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SURFACTANT/POLYMER FLOOD DESIGN FOR A HARD BRINE LIMESTONE RESERVOIR

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Epigraph

“La tierra es redonda como una naranja”

-Gabriel Garcia Marquez
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Abstract

Surfactant/Polymer Flood Design for a Hard Brine Limestone Reservoir

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A limited number of laboratory studies and pilot programs have been reported in chemical Enhanced Oil Recovery (EOR) flooding of carbonate reservoirs (Adams & Schievelbein, 1987). Fewer still have involved surfactants in limestone reservoirs. No surfactant/polymer flood on a field wide basis of a carbonate reservoir has ever been documented in the literature (Manrique, Muci, & Gurfinkel, 2010). This void represents a colossal opportunity given that nearly a third of the 32 billion barrels of oil consumed in the world each year come from carbonate reservoirs (Sheng, 2011, pp. 1, 254).

This thesis is based on experiments with a high hardness (~5,000 ppm divalent ions) carbonate field. Phase behavior, aqueous stability, and core flood experiments were performed using polymer and various surfactants and co-solvents. Both commercially available and laboratory synthesized surfactants were tested. The objective was to optimize the chemical injection design in order to lower interfacial tension between water and oil in the reservoir. Research was also done with alkali intended for use with hard brines.

The main challenges when working with hard brine were poor solubilization and low aqueous stability limits. However, highly propoxylated and ethoxylated surfactants mixed with internal olefin sulfonates, hydrophilic sulfates, and sec-butanol were observed to have very high solubilization ratios, fast phase behavior equilibration times, negligible
viscous macroemulsion effects, and excellent aqueous stability. Spinning drop interfacial
tensiometer tests confirmed low IFT values were obtained for a range of acceptable salinities with hard brine.

Three core floods were performed using one of the surfactant formulations developed. One flood was done with field core, brine, and crude oil and failed to meet expectations because of high levels of heterogeneity (vugs) within the core that lead to an elongated oil bank and low and slow oil recovery. The other floods were done with Estillades Limestone. The first Estillades flood used hard synthetic field brine and had better mobility but poor oil recovery. The last core flood had good mobility and recovered 90% of the residual oil to water flooding, but only after a total of 1.1 pore volumes of 1.0 wt% surfactant solution were injected. The results provided in this thesis constitute proof of concept that S/P flooding can be done in high salinity and hardness reservoirs.
APPENDIX .................................................................................................................. 253

BIBLIOGRAPHY ........................................................................................................... 298
LIST OF TABLES

Table 2.1: HLB group number by chemical structure ......................................................... 10
Table 2.2: Influence of fluid properties on phase behavior and aqueous stability. .................. 31
Table 5.1: Brine Chemistry Analyses .................................................................................... 82
Table 5.2: New Synthetic Field Brine .................................................................................... 83
Table 5.3: List of surfactants used in experiments. ................................................................. 85
Table 5.4: Abbreviations for chemical structures ................................................................. 85
Table 5.5: Comparison between total molar ion concentration between the water analyses.... 100
Table 5.6: Phase behavior experiments with hard and soft brines. ...................................... 116
Table 5.7: Aqueous stability experiments with hard and soft brines .................................... 116
Table 6.1: ECU core plug porosity and permeability ............................................................ 188
Table 6.2: Summary of EOR Floods. ..................................................................................... 205
Table 6.3: EOR coreflood results after 2 PV of chemical injection. ..................................... 206
Table 7.1: Sodium acetate pH experiments at 43.3 degrees Celsius. .................................. 239
Table 7.2: EDTA pH experiments. ......................................................................................... 239
Table 7.3: Characterization of brines used in pH experiments............................................. 240
Table 7.4a: EDTA-4Na at 43.3 degrees Celsius ................................................................. 241
Table 7.4b: EDTA-4Na at 43.3 degrees Celsius (continued) ............................................. 242
Table 7.5a: EDTA-4Na at 23 degrees Celsius ................................................................. 243
Table 7.5b: EDTA-4Na at 23 degrees Celsius (continued) ............................................. 244
Table 7.6a: EDTA-4Na at 43.3 degrees Celsius (hysteresis) ........................................... 245
Table 7.6b: EDTA-4Na at 43.3 degrees Celsius (hysteresis, continued) ......................... 246
Table 7.7: pH measurements at four temperatures ............................................................ 247
Table A.1: Experiments PB 1 through PB 19 ................................................................. 253
Table A.2: Experiments PB 20 through PB 28 ................................................................. 254
Table A.3: Experiments PB 29 through AS 37 ................................................................. 255
Table A.4: Experiments AS 38 through PB 46A ................................................................. 256
Table A.5: Experiments AS 47 through PB 51B ................................................................. 257
Table A.6: Experiments PB 52 through AS 61A ................................................................. 258
Table A.7: Experiments PB 62 through AS 65BA ............................................................. 259
Table A.8: Experiments AS 65C through AS 66G ............................................................. 260
Table A.9: Experiments AS 66H through PB 66Q ............................................................. 261
Table A.10: Experiments AS 66S through PB 69 ............................................................... 262
Table A.11: Experiments PB 70 through PB 75 ................................................................. 263
Table A.12: Experiments PB 76 through AS 77G ............................................................. 264
Table A.13: Experiments PB 78 through PB 81 ................................................................. 265
Table A.14: Experiments PB 82 through PB 90 ................................................................. 266
Table A.15: Experiments AS 91 through PB 98 ................................................................. 267
Table A.16: Experiments PB 99 through PB 108 ............................................................... 268
Table A.17: Experiments PB 109C through AS 116 ........................................................... 269
Table A.18: Experiments AS 117 through PB 124. ................................................................. 270
Table A.19: Experiments AS 124A through AS 131. ............................................................... 271
Table A.20: Experiments AS 132 through AS 141. ................................................................. 272
Table A.21: Experiments AS 142 through AS 148. ................................................................. 273
Table A.22: Experiments AS 149 through AS 157. ................................................................. 274
Table A.23: Experiments AS 158 through AS 163. ................................................................. 275
Table A.24: Experiments AS 164 through AS 169. ................................................................. 276
Table A.25: Experiments PB 169A through PB 177A. ............................................................. 277
Table A.26: Experiments AS 178 through PB 182A. ................................................................. 278
Table A.27: Experiments AS183 through AS 187. ................................................................. 279
Table A.28: Experiments AS 188 through AS 193. ................................................................. 280
Table A.29: Experiments AS 194 through AS 202. ................................................................. 281
Table A.30: Experiments AS 203 through AS 210. ................................................................. 282
Table A.31: Experiments AS 211 through PB 215B. ............................................................... 283
Table A.32: Experiments PB 215C through PB 217A. ............................................................. 284
Table A.33: Experiments AS 218 through AS 222. ................................................................. 285
Table A.34: Experiments PB 223 through AS 230BB. ............................................................ 286
Table A.35: Experiments PB 230CC through PB 236A. ......................................................... 287
Table A.36: Experiments PB 237 through AS 242A. ............................................................... 288
Table A.37: Experiments AS 242B through PB 243. ............................................................... 289
Table A.38: Experiments PB 244 through AS 247A. ............................................................... 290
Table A.39: Experiments AS 247B through PB 250A. ............................................................. 291
Table A.40: Experiments AS 251 through PB 254A. ............................................................... 292
Table A.41: Experiments AS 255 through AS 259. ................................................................. 293
Table A.42: Experiments PB 259A through AS 264. ............................................................... 294
Table A.43: Experiments PB 264A through PB 270. ............................................................... 295
Table A.44: Experiments PB 271 through AS 286. ................................................................. 296
Table A.45: Experiments AS 287 through AS 310. ................................................................. 297
LIST OF FIGURES

Figure 1.1: Capillary desaturation curve (Lake, 1989) ................................................................. 4
Figure 1.2: Capillary desaturation curves for four carbonate rocks ................................................ 4
Figure 2.1: Phase behavior microemulsion types ........................................................................ 16
Figure 3.1: Solubility of CaSO4 versus ionic strength of aqueous solutions ............................... 36
Figure 3.2: Solubility of SrSO4 versus ionic strength of aqueous solutions ............................ 36
Figure 3.3: Solubility of BaSO4 versus ionic strength of aqueous solutions ............................ 37
Figure 3.4: The effect of calcium on interfacial activity of aqueous systems with 5 percent sulfonate at 160°F ................................................................. 42
Figure 4.1: Core flood experimental setup ................................................................................... 79
Figure 5.1: SSFB vs. NaCl ionic strength equivalent ................................................................. 185
Figure 5.2: PB 18. After 11 weeks in the oven ......................................................................... 122
Figure 5.3: PB 9 after 15 weeks at 43.3°C. WOR=1. S*=~2.25 wt% TDS ........................... 123
Figure 5.4: PB 5 after 22 weeks at 43.3°C. WOR=1. S* between 1.80 and 2.20 wt% TDS. Viscous macroemulsions at 3.75 wt% TDS and above ................................. 124
Figure 5.5: PB 21 after 13 weeks in the oven .......................................................... 125
Figure 5.6: PB 6 after 25 weeks at reservoir temperature at 43.3°C. WOR=1. S*=~2.25 wt% TDS. Viscous macroemulsions at 4.50 wt% TDS and above ........................... 125
Figure 5.7: PB 3. WOR=1. S* around 1.5 wt% TDS. Viscous macroemulsions at 2.25 wt% TDS and above ........................................................................ 126
Figure 5.8: AS 34. Different surfactants in ECU Field Brine at reservoir temperature (43.3 °C) after agitation ................................................................. 126
Figure 5.9: AS 35. Sodium metaborate trials in ECU Field brine at 43.3 °C after agitation ...... 127
Figure 5.10: AS 44 indicating at least 0.8125 wt% N-25-12 is needed to prevent precipitation. 128
Figure 5.11: PB 56A. After 6 weeks in the oven ........................................................................ 129
Figure 5.12: PB 59. After 7 weeks in the oven ........................................................................... 130
Figure 5.13: AS 59A in NaCl brine ......................................................................................... 131
Figure 5.14: PB 64CA. After 7 weeks in the oven ................................................................. 132
Figure 5.15: PB 65 after 43 weeks in the oven .......................................................................... 133
Figure 5.16: PB 65AA after 7.5 weeks in the oven ................................................................. 134
Figure 5.17: AS 65BA. Phase separation at 4.5 wt% ............................................................ 135
Figure 5.18: AS 65C. Phase separation at 6.0 wt% ............................................................... 135
Figure 5.19: PB 66r after 7.5 weeks in the oven ................................................................. 136
Figure 5.20: PB 66r analysis ............................................................................................... 137
Figure 5.21: AS 66A with NaCl brine. All vials are stable ..................................................... 138
Figure 5.22: PB 66M after 13 weeks at reservoir temperature ................................................. 139
Figure 5.23: PB 66N after 13 weeks at reservoir temperature .................................................... 140
Figure 5.24: PB 69 after 5 weeks in the oven ......................................................................... 141
Figure 5.25: PB 70 after 5 weeks in the oven. 0.05 wt% less C9 than PB 69, but all type II with macroemulsions ......................................................................... 142
Figure 5.26: PB 74 after 33.5 weeks in the oven. More C9 and some co-solvent ................. 143
Figure 7.21: EDTA
Figure 7.20: pH trend with temperature at 5.0 wt% EDTA
Figure 7.19: pH trend with temperature at 0.50 wt% EDTA
Figure 7.18: pH trend with temperature at 0.25 wt% EDTA
Figure 7.17: EDTA
Figure 7.16: EDTA
Figure 7.15: EDTA
Figure 7.14: EDTA
Figure 7.13: EDTA
Figure 7.12: EDTA
Figure 7.11: EDTA
Figure 7.10: EDTA
Figure 7.9: EDTA
Figure 7.8: EDTA
Figure 7.7: EDTA
Figure 7.6: Wt% EDTA
Figure 7.5: EDTA
Figure 7.4: pH dependence on EDTA
Figure 7.3: AS 231. Sodium metaborate in formation
Figure 7.2: AS 230. Sodium acetate pH in different brines.
Figure 6.11: Viscosity data of EOR fluids at 43.3°C
Figure 6.10: Second Estillades SP EOR core flood pressure results.
Figure 6.9: Second Estillades SP EOR core flood produced oil results.
Figure 6.8: Estillades #2 water flood.
Figure 6.7: Assumed Estillades #1 Core relative permeability curves with n=2.
Figure 6.6: First Estillades SP EOR core flood produced oil results.
Figure 6.5: Estillades #1 water flood.
Figure 6.4: Assumed ECU core relative permeability curves with n=2 (for the first oil and water floods).
Figure 6.3: Eliasville Caddo Unit SP (PB 242) EOR core flood produced oil results.
Figure 6.2: Assumed ECU plugs used in the field core surfactant-polymer EOR floods.
Figure 5.75: AS 247B IFT with FB #1 augmented by SSFB.
Figure 5.74: AS 247A IFT with SSFB.
Figure 5.73: AS 246 IFT with SSFB.
Figure 5.72: AS 242D IFT with FB #1 augmented by SSFB.
Figure 5.71: AS 242C IFT with NaCl brine.
Figure 5.70: AS 242B IFT with SSFB.
Figure 5.69: AS 242A IFT with SSFB.

7.1: Sodium acetate pH in different brines.
7.2: AS 231. Sodium metaborate in formation brine #2. All samples precipitate.
7.3: pH dependence on EDTA-4Na concentration and Mg++, Ca++, and Sr++ salts at 43.3°C.
7.4: EDTA-4Na needed for pH 7.0 at 43.3°C.
7.5: EDTA-4Na:divalent ion chelating ratio dependency with divalent ion type and concentration at 43.3°C.
7.6: Wt% EDTA-4Na to wt% divalent ion for different brines at pH 7.0 and 43.3°C.
7.7: Wt% EDTA-4Na to divalent ion chelating ratio trends at pH 7.0 and 43.3°C.
7.8: EDTA-4Na Temperature effect on pH in 0.5 wt% MgCl2 (AS 287).
7.9: EDTA-4Na Temperature effect on pH in 1.0 wt% MgCl2 (AS 288).
7.10: EDTA-4Na Temperature effect on pH in 1.5 wt% MgCl2 (AS 289).
7.11: EDTA-4Na Temperature effect on pH in 3.0 wt% MgCl2 (AS 290).
7.12: EDTA-4Na Temperature effect on pH in 1.0 wt% SrCl2 (AS 296).
7.13: EDTA-4Na Temperature effect on pH in 3.0 wt% SrCl2 (AS 298).
7.14: EDTA-4Na Temperature effect on pH in 5.5 wt% SSFB (AS 230AA).
7.15: EDTA-4Na Temperature effect on pH in 3.0 wt% CaCl2 (AS 284).
7.16: EDTA-4Na Temperature effect on pH in 1.0 wt% CaCl2 (AS 286).
7.17: pH trend with temperature at 0.25 wt% EDTA-4Na.
7.18: pH trend with temperature at 0.50 wt% EDTA-4Na.
7.19: pH trend with temperature at 5.0 wt% EDTA-4Na.
7.20: EDTA-4Na with 1.0 wt% MgCl2; pH hysteresis due to temp (AS 288).
Figure 7.22: EDTA-4Na with 1.5 wt% MgCl2; pH hysteresis due to temp (AS 289) ............ 230
Figure 7.23: EDTA-4Na with 3.0 wt% MgCl2; pH hysteresis due to temperature (AS 290). .... 231
Figure 7.24: EDTA-4Na pH dependence on magnesium brine mixtures at 43.3°C. ............... 232
Figure 7.25: EDTA-4Na pH dependence on calcium brine mixtures at 43.3°C. .................. 233
Figure 7.26: Sodium metaborate pH dependence on divalent ion type and concentration and alkali concentration. .................................................................................................................. 235
Figure 7.27: Sodium metaborate pH dependence on magnesium brine mixtures. ............... 236
Figure 7.28: Sodium metaborate pH dependence on calcium brine mixtures. .................... 237
CHAPTER 1: INTRODUCTION

1.1 The Importance of EOR

The term Chemical Enhanced Oil Recovery is used in the petroleum industry literature to refer to a class of tertiary oil recovery. Chemical EOR is usually done after primary recovery (or natural depletion from expansion of reservoir fluids and reservoir compaction) and secondary waterflood recovery. However, Chemical EOR does not need to be performed last. It has been found that the earlier EOR is deployed, the larger the amount of hydrocarbons produced (Alvarado & Manrique, 2010, p. 5). In Wyoming, a polymer augmented alkaline flood was found to have a “considerably faster return on investment than any other process” for the production interval (Doll, 1988).

Tertiary recovery of oil is usually employed after a reservoir has been waterflooded for a number of years. Waterflooding is a process whereby water is injected into a reservoir to provide pressure support and to sweep oil to production wells. In time, the oil produced as a percentage of total liquids production will decline. Eventually the oil cut will become uneconomical. At this point, the reservoir is considered to be at residual oil saturation to waterflood.

There is, however, still oil in the reservoir that has been left behind either because it was not contacted and swept to a producer, or because it was cut off and isolated due to phase trapping mechanisms, primarily capillary forces.

1.2 A Brief Overview of Chemical EOR

The purpose of Chemical EOR is to recover the remaining oil in a reservoir that has had its mobile oil swept and produced during a waterflood. To achieve this objective, oil needs to be contacted and mobilized. Oil can be contacted by improving the sweep efficiency of injected fluids. One way to do improve sweep efficiency is to increase the viscosity of the injected fluid relative to the connate fluids. This provides a more
favorable mobility ratio, helps prevent viscous fingering, and helps to overcome reservoir heterogeneities (Sorbie, 1991). Mobility is defined as:

\[ \lambda = \frac{\mu}{k} \]  

Where \( \mu \) is the fluid viscosity and \( k \) is the permeability of the media to the fluid. The mobility ratio is defined as:

\[ M = \frac{\lambda_o}{\lambda_w} = \frac{\mu_o k_w}{\mu_w k_o} \]  

Where \( k_w \) and \( k_o \) are the water and oil relative permeabilities, respectively.

