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Experimental Study of Microemulsion Characterization and Optimization in Enhanced Oil Recovery: A Design Approach for Reservoirs with High Salinity and Hardness

by

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THESIS

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Experimental Study of Microemulsion Characterization and Optimization in Enhanced Oil Recovery: A Design Approach for Reservoirs with High Salinity and Hardness

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Dedication

To the lovely Cody Cox.
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Abstract

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The objective of this research was to develop a systematic laboratory approach, and design a high performance chemical flood for a problematic reservoir with formation brine having high salinity and hardness. Aqueous and microemulsion phase behavior tests have previously been shown to be a rapid, inexpensive and highly effective means to select the best chemicals and minimize the need for relatively expensive core flood tests. Phase behavior tests were therefore done with various combinations of surfactants, co-solvents and alkali for several crude oils and reservoir conditions, including the problematic reservoir of interest for design. Extensive phase behavior testing identified performance trends of chemicals at different concentrations, which could be interpolated for optimization. The trends were ultimately used to develop an approach to design
potential chemical flood formulations for the problematic reservoir of interest. Using this approach, several formulations were designed showing good performance in phase behavior testing. One of the formulations was then validated in a core flood experiment to give nearly 100% oil recovery with very low surfactant adsorption. The chemical flood design used a salinity gradient that was robust enough with withstand the sharp salinity contrast of the formation brine and surfactant slug at the displacement front. Salinity analysis of core flood effluent showed how Type III microemulsion conditions were targeted to most effectively mobilize residual oil.
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CHAPTER 1: INTRODUCTION

Replacing or following traditional water flooding with aqueous chemical mixtures can be a viable enhanced oil recovery (EOR) process. Mixtures typically contain several chemical components (i.e. surfactant, co-surfactant, co-solvent, polymer, electrolyte, and/or alkali) that are often mixed into the freshwater or formation brine. Obtaining an optimal formulation requires a strategic design methodology for quick and optimal formulation design. Chemical components are chosen based on their molecular design, and evaluated based upon both the aqueous phase behavior and the microemulsion phase behavior with a crude oil of interest. This research first identifies several parameters to characterize microemulsions, and then uses these parameters to evaluate molecular designs and interactions of EOR chemicals. A strategic design methodology then uses this information to create an optimal mixture for a crude oil and reservoir of interest, and to validate the mixture in a core flood experiment. This research emphasized designing for a reservoir with very high total dissolved solids (TDS) and hardness in the formation brine.

The research presented in subsequent chapters is only a small continuation of the vast knowledge on chemical EOR developed at the University of Texas at Austin and other research laboratories over the past 50 years. A general overview of this theoretical and experimental foundation in chemical EOR is referred to in the literature review chapter.

MOTIVATION

Many mature reservoirs under water flood have low economic production rates despite having 50 - 75% of the original oil still in place. These reservoirs are viable candidates for chemical enhanced oil recovery that uses both surfactant to reduce the IFT and polymer to improve sweep efficiency. However, designing these aqueous chemical mixtures is complex, and must be tailored to specific reservoir rock and fluids (i.e. crude oil and formation brine) properties. A strategic design methodology can help provide an
optimal, well-performing chemical formulation, even for challenging and problematic reservoir properties. Laboratory and field-testing can contribute to an expanding database in favor of broadening reservoir candidates for chemical EOR as a routine application.

Levitt (2006), Jackson (2006) and Levitt et al. (2006) describe a three-stage procedure developed at the University of Texas at Austin for surfactant selection and chemical formulation design for chemical EOR applications. The first stage selects a list of surfactants based upon data and knowledge of surfactant chemical structure and its interaction with crude oil and reservoir physics and chemistry. The second stage screens these surfactants as chemical mixtures (i.e. surfactant, co-surfactant, co-solvent, alkali, polymer, electrolytes, water) with crude oil in phase behavior experiments described that assesses phase behavior performance from the degree of micellar solubilization (which is related to interfacial tension), viscosity, equilibration time and optimum salinity among other characteristics.. The third stage tests the optimal formulation in a core flood experiment.

This research modifies the second design stage of the screening process and provides a systematic methodology of selecting and optimizing chemical mixtures that helps minimize experimental time and cost. Selecting an appropriate surfactant is only the first step in optimizing the total and relative concentrations of other co-surfactants, co-solvents, alkali, electrolytes, and/or polymer chemicals selected for the optimal formulation. This research tests how chemical components can affect phase behavior performance, and uses the findings to formulate a methodology for optimal design. The methodology is then used to design an optimal formulation for a specific crude oil from a candidate reservoir for a chemical EOR application.

Mature reservoirs that are candidates for chemical EOR applications frequently have characteristics regarding the chemistry and physics of their crude oil, formation brine, or reservoir rock that are problematic and challenging for design. Some of these characteristics are high salinity, and/or hardness for the formation brine, low API gravity oil, high oil viscosity, and low reactivity of the crude oil with alkali. Research and understanding into all of these challenging characteristics is important to expand the
potential candidate reservoirs for chemical EOR application. This research demonstrates how a good design methodology provides an optimal chemical formulation based on phase behavior data, and validated in core flood experimentation. As a practical design application, this research specifically addresses reservoirs with formation brine having very high TDS and hardness, and hopes to contribute to future commercial projects with these types of reservoirs.

**SUMMARY OF CHAPTERS**

Chapter 2 discusses literature and background information regarding chemical component structures and the advancement of chemical mixture design for EOR applications. Chapter 3 provides an experimental description of the phase behavior and core flood research, and describes the equipment, methodology, and data analyses used in the research. Chapter 4 presents the results for the microemulsion characterization, chemical formula design, and core flood application experiments. Chapter 5 is an additional chapter on natural imbibition experimentation, and consists of an experimental description, results, and discussion of this research. Chapter 6 presents a summary and conclusion of all experimental results, relating them to the literature and proposing a future direction for the research.
CHAPTER 2: LITERATURE REVIEW

INTRODUCTION

This chapter provides a literature review on the theory and methods used in this research. The review is segmented into a section on phase behavior experimentation, and a section on core flood experimentation. Early development and theory of phase behavior methods are described, and form the foundation of current experimental strategies. Similar theory and application for core flood experimentation are reviewed in the literature, and considered for experimental design. This research offers a continuation of the latest phase behavior and core flood methods described in the literature.

PHASE BEHAVIOR EXPERIMENTATION

Chemicals for EOR application are commonly characterized in phase behavior experiments by evaluating the microemulsion created with oil, water, and surfactant. A chemical formulation for an EOR application is first designed to work well in phase behavior before being tested in a core flood experiment.

Microemulsion Types

The interaction of an aqueous phase containing surfactant with a hydrocarbon phase will under some conditions produce a microemulsion containing surfactant, water, and oil, and this microemulsion has been a major scientific focus for chemical EOR. Windsor (1954) characterized these microemulsions as being of three different types: Type I, Type II, and Type III.

A Type I microemulsion is an oil-in-water microemulsion, where a portion of the oil has been solubilized by the surfactant. Conversely, a Type II microemulsion is a water-in-oil microemulsion, where a portion of the water has solubilized by the surfactant. A Type III microemulsion is an emulsion with the oil and water solubilized by the surfactant that is often assumed to be bicontinuous, and may be in equilibrium with excess oil and water phases. This bicontinuous microemulsion can have varying proportions of oil and water, and is assumed to contain essentially all of the surfactant...
originally in the aqueous phase. All microemulsions by definition are thermodynamically stable, and in theory will never separate out into their oil and water constituents.

**Microemulsion Characterization**

Aqueous and oil phase interaction under some conditions produces a microemulsion phase, which can transition (i.e. shift) from a Type I (oil in water) to Type III to Type II (water in oil) phase (or vice versa) with the systematic variation of several different parameters in the aqueous solution (Windsor, 1954; Bourrel and Schechter, 1988, Huh, 1979; Aoudia et al., 1995). Some parameters that cause a lower- to upper-phase transition for anionic surfactants such as sulfonates include increases in electrolyte strength (i.e. salinity), oil-soluble co-solvent concentration, alkyl chain length of the surfactant, oil aromaticity, and propylene oxide number (PON), and some parameters that cause a upper- to lower-phase transition include decreases equivalent alkane carbon number of the oil, ethylene oxide number and water-soluble co-solvent concentration (Huh, 1979; Aoudia and Wade, 1995). A temperature increase generally causes an upper-to lower-phase transition for anionic surfactants; however, the reverse has been shown to occur for anionic sulfates with a high PON (Aoudia and Wade, 1995). The most notable phase behavior transition for anionic surfactant applications is from type I to type III to type II as salinity increases.

Phase behavior microemulsions can be characterized using several different methods, and these methods evaluate properties relating to oil and water solubilization proportions, time of coalescence, interfacial tension between fluid phases, viscosity, and conductivity, with the most common method evaluating solubilized oil and water. Healy et al. (1976) devised a method to graphically represent the oil and water solubilized in the microemulsion. For each salinity, they would first measure the volumes of oil (Vo) and water (Vw) the microemulsion contained, and then normalize these volumes to the total volume of pure surfactant (Vs) to obtain oil and water solubilization ratio values (Vo/Vs and Vw/Vs, respectively). Then, these solubilization ratios would be plotted for each salinity, and subsequently fitted with curves to form solubilization curves. The
intersection of the oil and water solubilization ratio curves was defined as the optimal solubilization ratio and optimal salinity (other variables such as temperature can be used rather than salinity).

**Microemulsion Coalescence**

The time at which no further coalescence of the oil and water occurs is the equilibration time, which can often be lengthy or hindered when gels, macroemulsions, liquid crystals, etc. are present, and for this and other reasons such behavior is considered undesirable compared to the formation of microemulsions, which tend to equilibrate faster. Because microemulsions are thermodynamically stable, the coalesced volume at equilibrium should be constant indefinitely given no external perturbations or temperature/pressure changes.

**Microemulsion and Interfacial Tension**

The addition of surfactant reduces the interfacial tension (IFT) between oil and water, and this IFT reduction is the mechanism interest for mobilizing residual oil in chemical EOR (Huh, 1979). In a pipette containing a Type I microemulsion, the IFT of interest is between the microemulsion and oil phases. The IFT of this microemulsion/oil interface decreases as salinity is increased into the Type III region until the interface disappears at the Type III/Type II salinity boundary. Similarly, a pipette containing a Type II microemulsion will have an aqueous/microemulsion interface and the IFT decreases as the salinity is decreased into the Type III region. Both the aqueous/microemulsion and microemulsion/oil interfaces exist in a Type III environment, and the IFT of these two interfaces are equal at the optimal salinity. Determining this IFT value at optimal salinity is very important in surfactant selection and performance. Huh (1979) derived a theoretical relationship between solubilization ratio and IFT at optimum salinity. Huh's equation has been found to give a very good estimate of the IFT over a wide range of salinity and other variables for a large number of oils including crude oils. The relationship between IFT and solubilization ratio had previously been observed and
empirically correlated by Healy et al. (1976) and others and even used in simulation models (Pope et al., 1979), but Huh was the first to establish its theoretical basis.

**EOR Chemical Components and Structures**

A typical chemical EOR solution contains primary surfactant, co-surfactant, co-solvent, alkali, polymer, and electrolyte in an aqueous carrier. The primary surfactant is the component directly involved in microemulsion formation, with co-surfactant improving the action of the primary surfactant (Nelson et al., 1984). The co-solvent acts to prevent gel formation and reduce equilibration time among other benefits and is often needed to make the surfactant compatible with the polymer (Pope et al., 1982). Alkali agents can enable in-situ soap generation from crude components, and have also been shown to hasten microemulsion equilibration and coalescence (Jackson, 2006) with or without soap formation and also have other very significant benefits. Polymer acts to viscosity the solution for mobility control in the reservoir flood. Lastly, the electrolytes are adjusted to achieve optimal salinity and thus minimum IFT and are often also used to produce a negative salinity gradient (lower salinity in the polymer drive compared to the surfactant slug), which has numerous benefits in terms of making the chemical flood more efficient and robust (Pope et al., 1979).

**Primary Surfactant and Co-surfactant**

Surfactants cause the solubilization of water and oil into a microemulsion under some conditions, and are the primary component of interest in phase behavior studies. A specific surfactant or surfactant mixture must be selected based on its interaction with the crude oil, reservoir rock, and reservoir conditions (e.g. pressure and temperature), but the reservoir rock is not considered in phase behavior experimentation so additional testing is required to address those interactions.

Surfactants generally contain a hydrophilic head, a hydrophobic hydrocarbon tail, and possible intermediate neutral groups, which forms a structure loosely resembling male sperm. Several varieties of these groups are common in surfactant design, and
different combinations and permutations between these varieties can generate a plethora of surfactant structures to choose from. However, certain structures and combinations of structures have been shown to more effectively increase oil recovery performance. Chemical structures commonly found in the head, tail, and intermediate parts of the surfactant are discussed in the following sections.

**Carbon Chain (non-polar tail)**

The hydrophobic hydrocarbon chain forms the carbon backbone or tail of the surfactant molecule, with the number of carbons in the backbone typically varying from 12 to 16 but sometimes can be as high as 28. The best carbon number depends on the compatibility of a shorter or longer chain with the crude oil of interest, which can be highly dependent on the crude oil effective alkane carbon number (EACN) (Aoudia et al., 1995). Surfactants with long carbon chains and little branching are able to form microemulsions by closely packing their hydrocarbon tails together. For an oil-in-water microemulsion, the closer the carbon chains pack together, the smaller the microemulsion droplet can be. As microemulsion stability increases (e.g. with decreasing droplet size), the volume of Type III microemulsion increases, which is correlated with a very low oil/microemulsion and microemulsion/water IFT (Bourrel and Schechter, 1988). However, a more stable microemulsion generally has greater viscosity, and subsequently takes longer to equilibrate. Thus, it has been found that surfactants made from branched hydrophobes perform better overall. Other ways to avoid linear surfactants are also possible and have been used to advantage. Detergents used for almost all other purposes are typically linear since they are more easily biodegraded.

A branched hydrocarbon chain is desirable due to reduced packing at the oil/water interface, resulting in lower viscosity microemulsions, and the formation of less ordered oil/water structures that reduce gels and liquid crystal formations (Levitt et al., 2006, Schramm, 2000). Additionally, a longer hydrocarbon chain increases solubilization, decreases optimal salinity, but can increase both microemulsion viscosity and equilibrium time. A more extreme branching development where two separate carbon tails stem from the polar head group has also shown very good performance (Levitt et al., 2006).
Polar Head Groups

The hydrophilic head can be anionic, cationic, or neutral. The most common anionic heads are sulfonates and sulfates. Sulfates hydrolyze above about 60°C so are limited to low reservoir temperature applications. In aqueous chemical EOR, anionic surfactants are generally preferred to cationic and non-ionic surfactants due to several characteristics, which include a lower cost and lower adsorption to the negatively-charged surfaces of sandstones. Carbonates can also assume a negative surface charge when alkali has been included and the pH exceeds about 8.5.

Other Functional Groups

Intermediate groups encompass molecules that join the hydrocarbon tail to the hydrophilic head, and are often neutral (i.e. neither strongly hydrophilic or hydrophobic) in nature. The objective of these groups is to provide stability at the water/oil interface of a microemulsion droplet, and to contribute tolerance to divalent cations. Although several possible molecular groups can serve this function, the most commonly used groups are ethylene oxide (EO) and propylene oxide (PO), which have been shown to provide Ca$^{++}$ and Mg$^{++}$ tolerance (Austad and Milter, Bourrel and Schechter, Aoudia et al., DOE DE-FC26-03NT15406). EO groups are hydrophilic, whereas the PO is essentially neutral. Therefore, increasing the number of EO groups on a surfactant molecule increases the optimum salinity and the tolerance for divalent cations, preventing precipitation and other problems. PO groups increase the size and area of the surfactant without making it too hydrophilic and thus tend to promote lower IFT over a wider range of conditions, and also increase its divalent cation tolerance. Recent advancements in manufacturing technology allow surfactants with only PO groups, as well as only EO groups or a combination of PO/EO groups to be manufactured.

Co-solvent

The purpose of co-solvents are to introduce a small molecular weight compound to act at the oil-water interface, get between the surfactant hydrocarbon groups, and
reduce the viscosity of the oil/water microemulsion (Sanz and Pope, 1996). These co-solvents have been shown to reduce gel formation, microemulsion viscosity, and microemulsion equilibration time. An alcohol that is equally soluble in oil and water or has a partition coefficient between the oil and water of one (neutral) have been found to be good choices. Propyl, butyl, and pentyl alcohols are generally closest to neutrality, and have therefore been used the most in the past 40 years. However, adding alcohols has been shown to decrease the optimal solubilization ratio and increase the IFT and of course adds to the cost so there are disadvantages as well as advantages to using alcohol but the advantages often out weigh the disadvantages. Ethylene glycol butyl ether and other glycols also make good co-solvents and have some advantages over light alcohols such as a higher flash point (Jackson, 2006).

**Alkali**

The addition of alkali to an EOR solution serves to increase both electrolyte strength and pH. The additional electrolytes will reduce the NaCl requirement to achieve optimal salinity. However, because using the less expensive and non-scaling NaCl is more practical in contributing electrolyte strength, an optimal alkali quantity is only what satisfies the alkali consumption (Zhang and Hirasaki, 2004). In chemical EOR, alkali is consumed through ion exchange with the reservoir rock and possibly other geochemical reactions depending on the minerals and other factors, and through in situ saponification of naphthenic acids naturally present in crude oil. Maintaining a high pH throughout the entire chemical flood is needed to achieve these benefits in the entire reservoir. Therefore a high concentration may be needed for the injected fluid to account for consumption, meaning a significant concentration needs to be tested in phase behavior.

In phase behavior experiments, alkali is generally consumed through in situ saponification of naphthenic acids naturally present in crude oil. This saponification process creates natural soaps that mimic the action of synthetic surfactants, and also act as co-surfactants. However, some crude oils have a very low reactivity, and will therefore consume little to no alkali. The acid number of the crude oil (mg KOH / g oil) is often...
used as an indicator of the naphthenic/carboxylic acid concentration that could potentially be saponified, though there is not yet a perfect and quantifiable correlation to reactivity. Common alkali agents for EOR application are sodium hydroxide and sodium carbonate, with novel agents being sodium metaborate and organic alkalis. Alkalis of focus for this research have been sodium carbonate and sodium metaborate.

Sodium metaborate is of interest as an alternate alkali because it can prevent precipitation when gypsum or anhydrite (CaSO₄) deposits exist in reservoir rocks such as is often the case with dolomite rocks. If the sodium carbonate is present, the carbonate ions will form a precipitate with calcium ions from the gypsum. The advantage of sodium metaborate is that the borate ions form soluble complexes with dissolved calcium ions, and therefore formation damage and other problems can be mitigated.

**Polymer**

The addition of a high molecular weight water-soluble polymer to a chemical EOR solution increases the viscosity of the injected solution, the chemical slug. This increase in viscosity is needed to offset the increase in the aqueous relative permeability that occurs when the IFT is reduced by 1000s of fold. Higher viscosity (low mobility ratio) also increases the sweep efficiency in a reservoir by preventing an unstable displacement (fingering), channeling due to layering and other heterogeneities, and by passing among other mechanisms. For these and other reasons, polymer is needed in both the slug and the polymer drive pushing the slug. Oil recovery in the field has been shown to increase in portion to the amount of polymer used up to very high concentrations and pore volumes. Thus, the use of co-solvents to co-solubilize the surfactant and polymer is often (but not always) essential.

Hydrolyzed polyacrylamides (HPAMs) are a common, inexpensive class of polymers containing long, flexible structures (Sorbie, 1991; Lake, 1989; Wreath, 1989). The length of the polymer structure can be selected based on reservoir permeability and other rock characteristics such as pore structure but generally lower permeability means a
lower molecular weight polymer must be used. A comprehensive overview of polymers in chemical EOR can be found in Sorbie (1991).

**Electrolyte**

Phase behaviors are tested on a salinity gradient, and electrolyte is needed for this gradient, and for obtaining an optimal salinity. Sodium chloride is the most common electrolyte, though divalent cations (i.e. Ca$^{++}$ and Mg$^{++}$) are sometimes added to assess their interaction in phase behavior. Formation brine can also be used as the aqueous medium of the formulation, which can contain several different electrolyte ions.

**CORE FLOOD DESIGN AND EXPERIMENTATION**

Core flood experimentation in chemical EOR is a means to test how effectively a surfactant formulation can recover oil. A formulation showing good solubilization and aqueous stability in phase behavior can be selected for a core flood experiment. The target of a chemical flood is the residual oil saturation trapped by pore-scale capillary forces in a sample rock core (Levitt, 2006). The rock is similar or the same as reservoir rock that that the crude oil originated from.

**Interfacial Tension**

Mobilizing residual oil occurs when surfactant solution (new aqueous phase) replaces the initial water (old aqueous phase), and reduces the IFT between the residual oil and aqueous phase. Well performing surfactants commonly lower the IFT to $10^{-3}$ dynes/cm, compared to an oil-water IFT around 30 dynes/cm. An IFT of $10^{-3}$ dynes/cm nearly eliminates capillary pressure that originally trapped the residual oil, causing the oil to mobilize. The capillary number, $N_c$, is a non-dimensional parameter relating viscous forces to capillary forces, and is expressed as:

$$N_c = \frac{k V |\Phi|}{\gamma}$$
The capillary forces are represented by the interfacial tension, $\gamma$, and the viscous forces are represented by $k\nabla|\Phi|$ (which includes the viscous potential gradient). Empirical data for different porous media have shown the reduction of residual to correlate to an increase in capillary number (Delshad, 1986). A critical capillary number describes the lower limit where residual oil is first mobilized, and residual oil can become nearly zero when capillary number increases a few orders of magnitude greater. A surfactant-based chemical flood reducing IFT from 30 to $10^{-3}$ dynes/cm commonly achieves capillary numbers representing zero residual oil (Shen et al, 2006).

**Salinity Gradient**

Phase behavior experiments show IFT at oil-microemulsion and water-microemulsion interfaces to be most favorable (i.e. collectively low) at the optimal salinity, and optimal salinity is therefore desired for a core flood experiment. A salinity greater than optimal begins to lower the oil-microemulsion IFT to trap surfactant in the residual oil (i.e. surfactant loss), and increases water-microemulsion IFT, which reduces oil mobilization. A salinity lower than optimal lowers the water-microemulsion IFT to keep surfactant in the water phase, and increases oil-microemulsion IFT, which also reduces oil mobilization. An ideal scenario is to aim for optimal salinity somewhere in the displacement, but it is difficult to achieve optimum salinity everywhere given the narrow Type III salinity window, and several other factors (cation exchange, dilution, etc.). Pope et al. (1979) found a salinity gradient to offer a more robust chemical flood design, where initial water at a Type II salinity steps down to a surfactant slug at optimal salinity, followed by another step down to a polymer drive at Type I salinity. This salinity gradient significantly increases the chances of low IFT, Type III conditions somewhere in the mixing zone (Levitt, 2006). A polymer drive of salinity near the Type I/Type III boundary increases the risk of the system remaining in the Type II region, but increases the chances of more prolonged Type III, low IFT conditions. A more conservative polymer drive with salinity far into the Type I region can prevent it from being in the
Type II region, but it can also minimize the time spent at a Type III, low IFT salinity. Therefore, design of the salinity gradient is based on a desired risk-to-reward.

**Pressure Gradient**

Pressure gradient across the core is another important design consideration in a core flood experiment. A pressure gradient of 1 psi/ft is common for a field water flood with a frontal velocity on the order of 1 ft/D, and a chemical flood application should therefore be designed with a similar pressure gradient. Low microemulsion viscosity is required to achieve such a low pressure gradient.

**CRUDE OILS EVALUATED**

Every crude oil or hydrocarbon is unique, and therefore a unique chemical EOR formulation must be designed for that specific crude oil. However, research has attempted to find design trends for crude oils having similar properties, which can help reduce experimental time. One example is from Aoudia et al. (1995), who identified crude oil interactions by their equivalent alkane carbon number (EACN), finding this parameter to affect optimal salinity and solubilization ratio.

This research involved three different crude oils, which included: McElroy, Yates, and Crude D. McElroy crude oil was used to characterize phase behavior microemulsions, and to develop a general methodology for chemical formulation design. Yates crude oil was used in a small number of experiments for comparison with McElroy crude oil results. Crude D helped validate the design methodology developed with the McElroy crude, and was recovered in a core flood experiment.

**Yates**

Yates crude oil is from a fractured carbonate, low temperature (28°C) reservoir located in W. Texas in southern Pecos County. The field was discovered in the 1920s, and its long production period has made it a mature field, and therefore is a good candidate for tertiary recovery and chemical EOR. The type of Yates crude oil used in
experimentation was termed Yates batch 4 (MY4), which is identical to that used by Zhang and Hirasaki (2004, 2006). The crude oil is considered reactive with alkali.

**McElroy**

McElroy crude oil is from heterogeneous dolomite, low temperature (30°C) reservoir located in W. Texas on the eastern edge of the Central Basin platform, and the western margin of the Midland Basin. The field was discovered in 1926 and has been under continuous waterflooding since the 1960s. Because the field is nearing mature stages of secondary waterflood recovery, it is a good candidate for tertiary recovery and chemical EOR. The crude oil is light (API 36.2), low viscosity (10 cp), and considered non-reactive with alkali.

**Crude D**

Crude D is from a sandstone reservoir of moderate temperature (52°C) and permeability (90 md). The crude oil is very light (API 48) and of low viscosity (1.96 cp). The reservoir formation brine contains very high TDS (157,000 mg/L), with 6650 mg/L Ca^{++} and 2020 mg/L Mg^{++}, and this poses challenges to chemical EOR design.
CHAPTER 3: EXPERIMENTAL DESCRIPTION

INTRODUCTION

An experimental description of the materials, experimental methodology, and calculations used for data analysis are presented in this chapter. The chapter is segmented into three sections that include: chemical EOR fluids, aqueous/microemulsion phase behavior description, and core flood description. The EOR fluids segment gives an inventory of chemicals used and their preparation. The experimentation and analysis of these fluids to design a chemical EOR formulation is provided in the phase behavior description. The core flood description explains how a designed and optimized formulation is validated in a core flood experiment to recover residual oil.

Equipment used in the research can be categorized into experimental and analytical equipment. Experimental equipment performs and supports phase behavior and core flood experimentation, and includes: mass balances, water deionizer, convection ovens, borosilicate pipettes, fluid dispenser, flame torch, air minipermeameter, fluid reservoirs, pumps, tubing, pressure transducers, data acquisition recorder, fraction collector, and hot plate. Analytical equipment analyzes fluid properties, and includes: interfacial/surface tension meters, pH / conductivity meter, coquette viscometer, filter press, hyamine titrater. Descriptions and uses of the equipment are provided in this chapter, as well as their relevance for the overall research.

CHEMICAL EOR FLUIDS

The chemical EOR fluids used in the phase behavior and core flood experiments are described in this section. An inventory of surfactants, chemicals, and other fluids used in this research is provided, along with how these were prepared into useable mixtures for experimentation.
Primary and Co-surfactants

The surfactants used in this study contained a hydrophobic carbon backbone with 13 to 24 carbon atoms. The carbon backbones were either branched, kinked (e.g. internal olefins), or straight. Intermediate groups included propylene oxide (PO) and ethylene oxide (EO), and the polar head group was either a sulfate or a sulfonate.

The primary surfactant most extensively used in this experiment was C\textsubscript{16-17} - 7PO - SO\textsubscript{4} made by Stepan with the trade name of Petrostep S1. Some of the other primary surfactants included: C\textsubscript{13} - 4PO - SO\textsubscript{4}, C\textsubscript{13} - 8PO - SO\textsubscript{4}, C\textsubscript{14-15} - 8PO - SO\textsubscript{4}, C\textsubscript{12-13} - 8PO - SO\textsubscript{4}, C\textsubscript{12-13} - 5PO - SO\textsubscript{4}, C\textsubscript{16-18} - SO\textsubscript{3} (AOS), C\textsubscript{20-24} - SO\textsubscript{3} (AOS), C\textsubscript{12-14} - 3EO - SO\textsubscript{4}.

Note that the structure does not indicate the degree to which the surfactant branches. General information on these surfactants is given in Table 3.1.

The co-surfactants used were 15 to 24 carbon, twin-tailed molecules with a sulfonate head group. The most common one was the internal olefin sulfonate with 15 to 18 carbon atoms (IOS\textsubscript{15-18}) made by Stepan with the trade name Petrostep S2. An internal olefin sulfonate with 20 to 24 carbon atoms made by Stepan with the trade name Petrostep S3 was also tested.

Co-solvents

Several different alcohols ranging from C\textsubscript{3} to C\textsubscript{5} were available for experimentation; however, sec-butanol (SBA) was used in almost all of the phase behavior experiments. A small study did assess about eight potential co-solvents, which included: ethanol, 1-propanol, iso-propanol, 1-butanol, sec-butanol, tert-butanol, n-pentanol, 2-butoxy-ethanol. Sec-butanol, however, was found to offer the best performance for this low temperature (30\textdegreeC, 52\textdegreeC) study of light crude oils. Jackson (2006) found n-pentanol, t-pentanol and EGBE more suitable for a heavier crude oil at a higher temperature (85\textdegreeC). Iso-butanol (IBA) was not considered for this experiment even though it can offer similar performance to SBA at a lower cost.
Alkalis

Three different alkali agents were available for experimentation, and these included: sodium carbonate (Na₂CO₃), sodium metaborate pentahydrate (sodium metaborate), and sodium hydroxide (NaOH). Sodium carbonate was the primary alkali of interest based in part on the study of Jackson (2006). Sodium metaborate was used as an alternate, novel alkali, and sodium hydroxide was added to obtain very high pH values. At 1 wt% concentration under the conditions of temperature and salinity studied in this work, the pH of sodium carbonate is about 10.4, the pH of sodium metaborate is about 9.3, and the pH of sodium hydroxide is about 13.

Polymer

Several hydrolyzed polyacrylamine (HPAM) polymers from the Flopaam® polymer series were available; however, only the Flopaam® 3330S HPAM polymer was used for experimentation. The polymer is 30% hydrolyzed, with a molecular weight of 8 million Daltons. In this research, polymer was used in the aqueous stability tests and in the core flood experiment, but not in the microemulsion phase behavior tests.

Electrolytes

Sodium chloride was the electrolyte used for most phase behavior experiments, which contributed Na⁺ and Cl⁻ ions to provide the required salinity gradient. Other anions and cations used as electrolytes include Ca²⁺ and Mg²⁺, which were obtained from CaCl₂ and MgCl₂ salts. The use of alkali also contributed additional electrolytes to solutions.

Crude Oils

This research involved three different crude oils, which included: McElroy, Yates, and Crude D. McElroy crude oil was used to characterize microemulsion phase behavior, and to develop a general methodology for chemical formulation design. Yates crude oil was used in a small number of experiments for comparison with McElroy crude oil
results. Crude D helped validate the design methodology developed with the McElroy crude, and was recovered in a core flood experiment.

Prior to use, crude oil was tested for contamination by measuring the surface tension with respect to air. A ring tensiometer based on the du Nouy method is used to measure the surface tension between crude oil and air. The force required to pull a platinum-based ring from the water-oil interface is converted to an interfacial tension measurement. An expected value for uncontaminated crude oil is around 20 dynes/cm, so crude oil was assumed to be contaminated and subsequently rejected if values fell under 10 dynes/cm.

**Deionized Water**

Deionized water was used as the aqueous phase to prepare all stock solutions. A Nanopure™ filter system was used to de-ionize water for all experimental solutions. The system uses a recirculation pump to filter water to about an 18 megohm-cm resistivity value, which indicates that sufficient ions have been removed.

**FLUID PREPARATION**

**Equipment**

Several types of experimental and analytical equipment were used to prepare fluids for experimentation. Experimental equipment includes a mass balance and a filter press, and analytical equipment includes a coquette-type viscometer for measuring viscosity.

**Mass Balance**

Mass balances were used to measure chemical components for fluid mixtures and saturation and property values for cores. The Sartorius® ED623S mass balance with 0.001g resolution and 620g capacity measured masses of all chemical components (e.g. surfactant stocks, dry polymer, alkali and electrolyte salts) for various fluids (e.g. surfactant stock, brine, polymer stock). The Sartorius® ED620S mass balance with 0.01g
resolution and 6200g capacity measured dry and saturated cores contained in epoxy to obtain saturation and porosity values.

**Filter Press**

A FANN® Series 300 LPLT filter press was used to filter injection fluids. The filter press assembly consists of a stainless steel reservoir mounted in a frame, a pressure source, a filtering medium, and a graduated cylinder to collect and measure filtrate. Compressed air at 100 psi was the working pressure, which was regulated to 10-30 psi using a pressure regulator. The filtering mediums were Millipore™ hydrophilic cellulose filter paper at 0.45 microns for crude oil and brine solutions, and 1.2 microns for polymer solutions. For filtration tests of polymer solutions, a similar FANN® 12 BL filter press was also used that could be elevated above the graduated cylinder on a makeshift frame.

