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Enhanced Oil Recovery with Surfactant Flooding

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Enhanced Oil Recovery

with Surfactant Flooding

Ph.D.-Thesis

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Center for Energy Resources Engineering

Preface

This thesis constitutes the partial fulfillment of the requirements for obtaining the Ph.D. degree at the Technical University of Denmark. The work has been carried out at the Department of Chemical and Biochemical Engineering at the Technical University of Denmark (DTU) as a part of the research carried out in Center for Energy Resources Engineering (CERE) with Associate Professor Nicolas von Solms and with head of the Department of Chemistry at DTU Erling H. Stenby as supervisors.

During the course of the study a number of people have provided indispensable help and support, for which I am very grateful. I would like to give my thanks to Nicolas von Solms and Erling H. Stenby for supervision and increasing the quality of my work through fruitful discussions, encouragement, carefully reading of my manuscripts and their patience and allowing me to pursue my own ideas into the project.

I thank my colleagues at CERE, which has created an inspiring and collegial work environment at all times, with a high and challenging degree of knowledge exchange. Especially I want to address my thank to Tran Thoung Dang and Zacarias Tecle who has provided outstanding help during the experiments and to Christian Ove Carlsson for his help with taking pictures and recording the experimental setups.

Also a special thanks to Sidsel Marie Nielsen, with whom I have had the pleasure to share office with, which has led to a lively everyday at the office and mutual encouragement whenever needed.

At last I want to thank my dear family and concerned friends for their sincere interest in my project and for the help, guidance and support when needed and their understanding when the project demanded most of my time. Especially I thank my lovely husband, Jonas, and our two wonderful kids, August and Filippa for their continued support in my efforts of finishing this work and their constant everlasting effort to make this journey possible for me, which I could not have accomplished without them.

Kgs. Lyngby, May 2012

Sara Bülow Sandersen

Summary

Enhanced oil recovery (EOR) is being increasingly applied in the oil industry and several different technologies have emerged during, the last decades in order to optimize oil recovery after conventional recovery methods have been applied.

Surfactant flooding is an EOR technique in which the phase behavior inside the reservoir can be manipulated by the injection of surfactants and co-surfactants, creating advantageous conditions in order to mobilize trapped oil. Correctly designed surfactant systems together with the crude oil can create microemulsions at the interface between crude oil and water, thus reducing the interfacial tension (IFT) to ultra low (0.001 mN/m), which consequently will mobilize the residual oil and result in improved oil recovery. This EOR technology is, however, made challenging by a number of factors, such as the adsorption of surfactant and co-surfactant to the rock during the injection and chromatographic separation of the surfactant and co-surfactant in the reservoir. Therefore it would be a significant step forward to develop single surfactant systems, as this would minimize the consequences of adsorption and separation. Furthermore the surfactants must be resistant to and remain active at reservoir conditions such as high temperatures, pressures and salinities.

Understanding the underlying mechanisms of systems that exhibit liquid-liquid equilibrium (e.g. oil-brine systems) at reservoir conditions is an area of increasing interest within EOR. This is true both for complex surfactant systems as well as for oil and brine systems. It is widely accepted that an increase in oil recovery can be obtained through flooding, whether it is simple waterflooding, waterflooding where the salinity has been modified by the addition or removal of specific ions (so-called "smart" waterflooding) or surfactant flooding.

High pressure experiments have been carried out in this work on a surfactant system (surfactant/ oil/ brine) and on oil/ seawater systems (oil/ brine). The high pressure experiments were carried out on a DBR JEFRI PVT cell, where a glass window allows observation of the phase behavior of the different systems at various temperatures and pressures inside the high pressure cell. Phase volumes can also be measured visually through the glass window using precision equipment.

The surfactant system for which an experimental study was carried out consisted of the mixture heptane, sodium dodecyl sulfate (SDS)/ 1-butanol/ NaCl/ water. This system has previously been examined at ambient pressures and temperatures but this has been extended here to pressures up to 400 bar and to slightly higher temperatures (40 ˚C, 45 ˚C and 50 ˚C). Experiments were performed at constant salinity (6.56 %), constant surfactant-alcohol ratio (SAR) but with varying water-oil ratios (WOR). At all temperatures it was very clear that the effect of pressure was significant. The system changed from the two phase region, Winsor II, to the three phase region, Winsor III, as pressure increased. Increasing pressures also caused a shift from the three phase region (Winsor III), to a different two phase region, (Winsor I). These changes in equilibrium phase behavior were also dependent on the composition of the system. A number of different compositions of the surfactant system were studied. The effect of increased pressure became more significant when combined with increasing temperature.

The experiments performed on the oil/ seawater systems were similar to the high pressure experiments for the surfactant system discussed above. Oil was contacted with different brine solutions with varying sulfate concentrations at a WOR of 70/30. A series of experiments were performed on two crude oils; a Latin American crude oil and a Middle East crude oil. The two crude oils showed significantly different phase behavior when exposed to elevated temperatures and pressures. The Latin American crude showed a decrease in oil viscosity with an increase in sulfate concentration in the brine solution after contacting in the PVT cell. The Middle East crude oil formed emulsions in the PVT cell with increasing temperature and pressure which was more pronounced at higher sulfate concentrations. Further characterization of the two crude oils using gas chromatography and SARA analysis confirmed that the heavier components in the crude oils, (in the case of the Latin American crude oil), are correlated to the observed decrease of viscosity, where the viscosity decrease may be explained from change of the shape of the heavy components with the increase in sulfate concentration after contacting at high pressures and temperatures. A third model system consisting of heptane and seawater solutions was also studied. This system formed emulsions in the PVT cell similar to the Middle East crude oil, which indicates that the lighter components in the Middle East crude oil (compared to the Latin American crude oil) are responsible for the observed formation of emulsions.

The final part of the thesis is a phase behavior modeling study of alkane/ alkanol/ water systems relevant for surfactant flooding. Existing thermodynamic models, such as equations of state, while able to predict and correlate phase equilibrium in two liquid phases (with varying degrees of success) cannot account for the formation of a microemulsion phase. The presence of electrolytes

in the surfactant systems further complicates the problem, and the incorporation of electrolytes into equations of state is a problem that, while old, has not been satisfactorily solved. Furthermore the effect of pressure is presently not well accounted for. The simplified PC-SAFT equation of state is used to model the phase behavior of several binary systems. Typically, introducing a small binary interaction parameter, k_{ij}, results in good correlations. However, the interaction parameter must be fitted to each individual binary system.

A glycol ether/ water binary system was also included in the phase equilibrium modeling study. This system is so difficult to model adequately that an additional binary interaction parameter, l_{ij}, was introduced to see if the correlations of this system could be improved – especially with regard to the significant effect of pressure on the phase behavior. It was concluded that this additional binary parameter was not sufficient to substantially improve the performance of the model.

Resume

Forbedret olieindvinding (EOR) vinder større og større indpas i olieindustrien og flere forskellige teknologier er brudt frem gennem de sidste årtier, alle med det overordnede formål at bidrage til at optimere olieindvinding efter at traditionelle indvindingsmetoder er anvendt.

Gennemskylning med overfladeaktivt stof (surfactant flooding) er en EOR teknik, hvor faseadfærd og faseligevægt inde i reservoiret kan manipuleres via injektion af surfactanter og co-surfactanter. Herved dannes fordelagtige betingelser i forhold til at mobilisere den tilbageværende olie i reservoiret. Potentielt kan et rigtigt design af et surfactant system sammen med råolie danne microemulsioner ved grænsefladen mellem råolie og saltvands/surfactant-blanding og derved medføre en reducering af grænsefladespændingen (IFT) til ultra lav (0.001 mN/m), hvilket vil medføre en mobilisering af den tilbageværende råolie og endeligt resultere i en forbedret olieindvinding. Denne EOR teknologi udfordres dog af en række faktorer, som f.eks. adsorption af surfactant og co-surfactant til stenlaget i undergrunden under injektionen, samt kromatografisk separation af surfactant og co-surfactant fra surfactantblandingen undervejs i processen inde i reservoiret. Det vil være et betydeligt fremskridt, for at undgå disse udfordrende faktorer, at udvikle/ designe single surfactant systemer, da dette vil minimere de mulige konsekvenser der følger med den adsorption og separation som forekommer ved injektionen. Derudover er der en række andre krav til den anvendte surfactant, som skal kunne modstå, og samtidigt vedblive aktiv, ved såkaldte reservoir betingelser, hvilket blandt andet er høje temperaturer, høje tryk og varierende saltkoncentrationer.

Forståelsen for de mekanismer der dominere i væske-væske ligevægtssystemer (f.eks. olie-saltvands-systemer) ved reservoir betingelser er et område med fornyet og øget interesse indenfor EOR. Dette gælder både for de mere komplekse surfactant systemer, ligesåvel som det gælder mere simple olie-saltvandssystemer. Generelt er opfattelsen, at forøget olieindvinding kan opnås gennem såkaldt flooding. Dette er uanset om det er waterflooding, hvilket er gennemskylning af reservoiret med saltvand, hvor saltindholdet i injektionsvandet er modificeret ved enten at tilføre eller fjerne konkrete ioner (dette er også kaldet 'smart' waterflooding), eller det er surfactant flooding.

Der er udført eksperimenter ved højt tryk i dette projekt, hvor der er arbejdet med et surfactant system (surfactant/ olie/ saltvand) og et olie/ syntetisk havvand system (olie/ saltvand). Eksperimenterne ved højt tryk er udført i en højtrykscelle, DBR JEFRI PVT cell, der tillader direkte observationer gennem et glasvindue. Derved kan faseadfærd for de forskellige systemer, ved varierende temperaturer og tryk inde i højtrykscellen, observeres udefra. Det er endvidere muligt at bestemme fase volumenerne med et dertil egnet præcisionsmåleinstrument.

Det surfactant system, som er blevet anvendt til det eksperimentelle arbejde er sammensat af heptan, natrium dodecyl sulfat (SDS), 1-butanol, NaCl og vand. Tidligere har dette system været betragtet af andre uden trykpåvirkning og ved stuetemperatur. I dette projekt betragtes surfactant systemet ved højere tryk helt op til 400 bar og samtidigt også ved en anelse højere temperaturer (40 °C, 45 °C and 50 °C). Alle eksperimenter er udført ved konstant salinitet, det vil sige samme saltkoncentration i vandet (6.56%), konstant surfactant-alkohol forhold (SAR) og med varierende vand-olie forhold (WOR). Uanset valg af temperatur, var det klart fra resultaterne, at der var en betydelig effekt ved øget tryk på systemet. Surfactant systemet vekslede i antallet af væskefaser afhængigt af trykket. Et skift fra to-fase regionen, Winsor II, til tre-fase regionen, Winsor III, forekom i takt med at trykket i cellen blev øget. Øget tryk i cellen var også medvirkende til at surfactant systemet skiftede fra tre-fase regionen, Winsor III, til en anden to-fase region, Winsor I. Disse skift i ligevægtstilstande for faseadfærden var endvidere afhængigt af sammensætningen af surfactantsystemet. Forskellige sammensætninger af surfactant systemet blev undersøgt. Det var også observeret, at kombinationen af øget tryk, samt højere temperatur i højtrykscellen, forårsagede en mere betydelig påvirkning på surfactant systemet.

De eksperimenter, der er udført med olie/ syntetisk havvand, er udført efter en lignende fremgangsmåde som tilfældet med surfactant systemet, beskrevet ovenfor. I disse forsøg var olie og forskellige saltvandsopløsninger (syntetisk havvand) med varierende koncentration af sulfat blandet grundigt sammen ved en WOR på 70/30. Der er udført en række eksperimenter med to forskellige råolier, Latin American crude oil og Middle East crude oil. De to råolier viste bemærkelsesværdig forskellige faseadfærd når og efter, at systemerne med saltvandsopløsning var blevet påført høje temperaturer og højt tryk. For Latin American råolien blev viskositeten af råolien reduceret betydeligt som funktion af højere sulfat koncentration i saltvandsopløsningen efter at eksperimenter var gennemført i PVT cellen. Middle East råolien dannede emulsioner inde i PVT cellen som funktion af øget temperatur og tryk og endvidere var disse observationer mere udprægede ved højere koncentrationer af sulfat. De to råolier var yderligere karakteriseret ved hjælp af gas kromatografi (GC) og SARA analyse (karakterisering af indhold af Saturates,

Aromatics, Resins og Asphaltenes). Disse karakteriseringer bekræftede at de tungere komponenter i råolien (tilfældet for Latin American råolien) har en sammenhæng med den observerede reduktion i viskositeten af råolien. Reduktionen af viskositeten kan formentlig forklares ud fra ændringer af formen på de tunge komponenter som forekommer med øget koncentrationen af sulfat når systemet er under øget tryk og højere temeprature. Endnu et system er blevet undersøgt, heptan og havvand. Dette system dannede emulsioner inde i PVT cellen i samme stil som den foregående råolie system med Middle East råolien, hvilket indikere at det er de lettere komponenter i Middle East råolien (sammenholdt med Latin American råolien) som er den medvirkende årsag til de observerede dannelse af emulsioner.

Sidste del af denne PhD-afhandling omhandler et studie i modellering af faseadfærd og faseligevægte for alkan/ alkanol/ vand systemer, som kan være relevant for surfactant flooding. De nuværende termodynamiske modeller, som for eksempel tilstandsligninger, kan forudsige og korrelere faseligevægte for to væskefaser (med varierende grad af succes), dog er disse ikke i stand til at medregne dannelsen af en microemulsionsfase. Tilstedeværelsen af elektrolytter i surfacatant systemer bidrager til yderligere komplicering af problemet og inkorporering af elektrolytter i tilstandsligninger er et velkendt problem som endnu ikke er blevet løst tilfredsstillende. Desuden er effekten af tryk heller ikke velbeskrevet i termodynamiske modeller. I denne afhandling er sPC-SAFT tilstandsligningen anvendt for at modellere faseadfærd for en række binære systemer. Det typiske mønster for disse systemer er, at ved at introducere en mindre binær interaktionsparameter, k_{ij}, kan der opnås gode korrelationer. Dog skal interaktionsparameteren justeres til hvert enkelt binært system.

Inkluderet i faseligevægts-modelleringsstudiet er det binære system glykol æter/ vand. Dette system er vanskeligt at modellere tilfredsstillende og derfor introduceres en ekstra binær interaktionsparameter, l_{ij}, for at bestemme om der kunne opnås forbedret korrelationer for dette system. Særligt med hensyn til den betydelige effekt der kommer fra tryk på systemets faseadfærd. Konklusionen var, at den ekstra binære interaktionsparameter ikke var tilstrækkelig til at forbedre modellen væsentligt.

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Chapter 1

1 Introduction

By nature crude oil is a limited resource. Nevertheless, the amount of crude oil available has to meet the worldwide demands. From time to time, oil production has been intentionally reduced, and this has resulted in serious oil crises accompanied by a general increase in the oil price. This in turn has forced the oil industry to recover oil from more complicated areas, where the oil is less accessible meaning that recovery techniques are constantly advanced. This has contributed to the development of techniques for enhanced oil recovery, (EOR), which while used today, also constantly undergo further advancement and development. Up to two thirds of the crude oil remains trapped in the reservoirs after primary and secondary recovery in an average oil reservoir, [Rosen et al., 2005]. EOR is then required to optimize the depletion, as the remaining oil is trapped in the pore structure inside the reservoir. EOR covers several different advanced recovery techniques, which will be introduced in this chapter.

The focus in this thesis has been on the phase behavior properties inside the reservoir in connection with surfactant flooding and oil/ brine systems. The phase behavior in the surfactant system is overall the most important factor determining the success of a chemical flood [Skauge and Fotland, 1990]. Currently, there are no adequate models (such as equations of state) to describe phase behavior in such systems. Consequently phase behavior must be measured experimentally, which is both challenging and time-consuming.

The goal of this thesis has been to investigate the phase behavior of oil/water systems in relation to enhanced oil recovery. This chapter sets the basis for the experimental and modeling work presented subsequently. The general definitions of EOR are presented in this chapter. Surfactants and surfactant systems will be introduced, in order to explain the phase behavior which is essential to create an efficient surfactant flood and the difficulties in predicting the phase behavior of this type of systems. Furthermore the importance of the interaction between oil and water will be presented. Finally, the objectives of this Ph.D.-project are presented.

1.1 Enhanced Oil Recovery

Several mechanisms contribute to the primary production of oil. Primary production is in general understood as rather inefficient, as it produces less than 20 % of the original oil in place, [Morrow, 1991, p.5]. With the goal of improving oil recovery, EOR is introduced, employing more efficient recovery methods. Oil recovery methods usually fall into one of the following three categories:

- Primary recovery: Recovery by depletion
- Secondary recovery: Recovery by water or gas flooding
- Tertiary recovery: Recovery of the residual oil (also known as Enhanced Oil Recovery, (EOR))

It is not unusual that the so-called tertiary oil recovery takes place either as the primary or the secondary step chronologically, because this entails a more feasible process for certain reservoirs, [Green & Willhite, 1998, pp.1-10]. Another commonly used designation is improved oil recovery (IOR), which covers a broader range of activities. IOR can also include EOR, where IOR and EOR in general are defined as follows:

- Improved Oil Recovery (IOR): Injection of fluids, which are already present in the reservoir, e.g. water.
- Enhanced Oil Recovery (EOR): Injection of fluids, which are not normally present in the reservoir, e.g. surfactants.

The concepts of IOR and EOR in practice are often mixed. Nowadays, oil recovery processes are typically classified as primary, secondary and EOR processes. From a fundamental point of view EOR should be understood as methods or techniques whereby extrinsic energy and materials are added to a reservoir to control:

- Wettability
- Interfacial tensions (IFT)
- Fluid properties
- Establish pressure gradients necessary to overcome retaining forces
- Move the remaining crude oil in a controlled manner towards a production well.

One aspect of EOR operations, which in all processes has a considerable influence on the result, is the ability to control the flow of the displacement fluid, so-called mobility control. Since flow pattern prediction is very uncertain, predicting oil recovery becomes difficult. These uncertainties challenge EOR processes. While it is desirable to design the most efficient process in order to increase oil recovery, economic feasibility of the EOR process is more crucial than any other aspect, in order to commercialize the process [Sharp, 1975].

1.1.1 EOR Processes

Much work has been performed in the area of fluid injection with the objective of improving oil recovery by the natural drive mechanism. The most widely used technique is waterflooding, which has been applied for more than 60 years. The oil left in the swept zone after waterflooding then becomes the main target for tertiary oil recovery, [Morrow, 1991, p.6-10].

The primary goals in EOR operations are to displace or alter the mobility of the remaining oil in the reservoir. Using conventional waterflooding techniques is preferable as long as it is economically feasible. Remaining oil left after primary and secondary recovery operations over long time periods is usually distributed in pores in the reservoir, where the oil is trapped, mainly due to capillary forces and viscous forces. EOR techniques will contribute to a longer lifetime of already existing reservoirs. Unfortunately the application of EOR does not only bring advantages. Using EOR is correlated with higher risks and increases the requirement for additional facilities and investments. The common classifications of different EOR processes are [Green and Willhite, 1998, p.1-10]:

- Mobility-control
- Chemical processes
- Miscible processes

- Thermal Processes
- Other (e.g. microbial EOR)

In general the EOR processes involve injection of gas or fluids into the oil reservoir, displacing crude oil from the reservoir towards a production well. The injection processes supplement the natural energy present in the reservoir. The injected fluid also interacts with rock and oil trapped in the reservoir creating advantageous conditions for oil recovery.

Mobility-control is a process based on maintaining favorable mobility ratios between crude oil and water, by increasing water viscosity and decreasing water relative permeability. Can improve sweep efficiency over waterflooding during surfactant processes.

Chemical processes are injection of a specific liquid chemical that effectively creates desirable phase behavior properties, to improve oil displacement. The principles are illustrated in figure 1.1.
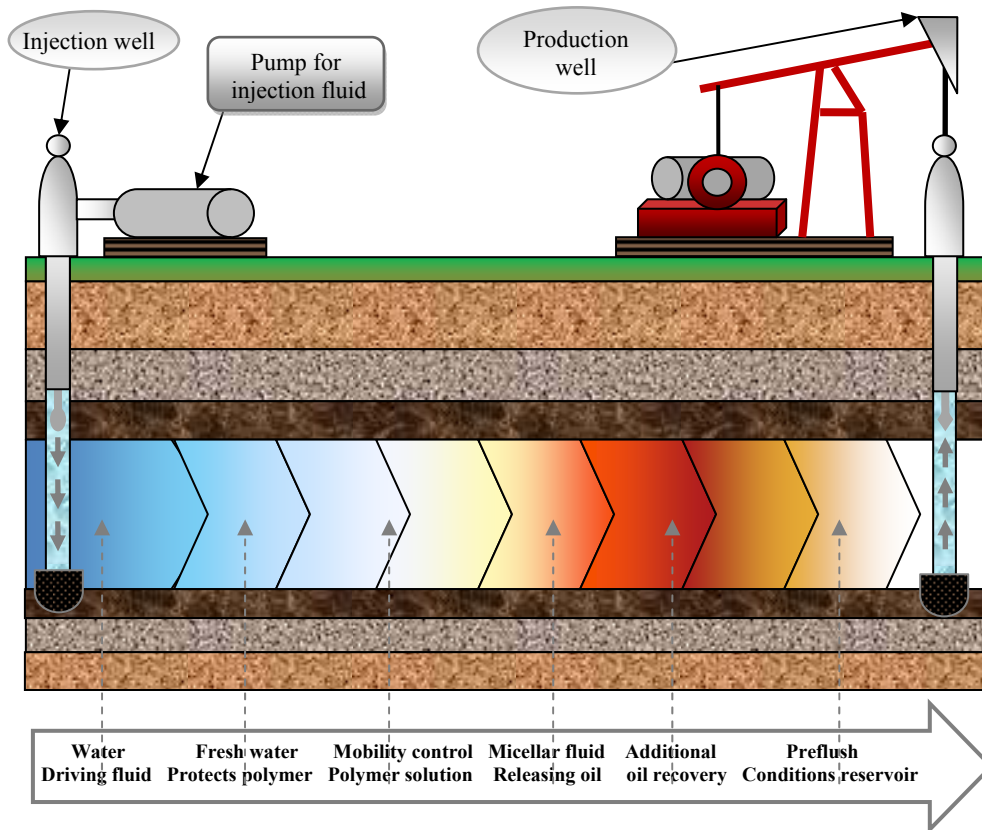
Figure 1.1. Chemical flooding, which is the injection of water and chemicals. Besides the economic point of view, the complexity rises as several additional tasks such as preflush of the reservoir and injection of additional fluids must be applied to accomplish an efficient process.

Surfactant flooding is an example of chemical flooding. This is a complex process, where the displacement is immiscible, as water or brine does not mix with oil. However, this condition is changed by the addition of surfactants. The technique creates low interfacial tension (IFT), where especially an ultra low IFT (0.001mN/m) between the displacing fluid and the oil is a requirement in order to mobilize the residual oil. The liquid surfactant injected into the reservoir is often a complex chemical system, which creates a so-called micelle solution. During surfactant flooding it is essential that the complex system forms microemulsions with the residual oil as this supports the decrease of the IFT and increases the mobility. However, the formation of microemulsions may also be a significant disadvantage, as microemulsions may plug the pores. It is also important to be aware of the high loss of surfactant, occurring as a result of adsorption and phase partitioning inside the reservoir. It is known that surfactant systems are sensitive to high temperatures and high salinity, leading to requirements for developing surfactant systems that can withstand such conditions. Other chemical processes have also been developed, such as alkaline flooding and various processes where alcohols are introduced. In alkaline flooding, alkaline chemicals are injected into the reservoir, where they react with certain components in the oil to generate

surfactants *in situ*. Alcohol processes have so far only been tested in laboratories and have not yet been applied in the field.

Miscible processes are based on the injection of a gas or fluid, which is miscible with the crude oil at reservoir conditions, in order to mobilize the crude oil in the reservoir. The process is illustrated in figure 1.2. This process relies on the modification of the components either in the injected phase or in the reservoir oil phase. Modification of either injected fluid or gas or the reservoir oil is achieved through multiple contacts between the injected phase and the oil phase with mass transfer of components between the phases, [Green & Willhite, 1998, p.7]. E.g. injection of CO_2 as a liquid will entail extraction of the heavier hydrocarbons from the reservoir oil, which will allow the displacement front to become miscible, [Holm, 1986].
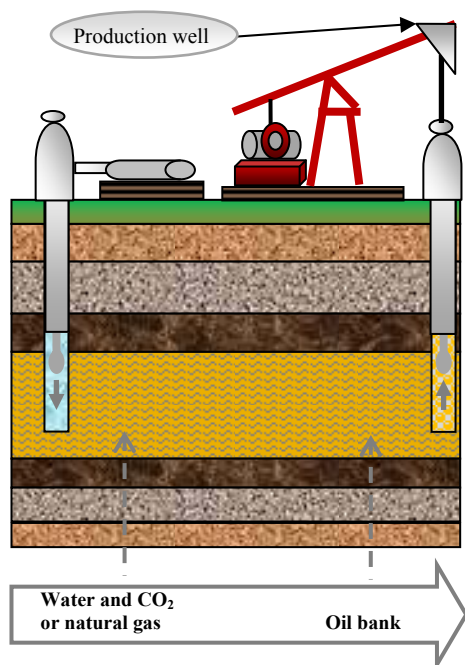
Figure 1.2. Miscible process control, where the injected fluid does mix with oil. In this process the oil is supposed to be mobilized while mixed with either injected gas or fluid.
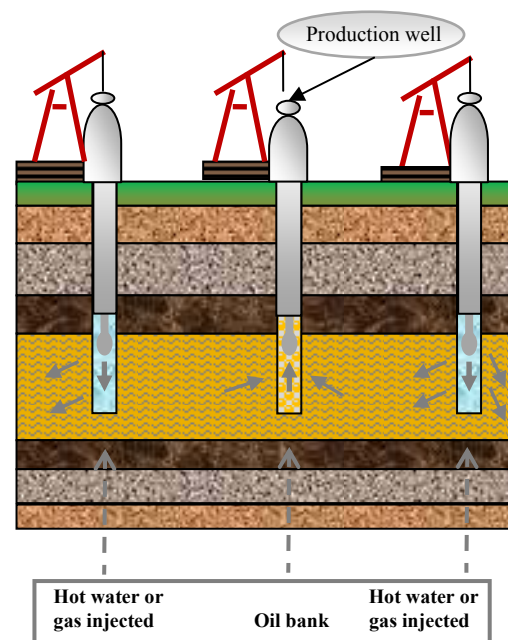
Figure 1.3. Thermal process control. Thermal energy is injected into the reservoir. The injected energy mobilizes the trapped oil and squeezes it away from the capillaries towards the reservoir.

Thermal processes are typically applied to heavy oils. Thermal recovery processes rely on the use of thermal energy. A hot phase of e.g. steam, hot water or a combustible gas is injected into the reservoir in order to increase the temperature of the trapped oil and gas and thereby reduce oil viscosity, [Green and Willhite, 1998, p.301]. The process is depicted in figure 1.3. The injected hot

stream facilitates the flow to the production wells by increasing the pressure and reducing the resistance to flow.

1.2 Surfactant Flooding

Surfactant flooding is injection of one or more liquid chemicals and surfactants. The injection effectively controls the phase behavior properties in the oil reservoir, thus mobilizing the trapped crude oil by lowering IFT between the injected liquid and the oil. The principle of surfactant flooding is illustrated in figure 1.4.
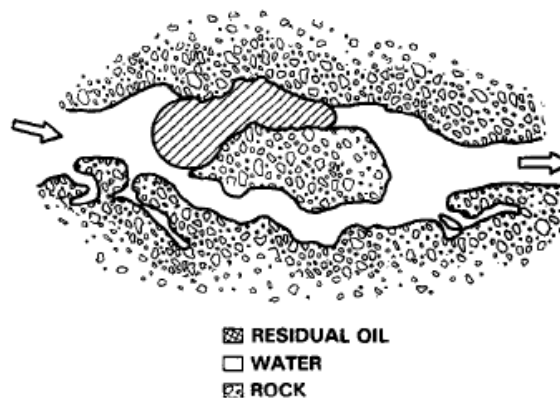
Figure 1.4. Principle of flooding, where residual oil is trapped in the reservoir, [O'Brien, 1982]. For the movement of oil through the narrow capillary pores, very low oil/water interfacial tension (IFT) is required; preferably ultra low IFT at 0.001 mN/m is desirable.

There is a great potential for chemical processes with surfactant flooding, since there is the possibility of designing a process where the overall displacement efficiency can be increased. Nowadays many mature reservoirs under waterflood have decreasing production rates despite having 50-75 % of the original oil left inside the reservoir [Flaaten et al., 2008]. In such cases it is likely that surfactant flooding can increase the economic productivity.

Surfactants are added to decrease the IFT between oil and water. Co-surfactants are blended into the liquid surfactant solution in order to improve the properties of the surfactant solution. The co-surfactant either serves as a promoter or as an active agent in the blended surfactant solution to provide optimal conditions with respect to temperature, pressure and salinity. Due to certain physical characteristics of the reservoir, such as adsorption to the rock and trapping of the fluid in the pore structure, considerable losses of the surfactant may occur. The stability of the surfactant system at reservoir conditions is also of great relevance. It is well known that surfactant systems

are sensitive to high temperature and high salinity and therefore surfactants that can resist these conditions should be used [Green and Willhite, 1998, p.7]. Surfactant flooding creates microemulsion solutions, which may contain different combinations of surfactants, co-surfactants, hydrocarbons, water and electrolytes [Green and Willhite, 1998, p.239-300]. Polymers are also often added to the injected surfactant solution, to increase viscosity, thus maintaining mobility control. In general there are three types of surfactant flooding for EOR [Rosen et al., 2005], shown in table 1.1:

Table 1.1. Types of surfactant flooding.

Type of surfactant flooding	Technique	Note
Micelle/polymer flooding:	A micelle slug usually of surfactant, co-surfactant, alcohol, brine and oil is injected into the reservoir.	Displacement efficiency close to 100 % (measured in laboratory).
Microemulsion flooding:	Surfactants, co-surfactants, alcohol and brine are injected into the reservoir to form microemulsions to obtain ultra low IFT.	Can be designed to perform well in e.g. high temperature or salinity or low permeable areas where polymer and/or alkali cannot work.
Alkaline/surfactant/polymer (ASP) flooding:	The addition of alkaline chemicals reduces the IFT at significantly lower surfactant concentrations.	Lower concentration of surfactants is involved in this process, which reduces the cost of chemicals.

Surfactant systems usually consist of both surfactants and co-surfactants. However the combination of multiple components in the surfactant solution system does not work well in practice as chromatographic separation occurs in the reservoir. The solution concentration quickly changes from its optimal value as the separation takes place. The optimization criterion in surfactant flooding is to maximize the amount of oil recovered, while minimizing the chemical cost. While it is necessary to reach low IFT for the surfactant system, minimizing only the IFT may not always coincide with optimal oil recovery, as low IFT is not the only essential condition to meet in order to get a successful and efficient oil recovery, [Fathi and Ramirez, 1984]. E.g. attention to the optimal salinity is crucial to include as well.

1.2.1 Surfactants

In surfactant flooding, the chemical system contains surface active agents, surfactants, which are polymeric molecules that lower the IFT between the liquid surfactant solution and the residual oil. Surfactants adsorb on a surface or fluid/fluid interface when present at low concentrations.

The most common structural form for surfactants is where they contain a nonpolar part, a hydrocarbon 'tail', and a polar or ionic part. The structure is shown in figure 1.5.
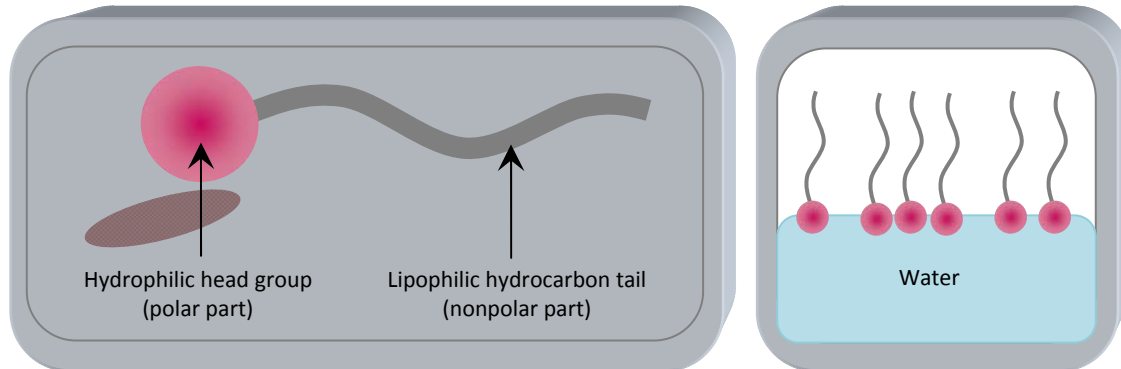
Figure 1.5. Surfactant molecule and surfactant orientation in water. Surfactants are also referred to as amphiphile molecules because they contain a nonpolar 'tail' and a polar 'head'-group within the same molecule, [Green and Willhite, 1998, p.241].

It is the balance between the hydrophilic and hydrophobic parts of the surfactant that generates the characteristics of the surface active agent. In EOR with surfactant flooding the hydrophilic head interacts with water molecules and the hydrophobic tail interacts with the residual oil. Thus, surfactants can form water-in-oil or oil-in-water emulsions. Surfactant molecules are amphiphilic, as they have both hydrophilic and hydrophobic moieties. Amphiphiles adsorb effectively to interfaces and typically contribute to significant reductions of the interfacial energy, [Pashley and Karaman, 2004, p. 62].

The primary surfactant is directly involved in the microemulsion formation with regards to the EOR surfactant flooding process. The co-surfactant, if any, promotes or improves the activities of the primary surfactant, by e.g. changing the surface energy or the viscosity of the liquids. Due to chromatographic separation of surfactant, co-surfactant and any other components, throughout the reservoir, it can be problematic to create a multicomponent surfactant system capable of maintaining optimal properties throughout the flooding process. The predominant disadvantage of separation is that the control of the system deteriorates in the reservoir and therefore it should be avoided if possible. As the co-surfactants prevent gel formation and reduce the equilibration time,

they are hard to eliminate from the surfactant systems used for flooding. Oil reservoirs have different characteristics and therefore the structure of added surfactant must be tailored to meet the reservoir conditions to achieve a low IFT. For example the temperature, pressure and rock vary significantly from one reservoir to another.

1.2.2 Classification of Surfactants

Surfactants are frequently classified on the basis of the ionic nature of the head group, as anionic, cationic, nonionic or zwitterionic. Each type possesses certain characteristics depending on how the surfactant molecules ionize in aqueous solutions. In table 1.2 a few commonly used surfactants are shown.

Table 1.2. List of common surfactant molecules with different types of charge: anionic, cationic and non-ionic. [Pashley & Karaman, 2004, p.63]

Anionic	
Sodium dodecyl sulfate (SDS)	$CH_3\left(CH_2\right)_{11} SO_4^- Na^+$
Sodium dodecyl benzene sulfonate	$CH_3\left(CH_2\right)_{11} C_6H_4 SO_3^- Na^+$
Cationic	
Cetyltrimethylammonium bromide (CTAB)	$CH_3\left(CH_2\right)_{15} N\left(CH_3\right)_3^+ Br^-$
Dodecylamine hydrochloride	$CH_3\left(CH_2\right)_{11} NH_3^+ Cl^-$
Non-ionic	
Polyethylene oxides	$CH_3\left(CH_2\right)_7 \left(O.CH_2CH_2\right)_8 OH$

Commonly used surfactants for EOR, are sulfonated hydrocarbons such as alcohol propoxylate sulfate or alcohol propoxylate sulfonate. To achieve an optimal surfactant flood for any given oil reservoir surfactants and polymers are often both included in the flooding. Surfactants are responsible for the reduction of the IFT and the polymer is added to improve the sweep efficiency, [Flaaten et al., 2008]. The demands on surfactants are numerous and it is a great challenge to distinguish which mechanisms are most dominant. Process conditions, such as high temperature and high pressure are often the reality in reservoir environments.

1.2.2.1 Use of Anionic Surfactants

Anionic surfactants are negatively charged. They are commonly used for various industrial applications, such as detergents (alkyl benzene sulfonates), soaps (fatty acids), foaming agents (lauryl sulfate), and wetting agents (di-alkyl sulfosuccinate). Anionic surfactants are also the most

commonly used in EOR. They display good surfactant properties, such as lowering the IFT, their ability to create self-assembled structures, are relatively stable, exhibit relatively low adsorption on reservoir rock and can be manufactured economically [Green & Willhite, 1998, p. 241]. Anionic surfactants dissociate in water to form an amphiphilic anion (negatively charged) and a cation (positively charged), which would typically be an alkaline metal such as sodium (Na^+) or potassium (K^+).