Mobilizing phase trapped oil is another way to recover additional petroleum resources from a reservoir. Oil is trapped in a reservoir by capillary forces, buoyancy forces, and viscous forces caused by a hydraulic gradient. For an oil globule to move, the following inequality must be true:

\((Viscous \ Force) + (Buoyancy \ Force) \geq (Capillary \ Force)\)

If a force balance is done on a trapped oil globule, the result is the trapping number, which is defined as:

\[ N_{T_\ell} = \frac{|\vec{k} \cdot [\nabla \Phi_\ell + g(\rho_\ell - \rho_\ell)\nabla D]|}{\sigma_{\ell\ell'}} \]  

Where \( \vec{k} \) is the permeability tensor, \( \Phi \) the potential, \( g \) is gravity, \( \rho \) the density, \( D \) the displacement vector, and \( \sigma \) the interfacial tension. \( \ell \) denotes the direction of the capillary force acting on the globule. A derivation of the trapping number can be found in Jin Minquan’s Doctoral Thesis (Minquan, 1995).

The capillary number is another way to understand the physical conditions impacting oil mobilization. The capillary number is defined as:

\[ N_{c_\ell} = \frac{|\vec{k} \cdot \nabla \Phi_\ell|}{\sigma_{\ell\ell'}} \]  

Which under simplified conditions can be expressed as:

\[ N_c = \frac{u \mu}{\sigma} \]
Where $u$ is the superficial or actual fluid velocity ($u = \frac{v}{\phi}$) in ft/day, $\mu$ the fluid viscosity in cp, and $\sigma$ the interfacial tension in dynes/cm.

Increasing the capillary number can be done by increasing the fluid velocity, increasing the fluid viscosity, or by lowering interfacial tension, or all three. The viscosity of a fluid can be increased by adding polymer. The velocity of the fluid can be increased by augmenting the rate of fluid injection, but this will cause a commensurate rise in the injection pressure. This rate of injection- and thus fluid velocity- will be limited by the formation rock’s fracture pressure. High flow rates (10 feet per day) can be obtained near in the wellbore region (up to perhaps 20 feet away from the wellbore), but the flow rate will decrease at increasing distances from the injection or production wells. The typical assumed velocity of fluids in the middle of a reservoir is 1 ft/d. The last variable in the capillary number is the interfacial tension (IFT). Oil will be mobilized at an ultra low IFT value of 0.001 dynes/cm or lower (Morgan, Schechter, & Wade, 1977, p. 102). The interfacial tension can be decreased with the addition of surface active agents, otherwise known as surfactants, to the fluid. Surfactants will be covered in more detail later.

The impact of increasing the capillary number on oil production can be observed from a capillary desaturation curve (Figure 1.1). As can be seen, for sandstones, there is a critical capillary number above which residual oil saturation decreases dramatically. The behavior of carbonates (Figure 1.2) can be very different. As seen in Figures 1 and 2, carbonates do not have sharp declines in residual saturation, but continually decline with an increasing capillary number. (Stegemeier, 1976). The difference between clastics and carbonates is likely due to the permeability, pore shape, and wettability of the rocks, which are fundamentally different in the two formation types.
Figure 1.1: Capillary desaturation curve (Lake, 1989).

Figure 1.2: Capillary desaturation curves for four carbonate rocks (Kamath, Meyer, & Nakagawa, 2001)

Connate and injection brine chemistry, formation rock composition and wettability, formation heterogeneity, and reservoir temperature and pressure also influence the success of a chemical EOR regime. Properties of the connate and injection
brines, including electrolyte composition and how it varies in the reservoir, influence surfactant behavior in terms of its ability to generate low IFT and to remain soluble. Brine composition also influences the viscosity of polymer solutions. The pH of the injection brine also has the ability to cause unfavorable precipitous reactions within the formation, generate in situ soaps, change rock wettability, influence surfactant and polymer molecular stability, and influence surfactant adsorption. The formation rock composition, including clays and evaporites such as gypsum or anhydrite, negatively influence the adsorption behavior of surfactants. Clays and evaporites also can react with injected water and dissolve, migrate, and cause scale build up and permeability reduction in the reservoir. A formation rock’s wettability influences the nature of oil distribution within pore spaces and the residual oil saturation to waterflooding. A water wet rock will have water in the smaller pores and oil in the larger, which means that the capillary forces on the oil will be lower (Peters, 2012, p. 59). A water wet rock is thus preferred for oil recovery. Formation heterogeneity includes properties such as mineral composition, dip angle, porosity, layering, formation thickness, fluid saturations, and areal and directional permeability. Finally, the pressure and temperature of a reservoir can influence the solubility of injected chemicals and their molecular stability.

1.3 Project Description and Objectives

The focus of this thesis is the design of a surfactant/polymer flood for a carbonate reservoir with a high hardness brine. The Eliasville Caddo Unit reservoir lies within the Caddo lime formation in North Texas. The field was economically polymer flooded in the early 1980’s and production has fallen off since then. As such, the reservoir is a target of tertiary oil recovery and it was decided that the reservoir be surfactant/polymer flooded to recover as much of the remaining oil as possible. The objectives of this project are to:

- Obtain clear aqueous stability at reservoir conditions
- Obtain ultralow interfacial tension at reservoir conditions
- Limit the amount of chemicals that are necessary for project completion
- Recover the maximum amount of oil

To achieve these objectives, aqueous stability tests were performed with synthetic formation brine at reservoir temperature on hundreds of chemical mixtures to ensure that no precipitations, phase separations, scales, or other negative effects would occur in the reservoir. Phase behavior experiments were also performed with synthetic formation brine at reservoir temperature to determine the optimum salinity of the system and the interfacial tension. Once a suitable chemical solution was obtained, core flood experiments with reservoir core plugs at reservoir temperature were done.

1.4 Summary and Conclusions

This chapter detailed the importance of enhanced oil recovery and introduced some of the known concepts that control chemical EOR. Project objectives and descriptions were given for the S/P design and Gemini surfactant core flooding portions of this thesis. An outline of this thesis will now be given.

**Chapter 2** introduces the particulars of alkali/surfactant/polymer design. It details different properties of alkalis, surfactants, co-solvents, and polymers and how these properties influence the design’s behavior. Special attention is given to describing phase behavior and aqueous stability experiments. Additional information is then provided on core flooding and pilot scale flooding.

**Chapter 3** is concerned with chemical enhanced oil recovery in carbonate reservoirs. The chapter identifies some key differences between siliciclastic and carbonate reservoirs. It also explains the challenges of carbonate formations with a focus on hard brines. Properties of hard brines and how they influence the different aspects of chemical EOR are discussed.

**Chapter 4** details the experimental methodology used to achieve the stated project objectives. Descriptions of how aqueous stability, phase behavior, and core floods
were performed are given in this chapter. This includes both the equipment used and the methodology.

A description and summary of aqueous stability, phase behavior, and interfacial tension experiments for the Eliasville Caddo Unit S/P flood are given in Chapter 5. This chapter also contains the characterization of the field brine samples and synthetic brines used. The end result of this experimental work was the chemical slug design that was recommended for core flood testing.

The results of core flooding experiments are presented in Chapter 6. This chapter also gives details of the ECU geology, oil, development, and other field properties. Polymer rheology is also presented for the different polymer concentrations used in synthetic and field brines at different salinities.

Chapter 7 presents research done with alkali in hard brines. The focus of this research was on establishing the aqueous stability and pH properties of two alkalis that had been proposed in the literature as being acceptable for use with hard brines. pH trends with divalent ion type, concentration, and mixture with monovalent ions was explored. pH trends with temperature and alkali concentration were also investigated.

The final chapter of this thesis is a summary and conclusion.
CHAPTER 2: CHEMICAL EOR BASICS

2.1 Introduction

This chapter seeks to inform the reader on the chemicals and standard experiments involved in EOR. First, each of the main chemicals—alkali, surfactants, cosolvents, and polymers—are introduced and their properties explained. Later, aqueous stability, phase behavior, and core flood experiments are described. The interactions of the chemicals within each experiment are explained, as are how reservoir conditions such as crude oil properties, brine salinity, brine hardness, temperature, and pressure can affect the results.

2.2 EOR Chemicals Characterization

2.2.1 Properties of surfactants

The basic configuration of a surfactant is a hydrophobic tail connected to a head group. The hydrophobic tail is generally an alcohol or hydrocarbon and can vary in length. In general, the longer the hydrophobe, the more hydrophobic the surfactant. Branching and other structures in the hydrophobe can influence the surfactant’s properties and will be discussed later in this section. The head group of the surfactant influences aqueous solubility and is the predominant influence in surfactant adsorption to rock surfaces (Sheng, 2011, p. 239). There are four fundamental types of surfactants which are categorized by the head group: cationic, anionic, non-ionic, and zwitterionic. Cationic surfactants have a positively charged head group, whereas anionic and non-ionic surfactants are negatively and neutrally charged respectively. Zwitterionic surfactants have variable electric potential based on brine pH. Anionic and non-ionic are the most commonly used surfactants in chemical EOR, predominantly because cationic surfactants interact strongly with electric double layer of many clastic reservoir minerals resulting in high adsorption rates (Sheng, 2011, p. 239). Cationic surfactants are sometimes used in
carbonates to alter rock wettability from oil wet to water wet. More information on alkali and surfactant adsorption and wettability alteration can be found in Hirasaki and Zhang (2003).

The Critical Micelle Concentration (CMC) is the requisite concentration of surfactant that allows micelles to form. When IFT is plotted versus surfactant concentration, the IFT is observed to decrease monotonically with increasing surfactant. However, at a certain concentration there is a discontinuity in the curve and IFT is observed to be relatively constant with increasing surfactant concentration. The surfactant concentration at this discontinuity is the CMC. Discontinuities in osmotic pressure, turbidity, and molar conductivity are also observed at the CMC. Critical micelle concentrations can be lowered by increasing the length of the hydrophobic tail of a surfactant, lowering the solution temperature, or adding ions to the solution. For more information, the reader is referred to Introduction to Colloid and Surface Chemistry (Shaw, 1980, pp. 79-81).

The Krafft point is the temperature at which phase separated surfactant will solubilize as the solution temperature is increased. Micellisation is inhibited below the Krafft point because unassociated surfactant is insoluble. As the temperature is increased, the surfactant becomes more soluble and micelles can form when the critical micelle concentration (CMC) has been reached at the Krafft point. Large amounts of surfactant can then be dispersed in the micelles and the solubility of the surfactant is observed to increase dramatically (Shaw, 1980, p. 87).

The cloud point is the temperature at which surfactant phase is no longer able to completely be solubilized by the aqueous phase. It is visually recognized with the solution becoming cloudy or phase separating. The cloud point is important for surfactants that exhibit reverse solubility behavior with increasing temperature. Such surfactants include molecules with polyoxy ethylene (PO) components and non-ionic surfactants (Sheng, 2011, p. 242).

The Hydrophilic-Lipophilic Balance (HLB) is a useful method for characterizing the hydrophobicity of a surfactant. It is a means for quantifying the interaction energy
with aqueous and oil phases that helps to more quickly identify appropriate surfactants for a given system. The HLB number varies between 0 and 20 (or sometimes even higher) and can be calculated as:

$$\text{HLB} = 7 + \sum (\text{hydrophilic group numbers}) - \sum (\text{lipophilic group numbers})$$

2.1

HLB values between 3-6 are considered emulsifiers of W/O (water in oil) emulsions. HLB values of 7-9 are considered wetting agents, and values from 8-18 are considered emulsifiers of O/W (oil in water) emulsions (Stein, 1996, pp. 163-165). HLB values are not constant; they vary slightly based on electrolyte concentration (Davies & Rideal, 1961, p. 375). The accepted hydrophilic and hydrophobic group numbers for different chemical structures can be found in Table 2.1: (Davies & Rideal, 1961, p. 374). More can be found on the HLB in Kruglyakov (2000).

<table>
<thead>
<tr>
<th>Group</th>
<th>Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrophilic:</td>
<td></td>
</tr>
<tr>
<td>$-\text{SO}_4^-$</td>
<td>38.7</td>
</tr>
<tr>
<td>$-\text{COO}^-$</td>
<td>21.1</td>
</tr>
<tr>
<td>$-\text{COO}^-\text{Na}^+$</td>
<td>19.1</td>
</tr>
<tr>
<td>Sulfonate</td>
<td>11</td>
</tr>
<tr>
<td>Ester (sorbitan ring)</td>
<td>6.8</td>
</tr>
<tr>
<td>Ester (free)</td>
<td>2.4</td>
</tr>
<tr>
<td>$-\text{COOH}$</td>
<td>2.1</td>
</tr>
<tr>
<td>OH $-$ (free)</td>
<td>1.3</td>
</tr>
<tr>
<td>$-\text{O}^-$</td>
<td>1.3</td>
</tr>
<tr>
<td>$-\text{OH}$ (sorbitan ring)</td>
<td>0.5</td>
</tr>
<tr>
<td>Lipophilic:</td>
<td></td>
</tr>
<tr>
<td>$-\text{CH}^-$</td>
<td>0.475</td>
</tr>
<tr>
<td>$-\text{CH}_2^-$</td>
<td>0.475</td>
</tr>
<tr>
<td>$-\text{CH}_3^-$</td>
<td>0.475</td>
</tr>
<tr>
<td>$=\text{CH}^-$</td>
<td>0.475</td>
</tr>
<tr>
<td>Combined:</td>
<td></td>
</tr>
<tr>
<td>$-\text{CH}_2 - \text{CH}_2 - \text{O}^-$</td>
<td>0.33</td>
</tr>
<tr>
<td>$-\text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{O}^-$</td>
<td>-0.15</td>
</tr>
</tbody>
</table>
The typical surfactants considered for chemical EOR are: alcohol propoxy sulfates (APS) with the general formula \( C_x - (PO)_y - SO_4 \), alcohol ethoxy sulfates (AES), internal olefin sulfonates (IOS), alpha olefin sulfonates (AOS), alkyl benzene sulfonates (ABS), alkyl-aryl sulfonates, alkyl-ether sulfates, carboxylates, and Gemini surfactants (Gao, 2012) (Alvarado & Manrique, 2010) (Levitt, 2006) (Flaaten, 2007) (Adkins, Arachchilage, Solairaj, Lu, Weerasooriya, & Pope, 2012). The addition of propoxylene oxide (PO) groups to the alkyl chain serves to make the surfactant molecule more hydrophobic, while the addition of ethylene oxide (EO) groups makes the molecule more hydrophilic. Zhang et al. found that propylene oxide increases the surfactant tolerance to higher salinities and divalent ions (2008). The same can also be said of ethylene oxide. PO groups also improve oil solubilization as do a limited number of EO groups (up to 10). Additional EO groups have been noted to decrease the solubilation ratio (Yang, et al., 2010). Branching of the surfactant molecules serves to increase solubilization and improve aqueous stability. Increasing the alkyl chain length has been reported to decrease the IFT at optimum salinity, but also to decrease the range over which the surfactant is effective (Reed & Healy, 1977, p. 417).

Synergy is also a common phenomenon of surfactant mixtures. It has been observed that when combining unlike surfactants (ABS and IOS, hydrophobic and hydrophilic surfactants, etc.) that the solubilization ratio can be higher than either of the surfactants by themselves. Yang et al. saw synergistic effects and attributed them to varying chains of hydrophobic backbones in their surfactants that matched up with the various crude oil components (2010). Synergy, however has not been fully characterized. Stein Notes that:

Implicit in the HLB system is the hypothesis that mixtures of surfactants behave additively. This is not exactly true, although the effect has been found not to be very pronounced as long as the HLB values between the various surfactants present do not differ too much. If the difference in the
HLB values between the various surfactants present is pronounced, then the surfactants may individually dissolve in the oil and water phases; this makes the composition of the interfacial layer at the oil-aqueous phase interface different from that expected on the basis of the weight average. In such cases, deviations from the additively rule are probable (Stein, 1996, pp. 181-182).

2.2.2 Properties of Co-Solvents

The purpose of co-solvents is to help solubilize surfactant, decrease microemulsion viscosity, and mitigate the effects or presence of macroemulsions. Co-solvents are fluids that are soluble in both polar and non-polar fluids. The degree to which a co-solvent is soluble in one type of fluid or another is dependent on its molecular composition and structure.

There are a wide range of co-solvents that are used or have been evaluated for chemical EOR purposes. The principal ones are alcohols: isopropyl alcohol, isobutyl alcohol, sec-butyl alcohol, methyl alcohol, ethyl alcohol, and isopentyl alcohol. Some of the less commonly used co-solvents include glycols: diethylene glycol monobutyl ether (DGBE) and triethylene glycol monobutyl ether (TGBE). Propy alcohol, penty alcohol, and hexyl alcohol are other potential co-solvents, as are ethoxylated alcohols (Sahni V. M., 2009, p. 43).

Co-solvent has an impact on optimum salinity. Larger solvents with higher molecular weights (like n-pentanol) tend to be more oil soluble and when mixed with surfactants have lower optimum salinities than smaller, lower molecular weight solvents (like methy alcohol). Sheng reports that propanol increases optimum salinity for sulfonate surfactants, while pentanol and hexanol decrease optimum salinity (2011, p. 278). This may be caused by the solvent preferentially increasing the aqueous solubility of surfactants of a specific molecular weight (Morgan, Schechter, & Wade, 1977, p. 115).
2.2.3 Properties of Polymers

The main purpose of including polymers in EOR surfactant flooding is to improve the mobility ratio between the injected and connate fluids. This is particularly important when reservoir heterogeneity is high or the mobility ratio is high. The mobility ratio between surfactant solutions without polymer and oil is typically high for a few reasons. First, adding surfactant changes the relative permeability curves by changing the residual saturations and by increasing the relative permeability values. This in turn causes the mobility ratio to increase. Second, low surface tension results in unstable fluid-fluid interfaces and accentuates the fingering effects caused by a more viscous fluid displacing a less viscous one (Homsy, 1987, p. 286). Third, a microemulsion phase will form between the chemical slug and the oil bank. The microemulsion viscosity depends on its composition of oil and brine, but the viscosity will often be greater than the viscosity of the oil; perhaps many times greater. This leads to the chemical slug unstably displacing the microemulsion phase because of an unfavorable mobility ratio. Thus, polymer is necessary to improve the mobility ratio for all of the reasons listed above.