**Couette Viscometer**

A Contraves Low Shear 30 (LS 30) couette-type viscometer was used to measure bulk viscosity of microemulsion and polymer/polymer-surfactant mixture. The instrument produces shear rates from 0.0174 to 128.5 sec⁻¹, and resulting shear stresses are measured between a spinning bob and about 1 mL of fluid in a small cup. Bulk viscosity values are calculated from shear stress and shear rate values using correlations and conversion factors.

**Surfactant/Co-Surfactant/Co-Solvent Stock Solution**

A stock solution containing surfactant, co-surfactant, and co-solvent are customized and mixed prior to each phase behavior experiment. Surfactant and co-surfactant feed stocks have an activity between 15% and 35% by mass percent of total solution, and these are mixed with co-solvent and diluted with de-ionized water to make a stock solution. Stock solutions generally have activities of 4 - 8%, or 4 to 8 times the 0.5 - 2% used in phase behavior and core flood experiments. The surfactant/co-surfactant/co-solvent stock solution will eventually be diluted to their desired concentration after
mixing with other chemical mixtures (e.g. alkali, brine, polymer) for either phase behavior experiments or core flood injection slugs.

**Polymer Stock Solution**

A hydrolyzed polyacrylamide (HPAM) polymer stock solution was prepared and then diluted later to the desired polymer concentration. An typical stock solution contains 5000 ppm polymer and 1000 ppm NaCl, and is prepared in 500 gram batches. To prepare a 500 gram-batch of stock, 2.5 grams of dry, desiccated polymer powder added into 497 grams of de-ionized water with 0.5 grams NaCl dissolved in it. The solution is slowly mixing on a magnetic stir plate while the powder is sprinkled into the shoulder of the vortex created by the rotating stir bar. Sprinkling must be slow enough to prevent clumping of the hydrated powder, and fast enough to prevent non-hydrated powder from floating on a solution too viscous for hydration. After the initial mixing, the polymer solution is mixed more slowly for at least 24 hours to ensure full hydration.

A filtration ratio is a measure of how well a prepared polymer solution has been hydrated. All polymer solutions were filtered through 1.2 μm Millipore filter paper under constant pressure of 15 psi in a Fann model filter press. All of a properly hydrated solution should filter at an almost constant rate throughout the filtration process, which indicates that non-hydrated components are not left behind on the filter paper. In actuality, some components build up on the filter paper during the filtration process, and decreases the filtration rate slightly during filtration.

Filtration ratio compares the time it takes to filter equal volumes of polymer solution near the beginning and end of the filtration process. For filtering a 120 mL polymer solution, a filtration ratio can be the time that 20 mL to 40 mL of solution filters to the time that 80 to 100 mL of solution filters. The following simple calculation expresses this as:
\[
\text{filtration ratio} = \frac{\Delta t_{80-100 \text{ mL}}}{\Delta t_{20-40 \text{ mL}}} \]  \hspace{1cm} \text{(3.1)}
\]

\[
\Delta t_{20-40 \text{ mL}} = \text{time for 20 to 40 mL of polymer to filter}
\]

\[
\Delta t_{80-100 \text{ mL}} = \text{time for 60 to 80 mL of polymer to filter}
\]

A polymer solution hydrated sufficiently should have a filtration ratio less than 1.2.

**Brine Stock Solutions**

Stock solutions of brines generally contain concentrated dissolved NaCl at 10 to 20 wt%, and are used to contribute electrolytes to surfactant and polymer solutions used in phase behavior and core flood experiments. In phase behavior experiments, concentrated stock solution of NaCl is added in varying amounts to an array of pipettes to create a salinity gradient, with each pipette assessing performance at a slightly different salinity than the others.

Synthetic formation brine (SFB) typically used to initially saturate a core, and injected during both the brine flood and water flood experiments. SFB is similar in composition to actual reservoir brine, and is based on water analysis data of actual reservoir brine that gives concentration values (mg/L) of each ion present. Ions usually consist of Na\(^+\), Ca\(^{++}\), Mg\(^{++}\), and Cl\(^-\), but can include trace ions such as Ba\(^{++}\), SO\(_4^{--}\), and HCO\(_3^-\). For simplicity, SFB is mixed by dissolving amounts of NaCl, CaCl\(_2\), and MgCl\(_2\) in de-ionized water that replicate the concentrations of Na\(^+\), Ca\(^{++}\), Mg\(^{++}\), and Cl\(^-\) present in the water analysis data. Trace ions are not considered unless of a significant concentration in the reservoir fluid. Note that in some studies, SFB is diluted in phase behavior experiments to mimic mixing produced water in a petroleum field setting to make injection fluids.
Crude Oil

To prepare crude oil for core injection, crude oil was filtered through a 0.45 micron Millipore filter paper to remove larger particulates that could plug the core. Crude D used in the core flood experiment was light and clean enough where filtration was relatively fast (~10 to 20 mL/min), and few particulates were removed by the filter paper. Heavier and more dirty crudes would need filtering more than once through different sized filter papers (i.e. 1.2 µm and 0.45 µm) and at reservoir temperature to dissolve paraffin components.

AQUEOUS / MICROEMULSION PHASE BEHAVIOR DESCRIPTION

Phase behavior experimentation of chemical EOR formulations is described in this chapter. These experiments offer a quick, economical method of screening chemicals for microemulsion properties and low interfacial tension prior to core flood experimentation. This section first describes some of the equipment used to prepare phase behavior pipettes, then discusses the actual preparation of pipettes using the prepared fluids and stock formulations discussed previously. Measurement and characterization created microemulsion is then discussed, along with quantitative methods for analyzing measurements.

Equipment

Several types of experimental and analytical equipment were used to prepare and analyze phase behavior pipettes. Experimental equipment includes pipettes and a pipette dispenser to hold and dispense fluid volumes, respectively, a flame torch to seal fluid-filled pipettes, and a convection oven to house and incubate pipettes. Analytical equipment used to characterize microemulsion formed in the pipettes includes a pH/conductivity meter, a spinning drop interfacial tensiometer, and a coquette-type viscometer.
**Borosilicate Pipettes**

Fisherbrand® standard 5 mL borosilicate serological pipettes with 5 mm inner diameter and 0.1 mL markings were used to hold fluid volumes in phase behavior experiments. The pipettes would hold volumes of aqueous solution and crude oil, as well as microemulsion formed from their interactions. The ends of pipettes were flame-sealed using a Benzomatic® Torch.

**Pipette Dispenser**

The Eppendorf Repeater Plus® handheld dispenser was used to dispense desired aqueous and crude oil volumes into the borosilicate pipettes. The dispenser could accurately deliver between 25 microliter and 1 ml volumes through disposable plastic tips, which were disposed after use with one fluid.

**Benzomatic® Torch**

After dispensing fluid volumes into pipettes, a Benzomatic® TS4000 flame torch was used to flame-seal the pipette ends. The flame torch burned MAPP gas from a 16 oz canister to create a hot blue flame about 3/4 inch long. The pipette end would melt and mold together to seal the end after about 30 seconds of exposure to the flame.

**Convection Ovens**

Pipettes that were sealed and mixed would be housed and incubated in a Blue M® convection oven. The oven would incubate pipettes for up to several months at reservoir temperature values in order to emulate reservoir temperature conditions. Mercury thermometers and oven temperature gauges helped guarantee a constant temperature with minimal fluctuation.

**Spinning Drop Interfacial Tensiometer**

Interfacial tension between microemulsion and aqueous phases was measured with a Model 500 Spinning Drop Interfacial Tensiometer. The apparatus was built at The
University of Texas at Austin. Interfacial tension of only a few microemulsions were measured with this apparatus, and interfacial tension was frequently inferred from the correlation by Huh (1979) mentioned previously.

**Couette Viscometer**

Microemulsion bulk viscosity was characterized using the Contraves Low Shear 30 (LS 30) couette-type viscometer. The instrument produces shear rates from 0.0174 to 128.5 sec\(^{-1}\), and resulting torque due to shear stresses are measured between a spinning bob and about 1 mL of fluid in a small cup. Bulk viscosity values are calculated from shear stress and shear rate values using conversion factors. This couette-type viscometer was also used to measure bulk viscosity of crude oil, brine, and polymer stock, polymer drive, and surfactant slug solutions.

**pH / Conductivity Meter**

Conductivity measurements was another method of characterizing microemulsion, and an Orion 5 Star benchtop digital conductivity meter was used to measure the conductivity of small microemulsion volumes. Prior to usage, the conductivity probe was calibrated with 1477 uS and 12.9 mS standard solutions. The meter was also capable of measuring pH, which was used to obtain pH values of aqueous phases used in phase behavior, and surfactant slugs used in core floods. Also prior to usage, a pH electrode was calibrated with 4.0, 7.0, and 10.0 pH standard solutions.

**Pipette Preparation**

A phase behavior experiment involves mixing certain proportions of an aqueous chemical EOR solution, salinated water, and crude oil in an array of pipettes. The pipettes used are generally 5 mL borosilicate pipettes, though 10 mL pipettes are used if larger microemulsion volumes are desired. The array of pipettes serves to create a salinity gradient, where different volumes of salinated water are added to each pipette to give different salinities. Additionally, equal volumes of aqueous chemical EOR solution
would be added to each pipette, with this EOR solution having a fixed concentration of surfactant, co-surfactant, co-solvent, polymer, and/or alkali.

**Order of Addition**

Stock solutions added to pipettes had concentrations several times that of the final concentration, and posed a risk if not mixed in an appropriate order. Contact of concentrated electrolyte stock with polymer or surfactant stock could adversely affect performance. To mitigate this risk, the electrolyte stock was added first, and was followed by de-ionized water. The surfactant and polymer stocks were then added in either order. Crude oil was the last component added after aqueous stability and aqueous fluid levels were recorded.

**Aqueous Stability and Initial Readings**

Prior to adding crude oil to pipettes, an aqueous stability assessment determines the clarity and homogeneity of all aqueous mixtures. The objective of the aqueous stability test is to determine compatibility of surfactants and polymer with electrolytes, and to ensure a stable surfactant slug that will not phase separate or contain precipitates prior to core flood or field injection. As a quick screening during phase behavior testing, aqueous fluids are agitated after being dispensed into pipettes, and then allowed to settle for one hour or more. The fluids in the phase behavior array are visually inspected, and the salinity is recorded where cloudiness and/or phase separation occurs. After this initial screen step, these mixtures were studied in a more detailed aqueous stability testing where larger, 10 mL volumes containing polymer are assessed in glass vials. A surfactant/polymer/electrolyte mixture that is injected into core or reservoir rock must be a clear, single phase mixture.

**Sealing and Mixing**

After assessing aqueous stability and adding crude oil, the ends of pipettes are heat-sealed with a Benzomatic® flame torch. Following heat-sealing, the pipettes are
allowed time to cool before being slowly inverted 12 times to allow the oil and aqueous phase mixing. Slow inversions is sufficient to generate microemulsion, but not rapid enough to generate foam. The greater contact between aqueous and oil phases is more representative of a pore-scale situation rather than the original contact area of the pipette cross-section. Microemulsion generation from oil and aqueous phases will yield a thermodynamically stable oil-in-water, water-in-oil, or bicontinuous microemulsion phase, and its analysis is the objective of phase behavior experimentation.

**Measurements and Observations**

Prepared pipettes are kept in a Blue M convection oven at a specified reservoir temperature of the crude oil for the duration of the phase behavior experiment. The visual and quantitative assessment of microemulsion properties and interfaces were recorded 1, 2, 3, 5, 7, 11, 15, 21, 30, and 50 days after the pipettes were mixed.

**Visual Assessment**

A qualitative, visual inspection of the phase behavior pipettes was used to assess the presence of gels or macroemulsion, the fluidity of interfaces, and the microemulsion viscosity. A gel and/or other highly viscous phases may cause plugging of the rock, high surfactant retention and other problems and thus should be avoided if at all possible. In some situations, a small accumulation of gel/macroemulsion at an interface would prevent oil and water phases from mixing, and the pipette would be inverted three more times to promote microemulsion formation. If the next inspection still showed gel/macroemulsion at the interface, the pipette would be assessed as having poor performance. Those mixtures where the macroemulsion breaks fast were considered superior to those where it broke slowly or not at all over the time period observed. Careful observations of droplet size and behavior when the pipettes are gently mixed can be used to indicate interfacial activity i.e. IFT.
Quantitative Assessment

Pipettes that were free of gels and macroemulsion and had freely flowing interfaces would be quantified to calculate phase volumes. Measurement of aqueous/microemulsion and/or microemulsion/oil interface levels would be interpolated to the nearest 0.01 mL using the markings on the pipette. From these interface measurements, the volumes of each phase (oil, water, and microemulsion) and the partial volumes of oil and water phases present in the microemulsion could be calculated. Further analyzing and comparing these volumes and volume fractions with respect to salinity and time could help determine optimal salinity, optimal solubilization ratio, and coalescence properties of the microemulsion. After pipettes have been incubated and measured over a period of time, microemulsion could be sampled from the pipettes and further characterized for viscosity, interfacial tension, and conductivity.

Microemulsion Characterization

Solubilization of oil and water phases with respect to available surfactant forms the basis of the solubilization ratio parameter used for microemulsion characterization. Solubilization ratios are calculated from interface measurements recorded while pipettes are incubating in the convection oven. The interfacial tension was then estimated using the equation from Huh (1979):

\[ \gamma = 0.3 / (\sigma^*)^2 \]

where \( \gamma \) is IFT, and \( \sigma^* \) is oil or water solubilization ratio at optimal salinity. Solubilization ratio values over time can also determine the microemulsion coalescence time, or the time after which little change in the solubilization ratios occur. Calculating and assessing solubilization ratio values versus both salinity and time is a simple and useful way to select the best surfactant formulations to test in core floods.

Microemulsions can undergo further characterization beyond screening calculations of solubilization ratio versus salinity and time. Additional characterization can come from measuring viscosity, interfacial tension, and conductivity. These additional analyses require microemulsion volumes larger than that generated in 5 mL
pipettes, and therefore 9 mL total of aqueous and oil are mixed in a larger 10 mL pipette. Microemulsion volumes are siphoned from these larger pipettes and analyzed for viscosity, conductivity, and interfacial tension. Viscosity was measured on 1 mL microemulsion volumes using the Contraves LS-30 couette-type viscometer. Conductivity was measured on 2 mL of microemulsion using a conductivity probe on an Orion 5-Star benchtop meter. Interfacial tension was measured using a spinning drop interfacial tensiometer by depositing a small droplet of microemulsion in an aqueous phase volume obtained from the same pipette as the microemulsion. A microemulsion droplet could only be observed in a clear aqueous phase, and therefore this aqueous/microemulsion interfacial tension could only be assessed in Type II and III microemulsions because a Type I microemulsion did not contain a separate aqueous phase. The following sections describe any calculations used in the characterization of microemulsion and fluid interfaces.

**Solubilization Ratio**

Original oil and water volumes are known from initial aqueous and oil interface readings, and changes in microemulsion interfaces after mixing can determine volumes of oil and water present in the microemulsion. Solubilization ratios of both oil and water can be calculated for each salinity, and subsequently plotted to determine trends in the data.

**Oil Solubilization Ratio**

Oil solubilization ratio is the volume of oil present in a microemulsion per volume of total active surfactant originally dispensed in the pipette. The basic equation is:

\[
\sigma_o = \frac{V_o}{V_s}
\]

where \(\sigma_o\) is the oil solubilization ratio, \(V_o\) is the oil volume present in the microemulsion, and \(V_s\) is the total surfactant volume present in the pipette. All of the surfactant is assumed to be in the microemulsion and only active surfactant is used in the calculation. This has been found to be a very good approximation for nearly pure
surfactants of the type used in this study (see Dwarakanath, 1997). High concentrations of co-solvent at low solubilization ratios can cause measurement error if not accounted for, but this was not a significant source of error in this study.

Water Solubilization Ratio

Water solubilization ratio is the volume of water present in a microemulsion per volume of total surfactant originally dispensed in the pipette. The basic equation is:

\[
\sigma_w = \frac{V_W}{V_s} \tag{3.4}
\]

\[\sigma_w = \text{water solubilization ratio} \]
\[V_W = \text{water volume in microemulsion} \]
\[V_s = \text{total surfactant volume in pipette} \]

One assumption is that all surfactant exists in the micromulsion phase. Water solubilization ratio is not characterized for Winsor Type I (oil-in-water) microemulsions because water is technically the continuous phase rather than a solubilized phase.

Optimum Solubilization Ratio and Salinity

The optimum solubilization ratio is the ratio at which the oil and water solubilization values are equal for the same microemulsion. The corresponding salinity value at the optimum solubilization ratio is called the optimum salinity, and microemulsions at this point of optimum are bicontinuous, Windsor Type III microemulsions. The solubilization ratio is a function of salinity, and this along with the optimum parameters are defined as such:
\[ \sigma = f(S) \]..................................................................................(3.5)

\[ \sigma = f(S^*) = \sigma^* \]..................................................................................(3.6)

\[ \sigma^* = \sigma_o = \sigma_w \]..................................................................................(3.7)

\[ \sigma = \text{solubilization ratio parameter} \]

\[ S = \text{salinity parameter} \]

\[ \sigma^* = \text{optimum solubilization ratio} \]

\[ S^* = \text{optimum salinity} \]

**Interfacial Tension**

The interfacial tension (IFT) measurement using the spinning drop tensiometer can be calculated from the equation below, as described by Vonnegut (1942). Additional theory behind the spinning drop method can be found in Cayias et al (1975) and Salager (2006).

\[ \gamma = \frac{\pi (\rho_1 - \rho_2) R_d^3 \omega^2}{4} \]..................................................................................(3.8)

\[ \gamma = \text{interfacial tension} \]

\[ \rho_1 = \text{density of continuous phase} \]

\[ \rho_2 = \text{density of droplet phase} \]

\[ R_d = \text{droplet diameter} \]

\[ \omega = \text{rotation speed} \]

An equation developed by Huh (1979) can be used to calculate IFT using the optimal solubilization ratio. This equation is given as:
\[
\gamma = \frac{0.3}{(\sigma^*)^2} \quad .................................................(3.9)
\]

\[
\gamma = \text{interfacial tension}
\]
\[
\sigma^* = \text{optimal solubilization ratio}
\]

**Viscosity and Conductivity**

Viscosity measurement output obtained from the couette-type viscometer is multiplied by various correction and calibration factors to arrive at the actual bulk viscosity value. Outputs from the conductivity meter are expressed as actual conductivity values, and require no further calculation.

**Screening and Scan Refinement**

Phase behavior mixtures had to pass several screening criteria to be further considered for a core flood design. A bi-continuous Type III microemulsion that existed at or near optimum salinity would need to visually appear gel/macroemulsion free, low viscosity, and free-flowing at interfaces. Quantitatively, this microemulsion needs a solubilization ratio equal to or greater than 10 at optimal salinity, and an equilibration/coalescence time of less than 7 days. A high oil and water solubilization ratio at optimal salinity is correlated with an ultra-low interfacial tension, which is the key mechanism driving surfactant-based chemical EOR.

Salinity scan refinement of a pipette series consists of re-creating the pipette series with smaller salinity increments between pipettes. The bicontinuous Type III microemulsion occurs in a narrow salinity range, and scan refinement can focus specifically on this range. Initial screening tests will commonly cover a broader salinity range to first identify roughly where the Type III region occurs, and the refined scan follows as a second test. If an accurate assessment of the Type III microemulsion properties of the refined scan shows good performance, then the aqueous formulation
passes the screening process, and will be considered at its optimal salinity for a core flood design.

**CORE FLOOD DESCRIPTION**

Core flood experimentation of a chemical EOR formulation designed in phase behavior experimentation is described in this section. The section begins by describing the core flood equipment setup, and the selecting, preparing, and measuring of a suitable core for flood experimentation. Brine, oil, and water flooding experiments are then performed to obtain core parameters, and prepare the core at residual oil saturation for the actual chemical flood. Following this, a detailed description of the design, experimentation, and analysis of the actual chemical flood is provided.

**Core flood Equipment Setup**

Simple schematic sketches of flooding experiments are shown in Figures ***. These sketches show simple equipment setups for the brine flood, oil flood, water flood, and chemical flood experiments. In these sketches, mineral oil acts as the displacing fluid, and is driven by a pump to displace the fluids of interest through the core. The core is kept in a convection oven at a constant temperature representative of the reservoir. Fluid exiting the core is collected into a burette or fraction collector depending on the flooding application. Descriptions of these and other types of equipment used in the setup are provided in this section.

**Fluid Reservoirs**

Fluids used in core flood experiments are stored in columns made of glass or stainless steel. The columns contain screw caps with valves on their ends, and are able to be shut-in and sealed air-tight. One of the ends functions as an inlet for displacing fluid, and the other functions as an outlet for dispensing fluid. The differing applications for stainless steel and glass columns are described below.
Stainless Steel Columns

Whitey® stainless steel columns are used to store fluids for delivery under high pressure, with high pressure being anything above about a 20 psi safety limit for the glass columns. The columns can hold a volume of 300 cc, and have a 5 cm outer diameter and 23 cm total length, with the last 3 cm on each end tapering to a 2 cm outer diameter. End pieces screw into the columns, and connect to Swagelok stainless steel connectors, tubing, and valves to form an air-tight seal. Columns are pressure tested to 100 psi prior to usage to test for leaks. Note that the oil flooding process is the only high-pressure scenario in the core flood experiment, with pressures from 20 to 100 psi.

Glass Columns

Spectra/Chrom™ LC glass columns are used to store fluids for delivery under low pressures, or pressures under a 20 psi safety limit. Small and large column types were used that contained inner diameters of 2.5 cm and 5 cm, respectively, and total lengths of 40 cm and 60 cm, respectively. The smaller column would store the surfactant slug and polymer drive mixtures, and the larger column stored synthetic reservoir brine. Synthetic reservoir brine was required at several stages (initial water saturation, brine flushing, and water flooding), which is the reason for using the glass column. All columns contained end pieces with Viton O rings to give an air-tight seal when hand tightened.

Convection Oven

LR Technologies® DK810 convection oven with a compact, vertical design enclosed cores and some injection fluids during core flood experiments. The ovens were set at temperatures representative of the reservoir that the crude oil was obtained from. Mercury thermometers and oven temperature gauges helped guarantee a constant temperature with minimal fluctuation.

Pre-flood Measurements (Bulk Volume, Pore Volume, and Porosity)

The Sartorius® ED620S mass balance with 0.01 g resolution and 6200 g capacity measured dry and saturated cores contained in epoxy to obtain saturation and porosity
values. The bulk volume of a core is calculated from measured dimensions of diameter and length according to the equation:

\[ V_b = \pi \frac{D^2}{4} L \] ..........................(3.10)

\[ V_b = \text{bulk volume} \]
\[ D = \text{core diameter} \]
\[ L = \text{core length} \]

The pore volume (also known as PV) of a core is calculated from the mass of brine (of known density) saturating the core according to the equation:

\[ V_p = \frac{M_{\text{sat}} - M_{\text{dry}}}{\rho_{\text{brine}}} \] ..........................(3.11)

\[ V_p = \text{pore volume} \]
\[ M_{\text{sat}} = \text{mass of brine saturated core} \]
\[ M_{\text{dry}} = \text{mass of vacuumed core} \]
\[ \rho_{\text{brine}} = \text{brine density} \]

Porosity can be determined from the above calculations according to the equation:

\[ \phi = \frac{V_p}{V_b} \] ..........................(3.12)

\[ \phi = \text{porosity} \]
\[ V_p = \text{pore volume} \]
\[ V_b = \text{bulk volume} \]

Note that the core dimensions used for the bulk volume calculation are measured on a bare core prior to applying epoxy. Dry and saturated masses, however, are measured
on prepared, epoxied cores. Therefore, one assumption is that epoxy penetration into the core walls is negligible, and does not decrease pore volume. Significant epoxy invasion would need to be accounted for by considering a reduced bulk volume within the epoxy-invaded areas of the core walls.

**Preliminary Flooding Experiments**

Prepared cores fully saturated with synthetic formation brine undergo a series of flooding experiments to measure core parameters, and to prepare cores for chemical flooding. Saturated cores are first flooded with synthetic formation brine to flush the core, and to obtain a brine permeability value as close to the absolute permeability as possible. Cores then undergo flooding with crude oil to residual brine saturation to calculate end point oil permeability and relative permeability parameters. A water flood experiment then completes the pre-chemical flooding by flooding the core again with synthetic formation brine to residual oil saturation. End point water permeability, relative permeability, and saturation parameters can then be calculated, and core now contains the residual oil saturation target for chemical flood design.

**Brine Flooding**

Brine flooding is the first and most simplistic flooding procedure. Synthetic formation brine with a composition similar to actual reservoir brine is used for the flood. Brine in a glass cylinder is initially heated in an oven, and then displaced through an initially brine saturated core by mineral oil displacing fluid. About three pore volumes of brine flood the core at a high injection rate (~6 mL/min), and are collected into a burette outside of the oven. Flow is calculated from collected burette volumes per time length, and pressure drop recorded with a 0-20 psi transducer connected to the core inlet.

**Crude Oil Flooding**

Crude oil flooding injects filtered crude oil from the top of the core to allow for gravity stability. Mineral oil cannot directly contact the crude oil, so it will displace a
brine column, which then displaces the crude oil. Both the brine and crude oil are initially heated in the oven, and stored in 300 mL stainless steel columns to withstand high injection pressures (~20 to 100 psi). About two pore volumes of crude oil (~200 mL) flood the core, making the 300 mL columns of sufficient volume to prevent mineral oil from reaching the core. Effluent is collected in 100 mL burettes, and a water cut of 1% with a steady pressure drop across the core indicates sufficient oil has been injected. Residual water saturation can be calculated using a mass balance and the known volume of water recovered. A 0-300 psi transducer connects to the core inlet to measure the high pressures across the core length.

**Water Flooding**

Water flooding uses the same brine as core saturation and brine flooding does. Mineral oil displaces the water into the bottom of the core so the displacement of the crude oil is gravity stable. The injection rate is very low (~1 to 2 PV/d) to represent typical reservoir pressure drops of 1 to 5 psi/ft, and to leave a residual oil saturation similar to an actual reservoir. Water is flooded until the effluent reduced to 1% oil cut and the pressure becomes nearly stable. The effluent collected in a burette can measure the recovered oil volume, and the residual oil saturation in the core is calculated using a mass balance. Pressure transducers are connected across three different length segments and the entire core, and have low ranges (0-5 psi to 0-20 psi) to measure the low-pressure drops to a sufficient resolution.

**Permeability Calculations**

Pressure and flow rate data from oil and brine flooding experiments are used with Darcy’s Law to calculate permeability and endpoint relative permeability values. An assumption in using Darcy’s Law is a steady state, single-phase flow regime, where either oil or water flows through the core at a constant pressure drop and flow rate. Steady state is assumed when the total pressure drop and flow rate vary by less than 5% over a 0.2 PV dimensionless time period.
Brine Permeability

Epoxied cores are initially saturated with brine, and further flooding with brine gives pressure and flow rate data used to calculate an absolute, or brine permeability. The core has no oil saturation at this time, and a single-phase Darcy’s Law is rearranged as such:

\[
k_{\text{brine}} = \frac{q \mu L}{A \Delta P}
\]

\[k_{\text{brine}}\] = absolute brine permeability

\[q\] = brine flow rate (steady-state)

\[\Delta P\] = total pressure drop (steady-state)

\[\mu\] = brine viscosity

\[L\] = core length

\[A\] = core cross sectional area

End-point Oil Permeability

Brine saturated cores undergo oil flooding until a residual brine saturation end-point has been reached. Flow at this end-point is assumed to be steady-state, single-phase, and constant pressure and flow rate. Given these assumptions, Darcy's Law is used to calculate the permeability of the oil phase as:

\[
k_o = \frac{q_o \mu_o L}{A \Delta P}
\]

\[k_o\] = permeability to oil

\[q_o\] = oil flow rate (steady-state)

\[\mu_o\] = oil viscosity

End-point Water Permeability

Cores now at residual brine saturation undergo brine flooding to a residual oil saturation end-point. Using the same assumptions as with oil, brine phase permeability is defined as \(k_w\) to distinguish it from total brine permeability, \(k_{\text{brine}}\).
End-Point Oil Relative Permeability

End-point relative permeability values are defined as the ratio of a certain phase permeability to the total brine permeability at \( S_w = 1 \). The calculations for both oil and brine end-point relative permeability is shown below:

\[
k_{ro}^o = \frac{k_o}{k_{brine}} \tag{3.16}
\]

- \( k_{ro}^o \) = end-point relative oil permeability
- \( k_o \) = oil phase permeability
- \( k_{brine} \) = total brine permeability

End-Point Water Relative Permeability

\[
k_{rw}^o = \frac{k_w}{k_{brine}} \tag{3.17}
\]

- \( k_{rw}^o \) = end-point relative brine permeability
- \( k_w \) = brine phase permeability
- \( k_{brine} \) = total brine permeability

Phase Saturation Calculations

Brine saturated cores were flooded with oil to residual brine saturation, and subsequently flooded with brine to residual oil saturation. Calculating these residual
saturation values are important for modeling relative permeability curves, and for determining recoverable oil for the chemical flood.

After the oil flood, the volume of water recovered can be used to calculate the initial oil saturation. The recovered water volume is replaced by oil in the core, and represents the oil volume that saturates the core. Initial oil saturation is therefore the ratio of recovered water to total pore volume. Subsequently, the water flood will recover an amount of oil, which is subtracted from the initial oil to determine the residual oil. These equations are as such:

\[
S_o = \frac{V_w}{V_p} \quad \text{(after oil flood)} \quad (3.18) \\
S_{ro} = \frac{V_w - V_o}{V_p} \quad \text{(after water flood)} \quad (3.19)
\]

\[
S_o = \text{initial oil saturation} \\
S_{ro} = \text{residual oil saturation} \\
V_w = \text{produced water volume during oil flood} \\
V_o = \text{produced oil volume during water flood} \\
V_p = \text{pore volume}
\]

**Chemical Flooding**

Many of the parameters calculated from the brine, oil, and water flooding experiments are used in designing the chemical flood experiment. Additionally, analysis of the effluent collected from the chemical flood can help in optimizing the core flood design and injection formulation for advancement towards a pilot project in the actual reservoir. This section discusses the calculations used for design of the chemical flood, the actual chemical flood procedure, and the analysis of recovered fluids following the chemical flood. The equipment setup can be referred to in the description provided previously.
Design Calculations

Other than the phase behavior and aqueous stability screening and design, several important calculations for chemical flood design are given in this section. The mobility and mobility ratio calculations are important to calculate a desired apparent viscosity for the injection fluid. They are based on viscosity and relative permeability parameters calculated previously, and ultimately determine the appropriate amount of polymer concentration for surfactant slug and polymer drive solutions for good mobility control. Estimating pressure drop is another important calculation made from core and fluid parameters using several assumptions. A pressure drop calculation predicts if the design is feasible if scaled to an actual reservoir, or if further design modification is required to lower the pressure gradient. Additional calculations of permeability resistance and reduction factors are also important, though they are often calculated from polymer injection data following the chemical flood experiment. However, predicted values of permeability reduction factor are required for estimating pressure drop, as will be shown.

Endpoint Mobility and Mobility Ratio

The mobility ratio is a dimensionless number that helps characterize the displacement efficiency between two fluids. Each fluid itself is defined by a mobility value, given as:

\[
\lambda_i = \frac{k_i}{\mu_i}
\]

\(\lambda_i\) = mobility of fluid i

\(k_i\) = effective permeability to fluid i

\(\mu_i\) = viscosity of fluid i

The mobility ratio is a ratio of the displacing fluid mobility to the displaced phase mobility (Lake, 1989). This can be generally expressed as:
\[ M = \frac{\lambda_{\text{displacing\_fluid}}}{\lambda_{\text{displaced\_fluid}}} \]  

**Mobility Ratio**

\[ M = \text{mobility ratio} \]

\[ \lambda_{\text{displacing\_fluid}} = \text{mobility of displacing fluid} \]

\[ \lambda_{\text{displaced\_fluid}} = \text{mobility of displaced fluid} \]

During the core flood procedure, effective permeability values of oil and water phases were measured as end-point permeability values relative to the total brine permeability, and these end-point relative permeability values can be used to calculate an end-point mobility ratio as such:

\[ M^O = \frac{\lambda^O_\text{w}}{\lambda^O_{\text{o}}} = \frac{k^O_\text{w}/\mu_\text{w}}{k^O_{\text{o}}/\mu_\text{o}} \]

\[ M^O = \text{end-point mobility ratio} \]

\[ k^O_{\text{o}} = \text{oil relative permeability} \]

\[ k^O_{\text{w}} = \text{water relative permeability} \]

\[ \mu_\text{o} = \text{oil viscosity} \]

\[ \mu_\text{w} = \text{water viscosity} \]

For core flood experiments, a mobility ratio less than one is considered favorable for displacement, while a ratio greater than one is unfavorable. Because the oil relative permeability is generally higher than the water relative permeability, a water viscosity higher than the oil viscosity is necessary to obtain a mobility ratio favorable for displacement.

