A Novel Approach to Surfactant Flooding Under Mixed-Wet Conditions

by

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PREFACE

This dissertation is submitted to the University of Stavanger (UiS) in partial fulfillment of the requirements for the degree of philosophiae doctor (PhD). The thesis includes the research work carried out during the academic duration of relevance. The outcome of this study is given through six papers.

ACKNOWLEDGEMENT

Without the support, patience and guidance of the following people, this study would not have been completed. It is to them that I owe my deepest gratitude.

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I came to Norway for studies through the educational cooperation between TUC (Telemark University College), Norway and UoM (University of Moratuwa), Sri Lanka. It seems appropriate at this point to express a special thanks to the staff at the Faculty of Technology, TUC and the lecturing staff at the Chemical & Process Engineering department, UoM.

My fellow doctoral students from both IRIS and UiS should be kindly remembered. A particular thank must be made to Anna Polanska for her friendly and constructive discussions. Few former master students from UiS who have been involved in the project are also acknowledged.

Finally, and most importantly, I express my warmest thanks to my loving parents and brother for their love and encouragement in all my pursuits. And most of all, my husband, Deshai Botheju for his loving words, faithfull support and encouragement is remarkable.

Thank you.

Kumuduni Abeysinghe
09.12.12
Sandefjord.

This thesis is dedicated to my loving parents…

SUMMARY

In early days, a large number of research studies have been done based on the assumption that most of the sandstone reservoirs are strongly water-wet. Now it is widely accepted that most of sandstone reservoirs are at wettability conditions other than strongly water-wet.

Surfactant flooding is one of the promising enhanced oil recovery methods that has been studied for many years. Traditional surfactant flooding studies have been reported utilizing mainly the mobilization of residual oil by increasing the capillary number and also assuming the water-wet formation. Capillary Desaturation Curve (CDC) represents the oil recovery potential by surfactants at water-wet conditions. Many investigations reported and assumed that this CDC concept is valid also for other wettability conditions.

This thesis represents the results from several core flooding experiments carried out in sandstone rock at different wettability conditions. The research study is focused on analyzing and understanding the oil recovery mechanisms by surfactants at mixed-wet conditions.

At mixed-wet / non water-wet conditions, it is found that the measured remaining oil and water saturation can be a function of the number of pore volume injected and can be also largely affected by capillary end effects. The residual oil saturation is difficult to obtain in core floods at mixed-wet / oil-wet conditions. Therefore the measured remaining saturation Vs capillary number in laboratory experiments does not represent the true CDC.

From the results of unsteady core floods, no conclusion can be drawn about the effect of surfactant on residual oil saturation at mixed/wet

conditions. Interpretation of experimental results show that the main oil recovery mechanism by surfactant at mixed-wet condition is accelerated oil production due to increased oil relative permeability at high N_c; not necessarily the reduction of residual oil.

When evaluating tertiary oil recovery at mixed-wet conditions, the focus should be directed towards relative permeability curves rather than residual oil saturation.

LIST OF PAPERS

Paper I :Chukwudeme, E. A., Fjelde, I., Abeysinghe, K. and Lohne, A. 2011. Effect of Interfacial Tension on Water/Oil Relative Permeability and Remaining Saturation with Consideration of Capillary Pressure. Paper SPE 143028, presented at the SPE EUROPEC/EAGE Annual Conference and Exhibition held in Vienna, Austria, 23-26 May. Submitted to SPE Reservoir Evaluation & Engineering.

Paper II :Abeysinghe, K. P., Fjelde, I. and Lohne, A. 2012. Dependency of Remaining Oil Saturation on Wettability and Capillary Number. Paper SPE 160883 prepared for the presentation at the 2012 SPE Saudi Arabia Section Technical Symposium and Exhibition held in Alkhobar, Saudi Arabia, 8 – 11 April.

Paper III :Abeysinghe, K. P., Fjelde, I. and Lohne, A. 2012. Acceleration of oil production in mixed-wet reservoirs by alteration of relative permeability curves using surfactants. Paper SPE 155626 prepared for the presentation at the SPE EOR Conference at Oil and gas West Asia held in Muscat, Oman 16 – 18 April. Submitted to SPE Reservoir Evaluation & Engineering.

Paper IV :Abeysinghe, K. P., Fjelde, I. and Lohne, A. 2012. Displacement of oil by surfactant flooding in mixed-wet condition. Paper SCA2012-23 prepared for the presentation at the International Symposium of the Society of Core Analysts held in Aberdeen, Scotland, UK, 27 – 30 August.

Paper V :Abeysinghe, K. P., Fjelde, I. and Lohne, A. 2012. Water flooding and surfactant flooding at different wettability conditions. Manuscript.

Paper VI :Abeysinghe, K. P., Fjelde, I. and Lohne, A. 2012. Effect of N_c on relative permeability at mixed-wet conditions. Manuscript.

CONTENTS

NOMENCLATURE

General Symbols

A = cross sectional area of the core
D = core diameter
fw = fractional water flow
I = Amott relative displacement index
k_{abs} = absolute permeability
k_r = relative permeability
k_{ro} = relative permeability to oil
k_{rw} = relative permeability to water
L = core length
n = saturation exponent
N_c = capillary number
N_{cc} = critical capillary number
N_{ct} = total capillary number
P_c = capillary pressure
Q = flow rate
R = resistivity
r = resistance
R_o = electrical resistivity of 100% water saturated rock
R_t = electrical resistivity of partially water saturated rock
S_o = oil saturation
S_{or} = residual oil saturation
S_{orw} = residual oil saturation after water flooding
S_{orc} = residual oil saturation after surfactant flooding
S_{of} = oil saturation determined by accessible water volume
S_w = water saturation
S_{wi} = initial oil saturation
S_{wr} = residual water saturation
t_D = dimensionless time
V_{osp} = oil displaced by spontaneous imbibition of water
V_{wsp} = water displaced by spontaneous imbibition of oil
V_{wt} = total amount of water displaced including V_{wsp}

v = darcy velocity
μ = viscosity
μ_o = viscosity of oil
μ_ω = viscosity of water

ρ = density
σ = interfacial tension
ϕ = porosity

Abbreviations

AN = Acid Number
BN = Basic Number
CDC = Capillary Desaturation Curve
CMC = Critical Micellar Concentration
DP = Differential Pressure
EOR = Enhanced Oil Recovery
FW = Formation Water
MW = Molecular Weight
NMR = Neuclear Magnetic Resonance
OF = Oil Flood
OP = Oil Production
OOIP = Original Oil In Place
PV = Pore Volume
RI = Resistivity Index
ROS = Remaining Oil Saturation
SF = Surfactant Flood
STO = Stock Tank Oil
WF = Water flood
WOR = Water Oil Ratio

SECTION 1

1 INTRODUCTION

1.1 Background of the study

Among the various Enhanced Oil Recovery (EOR) approaches, surfactant flooding is recognized as a promising method which has high potential for tertiary oil recovery (Reppert et al., 1990; Maerker and Gale, 1990; Alveskog et al., 1998).

The theory behind surfactant flooding was developed for water-wet formations considering the residual oil left after water flooding is trapped as discontinuous droplets (Zolotukhin and Ursin, 2000; Chatzis and Morrow, 1984). Mobilization of trapped oil depends on the ratio of viscous to capillary forces which is defined as capillary number (N_c).

The capillary number N_c is a dimensionless ratio of viscous forces to local capillary forces and can be defined in different ways (Sheng, 2011; Zolotukhin and Ursin, 2000; Lefebvre Du Prey, 1973).

$$N_c = \frac{\nu\mu}{\sigma} \tag{1}$$

Where v is Darcy velocity, μ is viscosity of the flowing phase and σ is interfacial tension between two phases.

It can also be defined as (Delshad et al., 1986; Mohanty and Salter, 1983)

$$N_c^{'} = \frac{k\ DP}{L\ \sigma} \tag{2}$$

Where k is absolute permeability of porous media, L is the length, DP is differential pressure and σ is interfacial tension between two phases.

The oil recovery potential by surfactant flooding is described by the capillary desaturation curve (CDC) that gives the variation of residual oil saturation (S_{or}) as a function of N_c. Commonly accepted CDC is based on water-wet conditions. It has a plateau in S_{or} at low N_c until a critical N_c (N_{cc}) is reached. Above N_{cc}, S_{or} will decrease as shown in Figure 1. Required increase in N_c can be achieved by surfactants which could significantly lower the interfacial tension (σ) between oil and water.

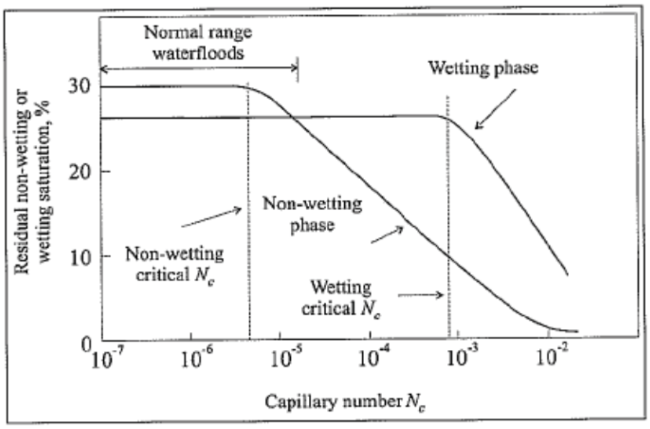


Figure 1 Capillary De-saturation curve [Lake,1989]

In early days, a large number of petroleum engineering studies were based on the assumption the most reservoirs were strongly water-wet. Now it is widely accepted and understood that the most reservoirs are at wettability conditions other than strongly water-wet. In several studies, mixed-wettability behavior proposed by Salathiel (1973) has been observed for reservoir core samples as well as model cores aged with crude oil.

It is assumed that the N_{cc} for wetting phase is two orders of magnitude higher than the N_{cc} for non-wetting phase (Lake, 1989). Some studies have been done to investigate the CDC for porous media at different wetting conditions. Mohanty and Salter (1983) measured CDC on water-wet, mixed-wet and oil-wet Berea sandstones (Figure 2). They observed typical CDC shape for water-wet cores where S_{or} decreased sharply above N_{cc}. In oil-wet and mixed-wet media, more gradual decrease in S_{or} was observed with increase in N_c. Chatzis and Morrow (1984) presented CDC for both continuous and discontinuous oil. They found that the corresponding N_c for the displacement of continuous oil is significantly lower than that required for mobilization of discontinuous oil. A similar observation was found by Johannesen and Graue (2007) after measuring CDC on outcrop chalk samples at different wettability conditions. They concluded that N_{cc} is low for weakly water-wet condition and increase as the wettability increase to strongly water-wet conditions. Garnes et al. (1990) measured CDC for some North Sea sandstone reservoirs and concluded that the CDC results showed a high potential for EOR. This conclusion was based on the observation of lower N_{cc} in the measured CDC shape. The correct shape of CDC at non water-wet conditions is a much debated subject.

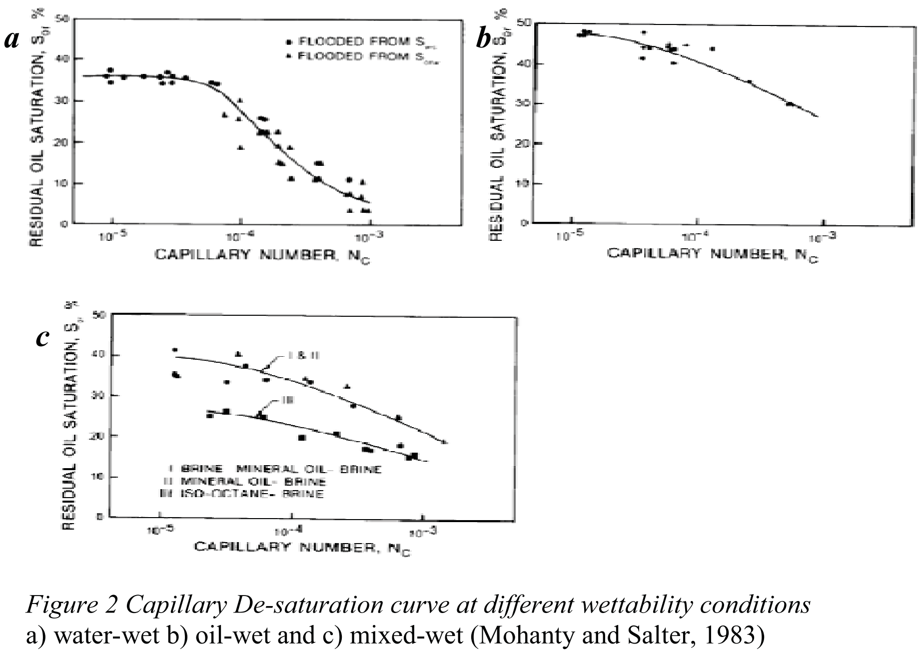


Figure 2 Capillary De-saturation curve at different wettability conditions
a) water-wet b) oil-wet and c) mixed-wet (Mohanty and Salter, 1983)

1.2 Scope

The focus in this PhD study has been investigating the recovery mechanisms in surfactant flooding at different wetting conditions, with the primary aim on the mixed-wet porous media. The work was mainly conducted in experimental basis but some simulation work has also been carried out in order to estimate the flow functions such as relative permeability and capillary pressure curves by history matching the experimental results.

The associated experimental work has been designed to measure the CDC under various wetting conditions with the primary focus on mixed-wet condition. Accordingly, core floods have been carried out under different wetting conditions, and the validity of measured CDC's is discussed.

In this study, relative permeability curves of oil-water at reduced interfacial tension have been estimated by history matching of experimental data. Two sets of k_r curves were established; one reference set with water-oil and a second set with surfactant-oil. These results are used to discuss the validity of measuring k_r curves for the prediction of oil recovery than measuring CDC at mixed-wet conditions. The oil recovery mechanisms using surfactants are also discussed and the main attention is kept on mixed-wet sandstone reservoirs.

1.3 Objectives

The basic objective of this PhD study has been to identify the governing oil recovery mechanisms during surfactant flooding at core-scale and at different wetting conditions. The work to fulfill this objective included laboratory measurements of CDC and water-oil k_r curves at reduced interfacial tension.

The following sub tasks have been the intended key stages of this study.

a) Selection of a suitable surfactant system that can be used for the intended experiments
b) Establish different wettability conditions in Berea sandstone rock
c) Characterize the established wetting conditions and the stability of wetting conditions during core floods
d) Measurement of CDC at different wettability conditions
e) Estimation of unsteady state k_r curves (low and high capillary numbers) at different wetting conditions (by history matchng)

1.4 Outlines of thesis

This thesis consists of two main sections. Section -1 includes six chapters. The current chapter (chapter 1) introduces the objectives of the study together with the general introduction. Chapter 2 gives a literature review of related topics such as wettability, surfactants and surfactant flooding in enhanced oil recovery. Chapter 3 describes the materials and experimental methods used in this study and chapter 4 is allocated to present the description of simulation method. Chapter 5 consists of eight sub chapters which present the main results and a discussion of main outcome of this research study. Chapter 6 presents a set of general conclusions derived from the overall study together with recommendations for further studies.

Section – 2 provides six research papers (published and unpublished) covering the spectrum of this research study.

2 LITERATURE REVIEW

This chapter provides a brief review of general concepts on related topics and previous research studies. The chapter starts from a discussion of the term ‘wettability’ which is one of the important properties of reservoir rock. After presenting different wettability conditions and the methods of measuring the wettability, a brief review of wettability alteration and effect of wettability on oil recovery are presented. The next, it presents a discussion of the fundamentals of surfactants such as classifications and basic principles. The third sub topic of this chapter is surfactant flooding.

2.1 Wettability

Wettability is defined as ‘the tendency of one fluid to spread on or adhere to a solid surface in the presence of other immiscible fluids’ (Anderson, 1986). The wettability of a reservoir rock affects the flow functions such as capillary pressure, relative permeability. It also affects electrical properties.

2.1.1 Wettability Classification

The literature has defined different types of wettability conditions ranging from strongly water-wet through neutral or intermediate wet to strongly oil-wet. The term mixed wettability was proposed by Salathiel (1973) to describe a special form of heterogeneous wettability condition with larger pores being oil-wet and smaller pores being water-wet. Fractional wettability is another type of heterogeneous wettability condition.

The different types of wettability conditions can be defined as follows.

Strongly water-wet: The rock has strong preference for water.

Neutral wet or Intermediate wet: The rock displays no preference for either oil or water; the system can be equally wetted by both oil and water.

Mixed wet: The smaller pores are occupied by water and are water-wet. The larger pores of the rock are oil-wet.

Fractional-wet: The scattered areas throughout the rock have different degrees of wettability (either water-wet or oil-wet).

Strongly oil-wet: The rock has strong preference for oil.

2.1.2 Wettability Measurements

A large number of qualitative and quantitative wettability measurements are available (Anderson, 1986). The mostly used quantitative methods include contact angle, Amott test and USBM test. Spontaneous imbibition curves, electrical resistivity measurements, NMR test, shape of recovery curves are classified as qualitative methods. However, the results from some qualitative wettability measurements can be interpreted to get a quantitative wettability index as suggested in literature. These methods are briefly discussed in the following sections.

2.1.2.1 Amott test

The Amott method combines spontaneous imbibition and forced displacement to measure the average wettability of a core (Anderson, 1986). This method is based on the principle that the wetting fluid will generally imbibe spontaneously into the core, displacing the non-wetting phase. The ratio of spontaneous imbibition to forced displacement is used to reduce the influence of other factors such as relative permeability, viscosity and the initial saturation of the rock.

The core is prepared by centrifuging (or by use of a high flowing pressure gradient) under brine until the residual oil saturation is reached. The test begins at the S_{or} and procedure involves four steps as follows.

I. The core is immersed in oil for 20 hours and the amount of water displaced by spontaneous imbibition of oil is recorded (V_{wsp}).
II. The core is centrifuged in oil (oil drive) until the residual water saturation S_{wi} is reached. The total amount of water displaced recorded including the V_{wsp} (V_{wt}).
III. The core is immersed in brine for 20 hours and the amount of oil displaced by spontaneous imbibition of brine is recorded (V_{osp}).
IV. The core is centrifuged in brine (brine drive) until the residual oil saturation S_{or} is reached. The total amount of oil displaced recorded including the V_{osp} (V_{ot}).

The test results are generally expressed as follows.

Displacement-by-oil ratio: $\delta_o = V_{wsp}/V_{wt}$

Displacement-by-water ratio: $\delta_w = V_{osp}/V_{ot}$

Amott relative displacement index: $I = \delta_w - \delta_o = V_{osp}/V_{ot} - V_{wsp}/V_{wt}$

Water-wet cores have a positive δ_w and zero value for δ_o. Similarly, oil-wet cores have a positive δ_o and zero value for δ_w. Both ratios are zero for neutrally-wet cores.

2.1.2.2 USBM test

The USBM method is quantitative test developed by Donaldson et al. (1969). This method is very similar to Amott method but measures the work required to do the imbibitions. Figure 3 illustrates the different P_c measurements (I, II & III) during the USBM test.

The wettability index is calculated from the areas under the capillary pressure curves (*A1* & *A2* in Figure 3). The capillary pressure curves are obtained by centrifuge method. The areas under the capillary pressure curves represent the thermodynamic work required for the respective fluid displacements. Displacement of a non-wetting phase by a wetting phase requires less energy than displacement of a wetting phase by a non-wetting phase. The wettability index W is calculated as;

$$W = \log (A1/A2)$$

where *A1* & *A2* are the areas under the oil and brine drive curves, respectively.

When *W* is greater than zero, the core is water-wet and when *W* is less than zero, the core is oil-wet. *W* value near zero, the core is neutrally wet.