The two main types of polymer used in chemical EOR are polyacrylamides and polysaccharides. While polysaccharides have better resistance to salinity and brine hardness, their effectiveness can be rapidly diminished by bacteria after injection into a reservoir. The main polymer considered in this thesis is a hydrolyzed polyacrylamide (HPAM). HPAMs have a negative electrical charge. They are typically very large molecules that are viscous because of their branching and electrically repulsive nature. The degree of hydrolysis of a polyacrylamide impacts its characteristics such as water solubility and sensitivity to salinity. High salinities tend to diminish the repulsive forces between polymer molecules due to ionic shielding. Additionally, high ion concentrations cause the polymer molecules to contract, reducing their interaction with each other and decreasing viscosity (Lake, 1989, p. 321).

HPAMs are also shear thinning fluids, which means that the more shear force is applied to them, the less viscous they are. This is beneficial for EOR purposes because it means that polymer can be injected at high rates since the force it takes to push the
polymer through the wellbore and into the formation is lower than it would be if the polymer behaved in a Newtonian manner. Once the polymer is in the formation, the shear forces on it are decreased and it becomes more viscous, thus improving the mobility ratio.

### 2.2.4 Properties of Alkalis

There are many benefits to adding alkali to a chemical EOR flood. Primarily, the alkali will increase the pH of the injected fluid. An increased pH helps to stabilize (meaning limit or halt degradation) certain surfactants, such as sulfates, for extended periods of time (Adkins, Arachchilage, Solairaj, Lu, Weerasooriya, & Pope, 2012). Increased pH also decreases the amount of surfactant adsorption during a chemical flood, thereby ensuring adequate propagation of the chemical slug and requiring a lower volume of chemicals which makes the flood more economical (Nelson, Lawson, Thigpen, & Stegemeier, 1984) (Mohammadi, Delshad, & Pope, 2008). Alkali can change the properties of reservoir rocks from oil wet or mixed wet to water wet, which is more favorable for oil production (Peters, 2012). Finally, the alkali can sometimes react with naphthenic acids in crude oil to produce in situ soap, which is beneficial because alkali is often cheaper than surfactant (Zhang, Liu, Yan, Puerto, Hirasaki, & Miller, 2006).

Some alkalis considered in EOR are: potassium or sodium hydroxide (KOH or NaOH), sodium carbonate (Na₂CO₃), sodium acetate (CH₃COONa), sodium metaborate (NaBO₂), and tetrasodium ethylenediaminetetraacetate ((HO₂CCH₂)₂NCH₂CH₂N(CH₂CO₂H)₂Na₄ or EDTA − 4Na). The choice of alkali is largely dependent on reservoir properties such as temperature, salinity, divalent ion concentration, reactivity of the crude oil, reservoir rock wettability, rock clay content, and adsorption. Related concerns are alkali cost and compatibility with injected surfactants. The different alkali can be varied in concentration injected to produce a specific pH value. Typically, a pH of at least 9 is desired to stabilize sulfate surfactants and to react with acids in the crude oil to produce soap.
The reactivity of alkali, besides helping to create in situ soap, can also be a disadvantage. One of the drawbacks to the use of alkalis is their propensity to react with divalent cations within reservoir brines and form precipitates (Wilson, 1977). Another disadvantage is that alkali can be consumed by reactions with certain reservoir rock minerals, such as anhydrite (CaSO₄) and gypsum (CaSO₄ · 2H₂O). Both of these types of reactions retard alkali in a flood and can lead to chromatic separation of the chemical slug and catastrophic breakdown of the flood design (Wilson, 1977) (Ehrlich, Hasiba, & Raimondi, 1974).

Phase Behavior and Aqueous stability will be discussed in the next section. However, using alkali in chemical flooding also releases additional ions into solution which affect these experiments. For a high salinity, high hardness brine, these additional ions can cause aqueous stability issues. The alkali ions complicate phase behavior by shifting the optimum salinity of the solution and crude oil. Therefore, the impact of adding alkali to a surfactant/polymer flood design may necessitate changing the surfactant(s) or co-solvent(s) used or their concentrations.

2.3 EOR Chemicals Experimental Behavior

2.3.1 Phase behavior

-What is phase behavior?

In a chemical EOR sense, phase behavior is how a composition of fluids macroscopically arranges itself when in a state of equilibrium. As an aqueous surfactant mixture and an oleic phase contact each other, surfactant will migrate to the interface. If the concentration of surfactant molecules is above the critical micelle concentration (CMC), the surfactant will form micelles, which are three dimensional structures that are dependent on brine chemistry. The micelle types are classified according to the type of microemulsion they form when the system has equilibrated (Figure 2.1). Microemulsions are a distinctly separate phase from oil and water because they are thermodynamically stable. They are also reported to behave as Newtonian fluids (Stein, 1996, p. 191).
Microemulsion droplets are on the order of 10 nm in diameter, which is smaller than normal emulsions of 1-10 μm diameter, and are believed to be spherical in nature (Stein, 1996, pp. 189-191) (Shaw, 1980, pp. 81-83).

Figure 2.1: Phase behavior microemulsion types.

In type I microemulsions, the micelles will form such that the hydrophobic part of the surfactant will face towards the interior of the structure and the hydrophilic part will face outwards. The micelle will solubilize hydrocarbons in the aqueous phase by trapping them in the interior of the micelle. Type I microemulsions are also called oil-in-water microemulsions or under optimum for their propensity to solubilize hydrocarbons in the aqueous phase.
In type II microemulsions, the micelles are arranged such that polar head groups conglomerate on the inner face and hydrophobic tails are directed outward. Type II microemulsions solubilize the aqueous phase by trapping it inside the micelles. The aqueous phase can thereby be transported within the oleic phase because the outside of the micelle is non-polar, like the hydrocarbons. Type II microemulsions are also called water-in-oil microemulsions or over-optimum.

Type III microemulsions are made up of micelles that solubilize hydrocarbons and micelles that solubilize the aqueous solution. Whereas type I and type II microemulsions form two phase systems (oleic and microemulsion, or microemulsion and aqueous), type III microemulsions form their own distinct third phase between the oleic and aqueous phases. This third phase is also referred to as the middle phase. Equilibrated three phase surfactant systems have been found to have the lowest interfacial tension (IFT) for a given surfactant mixture. Huh found that the size of the middle phase, as determined by the amounts of water and oil solubilized by surfactants, is related to the IFT by:

$$\gamma = \frac{C}{\sigma^2}$$  \hspace{1cm} (2.2)

Where $\sigma$ is the solubilization ratio and $C$ is usually taken to equal 0.3 ($C=0.3 \text{ mN/m}$). The solubilization ratio is defined as: $\sigma_o = \frac{V_o}{V_s}$ and $\sigma_w = \frac{V_w}{V_s}$, where $V_o$ and $V_w$ are the volumes of oil and water solubilized into the microemulsion, respectively. $V_s$ is the volume of surfactant solubilized into the microemulsion. It is assumed that all of the surfactant in the solution is in the microemulsion.

The optimum salinity of a surfactant solution is found by performing a phase behavior salinity scan in which the only variable between pipettes is the salinity of the brine. As the salinity is increased (if the range of the test is wide enough), the phase behavior goes from type I microemulsion (oil in water) to type III and then to type II (water in oil) microemulsion. From type I to type III microemulsion, the solubilization of oil in water will increase rapidly and then drop off very quickly after the type III region. Conversely, the solubilization of water in oil will increase rapidly as salinity decreases.
from the type II to type III region. The solubility of water in oil drops off precipitously in the type I region. The oil and aqueous solubilization ratios will cross each other at some point in the type III salinity range. This is defined as the optimum salinity. The solubilization ratio of oil and water are equal at this point. This solubilization ratio can be used to compare the results of the experiment to other chemical solutions. A minimum solubilization ratio of 10 cc/cc is considered the lowest value to incur ultra-low interfacial tension (0.001 dynes/cm).

Reed and Healy, Walker, and Winters observed that the optimum salinity varied with the water-oil ratio (WOR) (Reed & Healy, 1977, p. 416) (Walker, 2011) (Winters, 2012). They observed that the optimum salinity of a surfactant solution increases as the WOR increases. In other words, the higher the relative amount of brine present, the higher the optimum salinity. For example, Winters observed that a surfactant solution with Guerbet Alkoxy Carboxylate (GAC), Dodecylbenzene sulfonate (ABS), and iso-tridecanol-13PO-sulfate surfactants with triethylene glycol monobutyl ether (TGBE) co-solvent had its optimum salinity change from 30,000 ppm TDS at 10% oil concentration to 22,000 ppm TDS at 50% oil concentration (Winters, 2012, p. 63). Such a change in phase behavior is important given the natural variations in oil saturation within reservoirs. Therefore, an EOR chemical solution needs to be robust enough to handle saturation variance and still deliver ultra-low IFT.

Salinity gradients are important considerations from a phase behavior, heterogeneity, and surfactant retention standpoint (Hirasaki, van Domselaar, & Nelson, 1983). A salinity gradient is a method by which the salinity of the chemical slug is below that of the brine in the formation being displaced. The optimum salinity of the chemicals would be chosen so that it is between the chemical slug salinity and the formation brine salinity so that when the two brines mix, at some point the optimum salinity is passed through. This method helps reduce surfactant retention in the field, which improves recovery. Ahead of the chemical slug, the chemical mixture will be a type II emulsion, which retards the chemicals and can trap surfactant in the oil phase, leading to poor oil recovery (Reed & Healy, 1977, p. 426). Behind the chemical slug, the mixture will be a
type I microemulsion and the surfactant will be in the aqueous phase. Surfactant in the aqueous phase will propagate more quickly through the reservoir and be less likely to be retained in undisplaced oil phases. Thus, the type I and type II microemulsions in the salinity gradient help to stabilize the chemical flood front and lower surfactant retention. One drawback, however, is the tendency for alcohol co-solvents to undergo chromatic separation, which can negatively affect phase behavior.

The salinity gradient method of injection is preferred to the constant salinity method (whereby the injected salinity is the same as the formation salinity) because the constant salinity method requires the microemulsion to have a viscosity higher than the oil to prevent viscous fingering and phase trapping (Hirasaki, van Domselaar, & Nelson, 1983). This is caused by polymer’s inability to partition into the microemulsion phase, which means that there is no control on the microemulsion-oil mobility ratio. Changes in brine or oil saturation will change the microemulsion viscosity (see above), which can lead to viscous fingering and phase trapping. Once these instabilities are created, they will intensify and get worse. A salinity gradient, on the other hand, will help stabilize the chemical flood front with the type I-type II microemulsion interactions described previously.

-Microemulsion

Nonionic surfactants have been observed to have pronounced changes in phase behavior because of a sharp phase-inversion brought on by temperature increases (Skauge & Fotland, 1990). Levitt observed a decrease in solubilization with increased temperatures, which he attributed to the nonionic nature of the PO groups in his anionic surfactants (Levitt, 2006, pp. 54, 140). This is an important observation because large alkoxy surfactants with long chains of PO and EO groups have been found in this thesis and elsewhere (Adkins, Arachchilage, Solairaj, Lu, Weerasooriya, & Pope, 2012) to have the best aqueous stability and solubilization in high hardness brines.

Nelson found that microemulsion phase behavior did not change under pressure (Nelson R. C., 1983). Skauge and Fotland (1990) and others (Southwick, Svec, Chilek, &
Shahin, 2010) have found that the optimum salinity increases with temperature and methane gas pressure. Southwick et al. (2010) found that the methane, not pressure, was increasing the optimum salinity. Pressure was not observed to significantly change the phase behavior of the solutions. Rossen and Kohn (1984) observed that clouding or phase separation of micellar solutions and microemulsions is possible under low pressures (50 MPa, 7,250 Psi).

Lowering the surfactant concentration lowers the solubilization at optimum salinity (Skauge and Fotland). It has also been found to improve aqueous stability (Sahni, Dean, Britton, Kim, Weerasooriya, & Pope, 2010).

Microemulsion viscosity varies broadly for each surfactant solution and is dependent on surfactants used, oil properties, brine properties, temperature, co-solvent, etc. The main controllers of viscosity are thought to be relative oil and brine concentrations in the microemulsion. Often the microemulsion viscosity increases to some maximum point and then decreases. A type I microemulsion would have a viscosity similar to brine. A type II microemulsion would have a viscosity similar to crude oil. The microemulsion peak viscosity is often times much higher than these two endpoints. Sheng presents an example with microemulsion peak viscosity more than twice the viscosity of the crude oil (2011). Often this peak viscosity is close to the point where oil and brine concentrations are equal (Walker, 2011, p. 5). Flaaten found peak microemulsion viscosities near (but just below) optimum salinity on salinity scans. While using co-solvent, he also observed a maximum microemulsion viscosity of 25 cp with a 10 cp crude oil and brine (Flaaten, 2007, p. 52). Co-solvent is typically used to lower microemulsion viscosity, however, as Flaaten’s work shows, it is not always sufficient. During field injection, high microemulsion viscosity would need to be offset with higher viscosity chemical slugs, which can be done by increasing the polymer concentration, increasing the polymer molecular weight, changing the polymer structure, or by changing the chemical slug injection salinity. It is imperative to have chemical slug viscosity above the microemulsion viscosity to maintain mobility control and prevent viscous fingering, which can lead to early surfactant breakthrough and poor volumetric sweep efficiency.
Viscous macroemulsions and gels

Another objective of phase behavior experiments is to identify the presence of viscous macroemulsions and gels. Macroemulsions are different from microemulsions in that their droplet sizes are larger. In the phase behavior experiments done for the Eliasville Caddo Unit reservoir, macroemulsions and gels were typically observed to be heavier than the microemulsions and settled between the middle phase and brine. Macroemulsions and gels were observed to have colors ranging from brown to light tan or yellow.

Macroemulsions and gels are typically very viscous and form at the interface between oil and brine or micromulsion and brine. Often macroemulsions and gels will form a plug in the phase behavior pipette that can sometimes be broken by repeatedly inverting the pipette or shaking it. They will re-form as the fluids settle. Macroemulsions and gels are thermodynamically unstable and will break down over time. However, the time horizon can be very long; some macroemulsions and gels were observed to persist for over six months.

The formation of macroemulsions and gels often are present at relatively higher salinities during salinity scan phase behavior screening. However, this is not always the case. It appears that surfactant properties also influence the formation and persistence of macroemulsions and gels, specifically the hydrophobicity of the surfactant molecules (low HLB). In the laboratory work done for this thesis, it was found that macroemulsions were most prevalent when the surfactant solution became too hydrophobic (either by cutting the hydrophilic surfactant concentration, or by increasing the hydrophobic concentration) or the salinity was very high.

The presence, persistence, and severity of macroemulsions and gels can be mitigated with the use of adequate and sufficient co-solvent(s). Co-solvents, like surfactants, will often migrate to the brine-oil interface. Their ability to prevent the formation of macroemulsions, which are related to hydrophobicity and salinity, suggests that they are able to interact with the hydrophobe of a surfactant to make it soluble in the solution. Thus, while increased salinity will tend to condense the outer portion of the
electric double layers surrounding the hydrophilic head groups, thereby making the surfactants come closer to one another, and the hydrophobes will tend to coalesce, the co-solvent, because of its solubility in both oil and water, likely migrates to the areas between the hydrophobes and keeps these same hydrophobes from connecting. If macroemulsions are taken to be a poorly formed structure of surfactant, brine, and oil, then it stands to reason that co-solvents work by preventing the hydrophobes of surfactants from being so strongly attracted to each other and forming the macroemulsion structure.

Perhaps, in aqueous solution the addition of co-solvent creates a layer, buffer, or “shield” of co-solvent molecules around the hydrophobe of a surfactant, much like the hydrophilic head groups have layers of ions surrounding them. In a non-polar phase (i.e. oil) the opposite may be the case; the hydrophobe is free to interact with the other non-polar molecules, and the co-solvent has a higher affinity for the hydrophilic head group and creates a layer of co-solvent molecules around it. This may explain why co-solvents tend to reduce the solubilization of brine and oil in type III microemulsions. The co-solvent’s affinity for the hydrophobe of a surfactant could depress the hydrophobe’s ability to associate with non-polar fluids, much like the co-solvent depresses the hydrophobe’s association with other surfactant hydrophobes to prevent macroemulsions.

Concurrent with this idea is the observation that lower molecular weight co-solvents (like methanol and ethanol) have been reported to cause the optimum salinity of a surfactant solution to increase, and higher molecular weights (like sec-butanol) cause the optimum salinity to decrease (or not increase as much) (Morgan, Schechter, & Wade, 1977, p. 115). Lower molecular weight co-solvents tend to have a higher solubility in polar liquids like water because they have small hydrophobic sections. Much like the behavior of the electric double layer of ions around a charged surface depends on the type of ions in solution, so too would the aqueous stability and phase behavior of the surfactant hydrophobe depend on the co-solvent (and other surfactants) present. Thus, it would take many low molecular weight co-solvent molecules to form a layer around the surfactant hydrophobe. This, coupled with the co-solvent’s increased affinity for polar
fluids, may reduce the hydrophobicity of the surfactant tail, which limits the surfactant’s affinity for oil. A decrease in hydrophobicity promotes increased aqueous stability, ion tolerance, and a shift in optimum salinity to higher values. Conversely, it would take fewer high molecular weight co-solvent molecules to form around a surfactant hydrophobe because these co-solvent molecules are larger and have a lower solubility in polar fluids, which means they have a greater affinity for surfactant hydrophobes. Because these co-solvents are less soluble in polar fluids than low molecular weight co-solvents, and because fewer of them form around the hydrophobe, the impact to optimum salinity is lower. It also stands to reason that the aqueous stability of the hydrophobe would not be improved as much with large molecular weight co-solvents as with small ones.