**Apparent Viscosity**

Surfactant and polymer slugs are designed with an apparent viscosity equal to or greater than the inverse of the total relative mobility to ensure a mobility ratio less than one during chemical flood. The apparent viscosity equation is as such:
\[ \mu_{\text{app}} = \frac{1}{\lambda_{\text{trm}}} = \frac{1}{k_{\text{rw}}/\mu_{\text{w}} + k_{\text{ro}}/\mu_{\text{o}}} \]  

\( \mu_{\text{app}} \) = apparent viscosity  
\( \lambda_{\text{trm}} \) = total relative mobility  
\( \mu_{\text{w}} \) = brine viscosity  
\( \mu_{\text{o}} \) = oil viscosity  
\( k_{\text{RW}} \) = relative brine permeability  
\( k_{\text{RO}} \) = relative oil permeability

**Scaling Pressure Drop**

A pressure drop ratio between two flooding experiments can equal the inverse of the mobility values. The following assumptions must be met: equal flow rates, saturations, core properties, and salinity. The equation for this ratio for fluids i and j is expressed as:

\[ \frac{\Delta P_i}{\Delta P_j} = \frac{\lambda_j}{\lambda_i} = \frac{k_j/\mu_j}{k_i/\mu_i} \]  

(3.24)

This equation can be used to relate the polymer and brine floods, as long as flow rates are scaled accordingly. The equation can also be used to predict the pressure drop of a surfactant/polymer flood from water flood data, using an estimated value of the permeability reduction factor. This relationship is given as:

\[ \frac{\Delta P_{\text{slug}}}{\Delta P_{\text{wf}}} = \frac{k_{\text{wf}}/\mu_{\text{wf}}}{k_{\text{slug}}/\mu_{\text{slug}}} = \frac{k^o_{\text{rw}}k_{\text{w}}/\mu_{\text{w}}}{k_{\text{slug}}/\mu_{\text{slug}}} = \frac{k^o_{\text{rw}}R_k\mu_{\text{slug}}}{\mu_{\text{wf}}} \]  

(3.25)

Note that this can only provide a rough approximation because assumptions of equal salinity and saturation are violated.
**Polymer Resistance Factor**

Polymer resistance factor is the ratio of brine mobility to polymer mobility, and is a measure of polymer mobility relative to brine. Polymer mobility is generally much lower than brine mobility due to a higher viscosity and reduced effective permeability. Polymer resistance factor is calculated according to the following equation:

$$R_f = \frac{\lambda_w}{\lambda_p} = \frac{k_w \mu_p}{k_p \mu_w} \tag{3.26}$$

- $R_f$ = polymer resistance factor
- $\mu_p$ = polymer viscosity
- $\mu_w$ = brine viscosity
- $k_p$ = effective polymer permeability
- $k_w$ = effective brine permeability

**Polymer Permeability Reduction Factor**

The polymer permeability reduction factor is a ratio of the effective brine permeability to the effective polymer permeability. Both permeability values are calculated with the assumption that the brine or polymer are the only fluids present in the core during their respective flooding periods. Polymer effective permeability is generally less than brine permeability because polymer particles will adsorb onto rock surfaces to partially restrict flow. The polymer permeability reduction factor is calculated according to the following equation:

$$R_k = \frac{k_w}{k_p} \tag{3.27}$$

- $R_k$ = polymer permeability reduction factor
- $k_p$ = effective polymer permeability
- $k_w$ = effective brine permeability
Chemical Flood Procedure

The chemical flood follows the water flood. Mineral oil initially displaces a surfactant slug (~0.2 to 0.3 PV) into the bottom of the core (for gravity stability), and subsequently displaces a 1 to 2 PV polymer drive. Both surfactant and polymer are initially unheated to minimize degradation, and are assumed to sufficiently heat upon entering the core. The injection rate is very low (~1 to 2 PV/d) to represent typical reservoir pressure drops of 1 to 5 psi/ft. Effluent is collected in a fraction collector in 2 to 5mL increments for further analysis. Four pressure transducers (3 at 0-5 psi, 1 at 0-20psi) are connected similar to a water flood (across three length segments and the entire core), and can measure low pressures with sufficient resolution.

Effluent Collection, Preparation, and Analysis

Effluent samples collected throughout a chemical flood have compositions dependent on their time of recovery, which also determines what analysis techniques are used to further characterize them. A list of the chronology of effluent collected and the analyses performed on them is provided below, along with the types of equipment used in analyzing them:

1. Formation Brine Recovery
   The first effluent is recovered formation brine, which is characterized by its conductivity and pH.

2. Oil Bank Breakthrough
   Effluent will contain as much as 50% oil during breakthrough of the oil bank, which is characterized by oil volume and fraction, and conductivity and pH of the water cut.

3. Surfactant Breakthrough
   Effluent will contain microemulsion and/or emulsion, indicating the presence of surfactant. Samples are heated to break the emulsion, and characterize the oil fraction/volume. Some water cuts are analyzed for pH and conductivity, and
others for sulfates in a hyamine titrator to determine surfactant concentration.

4. Late Microemulsion

Recovered microemulsion will contain a decreasing proportion of oil as the polymer drive progresses. Samples are still heated, and analyzed for either pH and conductivity, or surfactant concentration. Samples can additionally be assessed for viscosity to determine the amount of shear degradation. The core flood is considered complete when almost entirely polymer solution is recovered.

Fraction Collector

A Teledyne ISO Retriever® 500 fraction collector was used to collect effluent samples from chemical floods. The collector has the capacity to hold 68 tubes (17 racks of 4 tubes each), and the tubes are 10 mL glass tubes with markings every 0.1 mL. The collector is automated, and will rotate to a new tube according to a user-specified time allotment based on flow rate and desired effluent volume per tube. Volumes of effluent usually vary from 2 - 5 mL depending on the desired resolution of the effluent data.

Hot Plate for Breaking Emulsions

A hot plate apparatus was used to heat effluent samples in order to break microemulsions into oil and aqueous phases. Two to five milliliter effluent samples were poured into glass vials and sealed tightly with screw caps. The vials were inserted into grooves on a hot plate that was then heated to 120 C for 24 hours. After this period, recovered oil volumes in the effluent could be measured more accurately than when the oil existed as microemulsion.

Hyamine Titrator

A hyamine titrator determined the amount of surfactant present in core flood effluent samples. The instrument first used 0.5 M citric acid to adjust the sample pH to 8, and then titrated with 0.005 M hyamine solution to determine surfactant concentration relative to SDS standards. The titration has a lower detection limit of 0.1%.
**Oil Recovery**

Chemical flooding will recover the residual oil remaining after the water flood. Effluent is collected in several glass tubes, with oil recovered in either a free or microemulsion phase. Free oil volumes are easily measured from the markings on the tubes, while microemulsions are first broken (through heat or dilution) before measuring the created free oil volume. The percentage of the residual oil recovered is given as:

\[
\%\text{Recovery} = \frac{\sum_{i=1}^{n} V_{o,i}}{S_{or} V_p} \times 100\% \quad \text{(3.28)}
\]

\%\text{Recovery} = \text{percent residual oil recovered}

\(V_{o,i}\) = volume of free oil in tube \(i\)

\(S_{ro}\) = residual oil saturation

\(V_p\) = pore volume
Table 3.1 - Name, vender, and chemical description of many of the surfactants used in the research.

<table>
<thead>
<tr>
<th>Name</th>
<th>Vender</th>
<th>Chemical Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Petrostep S1</td>
<td>Stepan</td>
<td>C_{16-17} - 7PO - SO_{4}^-</td>
</tr>
<tr>
<td>Petrostep S2</td>
<td>Stepan</td>
<td>IOS_{15-18} (internal olefin sulfonate)</td>
</tr>
<tr>
<td>Petrostep S3</td>
<td>Stepan</td>
<td>IOS_{20-24} (internal olefin sulfonate)</td>
</tr>
<tr>
<td>Exxal 13 TDA-4PO (Isotridecanol)</td>
<td>Harcros Chemical</td>
<td>C_{13} - 4PO - SO_{4}^-</td>
</tr>
<tr>
<td>Exxal 13 TDA-8PO (Isotridecanol)</td>
<td>Harcros Chemical</td>
<td>C_{13} - 8PO - SO_{4}^-</td>
</tr>
<tr>
<td>Alfoterra® 45 (Isalchem™ 123)</td>
<td>SASOL</td>
<td>C_{12-13} - 5PO - SO_{4}^-</td>
</tr>
<tr>
<td>Alfoterra® 58 (Isalchem™ 145)</td>
<td>SASOL</td>
<td>C_{14-15} - 8PO - SO_{4}^-</td>
</tr>
<tr>
<td>Alfoterra® 68 (Safo® 23)</td>
<td>SASOL</td>
<td>C_{12-13} - 8PO - SO_{4}^-</td>
</tr>
<tr>
<td>C_{12} Alpha Olefin Sulfonate (AOS)</td>
<td>Stepan</td>
<td>bC_{11-17}(OH)-CH_{2}-CH_{2}-SO_{3}^- (~75%), bC_{11-17}CH=CH-CH_{2}-SO_{3}^- (~25%)</td>
</tr>
<tr>
<td>C_{20-24} Alpha Olefin Sulfonate (AOS)</td>
<td>Stepan</td>
<td>bC_{17-21}(OH)-CH_{2}-CH_{2}-SO_{3}^- (~75%), bC_{17-21}CH=CH-CH_{2}-SO_{3}^- (~25%)</td>
</tr>
<tr>
<td>CS-330 (Sodium dodecyl 3EO sulfate)</td>
<td>Stepan</td>
<td>C_{12} - 3EO - SO_{4}^-</td>
</tr>
</tbody>
</table>
CHAPTER 4: EXPERIMENTAL RESULTS AND DISCUSSION

This chapter on experimental results and discussion consists of four sections that provide an experimental sequence from theory to design to application. The first section on microemulsion characterization for McElroy crude oil identifies five parameters to characterize microemulsions produced in phase behavior. The second section details chemical component interactions in phase behavior for McElroy crude, and identifies a methodology for designing an optimal formulation. The third section follows this methodology in finding an optimal formulation for Crude D from a reservoir with high TDS and hardness formation brine. The fourth section validates this formulation in a chemical flood by recovering residual oil from a sample core plug.

MICROEMULSION CHARACTERIZATION FOR McELROY CRUDE OIL

Chemical components and their molecular structures were initially assessed by characterizing the microemulsion produced with crude oil of known properties. Up to five parameters characterized the microemulsions: oil/water solubilization ratio (per surfactant volume), coalescence time, interfacial tension (IFT), viscosity, and conductivity. The objective was to observe trends between different parameters for microemulsions of different salinity within a phase behavior, and compare observed trends to previous research in the literature. These parameters also provided a better understanding of how phase behavior performance could be characterized when designing an optimal chemical formulation for chemical EOR.

Microemulsions used for the characterization was obtained from three phase behavior experiments labeled B4, B5, and B6. All experiments contained 1.5 wt% C_{16-17}^7PO - SO_4^-, 0.5 wt% IOS_{15-18}, and 2 wt% SBA aqueous phases, with McElroy crude as the oil phase. Experiment B4 contained no alkali, and experiments B5 and B6 contained 1 wt% Na_2CO_3 and 1 wt% sodium metaborate, respectively. Note that these mixtures were similar to high performing mixtures used in a previous study containing crude of similar characteristics (Levitt et al., 2006). Experiments were prepared in ten, 10mL borosilicate
pipettes differing by 0.1 wt% NaCl concentration over a 1 wt% NaCl range. The NaCl ranges for the no alkali, sodium carbonate, and sodium metaborate cases were 4.1 – 5.0 wt%, 3.3 – 4.2 wt%, and 3.8 – 4.7 wt%, respectively, which centered around their respective Type III microemulsion. Experiments were incubated in a 30°C oven for 60 days, which is the temperature of the McElroy reservoir. The pipettes are shown in Figures 4.1, 4.2, and 4.3 for the no alkali (B4), sodium carbonate (B5), and sodium metaborate (B6) experiments, respectively.

**Characteristic Parameters**

Five parameters were measured to characterize the microemulsions in the three phase behavior experiments: oil/water solubilization ratios, coalescence time, IFT, viscosity, and conductivity. These parameters were each evaluated individually, and a more systematic study is needed for accurate comparison and correlation.

**Solubilization Ratio**

For all three experiments, the volumes of oil and/or water in each microemulsion phase were quantified from water/microemulsion and microemulsion/oil fluid levels in the pipettes. Both oil and water solubilization ratios were subsequently calculated using the known total surfactant volume. Plots of these solubilization values versus NaCl concentration are shown in Figures 4.4, 4.5, and 4.6 for each of the three experiments. Optimum salinity and solubilization ratio were characterized at the intersection point between the oil and water solubilization curves, and the values are displayed in Table 4.14.

The optimal salinity for the no alkali, Na$_2$CO$_3$, and sodium metaborate (Na-metaborate) scenarios is 4.7, 3.9, and 4.4 wt% NaCl, respectively. Therefore, the optimal salinity in terms of wt% NaCl decreases from no alkali to Na-metaborate to Na$_2$CO$_3$. This indicates that alkali addition contributes electrolytes to act as a NaCl equivalent. However, calculating the Na$^+$ concentration for each optimal value gives 1.85, 1.86, and 1.97 wt% Na$^+$ for B4, B5, and B6, respectively. This indicates that B4 (no alkali)
contains a lower cation and anion (i.e. Cl\(^-\) only in this case) concentration, making sodium chloride a stronger electrolyte than either alkali. Alkali can have other advantages as will be shown later.

The optimal solubilization ratio for the no alkali, Na\(_2\)CO\(_3\), and sodium metaborate scenarios is 17.5, 18, and 16, respectively. Optimal solubilization ratio increases slightly from sodium metaborate to no alkali to Na\(_2\)CO\(_3\). However, the difference between an optimal solubilization ratio of 16 and 18 is relatively small, and both are acceptable values for chemical EOR since they are much greater than the minimum value of 10.

**Coalescence Time**

For each phase behavior experiment, the volumes of solubilized oil and water in each microemulsion were measured at time increments of 1, 2, 3, 5, 7, 11, 15, 21, and 40 days. As with the solubilization ratio plots, solubilized oil and water volumes were normalized to the total surfactant volume to obtain oil and water solubilization ratios. For each experiment, the oil and water solubilization ratios for the microemulsion most near optimal salinity were plotted for each time increment. Lines connected these solubilization ratio versus time plots for both oil and water, and the time at which both curves trended horizontally or in a similar fashion (i.e. minimal further change in solubilization ratio) was recorded as the coalescence time. Solubilization ratio versus time plots are displayed in Figures 4.7, 4.8, and 4.9, and the equilibration time data is displayed in Table 4.14.

From Table 4.14, the coalescence times for the no alkali, sodium carbonate, and sodium metaborate scenarios are 11, 5, and 7 days, respectively. Data for the no alkali and sodium carbonate experiments does show some drift, where solubilization values decrease slightly from horizontal at 40 days. Small fluctuations in the oven temperature could explain this drift. The coalescence times showed a decrease from no alkali to sodium metaborate to sodium carbonate. Given that the aqueous pH values are 8.56, 9.03, and 10.23 for the no alkali, sodium metaborate, and sodium carbonate experiments, respectively, and given the fact that Jackson (2006) observed similar trends with pH, the
higher pH is likely the reason for the observed decrease in coalescence time. The coalescence time for no alkali is much larger than desirable and is likely due in part to the low temperature. Higher temperature promotes faster equilibration everything else being equal. Regardless, the alkali clearly is very beneficial in this respect in addition to its better known benefits.

**Viscosity**

Microemulsion volumes were sampled from all pipettes for all three phase behavior experiments, and viscosity measurements were taken with a couette-type, low-shear viscometer. Figure 4.10 shows the plots of these viscosity values versus NaCl concentration for all three experiments.

Viscosity trends of all three experiments show a viscosity of approaching 1 cp at low NaCl concentrations, an increase to a maximum of 25 cp, and a decline approaching the crude oil viscosity of 10 cp at high NaCl concentrations. Microemulsions at low and high NaCl concentrations are almost pure aqueous or oil phases, respectively, and therefore viscosity values are expected to be similar to brine or oil values. Peak viscosity values occurred at 3.6, 4.2, and 4.5 wt% NaCl for Na₂CO₃, sodium metaborate, and no alkali scenarios, respectively. Note that these do not correlate with the optimum salinity values of 3.9, 4.4, and 4.7 wt% NaCl for Na₂CO₃, sodium metaborate, and no alkali, respectively. However, they do correlate to the NaCl concentrations of the Type I / Type III boundaries, which from the solubilization curves are 3.7, 4.2, and 4.5 wt% NaCl for Na₂CO₃, sodium metaborate, and no alkali, respectively. This is consistent with previous observations (Bourrel and Schechter, 1988). The peak microemulsion viscosities of about 25 cp are higher than desirable for chemical flooding, but would be much worse without the SBA co-solvent.

**Electrical Conductivity**

Microemulsion volumes were sampled from all pipettes in B4, B5, and B6 phase behavior experiments, and conductivity measurements were taken using with a
conductivity probe from an Orion 5-Star benchtop conductivity meter. Additionally, conductivity measurements were taken for pure aqueous solutions having NaCl concentrations identical to those in each pipette, and these were used to normalize the raw microemulsion conductivity data to a common NaCl concentration value (chosen as the lowest NaCl concentration for each experiment). Normalization eliminated conductivity effects caused by differences in NaCl concentration between microemulsions.

Figure 4.11 shows actual and normalized conductivity versus NaCl concentration for all three experiments. The conductivity of the pure aqueous solutions used for the normalization is also shown. All three graphs show a decrease in microemulsion conductivity as NaCl concentration increases, which is expected because the solubilization of the non-conductive oil phase increases with NaCl concentration. The conductivity decreases in a continuous, regular way for all three types of microemulsions, which implies that the microemulsion phase changes gradually and not discontinuously form one type to another type.

**Interfacial Tension (IFT)**

Pipettes in the Type III and Type II regions of experiments B4, B5, and B6 were sampled for microemulsion and aqueous phase volumes to measure IFT using a spinning drop tensiometer. The spinning drop apparatus measured the IFT between a microemulsion droplet and an aqueous phase that suspended the droplet. To observe the droplet deforming in the apparatus, a transparent phase must be used, which is why only the IFT between aqueous and microemulsion phases of the Type III and Type II regions could be measured in this case. Figure 4.12 plots the measured IFT values versus NaCl concentration for all three phase behavior experiments, and all graphs show aqueous/microemulsion IFT to increase with salinity as expected for the phase types measured. Although limited by the experimental difficulties, these IFT data do show that ultra-low IFT values were obtained for phases at equilibrium near the optimum salinity, as expected based upon the high solubilization ratios measured on the same phases.
CHEMICAL COMPONENT VARIATIONS AND INTERACTIONS IN PHASE BEHAVIOR

Obtaining an optimal formulation can be experimentally time-consuming, and requires a strategic design methodology for quick and optimal formulation design. Chemical components include surfactant, co-surfactant, co-solvent, polymer, electrolyte, and/or alkali, and these must be in a combination and concentration for optimal performance. A strategic design methodology assesses chemicals based on molecular design, and evaluates interactions of chemical components with each other and the crude oil. To develop a design methodology, the behavior and interactions between different chemical components in phase behavior needs to be understood. This section details how the presence and concentrations of different chemical components affect phase behavior performance when using McElroy crude oil. Performance was evaluated from microemulsion parameters of optimal solubilization ratio, optimal salinity, and coalescence time for each phase behavior experiment. Viscosity was inspected qualitatively by inclining pipettes for free-moving interfaces to eliminate the time-consuming measurements with a coquette-type viscometer. IFT was estimated using equation 3.9. Microemulsion conductivity was not considered as a microemulsion parameter for this study.

General Surfactant Screening

McElroy crude oil was first tested with several surfactants and co-surfactants in a general surfactant screening process. The objective of the general screening was to obtain a surfactant/co-surfactant combination and concentration that would provide high solubilization ratio at optimal salinity (i.e. large volume, type III microemulsion phase), which provides sufficiently low IFT when greater than about 10 cc/cc. This surfactant/co-surfactant combination could then be used for further testing and optimization with other chemical components. Additional objectives were a low viscosity (free-moving interfaces) without gels or viscous macroemulsion present, with a fast (<7 days) microemulsion coalescence time.
Of the potential hundreds of surfactant and co-surfactant varieties that the general screening process could have tested, only about ten were chosen for the McElroy crude oil. The types and chemical composition of the surfactants were chosen based on previous research and availability. For example, extensive surfactant research on a West Texas crude oil (having properties similar to McElroy crude oil) showed a branched, 16-17 carbon chain, propoxylated sulfate (i.e. C$_{16-17}$PO$_4^-$) mixed with a branched 15-18 carbon chain with internally attached sulfonate (i.e. IOS$_{15-18}$) to have very good performance (Jackson, 2006, Levitt, 2006). Therefore, these two surfactants were tested individually and in combination in the general screening, along with other potential surfactants. The carbon chain length, degree of propoxylation, degree of branching, and availability all factored into the other surfactants tested in the general screening. Table 4.1 lists the phase behavior experiments of the general screening, and Table 4.2 gives information about the structures of the surfactants used. Structural information includes information on the carbon-tail structure, the number of carbons in the tail backbone, the presence of carbons branching on the tail, the number of PO or EO intermediate groups, and the anionic group of the polar head. Plots of solubilization ratio versus NaCl concentration and versus time obtained during the general screening can be referred to in Figures 4.13 to 4.25, 4.30 to 4.31, and 4.56 to 4.57.

Table 4.1 shows experiments A10 and A50 to have the best performance based on an optimal solubilization ratio greater than or equal to 10. All other tests did not achieve this performance. The surfactant used in tests A10 and A50 was C$_{16-17}$PO$_4^-$, is one of the few with carbon branching on the tail. The only other surfactant with branching was the IOS$_{15-18}$. IOS$_{15-18}$ performed poorly when used alone in A9, but did give good performance in A10 when combined with C$_{16-17}$PO$_4^-$. The C$_{16-17}$PO$_4^-$ and IOS$_{15-18}$ surfactants were selected for further phase behavior testing alone and in combination.

Table 4.2 shows to general structures of surfactants referred to in Table 4.1. Most of the surfactant chains were nearly linear to slightly branched, with between 12 and 18 carbon molecules in their carbon backbones. The C$_{16-17}$PO$_4^-$ used in A10 A50 was
the only surfactants with more than 15 total carbons on their backbone, with the exception of IOS$_{15-18}$ which contained a twin-tail. These surfactants in combination were shown to have the best performance with respect to optimal solubilization ratio compared to other surfactants. Although the C$_{16-17}$-7PO-SO$_4^-$ has been selected as the best performer, other experiments were used to evaluate performance based on the presence of the PO and EO intermediate groups. Tests A7 and A8 compare two surfactants with a shorter hydrophobe made from isotridecyl alcohol (TDA) that only differ in the number of PO groups present. Test A7 with 4 PO groups had faster equilibration time, higher optimal salinity, and lower optimal solubilization ratio than Test A8 with 8 PO molecules. Both TDA surfactants show lower solubilization ratios than the C$_{16-17}$-7PO-SO$_4^-$, which implies the longer hydrophobe is needed for this particular crude oil. Tests A4 and A6 were the only ones containing EO groups and both of them showed viscous gels considered unacceptable, which has also been frequently observed by others.

All of the screening tests were performed with a SBA, which as with all co-solvents reduces the optimal solubilization ratio below an acceptable value for the poorer surfactants. The successful C$_{16-17}$-7PO-SO$_4^-$ surfactant performed well in the presence of SBA, and was therefore chosen for further experimentation. In further experimentation, the co-solvent concentration will be reduced incrementally to zero with performance being observed at each incremental decrease. Using alcohol as a co-solvent to achieve greater performance can be critical, as explained by Pope et al (1996).

Because the IOS$_{15-18}$ is further tested as a co-surfactant, the question exists of whether other poorer performing surfactants (meaning here one with an optimal solubilization ratio less than the C$_{16-17}$-7PO-SO$_4^-$. can be used as co-surfactants. To be an effective co-surfactant, the poorer performing surfactant would have to provide favorable properties that the primary surfactant may lack (e.g. low viscosity, salinity tolerance, fast equilibration, etc.). One criterion for co-surfactant selection that has worked well is to select a co-surfactant that is molecularly dissimilar to the primary surfactant but yet sufficiently similar to it that they form mixed micelles and transport without separating in
the porous medium as has been observed when for example a non-ionic and anionic are used together. This molecular dissimilarity can allow for several different effects:

1. Change the optimal salinity of the surfactant mixture compared to using only a primary surfactant. For instance, if a co-surfactant has a higher optimal salinity than a primary surfactant when both are used alone, a mixture will have a higher optimal salinity than if only the primary surfactant were used.

2. Decrease microemulsion viscosity and gel-formation. A co-surfactant that is molecularly dissimilar to a primary surfactant will create disorder when surfactant molecules align at the oil/water interface of a microemulsion droplet. This disorder will destabilize the microemulsion, and may reduce the viscosity and formation of gels.

As will be shown later, co-surfactant can prevent gel formation and viscous emulsions much like an alcohol co-solvent can, but at much smaller concentrations. Therefore, substituting a portion of the alcohol co-solvent with co-surfactant can be beneficial. Of the surfactants used in the general screening, the IOS15-18 contained the most extreme branching, with two carbon tails stemming from a polar head group. This extreme branching is believed to make it an effective co-surfactant according to the two criteria discussed above. All other poor performing surfactants have linear carbon chain tails, which would likely cause a close-packing condition, and viscous/gel-like emulsions. This is the rationale behind choosing the IOS15-18 over all other poor performing surfactants as a co-surfactant.

Surfactant and co-surfactant selection and optimization

The general screening phase behavior experiments showed the best performing surfactant to be C_{16-17}-7PO-SO_4^-, and therefore this surfactant was chosen for further experimentation. Additionally, IOS15-18 was considered as a co-surfactant because of its molecular structure and performance in previous research (Jackson, 2006).
The $\text{C}_{16-17}-7\text{PO-SO}_4^-$ and IOS$_{15-18}$ surfactant and co-surfactant were tested alone and as a mixture for the first segment of their experimentation. The results are displayed in Figures 4.18 to 4.21, and Figures 4.56 to 4.57, and tabulated in Table 4.3. Several conclusions can be made from characterizing these three tests:

1. The **optimal salinity** (wt% NaCl) increases as relative concentration of $\text{C}_{16-17}-7\text{PO-SO}_4^-$ decreases, and IOS$_{15-18}$ increases. The optimal salinity increases from 2 wt% to >7 wt% NaCl when the 2 wt% concentration of $\text{C}_{16-17}-7\text{PO-SO}_4^-$ is replaced by 2 wt% IOS$_{15-18}$. An optimal salinity of 4.3 wt% NaCl occurs when 1.5 wt% $\text{C}_{16-17}-7\text{PO-SO}_4^-$ and 0.5 wt% IOS$_{15-18}$ are used.

2. The **optimal solubilization ratio** tends to decrease as the relative concentration of $\text{C}_{16-17}-7\text{PO-SO}_4^-$ decreases and IOS$_{15-18}$ increases. The data show that the optimal solubilization ratio decreases from 15 to less than 5 as 2 wt% surfactant $\text{C}_{16-17}-7\text{PO-SO}_4^-$ is replaced with 2 wt% IOS$_{15-18}$, with 1.5 wt% $\text{C}_{16-17}-7\text{PO-SO}_4^-$ and 0.5 wt% IOS$_{15-18}$ having a value of 10. Note that the SBA concentration is 2 wt% higher when 2 wt% $\text{C}_{16-17}-7\text{PO-SO}_4^-$ is used; however, data discussed later will show that a higher SBA concentration should in fact decrease optimal solubilization ratio. Therefore, this ratio would likely be greater than 15 if 6 wt% SBA was reduced to 4 wt% SBA.

3. The **equilibration time (days)** tends to decrease as the relative concentration of $\text{C}_{16-17}-7\text{PO-SO}_4^-$ decreases and IOS$_{15-18}$ increases. The data show the equilibration time to decrease from 11 days to 1 day as 2 wt% surfactant $\text{C}_{16-17}-7\text{PO-SO}_4^-$ is replaced with 2 wt% IOS$_{15-18}$, with 1.5 wt% $\text{C}_{16-17}-7\text{PO-SO}_4^-$ and 0.5 wt% IOS$_{15-18}$ having an equilibration time of 7 days. Just as discussed previously, the SBA concentration is 2 wt% higher when 2 wt% $\text{C}_{16-17}-7\text{PO-SO}_4^-$ is used; however, data discussed later will also show that a higher SBA concentration should in fact decrease equilibration time. Therefore, the high value of 11 days would likely be greater if 6 wt% SBA was reduced to 4 wt% SBA.
The general conclusion is that replacing C_{16-17-PO-SO_4} with some or all IOS_{15-18} will tend to: increase optimal salinity, decrease optimal solubilization ratio, and decrease equilibration time. The slight variation in SBA concentration between experiments may have an influence on the measured values; however, in later experimental data this slight SBA variation will be shown to be small relative to the general trend between C_{16-17-PO-SO_4} and IOS_{15-18} surfactants. One flaw in this data is that Test A9 was not run at a sufficient range of NaCl concentration to cover all microemulsion types, and therefore only spanned the oil-in-water (Type I) and bicontinuous (Type III) microemulsion zones. Therefore, the optimal salinity, equilibration time, and optimal solubilization ratio were inferred from available data.

The important conclusion from these experiments is that some but not all co-surfactant is beneficial, and that the combination of surfactant, co-surfactant, and co-solvent should be further optimized for surfactant/co-surfactant ratio at as low a co-solvent concentration as possible. The C_{16-17-PO-SO_4} to IOS_{15-18} ratio of 3 tested here will serve as a starting point for the next set of experiments.

**Effect of surfactant and co-surfactant ratio**

From the previous section, the surfactant C_{16-17-PO-SO_4} was found to give a high optimal solubilization ratio when used at 2 wt%, and was found to give faster equilibration time when mixed with IOS_{15-18} in a 3:1 ratio. This section examines a few other experiments that use these two surfactants in slightly different concentrations and with slightly different SBA concentrations to determine the effects of varying the IOS_{15-18} concentration.

The surfactant-to-co-surfactant ratio was tested at 3, 7, and 8, and this data is tabulated in Table 6.4. Accompanying solubilization ratio plots are displayed in Figures 4.20 to 4.21, 4.56 to 4.59, and 4.72 to 4.73. All experiments except A70 contained a total surfactant concentration of 2 wt%. Experiments A10 and A51 with ratios of 3 and 7, respectively, show that as the surfactant/co-surfactant ratio decreases from 7 to 3, (i.e. increase IOS_{15-18} proportion), the optimal salinity increases from 3.05 to 4.0 wt% NaCl,
the optimal solubilization ratio decreases from 12.5 to 10, and the equilibration time decreases from 15 to 7 days. Two additional experiments A70 and A50 show an 8:1 ratio and only primary surfactant, respectively, and a comparison shows that optimal salinity increases from 2 to 2.65 wt% NaCl, optimal solubilization ratio decreases from 15 to 13.5, and equilibration time decreases from 11 to 7 days when 0.25 wt% IOS_{15-18} replaces the primary surfactant. These results are similar to when the surfactant ratio was changed, and the proportion of IOS_{15-18} was increased.

The following general conclusions can then be made:

1. Decreasing the C_{16-17-7PO-SO_4}^- to IOS_{15-18} ratio (i.e. more IOS_{15-18}) increases the optimal salinity, decreases the optimal solubilization ratio, and decreases the equilibration time.

2. Increasing IOS_{15-18} when C_{16-17-7PO-SO_4}^- is fixed will increase optimal salinity, decrease optimal solubilization ratio, and decrease equilibration time.

Co-solvent selection and optimization

The next stage of the experimental process was to select a good performing co-solvent, and optimize its concentration in the phase behavior formulation. Co-solvents are generally alcohol molecules with small carbon chain lengths that act at the oil-water interface to help destabilize any viscous emulsion or gel formation. An alcohol molecule of neutral hydrophobicity will target this interface rather than remaining in the oil or aqueous phases. Butyl alcohols containing four carbon atoms are generally closest to neutrality, with 3 carbon propyl alcohols being slightly hydrophilic, and 5 carbon pentyl alcohols being slightly hydrophobic. The four-carbon butyl-alcohols could be in the form of 1-butanol, sec-butanol, and tert-butanol, each with varying effectiveness. Sec-butanol tends to be most frequently used, with iso-butanol available as a cheaper alternative.
Co-solvent screening - effect of alcohol carbon-chain length

Several different alcohol molecules were selected and tested, and the best performing alcohol was chosen for further testing and optimization. Co-solvents were tested in phase behavior with similar proportions of surfactant and crude oil. The co-solvents tested ranged from C_2 to C_5 alcohol molecules, which included: ethanol, 1-propanol, 2-propanol, 1-butanol, sec-butanol, tert-butanol, 1-pentanol, and 2-butoxy ethanol. 2-butoxy ethanol is a glycol rather than an alcohol, but it was still tested to determine effectiveness. Iso-butanol was not tested in this study, even though it can be an alternative to SBA at a lower cost. Each phase behavior pipette contained 2 mL of aqueous phase with 6 wt% of one of the co-solvent species, and 2 wt% of C_{16-17}-7PO-SO_4^{-} primary surfactant. One milliliter of McElroy crude oil comprised the oil phase. The tests were also prepared using an NaCl salinity gradient, and therefore the aqueous phase ranged from 1 wt% to 4 wt% NaCl, with 0.5 wt% increments. Information about the different experiments and the measured data are tabulated in Table 4.5, and accompanying solubilization plots are displayed in Figures 4.60 to 4.71.