Wu et al. (2005) have investigated a series of branched alcohol propoxylate sulfate surfactants for the application in EOR. Their investigations show that the number of propoxylate groups has a significant influence on the IFT, the optimal salinity and the adsorption. Optimal salinity and adsorption are shown to decrease as the number of propoxy groups is increased. In their work the experiments are conducted at diluted surfactant concentrations, both with and without co-surfactants. Examples from Wu et al. (2005)'s work is shown in figure 1.6, where the results show that the average alkyl chain length has an influence on the performance of the system:

(A)   (B)
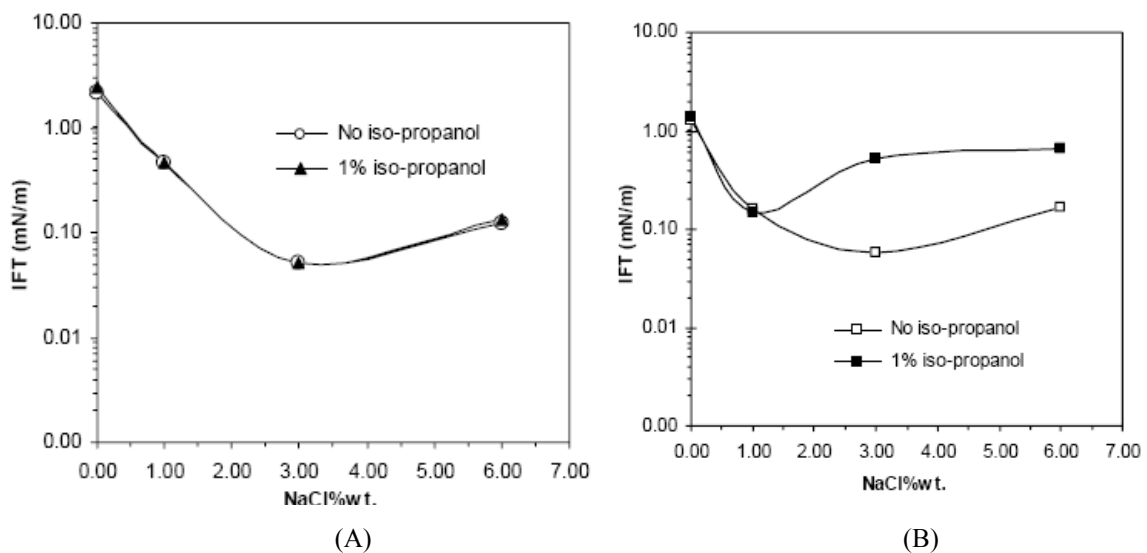
Figure 1.6. IFT versus salinity for two different alcohol propoxylate sulfate surfactant experiments. The surfactant concentration is 2wt. %. In (A): the average number of propoxy groups is 5 and the size of the branched alkyl chain is about C12. In (B): the average number of propoxy groups is 5 and the branched alkyl chain size is C14. Iso-propanol is added as co-surfactant. [Wu et al., 2005]

In figure 1.6 (A) the IFT values indicate that the optimal salinity is at 3 wt % NaCl with or without the co-surfactant iso-propanol. The effect of co-surfactants, if any, is very small. In figure 1.6 (B) the effect of co-surfactant is pronounced at salinities greater than 1 wt %, where it results in a significant increase in IFT which is undesirable.

Barnes et al. (2008) investigate families of anionic surfactants, internal olefin sulfonates, (IOS), for use in surfactant flooding at high temperatures, (up to 150 °C), and with varying optimal salinities from 1 % to 13 % depending on the carbon number range. The IOS surfactants show little sensitivity to temperature, which could be an advantage for reservoirs with temperature gradients. Overall the IOS surfactants exhibit promising over a range of reservoir conditions covering moderate to high temperatures and from low to high salinity conditions. Both alcohol propoxylate sulfates and IOS have been studied [Levitt et al., 2006 and Flaaten et al., 2008], where they are identified as promising surfactant candidates for EOR processes. These surfactant candidates are available at low cost and have been tested in different reservoir cores resulting in enhanced oil recovery and low surfactant retention, [Levitt et al., 2006]. It was found in Levitt et al. (2006)'s work that mixing the IOS and the alcohol propoxylate sulfate give the best result.

Furthermore Bryan and Kantzas (2007) have conducted an investigation of alkali surfactants for surfactant flooding of heavy oils. Their work showed that alkali surfactant flooding has a great potential for non-thermal heavy oil recovery, as the addition of alkali surfactants reduced the IFT between oil and water by such a magnitude that formation of emulsions was possible.

1.2.2.2 Use of Nonionic surfactants

Nonionic surfactants have no charged head group. They are also identified for use in EOR, [Gupta and Mohanty, 2007], mainly as co-surfactants to promote the surfactant process. Their hydrophilic group is of a non-dissociating type, not ionizing in aqueous solutions. Examples of nonionic surfactants include alcohols, phenols, ethers, esters or amides.

Curbelo et al. (2007) studied nonionic surfactants with different degree of ethoxylation to investigate the correlation with the adsorption of surfactant in porous media (sandstone). From the experiments the variations in the surface tension with surfactant concentration are shown in figure 1.7.

(A)   (B)
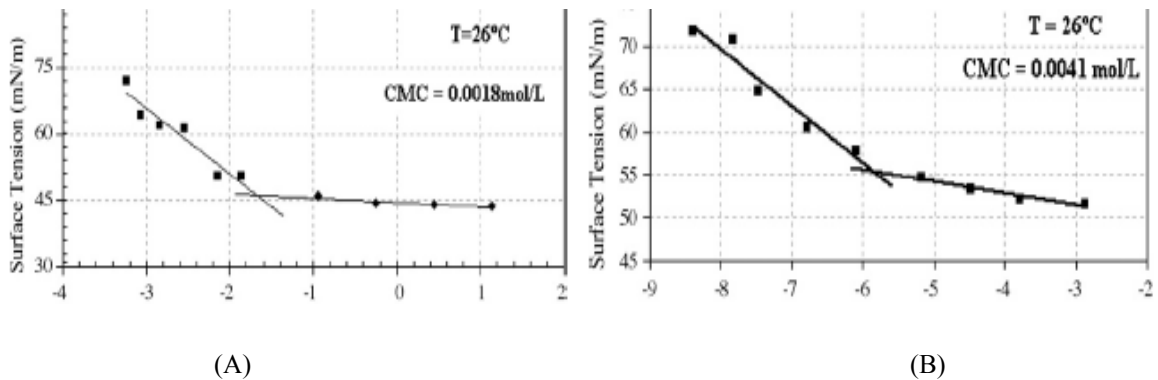
Figure 1.7. Determination of Critical Micelle Concentration (CMC) for two surfactants investigated. (A) is a surfactant with an ethoxylation degree of 9.5 and (B) is a surfactant with an ethoxylation degree of 15.0. The x-axis is the natural logarithm of the surfactant concentration. The break in both of the curves is where CMC is reached. [Curbelo et al., 2007]

Critical Micelle Concentration (CMC) is reached at a higher surfactant concentration for (B), with ethoxylation degree of 15.0, compared to (A), with ethoxylation degree at 9.5, seen in figure 1.7. With higher ethoxylation degree follows that the surfactant has a larger polar chain and consequently higher solubility towards the aqueous phase. Thus higher concentration of surfactant is required to assure formation of micelles. Curbelo et al. (2007) concluded that the adsorption to the sandstone core is higher in the case of the lower degree of ethoxylation, situation (A), which should be avoided in EOR surfactant flooding.

1.2.2.3 Use of Cationic Surfactants

Cationic surfactants have a positively charged head group. Cationic surfactants dissociate in water, forming an amphiphilic cation and anion, typically a halide (Br-, Cl- etc.). During the synthesis to produce cationic surfactants, they undergo a high pressure hydrogenation reaction, which is in general more expensive compared to anionic surfactants. As a direct consequence cationic surfactants are not as widely used as anionic and nonionic surfactants.

It is, however, reported that cationic surfactants can be used to improve the spontaneous imbibition rate of water into preferentially oil-wet carbonate. Water containing surfactants of the type alkyltrimethylammonium bromide or chloride was injected [Standnes & Austad, 2002]. The cationic surfactants are most likely dissolved in the oil phase as aggregates between the surfactant and the carboxylates, under creation of ion pairs. In this way the surface becomes more water-wet, thus the aqueous phase can better imbibe by capillary forces.

1.2.3 Single Component Surfactant Flooding

To obtain the optimal conditions for creating and maintaining the desired microemulsion phase during a surfactant flood, co-surfactants, such as low molecular alcohols as propanol and hexanol, are usually added to the surfactant solution, [Austad et al., 1996]. Chromatographic separation of the injected surfactant solution makes the operation challenging to control, as the original chemical composition in the surfactant solution will change in the reservoir and in consequence poor oil recovery may be experienced. A way to eliminate this problem is to reduce the amount of, co-surfactants, or even to omit them altogether. A few single component surfactants have been proposed in literature.

Austad et al. (1996) propose branched ethoxylated sulfonates, sulfate mixtures containing both ethoxy and propoxy groups in the same molecule, mixtures of ethoxylated and secondary alkane sulfonates and alkyl-o-xylene sulfonate. However, the ideal surfactant solution or combination will differ from one residual crude oil and reservoir to another. Austad et al. (1996) have examined the multiphase behavior of a single component alkyl-*o*-xylene sulfonate/brine/oil system at temperatures from 40 ˚C to 180 ˚C and pressures from 200 bar to 1000 bar with different crude oil, fractions of crude oil and model oil. The phase behavior observed with the increase in pressure was the same in all cases (II+ to III to II-). Regarding the increase in temperature, in the case of the crude oil the phase behavior showed II- to III to II+, while the opposite phase behavior (II+ to III to II-) was observed in the case of the model oil and the fraction of crude oil. It is suggested that the effect of temperature on the phase behavior is related to the interaction between the surfactant and the resin type material in the crude oil present at high temperatures.

Zhao et al. (2006) study IFT behavior of crude oil/single component surfactant/brine systems. Heavy alkyl benzene sulfonates have been found to be good surfactants for enhanced oil recovery in Chinese oil fields. On the basis of previous experiences Zhao et al. (2006) suggest alkyl methylnaphthalene sulfonates (AMNS) as surfactants for EOR. Different synthesized AMNS surfactants have been investigated; hexyl methylnaphthalene sulfonate, octyl methylnaphthalene sulfonate, decyl methylnaphthalene sulfonate and tetradecyl methylnaphthalene sulfonate. Zhao et al. (2006) reported that some synthesized single component surfactants of AMNS possess higher capacity and efficiency for lowering the surface tension than similar long-chain alkyl benzene sulfonates (LAS), when surfactants of the same chain length are compared. The structure of both AMNS and LAS is shown in figure 1.8.
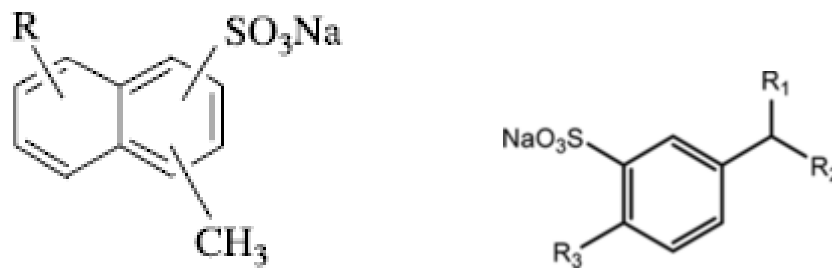
Figure 1.8. The structural formula of the alkyl methylnaphthalene sulfonates (AMNS), left, and alkyl benzene sulfonates (LAS), right.

The different AMNS were studied with respect to the IFT and the optimum salinity. It was concluded that the AMNS tetradecyl methylnaphthalene sulfonate was the most efficient in reducing the IFT. The surface tension of the crude oil/water IFT was reduced to 0.001 mN/m (ultra low) at low surfactant concentrations, 0.002 mass %, without addition of alkali or other additives. Surfactants with the longest chain length reduced IFT the most. This is in agreement with the expected behavior, as it is in general understood that IFT reduction increases with the increase in the chain length of the surfactant molecules. Zhao et al. (2006) conclude that both the chromatographic separation and the breakage of stratum are avoided effectively.

As mentioned earlier Wu et al. (2005) carried out a study with branched alcohol propoxylate sulfate surfactants and the influence of single component surfactants. They concluded that using only branched alcohol propoxylate surfactant in the formulation at low concentrations can create low IFT between brine and either *n*-octane or crude oil. The optimal salinity depended on the number of propoxy groups and decreases with an increase in propoxy groups. Adsorption experiments were carried out in this study as well. Adsorption of these surfactants on kaolinite clay decreases with an increase in the number of propoxy groups.

1.3 Microemulsions

Emulsions are colloids which are present in everyday life. Their high stability is both beneficial and challenging in for example the food industry, the production of detergents and in pesticide formulations [Sjöblom, 1996]. It is important to understand the stabilization of emulsions independent of whether they are desirable or undesirable for a process. In surfactant flooding the formation of microemulsions is essential. Water (brine) and crude oil are present as two immiscible phases together with surfactants. In microemulsions the emulsion phase is transparent, creates low IFT and a relatively low viscosity, all of which are crucial parameters in order to mobilize crude oil through the porous media.

1.3.1 Micelle Formation

At low concentrations of the dissolved surfactants, molecules are dispersed as monomers. Then as the concentration is increased, (by repeated injections in EOR), the surfactant molecules starts to aggregate and above the critical micelle concentration, (CMC), any further addition of surfactants will form into micelles. The formation from surfactants to aggregates to micelles is illustrated in figure 1.9. When the CMC is reached the concentration of surfactant monomers remains at an approximately constant level, meaning that further addition of surfactant molecules will primarily entail increased formation of micelles, [Green & Willhite, 1998, pp.242].
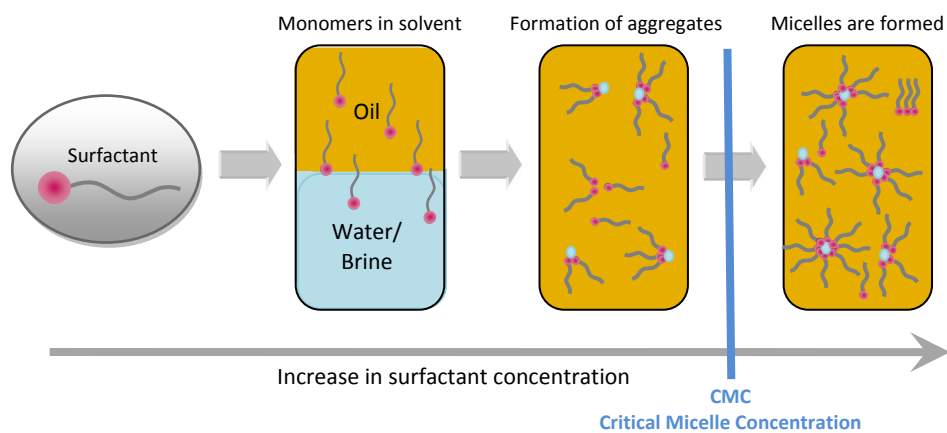
Figure 1.9. Micelle formation. The critical micelle concentration is at the blue vertical line.

The idea of surfactant flooding is based on the principles of lowering the surface energy, which is described by the Gibbs adsorption isotherm equation:

$$\Gamma_1 = -\frac{1}{2RT}\left(\frac{\partial \gamma}{\partial \ln c_1}\right) \tag{1.1}$$

Where Γ_1 is the surfactant adsorption density, R is the gas constant, T is the temperature, $\partial \gamma$ is the change in surface energy and ∂c_1 is the change in the concentration of the surfactant. The surface energy as a function of the concentration for a micelle forming surfactant follows the trend shown in figure 1.10. CMC will be reached, where $\partial \gamma / \partial \ln c_1$ is zero, marked by the vertical dotted line.
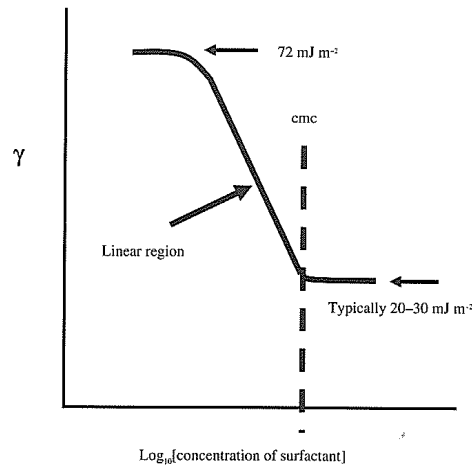
Figure 1.10. Surface energy versus concentration for a micelle forming surfactant, [Pashley and Karaman, pp. 53, 2004]. The vertical dotted line is the CMC.

The constant slope at surfactant concentrations just below the CMC value indicates that the surface energy is still decreasing, which is due to changes in the chemical potential. At the CMC a sharp transition is observed, as from CMC and at higher surfactant concentrations the slope, corresponding to $\dfrac{\partial \gamma}{\partial \ln c_1}$, is equal to zero. This observation can be explained by the fact that the surfactant monomers are forming aggregates, usually micelles, and all further addition of surfactant molecules to the solution will form aggregates. [Pashley and Karaman, 2004, pp. 52-52] The apparent solubility between oil and water are increased significantly as a function of the surfactant concentration at the CMC or above the CMC, due to the formation of micelles [Green & Willhite, 1998, pp.243].

1.3.1.1 Adsorption

Adsorption takes place when surfactant aggregates and micelles form on the surfaces. The surfactant concentration must exceed the CMC value. However, a loss of surfactants will be experienced due to adsorption and retention in the porous media in the reservoir. It is known that the adsorption isotherm is rather dependent on the type of surfactant and cosurfactant, the characteristics of the rock and the type of electrolytes present in the solution [Curbelo et al., 2007]. Adsorption starts with aggregates which are formed at the surface (e.g. rock). A monolayer begins to form and when the equilibrium monolayer adsorption has been reached, the system will form an additional layer. Multilayer adsorption can cause of significant surfactant losses, depicted in figure 1.11.
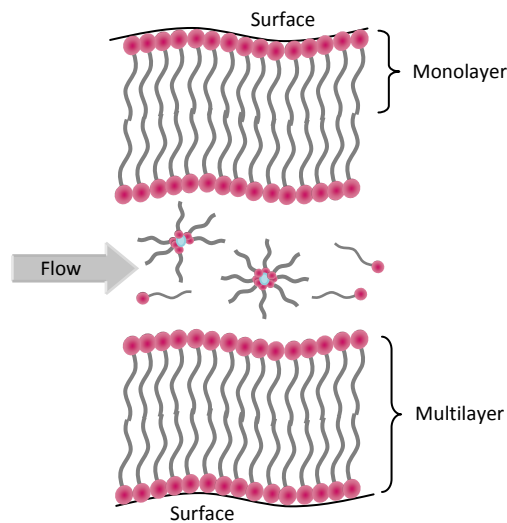
Figure 1.11. Illustration of multilayer adsorption. Initially the monolayer adsorption will take place until equilibration is reached. Subsequently the system will start forming an additional layer, thus forming multilayer adsorption.

Curbelo et al. (2007) found that the adsorption decreases with the degree of ethoxylation. In their work higher adsorption losses were experienced with surfactant molecules of lower ethoxylation degree.

1.3.2 Microemulsion Systems

Systems with two immiscible phases, such as oil and water, that are made soluble by micelles, are known as microemulsion systems. In contrast to macroemulsions systems, microemulsion systems have much larger particles and are thermodynamically stable, [Green & Willhite, 1998, pp.244]. The mechanisms in microemulsion systems are, however, not well understood and investigations and discussions are ongoing in order to ascertain their precise nature.

As oil consists of hydrocarbon molecules, which are nonpolar, they do not interact with the polar water molecules. When trying to mix water and oil it is possible to shake the mixture together to form a droplet emulsion, which will destabilize rather rapidly. Water and oil separate into two phases again, due to the high interfacial energy of the oil-water droplets. By addition of surfactants and co-surfactants the stability of these emulsions can be enhanced, as they reduce the interfacial energy. The addition of emulsifying agents, such as surface active agents (surfactants), results in either an opaque stable emulsion or a clear microemulsion. The most stable thermodynamic state for an oil-water system is phase separation, which means that oil-water emulsions are only

metastable. In contrast, microemulsion systems may be thermodynamically stable as the interfacial energy tends to zero, [Pashley and Karaman, 2004, pp. 80-81]. Microemulsion systems can be designed, such that they create ultra low IFT values, at about 0.001 mN/m, with either aqueous or hydrocarbon phases, [Green & Willhite, 1998, pp. 245], which is a property that is beneficial to EOR processes. Formation of the low interfacial energy surface is the basis of the stability of all microemulsions and most oil water emulsions, [Pashley and Karaman, 2004, pp.79].

In surfactant systems, salinity should be taken carefully into account, as this has significant influence on the phase behavior of the system. At low salinities the surfactant mixture will preferentially act as water soluble, thus forming an oil/water microemulsion as shown in figure 1.12.
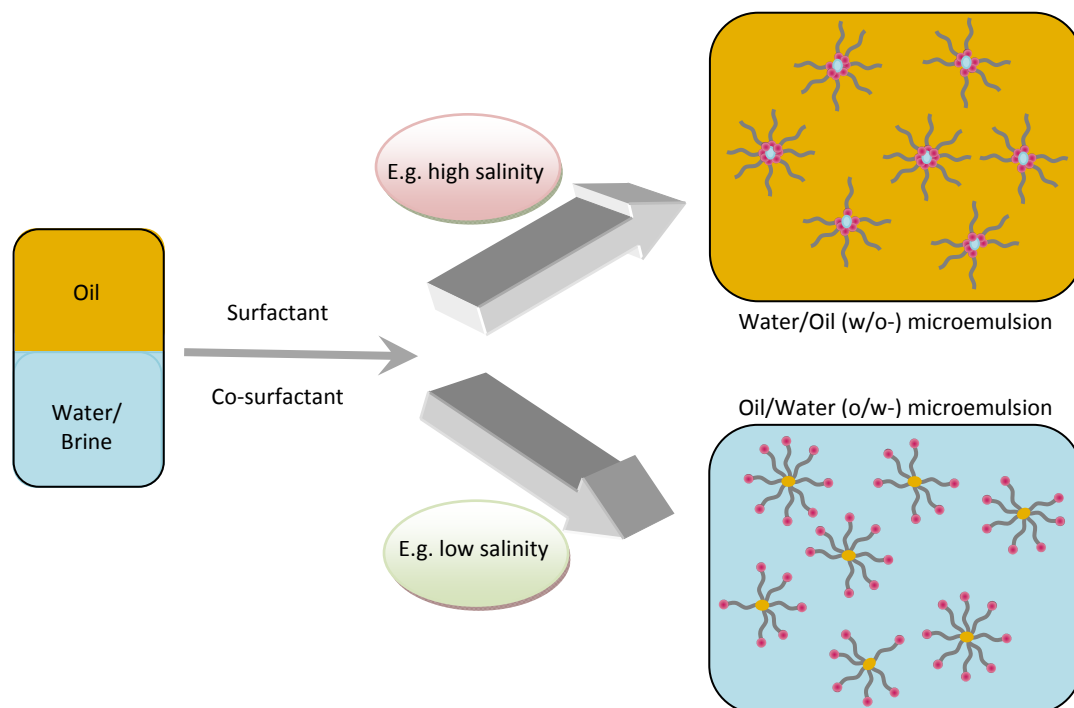
Figure 1.12. Oil and brine mixed with surfactants and co-surfactants, forming microemulsions.

An increase in the salinity will lead to different phase behavior as this will induce the surfactant system to form a three phase region at a lower critical endpoint. At the so called optimal salinity, the middle phase microemulsion solubilizes equal volumes of brine and oil. Finally the system will form a water/oil microemulsion at an upper critical endpoint as the surfactant becomes oil soluble when the salinity is high. [Raney and Miller, 1987]

1.4 Phase Behavior

The phase behavior of surfactant/oil/water mixtures is the single most critical factor determining the success of a chemical flood, [Skauge and Fotland, 1990]. The desired ultra low IFT in surfactant systems is usually measured by examining the phase behavior of the microemulsion system, where the regions with high solubilization are located. The phase behavior is dependent on the type and concentration of surfactant, the concentration of the co-surfactants, hydrocarbons and brine. Other important parameters are the effect of high temperature and pressure on the microemulsion properties (at typical reservoir conditions). Predictive models, such as equations of state, cannot describe the phase behavior of surfactant systems adequately, due to the presence of both surfactants and salts, which are not included in the available prediction tools. Therefore phase behavior of a particular system has to be measured experimentally.

1.4.1 Effect of Temperature and Pressure

It is in general understood that temperature has an impact on several important parameters for EOR processes, such as the wettability, IFT, the viscosity of the oil and imbibition rates, as well as having a profound influence on the phase behavior of surfactant/oil/water systems. Skauge and Fotland (1990) showed that an increase in temperature results in an increase in the optimal salinity. On the other hand Gupta and Mohanty (2007) showed that for most of the surfactants they tested at higher temperatures, the optimal salinity decreased or remained unchanged. These contradictory examples illustrate the complexity of surfactant systems where the phase behavior will be both component and composition dependent.

Even though the effect of pressure on the phase behavior of microemulsions has been the subject of some studies, there is no clear opinion as to when pressure has a significant effect on the phase behavior or not. Skauge and Fotland (1990) reported that an increase in pressure caused a shift in phase behavior toward a lower phase microemulsion. For experiments on secondary alkane sulfonates, it was observed that an increase in pressure leads to an increase in the optimal salinity. Skauge and Fotland (1990) reported the pressure dependence to be correlated with optimal salinity. Sassen et al. (1989, 1991, 1992) has studied several water/oil/surfactant systems with the goal of experimentally determining the influence of pressure on their phase behavior and to develop a thermodynamic model that can describe this influence. Conclusions from that work are that pressure has a considerable influence on the phase behavior of water/oil/surfactant systems for both nonionic and anionic surfactant systems.

1.4.2 Phase Equilibrium

In EOR by surfactant flooding the phase behavior and the phase equilibration between the displacing and the displaced fluids very likely will affect the recovery efficiency. Considering the phase behavior of surfactants systems, typically three types of systems are mentioned. They are depicted in figure 1.13. Winsor I systems are systems where the multiphase region has lower-phase microemulsion in equilibrium with excess of oil. The Winsor II systems are upper-phase microemulsions in equilibrium with excess of water or brine. Winsor III systems exhibit a middle phase microemulsion.
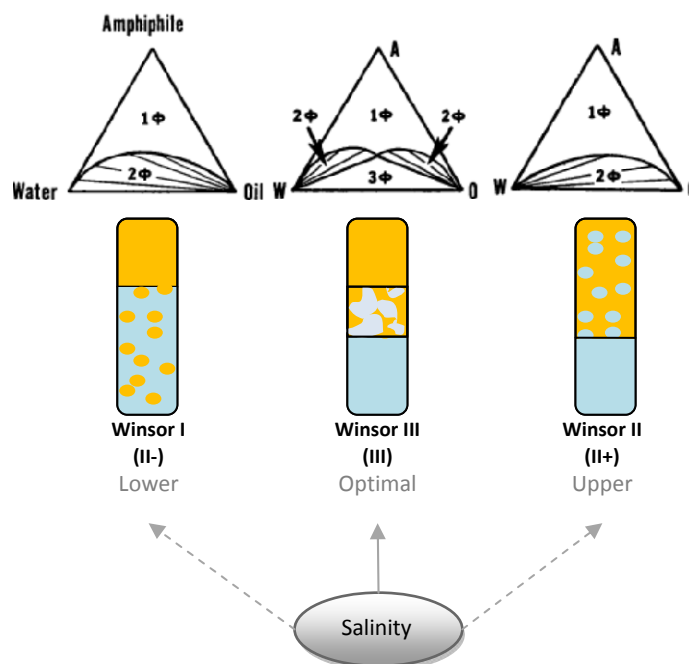
Figure 1.13. Ternary diagram types for surfactant/water/oil systems, [Salager et al., 1979]. Winsor type system; Winsor I is multiphase region with lower phase microemulsion in equilibrium with excess of oil, Winsor II, is the multiphase region with upper phase microemulsion in equilibrium with excess of water (or brine) and Winsor III, is the middle phase microemulsion at which the lowest IFT is observed between oil and water. As showed, optimal salinity is at the Winsor III system, where low or high salinity entails lower or upper phase microemulsions, respectively.

Figure 1.13 shows how a surfactant/water/oil system, in any of the three represented phase environments, can equilibrate as either a single phase or as multiple phases, depending on the overall composition. The Winsor I and II systems have the possibility of a maximum of two equilibrium phases. The Winsor III system has a maximum of three equilibrium phases, where this phase equilibrium system also contains both a type I node and type II node.

1.5 Modeling Surfactant Systems

No thermodynamic model is currently capable of correctly describing the phase behavior of surfactant systems. Based on the literature and the results, which are presented in this work, it would be useful to be able predict the phase behavior of surfactant systems (oil/water/surfactant) from equation of state (EoS) with accurate predictions of the influence of temperature and pressure. The model should ideally account for the presence of all components and all the possible phase behaviors including e.g. the formation of aggregates and microemulsions.

Sassen (1989) suggested an approach for describing the influence of pressure on the phase behavior on surfactant systems, using a modified Huron-Vidal model, where the pressure effect and the remaining interactions are separately taking care of by an EoS and by an excess Gibbs energy model, respectively. However, Sassen (1989) notes that due to the formation of aggregates and micelles in surfactant solutions, the Gibbs energy model must also account for these structured formations, which is challenging, as such models are not available in literature.

In Knudsen et al. (1993) an attempt was made to correlate the influence of pressure on the phase behavior of oil/water/surfactant containing systems. It is stated that experimental data from the binary subsystems are required to enable prediction of the ternary system. The experimental data for the binary subsystems are needed in order to estimate binary parameters used in the thermodynamic model.

The simplified Perturbed-Chain form of the Statistical Association Fluid Theory (sPC-SAFT) EOS, proposed by von Solms et al. (2003), has been applied in this work to carry out a phase equilibrium modeling study with the ultimate goal of applying the model to surfactant-containing systems.

1.6 Phase Behavior without Surfactants

A statement that most agree on is that oil and water (brine) do not mix. The precise interactions between oil and water are, however, poorly understood. Alongside development of understanding of surfactant flooding there is a need to increase understanding of interactions in oil/ water (brine) systems. Just as for the surfactant systems, oil/ water systems are very sensitive to the composition of the brine, the characterization of the crude oil, the rock inside the reservoir as well as temperature and pressure. Even in waterflooding this has gained interest as more detailed knowledge may contribute to more efficient oil recovery. To understand oil/ water interactions, an advanced study has been carried out and is reported in this thesis.

1.6.1 Effects of Ions in Sulfate-Rich Brine Solutions

The major focus of the research reported has been core flow and imbibition experiments. Bagci et al. (2001) studied the effect of brine composition on oil recovery by waterflooding. Different brine composition injections were tested; solutions of NaCl, KCl, $CaCl_2$ as well as mixed brines (2 wt% KCl + 2 wt% NaCl and 2 wt% KCl + 5 wt% $CaCl_2$). The highest oil recovery was observed for 2 wt% KCl brine. Extensive laboratory research was carried out by Austad and coworkers in order to understand improved oil recovery from chalk using modified sea water [Strand et al. 2006, Austad et al. 2005]. It was reported that SO_4^{2-} is a potential determining ion, in the sense as this particular ion and the amount of SO_4^{2-} was directly related to their observations, for improving oil recovery in chalk reservoirs. This ion must act together with Ca^{2+} and Mg^{2+} because sulfate alone is not able to increase spontaneous imbibition. In all the cases presented, wettability alteration was proposed as the reason for improved oil recovery.

1.7 Objectives

The main objective in this project was clarifying how the phase behavior of surfactant systems is influenced by temperature and pressure with the application to EOR in mind. The Ph.D.-project is mainly an experimental project concerning the understanding of fluid-fluid interactions in EOR. An experimental set up has been prepared, capable of carrying out phase equilibrium experiments at different temperatures and pressures. (Chapter 2).

The experimental set up has been used to carry out high pressure phase equilibrium experiments with an oil/ water/ surfactant model system, determining the phase behavior of the system at varying pressures. (Chapter 3.1 and appendix A)

As the apparatus was found appropriate for the study of oil/ water interactions, experimental work for this system was carried out as well, with the goal of measuring phase equilibrium at elevated temperatures and pressures. The oil/ brine study also includes a number of other analyses carried out after the high pressure operation to determine whether the compositions changed in either oil or water, e.g. viscosity of the oil before and after, pH value of brine, etc. (Chapter 3.2 and appendix B and C).

The results from the experiments with the two types of systems (oil/ water/ surfactant and oil/ brine) were analyzed with regards to their phase behavior of the liquid-liquid systems and carefully compared to relevant statements found in literature. (Chapter 3). The major results and conclusions are presented here in the thesis, as well as the relevant background and developments which are important in order to present a coherent picture of the work performed and its context. The results

have been presented in 3 articles (appendix A, appendix B and appendix C) and have been presented on conferences.

In addition to the experimental work, a modeling study of liquid-liquid systems of alkanes/ water/ alcohols/surfactants was initiated. The goal here was to establish that the equation of state model could describe phase behavior in simpler systems which are relevant to surfactant systems. This could then provide a basis for a complete model, predicting the phase behavior of surfactant systems. (Chapter 4).

1.8 Publications

Zahid, A., Sandersen, S.B., Stenby, E.H., von Solms, N., Shapiro, A., "Advanced Waterflooding in Chalk Reservoirs: Understanding of Underlying Mechanisms", Colloids and Surfaces A: Physicochemical and Engineering Aspects, 389 (1-3), 281-290, 2011

Sandersen, S.B., Zahid, A., Stenby, E.H., von Solms, N., Shapiro, A., "Mechanisms of Advanced Waterflooding in Chalk Reservoirs : Role of Seawater-Crude Oil Interactions", 2012 *(Submitted February 2012)*

Sandersen, .S.B, Stenby, E.H, von Solms, N., "The Effect of Pressure on the Phase Behavior of Surfactant Systems: An Experimental Study", 2012 *(Submitted April 2012)*

2 High Pressure Equipment for Phase Behavior Studies

It is of great importance to consider the effect of an increase in both temperature and pressure on the phase behavior inside an oil reservoir. In EOR processes, such as waterflooding and surfactant flooding, it can be devastating for the entire oil recovery if the phase behavior at reservoir conditions deviates significantly from the expected phase behavior, which could very well be known only at ambient conditions. Reservoir conditions (increased pressure and temperature among others) may change the interaction between the injected fluids in the EOR processes and it can change the optimal composition, which in the case of surfactant flooding, will influence the microemulsion properties of the system. In this work a high pressure cell, a so-called DBR JEFRI PVT cell is introduced and used to measure phase volumes in surfactant/ oil/ water/ brine systems.

2.1 High Pressure Cell

Phase equilibrium studies are carried out in a high pressure cell to examine the influence of pressure and temperature on the phase behavior of systems displaying liquid-liquid equilibrium, with up to three liquid phases. A DBR JEFRI PVT cell (model: JEFRI PVT 150-155 from DB Robinson) is used in the experimental work, illustrated in figure 2.1.
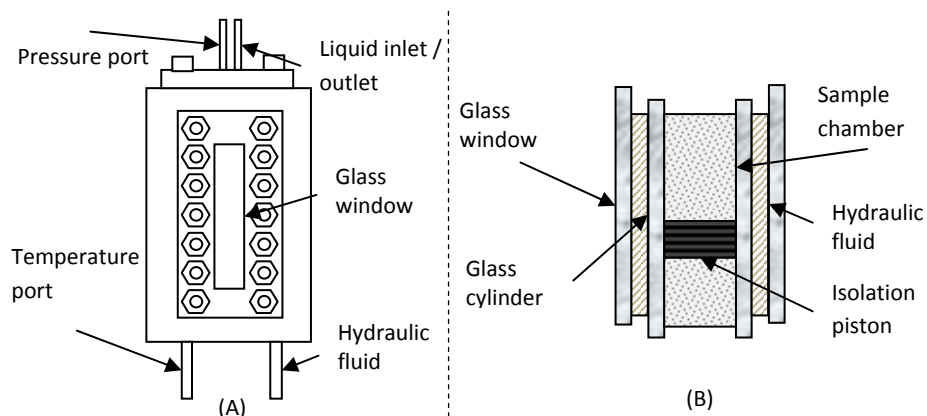

Figure 2.1. The experimental set up of the DBR JEFRI PVT cell. (A) is the cell from the outside, where the observation window, inlet/outlet and temperature and pressure ports are shown. (B) illustrates the cell from the inside, where the sample chamber, isolation piston and the surrounding hydraulic fluid is shown.

The DBR JEFRI PVT cell allows measurement and control of temperature and pressure in the range from 40 ˚C to 180 ˚C and from 1 bar to 700 bar, respectively. The DBR JEFRI PVT cell has been used in a variety of applications, such as solubilities of supercritical fluids, vapor-liquid-equilibrium (VLE) studies with gas condensates mixed with brine and other conventional PVT analysis of gas condensates and black oils [Staby et al. (1993), Pedersen et al. (2004)].

The DBR JEFRI PVT cell consists of a glass cylinder appropriate for high pressures and temperatures. The cylinder is 20.3 cm long and has an internal diameter of 3.2 cm, giving a total working volume of 163 cm^3 inside the chamber. Not all of the working volume is used, since there should be room for expansion and compression of the sample. The glass cylinder is covered by a steel shell with vertical glass plates, enabling observation of the system inside the glass cylinder. The pressure in the sample chamber is controlled with an ISCO displacement pump via a floating isolation piston. The whole PVT cell is attached to a rocking mechanism inside a temperature-controlled forced-air oven. The purpose of the rocking mechanism is to ensure thorough mixing inside the glass cylinder. The temperature is measured with an accuracy of ±0.3 ˚C with a PC100 thermocouple.

