contact angle θ can vary between 0 to 180°, depending on the relative affinity for the fluids towards the surface. An angle below 90° will therefore indicate a surface with higher affinity for water than oil, and it is classified as ***water-***

wet. Contrary, if the angle is above 90°, the surface has higher affinity for oil than for water, and it is termed ***oil-wet***. **Figure 2-2** shows three situations where water and oil have different affinities for the surface. Water is the wetting phase in **(a)**, so θ is below 90°. The opposite is the case in **(b)**, where oil is the wetting phase and θ is above 90°. In **(c)**, both fluids have equal affinity for the surface and it is said to be ***neutral-wet***.

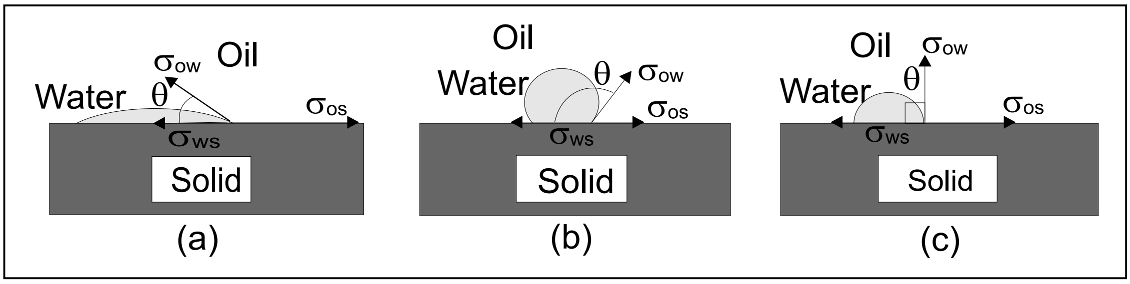


Figure 2-2. Three surfaces with different wettability. **(a)** Water-wet (θ < 90°), **(b)** Oil-wet (θ > 90°), and **(c)** Neutral-wet (θ = 90°).

Wettability is a very important parameter in oil recovery processes, because it has strong impacts on the distribution, location and flow of oil and water in the reservoir during production (Anderson, 1986b, 1987a, b, c; Cuiec, 1991; Hjelmeland and Torsaeter, 1980; Morrow, 1990). Water will occupy the narrowest pores and oil will reside as small droplets in the middle of the pores in a uniform water-wet system. The reverse fluid distribution will be the case in an oil-wet reservoir.

It is generally believed that oil reservoirs were created by accumulation of hydrocarbons in a rock originally filled with water (Chernicoff, 1999; Morrow, 1991). Most of the oil-bearing formations are located in sedimentary rocks consisting of either sandstone or carbonates (Boggs, 1995; Chernicoff, 1999). Minerals, which have never been contacted by crude oil, like quartz, carbonates and sulfates are strongly water-wet, but some exceptions exist (Anderson, 1986a). Initially, it was therefore believed that the mineral surface in all oil reservoirs was strongly water-wet, because the connate water would protect the invading crude oil from touching the rock surface (Benner and Bartell, 1942; Morrow, 1990). However, experience and observations from wettability tests on cores with preserved reservoir wettability, especially the work by Treiber *et al.* (1972), indicated that the observed oil-wetness was real. Tests showed that certain classes of components in the crude oil under certain conditions were able to alter the wettability of the original water-wet rock towards more oil-wet conditions, despite the protecting water-film. It was also recognized that wettability in porous media not necessary was a uniform quantity. Local chemical heterogeneities in the mineral composition and complexities of the pore system can generate non-uniform wettability. Core samples, ***which imbibe only water spontaneously, are said to be water-wet,*** whereas those who only ***take up oil spontaneously are described as oil-wet***. Samples imbibing/taking up neither water nor oil are said to be ***neutral wet***. ***Fractional (spotted-, dalmatian-, or speckled) wettability*** is characterized by isolated areas being water- and oil-wet (Cuiec, 1991). ***Mixed-wettability*** is a special type of fractional wettability, where water- and oil-wet areas are assumed to be inter-connected (Salathiel, 1973). Such cores contain continuous water- and oil-wet paths, respectively, and they are able to both imbibe and take up water and oil spontaneously (Anderson, 1986b).

The current status about wettability of oil reservoirs is therefore that most reservoirs are assumed to have a non-uniform wettability (Salathiel, 1973), and strongly water- and oil-wet conditions are regarded as exceptions rather than the rule (Cuiec, 1991; Heaviside, 1991).

2.2. Wettability modifying components in crude oils

Several authors recognized that a small fraction of certain components in the crude oil, mainly from the heavy asphaltene- and resin fraction, was able to alter the wettability of original strongly water-wet minerals (Anderson, 1986a; Benner and Bartell, 1942; Bobek *et al.*, 1958; Marsden and Nikias, 1962; Nutting, 1934; Reisberg and Doscher, 1956). This observation was further confirmed by Denekas *et al.* (1959), when performing wettability tests on cores, which had been contacted with different fractions of crude oils. The heavy fraction altered the wettability of the core material towards neutral- and oil-wet conditions, by far the most of all the distillation cuts tested (Sayyouh *et al.*, 1991). Since then, numerous researchers have confirmed this asphaltene/resin induced wettability alteration, which is now generally accepted as common knowledge (Clementz, 1982; Collins and Melrose, 1983; Crocker and Marchin, 1988; Cuiec, 1984; Dubey and Waxman, 1989; Gloton *et al.*, 1992; Wolcott *et al.*, 1993; Xie *et al.*, 2000; Xie and Morrow, 1999).

Asphaltenes are large complex molecules, somewhat polar, with molecular weights in the range 600-300,000 (Rønningsen, 1991). They are defined operationally as the components precipitate from crude oil when diluting with large excess of n-pentane, n-hexane or n-heptane. Resins are smaller molecules than asphaltenes, but have in general higher content of the polar elements nitrogen, sulfur and oxygen (NSO-compounds) and are therefore in general more polar than asphaltenes (Speight, 1999). Asphaltenes and resins are belonging to different solubility classes and they can be separated as shown in **Figure 2-3**.

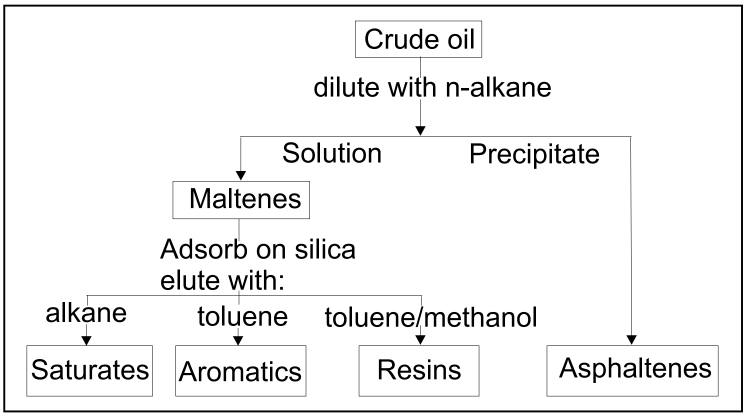


Figure 2-3. Solubility classes for crude oils. Separation of the asphaltene- and resin fraction. Redrawn after Buckley (1996).

Even though the presence of asphaltenes in crude oil seems to be necessary for wettability alteration to occur, there have never been demonstrated a correlation between the content of asphaltenes in crude oil and the extent of wetting alteration induced by the actual oil (Buckley, 1996). The best counter-example is the Athabasca tar sand in Canada containing approximately 15 % asphaltenes (Morrow, 1990), which has been shown to prevail its strongly water-wetness over geologic time (Takamura and Chow, 1983).

Although, asphaltenes are undoubtedly related to the wetting state of oil reservoirs (Xie *et al.*, 2000), experimental observations, however, point toward a smaller group of components from the asphaltene/resin fraction as more important regarding wettability alteration. These components are more specifically of ***acidic- and basic nature*** (Anderson, 1986b; Crocker and Marchin, 1988; Cuiec, 1984), and the content of these molecules are not necessary directly related to the content of asphaltenes in the oil as pointed out by Skauge *et al.* (1999).

Acidic- and basic components are more or less present in all crude oils, and these groups include components as phenols, carboxylic acids (Frye and Thomas, 1993; Reisberg and Doscher, 1956; Seifert and Howells, 1969; Seifert and Teeter, 1970; Somerville *et al.*, 1987), sulfur components like sulfides, thiophenes, mercaptanes and polysulfides and nitrogen components as amides, pyridines, quinolines and porphyrins (Anderson, 1986a). Many of these and similar components have been shown to have effect as wettability modifiers when adsorb to clean water-wet minerals (Benner and Bartell, 1942; Cuiec, 1977; Kowalewski *et al.*, 2000; Legens *et al.*, 1998a, b; Madsen *et al.*, 1996; Madsen and Lind; 1998; Morrow *et al.*, 1973; P III; Standal, 1999; Thomas *et al.*, 1993a, b; Torsæter *et al.*, 1997; Tweheyo *et al.*, 1999; Wagner and Leach, 1959). There also seem to be a difference in the way sandstone and carbonate rocks are responding to acidic- and basic components (Buckley and Liu, 1998; Denekas *et al.*, 1959). Carbonate rocks are usually more sensitive to acidic components (Cuiec, 1977; Madsen and Lind, 1998; P I, III; Thomas *et al.*, 1993a), whereas sandstone becomes more oil-wet after being contacted with basic components (Benner and Bartell, 1942; Cuiec, 1977; Kowalewski *et al.*, 2000; Michaels and Timmins, 1960; Skauge *et al.*, 1999; Torsæter *et al.*, 1997; Wagner and Leach, 1959). These observations can partly be explained by the difference in surface charge of these two types of rocks. Sandstone is negatively charged above pH = 2 (Menezes *et al.*, 1989; Skauge and Fosse, 1996), and therefore sensitive to positively charged ions. Carbonates are in general positively charged below pH 8 to 9 (Pierre *et al.*, 1990; Wesson and Harwell, 2000), and are therefore able to adsorb negatively charged acidic groups (Hall, 1986).

2.3. Wettability alteration mechanisms

The molecules containing polar functional groups are the most important regarding wettability alteration from water-wet to oil-wet conditions in oil reservoirs. Beside the amount of these components in the oil, the following parameters have been shown to be important governing the degree of wettability alteration for a given COBR system:

- Mineral composition and surface charge of the rock material (Anderson, 1986a; Buckley *et al.*, 1989; Dubey and Doe, 1993; Sayyouh *et al.*, 1990)
- Brine salinity and concentration of divalent- and other multivalent ions (Buckley, 1996; Morrow *et al.*, 1986, 1998; Tang and Morrow, 1999; Xie and Morrow, 1999)
- Capillary pressure and thin film forces, disjoining pressure (Hirasaki, 1991; Melrose, 1982)
- Water solubility of polar oil components (Anderson, 1986a; Kaminsky and Radke, 1998)
- The ability for the oil to stabilize heavy components (Al-Maamari and Buckley, 2000; Buckley, 1993; Buckley *et al.*, 1996, 1998; Buckley and Wang, 2000; Cimino *et al.*, 1995)
- Temperature (Al-Maamari and Buckley, 2000; Buckley *et al.*, 1996; Liu and Buckley, 1995), pressure (Al-Maamari and Buckley, 2000; Buckley *et al.*, 1998) and initial water saturation (Jadhunandan and Morrow, 1995; Salathiel, 1973; Zhou *et al.*, 2000b)

Based on this knowledge, four different mechanisms by which polar components are adsorbed to mineral surfaces, have been recognized and clearly defined by Buckley (1996):

- Polar binding. If no water is present in the porous medium, the adsorption of polar components is likely to happen between polar surface sites and molecules containing polar atoms (NSO-compunds)

- Surface precipitation. Precipitation of asphaltenes occurs when the oil is a poor solvent for the heavy fraction
- Acid/base interactions. This interaction takes place between sites of opposite electrical charge
- Ion binding. Divalent- or other multivalent ions in the brine are likely to bind to both the mineral surface and the oil/brine interface creating bridges

Buckley and Liu (1998) have furthermore shown that the potential for a given crude oil to alter wettability can be predicted to a first approximation by considering the API **G**ravity-**A**cid number (AN) and **B**ase number (BN) (G-AB) profile of the oil together with the rock material, i.e., sandstone vs. carbonate rock.

2.4. Measurement of wettability

Several methods (Anderson, 1986b), both quantitative and qualitative, exist to measure wettability of porous medium. The Amott-Harvey and contact angle measurements were the quantitative and the SI test the qualitative method used in this work, respectively. Other quantitative tests include the United States Bureau of Mines (USBM) test (Donaldson *et al.*, 1969), the Hammervold-Longeron index (Hammervold, 1994) and the SI index (Spinler, 1997), whereas microscopic examination (Castor *et al.*, 1981; Cooke *et al.*, 1974; Michaels *et al.*, 1964; Morris and Wieland, 1963), adhesion tests (Buckley *et al.*, 1989; Buckley and Morrow, 1990; Morrow, 1990), bottle tests (Dubey and Doe, 1993), flotation methods (Celik and Somasundaran, 1980), reservoir logs (Graham, 1958), relative permeability curves (Owens and Archer, 1971; Treiber *et al.*, 1972), NMR-measurements (Howard and Spinler, 1993) and capillary penetration tests (Varadaraj *et al.*, 1994) all have been used to evaluate wettability qualitatively. All methods have certain advantages and disadvantages and they should be interpreted with caution, because the wettability “index” generated by each method is depending on the method used (Anderson, 1986b; Cuiec, 1991; Hjelmeland and Torsaeter, 1980; Morrow, 1990).

2.4.1. Quantitative tests

Amott-Harvey Test

The Amott–Harvey test (Anderson, 1986b) is an extension of the wettability test introduced by Amott (1959). The method is based on the fact that the amount of water imbibing spontaneously into a core saturated with oil is depending on the surface energy of the system. The change in water saturation due to SI will decrease with decreasing water-wetness due to lower surface energy. After establishing the initial water saturation (S_{wi}) the test consists of the following steps, **Figure 2-4**:

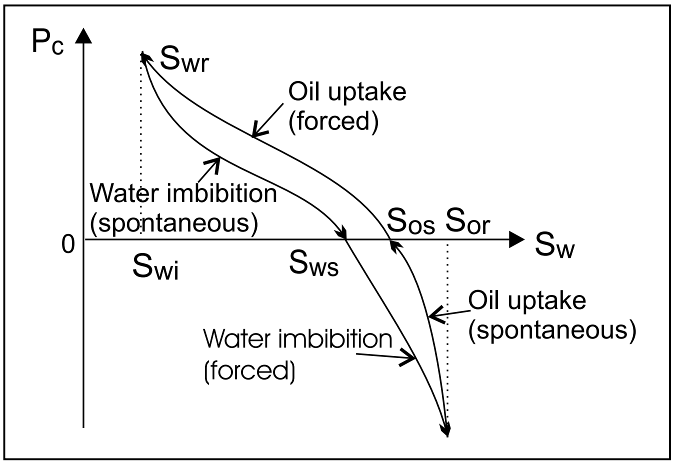


Figure 2-4. Capillary pressure vs. water saturation diagram illustrating the parameters needed to calculate the Amott-Harvey RDI.

- SI of water to reach, S_{ws}
- Flooding the core with water to reach residual oil saturation, S_{or}
- Spontaneous uptake of oil to reach, S_{os}
- Flooding the core with oil to reach residual water saturation, S_{wr}

The water index, I_w, the oil index, I_o, and the Amott-Harvey relative displacement index (RDI), $I_{A\text{-}H}$, can then be calculated from the formulas:

$$I_w = \frac{S_{ws} - S_{wi}}{S_{or} - S_{wi}} \quad , \quad I_o = \frac{S_{or} - S_{os}}{S_{or} - S_{wr}} \quad , \quad I_{A\text{-}H} = I_w - I_o \qquad [2\text{-}2]$$

where,

S_{wi}:	Initial water saturation, (%)	S_{or}:	Water saturation after forces water imbibition, (%)
S_{wr}:	Water saturation after forced uptake of oil, (%)	S_{ws}:	Water saturation after SI, (%)
S_{os}:	Water saturation after spontaneous uptake of oil, (%)		

$I_{A\text{-}H}$ varies between +1 for strongly water-wet systems to –1 for strongly oil-wet systems. Cuiec (1984) describes the system as water-wet when $+0.3 \leq I_{A\text{-}H} \leq +1$, intermediate for $-0.3 \leq I_{A\text{-}H} \leq +0.3$, and oil-wet for $-1 \leq I_{A\text{-}H} \leq -0.3$.

An advantage with the Amott-Harvey test is that both reservoir cores and fluids can be used. The drawbacks are its problem to differ between small differences in wettability, for cores having Amott index either close to unity (Morrow, 1990) or zero (Anderson, 1986b). Standardization of the timeframe for the imbibition tests is another problem, because different tests can require timeframes ranging from hours to months to reach zero capillary pressure, bringing some uncertainty to the S_{ws} and S_{os}-values. The method cannot handle dynamic IFT and wetting phenomena (Morrow, 1990), which may be important in the reservoir during the oil production. The latter problem also applies to the contact angle measurement method described below.

Contact angle measurements

Measuring contact angles is the most accurate way to determine the wettability for pure liquids and artificial core material (Morrow, 1990). However, some serious problems are related to this method when quantifying wettability for porous media using reservoir fluids. Since contact angles must be measured on smooth surfaces, they can usually not be measured directly on the porous medium (Sayyouh *et al.*, 1990, 1991). This problem has been solved by measuring the contact angle on smooth surfaces using minerals with a composition close to the porous medium. Calcite crystals are usually used as a substitute for carbonates, whereas different qualities of glass are used to represent sandstone cores (Morrow, 1990; Sharma and Wunderlich, 1985; Wagner and Leach, 1959). Test surface composition is therefore not exactly similar to composition of the porous medium (Hjelmeland and Torsaeter, 1980). Surface roughness (Morrow, 1975), mineralogical heterogeneity and pore structure are parameters apparently not taken into account when measuring contact angle on smooth surfaces (Anderson, 1986b). In addition, there are problems with hysteresis connected to contact angle measurements (Johnson and Dettre, 1969). The contact angles reported in the literature are usually the advancing- and the receding angles, because these are the most reproducible, **Figure 2-5**.

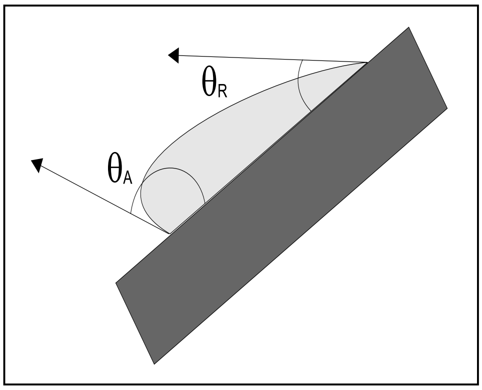


Figure 2-5. Advancing, θ_A, and receding, θ_R, contact angles. Redrawn after Johnsen and Dettre (1969).

Problems have also been reported when performing measurements with reservoir fluids, because naturally occurring surface-active components in the crude oil can disturb the measurement (Anderson, 1986b; Treiber *et al.*, 1972).

Different cut-off angles have been used to discriminate between water-wet, intermediate and oil-wet conditions. Morrow (1976) classifies surfaces having angles in the range from 0-62° as water-wet, 63-133° as intermediate and 134-180° as oil-wet. These cut off values was determined by performing SI tests into synthetic teflon cores. Treiber *et al.* (1972) classified cores having contact angles below 75° as water-wet, 75 to 105° for intermediate and above 105° for oil-wet, whereas Chilingar and Yen (1983) used the limits 80 and 100° to divide the three classes of wettability.

Recently, Rao and Girard (1996) published a new way of measuring contact angles called the Dual-Drop-Dual-Crystal (DDDC) technique, which according to the authors doesn't suffer from many of the traditional problems related to contact angle measurements.

2.4.2. Wettability of porous media based on SI data

Measuring the SI of water into core material is a qualitative way of assessing the wettability of the core material (Morrow, 1990). Both the rate and the amount of water imbibed, which is rapid and significant for strongly water-wet cores, will decrease as the wettability of the core material is approaching neutral-wet conditions.

Bobek *et al.* (1958) argued that wettability of porous media should be measured by methods related to capillary pressure measurement, because imbibition capacity is mainly depending on the water-wetness of the core and to a lesser degree the viscosities of the fluids involved and the pore structure of the core. Different methods have been suggested in an attempt to make this wettability test quantitative (Denekas *et al.*, 1959).

Morrow *et al.* (1999) introduced the wettability index, W_R, based on pseudo work of imbibition to differ between cores having Amott indices close to unity. The significance of this wettability index was confirmed by analyzing oil recovery from waterflooding tests. W_R gave a distinctly better resolution and correlation between oil recovery and wettability than Amott indices. Since W_R is based directly on SI curves, it has the advantage compared to the Amott and the USBM tests that it can provide information about dynamic IFT and wetting phenomena in the reservoir (Morrow, 1990). Zhou *et al.* (2000b) observed furthermore good correlation between W_R and an apparent dynamic advancing contact angle calculated from scaled dimensionless imbibition time. However, establishing reliable wettability tests based on SI still require improvements in scaling laws, which will make comparison between different COBR systems possible (Morrow, 1990). Such improvements have recently been reported over the past years (Al-Lawati and Saleh, 1996; Xie and Morrow, 2000; Zhou *et al.*, 2000a).

2.4.3. Correlation between different wettability tests

Rao and Bassiouni (2000) investigated and compared the Amott-Harvey, the USBM test and contact angle measurements. Their conclusion was that different wettability tests showed great scatter, and they recommended application of the DDDC technique to attain reproducible and more accurate contact angles for wettability evaluations (Rao, 1997). However, Lorenz *et al.* (1974) were able to correlate contact angles (cosθ-values) with the USBM wettability index and Kowalewski *et al.* (2000), Torsaeter (1988) and Tweheyo *et al.* (1999) observed good correlation between the Amott index and the USBM wettability index, using an improved USBM method developed by Sharma and Wunderlich (1985). Recently, Dixit *et al.* (1998) performed a theoretically analysis showing that the USBM index usually will be larger than the Amott-Harvey RDI.

Establishing a correlation between contact angles measured on smooth surfaces and displacement behavior in porous media would be of special interest and such correlations have been observed (Buckley *et al.*, 1995; Morrow *et al.*, 1998; Morrow and McCaffery, 1978; Owens and Archer, 1971; Rao, 1997; Treiber *et al.*, 1972; Zhou, *et al.*, 2000b). However, the correlation is far from straightforward due to the number of parameters other than wettability involved when performing displacement tests in porous media (Anderson, 1987a, b; Morrow *et al.*, 1986, 1998; Morrow and McCaffery, 1978). It seems that contact angles are a useful guide to evaluate relatively large changes in wettability induced by crude oils or surface-active materials for example, but they cannot be used to quantitatively predict SI or displacement efficiencies in porous media. It should therefore be clear from the above discussion that different wettability tests still show scatter, and no certain conclusion can be drawn regarding the "true" wettability of core samples.

Chapter 3. Fluid flow in porous media

3.1. Interfacial tension, capillary pressure and cylindrical tube model

The IFT between two immiscible fluids can be defined as force per unit distance acting parallel to the interface perpendicular to any line in the interface, or as the work needed to increase the surface area one unit (Mørk, 1997). When passing over a curved interface between oil and water, the pressure will increase to balance the interfacial tension forces. The pressure jump is called the capillary pressure and it is given by the Laplace equation (1806),

$$P_C = p_O - p_W = \sigma_{ow}\left(\frac{1}{R_1} + \frac{1}{R_2}\right) \qquad [3\text{-}1]$$

where,

σ_{ow}:	Oil-water IFT, (N/m)	P_c:	Capillary pressure, (Pa)
R_1, R_2:	Radii of curvature of the oil-water interface measured perpendicular to each other, (m)	p_o:	Pressure in the oil phase, (Pa)
		p_w:	Pressure in the water phase, (Pa)

By convention the capillary pressure is defined as the pressure in the non-reference phase (oil phase) minus the pressure in the reference phase (water phase). P_c can therefore both be positive and negative depending on which phase, oil or water, is the wetting phase. A positive capillary pressure means that water is the wetting- and oil the non-wetting phase in this thesis, and vice versa.

Because of its complexity, the cylindrical tube model is often used to idealize porous media. This geometry allows the relationship between wettability and oil-water IFT to be expressed explicitly. Thus, for a water-wet cylindrical tube with radius R filled with oil and water:

$$P_C = \frac{2\sigma_{ow} \cdot \cos\theta}{R} \qquad [3\text{-}2]$$

P_c:	Capillary pressure, (Pa)	θ:	Contact angle, (degree)
R:	Tube radius, (m)	σ_{ow}:	Oil-water IFT, (N/m)

The driving force underlying SI is proportional to the oil-water IFT, $\sigma_{ow} = F_c$, interpreted as force per unit length, F_c. It is the horizontal component of this force called the capillary force, $\sigma_{ow} \cdot \cos\theta$, which moves the water into the tube spontaneously, **Figure 3-1**. It follows that the rate of SI increases with both increasing capillary forces (Cuiec *et al.*, 1994; Schechter *et al.*, 1991) and water-wetness of the porous medium (Graue *et al.*, 1998; Jadhunandan and Morrow, 1991; Zhou *et al.*, 1993, 2000b).

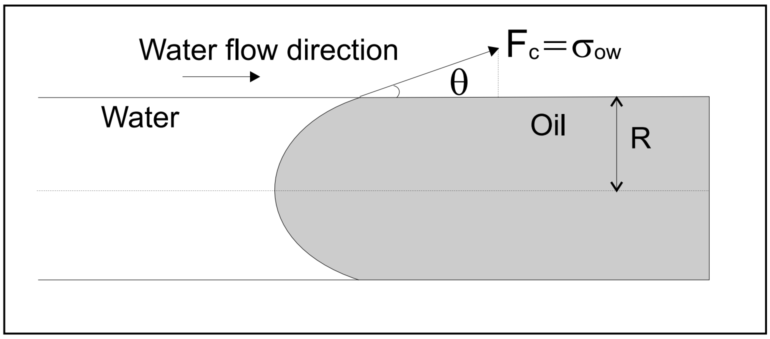


Figure 3-1. SI of water into an oil-filled water-wet tube. The horizontal component of the oil-water IFT is the driving force for the imbibition process.

3.2. Measuring oil-water IFT

Several methods exist to measure the oil-water IFT (Evans and Wennerström, 1994; Hiemenz and Rajagopalan, 1997). Three methods were used to evaluate this quantity in this work:

- The spinning drop technique is specially suited to measure low oil-water IFTs (Evans and Wennerström, 1994), and it was used to measure oil-water IFT in the presence of surfactants. The technique is based on the competition between centrifugal- and interfacial forces when small oil droplets are rotating rapidly in small tubes filled with aqueous surfactant solution. The IFT can be calculated from the shape of the oil droplet for a given angular velocity (Mørk, 1997)
- The ring tensiometer method for determines oil-water IFTs is based on the connection between the IFT and the force needed to detach the ring from the oil-water interface (Mørk, 1997)
- The pendant drop technique is based on the connection between oil-water IFT and the shape of an oil droplet residing in a fluid phase. The method is especially suited to evaluate IFTs at elevated temperatures (Mørk, 1997)

3.3. Gravity- and capillary forces in porous media

The most important forces determining the flow of oil and water during the oil production process are viscous-, gravity- and capillary forces (Morrow, 1979). Gravity- and capillary forces were the active forces during the experimental tests conducted in this thesis and only these two forces will be discussed here.

3.3.1. Gravity forces

Buoyancy forces are always present in mixtures of immiscible fluids. In such mixtures, the lighter phase will experience a pressure pointing upwards, and it is given by:

$$\Delta P_g = \Delta\rho \cdot g \cdot H \qquad [3\text{-}3]$$

where,

ΔP_g: Pressure difference between oil and water due to gravity, (Pa)
$\Delta\rho$: Density difference between oil and water, (kg/m^3)
g: Acceleration due to gravity, (= 9.8 m/s^2)
H: Height of the liquid column, (m)

Density difference between the fluid phases, height of the liquid column together with magnitude of capillary forces related to the IFT, wettability and permeability are the most important parameters deciding the influence of gravity forces on the fluid movements in the reservoir. In this thesis, the influence of gravity forces on the fluid flow in the SI experiments was investigated by varying the core height and the oil-water IFT.

Inverse Bond number

The relative influence of capillary- to gravity forces has been shown to have major impact on the oil expulsion mechanism. This ratio can be scaled according to the inverse Bond number, N_B^{-1} (Schechter *et al.*, 1994):

$$N_B^{-1} = C\frac{\sigma_{ow}\sqrt{\phi/k}}{\Delta\rho g H} \qquad [3\text{-}4]$$

where,

C:	0.4 dimensionless constant for capillary tube model (Zhou and Stenby, 1989)	σ_{ow}:	Oil-water IFT, (N/m)
		ϕ:	Porosity, (fraction)
		H	Height of the core material, (m)
k:	Absolute permeability, (m^2)	$\Delta\rho$:	Density difference between oil and water, (kg/m^3)
g:	Acceleration due to gravity, (9.8 m/s^2)		

For a system with well-defined wetting properties, Schechter *et al.* (1994), showed that capillary forces are dominant for $N_B^{-1} > 5$ and gravity forces for $N_B^{-1} << 1$. In the intermediate range, $0.2 < N_B^{-1} < 5$, both capillary- and gravity forces can be active in the displacement. **Figure 3-2** shows typical oil/water saturation profiles inside the porous medium for different ranges of N_B^{-1}. When the SI process is dominated by capillary forces, i.e. $N_B^{-1} > 5$, the oil is produced in a counter-current flow mode from all surfaces, **Figure 3-2 (a)**. The oil will be produced mainly from the upper part of the porous medium when N_B^{-1} is in the intermediate range, $0.2 < N_B^{-1} < 5$. Both capillary- and gravity forces are assumed to be active in the displacement process and the characteristic cone shaped oil/water interface is formed inside the porous medium, **Figure 3-2 (b)**. **Figure 3-2 (c)** shows an imibition process driven by gravity forces only. The oil recovery rate is slow, but ultimate recovery (UR) level can be very high due to strong reduction in the amount of trapped oil. Both the oil expulsion mechanism shown in **Figure 3-2 (a)** and **(b)** were demonstrated in the chalk tests performed in this work.

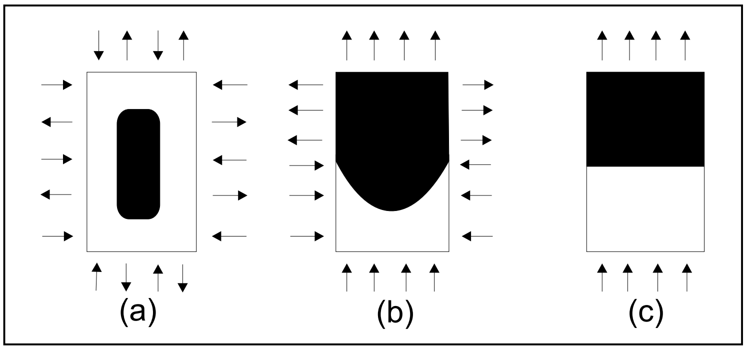


Figure 3-2. Distribution of oil and water inside cores where the driving forces for the SI is, **(a)** capillary forces **(b)** capillary- and gravity forces and **(c)** gravity forces. Redrawn after Schechter *et al.* (1994).

Gravity driven SI

Several authors have stressed the importance of gravity forces during the oil production process, especially in gas/oil systems (Haldorsen *et al.*, 1985; King *et al.*, 1970; Murty *et al.*, 1987; Torvund and Nipen, 1987) and under low oil-water IFT conditions (Austad and Milter, 1997; Gesztesi *et al.*, 1997; Hornof and Morrow, 1987; Hove *et al.*, 1995; Morrow and Songkran, 1981).

Chen *et al.* (2000) assumed that improved segregation of oil and water due to application of EA-surfactant at low oil-water IFT was the primary EOR mechanism when performing pilot tests in the Yates field. SI tests reported in this thesis showed that gravity forces were significant during low oil-water IFT tests confirming the above-cited statement.

3.3.2. Capillary forces

Capillary forces have decisive influence on oil recovery efficiency, but the influence differs in a fundamental way for non-fractured and fractured reservoirs. Strong capillary forces during waterflooding in a non-fractured reservoir will trap oil and cause relatively high residual oil saturation (Anderson, 1987c; Morrow *et al.*, 1973; Taber, 1980). Reduction in the oil-water IFT to remobilizing residual oil is therefore preferred under such conditions (Danielson et al., 1976; Davies and Jones, 1968; Gogarty, 1976; Kremesec and Treiber, 1978; Taber, 1980; Taugbøl, 1995). However, SI of water due to strong capillary forces is currently regarded as an important and necessary mechanism to attain high displacement efficiency in fractured reservoirs. The importance of the SI process is reflected in the numerous research papers treating this subject (Aronofsky *et al.*, 1958; Austad and Milter; 1997; Bourbiaux and Kalaydjian, 1990; Brownscombe and Dyes, 1952; Chen *et al.*, 2000; Cuiec *et al.*, 1994; Graham and Richardson, 1959; Hamon and Vidal, 1986; Mattax and Kyte, 1962; Parsons and Chaney, 1966; Reis and Cil, 1993; Thiebot *et al.*, 1990; Thomas *et al.*, 1987; Torsaeter, 1984). UR and the SI rate are the two most important quantities related to the SI process from a practical point of view (Xie and Morrow, 2000). It is therefore useful to take a closer look at the parameters governing these two crucial quantities. It is worth mentioning that all results cited here were obtained for water-wet core samples. SI into oil-wet material is reported in this thesis, and some of the cited conclusions may not apply to SI behavior under oil-wet conditions.

Matrix permeability

Graham and Richardson (1959) argued that the rate of SI should increase with increasing permeability of the porous medium. Several authors have later confirmed this relationship empirically (Al-Lawati and Saleh, 1996; Mattax and Kyte, 1962). No clear correlation has been observed between permeability and UR. However, Cuiec (1977) and Hamon and Vidal (1986) observed increase UR with increasing permeability when performing SI tests into Fontainebleau sandstone cores.