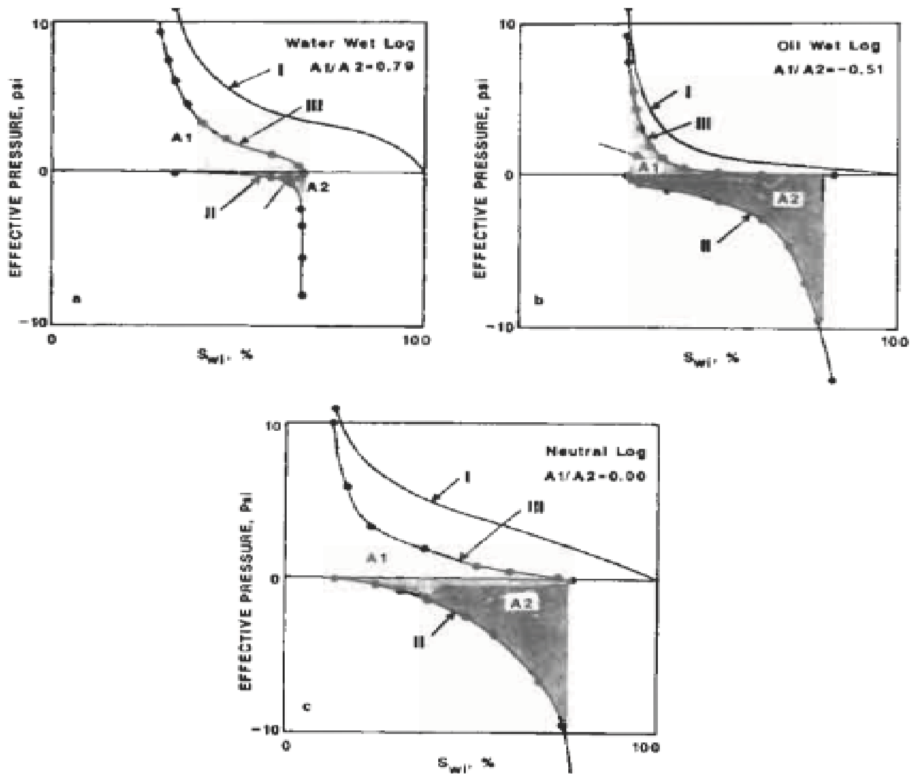


Figure 3 USBM wettability measurement (Donaldson et al. 1969)

2.1.2.3 Spontaneous imbibition curves

The spontaneous imbibition method is the most commonly used because it gives rough idea of the wettability (Zhou et al., 1996). The spontaneous imbibition rate (initial rate) and the total amount of fluid imbibed can be used to characterize the wettability. One problem with the spontaneous imbibition method is that, in addition to wettability, spontaneous imbibition rates also depend on rock permeability, viscosity of fluids, interfacial tension between wetting and non-wetting fluids and pore structure. This dependence on other variables can be reduced by comparison of the measured spontaneous imbibition rate with reference rate measured for strongly water wet cores. Based on the work of Mattax and Kyte (1961) the effects of above factors have been correlated by defining a dimensionless scaling parameter (t_D). This correlation has been adopted in many previous studies (Zhou et al., 1996; Ma et al., 1999).

Dimensionless time is defined as (Mattax and Kyte, 1961):

$$t_D = t\sqrt{\frac{k}{\phi}}\frac{\sigma}{\mu_w L^2} \tag{3}$$

where t is imbibition time (s) , k is permeability of rock (m^2), Φ is porosity (fraction), σ is interfacial tension (mN/m), μ_w is viscosity (cP) of water phase and L is core characteristic length (cm).

Zhou et al. (1996) used t_D including viscosity of oil (μ_o(cP)) as follows,

$$t_{D_1} = t\sqrt{\frac{k}{\phi}}\frac{\sigma}{\sqrt{\mu_w \mu_o} L^2} \tag{4}$$

Figure 4 shows an example of scaled spontaneous imbibition curves by using t_D.

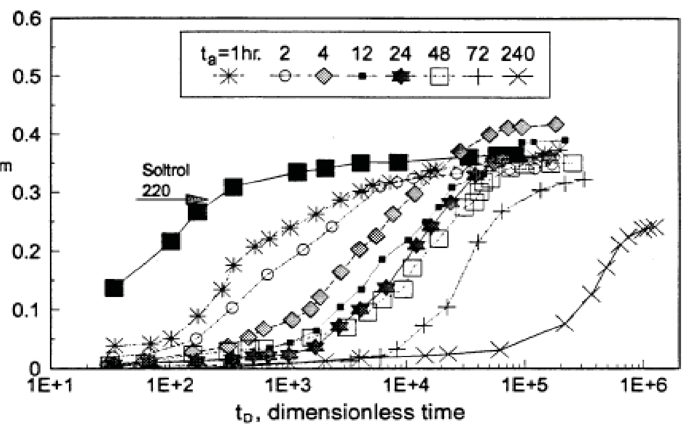


Figure 4 Example of scaled spontaneous inmibition curves (Ma et al., 1999)

2.1.2.4 Electrical resistivity measurements

As reported in literature, electrical resistivity measurements can be used to get an idea of wettability change in the rock (Anderson, 1986; Donaldson and Siddiqul, 1989; Sondenaa et al., 1991). Electrical resistivity of the plug (R) can be defined as follows.

$$R = r \ A/L$$

Where r is electrical resistance (Ω), A is cross sectional area (cm^2) of the core plug and L is length of the core plug (cm).

Relationship of R and water saturation is given by Archie's equation as follows,

$$RI = \frac{R_t}{R_o} = S_w^{-n} \qquad (5)$$

RI is defined as the resistivity index, and R_o and R_t are the electrical resistivity of 100% water saturated rock and only partially water saturated rock respectively. The exponent '***n***' relates water saturation to the resistivity and is called Archie saturation exponent.

$$n = -\frac{\log(RI)}{\log(S_w)} \qquad (6)$$

The resistivity value is dependent on temperature.

$$R_{25} = R_{measured}\left(\frac{T_{measured} + 21.5}{25 + 21.5}\right) \qquad (7)$$

where R_{25} is R (Ωcm) at 25°C and $R_{measured}$ is the R(Ωcm) at $T_{measured}$ temperature (°C). The number 21.5 is a constant.

Many studies have been done to examine the effects of wettability on the n (Anderson, 1986; Sondenaa et al., 1991; Tiab and Donaldson, 2004). For uniformly water-wet rocks, the value of n is approximately

2. In oil-wet rocks, large values of n (5 or higher) can be expected. Figure 5 shows the measured n values at different wettability conditions at two temperatures.

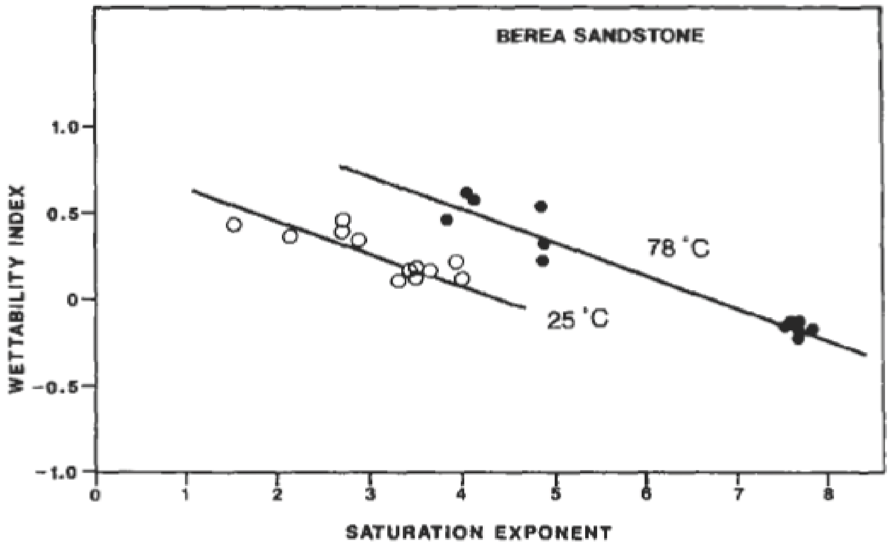
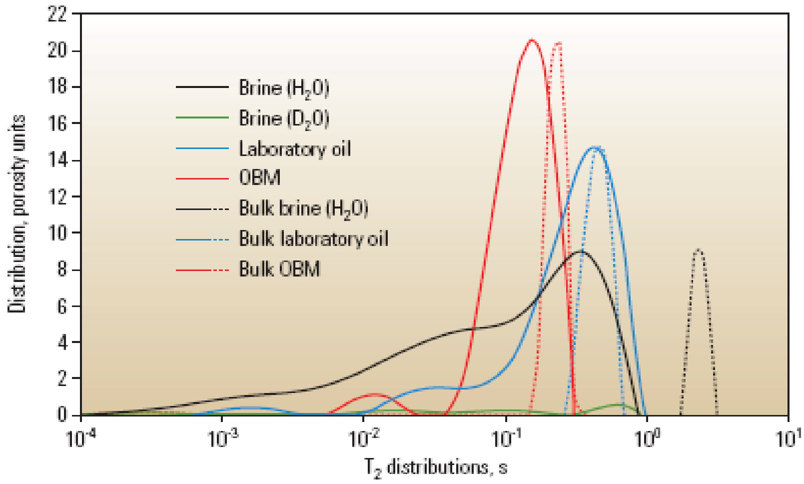


Figure 5 Example of change of the Archie saturation exponent as a fuction of wettability and temperature for Berea (Donaldson & Siddiqui, 1987)

2.1.2.5 NMR test

NMR is another qualitative method used to measure the wettability. Many previous studies have used the observation of a reduction in relaxation time of the oil from its bulk value as a qualitative wettability measurement (Brown and Fatt, 1956; Freedman et al. 2003).

This method is based on the observation that the surfaces of the rock can significantly reduce the measured relaxation time. When a proton is near a surface, it can become temporary bounded to the surface, and the relaxation is much faster than in the bulk fluid. Figure 6 shows NMR T2 distribution of a core plug at different conditions.



^ T_2 decay-time distributions. The T_2 distribution for a carbonate sample fully saturated with brine (H_2O) (solid black) is shifted to shorter time than the bulk-brine signal (dotted black) due to surface interactions. The brine is replaced with a brine made from deuterated water (D_2O), which has no NMR signal other than a small amount of residual H_2O (green). After the deuterated sample is flushed with OBM, the peak (solid red) is shifted from the bulk OBM (dotted red), indicating that the OBM wets the rock. The sample was cleaned and prepared again in the deuterated state, then flushed with laboratory oil. The main peak (solid blue) aligns with the bulk-oil signal (dotted blue), and so with laboratory oil, the surface remains water-wet.

Figure 6 Example of NMR test results (T2 distribution) for a carbonate sample at different conditions (Abdallah et al., 2007)

2.1.3 Wettability Alteration

Wettability alteration by aging rock with brine and oil is a complex process. There are several critical parameters which affect the wettability alteration of the rock surface such as brine composition, crude oil composition, rock mineralogy and history of the oil exposed to the rock surface (Anderson, 1986; Cuiec, 1987; Morrow et al., 1996; Buckley et al., 1998).

Studies conducted by Buckley et al. (1998) explain the importance of crude oil composition in wettability alteration. Polar crude oil components can adsorb on mineral surfaces and alter the wetting properties. Adsorption of polar components of crude oil depends upon factors such as brine composition, solvent quality of the oil, aging time and type of oil (Buckley et al., 1998). Previous studies done by Chattopdhyay et al. (2002) found that both Berea sandstone and limestone cores exhibit more water-wet behaviour with increasing brine salinity with Moutray oil. With Prudhoe Bay oil the water wetness decreases with increasing brine salinity. Increase in aging time provided a systematic change in wettability from water-wet to oil-wet direction, while other core and fluid properties are held essentially constant. Decrease in initial water saturation resulted in decrease in water wetness (Zhou et al., 1996).

Buckley et al. (1996) investigated wetting alteration of porous media using an asphaltic crude oil from Alaska and sodium chloride solution of varying pH. They used two core materials; Aerolith-10 (synthetic core composed of silica and alumina) and Clashach (a relatively clay free sandstone). In their study, they observed more water-wet conditions with high pH salt solution (pH 8, [NaCl] = 0.1M) compared to lower pH salt solution (pH 4, [NaCl] = 0.1M) for cores of Aerolith-10 aged in Alaska-93 crude oil. Also they noted that in Clashach sandstone cores, wetting is less directly influenced by the brine pH. Both high and low pH cores showed mixed-wet conditions.

The effect of brine composition on wettability alteration can be strongly dependent on the specific crude oil. For some crude oils, the wettability change is sensitive to the brine salinity while for other crude oils no such dependence can be observed (Morrow et al., 1996; Filoco et al., 1998). For Prudhoe Bay crude oil, the oil recovery data indicated that the brine films become more stable as the salinity is increased (Filoco et al., 1998).

Behbahani and Blunt (2005) performed several spontaneous imbibitions and waterflood experiments on Berea cores aged in Prudhoe Bay crude oil. They concluded that, as the aging time was increased, more of the pore space became oil-wet.

Tong et al. (2003) examined the reproducibility and stability of mixed wettability induced in Berea sandstones by using asphaltic crude oils (Minnelusa & Prudhoe Bay) and a paraffinic crude oil (Gullfaks). They observed that the paraffinic oil caused less change in wetting of Berea sandstone than the asphaltic crude oils. Due to the acidic surfaces, sandstones adsorb basic components readily, whereas acidic components are repelled. Most of the polar components in crude oils are weak acids. These do not adsorb readily on the sandstone surfaces. The basic components present in crude oils can react with and adsorb to the acidic silica and negatively charged clay surfaces, alternating the surface from water-wet to oil-wet direction. The degree of this wettability change depends on the amount and the type of basic components available.

Xie et al. (2002) made a study of the stability of wetting changes induced on quartz surfaces by adsorption of crude oil. They used 10 different crude oils and noted that the stable wetting appeared to be related to adsorption of positively charged oil species. The asphaltic crude oils that had high base numbers and high base-to-acid ratios produced stable wetting conditions. Buckley (2001) pointed out that the acid and base numbers of a crude oil should be considered together to identify the tendency of wettability alteration. Oils with high ratio of bases to acids will exhibit oil-wetting tendencies on sandstones.

2.1.4 Oil recovery Vs Wettability

The effect of wettability on oil recovery has been extensively studied in the literature (Donaldson et al., 1969; Jadhunadan and Morrow, 1991; McDougall and Sorbie, 1993; Moore, 1995; Torsaeter et al., 1997; Aziz, 2011). After analyzing several core flooding experiments in various porous media, Moore (1995) found that the wettability is the most important variable affecting the water flood oil recovery. Several researchers found the minimum residual oil saturation (Sor) at neutral or weakly water-wet conditions as shown in Figure 7.

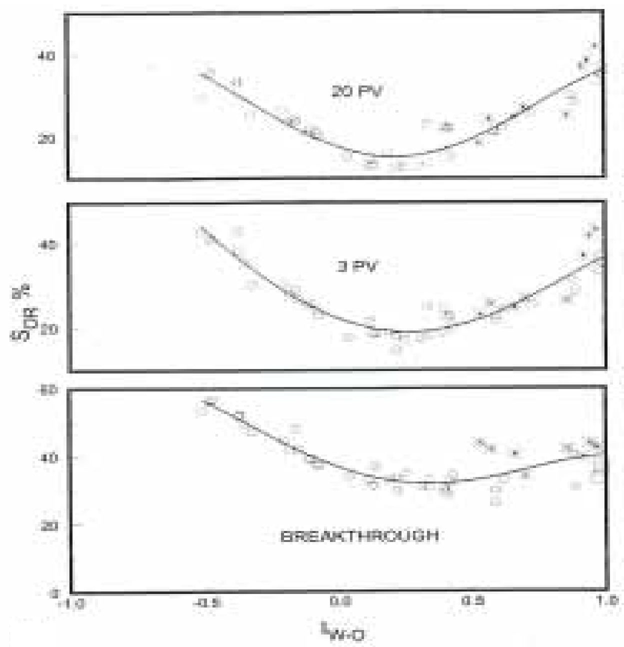


Figure 7 Residual oil saturation Vs Wettability (Jadhunandan and Morrow,1995)

2.2 Surfactants

Surfactants are organic compounds and the most common form of surfactants contains both a hydrocarbon portion (non polar) and a polar or ionic portion. The hydrocarbon portion is called the ‘tail’ and the ionic portion the ‘head’. The hydrocarbon portion (their tail) interacts very weakly with water molecules in aqueous solution. Thus the tail is called as hydrophobic part. The head interacts strongly with water molecules and it is called as hydrophilic part of the surfactant.

2.2.1 Classification

The most accepted classification of surfactants is based on the ionic nature of the head group as described in following sections (Pope and Baviere, 1991; Green and Willhite, 1998).

- *Anionic Surfactants*

  Anionic surfactants are the most widely used surfactants in EOR processes (Green and Willhite, 1998). In aqueous solution, ionization occurs and the surfactant head group has a negative charge.

- *Cationic Surfactants*

  The head group of cationic surfactants has a positive charge (Green and Willhite, 1998). This group of surfactants is rarely used in EOR applications because they are highly adsorbed on sandstone reservoir rocks.

- *Nonionic Surfactants*

Nonionic surfactants do not ionize or do not have an ionic charge (Green and Willhite, 1998). This group of surfactants has been used mostly as cosurfactants but also as a primary surfactants. Nonionic surfactants are much more tolerant of high salinities but the surface active properties are not generally as good as anionic surfactants. This group of surfactants is more sensitive to temperature.

- *Amphoteric or Zwitterionic Surfactants*

Zwitterionic surfactants have two groups that contain both positive and negative charges (Sheng, 2011). This type of surfactants is temperature and salinity tolerant. A term amphoteric is also used for such surfactants (Sheng, 2011).

2.2.2 Basic principles

2.2.2.1 CMC

At low concentration, dissolved surfactant molecules in a solution are dispersed as monomers. As the surfactant concentration increases in the aqueous solution, the surfactant molecules start to assemble into aggregates that are known as micelles (Green and Willhite, 1998). The concentration at which surfactants begin to form micelles is known as the critical micelle concentration (CMC) and this can be illustrated as shown in Figure 8. Above CMC, monomers and micelles exist in dynamic equilibrium.

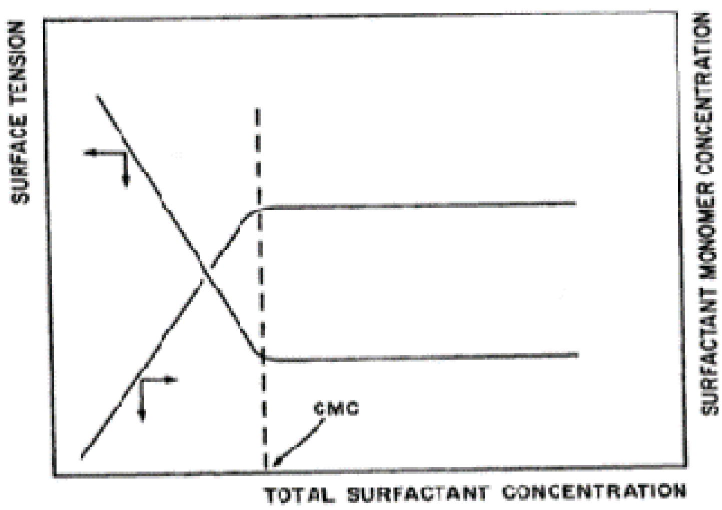


Figure 8 Schematic of surface tension versus surfactant concentration (Pope and Baviere, 1991)

2.2.2.2 Phase Behaviour

An example of surfactant-brine-oil phase behaviour is represented by a ternary diagram as shown in Figure 9. The micro emulsions or micellar solutions can exist in equilibrium with excess oil, water or both. Healy et al. (1976) referred to these respective equilibria as lower phase, upper phase and microemulsion middle phase. This equilibria is also known as Winsor type I, Winsor type II and Winsor type III respectively (Robbins, 1976; Green and Willhite, 1998;). Some authors used an alternative terminology as follows (Nelson and Pope, 1978; Sanz and Pope, 1995).

- Type II(-) : The lower phase micro emulsion which is Winsor type I. In this definition, II means no more than two phases can form and (-) means the tie lines have a negative slope.