2.3.2 Aqueous stability

Aqueous stability is an intrinsic characteristic that a chemical mixture has under specified temperature and pressure. Aqueous stability is often recorded as a mixture’s physical appearance, with stability defined as a clear, homogenous solution and instability displaying evidence of precipitation, haziness or cloudiness, and/or phase separation. Aqueous stability is important for petroleum systems to ensure propagation of chemicals in the reservoir.

Precipitation reactions, cloudiness, and phase separation will lead to excessive chemical consumption and retention within the reservoir, poor sweep efficiency, and ultimately poor oil recovery. Additionally, poor aqueous stability can lead to scale build up in production wells and to formation damage due to occlusion of pore throats (permeability reduction). Thus, not only will much of the chemicals injected be wasted and little additional oil produced, but wells will need to be worked over at an increased rate and facilities will need to be maintained with increased vigilance.

While the solubility of most salts in water will increase with temperature, the aqueous stability of many chemical EOR solutions will have the opposite behavior. This
is particularly true with non-ionic surfactants that have inverse solubility. However, in this thesis, branched sulfate surfactants were observed to have inverse solubility as well. Zhang et al. also observed that sulfates have reversed solubility (2006). Levitt found sulfate and IOS surfactants to have reversed solubility (2006).

According to Sheng, the influence of pressure on aqueous stability is generally assumed to be a minor effect and atmospheric pressure is used for the experiments (Sheng, 2011). This is plausible due to the small compressibility of the fluids involved and the high dependency of stability on brine composition, concentration, and temperature.

Aqueous stability measurements in petroleum systems typically consist of a brine, a primary surfactant, co-surfactants, co-solvents, a polymer, and possibly an alkali. Surfactant type and concentration are observed to impact aqueous stability. All things being equal, lower surfactant concentration solutions will often exhibit higher tolerance to dissolved electrolytes. Surfactants with a high Hydrophilic-Lipophilic Balance (HLB) tend to tolerate higher TDS content as well. These surfactants tend to have sulfate (or to a lesser extent, carboxylate) head groups, have many Ethylene Oxide (EO) groups, and/or have branching in their molecular structure (alkyl, benzene, etc). For example, Zhang et al. found that a branched C16-17 propoxylated sulfate and a C15-18 IOS were less likely to phase separate because the molecular branching inhibited liquid crystal formation (2006). Gemini surfactants are at this time an emerging technology in the chemical EOR community and also exhibit very high tolerance to electrolytes (Gao, 2012).

In his book Shaw discusses the salting out phenomena, whereby stable colloid dispersions flocculate as salinity is increased. He claims that “the ions of the added electrolyte dehydrate the hydrophilic colloid by competing for its water of hydration” (Shaw, 1980, p. 206). The salting out potential of an electrolyte therefore depends on the abilities of an ion to become hydrated. He lists the salting out power of common reservoir cations and anions as:

\[
\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+} > \text{Na}^+ \text{ and } \text{SO}_{4}^{2-} > \text{Cl}^-
\]

24
Shaw also discusses the impact of various physical phenomena on what he defines as the critical coagulation temperature: the minimum electrolyte concentration that is required to cause a visible change in the surfactant solution (Shaw, 1980). He discusses how electric double layers form around the charged head of surfactants and how these electric double layers are made of an inner Stern layer and an outer diffuse layer. The double layers of individual surfactant micelles repel each other and act over a relatively large distance, whereas van der Waals forces attract the molecules at close distances. When the electric double layers of colloids are condensed due to increasing electrolyte charge or concentration, the van der Waals forces of attraction have increasing importance. The critical coagulation concentration of an inert electrolytes is:

\[
c_{c.c} = \frac{9.85 \times 10^4 e^3 k^5 T^5 \gamma^4}{N_A e^6 A^2 z^6} \text{mol dm}^{-3}
\]

Where, \( e \) is the permittivity of the dispersion medium, \( k \) is Boltzmann’s constant, \( T \) is the absolute temperature, \( \gamma \) is a double layer parameter based on Stern layer potential, \( N_A \) is Avagadro’s number, \( e \) is the elementary charge, \( A \) is the Hamaker constant, and \( z \) is the ion charge number. For typical input values, the critical coagulation concentration for divalent ions (\( z=2 \)) is about eight times lower than that of monovalent ions (\( z=1 \)). This equation shows that temperature, ion potential, and Stern potential are the biggest drivers of the c.c.c. In most EOR surfactant-brine solutions, the impact of temperature is observed to be inverse to c.c.c., unlike the equation.

Aqueous stability can also be an issue with sulfonate surfactants and polymers. Zhang et al. reported surfactant rich and polymer rich phases with such a combination in relatively low concentrations at low salt concentrations (2.0-4.0 wt% NaCl, 1.0 wt% Na₂CO₃). They also claim that sulfonates and HPAM polymers are unlikely to complex due to electrical repulsion (Zhang, Liu, Yan, Puerto, Hirasaki, & Miller, 2006).

There are many methods for improving aqueous stability. The primary methods are to add co-solvents and/or hydrophilic co-surfactants. Another option is to add Ethylene Oxide (EO) groups to the surfactant molecule. Filtering, precipitating, or otherwise removing the divalent ions is also an option. In addition, injection schemes
involving salinity or chemical gradients can mitigate aqueous stability issues. If the brine is hard, chelating agents such as tetrasodium pyrophosphate (TSPP), nitrilo triacetic acid (NTA), EDTA, or sodium metaborate can be used to capture multivalent ions from solution (Yang, et al., 2010). Lowering the solution temperature will often improve stability as well.

Hydrophilic surfactants have high cloud points and can be added to a mixture to improve aqueous stability of the overall solution. Such surfactants include short hydrocarbon tail sulfates or surfactants with many EO groups. Blending unlike surfactants can also lead to synergistic behavior in which the type III microemulsion phase has a broader salinity range and a higher solubilization. The negative impacts are increased flood design complexity and increased risk of chromatic separation. Blending of surfactants can cause phase behavior to become highly dependent on relative surfactant composition.

Co-solvents have been found to improve aqueous stability. Shaw described surfactant stability in brine in terms of fundamental chemistry principles:

*The principal cause of aggregation is the van der Waals attractive forces between the particles, whereas stability against aggregation is a consequence of repulsive interaction between similarly charged electric double layers and particle-solvent affinity. Particle-solvent affinity promotes stability mainly by mechanical means, which can be considered in terms of the positive desolvation free energy change which accompanies particle aggregation. The adsorption of polymeric material on to the particle surfaces will usually promote stability through increased particle-solvent affinity and by an entropic mechanism, but may induce aggregation by a bridging mechanism.* (Shaw, 1980, p. 183)
Thus, Shaw states that surfactant-brine affinity is enhanced by the co-solvent adsorbing to the surfactants. The statement about co-solvent enhancing particle aggregation (decreasing aqueous stability) is not well supported by the EOR literature.

Chelating agents such as EDTA or sodium metaborate work by complexing to bind a multivalent ion, thus removing the ion from solution. Ideally the chelating agent and captured ion remain in suspension, however, this is not always the case. Chelating agents often release monovalent ions in order to capture multivalent ions, thus neither brine salinity nor ionic strength are reduced substantially (if at all). If low concentrations of hard ions are causing aqueous stability problems, then chelating agents may improve the situation.

Filtering or removing ions is a possible way to improve aqueous stability. This technique has been done in at least one field with low TDS and relative divalent ion concentration (Holm, 1982). Since higher ion concentrations compress electric double layers around surfactant molecules and reduce surfactant-brine affinity, they allow van der Waals attractive forces to predominate, resulting in particle conglomeration and aqueous stability failure. If the ion concentration is reduced, the opposite result occurs; electric double layers expand, surfactant-brine affinity increases, and attractive van der Waals forces are reduced.

The salinity gradient method may be able to mitigate the negative effects of poor aqueous stability at reservoir conditions (temperature, salinity, hardness, etc). Since the injected chemical slug is of a lower salinity and presumably a lower temperature than the formation, aqueous stability will be increased at least in the near wellbore region. Whether stability is maintained is another matter, as further into the reservoir brine mixing increases the slug salinity and geothermal sources heat up the slug.

Heterogeneities can also influence aqueous stability and phase behavior. Variations in salinity, divalent ion content, rock composition, permeability, oil and brine saturation, oil characteristics, and rock wettability all impact aqueous stability and phase behavior in different ways and to different degrees. For example, shifts in salinity, divalent ion content, and oil saturation can impact whether surfactant phase separates
from the chemical slug. They can also impact microemulsion type. Rock composition and wettability can influence surfactant adsorption and chemical slug propagation and effectiveness. Additionally, rock composition can impact chemical balances in the injected brines with constituents like anhydrite and gypsum dissolving into the interstitial brine. All these competing natural phenomena are part of reason for chemical or salinity gradient injection schemes.

2.3.3 Core flooding

Once acceptable phase behavior and aqueous stability are achieved, core floods are done. The purpose of core flooding is to design, test, and refine fluid injection schemes. Core floods are typically done with reservoir core plugs, but initial screening can be done with industry standards such as Berea Sandstone or Texas Cream Limestone. Successful core floods do not necessarily translate to successful reservoir floods. However, a failed core flood is usually sufficient evidence that the chemical EOR procedure tested will not work in the field.

Cores are often cleaned and conditioned before being used in a core flood. This involves flushing chemicals designed to remove impurities. Conditioning of cores is done by saturating them with fluid and storing them at elevated temperatures. Typically a core is saturated with brine, flushed with oil, and then waterflooded to residual oil saturation. After these steps have been taken, the core is ready for chemical flooding.

The fluid injection scheme of a core flood characterizes the flood for the: pre-flush (if any), the chemical slug, the polymer slug, and the drive water. The parameters that are controlled are the salinities of each stage, the chemical concentrations, and the amount of fluid injected for each stage. A pre-flush may be done to condition the core by changing the connate brine salinity or hardness. Typically the chemical and polymer slugs have a lower salinity in order to establish a salinity gradient. The polymer slug is normally tapered by decreasing the concentration of polymer as the flood progresses. This reduces the total amount of polymer needed and minimizes viscous fingering.
The results of a core flood typically include: the amount of additional oil recovered, the amount of residual oil, the oil cut (a percentage of the produced fluids), the oil bank breakthrough time, the amount of surfactant adsorption, and any changes in pressure. The most important of these parameters are the additional oil recovered and the surfactant adsorption. The cutoff for acceptable oil recovery is typically 90% of original oil in place. Oil recovery is important for project economics and feasibility. Surfactant adsorption is important because it gives an indication of surfactant propagation through the reservoir and the quantity of chemicals needed. Typically the amount of adsorption is about 0.10 to 0.30 milligrams of surfactant per gram of rock and is not affected by the type of rock (i.e. carbonate or sandstone) (Solairaj, Britton, Kim, Weerasooriya, & Pope, 2012). Excessive adsorption can cause core and reservoir flood failure.

2.3.4 Pilot

After core flooding is complete, a pilot test is normally done in the field before moving onto full field flooding. Typically core flooding is done in one to a few five spot blocks. Prior to chemical injection, the reservoir is characterized with well logs and tracer tests. Interwell tracer tests are effective in identifying reservoir heterogeneities, oil saturation, and flood conformance. An onsite laboratory is also crucial during and after chemical injection to control the injected fluids and monitor the effluents. Ordinarily the same properties that are monitored in a core flood are measured in the pilot test. Successful pilot testing may warrant a full field application.

2.4 Summary and Conclusions

In this chapter, the principal experiments used for evaluating EOR chemicals were presented. Phase behavior and aqueous stability tests were reviewed and discussed. A summary of the influences on phase behavior and aqueous stability can be found in Table
2.2. The objectives and expectations for core flooding and pilot testing were also presented.
Table 2.2: Influence of fluid properties on phase behavior and aqueous stability.

<table>
<thead>
<tr>
<th>Property Increased</th>
<th>Optimum Salinity</th>
<th>Solubilization Ratio</th>
<th>Aqueous Stability</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Decreases</td>
<td>No Effect</td>
<td>Increases</td>
</tr>
<tr>
<td>Temperature [as reported by (Reed &amp; Healy, 1977, p. 417)]</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Pressure</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Methane Concentration (i.e. Converting Dead Crude to Live Crude)</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Crude Density</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Surfactant Concentration (Hirasaki, van Domselaar, Nelson, 1983) (Reed &amp; Healy, 1977, p. 416)</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Surfactant Blending</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Low-MW Co-Solvent Concentration</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>High-MW Co-Solvent Concentration</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Brine TDS</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Brine Divalent Ion Relative Concentration (Sheng, 279) (Reed &amp; Healy, 1977, p. 422)</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>WOR (Reed &amp; Healy, 1977, p. 416)</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Polymer Concentration</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>
CHAPTER 3: CHEMICAL EOR IN CARBONATE FORMATIONS

3.1 Introduction

The target of oil remaining in carbonate fields is immense and alluring. Current production from carbonates is approximately 10 billion bbl/year out of 32 billion bbl/year consumed (Sheng, 2011). By some estimates, 60% of the world’s traditional oil reserves reside in carbonate reservoirs (Mohan, 2009). Additionally, the rate of new oilfield discoveries has been declining and the world’s largest oilfields have been on production for more than 30 years. So far, most of the Enhanced Oil Recovery techniques used in carbonates have employed gas injection methods (CO₂) or have been polymer floods (Alvarado & Manrique, 2010, p. 147). In fact, Alvarado and Manrique go so far as to state that “polymer flooding is the only proven EOR chemical method in carbonate formations” (Alvarado & Manrique, 2010, p. 147).


Sheng claims that anionic surfactants have high adsorption in carbonates, but this may not, in general, be true (Sheng, 2011, p. 8). Many studies show comparable adsorption in carbonates and sandstones (Levitt, 2006). Badakhshan and Bakes claim that surfactants have had limited application in carbonates because of fractures, low matrix
permeability, dead pore volume, high hardness and salinity, heterogeneity, and adsorption (Badakhshan & Bakes, 1990). Bernard found that the effect of calcium carbonate had no effect in oil recovery in surfactant polymer floods (Bernard, 1975). While Bernard’s results were done in unconsolidated sandpacks and only contained up to 2 wt% CaCO₃, perhaps the results are extendable to limestone formations.

### 3.2 Hard Brines and Divalent Cations

Carbonate formations are often times associated with high divalent cation concentrations, which are referred to as hard brines (Collins A., 1975). Divalent cations are atoms or molecules with a 2+ electrical charge, such as magnesium, calcium, barium, and strontium. Divalent ions significantly alter the properties of a formation brine (Collins A., 1975). High divalent ion concentrations drastically complicate the chemical EOR process because they tend to react with other ions and also more strongly influence the phase behavior and aqueous stability responses of a brine. For example, Winters observed that calcium ions in a brine have a disproportionate effect on the optimum salinity of a surfactant solution (Winters, 2012, p. 119). Divalent ions are also known to cause precipitation reactions with hydroxide and carbonate alkalis.

In municipal drinking water, hard water is usually defined as anything over 100 ppm magnesium and calcium, though some locations have water that far exceeds this. For example, the municipal drinking water hardness in Midland, Texas is 350-450 ppm divalent ions and approximately 2,000 ppm TDS (2010 Midland Water Quality Report: Drinking Water Quality Report, 2010). For comparison, the municipal drinking water for Houston, Texas and Austin, Texas are 145 ppm and 98 ppm divalent ions, respectively (Budget Water International, 2013A) (Austin Water Utility). Anchorage, Alaska’s municipal drinking water is sourced from the glacial runoff fed Lake Eklutna and has a water hardness of 57 ppm hard ions (Budget Water International, 2013B). These values are given as reference for the SP and ASP water hardness tolerances below. For
comparison, sea water contains: 32,600 ppm TDS, 1,270 ppm magnesium, 400 ppm calcium, and 8 ppm strontium (Collins A. , 1975, p. 195).

Hard brine for a reservoir can be defined as a concentration of over 300 ppm divalent ions in the formation brine. The screening criteria proposed by Alvarado and Manrique places the upper limit for water hardness at 20 ppm for ASP considerations and 1,000 ppm for SP floods (Alvarado & Manrique, 2010, p. 52). Sheng also had a similar upper limit of 1,000 ppm divalent ions (Sheng, 2011, p. 8). Thus, the divalent ion limits for Alkali floods are below the divalent ion content of many municipal drinking waters.

Flaaten has observed that the difference between how a hard brine and soft brine influence phase behavior may be related through the ionic strength of a mixture (Flaaten, 2007, p. 68). The ionic strength is a measure of the concentration of ions in a solution. It is the sum of the product of ion concentration and the square of ion charge for all electrolytes in solution. The ionic strength is defined as:

$$I = \frac{1}{2} \sum_{i=1}^{n} C_i z_i^2$$  \hspace{1cm} (3.1)

Where $C_i$ is the molar concentration of ion $I$ (M=mol/L) and $z_i$ is the charge of the ion. Monovalent electrolytes such as NaCl have a 1:1 correspondence to ionic strength. Divalent electrolytes such as CaCl$_2$ have a 4:1 impact on ionic strength.

Experiments are not always done at an ionic strength equivalent to hard brines. One example of this is in Walker’s Thesis. The softened synthetic brine he uses to duplicate the formation brine in his experiments is not an ionic strength equivalent and it’s not clear why that particular concentration is a valid substitute for the formation brine (Walker, 2011, p. 22). A similar observation can be made about the paper by Al-Hashim et al. on a study for EOR in Saudi Arabian carbonate fields (Al-Hashim, Obiora, Al-Yousef, Fernandez, & Nofal, 1996). However, these are not the only two examples of inexplicable brine substitutions.