Oil-water IFT

Austad and Milter (1997) decreased oil-water IFT by using surfactants when conducting SI tests on long low-permeability chalk cores. They found that the rate of SI decreased significantly for the surfactant solution compared to pure brine. Cuiec *et al.* (1994) observed the same tendency when testing rate of SI into low-permeability chalk from Mantes.

It is generally believed that the SI rate slows down when capillary forces are reduced, due to increased influence of weaker gravity forces. However, both theoretical simulations by Bourbiaux and Kalaydjian (1990) and experimental data by Schechter *et al.* (1994) using high-permeability core material, indicate that this is not necessary the case. Thus, the permeability of the porous medium seems to be a crucial parameter regarding rate of SI when gravity forces become active. It seems that when the permeability of the porous medium falls below a critical value, the rate of SI is likely to decrease with decreasing oil-water IFT. One reason for this can be that the simultaneous effect of capillary- and gravity driven imbibition will be much lesser in this case, because the gravity driven imbibition will be slower and more extended in time with low- than high-permeability cores. However, the UR is likely to increase for the low oil-water IFT case, due to suppression of snap-off of oil (Schechter *et al.*, 1994).

Core sample shape and boundary conditions

Torsæter and Silseth (1985) performed SI tests on cores having different shapes and boundary conditions. They found that the imbibition rate increased with increased imbibition area. The UR seemed to be nearly independent of the sample shape, which was also observed by Hamon and Vidal (1986).

Different boundary conditions are usually investigated by coating some of the sides of the core with impermeable layers. The purpose is to investigate how capillary forces are affected by change in flow geometry. The general trend shows that UR is independent of test geometry and the SI rate increases with increasing area available for imbibition (Torsæter and Silseth, 1985; Zhang *et al.*, 1995).

Pore structure

Milter and Øxnevad (1996) performed SI tests into two different chalk types, Stevns chalk from Denmark and Beer Stone from UK. Stevns chalk reached a UR level of 58 % OOIP, whereas only 22 % OOIP could be produced from the Beer Stone core. The difference in UR was attributed to different tendency to undergo wettability alteration, which they discussed in relation to geological parameters. Beer Stone chalk seemed more oil-wet than Stevns chalk after the aging process, which was assumed to account for the difference in UR. The higher oil-wetness of the Beer Stone chalk was attributed to (i) higher content of macro-pores (ii) more fine-grained chalk matrix and (iii) less pore-wall roughness.

Heterogeneities

Heterogeneities in the porous medium can be a serious source to erroneous interpretation of laboratory tests, and give non-representative data for predicting potential for field application. Hamon and Vidal (1986) demonstrated that heterogeneities in the permeability of a real outcrop sample was likely to slow down the recovery rate compared to the expected rate from a corresponding homogenous sample. Hamon has furthermore showed that the wettability of the reservoir rock is likely to vary considerably with the location in the field (Hamon, 2000), emphasizing the importance of knowing the origin of the core samples tested in the laboratory.

Fluid viscosities

Mattax and Kyte (1962) showed that SI decreased with increasing water viscosity, even though the oil-water viscosity ratio was held constant. However, later researchers have emphasized the importance of including the oil viscosity as a parameter when determine the rate of SI (Babadagli, 1996; Blair, 1964; Briggs *et al.*, 1988; Chimienti *et al.*, 1999; Donmez, 1997; Ruth *et al.*, 2000). Zhou *et al.* (2000a) showed that SI rate is inversely proportional to the geometrical mean of the oil- and the water viscosity as far as the mobility ratio was close to unity. This relationship gave a theoretical justification to the work by Zhang *et al.* (1995), which established the same relationship based on empirical data.

Initial water saturation

Viksund *et al.* (1998) performed SI tests with varying S_{wi} on Berea sandstone and 4 different chalk types, including Stevns chalk used in this study. The rate of SI was a complex function of S_{wi} and they explained the variations in the water imbibition rate as changes in capillary pressure and mobility of water with varying water saturation. Increased water saturation decreased the capillary pressure driving the imbibition, but the mobility of water increased at the same time. Hence, two opposing effects governed the SI rate. Decrease in capillary pressure seemed to be faster than increase in mobility of water for Berea sandstone cores, whereas the opposite probably was the case for chalk cores.

IFT gradients (Marangoni-effect)

The Marangoni-effect appears when surface-active molecules are distributed unevenly along an oil-water interface (Dukhin *et al.*, 1995). This non-uniform distribution can cause an IFT gradient pointing towards the center of the core, speeding up the imbibition rate compared to an imbibition conducted with equilibrium oil-water solutions. Several authors have suggested Marangoni flow as a method to increase oil recovery (Chen *et al.*, 2000; Lyford *et al.*, 1998a, b; Pratt, 1991; Schechter *et al.*, 1991).

Temperature

Two opposing effects will take place when performing SI tests at elevated temperature. Lower fluid viscosities will enhance oil production, whereas decreasing oil-water IFT will slow down the driving force for SI. Donmez (1997) performed SI tests using oils with different viscosities in the temperature range 20-80 °C. All tests showed increased rate and UR with increasing temperature, but the effect was much more pronounced for high- than low viscous oils. The reduction in oil viscosity seems therefore to be the most important factor governing the SI behavior at elevated temperature, as long as the viscosity reduction is significant.

3.3.3. Scaling laws

It should be mentioned that many of the parameters described above have been connected through so-called scaling laws. These scaling laws, which have undergone several improvements (Babadagli, 2000; Kazemi *et al.*, 1992; Ma *et al.*, 1995, 1997; Zhou *et al.*, 2000a) since Mattax and Kyte based on the theoretical work by Rapoport (1955) published the first one in 1962, express that the time require to reach the same recovery level should be the same for systems having different core-fluid properties as long as certain conditions are fulfilled. No contribution from gravity forces to the imbibition process is one of these conditions, implying that the core sample should be strongly water-wet (Mattax and Kyte, 1962).

Wettability conditions different from strongly water-wet have been included in the scaling laws by introducing a cosθ term in the numerator (Guo *et al.*, 1998; Gupta and Civan, 1994).

It is also interesting to notice that Xie and Morrow (2000) recently have reported a scaling law for SI into porous media with wettability different from strongly water-wet, which also includes the influence of gravity forces on the oil production rate:

$$t_D(c+g) = t\frac{k/\phi}{L_C^2\sqrt{\mu_W\mu_O}}\left(\frac{\sigma_{ow}}{\sqrt{k/\phi}}f(\theta)+\frac{\Delta\rho g L_C^2}{L_H}\right) \qquad [3\text{-}5]$$

where,

$t_D(c+g)$:	Dimensionless time including capillary- and gravity forces	μ_w:	Water viscosity, (Pa·s)
		μ_o:	Oil viscosity, (Pa·s)
t:	Imbibition time, (s)	σ_{ow}:	Oil-water IFT, (N/m)
k:	Permeability, (m^2)	$f(\theta)$:	Wettability factor, (-)
ϕ:	Porosity, (fraction)	$\Delta\rho$:	Density difference between oil and water, (kg/m^3)
L_C^2:	Characteristic length, (m)		
g:	Acceleration due to gravity, (= 9.8 m/s^2)	L_H:	Vertical height of core sample, (m)

3.4. Residual oil saturation after SI

The efficiency by which oil is displaced from an oil reservoir can be quantified by the pore scale displacement efficiency or MDE, E_m, defined by the following equation (Morrow, 1991):

$$E_m = \frac{S_{oi}-S_{or}}{S_{oi}} \qquad [3\text{-}6]$$

S_{oi}:	Initial oil saturation, (%)	S_{or}:	Residual oil saturation, (%)

The ultimate purpose for all EOR methods acting on the pore scale level is to reduce the residual oil saturation, S_{or}, as much as possible. The underlying mechanisms for the residual oil saturation can basically be divided into two broad classes:

- The macroscopic displacement efficiency can be low due to poor reservoir conditions like unfavorable wettability, fractures, impermeable layers and other heterogeneities
- The MDE on pore scale level can be low due to capillary trapped or bypassed oil

3.4.1. Residual oil saturation mechanisms

The reasons for poor displacement efficiency on pore scale level are the target for the discussions in this section. There are basically two mechanisms by which residual oil is trapped in the reservoir. The first is a mechanism referred to as ***bypassing of oil***, whereas the second is referred to as ***snap-off of oil*** (Chatzis *et al.*, 1983). When discussing porous media on a microscopic scale, the following definitions taken from Yu and Wardlaw (1991) will be used in this thesis. Pores are larger spaces inside the porous medium connected to each other by smaller spaces or constrictions referred to as throats. Pores are by definition larger than directly connected throats, but in some porous media the smallest pore can be smaller than the largest throat. The pore diameter or pore body diameter (D_{body}) can be defined as the diameter of the largest sphere restricted by the pore walls, which can be inscribed inside the pore space. Pore throat diameter (D_{throat}) is the diameter of an inscribed circle in a plane of minimum cross section between two adjacent pores. The ratio of pore body diameter to pore throat diameter (D_{body}/ D_{throat}) is called the aspect ratio (AR). The connectivity or coordination number of a pore is the number of pore connections leading to adjacent pores.

3.4.2. Bypass of oil

The porous medium is very heterogeneous in pore size, pore throat dimensions, ARs, pore-wall roughness and coordination number (Mohanty *et al.*, 1987). When the water is flowing through water-wet porous media containing oil, the oil can be bypassed due to several different unfavorable pore geometries. Two such geometries are shown for the pore doublets geometry in **Figure 3-3**. The oil-water interface is moving faster in the small pore causing bypassing of oil in the larger pore in **(a)**, while the opposite is shown in **(b)**. In the latter case, the flow pattern of the injected water may also depend on AR, wettability, pore-wall roughness, edges of ducts in addition to the radius of the pore.

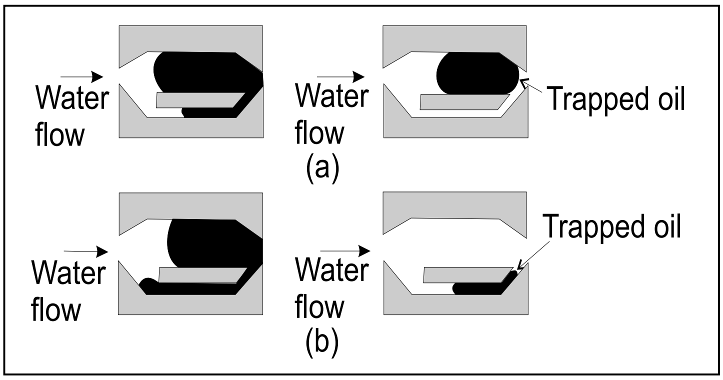


Figure 3-3. Bypassing of oil. **(a)** In a water-wet system, the oil-water interface is moving faster in the small pore than in the large pore, and the oil in the latter is partly bypassed. **(b)** In an oil-wet system, the oil-water interface is moving faster in the large pore than in the small pore, bypassing oil in the latter one.

Bypass of oil is the most important mechanism causing trapping of oil in porous media having low ARs (in the range 1-2), because snap-off is suppressed under such conditions (Chatzis *et al.*, 1983). As the AR increases, the trapping mechanism goes through a transition where bypassing of oil is the most important mechanism to snap-off as the dominant mechanism for trapping residual oil. The bypass mechanism is also the dominant mechanism for generating residual oil in systems containing large pores, clusters of large pores, and vugs accessible through smaller pores (Chatzis *et al.*, 1983).

3.4.3. Snap-off of oil

When oil is flowing from one pore into another filled with water through a narrow throat, the oil surface will at some point become unstable and a droplet will detach from the main bulk oil (Mohanty *et al.*, 1987; Wardlaw, 1980, 1982). This process is referred to as snap-off of oil, **Figure 3-4**.

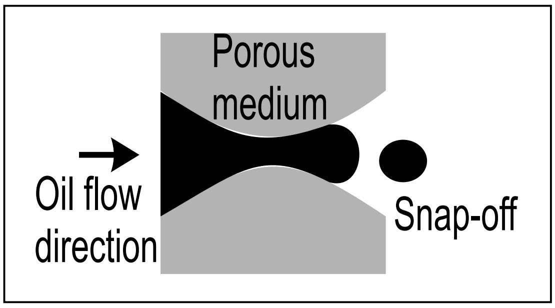


Figure 3-4. Snap-off of oil in porous media. Bulk oil is flowing through a narrow throat and droplets of oil are released by snap-off.

Snap-off of oil is a major mechanism causing residual oil in porous media, especially for strongly water-wet systems (Wardlaw, 1980). Chatzis *et al.* (1983) estimated that 80 % of the trapped oil in Berea sandstone cores occurred in snap-off geometries. The main parameters governing snap-off are AR (Chatzis *et al.*, 1983; Yu and Wardlaw, 1986), pore-wall roughness (Lenormand and Zarcone, 1984; Roof, 1970), connectivity of the pore system (Yu and Wardlaw, 1986), oil-water IFT (Arriola *et al.*, 1983; Wardlaw, 1982) and the wettability of the porous medium (Roof, 1970; Wardlaw, 1982).

Roof (1970) studied the physical mechanism for snap-off of oil on the scale of a single pore by pushing oil through strongly water-wet donut-hole shaped throats. He observed that the rate of the snap-off process was extremely sensitive to the geometry of the system, and the timeframe required for snap-off to occur was reduced significantly if a passageway for water to the pore throat region existed. Fast supply of water to this region will grow collars of water and thereby induce snap-off of oil. Both high AR (Milter, 1996) and increased pore-wall roughness (Roof, 1970) will promote fast supply of water to the pore throat region, and hence enhance snap-off.

The AR is, according to Chatzis *et al.* (1983), of first importance causing residual oil and the creation of the latter in water-wet systems with low- and high ARs is shown in **Figure 3-5 (a)** and **(b)**, respectively.

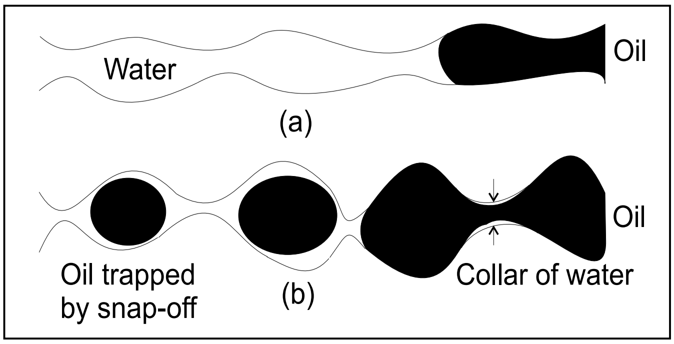


Figure 3-5. Sequences of pores having low- and high AR. **(a)** Low AR and no snap-off of oil. **(b)** High AR and increased tendency to snap-off of oil. Redrawn from Chatzis *et al.* (1983).

Slower supply of water to the pore throat region is in the same manner expected to be the reason for less snap-off in systems with low oil-water IFT or wettability close to neutral. Wardlaw (1982) observed lower tendency to snap-off when performing imbibition tests into glass-tube material with decreasing water-wetness. It was assumed that the wetting phase invaded the pores at a much slower rate close to neutral-wet condition, compared to strongly water-wet condition. The oil-water interface could therefore move through the pore body in a more piston-like manner and most of the oil could be displaced from the pore before enough water had reached the critical throat region to grow a collar of water and snap-off occurred. Reduced oil-water IFT is likewise likely to decrease the tendency for snap-off due to reduced capillary forces (Lenormand and Zarcone, 1984; Roof, 1970; S 3.1.; Schechter *et al.*, 1994).

Chapter 4. Surfactants: Types, phase behavior, ion-pair formation and stability

4.1. Types of surfactants

Surfactants are amphiphilic molecules containing two parts with different properties towards water. The usual structure is a long hydrophobic hydrocarbon chain bonded to a hydrophilic group, charged or non-charged (often referred to as the head-group). The hydrocarbon chain can be saturated or not, straight, branched, or aromatic. Surfactants are usually classified according to the charge of the hydrophilic group in the molecule. If the hydrophilic part is negatively or positively charged the surfactant is called anionic and cationic, respectively. If the hydrophilic part only contains polar groups, the surfactant is called non-ionic. The surfactant can also contain both negatively and positively charged groups within the same molecule and they are then classified as zwitter-ionic surfactants.

It is well known that cationic- and anionic surfactants have the ability to interact and create so-called ion-pairs (Eksborg *et al.*, 1973). Such surfactant systems have recently been studied in more detail and they are referred to as catanionic surfactant mixtures in the chemical literature (Jokela *et al.*, 1987; Karlsson, 2001; Khan and Marques, 1997). Khan and Marques (1997) define them as a new class of surfactants and they are believed to play a key role in the mechanism explaining the wettability alteration process put forward in this thesis. The terms, catanionic mixtures and surfactant ion-pairs, will be used interchangeable in this thesis. Examples of the different types of surfactants are:

Anionic surfactants: alkylsulfonates, $R\text{-}SO_3^-Na^+$, alkylethoxysulfonates $R\text{-}(OCH_2\text{-}CH_2)_x\text{-}SO_3^-Na^+$, alkylethoxy-propoxysulfonates $R\text{-}(OCH_2\text{-}CH_2\text{-}CH_2)_x\text{-}(OCH_2\text{-}CH_2)_y\text{-}SO_3^-Na^+$,
alkylsulfates $R\text{-}O\text{-}SO_3^-Na^+$ and fatty acids $R\text{-}COO^-Na^+$

Cationic surfactants: quaternary ammonium salts, $R\text{-}N(CH_3)_3^+Br^-$, and long chain primary amines, $R\text{-}NH_3^+Cl^-$

Non-ionic surfactants: ethoxylated alcohols, $R\text{-}CH_2\text{-}(C_2H_4O)_n\text{-}OH$

Zwitter-ionic surfactants: sulfobetaines, $RN^+(CH_3)_2(CH_2)_nSO_3^-$

Catanionic surfactants (ion-pair): alkyltrimethylammonium alkylcarboxylate,
$[R_1\text{-}N\text{-}(CH_3)_3^+]\ [R_2\text{-}COO^-]$

4.2. Oil-water IFT and critical micelle concentration (CMC)

Surfactants will accumulate at the oil-water interface and orient the charged head-groups towards the water phase and the hydrophobic hydrocarbon towards the oil phase. IFT between refined oils and water is typically in the range from 35-60 mN/m. These values can be lowered significantly by addition of surfactants, and ultra-low oil-water IFT values down to about $1\text{x}10^{-3}$ mN/m have been reported after addition of surfactants (Foster, 1973; Milter and Austad, 1996b; Wilson and Brander, 1977). Separate surfactant molecules in solution are often referred to as monomers. When increasing the monomer concentration the surfactant molecules will spontaneously aggregate into larger aggregates called micelles at some special concentration called the critical micelle concentration (CMC). If the concentration of the surfactant is not too high, the micelle aggregates will have a spherical shape (Hiemenz and Rajagopalan, 1997) where the charged head of the molecule will point out towards the water phase and the hydrophobic ends will create a hydrophobic environment in the inner of the micelle. **Figure 4-1** shows a sphere micelle **(a)** and a cylindrical micelle **(b)**, respectively. The latter one can be created at higher surfactant concentrations.

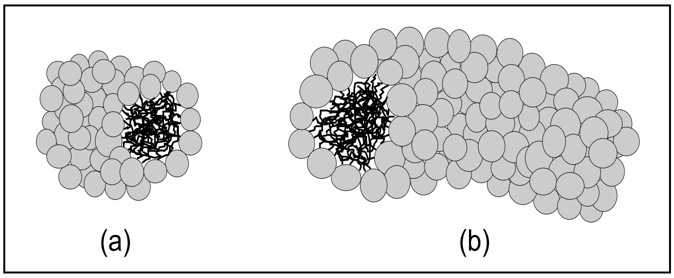


Figure 4-1. Micelles with different structures. **(a)** Spherical micelle, **(b)** Cylindrical micelle.

The monomer concentration stays almost constant above CMC, and addition of more surfactant will only increase the number of micelles or the size of preexisting micelles (aggregation number). For this reason, there is a sharp abrupt in many physical properties for solutions when passing through the CMC. Electric conductivity and oil-water IFT, shown on **Figure 4-2**, will level off and stay almost constant above CMC, because the number of monomers contributing to the conductivity and the packing density at the oil/water interface are almost the same above the CMC.

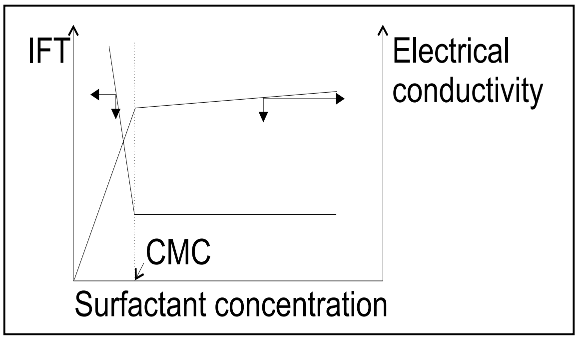


Figure 4-2. Change in physical properties for surfactant solutions exceeding the CMC. Oil-water IFT and electrical conductivity on the left and the right axis, respectively.

For ionic surfactants, the formation of micelles is usually an exothermic process, and CMC will therefore increase with increasing temperature (Zana, 1990). The opposite trend is usually the case for non-ionic surfactants (Evans and Wennerström, 1994). The CMC for a given surfactant is also depending on salinity of the water phase and the presence of other polar or surface-active molecules (co-surfactants). The effect on CMC from addition of salt is largest for ionic surfactants. Ions with opposite charge of the head-group are able to screen the electric repulsion between head-groups in the micelles and thereby lower the electrical barrier towards micelles formation. The result is a lowering in the CMC-value with increasing salt content. The same effect will also cause a closer packing of surfactant molecules at the oil-water interface, implying a decrease in oil-water IFT with increasing salinity. CMC also decreases with increasing hydrocarbon chain length for surfactants containing the same hydrophilic head-group (Mørk, 1997).

It is important to notice that catanionic surfactant mixtures show large synergistic effects on certain parameters compared to those of the individual surfactants from which the mixture is created. Reduced oil-water IFT and much lower CMC-values can occur in diluted solutions of these surfactants (Holland and Rubingh, 1991; Khan and Marques, 1997; Rosen, 1986).

4.3. Phase behavior

Solutions containing micelles have the ability to solubilize oil components in the interior of the micelles due to the hydrophobic environment. Micelles including more than one type of molecules are called ***mixed micelles***. The capacity for a given surfactant to solubilize organic components into the micelles is depending on surfactant concentration and factors promoting micelle formation (Rosen, 1989). Higher concentration of micelles will increase the capacity to solubilize organic material into the micelles. Addition of salt to ionic surfactants will lower CMC and likewise increase the solubility of solubilizates. Contrary, an increase in temperature usually increases the CMC and less material can be solubilized into the micelles. When mixing an aqueous phase containing surfactant with a concentration above the CMC together with an oil phase, several different scenarios can take place:

- The surfactant stays mainly in the water phase and oil is solubilized into the micelles. An oil-in-water microemulsion together with an excess oil phase exists at equilibrium. Such systems are called ***Type II(-)***
- Most of the surfactant can partition into the oil phase and solubilize water into the inverted micelles in the oil phase. A water-in-oil microemulsion together with an excess water phase exists at equilibrium. Such systems are called ***Type II(+)***
- The surfactant stays mainly in a surfactant rich middle phase, where both oil and water are assumed to be continuous (bicontinuous). The middle phase is in equilibrium with both excess water and oil. Such systems are called ***Type III***

The three systems are illustrated in **Figure 4-3**. A II(-) system is showed to the left in **(a)**, type III system in the middle **(b)** and type II(+) to the right **(c)**. Water-soluble surfactants are the most frequently used in connection with EOR, and all systems including surfactants are of type II(-) in this thesis.

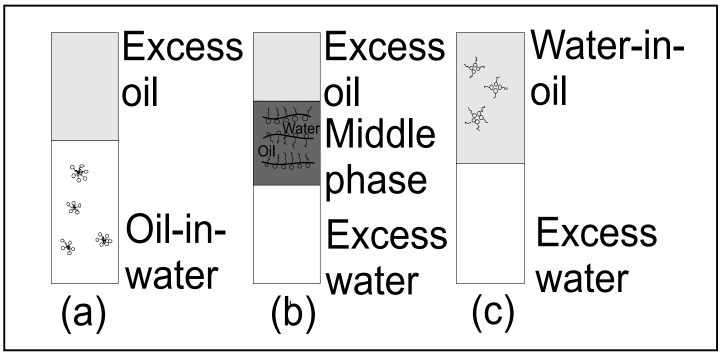


Figure 4-3. Phase systems generated upon mixing oil, water and surfactant. **(a)** Type II(-) system. **(b)** Type III system. **(c)** Type II(+) system. Redrawn after Veggeland and Lohne (1992).

4.4. Partitioning of surfactants into the oil phase as catanionic mixtures or ion-pairs

4.4.1. Partitioning coefficient

Some of the surfactant molecules can pass the oil-water interface and transfer to the oil phase in a II(-) system. There will be established a distribution of the surfactant between the oil- and the water phase, and the relative amount of the surfactant in each phase can be characterized by the partitioning coefficient, K. For a complex crude oil-brine system, a surfactant added to the system may be involved in different equilibriums (associations, etc.) in the two phases. The total amount of the surfactant in the water phase was analyzed during experimental work, and the partitioning coefficient is therefore defined as the total concentration of the surfactant in the oil phase divided by the total concentration of the surfactant in the water phase. Thus,

$$K = \frac{c_{\text{oilphase}}}{c_{\text{waterphase}}} \qquad [4\text{-}1]$$

c_{oilphase}: Total concentration of the surfactant in the oil phase, (mole/l)
$c_{\text{waterphase}}$: Total concentration of the surfactant in the water phase, (mole/l)

4.4.2. Ion-pair (catanionic mixtures) formation

Cationic- and anionic surfactants in mixture are able to interact strongly and create ion-pairs or catanionic surfactants (Caria and Khan, 1996; Jokela *et al.*, 1987; Karlsson, 2001; Khan and Marques, 1997). Electrostatic attraction is the main driving forces for creation of ion-pairs, but hydrophobic association has also been shown to be important, especially for surfactant ions having large hydrophobic groups (Mukhayer and Davis, 1975; Smith *et al.*, 1989). Ion-pairs will usually precipitate in water due to low solubility and they are likely to transfer to an oleic phase if it is available. This technique has been widely applied in chemical analysis like two-phase titration (Cross, 1994) and ion-pair chromatography (Eksborg *et al.*, 1973). Ion-pair formation can be illustrated by the equation (Eksborg *et al.*, 1973):

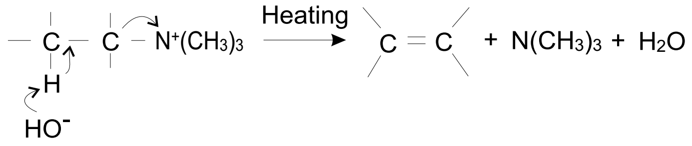
$$Q^+_{aq} + X^-_{aq} \leftrightarrow QX_{org} \qquad [4\text{-}2]$$

Q_{aq}^+: Cation in the water phase
X_{aq}^-: Negative counter ion in the water phase
QX_{org}: Ion-pair/catanionic mixture in the organic phase

The degree of partitioning into the oil phase is strongly depending on the ion-pair and the composition of the oil phase. Increased polarity of the oil phase is expected to increase the partitioning coefficient K (Eksborg *et al.*, 1973).

4.5. Chemical stability of cationic surfactants

Chemical degradation of surfactants can be a problem in high-temperature high salinity reservoirs (Bavière, 1989). Quaternary ammonium salts have in general high salt tolerance, but ammonium hydroxides have been shown to be unstable and undergo chemical degradation at temperatures in the 100-200 °C range. The degradation reaction is an example of Hofmann elimination reaction (Laue and Plagens, 1998):



[4-3]

In a neutral solution, however, the cationic surfactant is probably quite stable well above 100 °C for a long time.

Part 3 Experimental

Chapter 5. Apparatus, equipment and chemical analysis

5.1. Apparatus for measuring fluid- and interfacial properties

Density of the fluids was measured with Anton Paar DMA 4500 Density Meter and viscosities with Paar Physica UDS 200 METER. pH of aqueous solutions was measured using pHM 92 LAB pH METER. Oil-water IFT was determined with Du Nouy ring-tensiometer (Strand, 1996), whereas the spinning drop technique was used when measuring low IFT-values between oil and aqueous surfactant solutions. The oil-water IFT was also evaluated qualitatively as a function of temperature using the pendant drop technique (P VI; S 3.2.).

Asphaltenes in the crude oils were precipitated with excess of heptane (ratio 1:40 by volume) and determined by weight (P I). The oil companies providing the samples gave the wax-formation temperature for the different crude oils and West Lab Services AS determined acid- and base numbers according to the ASTM D-664 standard.

5.2. Core-flooding equipment

All core-floods connected to core preparation were performed using a Hassler coreholder and a Gilson High Performance Liquid Chromatography (HPLC) pump, except for some of the dolomite core tests, where gas was used to displace the oil through the core. The oil-floods were usually performed with a differential pressure of 23 bar over the core, and an overburden

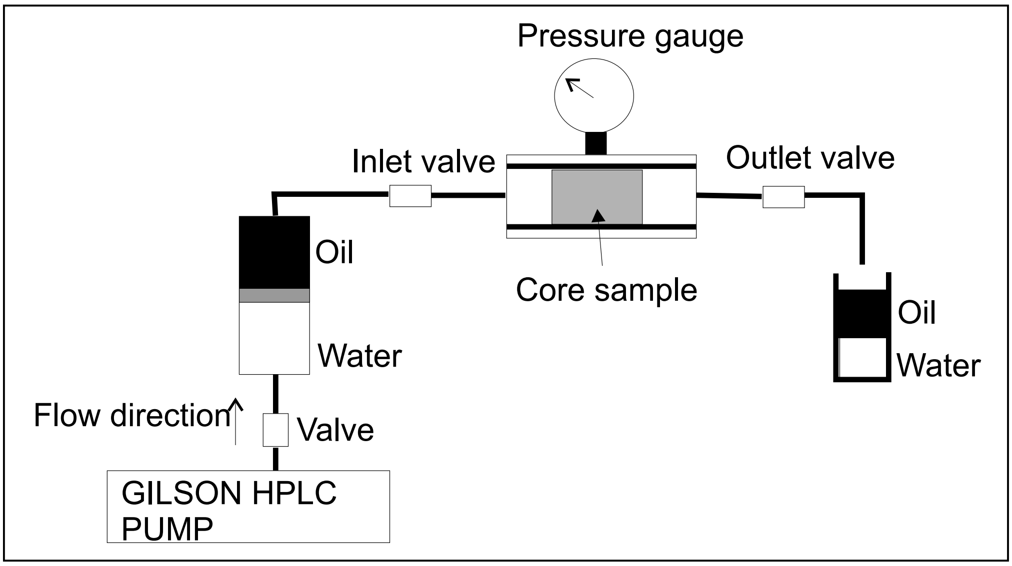


Figure 5-1. Experimental equipment and setup for preparation of cores for SI tests.

pressure not exceeding 33 bar. More detailed descriptions of the flooding procedures are given in the different papers. The experimental setup for the flooding procedure is shown in **Figure 5-1**.

5.3. SI test equipment

All low-temperature (≤ 70 °C) SI tests were conducted in standard Amott cells, whereas high-temperature tests (> 70 °C) were conducted in closed pressure bottles of metal. Short cores (5-6 cm long) were placed in a vertical position in the Amott cell/pressure bottle and surrounded by 350 and 70 ml of imbibition fluid, respectively. Long composite chalk cores (21-27 cm long) were stored in a rack, which was placed into a long Amott cell. The composite core was surrounded by approximately 500 ml liquid. **Figure 5-2 (a)** shows a picture of a short Amott cell containing a short chalk core and the rack used for long composite cores is shown in **Figure 5-2 (b)** together with a chalk core. More detailed information about temperatures and test procedures are given in the actual paper.

(a) (b)

Figure 5-2. **(a)** SI test in a short Amott cell. **(b)** Rack for mounting long composite cores from several short cores placed on top of each other, together with a chalk core.

5.4. Surfactant partitioning experiments

Partitioning experiments were performed by equilibrating equal volumes of the oil- and the water phase. Fatty acids were dissolved in the oil phase and the surfactants in the water phase, before bringing the two fluids together in a separatory funnel. pH was adjusted by adding small amounts of HCl or NaOH. The total amount of surfactants in the water phase was determined by two-phase titration, and the amount present in the oil phase was determined by material balance. The partitioning experiments were always performed with equal volumes of oil and water, so the partitioning coefficient K of the surfactant could be expressed as (SS 4.4.1.):

$$K = \frac{c_{\text{oilphase}}}{c_{\text{waterphase}}} = \frac{n_{\text{oilphase}}}{n_{\text{waterphase}}} \qquad [5\text{-}1]$$

$c_{\text{waterphase}}$: Total concentration of the surfactant in the water phase, (mole/l)
c_{oilphase}: Total concentration of the surfactant in the oil phase, (mole/l)
$n_{\text{waterphase}}$: Total number of surfactants in the water phase, (mole)
n_{oilphase}: Total number of surfactants in the oil phase, (mole)

5.5. Chemicals and chemical analysis

5.5.1. Chemicals

Synthetic brines were prepared from distilled water and chemicals of P.A. grade. The chemical formulas and abbreviations used in the text for the different surfactants are shown in **Table 5-1**.

Table 5-1. Surfactants and their abbreviations used in the experimental work.