2.2 Micro Meter Tool

Through the observation window in the DBR JEFRI PVT cell the evolution of the phase equilibrium can be closely monitored as a function of temperature and pressure. When the system attains equilibrium, the heights of the phases inside the PVT cell are measured with a micrometer (model: Precision Tools & Instruments Co. LTD., Surrey, England). From the phase heights and the known internal diameter, the phase volumes are calculated.

2.3 Measurements at High Pressure

Measurement at high pressure phase equilibria (with multiple liquid phases) can be carried out in many different ways. Especially in the field of EOR there is a need for experimental data in order to develop accurate simulations of the reservoirs. Thorough understanding of both the chemical and the physical processes, which occur in the reservoir, is essential to achieve efficient (or even optimal) recovery operations. At high pressures the deviation from ideal behavior becomes very significant and thereby accurate predictions of the phase behavior are much more difficult than at ambient pressures. The complex nature and composition of crude oils makes accurate modeling even more challenging. In the review papers by Dohrn et al. (2010) and Fonseca et al. (2011) different classifications of the experimental high pressure methods are mentioned. The two main classifications of high pressure phase equilibria are the so-called analytical method (overall mixture composition is not precisely known, composition of phases is analyzed) and the synthetic method

(overall mixture composition is precisely known). One of the advantages of using an analytical approach is that several components can be present in the experimental work without significant complication in the analysis. However, the compositional analysis is carried out by sampling and will then take place at ambient pressures outside the high pressure cell or by physicochemical methods at the system pressure (for example by spectroscopic methods). The synthetic approach is most suitable when the system is limited to two components, as compositional analysis is not performed when using this method. Analyzing multicomponent systems requires that additional measurements are performed after the phase equilibrium experiments. The synthetic method can allow experiments to be performed at both high pressures and high temperatures.

In this work the DBR JEFRI PVT cell is charged with fluid systems of different components and a known overall composition, which displays multiple liquid equilibriums. The methods employed correspond to the synthetic method type, according to the classification of Dohrn et al. (2010). Visual observations are carried out, knowing the overall composition, temperature and pressure and measuring the volume of all phases. In spite of the fact that the floating isolating piston can maintain the pressure in the cell, sampling from the cell is not performed, as this would change the overall composition of the system. The observed phase behavior would then not correlate with the original overall composition. As mentioned for the synthetic method, multicomponent systems require further analysis in order to yield compositional information about the individual phases (for example to determine phase boundaries and tie-lines for the system). These analyses were not performed in for the surfactant systems studied. For the oil/ brine systems studied several additional analysis was carried out to characterize, specially, the oil phase before and after operated in the PVT cell, which is described in the following chapter, section 3.2.

2.4 Application of DBR JEFRI PVT cell

The DBR JEFRI PVT cell was used in two types of experimental study; one with a model surfactant system (heptane/sodium dodecyl sulfate (SDS)/1-butanol/water/sodium chloride) and one with crude oils and different seawater solutions. In both studies the aim was to examine the phase behavior of the liquid-liquid equilibrium systems at elevated temperatures and pressures.

The general approach for the DBR JEFRI PVT cell, in this work, is that a specific amount of sample fluid is filled into the sample chamber. Temperature and pressure are then set. It takes approximately 12-24 hours to heat up the cell, depending on the desired temperature. After reaching the desired temperature the rocking mechanism is activated for 30 minutes to thoroughly mix the fluid in the PVT cell. When mixing is completed the system is left to equilibrate. This lasts from 30 minutes up to 2 hours, depending on the system in the cell and the temperature and

pressure conditions. It was found that higher temperature and pressure led to faster equilibration. The progress of the phase separation was closely monitored during equilibration. After equilibration of the system, the heights of the phases in the sample chamber were measured through the observation window. A micrometer provided from 'Precision Tools & Instruments Co. LTD., Surrey, England' was used for these measurements. From the volume height and the known internal diameter of the sample chamber, the phase volume is calculated. The interaction between the oil phases and water phases was in all cases examined carefully through the observation window, to determine (for example) whether emulsion phases were formed or had vanished, compared to the system's original phase behavior at ambient conditions. Any other changes, regarding the phases present, such as clarity, transparency and color changes, were also noted (due to the change in temperature and pressure). The overall specifications for the two types of systems operated in the high pressure cell are given in table 2.1.

Table 2.1. Specifications of the two systems studied in the DBR JEFRI PVT cell.

Type of system	Surfactant model system	Crude oil & seawater system
Components	heptane/SDS/1-butanol/brine	Crude oil/brine solution*
Sample volume	60 ml to 80 ml	50 ml
Temperature range	40 ˚C to 60 ˚C	37 ˚C to 110 ˚C
Pressure range	1 bar to 400 bar	15 bar to 300 bar
Compositions**	SAR = 0.5; WOR = not constant	WOR = 30 / 70

*The properties of the crude oils and the ions used for the brine solutions are from Paper II in appendix B, table 1 and table 2 and they are both reproduced below in chapter 3.2, table 3.2 and 3.3.

**SAR = surfactant alcohol ratio; WOR = water oil ratio; The exact weight fractions of the surfactant system is from Paper I in appendix A, table 1, 2 and 3 and they are reproduced below in chapter 3.1 as table 3.1.

Chapter 3

3 Influence of Pressure on Phase Behavior

In this chapter the experimental work carried out in this Ph.D. is presented. Most of the findings in this work have been submitted for publications and therefore many of the results from the experimental work are presented in either submitted paper manuscripts or in accepted papers. The paper manuscripts are all presented in appendix A: Paper I, appendix B: Paper II and appendix C: Paper III. The major results and conclusions are presented here in the thesis, as well as the relevant background and developments which are important in order to present a coherent picture of the work performed and its context.

3.1 Influence of Pressure on the Phase Behavior of Water/ NaCl/ Heptane/ SDS/ 1-Butanol Systems

This part of the chapter is regarding the phase behavior study of the surfactant system; water/ NaCl/ heptane/ 1-butanol/ SDS, referred to as the surfactant model system. The results from this work have contributed to one paper manuscript which will be submitted in the spring 2012, appendix A: Paper I.

3.1.1 Introduction

Typically in studies of surfactant flooding, mixtures are composed of water/ salt/ oil/ alcohol/ surfactant. Several phase behavior studies of such systems has been carried out, [van Nieuwkoop and Snoei (1985), Sassen et al. (1989), Sassen et al. (1991), Sassen et al. (1992), Kahlweit (1988), Bellocq et al. (1984)]. It varies whether the influence of temperature and pressure is included or not.

One surfactant model system is investigated in this Ph.D., with an anionic surfactant; specifically the surfactant model system of water/ NaCl/ heptane / SDS/ 1-butanol is used. Experiments have been carried out in a high pressure DBR JEFRI PVT cell. Primarily the aim has been ascertaining the influence of pressure on the phase behavior and furthermore to get an improved understanding of the influencing mechanisms for the surfactant model system. This surfactant model system has earlier been studied thoroughly by van Nieuwkoop and Snoei (1985), operated at ambient

temperatures and pressures with composition analysis. They obtained an observation pseudo ternary phase diagram showing a three phase region (Winsor type III), sandwiched between two different two phase regions (Winsor type II- and Winsor type II+), where they show that presence of this three phase region is correlated to the concentration of NaCl. The ternary phase diagram is shown in figure 3.1.
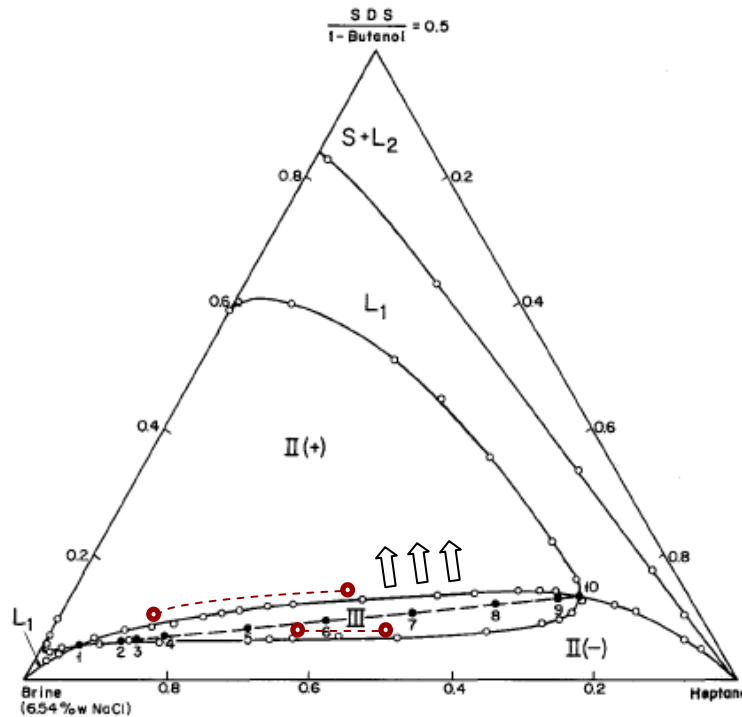
Figure 3.1. Pseudo ternary observation phase diagram of the system water/ NaCl/ heptane/ 1-butanol/ SDS, composed from the observations from the work conducted by van Nieuwkoop and Snoei (1985). The red bold circles mark the compositions at which the system has been operated in the DBR JEFRI PVT cell in this work. Significant change in the phase behavior was observed. The red dashed lines are drawn to illustrate the impact on the phase behavior due to increase in pressure.

Sassen et al. (1989) has also carried out an investigation of the influence of pressure and electrolyte on the phase behavior of the surfactant model system. According to their work, pressure had considerable influence on the phase behavior, when examining the model system at constant SAR and WOR with different salinities. In this present Ph.D.-project the surfactant model system has been further examined at varying WOR, constant SAR and constant salinity throughout all experiments.

As the opinions from literature regarding pressure influence on the phase behavior of surfactant systems are diverse, this study is initially carried out to ascertain if a significant effect from elevated pressure on the multiphase region is observable. The model system was studied at different overall compositions and at different temperatures and pressures.

3.1.2 Experimental Procedure

All high pressure phase behavior experiments were carried out on the DBR JEFRI PVT cell at temperatures from 40 ˚C to 60 ˚C and at pressures from 1 bar to 400 bar. Preliminary some simple phase behavior tests were carried out in glass tubes at atmospheric pressure and at room temperature on the surfactant model system, to assure the phase behavior at ambient conditions and to confirm that they were in agreement with the expectations from van Nieuwkoop and Snoei (1985). The PVT cell was loaded with a chosen composition of the surfactant model system, where the initial conditions at all times were 1 bar and temperature at 40 ˚C. Whenever the entire system in PVT cell has reached the chosen temperature, the rocking mechanism was activated to mix the surfactant system thoroughly and thereafter the system was left to equilibrate, where the system separated into either two or three phases. As the equipment allowed visual observations the phase volumes were measured. Further increase in pressure or both pressure and temperature was applied to the system and measurements of the phase volumes were carried out.

The mixtures used in all experiments were prepared with the overall compositions, given in table 3.1.

Table 3.1. Overview of the overall compositions of the surfactant model systems studied at the DBR JEFRI PVT cell. SAR is constant at 0.5, salinity is constant at 6.56 wt % and WOR is varied.

Compositions in weight fractions				
Sample	Water	SDS	1-Butanol	Heptane	NaCl
1	0.6156	0.0254	0.0509	0.2649	0.0432
2	0.5848	0.0242	0.0483	0.3016	0.0411
3	0.5570	0.0230	0.0460	0.3348	0.0391
4	0.5317	0.0220	0.0439	0.3651	0.0373

Note: Sample 1-4 was operated at different pressures from 1-400 bar and at different temperatures from 40-60°C.

Compositions in weight fractions				
Sample	Water	SDS	1-Butanol	Heptane	NaCl
5	0.7710	0.0300	0.0600	0.0850	0.0540
6	0.7396	0.0288	0.0576	0.1223	0.0518
7	0.7106	0.0276	0.0553	0.1567	0.0497
8	0.6590	0.0256	0.0513	0.2179	0.0461
9	0.6359	0.0247	0.0495	0.2804	0.0445

Note: Sample 5-9 was operated at different pressures from 1-400 bar to study the general phase behavior near the three phase area in the surfactant system.

Compositions in weight fractions				
Sample	Water	SDS	1-Butanol	Heptane	NaCl
10	0.6517	0.0359	0.0713	0.1953	0.0457
11	0.6211	0.0342	0.0680	0.2331	0.0436
12	0.6070	0.0334	0.0665	0.2504	0.0426
13	0.4687	0.0258	0.0513	0.4213	0.0329
14	0.4225	0.0233	0.0463	0.4783	0.0297
15	0.4406	0.0436	0.0888	0.3958	0.0313

Note: Sample 10-15 was operated at different pressures from 1-400 bar to study the general phase behavior above, inside and below the three phase area in the surfactant system.

3.1.3 Results

Phase volumes of the surfactant model system at elevated pressures and temperatures have been measured. Initially, experiments were carried out at room temperature to assure that the observations were in agreement with the observations obtained by van Nieuwkoop and Snoei (1985).

In a series of 15 different samples, with different compositions, the phase behavior is studied for the influence of increase in pressure and to some extend the increase in temperature as well. The results of the measured phase volumes are presented as the calculated phase volume fractions for

each phase as a function of pressure for various cases, featuring different overall compositions and temperatures. Among the 15 samples that have been studied, especially the observations of sample 4, 7, 14 and 15 stand out. The remaining results are presented in paper 1, appendix A, where the results for all 15 samples are discussed in details. Sample 4, 7, 14 and 15, all showed phase behavior with change in the number of phases present depending on the pressure. An overview of the change in number of phases is shown in table 3.2.

Table 3.2. Samples that showed most significant change in the phase behavior due to the increase in pressure. The red circles in figure 3.1 correspond to one of the four samples presented in this table.

Sample number	Shift in phases	Temperature [˚C]	Initial pressure [bar]	Pressure at phase shift [bar]
4	III → II-	40	1	160
7	II+ → III	40	1	100-200
14	III → II-	40	1	156
15	II+ →III	40	1	302

For compositions where the system, has three liquid phases present at ambient temperatures and pressures, increasing the pressure changes the system to a two phase system (II-) with an oil phase and an emulsion phase in excess of water. Furthermore for compositions where two phases are initially present (II+) with an emulsion phase in excess of oil and a lower water phase, increasing pressure changes the system to a three phase system (III) where the microemulsion phase appears, sandwiched between the oil phase on top and the water phase below. The denominator for these observations is that the phase behavior and the number of phases depend on an increase in pressure. Figure 3.2 shows calculated phase volume fractions for each phase as a function of pressure for the case of sample 4, 7, 14 and 15.
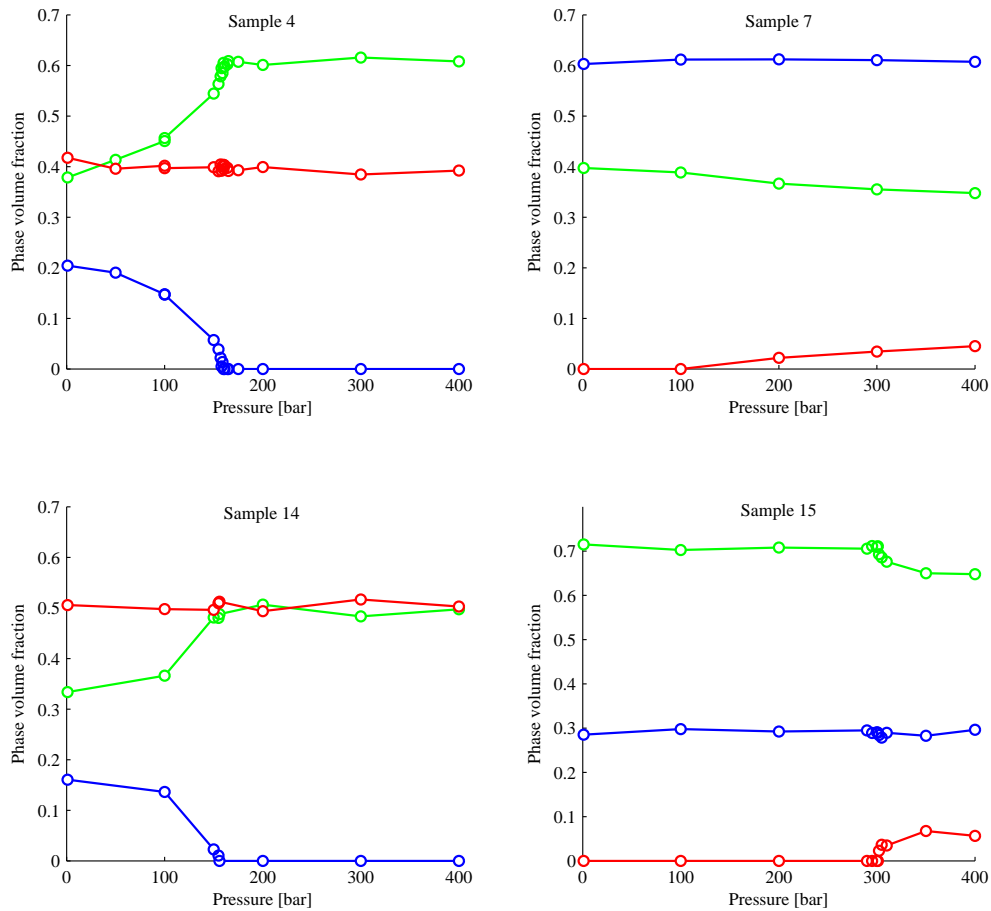
Figure 3.2. Calculated phase volume fractions calculated from the phase volume measurements obtained from the DBR JEFRI PVT cell at the temperature of 40 ˚C. Sample 4 and 14 shows examples of the water phase that disappears with the increase in pressure. Sample 7 and 15 shows examples of the oil phase rising due to increased pressure. Blue lines are water phase volume fractions, red lines are oil volume fractions and green lines are the microemulsions phase volume fractions.

Considering the phase volume fractions regarding sample 4, it is clearly seen that the increase in pressure has a significant influence on the phase behavior. The volume of the water phase decreases to zero very dramatically at 156 bar. Furthermore it is noticed that the phase volume of the oil phase remains constant, where the decrease in the phase volume of the water phase is directly correlated to an increase in the volume of the emulsion phase.

The phase behavior observed for sample 14 is similar to the observations for sample 4. Again the water phase vanishes from the system at around 150 bar and the decrease in the water phase volume is correlated with an increase in the emulsion phase volume.

In the case of sample 7 in figure 3.2, the oil phase appears between 100 bar and 200 bar as the increase of pressure is applied to the system. A slight decrease in the volume of the emulsion phase

is observed as the oil phase begins to increase in volume. This time the volume of the water phase remains constant.

Sample 15 goes through the same transformation, from two phases to three phases, as it is the case for sample 7. However, the significance of the influence of pressure is not present until pressure reaches 300 bar, which is higher than the 100 bar to 200 bar, which was sufficient to cause changes in the case of sample 7. This has to be explained from the fact, that sample 7 and 15 does not feature the same overall composition and also emphasizes that the composition can be crucial to the sensitivity of the influence on phase behavior of the surfactant system.

Along with the pressure influence on the phase behavior a minor study in the influence of the increased temperature was carried out as well. The change in number of phases and the phase volumes becomes more significant when the temperature is increased together with the increased pressure.

3.1.4 Discussion and Conclusions

From the experimental work carried out on the surfactant model system it is seen that pressure has an influence on the phase behavior. With the work of Sassen et al. (1989) in mind this was also expected. Experiments are carried out with constant salinity. From the experiments in the DBR JEFRI PVT cell the phase behavior changes significantly dependent on the pressure. The number of phases changed from Winsor II (two phase region) to Winsor III (three phase region) or from Winsor III (three phase region) to Winsor I (two phase region) dependent on the composition of the surfactant systems and the applied increase in pressure. Also the results induces that the increase in temperature enhances the effect and influence on the phase behavior becomes much more pronounced and significant, as the combined increase in both pressure and temperature resulted in a shift in the number of equilibrium phases at significantly lower pressures compared to the study with no increase in temperature.

As shown in figure 3.1 the location of the three phase envelope presented in the pseudo ternary phase diagram is displaced upwards due to the influence from increase in pressure. It is within this area, that the desired microemulsion phase is present, which is essential in order to lower the IFT and thus mobilizing the trapped crude oil. The results obtained in this work induces that the width of the three phase envelope remains unchanged and the influence of pressure thereby only shifts the three phase area, without changing the shape or volume of the three phase area.

This work clearly shows that the effect of pressure on the phase behavior of the surfactant system is profound.

3.2 Influence of Pressure on the Phase Behavior of Oil/ Seawater Systems

This second part of chapter 3 is regarding the phase behavior study of crude oil/ seawater systems. The study covers a broad range of measurements to study the exact interaction mechanisms of different crude oil/ seawater systems. The results from this work have contributed to two paper manuscripts. One has been accepted in August 2011 in Colloids and Surfaces A: Physicochemical and Engineering Aspects, [appendix B: Paper II: 'Advanced waterflooding in chalk reservoirs: Understanding the underlying mechanisms']. The second paper manuscript has been submitted to Colloids and Surfaces A: Physicochemical and Engineering Aspects in February 2012, [appendix C: Paper III: 'Mechanisms of advanced waterflooding in chalk reservoirs: Role of seawater-crude oil interactions'].

The experimental work and the paper manuscripts have been carried out in a fruitful collaboration with Adeel Zahid, with even contribution from all parties.

3.2.1 Introduction

A successful approach to improve the oil recovery from chalk reservoirs is the injection of brine with high salinity [e.g. Webb et al. (2005), Karoussi et al. (2007), Fjelde et al. (2009), Strand et al. (2006), etc.]. It is in general accepted that the high salinity may be responsible for the improved oil recovery for this type of reservoirs. However, the understanding of the dominating mechanisms in this advanced waterflooding process is poorly understood. The effect of the brine composition has been studied by several, e.g. Bagci et al. (2001) and Austad and co-workers (2005, 2006, 2007, 2009), where the major focus has been at core flow and imbibition experiments using modified seawater. Wettability alteration was suggested as the reason for the improved oil recovery in all studies. A number of studies documents that Ca^{2+}, SO_4^{2-} and Mg^{2+} are potential determining ions and the effect are pronounced with the increase in temperature. That the surface forces must be accounted for in oil production is well established, but so far this has not been in focus in the conducted studies. The experimental work available in literature, mentioned above, is mainly carried out using crude oil/ brine/ rock or brine/ rock systems. It is concluded from the work that it is the affinity of the potential determining ions for the chalk surface which increases with temperature and helps to improve the oil recovery. However, the conclusion has not yet been confirmed by studies of the oil/ brine interactions. Better understanding of the interactions between crude oil and brine (synthetic seawater) will make it possible to design more optimal brine solutions in order to improve the oil recovery.

The main focus in this experimental work has been to study the interaction between different crude oils contacted with different synthetic seawater solutions in both simple glass tubes at ambient temperature and atmospheric pressure and in the high pressure DBR JEFRI PVT cell at elevated pressures and temperatures. This work covers detailed observations of the phase behavior of the oil/ brine systems and measurements of density, viscosity, IFT, GC, SARA (Saturates, Aromatics, Resins and Asphaltenes) and water content of the oils are examined. A study of systems with heptane and different synthetic seawater solutions are also carried out.

3.2.2 Experimental Procedure

Three natural crude oils were used in this work; a North Sea crude oil, a Latin American crude oil and a Middle East crude oil. One model oil was also introduced; heptane. The crude oil properties are given in table 3.3.

Table 3.3. Crude oil properties.

Crude Oil	Density @ 20 °C [g/cm^3]	Acid Number [mg KOH/g oil]	Base Number [mg KOH/g oil]	Asphaltene [%]	Viscosity [cp]
Latin America	0.846	0.163	0.563	3.43	24.4
North Sea	0.847	0.095	2.442	0.302	8.837
Middle East	0.844	0.093	0.644	1.093	10.538

Different synthetic seawater brine solutions were prepared by mixing NaCl, NaHCO$_3$, KCl, MgCl$_2$·6H$_2$O, CaCl$_2$·2H$_2$O and Na$_2$SO$_4$. Seven brine solutions with different sulfate concentrations were prepared. The brine solutions are named SWXS. SW refers to synthetic seawater solution and XS refers to the sulfate concentration. One brine solution, with normal seawater sulfate concentration, was named SW and the XS notation thereafter is relatively to the sulfate concentration in the SW brine solution. SW0S, SW½S, SW, SW1½S, SW2S, SW2½S and SW3S were prepared. Table 3.4 shows the different brine compositions of the synthetic seawater solutions.

Table 3.4. Ion composition of the various synthetic seawater brine solutions.

Component	SW0S [mol/l]	SW0.5S [mol/l]	SW [mol/l]	SW1.5S [mol/l]	SW2S [mol/l]	SW2.5S [mol/l]	SW3S [mol/l]
Na^+	0.368	0.363	0.358	0.353	0.348	0.343	0.337
K^+	0.010	0.010	0.010	0.010	0.010	0.010	0.010
Mg^{2+}	0.045	0.045	0.045	0.045	0.045	0.045	0.045
Ca^{2+}	0.013	0.013	0.013	0.013	0.013	0.013	0.013
Cl^-	0.492	0.463	0.434	0.405	0.376	0.347	0.317
HCO_3^-	0.002	0.002	0.002	0.002	0.002	0.002	0.002
SO_4^{2-}	0.000	0.012	0.024	0.036	0.048	0.060	0.072
TDS [g/l]	33.39	33.39	33.39	33.39	33.39	33.39	33.39

Preliminary the three crude oils and heptane were studied in simple phase behavior experiments, carried out at ambient temperature and pressures in small glass tubes with different brine solutions. The water-oil ratio, (WOR), was 80/20 and the total sample volume were 10 ml. Five different brine solutions were contacted with the three crude oils. Visual observations of the phase behavior were carried out and after the separation of crude oil and water, the density and viscosity of the crude oil were measured.

All high pressure phase behavior experiments were carried out on the DBR JEFRI PVT cell at the conditions: (a) 37 ˚C, 15 bar; (b) 37 ˚C, 300 bar; (c) 110 ˚C, 15 bar; (d) 110 ˚C, 300 bar. Three oils were operated in the PVT cell. Two crude oils, the Latin American crude oil and the Middle East crude oil, and also the model oil, heptane. All three oils were contacted with the seven different brine solutions. As the equipment allowed visual observations the phase volumes were measured after phase equilibration, whenever changes in either pressure or temperature were applied to the system. The equilibration period was recorded with a video camera. On a volume basis the WOR is kept constant in all experiments at 70/30 with a total sample volume of 50 ml. Table 3.5 tabulates the range of experimental analysis that this work covers.

Table 3.5 Overview of the measurements carried out. All measurements listed are carried out at ambient conditions; room temperature and at atmospheric pressure.

Analysis	Method/ Tool	Measured sample
Viscosity	AMV-200 Automated Microviscometer	All oils before and after high pressure cell.
Water content in crude oil	Coulometric Karl Fisher titration method	The Latin American crude oil and the Middle East crude oil before and after high pressure cell.
Interfacial tension	Pendant drop method with a Data Physics OCA20 pendant drop apparatus.	The Latin American crude oil
SARA (Saturates, Aromatics, Resins, Asphaltenes)	Chromatography by gravity	The Latin American crude oil and the Middle East crude oil
GC	Agilent 7890A using ASTM method D6352	The Latin American crude oil and the Middle East crude oil before and after in high pressure cell
Turbiscan	Turbiscan MA 2000	The Latin American crude oil and the Middle East crude oil

Further details regarding the experimental activities such as the single methods with analysis description for each of the tabulated measurements from table 3.5 are given in the experimental sections of paper II and paper III in appendix B and C, respectively.

3.2.3 Results

An extensive research program has been carried out to study the oil/ brine interaction mechanisms. The preliminary tests carried out at room temperatures and atmospheric pressure indicates, in the case of the Latin American crude oil and the Middle East crude oil that salinity influences the formation of emulsions. No significant changes were observed regarding the North Sea crude oil and this crude oil is not discussed any further. Neither of the cases showed significant changes in viscosity and density. The heptane/ brine study at ambient conditions did not show any noticeable behavior regarding emulsion formations, changes in viscosity and density.

The high pressure phase behavior experiments in the DBR JEFRI PVT cell is carried out with the Latin American crude oil, the Middle East crude oil and the heptane contacted with the seven prepared synthetic seawater solutions. It is examined whether emulsions are present in certain oil/ brine systems and furthermore the oil phase is characterized to distinguish which components there

might be responsible for our observations with regards to the phase behavior at elevated pressures and temperatures.

Study of the crude oil/ brine interaction with light scattering at the Turbiscan showed that sulfate-rich brine solutions formed more stable emulsions compared to distilled water mixed with crude oil. In the preparation of the samples for the Turbiscan analysis, a 'gel'-like single phase was formed, when shaking crude oil and brine for thoroughly. This unexpected phase behavior challenge the mixing procedure, thus, inherent uncertainty of the mixing procedure for the light scattering analysis may have caused a significant margin of error to these results.

3.2.3.1 Latin American crude oil

An increase in pressure and temperature resulted in a de-emulsification of the crude oil almost independent on the sulfate concentration in the brine solution. Brine SW1½S had a slightly different phase behavior, as this sulfate concentration generates a less clear separation of the crude oil and brine, which resulted in a very cloudy and unclear interface between oil and brine at all conditions (pressure and temperature). Figure 3.3 gives an example of the observations from the high pressure cell at 37 ˚C and 15 bar.
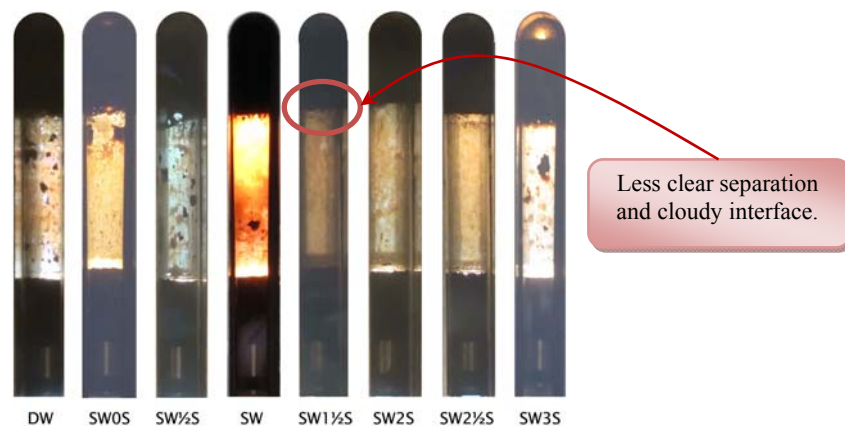
Figure 3.3. Latin American crude oil contacted with different brine solutions observed through the window in the DBR JEFRI PVT cell. Conditions are at 37 ˚C and 15 bar. The interface between crude oil and brine is very difficult to determine especially in the case of SW1½S.

Phase volumes were measured at every single test condition (combination of crude oil, seawater solution, temperature and pressure). No significant changes can be reported concerning the phase volumes, as they remained constant at all chosen conditions. Very small formation of emulsions was observed in the cases of DW, SW2S and SW2½S. The emulsions occupied such a small volumes, that it has been impossible to make useful measurements. A significant decrease in the viscosity of the Latin American crude oil was measured for the oil phase after the samples has left

the PVT cell. Viscosity results are shown in table 3.6 and compared to viscosity measurements of the same crude oil at room temperature in figure 3.4.

Table 3.6. Viscosity of Latin American crude oil after contacted with brine solutions in the DBR JEFRI PVT cell. The viscosity of the Latin American crude oil is measured for the oil phase and the measurement took place after the operation in the PVT cell.

Brine solution	Viscosity After high pressure cell [cp]
Crude oil	24.4
SW0S	21.5
SW	20.2
SW1½S	18.7
SW2S	18.1
SW2½S	18
SW3S	16.4
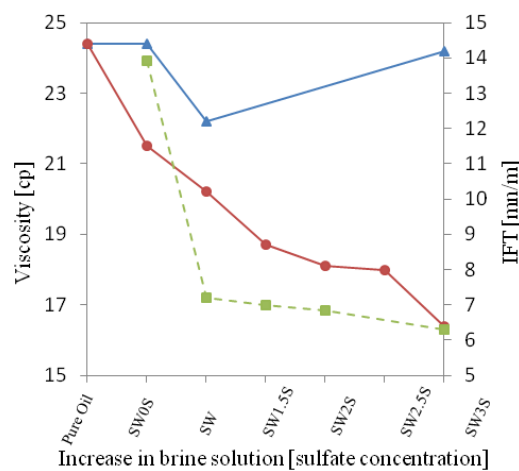
Figure 3.4. The vertical left axis is titled viscosity. It is seen that the viscosity, as a function of sulfate concentration in the synthetic seawater solutions, decreases significantly for the Latin American crude oil (red full line with circles) after contacted with brine solutions in the DBR JEFRI PVT cell. Blue full line with triangles is the viscosity of pure Latin American crude oil after contacted with the different brine solutions at ambient pressure and temperature. The vertical right axis is titled IFT. Green line with squares shows the IFT as a function of the sulfate concentration in the synthetic seawater solutions. It is seen that the IFT decreases with the increase in sulfate concentration.

The water content in the crude oil phase was also measured and those results make it clear that the observed viscosity decrease is not caused due to water present in the oil phase.

IFT was measured for this crude oil. The results show a decrease in IFT with the increase in sulfate concentration, as shown in figure 3.4. Even though the decrease in IFT is significant, as IFT for SW0S at 13.92 mN/m is reduced to 6.31 mN/m in the case of SW3S, this decrease seems to be insufficient to account for the observed increment in oil recovery.

The compositional combination of the Latin American crude oil is analyzed with the SARA analysis and compared with the Middle East crude oil. Results are shown in figure 3.5.
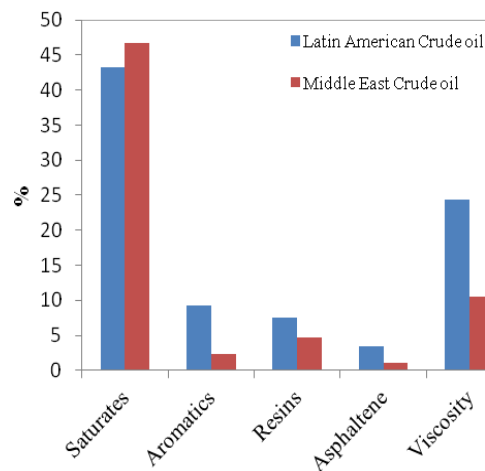
Figure 3.5. Summary of compositional difference between Latin American crude oil compared to the Middle East crude oil determined from the SARA analysis.

It was determined that the Latin American crude oil contained a much higher percentage of aromatics, resins and asphaltenes compared to the middle east crude oil. This strongly induces that the crude oil containing the highest amounts of heavy components are less inclined to form emulsions with brine.

3.2.3.2 Middle East crude oil

Similar to the observations in the previous section, it is seen for the Middle East crude oil that de-emulsification is observed as the increase in temperature and pressure is applied to the PVT cell for some samples. The Middle East crude oil showed formation of a third phase at the high temperature of 110 ˚C, with the increase in sulfate concentration. An example is given in figure 3.6.
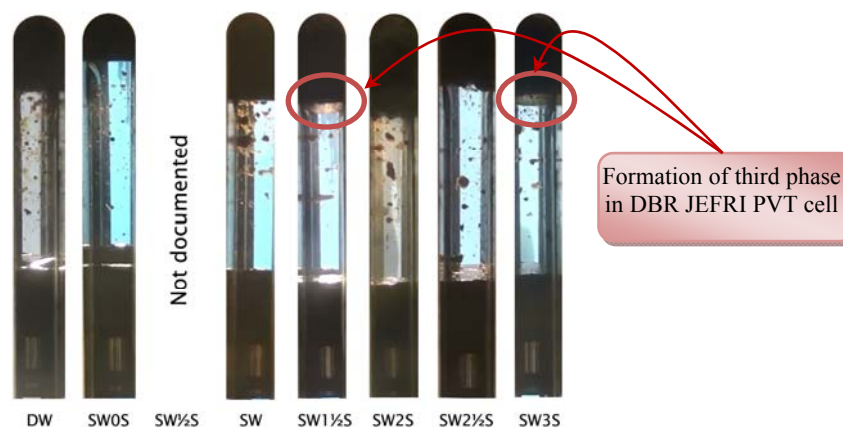
Figure 3.6. Middle East crude oil contacted with different brine solutions observed through the window in the DBR JEFRI PVT cell. Conditions are at 110 ˚C and 300 bar. The dark grey phase at the interface between crude oil and water in the case of SW1½S and SW3S is the third new phase.

Emulsions were observed specifically in the case of SW3S and SW1½S, at 110 ˚C and 300 bar and for SW3S also at 15 bar. The formation of the new emulsion phase was successfully reproduced to ensure the consistency of the observations. The uprising middle phase was measured to occupy a phase volume of approximately 2.5 ml out of the total sample volume at 50 ml. In contrast to the case of the Latin American crude oil, no significant changes were observed from the viscosity measurements.