There are other schools of thought. For example, Levitt claims that the effect of calcium on surfactant phase behavior is ten times that of sodium chloride (Levitt, 2006). However, this statement is vague and is not supported by the observations made in this
thesis. Reed and Healy found that the “addition of $Ca^{2+}$ to the aqueous phase in the ratio of 10:1 $NaCl:CaCl_2 \cdot 2H_2O$ decreased optimal salinity from 1.4% NaCl to 1.1% total dissolved solids, but the effect on optimal tension was very small” (1977, p. 422). Furthermore, they found that the “extent of the multiphase region was not significantly affected.” The work done in this thesis suggests that hard and soft brines in certain instances are comparable on an ionic strength basis.

### 3.3 Characteristics of Hard Brines

The purpose of this section is to discuss the geochemistry of hard brines. The four main contributors-calcium, magnesium, barium, and strontium- are discussed in turn. These elements are all members of the alkaline earth metals on the periodic table and have similar chemical behavior. They will be investigated both as electrolytes in brine and as constituents of minerals in sedimentary rocks.

The alkaline earth metals exist in a state of equilibrium between solid and aqueous phases within the reservoir. Flooding the reservoir with a chemical EOR slug- or even a salinity gradient by itself- will create an imbalance in the equilibrium. This imbalance is where many of the intricacies and nuances of hard brines can cause chemical floods to fail.

Collins summarized the effects of ionic strength on mineral solubility (1975). He found that the solubility of many compounds that form scales increases with increasing electrolyte composition (see Figure 3.1, Figure 3.2, and Figure 3.3 from (Collins A., 1975, pp. 381-2)). This is, of course, unless another solubility equilibrium is reached, such as the dissolution of gypsum or anhydrite and the precipitation of barium sulfate. This indicates that a chemical EOR flood with a salinity gradient in carbonate reservoirs may be at an elevated risk for precipitation reactions.
Figure 3.1: Solubility of CaSO₄ versus ionic strength of aqueous solutions (Collins A., 1975, p. 381).

Figure 3.2: Solubility of SrSO₄ versus ionic strength of aqueous solutions containing CaCl₂, MgCl₂, NaCl, KCl, and KBr (Collins A., 1975, p. 381).
3.3.1 Calcium

Calcium is present in the form of divalent ions in the connate waters of many reservoirs. This calcium can derive from the original depositional water, from dissolution of evaporites and carbonates, diagenesis of calcite or aragonite, or from brine transport.

Calcium can also be present in sandstones in clay particles such as montmorillonite (smectite) clay \((Ca_{0.35}(Al, Mg, Fe)_{4}[(Al, Si)_{6}O_{20}] \cdot nH_{2}O)\), feldspar \((CaAlSi_{3}O_{8})\), and plagioclase \((NaAlSi_{3}O_{8} - CaAl_{2}Si_{2}O_{8})\). Bernard found that the oil recovery from sandpack surfactant/polymer floods decreased as montmorillonite clay increased. He also observed that the negative effects of clay are amplified as the salinity of the interstitial water declines. Bernard postulated that the decline in flood performance is due to calcium clay adsorbing surfactant, adding \(Ca^{++}\) to the flood solution due to ion exchange thereby precipitating calcium sulfonate, and by adsorbing polymer leading to an increase in flood mobility (Bernard, 1975).
Calcium is present in limestone (CaCO₃) formations which are authigenic in nature and created in subaqueous environments due to chemical and biological means. Calcite (limestone) and aragonite can be formed by precipitation of minerals from super saturated solutions, such as in lagoons or tidal regions, or by biological means, such as reefs or pelagic sedimentation. Information on the many types of organisms that precipitate calcite or aragonite can be found in Geochemistry of Sedimentary carbonates (Morse & Mackenzie, 1990). Aragonite, like calcite, is made of calcium carbonate, but differs by the mineral’s crystal lattice (calcite is rhombohedral and aragonite is orthorhombic). Additionally, aragonite is typically formed near the earth’s surface under low temperature conditions. The mineral is unstable at higher temperatures and pressures and can dissolve and recrystallize as calcite, potentially adding calcium ions to interstitial waters (Morse & Mackenzie, 1990, p. 292).

Dolostone [(CaMg)(CO₃)₂] formations contain calcium and magnesium and arise due to chemical reactions. The formation of dolomite is caused by digenesis of limestone when interstitial water is hot, alkaline, CO₂ free, and rich in magnesium, conditions which typically occur in highly evaporative lagoon environments (Adams & Rhodes, 1960). Dolomitization also occurs at a quicker pace in aragonite than in calcite (Morse & Mackenzie, 1990, p. 299). Gypsum (CaSO₄ · 2H₂O) and anhydrite (CaSO₄) are formed in similar environments and are commonly found among carbonate rocks. The solubility of gypsum is 2,000 ppm in fresh water and about 7,000 ppm in NaCl brine (Bernard, 1975).

Calcium has the propensity to react with carbonate, hydroxide, sulfate, and acetate anions to create precipitates. It’s least soluble product is calcium carbonate. The solubility of some calcium salts, such as calcium sulfate, decrease with increasing temperature (Collins A., 1975).

3.3.1 Magnesium

Magnesium forms solids in many of the same ways as calcium. In many aqueous micro organisms, magnesium is incorporated into the skeletal structure of the organism in
the form of aragonite or calcite. Some organisms can contain more than 20 mole % MgCO₃. Magnesium ions have a high energy of hydration, which often causes magnesium carbonates to form hydrates. Magnesium can also inhibit the formation of calcite precipitation (Morse & Mackenzie, 1990).

Magnesium is commonly found in the following clays and sandstones: Biotite (KMg₃AlSi₃O₁₀(OH)₂), Montmorillonite, and Chlorite (Mg₃(Al, Si)₄O₁₀(OH)₂ · (Mg, Al)₃(OH)₆).

Magnesium is often found with calcite in limestone or dolostone formations. This is in part because calcite is formed in lacustrine or oceanic environments which contain both calcium and magnesium ions. A paper by Stanley and Hardie demonstrates how cyclical changes in calcium and magnesium concentrations in the oceans have led to periods of calcite formation and aragonite/high magnesium calcite formation over tens of millions of years (Stanley & Hardie, 1998).

Magnesium, like calcium, reacts with carbonates, hydroxides, sulfates, and acetate anions to form precipitates. However, in DI water, magnesium hydroxide has a lower water solubility than calcium hydroxide and will tend to precipitate those anions first in the presence of certain hydroxide alkali. Magnesium sulfate, on the other hand, is much more soluble than calcium sulfate. The solubilities of carbonates are all similar, but magnesium may be slightly more soluble.

Sheng claims that Mg²⁺ associates with surfactant to form a precipitate, but also causes a non-compatibility between surfactant and polymer (2011, p. 506).

3.3.3 Barium

Barium sulfate is highly insoluble and readily forms barium sulfate (BaSO₄) and barium carbonate ((BaCO₃). Barium is usually found in reservoir brines in concentrations less than 1,000 ppm, but concentrations over 200 ppm and even as high as 2,180 ppm have been reported from North Sea fields (Badr Bin Merdhah & Mohd Yassin, 2007). Because the barium atom is so large, it likely does not form in sediments appreciably by
biological means. Trace elements of aragonitic skeletons have been studied and the range of barium detected was 8-130 ppm (Reeder, 1983, p. 162). More likely, barium precipitates from concentrated sea water solutions in the form of barium sulfate or barium carbonate and then undergoes diagenesis after burial. There is evidence of barium sulfate (barite) reacting to form barium carbonate (celestite) at low temperatures (Reeder, 1983, p. 182). Given the complex interactions between calcium, magnesium, barium, strontium, sulfate, carbonate, temperature, and pressure, perhaps some barium remains in solution and this accounts for interstitial brine values.

3.3.4 Strontium

Strontium behaves much like calcium and magnesium. While it is present at a concentration of only 8 ppm in seawater, it can be found at concentrations from about 7,500 to 10,000 ppm in corals, aragonites, and ooids all over the world. Strontium seems to form at higher concentrations in organisms that form aragonitic skeletal structures, suggesting that it replaces calcium carbonate in lower phyla organisms (Morse & Mackenzie, 1990, pp. 212-215). As aragonite dissolves and re-precipitates as calcite or dolomite, strontium ions may get left suspended in the interstitial brine. Strontium remaining in the brine may occur because of competition for anions with other divalents, notably barium. Competition for anions would be dependent on solubility values and cation-anion ratios. This may explain why some reservoirs have such high quantities of strontium.

Strontium precipitates as SrCO₃ and SrSO₄.

3.4 Ubiquitous Nature of Hard Brines

Aqueous stability is a problem that needs to be solved because hard brines exist in both sandstone and carbonate reservoirs. In fact, most reservoirs contain at least some divalent ions. Collins summarized the analyses of over 4,000 petroleum reservoir brines
from various locations, formation types (e.g. clastic vs. carbonate), and reservoir depositional ages. His work shows that almost all of the reservoirs in the United States have divalent ion contents that exceed the ASP limitation of 10 ppm. Furthermore, the majority of reservoirs in the United States have divalent ion contents that exceed the SP limit of 1,000 ppm. His data suggests that the Gulf Coast, parts of East Texas, Wyoming, Colorado, and California (predominantly clastic reservoir production areas) are the only regions where SP and ASP flooding are within the divalent ion ranges defined above (Collins A., 1975). Collins and others (Lake, 1989, p. 316) also present data supporting a correlation between hardness and TDS.

3.5 Phase Behavior in Hard Brines

Hill et al. found that the salinity range of acceptable interfacial activity of a surfactant/brine solution decreased as the proportion of calcium increased (Hill, Reisberg, & Stegemeier, 1973). They also found that solutions containing five percent of a sulfonate surfactant in 0.1 molar NaCl solution at 160°F could tolerate up to 500 ppm of calcium (see Figure 3.4). Hill et al. designed a surfactant flood for the Benton field in Illinois. The field brine contained approximately 7.5 wt% TDS of which about 0.4 wt% were divalent ions. The flood water was from the nearby Lake Moses and contained 250 ppm TDS. They observed that blending, screening, and viscosity experiments with Benton reservoir water and Lake Moses injection water with sulfonate behaved similarly to NaCl and sulfonate solutions except that the salinity scale was compressed when reservoir brine was used because of the divalent ions (Hill, Reisberg, & Stegemeier, 1973).
Figure 3.4: The effect of calcium on interfacial activity of aqueous systems with 5 percent sulfonate at 160°F (Hill, Reisberg, & Stegemeier, 1973).

3.6 Aqueous Stability of Hard Brines

Aqueous stability is also influenced by brine hardness. The higher the divalent ion concentration in a brine, the lower the aqueous stability limit (Chandrasekar, 2010). Lower stability limits are expected with increasing multivalent ion concentrations
because multivalent ions have a greater impact to a brine’s hydration ability. This phenomenon may be related to ionic strength.

3.6.1 Aqueous Stability Failure in Hard Brines

3.6.1.1 Causes of Aqueous Stability Failure

Zhang et al. observed that when IOS composes more than 10% of a surfactant solution, the solution tolerance to calcium ions is about 1 wt% CaCl₂ (2006). Al-Hashim et al. found that as petroleum sulfonate surfactant concentration is increased in a CaCl₂ brine, the surfactants first precipitate, then redissolve into solution (Al-Hashim, Celik, Oskay, & Al-Yousef, 1988).

Chandrasekar observed a precipitation reaction with a 33,000 mg/l TDS brine of which 1,427 mg/l were Ca²⁺ ions in an ASP formulation of 0.75% C₁₆₋₁₇ 7PO SO₄, 0.25% C₁₅₋₁₈ IOS, 1% isobutyl alcohol (IBA), 0.3% sodium metaborate, and polymer (Chandrasekar, 2010, p. 65). He attributed the precipitation to high pH conditions and Ca²⁺ ions. In further experiments, Chandrasekar identified the 0.25% C₁₅₋₁₈ IOS with 0.3% sodium metaborate and 1.0% IBA in the brine to be the culprit of causing the precipitation. He suggested that sulfate ions present in the C₁₅₋₁₈ IOS sample would react with Ca²⁺ ions to form calcium sulfate at high pH. Why the C₁₅₋₁₈ Internal Olefin Sulfonate (IOS) would be more likely to precipitate than the C₁₆₋₁₇ 7PO Sulfate was unclear. One would think that the sulfate surfactant would be just as likely to interact with the Ca²⁺ ions, but this was not the case, even when the sulfate concentration was increased to three times that to the sulfonate.

Another concern was that the brine used in experiments for this thesis contained barium. It is well known that barium sulfate is highly insoluble in water. However, stability was achieved in this brine with IOS surfactants if enough co-surfactant and co-solvent were used. The low HLB value of most IOS surfactants already makes them susceptible to form precipitates or to phase separate, even with co-solvents like IBA. It could be that the most hydrophobic surfactant precipitates with the presence of sodium
metaborate, or that sodium metaborate is insoluble in the presence of sulfonate molecules of the surfactant (not that they are necessarily reacting and co-precipitating), much like Chandrasekhar determined that sodium metaborate was insoluble in the presence of sulfate ions.

Chandrasekar did not report on the compatibility of sodium metaborate and the brine without co-solvent, so one can only speculate on those results. However, it was found in experiments done for this thesis that sodium metaborate was not soluble in hard formation brine or in hard synthetic formation brine. Additionally, sodium metaborate was found to precipitate between 1.0 to 2.5 wt% NaBO$_4$ in 5.5 wt% NaCl brine at 43.3°C. The completeness of the sodium metaborate stability failure in hard brine led to the conclusion that co-solvent could not improve the situation.

Ultimately Chandrasekar was able to “mitigate” the precipitation issue by reducing the Ca$^{++}$ concentration by half and keeping the overall TDS the same. Why keeping the TDS the same was important, but not the ionic strength, was not clear. Chandrasekar also did not detect any surfactant in the effluent (meaning complete retention) whether alkali was used or not. Even when the calcium concentration was cut in half, he still did not detect any surfactant in the effluent, which indicates high adsorption (Chandrasekar, 2010, p. 65).

3.6.1.2 Impacts of Aqueous Stability Failure

Sanhi showed in his Master’s thesis that injecting a cloudy aqueous ASP solution in a core flood leads to poor oil recovery and high pressure drop (Sahni V. M., 2009, p. 48). By extension one would expect similar behavior if the ASP slug mixes with the connate brine and its temperature increases. Usually aqueous stability failure is observed in pilot tests as scale issues. Such scale issues have been observed in Alkali-Polymer and ASP floods in the Benton, Wilmington, White Castle, Daqing, and other fields (French, Keys, Stegemeier, Ueber, Abrams, & Hill, 1973) (Dauben, Easterly, & Western, 1987) (Falls, et al., 1992).
Cooke et al. performed an alkali enhanced water flood pilot in a Texas Gulf coast field with 0.3 molar sodium carbonate (pH 10.2). The pre-flushed the pilot zone with calcium free neutral water and chemical tracer. After breakthrough of the pre-flush, they began alkaline slug injection. They experienced a production rate drop of a factor of two when alkali water approached the production well. They found that the well was plugged with calcium carbonate after alkaline water breakthrough. Cooke et al. believed the scale was caused by the alkaline water mixing with resident water in the wellbore (Cooke, Williams, & Kolodzie, 1974).

Bernard performed surfactant/polymer core floods on unconsolidated sandpacks. He found that with no CaSO₄ present, oil recovery was 96 percent, but was reduced to 55 percent with the presence of 2 percent CaSO₄ in the sand. He attributed this decline in recovery to Ca²⁺ reacting with petroleum sulfonate surfactants and precipitating, as well as a reduction in the viscosity of polyacrylamide solution (Bernard, 1975).

3.6.2 Aqueous Stability Improvement of Hard Brines

Aqueous stability can be improved by a number of methods. The most common are: removing divalent ions (i.e. softening the water) by filtration, adding a chelating agent for divalent ions, precipitating out divalent ions with carbonate ions or alkali, diluting the hard brine with soft brine or fresh water, lowering the solution temperature, adding co-solvent, changing the structure of the surfactant used, and decreasing the amount of chemicals used (i.e. lowering the surfactant concentration). While any number of these options can be used or combined on a small scale in a laboratory, the feasibility of most of these options on a field wide scale is limited. Additionally, some of the methods employed to improve aqueous stability are counterproductive because they increase the optimum salinity and interfacial tension of a given formulation (Sahni V. M., 2009) (Mohan, 2009). The most feasible methods are decreasing the amount of chemicals used, adding co-solvent, and changing the structure of the surfactant used.
The first method that will be discussed is lowering the surfactant concentration. The problem with aqueous stability of surfactant solutions is that the surfactant becomes insoluble in the brine because of its hydrophobic nature, which causes the surfactant to separate out in polar solutions. However, if the surfactant solution is dilute enough, Brownian motion may keep the surfactant molecules from agglomerating and the solution from phase separating.

Changing the surfactant concentration has consequences for the behavior of the solution. Chandrasekar found that reducing the total amount of surfactant and co-surfactant improves aqueous stability and lowers optimum salinity (Chandrasekar, 2010, p. 49). Sanhi found that reducing the amount of surfactant above the CMC has no effect on IFT, but can increase the optimum salinity (Sahni V. M., 2009, p. 42). In addition, some schools of thought claim that large volumes of dilute surfactant solutions have increased adsorption rates in reservoirs and achieve worse results than small, concentrated solutions (Morgan, Schechter, & Wade, 1977, p. 101). However, others claim that small, concentrated solutions have lower adsorption rates and improved displacement properties (Gogarty & Tosch, 1968).

Co-solvent can be easily added to ASP formulas and is often inexpensive to do, a positive for field wide implementation. The benefits and consequences to adding co-solvent have been discussed in more detail previously. The benefits are increased aqueous stability, mitigated macroemulsion characteristics, and decreased microemulsion viscosity. The negatives include increased cost, decreased interfacial tension, possible chromatic separation upon injection, and possible shift of optimum salinity.