Surfactants	Abbreviation
Cationic surfactants	
n-C_8-$N(CH_3)_3Br$	C8TAB
n-C_{10}-$N(CH_3)_3Br$	C10TAB
n-C_{12}-$N(CH_3)_3Br$	C12TAB
n-C_{14}-$N(CH_3)_3Br$	C14TAB
n-C_{16}-$N(CH_3)_3Br$	C16TAB
n-C_8-Ph-$(C_2H_4O)_2$-$N(CH_3)_2(CH_2$-Ph)Cl	Hyamine
n-(C_8-C_{18})-$N(CH_3)_2(CH_2$-Ph)Cl	ADMBACl
n-C_{12}-NH_2	C12-amine
n-C_{10}-NH_2	C10-amine
n-C_{12}-$N(CH_3)_3Cl$, n-C_{14}-$N(CH_3)_3Cl$	Arquad (Arquad MC-50)
n-C_{12}-$N(CH_3)_3Cl$, n-C_{14}-$N(CH_3)_3Cl$, n-C_{16}-$N(CH_3)_3Cl$, n-C_{18}-$N(CH_3)_3Cl$	Dodigen (Dodigen 5462)
Anionic surfactants	
n-(C_{12}-C_{15})-$(C_2H_4O)_{15}$-SO_3Na	S-150
n-C_{13}-$(C_2H_4O)_8$-SO_3Na	B 1317
n-C_8-$(C_2H_4O)_3$-SO_3Na	S-74
n-(C_{12}-C_{15})-$(C_3H_6O)_4$-$(C_2H_4O)_2$-OSO_3Na	APES
(n-$C_8O_2CCH_2$)(n-C_8O_2C)CH-SO_3Na	Cropol
n-C_8-$(C_2H_4O)_8$-OCH_2-COONa	Akypo
n-C_9-Ph-$(C_2H_4O)_x$-PO_3Na	Gafac
n-C_{12}-OSO_3Na	SDS
Non-ionic surfactant	
$C_{9\text{-}11}$-$(C_2H_4O)_8OH$	EA

5.5.2. Quantitative analysis

Determination of calcium

West Lab Services AS analyzed the calcium content in the water phase by the Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) technique (P VI). The relative uncertainty was ± 10 %.

Determination of cationic surfactants

The total amount of cationic surfactants in the water phase during imbibition- and partitioning experiments was determined by the two-phase titration technique using the anionic surfactant, sodium dodecylsulfate (SDS), as described by Cross (1994).

Chapter 6. Porous media and fluid systems

6.1. Porous media and fluid systems

6.1.1. Porous media

All minerals containing the anion, CO_3^{2-}, are classified as carbonates. The most common carbonate minerals are shown in **Figure 6-1**.

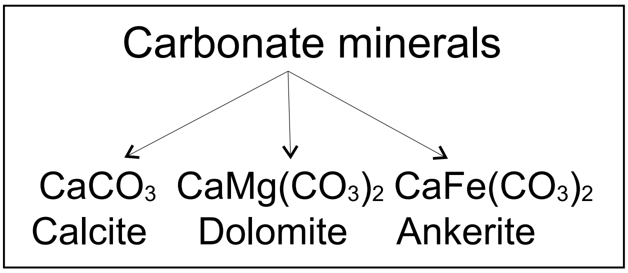


Figure 6-1. The most commonly carbonate minerals.

Sedimentary rocks containing more than 50 % of carbonate minerals are defined as carbonate rock. Furthermore, limestone (chalk) is most commonly defined as the sedimentary rock containing more than 50 % of the mineral $CaCO_3$, whereas dolomite is the sedimentary rock containing more than 50 % of the mineral dolomite (Mazzullo *et al.*, 1992), **Figure 6-2**. SI tests have been performed on both chalk and dolomite cores in this work.

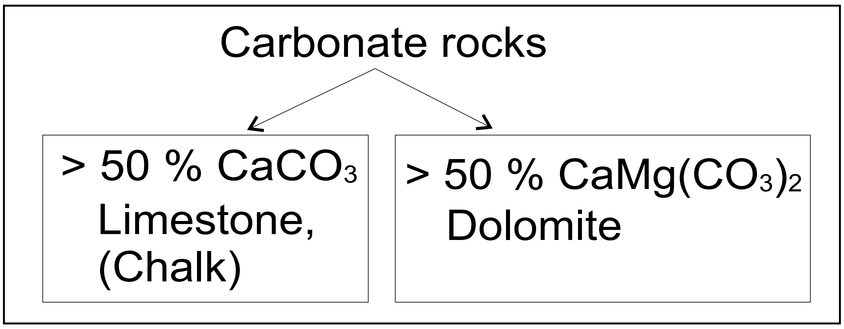


Figure 6-2. Classification of carbonate rocks according to Mazzullo *et al.* (1992).

Chalk

Chalk is a shallow-marine limestone, deposited by calcareous skeletal debris material originating from unicellular planktonic algae called coccolithophorid algae. The building blocks of these skeletons are calcite tablets or platelets with a typical diameter of 0.5 to 1 μm. The platelets are arranged in rings and rosettes known as coccoliths (3-15 μm across). The coccoliths can further combine into spheres called coccospheres (Kennedy, 1985), **Figure 6-3**.

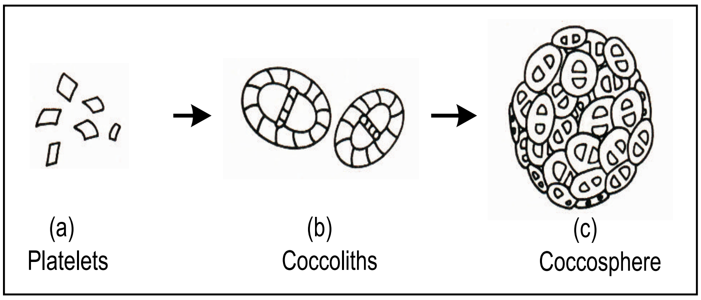
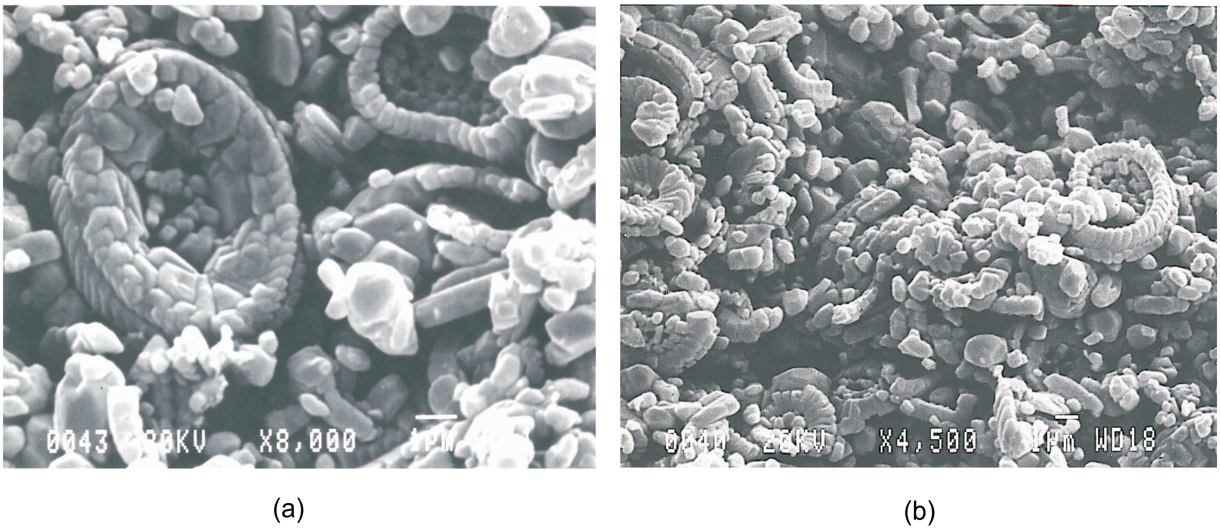


Figure 6-3. Platelets **(a)**, coccoliths **(b)** and coccosphere **(c)** are the building blocks of the chalk in the Ekofisk field. After Schatzinger *et al.* (1985).

Figure 6-4 shows a Scanning Electron Microscope (SEM) picture of a chalk sample from Stevns Klint, nearby Copenhagen, Denmark. Figure **(a)** has a magnification of 8,000X. Coccoliths can be seen in the middle and in the upper right corner. Figure **(b)** shows mainly platelets but coccolith fragments can be seen to the left and the right side. The magnification on this picture is 4,500X.



(a)

(b)

Figure 6-4. SEM pictures of Stevns Klint chalk. The picture to the left **(a)** is an 8,000X magnification. Coccoliths can clearly been seen in the middle and on the right side. The picture to the right **(b)** is magnified 4,500X. This picture shows mainly platelets, but coccoliths are also present to the right and to the left on this picture.

The Stevns chalk is a soft and highly porous material of Maastrichtian age. It is mainly composed (96 %) of a fine-graded coccolithic matrix, whereas larger bioclasts (mostly uncemented foraminifera) constitute the remaining part of the rock (Milter, 1996). The chalk has high porosity, up to 50 %, where most of the void volume originates from micro-interparticle pores between the skeletal of the coccoliths constituents. The microscopic size of the building blocks, the coccospheres and the coccoliths, causes matrix permeability in the range from 0.1-10 mD. The Stevns Klint chalk has a specific area of about 2 m^2/g as determined by the Braunauer-Emmett-Teller (BET) isotherm (Hiemenz and Rajagopalan, 1997). The pore throat size distribution is unimodal with a peak at approximately 0.4 μm, and a mean value of 0.5 μm as shown on **Figure 6-5**. The AR was estimated to about 3 (Milter, 1996) and the chalk was expected to be similar to the reservoir chalk in the Ekofisk field in the North Sea (Frykman, 1994).

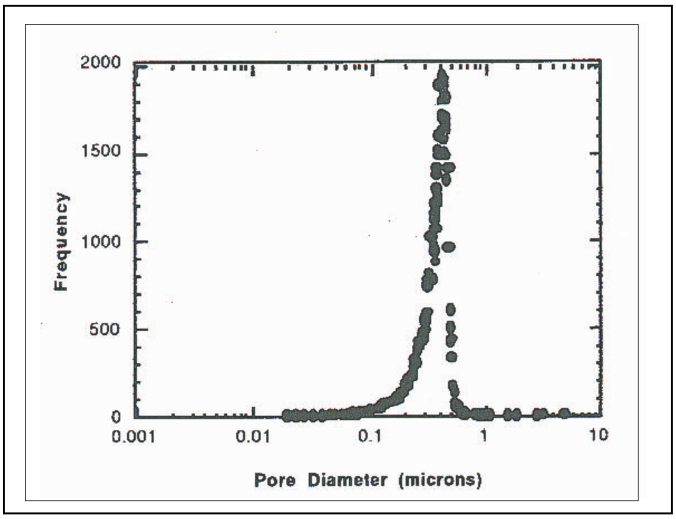


Figure 6-5. Pore size distribution in Stevns Klint chalk determined by mercury injection capillary pressure curve. Mean pore throat size is 0.5 μm. After Milter (1996).

The Ekofisk field in the North Sea is a highly fractured chalk reservoir, which has been waterflooded with great success since 1981 (Thomas *et al.*, 1987). The water is expected to imbibe spontaneously into the water-wet matrix blocks and expel the oil to the fracture system. However, laboratory investigations from the upper part of the field indicated that the reservoir rock was much less water-wet in this area. The decrease in water-wetness was believed to be due to an organic coating on the reservoir rock (Torsaeter, 1984).

This study was initiated with the purpose of investigating the potential for EOR from oil-wet low-permeability chalk, similar to the chalk type in the Ekofisk area. However, later investigation of the Upper Ekofisk formation has shown that water imbibes in a satisfactory way into this part of the field also, despite the decrease in water-wetness. Therefore, the EOR method investigated in this thesis does not seems like an actual way to enhance oil recovery from the Norwegian sector of the North Sea for the time being, since the Ekofisk field together with Valhall are the only two carbonate fields in this area. However, the potential for the method to enhance oil recovery from carbonate fields in general should be significant, because approximately 40 % of the oil production on world basis has its origin from carbonate reservoirs (Bjørlykke, 1984).

Dolomite

Carbonate rock with more than 50 % $CaMg(CO_3)_2$ is classified as dolomite, **Figure 6-2**. The dolomite cores tested in this work were from the San Andres formation in Texas and the carbonate in this formation is believed to have been mostly limestone at the time of karstification (Craig, 1988). The cores showed great differences in both properties and pore structure, **Figure 6-6 (a)** and **(b)**, which is likely to induce different wettabilities when exposed to crude oil (Hamon, 2000). Permeability varied between 22 to 352 mD and porosity between 14-30 %. One type of the cores appeared very heterogeneous with big holes and vugs in the pore structure, whereas the others appeared more homogenous with a sugary texture. Cores having more than 25 % of the total pore volume due to vugs (P IV), were classified as moldic and the others as sucrosic (Nogaret, 2000).


(a) **(b)**

Figure 6-6. Carbonate cores with different pore structure. The left picture **(a)** shows a homogeneous core with sugary texture called sucrosic, whereas the right picture **(b)** shows a heterogeneous core classified as moldic with big holes and vugs in the matrix.

6.1.2. Fluid systems

Synthetic high-salinity brine composed of 2/3 seawater (injection-water) and 1/3 formation-water (Thiebot *et al.*, 1990) was used in the SI tests using chalk (Brine 2, **Table 6-1**). The composition was therefore quite similar to the in situ brine composition during a water-injection process. Total dissolved solid (TDS) in Brine 2 was 44.9 g/l and pH, density and viscosity at 40 °C were 8.0, 1.02 g/cm^3 and 0.8 cP, respectively. The brine used in the tests with the dolomite reservoir cores (Brine 1, **Table 6-1**) was a low-salinity reservoir brine containing TDS of 9.25 g/l. pH and density at 20 °C was 5.9 and 1.0059 g/cm^3, respectively.

The composition of the two brines is given in **Table 6-1**. In addition, some other brine compositions were used in P III.

Table 6-1. Composition of the aqueous phases.

	Brine 1	**Brine 2**
Ion composition	**Concentration, (g/l)**	**Concentration, (g/l)**
Na^+	2.36	12.14
K^+	-	0.25
Ca^{2+}	0.80	3.43
Mg^{2+}	0.24	0.93
Sr^{2+}	0.02	-
Cl^-	5.67	26.54
SO_4^{2-}	0.16	1.56
HCO_3^-	-	0.09
Total dissolved solid (TDS)	9.25	44.94

The oil companies British Petroleum, Phillips Petroleum Company and Den Norske Stats Oljeselskap (Statoil) provided the crude oils used. The different oils are listed in **Table 6-2** and the oil properties are shown in **Table 6-3**.

Table 6-2. Pretreatment of the crude oils before used in spontaneous imbibition tests.

Oil	**Supply and pretreatment**
A	Pure n-heptane
B	Ekofisk stock tank oil filtered through 3-μ filter. No n-heptane added
C	Oil from BP. Diluted 1:1 with n-heptane
D	Asphaltenic oil. Diluted 1:1 with n-heptane
E [a]	Oil from Statoil. Diluted 70:30 crude oil: n-heptane
F [a]	Oil from Statoil. Diluted 60:40 crude oil:n-heptane
G	Oil from carbonate reservoir in west Texas. No n-heptane added

[a] Different initial crude oils.

Table 6-3. Properties of the crude oils used.

Oil	**Density [a] at 20 °C, (g/cm^3)**	**°API**	**AN [b], (mg KOH/g oil)**	**BN [b], (mg KOH/g oil)**	**Wax-form. temp.[b], (°C)**	**Asphaltenes [a], (wt. %)**	**Oil-Brine 2 IFT at 20 °C, (mN/m)**
A	0.684	75.3	-	-	-	-	55.4
B	0.835	38.0	0.12	Trace	29	0.90	19.8
C	0.815	42.1	0.52	Trace	53	0.33	20.3
D	0.798	45.8	0.055	Trace	33	2.57	28.1
E	0.846	35.8	0.41	Trace	22	0.19	15.7
F	0.816	41.9	1.73	Trace	25-30	0.23	15.4
G	0.874	30.4	≈ 1.0	unknown	unknown	unknown	11.1 [c]

[a] Measured on actual crude oils, [c] Brine 1

[b] Measured on initial crude oils before dilution with n-heptane

Chapter 7. Core restoration, wettability measurements and evaluation of flow modes

7.1. Procedure for altering the wettability of chalk- and dolomite cores

Restored outcrop chalk samples (Anderson, 1986a; Cuiec, 1977, 1991; Morrow, 1990; Wendel *et al.*, 1985; Wunderlich, 1991) were used in this study. The purpose was not to reproduce the wettability state related to some special field, but rather to make the core material as oil-wet as possible to establish the baseline for the EOR investigations. Oil F was used to alter the wettability of the chalk cores, whereas both oil F and oil G were used on the dolomite cores. The following procedures were used to restore the core samples:

7.1.1. Chalk cores with 100 % oil saturation

The dry weight of the cores was noted before saturating the cores with crude oil under vacuum. Porosity was calculated from weight difference and bulk volume. The cores were then flooded in a Hassler coreholder with 1.0 and 1.5 pore volume (PV) crude oil in each direction, before aging in closed containers surrounded by crude oil for 4 days at 50 °C. 2 mm. of the outermost layer of the cores were shaved off in a lathe just prior to the SI tests to avoid boundary effects.

7.1.2. Cores with initial water saturation (S_{wi})

After saturating the cores with brine under vacuum, the cores were flooded in a Hassler coreholder with 1.5 and 1.0 PV crude oil in each direction. The chalk cores were aged in closed containers surrounded by crude oil for 1 month at 90 °C. The dolomite cores were aged in crude oil for 3 weeks at 50 °C.

2 mm. of the outermost layer of the chalk cores were shaved off in a lathe just prior to the SI tests to avoid boundary effects. This procedure was not performed on the dolomite cores, due to a limited number of these cores.

7.2. Methods for measuring wettability

Three different methods were used to evaluate the wettability of the porous medium:

- The Amott-Harvey method (Anderson, 1986b) was applied to quantify the wettability state of an original oil-wet core after C12TAB imbibition (P II; SS 2.4.1.)
- Contact angle measurements were performed on calcite crystals pre-exposed to either crude oil or model oil containing fatty acids. The purpose was to evaluating the ability for different surfactants solutions to modify the wettability of the porous medium. The

contact angles were estimated from pictures of water droplets placed on the crystals (Johnson and Dettre, 1969; Neumann and Good, 1979; P II), and the repeatability of the measurements was approximately ± 4°. The contact angle measurements were not meant to represent wettability under reservoir conditions, but they were used as a rough method to evaluate the potential for different surfactants to modify carbonate surfaces covered by surface-active components (SS 2.4.1.). Calcite crystals originally from Chihuahua, Mexico and Poona, India where provided by J. Bromeland & Co.

- The rate and amount of brine imbibed by SI (SS 2.4.2.) was used to differ between oil-wet and weakly water-wet cores. The porous medium was characterized as oil-wet if no SI of water took place (Anderson, 1986b)

7.3. Evaluation of the influence of capillary- vs. gravity forces during SI tests

The relative influence of gravity- and capillary forces, i.e., the flow mode during the SI tests was evaluated in four different ways:

- By observing the residual oil saturation profile inside the core. These observations were performed by cutting the cores along the core axis
- By visual location of the oil expelled from the core surface (top- and lateral) during the imbibition tests
- By the shape and the UR level from the SI curves
- By calculations of N_B^{-1}-values from Eq. 3-4 (SS 3.3.1.)

7.3.1. Residual oil saturation profile inside the porous medium

Cutting the cores and observing the residual oil saturation inside the porous medium gave the most valuable information about the oil expulsion mechanism. **Figure 7-1** shows a typical example of a core where water has imbibed from all surfaces and expelled the oil in a counter-current flow mode driven by capillary forces.

Figure 7-1. Residual oil saturation profile inside an originally oil-wet chalk core. The core has been imbibed spontaneously by a 1.0 wt.% solution of C12TAB. The saturation profile shows that the surfactant solution has imbibed by means of capillary forces.

Figure 7-2 shows an oil-wet core, which has been imbibed by a surfactant solution at rather low oil-water IFT. The residual oil saturation profile points toward an oil expulsion mechanism mostly driven by gravity forces (SS 3.3.1.).

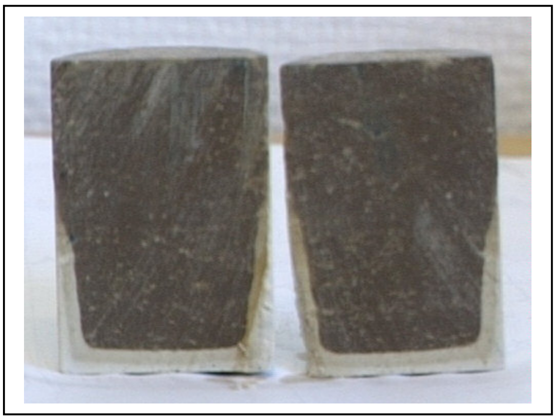


Figure 7-2. Residual oil saturation profile inside a chalk core imbibed at low oil-water IFT. The conic shape of the residual oil saturation profile shows that the surfactant solution has imbibed mainly by gravity forces (P II).

Unfortunately, this method could not be executed with reservoir dolomite cores due to a limited numbers of cores. Visual observation of the location of the expelled oil, shape of the SI curves and calculation of N_B^{-1}-values were used to evaluate the flow mode for these cores.

7.3.2. Visual location of expelled oil

It was shown in Section 3.3.1. that oil production appears as oil droplets from all sides of the core when capillary forces dominate the SI process, whereas oil droplets appeared mainly from the top surface of the core when gravity forces became more pronounced in the oil expulsion mechanism.

7.3.3. Oil expulsion mechanism related to shape of oil production curves

Several authors have observed that SI curves resulting from capillary driven imbibition tend to have a shape, which can be fitted to an exponential expression (Aronofsky *et al.*, 1958; Ma *et al.*, 1997; Reis and Cil, 1993). Reis and Cil (1993) derived the following expression for oil recovery as a function of time:

$$Q_0 = Q_\infty \left[1 - \exp\left\{ \ln\left(\frac{1}{2}\right) t_D \right\} \right] \qquad [7\text{-}1]$$

where,

Q_0: Cumulative oil production, (m^3)
Q_∞: Cumulative oil production after infinite time, (m^3)
t_D: Dimensionless imbibition time, (-)

Eq. 7-1 implies a shape as for the capillary driven imbibition curve shown in **Figure 7-3**.

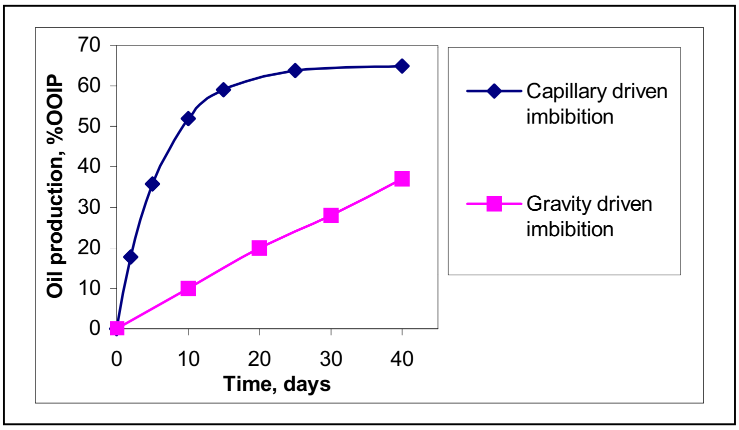


Figure 7-3. Typical shape of oil recovery curves as a function of time for imbibition processes mainly driven by capillary- and gravity forces.

The SI rate is usually lower when gravity forces become more dominate in the oil expulsion process. In the limit where capillary forces become insignificant, water is pushing the oil in a piston like manner and the flow of oil and water is totally co-current, **Figure 3-2 (c)**.

Milter and Austad (1996a) observed a linear relationship between oil recovery and time, which they interpreted as an imbibition driven by gravity forces. The shape of the residual oil inside the core confirmed the interpretation. Typical curve shapes for capillary- and gravity driven imbibition are illustrated schematically in **Figure 7-3**.

Schechter *et al.* (1994) performed tests on sandstone- and limestone cores at different oil-water IFT. **Figure 7-4** shows SI curves into a 45-mD limestone core for oil-water IFTs equal to 38.1, 1.07 and 0.1 mN/m, respectively. **Figure 7-4 (a)** shows the curves for early times whereas **(b)** shows the whole imbibition curves. Capillary forces were dominant at 38.1 mN/m and this curve shows the typical shape for an imbibition driven by capillary forces. Gravity forces were expected to be dominant at 0.1 mN/m, and the oil recovery was almost a linear function of time in this case. In addition, observations collected during the experimental work described in this thesis also points towards a tendency for a linear relationship between oil recovery and time to occur, when oil production is driven mainly by gravity forces (Chapter 10). The shape of the SI curve was therefore used as a qualitative measure of the relative influence of capillary- to gravity forces inside the porous medium.

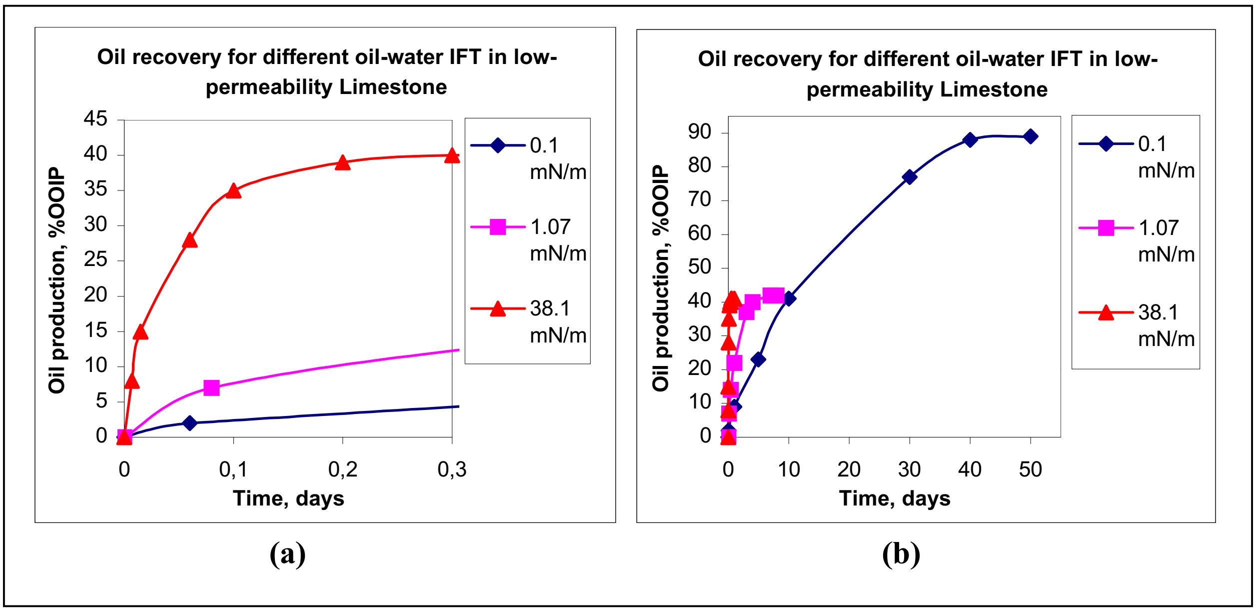


Figure 7-4. Experimental imbibition data from Schechter *et al.* (1994) showing the shape of the imbibition curves when capillary- and gravity forces are dominant. The imbibition curve for a capillary dominated imbibition process can be fitted to an exponential curve; whereas the imbibition curve for gravity dominated imbibition appears to be a linear function of time. **(a)** Imbibition curves for early times and, **(b)** Whole imbibition curves.

7.3.4. Calculation of inverse Bond numbers

It is important to notice that Eq. 3-4 for N_B^{-1} with corresponding cut-off values between the different flow domains, only is valid for systems with well-defined wetting- and non-wetting phases. Eq. 3-4 will overestimate N_B^{-1} when applied to less water-wet or neutral-wet systems. The situation will become even more complex when the imbibing phase contains agents, which are modifying the wettability properties of the rock material during the imbibition process as in this work. However, calculation of N_B^{-1}-values for the conducted SI tests showed that these values, even with the above-mentioned difficulties, could bring additional and useful information about the influence of gravity- and capillary forces. The method gave theoretical funded support to the conclusions drawn from the other tests, thereby helping to get a consistent and more complete picture of the driving forces during the SI experiments.

Part 4 Main results and discussions

This section of the thesis contains the main results from the experimental work obtained during the project. Most of the results are presented earlier in the enclosed papers. The purpose is to present the results in a way showing the connection between each paper and the development of the project.

Chapter 8. Establishing oil-wet core material

8.1. Heterogeneous wettability in outcrop chalk induced by crude oils

8.1.1. Cores with 100 % oil saturation

Outcrop chalk from Stevns Klint is strongly water-wet. This fact was confirmed when performing SI tests on chalk cores 100 % saturated with heptane. As expected, heptane did not influenced on the wettability of the chalk cores. **Figure 8-1** shows the oil recovery due to SI of brine into two chalk cores. The SI was fast and an UR of 72 % of OOIP was reached within 30 minutes and the curves showed excellent reproducibility.

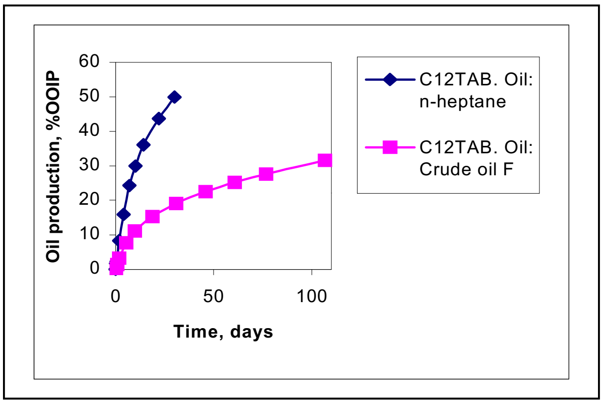


Figure 8-1. SI of Brine 2 into Stevns Klint chalk saturated 100 % with heptane at 26 °C.

Crude oil was used to alter the wettability of the water-wet chalk material to mimic the components adsorbed onto the reservoir rock in a real oil reservoir (Graue *et al.*, 1994, 1998; Graue and Bognø, 1999; Jadhunandan and Morrow, 1991; Jia *et al.*, 1991; S 2.2.; Xie and Morrow, 2000; Zhou *et al.*, 1993, 2000b). To interpret the results from SI tests correctly, it is very important that the wettability of the core material is homogenous. When saturating dry chalk cores with crude oil using vacuum, it was discovered that the adsorption of surface-active components took place in a non-uniform way. **Figure 8-2** shows the SI curve for a core prepared by just sucking the oil into the evacuated core. More than 500 minutes was required to initiate brine imbibition. Only 3.4 % of OOIP was produced after 1 day before the imbibition rate increased dramatically and approximately 47 % of OOIP was produced during the next 3 days. ***The shape of the SI curve was interpreted as an effect of a wettability gradient inside the core material***. The time delay before the imbibition initiated was expected to be due to higher adsorption of surface-active material at the boundary of the core. Increased water-wetness inside the core implied faster imbibition at a later stage in the imbibition process in line with the experimental observation. The oil-wet layer at the boundary was assumed to originate from a fast adsorption of surface-active components when the oil was sucked into the core during the saturation procedure in addition to continuous adsorption of surface-active components at the boundary during the aging process.

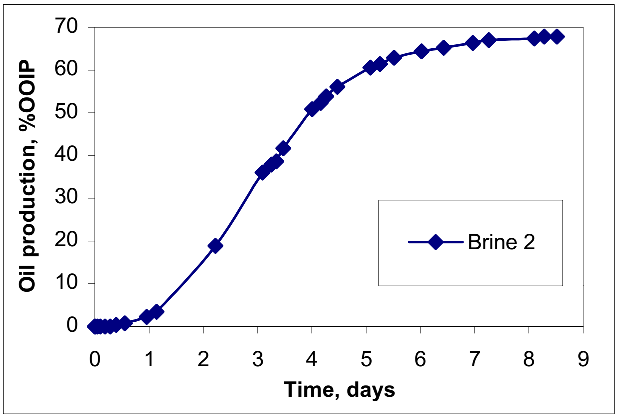


Figure 8-2. SI curve for chalk core saturated with crude oil in vacuum at 40 °C. The long initial SI delay time was assumed to be due to a wettability gradient at the outermost layer as resulting from the saturation- and the aging process.

The first assumption was confirmed when cleaving the core after saturating in vacuum. **Figure 8-3** indicates that there have been created a wettability gradient during the saturation process. The oil wettability was most pronounced at the boundary and the water-wetness increased towards the center.

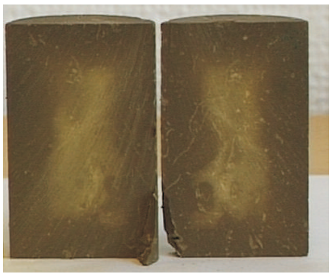


Figure 8-3. Chalk core saturated with crude oil using vacuum without flooding the core. The lighter areas in the middle of the core clearly show that there have been created a gradient in the adsorption of surface-active components as the crude oil flowed into the core.

Increased oil-wetness at the outermost layer was furthermore confirmed by submerging an oil-saturated core cut in different cross sections in brine. The brine imbibed into areas where the outermost layer had been removed and oil was expelled from the non-treated less water-wet areas, **Figure 8-4**.

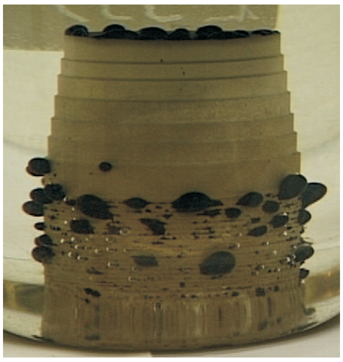


Figure 8-4. Core saturated with crude oil and cut in different cross-sections. Water imbibed in the more water-wet areas where the outermost layer had been removed, whereas oil was expelled from the less water-wet non-treated areas.

The experimental results in this section show that it is necessary to ***oil-flood the cores to obtain homogeneous wettability***, when crude oil is used to induce wettability alterations in outcrop chalk material.

The cores were aged in containers filled with crude oil after saturation in the vacuum chamber and the outermost layer of the cores had access to fresh oil containing surface-active components during the whole aging process. The amount of surface-active components in the pores inside the porous medium was, however, limited by the amount of oil residing in each individual pore. The aging procedure was therefore assumed to contribute to an increased oil-wetness of the outermost layer as well. It was therefore decided to remove a few millimeter of the outermost layer of the core after the aging process prior to the SI tests.