Another analysis carried out on the two crude oils is GC, which has been carried out before and after processed in the PVT cell. Considering the chromatograms of the Middle East crude oil the content of light components is significantly changed comparing the results before and after the crude oil has been contacted with synthetic seawater in the PVT cell. The content of lighter components in the Middle East crude oil is much higher before the crude oil has been contacted with brine in the DBR JEFRI cell than after. No changes were observed regarding the Latin American crude oil.

3.2.3.3 Model oil heptane

The purpose of this oil/ brine study was to understand the observed effects or mechanisms in the crude oil/ seawater interactions by analyzing this simple model system.

At room temperature, in contrast to the crude oil study at room temperature, no dispersion of the heptane in the brine solution was observed.

The results from the experiments carried out with heptane/ brine systems in the PVT cell were dominated with observations of the phase behavior forming of a third phase at the interface between heptane and brine. The formed, assumed, emulsion phase was more pronounced for this

type of system compared to the observations previously for the Middle East crude oil. Examples of the visual observations are given in figure 3.7.
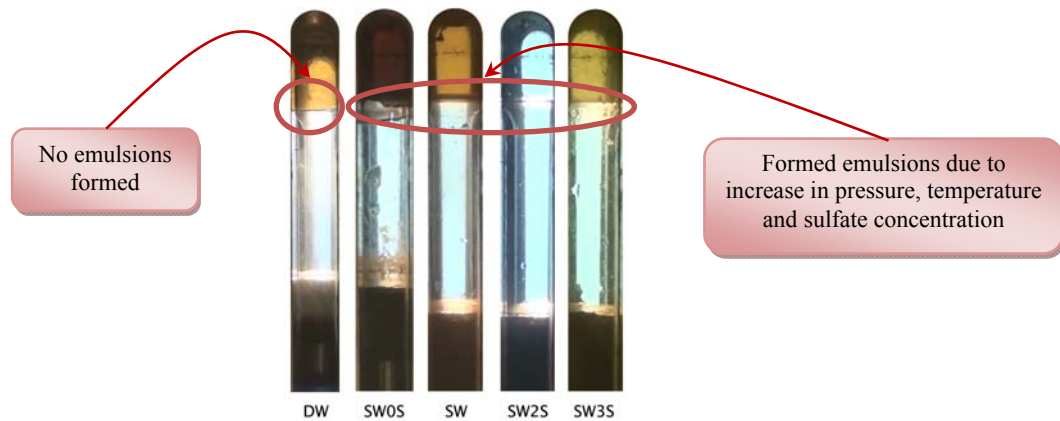
Figure 3.7. Heptane contacted with different brine solutions observed through the window in the DBR JEFRI PVT cell. Conditions are at 37 ˚C and 15 bar. The cloudy milky white emulsion phase is seen at the interface between heptane and water especially in the case of SW0S to SW3S.

The formation of the emulsion is sensitive to both pressure and temperature and the volume measurements concludes that the third phase is formed from the upper oil phase and the lower water phase evenly, as the phase volume of both of these phases is evenly reduced. No changes in either viscosity or density were observed.

A significant color change was observed for the operations of the heptane/ brine systems. The heptane/ brine systems begin at complete colorless. The water phase remains transparent and colorless, where the oil phase changes from colorless to yellow or brown, though still transparent. The change in color in the oil phase becomes more intense with increasing pressure and temperature. Color change persists after end experiments.

3.2.4 Discussion and Conclusions

The experiments carried out at room temperature and atmospheric pressure induced that the formation of emulsions in the present crude oil/ brine systems is affected by the salinity. The light scattering measurements showed that the presence of salt rather than distilled water facilitates more stable emulsions. Unexpected, an observation of a single phase formation was carried out, when mixing crude oil and brine. Possibly this could be a previously overseen mechanism, which could cause huge impact on the oil recovery.

Phase behavior experiments in the DBR JEFRI PVT cell showed interesting and different results, depending on the type of oil and the concentration of the sulfate in the brine solutions.

Significant decrease in the viscosity of the Latin American crude oil after contacted with brine, pronounced with the increase in sulfate concentration, could possibly be explained from change of the shape of the heavy component molecules. This has been detected in polymer solutions, where viscosity decrease is correlated with the addition of salt to the solution, [Hietala et al. (2005)]. Similar to observations from polymer studies, the sulfate ions along with other potential determining ions could influence the shape of the heavy components at elevated pressures and temperatures. As the viscosity decrease only is observed in the case of the Latin American crude oil this mechanism seems reasonable, especially when considering that the asphaltene content is three times higher for this oil compared to the Middle East crude oil. The SARA analysis confirmed that the Latin American crude oil contained high amounts of heavy components, which exhibits decrease in viscosity after contact with brine solution.

Formation of an emulsion phase in the case of the Middle East crude oil was another important finding in this work. To detect the emulsion phase, elevated pressures, temperatures and high sulfate concentration was required. Unfortunately, it has been out of the scope of this work to analyze the new formed phase, besides observations through the glass window in the high pressure equipment. As the third phase is formed upon simple mixing of components, do not require high shear conditions and presented stable at the experimental conditions, it is concluded that the emulsion phase very well could be a microemulsion phase, which then would serve as an IFT reducing agent in the phase behavior, which consequently would create conditions for an improvement of the oil recovery. From the SARA analysis it is revealed that the Middle East crude oil has high amount of lighter hydrocarbons. Furthermore the GC analysis showed that the content of light hydrocarbons changes significantly after the crude oil has been contacted with brine solutions in the high pressure cell. This indicates that the formation of emulsions in the crude oil is related to the light hydrocarbon components and from these results it is suggested that the light components are consumed in the formed emulsion phase.

In the case of the heptane/ brine phase behavior study in the PVT cell formation of emulsions at the oil/ brine interface was observed. The emulsion phases were formed similarly to those observed from the Middle East crude oil experiments, however, the heptane/ brine emulsion phases was much more pronounced. This observation supports the suggestion that emulsions in oil/ brine systems are formed by the lighter hydrocarbon components.

Both the determined decrease in viscosity and the formation of a possible emulsion could be possible explanations for the observed increase in oil recovery in advanced waterflooding. However, these oil/brine interaction results cannot stand alone and despite the further examinations

carried out in this work even more mechanisms must be taken into account to understand the EOR based on enhanced water salinity or 'smart'-water.

Chapter 4

4 Phase Behavior Modeling of Liquid Systems Relevant to Surfactant Flooding

In this chapter modeling the phase behavior of liquid systems relevant for surfactant flooding is considered. The simplified Perturbed Chain-Statistical Associating Fluid Theory (sPC-SAFT) is used to describe the phase behavior. Due to time consuming and expensive experimental work with surfactant systems it is desired to improve the development of the thermodynamic models used for such predictions, as the phase behavior predictions are not performing very accurately. Currently the predictions are not capable of including the microemulsion phase in surfactant systems, nor the presence of electrolytes. Furthermore the existing thermodynamic models cannot describe the effect from elevated pressures.

4.1 Introduction

As mentioned in chapter 1 and in other references [Fotland (1987), Sassen et al. (1989, 1991, 1992)], it is crucial to capture the influence of pressure when employing surfactant flooding as a method of enhanced oil recovery. Depending on the depth of the reservoir, pressures can be as high as 40, MPa [Sassen et al., 1989], which is challenging to the entire flooding process, as it will undergo extreme pressure changes thru the reservoir and therefore the understanding this effect is essential for efficient recovery of the residual oil.

The experimental work required to study surfactant systems is costly, and extremely time consuming. Furthermore the results are limited to the specific systems and conditions measured. However experimental work is essential, in order to provide relevant data for adapting and tuning thermodynamic models. One of the main goals of these thermodynamic models is to describe the phase behavior of the very complex systems resulting from surfactant floods. Equations of state are the natural choice for modeling phase equilibrium at high pressure (in high pressure surfactant systems in the presence of oil and brine, liquid-liquid-equilibrium (LLE) is of paramount importance, although vapor-liquid-equilibrium (VLE) may also be important). Nevertheless, existing thermodynamic models often perform poorly at elevated pressures and equations of state are not able to model phase behavior, in surfactant systems where a third liquid phase

(microemulsion) is formed. Even without the extra complication of a microemulsion phase, equations of state typically perform poorly when both surfactants and electrolytes are present.

In this chapter the simplified Perturbed Chain-Statistical Associating Fluid Theory (sPC-SAFT) is used to describe LLE for several binary and ternary alkane/ alcohol/ water systems. It is important and useful to be able to model these systems, since they represent the fluids present in a surfactant flood (oil, brine, co-surfactant), excluding only the surfactant itself. They are nevertheless still challenging to model, and any model which is being developed for surfactants should at the very least be able to adequately predict or correlate LLE in these simpler systems. In addition to these systems an LLE study of the binary surfactant system 2-butoxyethanol/ water is carried out.

As will be presented in this chapter, it was found that small changes in the interaction parameter, k_{ij}, entail significant improvements of the accuracy of the prediction of the phase behavior of the considered systems. However, it is dependent on the particular system which changes that is required to obtain the most suitable optimization of the predicted phase behavior.

The behavior of surfactant systems depends on a large number of variables such as temperature, pressure, salinity, surfactant structure, specific characteristics of the reservoir (rock and fluid) and so on. It is therefore difficult, time-consuming and expensive to conduct experiments at true reservoir conditions. It is thus necessary to be able to model (predict and correlate) the phase behavior in surfactant systems. However, no current thermodynamic models are capable of accurately describing such highly complex systems. Predicting the phase behavior of systems displaying liquid-liquid equilibrium, is already complex, especially in the presence of for example electrolytes, and is not possible with current models, where a third liquid phase exists, such as in surfactant systems. However, as a starting point at least alkane/ alcohol/ water systems should be modeled correctly, and most of the work presented in this chapter is concerned with such systems.

Surfactant systems have been studied by several investigators, both experimentally and also theoretically. Typically, simple systems are used as models to investigate the potential for more efficient recovery of the residual oil in surfactant flooding. Several research groups have reported experimental work with such model systems at both ambient and elevated pressures and temperatures [Bellocq et al. (1984), van Nieuwkoop and Snoei (1985), Kahlweit (1988), Levitt et al. (2006), Flaaten et al. (2008), Skauge and Fotland (1990), Sassen et al. (1989-1992)]. However, the few attempts to describe the experimentally observed phase behavior with thermodynamic models have not been successful [Sassen (1989-1992), Knudsen et al. (1994), Avlund et al.

(2012)], where in particular the pressure dependency is poorly described by the existing thermodynamic models.

This chapter focuses on the application of the simplified PC-SAFT equation of state (sPC-SAFT) to describe binary and ternary alkane/ alkanol/ water systems, in addition to looking at liquid-liquid equilibrium in a single water/surfactant system. The sPC-SAFT was proposed by von Solms et al. (2003) and differs only from the original version of PC-SAFT when considering mixtures. It may therefore be considered as a simplified mixing rule applied to PC-SAFT. One advantage of this is that existing pure-component parameters for PC-SAFT can also be used for sPC-SAFT. The binary systems considered (alkane/ alkanol, alkane/ water or alkanol/ water) are tabulated in table 4.1. The aim here is to study the capability of the sPC-SAFT for the simpler subsystems as well as to obtain binary parameters (k_{ij}) which can then be used for predictions when considering ternary or higher systems

Table 4.1. Overview of binary systems for which LLE or VLE was modeled using sPC-SAFT.

Binary systems		LLE/VLE	Fitted k_{ij}	Experimental data
Hexane	1-butanol	VLE	0.015	Berro et al. 1982
	1-octanol	VLE	-	Heintz et al. 1986
	water	LLE	0.05	Marche et al. 2003
				Tsonopolous 1983
Heptane	1-butanol	VLE	0.025	Kumar et al. 1980 (T=338.15 K)
				Berro et al. 1984 (T=333.15 K)
				Aristovich et al. 1965 (T=323.15 K)
	1-pentanol	VLE	0.015	Machova et al. 1988
	water	LLE	0.05	Marche et al. 2003
				Black et al. 1948
Octane	1-butanol	VLE	0.01	Gracia et al. 1992
	1-pentanol	VLE	0.01	Oracz 1976
	1-octanol	VLE	(0.01)	Schmelzer et al. 1984
	water	LLE	0.05	Marche et al. 2003
				Heidman 1985
				Sørensen et al. 1980
Water	1-butanol	LLE	-	Sørensen et al. 1980
	1-pentanol	LLE	-	Sørensen et al. 1980
	1-octanol	LLE	-	Góral et al.

Table 4.2. Overview of ternary systems modeled using sPC-SAFT and the source of relevant experimental data.

Ternary systems			Experimental data
Hexane	1-butanol	Water	Islam et al. 2011
			Sørensen et al. 1980
Benzene	1-butanol	Water	Sørensen et al. 1980
			Grenner et al. 2007
Heptane	1-propanol	Water	Sørensen et al. 1980
Dodecane	Ethanol	Water	Lasich et al. 2011
Dodecane	Propan-2-ol	Water	Lasich et al. 2011

Depending on the available experimental data, either LLE or VLE calculations were carried out for the binary systems listed in table 4.1. Table 4.2 lists the ternary systems which have been studied. Finally this study was concluded by considering the glycol ether, 2-butoxyethanol (C_4E_1) with water. This system has previously been considered by Knudsen et al. (1994) and Avlund et al. (2012).

4.2 The simplified PC-SAFT equation of state

The SAFT (Statistical Association Fluid Theory) equation of state, in the form of an engineering equation of state, was first proposed by Chapman et al. (1990) and Huang and Radosz (1990). A significant number of modifications of SAFT have later been proposed, where the Perturbed-Chain-SAFT proposed by Gross and Sadowski (2001) has probably been the SAFT variant which has been most widely applied. In 2003 the simplified Perturbed-Chain-Statistical Associating Fluid Theory (sPC-SAFT) was developed by von Solms et al. (2003).

PC-SAFT (and sPC-SAFT) can be presented in terms of the most general form of the reduced Helmholtz free energy for a mixture of associating or non-associating molecules:

$$\widetilde{a} \equiv \frac{A}{NkT} = \widetilde{a}^{id} + \widetilde{a}^{hc} + \widetilde{a}^{disp} + \widetilde{a}^{assoc} \qquad (4.1)$$

Where $\widetilde{a}^{id}$ is the reduced Helmholtz free energy of the ideal gas, $\widetilde{a}^{hc}$ is the contribution of the hard-sphere chain reference system, $\widetilde{a}^{disp}$ is the dispersion contribution from the attractive potential and $\widetilde{a}^{assoc}$ is the contribution from association. The expressions for the ideal gas contribution and the dispersion contribution are not changed from the original PC-SAFT version of

Gross and Sadowski (2001). For the hard chain term there are two contributions; the hard-sphere chain "connectivity" term and a reference hard-sphere term (i.e. a contribution from the chain segments which is reduced by joining them up). The hard-sphere chain term is given as follows:

$$\widetilde{a}^{hc} = \overline{m}\widetilde{a}^{hs} - \sum_i x_i(m_i - 1)\ln g_{ii}^{hs}(\sigma_{ii}) \tag{4.2}$$

The mean chain length is $\overline{m}$, defined as $\overline{m} = \sum_i x_i m_i$. m_i is the chain length and x_i is the mole fraction of component i. The hard-sphere term for mixtures of hard spheres is given by the mixture version of the Carnahan-Starling equation of state for hard-spheres (Mansoori et al. 1971):

$$\widetilde{a}^{hs} = \frac{1}{\zeta_0}\left[\frac{3\zeta_1\zeta_2}{1-\zeta_3} + \frac{\zeta_2^3}{\zeta_3(1-\zeta_3)^2} + \left(\frac{\zeta_2^3}{\zeta_3^2} - \zeta_0\right)\ln(1-\zeta_3)\right] \tag{4.3}$$

Where ζ_n are defined by:

$$\zeta_n = \frac{\pi\rho}{6}\sum_i x_i m_i d_i^n \tag{4.4}$$

ρ is the total density and d_i is the Chen and Kreglewski (1977) temperature-dependent segment diameter of component i given by:

$$d_i = \sigma_i\left[1 - 0.12\exp\left(-3\frac{\varepsilon_i}{kT}\right)\right] \tag{4.5}$$

Here ε_i is the segment energy parameter and σ_i is the temperature-independent segment diameter. The radial distribution function for mixtures of hard-spheres, at contact, required in the chain term from (4.2) is also given by Mansoori et al. (1971):

$$g_{ij}^{hs}(d_{ij}^+) = \frac{1}{1-\zeta_3} + \left(\frac{d_i d_j}{d_i + d_j}\right)\frac{3\zeta_2}{(1-\zeta_3)^2} + \left(\frac{d_i d_j}{d_i + d_j}\right)^2\frac{2\zeta_2^2}{(1-\zeta_3)^3} \tag{4.6}$$

To obtain sPC-SAFT from PC-SAFT, two modifications are introduced by von Solms et al. (2003), which affect the hard-sphere term, the hard-sphere chain term and the association term. Modification one is the assumption that all segments in the mixture have the same diameter, with the constraint that the mixture volume fraction using the new diameter gives the same volume

fraction as the actual mixture (i.e. it is defined, that $\eta \equiv \zeta_3$, where $\eta = \pi \rho d^3 \sum x_i m_i / 6$). The average diameter is thus given by:

$$d = \left(\frac{\sum_i x_i m_i d_i^3}{\sum_i x_i m_i} \right)^{1/3}$$
(4.7)

Introducing this diameter into (4.6), a much simpler expression for the radial distribution function in the chain and associating term is obtained:

$$g^{hs}(d^+) = \frac{1 - \eta/2}{(1-\eta)^3}$$
(4.8)

The second modification is to substitute (4.7) into (4.3), thus reducing the hard-sphere term to give the following simple expression:

$$\widetilde{a}^{hs} = \frac{4\eta - 3\eta^2}{(1-\eta)^2}$$
(4.9)

The sPC-SAFT also gives a slightly different expression for the association strength $\Delta^{A_i B_j}$ compared to the original PC-SAFT [Gross and Sadowski, 2001]. In the PC-SAFT equation of state the expression for the association strength is given as:

$$\widetilde{a}^{assoc} = \sum_i x_i \sum_{A_i} \left(\ln X_{A_i} - \frac{1}{2} X_{A_i} + \frac{1}{2} \right)$$
(4.10)

where x_i is the mole fraction of component i and X_{A_i} is the fraction of A-sites on molecule i that do not form associating bonds with other active sites, and is given by:

$$X_{A_i} = \frac{1}{1 + \sum_j \rho_j \sum_{B_j} X_{B_j} \Delta^{A_i B_j}}$$
(4.11)

Where ρ_j is the molar density of component j. $\Delta^{A_i B_j}$ is the association strength between site A on molecule i and site B on molecule j, given by the equation:

$$\Delta^{A_i B_j} = d_{ij}^3 g_{ij}(d_{ij}^+) \kappa^{A_i B_j} \left[\exp\left(\frac{\varepsilon^{A_i B_j}}{kT} \right) - 1 \right]$$
(4.12)

The association strength is a function of two pure-component parameters – the association volume $\kappa^{A_iB_j}$ and the association energy $\varepsilon^{A_iB_j}$. It also depends on the radial distribution function (4.6 for PC-SAFT or 4.8 for sPC-SAFT). For mixtures the Lorentz-Berthelot combining rules are applied, where the binary interaction parameter k_{ij} is introduced to correct the dispersion energies of unlike molecules:

$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}}\left(1 - k_{ij}\right) \qquad\qquad \sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \qquad\qquad (4.13)$$

An additional binary interaction parameter l_{ij}, can be applied in the calculation of the cross-size parameter [Kouskoumvekaki et al., 2004] in cases where corrections to the cross energy parameters have little effect. The cross-size parameter then becomes:

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}\left(1 - l_{ij}\right) \qquad\qquad (4.14)$$

The l_{ij} parameter is sometimes used to capture pressure effects, which are often poorly correlated using only a k_{ij} parameter

4.2.1 Pure-Component Parameters

Depending on the component, there are three or five pure component parameters for non-associating components and associating components, respectively. In the case of non-associating components, the three parameters are σ_i, the segment diameter, ε_i, the dispersion energy and m_i, the segment number. Two additional parameters are required for associating components. These are $\varepsilon^{A_iB_j}$, the associating energy and $\kappa^{A_iB_i}$, the associating volume.

The parameter sets used for the components studied here are given in table 4.3. Pure component parameters for alkanes are taken from Gross and Sadowski (2001). Pure component parameters for water are from the work of Grenner et al. (2006) and for alkanols from the work of Grenner et al. (2007). The pure component parameters for the glycol ether (2-butoxyethanol) are from Avlund et al. (2012).

Table 4.3 Pure component parameters for sPC-SAFT for alkanes, alkanols and water and for 2-butoxyethanol used in this study.

Component	σ [Å]	ε [K]	m	ε^{AB} [K]	κ^{AB}
Hexane	3.7983	236.77	3.0576	-	-
Heptane	3.8049	238.40	3.4831	-	-
Octane	3.8373	242.78	3.8176	-	-
Dodecane	3.8959	249.21	5.3060	-	-
Ethanol	4.1057	316.91	1.23058	2811.02	0.0033
1-Propanol	3.9044	292.11	1.79963	2811.02	0.0033
1-Butanol	3.7852	276.9	2.39832	2811.02	0.0033
1-Pentanol	3.9001	282.31	2.60475	2811.02	0.0033
1-Octanol	3.8872	273.92	3.84703	2811.02	0.0033
Water	2.6273	180.3	1.5	1804.22	0.0942
2-Butoxyethanol	3.518	257.63	4.194	1206.7	0.023353

No new pure-component parameters were obtained as part of this study, although these can readily be obtained if adequate experimental data for the pure component is available (e.g. saturated vapor pressure and liquid density data). Pure component parameters can, however, have a significant effect on the phase behavior of mixtures. For example Grenner et al. (2006) found that water parameters profoundly affected the description of liquid-liquid equilibrium in water-hydrocarbon systems.

4.3 Liquid-Liquid Equilibrium

This section presents the phase equilibrium results for the binary and ternary systems of alkane, alkanols and water with sPC-SAFT. The pure-component parameters for the compounds considered here are listed in table 4.3.

4.3.1 Phase Behavior for Binary Systems

A number of binary mixtures relevant to surfactant system modeling are considered. Grenner et al. (2006, 2007) applied sPC-SAFT to many of these types of systems and obtained good agreement with experimental data. Only LLE data at atmospheric pressures was modeled.

4.3.1.1 Water and Alkane Systems

Three different water/ alkane systems are considered in this work; hexane + water, heptane + water and octane + water. Figure 4.1 shows the LLE results for these three systems.
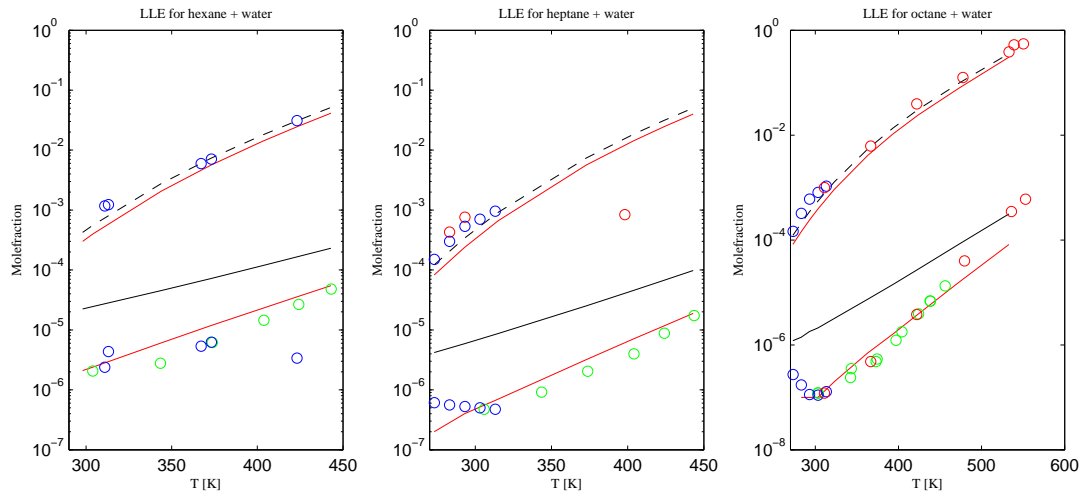

Figure 4.1. LLE for alkane + water systems. From left to right, hexane, heptane and octane, all mixed with water. Black lines are predicted (k_{ij}=0) with sPC-SAFT. The dashed black line is the oil rich phase and the solid black line is the water rich phase (so for example the solid black (lower) line shows the concentration of the alkane in the water phase). Red lines are correlated (k_{ij}=0.05). Experimental data: Blue circles are Sørensen et al. (1980), green circles are Marche et al (2003) and red circles are Black (1948) in the case of heptane and Heidman (1985) in the case of octane.

The results with sPC-SAFT for the three water/ alkane systems in figure 4.1 are similar, as the water rich phase is poorly described with k_{ij}=0. With a change in k_{ij} to 0.05 it is possible to correlate both phases, significantly improving the LLE description of these water/ alkane systems.

4.3.1.2 Water and Alkanol Systems

LLE calculations are carried out for three water/ alkanol systems. Binary systems of this kind have earlier been considered [Grenner et al., 2007] with similar results.
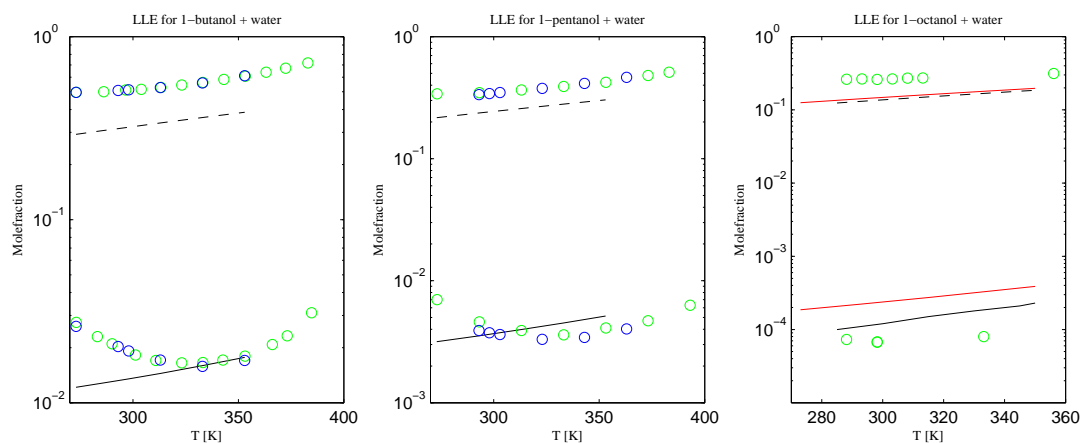
Figure 4.2. LLE for alkanol + water systems. From left to right, 1-butanol, 1-pentanol and 1-octanol. Black lines are predicted (k_{ij}=0) with sPC-SAFT. The dashed black line is the alcohol rich phase and the solid black line is the water rich phase. Red lines are correlations (k_{ij}=-0.01) with sPC-SAFT. Experimental data: Blue circles are Sørensen et al. (1980) and green circles are Góral et al. (2006). The two red lines in the plot for octanol + water show how changes in k_{ij} do not contribute to a more accurately description, since the binary parameter has little influence on the top line (concentration of water in alcohol).

The general picture is that sPC-SAFT does not predict the phase behavior very accurately. In all three examples both phases are estimated with deviations from the experimental data. For the water rich phase the error increases from the lighter 1-butanol towards the heavier 1-octanol. Changing the interaction parameter, k_{ij}, can improve the correlation for the water rich phase but has little effect on the alcohol rich phase. As illustrated in the water + 1-octanol system, changing the k_{ij} does little to improve the correlation of the alcohol rich phase while making the results for the water rich phase significantly worse.

4.3.1.3 Alkane and Alkanol Systems

Several alkane/ alkanol systems were also considered. No LLE data was available for these systems so VLE calculations are carried out instead. . The goal is to use these results subsequently in a ternary system. The approach is to correlate to binary LLE data if available or else to correlate to binary VLE data. VLE data are obtained for seven different alkane/ alkanol systems, as listed in table 4.1.

The VLE results for heptane + 1-butanol are shown in figure 4.3 at different temperatures.
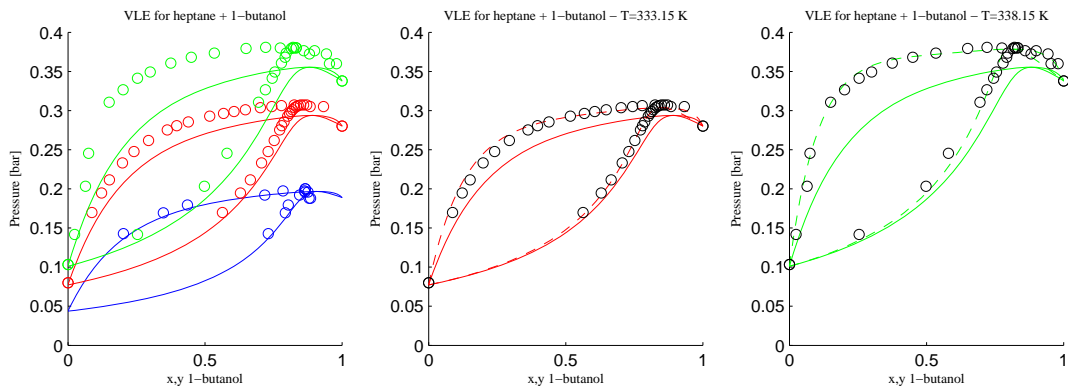

Figure 4.3. VLE for 1-butanol + heptane at different temperatures. Blue is at 323.15 K, red is at 333.15 K and green is at 338.15 K. Solid lines are predicted (k_{ij}=0) with sPC-SAFT, dashed lines are correlations (red with k_{ij}=0.015 and green with k_{ij}=0.025) with sPC-SAFT. Experimental data: Blue circles are from Aristovich et al. (1965), red circles from Berro et al. (1984) and green circles are from Kumar et al. (1980).

It is clearly seen that with no interaction parameter, (k_{ij}=0), the accuracy of the predictions with sPC-SAFT decreases with increasing temperature. Both at 333.15 K and 338.15 K significant deviation occurs for the system. An optimized prediction is obtained by introducing a small positive interaction parameter, where k_{ij} is increased from 0.0 to 0.015 and 0.025, respectively in the case of 333.15 K and 338.15 K.

In figure 4.4 from left to right the VLE results for 1-butanol + hexane, 1-octanol + hexane and 1-pentanol + heptane are shown.

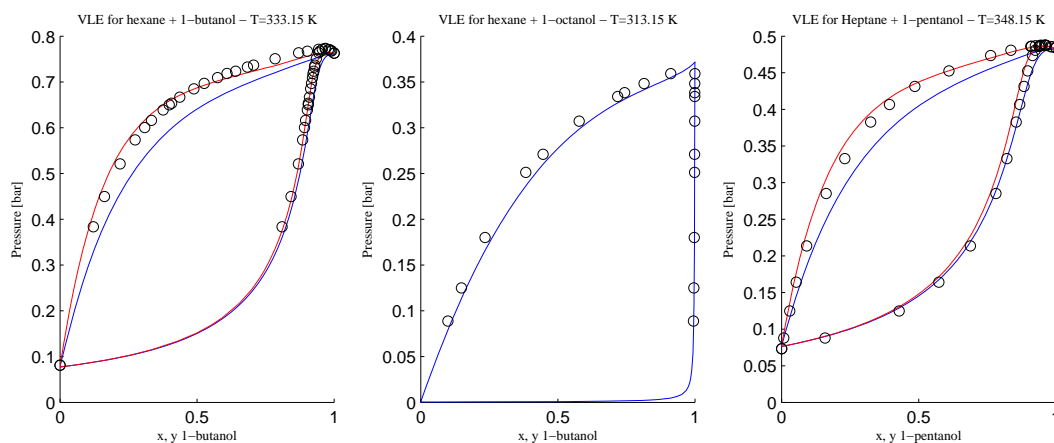Figure 4.4. VLE for 1-butanol + hexane, 1-octanol + hexane and 1-pentanol + heptane at different temperatures. Blue lines are predicted (k_{ij}=0) with sPC-SAFT and red lines are correlated (with k_{ij}=0.015) with sPC-SAFT. Black circles are experimental data. Experimental data: Berro et al. (1982) for 1-butanol + hexane, Heintz et al. (1986) for 1-octanol + hexane and Machova et al. (1988) for 1-pentanol + heptane.

In the case of 1-butanol + hexane and 1-pentanol + heptane the accuracy of the model is significantly improved by using a k_{ij}, of 0.015. In the case of 1-octanol + hexane the predictions obtained with sPC-SAFT are excellent and no binary parameter is required.

The VLE results for the final three alkane/ alkanol systems considered in this work are shown in figure 4.5. The systems octane + 1-butanol, octane + 1-pentanol and octane + 1-octanol are shown respectively from left to right.
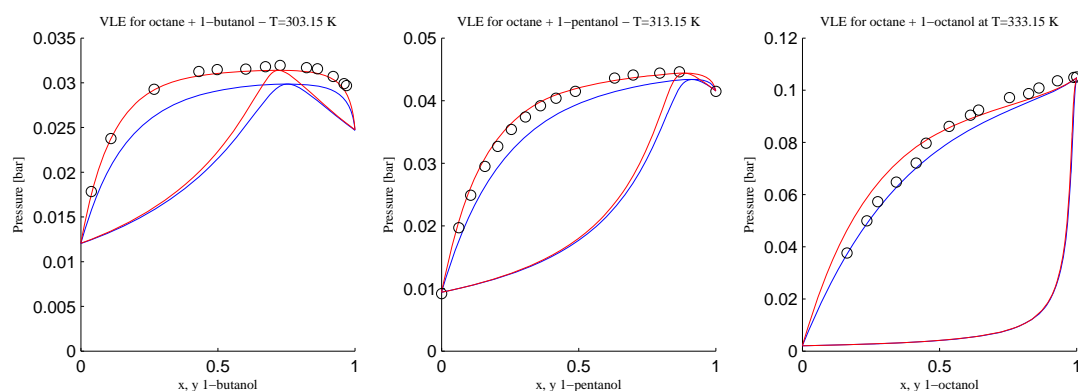
Figure 4.5. VLE for octane + 1-butanol, 1-pentanol and 1-octanol at different temperatures. Blue lines are predicted (k_{ij}=0) with sPC-SAFT and red lines are correlations (with k_{ij}=0.001) with sPC-SAFT. Black circles are experimental data. Experimental data: Gracia et al. (1992) for 1-butanol + octane, Oracz (1976) for 1-pentanol + octane and Schmelzer et al. (1984) for 1-octanol + octane.

In most cases VLE predictions with sPC-SAFT are not satisfactory, but in every case an excellent correlation can be obtained using a very small value of the binary interaction parameter k_{ij}.

4.3.2 Phase Behavior for Ternary Systems

In addition to these binary systems, the ternary systems shown in table 4.2 were also modeled. For all the ternary systems considered the predictions with sPC-SAFT have a slight tendency to overestimate the size of the two phase region. Figure 4.6 shows the results obtained for hexane/ 1-butanol/ water, benzene/ 1-butanol/ water and heptane/ 1-propanol/ water

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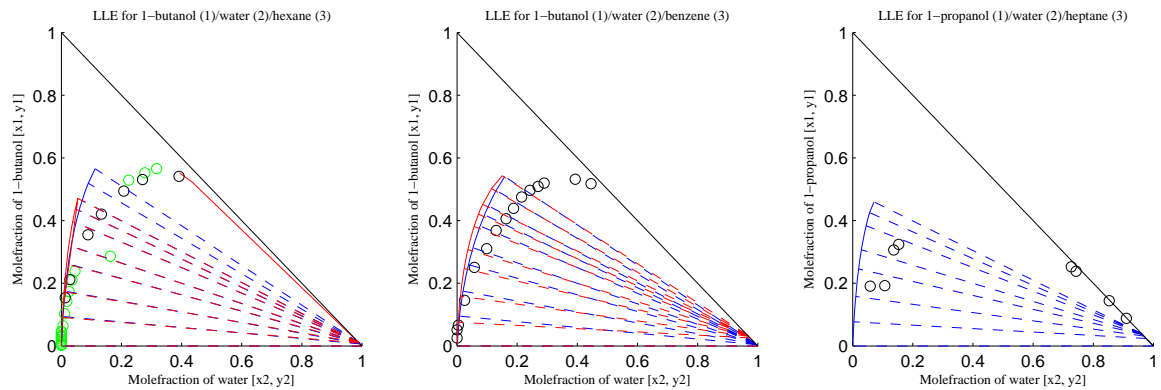
Figure 4.6. LLE for (from left to right) hexane + 1-butanol + water, benzene + 1-butanol + water and heptane + 1-propanol + water at 298.15 K. Blue dashed lines are predicted (k_{ij}=0) with sPC-SAFT, red are predictions for the ternary systems (using binary parameters correlated to the binary subsystems, given in table 4.1) and circles are experimental data: Green is Islam (2011), black is Sørensen et al. (1980).

In all cases deviations are obtained when comparing predicted results with the experimental data, where the two phase region is overestimated for all three systems. The results obtained using the binary interaction parameters obtained from the calculations on the binary subsystems (table 4.1) do not improve the results significantly.