Table 4.5 indicates that all co-solvents tested except 1-pentanol rendered useful phase behavior data, with 1-pentanol producing a gel-like microemulsion which was very slow to equilibrate. 1-pentanol contained the longest branching free carbon backbone, with 5 carbons aligned on a linear chain. For the co-solvents that rendered gel-free microemulsions, the results were varying with respect to equilibration time, optimal salinity, and optimal solubilization ratio. The 1-propanol and sec-butanol showed the highest solubilization ratios, with 18 cc/cc and 15 cc/cc, respectively. Equilibration times were 21 and 7 days for these co-solvents, respectively. The more branched tert-butanol, 2-butoxy ethanol, and 2-propanol gave lower optimal solubilization ratios of 12.5, 9, and 6, respectively.

Other than the poor performing 1-pentanol, co-solvents with a low carbon number such as ethanol and 2-propanol produced low solubilization ratios; however, the best performer was 1-propanol. 1-propanol has a three carbon linear chain in its backbone, and experiences no branching. One could therefore assume that increasing the linear
carbon backbone with increase solubilization and equilibration time (i.e. a more ordered microemulsion) until the carbon chain gets too long and produces a gel-like microemulsion (as with 1-pentanol). However, results from 1-butanol were surprising in that both solubilization and equilibration time were much lower than with 1-propanol, despite it having a 4 carbon linear backbone. Comparing the 2-carbon ethanol with 3-carbon 1-propanol shows much greater solubilization with the 1-propanol. 2-propanol also has three total carbons, but its structure has two one-carbon branches rather than a full three-carbon chain. Tert-butanol is similar to 2-propanol, except in having three one-carbon branches instead of two. Because of this, tert-butanol had slightly higher solubilization and lower equilibration time than 2-propanol. The 2-butoxyethanol structure differs from many of these in having a 6 carbon backbone with a polar oxygen between the second and third carbon. Relative to the other co-solvents, the performance of 2-butoxy-ethanol showed an average solubilization ratio and equilibration time of 9 cc/cc and 7 days, respectively.

To conclude, for the 6 wt% concentration of co-solvents that were used, the 1-propanol and sec-butanol produced the highest solubilization ratios, and are therefore most effective at reducing IFT. 2-butoxy ethanol, tert-butanol, and 1-butanol were less effective at solubilization, but did have lower equilibration time than 1-propanol, and a similar equilibration time to sec-butanol. Therefore, when desiring a high solubilization ratio and low equilibration time, sec-butanol seemed to perform the best when considering both of these factors. However, because 6 wt% co-solvent in oilfield EOR applications can be fairly expensive, co-solvent concentrations should be reduced to levels low enough, but where gel-free, fast equilibrating microemulsions still occur. Overall, SBA showed the best performance when considering both solubilization ratio and coalescence time, and was therefore selected for further testing and optimization.

Selecting and optimizing SBA co-solvent

SBA was selected as the co-solvent for further testing and optimization with McElroy crude oil. As mentioned, emulsions created in phase behavior can have high
viscosity and form gels, which are non-applicable for an EOR application. This was observable in phase behavior when only 2 wt% $\text{C}_{16-17}\text{-7PO-SO}_4^-$ was mixed with McElroy crude on a NaCl gradient. Adding co-solvent helped eliminate these gels and reduce the viscosity and equilibration time. The tradeoff is often a decrease in solubilization ratio. Therefore, the objective optimizing co-solvent concentration is to find the minimum co-solvent that reduced viscosity and gel formation, but does not significantly compromise solubilization ratio and cost.

Phase behavior experiments were performed using 1.5 wt% $\text{C}_{16-17}\text{-7PO-SO}_4^-$ and 0.5 wt% IOS$_{15-18}$, with 1, 2, and 4 wt% concentrations of SBA. These tests and measured data are tabulated in Table 4.6, with solubilization ratio plots displayed in 4.20, 4.21, 4.32, and 4.33. The experiment with 1 wt% SBA did not perform well, which represented a lower limit for the SBA concentration for this surfactant/co-surfactant ratio. The phase behavior with 2 wt% SBA had the higher solubilization ratio, and lower coalescence time compared to 4 wt% SBA. Further optimization should test SBA concentrations between 1 and 2 wt% to find the minimum concentration where equilibration can still occur, and performance is acceptable. An additional observation was that increasing SBA from 2 to 4 wt% caused the optimal salinity to decrease from 4.6 to 4.3 wt% NaCl.

The following conclusions can be made from this data analysis:

1. An increase in SBA concentration from 2 to 4 wt% slightly decreased both the optimal solubilization ratio and the optimal salinity.
2. When increasing the SBA concentration from 2 to 4 wt%, McElroy crude show a slightly greater coalescence time.
3. Decreasing SBA concentration from 2 to 1 wt% for McElroy crude produced viscous, gel-like emulsions that did not equilibrate.

**Co-effects between co-surfactant and co-solvent**

Several conclusions about the sec-butanol co-solvent and IOS$_{15-18}$ co-surfactant can be made from previous analyses. For instance, it was shown in Table 4.6 that
increasing SBA concentration will decrease both optimal salinity (wt% NaCl) and optimal solubilization ratio. It was also shown in Table 4.3 that increasing IOS\textsubscript{15-18} causes optimal salinity to increase, and optimal solubilization ratio to decrease. Further experimentation needs to be done that shows how each of these components can both interact and substitute for each other. A general conclusion thus far has been that a small amount of IOS\textsubscript{15-18} (~0.5 wt%) can replace a large amount (~2 to 4 wt%) of SBA, and still have similar surfactant performance with respect to high optimal solubilization ratio and equilibration time.

**Reducing surfactant, co-surfactant, and/or solvent concentration**

Phase behavior experiments performed thus far have contained relatively high concentrations of surfactant, co-surfactant, and co-solvent, with as much as 2 wt% total surfactant, and 6 wt% total co-solvent used. It is important to understand performance at lower concentrations for the option of lower concentration applications, and to understand dilution effects. The objective in a field application is to use the lowest chemical concentrations that will maximize oil recovery, whether a surfactant slug is small and of high concentration, or large and of low concentration.

Several experiments were performed using McElroy crude that reduced the total surfactant concentration from 2 wt% to 1 wt%, 0.5 wt%, and 0.2 wt%, with co-solvent concentration decreased proportionately as well. However, a first experiment was performed that reduced C\textsubscript{16-17}-7PO-SO\textsubscript{4} concentration from 2 to 1 wt%, while keeping SBA concentration at 6 wt%. Data are tabulated in Table 4.7, with Figures 4.56, 4.57, 4.74, and 4.75 showing solubilization plots. The results show that when the surfactant concentration is reduced from 2 to 1 wt%, the optimal solubilization ratio decreases slightly from 15 cc/cc to 12 cc/cc, the equilibration time decreases from 7 to 5 days, and the optimal salinity remains the same at 2 wt% NaCl. Note that the optimal solubilization ratio measures the oil volume solubilization per volume of surfactant, meaning that the surfactant performance decreased (i.e. a proportion of surfactant solubilized less oil) at the lower concentration. Also, note that the proportion of SBA to surfactant was higher at
the lower concentration, which may have decreased this performance measure. Increasing this SBA to surfactant ratio was expected to decrease the optimal salinity as shown in the previous section; however, the optimal salinity remained constant in this case. Additionally, the decrease in equilibration time may have resulted from this SBA to surfactant ratio increase, or from a decrease in total surfactant concentration.

Further experiments were performed that reduced surfactant, co-surfactant, and co-solvent in an incremental fashion. The original case tested previously used 1.5 wt% C_{16-17-7PO-SO_4}, 0.5 wt% IOS_{15-18}, and 2 wt% SBA, and in these experiments these concentrations were reduced by factors of 2, 4, and 10. This rendered total surfactant concentrations of 2 wt% to 1 wt%, 0.5 wt%, and 0.2 wt%. Table 6.8 shows the data from these experiments, and solubilization plots are displayed in Figures 4.32, 4.33, 4.42, and 4.44. The optimal solubilization ratio was highest at 11.5 in the 2 wt% total surfactant case, and decreased to 8 as the concentration was lowered to both 1 wt% and 0.5 wt%. Therefore, the optimal solubilization ratio tended to decrease as the total surfactant concentration was reduced. Additionally, the data shows that as the total concentration is reduced from 2 wt% surfactant to 0.5 wt% surfactant, the optimal salinity increases slightly from 4.3 to 4.95 wt% NaCl. Because the results of the lower concentration experiments were only measured once after 50 days (long after equilibration has occurred), the equilibration time was unable to be measured. Additionally, test A32 using 0.2 wt% total surfactant concentration did not provide useful data because the Type III microemulsion volumes were too small to measure. In conclusion, as chemical concentrations decreased, optimal salinity increased, and optimal solubilization ratio decreased.

**Alkali selection and optimization**

Adding alkali to the chemical EOR formulation and understanding its action can be beneficial, and therefore several alkali agents at varying pH concentrations were tested with the McElroy crude oil. As discussed previously, increasing the pH of the aqueous solution can cause saponification of naphthenic acids naturally present in crude oil to
create natural soaps that can mimic the actions of synthetic surfactants for a minimal increase in cost. Soaps are not molecularly identical to the synthetic surfactants, and can alter microemulsion characteristics (e.g. optimal salinity, viscosity, etc.). Not all crude oils contain reactive compounds. For McElroy crude oil, reactivity was tested by mixing the oil with varying concentrations of Na₂CO₃ alkali, which showed little reactivity and microemulsion generation relative to a more reactive Yates crude oil. McElroy crude was still tested with alkali to observe performance changes in phase behavior, which is the focus of this section.

**Effect of pH: using NaOH to vary pH**

Several alkali species were tested in phase behavior at varying concentrations to determine how they affected phase behavior parameters. One series of experiments tested several concentrations of NaOH, which provided a pH range from 8.56 to 12.34 of the aqueous solution. For all these experiments, McElroy crude oil was mixed in phase behavior with an aqueous solution containing 1.5 wt% C_{16-17}-7PO-SO₄⁻, 0.5 wt% IOS_{15-18}, 2 wt% sec-butanol, and 0 to 0.125wt% NaOH. Notice that the concentrations of surfactant and sec-butanol that worked well in the co-solvent testing were used in each experiment here, with alkali concentration being the only varying parameter. As with other tests, an appropriate NaCl gradient was created to cover all microemulsion types, and this gradient ranged from about 3.5 wt% to 5.5 wt% NaCl. The data from all phase behavior tests is tabulated in Table 4.9, and solubilization ratio plots are displayed in Figures 4.32, 4.33, and 4.46 to 4.55.

The data in Table 4.9 shows several tests with smaller NaOH concentrations (< 0.01 wt%) having pH values around 8.5 to 9, and consequently showing optimal solubilization ratios between 10 and 11.5. Optimal solubilization values increased to 14 when NaOH increased to both 0.016 wt% and 0.125 wt%, which resulted in a pH increase to 10.62 and 12.34, respectively. Little correlation in equilibration time or optimal salinity were observable with an increase in pH.
Increasing the pH beyond 10 for experiments A41 and A42 caused a significant increase in optimal solubilization ratio up to 14. This high pH increase could have caused in situ saponification of a small amount of crude oil components not detectable when previously testing for crude oil reactivity. Previous testing had only observed reactivity effects at pH values lower than about 10.5. Because the saponification was perhaps very minor in this case, no noticeable changes in viscosity, coalescence time, or optimal salinity were observed with increased NaOH concentration, and only solubilization ratio showed the significant increase.

After all soap has been generated, it is expected that the optimal salinity would level off above some pH threshold. This leveling off does appear in the results at 4.5, however, the pH at which it begins is very low. Experiment A41 is difficult to explain if optimal salinity levels do level off at 4.5 wt% NaCl. The increase in solubilization with an increase in pH is probably due to soap generation. Because this solubilization ratio increase reaches a ceiling of about 14 above pH 10, all soap generation is likely to have occurred above this pH. Also, a slight decrease in optimum salinity was observed as pH increased, which is likely due to soap generation. The generated soap would have an optimal salinity lower than the synthetic surfactant, and therefore its presence would decrease the optimal salinity.

**Effect of alkali type**

There are several other alkali components other than NaOH that can increase pH and contribute electrolytes to a chemical EOR formulation. Sodium carbonate (Na$_2$CO$_3$) and sodium tetrametaborate pentahydrate (referred to as sodium metaborate) were chosen as two alkali salts for experimentation with McElroy crude oil. These alkali agents are relatively inexpensive compared to surfactant and co-solvent molecules, and can be cheap enhancers of a chemical formula. As a standard, experiments containing alkali would have 1 wt% of either Na$_2$CO$_3$ or sodium metaborate, and the results were compared to experiments without alkali. Results are tabulated in Table 4.10, with solubilization ratio plots shown in Figures 4.32 to 4.37, 4.48, 4.49. When using Na$_2$CO$_3$ and sodium
metaborate as alkali agents in experiments with McElroy crude, the surfactant, co-
surfactant, and co-solvent types and concentrations remained constant.

Experiments containing alkali salts are compared to the experiment having no alkali, and the experiment containing NaOH from the previous section. The data in Table 4.10 shows that using 1 wt% Na$_2$CO$_3$ produces an optimal solubilization ratio of 15, which is greater than the no alkali situation where the ratio was 11.5. Notice, however, that the pH increased from 8.57 to 10.28 when Na$_2$CO$_3$ was used, which gives an optimal solubilization ratio increase relative to pH increase that is consistent with previous results using NaOH. Again, the previous results showed that increasing the pH beyond 10 was sufficient to increase the optimal solubilization ratio from about 11 to 14. The experiment using sodium metaborate gave an optimal solubilization ratio of 12 and a pH of 9.01, both of which are similar to the no alkali situation.

Regarding optimal salinity, Table 4.10 shows the wt% Na$^+$ optimal salinity to increase from 1.69 to 1.92 when Na$_2$CO$_3$ was used instead of no alkali. Note that the alkali itself contributes salinity, and therefore considering only wt% Na$^+$ is a reasonable salinity parameter to compare between the different experiments. The sodium metaborate did show a different optimal salinity (wt% Na$^+$) compared with the no alkali situation. Therefore, using Na$_2$CO$_3$ will slightly increase optimal salinity (wt% Na$^+$) compared with no alkali and sodium metaborate scenarios.

A related comparison can be shown from Table 4.10 between the no alkali, Na$_2$CO$_3$, and NaOH situations. Notice that the optimal salinity (wt% Na$^+$) increases from experiments containing no alkali to NaOH to Na$_2$CO$_3$. Additionally, the pH is similar between the NaOH and Na2CO3 experiments, and lower for the no alkali situation. This comparison shows that a simple increase in pH alone did not cause optimal salinity (wt% Na$^+$) to increase because optimal salinity did not increase for the NaOH situation. The optimal salinity increase is perhaps related to another mechanism like ionic strength of difference anions rather than simple pH increase.
The equilibrium time was 7 days for both the no alkali and Na$_2$CO$_3$ experiments, and increased to 11 days when sodium metaborate was used. Additionally, just as in the NaOH experiments, there seems to be no relationship between pH and equilibration time.

**Very low surfactant concentrations with alkali salts**

Previous data showed in Table 4.8 that the initial relatively high surfactant concentration of 2 wt% could be reduced to 1, 0.5, or even 0.2 wt%. However, experiments were performed in which solutions with reduced surfactant concentrations contained Na$_2$CO$_3$. These experiments are explained in this section, and consist of either 1 wt% Na$_2$CO$_3$, and either 2, 1, 0.5 or 0.2 wt% total surfactant. As a comparison, data from the no alkali situation shown before is also displayed again for comparison.

Table 4.11 displays data for Na$_2$CO$_3$ at varying surfactant, co-surfactant, and co-solvent concentrations, and solubilization plots are displayed in Figures 4.34, 4.35, 4.43, and 4.45. Table 4.8 can be referred to as a control using no alkali. Of mention is that microemulsion volumes at lower surfactant concentrations were observed to be small, and the measured values are of only moderate precision. For instance, optimal solubilization ratio varies from 15 to 18 to 12 as surfactant concentration decreases from 2 to 1 to 0.2 wt% in Table 4.11. Although these optimal solubilization values fluctuate widely, they are all relatively high (e.g. greater than 10), showing that good performance is maintained as low surfactant concentrations. Table 4.8 with no alkali, optimal solubilization ratio varies from 8 to 11 for surfactant concentrations of 0.5 to 2 wt%, which shows performance to be slightly compromised at lower concentrations. One important conclusion between the no alkali and Na$_2$CO$_3$ scenarios is that greater solubilization ratios are observed using Na$_2$CO$_3$ for all experiments.

**Co-effects between sec-butanol and alkali salts**

After understanding how varying individual parameters affects phase behaviors, two or more components can be varied to determine co-effects between different species. In this section, the co-effects of varying both sec-butanol and alkali salt concentrations
were tested to observe effects on phase behavior performance. For all the experiments, fixed concentrations of surfactant and co-surfactant of 1.5 wt% \( \text{C}_{16-17}-7\text{PO-SO}_4^- \), 0.5 wt% IOS\(_{15-18}\) were used in the aqueous solution, with McElroy crude as the oil phase. The sec-butanol concentrations used in these solutions were 1 wt%, 2 wt%, and 4 wt for experiments containing 1 wt% sodium carbonate, 1 wt% sodium metaborate, or no added alkali. As with other tests, appropriate NaCl quantities were added to the test tubes to create a salinity gradient to cover all microemulsion types. The components and data of all phase behavior tests are tabulated in Table 4.12, with solubilization ratio plots shown in Figures 4.20, 4.21, 4.26 to 4.29, 4.32 to 4.41. There are several conclusions that can be drawn from Table 4.12 for the McElroy crude oil:

1. For experiments producing microemulsion, the optimal solubilization ratio increases as sec-butanol concentration decreases from 4 to 2 wt%. The optimal solubilization ratio is greatest for sodium carbonate, intermediate for sodium metaborate, and lowest for no alkali with either 1 or 2 wt% SBA. This is possibly correlated with pH values, as the sodium carbonate had the highest pH, sodium metaborate intermediate pH, and no alkali had lowest pH. A decrease in sec-butanol increased the optimal salinity for each alkali situation and for the no alkali situation.

2. The addition of 1 wt% sodium carbonate or sodium metaborate enabled equilibration to occur at 1 wt% sec-butanol concentrations, without a significant change in phase behavior properties relative to 2 wt% sec-butanol. Therefore, either of these alkali salts can be used to replace a portion of sec-butanol in the EOR solution.

3. For experiments containing alkali, equilibration time decreased as SBA concentration increased.
From these data, several general conclusions can be made:

1. Sodium carbonate and sodium metaborate can supplement some sec-butanol, and enable equilibration with concentrations of sec-butanol that would not equilibrate if the alkali salts were not present.

2. The effect of alkali on the microemulsion is clearer at low co-solvent concentration. The experiment without alkali does not equilibrate at lower concentrations, and therefore alkali is shown to be beneficial at low SBA concentrations.

3. High pH may destabilize microemulsion at low co-solvent concentrations because the experiment with Na$_2$CO$_3$ showed a slightly lower solubilization ratio at 1 wt% SBA than at 2 wt% SBA. The experiment with sodium metaborate, however, showed incremental increases as SBA concentration was lowered. The destabilization mechanisms may be that soap as a co-surfactant has surface functionalities similar to IOS$_{15-18}$, and/or that pH does destabilize microemulsion. The latter are mostly likely because from A24 and A25, pH by sodium metaborate is about 9.02 compared to about 10.3 for Na$_2$CO$_3$, and hence soap generation at pH 9.02 is not significant compared to that at pH above 10 as shown in previous sections.

4. The optimal salinity shows a consistent increase in all alkali/no alkali situations as the SBA concentration decreases.

**Comparison between McElroy and Yates crude oils**

Most phase behavior experiments were performed using McElroy crude; however, Yates crude was used for some experiments to compare performance between two different crude oils. This study was performed at 22 C as a room temperature standard, although the reservoir temperatures of McElroy and Yates crudes are 30 C and 28 C, respectively. Lower temperature could compromise results and it is difficult to formulate conclusions for a higher temperature based on experiments at a lower temperature.
Table 4.13 shows the data for the phase behavior experiments used in the comparison, and solubilization ratio plots are shown in Figures 4.76 to 4.79, 4.83 to 4.86. All experiments contained the same concentrations of surfactant, co-surfactant, and co-solvent, and either no alkali or 1 wt% Na₂CO₃. Several conclusions can be made from this comparison:

1. Optimal salinity was higher for Yates crude oil for both no alkali and alkali experiments.
2. Equilibration time was longer for Yates crude oil for both no alkali and alkali experiments.
3. For Yates crude oil, the optimal solubilization ratio was higher when no alkali was used; the Yates crude oil is more reactive than McElroy crude oil so more soap is formed and the soap probably caused this difference.

**Additional Effects of Temperature**

Several additional experiments were conducted to explain the effects of temperature variation on surfactant solutions for McElroy crude oil. Only two difference temperatures of 22 C and 30 C were tested in these experiments, which correspond to room temperature and the reservoir temperature. Understanding surfactant performance at the reservoir temperature has obvious importance and relevance for field design and application. Understanding performance at room temperature was advantageous when conducting laboratory experiments, where heating to reservoir temperature was either difficult or impossible (e.g. like CT scanning of core samples). Comparison of the data between these two temperatures, however, did render some interesting results. Experiments were performed with the same concentrations of surfactant, co-surfactant, and co-solvent, with either no alkali, Na₂CO₃, or sodium metaborate. Minor differences other than temperature were that experiments performed at 30 C used 3 mL of McElroy crude oil, 6 mL of aqueous solution, and a fine resolution NaCl gradient varying at 0.1 wt% increments. The experiments performed at 22 C used 1mL of McElroy crude oil and 2 mL of aqueous solution, with a NaCl gradient of 0.25 wt% increments. Table 4.14
shows data for all experiments used for the comparison, with solubilization ratio plots displayed in Figures 4.4 to 4.9, 4.76 to 4.81. An additional Figure 4.82 compares experiments at two different temperatures when Na₂CO₃ was used.

The tests performed at 30°C showed higher optimal solubilization ratios for the no alkali and sodium metaborate experiments, and a similar optimal solubilization ratio for the Na₂CO₃ experiment. Additionally, there were similar equilibration times for the no alkali and Na₂CO₃ for both 22°C and 30°C temperatures, and a significant difference in equilibration time for the sodium metaborate experiments. The most marked difference though is the increase in optimal salinity for all three alkali experiments when temperature was decreased from 30°C to 22°C. This is shown in Figure 4.82 comparing experiments with Na₂CO₃ at two different temperatures. The solubilization ratio curves appear similar, except that they shift to a higher salinity when the temperature decreases.

**PHASE BEHAVIOR OPTIMIZATION FOR CRUDE D AND FORMATION BRINE WITH HIGH TDS AND HARDNESS**

Crude D is from a light oil reservoir with a temperature of 52°C. The formation brine has a high salinity and hardness. The goal was to find a high-performance formulation to test in a core flood as quickly as possible using the knowledge gained from the initial studies as well as previous studies.

**Primary Surfactant, Co-surfactant, and Co-solvent Selection**

Previous phase behavior experimentation with McElroy crude oil showed C₁₆₋₁₇ – 7PO – SO₄²⁻ primary surfactant and IOS₁₅₋₁₈ co-surfactant to perform well together when used with a sufficient concentration of sec-butanol (SBA). Therefore, these surfactants were selected for initial testing with Crude D since the reservoir temperature is also low enough to use sulfates and since it is also a light crude oil. IOS₂₀₋₂₄ was the only additional surfactant used in the initial testing experiments. All phase behavior experiments used a 2 wt% total surfactant concentration, and either 0.5 or 2 wt% of SBA.
Table 4.15 shows the first five phase behavior experiments performed with Crude D in an initial, coarse resolution scan to find optimal salinity. Solubilization ratio plots are shown in Figures 4.87 to 4.90 for experiments that produced measurable microemulsion interfaces. Three tests showed a combination of C_{16-17} – 7PO – SO_{4}^{-} and either IOS_{15-18} or IOS_{20-24}, and two tests used only IOS_{20-24} or IOS_{15-18}. The NaCl concentrations in the pipettes covered a wide range, and varied by 1.5 wt% between pipettes. This allowed for a coarse resolution NaCl scan to simply find the optimum salinity before preparing further tests at a finer NaCl resolution for in depth assessment.

The data in Table 4.15 show the surfactant/co-surfactant combination of C_{16-17} – 7PO – SO_{4}^{-} and IOS_{15-18} as the only mixture to perform well, and to not contain any gels or highly viscous microemulsion. Note that this combination performed well at both 0.5 and 2 wt% of SBA.

Finer resolution scans using smaller increments of NaCl between pipettes was performed in additional phase behavior experiments to focus in on the optimum salinity, Type III region. Table 4.15 shows data for the finer resolution phase behaviors, and accompanying figures showing solubilization ratio plots are displayed in Figures 4.91 to 4.94. These experiments were identical to the initial experiments, except that 0.25 wt% NaCl increments separated pipettes rather than a coarser resolution 1.5 wt% NaCl. The four additional experiments concluded that only the combination of C_{16-17} – 7PO – SO_{4}^{-} and IOS_{15-18} could produce gel-free microemulsions with results that could be further analyzed. Therefore, C_{16-17} – 7PO – SO_{4}^{-} and IOS_{15-18} surfactants were selected for more rigorous testing for the following effects: varying surfactant/co-surfactant ratio, reducing alcohol concentration, reducing total surfactant concentration, adding alkali, and final selection and optimization.

**Varying Surfactant-to-Co-Surfactant Ratio**

The ratio of C_{16-17} – 7PO – SO_{4}^{-} to IOS_{15-18} surfactant concentrations was systematically varied in phase behavior experiments, and the experimental results are shown in Table 4.16. Solubilization ratio plots of the experiments are shown in Figures
4.95 to 4.97, 4.102, 4.103, 4.108, and 4.109. The C\textsubscript{16-17}–7PO–SO\textsubscript{4}\textsuperscript{2−}–tO\textsubscript{15-18} ratios used were: 1:1, 5:3, 3:1, 7:1, and only C\textsubscript{16-17}–7PO–SO\textsubscript{4}\textsuperscript{2−}. All experiments used a 2 wt% total surfactant concentration, and a 1 wt% or 2 wt% SBA concentration at small or large ratios, respectively. Previous data using McElroy crude oil showed the necessity of high SBA concentrations at high proportions of C\textsubscript{16-17}–7PO–SO\textsubscript{4}\textsuperscript{2−}, and that a higher SBA concentration moderately reduced the solubilization ratio, and only slightly reduced the optimal salinity.

The most notable result in Table 6.16 is a consistent decrease in optimal salinity with an increase in surfactant ratio. The optimal salinity goes from 6.6 wt% NaCl at a 1:1 ratio to 2 wt% NaCl at a 7:1 ratio. Solubilization ratio results show only a slight upward trend as surfactant ratio increases; however, the 5:3 ratio solution did have a higher solubilization that the 3:1 ratio solution at the same SBA concentration of 1 wt%. Regardless, all solubilization ratio values are sufficiently high (i.e. > 10) to give a well-performing, low IFT microemulsion. Varying the surfactant ratio can therefore be used to give an optimal salinity value most fitting for reservoir salinity and conditions.

**Reducing Alcohol**

Reducing the concentration of alcohol (i.e. SBA) is desirable in terms of reducing the chemical costs, and therefore as little alcohol as possible should be used in the final formulation and still achieve acceptable performance. Table 4.17 shows data of several phase behavior experiments that varied the SBA concentration from 0.5 to 2 wt% at increments of 0.5 wt%. Different surfactant to co-surfactant ratios also assessed at each alcohol concentration as well. As mentioned, the objective is to reduce the SBA concentration as much as possible, and to still have a well performing (i.e. high solubilization ratio) mixture with a desirable optimal salinity. Solubilization ratio plots for all experiments in Table 4.17 are displayed in Figures 4.95 to 4.109.

From Table 4.17, 1:1 and 5:3 surfactant ratios were tested at a 0.5 wt% SBA concentration, and both found to give a high solubilization ratio (16 and 18, respectively). As expected, the optimal salinity was higher (6.9 wt% NaCl) for the 1:1 ratio than for the
Increasing the SBA concentration to 1 wt% for 1:1, 5:3, and 3:1 surfactant ratios showed slightly lower optimal solubilization ratio values, with a range from 12.5 to 15. A decrease in solubilization ratio with increase in SBA concentration was also observed with the McElroy crude oil. Increasing the SBA concentration slightly decreases the optimal salinity of the 1:1 ratio (from 6.9 to 6.6 wt% NaCl), and does not change the optimal salinity of the 5:3 ratio at 5 wt% NaCl. Table 4.17 shows three experiments1.5 and 2 wt% SBA, which all show good optimal solubilization values. Optimal salinity values show slight decreases for the 3:1 ratio and 5:3 ratio as SBA concentration increases from 1 to 1.5 wt% and 1 to 2 wt%, respectively. The overall conclusion from these experiments is that 2 wt% total surfactant solutions with 0.5 wt% SBA can give high solubilization ratios.

**Reducing Total Surfactant Concentration**

The amount of surfactant needed in a chemical flood depends first on the total mass of active surfactant, which is proportional to the slug size times the concentration, needed to satisfy surfactant adsorption (actually retention) in the reservoir and less so on the surfactant concentration per se within reasonable ranges of surfactant slug sizes and assuming the concentration is well above the CMC. However, it is important to understand how microemulsion performance changes with surfactant concentration and also there are some cost advantages to injecting dilute surfactant even for a fixed mass of surfactant, therefore variations in surfactant concentration were assessed in phase behavior experiments.

Table 4.18 shows phase behavior experiments that used 0.5, 1, and 2 wt% total surfactant concentrations for each surfactant to co-surfactant ratio of 3:1, 5:3, and 1:1. Solubilization ratio plots for these experiments are shown in Figures 4.98 to 4.101, 4.106 to 4.107, and 4.120 to 4.129. Experiments with 2 wt% total surfactant concentration had 1.5, 0.5, and 0.5 wt% SBA for 3:1, 1:1, and 5:3 surfactant ratios, respectively, and experiments at lower surfactant concentrations had SBA concentrations reduced proportionately. The results show optimal salinity and optimal solubilization ratios to be
very similar between 1 and 2 wt% total surfactant concentration for all surfactant ratios. The 5:3 ratio showed the highest solubilization ratio of 18 for both surfactant concentrations, and optimal salinity increased as surfactant ratio decreased.

Experiments at 0.5 wt% total surfactant showed mixed results, with only the 1:1 and 5:3 ratio experiments showing results. It should be noted that experiments at these low surfactant concentrations produce a small volume of microemulsion that can be difficult measure. Additionally, solubilization curves increase more abruptly, and require fine resolution data points centered around the optimal salinity for accurate assessment. This is possibly the reason why the 3:1 ratio experiment gave poor results, and why the solubilization ratios for the 1:1 and 5:3 ratio experiments differ slightly from the 1 and 2 wt% total surfactant experiments. Optimal salinity values for the 1:1 and 5:3 ratio experiments were lower with 0.5 wt% total surfactant than with 1 and 2 t% total surfactant.

General conclusions for the above experiments is that optimum solubilization ratio remains fairly constant as total surfactant concentration changes, and optimal salinity will decrease as total surfactant concentration decreases. Because mixtures generally perform well regardless of surfactant concentration, a small surfactant slug volume that is concentrated should perform as well as a larger volume, dilute surfactant slug, as long as the total amount of surfactant is the same.

Alkali Effect, Selection and Optimization

The effect of alkali, specifically sodium carbonate, on surfactant performance was assessed for several alkali concentrations for 1:1, 5:3, and 3:1 surfactant-to-co-surfactant ratios. Table 4.19 shows data from the phase behavior experiments using 0, 0.5 and 1 wt% Na₂CO₃, and an Na₂CO₃ scan. The Na₂CO₃ scan eliminates the use of NaCl, and lets Na₂CO₃ act as the electrolyte and alkali. Solubilization ratio plots of these experiments are shown in Figures 4.98 to 4.101, 4.106 to 4.107, 4.110 to 4.119, and 4.130 to 4.137.

The optimum solubilization ratios for all experiments are consistently around 16, and experience little change for all alkali concentrations. The 5:3 ratio experiment at 1
wt% Na₂CO₃ shows a higher solubilization ratio of 20, which cannot be explained due to solubilization ratios of around 16 for 5:3 ratio mixtures at other alkali concentrations. The optimal salinity with respect to NaCl shows a decrease as Na₂CO₃ concentration increases, which is expected because Na₂CO₃ is contributing to the electrolytes. Optimal salinity values for the Na₂CO₃ scan experiments show higher concentrations for all ratios than if only NaCl was used.