8.1.2. Cores with initial water saturation

Figure 8-5 shows the imbibition curve for a chalk core with initial water saturation prepared as described in SS 7.1.2. Some brine imbibed quickly and about 6 % of OOIP was produced during the first 2 days. The fast initial imbibition was not related to thermal expansion, because a similar effect was not observed for 100 % oil saturated cores at the same temperature. The core seemed to be more water-wet at the outermost layer, even though 2 mm. had been removed prior to the imbibition test. It is likely that the heterogeneous wettability was due to a decrease in oil saturation close to the core surface created when establishing S_{wi}. The recovery rate leveled off after 2 days and only 8.8 % of OOIP was produced within the experimental frame of 55 days. The small oil production of 2.8 % of OOIP between 2 and 55 days shows that the chalk material had become almost oil-wet inside the outermost layer.

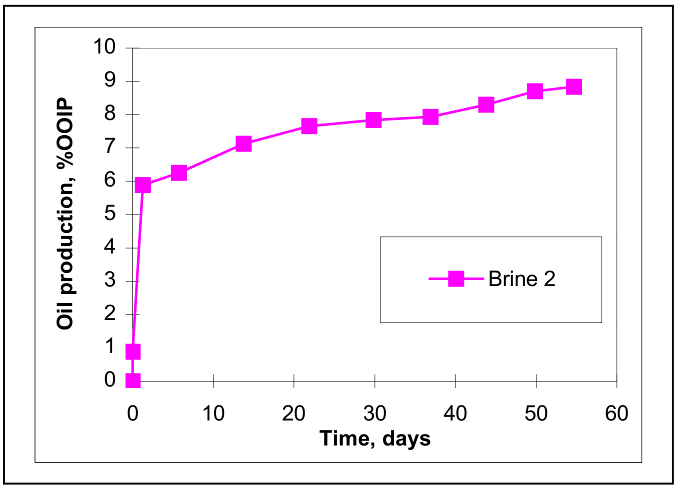


Figure 8-5. SI into chalk core with S_{wi} = 23.0 % aged for 1 month at 90 °C at 40 °C. The core behaved nearly oil-wet after a rapid imbibition of water during the first 2 days.

The results presented in this section show that ***care should be taken when using crude oils to alter wettability of core material***. Non-uniform adsorption of surface-active components when treating outcrop chalk cores with crude oil have also been reported by Graue *et al.* (2000) and Spinler *et al.* (1999, 2000a).

8.2. Relation: Acid number of crude oil-chalk wettability

Since the subject of this thesis is an exploration of the potential for EOR from oil-wet carbonate material, the crude oil should alter the wettability of the porous media in an efficient way towards oil-wet conditions, and thereby establish the baseline for the EOR tests. Outcrop chalk cores were saturated 100 % with oil using 6 different crude oils, and the relative wettability of the cores was determined by extent and rate of pure brine imbibition. The results from the tests are shown in **Figure 8-6**. The figure shows that ***the rate of SI decreased with increasing AN of the crude oil*** with an exception for oil C. In this case, however, it was observed that wax precipitated during the imbibition experiment, which influenced the imbibition process (Xie *et al.*, 2000). Similar relationship between wettability and AN has been reported earlier (Anderson, 1986a; Buckley and Liu, 1998; Dubey and Doe, 1993). No correlation could be established between the asphaltene content in the crude oils and the rate of SI (P I).

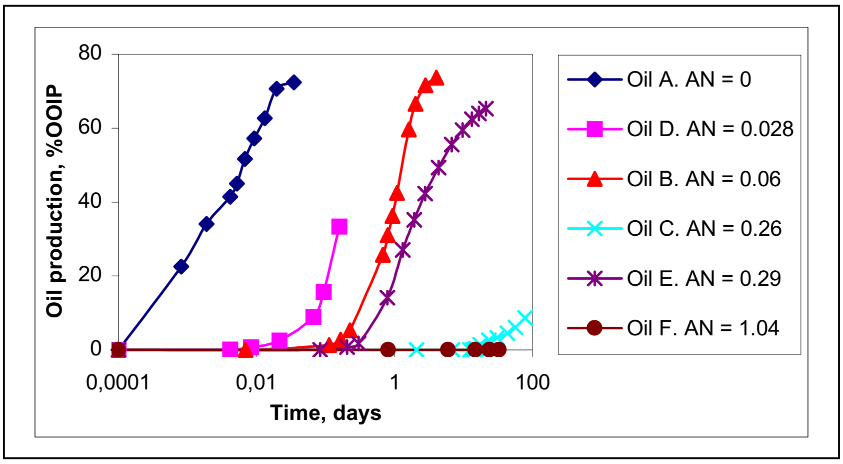


Figure 8-6. SI into chalk cores saturated with crude oils with different AN at 40°C. The rate of SI decreases with increasing AN of the crude oil.

Oil F rendered the chalk cores nearly oil-wet and this oil was therefore used to establish the baseline for the EOR investigations in all subsequent SI tests both with and without initial water, except for some of the dolomite core tests where oil G was used. The wettability alteration observed for the chalk material without S_{wi} was likely to take place by a polar binding mechanism, whereas the G-AB profile predicts acid/base interaction as the most likely mechanism for crude oil F with high AN in the presence of S_{wi} (Buckley and Liu, 1998). Since different adsorption mechanisms were involved depending on whether initial water was present or not, it is likely that both the type and the strengths of the adsorbed material may differ for the two cases. Buckley (1996) observed that components adsorbed by polar binding mechanism, usually were weaklier adsorbed than components adsorbed by mechanisms involving water.

Contact angle were measured through water droplets placed on calcite crystals pre-exposed to heptane containing fatty acids and heptane (SS 2.4.1.). Angles of 70, 90 and 10° were observed for lauric acid, stearic acid and heptane, respectively, as shown in **Figure 8-7**. The measured contact angles showed that carboxylic groups have high affinity for calcite surfaces in line with reported data in the literature (Cuiec, 1977; Madsen and Lind, 1998; P III; S 2.2.; Thomas *et al.*, 1993a, b).

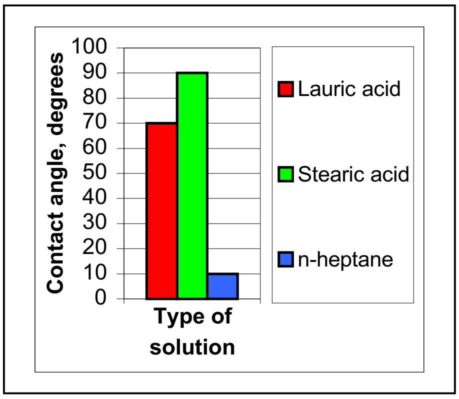


Figure 8-7. Contact angles measured through water droplets placed on calcite crystals exposed to pure heptane and heptane containing lauric- and stearic acid.

Chapter 9. Chemical mechanisms for wettability alteration of chalk from oil-wet to water-wet

9.1. SI of cationic- and anionic surfactants into oil-wet chalk. Imbibition mechanisms

The investigations described in the previous chapter showed that the oil-wetting components are negatively charged and attached to the chalk surface mainly by carboxylic groups. It therefore seems like a reasonable hypothesis that the SI of the cationic surfactant, C12TAB observed by Austad *et al.* (1998), was due to an ***interaction between positively charged surfactant head-groups and negatively charged carboxylic groups***. The surfactant monomers were believed to interact and desorb some organic material under formation of ion-pairs (SS 4.4.2.), thereby altering the wettability of the chalk towards a more water-wet state. Water can then imbibe spontaneously due to a positive capillary pressure (S 3.1.). A consequence of this hypothesis is that there should be a great difference in imbibition behavior when exposing oil-wet chalk to solutions of cationic- and anionic surfactants, because only cationic surfactants should be able to interact electrostatic with negatively charged groups.

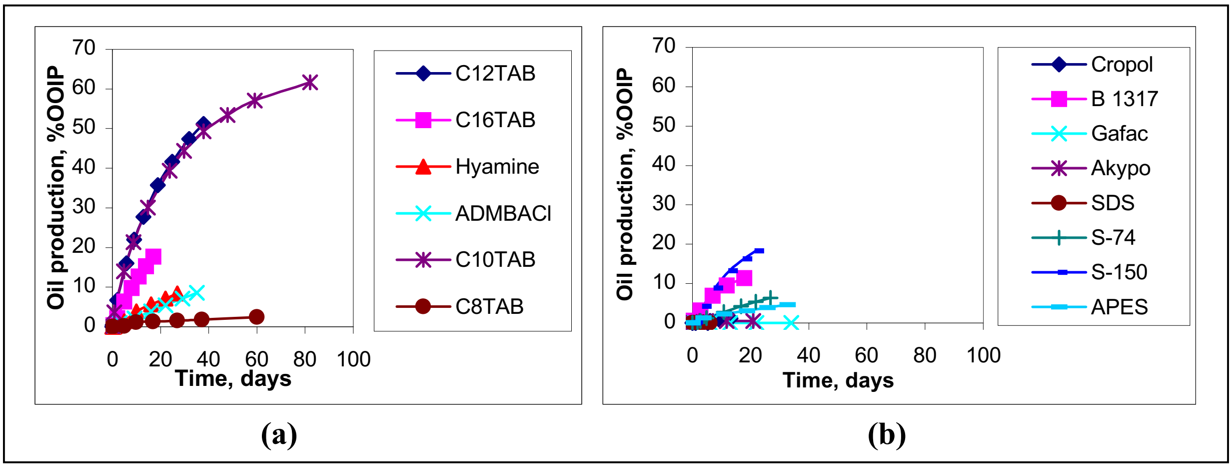


Figure 9-1. Oil recovery by SI of aqueous surfactant solutions into oil-wet chalk material. **(a)** Cationic surfactants, **(b)** Anionic surfactants.

Figure 9-1 (a) and **(b)** show the result from a screening test including 6 cationic- and 8 anionic surfactants. The cationic surfactants were in general more efficient than the anionic surfactants to produce oil. This fact supported and strengthened the hypothesis about an interaction between cationic surfactants and negatively charged organic material on the chalk surface as a key factor for the observed oil production. However, not all cationic surfactants were able to imbibed into the oil-wet cores in an efficient way. C10TAB and C12TAB were the most efficient cationic surfactants followed by C16TAB, while Hyamine, ADMBACl and C8TAB only produced minor amounts of oil at a very slow rate. Other effects than pure electrostatic interaction were therefore expected to be important in the desorption process as well.

Hyamine and ADMBACl are quaternary ammonium salts like C12TAB, but both molecules have two large hydrophobic groups attached to the N-atom (one methyl group is exchanged with a benzyl group, i.e., $-CH_2-Ph$). The poor imbibition response from these surfactants can maybe be related to weaker interaction between the charged centres on the interacting molecules due to repulsive steric forces, hindering the creation of ion-pairs (Smith et al., 1989). C8TAB showed poor response, whereas C10TAB and C12TAB performed quite well. C8TAB has a relatively short hydrophobic chain, and 8 methyl-groups were probably too short to interact efficiently with the hydrophobic surface at the oil-water contact. The hydrocarbon chain seems to require a certain lengths to interact efficiently with the organic material adsorbed into the mineral surface. C16TAB was relatively efficient, but it imbibed significantly slower than C10TAB and C12TAB. Only surfactant monomers are probably able to interact with the negatively charged carboxylic groups on the chalk surface. Thus, the desorption rate must be related to the number of surfactant monomers close to the oil-water-solid contact line. At a surfactant concentration above the CMC, the monomeric concentration will be determined by the CMC-value. Furthermore, the diffusion rate of the surfactant from the bulk phase to the water imbibition front will also be important. The CMC-value for C12TAB is 1.4×10^{-2} M (distilled water) compared to 8×10^{-4} M for C16TAB (Munkerjee and Mysels, 1971). The reason for the slower C16TAB imbibition can be explained by lower monomer concentration for this surfactant compared to C10TAB and C12TAB. Slower diffusion rate (Hiemenz and Rajagopalan, 1997) from the bulk phase to the water imbibition front due to higher molecular weight together with lower oil-water IFT (S 3.1.) may also contribute to slower imbibition rate for C16TAB, even though C16TAB should be more soluble in the organic phase than the other two surfactants.

The hypothesis that a wettability alteration had taken place in the chalk material during C12TAB imbibition was further supported by two other observations. **Figure 9-2** shows a picture of a cleaved core imbibed by C12TAB. The water saturation was about 45 % of PV. The residual oil saturation profile clearly shows that oil has been expelled in a counter-current flow mode driven by capillary forces (SS 3.3.1.). The existence of capillary forces indicated that a wettability alteration had taken place as the C12TAB solution imbibed.

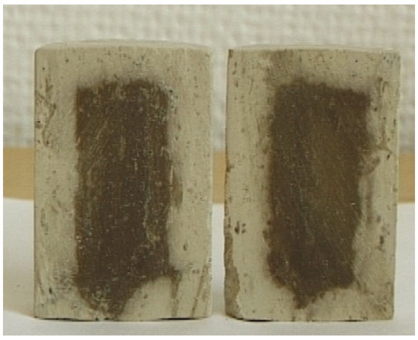


Figure 9-2. Picture of cleaved chalk core imbibed by 1.0 wt.% solution of C12TAB. The water saturation was approximately 45 % of PV.

An Amott-Harvey test (SS 2.4.1.) was performed on an oil-wet core previously imbibed by C12TAB. The surfactant was removed from the core by flooding the core with brine after the C12TAB imbibition was interrupted. The core was then flooded with crude oil and immediately loaded in an Amott cell and surrounded with Brine 2. The brine imbibed spontaneously and the Amott-Harvey RDI was determined to 0.6 (P II), indicating that a wettability alteration had taken place as a result of the previous C12TAB imbibition.

Some of the anionic surfactants also produced oil from the oil-wet chalk cores. The sequence in decreasing efficiency was S-150 > B1317 > S-74 > APES > Cropol. Only minor amount of oil was produced using Akypo, Gafac and SDS. Anionic surfactants cannot interact electrostatic with negatively charged material and no desorption of organic material can take place. However, it was noticed that the most efficient anionic surfactants (S-150, B 1317 and S-74) contained hydrophilic ethoxy-groups (EO-groups) as part of the hydrophilic section. The number of EO-groups decreased in the order 15, 8 and 3, respectively. It was therefore believed that the hydrophobic part of the surfactant was able to interact with the adsorbed organic material on the chalk surface, forming a bilayer with the hydrophilic EO-groups pointing out towards the water-phase. The EO-groups will point out from the surface increasing the water-wetness on top of the bilayer and brine can imbibe spontaneously due to the weak capillary forces created. This hypothesis was supported by the fact that the rate of SI increased with increasing numbers of EO-groups in the surfactant molecules. It should be mentioned that the anionic surfactant Akypo, even though it contained 8 EO-groups, only produced minor amounts of oil. This can again be explained by weak hydrophobic interaction between the short hydrocarbon chain in Akypo (C8) and the organic material on the mineral surface in a similar way as for the C8TAB surfactant.

It was also confirmed that the oil expulsion mechanism for anionic surfactants differed in a fundamental way from that of the cationic surfactants. **Figure 9-3** shows picture of the cleaved cores imbibed by the anionic surfactants, S-150 **(a)** and B 1317 **(b)**. There was no indication of oil production due to gravity segregation inside the cores. Brine seemed to imbibe in certain zones, probably due to weak capillary forces and no uniform imbibition front as for the capillary driven C12TAB imbibition, was observed.

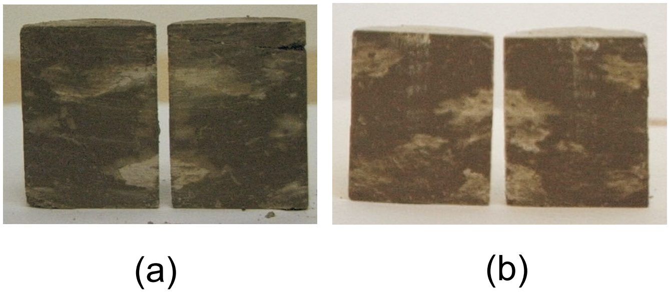


Figure 9-3. Pictures of cleaved chalk cores imbibed by the anionic surfactants from P II. **(a)** S-150 and **(b)** B 1317.

Advancing contact angles measurements on calcite crystals pre-exposed to crude oil followed by surfactant solutions brought further support to the hypothesis that cationic surfactants were more efficient to render chalk surfaces water-wet than anionic surfactants. **Figure 9-4** shows the measured angles for both types of surfactants. Cationic surfactants lowered the contact angles relative to brine significantly more than anionic surfactants. It should be noticed that the concentration of all surfactant solutions was above the respective CMC-values in these experiments.

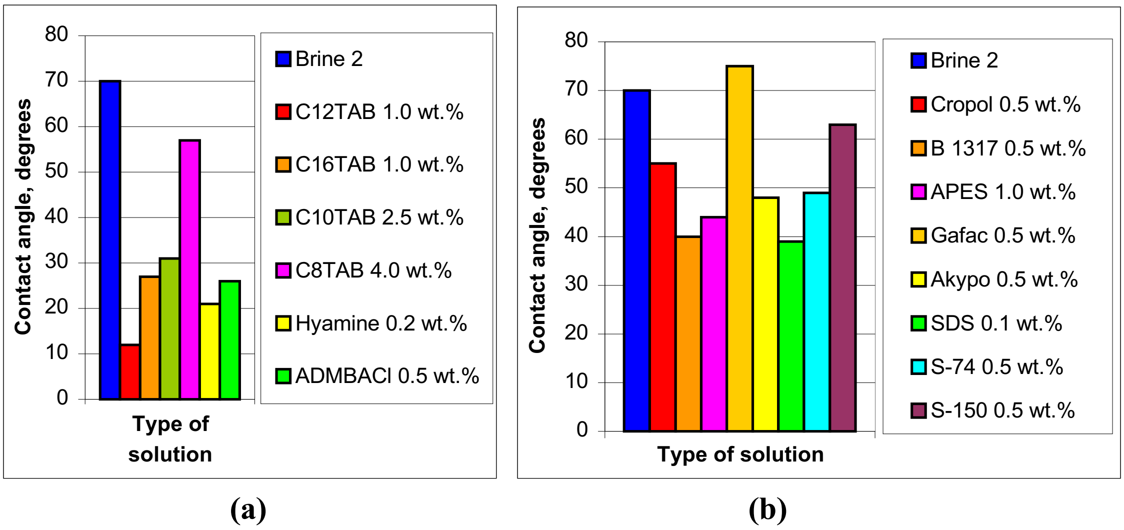


Figure 9-4. Advancing contact angles measured through water droplets on calcite crystals pre-exposed to crude oil followed by surfactants solutions. **(a)** Cationic surfactants and **(b)** Anionic surfactants.

Based on these experimental observations the following mechanisms are proposed for SI of cationic- and anionic surfactants solutions into oil-wet chalk, respectively.

9.1.1. Imbibition mechanism for cationic surfactants

The proposed mechanism for SI of cationic surfactants into oil-wet chalk is illustrated in **Figure 9-5**. The mechanism includes:

- Transport of surfactants to the oil-water-solid contact line
- A desorption process where the cationic surfactant monomers are interacting by means of electrostatic- and hydrophobic forces with negatively charged organic material attached to the mineral surface under the formation of ion-pairs
- Desorbed material is transported away from the surface as ion-pairs and assumed to either be part of the micellar system by forming mixed micelles or transfer to the oil phase as clusters of ion-pairs
- Water can then imbibe spontaneously into the water-wet chalk material

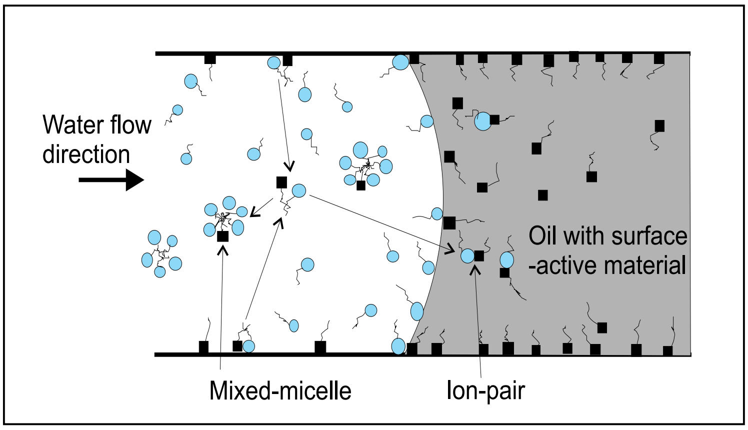


Figure 9-5. Proposed mechanism for SI of C12TAB into oil-wet chalk material. Blue circle are positively charged surfactant head-groups and black squares are polar components from the crude oil.

9.1.2. Imbibition mechanism for anionic EO-surfactants

The mechanism for SI of anionic EO-surfactants into oil-wet chalk, previously outlined by Chen *et al.* (2000) and Varadaraj *et al.* (1994), is illustrated in **Figure 9-6**. The EO-groups are believed to interact with the hydrophobic part on the material attached to the mineral surface, creating a bilayer structure. The EO-groups are pointing out from the surface creating a weakly water-wet layer allowing the water to imbibe (P II).

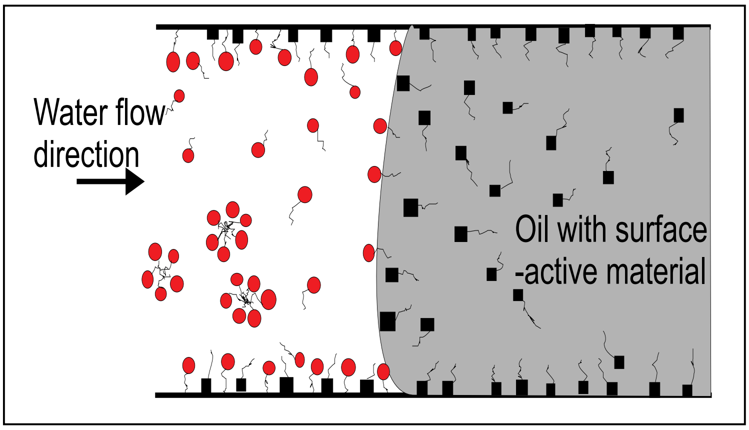


Figure 9-6. Mechanism for SI of anionic surfactants solutions containing hydrophilic EO-groups into oil-wet chalk. Red circles are negatively charged surfactant head-groups and black squares are polar components from the crude oil.

9.2. Removal and stabilizing of desorbed material

This section will focus on the oil-wetting organic material desorbed from the chalk surface upon contact with cationic surfactants. It is assumed that creation of ion-pairs through electrostatic interaction between oppositely charged molecules as well as hydrophobic interaction between hydrocarbon chains played a key role in the desorption process (Khan and Marques, 1997; SS 4.4.2.). The desorbed material is transported away from the surface as ion-pairs and it can either be part of the micellar system in the water phase under formation of mixed micelles, or transferred to the oil phase as clusters of ion-pairs (P III). These two mechanisms will be discussed in the following subsections.

9.2.1. Solubilization of desorbed material into micelles

Experiments using different concentration of the C12TAB surfactant were performed to investigate the influence of the presence of micelles on the desorption mechanism. **Figure 9-7** shows SI curves for different concentrations of C12TAB. The figure shows that SI was strongly depending on the C12TAB concentration. There was an abrupt decrease in the imbibition rate around the concentration approximately equal to CMC (C12TAB has a CMC equal to 0.4 wt.% in distilled water). Thus, the presence of micelles seemed to be of crucial importance for the SI to proceed into oil-wet chalk material (P II). They were expected to enhance the desorption rate of organic material in two ways. Micelles will act as surfactant monomer suppliers ensuring high concentration of monomers at the oil-water-solid contact line, and, in addition, to solubilize the desorbed materials. The higher UR for the 1.0 wt.% compared to the 5.0 wt.% solution was attributed to a stronger solubilization of oil into the II(-) micromulsion at the highest concentration (S 4.3.).

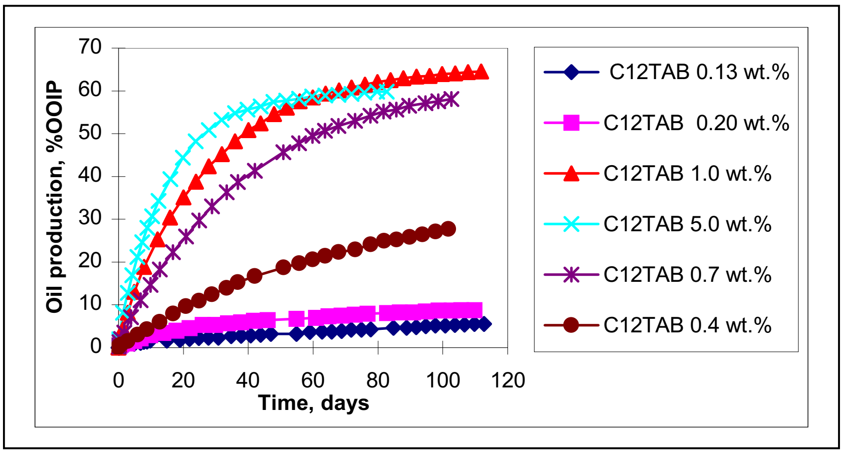


Figure 9-7. SI profiles for C12TAB into oil-wet chalk at 40 °C using different surfactant concentrations.

Advancing contact angles measurements on calcite crystals pre-exposed to lauric acid dissolved in heptane or crude oil followed by exposure to different surfactant solutions also confirmed the importance of surfactant concentration on the wettability alteration process. **Figure 9-8** shows angles measured by different surfactant solutions above and below the respective CMC-values. It can be seen that surfactant solutions having a concentration above CMC was much more efficient to desorb oil-wetting components from the calcite crystals than at concentrations below the CMC. Low solubility of the ion-pairs formed in the aqueous phase at a surfactant concentration below the CMC may be the reason for this observation.

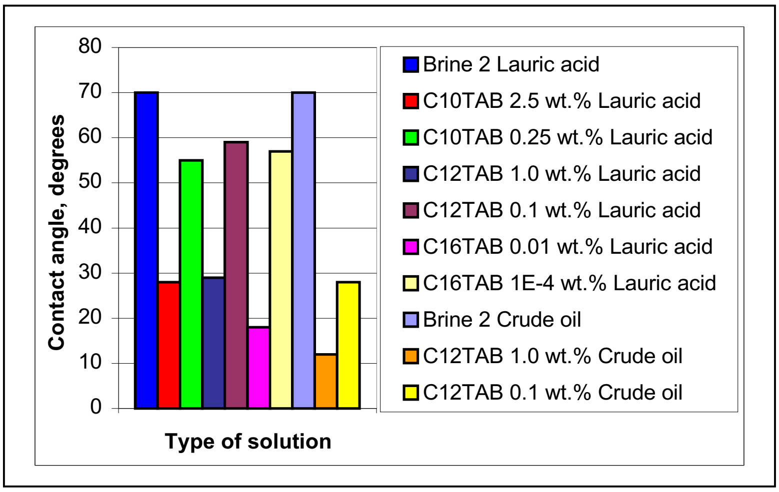


Figure 9-8. Advancing contact angles measured through water droplets on calcite crystals pre -exposed to crude oil or lauric acid dissolved in heptane followed by surfactant solutions at different concentrations above and below CMC.

9.2.2. Desorbed material transfer to the oil phase as ion -pairs

The desorption mechanism assumed that organic matter on the mineral surface was desorbed under formation of ion-pairs. The ion-pairs are scarcely soluble in water and can transfer to the oil phase (SS 4.4.2.). A detailed study regarding partitioning of C12TAB between water and oil was therefore performed to confirm the ability for C12TAB to partition into the oil phase together with negatively charged material as ion-pairs.

Model oils containing fatty acids, crude oil spiked with octanoic acid and crude oils having different ANs were used in the experiments. **Figure 9-9** shows partition coefficient (SS 4.4.1.) for C12TAB, C14TAB and C16TAB between model oil and brine as a function of pH in the water phase. The partitioning of surfactants into the oil phase increases with increasing pH. This increase was expected because more acids will be ionized at the oil/water interface at higher pH (Buckley, 1996), enhancing the formation of ion-pairs and the amount of surfactants transferring to the oil phase. Without octanoic acid present, the surfactant partition coefficient stayed constant.

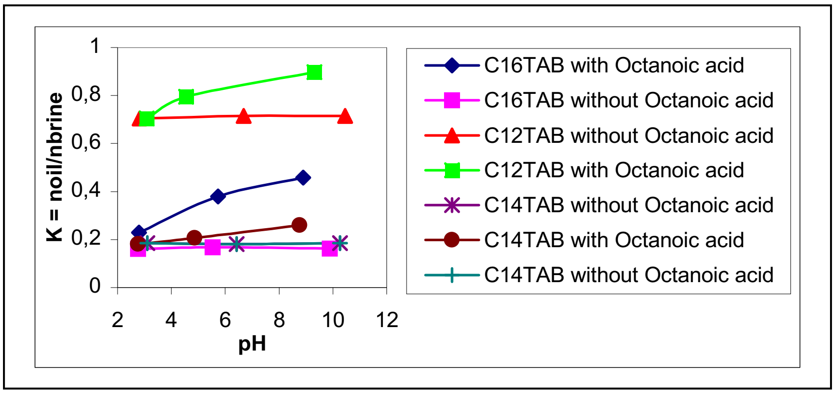


Figure 9-9. Partitioning coefficient for C12TAB, C14TAB and C16TAB between model oil and brine as a function of pH.

Crude oil B with AN 0.12 mg KOH/g oil was spiked with different amounts of octanoic acid. **Figure 9-10** shows partitioning of C12TAB for different concentration of added octanoic acid. The partitioning coefficient increased with increasing amount of octanoic acid added.

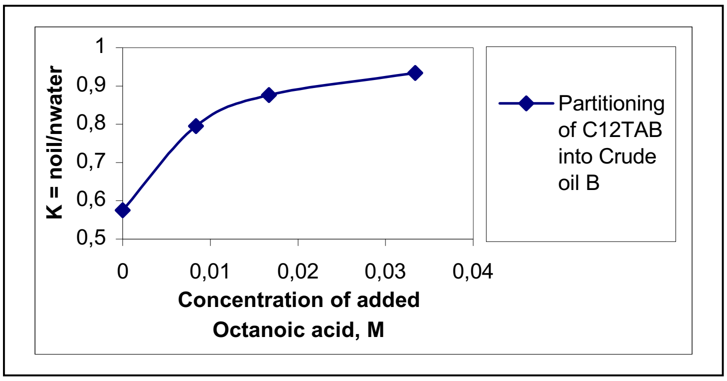


Figure 9-10. Partitioning of C12TAB into crude oil B spiked with octanoic acid.

Increased partitioning coefficient was also demonstrated for C12TAB using crude oils with different AN. **Figure 9-11** shows partitioning coefficient for 3 different crude oils. The partitioning of C12TAB increased with increasing AN of the oils (P III).

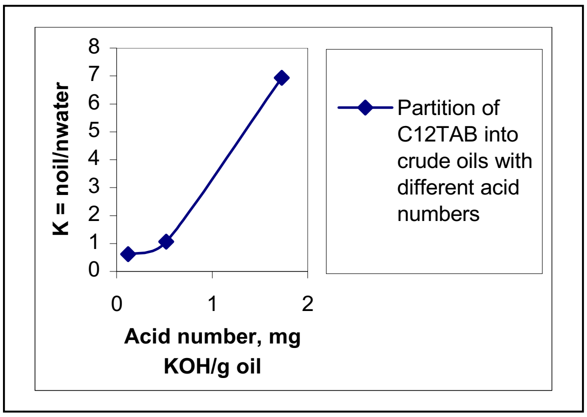


Figure 9-11. Partition coefficient, K, for partitioning of C12TAB into crude oils with different AN. The high K value for the crude oil with AN = 1.73 g KOH/g oil, was due to an initial surfactant concentration in the water phase approximately equal to CMC.

These tests confirm that cationic surfactants are likely to partition into the oil phase as ion-pairs or clusters of ion-pairs. The partitioning coefficient is depending on the surfactant concentration, the pH and salinity of the water phase, the composition of the oil phase and the amount and type of negatively charged counter ions available.

9.3. Influence of temperature on SI rate

The monomer concentration of surfactants at the oil-water-solid contact line is an important parameter governing the desorption rate of organic material from the mineral surface and hence for the imbibition rate. At a surfactant concentration above the CMC, the amount of monomers in the water phase is determined by the surfactant's CMC-value and the diffusion rate of the surfactant to the water imbibition front. **Figure 9-12** shows the rate of SI into oil-wet chalk at different temperatures and concentrations. A small increase in the imbibition rate was observed when increasing the concentration of surfactant from 1.0 to 5.0 wt.% at both 40 and 70 °C. It is important to notice that both concentrations were well above the CMC-value. The difference in UR for both concentrations at 40 and 70 °C was attributed to differences in oil solubilization into the II(-) microemulsion (S 4.3.). However, the SI rate seemed much more sensitive to changes in temperature than concentration and the rate and UR increased significantly for both concentrations when the temperature was raised from 40 to 70 °C.

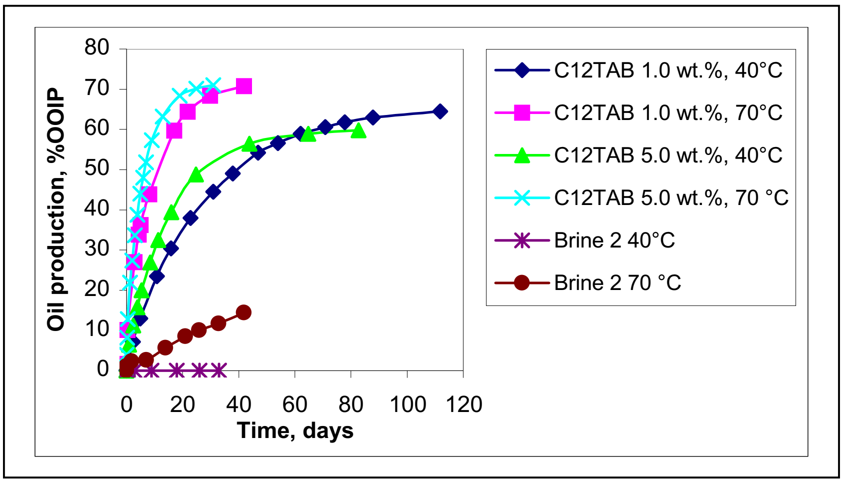


Figure 9-12. SI of C12TAB into oil-wet chalk material at 40 and 70 °C.