The results for the ternary dodecane systems are shown in figure 4.7.
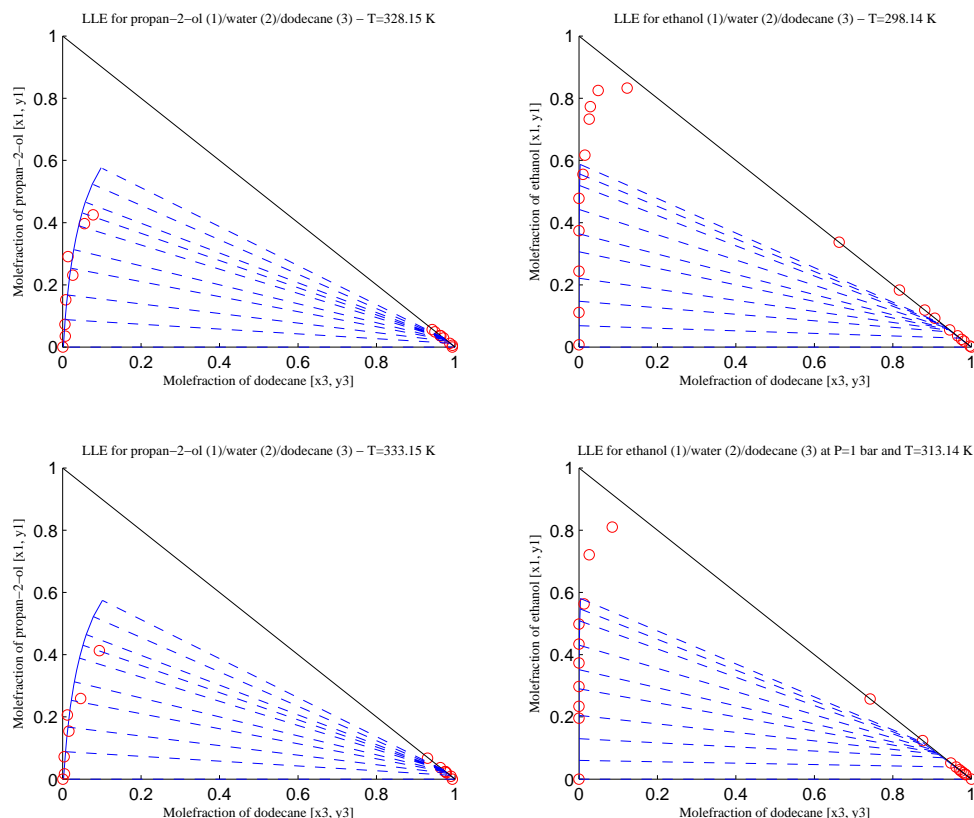
Figure 4.7. LLE for propan-2-ol + water + dodecane (left column) and ethanol + water + dodecane (right column) at different temperatures. Blue dashed lines are predicted (k_{ij}=0) with sPC-SAFT and red circles are experimental data. Experimental data are taken from Lasich et al. (2011).

The results are generally good, especially considering all three binary interaction parameters are set to zero. For propan-2-ol/ water /dodecane sPC-SAFT overestimates the size of the two-phase region when compared to the experimental data as is the case for the systems shown in figure 4.6. However, the results are still in rather good agreement with the experimental data and the deviations are low, when compared to the experimental values. The results are not noticeably affected by changing k_{ij} or pressure.

4.4 Glycol Ether and Water

With the ultimate objective of modeling surfactant systems with sPC-SAFT the glycol ether 2-butoxyethanol (C_4E_1), which is a nonionic surfactant, was considered. The binary system C_4E_1/ water have been measured by Schneider, and the system is interesting because it shows unusual closed-loop phase behavior as well as a significant effect of pressure. The system has been modeled by Knudsen et al. (1994) and by Avlund et al. (2012). Both works attempt to provide

thermodynamic models capable of describing this complex system (including the pressure dependency). Pure component parameters for sPC-SAFT for this glycol ether are from Avlund et al. (2012). It is worth noting that the glycol ether is treated as an ordinary associating component within the sPC-SAFT framework. Figure 4.8 shows the results obtained with the pure compound parameters from Avlund et al. (2012).
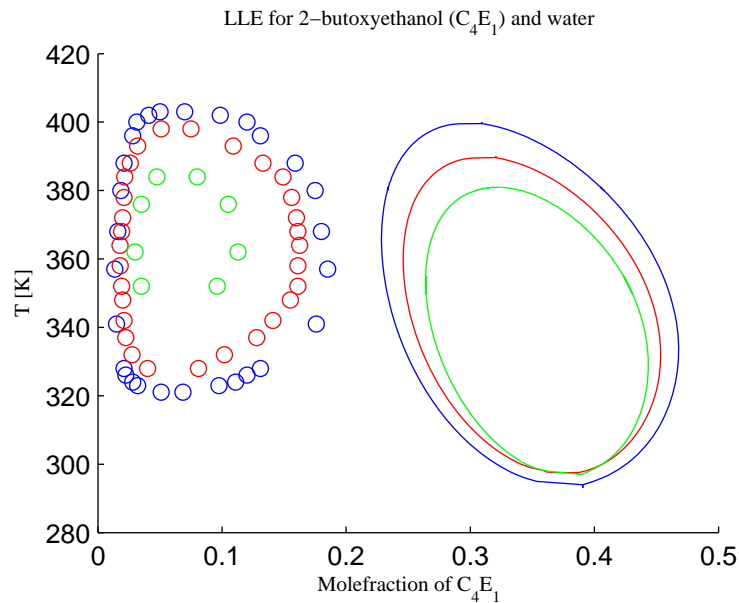
Figure 4.8. LLE for C_4E_1 + water. Lines are correlations (k_{ij}=-0.09) with sPC-SAFT. Blue is at 10 atm, red is at 200 atm and green is at 600 atm. Circles are experimental data, Schneider (1963), taken from Knudsen et al. (1994). The pressure effect is reasonably well captured, although the location of the two-phase region is off.

These results have already been presented by Avlund et al. (2012), and show that the experimental data are more influenced by pressure than the LLE modeling is capable of. However, the trend in the pressure dependency (higher pressure makes the loop smaller) is predicted correctly. The temperature interval where two phases occur is reasonably well captured by the model.

As shown in earlier sections of this chapter, the interaction parameter k_{ij} can significantly improve the correlation of experimental data. The results in figure 4.8 already include a non-zero interaction parameter. Since the pressure dependency in the C_4E_1/ water system only is qualitatively described in figure 4.8 an attempt was made to improve the correlation by the introduction of an additional binary interaction parameter, l_{ij}. Different combinations of k_{ij} and l_{ij} values are studied in order to improve the correlation of the data of Schneider (1963).

Table 4.4. Different combinations of k_{ij} and l_{ij}-values which have been studied.

		k_{ij}-values		
		0	-0.075	-0.09
l_{ij}-values	-0.01		X	X
	0	X	X	X
	0.01	X	X	X
	0.02	X	X	

The influence of the binary interaction parameter is studied in the temperature interval from 350 K to 380 K. The results are shown in figure 4.9.
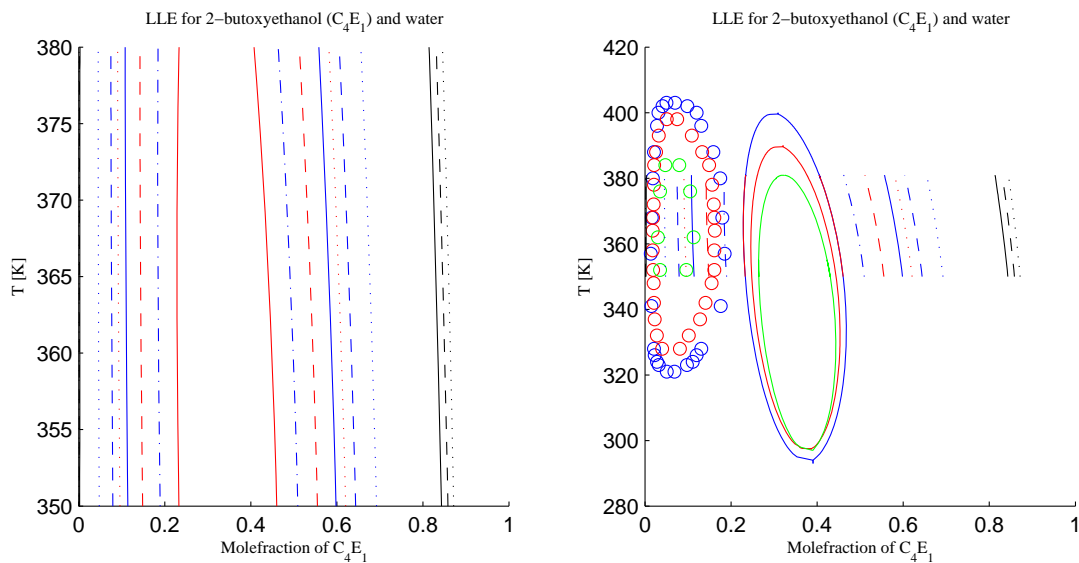
Figure 4.9. LLE for C_4E_1 + water. The figure on the left shows the influence of changing the interaction parameters k_{ij} and l_{ij} in the temperature interval 350 K to 380K and at constant pressure at 10 atm. The figure on the right shows the overall LLE results for C_4E_1 + water. Changing both interaction parameters increases the width of the closed loop significantly. Black is k_{ij}=0, blue is k_{ij}=-0.075 and red is k_{ij}=-0.09. Solid lines are l_{ij}=0, dashed lines are l_{ij}=0.01, dotted lines are l_{ij}=0.02 and dash-dotted line is l_{ij}=-0.01. The effect of l_{ij} is to expand the region of two phases. It was not possible to shift the region to the left without also changing its width.

The left part of figure 4.9 shows the results for the C_4E_1/ water system with sPC-SAFT as both k_{ij} and l_{ij} are varied. An appropriate value of k_{ij} results in a rather good match for the width of the two-phase region compared to the experimental data. No combination of the two binary parameters was able to improve the original correlation using only a single binary parameter, i.e. it was not possible to move the two phase region to the left without sacrificing the good modeling of the size and location (with respect to temperature).

4.5 Conclusions

Ideally we would like to build thermodynamic models capable of accounting for the complexity of surfactant systems, with the goal of performing good predictions of phase behavior in such systems. An equation of state model will very likely form the basis of such models in the future, so an initial study using the existing sPC-SAFT Equation of State was performed. Part of the goal of this study was to establish to what extent sPC-SAFT is able to predict multiphase equilibrium in systems which are relevant to surfactant systems, i.e. hydrocarbon/ water/ alcohol systems.

In the case of binary systems sPC-SAFT models LLE phase behavior with good results for water/ alkane systems. A small value of the binary interaction parameter is sufficient for accurate correlation. In the case of VLE behavior for alkane/ alkanol systems, accurate results are also obtained with a small binary interaction parameter. The same is not the case for water/ alkanol systems, where a single binary interaction parameter is unable to correlate the concentrations in both phases simultaneously. Using binary interaction parameters obtained from binary systems, ternary systems were then predicted with reasonable accuracy. Pressure did not have an effect on LLE for any of the systems studied.

The more complex binary system 2-butoxyethanol/ water (for which there is experimental evidence that the phase boundary is substantially dependent on pressure) were also studied. Introduction of the second binary interaction parameter, l_{ij}, was added to the model in order to try and correlate this pressure effect. However, it was concluded that the addition of this parameter is still not sufficient to improve the LLE modeling for this system. Further modifications of the sPC-SAFT model may be required, possibly coupled with an additional model where molecular interactions are more explicitly taken into account.

5 Conclusions

As significant amounts of crude oil remain trapped inside oil reservoirs, even a small increment in oil recovery efficiency would yield enormous benefits. The demand for oil is increasing and this gives rise to increased research in EOR techniques in order to optimize crude oil recovery. Surfactant flooding is a potentially promising EOR technique which is carried out by injection of fluids containing surfactants and (typically) co-surfactants. When the injection fluid is contacted with trapped crude oil, the surfactants cause a decrease in the interfacial tension between crude oil and injection water, which mobilizes the crude oil.

In order to design such a process to be sufficiently efficient there are many details and mechanisms that must be understood and tailored to match the specific reservoir and crude oil (rock, characteristics of the crude oil, optimal salinity, temperature, pressure). In practice it is nearly impossible to perform true reservoir simulations (whether experimental or theoretical), since understanding of the exact mechanisms is incomplete and reported results are often difficult to compare, due to different experimental setups, different crude oils, different simplifying assumptions and so forth. However, there is no doubt that correct modeling of the phase behavior of surfactant systems is essential in order to achieve the optimal surfactant flood design for improved oil recovery. Although several researchers have worked with surfactant systems with the goal of understanding the underlying mechanisms in the phase behavior of surfactant systems, opinions regarding the influence of pressure and temperature are diverse and, especially for pressure, are often neglected.

The model surfactant system (water/ NaCl/ SDS/ 1-butanol/ heptane) considered in this thesis is studied at elevated pressures and a range of temperatures. It was clearly seen that increased pressure had a significant influence on the phase behavior. The number of phases changed from Winsor II (two phase region) to Winsor III (three phase region) or from Winsor III (three phase region) to Winsor I (two phase region) depending on the pressure (and temperature) and the overall composition of the sample. The findings were even more pronounced when an increase in temperature was added. The results were compared to the observations from the work by van Nieuwkoop and Snoei (1985), who produced a pseudo ternary diagram (a so-called observation

diagram), showing the locations of the different single-, two- and three- phase regions for this surfactant system. The influence of elevated pressure resulted in a displacement of the three phase envelope within the ternary diagram although the size of the three phase region was not noticeably changed. It is concluded from this work that the effect of increased pressure (and temperature) on the phase behavior of the surfactant system is profound.

In order to improve understanding of the systems displaying liquid-liquid phase behavior a study of oil/ brine systems was performed with oil and different brine solutions, where the brine solutions were modified by changing the sulfate concentration. Three crude oils were used; a North Sea Crude, a Latin American Crude and a Middle East Crude. In addition, pure heptane was used as model oil. Experiments were carried out at ambient conditions and at elevated pressures and temperatures and a number of analyses were performed in order to characterize the equilibrium phases and explain the phase behavior observations. At room temperature the interaction experiments induced that formation of emulsions in the crude oil/ brine system was affected by salinity. One of the main conclusions from this experimental study carried in the PVT cell is that a significant decrease in the viscosity of the Latin American crude was measured after contacting with brine at high pressures. The viscosity decrease was more pronounced with increasing sulfate concentration in the brine. It is suggested that the viscosity decrease is explained by changes of the shape of the heavy component molecules present in the crude oil. It seems reasonable to suggest that the sulfate ions along with other potential determining ions is influencing the shape of the heavy components, which has been observed similarly for polymer studies, which consequently reduces the crude oil viscosity with increasing sulfate content ion the brine. As the viscosity decrease is only observed for the Latin American crude oil this seems reasonable, especially when considering that the asphaltene content is three times higher for this oil than for the Middle East crude oil.

A second main conclusion to this experimental work is that the Middle East crude oil formed emulsions while in the PVT cell at high sulfate concentrations, elevated pressures and elevated temperatures. The SARA analysis revealed that the Middle East crude oil has a large proportion of lighter components and the GC analysis confirmed that the amount of light hydrocarbons changed significantly after the Middle East crude oil was contacted with brine in the PVT cell at elevated temperatures and pressures. From these findings it is suggested that the formation of emulsions is related to the presence of lighter hydrocarbons in the Middle East crude oil. The heptane/ brine study showed similar formation of emulsions, which supports the hypothesis that the lighter hydrocarbons are responsible for this type of phase behavior.

As this type of experimental work is time consuming, costly and system-specific, it is desirable to develop thermodynamic models that are capable of accurate phase behavior modeling of complex systems (such as surfactant systems and systems with electrolytes). Ideally a model should also be able to include the influence of both pressure and temperature. To this end a modeling study with an equation of state model - sPC-SAFT was carried out. The goal here was accurate modeling of ternary water / alkane /alkanol systems which exhibit liquid-liquid equilibrium. Initially the binary systems water/ alkane, water/ alkanol and alkane/ alkanol were studied. LLE correlations for water/ alkane systems were satisfactory, while those for the water/ alkanol systems were less successful. VLE correlations for the alkanes/ alkanols are reasonable in most cases using a small value for the binary interaction parameter, k_{ij}. Based on the results from the various constitutive binary systems, ternary systems were then considered. Prediction of the phase behavior of the ternary systems was not significantly changed nor improved by using the binary parameters obtained from the binary systems. In all cases, changes in pressure did not noticeably change the model results obtained from sPC-SAFT. In other words pressure has little effect on liquid-liquid equilibrium for systems without surfactants.

Finally the system 2-butoxyethanol/ water were studied, where the influence from an additional binary interaction parameter, l_{ij}, was examined. This system was selected partly because experiments showed that the LLE phase behavior is dependent on pressure. It was concluded that the extra binary parameter does not improve the LLE correlations for this system. Further modifications of the sPC-SAFT model may be required, possibly coupled with an additional model where molecular interactions are more explicitly taken into account.

6 Future Work

There is no doubt that experimental work will continue to be the basis of any future development in this field and must therefore continue.

The focus of future experimental work should be on ´true´ surfactant systems. i.e. work with crude oils rather than model oils.

As the interaction between crude oil and brine is very dependent on the characteristics of the crude oil, it is important to explore these findings in more detail. Increased oil recovery should not come at the cost of (for example) unforeseen plugging due to emulsion formation caused by the mixing of the trapped crude oil with injection water. The study on crude oils and brine solution should be extended to include many more crude oils as well as both high and low salinity in the brine solutions.

In terms of equation of state modeling (for example with sPC-SAFT), phase equilibrium (vapor-liquid, liquid-liquid) in relatively simple systems is quite developed. However the correct handling of microemulsion phases, the effect of pressure and to some extent electrolytes is not yet possible. This modeling work would be a natural extension of the work performed in this study.

Abbreviations

AMNS	=	Alkyl Methyl Naphthalene Sulfonates
ASP	=	Alkaline/Surfactant/Polymer
CMC	=	Critical Micelle Concentration
DIT	=	Dynamic Interfacial Tension
EOR	=	Enhanced Oil Recovery
IFT	=	Interfacial Tension
IOR	=	Improved Oil Recovery
IOS	=	Internal Olefin Sulfonates
LAS	=	Long-chain Alkyl benzene Sulfonates
PC-SAFT	=	Perturbed Chain Statistical Associating Fluid Theory

List of symbols

A	=	Helmholtz energy, J
$\tilde{a}$	=	reduced Helmholtz energy
d	=	temperature dependent segment diameter, Å
g	=	radial distribution function
k	=	Boltzmann's constant J/K
m	=	segment number
N	=	number of molecules
n	=	mole number
T	=	temperature, K

X_A =   fraction of unbound sites

x =   mole fraction

Greek Letters

Δ^{AB} =   strength of attraction

ε =   depth of dispersion potential, J

ε^{AB} =   reduced association energy, K

κ^{AB} =   association volume

η =   volume fraction

ρ =   total number density, Å^{-3}

σ =   segment diameter, Å

ζ_n =   parameters in equation 4.3, $n = 0, 1, 2$ or 3

Superscripts

assoc   =   association

disp   =   dispersion

hc   =   hard chain

hs   =   hard sphere

id   =   ideal

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Appendix A

Paper I

The effect of pressure on the phase behavior of surfactant systems: An experimental study

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The effect of pressure on the phase behavior of surfactant systems: An experimental study

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Abstract

Enhanced oil recovery is employed in many mature oil reservoirs to maintain or increase the reservoir recovery factor. In this context, surfactant flooding has recently gained interest again. Surfactant flooding is the injection of surfactants (and co-surfactants) into the reservoir, in order to create microemulsions at the interface between crude oil and water, thus obtaining very low interfacial tension, which consequently helps mobilize the trapped oil.

In this work a surfactant system, which has been thoroughly described at atmospheric pressure, is examined at elevated pressure. The effect of temperature is also explored. It was found that the phase behavior in the system water/ sodium dodecyl sulfate (SDS)/ 1-butanol / heptane/ sodium chloride was significantly changed by an increase in pressure. When an increase in pressure is combined with an increased temperature the phase behavior of the system is influenced to an even greater extent. It was concluded that at certain compositions of the surfactant system (near to the phase boundary found at atmospheric pressure) the increase in pressure changed the phase behavior (for example causing the system to move from two phases to three or vice-versa). The sensitivity of the surfactant system depends very much on the overall composition as well as the magnitude of the pressure and temperature change.

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Key Words:

Phase behavior, surfactants, emulsions, high pressure, IFT, enhanced oil recovery, surfactant flooding

1 Introduction

Around half of the world's crude oil reserves remain trapped in reservoirs after conventional recovery methods have been applied. Enhanced oil recovery (EOR) is therefore increasingly applied in order to increase the reservoir recovery factor. In the EOR technique known as surfactant (or chemical) flooding, the phase behavior properties inside the reservoir can be advantageously manipulated by injecting surfactants (and usually co-surfactants) into the reservoir. The phase behavior in these surfactant systems is the decisive factor determining the success of a chemical flood [1]. However, there are at present no equations of state that can adequately describe the phase behavior of such complex systems. It is therefore essential that the phase behavior is experimentally determined in order to design a successful recovery process. In the design of the surfactant system the phase behavior should account for reservoir conditions (e.g. high pressure and high temperature), as it is crucial for this technique that the oil/ surfactant/ water system creates microemulsions during flooding. Formation of the microemulsion phase lowers the interfacial tension (IFT) between oil and water [2]. Ultra low IFT is further employed to mobilize trapped oil. It is well established that surfactant systems are sensitive to temperature and salinity [3], and widely accepted that detailed knowledge regarding the phase behavior of the oil/ surfactant/ water system is necessary to design an efficient surfactant flood.

Studies of the design of surfactants applicable for EOR have been carried out in several research groups. Anionic surfactants are those most commonly used for many applications (detergents, foaming agents, wetting agents etc.) and are therefore potential EOR candidates - especially due to their low cost. Levitt et al. [4] and Flaaten et al. [5] report that branched alcohol propoxylate sulfate and internal olefin sulfonates are promising candidates with respect to both oil recovery and surfactant retention in the cores, where both studies show high oil recovery and low surfactant adsorption. Wu et al. [6] show that the average alkyl chain length and the number of propoxylate groups may influence optimal salinity, IFT and adsorption.

The phase behavior of surfactant systems has been studied both experimentally [e.g. 7, 12-14] and theoretically [e.g. 8-16] in several projects and it varies whether the temperature and pressure dependency is included and considered as influencing parameters. Among the theoretical attempts to develop an approach to predict the influence from pressure accurately there are so far no true

success regarding predictions of the phase behavior and as the understanding of the exact mechanisms, which is caused by high pressures, is poor this task is an ongoing challenge in the oil recovery field. Surfactant systems used for EOR will necessarily be at high (reservoir) pressures and improved understanding of the effect of high pressure will be beneficial in order to design optimized oil recovery processes.

The experiments in this study have been carried out in a high pressure DBR JEFRI PVT cell with the primary aim of ascertaining the influence of pressure on the phase behavior of a surfactant system and further to obtain an improved understanding of the influencing mechanisms. The model surfactant system water/ sodium chloride (NaCl)/ sodium dodecyl sulfate (SDS)/ 1-butanol/ heptane was chosen. In the work by van Nieuwkoop and Snoei [7] this system has been operated and investigated thoroughly at ambient temperature and pressure. van Nieuwkoop and Snoei [7] observed that the three-phase region depends strongly on the overall composition parameters, such as salinity, water oil ratio (WOR), surfactant alcohol ratio (SAR) and total surfactant concentration. Sassen [12] has also studied this surfactant system as well as the subsystems influenced by pressure. Influence from pressure showed considerable influence on the phase behavior, where the surfactant system is studied at constant SAR and WOR, with both constant and varying salinity. In this work the starting point is from the results from van Nieuwkoop and Snoei [7] and in contrast to or a continuation of Sassen et al. [12] the surfactant system is studied with varying WOR and kept at constant SAR and constant salinity throughout all experiments. Several investigations of the phase behavior of water + oil + surfactant + alcohol systems are carried out at atmospheric pressure [9, 10], and there is no consensus on the exact significance of the influence from pressure on such systems or how pressure possibly changes the phase behavior. Surfactant systems are in general classified according to the so-called Winsor type systems as shown in figure 1 and described by Nelson and Pope [11], where the desired ultra low IFT is achieved with the formation of a microemulsion phase, which is the Winsor III situation.
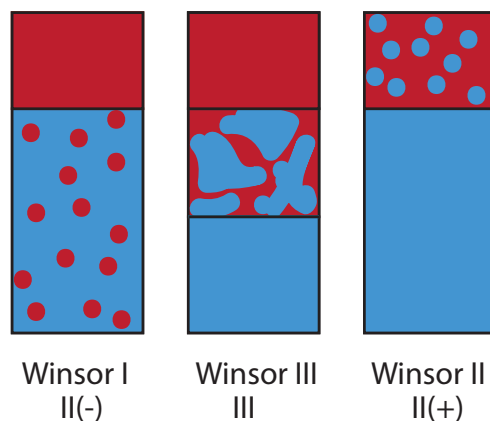
Figure 1. Drawing of the Winsor type system [11] showing how surfactants are usually considered. From left to right is; Winsor I where oil/water microemulsions are present below the oil phase, Winsor III where the microemulsion phase is present as a third phase and finally Winsor II water/oil emulsions are present above the water phase.

This phase behavior study is based on the diverse opinions from literature as to whether elevated pressure has a significant effect on the multiphase region. Initially the purpose of the phase behavior study was to establish if pressure induces a change in the phase behavior of the system. Subsequently the model system was tested with different overall compositions at several different temperatures and pressures.

2 Experimental and Equipment

This experimental study consists mainly of a thorough investigation of phase equilibrium study in the surfactant system mentioned, specifically the number of phases present and the volumes of the phases.

2.1 Chemicals

The system of pure heptane (SIGMA, Aldrich), sodium dodecyl sulfate (FLUKA, > 99%), 1-butanol (SIGMA, Aldrich), distilled water (from tap) and sodium chloride (FLUKA, > 99.5%) was used in the experimental work. All chemicals were used as purchased without any further purification. This system is used as a model system where several different compositions were examined. As the system is already described at room temperature and atmospheric pressure by van Nieuwkoop and Snoei [7] a good reference point is established in order to ascertain the effect of temperature and pressure.

2.2 Preparation of the Starting Composition of the Samples

All chemicals were weighed on an analytical balance and transferred into a flask and stirred well together until SDS and NaCl were dissolved in the water/1-butanol/oil solution. To perform accurate phase volume measurements it was found that a total volume of 50-100 ml is necessary for each sample. Therefore all starting composition of the samples was prepared with a starting volume of 60-80 ml. The overall component weight fractions of the different surfactant systems are shown in table 1, 2 and 3. The surfactant alcohol ratio (SAR) is held constant in all experiments at 0.5; similarly the overall salinity is kept constant at 6.56%. The water oil ratio (WOR) is varied from experiment to experiment.

Table 1. Overview of the overall composition of the systems in sample 1-4 for the system water/SDS/1-butanol/heptane/NaCl (6.56 wt %) and the measured phase volume fractions of the present three phases before the high pressure operation was started.

	Compositions in weight fractions				
Sample	Water	SDS	1-Butanol	Heptane	NaCl
1	0.6156	0.0254	0.0509	0.2649	0.0432
2	0.5848	0.0242	0.0483	0.3016	0.0411
3	0.5570	0.0230	0.0460	0.3348	0.0391
4	0.5317	0.0220	0.0439	0.3651	0.0373
	Phase volume fractions at start conditions (P = 1 bar and T = 40˚C)				
	Lower		Middle		Upper
1	0.451		0.283		0.266
2	0.383		0.291		0.326
3	0.318		0.312		0.370
4	0.204		0.378		0.417
Note:	Sample 1-4 was operated at different pressures from 1-400 bar and at different temperatures from 40-60˚C.				

Table 2. Overview of the overall composition of the systems in sample 5-9 for the system water/SDS/1-butanol/heptane/NaCl (6.56 wt %) and the measured phase volume fractions of the present three phases before the high pressure operation was started.

Compositions in weight fractions				
Sample	Water	SDS	1-Butanol	Heptane	NaCl
5	0.7710	0.0300	0.0600	0.0850	0.0540
6	0.7396	0.0288	0.0576	0.1223	0.0518
7	0.7106	0.0276	0.0553	0.1567	0.0497
8	0.6590	0.0256	0.0513	0.2179	0.0461
9	0.6359	0.0247	0.0495	0.2804	0.0445

Phase volume fractions at start conditions
(P = 1 bar and T = 40°C)

Sample	Lower	Middle	Upper
5	0.715	0.285	0
6	0.667	0.333	0
7	0.603	0.397	0
8	0.519	0.299	0.182
9	0.431	0.290	0.279

Note: Sample 5-9 was operated at different pressures from 1-400 bar to study the general phase behavior near the three phase area in the surfactant system.

Table 3. Overview of the overall composition of the systems in sample 10-15 for the system water/SDS/1-butanol/heptane/NaCl (6.56 wt %) and the measured phase volume fractions of the present three phases before the high pressure operation was started.

Compositions in weight fractions				
Sample	Water	SDS	1-Butanol	Heptane	NaCl
10	0.6517	0.0359	0.0713	0.1953	0.0457
11	0.6211	0.0342	0.0680	0.2331	0.0436
12	0.6070	0.0334	0.0665	0.2504	0.0426
13	0.4687	0.0258	0.0513	0.4213	0.0329
14	0.4225	0.0233	0.0463	0.4783	0.0297
15	0.4406	0.0436	0.0888	0.3958	0.0313

Phase volume fractions at start conditions
(P = 1 bar and T = 40°C)

Sample	Lower	Middle	Upper
10	0.531	0.458	0
11	0.492	0.508	0
12	0.478	0.437	0.115
13	0.204	0.349	0.446
14	0.161	0.334	0.506
15	0.285	0.715	0

Note: Sample 10-15 was operated at different pressures from 1-400 bar to study the general phase behavior above, inside and below the three phase area in the surfactant system.

2.3 High Pressure Equipment

The phase behavior observations and the phase volume measurements are carried out in a DBR JEFRI PVT cell (model: JEFRI PVT 150-155 from D B Robinson). A detailed drawing of the cell is given in figure 2 and a photograph of the cell inside the oven is shown in figure 3. A complete description of the DBR JEFRI PVT cell has been given previously [12]. This high pressure equipment allows visual observation of phase behavior at elevated pressures and temperatures.
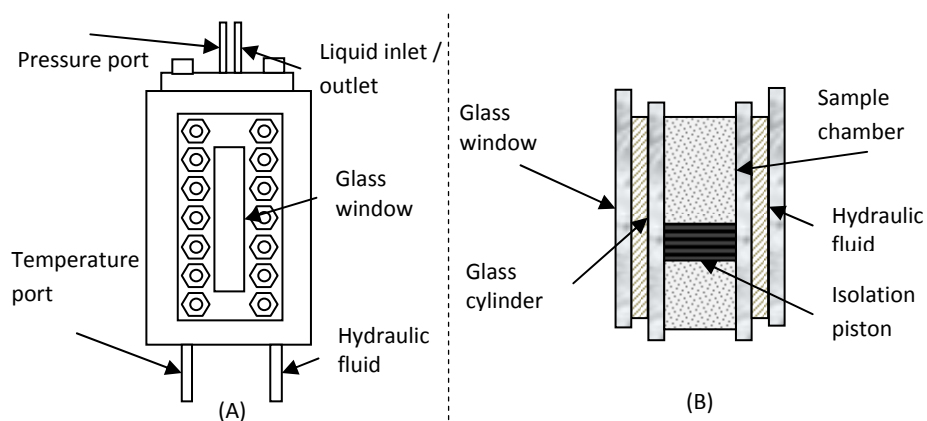
Figure 2. Experimental setup of the DBR JEFRI PVT cell. (A) is a sketch of the cell from the outside and (B) is a segment illustrating the construction of the cell from the inside, showing the isolation piston which moves up and down to adjust the pressure inside the sample chamber.


Figure 3. Picture of the DBR JEFRI PVT cell. This is high pressure equipment for phase behavior measurements at various temperatures and pressures. The surrounding steel is the inside of the temperature controlled forced air oven. The cell is monitored on a rocking mechanism suitable for mixing the systems inside the sample chamber. The glass window in the middle allows visual observations.

The PVT cell is operated at temperatures from 40 ˚C up to 180 ˚C and at pressures up to 700 bar. Through the glass window it is possible to follow the equilibration of the particular system as well as the heights of the phases. As seen in figure 4 the equilibrated liquid-liquid system is seen through the glass window, three different situations are pictured. These are measured using a micrometer from 'Precision Tools & Instrument C˚ LTD, Surrey, England'.

2.4 Experimental Procedure

Phase behavior studies have been carried out on a surfactant system. The initial composition of the system is changed several times during the experiments on the DBR JEFRI cell. This variation generates starting compositions with a different number of phases (initially at ambient conditions) in the surfactant system.

a.   P=78 bar and T=45 ˚C

b.   P=50 bar and T=40 ˚C

c.   P=150 bar and T=40 ˚C
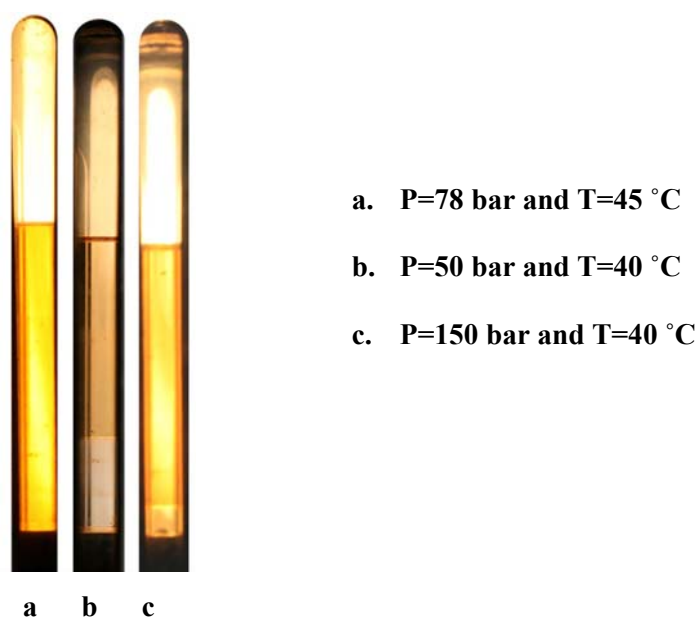
Figure 4. View of the surfactant system from the glass window at the DBR JEFRI cell. A, B and C depicts different equilibrations of the surfactant system, with different thermodynamic conditions. Red circles are at the interfaces between the present phases in each system. In A, a two phase system is present with an upper oil phase in contact with a microemulsion phase. In B the surfactant system is present with three phases; an upper oil phase, microemulsion phase in the middle and a lower water/ brine phase. In situation C the surfactant system shows a decrease in the lower water phase volume, compared to B, due to the increase in pressure. The decrease in temperature, comparing A to B and C, changes the number of present phases from two to three.

Thus the surfactant system has been composed such that it has been operated from the possible two phase area (II+), with microemulsion in contact with the lower aqueous phase, towards the three phase envelope and further from the three phase envelope towards the other two phase area (II-), with a microemulsion phase in contact with an upper oil phase. From the observation phase diagram in figure 5 the different starting compositions can be followed and the three phase area (III) is shown.

Samples are initially prepared in the laboratory at atmospheric pressure and room temperature, and then transferred into the sample chamber in the DBR JEFRI PVT cell by creating vacuum inside the cell and then sucking the prepared sample into the sample chamber. Operations were originally started at the component composition given for sample 1 in table 1, sample 5 in table 2 and sample 10 in table 3. The subsequent compositions in each of the three tables are then formed by direct addition of components into the sample chamber.
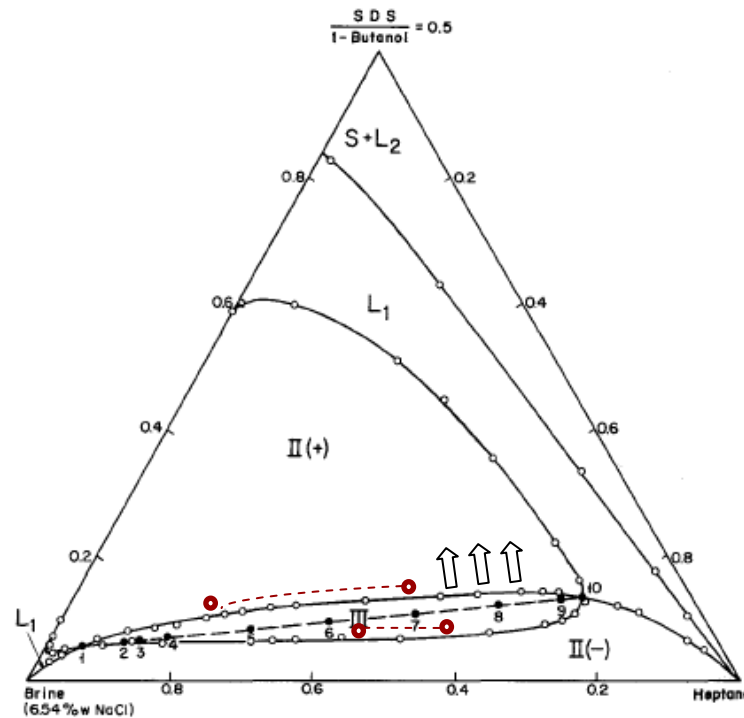
Figure 5. Phase diagram of the system sodium dodecyl sulfate/ 1-butanol/brine/ heptane, composed from the observations from the work conducted by van Nieuwkoop and Snoei 1985 [7]. The figure shows a pseudo ternary phase diagram of the present system. Furthermore the red bold circles mark the compositions at which the system has been operated in the DBR JEFRI PVT cell, where significant change in phase behavior was observed. The red dashed lines are drawn to emphasize the effect observed due to increase in both pressure and temperature.