- Type II(+) : The upper phase micro emulsion which is Winsor type II. In this definition, II means no more than two phases can form and (+) means the tie lines have a positive slope.
- Type III : The middle phase micro emulsion which is Winsor type III.

Above terminology has been used in this study.

Figure 10 shows an example of the relationships between σ values of equilibrium phases, solubilization parameters, phase behaviour and salinity.

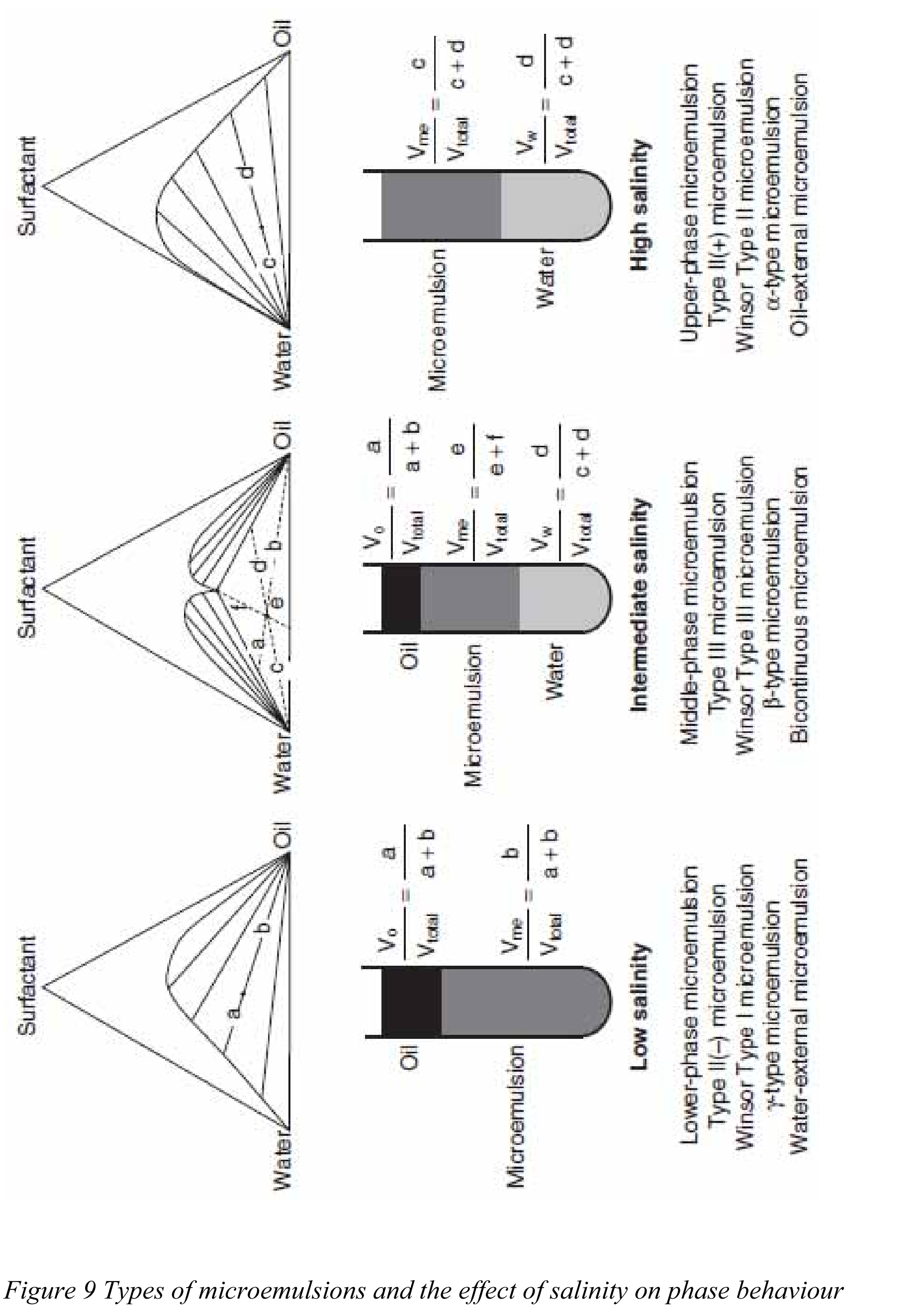


Figure 9 Types of microemulsions and the effect of salinity on phase behaviour (Sheng, 2011)

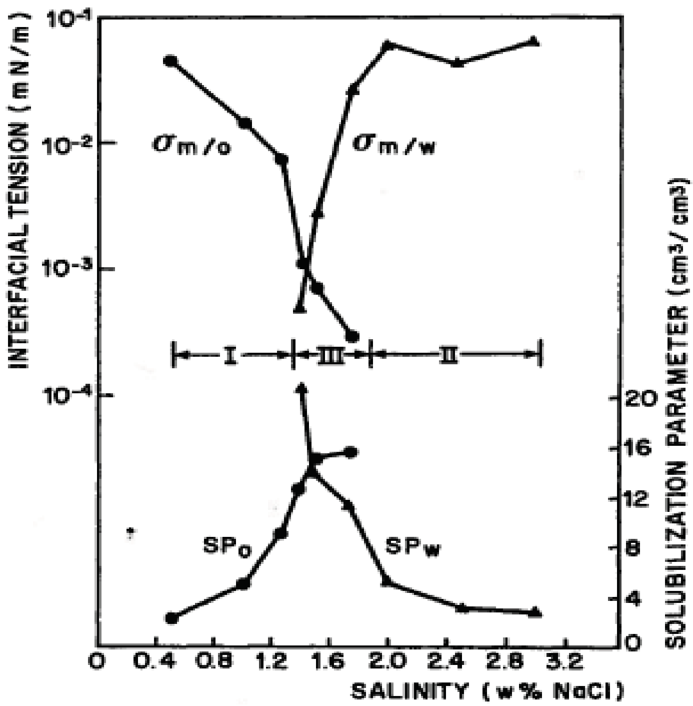


Figure 10 Interfacial tension and solubilization parameters Vs salinity (Pope and Baviere, 1991)

2.3 Surfactant Flooding in Enhanced Oil Recovery

The use of surfactants has long been considered in the oil industry as a major chemical EOR process (Green and Willhite, 1998). Surfactant flooding is also known as microemulsion flooding or micellar flooding. Surfactants are used in EOR, especially because of their ability to reduce oil-water interfacial tension.

2.3.1 Oil Recovery Mechanisms

Conventional surfactant floods have been practiced in industry considering only through reduction in oil-water interfacial tension (Ayirala and Rao, 2006; Rao et al., 2006) and it is briefly discussed in this section. The capability of surfactants to enhance oil recovery through other mechanisms such as alteration of relative permeability, wettability alteration is also reviewed in this section.

2.3.1.1 Reduced S_{or} by increase N_c

Surfactants are able of reducing σ between oil-water and thereby increase the N_c. This is known to be a main mechanism in surfactant flooding at water-wet formations. As described in section 1.1, measured CDC at water-wet condition represents the potential for surfactant flooding. Validity of CDC concept for other wettability conditions such as mixed-wet or oil-wet is not well understood.

2.3.1.2 Altered relative permeability

Apart from CDC, surfactants can cause significant changes in two phase flow behavior. One possible effect could be the changes in relative permeability curves (k_r). Flucher et al. (1985) performed a series of steady state experiments on Berea sandstone cores. They concluded that k_{ro} curves become a function of σ rather than function of N_c. Furthermore, they observed that k_{rw} curves behaved as a function of N_c. Harbert (1983), Kalaydjan (1992) and Al-Wahaibi et al. (2006) showed that the k_r for non wetting phase was more affected than the wetting phase at reduced σ.

Batycky and McCaffery (1978) measured k_{rw} and k_{ro} curves on unconsolidated sand packs with varying σ from 50 to 0.02 mN/m. They concluded that k_r curves become less curved when σ decreases. They further found that the removal of hysteresis in k_r curves at low σ. Shen et al. (2006) examined the influence of σ on k_{rw} and k_{ro} curves using strongly water-wet outcrop sandstone cores. They found that both k_{rw} and k_{ro} curves become less curved below σ value of 3 mN/m. A little impact on the k_r curves was observed when σ was higher than 3 mN/m.

Figure 11 shows that as the σ is reduced, the ratio of k_{rw}/k_{ro} increases for the low S_w and decreases for high S_w. Surfactant flooding is normally applied after water flood (that means at high S_w). Figure 11 shows the k_{rw}/k_{ro} ratio becomes lower in surfactant flood than in water flood at higher S_w.

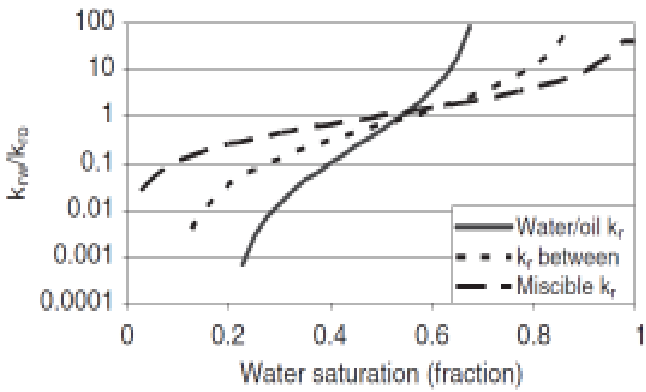


Figure 11 Effect of interfacial tension on kr ratio (Sheng, 2011)

The fraction of the displacing water (f_w) can be defined as follows and f_w is a function of k_{rw}/k_{ro}.

$$f_w = \frac{1}{1 + \frac{kro}{krw}\frac{\mu_w}{\mu_o}} \tag{8}$$

The decrease in k_{rw}/k_{ro} ratio (at reduced σ) results in lower water cut thereby improves the oil displacement efficiency.

2.3.1.3 Wettability alteration

Surfactants can change the wettability of the rock. Standnes and Austad (2003), Chen et al. (2004), Seethepalli et al. (2004), Li et al. (2004) have studied the effect of surfactants on wettability alteration of rock to improve spontaneous imbibitions.

2.3.1.4 Other mechanisms

The macro-scale effects such as reduced capillary trapping due to the presence of heterogeneities and segregated flow due to gravity are other possible oil recovery mechanisms by surfactants. Investigation of these two mechanisms has been reported by Lohne et al. (2012) and Lohne & Fjelde (2012). Both mechanisms have been investigated by numerical simulation. The work presented by Lohne et al. (2012) described the gravity segregation in water and surfactant flooding using simple homogeneous model. Furthermore, they demonstrated the effect of surfactant flooding on field scale gravity segregation by simulations and steady state upscaling. Lohne and Fjelde (2012) demonstrated that the capillary trapping of heterogeneous formations depends on the geometric distribution of permeability and wettability and σ.

2.3.2 Surfactant Retention

Surfactant retention mechanisms can be precipitation, adsorption, phase partition and phase trapping (Sheng, 2011). Usually, total surfactant loss by the different mechanisms is considered as surfactant retention.

Surfactant retention in reservoirs depends on surfactant type, surfactant equivalent weight, surfactant concentration, rock minerals, clay content, electrolyte composition, temperature and pH of the brine.

The efficiency of the surfactant flooding process can be reduced because of surfactant loss impairing the reduction of σ. Surfactant adsorption increases as the surfactant concentration increases until a plateau value is reached at the CMC (Figure 12).

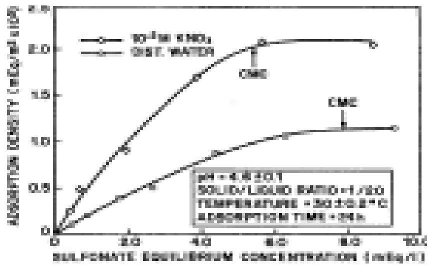


Figure 12 Adsorption isotherm of sodium dodecylsulfonate on kaolinite (Pope and Baviere, 1991)

3. MATERIALS AND EXPERIMENTAL METHODS

In this section, a description of different types of materials and methods used in the experimental work of this study is presented. The experimental conditions (Formation water composition, Stock tank oil and temperature) used in this thesis were related to a specific sandstone oil reservoir. In the Petromaks project where the PhD research was included, the oil reservoir was selected.

3.1 Surfactant Screening

The evaluation of surfactant systems was done by using several surfactants products from different suppliers.

3.1.1 Solubility Test

Solubility test was carried out by mixing surfactant products in Formation Water (FW) and dilutions of formation water and visually observed. The composition of FW is given in Paper II & III.

3.1.2 Phase Behaviour Test

Phase behaviour tests were first carried out at 38°C and with 1:1 volume ratio of brine to oil. Synthetic formation brine and dilutions were used as brine. N-decane and Stock Tank Oil (STO from selected reservoir) were used as oil. To identify the type of phase behaviour, surfactant concentration in the water and oil phase was determined by two phase titration. For promising systems, σ was measured using spinning drop method. Samples were observed visually to evaluate the macro emulsion formation, and injectivity tests were carried out for promising surfactant system.

3.1.3 Analytical Methods

3.1.3.1 Two Phase Titration

Surfactant concentration of the samples was determined by two phase titration method (Schmitt, 2001). The analyses were performed by using surfactant Hyamine, methylene blue indicator and chloroform as organic phase.

3.1.3.2 Interfacial Tension Measurement

Interfacial tension (σ) between surfactant solution and oil (n-decane or STO) was measured using the Spinning Drop Interfacial Tensiometer supplied by KRUSS GmbH, Germany. The oil-surfactant interfacial tension is estimated with built-in software system according to the following equation.

$$\sigma = \frac{D_*^3(\rho_H - \rho_L)}{R_*^2} \tag{9}$$

Where σ (mN/m) is the oil-surfactant interfacial tension, D_* is the diameter of the oil drop, ρ_H and ρ_L are the density of the heavy phase (surfactant) and light phase (oil) respectively. R_* is the rotational speed.

3.2 Wettability Alteration

3.2.1 Aging with stock tank oil

Two types of Berea rock samples (100mD & 500mD) were used in the aging with STO. Brine pH, brine salinity, S_{wi} and aging time were varied in the aging process. The compositions of the different brine types used in this study are given in Table 1. Core plugs were saturated with brine and flooded by STO (at 38 °C) to establish S_{wi} (higher than 0.15). Lower S_{wi} (lower than 0.15) was established by means of unconfined porous disk method using N_2 gas. After the drainage to S_{wi}, N_2 was replaced by STO. The core plugs at S_{wi} were aged for 10 days at 90°C. For some core plugs, aging time was longer. After the aging process, wettability conditions were characterized by spontaneous imbibitions test at 38°C. After the spontaneous imbibitions test, forced imbibition (water flooding) was carried out at 38°C.

Table 1. Brine compositions

Salt	Units	FW	Brine 1*	Brine 2	Brine 3	Brine 4	Brine 5**
$CaCl_2.2H_2O$	g/L	37.600	7.520	37.600	37.600	0.000	0.376
$MgCl_2.6H_2O$	g/L	15.000	3.000	15.000	15.000	0.000	0.150
NaCl	g/L	88.000	17.600	88.000	88.000	5.800	0.880
Na_2SO_4	g/L	0.200	0.040	0.200	0.200	0.000	0.002
$NaHCO_3$	g/L	0.000	0.000	0.069	0.920	0.000	0.000
1 M HCl	ml/L	0.000	0.000	0.800	3.960	0.000	0.000
pH	-	5.50	-	4.60	6.05	-	-

*5 times dilution of FW (20 % FW)

**100 times dilution of FW (1% FW)

3.2.2 Chemical treatment

Outcrop Berea (500 mD) core plugs were treated with chemicals to alter wettability to less water-wet. STO and n-decane were used as oil and synthetic FW was used as brine. A wettability altering agent, Quilon L was used to artificially alter the wettability of strongly water wet Berea core plugs to less water-wet. This is a fatty acid chromium complex that binds irreversibly to negatively charge surfaces leaving a hydrophobic surface (Maini et al., 1986).

(a) Modification of wettability before drainage

Dry core plugs were mounted in tri-axial core holders with 50 bar overburden pressure and Quilon L (0.1, 1.0 or 3.0%) solution was injected in both directions (5 PV in each at 0.5 ml/min) at 5 or 10 bar back pressure and room temperature. The core plugs saturated with the Quilon L solution were demounted from the core holders and placed in an oven at 90 ºC for 5 days.

(b) Establish initial water saturation (S_{wi})

Treated and untreated core plugs were saturated with FW and drained to S_{wi} by using the unconfined porous plate method. Pressures from 0.3 bar up to 15 bar were applied gradually using N_2 gas when water production was ceased at that pressure.

(c) Modification of wettability after drainage

To obtain mixed wettability samples, Quilon L was mixed with n-decane (concentration equal to 3%) and filtered through 0.45 µm oil filter. The filtered solution was injected to an untreated core plugs at S_{wi} in both directions (5 PV in each) at 0.5 ml/min. After the treatment, n-decane was injected to remove excess of treatment chemicals. For the core floods with STO as oil, n-decane was replaced by STO by injecting STO at 0.5ml/min for 5 PV.

The purpose of the treatment at S_{wi} was to get oil-wet larger pores and water-wet smaller pores which is similar distribution of pore wettability proposed by Salathiel (1973).

3.3 Wettability Measurements

3.3.1 Resistivity Measurement

Electrical resistance (Ω) was measured using PM 6304 Programmable automatic RCL (Resistance (R), Capacitance (C), Inductance (L)) Meter. Three or two measurements were made as follows.

For the wettability establishment after primary drainage (at S_{wi}):

r_o : Brine saturated core plug (S_w=100%)

r_{t1}: Core plug filled with oil at S_{wi} (before wettability change)

r_{t2}: Core plug after establishing the wettability (aged with STO or chemically treated)

For the artificial wettability alteration before primary drainage (100% chemically treated cores):

r_o' : Brine saturated core plug (S_w=100%)

r_{t1}': Core plug filled with oil at S_{wi} (after primary drainage)

The measured resistance values were used to estimate the *n* as described in section 2.1.2.4.

$$RI = \frac{R_t}{R_o} = \frac{r_{t1}(A/L)}{r_o(A/L)} = S_w^{-n_1} \quad \text{=====> Estimate } \boldsymbol{n_1} \text{ or } \boldsymbol{n_1'}$$

$$RI = \frac{R_t}{R_o} = \frac{r_{t2}(A/L)}{r_o(A/L)} = S_w^{-n_2} \quad \text{=====> } \textit{Estimate } \boldsymbol{n_2}$$

A: cross sectional area of the core

L: core length

$\boldsymbol{n_1}$: untreated core or before wettability alteration

$\boldsymbol{n_1'}$: 100% chemically treated cores (chemical treatment before drainage)

$\boldsymbol{n_2}$: Wettability changed after primary drainage (at S_{wi})

3.3.2 Spontaneous Imbibition Test

After establishing the wettability conditions (aged with STO or chemically treated), the core plugs were demounted from the core holder and placed in an Amott cell filled with the brine which was used in the core preparation. The test was carried out at 38 °C. The volume of oil produced was recorded as a function of time until the oil production was stopped. Scaled spontaneous imbibition curves (as described in section 2.1.2.3) were compared with the results from strongly water-wet core.

3.3.3 Nuclear Magnetic Resonance Relaxation Test

The Nuclear Magnetic Resonance relaxation T2 tests were carried out only for the chemically treated core plugs with comparison to untreated core plugs.

Core plugs at S_{wi} (with n-decane as oil) before the core floods:

1) Untreated core at S_{wi}
2) Core plug treated before drainage (100% treated)
3) Core plug treated after drainage (treated at S_{wi})

Core plugs at S_o=100% (with n-decane as oil) before the core floods:

4) Untreated core plug saturated with n-decane
5) Core plug treated before drainage saturated with n-decane
6) Bulk n-decane

Core plugs at S_{wi} (with n-decane as oil) after the core floods (oil flooded back to S_{wi}):

7) Core plug treated before drainage (100% treated)
8) Core plug treated after drainage (treated at S_{wi})

3.4 Core flooding experiments

3.4.1 Core floods – Berea rock

Most of the experiments in this research study were carried out on Berea rock. In the first attempt, CDC's on water-wet Berea (both non wetting phase and wetting phase CDC's) were measured using solvent system. Later, core floods at different wettability conditions were carried out including the measurement of CDC's.