Several mechanisms can contribute to increase the SI rate at elevated temperature:

- Increased rate of the chemical desorption process. The chemical desorption process was assumed to be the rate-limiting parameter in the wettability alteration mechanism. The rate of most chemical reactions increases with increasing temperature and desorption reactions will speed up as the temperature increases
- Increased diffusion rate of surfactants. The surfactant molecules must diffuse to the water imbibition front to desorb oil-wetting components as the imbibition front moves into the porous medium. It is well known that increase in the diffusion coefficient and viscosity reduction of the solvent are the main parameters governing increase in diffusion rate for molecules in bulk solution at elevated temperature (Hiemenz and Rajagopalan, 1997). In addition, surfactants are also able to spread very fast along the oil-water interface
- Increased oil-water IFT. Measurements have shown that the oil-water IFT increases with increasing temperature for C_nTAB surfactants (Austad *et al.*, 1998; P V). This will increase the imbibition rate when the oil-wetting components have been removed and water is imbibing (S 3.1.)
- Lowering of the fluid viscosities. The contribution from reduction in fluid viscosities has been shown to be most important for heavy oils (Babadagli, 1996; Briggs *et al.*, 1988; Donmez, 1997; Reis, 1992). Effects from reduction in oil viscosity were therefore assumed to have only slightly influences in this study, due to relative low oil viscosity at 20 °C (2.5 cP)
- Thermal expansion of oil. Thermal expansion of the oil phase was assumed to have small effect in the temperature range 40-70 °C according to reported expansion values

for typical oils ranging from 0-6 % for temperatures between 15-80 °C (Babadagli, 1996)

- Wettability alteration effects. There are reasons to believe that oil-wet chalk becomes more water-wet at elevated temperature (Chapter 14). Increased water-wetness of the chalk was therefore assumed to give a small contribution to the oil production at 70 °C (slow imbibition of brine at 70 °C)

It is of course, impossible to relate the increased oil recovery rate observed at 70 °C directly to one of the parameters mentioned above. What can be said is that raising the temperature had a large influence on the SI rate and this fact does not seem to contradict the proposed wettability alteration mechanism.

9.4. Main parameters and kinetics in the wettability alteration mechanism

A mechanism for wettability alteration of oil-wet chalk to water-wet conditions by use of cationic surfactants of the type, C_nTAB, have been proposed. The cylindrical tube model in **Figure 9-13** can illustrate the wettability alteration process.

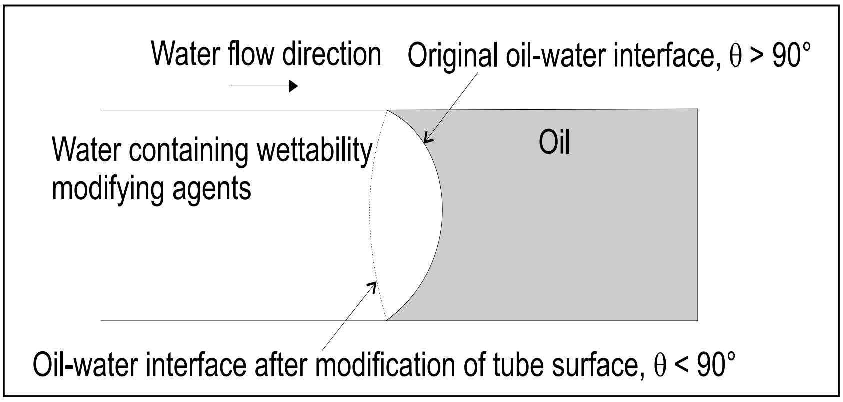


Figure 9-13. SI of water into oil-wet tube by modification of the tube material so the contact angle drops below 90°.

Young's equation, Eq. 2-1, solved for the contact angle yields,

$$\cos\theta = \frac{\sigma_{os} - \sigma_{ws}}{\sigma_{ow}} \qquad [9\text{-}1]$$

The capillary pressure is negative for θ > 90°, and it can be seen from Eq. 9-1 that the surfactant is modifying the water-solid IFT, σ_{ws}, so the numerator, σ_{os} - σ_{ws}, turns positive. The contact angle decreases below 90° and water can imbibe spontaneously.

The results in the previous subsection showed that raising the temperature had large effect on the SI rate into oil-wet chalk. The increase in temperature is expected to increase the kinetics of the wettability alteration process, especially the desorption process, and the efficiency of the surfactant is therefore expected to increase significantly with increasing temperature of the actual COBR system under treatment. However, the temperature will usually stay constant or decrease when injecting water into a reservoir. The following surfactant parameters are therefore assumed to be most important regarding the kinetics of the SI rate at constant temperature:

- The size of the hydrocarbon chains attached to the N-atom in the surfactant (Khan and Marques, 1997). Too large carbon-groups attached is believed to lower the interaction between the charged centers of the surfactants and the negatively charged organic molecules due to steric repulsion (Hyamine and ADMBACl vs. C10TAB and C12TAB)
- Hydrophobic interaction between the hydrocarbon chain of the surfactant and the organic material attached to the mineral surface. The surfactant carbon chain should contain at least 10 carbon atoms to interact efficiently with the organic matter on the mineral surface (C8TAB vs. C10TAB and C12TAB)
- Since only surfactant monomers were assumed to take part in the desorption process, the CMC of the surfactant should be high and the surfactant concentration should be kept above the CMC to ensure high desorption rate and fast imbibition of water as this step is assumed to be the rate-determine step in the wettability alteration mechanism (C12TAB vs. C16TAB)
- The surfactant should only lower the oil-water IFT moderately, ensuring fast capillary driven imbibition of water after the desorption process. Otherwise, gravity forces may become active as discussed in the next chapter

9.5. Application of wettability modifying agents for EOR

Earlier reported work involving wettability alteration of reservoir rock with the aim of EOR includes mostly addition of caustic to the injection water during waterflooding. The alkaline water was assumed to alter the wettability of the oil-wet reservoir rock to water-wet and thereby improve the displacement efficiency (Arteaga-Cardona *et al.*, 1996; Emery *et al.*, 1970; Froning and Leach, 1967; Graue and Johnson, 1974; Leach *et al.*, 1962; Spinler and Baldwin, 2000). In addition, Blair and Stout (1985) and Downs and Hoover (1989) and reported promising results from pilot tests injecting thin film spreading agents (Blair, 1982), which was assumed to alter the wettability of the reservoir rock towards water-wet. It should be noticed that all the tests in the cited articles were performed using sandstone rocks.

The EOR in the above cited works was due to the fact that several authors have reported that optimal oil recovery during waterflooding usually appears when the wettability of the porous medium is weakly water-wet (Alveskog *et al.*, 1998; Anderson, 1987c; Jadhunandan and Morrow, 1995; Lorenz *et al.*, 1974; Morrow, 1987; Morrow *et al.*, 1986; Rathmell *et al.*, 1973; Torsæter *et al.*, 1997; Tweheyo *et al.*, 1999; Zhou *et al.*, 2000b). This knowledge has furthermore given rise to laboratory investigations with the purpose of reversing the wettability of strongly water-wet sandstone rock towards neutral-wet (Michaels *et al.*, 1964; Michaels and Porter, 1965; Michaels and Timmins, 1960; Kowalewski *et al.*, 2000; Tweheyo *et al.*, 1999; Wagner and Leach, 1959). It is important to notice that all the cited works are aiming to take advantage of a wettability alteration in previously waterflooded zones. The injected chemicals were only assumed to be efficient in areas reached by the injected water. However, a wettability alteration process allowing SI of water into oil-wet carbonate media has, with the exception of the article by Austad and Milter (1997), to the knowledge of the author not been reported in the literature. The results presented in this thesis should therefore be considered as an interesting method to enhanced the displacement efficiency in fractured oil-wet carbonate reservoirs producing in the secondary- or tertiary stage.

Chapter 10. The relative influence of capillary- vs. gravity forces during imbibition into low-permeable oil-wet chalk

It is important to gain information about the relative influence of gravity- to capillary forces acting on the fluids during the SI tests in the laboratory. The reason is that the height of the matrix blocks in fractured carbonate reservoirs may vary significantly (Thomas *et al.*, 1987). Tests have shown that SI rate is likely to slow down under increased influence of gravity forces, especially for low-permeable porous media (Cuiec *et al.*, 1994; Milter and Austad, 1996a; S 3.3.). Incorrect conclusions about displacement efficiency for field application can be the outcome, if tests only are performed on short cores when adding surfactants to the injection water.

10.1. Influence of capillary- vs. gravity forces during C12TAB imbibition

The influence of gravity- and capillary forces during SI into low-permeability oil-wet chalk was investigated by varying the height of the cores, the temperature, the oil-water IFT and the initial water saturation (P V). **Figure 10-1** shows SI of C12TAB into long cores with and without S_{wi} at 40 and 70 °C, respectively. The shapes of the imbibition curves at 40 °C are quite similar for cores with and without S_{wi}. There was a break on the curves, which were interpreted as a crossover in imbibition mechanism from an imbibition mainly driven by capillary forces to an imbibition mainly dominated by gravity forces (S 7.3.). Calculated values of N_B^{-1} also indicated that gravity forces should be active in the oil expulsion process. The core without S_{wi} produced oil with a slightly higher rate than the core with S_{wi}. However, the imbibition rate increased significantly for both cores with and without S_{wi} when raising the temperature to 70 °C. Contrary to the curves at 40 °C, no break on the imbibition curves similar to the curves at 40 °C was observed, indicating that capillary forces were more pronounced at 70 °C. This assumption was confirmed when studying the residual oil saturation inside the cores.

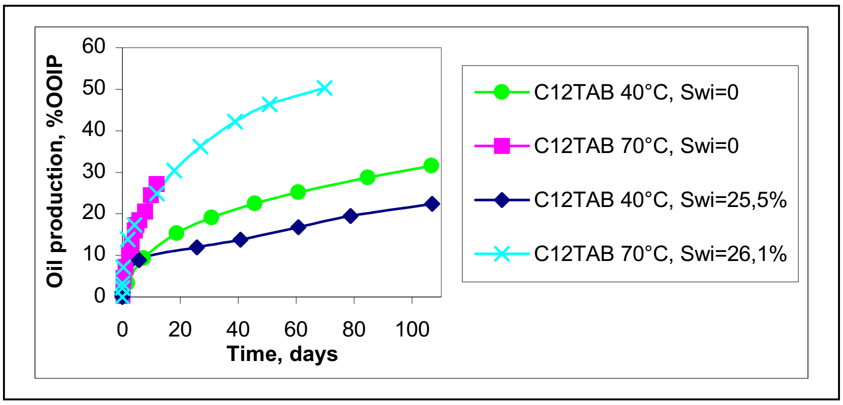


Figure 10-1. SI of C12TAB into long oil-wet chalk with and without S_{wi} at 40 and 70 °C.

There was no sign of gravity segregation in the cores imbibed at 70 °C, **Figure 10-2**. A faster wettability alteration process and higher oil-water IFT are probably the main reasons for the change in imbibition mechanism when increasing the temperature from 40 to 70 °C.

Figure 10-2. Pictures of cleaved long composite chalk cores.**(a)** C12TAB 40 °C and S_{wi} = 0, **(b)** C12TAB 70 °C and S_{wi} = 0.

Tests were also performed on long chalk cores where crude oil was exchanged with heptane prior to C12TAB imbibition. The IFT between C12TAB solution and heptane was 6.4 mN/m at 40 °C, which resulted in an imbibition mechanism dominated mainly by capillary forces as confirmed by the shape of the imbibition curve in **Figure 10-3**. The curve for C12TAB imbibition into long core saturated with oil F is included for comparison. S_{wi} was zero in both cases.

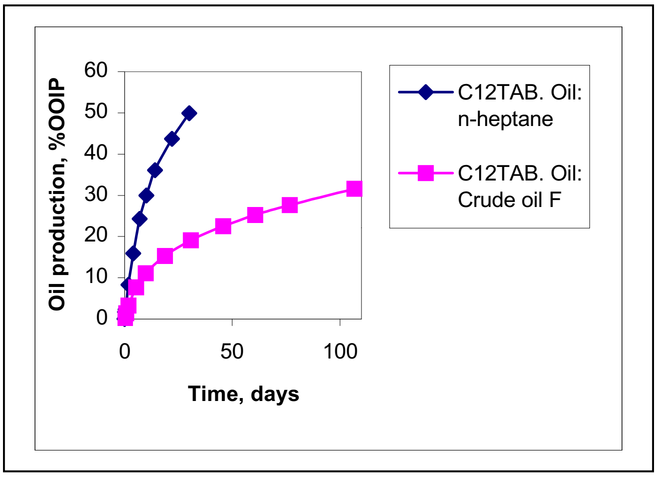
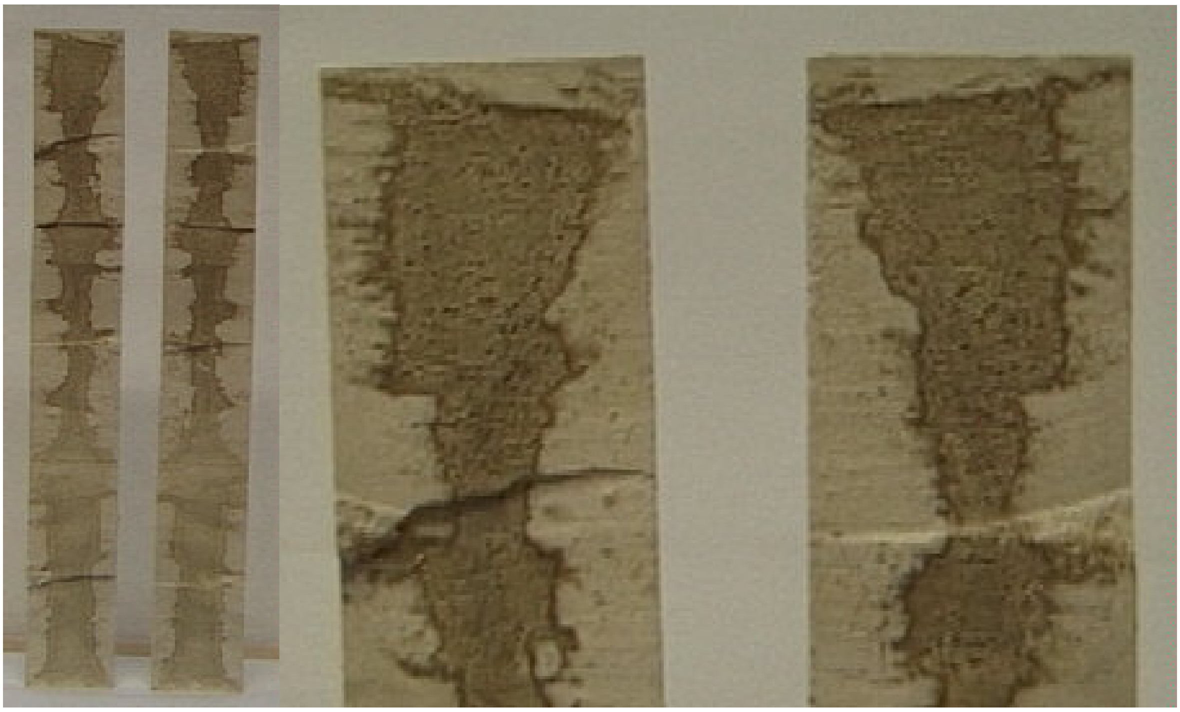


Figure 10-3. SI of C12TAB surfactant into long oil chalk cores 100 % saturated with heptane and crude oil F as oil phases. The temperature was 40 °.



(a) **(b)**

Figure 10-4. Cleaved long composite chalk core saturated with heptane before imbibition with C12TAB. **(b)** Upper part of the same core as in **(a)**.

Figure 10-4 (a) shows a picture of the cleaved long composite chalk core where crude oil was exchanged with heptane before initiating the SI test. The residual oil saturation profile points to an imbibition dominated by capillary forces. The picture gives interesting information about flow behavior in porous medium during a SI process, where oil and water are flowing counter-currently. Water tends to imbibe into the core in certain zones and oil is expelled in other zones with higher oil saturation. These patterns are showed in more detail in the upper part of the core **(b)**. Whether such patterns are created in general or are a result of small heterogeneities in the chalk material is not clear.

Chapter 11. Comparison of C12TAB vs. a non-ionic surfactant for their ability to imbibe into short and long oil-wet dolomite reservoir cores

At this point in the project, the C12TAB surfactant system had only been tested on outcrop chalk cores. It was therefore interesting to see if the surfactant system was able to benefit oil production from restored reservoir cores. This section will present results from SI tests performed on restored dolomite reservoir cores from a field in west Texas. A comparison between C12TAB and an ethoxylated alcohol, $C_{9\text{-}11}(EO)_8OH$ (termed EA), for their ability to enhance oil production from short and long oil-wet dolomite reservoir cores is also reported (P IV).

11.1. SI of C12TAB vs. EA into short and long oil-wet dolomite reservoir cores

11.1.1. Short core tests

Figures 11-1 and **11-2** show imbibition of C12TAB and EA into 4 moldic and 3 sucrosic dolomite cores (SS 6.1.1.). ***C12TAB was in general more efficient to expel oil from the oil-wet cores compared to EA***. Approximately 40-50 % of OOIP was produced using C12TAB, roughly 2-3 times more than for EA. No correlation could be established between oil production and moldic and sucrosic type of core. However, the relative efficiency of C12TAB and EA to displace oil decreased with increasing permeability for the moldic cores. Increased influence of gravity forces with increasing permeability was assumed to be the reason for this tendency (P IV).

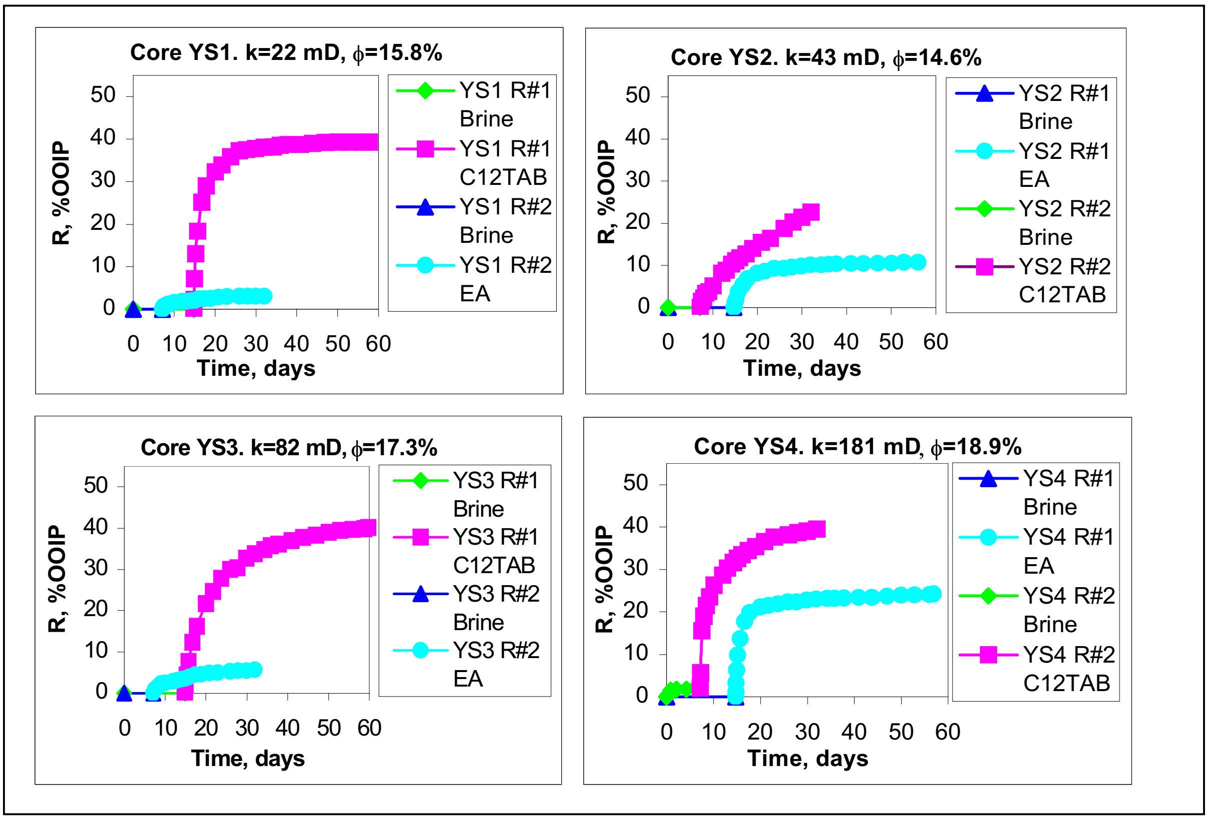


Figure 11-1. SI of C12TAB and EA into oil-wet dolomite reservoir cores classified as moldic.

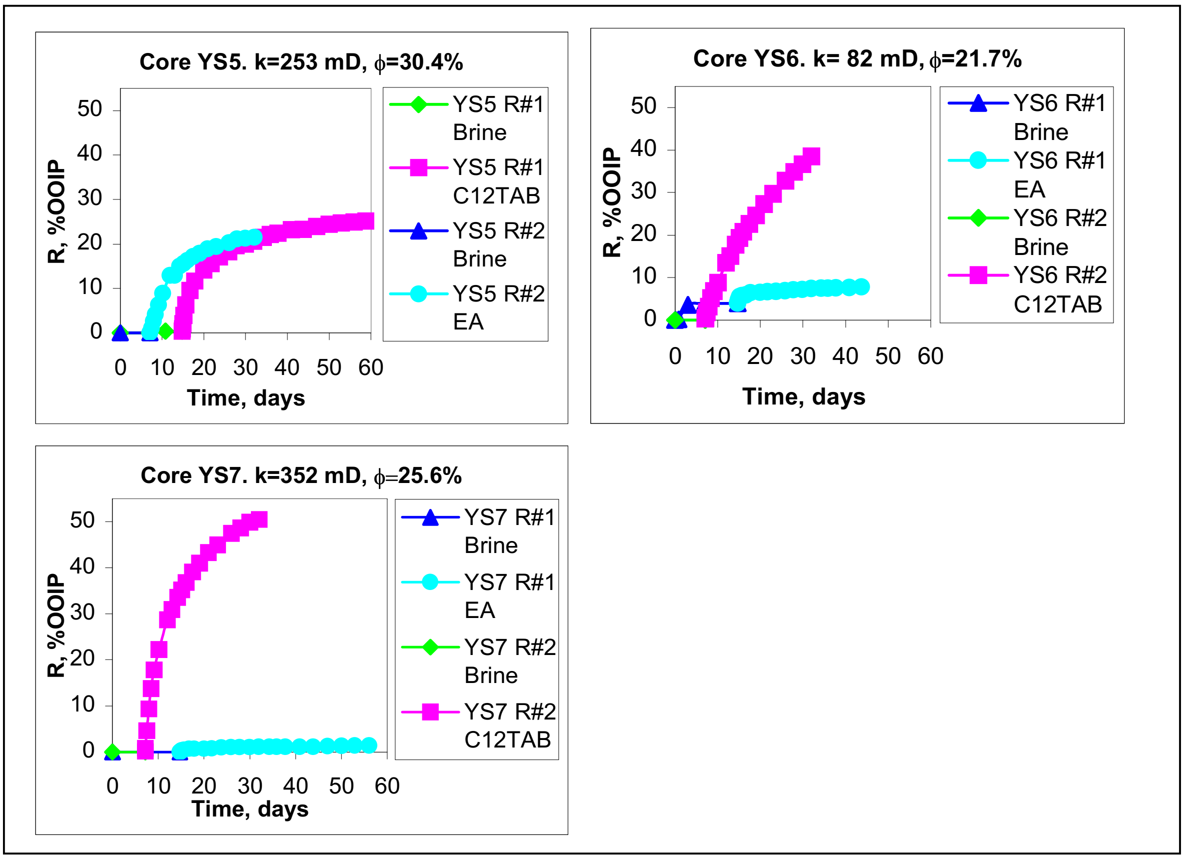


Figure 11-2. SI of C12TAB and EA into oil-wet dolomite reservoir cores classified as sucrosic.

The curves confirmed that C12TAB was able to expel oil in an efficient way from real reservoir core material restored to mimic reservoir wettability. C12TAB was expected to increase the water-wetness of the dolomite cores in a similar way as for chalk cores, whereas EA was believed to enhance oil recovery by oil-water IFT reduction and creation of a water-wet bilayer similar to the mechanism previously described for anionic EO-surfactants. Hence, the difference in oil recovery efficiency was assumed to be a result of the different imbibition mechanisms involved for the two types of surfactants. It should be noticed that the IFT between C12TAB and EA solutions towards oil were approximately the same.

Contact angle measurements were performed on calcite crystals pre-exposed to crude oil G followed by Brine 1, C12TAB and EA solution. The angles were measured to 55, 29 and 45°, respectively, showing that C12TAB was much more efficient than EA to alter the wettability of the calcite crystals towards a more water-wet state, **Figure 11-3**.

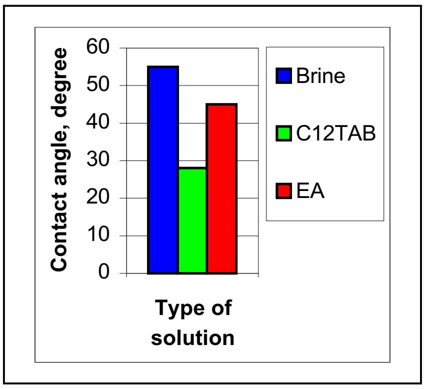


Figure 11-3. Contact angles measured on calcite crystals pre-exposed to crude oil G followed by Brine 1, C12TAB or EA solution.

11.1.2. Long core tests

Tests were performed on two long dolomite reservoir cores with permeability of 162 and 45 mD. **Figure 11-4** shows that C12TAB imbibed quickly into the 162-mD YL1 core and more than 60 % of OOIP was produced during 33 days. The 45-mD YL2 core was first surrounded with EA and only 4 % OOIP was produced during 37 days; thereafter EA was exchanged with C12TAB. Oil production was immediately initiated, but the rate was significant lower than for the 162-mD core. Lower permeability of the core and synergistic effects (Rosen, 1986) between previously imbibed EA and C12TAB was believed to be the main reasons for the slower oil expulsion rate from YL2 compared to YL1 (P IV).

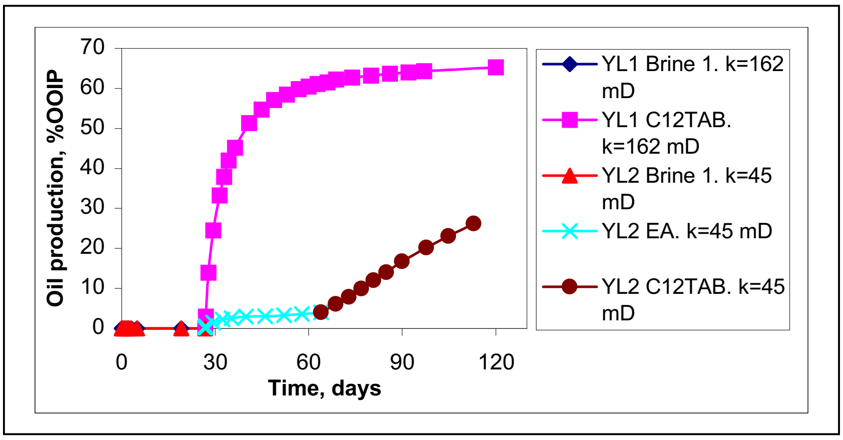


Figure 11-4. SI of C12TAB into long oil-wet dolomite reservoir cores at 22 °C.

11.1.3. Spontaneous uptake of oil

Spontaneous uptake of oil was observed for dolomite cores previously imbibed by EA and C12TAB. **Figure 11-5** shows uptake of oil in a core previously imbibed by C12TAB. Low oil-water IFT and gravity segregation were assumed to be the reasons for the oil uptake (P IV). It is therefore important to avoid contact between oil and reservoir areas previously flooded by surfactant in the field, because the oil saturation is then likely to increase again.

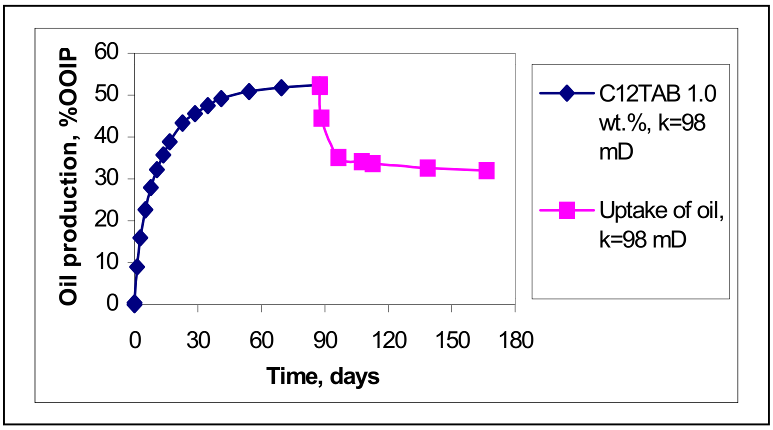


Figure 11-5. SI of C12TAB into dolomite reservoir core followed by spontaneous uptake of oil at 22 °C.

Chapter 12. Amines as wettability modifiers for oil-wet carbonate

This chapter presents results from SI tests into oil-wet chalk- and dolomite cores using amine solutions. Amines containing long hydrocarbon chain will act as cationic surfactants at pH below 7-8. The purpose of applying amines in SI tests was to evaluate their ability to imbibe into oil-wet carbonate according to the same mechanism as C12TAB. Amines are much cheaper than quaternary ammonium salts, which make them more attractive to be used in actual fields.

12.1. Imbibition of C12-amine into oil-wet chalk

It was natural to start the screening test of amines with C12-amine, since the corresponding quaternary ammonium salt, C12TAB, was the most efficient surfactant to expel oil under oil-wet conditions. However, the C12-amine solution became cloudy and solubility data indicated that C12-amine precipitated out of solution. Nevertheless, the C12-amine solution was able to imbibe into oil-wet chalk and SI profiles at 40 and 70 °C are shown in **Figure 12-1**. It should be noticed that the amine was dissolved in distilled water in these tests to enhance the water solubility.

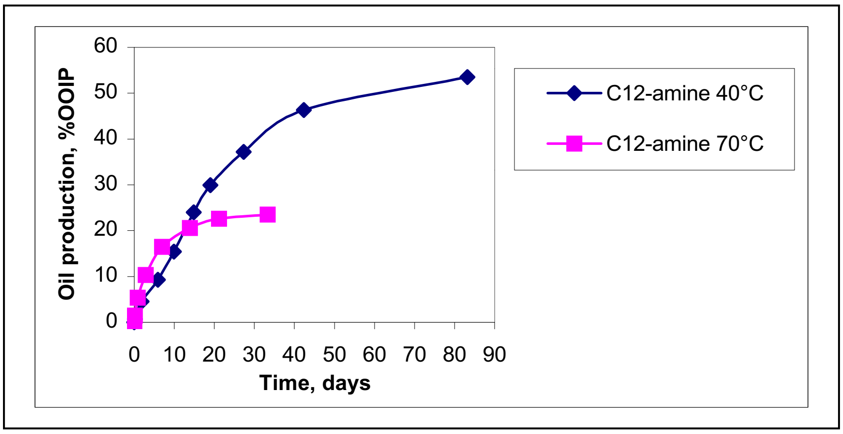


Figure 12-1. SI profiles for C12-amine solutions dissolved in distilled water into oil-wet chalk cores at 40 and 70 °C.

Figure 12-2 shows a picture of a cleaved core imbibed by C12-amine solution at 40 °C. The residual oil saturation profile indicates that the oil was expelled in a counter-current flow mode by capillary forces. Hence, the imbibition of C12-amine was believed to proceeds in the same manner as for C12TAB, i.e., the C12-NH_3^+ was the active cationic surfactant desorbing the organic material from the chalk surface. However, the instability of the C12-amine solution makes it improper as EOR chemical. The poor imbibition behavior at 70 compared to 40 °C, was believed to be related to dissolution of chalk as discussed in the next section.

Figure 12-2. Picture of a cleaved chalk core Imbibed by C12-amine dissolved in distilled water at 40 °C.

12.2. SI of C10-amine into oil-wet dolomite cores at different temperatures

C10-amine has higher solubility than C12-amine in water (Shergold, 1987) and a 1.0 wt.% solution of C10-amine stayed clear and transparent, even when dissolved in the high salinity Brine 1. **Figure 12-3** shows imbibition of C10-amine into dolomite cores at 40 °C. The absence of brine imbibition confirmed that the cores were completely oil-wet. However, C10-amine solution imbibed spontaneously and UR of 73 % of OOIP was reached within 3 weeks for the high-permeable 352-mD core. The 101-mD core also imbibed quite efficiently and the oil recovery approached 70 % of OOIP after 55 days. Initially, the 22-mD core imbibed very fast initially, but UR leveled off at approximately 50 % of OOIP after 3 weeks. This core was highly moldic and the high residual oil saturation in this core was expected to be due to higher degree of snap-off and bypass of oil in such pore systems (S 3.4.). These results confirmed that C10-amine solution has the ability to alter the wettability of oil-wet dolomite and induce SI into oil-wet material at pH values below 7.0.