Each sample was processed as follows: First the temperature and pressure were set. Samples are tested at pressures in the range from 1 bar to 400 bar and temperatures in the range of 40 ˚C to 60 ˚C. Initial conditions for a sample were pressure at 1 bar and temperature at 40 ˚C. The second step in the operation was to ensure thorough mixing of the sample. This was accomplished by activating the cell's rocking mechanism for 30 minutes. Thereafter the system is left to equilibrate. It was found sufficient to leave the system to equilibrate for 2 hours. After this time the phase volumes were no longer changing, the samples were completely separated, and all phases were transparent. Finally, the phase heights were measured through the observation window. Phase volumes were calculated from the measured heights and the internal diameter of the sample chamber. At this point the number of phases and how they appeared (color) were noted. Hereafter the pressure was increased, typically in steps of 100 bar up to 400 bar and the procedure for rocking, equilibrating the system, calculating the phase volumes from the measured heights and observations of the appearance of the present phases was repeated at least at every 100 bar. This is considered as a complete sample study in the chosen pressure range.

In a few cases changes from increase in temperature were also studied, where the temperature increase was applied after a complete study in the chosen pressure range. Also the addition of components to change the overall composition of the system was applied after a complete study in the chosen pressure range and then followed by another complete study of effect of pressure on the surfactant system with the new overall composition.

2.4.1 Experiments at Room Temperature

Initially four experiments, representing different locations and different phase volumes in the surfactant system in figure 5, were conducted at conditions with atmospheric pressure and room temperature. This was in order to confirm the reported observations by van Nieuwkoop and Snoei [7]. Our study was in complete agreement with the reported observations for the compositions tested.

2.4.2 Experiments at Elevated Pressures and Temperatures

As the equipment does not allow temperatures lower than 40 ˚C it was not possible to study the system at room temperature and different pressures. Therefore it was initially confirmed that the system given by sample 1 in table 1, despite the temperature increase from 23 ˚C to 40 ˚C, still showed the same phase behavior (same number of present phases and same measured phase volumes). One complete cycle of measurements for any of the 15 samples in table 1, 2 and 3 begins at a pressure of 1 bar. The pressure is then increased, in most cases, to 100 bar, then 200 bar, then

300 bar and finally 400 bar. At each pressure the surfactant system is observed through the observation window, and the separation is followed. When equilibrium has been reached, the phase volumes of the present phases are measured.

In the case of samples 1 and 4 the effect of an increase of temperature was also examined. The temperature was increased from 40 ˚C to 60 ˚C and then reduced to 50 ˚C. The temperature variation was applied after a complete range of pressure experiments at 40 ˚C and followed by another complete range of pressure experiments at the new temperature.

3 Results and Discussion

The effect of pressure on the surfactant system water/ NaCl/ SDS/ 1-butanol/ heptane is an example of a surfactant system which is influenced from high pressures, as would be experienced at reservoir conditions in EOR operations. The understanding of the exact effect of pressure and how it influences the phase behavior is however, poorly examined. This work is the results of an experimental study of the exact changes in the phase behavior in the surfactant system at various thermodynamic conditions.

3.1 Phase Volumes from the DBR JEFRI PVT Cell

The volume of each of the phases present at a particular set of conditions, (composition, temperature, pressure), was obtained by measuring the height of the phase through the glass window. The total volume was also checked to ensure that no leakage had occurred. Figure 6, 7 and 8 shows measured phase volumes for each phase as a function of pressure for various cases, featuring different overall compositions and in some cases different temperatures.

The top part of figure 6 shows results for sample 1 at different temperatures (40 ˚C, 53 ˚C and 60 ˚C), where the neither the influence from pressure or temperature changes the observed phase volumes. The middle of figure 6 shows the results obtained for sample 2, 3 and 4 at constant temperature (40 ˚C), as a function of pressure. It is clearly seen that sample 2 has similar phase behavior as sample 1, regarding the phase volumes. In the case of sample 3 when increase in pressure has taken place, it is observed that the volume of the water phase (blue line with squares) begins to decrease along with an increase in the middle phase volume. This induces that the solution, dependent on the pressure, goes toward Winsor type I system with a lower microemulsion phase. Considering the results for sample 4, the influence from pressure becomes very significant, as the volume of the water phase decrease to zero very dramatically at 156 bar. The lower graph in figure 6 only concerns the overall composition of sample 4 at three different temperatures (40 ˚C, 45 ˚C and 50 ˚C).
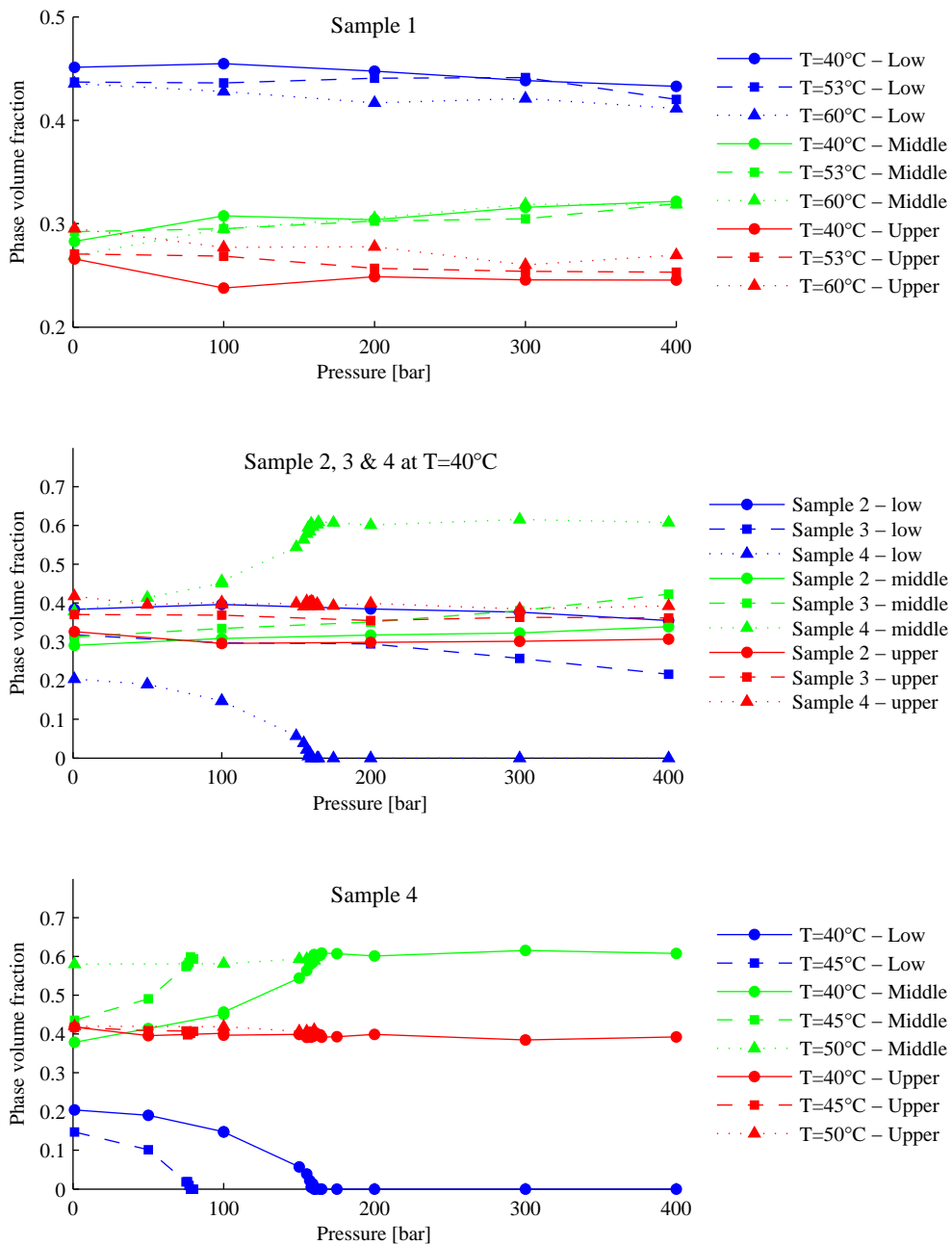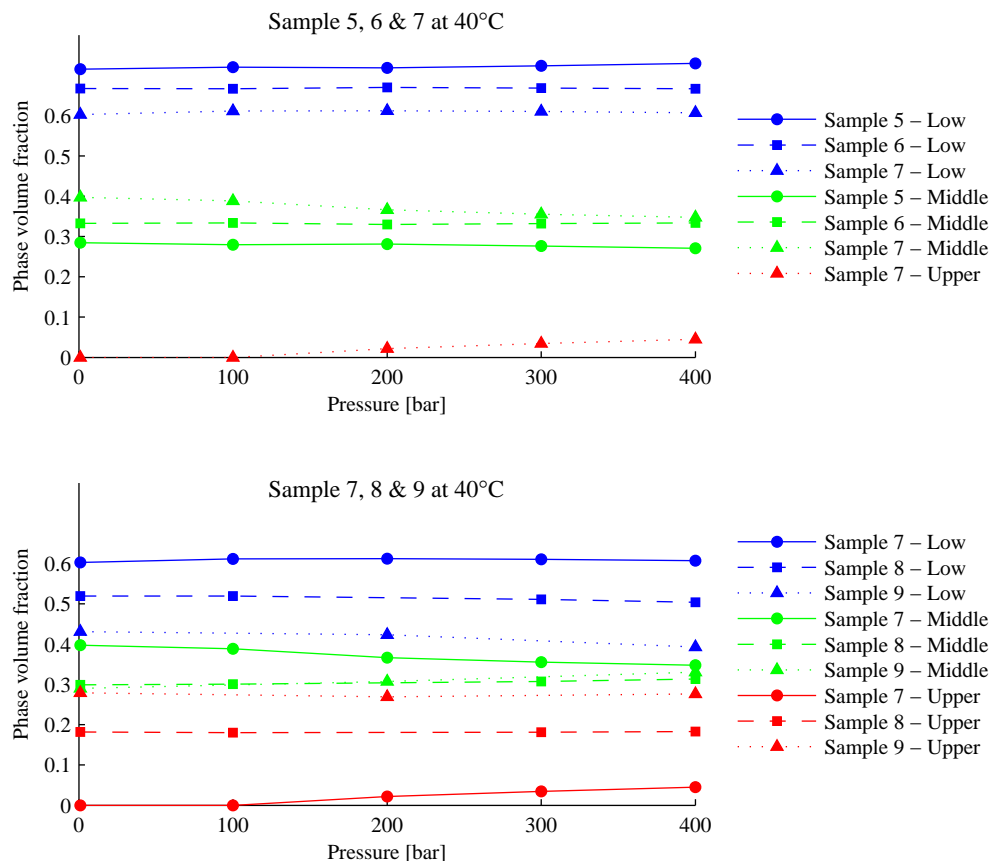
Figure 6. Graphical representation of the phase volume measurements obtained from the DBR JEFRI cell. Blue lines are water volume, green lines are oil volume and red lines are the middle phase volume. Sample 1 is the same system at varying temperatures with no significant changes in the phase volumes. Sample 4 is compositional wise another system compared to sample 1. Sample 4 is also at varying temperatures. In this case the pressure clearly has an effect on the observed phase volumes, as the water phase disappears with increasing pressure. Sample 2, 3 and 4 are plotted together to illustrate how close the phase volume measurements are until the break point where the effect from pressure changes the phase behavior of the system completely, which is the case for sample 4.

The addition of an increase in temperature together with the elevated pressure clearly enhances the decrease in the water phase volume and the increase in the middle phase volume, which occurs at 156 bar at 40 ˚C, at 78 bar at 45 ˚C and simple has vanished completely in case of an increase to 50 ˚C.

Figure 7 shows the results of an, compositional wise, other starting point of the surfactant system, with a two phase system at ambient conditions. All samples presented in figure 7 are at the same temperature, 40 ˚C as a function of pressure. The top of figure 7 shows the results for sample 5, 6 and 7. Both sample 5 and 6 shows similar results regarding the measured phase volumes of the two present phases; the water phase and the upper microemulsion phase. In the case of sample 7, the oil phase appears with the increase in pressure between 100 bar and 200 bar and a slight decrease in the upper microemulsion phase is observed as well.

Compositional the three samples have been changed in the WOR by increasing the amount of heptane present in the system. In the lower part of figure 7, the results of sample 7, 8 and 9 are shown. It is noticeable to see that in the case of sample 7 the oil phase appears with a rather small phase volume. In the case of sample 8 the oil phase and thus a middle microemulsion phase is well established. Sample 9 shows a further increase in the oil phase and at this point the system seems independent on the influence from pressure, as the phase volumes of all three phases is almost constant at all measured pressures.

Figure 8 shows the results of the last set of samples, which are carried out at constant temperature at 40 ˚C as a function of pressure. In the top part of the figure the results for sample 10, 11 and 12 are shown. They are compositionally different as the amount of heptane is increased. The starting point for these samples is similar to that of the samples from figure 7, as the surfactant systems are a two phase system at ambient conditions, however, the WOR is different. Sample 10 and 11 show no significant changes in the phase volumes due to the increase in pressure. In contrast the influence of increased pressure on sample 12 is resulting in the appearance of an additional third phase, as the oil phase volume increases with increasing pressure. Similar to the earlier observations, the volume of the water phase remains almost constant and the volume of the microemulsion phase decreases with the increase in pressure. The middle part of figure 8 shows the results for sample 12, 13 and 14. Overall composition in these samples is different, as the heptane amount is increased with the sample number.

Figure 7. Graphical representation of the phase volume measurements obtained from the DBR JEFRI cell. Blue lines are water volume, green lines are oil volume and red lines are the middle phase volume. Sample 5, 6 and 7 are plotted together at constant temperature at 40 ˚C. All three samples are compositionally different as the amount of heptane is increased through sample 5, 6 and 7. It is seen that the phase volumes are relatively constant until the break point in sample 7, where the microemulsion phase arises as the third phase due to pressure change. At the same time the oil phase volume decreases and the water phase volume line is remaining the same.

In the lower graph sample 7, 8 and 9 are plotted together showing that the middle phase is well established and that the volume increases as more heptane is added.

As just described, the case of sample 12 shows change in phase behavior with increase in pressure, as the volume of the oil phase increases. Regarding sample 13, it is seen that the three phases are measured at all investigated temperatures and the phase volumes of each phase does not change remarkably with the change in pressure. Considering sample 14, this is quiet another story, as this sample suddenly changes from three phases to two phases at a pressure of approximately 150 bar. Simply the water phase vanishes from the system. Finally, the result for sample 15 is shown in the lower part of figure 8. The phase behavior is clearly influenced by the increase of pressure, as the oil phase appears around 300 bar and the oil phase volume increases significantly when pressure is further increased. This final observation emphasize that the pressure dependency is correlated to

composition of the surfactant system and small compositional changes can cause a much more sensitive system with regard to the phase behavior when physical conditions, such as temperature and pressure, are changed.

3.2 Pressure and Temperature Dependency

As already shown, the number of phases and their volumes are dependent on the pressure of the system for various compositions. In the case of sample 4 and 14 the surfactant system goes from a three phase system to a two phase system consisting of an upper oil phase and a microemulsion phase with oil emulsions in excess of water, which graphically shown in figure 6 and 8, respectively. In the case of sample 7 and sample 12 the surfactant system begins as a two phase system, with the microemulsion phase of water emulsions in excess of oil and a lower aqueous phase, changing to a three phase system, graphically depicted in figure 7 and 8. The denominator for all 4 mentioned samples are that the observed changes in phase volumes and thus in number of present phases are the supplied increase in pressure.

It is noticeable, that the effect on the surfactant system from pressure occurs rather rapidly. In almost all the samples the significant effects from pressure arise after several more or less constant phase volumes and suddenly the system changes phase behavior dependent on the pressure. As the presence of a microemulsion phase is crucial for industrial applications such as surfactant flooding for enhanced oil recovery, this observation is worth bearing in mind, since it is likely that the pressure conditions present in an oil reservoir and during oil recovery with surfactants could yield the possibility of such phase behavior.

To confirm the observed pressure effects, experiments were repeated with the same results. It was also verified that the change in number of phases present was a reversible phenomenon, i.e. the effects obtained by increasing pressure could be reversed by decreasing the pressure again.

In addition to the effects of pressure on phase behavior, it is well known that temperature also affects the phase behavior of a surfactant system. (For example it has been established that for example the optimal salinity of injection water will change depending on the temperature. In agreement with previous observation, it is noticeable that in the case of sample 4, seen in figure 6 at the bottom, the change in phase volumes and the change in number of phases present become more significant when temperature is increased along with the increase in pressure.
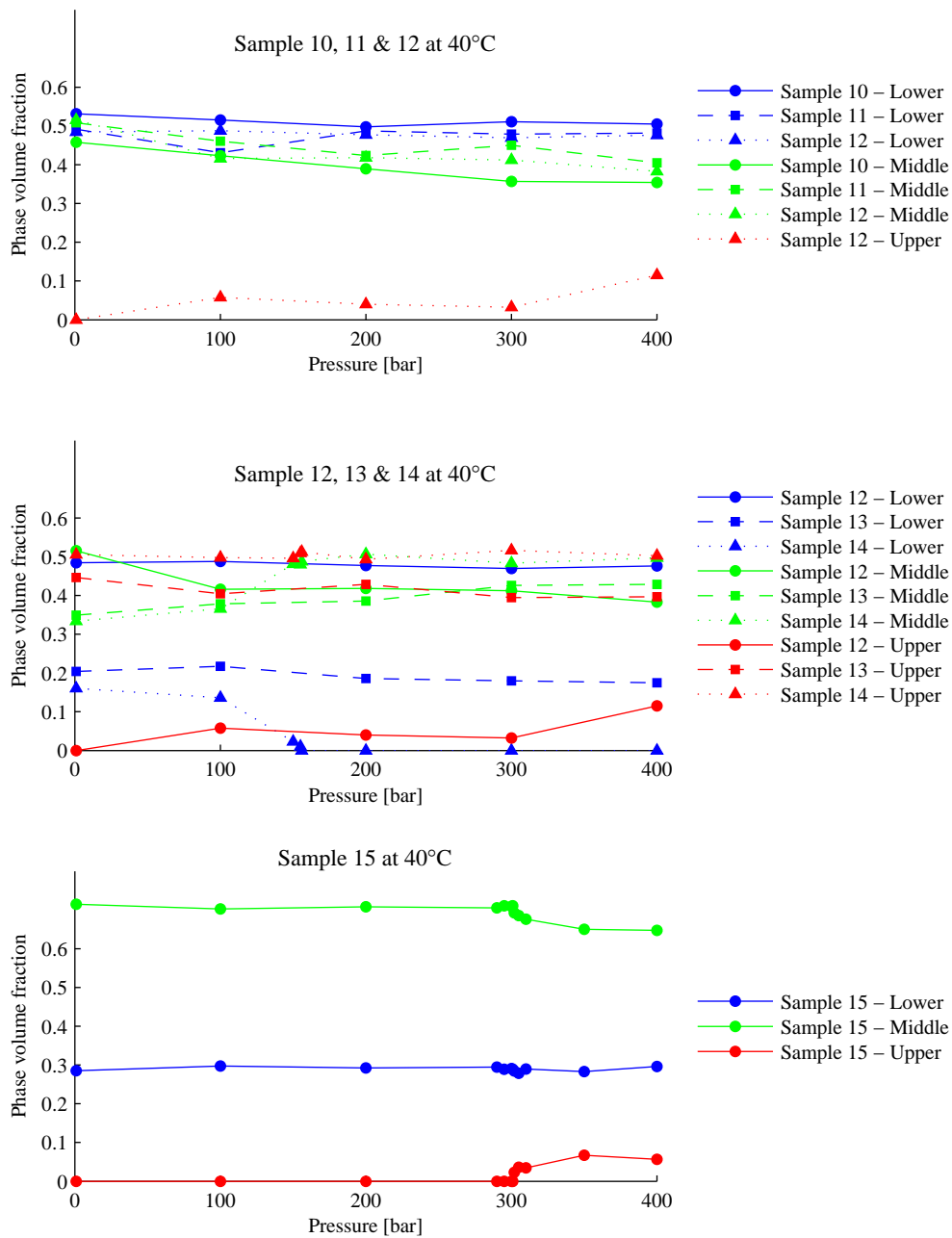
Figure 8. Graphical representation of the phase volume measurements obtained from the DBR JEFRI cell. Blue lines are water volume, green lines are oil volume and red lines are the middle phase volume. Sample 10, 11 and 12 are compositionally different. In the case of sample 12 the pressure change results in the formation of a middle phase region, which increases as the pressure is increased.

In the plot with sample 12, 13 and 14, at constant temperature at 40 ˚C, the pressure effect changes the systems from the two phase (Winsor II) region to the middle phase region (Winsor III) in the case of sample 12 and from the middle phase region to the two phase region (Winsor I) in the case of sample 14.

Sample 15 clearly shows the effect from pressure, which changes the present phase behavior in the surfactant system.

3.3 Displacement of Expected Three Phase Area

In the work carried out by van Nieuwkoop and Snoei [7], they reported a pseudo-ternary phase diagram based on their observations. From the diagram the studied surfactant system are expected to show a three phase area which is sandwiched between the two phase area with water in oil emulsions (area II+) and water, and another two phase area with oil in water emulsion ins (area II-). This diagram is pictured in figure 5. Comparison of our results, at varying overall compositions with different WOR, to those presented in figure 5 shows that the three phase area is displaced upwards and to the left as the system pressure increases. Furthermore the obtained results induce that the shape and volume of the three phase envelope remains unchanged. As this study does not cover a very detailed work on the influence of pressure and temperature together, it is not to conclude how these parameters together would change the two and three phase areas in the pseudo-ternary diagram. However, one single system was studied for the combined effects, sample 4, depicted in figure 6. From that single set of compositions the effects of combined increase in temperature and pressure seems rather significant, as a increase in temperature of on 5 ˚C cause an even more significant change in the phase behavior compared to the same system, where only pressure is elevated.

4. Conclusions

1. An atmospheric pressure study at room temperature of the surfactant system verified the observations reported by van Nieuwkoop and Snoei [7].

2. The experimental studies on the DBR JEFRI PVT cell show that at the studied component compositions of the surfactant system, the phase behavior changes significantly dependent on the pressure. The number of phases was changed from either a two phase system (Winsor II) to a three phase system (Winsor III) or a three phase system (Winsor III) to another two phase system (Winsor I) as the pressure on the system was increased.

3. Further studies also indicate that temperature enhances the effect observed from pressure, as combined increase in temperature and pressure resulted in a shift in number of phases at a significant lower pressure compared to the same study with no temperature increase.

4. High pressure displaces the location of the three phase area, which is the desired area for surfactant flooding. It is within this area, that the microemulsion phase is present, which is crucial to mobilize the oil in this oil recovery technique.

5. In this work it is clearly shown that the effect of pressure on the phase behavior of a surfactant system is profound.

Acknowledgements

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Paper II

Advanced waterflooding in chalk reservoirs: Understanding of underlying mechanisms

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Advanced Waterflooding in Chalk Reservoirs: Understanding of Underlying Mechanisms

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Abstract

Over the last decade, a number of studies have shown SO_4^{2-}, Ca^{2+} and Mg^{2+} to be potential determining ions, which may be added to the injected brine for improving oil recovery during waterflooding in chalk reservoirs. However the understanding of the mechanism leading to an increase in oil recovery is still not clear. In this work the crude oil/seawater ions interaction at different temperatures, pressures and sulfate ion concentrations is investigated. Our results show that sulfate ions may help decrease the crude oil viscosity when brine is contacted with oil under high temperature and pressure. We have also observed formation of a microemulsion phase between brine and oil with the increase in sulfate ion concentration at high temperature and pressure. In addition, sulfate ions can reduce interfacial tension (IFT) between oil and water. We propose that the decrease in viscosity and formation of a microemulsion phase could be the possible reasons for the observed increase in oil recovery with sulfate ions at high temperature in chalk reservoirs besides the mechanism of the rock wettability alteration, which has been reported in most previous studies.

Key Words:

Chalk reservoirs, waterflooding, emulsification, viscosity, IFT, oil recovery

1. Introduction

More than half of the world's oil is found in carbonate formations (chalk and limestone)[1]. Due to the potential for enhanced oil recovery (EOR), different techniques have been applied in order to

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improve oil recovery from carbonate formations. During the last decade, injection of brines with high salinity has been developed into an emerging EOR technology for chalk reservoirs that does not require toxic or expensive chemicals [2-7]. Although it is widely accepted that high salinity brine may increase the oil recovery for chalk reservoirs [2, 3, 7], understanding of the mechanism of this increase is still developing. To understand this advanced waterflooding process, an extensive research program has been carried out covering a broad range of disciplines within colloid and surface chemistry, the thermodynamics of crude oil and brine, as well as their behavior in porous media.

The major focus of the research has been core flow and imbibition experiments. Bagci et al. [8] studied the effect of brine composition on oil recovery by waterflooding and tested injection of NaCl, KCl, $CaCl_2$ and mixed brines such as 2 wt% KCl + 2 wt% NaCl and 2 wt% KCl + 5 wt% $CaCl_2$. The highest oil recovery was observed for 2 wt% KCl brine. Extensive laboratory research was carried out by Austad and co-workers in order to understand improved oil recovery from chalk using modified sea water [5, 7, 9-11]. It was reported that SO_4^{2-} is a potential determining ion for improving oil recovery in chalk reservoirs. This ion must act together with Ca^{2+} and Mg^{2+} because sulfate alone is not able to increase the spontaneous imbibition. In all the presented cases, wettability alteration was proposed as a reason for improved oil recovery.

| A | B | C |
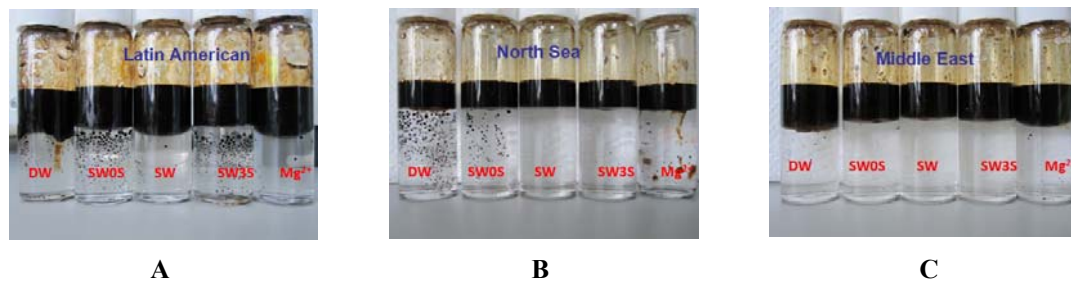
Figure 1. Different crude oils and brine samples after stirring them @ 1000 rpm for 15 minutes at room temperature. The sample bottles are filled with crude oil and brine solution and have been equilibrating for two to three hours. In each picture; A, B and C, the same crude oil is mixed with different brine solutions and after equilibration the sample bottles are compared to define if any phase behavior has changed simply due to the content of the brine solutions.

Zeta potential, contact angle and interfacial tension (IFT) measurements were also carried out with brine solutions of different Ca^{2+}, SO_4^{2-} and Mg^{2+} ion concentrations. Strand et al. [5] carried out zeta potential measurements on mild Stevns Klint chalk suspended in brine solutions of different ionic ratios of Ca^{2+} and SO_4^{2-}. It was reported that surface charge is dictated by the relative concentration of Ca^{2+} and SO_4^{2-} . Gomari et al. [12] performed zeta potential measurements with calcite powder. Zeta potential is decreased from +15.03 to +1.23 mV for the sodium sulfate

solution and is increased from +15.03 to 17.7 mV in case of magnesium chloride solution. This also documented the affinity of these ions towards the calcite surface. Tweheyo et al. [6] and Gomari et al. [12] carried out contact angle measurements on calcite surface modified with oil and then exposed to brines of different compositions at different temperatures. It was observed that Ca^{2+}, SO_4^{2-} and Mg^{2+} are potential determining ions and these ions become more effective as temperature increases. It has been established in the literature that surface forces play an active part in oil production. The magnitude of these forces is partly determined by the interfacial tension value [13]. Zhang et al. [14] carried out IFT measurements between oil and brine (with different concentration of SO_4^{2-}) at room temperature. It was observed that sulfate ions did not contribute to decreasing the IFT.

Most of above reported experimental work has been carried out using crude oil/brine/rock or brine/rock systems. The main conclusion from this extensive work was that it is the affinity of potential determining ions for the chalk surface which increases with temperature, and that this helps to improve oil recovery. However, this conclusion has not been confirmed by studies of the oil/brine interactions, which might also be contributing to recovery increase. In the study presented here we demonstrate that these interactions may also be partly responsible for the increase in oil recovery.

We have studied crude oil/ brine interactions at room temperature in normal glassware and also in a DBR JEFRI PVT cell at the different temperatures and pressures. Three crude oils have been used for the study. Detailed measurements of density, viscosity and water content before and after the experiment are presented. We also carried out IFT measurements at room temperature. The details are given below.

2. Experimental

2.1 Crude Oil

We used three natural crude oils from three different parts of the world: a North Sea crude oil; a Latin American crude oil and a crude oil from a Middle East field. No model oil was used in this study, since the goal was to study more realistic fluid/fluid interactions.

Acid and base numbers of the crude oils were measured using Metrohm 702 SM Titrino by the methods developed by Fan et al. [15](the modified versions of ASTM D2896 for the base titration and ASTM D664 for acid number titration). Density, acid number, base number and viscosity of the crude oils are given in Table 1.

Table 1. Crude oil properties.

Crude Oil	Density @ 20 °C [g/cm^3]	Acid Number [mg KOH/g oil]	Base Number [mg KOH/g oil]	Asphaltene [%]	Viscosity [cp]
Latin America	0.846	0.163	0.563	3.43	24.4
North Sea	0.847	0.095	2.442	0.302	8.837
Middle East	0.844	0.093	0.644	1.093	10.538

Table 2. Brine compositions.

Component	SW0S [mol/l]	SW0.5S [mol/l]	SW [mol/l]	SW1.5S [mol/l]	SW2S [mol/l]	SW2.5S [mol/l]	SW3S [mol/l]
Na^+	0.368	0.363	0.358	0.353	0.348	0.343	0.337
K^+	0.010	0.010	0.010	0.010	0.010	0.010	0.010
Mg^{2+}	0.045	0.045	0.045	0.045	0.045	0.045	0.045
Ca^{2+}	0.013	0.013	0.013	0.013	0.013	0.013	0.013
Cl^-	0.492	0.463	0.434	0.405	0.376	0.347	0.317
HCO_3^-	0.002	0.002	0.002	0.002	0.002	0.002	0.002
SO_4^{2-}	0.000	0.012	0.024	0.036	0.048	0.060	0.072
TDS [g/l]	33.39	33.39	33.39	33.39	33.39	33.39	33.39

2.2 Brine Solutions

The synthetic brine solutions were prepared by adding different amounts of NaCl, NaHCO$_3$, KCl, MgCl$_2$.6H$_2$O, CaCl$_2$.2H$_2$O and Na$_2$SO$_4$ to the distilled water. Seven brine solutions with different sulfate concentrations were prepared. The first brine solution is synthetic seawater without sulfate ions (SW0S); the second solution is synthetic seawater with normal sulfate ions (SW). The detailed composition and names of all seven brine solutions is given in Table 2. In this Table, various brines are termed as SWXS. The notation X represents relative concentration of sulfate ions related to SW (so for example SW2.5S was brine containing 2.5 times more sulfate than SW). The total dissolved solid for all the brine solutions was made the same by adjusting the quantity of NaCl. All the brine chemicals were delivered by Fluka and have a purity of $\geq$ 99.5%.

pH measurements of the brine solutions were carried out before and after the experiment in the PVT cell. The radiometer analytical 'Red Rod' combined pH electrode was used to measure pH.

2.3 Crude Oil/Brine Interaction Experiment at Room Temperature

The initial experiments were carried out at room temperature and atmospheric pressure. All three crude oils with five different synthetic brine solutions were used for this part of the study. The crude oils were mixed with the brine solutions such that each system consisted of 20 vol% (2 ml) of crude oil and 80 vol% (8 ml) of brine placed in a small sample bottle. The mixtures were thoroughly stirred at 1000 rpm for 15 minutes in a centrifuge. Afterwards the samples were left for two to three hours, until the crude oil and the brine solution separated. After equilibration, the system spontaneously divided into two phases; the oil phase on the top and the water phase on the bottom.

All five systems were photographed. The formation of emulsions was determined by visual observation of the interface between the crude oil and the brine. The mixtures after separation are shown in Figure 1. The viscosity and density of the crude oil were measured again after separation of the mixtures.

2.4 Crude Oil/Brine Interaction in DBR PVT JEFRI Cell

The high pressure experimental measurements were carried out in a DBR JEFRI PVT cell (model: JEFRI PVT 150-155 from D B Robinson), which is shown in detail in Figure 2. This is a high pressure cell allowing measurements for up to 700 bar and 180 ˚C. The DBR JEFRI PVT cell has been used in a variety of applications such as solubilities of supercritical fluids, VLE studies with gas condensates mixed with brine and other conventional PVT analysis of gas condensates and black oils[16, 17].

The main body of the DBR JEFRI PVT cell consists of a glass cylinder appropriate for measurements at high pressures and temperatures. The glass cylinder is 20.3 cm long and has an internal diameter of 3.2 cm, which gives a total working volume of 163 cm^3 inside the sample chamber. However, it is not recommended to use the full capacity of the working volume because there must be some room for expansion and compression of the sample. The cylinder is located inside a steel shell with vertical glass plates, which makes possible visual observations of the glass cylinder. An ISCO displacement pump is used to control the pressure inside the sample chamber via a floating isolation piston, which ensures that the pressure will remain constant. The entire PVT cell is installed on a rocking mechanism inside a temperature controlled forced air oven in the so-called air bath. The arrangement of the entire JEFRI cell in its rocking mechanism and inside the oven is showed in Figure 3. The rocking mechanism is used to ensure thorough mixing of the

samples in the glass cylinder. The temperature is read from a digital display mounted on the PVT cell and is measured with a PC100 with an accuracy of ±0.3 ˚C.
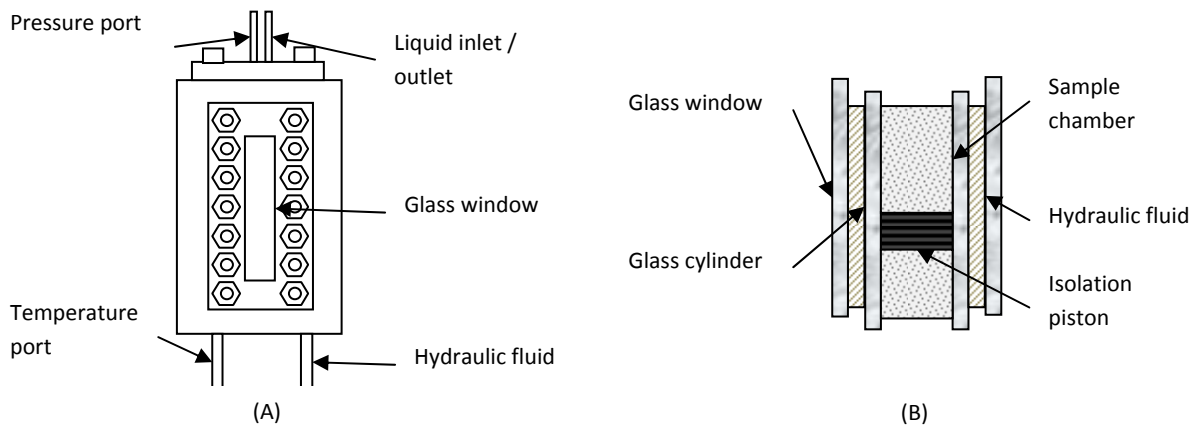
Figure 2. Experimental setup of the DBR JEFRI PVT cell. (A) is a sketch of the cell from the outside and (B) is a segment illustrating the construction of the cell from the inside.

Figure 3. Picture of the DBR JEFRI PVT cell. This is high pressure equipment for phase behavior measurements at various temperatures and pressures. The surrounding steel is the inside of the temperature controlled forced air oven. The cell is monitored on a rocking mechanism suitable for mixing the systems inside the glass chamber. In the middle the glass window is seen which allows visual observations.