(a) CDC measurement using solvent system

In this study, a solvent system of 2wt% $CaCl_2$ brine, isooctane and isopropanol was used instead of a surfactant system with the assumption that both systems have similar effect on reducing σ. Detailed study of this solvent system is reported by Morrow et al. (1998). Core floods were carried out in water-wet Berea rock samples (500mD) of length 30 cm and diameter 3.7 cm at room temperature (20 °C). Oil (non-wetting phase) and water (wetting phase) floods were performed at multiple rates for three brine/iso-octane/iso-propanol systems varying σ.

The compositions of the three used two phase systems with varying σ are listed in Table 2. The overall composition of each system was well shaken in a separating funnel and allowed to equilibrate at room temperature. The prepared systems were stored at least one day to reach equilibrium before the phases were separated.

Table 2. Equilibrium system 2 wt% CaCl2/isopropanol/isooctane.

Fluid system	2 weight% CaCl2 (aq) [vol%]	Isopropanol [vol%]	Isooctane [vol%]
1	50	0	50
2	23	33	44
3	12	44	44

For each fluid system, the flooding steps in Table 3 were carried out after saturating the core with water phase of the selected flooding system (paper I).

Table 3. Flooding procedure

Main flooding step	Injection rate for oil flood (non-wetting phase) [ml/min]		Injection rate for water flood (wetting phase) [ml/min]	
1	1a	0.1→0.3→1.0→ 3.0→Q3=10.0	1b	0.1→0.3→1.0→ 3.0→10.0
2	2a	3.0→10.0	2b	3.0→10.0
3	3a	10.0	3b	10.0

a and *b* represent the drainage and imbibitions process respectively.

After the flooding process, the core plug was cleaned by injecting approximately 10 pore volume of isopropanol and the flood with the next solvent system was carried out

(b) Water flooding & surfactant flooding experiments

Water and surfactant flooding experiments were carried out on Berea rock (500 mD) at different wettability conditions. Wettability conditions were prepared by chemical treatment using Quilon L (Paper V). N-decane or STO were used as oil in all experiments except for one core flood at strongly water-wet condition where Silicone oil was used. Three surfactant systems (anionic) were used for the surfactant floods. Surfactant solution – 1 is a mixture of a hydrophobic surfactant product T12 (C13-propoxy sulphate) and a hydrophilic surfactant product T13 (C12-ethoxy-sulphate) in 3 to 1 weight ratio dissolved in lower salinity FW (20% FW) as 0.4 wt% active. Surfactant solution – 2 is a product of sodium lauryl ethoxy sulphate (A17) dissolved in FW as 0.1 wt% active. Active 1 wt% of anionic surfactant A16 (Sodium C6-10 Alcohol Ether Sulfate) prepared in FW was used as surfactant solution– 3. Type II (-) phase behaviour was shown for all surfactant systems.

(i) Water Flooding

FW was injected to the core plugs of different wettability with gradually increasing the injection rate from 0.1, 0.3, 1.0, 3.0 and 10.0 or 7.5 ml/min. The criteria for increasing the rate were that the oil production rate had approached close to zero and the differential pressure was stabilized with time.

(ii) Surfactant Flooding

Surfactant flooding at S_{orw}: After the water flooding was finished, surfactant solution was injected to the core plugs with gradually increasing the injection rate from 0.1, 0.3, 1.0, 3.0 and 10.0 or 7.5 ml/min. The criteria for increasing the rate were that the oil production was very low and the differential pressure across core plug was constant.

At the lowest rate (0.1 ml/min), effluent samples were taken out and analyzed for surfactant concentration to be sure that the core plug was saturated with the surfactant.

Single rate surfactant flooding at S_{wi}: Surfactant solution was injected to the core plugs (at S_{wi}) at single flow rates (0.3 or 3.0 ml/min).

Multiple rates surfactant flooding at S_{wi}: Surfactant solution was injected to the core plugs (at S_{wi}) with gradually increasing the injection rate from 0.3, 3.0 and 7.5 ml/min.

(iii) Oil Flooding

After the surfactant flooding, FW was injected at 1.0 ml/min to replace the surfactant solution from the core plugs. Oil flooding was carried out by injecting n-decane (Paper II) or STO with gradually increasing the injection rate from 0.1, 0.3, 1.0, 3.0 and 10.0 or 7.5 ml/min. The criteria for increasing the rate were that the water production had stopped and the differential pressure across core plug was constant.

3.4.2 Core floods – Reservoir rock

A single reservoir core sample was used for all flooding experiments. The core plug was selected on the basis of having relatively homogeneous computerized tomography (CT) scan images.

The core plug was cleaned by injecting toluene followed by methanol at 60 °C. The methanol in the plug was replaced with FW. Then the core plug was drained to S_{wi} with Isopar H at room temperature using confined porous disc method. Wettability was established by injecting STO. This was done by first injecting a mixture of Isopar H/toluene in the ratio of 4:1 and next STO (5 PV) at 90 °C. The plug was aged at 90 °C for 14 days. The core floods were carried out at 38 °C.

(a) Water/oil flooding cycles

Marcol 82 was injected to the core plug at S_{wi} to replace the STO (Marcol was used as oil to get better production data with faster separation). FW was injected to the core plugs of different wettability with gradually increasing the injection rate from 0.1, 0.3, 1.0, 3.0 and 7.0 ml/min. After the water flood, oil flooding was carried out by injecting Marcol 82 with gradually increasing the injection rate from 0.1, 0.3, 1.0, 3.0 and 7.0 ml/min. Two flooding cycles (water flood followed by oil flood) were carried out.

(b) Water and surfactant floods

FW was injected to the core plug at S_{wi} with gradually increasing the injection rate from 0.3, 1.0, 3.0 to 7.0 ml/min. After the water flood, surfactant solution was injected at multiple rates (0.1, 0.3, 1.0, 3.0 and 7.0 ml/min).

4 SIMULATION METHOD

This chapter give a brief description of the numerical simulation used in the analysis of the experimental results.

Short description is also given in the attached papers :

Paper I - estimation of k_r curves by history matching the experimental data and measured P_c curve

Paper II & III – estimation of both k_r & P_c curves by history matching the experimental data

Most of simulation work was carried out using Sendra simulator. Sendra is a 1D black-oil simulation model used for analysing SCAL experiments (Sendra, 2011). It is tailor made for revealing relative permeability and capillary pressure from two-phase and multi-phase flow experiments handling both imbibition and drainage experiments.

Sendra analyses includes two modes termed simulation and estimation. Estimation mode is a history matching tool in the simulator which used to reconcile the experimental data. Simulation mode is the forward simulation of an experimental scenario which used to predict the experimental performance. Both estimation and simulation modes were used in this study.

Relative permeability (k_r) functions and capillary pressure curves were estimated by history matching the oil recovery and the pressure drop data obtained from the core floods. LET correlation (Lomeland et al. 2005) was used to obtain the water-oil k_r curves given by the following equation:

$$k_{rj} = k_{rje} \frac{(S_{jn})^{L_j}}{(S_{jn})^{L_j} + E_j(1-S_{jn})^{T_j}}, \quad S_{jn} = \frac{S_j - S_{jr}}{1 - S_{wr} - S_{or}}, \quad j = w, o \qquad (10)$$

where S_{jn} is the normalized saturation; S_{wr} and S_{or} are residual water and oil saturation; k_{rje} represents phase end point relative permeability; L, E, and T are empirical constants. The parameter L describes the lower part of the curve, T describes the top part of the curve and E describes the elevation of the curves.

The capillary pressure curves were obtained using Skjæveland model (Skjæveland et al. 2000).

$$P_c = \frac{C_w}{\left(\frac{S_w - S_{wr}}{1 - S_{wr}}\right)^{a_w}} - \frac{C_o}{\left(\frac{1 - S_w - S_{or}}{1 - S_{or}}\right)^{a_o}} \qquad (11)$$

Where C_w and C_o [≥ 0] are capillary threshold pressures for water-wet and oil-wet region, and a_w and a_o [0.25 to 2.0] are the shape factors.

5 MAIN RESULTS AND DISCUSSION

The work presented in this thesis has improved the understanding of the oil recovery and the behavior of flow functions as well as the interpretation of laboratory data at different wettability conditions in sandstone reservoirs. Also a novel approach to surfactant flooding under mixed-wet sandstone reservoirs is presented and discussed.

5.1 Evaluation of surfactant systems

Screening has been carried out to identify surfactant systems that can be used in this research study.

It was in the study also possible to use lower salinities than FW. Surfactant products which were soluble in FW and dilutions of FW with low-moderate σ was therefore also of interest. For core flooding experiments, it is easier to use two phase system rather than type III system. The best is to use type II (-) because of several reasons. For type II(-) systems adsorption of surfactant is lower and the possibility of plugging by macroemulsions is less. In type III systems solubilisation of oil are higher than in II (-) systems. The oil is then produced not only due to lower σ but also due to the solubilisation of oil into the microemulsion phase.

Table 4 summarises the main results from the phase behaviour study. Combination of T12 & T13 products (at different ratios) showed promising results with low σ (0.01 -0.05 mN/m) at lower salinities (20% - 40%FW). The product A17 showed moderate σ (0.1 mN/m) at 100%FW salinity with STO and was also used.

Table 4. Summary of main resultsfrom phase behaviour study

Surfactant	n-decane + Formation Water					STO + Formation Water				
	20%	40%	60%	80%	100%	20%	40%	60%	80%	100%
(T13)-0.1%	II(-) 1.5	II(-)	II(-) 0.8	II(-)	II(-) 0.6	II(-)	II(-)	II(-) 0.3	II(-)	II(-) 0.12
(T12)-0.2% (T13)-0.2%	II(-)	II(-) 0.04	II(-)	II(-)	II(-)	II(-)	II(-) 0.05	II(-)	II(-)	II(-)
(T12)-0.3% (T13)-0.1%	II(-)	II(-) 0.02	II(+)	II(+)	II(+)	II(-) 0.01	II(-)			
(T12)-0.1% (T13)-0.3%	II(-) 0.2			II(-) 0.14		II(-) 0.26			II(-) 0.08	
(A16)-1.0%	II(-)	II(-)	II(-)	II(-)	II(-) 1.5	II(-)	II(-)	II(-)	II(-)	II(-) 0.8
(A17)-0.1%	II(-)	II(-)	II(-)	II(-)	II(-) 0.48	II(-) 0.4	II(-)	II(-)	II(-)	II(-) 0.1

B - σ (mN/m) **Type**

Surfactant is insoluble in water	Surfactant is soluble in water

For the combined products T12 & T13 increasing salinity causes a transition from II (-) to III to II (+) type. Increasing the amount of hydrophilic product (T13), increases the solubility and increases σ.

The selected systems are summarized in Table 5.

Table 5. Selected surfactant systems

No	Surfactant system	Brine salinity	σ at 38 °C (mN/m)	
			n C10	STO
Solution - 1	T12 – 0.3% + T13 – 0.1%	20 % FW	0.01	0.01
Solution - 2	A17 – 0.1%	100 % FW	0.5	0.1
Solution - 3	A16 – 1.0%	100 % FW	1.5	0.8

Selected systems gave no pressure build-up during injection to water-wet Berea (500mD) core plug at S_{orw}.

5.2 Establishing different wettability conditions in Berea sandstone

5.2.1 Aging with STO

Overviews of the core plugs used to investigate the wettability alteration by aging with STO are given in Table 6 and Table 7. Isopar H and Marcol 82 were used as oil to represent the strongly water-wet conditions.

Table 6. Core data (Berea 500mD)_wettability alteration with STO

Core No	Brine	Aging time (days)	S_{wi} (fraction)	S_o (fraction)	S_{orw} (fraction)	k_{rw}	***n*** after aging
1a	FW	10	0.29	0.37	0.37	0.10	-
2a	Brine 2	10	0.26	0.45	0.43	0.10	-
3a	Brine 3	10	0.36	0.45	0.43	0.11	-
6b*	FW	0	0.09	0.42	0.42	0.13	-
1b	FW	10	0.08	0.42	0.42	-	2.1
3b	FW	10	0.07	0.32	0.32	0.14	-
7b	FW	90+	0.09	-	-	-	1.9
1h	Brine 4	10	0.23	0.23	-	-	-
2h	Brine 5	10	0.33	0.15	-	-	2.0

*Isopar H as oil to represent strongly water-wet condition

Table 7. Core data (Berea 100mD)_wettability alteration with STO

Core No	Brine	Aging time (days)	S_{wi} (fraction)	S_o (fraction)	S_{orw} (fraction)	k_{rw}	***n*** after aging
3c	FW	10	0.35	0.34	0.34	0.12	-
1d	FW	10	0.12	0.46	-	-	-
2c	Brine1	10	0.35	0.37	0.37	0.08	-
5d	FW	15	0.09	0.49	-	-	1.7
6d	FW	90+	0.10	-	-	-	1.6
3d**	FW	0	0.16	0.38	-	-	-

**Marcol 82 as oil to represent strongly water-wet condition

Core plugs were usually aged for 10 days. Longer aging times (3 months) were applied for two core plugs (7b and 6d) as shown in Table 6 and Table 7. They were continued with aging while measuring the electrical resistivity.

Table 8 gives an overview of the core plugs used in the different experiments including the parameters varied.

Table 8. Core plugs used in different studies

Parameter	Berea 500mD	Berea 100mD
Brine pH	1a, 2a, 3a, 6b	-
S_{wi}	1a, 1b, 3b, 6b	3c, 1d, 3d
Brine salinity	1a, 1h, 2h, 6b	2c, 3c, 3d
Aging time	1a, 7b, 6b	1d, 5d, 6d, 3d

Scaled spontaneous imbibition results are plotted in Figure 13. The high spontaneous imbibition of brine and the low $k_{rw}(S_{orw})$ values observed during forced imbibition indicated that there was no/minor change in the wettability in aging with STO, even though several parameters were varied. Estimated n values, indicated that the core plugs are water-wet.

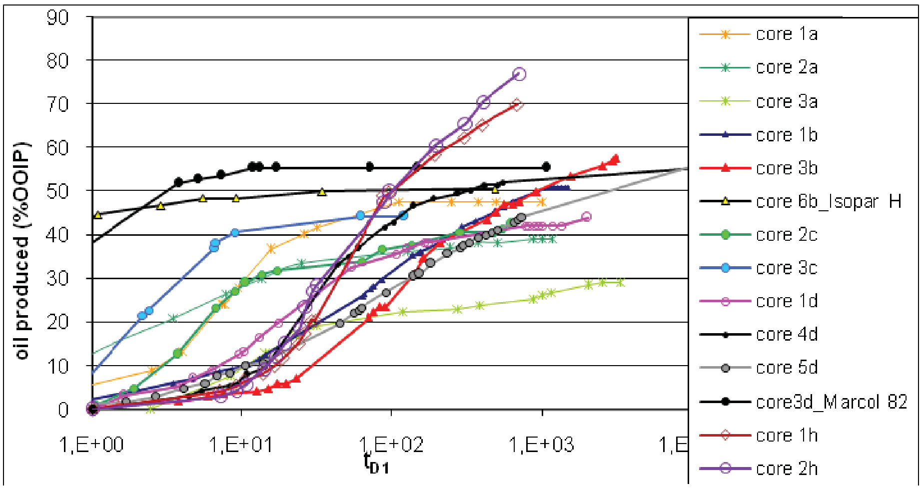


Figure 13. Oil produced by spontaneous imbibition vs dimensionless time for Berea 500mD & 100mD cores.

Table 9 presents a comparison of different crude oils used in other studies to age the Berea sandstone.

Table 9. Comparison of different crude oils (Filoco et al., 1998, 2000; Xie et al., 2002; Tong et al., 2003)

Crude oil	Acid number (AN)	Base number (BN)	BN/ AN	wettability from literature
Shell A-1 (Pink)	1.93	2.22	**1.2**	Water-wet[f]
Shell A-20 (Terracota)	0.24	2.60	10.8	Mixed-wet[f]
Prudhoe Bay (A95)	0.24	2.20	9.2	Mixed-wet[fx]
CS	0.33	**1.16**	**3.5**	Unstable[x]
DaGang	0.66	4.67	7.1	Mixed-wet[x]
Gullfaks-96	0.24	**1.19**	**5.0**	Water-wet[fxt]
KC	0.13	**0.92**	**7.1**	Unstable[x]
Lost Hills	1.9	6.05	3.2	Mixed-wet[x]
Mars Pink	3.92	**2.30**	**0.6**	Unstable[x]
Minnelusa	0.17	2.29	13.5	Mixed-wet[xt]
Sulimar Queen (SQ 95)	0.17	**0.62**	**3.6**	Unstable[x]
STO in this study	0.83	**2.0**	**2.4**	**Water-wet or unstable wettability?**

[[f] **-** Filoco et al., 1998, [x] - Xie et al., 2002, [t] - Tong et al., 2003]

By comparing the result of this study with previous literature (see Table 9), the reason for the minor/no change in wettability of Berea sandstone could be interpreted considering the lower value of base-to-acid ratio of STO used in this study.

5.2.2 Chemical treatment

Different wettability conditions on Berea core plugs were established using Quilon L as wettability modifier (Paper V). The chemical treatment was done in two ways i.e. the core plugs were treated before drainage and treated after drainage to S_{wi}. The established wettability conditions were satisfactorily characterized by different methods as described below.

5.2.2.1 Resistivity measurements

Resistivity of core was measured before and after primary drainage (at S_w=100% and at S_{wi}). Measured resistivity values were used to estimate the Archie saturation exponent (***n***) as described in Section 3.3.1. The results are summarized in Table 10. Untreated core plugs showed ***n*** value of 2, and ***n*** was close to 5 for the core plugs treated with higher concentration of Quilon L (treated before drainage). Similar ***n*** values were reported by Sondenaa et al. (1991) for water-wet Berea and oil-wet Berea. The core plugs treated at S_{wi} showed ***n*** value closer to 3.

The core plug treated (before drainage) with the lowest concentration of Quilon L (0.1%) was found to be mildly water-wet and the core plug treated with 1.0 wt% of Quilon L was mildly oil-wet. Meanwhile, the core plug treated with the highest Quilon L concentration (3.0%) was strongly oil-wet. The decrease in water-wetness resulted in increase in ***n***.

Estimated ***n*** values were similar before water flood (after primary drainage) and after oil flood (secondary drainage) and the results are shown in Paper II and Paper III. This indicates that the establish wettability conditions are stable during water/oil flooding cycle. Also it can be concluded that the wettability of the system is not changed during surfactant flood.

Table 10. Saturation exponent at different wettability conditions

Core No.	Treatment before drainage (concentration % of Quilon in distilled water)	S_{wi}	Estimated ***n***		Oil type	Wettability
5e	0.1	0.15	2.3		n-decane	Mildly water-wet
9e	1.0	0.18	3.5		n-decane	Mildly oil-wet
1e	3.0	0.16	4.6		n-decane	Strongly oil-wet
24j	0.0	0.10	2.1		n-decane	Strongly water-wet
7L	0.0	0.09	2.0		Silicone oil	Strongly water-wet
28L	0.0	0.09	2.1		STO	Strongly water-wet
20L	0.0	0.06	1.8		STO	Strongly water-wet
Core No.	Treatment after drainage (concentration % of Quilon in n-decane)	S_{wi}	Estimated ***n***		Oil type	Wettability
			Before treatment	After treatment		
10f	3.0	0.10	2.0	3.0	n-decane	Mixed-wet
6f	3.0	0.16	1.7	3.6	n-decane	Mixed-wet
1f	3.0	0.18	1.7	3.6	n-decane	Mixed-wet
12f	3.0 with 5 days aging at 90 C	0.07	1.8	3.0	n-decane	Unstable wettability
26L	3.0	0.09	2.1	3.1	STO	Mixed-wet
18L	3.0	0.08	2.0	3.0	STO	Mixed-wet
14j	3.0	0.08	1.9	2.9	STO	Mixed-wet

5.2.2.2 Spontaneous imbibition test

Spontaneous imbibition curves for some selected core plugs at different wettabilities are presented in Figure 14. Spontaneous imbibition rate and final oil recovery decrease with increasing oil wetness (wettability conditions were evaluated based on resistivity measurements presented in Section 5.2.2.1). However, the mixed-wet core plug aged after the Quilon L treatment at S_{wi} (12f) showed higher spontaneous imbibitions of FW compared to the other mixed-wet core plugs. The reason for this observation is not clearly understood.