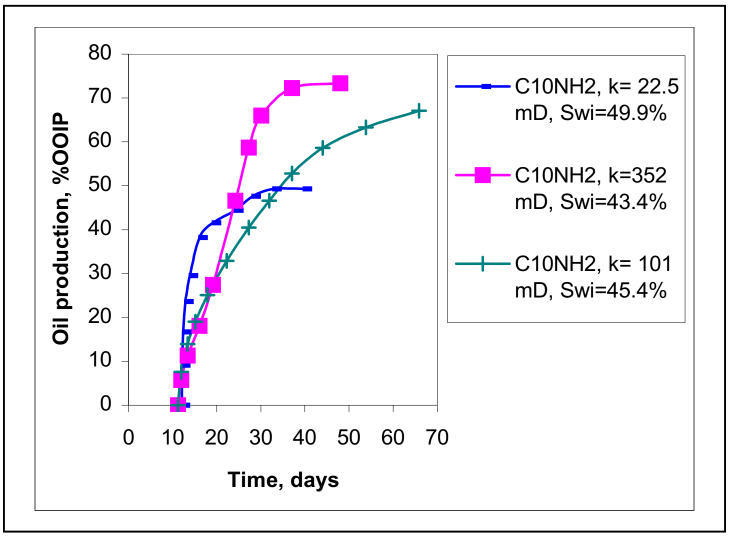


Figure 12-3. SI of C10-amine solutions into oil-wet dolomite reservoir cores at 40 °C.

However, raising the temperature to 70 °C resulted in a tremendous decrease in oil recovery for the dolomite cores with highest permeability (101 and 352 mD). The low-permeable moldic core imbibed C10-amine solution and 43 % of OOIP was produced within 1 week. When lowering the temperature to 20 °C, both of the high-permeable cores imbibed quite efficiently as shown in **Figure 12-4**.

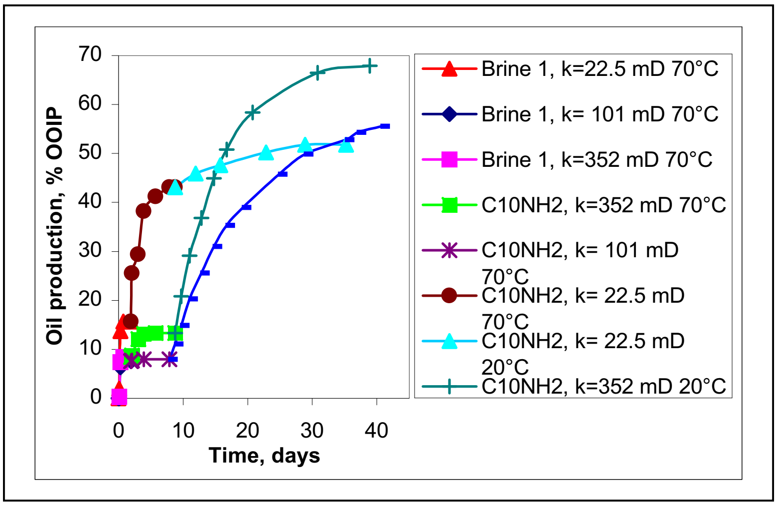


Figure 12-4. SI of C10-amine into oil-wet dolomite reservoir cores at 70 and 20 °C. pH about 6.5.

The decrease in imbibition rate at 70 °C was expected to be due to increased dissolution of dolomite, which will decrease the amount of active $C10NH_3^+$ surfactant according to the following reaction:

$$CaMg(CO_3)_2(s) + 2C_{10}NH_3^+ \Leftrightarrow Ca^{2+} + Mg^{2+} + 2HCO_3^- + 2C_{10}NH_2 \qquad [12\text{-}1]$$

This interpretation was supported by a dissolution tests performed on chalk powder added to distilled water and to C10-amine dissolved in distilled water, **Table 12-1**.

Table 12-1. Dissolution of chalk powder as a function of temperature for powder suspended in distilled water and C10-amine solution with pH adjusted to about 6.5.

Chalk powder suspended in	Temp., (°C)	Mass chalk powder, (g)	Calcium conc. in the water, (mg/l)	Mass dissolved calculated as mg $CaCO_3$	% $CaCO_3$ dissolved
Distilled water	20	1.0126	32.2	4.0	0.4
Distilled water	90	1.0043	11.3	1.4	0.14
1.0 wt.% C10-amine	20	1.0105	86	10.8	1.07
1.0 wt.% C10-amine	90	1.0079	186	23.3	2.31

The solubility of calcium carbonate in water decreases with increasing temperature. The concentration of calcium in distilled water at 20 °C was therefore higher than at 90 °C. The opposite trend was, however, observed when the water contained $C10NH_3^+$. The amount of calcium was approximately 2 times higher at 90 °C than at 20 °C in this case. Furthermore, the concentration of calcium in the $C10NH_3^+$ solution was approximately 16 times the concentration of calcium in water at 90 °C. Increased dissolution rate of calcium carbonate induced by $C10NH_3^+$ with increasing temperature was assumed to be the reason for this.

The $C10NH_3^+$ surfactant will desorb organic material from the dolomite surface and thereby give the $C10NH_3^+$ ions free access to the water-wet mineral surface. There will be a competition between $C10NH_3^+$ ions used to dissolve dolomite and $C10NH_3^+$ ions used to desorb organic material from the surface. The dissolution reaction was assumed to become dominant at temperatures approaching 70 °C. In the water-wet pores, the concentration of active $C10NH_3^+$ surfactants close to the oil-water interface then becomes very low at 70 °C, and the SI process ceased (P VI).

Contact angle measurement confirmed the strong ability for amine solutions to increase the water-wetness of a calcite surface covered by oil-wetting components. A 1.0 wt.% solution of C10-amine lowered the contact angle to 12° compared to 68° for Brine 1,

Figure 12-5.

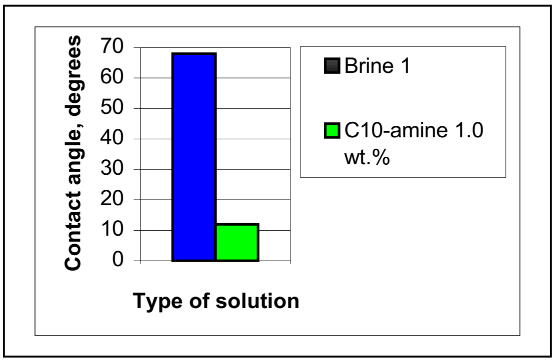


Figure 12-5. Contact angles measured on calcite pre-exposed to crude oil followed by Brine 1 and C10-amine solution. pH about 6.5.

Chapter 13. Low-cost bio-derivate products from coconut as wettability modifiers for oil-wet chalk and dolomite

This chapter is also concentrated on finding cheaper surfactants for application in the field. SI results are presented for two cationic surfactant mixtures Arquad MC-50 and Dodigen 5462, termed Dodigen and Arquad, using oil-wet chalk and dolomite at 40 and 70 °C (P VII). The mixtures contain different amounts of quaternary ammonium salts with chloride as counter-ion. Each individual component will be referred to as C12TAC, C14TAC, C16TAC and C18TAC in accordance with the abbreviation used for the corresponding bromide compounds (C12TAB, etc.). Arquad contains 50 wt.% C12TAC and C14TAC mixed with 35-40 wt.% iso-propanol and 13 wt.% water, whereas Dodigen contains 50 wt.% C12TAC, 24 wt.% C14TAC, 11 wt.% C16TAC and 13 wt.% C18TAC (Hegnauer, 1963; P VII).

13.1. SI of Dodigen and Arquad into oil-wet chalk at 40 and 70 °C

Figure 13-1 shows imbibition of Arquad and Dodigen into chalk cores at 40 °C. Both surfactants were assumed to imbibe according to the same mechanism as C12TAB. Arquad imbibed quickly with a rate slightly higher compared to pure C12TAB. Approximately, 67 % of OOIP was produced after 80 days. This behavior was in strong contrast to Dodigen, which imbibed at a much lower rate. For Dodigen, the oil production appeared to be a nearly linear function of time. The different shape of the imbibition curves points to a different mechanism for the oil expulsion. Different values of the oil-water IFT and the CMC for the two surfactant systems are probably the reasons. The oil-water IFT for Dodigen and Arquad were 0.08 and 0.9 mN/m, respectively (P VII).

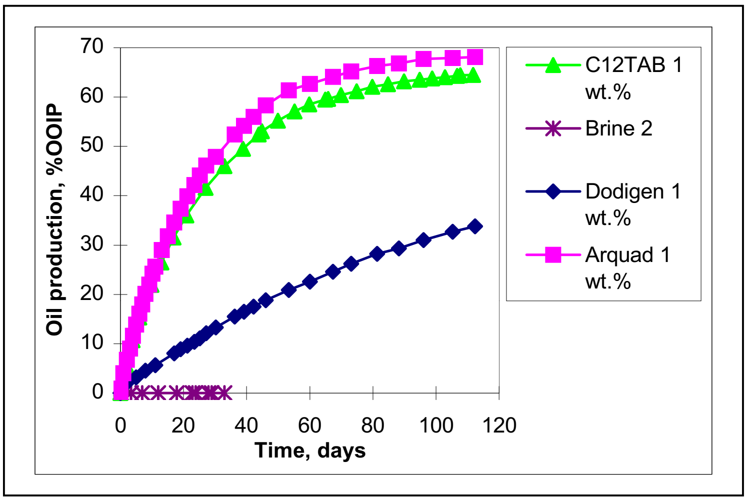


Figure 13-1. SI of Arquad and Dodigen into oil-wet chalk at 40 °C. The curve for C12TAB is included for comparison.

Likewise, the CMC-value of the Dodigen system was also assumed to be much lower than for the Arquad system, due to the content of C16TAC and C18TAC. **Figure 13-2** shows variation in CMC as a function of the number of carbon-atoms in the hydrophobic chain for C_nTAC surfactants. The residual oil saturation profile inside the cores also confirmed that gravity forces were much more pronounced for the Dodigen system than for Arquad.

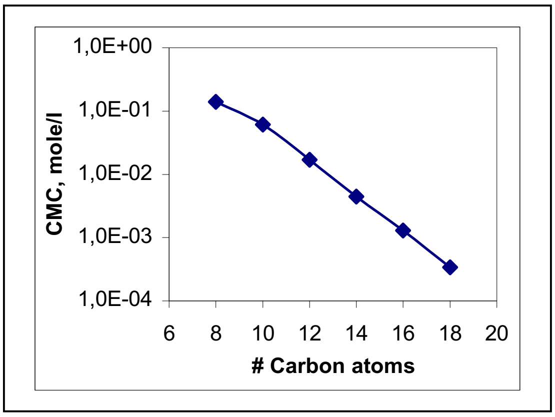


Figure 13-2. CMC as a function of # carbon atoms in the hydrophobic part of C_nTAC surfactants.

Figure 13-3 shows the typical cone shaped oil-water interface created when gravity forces are dominating the fluid flow (SS 3.3.1.). Thus, at 40 °C, Arquad appeared to expel the oil in a counter-current flow dominated by capillary forces, but in the case of Dodigen, gravity forces appeared to be more active determining the fluid flow.

Figure 13-3. Cleaved core imbibed by Dodigen solution at 40 °C.

However, both surfactants were shown to lower the contact angle measured on calcite crystals pre-exposed to crude oil, **Figure 13-4**.

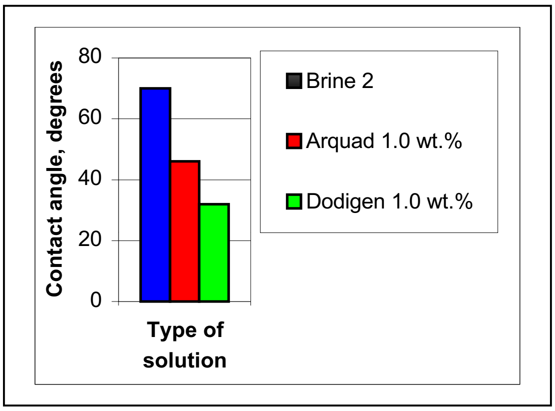


Figure 13-4. Contact angles measured on calcite crystals pre-exposed to crude oil followed by Arquad and Dodigen.

It has been shown that oil-water IFT increases with increasing temperature for quaternary cationic surfactants (Austad *et al.*, 1998; P V). **Figure 13-5** shows SI curves for Arquad and Dodigen with and without S_{wi} into chalk cores at 70 °C.

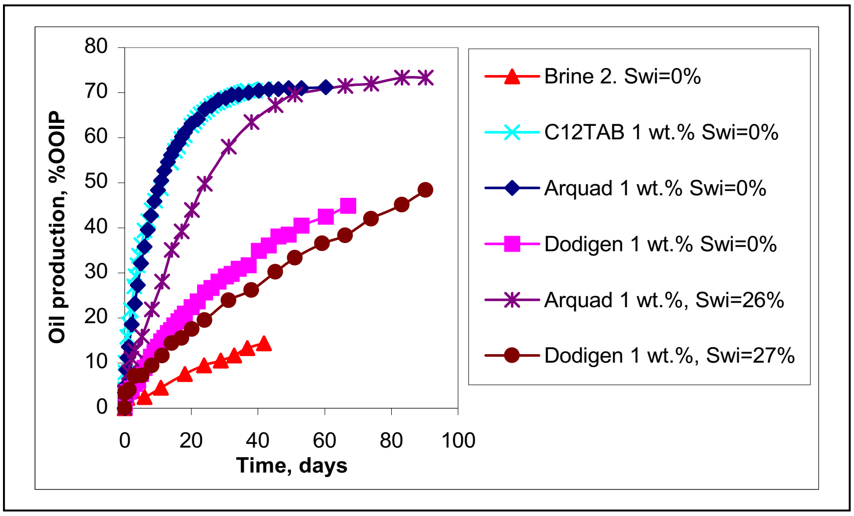


Figure 13-5. SI of Arquad and Dodigen with and without S_{wi} into oil-wet chalk at 70 °C. The curve for C12TAB is included for comparison.

Without S_{wi}

Arquad reproduced the curve for C12TAB also for this temperature. The imbibition was fast and maximum oil recovery of 70 % of OOIP was reached after 30 days. The imbibition rate for Dodigen was much slower, but the shape of the imbibition curve indicated that capillary forces had greater influence on the imbibition process compared to what was observed at 40 °C. This assumption was confirmed when cleaving the core. The residual oil saturation indicated an imbibition mainly driven by capillary forces, which was assumed to be due to higher oil-water IFT and higher desorption rate of oil-wetting components from the chalk surface at 70 compared to 40 °C, **Figure 13-6 (a)**

With S_{wi}

The imbibition rates were slightly lower for cores containing initial water compared to cores without S_{wi} for both Arquad and Dodigen. However, UR seems to be unaffected by S_{wi} and the core imbibing Arquad reached 70 % of OOIP after approximately 50 days. Picture of the core imbibed by Dodigen containing S_{wi} are shown in **Figure 13-6 (b)**. It is clear from the picture that capillary forces were much more dominate during the imbibition process at 70 compared to 40 °C, and no indications of gravity segregation can be observed in the former case. Capillary forces mainly governed the imbibition for both Arquad and Dodigen imbibition at 70 °C, but Arquad imbibition was much faster due to higher oil-water IFT and higher monomer concentration of surfactant.

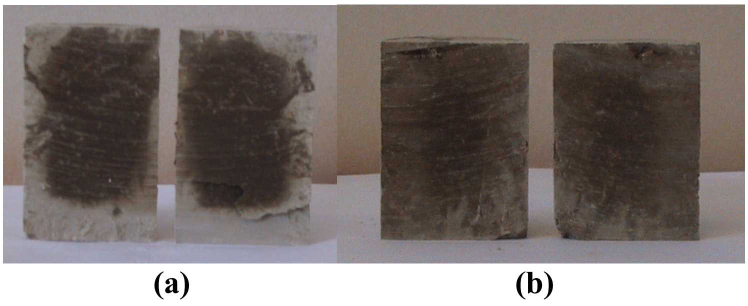


Figure 13-6. Residual oil saturation profiles in chalk cores without **(a)** and with **(b)** S_{wi} imbibed by Dodigen at 70 °C.

3.2. SI of Arquad into long composite oil-wet chalk core at 70 °C

Figure 13-7 shows imbibition of Arquad and C12TAB into long composite chalk cores at 70 °C (20 and 27 cm, respectively). Arquad imbibed faster than pure C12TAB and 60 % of OOIP was produced during 32 days.

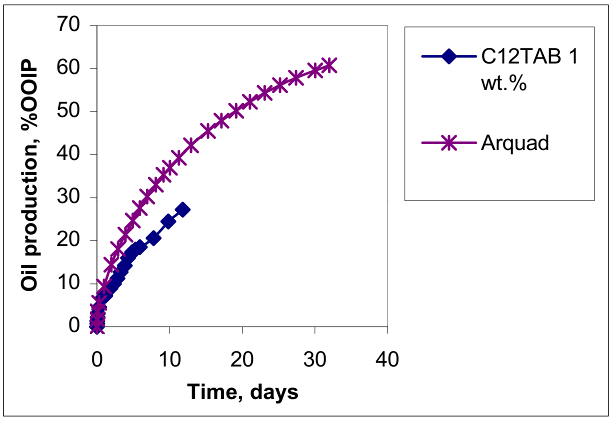


Figure 13-7. SI of Arquad into long composite oil-wet chalk core at 70 °C. The curve for C12TAB is included for comparison.

Picture of the cleaved core imbibed by Arquad, **Figure 13-8**, confirmed that capillary forces mainly determined the fluid flow, even though the magnitude of the gravity forces were increased about 5 times compared to the short core experiments.

Figure 13-8. Cleaved long composite chalk core imbibed by Arquad at 70 °C. The residual oil saturation profile points towards an imbibition mechanism mainly driven by capillary forces.

13.3. SI of Dodigen and Arquad into oil-wet dolomite at 40 °C

Figure 13-9 shows SI of Arquad and Dodigen into two dolomite reservoir cores with permeability of 352 and 101 mD. No SI of water during 5 days confirmed the oil-wetness of the cores. Arquad imbibed very fast into both cores and UR of 90 % of OOIP was reached within 12 and 25 days for the 352 and the 101-mD core, respectively. The shape of the curves indicated an imbibition process driven by capillary forces. The curves for Dodigen imbibition was quite fast initially, but later on they turned almost into straight lines indicating increased influence of gravity forces on the imbibition mechanism, especially for the 101-mD core. These observations point towards the importance of keeping capillary forces as the main driving forces for imbibition. Increased influence of gravity forces is, even for these high-permeable cores, likely to decrease the imbibition rate, which is a major parameter regarding oil recovery from the field.

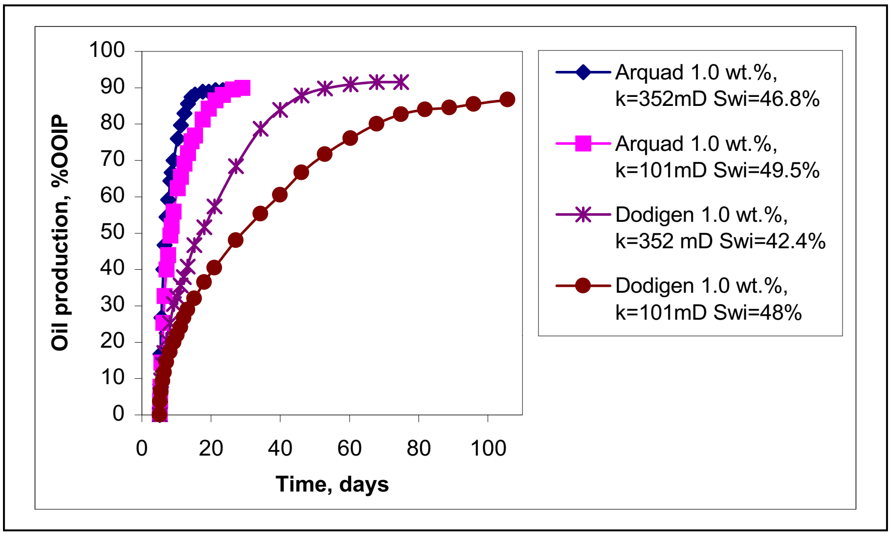


Figure 13-9. SI of Arquad and Dodigen into oil-wet dolomite reservoir cores at 40 °C.

13.4. Summary on SI by Arquad and Dodigen

The results presented in this section show promising SI behavior into oil-wet carbonates when using cheap blends of commercially surfactants. Arquad responded much better than Dodigen, which was attributed to differences in CMC-value and oil-water IFT for the two systems. It is also interesting to note that Arquad in some cases performed better than the pure C12TAB surfactant. When applying surfactants for cleaning, it has been observed that blends of surfactants usually perform better than a single component surfactant (Bäckström *et al.*, 1988; Khan and Marques, 1997; Malmsten and Lindman, 1989). This was explained by the complexity of the detergency process. Since the process consists of many steps, it is likely that different steps require surfactants with different properties to work optimal. The same reasoning can probably be applied to the present problem, where the “cleaning” process involves desorption and removal of complex organic molecules, which are assumed to differ largely in size and shape.

Chapter 14. Thermally induced wettability alteration in chalk

Many authors have observed increased water-wetness of carbonate rock with increasing temperature (Al-Hadhrami and Blunt, 2000; Anderson, 1986b; Hjelmeland and Larrondo, 1983; Kyte and Mattax, 1961; Macaulay *et al.*, 1995; Rao, 1996; Wang and Gupta, 1995). Al-Hadhrami and Blunt (2000) suggested an improved oil recovery method for the Ghaba North field in Oman, based on a thermally induced wettability alteration from oil-wet to water-wet conditions. Preliminary experimental results confirming Al-Hadhrami and Blunt’s observation are presented in this chapter and a wettability alteration mechanism is suggested and discussed in light of these data and reported data in the literature.

14.1. High-temperature SI of brine into oil-wet chalk

SI curves for imbibition of pure brine into oil-wet chalk are shown in **Figure 14-1**. The figure shows that water imbibition increased with increasing temperature. At 130 °C, the oil recovery level reached 38 % of OOIP after 28 days. Besides wettability alteration, several other factors can contribute to increased oil production at high temperature like thermal expansion of the fluids, generation of free gas inside the pores and reduction of fluid viscosities. The latter effect was expected to only give a minor contribution, due to low viscosity of the oil phase at 20 °C (2.5 cP). In the present case, however, a wettability alteration of the chalk material from oil-wet to water-wet with increasing temperature seems to be the most likely explanation to account for the observed oil recovery curves.

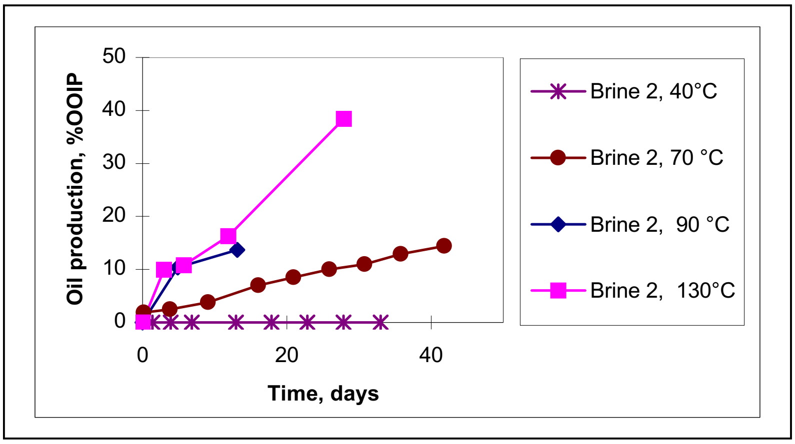


Figure 14-1. SI of brine into oil-wet chalk at different temperatures.

Figure 14-2 shows pictures of two cores imbibed at 90 and 130 °C. The pictures indicate that water has imbibed into certain zones, due to weak capillary forces. It is interesting to notice that the imbibition profiles are quite similar to the profiles observed for imbibition of anionic EO-surfactants into oil-wet chalk at 40 °C shown in **Figure 9-3**.

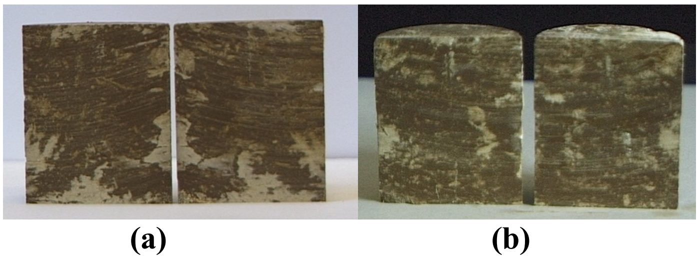
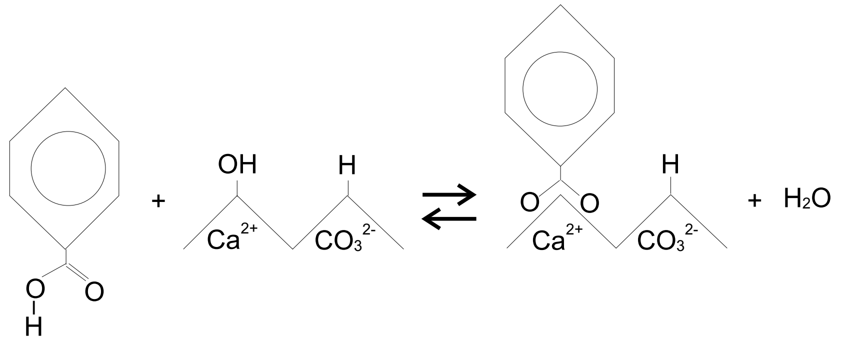


Figure 14-2. Residual oil saturation profile inside cleaved oil-wet chalk cores imbibed by pure brine. **(a)** Core tested at 90 °C, and **(b)** Core tested at 130 °C.

14.2. Thermal effects upon heating carbonate reservoirs

14.2.1. Adsorption of benzoic acid on calcium carbonate

Carbonate reservoirs become oil-wet when organic components, mainly negatively charged components, are adsorbed to the mineral surface from the crude oil. Legens *et al.* (1998b) calculated the binding energy for benzoic acid and water molecules towards clusters of calcium carbonate. The energies were calculated to be –221.3 and –225.9 kJ/mol for benzoic acid and water, respectively. Furthermore, calculations showed that the change in free energy for the saponification reaction in Eq. 14-1 (Legens *et al.*, 1998b) was approximately zero.



[14-1]

This means that the equilibrium is sensitive to respective concentration of free water and benzoic acid molecules. Most of the carbonate surface will be hydrated in excess of water and the equilibrium is displaced to the left. In excess of benzoic acid, the equilibrium will be displaced to the right and the saponification reaction will take place. Adsorption of benzoic acid will therefore preferentially take place from an oil phase where the water activity is low compared to an aqueous phase.

14.2.2. Dissolution of water in oil

Several authors have reported increased dissolution of water in the oil phase with increasing temperature (Glandt and Chapman, 1995; Griswold and Kasch, 1942; Liu and Buckley, 1995). **Figure 14-3** shows dissolution of water in mole % into different oils as the temperature increases.

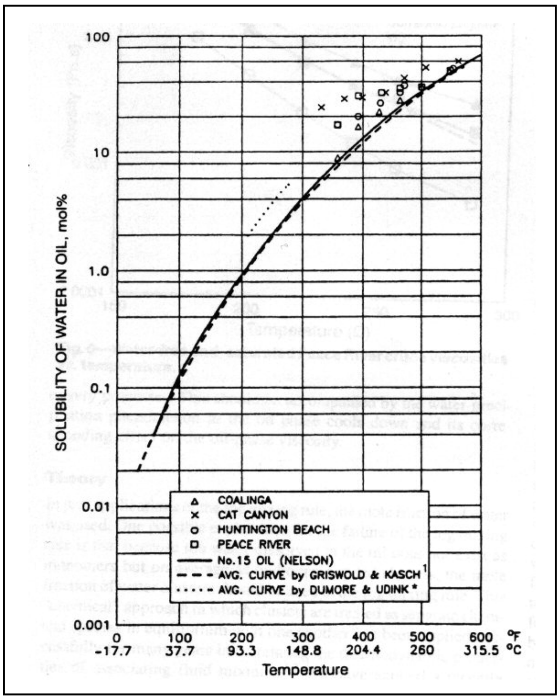


Figure 14-3. Solubility curves for water into different oils (mole %) as a function of temperature. After Glandt and Chapman (1995).

Approximately 0.1 mole % water can be dissolved in crude oil at 38 °C and the amount increases to approximately 2 mole % at 130 °C. These values indicate that the activity of water in the oil phase can be significant as the temperature increases. The water molecules are expected to exist as clusters in the oil phase. Each cluster contained 2-8 water molecules, and the cluster size and the cluster size increased with increased polarity of the crude (Glandt and Chapman, 1995).

Furthermore, the reactivity of water molecules in the oil phase increases significantly compared to water present in the aqueous phase, due to difference in solubilization energies for water molecules in the oil phase and the aqueous phase (Parker, 1969). Thomas *et al.* (1993a) observed that fatty acids adsorbed irreversible into a carbonate surface. Only water-saturated toluene and 40 % iso-propanol in water were able to desorb the acids from the mineral surface. Water molecules dissolved in the oil phase were therefore ***assumed to have the ability to displace organic material adsorbed to the chalk and alter the wettability of the mineral surface***, when the water concentration exceeds some critical concentration.

14.2.3. Mechanism for increased water-wetness of carbonate at elevated temperatures

Based on these observations, the following scenario can possibly take place in a crude oil/brine/oil-wet carbonate system when raising the temperature. There will exist a competition between polar oil components and water molecules to adsorb to the mineral surface from the oil phase. The outcome is governed by the activity of the respective components given by the equilibrium reaction in **Figure 14-4**.

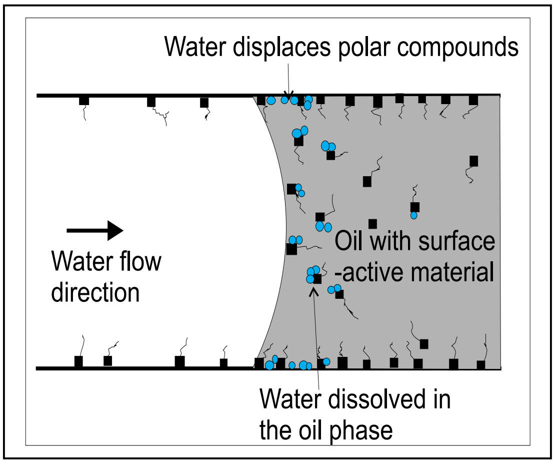


Figure 14-4. Proposed mechanism for increased water-wetness in oil-wet carbonate with increasing temperature. The dissolution of water into the oil phase increased with increasing temperature. The high water activity in the oil phase causes water to displace oil-wetting organic components from the mineral surface and the water-wetness increases.

At low temperatures, the water activity in the oil phase is low and the polar oil components will cover most of the mineral surface. Hence, the surface will act oil-wet under these conditions. When the temperature increases, the dissolution of water in the oil phase increases and water molecules can start to compete with the polar oil components, especially the carboxylates, for sites on the calcium carbonate surface. Water will displace polar components from the mineral surface with increasing water activity and the surface will become more water-wet. The critical temperature where the original oil-wet carbonate rock starts to act water-wet, will depend on the original concentration of polar oil components, the AN of the oil, the ability for the crude to dissolve water and the chemical nature of the polar components originally adsorbed to the mineral surface.

Another contribution to increased water-wetness with increasing temperature is based on the assumption that the following reaction is exothermic, which will displace the equilibrium of the following reaction to the right:

$$\text{Polar components (oil phase) + carbonate surface} \rightleftarrows \text{Polar components (carbonate surface) + Heat} \qquad [14\text{-}2]$$

The assumption seems reasonable due to reported values for ΔG. Madsen and Lind (1998) calculated $\Delta G \approx -22$ kJ/mol from adsorption data for adsorption of benzoic acid from organic solution into Stevns Klint chalk. Johnson and Dettre (1969) suggested that increase in temperature could have large effect on wettability due to desorption of monolayers. Thus, the number of polar oil components adsorbed to an oil-wet mineral surface will decrease in a COBR system where the oil phase is totally free for water upon increasing the temperature.

14.3. Summary on thermally induced wettability alteration

The presented results show that EOR due to a wettability alteration towards more water-wet conditions can be a significant effect when supplying heat to oil-wet carbonate reservoirs. The mechanism underlying the wettability alteration was discussed by increased dissolution of water in the oil phase at elevated temperature. The water will displace the oil-wetting components from the carbonate surface when the water activity in the oil phase exceeds some critical value.

The results presented here should, however, not be regarded as conclusive, but rather as preliminary suggestions and a starting point for further investigation, both experimentally as well as theoretically.

Part 5 Concluding remarks

This part of the thesis presents the conclusions, which can be drawn from the work. Also recommendations for future work are suggested.

Chapter 15. Conclusions and future work

15.1. Conclusions

The first objective of this work was to put forward a hypothesis about the mechanism for SI of aqueous surfactant solution, C12TAB, into oil-wet chalk material. A mechanism explaining the imbibition process based on several experimental approaches and tests is presented.