In each experiment the water-oil ratio (WOR) is kept constant. Each system consists of 30 vol% crude oil (15 ml) and 70 vol% brine solution (35 ml). During the operation, the system is exposed to the following temperature and pressure conditions: (a) 37 ˚C, 15 bar (b) 37 ˚C, 300 bar (c) 110

˚C, 15 bar (d) 110 ˚C, 300 bar. When the PVT cell is loaded with the desired system, the rocking mechanism is activated for 30 minutes and thereafter the system is left to equilibrate for 30 minutes to 2 hours depending on the conditions. The equilibration period is recorded with video camera in order to evaluate the equilibration for different systems and to have pictures of the equilibrated system. Finally the heights of the phases inside the PVT cell were measured through the observation window using a micrometer from 'Precision Tools & Instrument C˚ LTD, Surrey, England'. Phase volumes were calculated from the measured heights of the phases and the known internal diameter of the cell. The interface between the oil phase and the brine phase was thoroughly studied for every test case to see if any emulsion phase is formed at the interface.

We used the Latin American and the Middle East crude oils for this part of the study where they were tested with the different brine solutions. The properties of the crude oils are presented in Table 1.

2.5 Viscosity Measurement

We measured the viscosity of the crude oil using an AMV-200 Automated Microviscometer. The viscometer operates on the rolling ball principle, according to which a ball is introduced into an inclined, sample-filled capillary. The time it takes for the ball to roll a fixed distance is measured and from this viscosity is calculated. After all the experiments were completed – both those in normal glassware at ambient conditions and those at higher temperature and pressure in the JEFRI cell - the oil samples were transferred from the cell into a sample bottle. The sample was left overnight to ensure complete separation of crude oil and water. Then approximately 3 ml of oil sample from the middle of the oil phase was used for viscosity measurements, as shown in Figure 4.
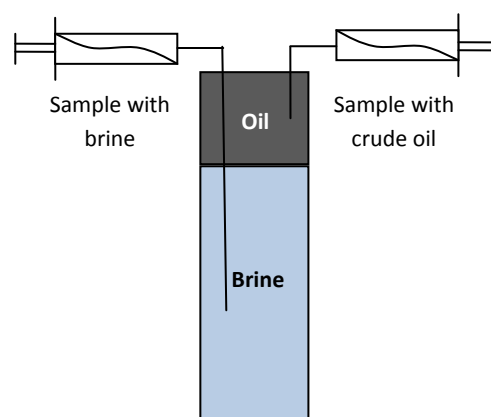
Figure 4. Illustration of how crude oil and brine samples are extracted for further viscosity examination.

2.6 Water Content Measurement in Crude Oil

We also measured the water content in the crude oil before and after the experiments in the JEFRI cell by the coulometric Karl Fisher (KF) titration method. A Metrohm 756 KF coulometer was used for this. Several reactions take place during titration of a sample. They can be summed up by the following overall reaction equation:

$$H_2O + I_2 + [RNH]SO_3 CH_3 + 2 RN \rightarrow [RNH]SO_4 CH_3 + 2[RNH]I$$

In the coulometric KF titration, the iodine needed is generated directly in the electrolyte by electrochemical means (electronic burette). The end point is indicated voltametrically by applying an alternating current of constant strength to a double platinum electrode. The reagent used for the titration is HYDRANAL-Coulmat AG from Fluka which is filled into the titration vessel. We also added 20 % toluene to the reagent to avoid contamination of the cell and electrode. This method is described in API Manual of Petroleum Measurement Standards (MPMS) chapter 10.9 and in ASTM D 4928.

The coulometer was calibrated by measuring the water content of a water standard Hydranal 34847 delivered by Riedel-de Haen after which the water content in the crude oil samples was measured. The measurements were repeated 2-3 times to confirm the repeatability of the results.

2.7 Interfacial Tension Measurement

Interfacial tension (IFT) was measured using a pendant drop method. This was conducted with a Data Physics OCA20 pendant drop apparatus, with a small drop of oil formed upwards at the tip of a stainless steel needle immersed in aqueous brine. IFT was calculated from the shape of the drop by fitting to the Young-Laplace equation. To get reliable results with the pendant drop method, a stable drop should be formed. For this, we used a needle of 0.63 mm diameter. IFT measurements were carried out only for the fresh Latin American crude oil and at ambient conditions.

3. Results

The effect of oil/brine interaction may be compared, to some extent, to the effects arising from surfactant/oil/brine systems characteristic of surfactant flooding. It is known that such systems are sensitive to salinity and temperature [18]. Our work indicates that similar effects are observed for selected crude oil/brine systems. Surfactants create emulsions, which reduce the interfacial tensions to ultra-low values. In this work it is examined whether emulsions are present in certain crude oil/brines systems. The effect of significant viscosity reduction of oil in contact with particular

brine is also observed but this strongly depends on the thermodynamic conditions, as well as on the brine and oil compositions

3.1 Room Temperature Crude Oil/Brine Study

A preliminary de-emulsification test was carried out initially with the Latin American crude oil and different brine solutions at room temperature. As shown in Figure 1a, in some of the sample bottles (SW0S and SW3S), dispersion of crude oil droplets in the brine solution is observed, while in other bottles formation of emulsions is observed and some crude oil is suspended in the brine solution. This emulsion formation is more noticeable in distilled water and in the brine saturated by Mg^{2+} ions. This indicates that salinity affects the emulsion formation, but no clear trend is observed at this stage. As some of the crude oil components may dissolve in the brine solution, the density and viscosity of the crude oil was measured before and after stirring in the sample bottle with different brine solutions. Table 3 provides the density and viscosity of the crude oils for the different tests. No significant change in viscosity and density of the crude oil was observed.

Table 3. Density and viscosity data of three crude oils after interacting with brine solutions at room temperature.

| Brine	Latin American		North Sea		Middle East	
	Viscosity (cp)	Density (g/cm^3)	Viscosity (cp)	Density (g/cm^3)	Viscosity (cp)	Density (g/cm^3)
Only Oil	24.4	0.877	13.5	0.845	12.7	0.865
DW	-	-	13.5	0.846	13.3	0.865
SW0S	24.4	0.897	13.9	0.847	12.6	0.866
SW	22.2	0.901	14.0	0.848	12.9	0.866
SW3S	24.2	0.894	14.1	0.848	13.2	0.884
0.1 M MgCl$_2$	24.7	0.890	13.1	0.849	13.9	0.866

In the next stage, the two other crude oils were studied. Figure 1b shows the result of the mixing tests for the North Sea crude oil and Figure 1c for the Middle East crude oil. In the case of the North Sea crude oil, no formation of emulsion was observed, although there is some dispersion of crude oil in the distilled water (DW) and in the SW0S brine. In the case of the Middle East crude oil, dispersion of the crude oil in the brine was not observed in any of the experiments. However, more noticeable emulsion formation is observed for DW and for the brine saturated with Mg^{2+} ions. No significant change in viscosity and density was observed for either of the crude oils after contacting with brine solutions, as presented in Table 3. With respect to emulsion formation, both the Middle East and the Latin American crude oil behave in the same way, i.e. both show more

noticeable emulsion formation with the DW and with the brine solution saturated by Mg^{2+} ions. The potential determining ions, especially the sulfate ions, did not help to de-emulsify the crude oil at room temperature, for any of the three crudes.

3.2 DBR JEFRI Cell Crude Oil/Brine Study

A preliminary test was carried out with the Latin American crude oil and DW as a base case. After loading the samples in the cell, the liquid-liquid system was rocked and then left to equilibrate. After that phase volumes were measured and photographs were taken at every temperature and pressure condition. More experiments were carried out for the same crude oil with other brine solutions in a similar way. The photographs taken of the various crude oil and brine systems are shown in Figures 5, 6, 7 and 8. Comparison of Figures 5 and 7, as well as Figures 6 and 8 clearly shows that increasing the temperature results in de-emulsification of the crude oil in almost all cases. Brine SW1.5S is an exception as this particular brine solution generates a less clear separation of the crude oil and brine. Interesting about this observation is that the same trend occurs very similar in at all conditions, which indicates that this sulfate concentration is responsible. At the lower temperature, T = 37 ˚C, sulfate ions at certain concentrations (SW to SW2.5S) help to clarify the oil/brine interface, see Figures 5 and 6. At a higher temperature, T = 110 ˚C, sulfate does not de-emulsify the oil at all, see Figure 7 and 8. We measured the phase volumes at every test conditions, but no significant change was observed at any combination of the pressure and temperature conditions. The observed formation of emulsions has been of such a small volume, that it has not been possible to make useful measurements of their volumes. It was only possible to detect through the used microscope.
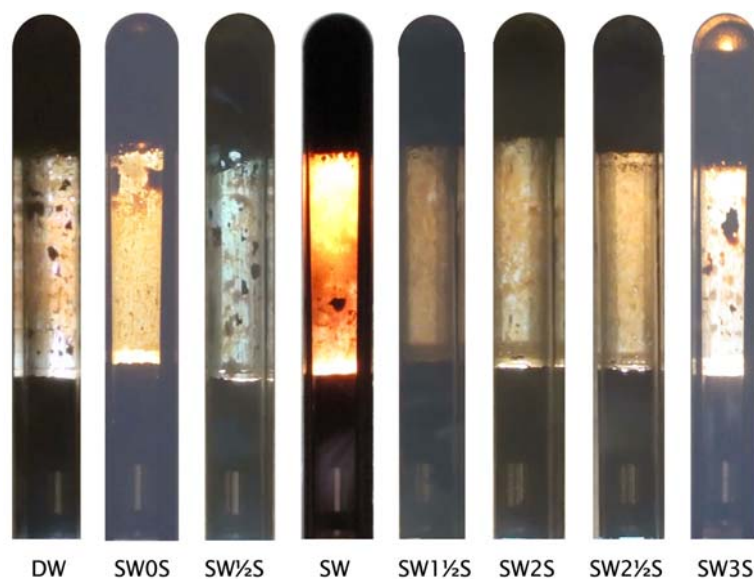
Figure 5. Latin American Crude Oil and different brine solutions after processed in the JEFRI PVT cell, all at 37 ˚C and 15 bar.
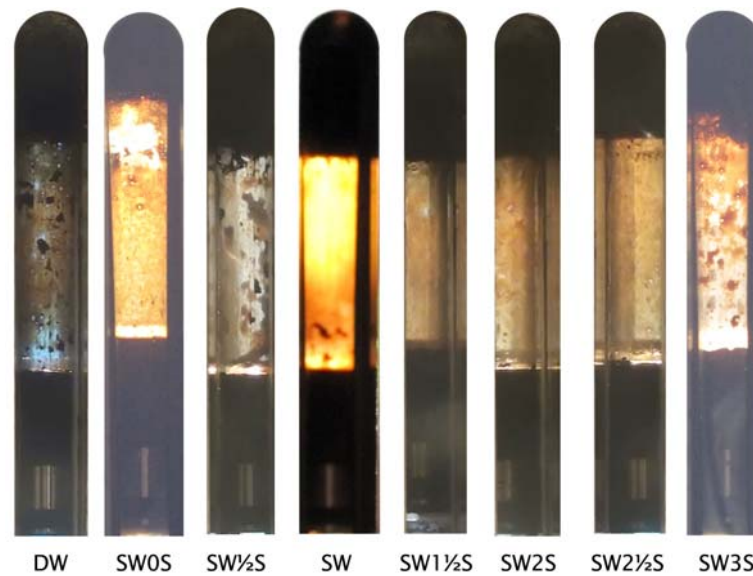
Figure 6. Latin American Crude Oil and different brine solutions after processed in the JEFRI PVT cell, all at 37 ˚C and 300 bar.

After finishing the experiment in the JEFRI cell, the samples were transferred from the cell into a sample bottle and left overnight. Then viscosity measurements of the crude oil phase were performed for every experiment. Results are shown in Table 4. In the case of the Latin American crude oil it can be seen that the viscosity of the crude oil decreased with the increase in sulfate concentration when the system was exposed to high temperatures and pressures.

Table 4. Crude oil viscosity data after interacting with brine solutions in JEFRI Cell.

Brine solution	Viscosity After high pressure cell [cp]
Crude oil	24.4
SW0S	21.5
SW	20.2
SW1½S	18.7
SW2S	18.1
SW2½S	18
SW3S	16.4

In order to check solubility of the crude oils in the brine phase, we measured the pH of the brine phases in all cases. Results for the pH of different brine solutions are shown in Table 5. A decrease in pH was experienced in all cases. In highly sulfated brine solutions, less change in pH was

observed as compared to DW and SW0S. This suggests that some of the acidic components of the crude oil are being washed into the brine solution, causing the decrease in pH of the brine solutions. However, this change in pH is not sufficient to explain the decrease in viscosity of the Latin American crude oil. Furthermore, the measured water content in the crude oil phase (Table 6) makes it clear that the observed decrease of viscosity cannot be explained by water present in the oil phase. We did not observe a significant change in the viscosity of oil in contacted with SW0S, but on the other hand it has comparatively high water content with respect to other tests.
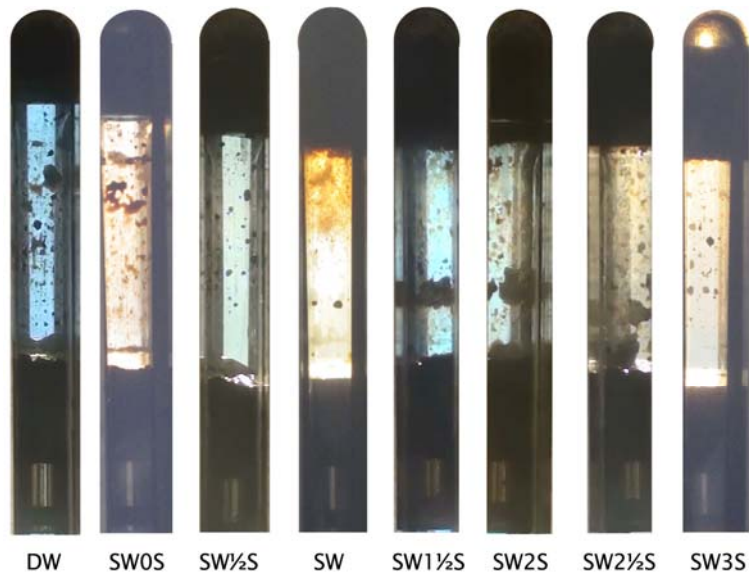
Figure 7. Latin American Crude Oil and different brine solutions after processed in the JEFRI PVT cell, all at 110 ˚C and 15 bar.
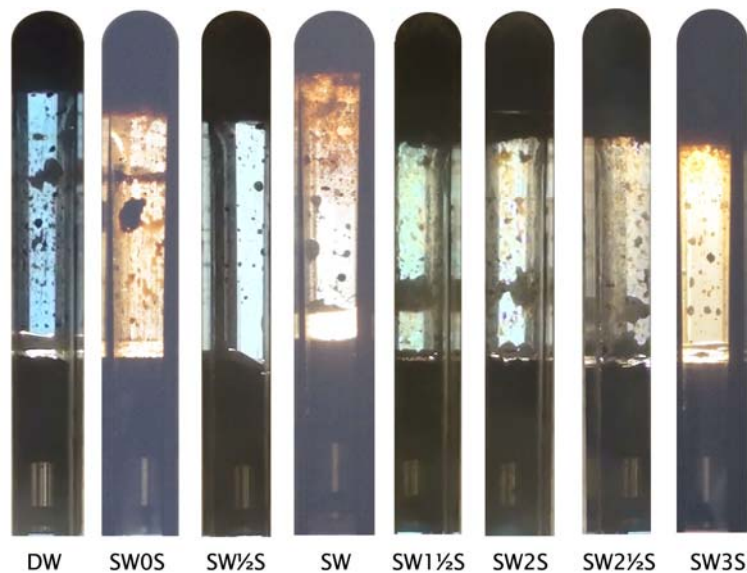
Figure 8. Latin American Crude Oil and different brine solutions after processed in the JEFRI PVT cell, all at 110 ˚C and 300 bar.

To confirm that viscosity indeed decreases, further experiments were carried out with the Middle East crude oil and different brine solutions in the same way as for Latin American crude oil. The Middle East crude oil and different brine solutions at various temperature and pressure conditions (the same as reported for the experiments with the Latin American crude oil) are photographed, as shown in Figures 9, 10, 11 and 12. If we compare Figure 9 and 11, as well as Figure 10 and 12, we can see that the high operating temperature de-emulsifies the Middle East crude oil also. A more interesting feature is the formation of a new phase (probably microemulsion) at the high temperature, T = 110 °C, with the increase in sulfate concentration (see Figures 11 and 12). The microemulsion phase formed can be seen for SW3S in Figure 11 and for SW1.5S and SW3S case in Figure 12.

Table 5. pH of brine solutions before and after experiments.

Brine solutions from Latin American crude oil sample		
Samples	pH (before)	pH (after)
DW	5.97	3.49
SW0S	6.29	4.30
SW½S	-	7.07
SW1½S	8.02	7.50
SW2S	8.09	7.51

Table 6. Water contents in crude oils after interacting.

| Latin American crude oil	
Samples	Water content [%]
Only oil	0.017
DW	0.024
SW0S	0.645
SW½S	0.029
SW1½S	0.473
SW2S	0.045

Table 7. Interfacial tension of Latin American oil/brines @ 25 °C with brine solutions in JEFRI Cell.

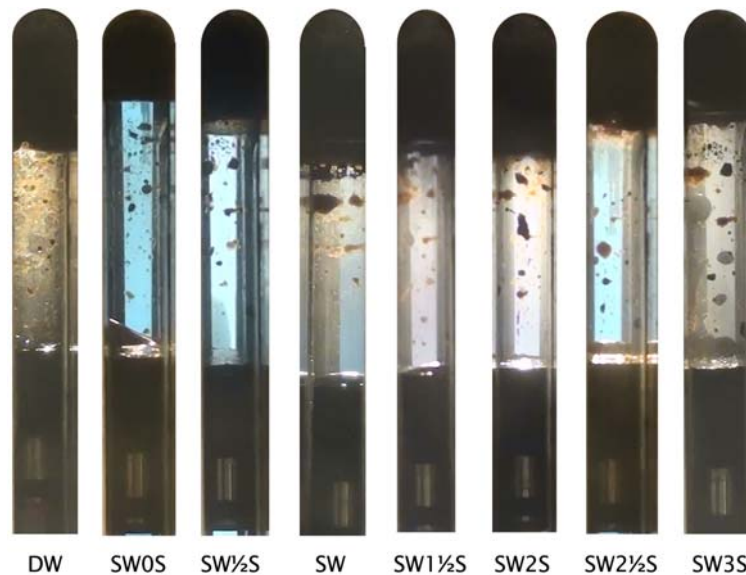| Latin American crude oil	
Samples	IFT [mN/m]
SW0S	13.92
SW	7.19
SW1½S	6.98
SW2S	6.83
SW3S	6.31

Table 8. Crude oil viscosity data after interacting with brine solutions in JEFRI Cell.

Middle East crude oil	
Samples	Viscosity [cP]
Only oil	10.54
DW	9.03
SW0S	8.02
SW½S	7.88
SW	7.92
SW2S	8.00

After completing the experiment with the Middle East crude oil and brine solutions in the DBR JEFRI PVT cell, the samples were removed from the cell and left overnight in the same way as for the Latin American crude oil. Viscosity measurements of the crude oil samples were then carried out. Results are shown in Table 8. No significant change in the viscosity of the crude oil was observed in this case.
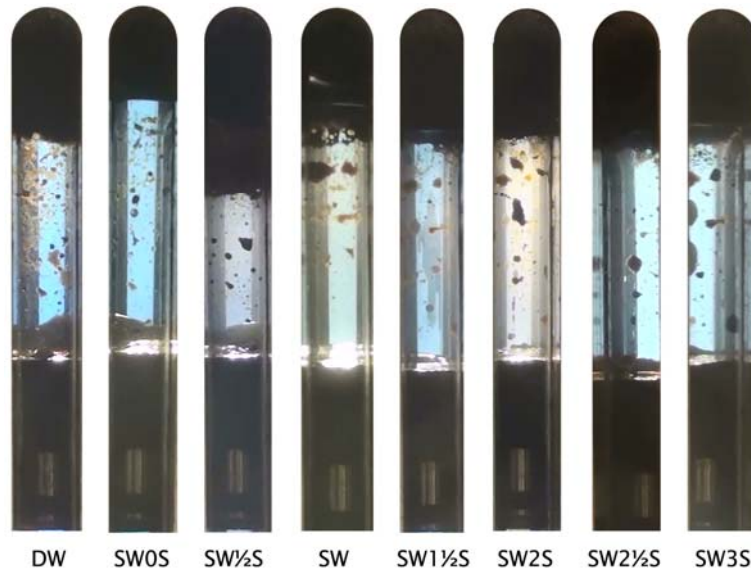
Figure 9. Middle East Crude Oil and different brine solutions after processed in the JEFRI PVT cell, all at 37 ˚C and 15 bar.

Figure 10. Middle East Crude Oil and different brine solutions after processed in the JEFRI PVT cell, all at 37 ˚C and 300 bar.

3.3 Interfacial Tension Measurements

IFT measurements were performed between the Latin American crude oil and brine at room temperature and atmospheric pressure in order to study the effect of brine salinity on interfacial tension. IFT values between oil and different brines are summarized in Table 7. Results show that IFT decreases with the increase in sulfate concentration. IFT for SW0S/oil is 13.92 mN/m and this decreased to 6.31 mN/m for SW3S/oil. This demonstrates that sulfate helps to decrease the IFT. However, this decrease seems to be insufficient to account for the observed increment in oil recovery.

4. Discussion

We observed that viscosity of Latin American crude oil in contacted with brine solution decreased with the increase in sulfate concentration at high temperature and pressure condition. One possible reason for decrease in viscosity of crude oil may be the change of shape of heavy component (aromatics, asphaltenes and resins) molecules. This happens in polymer solutions. Many authors reported decrease in viscosity of polymer solution when salt is added to solution [19-21]. If a polymer is poly-acid, it may dissociate in a solution. The molecules of non-dissociated polymer are normally coiled. Most of the interaction forces are hidden inside the coiled molecules. The effect on viscosity is relatively small. When acidity of the solution changes the molecules of the polymeric acid may dissociate. The segments of such molecules become negatively charged and repel from each other. As a result, the molecules stretch. In the flow, the negatively charged stretched molecules occupy a larger volume and interact stronger with each other. This is likely to increase the viscosity of the solution (although there may be other considerations). Addition of some salts or into the solution may result in the fact that the salt ions neutralize the negatively charged segments, and the polymer molecules become coiled again, which decreases the viscosity. In the same way, sulfate ions along with other potential determining ions could affect the shape of heavy components of crude oils at high temperature and pressure. This mechanism looks reasonable because we have observed decrease in viscosity only in the case of Latin American crude oil whose asphaltene content is three times higher than of the Middle East crude oil where we did not observe any decrease in viscosity. The exact mechanism of interaction of the sulfate ions with the crude oil which leads to viscosity decrease is still not clear and the role of the potential determining ions with respect to temperature and pressure needs further study. However, the effect is pronounced and repeatable, and may definitely affect the oil recovery under reservoir conditions.

Another important finding is the formation of a new phase (probably microemulsion) with the Middle East crude oil at high temperature, pressure, and sulfate concentration. Although we could not analyze the new formed phase, we believe that it was a microemulsion, since microemulsions may form upon simple mixing of the components, as in our experiments, and do not require the high shear conditions generally used in the formation of ordinary emulsions. The newly formed phase was stable under experimental conditions. Investigation of the new phase under high temperature and pressure conditions in JEFRI cell requires specialized equipment and is outside the scope of the present work. Even if it is not microemulsion, it may have an important influence on oil recovery mechanisms that was not studied previously.
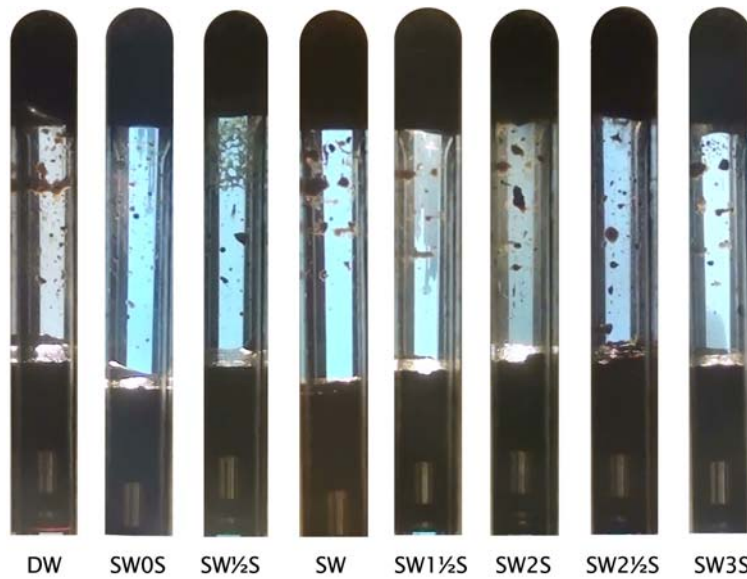
Figure 11. Middle East Crude Oil and different brine solutions after processed in the JEFRI PVT cell, all at 110 ˚C and 15 bar. The formation of a microemulsion phase can be observed in case of SW3S, present as a dark grey phase between the oil and the brine phases.
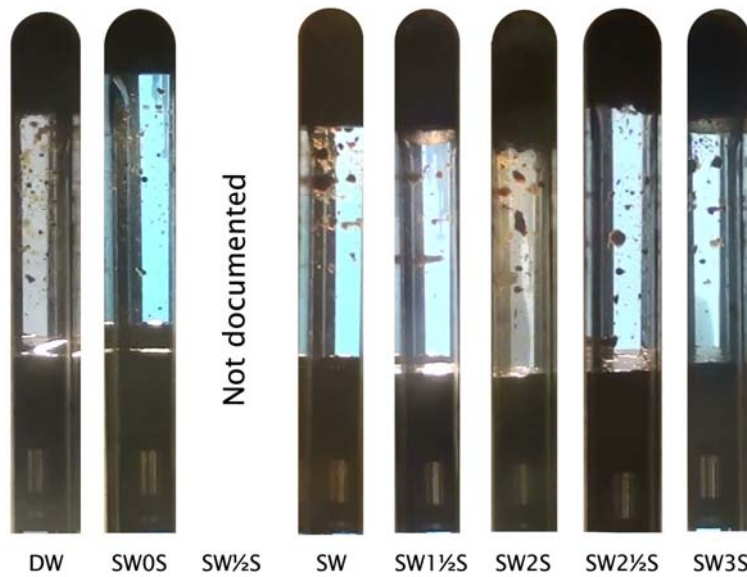
Figure 12. Middle East Crude Oil and different brine solutions after processed in the JEFRI PVT cell, all at 110 ˚C and 300 bar. The formation of a microemulsion phase can be observed in case of Sw1½ and SW3S, present as a dark grey phase between the oil and the brine phases.

It has been established that seawater is an excellent EOR fluid for chalk reservoirs at high temperature [22]. On the other hand both the decrease in viscosity of the Latin American crude oil and formation of the microemulsion phase with the Middle East crude oil were also observed at high temperature. This clearly shows that these two factors could be possible explanations for the observed increase in oil recovery. On the other hand, recent studies in our laboratory [23] indicate that the rock may also determine whether the effect of the temperature on the recovery is observed.

Thus, brine/crude oil interaction alone may be insufficient to explain all the mechanisms of the EOR based on enhanced water salinity.

Experimental results show that both crude oils interact differently with the same brine solutions regarding phase behavior and viscosity measurements. This difference is attributed to the difference in composition of the different crude oils. Thus, variation of the oil viscosity with brine salinity is oil-dependent. Unless an explanation is given, this viscosity variation needs to be checked in each particular case of application of the salinity-based EOR. Further experimental studies are in progress in our laboratory in order to understand the complex interaction of crude oil components with brine solutions.

5. Conclusions

1. Room temperature crude oil/brine studies indicate that the salinity of the brine affects the emulsion formation. No trend was observed with regard to amounts of the potential determining ions and especially with sulfate ions. Brine solutions did not affect the viscosity and density of crude oils at room temperature.

2. The DBR JEFRI PVT cell high-pressure studies show that an increase in temperature de-emulsifies crude oils in all cases.

3. The viscosity of the Latin American crude oil was significantly reduced after interacting with sulfate ions at high temperature and pressure conditions in the DBR JEFRI PVT cell. A trend of decrease in viscosity with the increase in sulfate concentration was observed.

4. Formation of a probably microemulsion phase was observed with the Middle East crude oil with the increase in sulfate concentration especially at the high temperature and pressure conditions in the DBR JEFRI PVT Cell. No significant viscosity change was observed in this case.

5. At room temperature sulfate ions helped to reduce the IFT between the Latin American crude oil and brine. However decrease of the IFT with sulfate concentration seems to be insufficient to significantly affect the oil recovery.

6. The viscosity decrease for the Latin American crude oil and formation of the microemulsion phase with the Middle East crude oil are possible reasons for the increment in oil recovery with sulfate ions. Increase in oil recovery in Stevns Klint chalk was reported at higher temperatures (over 90 ˚C)[19] and both these effects were also observed at the high temperature conditions. Further experimental studies are required in order to understand this complex interaction of crude oil components with brine solutions.

Acknowledgements

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            Submitted.

Appendix C

Paper III

Mechanisms of advanced waterflooding in chalk reservoirs: Role of seawater-crude oil- interactions

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Mechanisms of Advanced Waterflooding in Chalk Reservoirs: Role of Seawater-Crude Oil Interactions

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Abstract

It is experimentally documented that seawater with increased amounts of the potential determining ions, SO_4^{2-}, Ca^{2+} and Mg^{2+}, can significantly improve the oil recovery in chalk reservoirs at high temperatures. Usually, wettability alteration is reported as the main mechanism for the improvement in oil recovery. Our recent study proposed that the decrease in viscosity and formation of an emulsion phase could also be a possible reason for the observed increase in oil recovery. It was found that two crude oils exhibited different phase behavior and viscosity variation in contact with the same brine solutions. In this work, we study crude oil/brine interactions further: We investigate the effects of compositional differences of crude oils and also study heptane/seawater interactions under different temperatures, pressures and sulfate ion concentrations. For the two crude oils studied, the heavier oil (that with a large fraction of heavy components) exhibited viscosity reduction in contact with brine, while the lighter crude oil exhibited emulsion formation. We have also observed formation of an emulsion phase in the heptane/brine systems under high pressures and temperatures. It is concluded that viscosity reduction for a crude oil in contact with brine is connected to the presence of heavy components in the crude oil, while formation of emulsions with brine is a phenomenon related to the presence of lighter components in the crude oil.

Key Words:

Waterflooding, oil recovery, crude oils, heptane, viscosity, emulsification, emulsion, phase behavior

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1 Introduction

Although waterflooding is an extensively practiced recovery method for mechanical displacement of oil and for pressure maintenance, the composition of the injection water has not generally been considered an important factor in waterflood design. In recent years, however, research on so-called "smart" waterflooding has shown that injection of suitably composed brine can substantially increase oil recovery from both sandstone and carbonate reservoirs. For example it has been documented experimentally that low salinity waterflooding in sandstones and high salinity seawater flooding in carbonates contribute to an increase in oil recovery [1-3]. Understanding the underlying mechanisms behind these effects is, however, still in progress.

Several experimental studies have been carried out on seawater flooding in chalk reservoirs by Austad and co-workers [3-9]. Concentrations of the active ions Ca^{2+}, SO_4^{2-} and Mg^{2+} as well as temperature were documented as governing parameters in determining the amount of oil recovered both by spontaneous imbibition and by forced displacement. Recently, Fathi et al. [10] reported that not only are the concentrations of the active ions Ca^{2+}, SO_4^{2-}, and Mg^{2+} important, but also the amount of NaCl has an impact on oil recovery. Other experimental studies also reported positive effects from different seawater ions (SO_4^{2-} and Mg^{2+}) on oil recovery from carbonate rocks [1, 2, 11].

To understand the mechanism of improved oil recovery, surface chemistry was the major focus in most of the studies mentioned, and wettability alteration of the porous surface was reported as a key reason for recovery improvement. The main conclusion from this earlier work is that it is the affinity of the potential determining ions to the chalk surface, which increases with temperature, which helps to improve the oil recovery [3, 6].

Crude oil/brine interactions have generally been ignored in most reported studies. Our recent laboratory study [12] was one of the first to demonstrate that these interactions may also be responsible for an increase in oil recovery. We studied crude oil/brine interactions at room temperature and atmospheric pressure, as well as at high temperature and pressure in a DBR JEFRI cell. Two different crude oils (from Latin America and the Middle East) were studied. Our results showed that sulfate ions could help decrease the viscosity of one of the crude oils when brine is contacted with it at high temperature and pressure. For the other crude oil, sulfate ions in brine could also be responsible for creation of an emulsion phase at the interface between crude oil and brine. Decrease of viscosity of a crude oil and formation of emulsion phase were reported as possible reasons for improved oil recovery, aside from the wettability alteration reported in other works. Formation of emulsions between water and crude oil is a known effect during oil

production. Appearance of emulsions may result in major processing problems and can affect the quality of the produced crude oil [13, 14]. However, most often formation of emulsions (especially, microemulsions) is considered to be a positive effect, as the interfacial tension (IFT) is lowered such that the mobility of the crude oil inside the reservoir is enhanced [15].

Both crude oils used in our previous study interacted in a different way with the same brine solutions in terms of phase behavior and viscosity. This difference is ascribed to the different compositions of the crude oils. The motivation of the present work is to understand the interactions of the crude oil components with the brine solutions. Specifically we address the following questions:

What is the mechanism for crude oil viscosity reduction?

Which components of the crude oil are responsible for the formation of emulsions?

Why do different crude oils interact in a significantly different way with the same brine solutions?

In this work, gas chromatography (GC) analysis of the crude oils (before and after contacting with brine solutions in a DBR JEFRI cell) is carried out in order to determine the effect of brine on the compositions of the crude oils. A SARA (Saturates, Aromatics, Resins, Asphaltenes) analysis of both crude oils is also carried out. For comparison, we carried out a similar study with heptane instead of crude oil in order to determine whether formation of the emulsion phase and viscosity reduction could also occur in such a simple, single hydrocarbon/brine system. The procedure described previously was followed [17]. Attention was also given to any possible color change in the heptane after interacting with brine solutions, since it was recently reported that the amount of sulfate in the brine solution is correlated to discoloration of decane [16]. We also conducted light scattering analysis of the emulsions using a TurbiScan apparatus [24]. Moradi et al. [17] reported the measurement of droplet size and stability of emulsions using a transmitted-light microscope. Our target was to make a detailed analysis of the formation of emulsions in order to characterize the emulsion (which kind of emulsion the system forms size of droplets, the time range of separation between oil and water phase, and the stability of the emulsions)

2 Experiments

Experiments designed in this study are based on the results from our previous work [12]. The experimental work consists of two parts: The first part is a compositional analysis of the crude oils studied in previous work. In the second part, a new model oil/brine system (heptane/brine) is studied in order to clarify whether the lighter components in the oil are responsible for one of our previous observations, either that viscosity of the oil decreases after operation in high pressure and temperature equipment or that formation of oil and water emulsions are experienced when the

system is at high pressure and temperature. In addition, Turbiscan analysis of a crude oil/brine system is also carried out.

2.1 Crude Oils

The same two crude oils, the middle east crude oil and the latin American crude oil, reported on previously, [12] were also used in this study for detailed compositional analysis. The properties of the crude oils, (density, viscosity, acid number and base number) are given in Table1. In addition to the crude oils, *n*-heptane was also used as a model fluid to understand the complex crude oil/brine interactions.

Table 1. Crude oil properties.

Crude Oil	Density @ 20 °C [g/cm³]	Acid Number [mg KOH/g oil]	Base Number [mg KOH/g oil]	Asphaltene [%]	Viscosity [cp]
Latin America	0.846	0.163	0.563	3.43	24.4
Middle East	0.844	0.093	0.644	1.093	10.538

Table 2. Brine compositions.

Component	SW0S [mol/l]	SW0.5S [mol/l]	SW [mol/l]	SW1.5S [mol/l]	SW2S [mol/l]	SW2.5S [mol/l]	SW3S [mol/l]
Na^+	0.368	0.363	0.358	0.353	0.348	0.343	0.337
K^+	0.010	0.010	0.010	0.010	0.010	0.010	0.010
Mg^{2+}	0.045	0.045	0.045	0.045	0.045	0.045	0.045
Ca^{2+}	0.013	0.013	0.013	0.013	0.013	0.013	0.013
Cl^-	0.492	0.463	0.434	0.405	0.376	0.347	0.317
HCO_3^-	0.002	0.002	0.002	0.002	0.002	0.002	0.002
SO_4^{2-}	0.000	0.012	0.024	0.036	0.048	0.060	0.072
TDS [g/l]	33.39	33.39	33.39	33.39	33.39	33.39	33.39

2.2 Brine Solutions

Synthetic brine solutions with different sulfate concentrations are prepared by adding different amounts of NaCl, NaHCO₃, KCl, MgCl₂.6H₂O, CaCl₂.2H₂O and Na₂SO₄ to distilled water. The first brine solution is synthetic seawater with no sulfate ions, (SW0S); the second brine solution is the synthetic seawater with the normal concentration of sulfate ions (SW). The detailed compositions of other brine solutions used are given in Table 2. The various brine solutions are

named SWXS, where X denotes the relative sulfate concentration with respect to SW. Experiments with heptane and previous experiment with crude oil are carried out with the seven different brine solutions: SW0S, SW0.5S, SW, SW1.5S, SW2S, SW2.5S and SW3S.