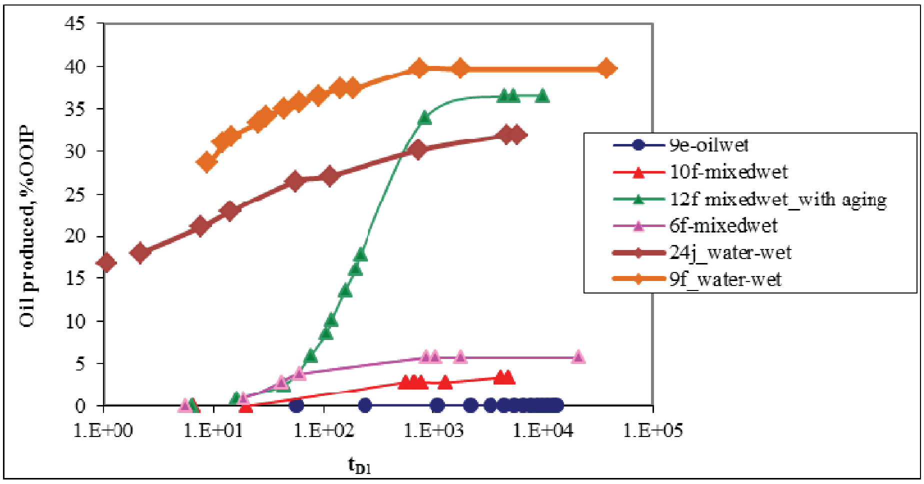


Figure 14. Oil recovery by spontaneous imbibition for the core plugs (after the core floods) at different wettability conditions with n-decane as oil.

5.2.2.3 NMR test

NMR relaxation T2 measurements were carried out for core plugs at different wettability conditions (based on resistivity measurements as presented in Section 5.2.2.1) such as mixed-wet, mildly oil-wet and strongly water-wet (Paper V). The mixed-wet (core 10f) and mildly oil-wet (core 9e) core plugs analyzed by NMR T2 relaxation after the core floods. Another mixed-wet core plug (core 7f) and mildly oil-wet core plug (core 11e) were analyzed before the core floods. NMR test for the reference core at water-wet condition was carried out with untreated core plug (core 4f) before the core floods. The results are shown in Figure 15.

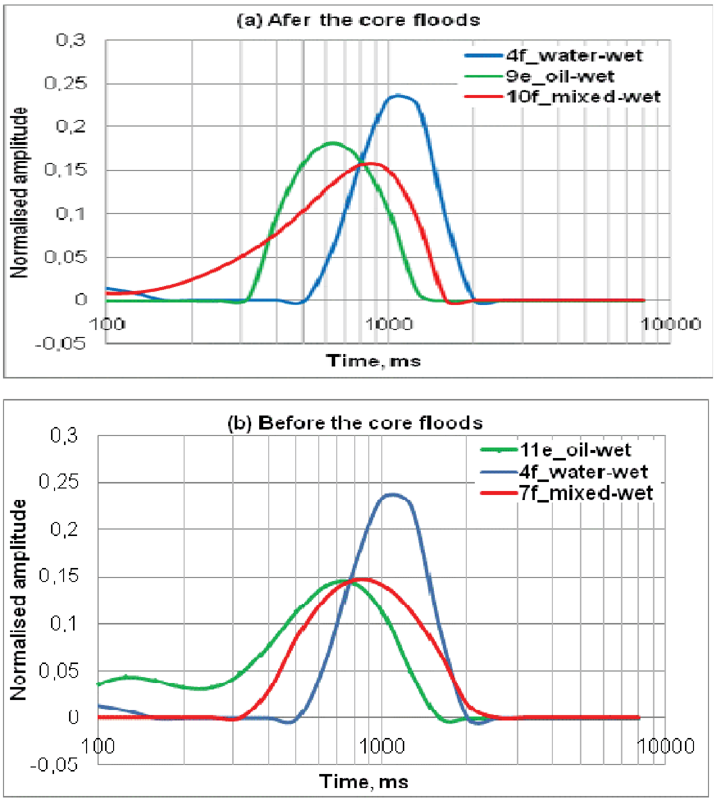


Figure 15. NMR T2 distribution of core plugs at different wettability conditions (a) After the core floods (b) Before the core floods

The oil peak value was closer to 1000ms for the water-wet core. The peak value for the mixed-wet core was shifted to lower value (800 ms) and for the oil-wet core, much lower peak value (600 ms) was observed. Shifting the wettability in oil-wet direction gave shorter time for the main peak of NMR signal compared to water-wet condition. This observation is further supported by the wettability conditions indicated in resistivity data and spontaneous imbibition tests.

Additional NMR measurements were carried out on strongly water-wet and strongly oil-wet Berea core plugs at 100% oil saturation. The results are shown in Figure 16 comparison with the bulk relaxation time of oil (n-decane). The peak value of T2 distribution of water-wet core (at S_{oi}=100%) centers on the T2 distribution of bulk oil. This indicates that the oil does not wet the rock surface. At oil-wet condition (at S_{oi}=100%), the main peak has shorter relaxation time than the bulk oil indicating that the oil wets the rock surface.

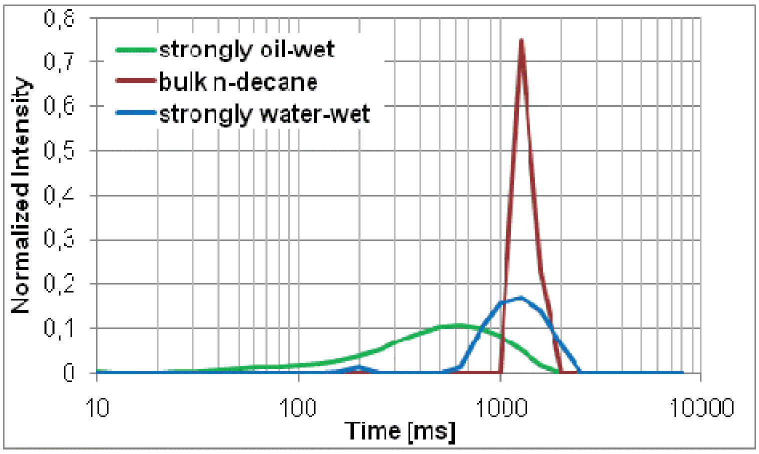


Figure 16. NMR T2 distribution of water-wet and oil-wet core plugs at 100% oil saturation with compare to the bulk relaxation time of oil.

5.3 CDC of water-wet Berea using Solvent system

The core floods with the solvent system 2wt% CaCl2 brine, isooctane and isopropanol were carried out to demonstrate CDCs (both wetting and non wetting) for strongly water-wet Berea rock (Paper I). The experiments were done using the solvent systems as described in Section 3.4.1 (a). N_c was increased by both reducing σ and increasing flow rate.

The properties of the core plugs used in this experiment are summarized in Table 11.

Table 11 Core data (Berea 500mD)_CDC measurement with solvent sysytems

Core No.	Length (cm)	Diameter (cm)	PV (ml)	Φ (fraction)	k_{abs} (mD)
1	30.0	3.77	77.0	0.23	675
2	30.0	3.77	83.3	0.25	866

The experimental remaining saturation from all drainage and imbibitions steps are plotted as CDCs in Figure 17. The measured CDC for the oil (non wetting phase) shows a roughly constant plateau below a N_{cc} and a declining slope above N_{cc}. This is similar to the characteristic shape for a typical CDC for the non wetting phase reported by Mohanty and Salter (1983), Lake (1989) and Delshad et al. (1986).

The measured CDC for water (wetting phase) has a declining slope with no N_{cc} as shown in Figure 17 b. Analysis of the wetting phase results (Paper I) suggest that the measured CDC for wetting phase in Figure 17 b is not a true CDC. The saturation point plotted in Figure 17 b are average remaining saturations in the core which are higher than the residual saturations. At low N_c, the water production is limited by capillary end effects. Also remaining water saturation strongly depends on number of PV injected. In this experiment, water displacement behaviour by oil is used to analyze the flooding characteristics of the wetting phase. This is relevant for oil production in mixed-wet or oil-wet systems.

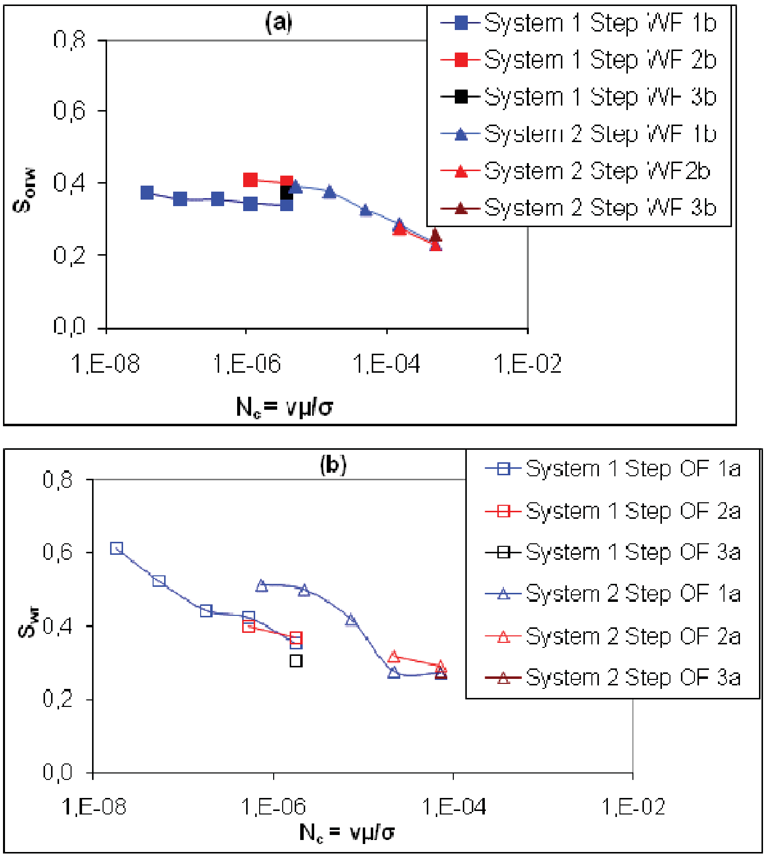


Figure 17. (a) Measured CDC for non wetting phase (b)measured CDC for wetting phase

5.4 Water flooding behaviour at different wettability conditions

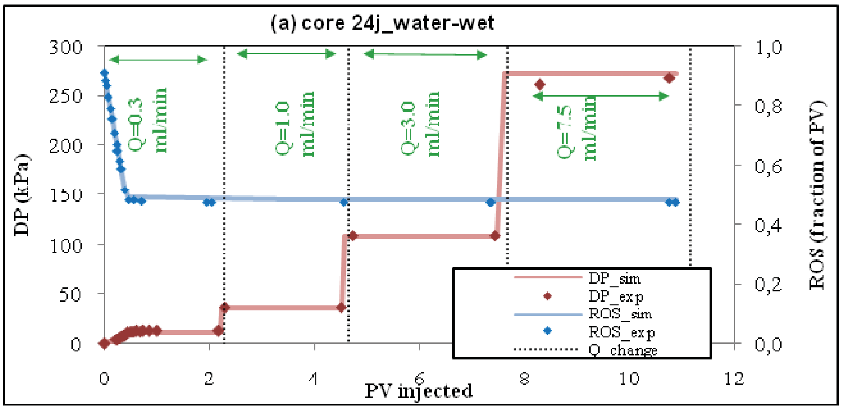
The specific study was aimed at understanding the nature of water flooding behaviour at different wettability conditions (Paper V). Untreated Berea core plugs (500mD) were used for strongly water-wet conditions. Other wettability conditions (mildly water-wet, mixed-wet, mildly oil-wet and strongly oil-wet) were established by chemical treatment as described in Section 3.2.2. Characterization of prepared wettability conditions is presented in Section 5.2.2 and Paper V. Multiple rates water flooding experiments were carried out in several core plugs at different wettability conditions according to the procedure explained in Section 3.4.1 (b). Table 12 presents an overview of the core plugs used in these experiments.

Table 12. Core properties (Berea 500mD)_core floods with model oils

Core No.	PV (ml)	Φ (fraction)	k_{abs} (mD)	S_{wi} (fraction)	Oil type
5e	22.61	0.23	629	0.15	n-decane
9e	22.85	0.23	673	0.18	n-decane
1e	22.80	0.23	723	0.16	n-decane
24j	23.41	0.23	496	0.10	n-decane
10f	23.60	0.23	418	0.10	n-decane
6f	23.11	0.23	460	0.16	n-decane
1f	23.19	0.23	429	0.18	n-decane
12f	23.63	0.23	432	0.07	n-decane
7L	22.63	0.23	568	0.09	Silicone oil
4j	23.18	0.23	531	0.11	n-decane

5.4.1 Water-wet conditions

Untreated Berea core plugs were used with two types of oils (n-decane and silicone oil). Remaining oil saturation (ROS) and pressure drop (DP) profiles during the water flooding at water-wet conditions (core 24j & core 7L) are shown in Figure 18 with the corresponding history matched profiles.



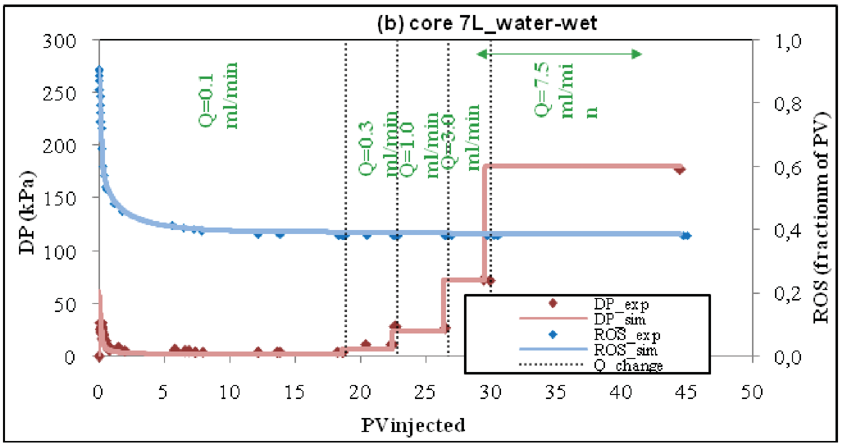


Figure 18. Remaining oil saturation (ROS) and differential pressure (DP) during water flooding at strongly water-wet conditions (a) core 24j – n-decane as oil (b) core 7L – silicone oil as oil

In water flooding of core 24j where n-decane was used as oil, oil /water viscosity ratio was less than unity. At this situation, piston like displacement was observed with no oil production after the breakthrough. In core 7L where high viscous silicone oil was used, the oil/water viscosity ratio was around 320. During the water flooding of core 7L, early water breakthrough was observed and a prolonged period of two phase flow occurred after the breakthrough of water. The difference in water flood behavior in core 7L compared to core 24j is caused by the difference in the viscosity ratio.

In both water floods (core 24j & core 7L), constant oil recovery and stable DP profiles can be seen as the rate is increased as shown in Figure 18.

5.4.2 Mildly water-wet

The measured ROS and DP profiles during the water flood at mildly water-wet condition are plotted in Figure 19 with the corresponding history matched profiles (Paper V).

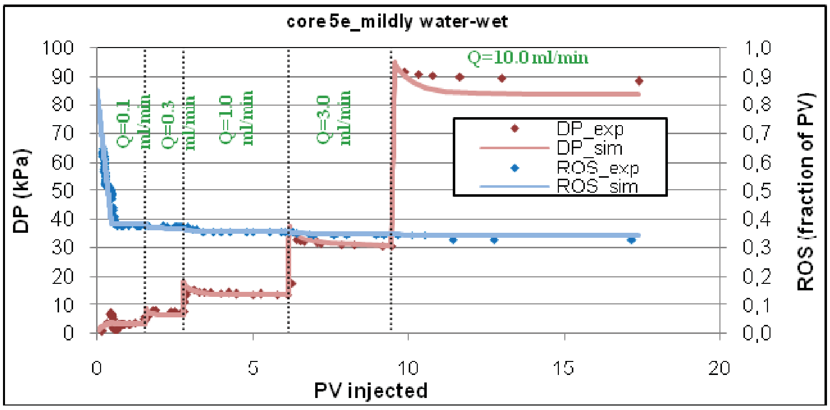


Figure 19. Remaining oil saturation (ROS) and differential pressure (DP) during water flooding of mildly water-wet (core 5e) condition.

During the water flooding at mildly water-wet condition, two phase production after water breakthrough was observed. The ROS was gradually decreased as the flow rate was increased. Also a declining trend was observed in DP profiles at each flow rate as shown in Figure 19.

The observed rate dependency (in Figure 19) can be explained by that the relative permeabilities themselves are rate dependent or that the production is affected by capillary end effects. The rate dependency is fully reproduced in the simulations using rate independent relative permeability and capillary pressure. Rate dependency in relative permeability functions is normally expected at high N_c (above 10^{-5}). In this case, N_c ranged from 10^{-8} to 10^{-6}. The rate dependency observed in this case is most likely caused by capillary end effects.

5.4.3 Oil-wet conditions

The water flooding behaviors at strongly oil-wet condition (core 1e) and mildly oil-wet condition (core 9e) are shown in Figure 20 (Paper V). Two phase production after the water breakthrough was observed in both water floods (core 1e and core 9e). The ROS was gradually decreased as the flow rate was increased and a declining trend was observed in DP profiles at each flow rate.

Interpretation of results by simulations indicates that the rate dependency is most likely due to the elimination of capillary end effects with the increase of flow rate.

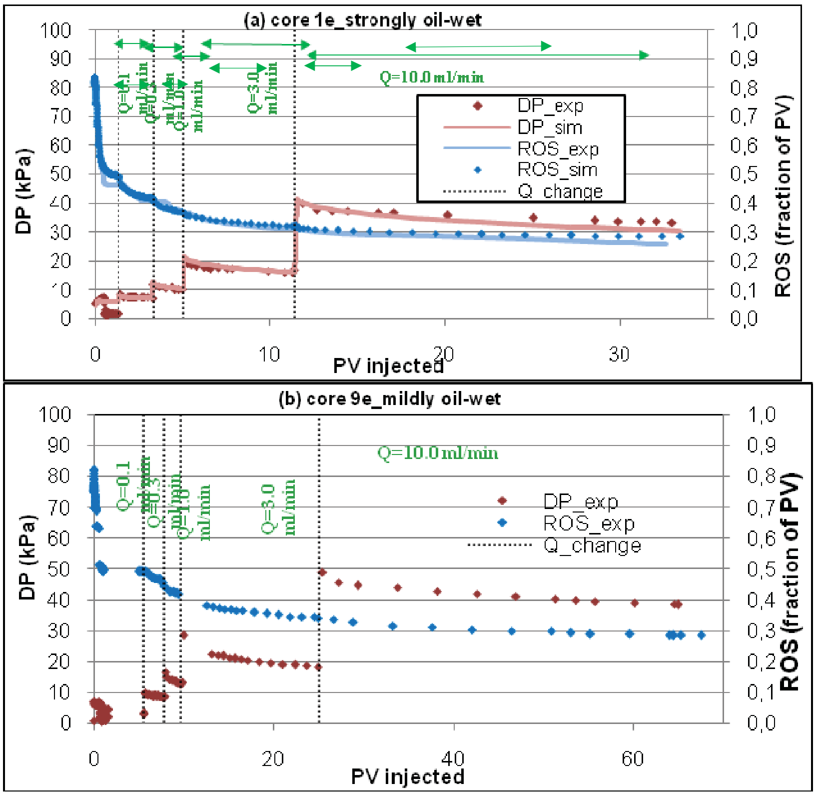


Figure 20. Remaining oil saturation (ROS) and differential pressure (DP) during water flooding of (a) Strongly oil-wet (core 1e); (b) Mildly oil-wet (core 9e)

5.4.4 Mixed-wet conditions

Few core plugs with different S_{wi} were treated in same way to prepare mixed-wet cores as described in section 3.2.2.1 (c). Figure 21 shows ROS and DP profiles during the water flooding of mixed-wet core plugs (core 10f and core 6f). In all cases, two-phase production was observed after water breakthrough. ROS varied with flow rate and tail oil production was observed (Paper II & Paper V).