The general conclusion from the alkali experiments is that adding alkali will not affect solubilization ratio. However, alkali could be beneficial in preventing surfactant adsorption onto the rock surface, or in replacing SBA as is shown in the next section.

**Formulations for Core flood**

Most of the phase behavior experiments for Crude D performed well in achieving high optimum solubilization ratios over a wide range for several variables: surfactant ratio, total surfactant concentration, alkali concentration, and SBA concentration. This information was then used to design a few good formulations suitable for a core flood using Berea sandstone, and saturated with a high TDS and hardness synthetic formation brine.

Of the range of surfactant ratios tested, only a 5:3 and 1:1 surfactant-to-co-surfactant ratio was considered because of their higher optimal salinity compared to ratios of 3:1 and greater. The higher optimal salinity would reduce the salinity shock at the displacement from with the high TDS and hardness synthetic formation brine. Between the 5:3 and 1:1 ratio, the optimal solubilization values were generally greater for the 5:3 ratio than for the 1:1 ratio. Therefore, the first core flood formulation would contain a 5:3 surfactant-to-co-surfactant ratio, with the option available to optimize future core floods with a lower ratio.

A suitable concentration of SBA was selected based on the data in Table 4.17, where SBA concentration was varied from 0.5 to 2 wt% for phase behavior experiments containing 2 wt% total surfactant for the 5:3 ratio of surfactant to co-surfactant, the phase behavior with 0.5 wt% SBA had the highest optimal solubilization ratio of 18.
Additionally, the low SBA concentration offered a cost savings over formulations with higher SBA concentrations. Therefore, a 0.5 wt% concentration of SBA per 2 wt% total surfactant was the best choice based on the SBA data.

A total surfactant concentration of 1 wt% was chosen based on the data in Table 4.18 for the 5:3 ratio of surfactant-to-co-surfactant. For the phase behavior experiments with 5:3 ratio, 2 wt% total surfactant, 0.5 wt% SBA and 1 wt% total surfactant, 0.25 wt% SBA had the same optimal solubilization ratio of 18, while 0.5 wt% total surfactant, 0.125 wt% SBA had a smaller optimal solubilization ratio of 15. The 1 wt% total surfactant was chosen as the first core flood formulation, with the option available to optimize future core flood experiments with perhaps a lower total surfactant concentration.

Data on adding alkali (i.e. Na₂CO₃) to phase behavior experiments with 5:3 surfactant to co-surfactant ratio is shown in Table 4.19 for 2 wt% total surfactant. 0, 0.5, 1, and max wt% Na₂CO₃ experimental data shows the highest solubilization ratio of 20 to occur for 1 wt% Na₂CO₃ at 5:3 surfactant to co-surfactant ratio. Therefore, 1 wt% Na₂CO₃ was chosen as the alkali concentration for a core flood formula option.

Table 4.20 shows three different chemical formula options concluded from the selection process based on surfactant ratio, total surfactant concentration, SBA concentration, and alkali concentration. Solubilization ratio plots of these three options are shown in Figures 4.124 to 4.125, and 4.138 to 4.141. All three selections use a 5:3 surfactant to co-surfactant ratio and 1 wt% total surfactant. Test 28 in Table 4.20 also contains 0.25 wt% SBA, and does not contain Na₂CO₃. Test 41 in Table 4.20 is similar to Test 28, except that it contains 1 wt% Na₂CO₃. Adding the 1 wt% Na₂CO₃ shows an advantage in increasing the solubilization ratio from 18 to 24. Test 42 is an additional experiment using a formula with no SBA and with 1 wt% Na₂CO₃. The solubilization ratios are similar for Tests 41 and 42, showing that eliminating SBA when 1 wt% alkali was used is a viable option. If a formulation containing alkali was chosen for the chemical flood, test 42 would be preferred over 41 due to the absence of SBA.
**Aqueous Stability**

An aqueous stability test of the surfactant slug used in the core flood was performed at room temperature for 24 hours. The chemical components and concentrations in the surfactant slug are shown in Table 4.29, except the NaCl concentration was varied for the aqueous stability test. The results of the aqueous stability test are displayed in Table 4.21 for Test 28, which is the formulation used in the surfactant slug. The formulation of Test 42 containing alkali was also tested for aqueous stability as an alternative solution for ASP flooding. Note that 2000 ppm Flopaam 3330-S polymer was included in the formulations for the aqueous stability test.

Table 4.21 shows the Test 28 formulation tested for aqueous stability at increments of 1 wt% NaCl. Solutions remain clear and homogeneous through 6 wt% NaCl, and become cloudy at 7 wt% NaCl. The optimal salinity is 4.9 wt% NaCl, which is lower than the 6 to 7 wt% NaCl concentration at which the solution becomes unstable. Therefore, the surfactant slug at optimal salinity passes the aqueous stability test, and is acceptable for a chemical flood. The alternative formulation containing alkali (Test 42) is aqueous stable through 5 wt% NaCl, and the solution is therefore aqueous stable at its optimal salinity value of 4.42 wt% NaCl.

**COREFLOOD RECOVERY IN BEREA SANDSTONE CONTAINING SYNTHETIC FORMATION BRINE OF HIGH TDS AND HARDNESS**

A core flood experiment is a means to test whether a selected chemical formulation that performs well in phase behavior is capable of recovering a significant volume of residual oil from a core. The core flood performed in this research was unique in recovering residual oil from a core initially saturated with synthetic formation brine of high TDS and hardness. It was initially uncertain whether the salinity contrast between the synthetic formation brine and the surfactant slug at the displacement front would hinder the oil recovery process, which was the focus of this core flood.
Core Data

A Berea sandstone core was used in the core flood experiment, and property data used to characterize the core are shown in Tables 4.22 to 4.25. These property data include: core dimensions and pore volume, permeability and relative permeability, and initial and residual saturation values. The crude oil used in the core flood, Crude D, is produced from a sandstone reservoir, and therefore Berea sandstone was used in place of actual reservoir core.

The core was 1 foot long (30.4 cm) and 2 inches in diameter (5.1 cm), with 20.4% porosity and 126.7 mL pore volume. Air permeability measurements were taken at the inlet, outlet, and middle of the bare, dry core prior to applying epoxy, and these permeability values were 867 md, 777 md, and 800 md, respectively. Air permeability was measured again at the inlet after applying epoxy, and the permeability was similar at 859 md.

The sequence of flooding experiments (i.e. brine flood, oil flood, water flood, and chemical flood) allowed permeability and relative permeability values to be calculated from collected pressure and flow rate data. During brine flooding, the core was saturated with a single, brine phase, and the absolute brine permeability was calculated to be 603 md. An end-point oil permeability of 376 md was calculated at residual water saturation, which gave a 0.623 end-point oil relative permeability (relative to absolute brine permeability). End-point water permeability of 72 md was calculated from water flood data at residual oil saturation, giving a 0.119 end-point relative water permeability.

Initial and residual saturation values were calculated from recovered oil and water volumes during the oil and water flood experiments. The oil flood experiment rendered an initial oil saturation of 0.61, with a residual water saturation of 0.39. The water flood experiment rendered an initial water saturation of 0.706, with a residual oil saturation of 0.294. Recovering the residual oil remaining after the water flood was the target of the chemical flood.
Injected Fluid Data

Synthetic Formation Brine

Synthetic formation brine was used to initially saturate the dry core, and to flood the core during the brine flood and water flood experiments. Table 4.26 gives the concentration values of Na⁺, Ca²⁺, Mg²⁺, and Cl⁻ ions composing the synthetic formation brine, which are similar to water analysis data from actual formation brine. The synthetic brine contained 156525 mg/L TDS and 8667 mg/L Ca²⁺ + Mg²⁺, which was the major challenge for this core flood experiment. The brine viscosity at reservoir temperature (i.e. 52 °C) was found to be 0.73 cp (shown in Table 4.27) at a shear rate of 11 sec⁻¹, and Figure 4.142 can be referred to for a plot of viscosity versus a range shear rates.

Surfactant Slug and Polymer Drive

The chemical formulation selected for the surfactant slug contained 0.625 wt% C₁₆₋₁₇ - 7PO - SO₄⁻, 0.375 wt% IOS₁₅₋₁₈, 0.25 wt% SBA, 2000 ppm Flopaam 3330-S, 4.9 wt% NaCl, and this selection was based on a good phase behavior performance and aqueous stability at optimum salinity. Figure 6.151 shows the solubilization ratio versus NaCl concentration phase behavior data for the surfactant slug (excluding 2000 ppm Flopaam 3330-S). Note that the optimal salinity is 4.9 wt% NaCl, the same as the surfactant slug prepared for injection. The optimal solubilization ratio of 16 can approximate the interfacial tension as 0.0012 dynes/cm, according to equation 3.9. Figure 4.151 also shows the Type III region to span from 4.6 to 5.15 wt% NaCl, though Type I and II microemulsions were not found until 4.5 and 5.25 wt% NaCl, respectively.

An aqueous stability test was performed using the chemical concentrations of the surfactant slug for a range of NaCl concentrations. This aqueous stability test is shown in Table 4.21 as Test 28, and it did contain 2000 ppm Flopaam 3330-S polymer. Table 6.21 shows aqueous mixtures remain clear when containing at least 6 wt% NaCl, and are cloudy when containing 7 wt% or more NaCl. Because the surfactant slug contains 4.9 wt% NaCl, it is therefore aqueous stable, and will not segregate or precipitate prior to core flood injection.
The formulation selected for the polymer drive was 2000 ppm Flopaam 3330-S and 3 wt% NaCl. The NaCl concentration was about 60% that of the surfactant slug to ensure that the salinity gradient in the core flood reaches the Type I region based on the surfactant formulation phase behavior. The phase behavior data shows the Type I / Type III boundary at around 4.6 wt% NaCl. Polymer drive salinity closer to this boundary would have increased the risk of not reaching the Type I region, especially with the high synthetic formation brine salinity at the displacement front.

Surfactant slug and polymer drive viscosity is designed based on a polymer apparent viscosity calculation that aims for a target mobility ratio less than one. As shown in the data analysis chapter, the apparent viscosity (equation 3.23), and the calculation using the core data is as such:

\[
\mu_{\text{app}} = \frac{1}{\lambda_{\text{trm}}} = 0.73 + 1.96 \left(\frac{0.119}{0.623}\right) = 9.28 \text{cp}
\]

Both the surfactant slug and the polymer drive contained 2000 ppm of Flopaam 3330-S polymer, and their respective viscosities were 10.9cp and 8.7cp at 52°C and an 11 sec\(^{-1}\) shear rate, respectively (Table 4.27). Figures 4.143 and 4.144 contain plots of viscosity versus a range shear rates for both the surfactant slug and polymer drive, respectively. Although the polymer drive viscosity of 8.7cp at 11 sec\(^{-1}\) was slightly lower than the calculated apparent viscosity of 9.28cp, Figure 4.144 shows the polymer drive viscosity to trend around 10 cp at shear rates expected in the core flood, which will provide sufficient mobility control.

**Polymer Filtration**

A polymer stock solution with 5000 ppm Flopaam 3330-S and 1000 ppm NaCl was prepared and filtered prior to mixing surfactant slug and polymer drive solutions. A total of 140 mL of stock solution was filtered with 1.2 um Millipore filter paper in a Fann model filter press under a constant 12 psig pressure. The solution was collected in a graduated cylinder, and the time was recorded after every 10mL collected. Table 4.35
shows the collected data from the filtration, and the filtration ratio is calculated equation 3.1:

\[
\text{filtration ratio} = \frac{\Delta t_{21.13\text{min}80-100\text{mL}}}{\Delta t_{19.18\text{min}20-40\text{mL}}} = \frac{21.13\text{min}}{19.18\text{min}} = 1.1
\]

A filtration ratio of 1.1 is considered acceptable with respect to the 1 to 1.2 allowable range.

**Core Saturation and Preliminary Fluid Injections**

**Brine Flooding**

The brine flood experiment used 2.5 PV of the synthetic formation brine (described in Table 4.26) under a constant flow rate of 7.23 mL/min. This was the highest flow rate at which the displacement pump could deliver displacing fluid. The average pressure drop across the entire core was 3.1 psi after reaching steady state conditions (as shown in Figure 4.146), which gave a total brine permeability of 603md. This permeability represents the absolute permeability of the core, and is the basis for relative permeability calculations.

**Crude Oil Flooding**

The oil flood experiment used a total of 2.2 PV Crude D under a constant flow rate of 7.34 mL/min (described in Table 4.32). This was the highest flow rate at which the displacement pump could deliver displacing fluid. Figure 4.147 shows the pressure drop across the whole core, as well as the inlet, outlet, and middle core sections versus pore volumes of crude injected. The oil flood was stopped temporarily after 1.8 pore volumes had been injected before injecting an additional 0.4 pore volumes. The pressure data in Figure 4.147 shows pressure data to follow the same trend for both injection periods, and the pressure was assumed to have reached steady state at the end of the second injection period. The pressure drop across the entire core after reaching an
assumed steady state was 14 psi, and the oil permeability was calculated to be 376md with a relative permeability of 0.623.

**Water Flooding**

The water flood experiment injected a total of 1.12 PV of synthetic formation brine at a constant flow rate of 12.6 mL/hr (described in Table 4.33). The target flow rate was 10.6 mL/hr (i.e. 2 PV/d); however the displacement pump set at this flow rate delivered a slightly higher flow rate of 12.6 mL/hr (i.e. 2.39 PV/d). Figure 4.148 shows the pressure drop across the whole core, inlet, outlet, and middle core sections versus pore volumes of synthetic brine injected. A pressure drop of 0.76 psi was measured across the whole core when the pressure was nearly steady towards the end of the water flood. An end-point brine permeability of 72 md was calculated for the core, which corresponded to an end-point relative brine permeability of 0.119.

**Surfactant/Polymer Flooding**

The waterflood pressure drop at steady state was 0.76 psi per 1 foot core length (i.e. 0.76 psi/ft). Given that the surfactant slug will flow at the same rate as the waterflood, the total pressure drop for the surfactant slug can be approximated with the pressure scaling equation given in the Data Analysis chapter. The following calculation is as such (from equation 3.25):

\[
\Delta P_{\text{slug}} = \frac{\mu_{\text{slug}} R_k^0}{\mu_{\text{wf}}} \Delta P_{\text{wf}}
\]

\[
\Delta P_{\text{slug}} = \frac{10.89*1.5*0.119}{0.733} * 0.76 = 2.01 \text{psi/ft}
\]

A pressure drop around 2 psi/ft is expected for the surfactant slug. Note that this is a rough approximation, as it assumes equal saturations, core properties, and salinity, of which are violated.

During the surfactant/polymer flood, a 0.3 PV surfactant slug was initially injected, and was followed by a 2.3 PV polymer drive (described in Table 4.34).
flow rate was held at a constant 11.2 mL/hr corresponding to 2.12 PV/d (i.e. 2.12 ft/d),
which was close to the target flow rate of 2 PV/d. Figure 4.149 shows the pressure drop
across the whole core, inlet, outlet, and middle core sections versus pore volumes
injected. A maximum pressure drop of 2.5 psi over the 1 foot core length at the 2.12 ft/d
flow rate was measured after about 0.45 PV was injected. Normalizing to a 1 ft/day flow
rate will give a maximum pressure drop of 1.2 psi/ft per 1 ft/day, well within the 2 psi/ft
per 1 ft/day design constraint. Most of the data mentioned is displayed graphically in
Figure 4.150.

**Effluent Analysis**

Effluent was collected in 10mL glass tubes at 30 minute collection intervals per
tube, giving an average of about 5.6 mL fluid per tube. An oil bank recovered from about
0.25 PV to 0.83 PV, after which microemulsion was produced. Surfactant breakthrough
occurred when microemulsion production began after about 0.83 PV of injection.
Measurable surfactant was recovered with the microemulsion from about 0.83 PV to 1.5
PV injection, after which both oil recovery and microemulsion production was negligible.

**Oil Recovery**

Figure 4.152 shows plots of cumulative recovery and oil fraction versus pore
volumes injected. The oil fractions in the effluent during oil bank production (0.25 to
0.83 PV) was around 0.4, and drastically decreases to less than 0.1 during microemulsion
production (0.83 to 1.50 PV). The chemical flood recovered about 97% of the residual
oil, with 80% the residual oil recovered during oil bank production, and 17% recovered
during microemulsion production.

**Surfactant Recovery / Surfactant Adsorption**

Figure 4.153 shows the surfactant concentration (mg/L) present in collected
effluent versus pore volumes injected. The data points are rather scarce, but are still
sufficient to approximate a curve. Surfactant was recovered from 0.83 to 1.5 PV, which
corresponds to the microemulsion production period. The curve surfactant recovery curve in Figure 4.153 approximates a peak just after 1.0 PV, and the curvilinear nature of the recovery curve is illustrative of dispersion effects in the core.

Approximately 380 milligrams of total surfactant was injected with the 0.3PV surfactant slug and about 69 milligrams of total surfactant was recovered. Therefore, about 311 milligrams of surfactant was retained in the rock, which corresponds to about 0.24 milligrams surfactant per gram of rock (for a 1305 gram rock mass).

**Conductivity / Salinity Gradient**

Aqueous phases in several of the effluent samples were used to measure conductivity with an Orion 5-star benchtop conductivity meter. Figure 4.153 plots effluent conductivity versus injected pore volume, and shows the Type I, II, and III regions corresponding to the phase behavior microemulsions that exist at the respective conductivity values. The graph shows effluent collected during 0 to 0.75 PV injected to have a conductivity similar to the synthetic formation brine, indicating that synthetic brine saturating the core from the water flood was recovered initially. This period was also during oil bank production. Effluent conductivity decreases sharply once surfactant breakthrough occurs around 0.83 PV, and Figure 6.153 shows the conductivity curve entering the Type III region during early surfactant/microemulsion production. With further injection, conductivity drops into the Type I region just after 1.0 PV injection, and continues a slow decline towards a conductivity value of the polymer drive. Effluent conductivity at the end of the polymer flood is equal to the polymer drive conductivity, which indicates the effluent to be recovered polymer solution.
Table 4.1. – Phase behavior experiments performed in a general surfactant screening with McElroy crude oil at 30 C.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A5</td>
<td>TDA - 4PO - SO4-</td>
<td>none</td>
<td>0</td>
<td>4</td>
<td>1% - 8%, (1%)</td>
<td>7.40</td>
<td>3.5</td>
</tr>
<tr>
<td>A6</td>
<td>C12 - 3EO - SO4-</td>
<td>none</td>
<td>0</td>
<td>4</td>
<td>1% - 8%, (1%)</td>
<td>only Type I</td>
<td>only Type I</td>
</tr>
<tr>
<td>A7</td>
<td>TDA - 4PO - SO4-</td>
<td>none</td>
<td>0</td>
<td>4</td>
<td>1.5 - 7%, (0.6%)</td>
<td>7.50</td>
<td>3.5</td>
</tr>
<tr>
<td>A8</td>
<td>TDA - 8PO - SO4-</td>
<td>none</td>
<td>0</td>
<td>4</td>
<td>2.5 - 7%, (0.5%)</td>
<td>3.50</td>
<td>6.5</td>
</tr>
<tr>
<td>A9</td>
<td>IOS15-18</td>
<td>none</td>
<td>0</td>
<td>4</td>
<td>2 - 7%, (1%)</td>
<td>&gt;7</td>
<td>2 to 4</td>
</tr>
<tr>
<td>A10</td>
<td>C16,17-7PO-SO4-</td>
<td>IOS-1518</td>
<td>0.5</td>
<td>4</td>
<td>2 - 7%, (1%)</td>
<td>4.3</td>
<td>10</td>
</tr>
<tr>
<td>A11</td>
<td>C14,16 - 8EO - SO4-</td>
<td>none</td>
<td>0</td>
<td>2</td>
<td>1 - 8%, (1%)</td>
<td>gel/viscous</td>
<td>gel/viscous</td>
</tr>
<tr>
<td>A12</td>
<td>C12,13 - 8EO - SO4-</td>
<td>none</td>
<td>0</td>
<td>2</td>
<td>1 - 8%, (1%)</td>
<td>4.60</td>
<td>4.0</td>
</tr>
<tr>
<td>A13</td>
<td>C12,13 - 5EO - SO4-</td>
<td>none</td>
<td>0</td>
<td>2</td>
<td>1 - 8%, (1%)</td>
<td>5.00</td>
<td>5.0</td>
</tr>
<tr>
<td>A18</td>
<td>TDA - 8PO - SO4-</td>
<td>none</td>
<td>0</td>
<td>2</td>
<td>2 - 4.5%, (0.25%)</td>
<td>3.50</td>
<td>7.0</td>
</tr>
<tr>
<td>A50</td>
<td>C16,17-7PO-SO4-</td>
<td>IOS-1518</td>
<td>0</td>
<td>6</td>
<td>1 - 3%, (0.25%)</td>
<td>2</td>
<td>15</td>
</tr>
</tbody>
</table>
Table 4.2. – General structures and names of the surfactants used in the general screening experiments referred to in Table 4.1.

<table>
<thead>
<tr>
<th>Name</th>
<th>Vender</th>
<th>Chemical Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Petrostep S1</td>
<td>Stepan</td>
<td>C_{16-17} - 7PO - SO_4^-</td>
</tr>
<tr>
<td>Petrostep S2</td>
<td>Stepan</td>
<td>IOS_{15-18} (internal olefin sulfonate)</td>
</tr>
<tr>
<td>Petrostep S3</td>
<td>Stepan</td>
<td>IOS_{20-24} (internal olefin sulfonate)</td>
</tr>
<tr>
<td>Exxal 13 TDA-4PO (Isotridecanol)</td>
<td>Harcros Chemical</td>
<td>C_{13} - 4PO - SO_4^-</td>
</tr>
<tr>
<td>Exxal 13 TDA-8PO (Isotridecanol)</td>
<td>Harcros Chemical</td>
<td>C_{13} - 8PO - SO_4^-</td>
</tr>
<tr>
<td>Alfoterra® 45 (Isalchem™ 123)</td>
<td>SASOL</td>
<td>C_{12-13} - 5PO - SO_4^-</td>
</tr>
<tr>
<td>Alfoterra® 58 (Isalchem™ 145)</td>
<td>SASOL</td>
<td>C_{14-15} - 8PO - SO_4^-</td>
</tr>
<tr>
<td>Alfoterra® 68 (Safol® 23)</td>
<td>SASOL</td>
<td>C_{12-13} - 8PO - SO_4^-</td>
</tr>
<tr>
<td>C_{14} Alpha Olefin Sulfonate (AOS)</td>
<td>Stepan</td>
<td>bC_{11-14}-(CH(OH)-CH_2CH_2-SO_3^- (~75%), bC_{11-13}-(CH=CHCH_2-SO_3^- (~25%)</td>
</tr>
<tr>
<td>C_{20-24} Alpha Olefin Sulfonate (AOS)</td>
<td>Stepan</td>
<td>bC_{17-21}-(CH(OH)-CH_2CH_2-SO_3^- (~75%), bC_{17-21}-(CH=CHCH_2-SO_3^- (~25%)</td>
</tr>
<tr>
<td>CS-330 (Sodium dodecyl 3EO sulfate)</td>
<td>Stepan</td>
<td>C_{12} - 3EO - SO_4^-</td>
</tr>
</tbody>
</table>

Table 4.3. – Phase behavior experiments showing C16/17-7PO-SO4- and IOS 15/18 surfactant and co-surfactant tested alone and in combination McElroy crude oil at 30°C.

<table>
<thead>
<tr>
<th>TEST</th>
<th>1° Surfactant</th>
<th>Co-surfactant</th>
<th>Co-solvent</th>
<th>%NaCl</th>
<th>Opt. Salinity S* (wt% NaCl)</th>
<th>Opt. Sol. Ratio, σ (cc/cc)</th>
<th>Eq. Time at S* (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Name</td>
<td>Wt %</td>
<td>Name</td>
<td>Wt %</td>
<td>SBA (wt%)</td>
<td>Scan</td>
<td></td>
</tr>
<tr>
<td>A9</td>
<td>IOS-1518</td>
<td>2</td>
<td>none</td>
<td>0</td>
<td>4</td>
<td>2 - 7%, [1%]</td>
<td>&gt;7</td>
</tr>
<tr>
<td>A10</td>
<td>C16/17 - 7PO - SO4-</td>
<td>1.5</td>
<td>IOS-1518</td>
<td>0.5</td>
<td>4</td>
<td>2 - 7%, [1%]</td>
<td>4.3</td>
</tr>
<tr>
<td>A50</td>
<td>C16/17 - 7PO - SO4-</td>
<td>2</td>
<td>none</td>
<td>0</td>
<td>6</td>
<td>1 - 3%, [0.25%]</td>
<td>2</td>
</tr>
</tbody>
</table>
Table 4.4. – Phase behavior experiments varying the C16/17-7PO-SO4- to IOS 15/18 ratio for using McElroy crude oil at 30 C.

<table>
<thead>
<tr>
<th>TEST</th>
<th>1° Surfactant C16/17 - 7PO-SO4- (wt%)</th>
<th>Co-surfactant IOS-1518 (wt%)</th>
<th>Ratio 1o Surf : co-surf</th>
<th>Co-solvent SBA (wt%)</th>
<th>%NaCl Scan</th>
<th>Opt. Salinity S* (wt% NaCl)</th>
<th>Opt. Sol. Ratio, σ (cc/cc)</th>
<th>Eq. Time at S* (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A10</td>
<td>1.5</td>
<td>0.5</td>
<td>3 : 1</td>
<td>4</td>
<td>2 - 7%, [1%]</td>
<td>4.3</td>
<td>10</td>
<td>7</td>
</tr>
<tr>
<td>A51</td>
<td>1.75</td>
<td>0.25</td>
<td>7 : 1</td>
<td>4</td>
<td>2.5 - 4.5%, [0.5%]</td>
<td>3.05</td>
<td>12.5</td>
<td>11</td>
</tr>
<tr>
<td>A70</td>
<td>2</td>
<td>0.25</td>
<td>8 : 1</td>
<td>6</td>
<td>0.325%</td>
<td>2.65</td>
<td>13.5</td>
<td>5</td>
</tr>
<tr>
<td>A50</td>
<td>2</td>
<td>0</td>
<td>-</td>
<td>6</td>
<td>1 - 3%, [0.25%]</td>
<td>21</td>
<td>5</td>
<td>7</td>
</tr>
</tbody>
</table>

Table 4.5. – Phase behavior experiments screening different co-solvents using McElroy crude oil at 30 C.

<table>
<thead>
<tr>
<th>TEST</th>
<th>1° Surfactant C16/17 - 7PO-SO4- (wt%)</th>
<th>Co-surfactant IOS-1518 (wt%)</th>
<th>Co-solvent Name Wt %</th>
<th>%NaCl Scan</th>
<th>Opt. Salinity S* (wt% NaCl)</th>
<th>Opt. Sol. Ratio, σ (cc/cc)</th>
<th>Eq. Time at S* (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A61</td>
<td>2</td>
<td>0</td>
<td>ethanol 6</td>
<td>1 - 4%, [0.5%]</td>
<td>2.1</td>
<td>4</td>
<td>7</td>
</tr>
<tr>
<td>A60</td>
<td>2</td>
<td>0</td>
<td>1-propanol 6</td>
<td>1 - 4%, [0.5%]</td>
<td>2.5</td>
<td>18</td>
<td>21</td>
</tr>
<tr>
<td>A52</td>
<td>2</td>
<td>0</td>
<td>2-propanol 6</td>
<td>1 - 3.5%, [0.5%]</td>
<td>2.3</td>
<td>6</td>
<td>21</td>
</tr>
<tr>
<td>A67</td>
<td>2</td>
<td>0</td>
<td>1-butanol 6</td>
<td>1 - 4%, [0.5%]</td>
<td>1.25</td>
<td>10</td>
<td>3</td>
</tr>
<tr>
<td>A50</td>
<td>2</td>
<td>0</td>
<td>SBA 6</td>
<td>1 - 3%, [0.25%]</td>
<td>21</td>
<td>15</td>
<td>7</td>
</tr>
<tr>
<td>A65</td>
<td>2</td>
<td>0</td>
<td>tert-butanol 6</td>
<td>1 - 4%, [0.5%]</td>
<td>2.4</td>
<td>12.5</td>
<td>7</td>
</tr>
<tr>
<td>A66</td>
<td>2</td>
<td>0</td>
<td>1-pentanol 6</td>
<td>1 - 3.5%, [0.5%]</td>
<td>gel/viscous</td>
<td>gel/viscous</td>
<td>gel/viscous</td>
</tr>
<tr>
<td>A64</td>
<td>2</td>
<td>0</td>
<td>2-butoxy ethanol 6</td>
<td>1 - 4%, [0.5%]</td>
<td>2.1</td>
<td>9</td>
<td>7</td>
</tr>
</tbody>
</table>
Table 4.6. – Phase behavior experiments using different concentrations of SBA with McElroy crude oil at 30 C.

<table>
<thead>
<tr>
<th>TEST</th>
<th>1° Surfactant</th>
<th>Co-surfactant</th>
<th>Co-solvent</th>
<th>%NaCl</th>
<th>Opt. Salinity S*(wt% NaCl)</th>
<th>Opt. Sol. Ratio, σ (cc/cc)</th>
<th>Eq. Time at S* (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C16/17 - 7PO - SO4- (wt%)</td>
<td>IOS-1518 (wt%)</td>
<td>SBA (wt%)</td>
<td>Scan</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A10</td>
<td>1.5</td>
<td>0.5</td>
<td>4</td>
<td>2 - 7%, [1%]</td>
<td>4.3</td>
<td>10</td>
<td>7</td>
</tr>
<tr>
<td>A19</td>
<td>1.5</td>
<td>0.5</td>
<td>2</td>
<td>3 - 6%, [0.25%]</td>
<td>4.6</td>
<td>11.5</td>
<td>5</td>
</tr>
<tr>
<td>A23b</td>
<td>1.5</td>
<td>0.5</td>
<td>1</td>
<td>4.25 - 6%, [0.25%]</td>
<td>gel/viscous</td>
<td>gel/viscous</td>
<td>gel/viscous</td>
</tr>
</tbody>
</table>

Table 4.7. – Phase behavior experiments with different primary surfactant concentration and the same SBA concentration using McElroy crude oil at 30 C.

<table>
<thead>
<tr>
<th>TEST</th>
<th>1° Surfactant</th>
<th>Co-surfactant</th>
<th>Co-solvent</th>
<th>%NaCl</th>
<th>Opt. Salinity S*(wt% NaCl)</th>
<th>Opt. Sol. Ratio, σ (cc/cc)</th>
<th>Eq. Time at S* (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C16/17 - 7PO - SO4- (wt%)</td>
<td>IOS-1518 (wt%)</td>
<td>SBA (wt%)</td>
<td>Scan</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A50</td>
<td>2</td>
<td>0</td>
<td>6</td>
<td>1 - 3%, [0.25%]</td>
<td>2</td>
<td>15</td>
<td>7</td>
</tr>
<tr>
<td>A80</td>
<td>1</td>
<td>0</td>
<td>6</td>
<td>1 - 3%, [0.25%]</td>
<td>2</td>
<td>12</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 4.8. – Phase behavior experiments showing a decrease in surfactant, co-surfactant, and co-solvent concentrations using McElroy crude oil at 30 C.

<table>
<thead>
<tr>
<th>TEST</th>
<th>1° Surfactant</th>
<th>Co-surfactant</th>
<th>Co-solvent</th>
<th>%NaCl</th>
<th>Opt. Salinity S*(wt% NaCl)</th>
<th>Opt. Sol. Ratio, σ (cc/cc)</th>
<th>Eq. Time at S* (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C16/17 - 7PO - SO4- (wt%)</td>
<td>IOS-1518 (wt%)</td>
<td>SBA (wt%)</td>
<td>Scan</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A19</td>
<td>1.5</td>
<td>0.5</td>
<td>2</td>
<td>3 - 6%, [0.25%]</td>
<td>4.3</td>
<td>11.5</td>
<td>5</td>
</tr>
<tr>
<td>A35</td>
<td>0.75</td>
<td>0.25</td>
<td>1</td>
<td>3.75 - 5.5%, [0.25%]</td>
<td>4.85</td>
<td>8</td>
<td>-</td>
</tr>
<tr>
<td>A29</td>
<td>0.375</td>
<td>0.13</td>
<td>0.5</td>
<td>3.75 - 5.25%, [0.25%]</td>
<td>4.95</td>
<td>8</td>
<td>-</td>
</tr>
<tr>
<td>A32</td>
<td>0.15</td>
<td>0.05</td>
<td>0.2</td>
<td>3.75 - 5.25%, [0.25%]</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 4.9. – Phase behavior experiments showing a varying concentrations of sodium hydroxide as the alkali agent, with McElroy crude oil at 30 C.