2.3 SARA Analysis

SARA analysis was first described by Jewell et al. [18], where it was based on adsorption chromatography by gravity. In the present work SARA analysis was applied to two crude oils. Component separation was carried out in five different steps: A column was prepared with heptane and silica was carefully added to avoid air bubbles. Heptane must be present at all times and the column cannot dry out. 100 g of silica and 5 g of oil was used. The separation was carried out in 5 steps:

1. 1.25 L heptane solution was added to the column and the separation begins.
2. Separation with 1.25 L heptane-toluene 1:1 solution was carried out. The fractions collected from step 1 and step 2 is the saturate fractions. In a new collector the process was continued with heptane-toluene solution until the eluent was light yellow.
3. The separation was continued with 1.5 L toluene. The collected fraction is the first part of the aromatics. Toluene was added until the eluent was almost colorless.
4. 1.5 L toluene-methanol solution in a 4:1 relation was added to the column. From step 3 and 4 the first and the second part of the aromatics was collected. With another new collector the separation continues with the toluene-methanol solution until the eluent was almost colorless. In the final step 0.5 L dichloromethane-methanol solution in the ratio of 4:1 was added until the eluent became colorless. The resins were collected from the final separation part. The asphaltenes stay in the column, held there due to the silica powder.

2.4 GC Analysis

The two crude oils were analyzed with simulated distillation gas chromatography, both before and after they were contacted in the high pressure cell with different brine solutions. An Agilent 7890A gas chromatograph was used. In order to determine the carbon numbers of each of the fractions obtained in the simulated distillation, ASTM method D6352 was applied. This method covers hydrocarbons with boiling points up 700 °C, which is the boiling point of C94. The method is not applicable to fractions with carbon numbers lower than C10-C11. To overcome this, the GC was also fitted with a sub-ambient column oven, where liquid carbon dioxide was used to extend the 7890A lower oven temperature down to -40 °C. Table 3 gives details of the setup.

Table 3. Instrument conditions for the cryogenic ASTM D6352 simulated distillation.

|	
Auto injector	Agilent 7693 ALS Syringe size: 1µL Injection volume: 0.05 µL
Inlet	Split/splitless operated in split mode Temperature: 50 ºC for 0 min then 200 ºC/min to 430 ºC for 6 min
Column	Dimensions: 5m x 530µm x 0.15µm Temperature: 450 °C
Oven	-20 ºC for 1 min then 20 ºC/min to 430 ºC for 5 min.
Detector	Flame Ionization Detector (FID) Temperature 400 ºC FID Hydrogen flow rate: 40mL/min FID Air flow rate: 450mL/min Make-up flow: 45mL/min nitrogen Data acquisition rate 5Hz
Data system	Agilent Chemstation

Calibration was done in two steps in order to identify the retention times of the fractions with the carbon numbers ranging from C5 to C90. Initially a known solution of C5-C18 (Agilent 5080-8768) was injected into the gas chromatograph, from which the corresponding retention time could be obtained. Second, a solution of 10 mg of polywax 655 (Agilent 5188-5317) was injected with 1.5 ml of toluene to identify the retention times of carbon numbers C20 to C94. To analyze the crude oils, the two samples were injected into the GC before and after the high pressure experiments. From the resulting chromatograms the amounts of the carbon fractions from C5 to C94 could then be calculated.

2.5 Heptane/Brine Interaction Study at Ambient Conditions

Initially the heptane/brine interactions were studied at room temperature and atmospheric pressure. Heptane and different synthetic brines were mixed in a volumetric ratio of 20/80 and stirred. The mixture was centrifuged at 1000 rpm for 15 minutes as in the previous study [12]. After equilibration, the systems were photographed and examined for any possible color change or emulsion formation.

2.6 Heptane/Brine Interaction Study in DBR JEFRI PVT Cell

The heptane/brine interactions at high pressures and temperatures were studied in the DBR JEFRI PVT cell. The equipment details and the experimental procedures are described in Zahid et al. [12]. The cell is shown in figures 1 and 2. The four sets of experimental conditions were: (a) 37 ˚C, 15 bar (b) 37 ˚C, 300 bar (c) 110 ˚C, 15 bar (d) 110 ˚C, 300 bar.
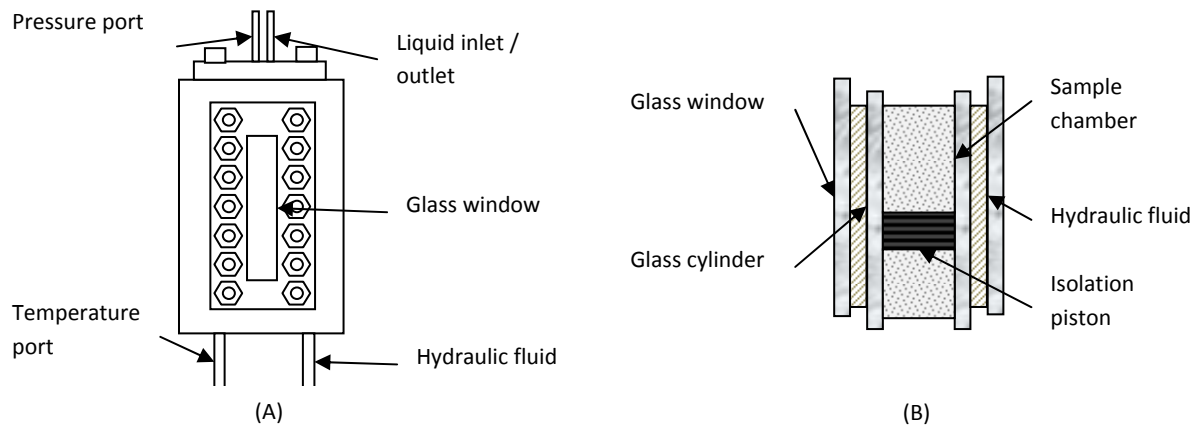
Figure 1. Experimental setup of the DBR JEFRI PVT cell. (A) is a sketch of the cell from the outside and (B) is a segment illustrating the construction of the cell from the inside.

The brine-heptane volumetric ratio (WOR) was 30/70 which corresponds to 15 ml heptane and 35 ml brine in each experiment. The sulfate content of the brine solutions is given in Table 2.

Figure 2. Picture of the DBR JEFRI PVT cell -high pressure equipment for phase behavior measurements at elevated temperatures and pressures. The surrounding steel is the inside of the temperature controlled forced air oven. The cell is mounted on a rocking mechanism suitable for mixing the systems inside the glass chamber. The glass window allows visual observations.

After the heptane/brine systems were contacted in the DBR JEFRI PVT cell, the density and viscosity of the heptane were measured. The heptane was also examined for any possible color change.

2.7 Turbiscan Analysis of the Crude Oil/Brine Emulsions

The crude oil/brine systems were also analyzed in the Turbiscan [24]. This is a light scattering measurement tool for analysis of concentrated dispersions. Typically the Turbiscan is used to analyze formulations, documenting stability. In the present work the Turbiscan was used to monitor equilibrium in the mixed crude oil/brine systems. To determine if the observed emulsions could be quantified with regard to the droplet size and stability.

For this work a commercial apparatus Turbiscan MA 2000 was used. A cylindrical glass test-tube is placed vertically into the device. A reading head moves up and down in order to scan the entire sample length, as shown in figure 3.
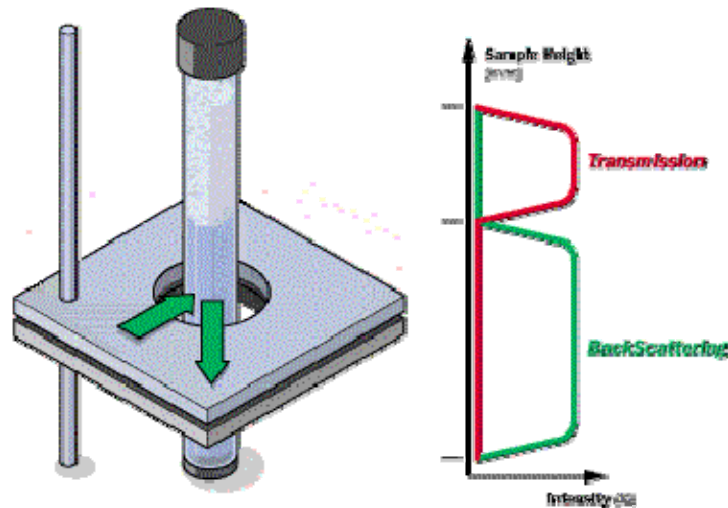
Figure 3. Drawing of the inside of the TurbiScan. The squared platform is the reading head, which is moving up and down along the cylindrical cell to scan the entire sample length. [Tutorial from Turbiscan MA 2000]

There are two detectors, one to detect the light transmitted through the sample from the light source, and another to receive the light backscattered by the sample. The Turbiscan operates at room temperature and atmospheric pressure. The details of the Turbiscan MA 2000 operation are reported by Mengual et al. [19].

In the Turbiscan experiments, the crude oil/brine ratio is kept similar to the crude oil/brine study in the DBR JEFRI PVT cell: 30 vol% crude oil (2.1 ml) and 70 vol% brine solution (4.9 ml). Two brine/water solutions were used: DW and SW3S. The crude oil/brine samples were loaded into the glass tubes and mixed by vigorous hand-shaking. Thereafter the tube was placed inside the Turbiscan and the sample was scanned for 12 hours with a measurement every hour. The results were stored in the enclosed software and the output graphs were analyzed.

Due to some unexpected phase behavior, where the two phase crude oil brine system changed into a relatively stable single gel-like phase, during the preparation of the samples in the glass tubes other water-oil ratios were also analyzed: 50 vol% crude oil and 50 vol% distilled water; 20 vol% crude oil and 80 vol% distilled water, and 10 vol% crude oil and 90 vol% distilled water. The Latin American Crude oil and the Middle East Crude oil were used for these analyses, in combinations with the two different brine/water solutions.

3 Results

3.1 SARA Analysis

Our previous experimental results [17] showed that both crude oils interact differently with the same brine solution at high temperatures and pressures. While the viscosity of the highly viscous Latin American oil is strongly reduced after contact with brines containing high amounts of sulfates, the Middle East oil forms emulsions with them. However, the Latin American oil does not form emulsions, nor is the viscosity of the Middle East oil reduced. This difference is attributed to compositional differences between the oils. SARA analysis of both crude oils was performed to study this difference and the results are summarized in Table 4.

Table 4. SARA Analysis of Crude Oils.

| Crude Oil	Saturates (%)	Aromatics (%)	Resins (%)	Asphaltene (%)	Viscosity (cP)
Latin America	43.26	9.19	7.49	3.43	24.4
Middle East	46.78	2.34	4.66	1.093	10.538

The Latin American crude oil has (as expected) a much higher percentage of aromatics, resins and asphaltenes compared to the Middle East crude oil. The conclusion is that the oil containing the highest amounts of heavy components was less inclined to form emulsions with brines, while at the same time demonstrating viscosity reduction after contact with them.

3.2 GC Analysis of crude oils

The graphical results from GC analysis are shown in figures 4 and 5. For the Latin American crude oil, there are no noticeable changes in the GC profiles when comparing the unprocessed crude oil with crude oil samples that have been contacted with brine in the DBR JEFRI PVT cell. On the other hand, there are changes in the chromatograms of the Middle East Crude Oil. From figure 6 it is seen that the unprocessed crude oil has a significantly higher content of light components than the crude oil after contact with brine. To verify this observation, measurements with the original crude oil were repeated 3 times, and the conclusion was the same in each case.
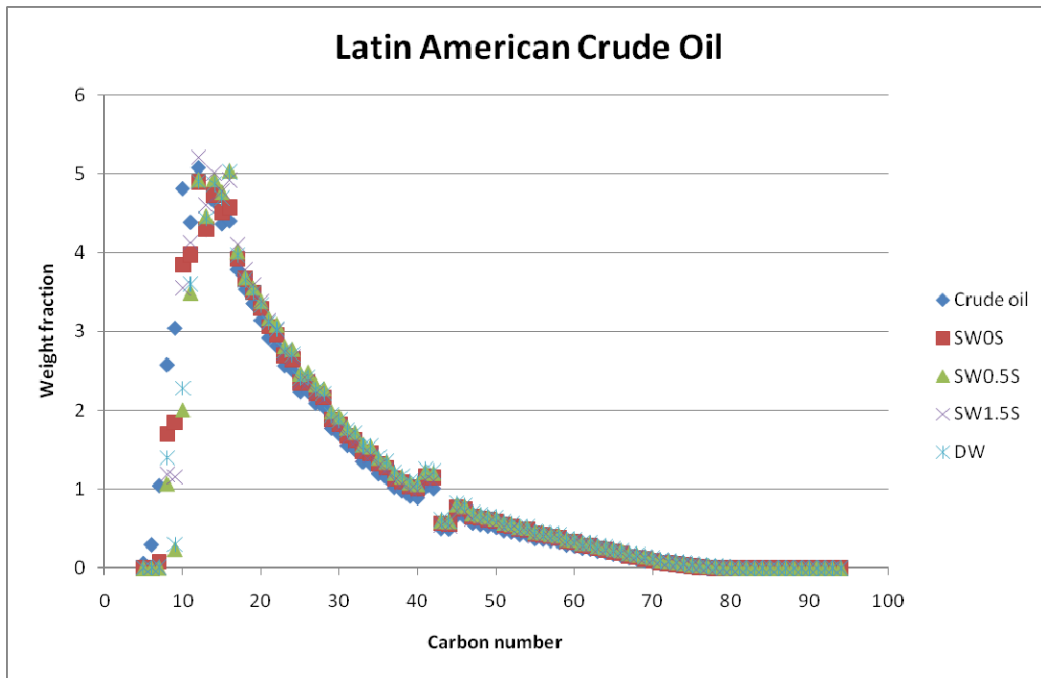
Figure 4. Graphical results from GC analysis of the Latin American Crude Oil before and after contact in the JEFRI cell with brines of varying sulfate concentration. For the GC analysis the required sample amount is removed from the full original oil/brine sample, which was operated in the high pressure cell.
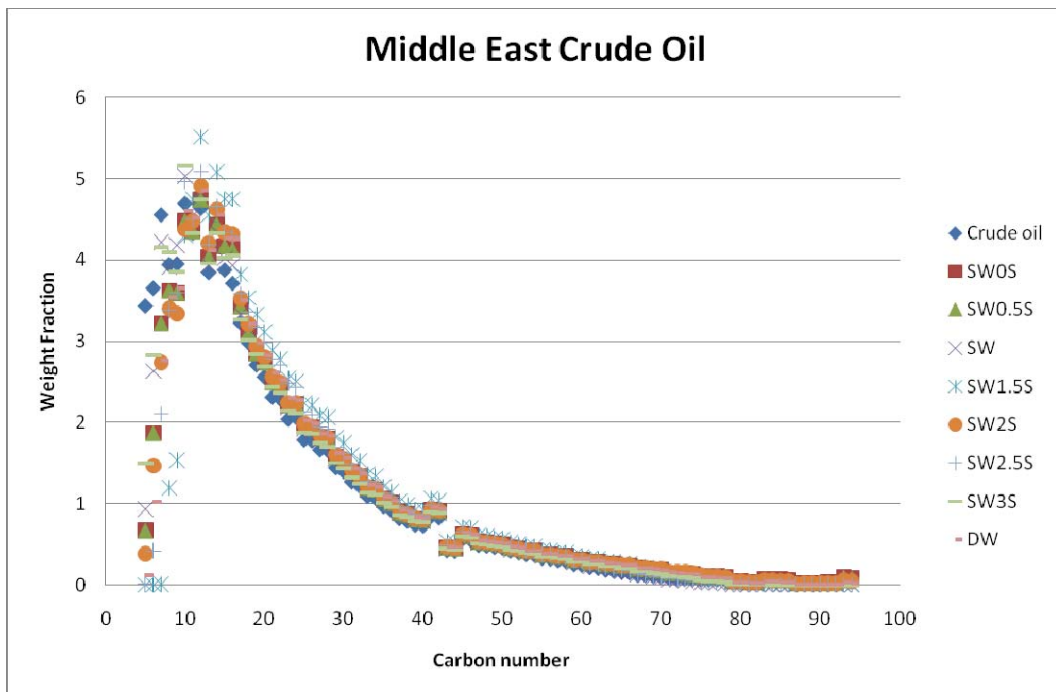
Figure 5. Graphical results from GC analysis of the Middle East Crude Oil before and after contact in the JEFRI cell with brines of varying sulfate concentration. For the GC analysis the required sample amount is removed from the full original oil/brine sample, which was operated in the high pressure cell.

3.3 The Room Temperature Heptane/Brine Study

The purpose of the heptane-brine interaction study was to understand the effects observed in the seawater-crude oils interaction study by analyzing a simple model system. The experiments with crude oil indicated that the light oil components are most probably responsible for formation of emulsions, while heavy components may participate in viscosity reduction. In order to support this conclusion, we determined whether formation of emulsions and viscosity reduction could be obtained in heptane/brine systems.

The heptane-brine interactions were initially studied at room temperature. Unlike in the crude oil study [12], no dispersion of the heptane droplets in the brine solution was observed (figure 6).
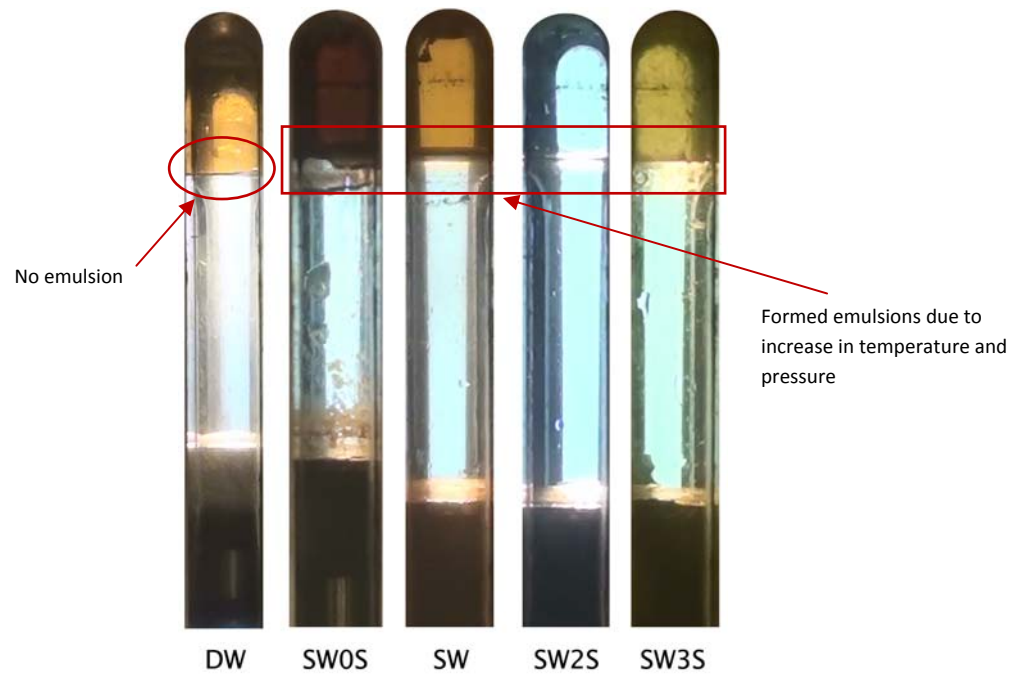

Figure 6. Heptane and different brine solutions after stirring them @ 1000 rpm for 15 mins at room temperature. The sample bottles are filled with heptane and brine solution and have been equilibrated for 1-2 hrs. These tests at ambient conditions were performed to see whether unusual phase behavior or discoloration of the heptane was solely due to the composition of the brine solutions.

Density and viscosity of heptane was measured before and after stirring the sample bottle with different brine solutions (SW0S, SW, SW2S, SW2.5S and SW3S). No significant changes were observed.

3.4 Heptane/ Brine Interaction in the DBR JEFRI PVT Cell

Heptane/brine interactions were also investigated under different temperatures and pressures in the DBR JEFRI cell. The system was monitored continuously to detect any changes in the number of phases or in the color of the heptane phase.
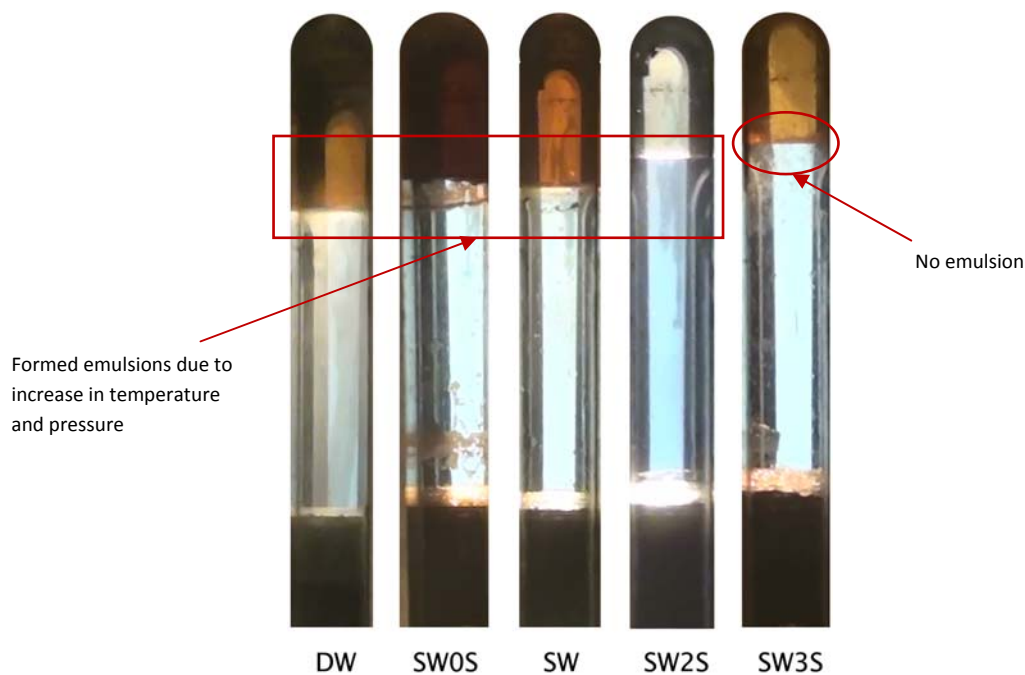
Figure 7. Heptane with different brine solutions after processed in the JEFRI PVT cell, all at 37 ˚C and 15 bar. Sample with DW shows no emulsion at the interface between oil and brine. Sample SW0S, SW, SW2S and SW3S shows formed emulsions. The emulsions are formed as the temperature and pressure has been increased.
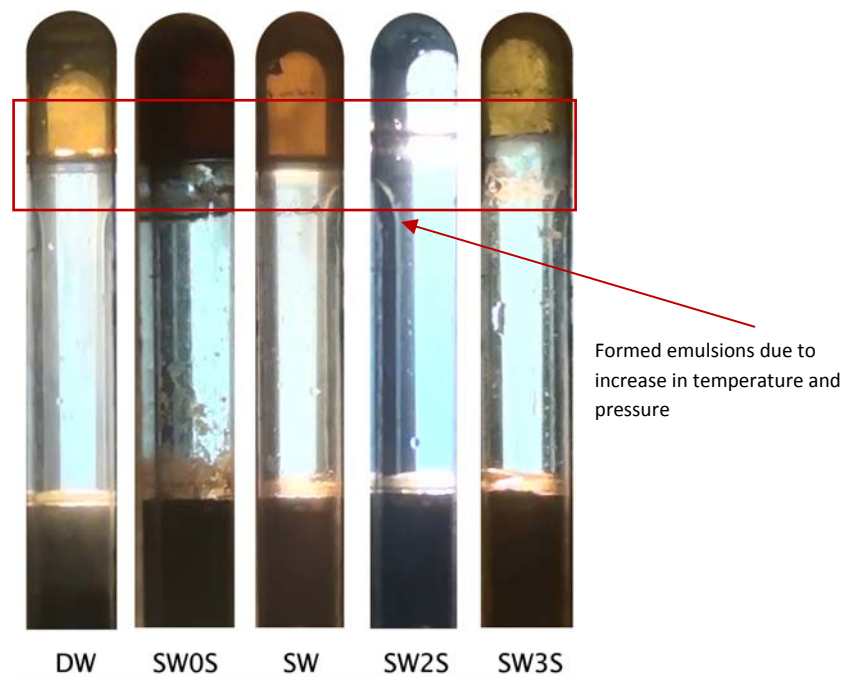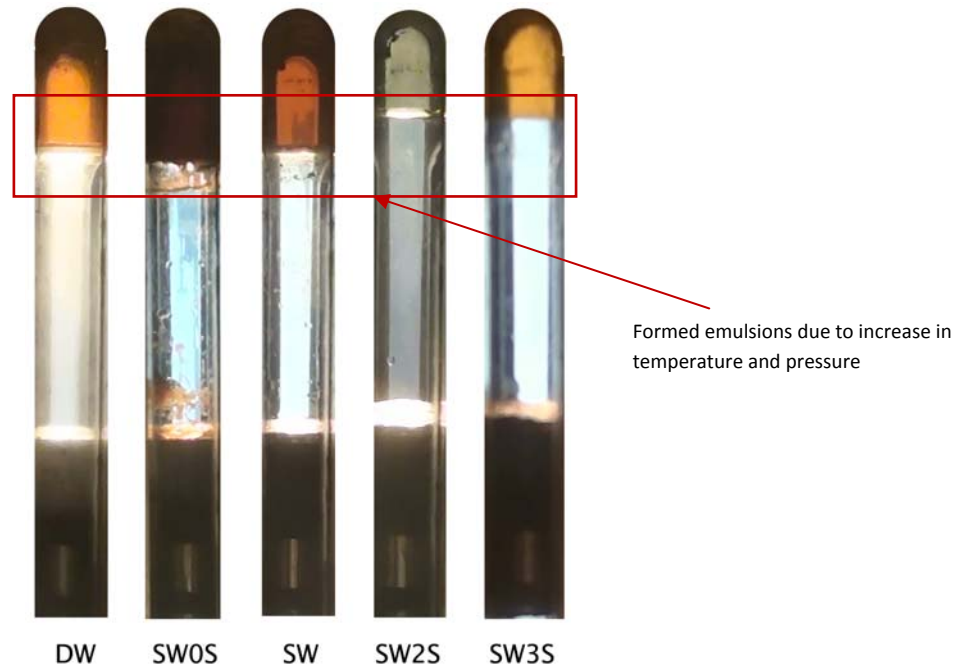

Figure 8. Heptane with different brine solutions after processed in the JEFRI PVT cell, all at 37 ˚C and 300 bar. All samples show formed emulsions. The emulsions are formed as the temperature and pressure has been increased.

After equilibration of the liquid-liquid systems the separation was monitored until the liquids were stabilized. Phase volumes were measured and the equilibrated systems were photographed. The photographs taken of different heptane/ brine systems (brine solutions having different sulfate concentration) at different temperatures and pressures are shown in figures 7 to 10. Besides the cases of DW at 37 ˚C and 15 bar and SW3S at 110 ˚C and 15 bar, the heptane/ brine systems formed a cloudy milky white emulsion phase at the interface between heptane and water. This emulsion phase is even more significant than the emulsion formed by the Middle East crude oil described previously. Formation of the emulsion phase is sensitive to both temperature and pressure. By observation of the volumes involved it may be concluded that this phase is formed from both the upper oil phase and the lower water phase.

After removal from the cell the heptane/brine systems were stored in a sample bottle and later examined for any changes. A significant color change in the heptane/ brine system was observed. As can be seen in figure 11, the system is completely colorless at the beginning of an experiment. The heptane and water phases remain transparent throughout the operation in the high pressure cell, but heptane containing phase changes from colorless to yellow or brown. As the system is exposed to higher temperatures and pressures, the change in color becomes more intense and as figure 11 shows, the color of the heptane phase persists after the experiment.
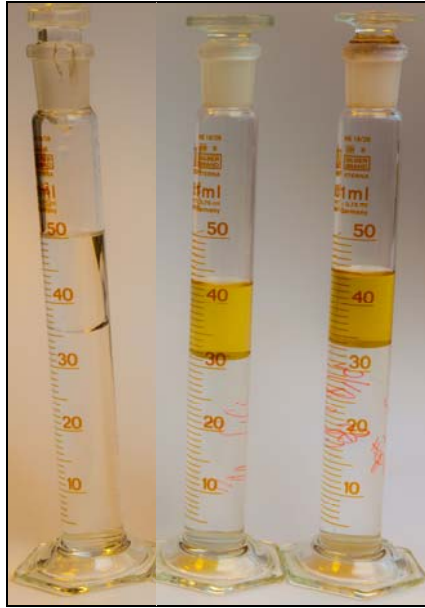

Figure 9. Heptane with different brine solutions after processed in the JEFRI PVT cell, all at 110 ˚C and 15 bar. Sample with SW3S shows no emulsion at the interface between oil and brine. Sample DW, SW0S, SW and SW2S shows formed emulsions. The emulsions are formed as the temperature and pressure has been increased.

Formed emulsions due to increase in temperature and pressure

Figure 10. Heptane with different brine solutions after processed in the JEFRI PVT cell, all at 110 ˚C and 300 bar. All samples show formed emulsions. The emulsions are formed as the temperature and pressure has been increased.

Table 5. Density and Viscosity Data of heptane before and after interacting with brine solutions inside the JEFRI cell.

Brine	Heptane	
	Viscosity (cP)	**Density (g/cm^3)**
Only Heptane	0.385	0.68
DW	0.403	0.68
SW0S	0.424	0.69
SW	0.412	0.68
SW2S	0.387	0.68
SW3S	0.394	0.68

Figure 11. Heptane with different brine solutions after processing in the JEFRI cell at ambient temperature and atmospheric pressure. From left to right heptane with DW (not processed in the JEFRI cell), SW2S and SW3S.

3.5 Turbiscan

Initially the crude oil and brine solution were mixed in a glass tube appropriate for the Turbiscan MA 2000 with 30/70 vol% ratio. During mixing the oil/brine system by hand shaking, it was immediately observed that the system changed from a two-phase liquid system to a single gel-like phase (very sticky, jelly and basically immobile). This observation was the same for both crude oils. This effect was never observed under high pressures and temperatures (in the PVT cell). Therefore, the new system was investigated more thoroughly.

Initially the gel-like phase was observed over a period of time to find out whether the system would eventually return to the original two-phase form. As no change was observed after one week, it was concluded that at room temperature and atmospheric pressure the 'gel' phase was stable. In figure 12 the 'gel' formations produced by both crude oils are pictured.

Middle East Crude Oil
with
SW0S

Latin American Crude Oil
with
SW0S

Figure 12. Picture of the formation of a 'gel' phase occurring from hand shaking crude oil and brine solution together. This form is stable as long as the glass tubes are at room temperature and atmospheric pressure. The formed phase is sticky and jelly-like. It is immobile, even though it is not completely solid.

After one week, the gel-like phases were exposed to heat. At 50 ˚C the crude oil/brine systems reformed back to their original two phase liquid-liquid form and stayed in this state during cooling to room temperature. The effect of pressure on the gel-like phasewas not considered in this work.

Light scattering analysis from the Turbiscan confirms that the stabilities of the oil/brine emulsions may be different. The emulsions formed by crude oils and DW are less stable than those from the crude oils and SW3S. For both crude oils the presence of brine rather than distilled water results in a larger emulsion phase which also persists for longer.

The Latin American crude oil mixed with distilled water was chosen to conduct further research on the gel-like phase formation. Different WOR were tested: 50/50 vol%, 20/80 vol% and 10/90 vol%. The gel-like behavior was observed for all the tested systems. A way to avoid the formation of a gel phase was to mix the crude oil and water in a tube of a larger diameter, (1.5 cm rather than 1.1 cm).

Four further experiments were conducted with 30/70 vol% WOR: two experiments with the Middle East Crude mixed with DW and SW3S and two with the Latin American Crude mixed with DW and SW3S. This time the glass tubes were only shaken gently, in order not to reach the 'gel' state, and immediately placed in the Turbiscan. They were operated for 2 hours and the samples were scanned every two minutes.

For the Latin American crude, separation of oil and brine takes longer in the case of DW compared with SW3S. This is in agreement with the observations of the phase separation of the samples. This

indicates also that the sulfate ions in the SW3S solution act as emulsion destabilizing ions. Similar results were obtained in the experiments with the Middle East crude and DW and SW3S, where the separation of oil and water is faster in the case with no sulfate ions. It should be mentioned that these four experiments may have a significant margin of error due to the inherent uncertainty of the mixing procedure.

4 Discussion

4.1 Viscosity Variation of Crude oil

In the previous work [12] it was found that decrease in viscosity and formation of an emulsion phase could be a possible reason for the observed increase in oil recovery under high salinity flooding In the SARA analysis it was observed that the Latin American crude oil exhibited greatest viscosity variation on contact with brine. Since this oil has a higher amount of heavy components (aromatics, resins and asphaltenes) compared to the Middle East crude oil, this suggests that viscosity of a crude oil with a high percentage of heavy components will vary most after interaction with brine solutions.

However, the GC analysis of the Latin American crude oil samples did not show any significant compositional change before and after contacting with the brine solutions in the PVT cell. Based on this finding, we propose that variation of viscosity of the crude oil, after contact with the brine solutions at high temperature and pressure, could be explained by a change in shape of heavy petroleum molecules in contact with the different ions. This happens in polymer solutions. Many authors reported decrease in viscosity of polymer solution when salt is added to solution [20, 21].

4.2 Emulsion Formation

SARA analysis revealed that the Middle East crude oil has a relatively high amount of light hydrocarbons. Furthermore, the GC analysis of the Middle East crude oil before and after interacting with the brine solutions in the PVT JEFRI cell showed that this oil originally had a higher content of light components compared to the oil after the experiment. The light components were possibly consumed by the emulsion phase formed. This indicates that formation of emulsions is correlated to the lighter components of the crude oil. In the heptane/brine interaction study, we observed formation of a significant emulsion phase after interacting with the brine solution in the PVT JEFRI cell. This also supports the hypothesis that the emulsions are formed by the lighter components of the crude oil.

A significant change in color of heptane was observed in the heptane/brine study in the PVT JEFRI cell. The heptane changed from colorless to yellow or brown after interacting with brine solutions with high sulfate concentration. The possibility of impurities in the equipment has been excluded: its cleaning has been carried out very thoroughly, and the color change was observed in repeated experiments with the same intensity of yellow or brown. Fernø et al. [14] also observed a color change in decane (from transparent to dark yellow) during high temperature spontaneous imbibition experiments with a brine solution having high sulfate concentration. Liberation of carboxylic components of crude oil from the chalk surface, by ion exchange or dissolution, was reported to be a reason for the color change. However, in our experiments the color changed in the absence of a porous medium, solely by interaction with the brine solution. The reason behind this change is not clear yet. However, the effect is pronounced and repeatable.

From the light scattering measurements it was observed that the crude oil/brine samples produced larger and more stable emulsions compared to crude oil/DW samples. This confirms that sulfate participates in mechanisms that control emulsion formation. Furthermore, the unexpected observation of a 'gel-like' phase formed from DW and crude oil creates a basis for speculation as to whether the crude oil/brine system could possibly act similarly under reservoir or production conditions. Formation of such a phase might be a problem for oil recovery. Unfortunately, due to the blackness of the crude oils, it was not possible to extract information about the droplet sizes of the dispersed phase in the Turbiscan experiments.

Emulsions of crude oil and water have been encountered at different stages of oil production (drilling, producing, transporting, processing etc.). These emulsions may be dispersions of water particles in oil (W/O) or fine dispersions of oil in water (O/W), in some cases multiple emulsions may also be found [22, 23]. Pressure gradients over chokes and valves introduce high shear stress that causes dispersion of oil drops. Generally, crude oil components like asphaltenes, resins, waxes and naphthenic acids are considered to be surface active natural emulsifiers that are responsible for producing stable emulsions [23]. However, the emulsion phase (related to lighter components of the crude oil) that we observed in our experiments is apparently formed by a different mechanism. First, it is not produced under high shear stresses; its formation requires only gentle shaking. Secondly, it is formed without participation of heavy and complex petroleum components, which is confirmed in experiments with pure *n*-heptane. Our experiments show that formation of emulsions in the reservoirs and during production might be a much more widespread phenomenon, and probably much more important for petroleum recovery, than was previously believed.

5 Conclusions

1. SARA analysis of Latin American crude oil revealed that a crude oil with high amounts of heavy components exhibits viscosity decrease after contact with brine solutions.

2. No significant compositional change in GC analysis of the Latin American crude oil suggested that viscosity variation is possibly because of change of conformations of the heavy molecules like in polymer solutions [20].

3. SARA analysis of the Middle East crude oil and compositional changes in the range of lighter components in the GC analysis demonstrated that formation of emulsions is related to lighter components of a crude oil.

4. The heptane-brine systems formed emulsions in the JEFRI cell. But no change in heptane viscosity was observed. This may support the conclusion that viscosity variation in crude oil is attributed to the presence of heavy components, while formation of emulsions is related to lighter components.

5. The measurements in the Turbiscan confirmed that the presence of sulfate in the brine facilitates creation of the water-brine emulsions. A new observation was the formation of a 'gel-like' single phase under shaking the oil/brine samples in the course of their preparation for the Turbiscan.This may be an important, previously overseen mechanism affecting oil production.

Acknowledgements

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