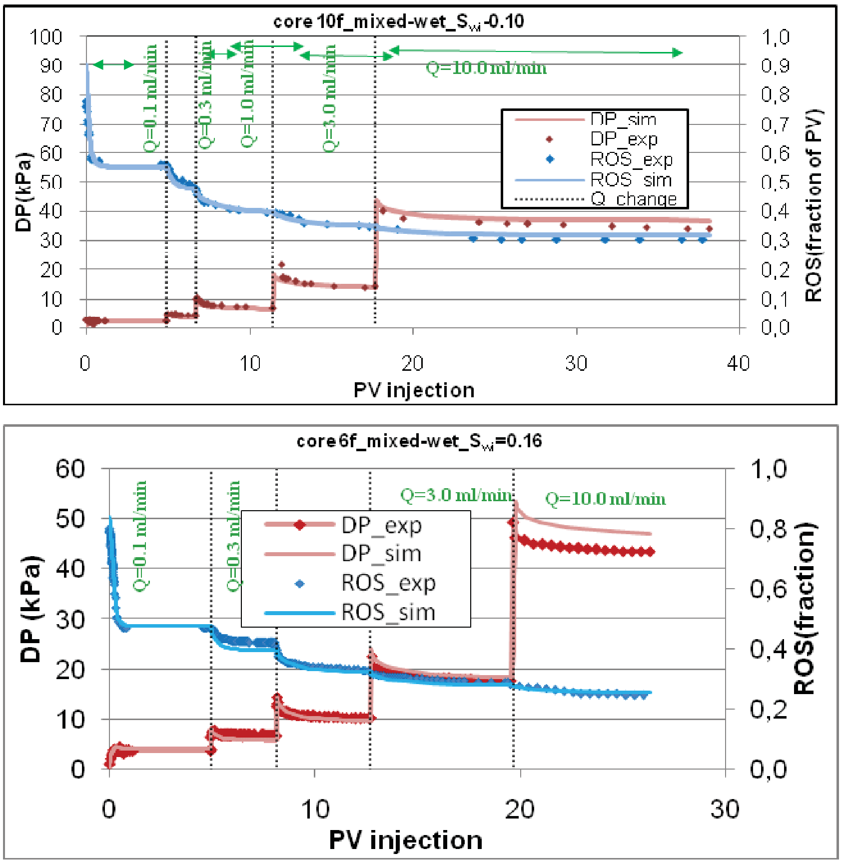


Figure 21. Remaining oil saturation (ROS) and differential pressure (DP) during water flooding of mixed-wet core plugs

5.4.5 Capillary pressure (P_c) and relative permeability (k_r) curves

The capillary pressure (P_c) and relative permeability (k_r) curves were obtained by history matching the oil production and differential pressure data obtained from the water flood experiments using Sendra simulator. The main output from history matching is the relative permeability functions. The primary purpose of estimating the P_c is to correct the relative permeability for the influence of P_c.

(a) Water-wet & oil-wet conditions

The estimated P_c curves are plotted in Figure 22. In strongly water-wet condition, the P_c curve is positive over most of the saturation range. It shows that the oil was produced mainly by spontaneous imbibition which is represented by the lowest rate 0.1 ml/min. No additional oil was produced during the forced imbibition (at higher rates) at strongly water-wet condition. The P_c curve for mildly water-wet conditions indicates that the oil was produced by both spontaneous imbibition and forced imbibition of water. The initial part of the lowest rate injection (0.1 ml/min) represents the spontaneous imbibition process while the end of the lowest rate injection and higher rates represent the forced imbibition of water. At the oil-wet conditions, when the system was contacted with water, it did not spontaneously imbibe water. Therefore P_c immediately becomes negative during forced imbibition. P_c curves for oil-wet systems show that a threshold pressure was required for entry of water before the displacement of oil by forced imbibition of water. The cross point water saturation of the P_c curve shifts to the lower S_w when the system wettability conditions were changed from water-wet to oil-wet. The estimated P_c curves are similar to the ones obtained by Masalmeh (2002).

The estimated k_r curves are shown in Figure 23. The k_{ro} values are less at low S_{wi} in oil-wet systems compared to the water-wet conditions. This is because the water in the larger pores hinders the relative movement of the oil. The cross point for the k_{ro} and k_{rw} curves shifts towards the left (lower S_w) from the water-wet to oil-wet systems as expected. The estimated relative permeability was not a function of saturation only but also varies with wettability.

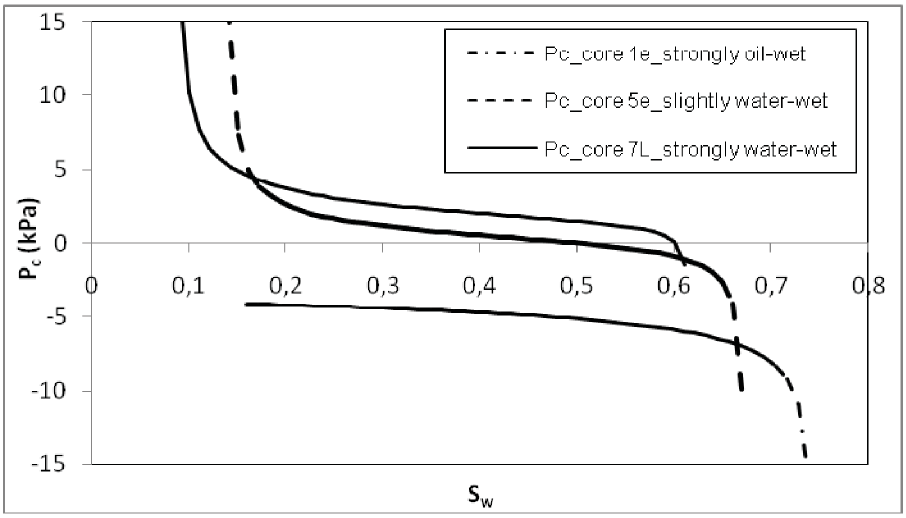


Figure 22. Estimated capillary pressure (P_c) curves at different wettability conditions

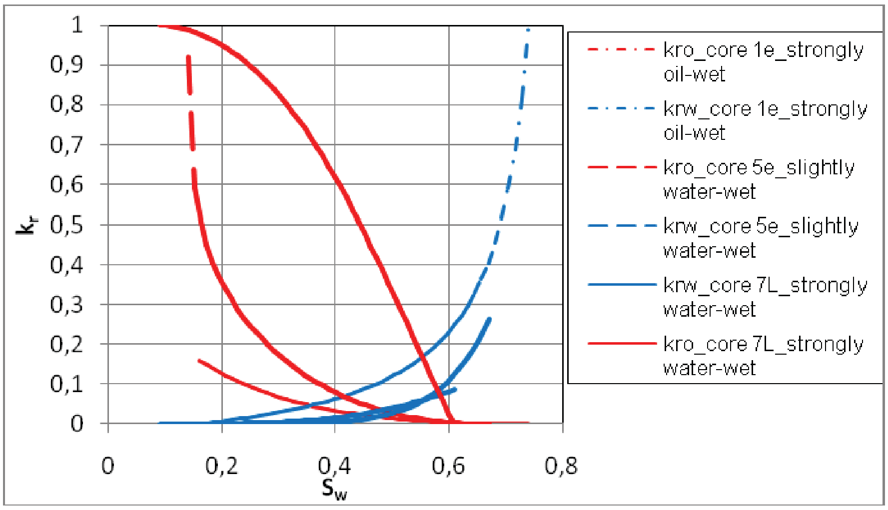


Figure 23. Estimated relative permeability (k_r) curves at different wettability conditions

(b) Mixed-wet conditions

The estimated capillary pressure (P_c) and relative permeability (k_r) functions for two mixed-wet core plugs (core 10f & core 6f) are plotted in Figure 24. In two cases, the P_c curve indicated that the oil production occurred by both spontaneous imbibition and force imbibition. Water is first spontaneously imbibed along continuous water-wet smaller pores. When spontaneous imbibition has stopped, P_c becomes negative and water acts as non-wetting fluid. Both positive and negative values of P_c indicate the typical mixed-wet condition.

The cross point of k_{ro} and k_{rw} was the main difference between mixed-wet and slightly water-wet P_c curves. The cross point water saturation for two mixed-wet cores was around 0.3. The P_c curve for core 6f (S_{wi} = 0.16) was shifted to higher S_w compared to that of the core 10f (S_{wi} =0.10).

The k_r curves for both water and oil show high curvature. The end point relative permeability to water (k_{rw}) values are lower (closer to 0.6) for the core plugs treated with Quilon L at higher S_{wi} (core 6f) compared to the core plugs treated at lower S_{wi} (core 10f). The core plugs treated at lower S_{wi} (core 10f) show higher k_{rw} end points (close to 0.9) which indicate higher degree of oil wetness.

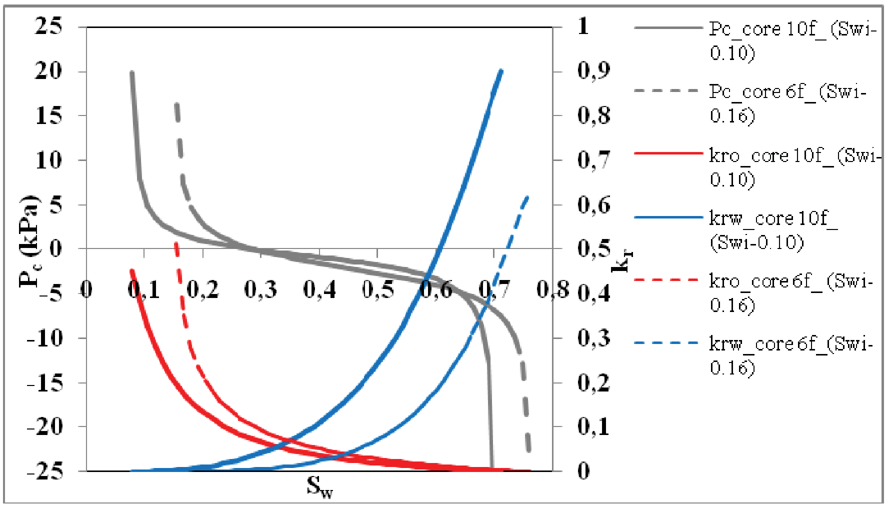


Figure 24. Estimated water-oil relative permeability curves (k_r) and capillary pressure (P_c) curves for the prepared mixed-wet core plugs (core 10f with S_{wi}-0.10 and core 6f S_{wi}-0.16)

5.5 Accelerated oil production by surfactants at mixed-wet conditions

Both water-wet Berea (untreated) and mixed-wet Berea (treated after drainage to S_{wi}) were used in this study (paper III). Multiple rate water floods and single rate surfactant floods (at S_{wi}) were carried out on both water-wet and mixed-wet Berea core plugs according to the procedure described in section 3.4.1. (b). For all the core floods, STO was used as oil and for the surfactant floods, surfactant solution -1 was used. Core plugs with similar properties were used as listed in Table 13.

Table 13. Core properties(Berea 500mD)_core floods with STO

Core No.	PV (ml)	Φ (fraction)	k_{abs} (mD)	S_{wi} *(fraction)*
28L	22.81	0.23	633	0.09
26L	22.56	0.22	562	0.09
18L	22.58	0.22	558	0.08
20L	22.28	0.22	652	0.06
14j	22.50	0.22	608	0.08
2j	22.52	0.22	552	0.11

Figure 25 and Figure 26 shows the remaining oil saturation (ROS) and pressure drop (DP) for the water flooding experiments in water-wet and mixed-wet Berea core plugs. The corresponding history matched profiles for ROS and DP by Sendra are plotted in the same figures. The experimental data are consistent with the simulated profiles. To reduce the capillary end effects in the core flooding experiments, higher flow rates and multiple rates were used.

In theses experiments, the viscosity ratio of fluids (STO/FW) was around 40. At water-wet condition (core 28L), significant two-phase production was observed after the breakthrough of oil. It was therefore possible to estimate the k_r functions at water-wet condition. Remaining oil saturation (ROS) was stable after injecting 7 PVs of FW at flow rate of 1.0 ml/min. No additional oil was produced as the flow rate was increased to 3.0 ml/min and 7.5 ml/min. Stable ROS and DP profiles were observed under increasing flow rates. This confirms the rate independent production at water-wet condition. Therefore residual oil saturation (S_{or}) of 33% was reached after injecting 7 PV's of water to water-wet core plug.

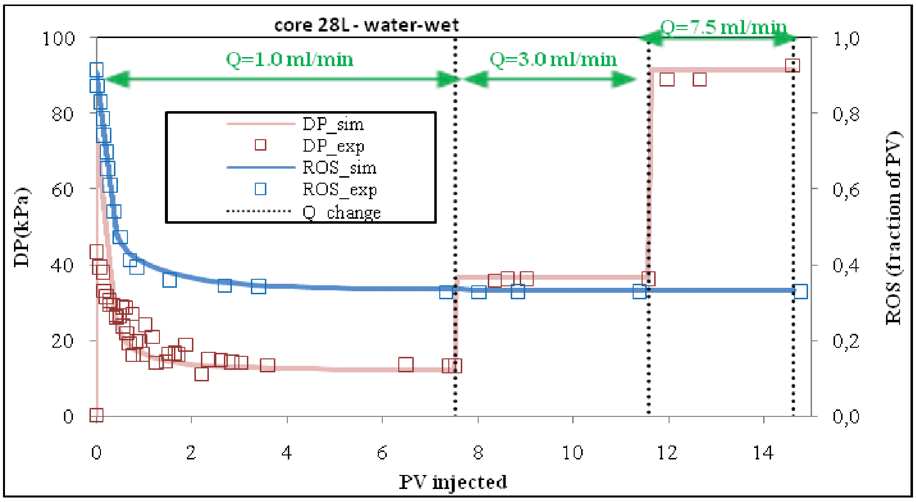
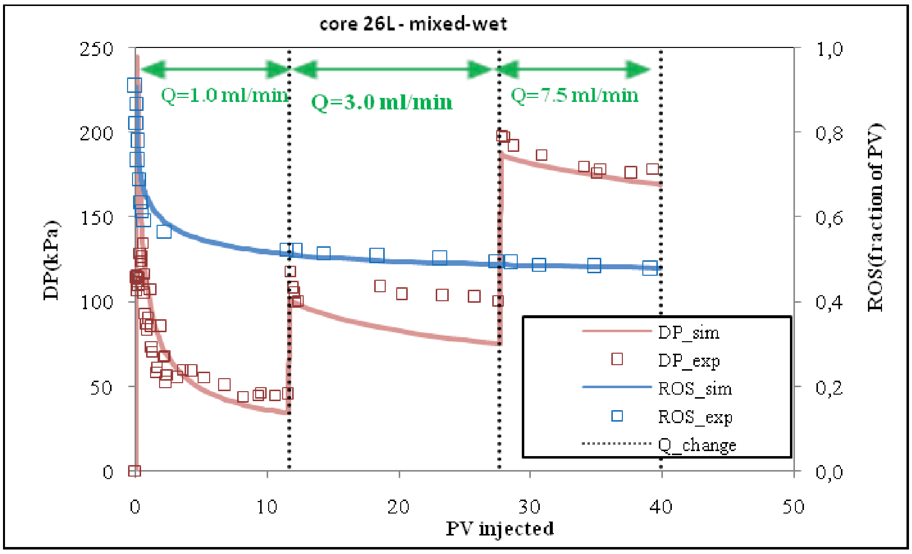


Figure 25. Remaining oil saturation (ROS) and differential pressure (DP) during water flooding of water-wet core plug with STO as oil

At mixed-wet conditions (core 26L and core 18L), oil production was not stable even after about 40 PV's of water injection. Increase in flow rate resulted in additional production of oil. Declining trend in DP profiles indicated two-phase production. This means that the oil production has not stopped. Continuous, but slow, production of oil was observed for longer time duration at mixed-wet condition. This is in contrast to the water-wet case. Therefore S_{or} (the lowest saturation of oil that can be drained by water) has not been achieved during water flooding of the two mixed-wet core plugs (core 26L and core 18L). This observation is similar to the characteristic mixed-wet behavior observed on preserved cores from East Texas Woodbine reservoir (Salathiel, 1973). Wood et al. (1991) studied the effectiveness of waterflood on preserved cores from Alaska Endicott Field. In their study, continuous oil production was observed for many PVs in both unsteady state and steady state water floods.



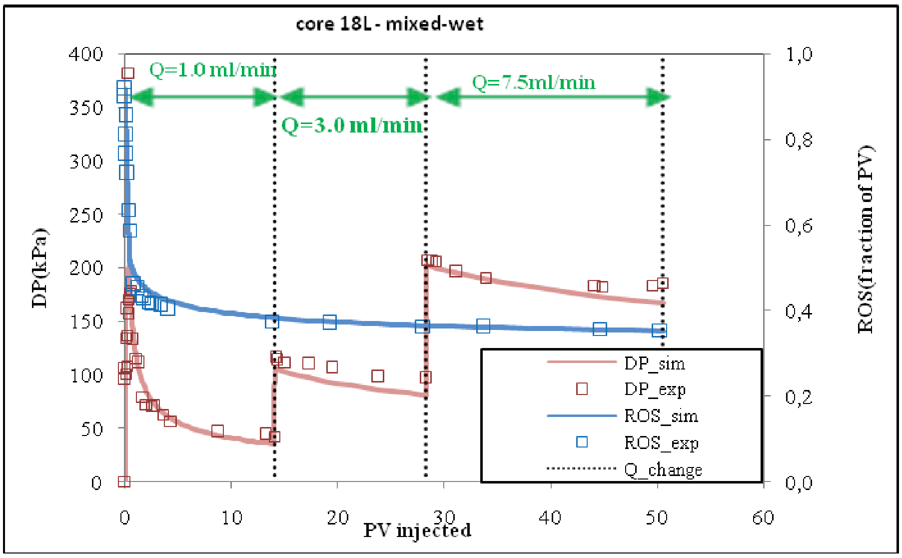


Figure 26. Remaining oil saturation (ROS) and differential pressure (DP) during water flooding of mixed-wet core plugs with STO as oil

When the economical saturation is reached (practical S_{or}), there are still continuous connections between much of the oil throughout the rock at mixed-wet conditions. Small amounts of oil will then be produced at very high water oil ratio (WOR). The true S_{or} in mixed-wet systems can be achieved by the injection of thousands of PVs of water. Sorbie et al. (2011) reported theoretically calculated S_{or} values for mixed-wet conditions at infinite PV throughput. In practice, this situation is difficult or not achieved in water flooding. However, this slow production of oil at mixed-wet conditions could be accelerated by surfactants. The accelerated production will indicate alteration of k_r curves. In order to estimate k_r curves to oil and surfactant (increased N_c), surfactant floods starting from S_{wi} were carried out at water-wet and mixed-wet core plugs.

Figure 27 shows the remaining oil saturation (ROS) and pressure drop (DP) for the surfactant flood experiments (started at S_{wi}) on water-wet and mixed-wet Berea core plugs.