Increasing co-solvent concentration often increases the optimum salinity of the system (Sahni V. M., 2009, p. 41). Co-solvent increases aqueous stability and sometimes the optimum salinity. Co-solvent also lowers the solubilization ratio, which indicates an increase in interfacial tension from the Chun Huh equation. Co-solvent mitigates the formation and effects of gels, liquid crystals, and macroemulsions. It also causes faster phase behavior equilibration and aids the formation of low viscosity microemulsions.
Levitt noted that surfactants have better aqueous stability at low temperatures (Levitt, 2006).

Another method which has been found to be effective at improving the aqueous stability in hard brines is changing the structure of the surfactant used (Gao, 2012) (Liyanage, et al., 2012). Zhang et al. (2006) found that branched hydrophobes and IOS surfactants had a higher resistance to liquid crystal formation (phase separation) than an iso-C13 propoxylated, ethoxylated sulfate. Gemini surfactants differ from traditional surfactants because they have two hydrophobic tails connected to each other by a bridge molecule. In addition, they have one or two hydrophilic head groups. Changing the size or position of the bridge molecule, the length of the tail groups, or changing the number or type of the head groups can alter the properties of the surfactant molecule considerably. Gao found Gemini surfactants to be very hydrophilic and tolerant to divalent ions and high temperatures, while still achieving ultra low IFT (Gao, 2012). However, geminis often tend to be too hydrophilic.

Altering the structure of a surfactant can also be done by adding Ethylene Oxide (EO) and Propylene Oxide (PO) groups to it. Such methods have been employed widely in the past, but usually no more than 15 EO or PO groups were added to a molecule. Liyanage et al. reported in 2012 their application of dozens of EO and PO groups to surfactant molecules to improve aqueous stability (2012). The EO groups serve to improve TDS, divalent ion, heavy oil, and temperature tolerance. However, too many EO groups can make the molecule more hydrophilic than desired, in which case PO groups can be added to bring the HLB and optimum salinity of the molecule down.

The benefits of changing the surfactant structure are increased tolerance to high temperatures, divalent ions, and total salinity. In addition, large hydrophobe surfactants are often inexpensive to produce because the EO and PO groups are relatively inexpensive compared to the alcohol feedstock used to make the hydrophobe. The major downsides of large hydrophobe and Gemini surfactants are their scarcity (currently they are only made by special order in small scales or in a laboratory) and their tendency to be very hydrophilic.
The least field feasible of the previously listed options are: lowering the solution temperature, removing the divalent ions, precipitating out divalent ions, and diluting the hard brine.

Lowering the solution temperature is not a feasible means to addressing the aqueous stability dilemma. While the solution injected into a reservoir may be injected at relatively low temperatures, it will heat up within the wellbore and reservoir due to natural geothermal phenomena. Even if it is assumed that the injected solution does not heat up appreciably in the wellbore and therefore remains stable going into the reservoir, it may not remain so as it heats up in the formation. The point could be made that phase separation of surfactant solutions is a very common form of aqueous stability failure and is caused by the surfactant being driven into more hydrophobic behavior as the temperature is increased. Thus, as is observed in phase behavior experiments, if a non-polar phase is present, the surfactant will be driven into it and aqueous stability will be maintained.

Two problems arise from this. First, that the surfactant is being driven into the non-polar phase by temperature, and it has already been established that temperature affects phase behavior. Hence, the optimum salinity and solubilization (and therefore the effectiveness of the flood) will be in flux in the near wellbore region while the temperature of the injected solution increases. If the near wellbore region remains at a lower temperature because of long term and continuous injection plans, it is possible that oil in this region may not be mobilized very efficiently because this zone will likely fall outside of design parameters for salinity and temperature dependent phase behavior. Second, if it is assumed that the near wellbore region oil is quickly mobilized and swept away, then as the flood progresses and the oil bank moves further away from the injection wells, there will ideally be little oil left behind in the swept area of the formation. However, ASP solution will continue to be injected into the formation. Since there is little or no oil for the surfactant to migrate to as the ASP solution temperature increases, it will become unstable. This will lead to a decrease in ASP EOR flood effectiveness.
This is also the reason why it is paramount to do aqueous stability tests at reservoir temperature.

Removing divalent ions in laboratory experiments is also a questionable practice. This is often accomplished by substituting sodium chloride for calcium, magnesium, strontium, and barium when making a synthetic reservoir brine. Soft brines will have different impacts to optimum salinity, type III microemulsion volume, type III microemulsion salinity range, phase separation, and precipitation reactions. The ways in which divalent ions could be removed in a field would be due to filtering them out, flushing the reservoir with many pore volumes (PV) of soft brine, or by precipitation reactions.

Precipitating divalent ions out of solution can be done relatively easily with certain alkali, notably carbonates (e.g. sodium carbonate) and hydroxides (e.g. potassium hydroxide, sodium hydroxide, etc.). However, the effects of precipitating divalent ions in the reservoir could be detrimental. For example, pore throats can be occluded and permeability reduced, or scales can build up in wells or surface facilities. Precipitating divalent ions may not be effective because of the amount of consumption of the alkali required for the field, the impacts to well injectivity due to scales, and because of dissolution reactions from the reservoir rock (anhydrite, gypsum, clays, etc). It could be that the divalent ions in the connate brine are precipitated with alkali, only to have them leach back into the new reservoir brine. Such complications would make determining the salinity of the reservoir difficult, and the design of the chemical slug for that salinity even more difficult.

Another method commonly used in laboratory studies is to dilute reservoir brine (or synthetic reservoir brine) with soft brine. The claim is that the hardness of a pre-flush, or that of the chemical slug itself, will be lower than the hardness of the reservoir connate water and some degree of mixing will occur in the reservoir. This scenario is a rationalization of substituting a problem that could be solved with one that could not be. The ratio of reservoir brine to soft brine used in studies is often subjective and happens to be low enough so that the negative effects of divalent ions, such as precipitation
reactions, are minor to non-existent. In such a case, the laboratory experiments are unreflective of the reservoir characteristics. Best practice is to test potential chemical solutions at connate reservoir conditions, regardless of flooding strategy.

3.7 Alkali Behavior in Hard Brines

As mentioned previously, the main alkalis considered in EOR are: potassium or sodium hydroxide (KOH or NaOH), sodium carbonate (Na$_2$CO$_3$), sodium acetate (CH$_3$COONa), sodium metaborate (NaBO$_2$), and tetrasodium ethylenediaminetetraacetate (($\text{HO}_2\text{CCH}_2$)$_2\text{NCH}_2\text{CH}_2\text{N(CH}_2\text{CO}_2\text{H})_2\text{Na}_4$ or EDTA – 4Na). Sodium hydroxide is a very strong alkali and is often times too reactive with reservoir formations and brines to be effective. Sodium hydroxide can dissociate and react with CO$_2$ to produce carbonate ions (CO$_3^{2-}$). Carbonate ions then react with Ca$^{++}$ ions to produce CaCO$_3$ which may precipitate out of solution. Barium and strontium carbonate (BaCO$_3$ and SrCO$_3$) are relatively insoluble in water and would also likely precipitate. Sodium carbonate would cause similar precipitates. Sodium carbonate is commonly thought of as a good alkali for ASP flooding because it produces a relatively high pH and has lower reaction rates with clays than the hydroxide alkalis. Additionally, sodium carbonate is inexpensive and carbonate precipitates do not adversely affect permeability to the same extent as hydroxides and silicates (Hirasaki & Zhang, 2003). Hydroxide ions will react directly with many transition metals like Ca$^{++}$, Mg$^{++}$, and to a lesser extent Sr$^{++}$ and Ba$^{++}$ to produce precipitates. Sodium acetate can complex with transition metals and may mitigate some of the effects of divalent ions. In addition, many of the metal acetates are highly soluble in water (Winters, 2012, p. 20). Sodium metaborate can act as a chelating agent for divalent ions and mitigate some of their impacts to aqueous stability when present in lower concentrations (Chandrasekar, 2010, pp. 10-11). However, at higher concentrations of divalent ions, sodium metaborate will cause precipitation reactions.

Ehrlich et al. investigated alkaline enhanced waterflooding. They found that when gypsum or anhydrite are present in more than trace quantities, a NaOH slug would be
ineffective because of the dissolution of \( \text{CaSO}_4 \) and the precipitation of \( \text{Ca(OH)}_2 \) (Ehrlich, Hasiba, & Raimondi, 1974).

Cooke et al. observed that higher concentrations of sodium chloride lowered the pH required to achieve a particular interfacial tension. This means that for higher salinity brines, less alkali is needed to achieve low interfacial tension. They also found that the presence of calcium and magnesium in the brine, even at low concentrations, increased the interfacial tension between an acidic oil and alkaline brine. They claim that the divalent ions react with organic acids to form calcium and magnesium soaps that are less surface active. Cooke et al. assert that calcium is more detrimental than magnesium in its impact to IFT. Their figures show that, depending on the oil type, less than 25 ppm of calcium is tolerable in a 5.8 wt% NaCl brine if IFT is to be kept below 0.1 dynes/cm. They observed that the same experiment using magnesium required about five times as much magnesium as calcium for the same drop in IFT. Similar results were obtained for a 17.4 wt% NaCl brine (Cooke, Williams, & Kolodzie, 1974).

Cooke et al. noted that when calcium-free alkaline brine contacts clays, calcium ions on the rock surface are released. They proposed using ion-chelating chemicals and the addition of Na\(_2\)CO\(_3\) to the alkaline water to precipitate out the calcium ions as calcium carbonate. Na\(_2\)CO\(_3\) is typically the principal alkali used in modern ASP floods. This makes alkali injection in reservoirs with hard brines untenable (Cooke, Williams, & Kolodzie, 1974).

EDTA-4Na has been used as an alkali as well (Winters, 2012, p. 220). Winters found that Ca\(_2\)EDTA would precipitate at a Ca\(^{++}\) concentration somewhere between 1000 and 2000 ppm in DI water. He also observed that Mg\(_2\)EDTA precipitated at concentrations less than 1000 ppm Mg\(^{++}\) in DI water. The EDTA solution pH decreased as temperature, divalent ion concentration, and aging time increased. EDTA had a high retardation rate in core floods and therefore was not a suitable alkali when anhydrite or gypsum were present.

Winters also explored sodium acetate as an alkali (Winters, 2012, p. 197). He observed that the solution pH decreased as calcium concentration and temperature
increased. With solutions of Ca++ and sodium acetate varying between 0 to 2,000 ppm and 1 to 4 wt% respectively, Winters observed most pH readings to be between 8 and 9. This is below the pH value of 10 needed for saponification of naphthenic acid to occur. While sodium acetate is very resistant to divalent ions, Winters performed core floods with 4.3 wt% sodium acetate and found that it had been neutralized in the core. Even after injecting two pore volumes, he did not see an appreciable increase in pH. Thus, the pH benefits of injecting sodium acetate would not be expected to carry very far into the reservoir. The high concentration of sodium acetate necessary for even a small increase in pH may add too many ions to the reservoir brine to make its use tenable.

Many researchers have identified sodium metaborate (NaB(OH)₄) as a suitable alkali for reservoirs with hard brine (Flaaten, 2007, pp. 49-52) (Zhang, Nguyen, Flaaten, & Pope, 2008) (Chandrasekar, 2010, p. 67) (Sahni V. M., 2009, p. 15). Zhang et al. (2008) found that sodium metaborate could tolerate calcium up to 6,000 ppm. However, this is contradictory to other researchers who have observed precipitation in sea water (Bataweel & Nasr-El-Din, 2011). Zhang et al. also observed that the consumption of sodium metaborate in silica and carbonate rocks was considerably lower than that of sodium carbonate and sodium hydroxide.

Chandrasekar performed many experiments with sodium metaborate and ultimately concluded that a major limitation of sodium metaborate was its inability to sequester calcium ions in the presence of sulfate ions (which is the opposite assertion of Flaaten (2007, p. 11); he claimed that sodium metaborate could prevent precipitation when evaporites were present). He states: “the calcium tolerance in the presence of 50 ppm of sulfate ions was found to be less than 1500 ppm when the salinity of the solution was 35,000 ppm TDS” (Chandrasekar, 2010, p. 75). This may explain why sodium metaborate precipitates in sea water, but not other high divalent ion solutions. Bataweel and Nasr-El-Din found that sodium metaborate precipitated in seawater (including 664 ppm Ca++ and 2,279 ppm Mg++) and formation brines (including 30,000 ppm Ca++ and 4,000 ppm Mg++) (Bataweel & Nasr-El-Din, 2011). They also performed core floods and observed that sodium metaborate had minimum
alkalinity loss in seawater and formation brine. Finally, Bataweel and Nasr-El-Din found that sodium metaborate did not cause a decrease in permeability for carbonate cores when seawater was used as the brine. While they did observe a permeability reduction when using formation brine, the permeability was reduced less with sodium metaborate than with sodium carbonate.

3.8 Polymer Behavior in Hard Brines

Polymer viscosity is also influenced by brine (Levitt, 2006) (Lake, 1989) (Choi, 2008). Divalent cations like calcium reduce viscosity of HPAMs more dramatically than monovalent cations. This forced Levitt use higher molecular weight polymer for his experiments to achieve sufficient injected fluid viscosity. Bernard similarly observed a decrease in viscosity of a polyacrylamide solution when gypsum dissolved and released Ca$^{2+}$ ions in surfactant/polymer core floods of unconsolidated sandpacks. He found that with no CaSO$_4$ present, oil recovery was 96 percent, but was reduced to 55 percent with the presence of 2 percent CaSO$_4$ in the sand (Bernard, 1975).

Gao found that HPAM polymer did not influence aqueous stability (Gao, 2012). Similar results are echoed in this thesis. Zhang et al. (2006) used both hard and soft brines. They asserted that chemical EOR mixtures with sulfate or sulfonate surfactants and high molecular weight polymer can cause phase separation. They observed separation of surfactant rich and polymer-rich phases at higher salinities and attributed this in part due to the electrical repulsion between the anionic surfactant and anionic polymer.

3.9 EOR Research with Hard Brines

Levitt’s Master’s thesis focused on tailoring the ASP process to a dolomite reservoir. To do this, he tested different ASP mixtures with various brines in Barea
sandstone, Texas Cream limestone, and a dolostone. Levitt initially flooded most of the cores with synthetic formation or high divalent cationic brines. However, the ASP and polymer drive slugs were done in a salinity gradient fashion with significantly reduced TDS content and in only one case was the divalent ion content greater than 1,000 ppm (1381 ppm Ca\(^{++}\) and 9 ppm Mg\(^{++}\)) (Levitt, 2006). Given the steep salinity gradients, presence of hydrocarbons, piston-like displacement of fluids in cores, and relatively low brine mixing because of the short distances involved, it is likely that the divalent ions from the connate brine and anhydrite dissolution did not severely hamper the core flood results.

Levitt noted the infeasibility of using sodium carbonate with anhydrite and calcium in general. He proposed sodium metaborate as a possible solution, but from other research, it is known that sodium metaborate does not work well in the presence of sulfate ions or very high divalent ion concentrations (Bataweel & Nasr-El-Din, 2011) (Chandrasekar, 2010). He noted the pickup of calcium and sulfate from anhydrite and quick reaction (equilibration) time. However, according to Morse and Mackenzie, the true equilibration requires weeks or longer to obtain:

...One of the major criteria for determining if a solution is in equilibrium with a solid is the constancy of the solution composition with time. Many investigators have failed to carry out experimental solubility studies long enough to establish clearly this constancy in a satisfactory manner. All too often no observable change over a period of only an hour to a day has been used as a satisfactory time period (Morse & Mackenzie, 1990, p. 51).

Levitt’s solution to was to emphasize the salinity gradient concept to compensate for calcium pick up. Levitt claimed that the effect of calcium is ten times that of monovalent ions on phase behavior. Supposedly this means the breadth and strength of the type III region are impacted by divalent ions at ten times the rate of monovalent ions. Levitt and
many others have stated that the effect of calcium on HPAM was more dramatic than monovalent ions (Levitt, 2006) (Lake, 1989) (Choi, 2008).

Although Levitt did not provide detailed results of aqueous stability tests, he did note the temperature dependence of aqueous stability and phase behavior. When one of Levitt’s SP slugs phase separated into a surfactant rich upper phase and a polymer rich lower phase at 38 degrees Celcius, his solution was to cool the SP solution reservoir to aqueous stable temperatures. He also stated that “Aqueous phase stability is not an issue in the presence of oil” (Levitt, 2006, p. 95). For a detailed rebuttal to the feasibility of the latter two points in field applications, the reader is referred to the discussion on page 45.

While Adam Flaaten incorporated aqueous stability tests into his Chemical EOR design approach for reservoirs with high salinity and hardness in his Master’s thesis, his approach did not incorporate the major aspects that present challenges to achieving good aqueous stability; namely elevated temperatures and divalent ion concentrations. Adam Flaaten’s work involved mixtures of surfactants, co-solvents, and polymer in NaCl salinity scans at room temperature (Flaaten, 2007, p. 80). However, as will be seen in this thesis, achieving aqueous stability under these conditions is not particularly difficult. A much greater challenge is achieving aqueous stability under reservoir conditions. Such conditions include elevated temperature and high concentrations of Ca$^{2+}$, Mg$^{2+}$, Ba$^{2+}$, and Sr$^{2+}$. This is an important distinction because solutions that are aqueously stable at room temperature tend to precipitate at substantially lower TDS concentrations with only a moderate increase in temperature. Similarly, aqueous stability diminishes rapidly as the concentration of divalent ions increases (Chandrasekar, 2010). Thus, for reservoirs in which the surfactant and polymer slugs cannot be softened, or severe heterogeneity and mixing are anticipated, a precipitous reaction is expected. In addition, it is expected that while cooler temperatures will prevail in the near wellbore region of an injection well, substantial aqueous stability failure will occur farther into the reservoir where conditions are warmer and the oil into which surfactants would normally separate has already been displaced.
Winters performed experiments with a synthetic formation brine of 5157 ppm TDS, of which 440 ppm were Ca\(^{++}\) and 148 ppm were Mg\(^{++}\). He performed his aqueous stability and phase behavior experiments at reservoir temperature. He also advocated the use of Guerbet Alkoxy Carboxylate (GAC) surfactants for temperature and divalent ion tolerance and Triethylene glycol monobutyl ether (TEGBE) as a co-solvent. Winters observed that some surfactants that have the highest tolerance to calcium ions also have undesirably high optimum salinities. Winters presented his findings on the impact of Ca\(^{++}\) ions on optimum salinity for GAC surfactants of different numbers of PO groups. His data suggests that the impact of calcium ions on optimum salinity is between 1:1 and 1:4, meaning that an increase of calcium ions of 500 ppm can cause an optimum salinity decrease of 500 ppm to 2,000 ppm TDS. As discussed in his conclusions (pg 238) his experiments seem to conclude that sodium acetate is not a good alkali. His experiments with EDTA as an alkali are somewhat contentious given that they contained less than 1,000 ppm calcium ions and no magnesium. Presumably, magnesium was removed because it reacted more strongly with EDTA to form precipitates (Winters, 2012).