Knowing the mechanism, the second objective was to screen different cheaper surfactants systems for their ability to displace oil in the same manner as for C12TAB surfactant. Knowledge about the mechanism underlying the SI process simplified this work, and several different cheaper surfactants, which are believed to act in the same way as C12TAB, have been screened and tested for their ability to spontaneously imbibe water into oil-wet carbonates. The following conclusions can be drawn from the experimental results:

Saturation procedures and restoration of oil-wet carbonate cores

- Strongly water-wet outcrop chalk cores have to be flooded in each direction with the actual oil in order to obtain homogeneous wettability when using crude oil to alter the wettability towards more oil-wet conditions
- Strongly water-wet outcrop chalk cores and dolomite reservoir cores can be rendered oil-wet by aging the cores in crude oils having an AN of about 1 mg KOH/g oil

Imibition mechanisms for cationic- and anionic surfactants into oil-wet chalk

- Oil-wetting components containing carboxylate groups adsorbing strongly onto the chalk surface can be desorbed by cationic surfactants under the formation of ion-pairs. Electrostatic- and hydrophobic interaction between the two species appeared to drive the desorption process
- Contact angle measurements on calcite crystals pre-exposed to crude oil and model oils containing fatty acids and then exposed to cationic surfactant solutions confirmed the ability for cationic surfactants to alter the wettability towards a more water-wet condition

- The desorbed material can either stay in the water-phase under formation of mixed micelles or be transferred to the oil-phase as oil-pairs or clusters of ion-pairs
- The surfactant concentration should stay above CMC to ensure a maximum concentration of surfactant monomers during the desorption process. In addition, the micelles will solubilize the desorbed material
- The surfactant should not lower the oil-water IFT too much in order to maintain a strong capillary driven imbibition of water when the oil-wetting components have been desorbed
- Anionic EO-surfactants are able to render oil-wet chalk weakly water-wet by creating a bilayer structure where hydrophilic EO-groups are pointing out from the organic coating. Water can then imbibe slowly due to weak capillary forces

The relative influence of capillary- to gravity forces during SI into oil-wet low-permeable chalk

- Increasing the length of the core samples and lowering the oil-water IFT will increase the influence of the gravity forces compared to the capillary forces. Increased influence of gravity forces is likely to imply a decrease in the imbibition rate as demonstrated for C12TAB at 40 °C
- Oil-water IFT increases with increasing temperature for cationic surfactants of the type C_nTAB. Long-core experiments using C12TAB at 70 °C confirmed that capillary forces dominated the SI process at this temperature. The oil production rate did not decreased significantly compared to short core experiments at 70 °C

SI into short- and long oil-wet dolomite reservoir cores

- C12TAB solution is able to alter the wettability from oil-wet to more water-wet conditions and thereby spontaneously imbibe into restored dolomite reservoir cores
- The oil production rate and the ultimate oil recovery level are depending on each individual core, but C12TAB is in general 2-3 times more efficient to produce oil compared to the ethoxylated alcohol, $C_{9\text{-}11}(C_2H_4O)_8OH$, from the short cores
- C12TAB is able to expel oil efficiently in a counter-current flow mode from long oil-wet dolomite reservoir cores at 22 °C
- Dolomite reservoir cores previously imbibed by C12TAB are able to take up oil spontaneously when the core is surrounded by oil

Amines as wettability alteration modifiers for oil-wet carbonate

- C10-amine solutions, which are stable at high salinities and pH of about 6.5, altered the wettability of oil-wet carbonate towards a more water-wet state in the same way as C12TAB
- C10-amine solutions imbibe fast into oil-wet dolomite reservoir cores at 40 °C. However, the imbibition process almost ceased when raising the temperature to 70 °C, probably because of decrease in the concentration of the active $C10NH_3^+$ surfactant due to reaction with the dolomite surface. Thus, amines can probably only be applied as wettability modifiers in low-temperature carbonate reservoirs
- Contact angle measurements on calcite crystals confirm the ability for C10-amine solutions to render calcite surfaces pre-exposed to crude oil more water-wet

Low-cost bio-derivate products from coconut as wettability modifier for oil-wet carbonate

- Arquad and Dodigen, containing cationic surfactants of the type C_nTAC (n = 12 and 14 for Arquad and n = 12, 14, 16 and 18 for Dodigen), are able to alter the wettability of oil-wet chalk- and dolomite cores towards a more water-wet state in the same way as C12TAB
- Arquad was much more efficient than Dodigen to produce oil from both oil-wet chalk cores and oil-wet dolomite reservoir cores. The reasons were discussed in relationship to both lower CMC and oil-water IFT for Dodigen compared to Arquad
- Contact angle measurements on calcite crystals confirm the ability for Arquad and Dodigen solutions to alter the wettability of calcite surfaces pre-exposed to crude oil towards a more water-wet state
- Experimental results so far point towards Arquad to be the most promising chemical for field application in fractured oil-wet carbonate reservoirs, due to high displacement efficiency in the laboratory tests and low price

Thermally induced wettability alteration in chalk

- Water imbibes into oil-wet chalk at elevated temperature. Increased water-wetness at elevated temperature for carbonates reported in several articles was assumed to be the reason for this observation
- The increase in water-wetness at elevated temperature is suggested to be due to increased dissolution of water in the oil phase as the temperature increases. The water molecules are believed to compete with the organic oil-wetting components in the oil

phase for sites on the carbonate surface. Water molecules are believed to displace oil-wetting components like carboxylates from the carbonate surface as the concentration of water increases (elevated temperature) and water can then imbibe spontaneously into the porous medium

The overall new scientific contribution presented in this work is the demonstration of very high oil recoveries by SI of aqueous solutions into oil-wet porous carbonates. Based on the experimental observations, a reasonable chemical mechanism for the wettability alteration is also suggested, which must be regarded as an important contribution to the topic, wettability and surface phenomena in enhanced oil recovery processes

15.2. Future work

Research related to the mechanism for SI of surfactant solutions onto oil-wet material is of course far from closed with this thesis. Further work on the subject can be divided into two main areas, i.e., more fundamental work is needed, and then, more field-related problems must be handled. Examples of more fundamental work are:

- Characterization of the organic components/functional groups in the crude oil which adsorbed to the carbonate surface
- A closer look at the rock-amine solution interaction to improve the understanding about the decrease in imbibition rate for amines at elevated temperature
- More detailed investigations of physico-chemical processes related to the SI of brine into oil-wet chalk at elevated temperature
- Develop scaling laws for SI into oil-wet material

Work related to field application:

- A model describing the wettability alteration mechanism should be included into commercial reservoir simulators for predicting laboratory- and field behavior
- Loss of surface-active chemicals/surfactants like adsorption and phase partitioning must be quantified for specific field conditions
- Optimal surfactant concentration and compositional distribution for the C_nTAC must be tested and related to the specific field
- Regarding the oil-water transition zone: Is water-wet carbonate able to take up crude oil spontaneously?

References

Adams, W. T. and Schievelbein, V. H., 1987. ***Surfactant flooding carbonate reservoirs***. SPE Reservoir Engineering, November, pp. 619-626.

Al-Hadhrami, H. S., and Blunt, M. J., 2000. ***Thermally induced wettability alteration to improve oil recovery in fractured reservoirs***. Paper SPE 59289 presented at the SPE/DOE Improved Oil Recovery Symposium held in Tulsa, OK, USA, April 3-5.

Al-Lawati, S. and Saleh, S., 1996. ***Oil recovery in fractured oil reservoirs by low IFT imbibition process***. Paper SPE 36688 presented at the SPE Annual Technical Conference and Exhibition held in Denver, CO, USA, October 6-9.

Al-Maamari, R. S. H. and Buckley, J. S., 2000. ***Asphaltene precipitation and alteration of wetting: Can wettability change during oil production?*** Paper SPE 59292 presented at the SPE/DOE Improved Oil Recovery Symposium held in Tulsa, OK, USA, April 3-5.

Alveskog, P. L., Holt, T., and Torsæter, O., 1998. ***The effect of surfactant concentration on the Amott wettability index and residual oil saturation***. Journal of Petroleum Science and Engineering, 20, pp. 247-252.

Amott, E., 1959. ***Observations relating to the wettability of porous rock***. Petroleum Transactions, AIME, pp. 156-162.

Anderson, W. G., 1986a. ***Wettability literature survey - Part 1: Rock/oil/brine interactions and the effects of core handling on wettability***. Journal of Petroleum Technology, Trans., AIME 281, pp. 1125-1144.

Anderson, W. G., 1986b. ***Wettability literature survey - Part 2: Wettability measurements***. Journal of Petroleum Technology, Trans., AIME 281, pp. 1246-1262.

Anderson, W. G., 1987a. ***Wettability literature survey- Part 4: Effect of wettability on capillary pressure***. Journal of Petroleum Technology, October, pp. 1283-1300.

Anderson, W. G., 1987b. ***Wettability literature survey- Part 5: The effect of wettability on relative permeability***. Journal of Petroleum Technology, November, pp. 1453-1468.

Anderson, W. G., 1987c. ***Wettability literature survey- Part 6: The effect of wettability on waterflooding***. Journal of Petroleum Technology, December, pp. 1605-1622.

Aronofsky, J. S., Masse, L., and Natanson, S. G., 1958. ***A model for the mechanism of oil recovery from the porous matrix due to water invasion in fractured reservoirs***. Petroleum Transactions, AIME, Vol. 213, pp. 17-19.

Arriola, A., Willhite, G. P., and Green, D. W., 1983. ***Trapping of oil drops in a noncircular pore throat and mobilization upon contact with a surfactant***. SPE Journal, February, pp. 99-114.

Arteaga-Cardona, M., Pineda-Muñoz, A., and Islas-Juárez, R., 1996. ***Injection of dilute alkaline solutions to improve the recovery factor in oil-wet reservoirs***. Paper SPE 35340 presented at the SPE International Petroleum Conference and Exhibition held in Villahermosa, Mexico, March.

Ashayer, R., Grattoni, C. A., and Luckham, P. F., 2000. ***Wettability changes due to surfactant adsorption***. Paper presented at the 6th International Symposium on Reservoir Wettability and Its Effect on Oil Recovery, Socorro, NM, USA, September 27-28.

Austad, T., Matre, B., Milter, J., Sævareid, A., and Øyno, L., 1998. ***Chemical flooding of oil reservoirs 8. Spontaneous oil expulsion from oil- and water-wet low permeable chalk material by imbibition of aqueous surfactant solutions***. Colloid and Surfaces A: Physicochemical and Engineering Aspects 137, pp. 117-129.

Austad, T. and Milter, J., 1997. ***Spontaneous imbibition of water into low permeable chalk at different wettabilities using surfactants***. Paper SPE 37236 presented at the International Symposium on Oilfield Chemistry held in Houston, TX, USA, February 18-21.

Bäckström, K., Lindman, B., and Engström, S., 1988. ***Removal of triglycerides from polymer surfaces in relation to surface packing. Ellipsometry studies***. Langmuir, Vol. 4, No. 4, pp. 872-878.

Babadagli, T., 1996. ***Temperature effect on heavy-oil recovery by imbibition in fractured reservoirs.*** Journal of Petroleum Science and Engineering, 14, pp. 197-208.

Babadagli, T., 2000. ***Scaling of co-current and counter-current capillary imbibition for surfactant and polymer injection in naturally fractured reservoirs***. Paper SPE 62848 presented at the SPE/AAPG Western Meeting held in Long Beach, CA, USA, June 19 -23.

Bavière, M., 1991. ***Preface***. In: Critical Reports on Applied Chemistry Volume 33. Basic Concepts in Enhanced Oil Recovery Processes. Ed. Bavière, M. Published for SCI by Elsevier Applied Science, London and New York, pp. V-VIII.

Bavière, M., Bazin, B., and Labrid, J., 1989. ***Chemical stability of surfactants for micellar flooding under North Sea conditions***. In situ, 13(3), pp. 101-120.

Benner, F. C. and Bartell, F. E., 1942. ***The effect of polar impurities upon capillary and surface phenomena in petroleum production***. Drill. and Prod. Prac., API, New York City, pp. 341-348.

Bjørlykke, K., 1984. ***Lærebok i sedimentologi og petroleumsgeologi***. Universitetsforlaget.

Blair, Jr., C. M., 1982. ***United States Patent 4,341,265***. July 27.

Blair, Jr., C. M. and Stout, C. A., 1985. ***Interfacial spreading agents increase waterflood production***. Oil and Gas Journal, May 20, pp. 55-59.

Blair, P. M., 1964. ***Calculation of oil displacement by countercurrent water imbibition***. SPE Journal, September, pp. 195-202.

Bobek, J. E., Mattax, C. C., and Denekas, M. O., 1958. ***Reservoir rock wettability-its significance and evaluation***. Pet. Trans. AIME 213, pp. 155-160.

Boggs, S., Jr., 1995. ***Principles of sedimentology and stratigraphy. Second edition***. Prentice-Hall, Inc.

Boneau, D. F. and Clampitt, R. L., 1977. ***A surfactant system for the oil-wet sandstone of the North Burbank Unit***. Journal of Petroleum Technology, May, pp. 501-506.

Bourbiaux, B. J. and Kalaydjian, F. J., 1990. ***Experimental study of cocurrent and countercurrent flows in natural porous media***. SPE Reservoir Engineering, August, pp. 361-368

Briggs, P. J., Baron, R. P., Fulleylove, R. J., and Wright, M. S., 1988. ***Development of heavy-oil reservoirs***. Journal of Petroleum Technology, February, pp. 206-214.

Brownscombe, E. R. and Dyes, A. B., 1952. ***Water-imbibition displacement … Can it release reluctant Spraberry oil?*** The Oil and Gas Journal, November 17th, pp. 264-267.

Buckley, J. S., 1993. ***Asphaltene precipitation and crude oil wetting***. Paper SPE 26675 presented at the SPE 68th Annual Technical Conference and Exhibition held in Houston, TX, USA, October 3-6.

Buckley, J. S., 1996. ***Mechanisms and consequences of wettability alteration by crude oils***. Doctor of Philosophy Thesis. Department of Petroleum Engineering, Heriot-Watt University, Edinburgh, UK.

Buckley, J. S., Bousseau, C., and Liu, Y., 1995. ***Wettability alteration by brine and crude oil: From contact angles to cores***. Paper SPE 30765 presented at the SPE Annual Technical Conference and Exhibition held in Dallas, TX, USA, October 22-25.

Chauveteau, G. and Sorbie, K. S., 1991. ***Mobility Control by polymers***. In: Critical Reports on Applied Chemistry Volume 33. Basic Concepts in Enhanced Oil Recovery Processes. Ed. Bavière, M. Published for SCI by Elsevier Applied Science, London and NewYork, pp. 43-87.

Chen, H. L., Lucas, L. R., Nogaret, L. A. D., Yang, H. D., and Kenyon, D. E., 2000. ***Laboratory monitoring of surfactant imbibition using computerized tomography***. Paper SPE 59006 presented at the SPE International Petroleum Conference held in Villahermosa, Mexico, February 1-3.

Chernicoff, S., 1999. ***Geology. Second edition***. Houghton Mifflin Company, Boston, MA, USA.

Chilingar, G. V. and Yen, T. F., 1983. ***Some notes on wettability and relative permeabilities of carbonate reservoir rocks, II***. Energy Sources, Volume 7, Number 1, pp. 67-75.

Chimienti, M. E., Illiano, S. N., and Najurieta, H. L., 1999. ***Influence of temperature and interfacial tension on spontaneous imbibition process***. Paper SPE 53668 presented at the SPE Latin America and Caribbean Petroleum Engineering Conference held in Caracas, Venezuela, April 21-23.

Cimino, R., Correra, S., Del Bianco, A., and Lockhart, T. P., 1995. ***Solubility and phase behavior of asphaltenes in hydrocarbon media***. In: Asphaltenes: Fundamentals and Applications. Eds. Sheu, E. Y. and Mullins, O. C. Plenum Press, New York, pp. 97 -130.

Clampitt, R. L. and Reid, T. B., 1975. ***An economic polymerflood in the North Burbank Unit Osage County, Oklahoma***. Paper SPE 5552 presented at the 50th Annual Fall Meeting of the SPE of AIME held in Dallas, TX, USA, September 28-October 1.

Clementz, D. M., 1982. ***Alteration of rock properties by adsorption of petroleum heavy ends: Implications for enhanced oil recovery***. Paper SPE/DOE 10683 presented at the SPE/DOE third joint Symposium on EOR held in Tulsa, OK, USA, April 4-7.

Collins, S. H. and Melrose, J. C., 1983. ***Adsorption of asphaltenes and water on reservoir rock minerals***. Paper SPE 11800 presented at the International Symposium on Oilfield and Geothermal Chemistry held in Denver, CO, USA, June 1-3.

Cooke, Jr., C. E., Williams, R. E., and Kolodzie, P. A., 1974. ***Oil recovery by alkaline waterflooding***. Journal of Petroleum Technology, December, pp. 1365-1374.

Buckley, J. S., Hirasaki, G. J., Liu, Y., Von Drasek, S., Wang, J-X., and Gill, B. S., 1998. ***Asphaltene precipitation and solvent properties of crude oils***. Petroleum Science and Technology, 16 (3 & 4), pp. 251-285.

Buckley, J. S. and Liu, Y., 1998. ***Some mechanisms of crude oil/brine/solid interactions***. Journal of Petroleum Science and Engineering, 20, pp. 155-160.

Buckley, J. S., Liu, Y., Xie, X., and Morrow, N. R., 1996. ***Asphaltenes and crude oil wetting-The effect of oil composition***. Paper SPE/DOE 35366 presented at the SPE/DOE Improved Oil Recovery Symposium held in Tulsa, OK, USA, April 21-24.

Buckley, J. S. and Morrow, N. R., 1990. ***Characterization of crude oil wetting behavior by adhesion tests***. Paper SPE/DOE 20263 presented at the 7th Symposium on EOR held in Tulsa, OK, USA, April 22-25.

Buckley, J. S., Takamura, K., and Morrow, N. R., 1989. ***Influence of electrical surface charges on the wetting properties of crude oils***. SPE Reservoir Engineering, August, pp. 332-340.

Buckley, J. S. and Wang, J., 2000. ***Crude oil characterization for prediction of wetting alteration***. Paper presented at the 6th International Symposium on Reservoir Wettability and Its Effect on Oil Recovery held in Soccoro, NM, USA, September 27-28.

Caria, A. and Khan, A., 1996. ***Phase behavior of catanionic surfactant mixtures: Sodium bis(2-ethylhexyl)sulfosuccinate-didodecyldimethylammonium bromide-water system***. Langmuir, 12, pp. 6282-6290.

Castor, T. P., Somerton, W. H., and Kelly, J. F., 1981. ***Recovery mechanisms of alkaline flooding***. In: Surface Phenomena in Enhanced Oil Recovery. Ed. Shah, D. O. Plenum Press, New York City, pp. 249-291.

Celik, M. S. and Somasundaran, P., 1980. ***Wettability of reservoir minerals by flotation and correlation with surfactant adsorption***. Paper SPE 9002 presented at the SPE International Symposium on Oilfield and Geothermal Chemistry held at Stanford, CA, USA, May 28-30.

Chatzis, I., Morrow, N. R., and Lim, H. T., 1983. ***Magnitude and detailed structure of residual oil saturation***. SPE Journal, April, pp. 311-326.

Chaumet, P. and Cottin, R. H., 1991. ***Methodology and screening criteria-implementation of EOR processes***. In: Critical Reports on Applied Chemistry Volume 33. Basic Concepts in Enhanced Oil Recovery Processes. Ed. Bavière, M. Published for SCI by Elsevier Applied Science, London and New York, pp. V-VIII.

Craig, D. H., 1988. ***Cave and other features of the Permian karst in San Andres dolomite, Yates field reservoir, west Texas***. In: Paleokarst. Eds. James, N. P. and Choquette, P. W. Springer-Verlag, Berlin, pp. 342-363.

Crocker, M. E. and Marchin, L. M., 1988. ***Wettability and adsorption characteristics of crude-oil asphaltene and polar fractions***. Journal of Petroleum Technology, April, pp. 470-474.

Cross, J. 1994. ***Volumetric analysis of cationic surfactants***. In: Surfactant science series vol. 53. Cationic surfactants. Analytical and biological evaluation. Eds. Cross, J. and Singer, E. J. Marcel Dekker, Inc., New York, pp. 140-175.

Cuiec, L., 1977. ***Study of problems related to the restoration of the natural state of core samples***. The Journal of Canadian Petroleum Technology, October-December, pp. 68-80.

Cuiec, L., 1984. ***Rock/crude-oil interactions and wettability: An attempt to understand their interrelation***. Paper SPE 13211 presented at the SPE 59th Annual Technical Conference and Exhibition held in Houston, TX, USA, September 16-19.

Cuiec, L. E., 1991. ***Evaluation of reservoir wettability and its effect on oil recovery***. In: Surfactant science series vol. 36. Interfacial Phenomena in Petroleum Recovery. Ed. Morrow, N. R. Marcel Dekker, Inc., New York and Basel.

Cuiec, L., Bourbiaux, B., and Kalaydjian, F., 1994. ***Oil recovery by imbibition in low permeability chalk***. SPE Formation Evaluation 9, pp. 200-208.

Danielson, H. H., Paynter, W. T., and Milton, Jr., H. W., 1976. ***Tertiary recovery by the Maraflood process in the Bradford field***. Journal of Petroleum Technology, February, pp. 129-138.

Davis, J. A. and Jones, S. C., 1968. ***Displacement mechanisms of micellar solutions***. Journal of Petroleum Technology, December, pp. 1415-1428.

Denekas, M. O., Mattax, C. C., and Davies, G. T., 1959. ***Effects of crude oil components on rock wettability***. Trans., AIME, 216, pp. 330-333.

Dixit, A. B., Buckley, J. S., McDougall, S. R., and Sorbie, K. S., 1998. ***Core wettability: Should I_{AH} equal I_{USBM}?*** Paper SCA-9809 presented at the Society of Core Analysts International Symposium held in Hague, The Netherlands, September 14-16.

Donaldson, E. C., Thomas, R. D., and Lorenz, P. B., 1969. ***Wettability determination and its effect on recovery efficiency***. SPE Journal, March, pp. 13-20.

Donmez, A., 1997. ***Investigation of the effect of temperature on heavy oil recovery by imbibition mechanism***. Paper SPE 37555 presented at the SPE International Thermal Operations and Heavy Oil Symposium held in Bakersfield, CA, USA, February 10-12.

Downs, H. H. and Hoover, P. D., 1989. ***Enhanced oil recovery by wettability alteration***. In: Oil-Field Chemistry. Enhanced Recovery and Production Stimulation. Eds. Borchardt, J. K. and Yen, T. F. A. C. S. Symposium Series 396. Washington D. C.

Dubey, S. T. and Doe, P. H., 1993. ***Base number and wetting properties of crude oils***. SPE Reservoir Engineering, August, pp. 195-200.

Dubey, S. T. and Waxman, M. H., 1989. ***Asphaltene adsorption and desorption from mineral surfaces***. Paper SPE 18462 presented at the SPE International Symposium on Oilfield Chemistry in Houston, TX, USA, February 8-10.

Dukhin, S. S., Kretzschmar, G., and Miller, R., 1995. ***Dynamics of adsorption at liquid interfaces. Theory, experiment, application***. Studies in interface science Vol. 1. Eds. Möbius, D. and Miller, R. Elsevier Science B. V.

Eksborg, S., Lagerström, P. O., Modin, R., and Schill, G., 1973. ***Ion-pair chromatography of organic compounds***. J. Chromatography, 83, pp. 99-110.

Ely, R., 1972. ***The Guerra experiment - A field test of tertiary detergent flooding***. Paper SPE 3800 presented at the Improved Oil Recovery Symposium of the SPE of AIME held in Tulsa, OK, USA, April 16-19.

Emery, L. W., Mungan, N., and Nicholson, R. W., 1970. ***Caustic slug injection in the Singleton field***. Journal of Petroleum Technology, December, pp. 1569-1576.

Evans, D. F. and Wennerström, H., 1994. ***The Colloidal Domain: Where Physics, Chemistry, Biology and Technology Meet***. VCH Publishers, Inc.

Farouq-Ali, S. M. and Stahl, C. D., 1970. ***Increased oil recovery by improved waterflooding***. Earth and Mineral Sciences, Volume 39, No. 4, January, pp. 25-28.

Foster, W. R., 1973. ***A low-tension waterflooding process***. Journal of Petroleum Technology, February, pp. 205-210.

French, M. S., Keys, G. W., Stegemeier, G. L., Ueber, R. C., Abrams, A., and Hill, H. J., 1973. ***Field test of an aqueous surfactant system for oil recovery, Benton field, Illinois***. Journal of Petroleum Technology, February, pp. 195-204.

Froning, H. R. and Leach, R. O., 1967. ***Determination of chemical requirements and applicability of wettability alteration flooding***. Journal of Petroleum Technology, June, pp. 839-843.

Frye, G. C., and Thomas, M. M., 1993. ***Adsorption of organic compounds on carbonate minerals. 2. Extraction of carboxylic acids from recent and ancient carbonates***. Chemical Geology, 109, pp. 215-226.

Frykman, P., 1994. ***Variability in petrophysical properties in Maastrichtian chalk outcrops at Stevns, Denmark***. DGU service report No. 38.

Gesztesi, G., Bodola, M., Török, J., Tóth, J., and Mating, B., 1997. ***Laboratory and field studies on gravitational effect in low-tension waterflooding***. Paper presented at the 9th European Symposium on Improved Oil Recovery held in Hague, The Netherlands, October 20-22.

Glandt, C. A. and Chapman, W. G., 1995. ***Effect of water dissolution on oil viscosity***. SPE Reservoir Engineering, February, pp. 59 64.

Gloton, M. P., Turmine, M., Mayaffre, A., Letellier, P., and Toulhoat, H., 1992. ***Study of asphaltenes adsorption on mineral surfaces by contact measurements: Kinetics of wettability changes***. In: Physical Chemistry of Colloids and Interfaces in Oil Production. Eds. Toulhoat, H. and Lecourtier, J., Paris, pp. 89-96.

Gogarty, W. B., 1976. ***Status of surfactant or micellar methods***. Journal of Petroleum Technology, January 1976, pp. 93-102.

Graham, J. W., 1958. ***Reverse-wetting logging***. Petroleum Transactions, AIME, Vol. 213, pp. 304-309.

Graham, J. W. and Richardson, J. G., 1959. ***Theory and application of imbibition phenomena in recovery of oil***. Petroleum Transactions, AIME, vol. 216, pp. 377-381.

Graue, A., Aspenes, E., Bognø, T., Moe, R. W., and Ramsdal, J., 2000. ***Alteration of wettability and wettability heterogeneity***. Paper presented at the 6th International Symposium on Reservoir Wettability and Its Effect on Oil Recovery held in Soccoro, NM, USA, September 27-28.

Graue, A. and Bognø, T., 1999. ***Wettability effects on oil recovery mechanisms in fractured reservoirs***. Paper SPE 56672 presented at the SPE Annual Technical Conference and Exhibition held in Houston, TX, USA, October 3-6.

Graue, A., Tonheim, E., and Baldwin, B., 1994. ***Control and alteration of wettability in low-permeability chalk***. Paper presented at the 3rd International Symposium on Evaluation of Reservoir Wettability and Its Effect on Oil Recovery held in Laramie, WY, USA, September 21-23.

Graue, A., Viksund, B. G., and Baldwin, B. A., 1998. ***Reproducible wettability alteration of low-permeable outcrop chalk***. Paper SPE 39662 presented at the SPE/DOE Improved Oil Recovery Symposium held in Tulsa, OK, USA, April 19-22.

Graue, D. J. and Johnson, Jr., C. E., 1974. ***Field trial of caustic flooding process***. Journal of Petroleum Technology, December, pp. 1353-1358.

Griswold, J. and Kasch, J. E., 1942. ***Hydrocarbon-water solubilities at elevated temperatures and pressures***. Ind. Eng. Chem. 34, No. 7, pp. 804-806.

Guo, B., Schechter, D. S., and Baker, R. O., 1998. ***An integrated study of imbibition waterflooding in the naturally fractured Spraberry trend area reservoirs***. Paper SPE 39801 presented at the SPE Permian Basin Oil and Gas Recovery Conference held in Midland, TX, USA, March 25-27.

Gupta, A. and Civan, F., 1994. ***An improved model for laboratory measurement of matrix to fracture transfer function parameters in immiscible displacement***. Paper SPE 28929 presented at the SPE 69th Annual Technical Conference and Exhibition held in New Orleans, LA, USA, September 25-28.

Haldorsen, H. H., Rego, C. A., Chang, D. M., Mayson, H. J., Creveling, Jr., D. M., 1985. ***An evaluation of the Prudhoe Bay gravity drainage mechanism by complementary techniques***. Paper SPE 13651 presented at the SPE California Regional Meeting held in Bakersfield, USA, March 27-29.

Hall, B. E., 1986. ***Workover fluids. Part 1-Surfactants have different chemical properties that should be understood to ensure proper application***. World Oil, May, pp. 111-114.

Hammervold, W. L., 1994. ***Capillary pressure and wettability measurements by improved diaphragm method***. Ph. D. Thesis, Stavanger University College.

Hamon, G., 2000. ***Field-wide variations of wettability***. Paper SPE 63144 presented at the SPE Annual Technical Conference and Exhibition held in Dallas, TX, USA, October 1-4.

Hamon, G. and Vidal, J., 1986. ***Scaling-up the capillary imbibition process from laboratory experiments on homogeneous and heterogeneous samples***. Paper SPE 15852 presented at the SPE European Petroleum Conference held in London, UK, October 20-22.

Heaviside, J., 1991. ***Measurement of relative permeability***. In: Surfactant science series vol. 36. Interfacial Phenomena in Petroleum Recovery. Ed. Morrow, N. R. Marcel Dekker, Inc., New York and Basel.

Hegnauer, R., 1963. ***Chemotaxonomie der Pflanzen II***. Birkhauser Verlag Basel and Stuttgart, pp. 390-415.

Hiemenz, P. C., and Rajagopalan, R., 1997. ***Principles of colloid and surface chemistry. Third edition, revised and expanded***. Marcel Dekker, Inc. New York, Basel, Hong Kong.

Hirasaki, G. J., 1991. ***Wettability: Fundamentals and surface forces***. SPE Formation Evaluation, June, pp. 217- 226.

Hjelmeland, O. S. and Larrondo, L. E., 1983. ***Experimental investigation of the effects of temperature, pressure, and crude oil composition on interfacial properties***. Paper SPE 12124 presented at the SPE 58th Annual Technical Conference and Exhibition held in San Francisco, CA, USA, October 5-8.

Hjelmeland, O. S. and Torsaeter, O., 1980. ***Wettability, the key to proper laboratory waterflooding experiments***. U. S. DOE CONF-8004140, Proc., International Energy Agency Workshop on EOR, Bartlesville Energy Technology Center, Bartlesville, OK, USA, pp. 1-24.

Holland, P. M. and Rubingh, R. H., 1991. ***Cationic surfactants in mixed surfactant systems***. In: Surfactant science series vol. 37. Cationic surfactants, Physical Chemistry. Eds. Rubingh, D. N. and Holland, P. M. Marcel Dekker, Inc., New York, pp. 141-187.

Hornof, V. and Morrow, N. R., 1987. ***Gravity effects in the displacement of oil by surfactant solutions***. SPE Reservoir Engineering, November, pp. 627-633.

Hove, A. O., Dawe, R. A., and Evans, R. N., 1995. ***Gravity segregation at the pore scale in cores under miscible and low interfacial tension conditions including in-situ tomography***. Journal of Petroleum Science and Engineering, 14, pp. 89-98.

Howard, J. J. and Spinler, E. A., 1993. ***Nuclear magnetic resonance measurements of wettability and fluid saturations in chalk***. Paper SPE 26471 presented at the SPE 68th Annual Technical Conference and Exhibition held in Houston, TX, USA, October 3-6

Inks, C. G. and Lahring, R. I., 1968. ***Controlled evaluation of a surfactant in secondary recovery***. Journal of Petroleum Technology, November, pp. 1320-1324.

Jadhunandan, P. P. and Morrow, N. R., 1991. ***Spontaneous imbibition of water by crude oil/brine/rock systems***. In situ 15(4), pp. 319-345.

Jadhunandan, P. P. and Morrow, N. R., 1995. ***Effect of wettability on waterflooding recovery for Crude-oil/Brine/Rock systems***. SPE Reservoir Engineering, February, pp. 40-46.

Jennings, Jr., H. Y., Johnson, Jr., C. E., and McAuliffe, C. D., 1974. ***A caustic waterflooding process for heavy oils***. Journal of Petroleum Technology, December, pp. 1344-1352.

Jia, D., Buckley, J. S., Morrow, N. R., 1991. ***Control of core wettability with crude oil***. Paper SPE 21041 presented at the SPE International Symposium on Oilfield Chemistry held in Anaheim, CA, USA, February 20-22.

Johnson, Jr., C. E., 1976. ***Status of caustic and emulsion methods***. Journal of Petroleum Technology, January, pp. 85-92.

Johnson, R. E. and Dettre, R. H., 1969. ***Wettability and contact angles***. In: Surface and Colloid Science. Ed. Matijevic, E. Wiley Interscience, New York City, 2, pp. 85-153.

Jokela, P., Jönsson, B., and Khan, A., 1987. ***Phase equilibrium of catanionic surfactant-water systems***. Journal of Physical Chemistry, Vol. 91, No. 12, pp. 3291-3298.

Kaminsky, R. and Radke, C. J., 1998. ***Water films, asphaltenes, and wettability alteration***. Paper SPE 39087 presented at the SPE/DOE Improved Oil Recovery Symposium held in Tulsa, OK, USA, April 19-22.

Karlsson, J. S., 2001. ***Alkanoic acid-alkylamine complexation and surfactant phase behaviour***. Dr. Thesis, Department of Physical Chemistry, Faculty of Mathematics and Natural Sciences, Åbo Akademi University, Finland.

Kazemi, H., Gilman, J. R., and Eisharkawy, A. M., 1992. ***Analytical and numerical solution of oil recovery from fractured reservoirs with empirical transfer functions***. SPE Reservoir Engineering, May, pp. 219-227.

Kennedy, W. J., 1985. ***Sedimentology of the late cretaceous and early palaeocene chalk group, North Sea Central Graben***. Paper presented at the Norwegian Petroleum Directorate/Danish Energy Agency Chalk Research Program Symposium/Seminar held in Stavanger, Norway, May 21-22.

Khan, A. and Marques, E., 1997. ***Catanionic surfactants***. In: Specialist surfactants, Ed. Robb, I. D. Blakie Academic & Professional, London, Chapter 3.

King, R. L., Stiles Jr., J. H., and Waggoner, J. M., 1970. ***A reservoir study of the Hawkins Woodbine field***. Paper SPE 2972 presented at the 45th Annual Fall Meeting of the SPE of AIME held in Houston, TX, USA, October 4-7.

Knight, R. K. and Baer, P. J., 1973. ***A field test of soluble-oil flooding at Higgs Unit***. Journal of Petroleum Technology, January, pp. 9-15.

Kowalewski, E., Holt, T., and Torsaeter, O., 2000. ***Wettability alterations due to an oil soluble additive***. Paper presented at the 6th International Symposium on Reservoir Wettability and Its Effect on Oil Recovery held in Soccoro, NM, USA, September 27-28.

Kremesec, V. J. and Treiber, L. E., 1978. ***Effect of system wettability on oil displacement by micellar flooding***. Journal of Petroleum Technology, January, pp. 52-60.

Kyte, J. R. and Mattax, C. C., 1961. ***Effect of reservoir environment on water-oil displacements***. Journal of Petroleum Technology, June, pp. 579-582.