The history matching and experimental data are in good agreement both for the oil recovery and pressure drop profiles. The oil production was increased in both water-wet and mixed-wet cases. Increased oil production at water-wet conditions was due to the N_c higher than N_{cc}. At mixed-wet condition, tail oil production was observed.

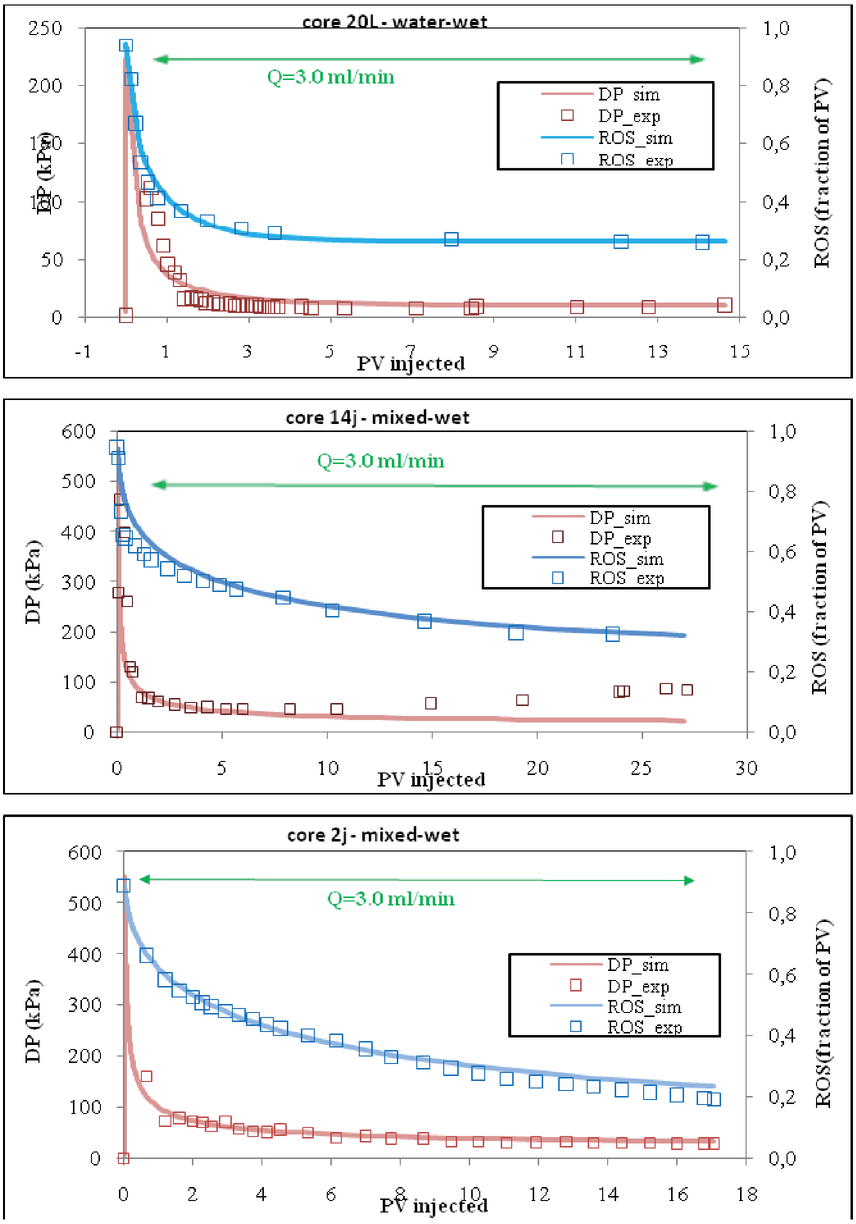


Figure 27. Remaining oil saturation (ROS) and differential pressure (DP) during surfactant flooding at Swi of water-wet & mixed-wet core plugs with STO as oil

Estimated k_r curves to oil/water and oil/surfactant are shown in Figure 28.

At water-wet conditions, k_{rw} has higher curvature and k_{ro} curve has no/less curvature. At mixed-wet conditions, both k_{ro} and k_{rw} show high curvature. At water-wet conditions water is the wetting phase and at mixed-wet conditions the wettability is not homogeneous. According to the treatment at S_{wi}, the smaller pores filled with water are remained as water-wet and the larger pores become oil-wet in the mixed-wet core plugs.

Oil/surfactant k_r curves for the surfactant floods (in Figure 28), has a less curvature compared to the curves obtained at higher σ. Surfactant flood shifts the k_{ro} curve to the higher S_w at both water-wet and oil-wet conditions. The cross point for k_{ro} and k_{rw} shifts to higher S_w in surfactant flood compared to water flood at water-wet condition. This observation is similar to the k_r curves (at low σ) reported by Gilliland and Conley (1975) and Shen et al. (2006). The increased in k_{ro} indicates an accelerated oil production at mixed-wet conditions.

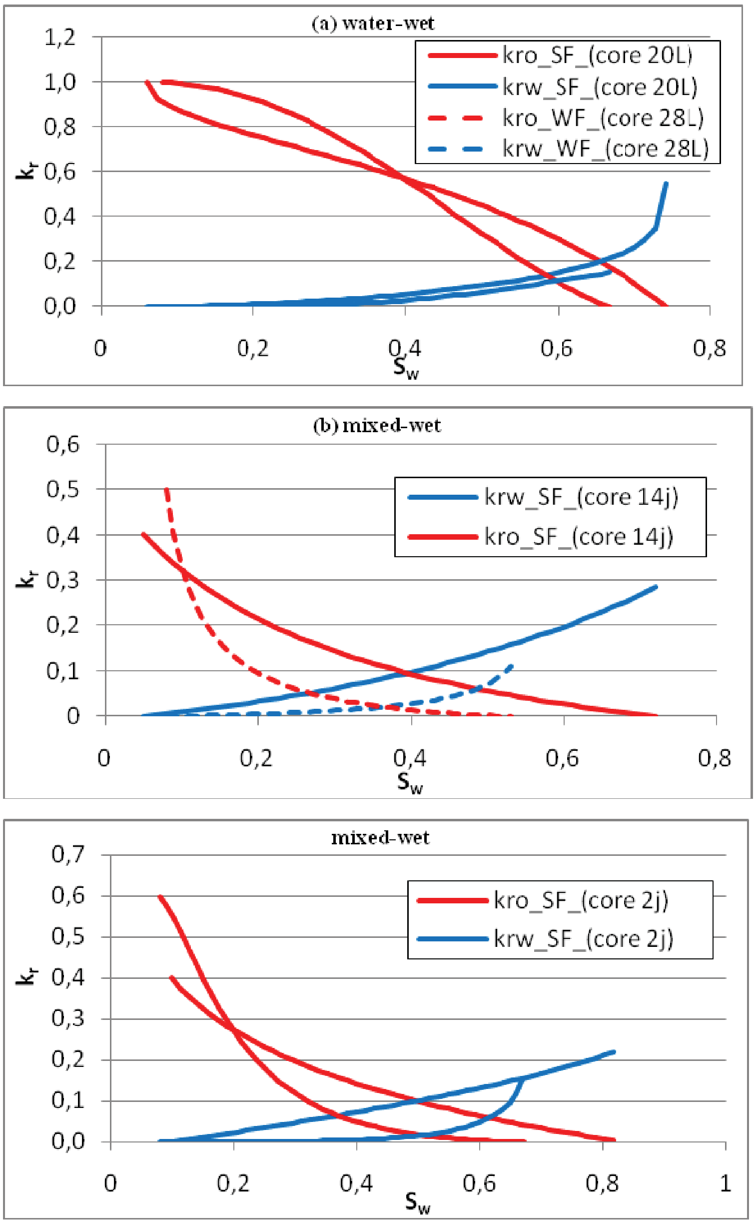


Figure 28 Estimated kr function for oil/water (WF) and oil/surfactant (SF) at (a) water-wet and (b) mixed-wet conditions (Nc for SF is around 4 x 10-3)

5.6 Effect of N_c on relative permeability at mixed-wet conditions

In this study, single rate surfactant floods (at different N_c) and multiple rates surfactant flood were carried out in mixed-wet Berea core plugs at S_{wi} (Paper VI). STO was used as oil in all the experiments. Two surfactant systems (surfactant solution-1 and surfactant solution-3) were used for the surfactant floods. In order to minimize the uncertainty in saturation caused by oil solubilization, surfactant solution after equilibrium with STO was used in the surfactant flooding experiment. Table 14 presents an overview of the core plugs used in this study.

Table 14. Core properties(Berea 500mD)_core floods with STO

Core No.	PV (ml)	Φ (fraction)	k_{abs} (mD)
26L*	22.56	0.22	562
9M	22.35	0.22	655
11M	22.06	0.22	593
12M	22.24	0.22	675
4M	22.79	0.23	594

*from previous section 5.5

Table 15 gives an overview of the oil displacement experiments at different N_c. N_c was changed by varying the injection flow rate and also varying the σ between oil and water. The water flood experiment at mixed-wet condition (core 26L) is considered as reference for low N_c.

Table 15. Summary of core floods at different N_c

Core No.	Q (ml/min)	Surfactant solution	σ (mN/m)	μ_w (cP)	N_c
26L	1.0→3.0→7.5	-	22	1.08	$6x10^{-7}$→$2x10^{-6}$→$5x10^{-6}$
9M	0.3→ 3.0→7.5	Solution -1	0.01	0.76	$3x10^{-4}$→$3x10^{-3}$→$8x10^{-3}$
11M	0.3	Solution -1	0.01	0.76	$3x10^{-4}$
12M	3.0	Solution -1	0.01	0.76	$3x10^{-3}$
4M	3.0	Solution -3	0.8	0.96	$5x10^{-5}$

The experimental ROS and simulated results using Sendra for the core floods at different N_c is shown in Figure 29. At low N_c (water flood in core 26L), multiple flow rates were used. At high N_c (surfactant floods in core 11M, 12M & 4M), single flow rates were used. The experimental ROS profiles are well reproduced by simulations as shown in Figure 29. The oil production is increased as the N_c is increased. More efficient oil displacement is observed at high N_c (surfactant floods) compared to low N_c (water flood).

Figure 30 shows the measured ROS and differential pressure (DP) profiles from the multiple rates surfactant flood in core 9M. The corresponding history matched profiles generated by Sendra are also plotted in Figure 30. When the flow rate is increased, the stepwise reduction in ROS is observed. The reduction in ROS is significant when the flow rate is increased from 0.3 ml/min to 3.0 ml/min. This rate dependent oil production is not reproduced in simulations as shown in Figure 30.

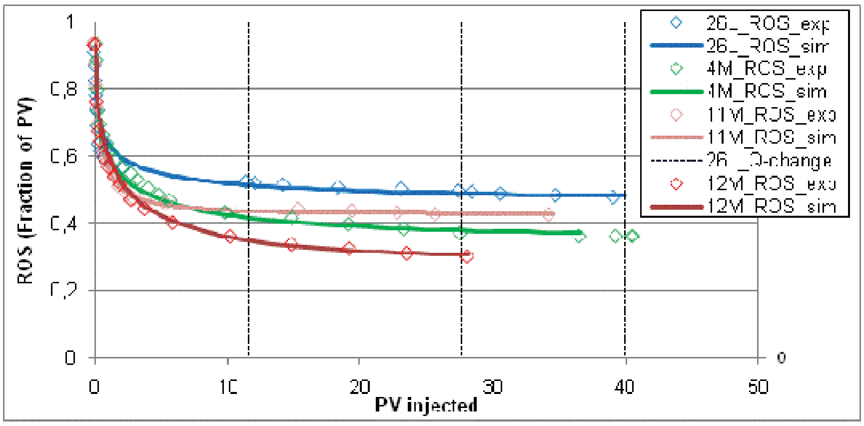


Figure 29. Experimental and simulated remaining oil saturation at different N_c (order of increasing N_c)

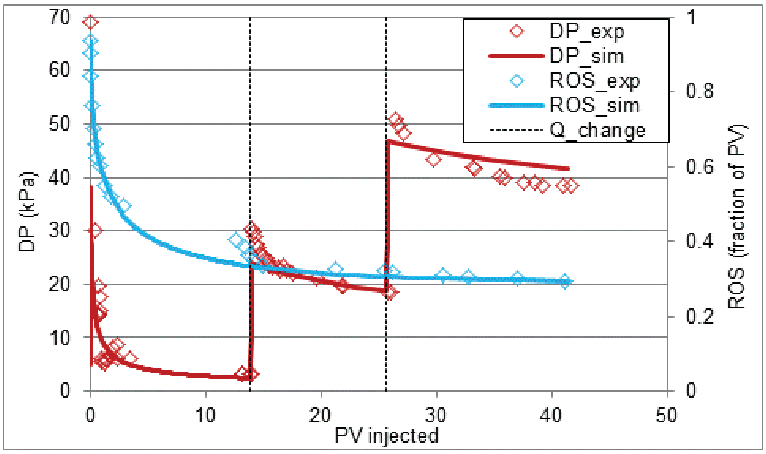


Figure 30. Experimental and simulated remaining oil saturation at high N_c (multiple flow rates surfactant flood - core 9M)

The observed rate dependent production at high N_c (core 9M) is an indication of rate dependent relative permeability functions. This observation is in line with the observations reported in Paper I from the core floods carried out with solvent systems.

The estimated k_r curves (by history matching of experimental data) at different N_c are shown in Figure 31. A significant increase in k_{ro} can be seen at high N_c. Figure 32 gives the k_r ratio (k_{rw}/k_{ro}) curves at different N_c.

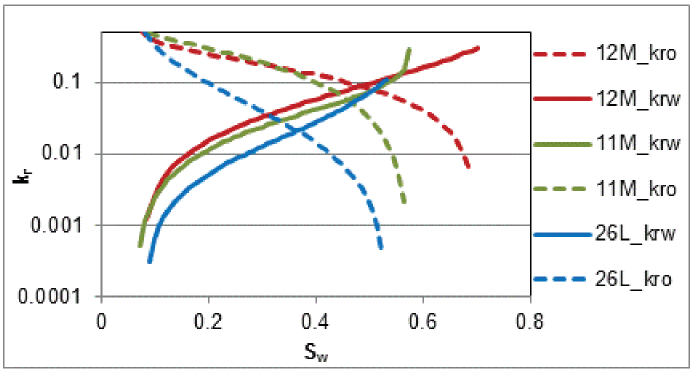


Figure 31. Computed k_r curves at different N_c (in the order of decreasing N_c)

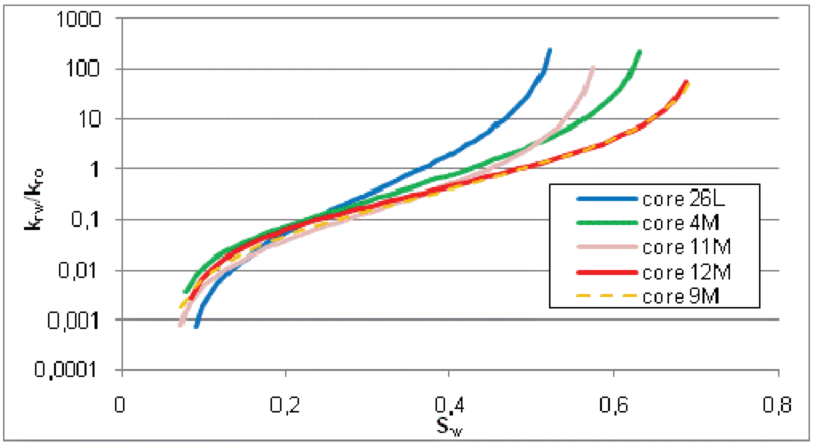


Figure 32. Ratio of k_{rw} to k_{ro} during water flood and surfactant (order of increasing N_c)

At high S_w, decreasing k_{rw}/k_{ro} ratio is observed with increasing N_c. This indicates the lower water cut at high N_c which results improvement of oil displacement.

Figure 33 shows the relationship between fractional flow of water (f_w) and water saturation (S_w). F_w was found to decrease with increasing N_c. Fractional flow analysis supports the observations made in above where oil recovery increased with increasing N_c.

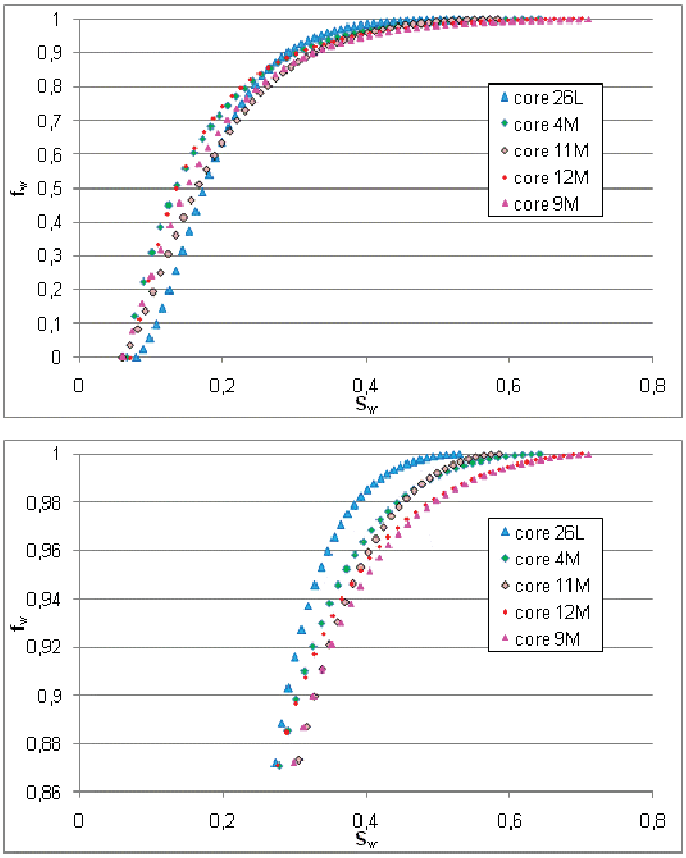


Figure 33. Fractional flow curves during water flood and surfactant floods at mixed-wet conditions (order of increasing N_c)

5.7 Measured CDC (remaining saturation Vs N_c)

Multiple rates water floods (with n-decane as oil) presented in section 5.4 were continued with multiple rates surfactant floods (surfactant flood at S_{orw}) using surfactant solution-3 (Paper V). The measured CDCs during these water floods and surfactant floods at different wettability conditions are shown in Figure 34. N_c was increased by stepwise increases in the flow rate (0.1 ml/min – 10.0 ml/min) and by reducing the interfacial tension from 40 to 1.5 mN/m during the surfactant floods.

At water-wet conditions, CDC measured for the non-wetting phase has a plateau at low N_c and declining slope above N_{cc} (Figure 34). This is quite similar to the typical CDCs observed for non-wetting phase at water-wet conditions (Mohanty and Salter, 1983; Lake, 1989; Delshad et al., 1986; Garnes et al., 1990).

Under mixed-wet and oil-wet conditions, the remaining oil saturation was found to decrease with increasing N_c. No N_{cc} was observed. This is similar to the atypical CDC presented by Garnes et al. (1990) on some North Sea sandstones. Mohanty and Salter (1983) determined similar shape of CDC's for oil-wet and mixed-wet conditions. At mixed-wet and oil-wet conditions, oil is the wetting phase and during water/surfactant flood wetting phase is displaced by non-wetting phase. At low N_c (water flood), the reduction in ROS with increase in N_c is mainly due to the removal of capillary end effects and also due to the number of PV of water injected.

Few of the core plugs were flooded back to S_{wi} by multiple rates oil floods. The measured CDCs during the oil floods at different wettability conditions are plotted in Figure 35. The capillary number was increased only by increasing the flow rate during oil flooding experiments. Comparable atypical CDC shape was observed for the wetting phase at the water-wet condition.