<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A41</td>
<td>1.5</td>
<td>0.5</td>
<td>2</td>
<td>NaOH</td>
<td>0.125</td>
<td>12.34</td>
<td>3.5 - 5.5%, (0.25%)</td>
<td>4.35</td>
<td>14</td>
</tr>
<tr>
<td>A42</td>
<td>1.5</td>
<td>0.5</td>
<td>2</td>
<td>NaOH</td>
<td>0.015625</td>
<td>10.62</td>
<td>3.5 - 5.5%, (0.25%)</td>
<td>4.5</td>
<td>14</td>
</tr>
<tr>
<td>A47</td>
<td>1.5</td>
<td>0.5</td>
<td>2</td>
<td>NaOH</td>
<td>0.004</td>
<td>9.07</td>
<td>3.75 - 5.0%, (0.25%)</td>
<td>4.5</td>
<td>10</td>
</tr>
<tr>
<td>A46</td>
<td>1.5</td>
<td>0.5</td>
<td>2</td>
<td>NaOH</td>
<td>0.0004</td>
<td>8.56</td>
<td>3.5 - 5.0%, (0.25%)</td>
<td>4.5</td>
<td>10</td>
</tr>
<tr>
<td>A44</td>
<td>1.5</td>
<td>0.5</td>
<td>2</td>
<td>NaOH</td>
<td>0.00004</td>
<td>8.47</td>
<td>3.5 - 5.5%, (0.25%)</td>
<td>4.65</td>
<td>11</td>
</tr>
<tr>
<td>A19</td>
<td>1.5</td>
<td>0.5</td>
<td>2</td>
<td>none</td>
<td>0</td>
<td>8.57</td>
<td>3 - 6%, (0.25%)</td>
<td>4.3</td>
<td>11.5</td>
</tr>
</tbody>
</table>

Table 4.10. – Phase behavior experiments showing sodium carbonate and sodium metaborate used as alkali salts, with sodium hydroxide shown for comparison. All tests use McElroy crude oil at 30 C.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A19</td>
<td>1.5</td>
<td>0.5</td>
<td>2</td>
<td>None</td>
<td>0</td>
<td>8.57</td>
<td>3 - 6%, (0.25%)</td>
<td>4.3</td>
<td>11.5</td>
<td>5</td>
</tr>
<tr>
<td>A21</td>
<td>1.5</td>
<td>0.5</td>
<td>2</td>
<td>Na2CO3</td>
<td>1</td>
<td>10.28</td>
<td>3.25 - 4.75%, (0.25%)</td>
<td>3.77</td>
<td>15</td>
<td>7</td>
</tr>
<tr>
<td>A22</td>
<td>1.5</td>
<td>0.5</td>
<td>2</td>
<td>NaMetaborate</td>
<td>1</td>
<td>9.01</td>
<td>3.25 - 4.75%, (0.25%)</td>
<td>4.25</td>
<td>12</td>
<td>15</td>
</tr>
<tr>
<td>A42</td>
<td>1.5</td>
<td>0.5</td>
<td>2</td>
<td>NaOH</td>
<td>0.015625</td>
<td>10.62</td>
<td>3.5 - 5.5%, (0.25%)</td>
<td>4.5</td>
<td>14</td>
<td>5</td>
</tr>
</tbody>
</table>
Table 4.11. – Phase behavior experiments showing a decrease in surfactant, co-surfactant, and co-solvent concentrations with the addition of sodium carbonate. All tests use McElroy crude oil at 30 °C.

<table>
<thead>
<tr>
<th>TEST</th>
<th>1° Surfactant</th>
<th>Co-surfactant</th>
<th>Co-solvent</th>
<th>Alkali</th>
<th>pH</th>
<th>%NaCl</th>
<th>Opt. Salinity S* (wt% NaCl)</th>
<th>Opt. Sol. Ratio, σ (cc/cc)</th>
<th>Eq. Time at S* (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C16/17 - 7PO - SO4- (wt%)</td>
<td>IOS-1518 (wt%)</td>
<td>SBA (wt%)</td>
<td>Name</td>
<td>Wt %</td>
<td>Scan</td>
<td>3.25 - 4.75%, [0.25%]</td>
<td>3.77</td>
<td>15</td>
<td>7</td>
</tr>
<tr>
<td>A21</td>
<td>1.5</td>
<td>0.5</td>
<td>2</td>
<td>Na2CO3</td>
<td>1</td>
<td>10.28</td>
<td>3.25 - 4.75%, [0.25%]</td>
<td>3.77</td>
<td>15</td>
</tr>
<tr>
<td>A36b</td>
<td>0.75</td>
<td>0.25</td>
<td>1</td>
<td>Na2CO3</td>
<td>1</td>
<td>15 - 5%, [0.5%]</td>
<td>4</td>
<td>18.5</td>
<td>-</td>
</tr>
<tr>
<td>A33</td>
<td>0.15</td>
<td>0.05</td>
<td>0.2</td>
<td>Na2CO3</td>
<td>1</td>
<td>3.4 - 4.5%, [0.25%]</td>
<td>3.6</td>
<td>12</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4.12. – Phase behavior experiments showing variations in sec-butanol concentration for no alkali, sodium carbonate, and sodium metaborate scenarios. All tests use McElroy crude oil at 30 °C.

<table>
<thead>
<tr>
<th>TEST</th>
<th>1° Surfactant</th>
<th>Co-surfactant</th>
<th>Co-solvent</th>
<th>Alkali</th>
<th>pH</th>
<th>%NaCl</th>
<th>Opt. Salinity S* (wt% NaCl)</th>
<th>Opt. Sol. Ratio, σ (cc/cc)</th>
<th>Eq. Time at S* (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C16/17 - 7PO - SO4- (wt%)</td>
<td>IOS-1518 (wt%)</td>
<td>SBA (wt%)</td>
<td>Name</td>
<td>Wt %</td>
<td>Scan</td>
<td>3.25 - 4.75%, [0.25%]</td>
<td>3.77</td>
<td>15</td>
<td>7</td>
</tr>
<tr>
<td>A10</td>
<td>1.5</td>
<td>0.5</td>
<td>4</td>
<td>none</td>
<td>0</td>
<td>8.64</td>
<td>2% - 7%, [1%]</td>
<td>4.3</td>
<td>10</td>
</tr>
<tr>
<td>A16</td>
<td>1.5</td>
<td>0.5</td>
<td>4</td>
<td>Na2CO3</td>
<td>1</td>
<td>10.35</td>
<td>2.25% - 4.5%, [0.25%]</td>
<td>3.6</td>
<td>8.5</td>
</tr>
<tr>
<td>A17</td>
<td>1.5</td>
<td>0.5</td>
<td>4</td>
<td>NaN3</td>
<td>1</td>
<td>9.07</td>
<td>2.25% - 4.5%, [0.25%]</td>
<td>3.9</td>
<td>10</td>
</tr>
<tr>
<td>A19</td>
<td>1.5</td>
<td>0.5</td>
<td>2</td>
<td>none</td>
<td>0</td>
<td>8.57</td>
<td>3% - 6%, [0.25%]</td>
<td>4.3</td>
<td>11.5</td>
</tr>
<tr>
<td>A21</td>
<td>1.5</td>
<td>0.5</td>
<td>2</td>
<td>Na2CO3</td>
<td>1</td>
<td>10.28</td>
<td>3.25% - 4.75%, [0.25%]</td>
<td>3.77</td>
<td>15</td>
</tr>
<tr>
<td>A22</td>
<td>1.5</td>
<td>0.5</td>
<td>2</td>
<td>NaN3</td>
<td>1</td>
<td>9.01</td>
<td>3.25% - 4.75%, [0.25%]</td>
<td>4.25</td>
<td>12</td>
</tr>
<tr>
<td>A23b</td>
<td>1.5</td>
<td>0.5</td>
<td>1</td>
<td>none</td>
<td>0</td>
<td>4.25</td>
<td>4.25% - 6%, [0.25%]</td>
<td>gel/viscous</td>
<td>gel/viscous</td>
</tr>
<tr>
<td>A24</td>
<td>1.5</td>
<td>0.5</td>
<td>1</td>
<td>Na2CO3</td>
<td>1</td>
<td>4.05</td>
<td>4.25% - 6%, [0.25%]</td>
<td>4.25</td>
<td>12</td>
</tr>
<tr>
<td>A25</td>
<td>1.5</td>
<td>0.5</td>
<td>1</td>
<td>NaN3</td>
<td>1</td>
<td>4.25</td>
<td>4.25% - 6%, [0.25%]</td>
<td>4.25</td>
<td>12</td>
</tr>
</tbody>
</table>
Table 4.13. — Phase behavior experiments comparing McElroy and Yates crude oils. All experiments were performed at 22 C.

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</thead>
<tbody>
<tr>
<td></td>
<td>C16/17-7PO-SO4- (wt%)</td>
<td>IOS-1518 (wt%)</td>
<td>SBA (wt%)</td>
<td>Name</td>
<td>Wt %</td>
<td>Scan</td>
<td>°C</td>
<td>S* (wt% NaCl)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>McElroy</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C1</td>
<td>1.50</td>
<td>0.5</td>
<td>2</td>
<td>none</td>
<td>0</td>
<td>8.57</td>
<td>22</td>
<td>3.0% - 6.0%, [0.25%]</td>
<td>5</td>
<td>13</td>
</tr>
<tr>
<td>C2</td>
<td>1.50</td>
<td>0.5</td>
<td>2</td>
<td>Na2CO3</td>
<td>1</td>
<td>10.28</td>
<td>22</td>
<td>3.25% - 4.75%, [0.25%]</td>
<td>4.25</td>
<td>18</td>
</tr>
<tr>
<td>YA6</td>
<td>1.50</td>
<td>0.50</td>
<td>2</td>
<td>Na2CO3</td>
<td>0</td>
<td>8.57</td>
<td>22</td>
<td>2.5% - 6.5%, [0.5%]</td>
<td>5.60</td>
<td>14.0</td>
</tr>
<tr>
<td>YA3</td>
<td>1.50</td>
<td>0.50</td>
<td>2</td>
<td>Na2CO3</td>
<td>1</td>
<td>10.28</td>
<td>22</td>
<td>2% - 6%, [0.5%]</td>
<td>4.85</td>
<td>17.0</td>
</tr>
</tbody>
</table>

Table 4.14. — Phase behavior experiments B4, B5, and B6 used for microemulsion characterization at 30 C. Experiments C1, C2, and C3 are similar, but are performed at 22 C. All tests contain McElroy crude oil.

<table>
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</thead>
<tbody>
<tr>
<td></td>
<td>C16/17-7PO-SO4- (wt%)</td>
<td>IOS-1518 (wt%)</td>
<td>SBA (wt%)</td>
<td>Name</td>
<td>Wt %</td>
<td>Scan</td>
<td>°C</td>
<td>S* (wt% NaCl)</td>
<td></td>
</tr>
<tr>
<td>30 C</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>B4</td>
<td>1.5</td>
<td>0.5</td>
<td>2</td>
<td>none</td>
<td>0</td>
<td>4.1 - 5.0%, [0.1%]</td>
<td>30</td>
<td>4.7</td>
<td>17.5</td>
</tr>
<tr>
<td>B5</td>
<td>1.5</td>
<td>0.5</td>
<td>2</td>
<td>Na2CO3</td>
<td>1</td>
<td>3.3 - 4.2%, [0.1%]</td>
<td>30</td>
<td>3.9</td>
<td>18</td>
</tr>
<tr>
<td>B6</td>
<td>1.5</td>
<td>0.5</td>
<td>2</td>
<td>NaMetaborate</td>
<td>1</td>
<td>3.8 - 4.7%, [0.1%]</td>
<td>30</td>
<td>4.4</td>
<td>16</td>
</tr>
<tr>
<td>22 C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C1</td>
<td>1.5</td>
<td>0.5</td>
<td>2</td>
<td>none</td>
<td>0</td>
<td>3 - 6%, [0.25%]</td>
<td>22</td>
<td>5</td>
<td>13</td>
</tr>
<tr>
<td>C2</td>
<td>1.5</td>
<td>0.5</td>
<td>2</td>
<td>Na2CO3</td>
<td>1</td>
<td>3.25 - 4.75%, [0.25%]</td>
<td>22</td>
<td>4.25</td>
<td>18</td>
</tr>
<tr>
<td>C3</td>
<td>1.5</td>
<td>0.5</td>
<td>2</td>
<td>NaMetaborate</td>
<td>1</td>
<td>3.5 - 5.0%, [0.25%]</td>
<td>22</td>
<td>5.1</td>
<td>12.5</td>
</tr>
</tbody>
</table>
Table 4.15. – Phase behavior experiments showing coarse and fine resolution salinity scans using Crude D at 52°C. Surfactants and co-surfactants were similar to those used for McElroy crude oil.

<table>
<thead>
<tr>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Name Wt %</td>
<td>Name Wt %</td>
<td>Name Wt %</td>
<td>Scan</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>D</td>
<td>C16/17-7PO-SO4- 1.5</td>
<td>IOS-1518 0.5</td>
<td>SBA 2.0</td>
<td>2-8%, [1.5%]</td>
<td>3.1</td>
<td>12</td>
<td>NA</td>
</tr>
<tr>
<td>2</td>
<td>D</td>
<td>C16/17-7PO-SO4- 1.0</td>
<td>IOS-1518 1.0</td>
<td>SBA 0.5</td>
<td>3-9%, [1.5%]</td>
<td>6.5</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>3</td>
<td>D</td>
<td>C16/17-7PO-SO4- 1.5</td>
<td>IOS-2024 0.5</td>
<td>SBA 2.0</td>
<td>2-8%, [1.5%]</td>
<td>gel/viscous</td>
<td>gel/viscous</td>
<td>gel/viscous</td>
</tr>
<tr>
<td>4</td>
<td>D</td>
<td>IOS-2024 2.0</td>
<td>none 0</td>
<td>SBA 0.5</td>
<td>3.5-9.0%, [1.5%]</td>
<td>gel/viscous</td>
<td>gel/viscous</td>
<td>gel/viscous</td>
</tr>
<tr>
<td>5</td>
<td>D</td>
<td>IOS-1518 2.0</td>
<td>none 0</td>
<td>SBA 0.5</td>
<td>3.5-9.0%, [1.5%]</td>
<td>gel/viscous</td>
<td>gel/viscous</td>
<td>gel/viscous</td>
</tr>
<tr>
<td>6</td>
<td>D</td>
<td>C16/17-7PO-SO4- 1.5</td>
<td>IOS-1518 0.5</td>
<td>SBA 2.0</td>
<td>2.3-4%, [0.25%]</td>
<td>3.25</td>
<td>15</td>
<td>75</td>
</tr>
<tr>
<td>7</td>
<td>D</td>
<td>C16/17-7PO-SO4- 1.0</td>
<td>IOS-1518 1.0</td>
<td>SBA 0.5</td>
<td>5.25-6.75%, [0.25%]</td>
<td>6.6</td>
<td>5</td>
<td>11</td>
</tr>
<tr>
<td>8</td>
<td>D</td>
<td>C16/17-7PO-SO4- 1.5</td>
<td>IOS-2024 0.5</td>
<td>SBA 2.0</td>
<td>1.25-2.75%, [0.25%]</td>
<td>gel/viscous</td>
<td>gel/viscous</td>
<td>gel/viscous</td>
</tr>
<tr>
<td>9</td>
<td>D</td>
<td>IOS-2024 2.0</td>
<td>none 0</td>
<td>SBA 0.5</td>
<td>1.5-4%, [0.5%]</td>
<td>gel/viscous</td>
<td>gel/viscous</td>
<td>gel/viscous</td>
</tr>
</tbody>
</table>

Table 4.16. – Phase behavior experiments showing a variation in the surfactant/co-surfactant ratio used with Crude D at 52°C.

<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C16/17 - 7PO-SO4- (wt%)</td>
<td>IOS-1518 (wt%)</td>
<td>1st Surf : co-surf</td>
<td>SBA (wt%)</td>
<td>Scan</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>D</td>
<td>1.0</td>
<td>1.0</td>
<td>1 : 1</td>
<td>1.0</td>
<td>6.0 - 7.5%, [0.20%]</td>
<td>6.6</td>
<td>12.5</td>
<td>21</td>
</tr>
<tr>
<td>13</td>
<td>D</td>
<td>1.25</td>
<td>0.75</td>
<td>5 : 3</td>
<td>1.0</td>
<td>3.5 - 6.5%, [0.25%]</td>
<td>5</td>
<td>15</td>
<td>5</td>
</tr>
<tr>
<td>12</td>
<td>D</td>
<td>1.5</td>
<td>0.5</td>
<td>3 : 1</td>
<td>1.0</td>
<td>2.75 - 4.25%, [0.25%]</td>
<td>3.4</td>
<td>13</td>
<td>NA</td>
</tr>
<tr>
<td>19</td>
<td>D</td>
<td>1.75</td>
<td>0.25</td>
<td>7 : 1</td>
<td>2.0</td>
<td>2 - 3.5%, [0.25%]</td>
<td>2</td>
<td>17</td>
<td>21</td>
</tr>
<tr>
<td>11</td>
<td>D</td>
<td>2.0</td>
<td>0</td>
<td>-</td>
<td>2.0</td>
<td>0.5 - 3.5%, [0.25%]</td>
<td>gel/viscous</td>
<td>gel/viscous</td>
<td>gel/viscous</td>
</tr>
</tbody>
</table>
Table 4.17. – Phase behavior experiments showing a variation in SBA concentration for several different surfactant/co-surfactant ratios. Crude D was used, and the temperature was 52 C.

<table>
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<tbody>
<tr>
<td>15</td>
<td>D</td>
<td>1.0</td>
<td>1.0</td>
<td>1 : 1</td>
<td>0.5</td>
<td>6.9</td>
<td>6.25 - 7.5%, [0.25%]</td>
<td>16</td>
<td>21</td>
</tr>
<tr>
<td>18</td>
<td>D</td>
<td>1.25</td>
<td>0.75</td>
<td>5 : 3</td>
<td>0.5</td>
<td>5</td>
<td>3.5 - 6.5%, [0.5%]</td>
<td>18</td>
<td>21</td>
</tr>
<tr>
<td>16</td>
<td>D</td>
<td>1.0</td>
<td>1.0</td>
<td>1 : 1</td>
<td>1.0</td>
<td>6.6</td>
<td>6.0 - 7.5%, [0.25%]</td>
<td>12.5</td>
<td>21</td>
</tr>
<tr>
<td>13</td>
<td>D</td>
<td>1.25</td>
<td>0.75</td>
<td>5 : 3</td>
<td>1.0</td>
<td>5</td>
<td>3.5 - 6.5%, [0.5%]</td>
<td>15</td>
<td>5</td>
</tr>
<tr>
<td>12</td>
<td>D</td>
<td>1.5</td>
<td>0.5</td>
<td>3 : 1</td>
<td>1.5</td>
<td>3.4</td>
<td>2.75 - 4.25%, [0.25%]</td>
<td>13</td>
<td>NA</td>
</tr>
<tr>
<td>14</td>
<td>D</td>
<td>1.5</td>
<td>0.5</td>
<td>3 : 1</td>
<td>3.5 - 6.5%</td>
<td>4.50</td>
<td>13.0</td>
<td>5</td>
<td>21</td>
</tr>
<tr>
<td>17</td>
<td>D</td>
<td>1.25</td>
<td>0.75</td>
<td>5 : 3</td>
<td>2.0</td>
<td>2</td>
<td>2 - 3.5%, [0.25%]</td>
<td>17</td>
<td>21</td>
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</table>

Table 4.18. – Phase behavior experiments showing a variation in total surfactant concentration for several different surfactant/co-surfactant ratios. Crude D was used, and the temperature was 52 C.

<table>
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</thead>
<tbody>
<tr>
<td>14</td>
<td>D</td>
<td>1.5</td>
<td>0.5</td>
<td>3 : 1</td>
<td>1.5</td>
<td>3.25</td>
<td>2.75 - 4.25%, [0.25%]</td>
<td>16</td>
<td>21</td>
</tr>
<tr>
<td>15</td>
<td>D</td>
<td>1.0</td>
<td>1.0</td>
<td>1 : 1</td>
<td>0.5</td>
<td>6.9</td>
<td>6.25 - 7.5%, [0.25%]</td>
<td>16</td>
<td>21</td>
</tr>
<tr>
<td>18</td>
<td>D</td>
<td>1.25</td>
<td>0.75</td>
<td>5 : 3</td>
<td>0.5</td>
<td>5</td>
<td>3.5 - 6.5%, [0.5%]</td>
<td>18</td>
<td>21</td>
</tr>
<tr>
<td>26</td>
<td>D</td>
<td>0.75</td>
<td>0.25</td>
<td>3 : 1</td>
<td>0.75</td>
<td>3.25</td>
<td>2.5 - 4.0%, [0.25%]</td>
<td>15</td>
<td>3</td>
</tr>
<tr>
<td>27</td>
<td>D</td>
<td>0.50</td>
<td>0.50</td>
<td>1 : 1</td>
<td>0.25</td>
<td>6.7</td>
<td>6 - 7.5%, [0.25%]</td>
<td>16</td>
<td>15</td>
</tr>
<tr>
<td>28</td>
<td>D</td>
<td>0.625</td>
<td>0.375</td>
<td>5 : 3</td>
<td>0.25</td>
<td>4.9</td>
<td>4.25 - 5.75%, [0.25%]</td>
<td>18</td>
<td>NA</td>
</tr>
<tr>
<td>29</td>
<td>D</td>
<td>0.375</td>
<td>0.125</td>
<td>3 : 1</td>
<td>0.375</td>
<td>poor results</td>
<td>poor results</td>
<td>poor results</td>
<td>3</td>
</tr>
<tr>
<td>30</td>
<td>D</td>
<td>0.25</td>
<td>0.25</td>
<td>1 : 1</td>
<td>0.13</td>
<td>6.1</td>
<td>6 - 7.5%, [0.25%]</td>
<td>18</td>
<td>3</td>
</tr>
<tr>
<td>31</td>
<td>D</td>
<td>0.3125</td>
<td>0.1875</td>
<td>5 : 3</td>
<td>0.1250</td>
<td>4.4</td>
<td>4.25 - 5.75%, [0.25%]</td>
<td>15</td>
<td>15</td>
</tr>
</tbody>
</table>

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Table 4.19. – Phase behavior experiments showing a variation in Na2CO3 concentration for several different surfactant/co-surfactant ratios using Crude D at 52 C. Na2CO3 concentrations include 0, 0.5, and 1 wt%, as well as using only Na2CO3 as the electrolyte.

<table>
<thead>
<tr>
<th>TEST</th>
<th>OIL</th>
<th>1st Surfactant C16/17 - 7PO - SO4- (wt%)</th>
<th>Co-surfactant IOS-1518 (wt%)</th>
<th>Ratio 1o Surf: co-surf</th>
<th>Co-solvent SBA (wt%)</th>
<th>Alkali Na2CO3 (wt%)</th>
<th>Scan</th>
<th>Opt. Salinity S* (wt% NaCl)</th>
<th>Opt. Sol. Ratio, σ (cc/cc)</th>
<th>Eq. Time at S* (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>D</td>
<td>1.5</td>
<td>0.5</td>
<td>3 : 1</td>
<td>1.5</td>
<td>0</td>
<td>0.25</td>
<td>2.75 - 3.25%, [0.25%]</td>
<td>3.25</td>
<td>16.5</td>
</tr>
<tr>
<td>15</td>
<td>D</td>
<td>1.0</td>
<td>1.0</td>
<td>1 : 1</td>
<td>0.5</td>
<td>0</td>
<td>0.5</td>
<td>6.25 - 7.5%, [0.25%]</td>
<td>6.9</td>
<td>16</td>
</tr>
<tr>
<td>18</td>
<td>D</td>
<td>1.25</td>
<td>0.75</td>
<td>5 : 3</td>
<td>0.5</td>
<td>0</td>
<td>0.5</td>
<td>9.25 - 10.5%, [0.5%]</td>
<td>5</td>
<td>18</td>
</tr>
<tr>
<td>20</td>
<td>D</td>
<td>1.5</td>
<td>0.5</td>
<td>3 : 1</td>
<td>1.5</td>
<td>0.5</td>
<td>0.5</td>
<td>5.75 - 7.25%, [0.25%]</td>
<td>6.25</td>
<td>16</td>
</tr>
<tr>
<td>21</td>
<td>D</td>
<td>1.0</td>
<td>1.0</td>
<td>1 : 1</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>3 - 4.5%, [0.25%]</td>
<td>4.75</td>
<td>16</td>
</tr>
<tr>
<td>22</td>
<td>D</td>
<td>1.25</td>
<td>0.75</td>
<td>5 : 3</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>4.25 - 5.25%, [0.25%]</td>
<td>4.75</td>
<td>16</td>
</tr>
<tr>
<td>23</td>
<td>D</td>
<td>1.5</td>
<td>0.5</td>
<td>3 : 1</td>
<td>1.5</td>
<td>1</td>
<td>1.75</td>
<td>3.75 - 4.75%, [0.25%]</td>
<td>2.5</td>
<td>17</td>
</tr>
<tr>
<td>24</td>
<td>D</td>
<td>1.0</td>
<td>1.0</td>
<td>1 : 1</td>
<td>0.5</td>
<td>1</td>
<td>5.25</td>
<td>6.75 - 8.75%, [0.25%]</td>
<td>6.00</td>
<td>16</td>
</tr>
<tr>
<td>25</td>
<td>D</td>
<td>1.25</td>
<td>0.75</td>
<td>5 : 3</td>
<td>0.5</td>
<td>1</td>
<td>4.125</td>
<td>4.75 - 5.75%, [0.25%]</td>
<td>4.375</td>
<td>20</td>
</tr>
<tr>
<td>32</td>
<td>D</td>
<td>1.5</td>
<td>0.5</td>
<td>3 : 1</td>
<td>1.5</td>
<td>2.75</td>
<td>6.5% - 7.5%, [0.75%]</td>
<td>none</td>
<td>4.7 (Na2CO3)</td>
<td>16</td>
</tr>
<tr>
<td>33</td>
<td>D</td>
<td>1.0</td>
<td>1.0</td>
<td>1 : 1</td>
<td>0.5</td>
<td>6.25</td>
<td>10% - 12%, [0.75%]</td>
<td>none</td>
<td>9.2 (Na2CO3)</td>
<td>15</td>
</tr>
<tr>
<td>34</td>
<td>D</td>
<td>1.25</td>
<td>0.75</td>
<td>5 : 3</td>
<td>0.5</td>
<td>4.5 - 6.25%, [0.75%]</td>
<td>none</td>
<td>6.8 (Na2CO3)</td>
<td>15</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 4.20. – Phase behavior experiments showing three different formulation options for a chemical flood experiment based on the design methodology of previous phase behavior experiments. Crude D was used at 52 C.

<table>
<thead>
<tr>
<th>TEST</th>
<th>OIL</th>
<th>1st Surfactant C16/17 - 7PO - SO4- (wt%)</th>
<th>Co-surfactant IOS-1518 (wt%)</th>
<th>Ratio 1st Surf: co-surf</th>
<th>Co-solvent SBA (wt%)</th>
<th>Alkali Na2CO3 (wt%)</th>
<th>Scan</th>
<th>Opt. Salinity S* (wt% NaCl)</th>
<th>Opt. Sol. Ratio, σ (cc/cc)</th>
<th>Eq. Time at S* (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>28</td>
<td>D</td>
<td>0.625</td>
<td>0.375</td>
<td>5 : 3</td>
<td>0.25</td>
<td>0</td>
<td>4.25</td>
<td>4.25 - 5.75%, [0.25%]</td>
<td>4.9</td>
<td>18</td>
</tr>
<tr>
<td>41</td>
<td>D</td>
<td>0.625</td>
<td>0.375</td>
<td>5 : 3</td>
<td>0.25</td>
<td>1</td>
<td>4.125</td>
<td>4.125 - 5.125%, [0.125%]</td>
<td>4.25</td>
<td>24</td>
</tr>
<tr>
<td>42</td>
<td>D</td>
<td>0.625</td>
<td>0.375</td>
<td>5 : 3</td>
<td>0</td>
<td>1</td>
<td>4.125</td>
<td>4.125 - 5.25%, [0.125%]</td>
<td>4.42</td>
<td>23</td>
</tr>
</tbody>
</table>
Table 4.21. – Aqueous stability experiments of two different formula options having good phase behavior performance with Crude D. Aqueous stability experiments were performed at room temperature, or 22 C. Note that 2000 ppm Flopaam 3330-S polymer was added to each formulation.

<table>
<thead>
<tr>
<th>TEST</th>
<th>OIL</th>
<th>1st Surfactant C16/17 -7PO- SO4- (wt%)</th>
<th>Co-surfactant IOS-1518 (wt%)</th>
<th>Ratio 1o Surf: co-surf 5 : 3</th>
<th>Co-solvent SBA (wt%)</th>
<th>Alkali Na2CO3 (wt%)</th>
<th>%NaCl</th>
<th>Temp Scan</th>
<th>NaCl Scan</th>
<th>Opt. Salinity S* (wt% NaCl)</th>
<th>wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>28</td>
<td>D</td>
<td>0.625</td>
<td>0.375</td>
<td>5 : 3</td>
<td>0.25</td>
<td>0</td>
<td>4.25%</td>
<td>0.25 21</td>
<td>clear</td>
<td>clear clear clear clear clear cloudy cloudy cloudy</td>
<td></td>
</tr>
<tr>
<td>42</td>
<td>D</td>
<td>0.625</td>
<td>0.375</td>
<td>5 : 3</td>
<td>0</td>
<td>1</td>
<td>4.125%</td>
<td>0.125% 21</td>
<td>clear</td>
<td>clear clear clear clear cloudy cloudy cloudy cloudy</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.22. – Dimensions of the Berea Sandstone core used in the chemical flood experiment with Crude D.

<table>
<thead>
<tr>
<th>Pore Volume PV</th>
<th>Porosity φ</th>
<th>Total length L</th>
<th>Diameter D</th>
</tr>
</thead>
<tbody>
<tr>
<td>126.7 mL</td>
<td>0.204</td>
<td>30.4 cm</td>
<td>5.1 cm</td>
</tr>
</tbody>
</table>

Table 4.23. – Air permeability measurements for the unepoxied and epoxied Berea Sandstone core used in the chemical flood experiment with Crude D.

<table>
<thead>
<tr>
<th>Air permeability (unepoxied core)</th>
<th>inlet</th>
<th>outlet</th>
<th>middle</th>
<th>867 md</th>
<th>777 md</th>
<th>800 md</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air permeability (epoxied core)</td>
<td>inlet</td>
<td>859 md</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 4.24. – Permeability and relative permeability values of the Berea Sandstone core used in the chemical flood experiment with Crude D.

<table>
<thead>
<tr>
<th>Permeability</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absolute brine permeability</td>
<td>$k_{br}$</td>
<td>603 md</td>
</tr>
<tr>
<td>End-point oil permeability</td>
<td>$k_{o^o}$</td>
<td>376 md</td>
</tr>
<tr>
<td>End-point brine permeability</td>
<td>$k_{w^o}$</td>
<td>72 md</td>
</tr>
<tr>
<td>End-point relative oil permeability</td>
<td>$k_{ro^o}$</td>
<td>0.623</td>
</tr>
<tr>
<td>End-point relative brine permeability</td>
<td>$k_{rw^o}$</td>
<td>0.119</td>
</tr>
<tr>
<td>Polymer permeability</td>
<td>$k_p$</td>
<td>424 md</td>
</tr>
</tbody>
</table>

Table 4.25. – Saturation data calculated for the Berea Sandstone core used in the chemical flood experiment with Crude D.

<table>
<thead>
<tr>
<th>Saturation</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial water saturation</td>
<td>$S_w$</td>
<td>0.706</td>
</tr>
<tr>
<td>Residual water saturation</td>
<td>$S_{wr}$</td>
<td>0.39</td>
</tr>
<tr>
<td>Initial oil saturation</td>
<td>$S_o$</td>
<td>0.61</td>
</tr>
<tr>
<td>Residual oil saturation</td>
<td>$S_{or}$</td>
<td>0.294</td>
</tr>
</tbody>
</table>

Table 4.26. – Ion concentrations in the synthetic formation brine.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na+</td>
<td>51288</td>
</tr>
<tr>
<td>Ca++</td>
<td>6648</td>
</tr>
<tr>
<td>Mg++</td>
<td>2019</td>
</tr>
<tr>
<td>Cl-</td>
<td>96570</td>
</tr>
<tr>
<td><strong>TDS</strong></td>
<td><strong>156525</strong></td>
</tr>
</tbody>
</table>
Table 4.27. – Viscosity of fluids used in the chemical flood. All viscosity values were measured at 52 C, and measured values are at 11 sec\(^{-1}\) shear rate. Further data is in Figures 6.142 to 6.145.

<table>
<thead>
<tr>
<th>Fluid Type</th>
<th>μ</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brine viscosity</td>
<td>(\mu_w)</td>
<td>0.73 cp</td>
</tr>
<tr>
<td>Crude oil viscosity</td>
<td>(\mu_o)</td>
<td>1.96 cp</td>
</tr>
<tr>
<td>Surfactant slug viscosity</td>
<td>(\mu_s)</td>
<td>10.9 cp</td>
</tr>
<tr>
<td>Polymer drive viscosity</td>
<td>(\mu_p)</td>
<td>8.7 cp</td>
</tr>
</tbody>
</table>

Table 4.28. – Density of the synthetic formation brine and crude oil (Crude D) used in the chemical flood.