Laplace, P. S., 1806. ***Mechanique Celeste, Supplement to Book 10***. Duprat, J. B. M., Paris.

Laue, T. and Plagens, A., 1998. ***Named organic reactions***. John Wiley & Sons Ltd, Baffins Lane, Chichester, West Sussex PO19 1UD, England.

Leach, R. O., Wagner, O. R., Wood, H. W., and Harpke, C. F., 1962. ***A laboratory field study of wettability adjustment in water flooding***. Journal of Petroleum Technology, February, pp. 206-212.

Legens, C., Palermo, T., Toulhoat, H., Fafet, A., and Koutsoukos, P., 1998a. ***Carbonate rock wettability changes induced by organic compound adsorption***. Journal of Petroleum Science and Engineering 20, pp. 277-282.

Legens,C., Toulhoat, H., Cuiec, L., Villiéras, F., and Palermo, T., 1998b. ***Wettability change related to the adsorption of organic acids on calcite: experimental and ab initio computational studies***. Paper SPE 49319 presented at the SPE Annual Technical Conference and Exhibition held in New Orleans, LA, USA, September 27-30.

Lenormand, R. and Zarcone, C., 1984. ***Role of roughness and edges during imbibition in square capillaries***. Paper SPE 13264 presented at the SPE 59th Annual Technical Conference and Exhibition held in Houston, TX, USA, September 16-19.

Liu, Y. and Buckley, J. S., 1995. ***Evolution of wetting alteration by adsorption from crude oil***. Paper SPE 28970 presented at the International Symposium on Oilfield Chemistry held in San Antonio, TX, USA, February 14-17.

Lorenz, P. B., Donaldson, E. C., and Thomas, R. D., 1974. ***Use of centrifugal measurements of wettability to predict oil recovery***. Report 7873, U. S. Bureau of Mines, Bartlesville Energy Technology Center, Bartlesville, OK, USA.

Lund, T. A. T., Berge, H. I., Espedal, S., Kristensen, R., Rolfsvåg, T. A., and Strømsvik, G., 1995. ***The technical performance and results from a large scale Na-silicate gel treatment of a production well at the Gullfaks field***. Paper presented at the 8th European Symposium on Improved Oil Recovery held in Vienna, Austria, May 15-17.

Lyford, P. A., Pratt, H. R. C., Grieser, F., and Shallcross, D. C., 1998a. ***The Marangoni effect and enhanced oil recovery part 1. Porous media studies***. The Canadian Journal of Chemical Engineering, Vol. 76, April, pp. 167-174.

Lyford, P. A., Shallcross, D. C., Grieser, F., and Pratt, H. R. C., 1998b. ***The Marangoni effect and enhanced oil recovery part 2. Interfacial tension and drop instability***. The Canadian Journal of Chemical Engineering, Volume 76, April, pp. 175-182.

Ma, S., Morrow, N. R., and Zhang, X., 1997. ***Generalized scaling of spontaneous Imbibition data for strongly water-wet systems***. Journal of Petroleum Science and Engineering, 18, pp. 165-178.

Ma, S., Zhang, X., and Morrow, N. R., 1995. ***Influence of fluid viscosity on mass transfer between fractures and matrix***. Paper CIM 95-94 presented at the Petroleum Society of CIM Annual Technical Meeting held in Banff, Alberta, Canada, May 14-17.

Macaulay, R. C., Krafft, J. M., Hartemink, M., and Escovedo, B., 1995. ***Design of a steam pilot in a fractured carbonate reservoir-Qarn Alam Field, Oman***. Paper SPE 30300 presented at the International Heavy Oil Symposium held in Calgary, Canada, June 19-21.

Madsen, L., Grahl-Madsen, L., Grøn, C., Lind, I., and Engell, J., 1996. ***Adsorption of polar aromatic hydrocarbons on synthetic calcite***. Organic Geochemistry, Vol. 24, No. 12, pp. 1151-1155.

Madsen, L. and Lind, I., 1998. ***Adsorption of carboxylic acids on reservoir minerals from organic and aqueous phase***. SPE Reservoir Evaluation and Engineering, February, pp. 47-51.

Malmsten, M. and Lindman, B., 1989. ***Ellipsometry studies of cleaning of hard surfaces. Related to the spontaneous curvature of the surfactant monolayer***. Langmuir, Vol. 5, No. 4, pp. 1105-1111.

Marsden, S. S. and Nikias, P. A., 1962. ***The wettability of the Bradford sand. I***. Producers Monthly 26, No. 5, pp. 2-5.

Marle, C. M., 1991. ***Oil entrapment and mobilization***. In: Critical Reports on Applied Chemistry Volume 33. Basic Concepts in Enhanced Oil Recovery Processes. Ed. Bavière, M. Published for SCI by Elsevier Applied Science, London and New York, pp. 3-39.

Mattax, C. C. and Kyte, J. R., 1962. ***Imbibition oil recovery from fractured, water-drive reservoir***. SPE Journal, June, pp. 177-184.

Mazzullo, S. J., Chilingarian, G. V., and Bissell, H. J., 1992. ***Carbonate rock classifications***. In: Development in Petroleum Science, 30. Carbonate reservoir characterization: A Geologic-Engineering Analysis, Part I. Eds. Chilingarian, G. V., Mazzullo, S. J., and Rieke, H. H. Elsevier Science Publishers B. V., pp. 59-108.

Melrose, J. C., 1982. ***Interpretation of mixed wettability states in reservoir rocks***. Paper SPE 10971 presented at the SPE 57th Annual Fall Technical Conference and Exhibition held in New Orleans, LA, USA, September 26-29.

Menezes, J. L., Yan, J., and Sharma, M. M., 1989. ***The mechanism of wettability alteration due to surfactants in oil-based muds***. Paper SPE 18460 presented at the SPE International Symposium on Oilfield Chemistry held in Houston, TX, USA, February 8-10.

Michaels, A. S. and Porter, M. C., 1965. ***Water-oil displacements from porous media utilizing transient adhesion-tension alterations***. A. I. Ch. E. Journal, Vol. 11, No. 4, July.

Michaels, A. S. and Timmins, R. S., 1960. ***Chromatographic transport of reverse-wetting agents and its effect on oil displacement in porous media***. Petroleum Transactions, AIME, 219, pp. 150-157.

Michaels, A. S., Stancell, A., and Porter, M. C., 1964. ***Effect of chromatographic transport in hexylamine on displacement of oil by water in porous media***. SPE Journal, September, pp. 231-239.

Michels, A. M., Djojosoeparto, R. S., Haas, H., Mattern, R. B., van der Weg, P. B., and Schulte, W. M., 1996. ***Enhanced water flooding design using dilute surfactant concentrations for North Sea conditions***. Paper SPE/DOE 35372 presented at the 10th Symposium on Improved Oil Recovery held in Tulsa, OK, USA, April 21-24.

Milter, J., 1996. ***Improved Oil Recovery in Chalk. Spontaneous imbibition affected by wettability, rock framework and interfacial tension***. Dr. Sc. Thesis. Department of Chemistry, University of Bergen, Norway.

Milter, J. and Austad, T., 1996a. ***Chemical flooding of oil reservoirs 6. Evaluation of the mechanism for oil expulsion by spontaneous imbibition of brine with and without surfactant in water-wet, low-permeable chalk material***. Colloids and Surfaces A: Physicochemical and Engineering Aspects 113, pp. 269-278.

Milter, J. and Austad, T., 1996b. ***Chemical flooding of oil reservoirs 7. Oil expulsion by spontaneous imbibition of brine with and without surfactant in mixed-wet, low-permeable chalk material***. Colloids and Surfaces A: Physicochemical and Engineering Aspects 117, pp. 109-115.

Milter, J. and Øxnevad, I. E. I., 1996. ***Spontaneous imbibition in two different chalk facies.*** Petroleum Geoscience 2, pp. 231-240.

Mohanty, K. K., Davis, H. T., and Scriven, L. E., 1987. ***Physics of oil entrapment in water-wet rock***. SPE Reservoir Engineering, February, pp. 113-128.

Morris, E. E. and Wieland, D. R., 1963. ***A microscopic study of the effect of variable wettability conditions on immiscible fluid displacement***. Paper SPE 704 presented at the 38th Annual Fall Meeting of the SPE of AIME in New Orleans, LA, USA, October 6-9.

Morrow, N. R., 1970. ***Physics and thermodynamics of capillary***. Industrial and Engineering Chemistry, Vol. 62, No. 6, June, pp. 32-56.

Morrow, N. R., 1975. ***The effects of surface roughness on contact angle with special reference to petroleum recovery***. The Journal of Canadian Petroleum Technology, October-December, pp. 42-53.

Morrow, N. R., 1976. ***Capillary pressure correlations for uniformly wetted porous media***. Journal of Canadian Petroleum Technology, October-December, 15, No. 4, pp. 49-69.

Morrow, N. R., 1979. ***Interplay of capillary, viscous and buoyancy forces in the mobilization of residual oil***. Journal Canadian Petroleum Technology, September, pp. 35-46.

Morrow, N. R., 1987. ***A review of the effects of initial saturation, pore structure and wettability on oil recovery by waterflooding***. North Sea Oil and Gas Reservoirs. The Norwegian Institute of Technology, Graham and Trotman, pp. 179-191.

Morrow, N. R., 1990. ***Wettability and its effect on oil recovery***. Journal of Petroleum Technology, December, pp. 1476-1484.

Morrow, N. R., 1991. ***Introduction to interfacial phenomena in oil recovery***. In: Surfactant science series volume 36. Interfacial Phenomena in Petroleum Recovery. Ed. Morrow, N. R. Marcel Dekker, Inc., New York, pp. 1-21.

Morrow, N. R. and McCaffery, F. G., 1978. ***Displacement studies in uniformly wetted porous media***. In: Wetting, Spreading, and Adhesion. Ed. Padday, G. F. Academic Press, NewYork City, pp. 289-319.

Morrow, N. R., Cram, P. J., and McCaffery, F. G., 1973. ***Displacement studies in dolomite with wettability control by octanoic acid***. SPE Journal, August, pp. 221-232.

Morrow, N. R., Lim, H. T., and Ward, J. S., 1986. ***Effect of crude-oil-induced wettability changes on oil recovery***. SPE Formation Evaluation, February, pp. 89-103.

Morrow, N. R., Ma, S., Zhou, X., and Zhang, X., 1999. ***Characterization of wettability from spontaneous imbibition measurements***. Journal of Canadian Petroleum Technology. Special Edition, Volume 38, No. 13, Paper: 94-47.

Morrow, N. R. and Songkran, B., 1981. ***Effect of viscous and buoyancy forces on nonwetting phase trapping in porous media***. In: Surface Phenomena in Enhanced Oil Recovery. Ed. Shah, D. D. Plenum Press, New York, pp. 387 –411.

Morrow, N. R., Tang, G., Valat, M., and Xie, X., 1998. ***Prospects of improved oil recovery related to wettability and brine composition***. Journal of Petroleum Science and Engineering, 20, pp. 267-276.

Mukhayer, G. I. and Davis, S. S., 1975. ***Interactions between large organic ions of opposite charge 1. Stoichiometry of the interactions of sodium dodecyl sulfate with benzyltriphenylphosphonium chloride***. Journal of Colloid and Interface Science, Vol. 53, No. 2, November, pp. 224-234.

Munkerjee, P. and Mysels, K. J., 1971. ***Critical micelle concentration of aqueous surfactant systems***. NSRDS-NBS-36, National Bureau of Standards, Washington, D. C.

Murty, C. R. K., Al-Saleh, N., and Dakessian, B. A., 1987. ***Forty-seven years' gas injection in a preferentially oil-wet, low-dip reservoir***. Journal of Petroleum Technology, March, pp. 363-368.

Mørk, P. C., 1997. ***Overflate og kolloidkjemi. Grunnleggende prinsipper og teorier. 5. utgave***. Institutt for Industriell kjemi, Fakultet for Kjemi og Biologi. NTNU.

Neumann, A. W. and Good, R. J., 1979. ***Techniques of measuring contact angles***. In: Surface and Colloid Science. Eds. Good, R. J. and Stromberg, R. R. Plenum Press, New York City 11, pp. 31-91.

Nogaret, L. A. D., 2000. ***Personal communication***. Marathon Oil Company, Petroleum Technology Center, Littleton, CO, USA, May.

Norwegian Petroleum Directorate, 1993. ***Improved Oil Recovery – Norwegian Continental shelf***. The Norwegian Petroleum Directorate (NPD).

Nutting, P. G., 1934. ***Some physical and chemical properties of reservoir rocks bearing on the accumulation and discharge of oil***. In: Problems of Petroleum Geology. Eds. Wrather, W. E. and Lahee, F. H. AAPG, Tulsa, pp. 825-832.

Olsen, D. K., Hicks, M. D., Hurd, B. G., Sinnokrot, A. A., and Sweigart, C. N., 1990. ***Design of a novel flooding system for an oil-wet central Texas carbonate reservoir***. Paper SPE 20224 presented at the SPE/DOE 7th Symposium on EOR held in Tulsa, OK, USA, April 22-25.

Owens, W. W. and Archer, D. L., 1971. ***The effect of rock wettability on oil-water relative permeability relationships***. Journal of Petroleum Technology, July, pp. 873-878.

Parker, A. J., 1969. ***Protic-diprotic aprotic solvent effects on rates of bimolecular reactions***. Chemical Reviews, Volume 69, No. 1, February, pp. 1-32.

Parsons, R. W. and Chaney, P. R., 1966. ***Imbibition model studies on water-wet carbonate rocks***. SPE Journal, March, pp. 26-34.

Pierre, A., Lamarche, J. M., Mercier, R., Foissy, A., and Persello, J., 1990. ***Calcium as potential determing ion in aqueous calcite suspensions***. J. Dispersion Science and Technology, 11, No. 6, pp. 611-635.

Pope, G. A. and Bavière, M., 1991. ***Reduction of capillary forces by surfactants***. In: Critical Reports on Applied Chemistry Volume 33. Basic Concepts in Enhanced Oil Recovery Processes. Ed. Bavière, M. Published for SCI by Elsevier Applied Science, London and New York, pp. 89-122.

Pratt, H. R. C., 1991. ***Marangoni flooding with water drives: A novel method for EOR?*** Paper SPE 22982 presented at the SPE Asian-Pacific Conference held in Perth, Australia, November 4-7.

Pursley, S. A., Healy, R. N., and Sandvik, E. I., 1973. ***A field test of surfactant flooding, Loudon, Illinois***. Journal of Petroleum Technology, July, pp. 793-802.

Raimondi, P., Gallagher, B. J., Ehrlich, R., Messmer, J. H., and Bennett, G. S., 1976. ***Alkaline waterflooding: Design and implementation of a field pilot***. Paper SPE 5831 presented at the SPE-AIME 4th Symposium on Improved Oil Recovery held in Tulsa, OK, USA, March 22-24.

Rao, D. N., 1996. ***Wettability effects in thermal recovery operations***. Paper SPE/DOE 35462 presented at the SPE/DOE 10th Symposium on Improved Oil Recovery held in Tulsa, OK, USA, April 21-24.

Rao, D. N., 1997. ***Is there a correlation between wettability from corefloods and contact angles?*** Paper SPE 37234 presented at the SPE International Symposium on Oilfield Chemistry held in Houston, TX, USA, February 18-21.

Rao, D. N. and Bassiouni, Z. A., 2000. ***A new technique to confidently characterize wettability alterations induced by drilling/completion/workover fluids***. Paper SPE 59516 presented at the SPE International Symposium on Formation Damage Control held in Lafeyette, LA, USA, February 23-24.

Rao, D. N. and Girard, M. G., 1996. ***A new technique for reservoir wettability characterization***. Journal of Canadian Petroleum Technology Volume 35, No. 1, January, pp. 31-39.

Rapoport, L. A., 1955. ***Scaling laws for use in design and operation of water-oil flow models***. Petroleum Transactions, AIME, Vol. 204, pp. 143-150.

Rathmell, J. J., Braun, P. H., and Perkins, T. K., 1973. ***Reservoir waterflood residual oil saturation from laboratory tests***. Journal of Petroleum Technology, February, pp. 175-185.

Reis, J. C., 1992. ***An analysis of oil expulsion mechanisms from matrix blocks during steam injection in naturally fractured reservoirs***. In situ vol. 16, No. 1, pp. 43-73.

Reis, J. C. and Cil, M., 1993. ***A model for oil expulsion by counter-current water imbibition in rocks: one-dimensional geometry***. Journal of Petroleum Science and Engineering, 19, pp. 97-107.

Reisberg, J. and Doscher, T. M., 1956. ***Interfacial phenomena in crude-oil-water systems***. Producers Monthly, November, pp. 43-50.

Roof, J. G., 1970. ***Snap-off of oil droplets in water-wet pores***. SPE Journal, March, pp. 85-90.

Rosen, M. J., 1986. ***Molecular interaction and synergism in binary mixtures of surfactants***. In: Am. Chem. Soc. Symposium Series 311. Phenomena in Mixed Surfactant Systems. Ed. Scamehorn, J. F. Washington, D. C., pp. 144-162.

Rosen, M. J., 1989. ***Surfactants and interfacial phenomena***. Second Edition. John Wiley & Sons, Inc.

Ruth, D., Morrow, N., Yu, L., and Buckley, J. S., 2000. ***Simulation study of spontaneous imbibition***. Proceedings to the International Symposium of the Society of Core Analysts Annual Meeting held in Abu Dhabi, United Arabian Emirates, October.

Rønningsen, H. P., 1991. ***The chemistry of asphaltenes and their significance in crude oil exploration and production***. Lecture for the Degree of Doctor of Philosophy, December 13, Oslo, Norway.

Salathiel, R. A., 1973. ***Oil recovery by surface film drainage in mixed-wettability rocks***. Journal of Petroleum Technology, October, pp. 1216-1224.

Sayyouh, M. H., Dahab, A. S., and Omar, A. E., 1990. ***Effect of clay content on wettability of sandstone reservoirs***. Journal of Petroleum Science and Engineering, 4, pp. 119-125.

Sayyouh, M. H., Hemeida, A. M., Al-Blehed, M. S., and Desouky, S. M., 1991. ***Role of polar compounds in crude oils on rock wettability***. Journal of Petroleum Science and Engineering, 6, pp. 225-233.

Schatzinger, R. A., Feazel, C. T., and Henry, W. E., 1985. ***Evidence of resedimentation in chalk from the Central Graben, North Sea***. Paper presented at the Norwegian Petroleum Directorate/Danish Energy Agency Chalk Research Program Symposium/ Seminar held in Stavanger, Norway, May 21-22.

Schechter, D. S., Zhou, D., and Orr, F. M. Jr., 1991. ***Capillary imbibition and gravity segregation in low IFT systems***. Paper SPE 22594 presented at the SPE 66th Annual Technical Conference and Exhibition held in Dallas, TX, USA, October 6-9.

Schechter, D. S., Zhou, D., and Orr, F. M. Jr., 1994. ***Low IFT drainage and imbibition***. Journal of Petroleum Science and Engineering, 11, pp. 283-300.

Schumacher, M. M., 1978. ***Secondary recovery of crude oil***. In: Enhanced Oil Recovery. Secondary and tertiary methods. Ed. Schumacher, M. M. Noyes Data Corporation, Park Ridge, New Jersey, USA, pp. 17-32.

Seifert, W. K. and Howells, W. G., 1969. ***Interfacially active acids in a California crude oil. Isolation of carboxylic acids and phenols***. Analytical Chemistry Vol. 41, No. 4, April, pp. 554-562.

Seifert, W. K. and Teeter, R. M., 1970. ***Identification of polycyclic aromatic and heterocyclic crude oil carboxylic acids***. Analytical Chemistry, Vol. 42, No. 7, June, pp. 750-758.

Seright, R. S. and Liang, J., 1994. ***A survey of field application of gel treatments for water shutoff***. Paper SPE 26991 presented at the III Latin American/Caribbean Petroleum Engineering Conference held in Buenos Aires, Argentina, April 27-29.

Sharma, M. M., and Wunderlich, R. W., 1985. ***The alteration of rock properties due to interactions with drilling fluid components***. Paper SPE 14302 presented at the SPE Annual Technical Conference and Exhibition held in Las Vegas, NV, USA, September 22-25.

Shergold, H. L., 1987. ***Cationic surfactants in mineral processing***. In: Industrial Applications of Surfactants. The Proceedings of a Symposium organized by the North West Region of the Industrial Division of the Royal Society of Chemistry, University of Salford, April 15th-17th 1986. Ed. Karsa, D. R. The Royal Society of Chemistry, Burlington House, London W1V 0BN.

Skauge, A. and Fosse, B., 1996. ***A study of the adhesion, interfacial tension, and contact angles for a brine, quartz, crude oil system***. Paper presented at the 3th International Symposium on Evaluation of Reservoir Wettability and Its Effect on Oil Recovery held in Laramie,WY, USA, September 21-23.

Skauge, A., Standal, S., Boe, S. O., Skauge, T., and Blokhus, A. M., 1999. ***Effects of organic acids and bases, and oil composition on wettability***. Paper SPE 56673 presented at the SPE Annual Technical Conference and Exhibition held in Houston, TX, USA, October 3-6.

Smith, D. L., Cox, M. F., Russell, G. L., Earl, G. W., Lacke, P. M., Mays, R. L., and Fink, J. M., 1989. ***The interaction of dimethyl diallow ammonium chloride and sodium linear alkylbenzene sulfonate***. J. Am. Oil Chem. Soc., Vol. 66, no. 5, May, pp. 718-727.

Somerville, H. J., Bennett, D., Davenport, J. N., Holt, M. S., Lynes, A., Mahieu, A., McCourt, B., Parker, J. G., Stephenson, R. R., Watkinson, R. J., and Wilkinson, T. G., 1987. ***Environmental effect of produced water from North Sea oil operations***. Marine pollution bulletin, Volume 18/Number 10/October.

Sorbie, K. S., 1991. ***Polymer-improved oil recovery***. Blackie USA and Canada: CRC Press, Inc.

Speight, J. G., 1999. ***The chemistry and technology of petroleum. Third edition, revised and expanded***. Marcel Dekker, Inc. New York and Basel.

Spinler, E. A., 1997. ***Determination of in-situ wettability from laboratory and well log measurements for a carbonate field***. Paper SPE 38733 presented at the SPE Annual Technical Conference and Exhibition held in San Antonio, TX, USA, October 5-8.

Spinler, E. A, and Baldwin, B. A., 2000. ***Surfactant induced wettability alteration in porous media***. In: Surfactants, Fundamentals and Applications in the Petroleum Industry. Ed. Schramm, L. L. Cambridge University Press 2000.

Spinler, E. A., Baldwin, B. A., and Graue, A., 1999. ***Simultaneous measurement of multiple capillary pressure curves from wettability and rock property variations within single rock plugs***. Paper SCA-9957. Reviewed proceedings to the International Symposium of the Society of Core Analysts held in Golden, CO, USA, August 1-4.

Spinler, E. A., Baldwin, B. A., and Graue, A., 2000a. ***Experimental artifacts caused by wettability variations in chalk***. Paper presented at the 6th International Symposium on Reservoir Wettability and Its Effect on Oil Recovery held in Soccoro, NM, USA, September 27-28.

Spinler, E. A., Zornes, D. R., Tobola, D. P., and Moradi-Araghi, A., 2000b. ***Enhancement of oil recovery using a low concentration of surfactant to improve spontaneous and forces imbibition in chalk***. Paper SPE 59290 presented at the SPE/DOE Improved Oil Recovery Symposium held in Tulsa, OK, USA, April 3-5.

Standal, S., 1999. ***Wettability of solid surfaces induced by adsorption of polar organic components in crude oil***. Dr. Sc. Thesis, Department of Chemistry, University of Bergen, Norway.

Strand, S., 1996. ***Øvelser i Petroleumsproduksjon***. Laboratoriehefte i Petroleumsproduksjon, Institutt for Petroleumsteknologi, Høgskolen i Stavanger.

Sydansk, R. D. and Southwell, G. P., 1998. ***More than 12 years of experience with a successful conformance-control polymer gel technology***. Paper SPE 49315 presented at the SPE Annual Technical Conference and Exhibition held in New Orleans, LA, USA, September 27-30.

Szabo, M. T., 1975. ***Laboratory investigation of factors influencing polymer flood performance***. Society of Petroleum Engineers Journal, August, pp. 338- 346.

Taber, J. J., 1980. ***Research on Enhanced oil recovery: Past, present and future***. Pure and Appl. Chemistry, Vol. 52, pp. 1323-1347.

Takamura, K. and Chow, R. S., 1983. ***A mechanism for initiation of bitumen displacement from oil sand***. Journal of Canadian Petroleum Technology, November-December, pp. 22-30.

Tang, G. and Morrow, N. R., 1999. ***Oil recovery by waterflooding and imbibition-invading brine cation valency and salinity***. Paper SCA-9911 presented at the Annual Symposium of the Society of Core Analysts.

Taugbøl, K., 1995. ***Chemical flooding of oil reservoirs. Low tension polymer water flood***. Dr. Sc. Thesis. Department of Chemistry, University of Bergen, Norway.

Thiebot, B., Barroux, C., Bouvier L., Heugas, O., and Plazanet, V., 1990. ***Improvement of imbibition oil recovery from chalky fractured reservoirs by additives***. Presented at the 3th North Sea Chalk Symposium held in Copenhagen, Denmark.

Thomas, L. K., Dixon, T. N., Evans, C. E., Vienot, M. E., 1987. ***Ekofisk waterflood pilot***. J. Petroleum Technology, Trans., AIME 283, pp. 221-232.

Thomas, M. M., Clouse, J. A. and Longo, J. M., 1993a. ***Adsorption of organic compounds on carbonate minerals 1. Model compounds and their influence on mineral wettability***. Chemical Geology 109, pp. 201-213.

Thomas, M. M., Clouse, J. A. and Longo, J. M., 1993b. ***Adsorption of organic compounds on carbonate minerals 3. Influence on dissolution rates***. Chemical Geology 109, pp. 227-237.

Torsaeter, O., 1984. ***An experimental study of water imbibition in chalk from the Ekofisk field***. Paper SPE/DOE 12688 presented at the 4th Symposium on EOR held in Tulsa, OK, USA, April 15-18.

Torsaeter, O., 1988. ***A comparative study of wettability test methods based on experimental results from North Sea reservoir rocks***. Paper SPE 18281 presented at the SPE 63th Annual Technical Conference and Exhibition held in Houston, TX, USA, October 2-5.

Torsæter, O., Bøe, R., and Holt, T., 1997. ***An experimental study of the relationship between rock surface properties, wettability and oil production characteristics***. Paper SCA-9739. Proceedings to the International Symposium of the Society of Core Analysts held in Calgary, Canada, September 7-10.

Torsæter, O. and Silseth, J. K., 1985. ***The effects of sample shape and boundary conditions on capillary imbibition***. North Sea Chalk Symposium. Paper 10 presented at the Norwegian Petroleum Directorate/Danish Energy Agency Chalk research program Symposium/Seminar held in Stavanger, Norway, May 21-22.

Torvund, T. and Nipen, O., 1987. ***The Oseberg field: potential for increased oil recovery by gas injection in a high permeability environment***. North Sea Oil and Gas Reservoirs, NIT, Graham and Trotman, pp. 61-74.

Treiber, L. E., Archer, D. L., and Owens, W. W., 1972. ***A laboratory evaluation of the wettability of fifty oil producing reservoirs***. SPE Journal, December, Trans., AIME, 253, pp. 531-540.

Tweheyo, M. T., Holt, T., and Torsæter, O., 1999. ***An experimental study of the relationship between wettability and oil production characteristics***. Journal of Petroleum Science and Engineering, 24, pp. 179-188.

Varadaraj, R., Bock, J., Brons, N., and Zushma, S., 1994. ***Influence of surfactant structure on wettability modification of hydrophobic granular surfaces***. Journal of Colloid and Interface Science 167, pp. 207-210.

Veggeland, K. and Lohne, A., 1992. ***Phase behavior***. In: SPOR Monograph. Recent Advances in Improved Oil Recovery Methods for North Sea Sandstone Reservoirs. Eds. Skjæveland, S. M. and Kleppe, J. Norwegian Petroleum Directorate, Stavanger, Norway, pp. 248-256.

Viksund, B. G., Morrow, N. R., Ma, S., Wang, W., and Graue, A., 1998. ***Initial water saturation and oil recovery from chalk and sandstone by spontaneous imbibition***. Paper SCA-9814 presented at the Society of Core Analysts International Symposium held in Hague, The Netherlands, September 14-16.

Wagner, O. R. and Leach, R. O., 1959. ***Improved oil displacement efficiency by wettability adjustment***. Petroleum Transactions, AIME, Vol. 216, pp. 65-72.

Wang, W. and Gupta, A., 1995. *Investigation of the effect of temperature and pressure on wettability using modified pendant drop method*. Paper SPE 30544 presented at the SPE Annual Technical Conference and Exhibition held in Dallas, TX, USA, October 22-25.

Wardlaw, N. C., 1980. ***The effects of pore structure on displacement efficiency in reservoir rocks and in glass micromodels***. Paper SPE 8843 presented at the first joint SPE/DOE Symposium on EOR held in Tulsa, OK, USA, April 20-23.

Wardlaw, N. C., 1982. ***The effects of geometry, wettability, viscosity and interfacial tension on trapping in single pore-throat pairs***. The Journal of Canadian Petroleum Technology, May-June, pp. 21-27.

Wendel, D. J., Anderson, W. G., and Meyers, J. D., 1985. ***Restored-state core analysis for the Hutton reservoir***. Paper SPE 14298 presented at the SPE 60th Annual Technical Conference and Exhibition held in Las Vegas, NV, USA, September 22-25.

Wellington, S. L. and Richardson, E. A., 1997. ***Low surfactant concentration enhanced waterflooding***. SPE Journal, Volume 2, December, pp.389-405.

Wesson, L. L. and Harwell, J. H., 2000. ***Surfactant adsorption in porous media***. In: Surfactants: Fundamentals and Application in the Petroleum Industry. Ed. Scramm, L. L. Cambridge University Press.

Wilson, P. M. D. and Brander, C. F., 1977. ***Aqueous surfactant solutions which exhibit ultra-low tensions at the oil-water interface***. Journal of Colloid and Interface Science, Vol. 60, No. 3, July, pp. 473-479.

Wolcott, J. M., Groves, Jr., F. R., and Lee, H-G., 1993. ***Investigation of crude-oil/mineral interactions: Influence of oil chemistry on wettability alteration***. Paper SPE 25194 presented at the SPE International Symposium on Oilfield Chemistry held in New Orleans, LA, USA, March 2-5.

Wunderlich, R. W., 1991. ***Obtaining samples with preserved wettability***. In: Surfactant science series vol. 36. Interfacial Phenomena in Petroleum Recovery. Ed. Morrow, N. R. Marcel Dekker, Inc., New York and Basel.

Xie, X. and Morrow, N. R., 1999. ***Contact angles on quartz induced by adsorption of heteropolar hydrocarbons***. J. Adhesion Sci. Technol. Vol. 13, No 10, pp. 1119-1135.

Xie, X. and Morrow, N. R., 2000. ***Oil recovery by spontaneous imbibition from weakly water-wet rocks***. Paper 26 presented at the Annual Meeting of the Society of Core Analysts held in Abu Dhabi, United Arabian Emirates, October.

Xie, X., Morrow, N. R., and Buckley, J. S., 2000. ***Contact angle hysteresis and the stability of wetting changes induced by adsorption from crude oil***. Paper presented at the 6th International Symposium on Reservoir Wettability and Its Effect on Oil Recovery held in Socorro, NM, USA, September 27-28.

Yang, H. D. and Wadleigh, E. E., 2000. ***Dilute surfactant IOR-Design improvements for massive, fractured carbonate applications***. Paper SPE 59009 presented at the SPE International Petroleum Conference and Exhibition held in Villahermosa, Mexico, February 1-3.

Young, T., 1805. ***Philosophical Transactions***. Royal Society London, 95, p. 65

Yu, L. and Wardlaw, N. C., 1986. ***Mechanisms of nonwetting phase trapping during imbibition at slow rates***. Journal of Colloid and Interface Science, Vol. 109, No. 2, February, pp. 473-486.

Yu, L. and Wardlaw, N. C., 1991. ***Quantitative determination of pore structure from mercury capillary pressure curves***. In: Surfactant science series volume 36. Interfacial Phenomena in Petroleum Recovery. Ed. Morrow, N. R. Marcel Dekker, Inc., New York, pp. 101-156.

Zana, R., 1990. ***Micellization of cationic surfactants***. In: Surfactant science series vol. 37. Cationic Surfactants. Physical Chemistry. Eds. D. N. Rubingh and P. M. Holland. Marcel Dekker, Inc. New York and Basel, pp. 41-85.

Zhang, X., Morrow, N. R., and Ma, S., 1995. ***Experimental verification of a modified scaling group for spontaneous imbibition***. Paper SPE 30762 presented at the SPE Annual Technical Conference and Exhibition held in Dallas, TX, USA, October 22-25.

Zhou, D., Jia, L., Kamath, J., and Kovscek, A. R., 2000a. ***Scaling of counter-current imbibition processes in low-permeability porous media***. Paper presented at the 6th International Symposium on Reservoir Wettability and Its Effect on Oil Recovery held in Socorro, NM, USA, September 27-28.

Zhou, D. and Stenby, E. H., 1989. ***Immiscible displacement in a porous medium simulated by a statistical model***. In: North Sea oil and Gas Reservoirs-II. Ed. Buller *et al.*, Graham and Trotman, London, UK, pp. 271-280.

Zhou, X., Morrow, N. R., and Ma, S., 2000b. ***Interrelationship of wettability, initial water saturation, aging time, and oil recovery by spontaneous imbibition and waterflooding***. SPE Journal 5 (2), June, pp. 199-207. Revised for publication from Paper SPE 35436.

Zhou, X., Torsæter, O., Xie, X., and Morrow, N. R., 1993. ***The effect of crude-oil aging time and temperature on the rate of water imbibition and long-term recovery by imbibition***. Paper SPE 26674 presented at the SPE 68th Annual Technical Conference and Exhibition held in Houston, TX, USA, October 3-6.

Paper I

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