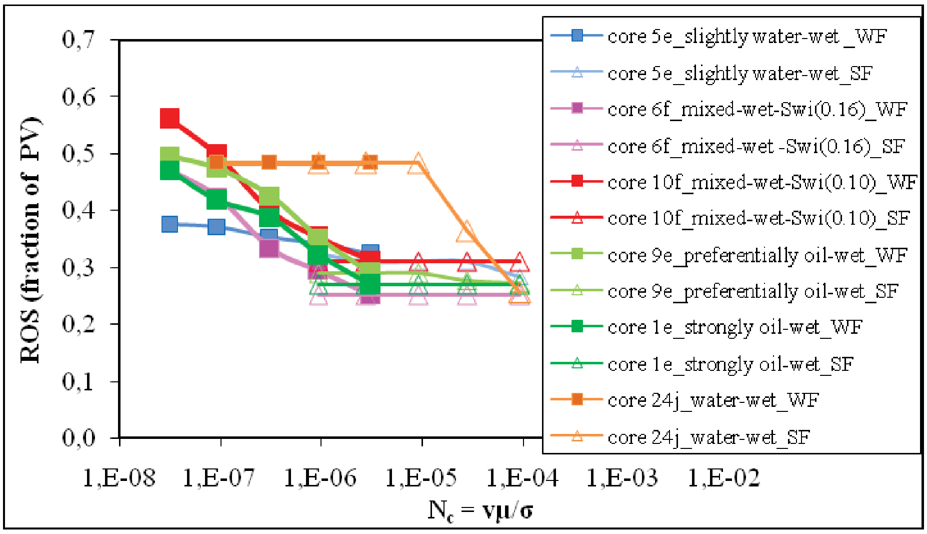


Figure 34. Measured CDC during water flood and surfactant flood at different wettability conditions (n-decane as oil)

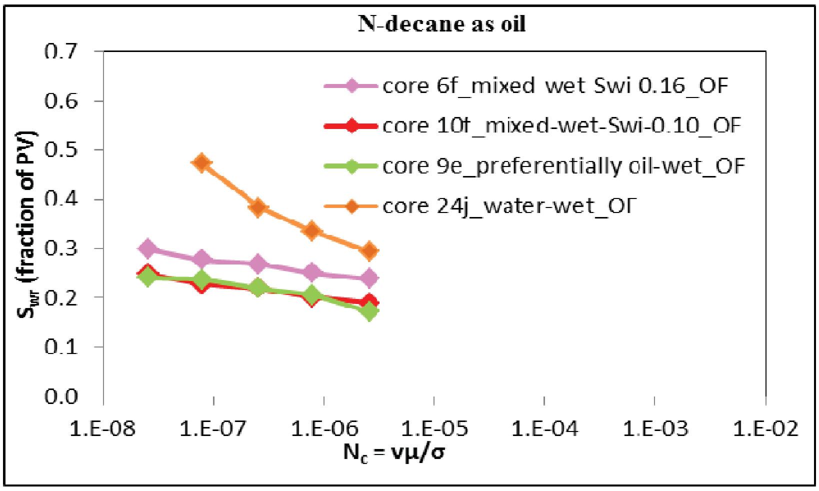


Figure 35. Measured CDC during oil flood at different wettability conditions

Measured CDCs during the water floods and surfactant floods presented in section 5.5 and section 5.6 (STO as oil) are shown in Figure 36 (Paper III).

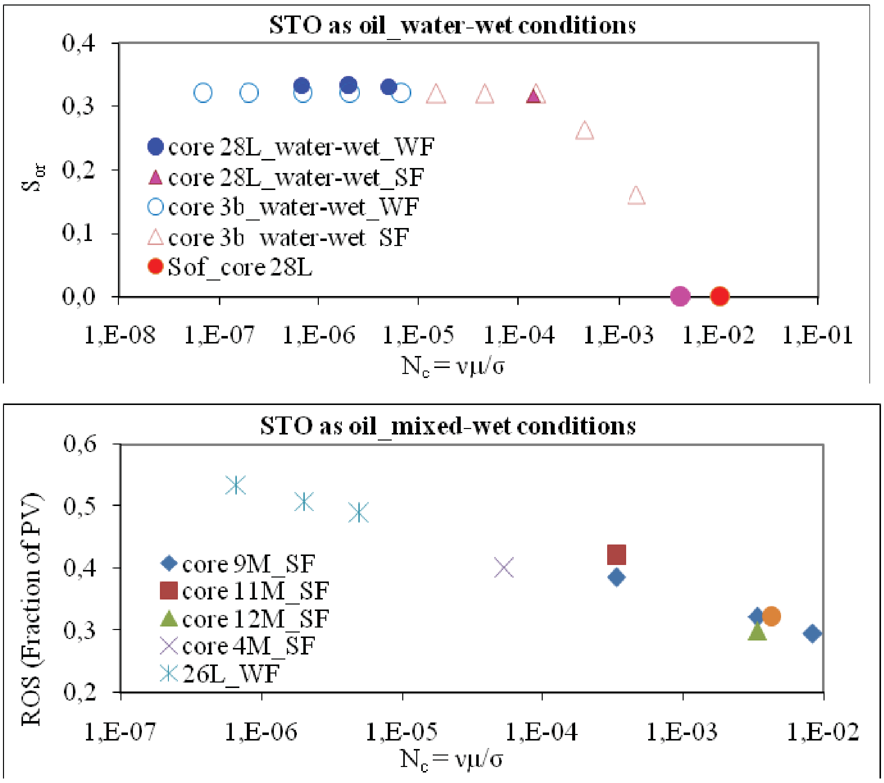


Figure 36. Measured CDC during water flood and surfactant flood at different wettability conditions (S_{of} is the oil saturation determined by accessible water volume)

The typical CDC shape was observed for the non wetting phase at water-wet conditions as shown in Figure 36 (a). Similar non representative shape of CDC was observed at mixed-wet conditions as described earlier (with n-decane as oil). In Figure 36 at low N_c (water flood with STO as oil), much higher ROS values were observed compared to when n-decane was displaced (Figure 34). The reason for this is the higher viscosity ratio of oil to water when STO was used. To displace high viscous oil, much higher throughput of water is required. Higher flow rates were used in this experiment (water flood in core 26L) and therefore influence of capillary end effects are less. Smaller jumps in ROS with increase in N_c compared to the water floods with n-decane as oil, is also an indication of reduced influence of capillary forces. At mixed-wet conditions, ROS is a function of number of PV of water injected and the oil production is limited by the relative permeability. During the surfactant flooding (Figure 36), the reduction of ROS with increase in N_c can be partly due to the number of PV injected and also due to the acceleration of oil production.

5.8 Core flooding experiments on reservoir rock

Water-oil flooding cycles (FW-Marcol 82) and water & surfactant floods (Paper IV) were carried out on the selected core plug according to the procedure described in section 3.4.2. The properties of the selected core plug are listed in Table 16.

Table 16. Core properties_Reservoir core floods

Core No.	PV (ml)	Φ (fraction)	k_{abs} (mD)
Res_66	16.33	0.25	508

5.8.1 Water-oil flooding cycles

Water-oil flooding cycles (WF→OF→WF→OF) were carried out in the reservoir core (Res 66) with FW-Marcol 82. Crude oil in the aged core plug was replaced with Marcol 82 to get easier separation of phases and volume reading. Multiple rate water floods and multiple rate oil floods were carried out at 38 °C. Two flooding cycles were carried out. Figure 37 shows the experimental and simulated oil production (OP) and differential pressure (DP) during water floods.

Rate dependent production was observed in both water floods and oil floods. The capillary pressure (P_c) and relative permeability (k_r) curves were obtained by history matching the oil production and differential pressure data obtained from the water flood experiments.

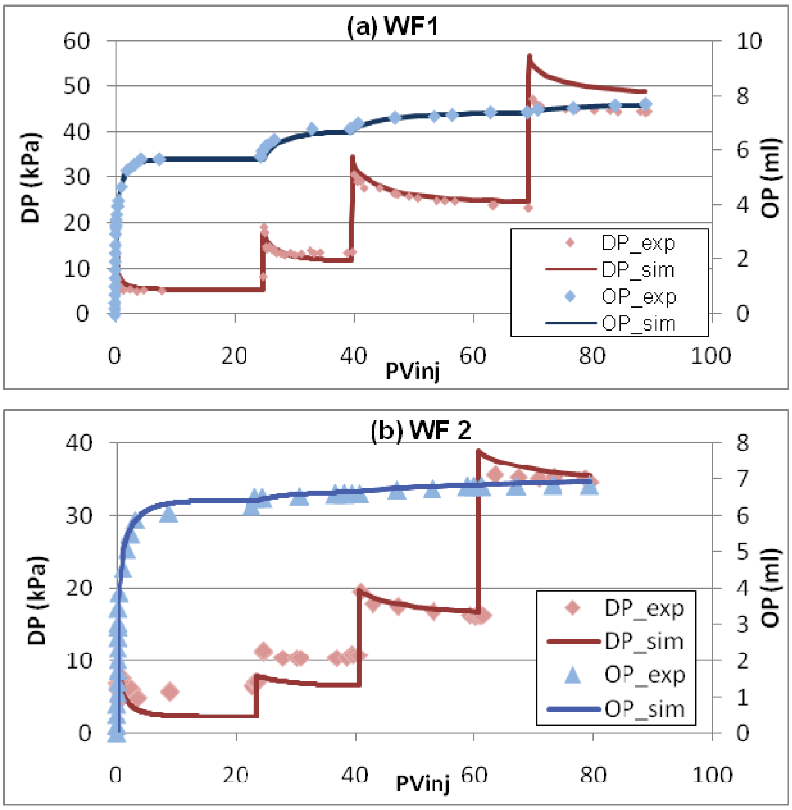


Figure 37. Oil production and differential pressure during water flooding of Reservoir core (a) 1st Water Flood (WF 1) (b)2nd Water Flood (WF 2)

The experimental productions were reproduced by assuming constant k_r and P_c curves in the simulations. Rate dependent production observed in water floods is most likely due to the capillary end effects. The estimated k_r and P_c curves are shown in Figure 38. The P_c curve has both positive and negative parts which indicate that oil was produced by both spontaneous imbibition and forced imbibition of water. The cross point water saturation is around 0.5 in the first water flood and 0.69 in the second water flood.

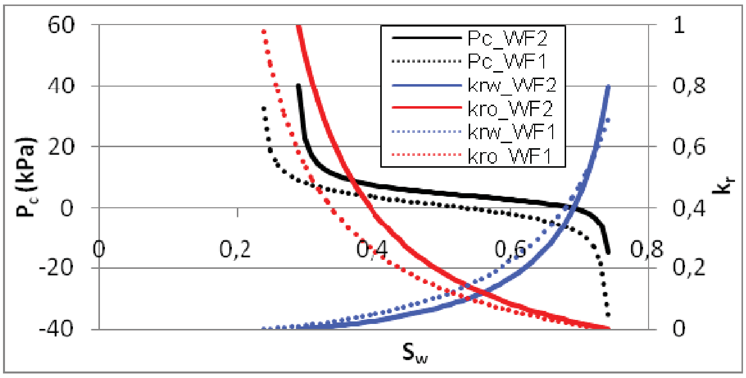


Figure 38. Oil-water relative permeability and capillary pressure curves estimated by history matching.

5.8.2 Water flooding and surfactant flooding

Both ROS and DP profiles during water flooding of the reservoir core are shown in Figure 39 (a) together with the history matched profiles. Estimated k_r curves by Sendra using P_c curve measured on another reservoir sample (from same reservoir) are plotted in Figure 39 (b).

Surfactant flooding was carried out after the water flooding with stepwise increase in the flow rate. In order to minimize the uncertainty in saturation caused by oil solubilization, surfactant solution after equilibrium with STO was used in the surfactant flooding experiment. Measured ROS vs N_c is shown in Figure 40. Declining slope at low N_c (water flooding) is mainly due to the capillary end effects and the number of PV injected in the experiment. A gentle slope was observed at high N_c (surfactant flooding). During surfactant flooding, reduction of ROS can be partly due to the number of PVs injected. Based on the experience with mixed-wet Berea core plugs, the reduction in ROS can also be due acceleration of oil production by improvement of relative permeability. Similar non representative CDC shapes were also observed in the experiments on mixed-wet Berea core plugs.

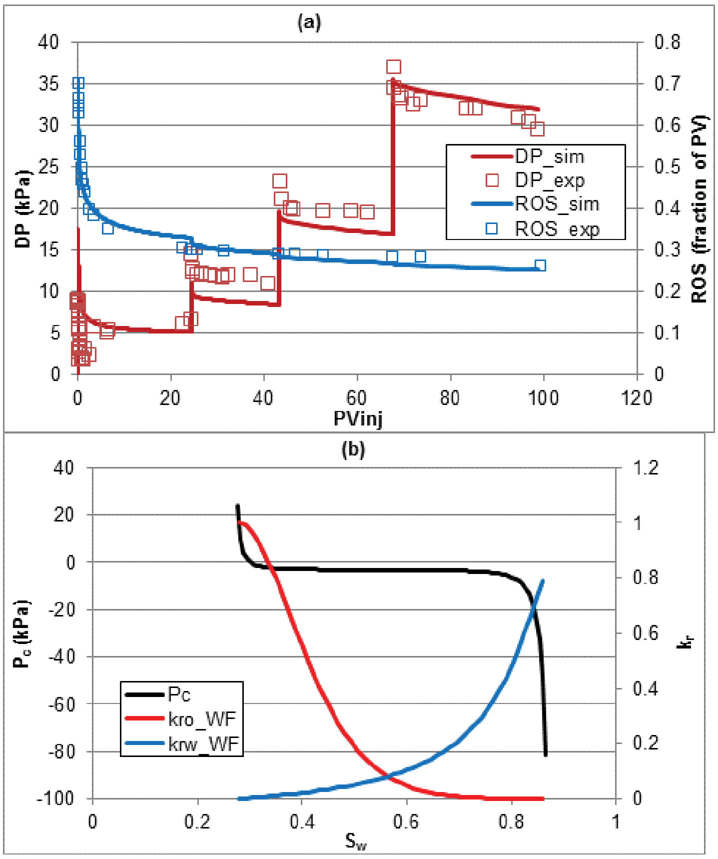


Figure 39. (a) Remaining oil saturation and differential pressure during water flooding of Reservoir core (b) Oil-water relative permeability and capillary pressure curves for the reservoir core.

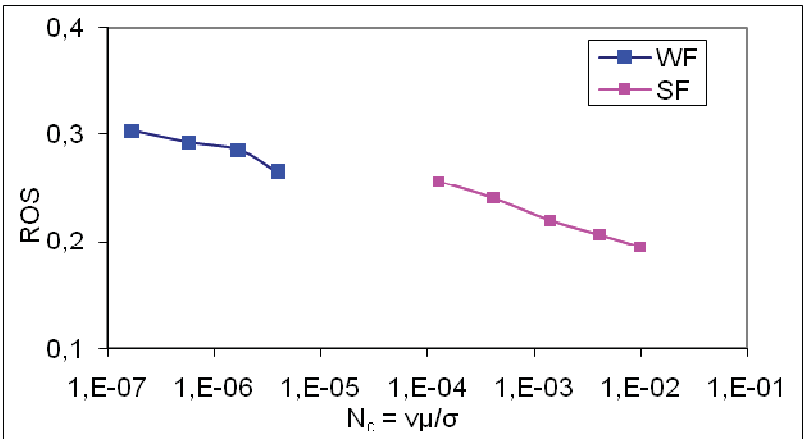


Figure 40. Measured remaining oil saturation Vs N_c during water flooding and surfactant flooding of the reservoir core.

5.9 Further Discussion

Oil displacement behavior at different wettability conditions was examined and discussed in this study. In strongly water-wet conditions, the displacement of oil by water is almost imbibitions controlled and do not show any capillary end effects. Therefore, in water-wet rock, core data produced by laboratory core floods are applicable to the reservoir. Similar conclusion was reported by Moore and Slobod (1955) after measuring the oil recovery in different core materials at water-wet conditions. They observed the same recovery in shorter cores as in long cores and also reported that the residual oil saturation by spontaneous imbibitions and water flooding were very similar at water-wet conditions.

According to the results in this study, at mixed-wet (or less water-wet) conditions, ROS after water flooding is largely influence by capillary end effects (significantly at lower flow rates). The lowest flow rate (0.1

ml/min) is close enough in the order of magnitude for a direct field comparison. The capillary end effect is only a laboratory artifact which does not exist in the reservoir floe behavior. Therefore, the core data from laboratory core floods at mixed-wet or less water-wet conditions are not applicable to reservoir scale and must be corrected for capillary end effects before scaling to reservoir scale simulation.

The measured ROS at mixed-wet conditions can not be considered as true S_{or}. Therefore, the plot of ROS versus N_c does not represent true CDC for mixed-wet or less water-wet conditions. Similar atypical CDC shapes were reported by Abrams (1975), Delshad et al. (1986) and Granes et al. (1990). Wrong representation of CDC shape may lead to wrong predictions in evaluating the potential for surfactant flooding. The slow oil production by water flooding at mixed-wet conditions is accelerated by surfactants. The results of this study show that the more important effect of surfactant flooding at mixed-wet conditions is the acceleration of oil production due to the improvement of k_{ro}. In reservoir simulations of surfactant flooding at mixed-wet conditions, relative permeability measured at different N_c should be considered as main input.

An increasing tail production of oil is seen at increasing oil wetness conditions (Salathiel, 1973; Wood and Wilcox, 1991; Jadhunandan and Morrow, 1995). Increasing the oil relative permeability at low oil saturation will increase the amount of recoverable oil with less water production at mixed-wet reservoirs. The outcome of this study gives additional knowledge for the field application of surfactant flooding in reservoirs other than water-wet conditions.

6 CONCLUDING REMARKS AND FUTURE WORK

6.1 Conclusions

No significant wettability change was observed by aging with the STO used in this study by varying brine pH, S_{wi}, rock permeability, brine salinity and aging time.

Quilon L appeared to be promising wettability modifier for Berea sandstone cores. Treating core plugs with increasing concentrations of Quilon L can be used as a method to produce core plugs of different wettability.

A procedure to establish mixed-wet Berea core plugs using Quilon L treatment is presented here. The established mixed-wet conditions are stable during water/oil flooding cycle and the method is reproducible.

Lower remaining oil saturation was observed at mixed-wet conditions than water-wet conditions, but higher throughput of water had to be injected at mixed-wet conditions.

Oil recovery can be accelerated by surfactants at mixed-wet conditions. The accelerated oil production is due to increase of k_{ro} values by surfactants (at lower S_o).

When evaluating tertiary oil recovery at mixed-wet conditions, the focus should be directed at k_r curves rather than S_{or}.

The measured CDC for oil in mixed-wet condition and the CDC for water in water-wet condition deviate from typical CDC shape due to the following reasons:

- Influence of capillary end effects especially low N_c
- ROS is a strong function of number of PV's injected

- S_{or} is poorly defined and difficult to obtain in core floods

Therefore plotting the measured ROS values vs N_c does not represent the true CDC behavior. In mixed-wet or non water-wet conditions, the most important effect of surfactants can be the acceleration of oil production; not necessarily the reduction of S_{or}.

6.2 Limitations of this study and further work

The work in this thesis has been carried out with some limitations and continued research is necessary to fully understand the evaluation of surfactant flooding at mixed-wet conditions. The following are some limitations in this study and suggested recommendations for future work.

- The mixed-wet conditions in outcrop Berea sandstone has been established by artificially (not by aging with crude oil). Nevertherless, it is assumed that these mixed-wet conditions are very similar to mixed-wet conditions established by aging with crude oil since the chemical treatment was done at S_{wi}. However, it would be interesting to investigate the proposed mechanism at mixed-wet conditions established by crude oil (more realitic wettability conditions).
- Independent P_c or in situ saturation measurements could give direct indication of capillary end effects and it would minimize the uncertainity of estimated k_r curves.
- Rate dependent production at reduced interfacial tension is attributed to rate dependent relative permeability which can not be simulated with a single set of relative permeability. Further work is needed for simulations considering rate dependent relative permeability functions.

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SECTION 2

Paper I

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Paper IV

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Paper V

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Paper VI

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