<table>
<thead>
<tr>
<th>Fluid Type</th>
<th>ρ</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brine density</td>
<td>(\rho_w)</td>
<td>1.098 g/cc</td>
</tr>
<tr>
<td>Crude oil density</td>
<td>(\rho_o)</td>
<td>0.8 g/cc</td>
</tr>
</tbody>
</table>

Table 4.29. – Chemical concentrations used in the surfactant slug for the chemical flood experiment.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>C, 16/17-7PO-SO4-</td>
<td>0.625 wt%</td>
</tr>
<tr>
<td>IOS 15-18</td>
<td>0.375 wt%</td>
</tr>
<tr>
<td>sec-butanol</td>
<td>0.25 wt%</td>
</tr>
<tr>
<td>Flopaam 3330S</td>
<td>2000 ppm</td>
</tr>
<tr>
<td>NaCl (optimal salinity)</td>
<td>4.9 wt%</td>
</tr>
</tbody>
</table>
Table 4.30. – Chemical concentrations used in the polymer drive solution for the chemical flood.

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Flopaam 3330S</td>
<td>2000 ppm</td>
<td></td>
</tr>
<tr>
<td>NaCl</td>
<td>3 wt%</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.31. – Flow rate, average pressure drop, and injection volume data for the brine flood experiment.

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate</td>
<td>7.23 mL/min</td>
<td></td>
</tr>
<tr>
<td>Pressure drop (average)</td>
<td>3.1 psi</td>
<td></td>
</tr>
<tr>
<td>Brine volume injected</td>
<td>2.5 PV</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.32. – Flow rate, average pressure drop, and injection volume data for the oil flood experiment.

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate</td>
<td>7.34 mL/min</td>
<td></td>
</tr>
<tr>
<td>Pressure drop (average)</td>
<td>14 psi</td>
<td></td>
</tr>
<tr>
<td>Oil volume injected</td>
<td>2.2 PV</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.33. – Flow rate, average pressure drop, and injection volume data for the water flood experiment.

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate</td>
<td>12.6 mL/hr</td>
<td></td>
</tr>
<tr>
<td>Pressure drop (average)</td>
<td>0.76 psi</td>
<td></td>
</tr>
<tr>
<td>Water volume injected</td>
<td>1.12 PV</td>
<td></td>
</tr>
</tbody>
</table>
Table 4.34. – Flow rate, average pressure drop, maximum pressure drop, and injection volume data for the chemical flood experiment.

<table>
<thead>
<tr>
<th>Flow rate</th>
<th>11.2 mL/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure drop (average)</td>
<td>1.6 psi</td>
</tr>
<tr>
<td>Max pressure drop</td>
<td>2.5 psi</td>
</tr>
<tr>
<td>Surfactant slug volume</td>
<td>0.3 PV</td>
</tr>
<tr>
<td>Polymer drive volume</td>
<td>2.3 PV</td>
</tr>
</tbody>
</table>

Table 4.35. – Filtration data for the polymer stock solution used to make the polymer drive solution. This data was used to calculate the filtration ratio.

<table>
<thead>
<tr>
<th>Volume</th>
<th>Pressure</th>
<th>Time</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>mL</td>
<td>psig</td>
<td>min</td>
<td>sec</td>
</tr>
<tr>
<td>10</td>
<td>12</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>20</td>
<td>12</td>
<td>9</td>
<td>30</td>
</tr>
<tr>
<td>30</td>
<td>12</td>
<td>19</td>
<td>2</td>
</tr>
<tr>
<td>40</td>
<td>12</td>
<td>28</td>
<td>41</td>
</tr>
<tr>
<td>50</td>
<td>12</td>
<td>38</td>
<td>23</td>
</tr>
<tr>
<td>60</td>
<td>12</td>
<td>48</td>
<td>16</td>
</tr>
<tr>
<td>70</td>
<td>12</td>
<td>58</td>
<td>19</td>
</tr>
<tr>
<td>80</td>
<td>12</td>
<td>68</td>
<td>34</td>
</tr>
<tr>
<td>90</td>
<td>12</td>
<td>78</td>
<td>57</td>
</tr>
<tr>
<td>100</td>
<td>12</td>
<td>89</td>
<td>42</td>
</tr>
<tr>
<td>110</td>
<td>12</td>
<td>100</td>
<td>45</td>
</tr>
<tr>
<td>120</td>
<td>12</td>
<td>112</td>
<td>10</td>
</tr>
</tbody>
</table>

Filtration test
FR = 1.1
Figure 4.1. - Phase behavior pipettes for experiment B4 (no alkali), and NaCl concentration increases from 4.1 - 5.0 wt% from left to right at 0.1 wt% increments.
Figure 4.2. - Phase behavior pipettes for experiment B5 (sodium carbonate), and NaCl concentration increases from 3.3 – 4.2 wt% from left to right at 0.1 wt% increments.
Figure 4.3. - Phase behavior pipettes for experiment B6 (sodium metaborate), and NaCl concentration increases from 3.8 – 4.7 wt% from left to right at 0.1 wt% increments.
Figure 4.4. - Oil and water solubilization curves for phase behavior experiment B4 using McElroy crude for microemulsion characterization. The formulation contained 1.5 wt% \( \text{C}_{16-17} \text{PO} \text{SO}_4^- \), 0.5 wt% \( \text{IOS}_{15-18} \), 2 wt% SBA.
Figure 4.5. - Oil and water solubilization curves for phase behavior experiment B5 using McElroy crude for microemulsion characterization. The formulation contained 1.5 wt% C_{16-17}–7PO–SO_{4}^−, 0.5 wt% IOS_{15-18}, 2 wt% SBA, and 1 wt% Na₂CO₃.
Figure 4.6. - Oil and water solubilization curves for phase behavior experiment B6 using McElroy crude for microemulsion characterization. The formulation contained 1.5 wt% C_{16-17}-7PO–SO\textsubscript{4}\textsuperscript{2−}, 0.5 wt% IOS\textsubscript{15-18}, 2 wt% SBA, and 1 wt% NaMetaborate.
Figure 4.7. - Oil and water solubilization ratio versus time at a salinity of 4.7 wt% (near optimum) for experiment B4 using McElroy crude for microemulsion characterization. The formulation contained 1.5 wt% C_{16-17}−7PO−SO_4^−, 0.5 wt% IOS_{15-18}, 2 wt% SBA.
Figure 4.8. - Oil and water solubilization ratio versus time at a salinity of 3.9 wt% (near optimum) for experiment B5 using McElroy crude for microemulsion characterization. The formulation contained 1.5 wt% C_{16-17}–7PO–SO_4^−, 0.5 wt% IOS_{15-18}, 2 wt% SBA, and 1 wt% Na_2CO_3.
Figure 4.9. - Oil and water solubilization ratio versus time at a salinity of 4.4 wt% (near optimum) for experiment B6 using McElroy crude for microemulsion characterization. The formulation contained 1.5 wt% C_{16-17}-7PO-SO_4^-, 0.5 wt% IOS_{15-18}, 2 wt% SBA, and 1 wt% NaMetaborate.
Figure 4.10. - Microemulsion viscosity for experiments B4, B5, B6 measured at 30 C.
Figure 4.11. - Conductivity measurements of microemulsions and pure aqueous phases for experiments B4, B5, B6 measured at 30°C. Non-normalized microemulsions conductivity is normalized to pure aqueous phase conductivity.
Figure 4.12. - IFT measurements between microemulsion droplets in pure aqueous phase using a spinning drop tensiometer. Microemulsions were collected from B4, B5, B6, and measured at a temperature of 30°C.
Figure 4.13. - Solubilization ratio plot of phase behavior A5 using McElroy crude oil at
30 C. The formulation contained 2 wt% TDA –4PO–SO$_4^-$, 4 wt% SBA.
Figure 4.14. - Solubilization ratio plot of phase behavior A7 using McElroy crude oil at 30 C. The formulation contained 2 wt% TDA –4PO–SO₄⁻, 4 wt% SBA.
Figure 4.15. - Change in solubilization ratios versus time for phase behavior A7 using McElroy crude oil at 30°C. The formulation contained 2 wt% TDA–4PO–SO₄⁻, 4 wt% SBA, and was evaluated at 7 wt% NaCl (near optimum).
Figure 4.16. - Solubilization ratio plot of phase behavior A8 using McElroy crude oil at 30 C. The formulation contained 2 wt% TDA –8PO–SO₄⁻, 4 wt% SBA.
Figure 4.17. - Change in solubilization ratios versus time for phase behavior A8 using McElroy crude oil at 30 C. The formulation contained 2 wt% TDA - 8PO–SO₄⁻, 4 wt% SBA, and was evaluated at 3.5 wt% NaCl (near optimum).
Figure 4.18. - Solubilization ratio plot of phase behavior A9 using McElroy crude oil at 30°C. The formulation contained 2 wt% IOS\textsubscript{15-18}, 4 wt% SBA.
Figure 4.19. - Change in solubilization ratios versus time for phase behavior A9 using McElroy crude oil at 30 C. The formulation contained 2 wt% IOS15-18, 4 wt% SBA, and was evaluated at 7.0 wt% NaCl (near optimum)
Figure 4.20. - Solubilization ratio plot of phase behavior A10 using McElroy crude oil at 30 C. The formulation contained 1.5 wt% C_{16-17}-7PO-SO_4^-, 0.5 wt% IOS_{15-18}, 4 wt% SBA.
Figure 4.21. - Change in solubilization ratios versus time for phase behavior A10 using McElroy crude oil at 30 C. The formulation contained 1.5 wt% C_{16-17}–7PO–SO_4, 0.5 wt% IOS_{15-18}, 4 wt% SBA, and was evaluated at 4.5 wt% NaCl (near optimum).
Figure 4.22. - Solubilization ratio plot of phase behavior A12 using McElroy crude oil at 30 °C. The formulation contained 2wt% C_{12-13} –8PO–SO_4^−, 2 wt% SBA.
Figure 4.23. - Change in solubilization ratios versus time for phase behavior A12 using McElroy crude oil at 30 C. The formulation contained 2wt% C_{12-13} –8PO–SO_4^–, 2 wt% SBA, and was evaluated at 5 wt% NaCl (near optimum).
Figure 4.24. - Solubilization ratio plot of phase behavior A13 using McElroy crude oil at 30°C. The formulation contained 2 wt% C_{12-13} \text{–}5PO\text{–}SO_4^–, 2 wt% SBA.
Figure 4.25. - Change in solubilization ratios versus time for phase behavior A13 using McElroy crude oil at 30°C. The formulation contained 2 wt% C_{12-13} –5PO–SO_4^−, 2 wt% SBA, and was evaluated at 5 wt% NaCl (near optimum).
Figure 4.26. - Solubilization ratio plot of phase behavior A16 using McElroy crude oil at 30 C. The formulation contained 1.5 wt% C_{16-17} –7PO–SO_4^–, 0.5 wt% IOS_{15-18}, 4 wt% SBA, and 1 wt% Na_2CO_3.
Figure 4.27. - Change in solubilization ratios versus time for phase behavior A16 using McElroy crude oil at 30 C. The formulation contained 1.5 wt% C_{16-17}–7PO–SO₄, 0.5 wt% IOS_{15-18}, 4 wt% SBA, and 1 wt% Na₂CO₃, and was evaluated at 3.5 wt% NaCl (near optimum).
Figure 4.28. - Solubilization ratio plot of phase behavior A17 using McElroy crude oil at 30°C. The formulation contained 1.5 wt% \( C_{16-17} \)–7PO–SO\(_4\)\(^{-}\), 0.5 wt% IOS\(_{15-18}\), 4 wt% SBA, and 1 wt% NaMetaborate.
Figure 4.29. - Change in solubilization ratios versus time for phase behavior A17 using McElroy crude oil at 30 C. The formulation contained 1.5 wt% C_{16-17} – 7PO–SO_4^−, 0.5 wt% IOS_{15-18}, 4 wt% SBA, and 1 wt% NaMetaborate, and was evaluated at 3.75 wt% NaCl (near optimum).
Figure 4.30. - Solubilization ratio plot of phase behavior A18 using McElroy crude oil at 30 C. The formulation contained 2 wt% TDA –8PO–SO₄⁻, 2 wt% SBA.
Figure 4.31. - Change in solubilization ratios versus time for phase behavior A18 using McElroy crude oil at 30 C. The formulation contained 2 wt% TDA –8PO–SO₄⁻, 2 wt% SBA, and was evaluated at 3.5 wt% NaCl (near optimum).
Figure 4.32. - Solubilization ratio plot of phase behavior A19 using McElroy crude oil at 30 C. The formulation contained 1.5 wt% C_{16-17}–7PO–SO_4^- , 0.5 wt% IOS_{15-18} , 2 wt% SBA.
Figure 4.33. - Change in solubilization ratios versus time for phase behavior A19 using McElroy crude oil at 30 C. The formulation contained 1.5 wt% C$_{16-17}$ – 7PO–SO$_4^-$, 0.5 wt% IOS$_{15-18}$, 2 wt% SBA, and was evaluated at 4.5 wt% NaCl (near optimum).
Figure 4.34. - Solubilization ratio plot of phase behavior A21 using McElroy crude oil at 30 °C. The formulation contained 1.5 wt% C_{16-17}-7PO-SO_{4}–, 0.5 wt% IOS_{15-18}, 2 wt% SBA, and 1 wt% Na_{2}CO_{3}. 
Figure 4.35. - Change in solubilization ratios versus time for phase behavior A21 using McElroy crude oil at 30 C. The formulation contained 1.5 wt% C_{16-17} – 7PO–SO_4^−, 0.5 wt% IOS_{15-18}, 2 wt% SBA, and 1 wt% Na_2CO_3, and was evaluated at 3.75 wt% NaCl (near optimum).
Figure 4.36. - Solubilization ratio plot of phase behavior A22 using McElroy crude oil at 30 C. The formulation contained 1.5 wt% C_{16-17–7PO–SO_4^-}, 0.5 wt% IOS_{15-18}, 2 wt% SBA, and 1 wt% NaMetaborate.
Figure 4.37. - Change in solubilization ratios versus time for phase behavior A22 using McElroy crude oil at 30 C. The formulation contained 1.5 wt\% C_{16-17}–7PO–SO_4^–, 0.5 wt\% IOS_{15-18}, 2 wt\% SBA, and 1 wt\% NaMetaborate, and was evaluated at 4.25 wt\% NaCl (near optimum).
Figure 4.38. - Solubilization ratio plot of phase behavior A24 using McElroy crude oil at 30 C. The formulation contained 1.5 wt% C_{16-17}–7PO–SO_4^–, 0.5 wt% IOS_{15-18}, 1 wt% SBA, and 1 wt% Na_2CO_3.
Figure 4.39. - Change in solubilization ratios versus time for phase behavior A24 using McElroy crude oil at 30 C. The formulation contained 1.5 wt% C_{16-17} – 7PO–SO_{4}^{-}, 0.5 wt% IOS_{15-18}, 1 wt% SBA, and 1 wt% Na_{2}CO_{3}, and was evaluated at 4 wt% NaCl (near optimum).
Figure 4.40. - Solubilization ratio plot of phase behavior A25 using McElroy crude oil at 30°C. The formulation contained 1.5 wt% C_{16-17} –7PO–SO_4^- , 0.5 wt% IOS_{15-18} , 1 wt% SBA, and 1 wt% NaMetaborate.
Figure 4.41. - Change in solubilization ratios versus time for phase behavior A25 using McElroy crude oil at 30 C. The formulation contained 1.5 wt% $C_{16-17}-7PO-SO_4^-$, 0.5 wt% IOS$_{15-18}$, 1 wt% SBA, and 1 wt% NaMetaborate, and was evaluated at 4.5 wt% NaCl (near optimum).
Figure 4.42. - Solubilization ratio plot of phase behavior A29 using McElroy crude oil at 30 C. The formulation contained 0.375 wt% C_{16-17} –7PO–SO\text{4}^{-}, 0.125 wt% IOS_{15-18}, 0.5 wt% SBA.
Figure 4.43. - Solubilization ratio plot of phase behavior A33 using McElroy crude oil at 30 C. The formulation contained 0.15 wt% C\textsubscript{16-17} –7PO–SO\textsubscript{4}\textsuperscript{−}, 0.05 wt% IOS\textsubscript{15-18}, 0.2 wt% SBA, and 1 wt% Na\textsubscript{2}CO\textsubscript{3}.
Figure 4.44. - Solubilization ratio plot of phase behavior A35 using McElroy crude oil at 30 C. The formulation contained 0.75 wt% C_{16-17–7PO–SO_4}^-, 0.25 wt% IOS_{15-18}, 1 wt% SBA.
Figure 6.45. - Solubilization ratio plot of phase behavior A36b using McElroy crude oil at 30 C. The formulation contained 0.75 wt% C_{16-17}–7PO–SO_{4}^{-}, 0.25 wt% IOS_{15-18}, 1 wt% SBA, and 1 wt% Na_{2}CO_{3}. 
Figure 4.46. - Solubilization ratio plot of phase behavior A41 using McElroy crude oil at 30°C. The formulation contained 1.5 wt% C_{16-17} –7PO–SO_4^−, 0.5 wt% IOS_{15-18}, 2 wt% SBA, and 0.125 wt% NaOH.
Figure 4.47. - Change in solubilization ratios versus time for phase behavior A41 using McElroy crude oil at 30 C. The formulation contained 1.5 wt% C_{16-17}\text{–}\text{7PO}\text{–SO}_4^-, 0.5 wt% IOS_{15-18}, 2 wt% SBA, and 0.125 wt% NaOH and was evaluated at 4.25 wt% NaCl (near optimum).
Figure 4.48. - Solubilization ratio plot of phase behavior A42 using McElroy crude oil at 30 C. The formulation contained 1.5 wt% C_{16-17} –7PO–SO_4^−, 0.5 wt% IOS_{15-18}, 2 wt% SBA, and 0.015625 wt% NaOH.
Figure 4.49. - Change in solubilization ratios versus time for phase behavior A42 using McElroy crude oil at 30 °C. The formulation contained 1.5 wt% C_{16-17} - 7PO–SO_4^−, 0.5 wt% IOS_{15-18}, 2 wt% SBA, and 0.015625 wt% NaOH, and was evaluated at 4.5 wt% NaCl (near optimum).
Figure 4.50. - Solubilization ratio plot of phase behavior A44 using McElroy crude oil at 30 C. The formulation contained 1.5 wt% C_{16-17} –7PO–SO_4^–, 0.5 wt% IOS_{15-18}, 2 wt% SBA, and 0.00004 wt% NaOH.
Figure 4.51. - Change in solubilization ratios versus time for phase behavior A44 using McElroy crude oil at 30 C. The formulation contained 1.5 wt% $C_{16-17-7PO-SO_4}$, 0.5 wt% IOS$_{15-18}$, 2 wt% SBA, and 0.00004 wt% NaOH, and was evaluated at 4.75 wt% NaCl (near optimum).
Figure 4.52. - Solubilization ratio plot of phase behavior A46 using McElroy crude oil at 30 C. The formulation contained 1.5 wt% C_{16-17} –7PO–SO_4^–, 0.5 wt% IOS_{15-18}, 2 wt% SBA, and 0.0004 wt% NaOH.
Figure 4.53. - Change in solubilization ratios versus time for phase behavior A46 using McElroy crude oil at 30 C. The formulation contained 1.5 wt% C_{16-17} – 7PO–SO_4^–, 0.5 wt% IOS_{15-18}, 2 wt% SBA, and 0.0004 wt% NaOH, and was evaluated at 4.5 wt% NaCl (near optimum).
Figure 4.54. - Solubilization ratio plot of phase behavior A47 using McElroy crude oil at 30 C. The formulation contained 1.5 wt% C_{16-17}–SO_4^{2−}, 0.5 wt% IOS_{15-18}, 2 wt% SBA, and 0.004 wt% NaOH.
Figure 4.55. - Change in solubilization ratios versus time for phase behavior A47 using McElroy crude oil at 30 C. The formulation contained 1.5 wt% C_{16-17}–7PO–SO_{4}^{−}, 0.5 wt% IOS_{15-18}, 2 wt% SBA, and 0.004 wt% NaOH, and was evaluated at 4.5 wt% NaCl (near optimum).
Figure 4.56. - Solubilization ratio plot of phase behavior A50 using McElroy crude oil at 30 C. The formulation contained 2 wt% $C_{16-17}-\text{PO-SO}_4^-$, 6 wt% SBA.
Figure 4.57. - Change in solubilization ratios versus time for phase behavior A50 using McElroy crude oil at 30 C. The formulation contained 2 wt% C_{16-17}–7PO–SO_{4}^–, 6 wt% SBA, and was evaluated at 2 wt% NaCl (near optimum).
Figure 4.58. - Solubilization ratio plot of phase behavior A51 using McElroy crude oil at 30 C. The formulation contained 1.75 wt% C_{16-17}–7PO–SO_4^−, 0.25 wt% IOS_{15-18}, 4 wt% SBA.
Figure 4.59. - Change in solubilization ratios versus time for phase behavior A51 using McElroy crude oil at 30°C. The formulation contained 1.75 wt% C\textsubscript{16-17} – 7PO–SO\textsubscript{4}\textsuperscript{−}, 0.25 wt% IOS\textsubscript{15-18}, 4 wt% SBA, and was evaluated at 3 wt% NaCl (near optimum).
Figure 4.60. - Solubilization ratio plot of phase behavior A52 using McElroy crude oil at 30 C. The formulation contained 2 wt% C_{16-17} -7PO–SO$_4^-$, 6 wt% IPA.
Figure 4.61. - Change in solubilization ratios versus time for phase behavior A52 using McElroy crude oil at 30 C. The formulation contained 2 wt% C_{16-17} -7PO–SO_4^−, 6 wt% IPA, and was evaluated at 2 wt% NaCl (near optimum).
Figure 4.62. - Solubilization ratio plot of phase behavior A60 using McElroy crude oil at 30 °C. The formulation contained 2 wt% C_{16-17}PO–SO_4^–, 6 wt% 1-propanol.
Figure 4.63. - Change in solubilization ratios versus time for phase behavior A60 using McElroy crude oil at 30 C. The formulation contained 2 wt% C<sub>16-17</sub>–7PO–SO₄⁻, 6 wt% 1-propanol, and was evaluated at 2.5 wt% NaCl (near optimum).
Figure 4.64. - Solubilization ratio plot of phase behavior A61 using McElroy crude oil at 30 C. The formulation contained 2 wt% C_{16-17}–7PO–SO_4^−, 6 wt% ethanol.
Figure 4.65. - Change in solubilization ratios versus time for phase behavior A61 using McElroy crude oil at 30 C. The formulation contained 2 wt% C$_{16-17}$-7PO–SO$_4^-$, 6 wt% ethanol, and was evaluated at 2 wt% NaCl (near optimum).
Figure 4.66. - Solubilization ratio plot of phase behavior A64 using McElroy crude oil at 30 °C. The formulation contained 2 wt% C_{16-17}-7PO-SO_4^-, 6 wt% sec-butoxy ethanol.
Figure 4.67. - Change in solubilization ratios versus time for phase behavior A64 using McElroy crude oil at 30 C. The formulation contained 2 wt% C\textsubscript{16-17}−PO−SO\textsubscript{4}\textsuperscript{−}, 6 wt% sec-butoxy-ethanol, and was evaluated at 2 wt% NaCl (near optimum).
Figure 4.68. - Solubilization ratio plot of phase behavior A65 using McElroy crude oil at 30 C. The formulation contained 2 wt% C_{16-17}-7PO–SO_{4}^{-}, 6 wt% tert-butanol.
Figure 4.69. - Change in solubilization ratios versus time for phase behavior A65 using McElroy crude oil at 30°C. The formulation contained 2 wt% C_{16-17}–7PO–SO_4^−, 6 wt% tert-butanol, and was evaluated at 2 wt% NaCl (near optimum).
Figure 4.70. - Solubilization ratio plot of phase behavior A67 using McElroy crude oil at 30°C. The formulation contained 2 wt% C_{16-17–7}PO–SO_4^–, 6 wt% 1-butanol.
Figure 4.71. - Change in solubilization ratios versus time for phase behavior A67 using McElroy crude oil at 30 C. The formulation contained 2 wt% C_{16-17}–7PO–SO_4^−, 6 wt% 1-butanol1.25 wt% NaCl (near optimum).
Figure 4.72. - Solubilization ratio plot of phase behavior A70 using McElroy crude oil at 30 C. The formulation contained 2 wt% C_{16-17}–7PO–SO_4^−, 0.25 wt% IOS_{15-18}, 6 wt% SBA.
Figure 4.73. - Change in solubilization ratios versus time for phase behavior A70 using McElroy crude oil at 30 C. The formulation contained 2 wt% C_{16-17-7PO-SO_4}^-, 0.25 wt% IOS_{15-18}, 6 wt% SBA, and was evaluated at 2.5 wt% NaCl (near optimum).
Figure 4.74. - Solubilization ratio plot of phase behavior A80 using McElroy crude oil at 30 °C. The formulation contained 1 wt% C_{16-17} –7PO–SO_4^- , 6 wt% SBA.
Figure 4.75. - Change in solubilization ratios versus time for phase behavior A80 using McElroy crude oil at 30 C. The formulation contained 1 wt% C_{16-17} –7PO–SO_4^−, 6 wt% SBA, and was evaluated at 2 wt% NaCl (near optimum).
Figure 4.76. - Solubilization ratio plot of phase behavior C1 using McElroy crude oil at 22 C. The formulation contained 1.5 wt% C_{16-17} –7PO–SO_{4}^−, 0.5 wt% IOS_{15-18}, 2 wt% SBA.
Figure 4.77. - Change in solubilization ratios versus time for phase behavior C1 using McElroy crude oil at 22 C. The formulation contained 1.5 wt% C_{16-17}-7PO-SO_4^-, 0.5 wt% IOS_{15-18}, 2 wt% SBA, and was evaluated at 5 wt% NaCl (near optimum).
Figure 4.78. - Solubilization ratio plot of phase behavior C2 using McElroy crude oil at 22°C. The formulation contained 1.5 wt% C<sub>16-17</sub>PO–SO<sub>4</sub><sup>−</sup>, 0.5 wt% IOS<sub>15-18</sub>, 2 wt% SBA, and 1 wt% Na<sub>2</sub>CO<sub>3</sub>. 
Figure 4.79. - Change in solubilization ratios versus time for phase behavior C2 using McElroy crude oil at 22 C. The formulation contained 1.5 wt% C_{16-17–7PO–SO_4}^−, 0.5 wt% IOS_{15-18}, 2 wt% SBA, and 1 wt% Na_2CO_3, and was evaluated at 4.25 wt% NaCl (near optimum).
Figure 4.80. - Solubilization ratio plot of phase behavior C3 using McElroy crude oil at 22 C. The formulation contained 1.5 wt% $C_{16-17}$PO–SO$_4^-$, 0.5 wt% IOS$_{15-18}$, 2 wt% SBA, and 1 wt% NaMetaborate.
Figure 4.81. - Change in solubilization ratios versus time for phase behavior C3 using McElroy crude oil at 22 C. The formulation contained 1.5 wt% C_{16-17} - 7PO–SO_{4}^{2-}, 0.5 wt% IOS_{15-18}, 2 wt% SBA, and 1 wt% NaMetaborate, and was evaluated at 5 wt% NaCl (near optimum).
Figure 4.82. - Comparison of solubilization ratio plots of phase behaviors B5 at 30 C and C2 at 22 C using McElroy crude oil. The temperature differs between the two experiments. The formulation contained 1.5 wt% $C_{16-17-7}PO-SO_4^-$, 0.5 wt% $IOS_{15-18}$, 2 wt% SBA, and 1 wt% $Na_2CO_3$. 
Figure 4.83. - Solubilization ratio plot of phase behavior YA3 using Yates crude oil at 22 C. The formulation contained 1.5 wt% C_{16-17-7PO−SO_{4}^-}, 0.5 wt% IOS_{15-18}, 2 wt% SBA.
Figure 4.84. - Change in solubilization ratios versus time for phase behavior YA4 using Yates crude oil at 22 C. The formulation contained 1.5 wt% C$_{16-17}$ –PO–SO$_4^-$, 0.5 wt% IOS$_{15-18}$, 2 wt% SBA, and was evaluated at 4.5 wt% NaCl (near optimum).
Figure 4.85. - Solubilization ratio plot of phase behavior YA6 using Yates crude oil at 22 C. The formulation contained 1.5 wt% \( C_{16-17}^{\text{PO}_7} \text{SO}_4^- \), 0.5 wt% IOS\(_{15-18} \), 2 wt% SBA.
Figure 4.86. - Change in solubilization ratios versus time for phase behavior YA6 using Yates crude oil at 22 C. The formulation contained 1.5 wt% $C_{16-17}-7PO-$SO$_4^-$, 0.5 wt% IOS$_{15-18}$, 2 wt% SBA, and was evaluated at 5.5 wt% NaCl (near optimum).
Figure 4.87. - Solubilization ratio plot of phase behavior D1 using Crude D at 52 C. The formulation contained 1.5 wt% C_{16-17–7PO–SO_4}^-, 0.5 wt% IOS_{15-18}, 2 wt% SBA.
Figure 4.88. - Change in solubilization ratios versus time for phase behavior D1 using Crude D at 52°C. The formulation contained 1.5 wt% C_{16-17}−7PO−SO_4^{−}, 0.5 wt% IOS_{15-18}, 2 wt% SBA, and was evaluated at 3.5 wt% NaCl (near optimum).
Figure 4.89. - Solubilization ratio plot of phase behavior D2 using Crude D at 52 C. The formulation contained 1 wt% C_{16-17} –7PO–SO_4^–, 1 wt% IOS_{15-18}, 0.5 wt% SBA.
Figure 4.90. - Change in solubilization ratios versus time for phase behavior D2 using Crude D at 52 C. The formulation contained 1 wt% C_{16-17} -7PO-SO_4^-, 1 wt% IOS_{15-18}, 0.5 wt% SBA, and was evaluated at 6 wt% NaCl (near optimum).
Figure 4.91. - Solubilization ratio plot of phase behavior D7 using Crude D at 52 C. The formulation contained 1.5 wt% $\text{C}_{16-17}-7\text{PO}\text{--SO}_4^-$, 0.5 wt% IOS$\text{15-18}$, 2 wt% SBA.
Figure 4.92. - Change in solubilization ratios versus time for phase behavior D7 using Crude D at 52 C. The formulation contained 1.5 wt% C₁₆₋₁₇−₇PO−SO₄⁻, 0.5 wt% IOS₁₅₋₁₈, 2 wt% SBA, and was evaluated at 3.25 wt% NaCl (near optimum).
Figure 4.93. - Solubilization ratio plot of phase behavior D8 using Crude D at 52 C. The formulation contained 1 wt% C\textsubscript{16-17}–7PO–SO\textsubscript{4}\textsuperscript{2–}, 1 wt% IOS\textsubscript{15-18}, 0.5 wt% SBA.
Figure 4.94. - Change in solubilization ratios versus time for phase behavior D8 using Crude D at 52 C. The formulation contained 1 wt% $C_{16-17}$–7PO–SO$_4^-$, 1 wt% IOS$_{15-18}$, 0.5 wt% SBA, and was evaluated at 6.75 wt% NaCl (near optimum).
Figure 4.95. - Solubilization ratio plot of phase behavior D12 using Crude D at 52 C.
The formulation contained 1.5 wt% C_{16-17} \text{-7PO\textendashSO}_4^-, 0.5 wt% IOS_{15-18},
1 wt% SBA.
Figure 4.96. - Solubilization ratio plot of phase behavior D13 using Crude D at 52 C. The formulation contained 1.25 wt% $C_{16-17}-7PO–SO_4^-$, 0.75 wt% IOS$_{15-18}$, 1 wt% SBA.
Figure 4.97. - Change in solubilization ratios versus time for phase behavior D13 using Crude D at 52 C. The formulation contained 1.25 wt% $\text{C}_{16-17}-7\text{PO}-\text{SO}_4^-$, 0.75 wt% IOS$_{15-18}$, 1 wt% SBA, and was evaluated at 5 wt% NaCl (near optimum).
Figure 4.98. - Solubilization ratio plot of phase behavior D14 using Crude D at 52 C. The formulation contained 1.5 wt% $\text{C}_{16-17}-\text{7PO–SO}_4^-$, 0.5 wt% IOS$_{15-18}$, 1.5 wt% SBA.
Figure 4.99. - Change in solubilization ratios versus time for phase behavior D14 using Crude D at 52 C. The formulation contained 1.5 wt% $C_{16-17}$-7PO–SO$_4$ $^-$, 0.5 wt% IOS$_{15-18}$, 1.5 wt% SBA, and was evaluated at 3.5 wt% NaCl (near optimum).
Figure 4.100. - Solubilization ratio plot of phase behavior D15 using Crude D at 52 C. The formulation contained 1 wt% $C_{16-17}^{-7PO-SO_4}$, 1 wt% IOS$_{15-18}$, 0.5 wt% SBA.
Figure 4.101. - Change in solubilization ratios versus time for phase behavior D15 using Crude D at 52 C. The formulation contained 1 wt% C_{16-17} - 7PO–SO_4^−, 1 wt% IOS_{15-18}, 0.5 wt% SBA, and was evaluated at 7 wt% NaCl (near optimum).
Figure 4.102. - Solubilization ratio plot of phase behavior D16 using Crude D at 52 C. The formulation contained 1 wt% C_{16-17}−7PO−SO_4^−, 1 wt% IOS_{15-18}, 1 wt% SBA.
Figure 4.103. - Change in solubilization ratios versus time for phase behavior D16 using Crude D at 52 C. The formulation contained 1 wt% C_{16-17}^{7PO–SO_4^-}, 1 wt% IOS_{15-18}, 1 wt% SBA, and was evaluated at 6.5 wt% NaCl (near optimum).
Figure 4.104. - Solubilization ratio plot of phase behavior D17 using Crude D at 52 C. The formulation contained 1.25 wt% C_{16-17}–7PO–SO_4^- , 0.75 wt% IOS_{15-18} , 2 wt% SBA.
Figure 4.105. - Change in solubilization ratios versus time for phase behavior D17 using Crude D at 52 C. The formulation contained 1.25 wt% C_{16-17} \text{–7PO–SO}_4^– , 0.75 wt% IOS_{15-18} , 2 wt% SBA, and was evaluated at 4.5 wt% NaCl (near optimum).
Figure 4.106. - Solubilization ratio plot of phase behavior D18 using Crude D at 52 C. The formulation contained 1.25 wt% $C_{16-17}-7PO-SO_4^-$, 0.75 wt% IOS$_{15-18}$, 0.5 wt% SBA.
Figure 4.107. - Change in solubilization ratios versus time for phase behavior D18 using Crude D at 52 C. The formulation contained 1.25 wt% $C_{16-17}$–7PO–SO$_4^-$, 0.75 wt% IOS$_{15-18}$, 0.5 wt% SBA, and was evaluated at 5 wt% NaCl (near optimum).
Figure 4.108. Solubilization ratio plot of phase behavior D19 using Crude D at 52 C. The formulation contained 1.75 wt% C\textsubscript{16-17} –7PO–SO\textsubscript{4}\textsuperscript{2-}, 0.25 wt% IOS\textsubscript{15-18}, 2 wt% SBA.
Figure 4.109. - Change in solubilization ratios versus time for phase behavior D19 using Crude D at 52 C. The formulation contained 1.75 wt% $C_{16-17}$–7PO–SO$_4^-$, 0.25 wt% IOS$_{15-18}$, 2 wt% SBA, and was evaluated at 2 wt% NaCl (near optimum).
Solubilization ratio plot of phase behavior D20 using Crude D at 52 C. The formulation contained 1.5 wt% C_{16-17} -7PO-SO_4^-, 0.5 wt% IOS_{15-18}, 1.5 wt% SBA, and 0.5 wt% Na_2CO_3.
Figure 4.111. - Change in solubilization ratios versus time for phase behavior D20 using Crude D at 52 C. The formulation contained 1.5 wt% $\text{C}_{16-17}-7\text{PO-SO}_4^-$, 0.5 wt% IOS$_{15-18}$, 1.5 wt% SBA, and 1 wt% Na$_2$CO$_3$, and was evaluated at 3 wt% NaCl (near optimum).
Figure 4.112. - Solubilization ratio plot of phase behavior D21 using Crude D at 52 C. The formulation contained 1 wt% C_{16-17} –7PO–SO₄⁻, 1 wt% IOS_{15-18}, 0.5 wt% SBA, and 0.5 wt% Na₂CO₃.
Figure 4.113. - Change in solubilization ratios versus time for phase behavior D21 using Crude D at 52 C. The formulation contained 1 wt% C_{16-17} – 7PO–SO_{4}, 1 wt% IOS_{15-18}, 0.5 wt% SBA, and 0.5 wt% Na_{2}CO_{3}, and was evaluated at 6.25 wt% NaCl (near optimum).
Figure 4.114. - Solubilization ratio plot of phase behavior D22 using Crude D at 52 °C. The formulation contained 1.25 wt% C_{16-17}–7PO–SO_{4}^{−}, 0.75 wt% IOS_{15-18}, 0.5 wt% SBA, and 0.5 wt% Na_{2}CO_{3}. 
Change in solubilization ratios versus time for phase behavior D22 using Crude D at 52°C. The formulation contained 1.25 wt% C_{16-17}−7PO−SO_4^{−}, 0.75 wt% IOS_{15-18}, 0.5 wt% SBA, and 0.5 wt% Na_2CO_3, and was evaluated at 4.75 wt% NaCl (near optimum).
Solubilization ratio plot of phase behavior D23 using Crude D at 52 C. The formulation contained 1.5 wt% C_{16-17}–7PO–SO_4^−, 0.5 wt% IOS_{15-18}, 1.5 wt% SBA, and 1 wt% Na_2CO_3.