It is good practice to design as robust a system as possible. Removing divalent ions and neglecting the effects of temperature inaccurately represents the reservoir and provides misleading data. Best practice principals would be to perform aqueous stability experiments at connate reservoir conditions, as was done by Walker. This was the stance taken for the work done in this thesis. While Flaaten’s aqueous stability objective was to make sure that “The surfactant slug…will not segregate or precipitate prior to core flood injection”, the objective of this thesis was to make sure that there would be no aqueous stability failure at any conditions (Flaaten, 2007, p. 82).
3.10 Mitigation of Divalent Ions in Hard Brines Impact to Chemical EOR Processes

3.10.1 Ineffectiveness of Pre-flushing

Often times aqueous stability is predicated on a successful pre-flush of the reservoir. Pre-flush is the term that refers to the injection of a brine with a controlled dissolved solids composition in order to condition the reservoir prior to chemical flooding. Typically this is done by injecting a brine with a lower divalent ion and TDS content than the connate brine. Ideally this pre-flush displaces the connate fluids from the reservoir and all that is left is the pre-flush fluid, which is optimally designed for the subsequent EOR flood. Occasionally polymer will be added to a pre-flush to improve sweep efficiency.

Pre-flushes sometimes work in laboratory corefloods. Low heterogeneity impairs mixing and improves the effectiveness of a pre-flush. Clean sandstones with low clay content seem to be the best candidates for pre-flushing. Carbonates can also have good laboratory pre-flush results, but they are complicated by vugginess and the propensity for carbonate and sulfate dissolution. When displacing 38°C hard\(^1\) synthetic formation brine with 31,000 ppm NaCl and polymer, and using 28.1 x 5.6 cm dolomite cores at an injection rate of 1.1 ft/day, Levitt observed calcium, magnesium, and sulfate pickups in the effluent (Levitt, 2006, p. 101). The pickups of calcium and sulfate were highest and varied between 80 and 612 ppm calcium with a median of 423 ppm (sample size of five). He observed calcium equilibration after a few hours of rock-fluid contact time (Levitt, 2006, p. 90). Levitt attributed these increases in divalent ions to anhydrite dissolution.

The divalent ion pickup of effluent brines from coreflood experiments should be considered carefully. Morse and Mackenzie note that solubility data for carbonates is dependent on equilibration time. They claim that long periods (weeks or more) need to be used to establish constancy, but often a few hours or a day with no observable change is used as a satisfactory period (Morse & Mackenzie, 1990, p. 51). They also present

\(^1\) 2,000 ppm Ca\(^{++}\), 600 ppm Mg\(^{++}\), no carbonate or sulfate, and 59,812 TDS.
information that shows how dissolution of a particular foraminifera (*Amphiroa rigida*) dissolves in DI water. This data shows that over the course of a day, the calcium and magnesium ion concentrations in the water will increase, but after eight hours, calcium will begin to precipitate out of solution (Morse & Mackenzie, 1990, p. 111).

Levitt observed anhydrite dissolution in his experiments, which may have overshadowed the effects of carbonate dissolution. With regards to sulfate dissolution in sandstones, Bernard states:

> It has been suggested that a small pre-flush before the soluble oil would eliminate the gypsum problem. Our calculations show that this is not the case; when the sand contains 1 percent gypsum, 4 to 20 PV of water will be required to dissolve the gypsum. This shows that if the formation contains gypsum or some other calcium-containing mineral of similar solubility, it is likely that a soluble oil flood would be relatively inefficient (Bernard, 1975).

Obtaining, treating, injecting, and disposing four to twenty pore volumes of fresh and waste water is not feasible. This information suggests that the dissolution of reservoir rock must be dealt with, and cannot realistically be negated by pre-flushing or modifying the chemical slug injection salinity.

In practice, preconditioning reservoirs on a large scale has met with little success. Evidence in the literature of preflood failure exists for the Wilmington, White Castle, Brookshire Dome, Bell Creek, and Benton Creek fields. Preflood failure can be observed by scale formation. For example, the White Castle sandstone field in Louisiana underwent a preflood consisting of 3.16 PV of soft brines without polymer being injected into the pilot block to displace the hard connate water. The authors observed calcium scale one of the wells was chemically treated five separate times during the pilot. They attributed the scale to multivalent ions due to ineffective preflooding. They also noted heterogeneity in the pilot area, and this likely contributed to the poor brine displacement.
The authors claimed that the pilot was not a fair assessment of the scaling problems that would occur in a full field test in part because of the large preflood that was used to characterize the reservoir (Falls, et al., 1992).

The Wilmington field is sandstone formation located in California and underwent a full field alkali flood in the 1980’s after a pre-flush. Over the course of 14 months, 11.5 MSTB of soft brine (10-25 ppm divalent ions, 1,000 ppm TDS), or 10.2% PV, was injected without polymer for the pre-flush to displace the hard reservoir brine of 355 ppm Ca$$^{++}$$, 315 ppm Mg$$^{++}$$, and 21,097 ppm TDS. An additional 41 MSTB (67% PV) was injected for the alkaline slug. Despite this, 200-300 ppm of divalent ions continued to be measured at the production wells. The authors concluded that “the pre-flush was ineffective in removing hardness, as evidenced by the high concentration of calcium and magnesium in the waters from producing wells.” High consumption of alkaline was observed and attributed to mixing and precipitation of the alkaline fluids with high hardness connate brine and dissolution of reservoir minerals. In addition, scales and precipitates in the producing wells “greatly curtailed” oil production. The results of the flood made the authors question the viability of alkaline flooding (Dauben, Easterly, & Western, 1987).

The failure of pre-flushes to adequately condition reservoirs for chemical flooding has occurred in many more fields. The Brookshire Dome field is a sandstone reservoir about 20 miles west of Houston, TX on I-10. This field underwent a 0.05 PV polymer drive pre-flush and also had results that were below expectations, possibly due to high alkali consumption due to clays (Gao, 2012). An EOR pilot in the high salinity Benton Field of Illinois observed calcium scales and production well problems, despite performing a preflood (French, Keys, Stegemeier, Ueber, Abrams, & Hill, 1973).
3.10.2 Infeasibility of Sequestering Divalent Ions

The principal chemicals used to sequester divalent ions in chemical EOR are sodium tripolyphosphate, EDTA, and sodium metaborate. Sodium metaborate has already been discussed extensively and it was found that it will precipitate when sulfate is present, which is commonly found in carbonate formations. Hill et al. report that 0.5 percent sodium tripolyphosphate \((Na_5P_3O_{10})\) and sulfonate surfactants could tolerate up to 1.9 wt% TDS of hard brine at 95°F. The brine contained approximately 0.1 wt% (1,000 ppm) of barium, calcium, and magnesium (Hill, Reisberg, & Stegemeier, 1973). However, they were unable to use STP in formation water without diluting it with DI water because of precipitation reactions. While STP may work for low to moderately hard brines, it fails for high hardness brines typically encountered in many carbonate and clastic reservoirs.

The main chelating agent considered in chemical EOR is Tetrasodium Ethylenediaminetetraacetate (EDTA-Na₄). Besides being an expensive chemical, a relatively large concentration of EDTA is required to sequester each multivalent ion. The weight ratio of EDTA to divalent ions for complete sequestration is 9:1 (Yang, et al., 2010). This ratio gets even higher with increased temperature. For a carbonate reservoir such as the Eliasville Caddo Unit studied in this thesis, the brine would require approximately 45,000 ppm of EDTA to sequester the 5,000 ppm of divalent ions While EDTA sequesters multivalent ions, it also releases four moles of \(Na^+\) for every one mole of EDTA dissolved. This would push the field brine salinity from 54,000 ppm to about 229,000 ppm TDS\(^2\). Such a massive shift in salinity would have to be designed for in phase behavior, but it probably would not even be stable. All the experiments done for this thesis with EDTA showed precipitation in hard ECU formation brine, even with EDTA concentrations as low as 0.25 wt%.

\[2 \text{TDS} = 49,000 \text{ ppm monovalents} + (5,000 \text{ ppm divalents}) \left(\frac{9 \text{ ppm EDTA}}{1 \text{ ppm divalents}}\right) \left(\frac{4 \text{ ppm Na}^+}{1 \text{ ppm EDTA}}\right) = 229,000 \text{ ppm}\]
3.10.3 Infeasibility of Removing Divalent Ions

The methods for removing ions from produced water for EOR purposes are limited and expensive. The two most feasible methods would be to add alkali to the produced brine or to pass it through a reverse osmosis process.

Adding high concentrations of alkali would precipitate many of the hard ions out of the brine. The precipitate would then need to be collected and disposed of. For a field with a high concentration of divalent ions, a very large amount of alkali would be needed. While alkali is relatively inexpensive, the disposal costs for the precipitates could be high because of impurities or contamination with toxic elements like barium.

Reducing the brine salinity and hardness can also be done by passing the produced water through a semi permeable membrane. In this process, brine is placed under pressure on one side of the membrane, which forces water to the other side. Thus, the formation brine is separated into a brine with a higher concentration of ions and one with a lower concentration. The pressure needed to drive the reverse osmosis process could be over 1,000 psi, depending on the brine salinity. The equipment and energy costs associated with reverse osmosis are high. The wastewater would also need to be disposed of, perhaps in a wastewater well that is not connected to the reservoir interval.

A final concern with removing the divalent ions in carbonate fields is one that has already been discussed in detail: the dissolution of reservoir minerals to increase divalent ion content of the interstitial brine. Even if the produced water can be economically softened, it will pick up divalent ions when injected into the formation. Gypsum and anhydrite are particularly susceptible to dissolution, but calcium carbonate and many other minerals will also dissolve. In such a case, softening the brine is ultimately a futile attempt to battle the fundamental nature of the reservoir.
3.10.3 Salinity Gradient

The salinity gradient concept is generally considered to be a good method for combating reservoir heterogeneity and unknown reservoir properties. It has been shown to work well in core floods (Hirasaki, van Domselaar, & Nelson, 1983). A salinity gradient is created when the injected brine has a lower TDS concentration than the brine it is displacing. In a reverse salinity gradient, the injected fluid has a higher salinity content than the water it is displacing and is usually used in a low salinity reservoir. In a salinity gradient, the optimum salinity of the surfactant solution is designed to be lower than that of the formation, but above that of the injected brine. The theory is that the two brines will comingle as they progress through the reservoir and at some location in the mixing zone the optimum salinity will be reached. Thus, moderate variances in the salinity will not hamper the flood efficiency.

The primary downsides of the salinity gradient are obtaining softened water, disposing and/or treating produced water, mineral dissolution, and brine mixing. The first three limitations have already been discussed in detail above. As discussed previously, mineral dissolution would impact the salinity and hardness of the softened injection water. It is worth noting that the degree of dissolution will be dependent on many things, including the ionic strength of the injected water. This means that the lower the TDS content of the injected brine, the worse the dissolution will be. The dissolution phenomenon will make designing a salinity gradient very difficult for carbonates or reservoirs with high clay or anhydrite content. Dissolution could cause a softened injection brine to pick up so many divalent ions that the brine passes the optimum salinity, which is supposed to be between the injection brine and formation brine salinity.

For example, suppose a chemical EOR flood design consists of a formation brine with TDS of 55,000 ppm, an injection brine of 45,000 ppm TDS, and an optimum salinity of 50,000 ppm TDS. Without mineral dissolution, this design should work well. On the other hand, suppose that mineral dissolution releases 8,000 ppm TDS, bringing the injected brine salinity up to 53,000 ppm. The optimum salinity is now below the injection and formation brine salinities, which is undesirable because it could lead to a type II
microemulsion that traps surfactant in the oil phase and very strongly degrades the flood performance. With enough resources and capital, suppose the injected brine salinity can be reduced to 40,000 ppm. The reduced salinity will induce a higher amount of mineral dissolution. If the new salinity dissolution is 10,000 ppm TDS, then the injection salinity will become 50,000 ppm in the formation, which is the same as the optimum salinity. This design may still fail because the injection salinity with dissolution is too high.

Another concern with mineral dissolution is that the amount of TDS released by the minerals is dependent on time. Thus, the longer the injected brine is in the reservoir, the closer the geochemical system comes to equilibrium. This generally leads to an increase in TDS, but can lead to precipitation later on (Morse & Mackenzie, 1990, p. 111). Thus, a situation could develop in which the salinity gradient is very effective in the near wellbore region of an injector and displaces most of the oil there, but breaks down further away. While oil production will suffer, the increased oil saturation and increased oil relative permeability should result in increased oil production from the baseline, even though the oil bank in the reservoir will erode as the flood degenerates.

Mixing of the injection brine with formation brine is very complex and not well represented by core flooding. Core floods are largely one dimensional and have short mixing zones, relatively low levels of heterogeneity, and low fluid-rock residency times. In reservoirs, variations in permeability, pore size, saturation, salinity, and mineral dissolution will play a part the degree of brine mixing. While polymer helps to improve the displacement front between the two brines, inevitably some equilibrium will be obtained after a certain distance from the injector. If the well spacing in the field is tight, this may not be a significant problem. Otherwise, the new formation salinity may approach some intermediate and variable salinity which would be difficult to characterize let alone correct.

The variance in ions during a salinity gradient flood will also have an impact on polymer. Since polymer is highly sensitive to TDS and divalent ion content, mineral dissolution and brine mixing may have significant impacts to polymer viscosity and flood mobility. Perhaps a good practice is to test the polymer viscosity at different
concentrations in reservoir brine. This will give an indication of the mobility under worst case conditions, which can then be accounted for by changing the polymer or the injected polymer concentration.

3.11 Summary and Conclusions

This chapter investigated some of the complexities of working with carbonate reservoirs and emphasized the importance of divalent ions in the formation brine as well as formation mineralogy. Many of the principles in this chapter are applicable to clastic reservoirs as well. Phase behavior and aqueous stability in hard brines were discussed, as were methods to improve them. Previous research with hard brines was reviewed. The feasibility and robustness of aqueous stability improvements were investigated. The behavior of alkali and sequestering agents in hard brines was explored, as was potential methods for mitigating the divalent ion content in carbonate reservoirs, namely: pre-flushing, removing divalent ions by precipitation or reverse osmosis, and salinity gradients. The takeaways from this chapter are summarized below:

- Most reservoirs in the United States would be considered to have hard brines by chemical EOR standards.
- Most alkali reviewed fail in hard brines, including sodium metaborate
- Sodium acetate is aqueous stable as an alkali, but its pH is too low for spontaneous saponification with crude oil, its pH is below optimum for sulfate stability surfactant, and it is very quickly neutralized in core floods.
- HPAM polymer viscosity is reduced with increasing salinity or divalent ion content.
- Sequestering divalent ions with EDTA or sodium metaborate is infeasible because of mineral dissolution, added electrolytes, precipitation reactions, and the quantity of chemical needed.
- Pre-flushing does not work.
• Precipitation or reverse osmosis to remove divalent ions from produced waters for chemical EOR injection is not feasible.

• Salinity gradients have added complexities in carbonates because of mineral dissolution and may not be practical.

• Most hard brine research to date has neglected or downplayed the:
  o Importance of ionic strength equivalency when using soft brines.
  o Necessity of performing aqueous stability experiments at reservoir temperature.
  o Effects of mineral dissolution.
CHAPTER 4: EXPERIMENTAL EQUIPMENT AND METHODOLOGY

4.1 Introduction

This chapter details the experimental equipment, materials, and procedures used to screen different EOR chemicals and concentrations. The objective of these processes is to develop quick, accurate, repeatable (precise), and comparable results. Tailoring can then be done to select for desired solution properties.

The purpose of an aqueous stability experiment is to test the conditions under which a chemical solution will cloud up, phase separate, or precipitate. A phase behavior test examines the conditions that affect microemulsion characteristics (solubilization strength and breadth, viscosity, etc.). The conditions typically tested are salinity, temperature, chemical type, and chemical concentration. Since phase behavior is used as a proxy for interfacial tension, it can be useful to verify that ultra low IFT is obtained with good phase behavior. This is done with a spinning drop tensiometer. Measuring the IFT is a long and labor intensive process, which is why it is done sparingly and only after good phase behavior results. Core floods are done to simulate the EOR process in a permeable rock and are used as a means of screening and tweaking EOR chemicals and injection procedures.

All phase behavior and aqueous stability solutions were initially mixed in atmospheric conditions at room temperature and pressure. Samples were then equilibrated in an oven. Fluids were also at room conditions prior to the start of the spinning drop tensiometer and core flood experiments. The core flood fluids were kept at room temperature, but they were raised to reservoir temperature via electrical heating tape prior to entering the core.
4.2 Aqueous Stability and Microemulsion Phase Behavior Experiments

4.2.1 Experimental Nomenclature

The aqueous stability and phase behavior experiments were all given names with the format “PB ###” or “AS ###”. PB stands for “phase behavior” and AS for “aqueous stability”. The number that follows PB or AS is the experiment series identifier. This number was used to identify the surfactant composition for each experiment.