Figure 4.116.
Figure 4.117. - Change in solubilization ratios versus time for phase behavior D23 using Crude D at 52 C. The formulation contained 1.5 wt% C_{16-17}–7PO–SO_4^–, 0.5 wt% IOS_{15-18}, 1.5 wt% SBA, and 1 wt% Na_2CO_3, and was evaluated at 2.75 wt% NaCl (near optimum).
Figure 4.118. - Solubilization ratio plot of phase behavior D24 using Crude D at 52 C. The formulation contained 1 wt% C_{16-17} –7PO–SO_4^–, 1 wt% IOS_{15-18}, 0.5 wt% SBA, and 1 wt% Na_2CO_3.
Figure 4.119. - Change in solubilization ratios versus time for phase behavior D24 using Crude D at 52 C. The formulation contained 1 wt% C\textsubscript{16-17}–\textsubscript{7PO–SO}_4^–, 1 wt% IOS\textsubscript{15-18}, 0.5 wt% SBA, and 1 wt% Na\textsubscript{2}CO\textsubscript{3}, and was evaluated at 6 wt% NaCl (near optimum).
Figure 4.120. - Solubilization ratio plot of phase behavior D26 using Crude D at 52 C. The formulation contained 0.75 wt% C_{16-17}–PO–SO_4^{−}, 0.25 wt% IOS_{15-18}, 0.75 wt% SBA.
Figure 4.121. - Change in solubilization ratios versus time for phase behavior D26 using Crude D at 52 C. The formulation contained 0.75 wt% $C_{16-17}-7PO-SO_4^-$, 0.25 wt% IOS$_{15-18}$, 0.75 wt% SBA, and was evaluated at 4.5 wt% NaCl (near optimum).
Figure 4.122. - Solubilization ratio plot of phase behavior D27 using Crude D at 52 C. The formulation contained 0.5 wt% C_{16-17}–SO_4^–, 0.5 wt% IOS_{15-18}, 0.25 wt% SBA.
Figure 4.123. - Change in solubilization ratios versus time for phase behavior D27 using Crude D at 52 C. The formulation contained 0.5 wt% C_{16-17} – 7PO–SO_4^–, 0.5 wt% IOS_{15-18}, 0.25 wt% SBA, and was evaluated at 6.75 wt% NaCl (near optimum).
Figure 4.124. - Solubilization ratio plot of phase behavior D28 using Crude D at 52 C. The formulation contained 0.625 wt% C_{16-17}–7PO–SO_{4}^{−}, 0.375 wt% IOS_{15-18}, 0.25 wt% SBA.
Figure 4.125. - Change in solubilization ratios versus time for phase behavior D28 using Crude D at 52 C. The formulation contained 0.625 wt% C_{16-17} \text{PO}_7 \text{SO}_4^-, 0.375 wt% IOS_{15-18}, 0.25 wt% SBA, and was evaluated at 4.5 wt% NaCl (near optimum).
Figure 4.126. - Solubilization ratio plot of phase behavior D30 using Crude D at 52 C. The formulation contained 0.25 wt% $C_{16-17}$–7PO–SO$_4^-$, 0.25 wt% IOS$_{15-18}$, 0.125 wt% SBA.
Change in solubilization ratios versus time for phase behavior D30 using Crude D at 52 C. The formulation contained 0.25 wt% \( C_{16-17} \) –7PO–SO\(_4\) -, 0.25 wt% IOS\(_{15-18}\) , 0.125 wt% SBA, and was evaluated at 4.5 wt% NaCl (near optimum).
Figure 4.128. - Solubilization ratio plot of phase behavior D31 using Crude D at 52 C. The formulation contained 0.3125 wt% $\text{C}_{16-17}-7\text{PO-SO}_4^-$, 0.1875 wt% $\text{IOS}_{15-18}$, 0.125 wt% SBA.
Change in solubilization ratios versus time for phase behavior D31 using Crude D at 52 C. The formulation contained 0.3125 wt% $C_{16-17}-7PO-SO_4^-$, 0.1875 wt% IOS$_{15-18}$, 0.125 wt% SBA, and was evaluated at 4.5 wt% NaCl (near optimum).
Figure 4.130. - Solubilization ratio plot of phase behavior D32 using Crude D at 52 C. The formulation contained 1.5 wt% C_{16-17}–7PO–SO_4^−, 0.5 wt% IOS_{15-18}, 1.5 wt% SBA.
Figure 4.131. - Change in solubilization ratios versus time for phase behavior D32 using Crude D at 52 C. The formulation contained 1.5 wt% C\textsubscript{16-17} - 7PO – SO\textsubscript{4}, 0.5 wt% IOS\textsubscript{15-18}, 1.5 wt% SBA, and was evaluated at 4.5 wt% Na2CO3 (near optimum).
Figure 4.132. - Solubilization ratio plot of phase behavior D33 using Crude D at 52 C. The formulation contained 1 wt% C\textsubscript{16-17}–7PO–SO\textsubscript{4}\textsuperscript{−}, 1 wt% IOS\textsubscript{15-18}, 0.5 wt% SBA.
Figure 4.133. - Change in solubilization ratios versus time for phase behavior D33 using Crude D at 52 C. The formulation contained 1 wt% C_{16-17} - 7PO–SO_4^−, 1 wt% IOS_{15-18}, 0.5 wt% SBA, and was evaluated at 9.25 wt% Na2CO3 (near optimum).
Figure 4.134. - Solubilization ratio plot of phase behavior D34 using Crude D at 52 C. The formulation contained 1.25 wt% $C_{16-17}$–7PO–SO$_4^-$, 0.75 wt% IOS$_{15-18}$, 0.5 wt% SBA.
Figure 4.135. - Change in solubilization ratios versus time for phase behavior D34 using Crude D at 52 C. The formulation contained 1.25 wt% C_{16-17}-7PO–SO_4^{2–}, 0.75 wt% IOS_{15-18}, 0.5 wt% SBA, and was evaluated at 7.5 wt% Na2CO3 (near optimum).
Figure 4.136. - Solubilization ratio plot of phase behavior D40 using Crude D at 52°C. The formulation contained 1.25 wt% C_{16-17} –7PO–SO_4 \^2, 0.75 wt% IOS_{15-18}, 0.5 wt% SBA, and 1 wt% Na_2CO_3.
Figure 4.137. - Change in solubilization ratios versus time for phase behavior D40 using Crude D at 52°C. The formulation contained 1.25 wt% C_{16-17}-\text{PO-SO}_4^-, 0.75 wt% IOS_{15-18}, 0.5 wt% SBA, and 1 wt% Na_2CO_3, and was evaluated at 4.5 wt% NaCl (near optimum).
Figure 4.138. - Solubilization ratio plot of phase behavior D41 using Crude D at 52 C. The formulation contained 0.625 wt% C_{16-17}-7PO–SO_{4}^−, 0.375 wt% IOS_{15-18}, 0.25 wt% SBA, and 1 wt% Na_{2}CO_{3}.
Figure 4.139. - Change in solubilization ratios versus time for phase behavior D41 using Crude D at 52 C. The formulation contained 0.625 wt% C_{16-17-7}PO–SO_4^–, 0.375 wt% IOS_{15-18}, 0.25 wt% SBA, and 1 wt% Na_2CO_3, and was evaluated at 4.375 wt% NaCl (near optimum).
Figure 4.140. - Solubilization ratio plot of phase behavior D42 using Crude D at 52°C. The formulation contained 0.625 wt% C\textsubscript{16-17} –7PO–SO\textsubscript{4}\textsuperscript{−}, 0.375 wt% IOS\textsubscript{15-18}, and 1 wt% Na\textsubscript{2}CO\textsubscript{3}.
Figure 4.141. - Change in solubilization ratios versus time for phase behavior D42 using Crude D at 52 C. The formulation contained 0.625 wt% C_{16-17}–7PO–SO_4^–, 0.375 wt% IOS_{15-18}, and 1 wt% Na_2CO_3, and was evaluated at 4.375 wt% NaCl (near optimum).
Figure 4.142 - Viscosity versus shear rate measurements for synthetic formation brine using a coquette-type viscometer.
Figure 4.143 - Viscosity versus shear rate measurements for the surfactant slug using a coquette type viscometer.
Figure 4.144 - Viscosity versus shear rate measurements for the polymer drive solution using a coquette-type viscometer.
Figure 4.145 - Viscosity versus shear rate measurements for Crude D using a coquette-type viscometer.
Figure 4.146 - Pressure drop across the entire core versus pore volumes of injected synthetic formation brine during the brine flood experiment at 52 C.
Figure 4.147 - Pressure drop across the entire core, and inlet, middle, and outlet sections of the core versus pore volumes of Crude D injected during the oil flood experiment at 52 C.
Figure 4.148 - Pressure drop across the entire core, and inlet, middle, and outlet sections of the core versus pore volumes of synthetic formation brine injected during the water flood experiment at 52 \( ^\circ \)C.
Figure 4.149 - Pressure drop across the entire core, and inlet, middle, and outlet sections of the core versus pore volumes injected. Surfactant slug was injected for the first 0.3 pore volumes, and polymer drive for the remaining 2.3 pore volumes. The experiment was performed at 52 °C.
Figure 4.150 - Pressure drop across the entire core versus pore volumes injected. Surfactant slug was injected for the first 0.3 pore volumes, and polymer drive for the remaining 2.3 pore volumes. The experiment was performed at 52 C.
Figure 4.151 - Phase behavior data for Test 28 using Crude D at 52 C. This same formulation was used for the surfactant slug, only this formulation does not contain polymer. The formulation contained 0.625 wt% C$_{16-17}$–PO–SO$_4^-$, 0.375 wt% IOS$_{15-18}$, 0.25 wt% SBA.
Figure 4.152 - Oil fraction and cumulative oil recovery data obtained from effluent analysis of the core flood with Crude D.
Figure 4.153  -  Conductivity and surfactant concentration data from analysis of the effluent obtained from the core flood experiment using Crude D.
CHAPTER 5: CT SCANNING OF NATURAL IMBIBITION IN CORES

INTRODUCTION

The objective of the natural imbibition study was to observe fluid imbibition processes inside of a limestone core using CT scanning technology. An additional objective was to compare differences in imbibition processes using different chemical EOR formulations. The formulations contain a mixture of surfactant, co-surfactant, co-solvent, electrolyte, and/or alkali. The selection of chemicals was based upon the phase behavior and core flood data presented in Chapter 4.

EXPERIMENTAL DESCRIPTION

A description of the experimental setup, materials, and procedure is provided in this section. The experiment consisted of first selecting and preparing imbibition fluids, and preparing cores that will undergo imbibition processes. An experimental apparatus is then constructed to house the cores while being immersed in imbibition fluids. The process is characterized by the use of CT scanning technology, and obtained images are processed and interpreted. Example imbibition cells are shown in Figure 5.7, where two cores are immersed in either brine or a solution containing surfactant.

Imbibition Fluids

Four different types of fluids were prepared for four different imbibition experiments. Table 5.1 lists the four fluid types as control, no alkali, sodium carbonate, and sodium metaborate. The control fluid was the only fluid that did not contain surfactant, and would therefore render an oil-water interfacial tension (IFT) of about 20 dynes/cm. All other solutions contained surfactant with an estimated IFT with the oil on the order of $10^{-3}$ to $10^{-2}$ dynes/cm. Two of the three solutions with surfactant contained alkali, which included sodium carbonate and sodium metaborate.
Control

The control fluid contains 4.6 wt% NaCl, and essentially mimics the use of formation brine.

No Alkali

The formulation labeled ‘No Alkali’ in Table 5.1 contained 1.5 wt% C_{16-17} – 7PO – SO_4^-, 0.5 wt% IOS_{15-18}, 2 wt% SBA, and 4.6 wt% NaCl. This formulation was found to show good phase behavior with McElroy crude as shown from solubilization ratio plots in Figures 5.1 and 5.2. Note that 4.6 wt% NaCl is the optimal salinity shown in Figure 5.1. Figure 5.2 shows fast equilibration in only about 3 days.

Sodium Carbonate

The formulation labeled ‘Sodium Carbonate’ in Table 5.1 contained 1.5 wt% C_{16-17} – 7PO – SO_4^-, 0.5 wt% IOS_{15-18}, 2 wt% SBA, 1 wt% sodium carbonate, and 3.8 wt% NaCl. This formulation was found to show good phase behavior with McElroy crude as shown from solubilization ratio plots in Figures 5.3 and 5.4. 3.8 wt% NaCl is the optimal salinity shown in Figure 5.3. Figure 5.4 shows fast equilibration.

Sodium Metaborate

The formulation labeled ‘Sodium Metaborate’ in Table 5.1 contained 1.5 wt% C_{16-17} – 7PO – SO_4^-, 0.5 wt% IOS_{15-18}, 2 wt% SBA, 1 wt% sodium tetrametaborate pentahydrate, and 4.3 wt% NaCl. This formulation was also found to show good phase behavior with McElroy crude as shown from solubilization ratio plots in Figures 5.5 and 5.6. Note that 4.6 wt% NaCl is the optimal salinity shown in Figure 5.5. Figure 5.6 shows fast equilibration.

Core Preparation

Texas Crème Limestone cores of three inches in length and one inch diameter were drilled from a source block. Cores were then dried, weighed, measured, and
vacuumed in a glass cylinder for 1 hour to remove air particles. While still under vacuum, a de-aired brine solution with 3 wt% NaCl and 200 ppm CaCl₂ was then allowed to fill the cylinder, and saturate the cores. Cores were kept in the brine solution for thirty days to achieve ionic equilibrium. Brine saturated cores were then placed in a Hassler core holder, and injected with about 10 pore volumes of a similar brine solution. Following brine flooding, cores were injected with three pore volumes or McElroy crude oil to displace the brine, and achieve residual water saturation conditions. Pressure and flow rate data were recorded throughout the brine and oil flooding processes. After cores were saturated with crude oil, they were immersed a jar filled with crude oil, and allowed to age for 30 days at room temperature (22 C).

**Experimental Setup**

Four prepared cores were sealed at both ends with Teflon® tape to prevent fluid flow from the ends. The cores were then each placed into a Pyrex® 100 mL graduated cylinder, and all four cylinders were fastened together and mounted for CT scanning. Just prior to CT scanning, each cylinder was filled with a different imbibition solution described previous, and sealed with paraffin. Figure 5.8 shows a picture of the experimental setup.

**CT Scanner**

The High-Resolution X-ray Computed Tomography Facility at the University of Texas at Austin, Department of Geological Sciences was used to conduct natural imbibition experiment.

**Imbibition Experiment**

The natural imbibition experiment was performed for a total of 30 days. CT scans were taken at 1, 2, 3, 4, 8, 15, 22, and 29 days. The CT scanner was used to scan 1 mm thick slices over the middle sections of the cores. A total of 26 slices were scanned, or about one-third of the total core length. CT data was initially processed at the scanning
facility, and then further modified with color to distinguish density contrasts. Figure 5.10 shows an example of two images, where the image on the left was the processed raw CT data, and the image on the right is modified with color to show contrasting densities in the core.

RESULTS AND DISCUSSION

The experimental results of the natural imbibition experiments are shown in a series of processed and colored CT scanner images in Figures 5.11 to 5.15. Figures 5.11 and 5.12 show images from the top and bottom slices after 1, 2, 3, 4, 8, and 15 days. Figures 5.13 and 5.14 show images from the top and bottom slices after 15, 22, and 29 days. Figure 5.15 compares the top, middle, and bottom slices between 1 and 15 days. Note that the color contrasts represent different densities within the core, where blues and greens represent lower density (e.g. oil), and reds and oranges represent higher densities (e.g. water).

Based on color contrasts (i.e. density contrasts) in the cores, there is a general trend showing low densities at 1 to 2 days, higher densities from 3 to 8 days, and lower densities again from 15 days onward. Figures 5.11 and 5.12 show largely blue and green cores at 1 and 2 days significantly change to reds and yellows from 3 to 8 days, which could indicate the imbibition of water into the core. Figures 5.11 and 5.12 also show blue and green colors to return at 15 days, which could indicate that oil has returned to the scanned core section. From 15 to 29 days, cores show little change in color (Figures 5.13 and 5.14), which could indicate that a steady state has been achieved. A steady state scenario is further supported by Figure 5.13 showing only a small amount of color change from 15 to 60 days. Figure 5.15 compares the top, middle, and bottom sections of the scanning region between 1 and 15 days. Assuming that steady-state conditions were achieved after 15 days (from Figures 5.13 and 5.14), Figure 5.15 shows the top section having the least color contrast, and the bottom section having the greatest color contrast. This could indicate a greater amount of water in the bottom section than the top section after steady state conditions have been reached.
An overall interpretation of the images from the CT scanning shows a significant amount of water imbibition for all cores on day 3. The amount of imbibed water present in the middle section is at a maximum around days 3 and 4, and afterwards is slowly replaced by oil. This continues until after day 15 when steady state conditions appear to have been reached. During this process, water uniformly imbibes the scanned middle section of the core, and oil from the bottom portion of the core eventually becomes displaced through buoyancy to the middle and top sections of the core. After reaching equilibrium, the middle section shows a non-uniform distribution of fluids in the core, with the top section containing more oil than water relative to the bottom section.

Although only the middle portion of the core was scanned, the entire core is expected to show a non-uniform distribution of oil and water. A plausible interpretation situation is for the bottom section to contain mostly water, the middle section a combination of oil and water, and the top section a bank of oil that has pooled behind the sealed top of the core.
Table 5.1 - Four different fluid formulations used for the four cores of the imbibition experiment.

<table>
<thead>
<tr>
<th>CORE 1 - Control</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>4.6 wt%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CORE 2 - No Alkali</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C 16/17-7PO-SO4-</td>
<td>1.5 wt%</td>
</tr>
<tr>
<td>IOS 15-18</td>
<td>0.5 wt%</td>
</tr>
<tr>
<td>sec-butanol</td>
<td>2 wt%</td>
</tr>
<tr>
<td>NaCl (optimal salinity)</td>
<td>4.6 wt%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CORE 3 - Sodium Carbonate</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C 16/17-7PO-SO4-</td>
<td>1.5 wt%</td>
</tr>
<tr>
<td>IOS 15-18</td>
<td>0.5 wt%</td>
</tr>
<tr>
<td>sec-butanol</td>
<td>2 wt%</td>
</tr>
<tr>
<td>Sodium Carbonate</td>
<td>1 wt%</td>
</tr>
<tr>
<td>NaCl (optimal salinity)</td>
<td>3.8 wt%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CORE 4 - Sodium Metaborate</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C 16/17-7PO-SO4-</td>
<td>1.5 wt%</td>
</tr>
<tr>
<td>IOS 15-18</td>
<td>0.5 wt%</td>
</tr>
<tr>
<td>sec-butanol</td>
<td>2 wt%</td>
</tr>
<tr>
<td>Sodium Metaborate</td>
<td>1 wt%</td>
</tr>
<tr>
<td>NaCl (optimal salinity)</td>
<td>4.3 wt%</td>
</tr>
</tbody>
</table>
Table 5.2 - A general description of the core and CT scanning information for the natural imbibition experiment.

<table>
<thead>
<tr>
<th>Description</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Height</td>
<td>3 inches</td>
</tr>
<tr>
<td>Diameter</td>
<td>1 inch</td>
</tr>
<tr>
<td>Rock Type</td>
<td>Texas Cream Limestone</td>
</tr>
<tr>
<td>Saturation</td>
<td>Initial 4 wt% NaCl saturation, then saturate with McElroy crude oil to residual water saturation</td>
</tr>
<tr>
<td>Aging</td>
<td>30 days at 21 C</td>
</tr>
<tr>
<td>Scan</td>
<td>1 mm thick slices over the middle 1 inch, total of 26 slices</td>
</tr>
<tr>
<td>Temperature</td>
<td>21 C</td>
</tr>
</tbody>
</table>
Figure 5.1 - Solubilization ratio plot of phase behavior A19 using McElroy crude oil at 30 C. This formulation comprised the ‘No Alkali’ fluid the natural imbibition experiment. The formulation contained 1.5 wt% C_{16-17} –7PO–SO_{4}^{–}, 0.5 wt% IOS_{15-18}, 2 wt% SBA.
Figure 5.2. - Change in solubilization ratios versus time for phase behavior A19 using McElroy crude oil at 30°C. This fluid comprised the ‘No Alkali’ fluid type for the natural imbibition experiment. The formulation contained 1.5 wt% C_{16-17}–7PO–SO_{4}^{−}, 0.5 wt% IOS_{15-18}, 2 wt% SBA, and was evaluated at 4.5 wt% NaCl (near optimum).
Figure 5.3 - Solubilization ratio plot of phase behavior A21 using McElroy crude oil at 30 C. This formulation comprised the ‘Sodium Carbonate’ fluid the natural imbibition experiment. The formulation contained 1.5 wt% C_{16-17} – 7PO–SO_{4}^{-}, 0.5 wt% IOS_{15-18}, 2 wt% SBA, and 1 wt% Na_{2}CO_{3}. 
Figure 5.4. - Change in solubilization ratios versus time for phase behavior A21 using McElroy crude oil at 30°C. This fluid comprised the ‘Sodium Carbonate’ fluid type for the natural imbibition experiment. The formulation contained 1.5 wt% C_{16-17}–7PO–SO_4, 0.5 wt% IOS_{15-18}, 2 wt% SBA, and 1 wt% Na_2CO_3, and was evaluated at 3.75 wt% NaCl (near optimum).
Figure 5.5 - Solubilization ratio plot of phase behavior A22 using McElroy crude oil at 30 C. This formulation comprised the ‘Sodium Metaborate’ fluid the natural imbibition experiment. The formulation contained 1.5 wt% \( \text{C}_{16-17} - 7\text{PO-SO}_4^- \), 0.5 wt% IOS\(_{15-18}^-\), 2 wt% SBA, and 1 wt% NaMetaborate.
Figure 5.6. - Change in solubilization ratios versus time for phase behavior A22 using McElroy crude oil at 30°C. This fluid comprised the ‘Sodium Metaborate’ fluid type for the natural imbibition experiment. The formulation contained 1.5 wt% C_{16-17} -7PO–SO_4^- , 0.5 wt% IOS_{15-18} , 2 wt% SBA, and 1 wt% NaMetaborate, and was evaluated at 4.25 wt% NaCl (near optimum).
Figure 5.7 - An example imbibition experiment using a brine solution and a surfactant formulation.
Figure 5.8 – Experimental setup for the natural imbibition experiment using the CT scanner.
Figure 5.9 – Simple diagram showing how imbibition cores were sealed at the top and bottom, and only the middle one-third of the core was scanned.
Figure 5.10 – Example CT scan and processed image of a 1 mm thick slice of each core.
Figure 5.11 – Processed CT scanner images up to 15 days for the top slice. Blues greens represent a lower density region (e.g. oil present), and reds and oranges represent higher density regions (e.g. water present).
Figure 5.12 – Processed CT scanner images up to 15 days for the bottom slice. Blues greens represent a lower density region (e.g. oil present), and reds and oranges represent higher density regions (e.g. water present).
Figure 5.13 – Processed CT scanner images for 15 days and longer of the top slice. Blues greens represent a lower density region (e.g. oil present), and reds and oranges represent higher density regions (e.g. water present).
Figure 5.14 – Processed CT scanner images for 15 days and longer of the bottom slice. Blues greens represent a lower density region (e.g. oil present), and reds and oranges represent higher density regions (e.g. water present).
Figure 5.15 – Processed CT scanner images comparing top, middle, and bottom slices at 1 day and 15 days. Blues greens represent a lower density region (e.g. oil present), and reds and oranges represent higher density regions (e.g. water present).
CHAPTER 6: SUMMARY AND CONCLUSIONS

SUMMARY

This chapter discusses some of the important knowledge learned from the phase behavior and core flood research. The research helped to understand many of the objectives that motivated this work in the field of chemical EOR. A systematic study with phase behavior experiments helped understand how different chemical components and environmental conditions affect microemulsion properties and phase behavior performance. This information was then used to develop a strategic design methodology for screening and optimizing chemical formulations for a crude oil of interest. The surfactants Petrostep S1 (C_{16-17} – 7PO – SO_4^-) and Petrostep S2 (IOS_{15-18}) provided by Stepan offered very good performance in microemulsion phase behavior, and in oil recovery from actual rock core. The performance of a mixture of these two surfactants was successfully validated in a core flood experiment by recovering nearly 100% of the water flood residual oil.

PHASE BEHAVIOR

A strategic design methodology based primarily on phase behavior was successful in developing a formulation that performed well with Crude D. The design process first selected a primary surfactant, co-surfactant, and co-solvent based on previous research at the University of Texas. Without previous research, testing several surfactant, co-surfactant, and co-solvent structures would have been performed individually, which shows the importance of having a chemical EOR database as a starting point for a formulation design. The surfactant and co-surfactant were first optimized with respect to their concentration ratio, and then the best performing ratio was considered for further design. The co-solvent concentration was then reduced to a low concentration that still showed good phase behavior performance. Concentrations of surfactant, co-surfactant, and co-solvent were then all reduced proportionately to observe dilution effects. The addition of alkali was then tested and evaluated as an alternative for chemical flooding. After performing this methodology, an optimal formulation for Crude D was designed
that showed good phase behavior performance and thus was ready to test in a core flood experiment and expected to perform well based upon previous experience.

**CORE FLOOD**

A core flood experiment was performed to validate the performance of an optimized phase behavior formulation design, and its ability to recover residual oil (Crude D) from Berea Sandstone. The validation was a means to test whether a selected chemical formulation performing well in phase behavior was capable of performing well in a core. The core flood experiment using the designed formulation was successful in recovering nearly 100% of residual oil remaining in the core after water flooding.

The core flood performed in this research demonstrated that properly selected, high-performance surfactants can reduce the water flood residual oil saturation in a core to less than 1% even when displacing a formation brine of high TDS and hardness without a pre-flood and with very low surfactant adsorption. The salinity contrast between the synthetic formation brine and the surfactant slug at the displacement front did not significantly hinder the oil recovery process. Conductivity analysis of core effluent showed surfactant breakthrough in the Type III region, and slowly grading into the Type I region with the polymer drive. A large oil bank with high oil cut was produced before the surfactant displacement front, which accounted for about 80% of the produced residual oil. This core flood shows very clearly the robustness of a chemical flood with a properly designed salinity gradient.

**SPONTANEOUS IMBIBITION**

The same surfactants that performed well in the Berea sandstone core flood were tested in a novel imbibition experiment to determine their behavior in a low-permeability limestone core. The natural imbibition study used CT scanning technology to remote sense fluid imbibition processes inside of the rock. Different imbibition fluids consisted of brine control and several surfactant formulations. This study on natural imbibition
processes in porous media is to evaluate the ability of the optimum chemical formulations identified from the phase behavior enhance water imbibition.

CT images successfully showed changes in density within the scanned rock over time, which indicated an interchange of fluids (oil and water) of different densities. The images showed the density increased (e.g. water imbibition) after about 3 days, followed by a density decrease (e.g. mobilized oil within the core) after about 15 days. The conclusion was that water initially imbibed uniformly into the limestone, and then oil later flowed from the bottom to the top under the buoyancy force. No oil was produced from the top since it was sealed, and oil either pooled behind the seal, or flowed out of the sides of the core.

GENERAL CONCLUSIONS

An increasing worldwide demand for crude oil is making many oil reservoirs viable candidates for chemical EOR. Although chemical flooding has the potential to achieve very high oil recoveries, it is complex, and can require extensive laboratory testing and expertise for a successful design and implementation. Additionally, many types of reservoir have problematic characteristics such as: high temperature, low permeability, fractures, high formation brine salinity and hardness and/or high oil viscosity that make it challenging to develop an economic process. Research and understanding into all of these challenging characteristics is important to expand the potential candidate reservoirs for chemical EOR application.

This research has demonstrated how a good design methodology provides an optimal chemical formulation based on phase behavior data, and validated in core flood experimentation. As a practical design application, this research specifically addressed reservoirs with formation brine having high salinity and hardness, with the objective of contributing to future commercial projects with these types of reservoirs. Hopefully this research has helped continue the advancement of chemical EOR research in the Center for Petroleum and Geosystems Engineering at the University of Texas.
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