The experimental numbers are occasionally succeeded by a letter. These letters indicate successive experiments with the same surfactants and concentrations. Often the aqueous stability experiment is labeled “AS ###” and the phase behavior experiment “PB ###A”, or vice versa. This indicates the order in which the experiments were done (sometimes phase behavior tests were done later because the aqueous stability was promising, and sometimes the reverse was true). Families of experiments often had changes in co-solvent, co-solvent concentration, brine, the range, or precision of the experimental parameter (i.e. salinity).

4.2.2 Aqueous Stability Experiment Equipment

Aqueous stability experiments were done by mixing salts, polymer, surfactants, and co-solvents with de-ionized (DI) water. All chemicals were used as received. The majority of the salts consumed were Fisher Scientific ACS, lab grade chemicals with assays greater than 99%. Two exceptions were Sigma Aldrich lab grade salts which included strontium chloride hexahydrate and sodium metaborate tetrahydrate, both with assays greater than 99%. The barium chloride dihydrate used was from EM Science and had an assay greater than 99%. The majority of the surfactants were supplied by Tiorco (a Stepan company) under the Petrostep brand name. Some of the surfactants, including the large hydrophobe surfactants, were created in, and obtained from, Dr. Gary Pope’s lab with the assistance of Dr. Stephanie Adkins and Dr. Upali Weerasooriya here at The University of Texas. The co-solvents used were Methanol, Ethanol, Iso-butyl alcohol, 1-
Butanol, Sec-Butanol, TGBE, DGBE, and glycerol. These fluids were all Sigma Aldrich and Fisher Scientific lab grade chemicals.

Flopaam 3330S (a product of SNF Floerger) was the polymer used in almost all of the aqueous stability tests. Flopaam 3330S is a partially hydrolyzed polyacrylamide with a molecular weight of 8M and a 25-30% degree of hydrolysis. More information on this particular polymer can be found in Suk Kyoong Choi’s doctoral dissertation (Choi, 2008, p. 22).

The oven used was a GCA Mechanical Convection Incubator 6LM with solid state digital control. The oven was set to 43.3°C (110°F) and maintained at that temperature. Both aqueous stability vials and phase behavior pipettes were stored in the oven, sometimes for months at a time.

Mettler PL200 and a Sartorius 3862 MP8-1 scales were used. The Mettler scale was sensitive to 1.0 mg but had a limited upper range of 200 g. The Sartorius scale, on the other hand, had a precision of 0.1 grams, but an upper limit of 16 kg. Both scales were calibrated yearly by contracted professionals.

The pipette dispenser used was an Eppendorf Repeater Plus model with 10 ml and 5 ml Eppendorf combtips.

The glassware used was Fisher Scientific brand borosilicate glass with no calcium, magnesium, or zinc and low alkali content. Containers of 125 ml were used to contain stock surfactant solutions with concentrated surfactant diluted in DI water. Stock solutions typically contained 2, 4, or 10 wt% surfactant. The aqueous stability experimental solutions were then mixed in 23 x 85 mm Fischer vials with rubber lined caps.

4.2.3 Aqueous Stability Description

The following is a description of the procedure used for performing an aqueous stability experiment. All solutions were initially mixed in atmospheric conditions at room temperature and pressure. Samples were then equilibrated in an oven.
First, concentrated stock synthetic brine was required to perform experiments at and above the formation salinity. The stock synthetic brine was produced using the mean of field brine chemical analyses from different wells. In addition, Tiorco performed a test on well AA Atkins #21 twice and found a discrepancy with the previous analyses with respect to strontium, calcium, and barium concentrations. This led to a shift in the synthetic reservoir brine used after so many tests. However, the impact of the changing salinity composition on aqueous stability and phase behavior was minimal. This is probably because the total concentration of divalent ions remained approximately the same on a weight percent basis.

The concentrated stock synthetic brine used had a concentration of 20 wt%. Its composition can be found in Table 5.2. Care was taken when making the stock brine from the chemical compositions because some of the chemicals contained hydrates. To properly mimic the field brine composition, the hydrates needed to be taken into account in order to determine the amount of each chemical added. Unless otherwise indicated, all experiments were performed with dilutions of stock synthetic field brine, which is hard in nature.

Secondly, surfactants and co-solvents were diluted with DI water from their original concentrations to more manageable concentrations (typically 2, 4, or 10 wt%). This was done to control the amount of each chemical used in the experiments and to compensate for the pipette dispenser’s fixed intervals of precision. The pipette dispenser was only able to release fluid at 50 to 100 \( \mu m \) increments, depending on the combtip used. It was found to be more convenient to change the stock solution concentration than to continuously manipulate the combtip used.

In the second step we went from a weight based measurement to a volume based one. This was done to make mixing the chemicals easier. In switching from a weight based to a volume based measurement, the inherent assumption is that the densities of fluids being mixed are approximately the same. The density of synthetic formation brine stock solution has a TDS of 200,000 ppm hard brine and has a specific gravity of 1.15 at 22.4 degrees Celsius. This is significantly more than the other solutions being mixed
together. This will tend to skew the resulting solution to have a higher salinity than what we record. However, the salinity is typically at most a third of the total solution, so the salinity will only be above the recorded salinity by approximately 5% on the high side (a 7.0 wt% solution would actually be 7.35 wt%) and approximately 2% on the low side (a 4.0 wt% solution would actually be ~4.08 wt%). These values are within engineering tolerances, are likely smaller than the variances in salinity in the reservoir, and would be cumbersome to continuously mitigate. Additionally, the intent of mixing the solutions together is to be able to do quick aqueous stability and phase behavior experiments to screen chemicals and concentrations and get a reasonable idea of system behavior. Mixing mass based and volumetric based measuring systems is perhaps the simplest method for achieving this objective.

Third, polymer, surfactants, co-solvents, DI water, and synthetic brine (in that order) were dispensed into vials. Typically a total of 4 ml or 8 ml of solution were dispensed into each container. Most of the aqueous stability experiments done were salinity scans. This means that for a given experiment, salinity is the only variable in the series of vials. The salinity was varied by adding different amounts of stock brine solution and DI water in each vial. After the chemicals were added, the vials were then vigorously shaken by hand, placed in racks, and allowed to equilibrate in an oven. Experiments were given at least a week to equilibrate and many were kept in the oven for months. Equilibrium was typically reached in 48 to 72 hours or less.

Fourth, measurements were made by visually inspecting each sample for signs of phase separation, cloudiness, or precipitation. Inspections were generally done in less than a minute after the sample was removed from the oven. Photographs of the samples were taken shortly (less than 5 minutes) after samples were removed from the oven. The discrepancy between measurements and photographs arises because of the set up time required for photographing each experiment.

All aqueous stability experiments were completed and sealed under atmospheric conditions. An inert gas, such as argon or nitrogen, was not put into the vials. One reason an inert gas was not used was that the other chemical stocks and the DI water were all
prepared in atmospheric conditions. Using $O_2$ scrubbers would have added complexity. Secondly, it would have been difficult to prevent contact of the solutions with oxygen during transfer to the vials. Thirdly, residual oil on the glass walls is often combusted when sealing the pipettes. This consumes oxygen and circulates the combusted gases in the pipette. Finally, the volume of oxygen in the vial is not that great, and a significant portion of it would already be concentrated in the liquids, which would not change much by flushing the vial with an inert gas.

The impacts of evaporation were also assumed to be of small consequence. The vials were all sealed and could be considered closed systems. However, in the case of methanol or ethanol as the co-solvent, the effects of evaporation could have been more dramatic. This is because these chemicals have a boiling point lower than water and are more likely to evaporate. There is a real possibility that the majority of these chemicals evaporated and their concentration in the aqueous solution was much lower than believed. For this reason, the vials were also shaken after recording the aqueous stability limit. Shaking the vials sometimes revealed a clear mixture when the unshaken vial showed precipitation, or vice versa.

4.2.4 Phase Behavior Experiment Equipment

The chemicals used for the phase behavior experiments were the same as those used in the aqueous stability tests. The fundamental difference between the two experiments is that crude oil is added to the aqueous solution in phase behavior pipettes. Dead crude oil from the Eliasville Caddo Unit field was used as the oleic phase. Polymer was also omitted from the phase behavior experiments.

Graduated pipettes are typically used for conducting phase behavior experiments because they allow for easy visibility and quantification of the different phases. Quantifying the volume of the type III (middle phase) microemulsion, and recording its boundaries with the aqueous and oil phases allows for the solubilization volumes to be
calculated and the Chun Huh equation to be used. The glassware used in the experiments was sterilized 5 ml borosilicate Fisherbrand pipettes with 1/10 ml subdivisions.

4.2.5 Phase Behavior Description

First, each pipette was fused shut with a propane torch at the bottom (tapered) end. Then the aqueous components were added typically starting with the surfactants, then DI water, and finally the brine. Next, the aqueous fluid level was measured by reading the bottom of the meniscus against the gradations in the pipette. Eliasville Caddo Unit dead oil was then added to the pipette and the bottom of this meniscus was also read. After the fluids were in the pipette and their volumes were measured, the top of the pipette was fused shut with a propane torch. The pipettes were then inverted at least ten times each. The pipettes were placed in racks and into an oven at reservoir temperature (43.3 degrees Celsius) and allowed to equilibrate.

Readings and photographs of the phase behavior were then made periodically. Depending on the favorable response of the experiment, some phase behavior tubes were left in the oven upwards of six months. Most experiments, however, were typically in the oven for one to three months. The recorded data included the liquid-liquid interface position(s), the presence of macro-emulsions and gels, a visual inspection of the relative viscosity of the interfaces, and the color of the microemulsion or other interesting results.

These results was then put into a spreadsheet that would, taking into account initial and equilibrated fluid volumes as well as surfactant concentrations, determine the volumes of oil and brine solubilized by the chemical solution. The ratio of the volume of oil solubilized to the volume of surfactant in the solution is the oil solubilization ratio. The ratio of the volume of brine solubilized to the volume of surfactant in the solution gives the aqueous solubilization ratio. Since most phase behavior experiments are scans of some sort (usually salinity, but occasionally surfactant concentration, alkali concentration, or water-oil ratio), when graphed, the abscissa will be the scanned variable and the ordinate will be the solubilization ratio. If the variable is salinity, the graph will
produced a plot with two curves: one of oil solubilization and one of brine solubilization. The two curves intersect at the optimum salinity. The solubilization ratio at the optimum salinity is worth noting, as it is often used to compare the behavior of different surfactant solutions. At this point, both the oil and brine solubilization are the same.

4.3 Spinning Drop Interfacial Tension Experiments

4.3.1 Spinning Drop Interfacial Tension Equipment

A spinning drop interfacial tensiometer is a device used to measure ultra low IFT values (~0.001 dynes/cm, for comparison, DI water at 25 °C has an IFT of 72 dynes/cm). Interfacial tension tests were done for some of the chemical solutions that showed promising aqueous stability and phase behavior. Besides the spinning drop interfacial tensiometer, other equipment such as capillary tubes and caps, syringes, acetone, and a heat gun are necessary.

A Gaertner Scientific Co. Model 500 spinning drop interfacial tensiometer was used for all interfacial experiments. This model has a top speed of 6.5 microseconds/revolution and can heat samples to a maximum temperature of 100 °C. It also has an adjustable microscope for precise measurement of drop diameters.

Clear, thin capillary tubes held the aqueous solutions and oil drops. Caps with o-ring seals were also used to prevent air bubbles from entering the samples. A National Scientific 10 mL syringe with a six inch long needle and a Hamilton Co. 10 μL syringe were needed to move fluids from their containers to the capillary tubes. Fischer Scientific ACS grade acetone was used to wash the capillary tubes, caps, and syringes after each experiment. A heat gun helped dry the capillary tubes.

4.3.2 Spinning Drop Interfacial Tension Description and Calculations

The procedure followed for the spinning drop interfacial tensiometer was similar to that used by Bo Gao in the appendix section of his doctoral dissertation (2012). First,
surfactant solutions were prepared in a manner similar to aqueous stability experiments, with the exception that polymer was not used in the tensiometer experiments in order to accelerate equilibration time. Next, the 10 ml syringe was used to transfer the surfactant solution to a 2 mm outer diameter capillary tube. This was done by placing the needle at the bottom of the capillary tube and injecting fluid continuously while removing the needle. Careful attention was paid to ensuring no air bubbles remained trapped in the tube. Air bubbles can confound results by mingling with oil drops, which impedes the oil drops’ ability to elongate. Aqueous solution was then added to the capillary tube cap. Next, the tube was quickly inverted and sealed with the cap, again making sure to prevent air bubbles from entering the tube.

After the capillary tube was sealed and the exterior cleaned of excess solution, the 10 μL syringe was used to place an approximately 2 μL crude oil droplet into the tube via a small elastomer sealed hole in the center of the cap. Care was taken not to introduce air bubbles to the tube and to place the oil droplet in the center of the tube where it could move freely.

Next, the capillary tube was inserted into the spinning drop interfacial tensiometer and the machine was started. The speed used in the experiments was approximately 6.50 ms/rev, the fastest setting. The machine was then brought up to 43.3 °C and allowed to equilibrate for 45 minutes. This was the amount of time recommended by Bo Gao in his dissertation to prevent reading errors due to transient effects. Additionally, the inclination of the machine was adjusted with a built in screw to keep the oil droplet in the center of the capillary tube.

Once the sample had equilibrated, measurements were made on the upper and lower extremities of the center of the oil droplet. These measurements were done with the built-in microscope and fine tuned measurement dial. Once the oil droplet diameter was obtained, the spinning drop tensiometer was turned off and allowed to cool. The capillary tube and cap were removed and rinsed repeatedly with acetone and DI water. They were then dried with a heat gun.

The equation used to determine the interfacial tensions was:
In this equation, $\gamma$ is the interfacial tension in dynes/cm (which is $10 \mu N/cm$), $\Delta \rho$ is the difference in density between the oil droplet and the aqueous solution in g/cc, $\omega$ is the rotational velocity in rad/s, $R$ is the oil droplet radius in cm. The oil droplet reading using the tensiometer measurement dial can be converted to get $R$ in cm by dividing the recorded diameter by 200.

The IFT measurements for this thesis were all done at reservoir temperature (43.3 °C) unless otherwise specified. The fluids were all prepared and stored at room conditions. The oil droplet and the surfactant solution were not pre-equilibrated before being placed in the capillary tube.

4.4 Core Flood Experiments

4.4.1 Core Flood Experiment Equipment

Core flooding is a common method used to test the effectiveness of a chemical EOR design. The core flood experimental setup used in this thesis consisted of an ISCO LC-5000 Syringe Pump, one 700 cc polyurethane accumulator, one metal accumulator, two high pressure core holders, electrical heating tape, a Coleman cooler, pressure gauges, and a retriever for collecting samples of the effluent fluids. A diagram of the set-up can be seen in Figure 4.1. The syringe pump had a maximum flow rate of 400 ml/hr. The polyurethane accumulator had a pressure rating of 150 psi and was used with the preliminary brine flush and surfactant solution injection. The metal accumulator was used for crude oil and polymer injection.

Two core holders were used to accommodate different core sizes. The first one was able to incorporate a core up to one inch in diameter by six inches long. The second could fit a 1.5 inch diameter by 12 inch long core.

The core holders were placed on a rack inside of an insulated cooler. BriskHeat 120 Volt, 144 Watt 24” electrical heating tape was coiled around the incoming tubing and
core holder. Three thermometers were placed in the cooler to monitor the temperature: one at the cooler inlet, one at the cooler outlet, and one on the rack next to the core holder.

Two pressure gauges were used as well. One was a Solfrunt gauge with a mechanical interface. This gauge placed just before the cooler inlet. The other was a Validyne digital pressure transducer with an output to a data acquisition device (DAQ), which was connected to a computer and controlled with LABVIEW software.

4.4.2 Core Flood Description

First, the dead volume of the core flood tubing was determined. Next, the cores were cut to a specific length and aged in brine at reservoir temperature. The weight of the core when dry and after aging was recorded to determine the porosity. The aged cores were helically wrapped in Teflon tape and placed into an elastomeric core sleeve. The core sleeve was placed into the core holder and axial pressure was applied by screwing in the core holder end pieces. Confining pressure was applied by using a hand pump to pressurize the core holder annulus with hydraulic oil. The confining pressure was maintained at 500 psi or greater.

With the sample secured in the holder, a vacuum was then pulled on the cores for at least six hours. Next, the core was flooded with brine and the liquid permeability was determined. Crude oil was then injected and to residual water saturation. Fluid effluents were measured and the oil and water saturations were determined volumetrically. Next, the core was water flooded to residual oil saturation. Fluid saturations were again measured volumetrically. The relative permeability at residual water and residual oil saturation were obtained from pressure data.

Next, the surfactant and polymer slugs were injected and the injection pressure was monitored. Effluent samples were analyzed and the surfactant concentration and adsorption were determined. The effluent volume of oil was analyzed to determine the oil cut of the oil bank, the amount of oil recovered, and the residual oil saturation.
4.4.3 Core Flood Calculations

The porosity of each core was determined by weighing the core when it was dry and after it had been aged in brine. The following equation was used:

\[ \phi = \frac{m_{\text{aged core}} - m_{\text{dry core}}}{\rho_{\text{fluid}} V_{\text{bulk of core}}} \]  

Where \( m \) is mass, \( \rho \) is density, and \( V \) is volume.

The permeability was determined according to Darcy’s law:

\[ q = -\frac{kA\Delta P}{\mu L} \]  

Where \( k \) is permeability, \( A \) is the cross-sectional area of the core, \( P \) is pressure, \( \mu \) is fluid viscosity, and \( L \) is the length of the core.

Fluid saturations were determined according to:

\[ S_i = \frac{V_i}{V_p} \]  

Where \( S_i \) is the saturation of fluid \( i \), \( V_i \) is the volume of fluid \( i \) in the core, and \( V_p \) is the total core pore volume. \( V_i \) for oil would be \( V_o \). The volume of oil in the core at residual water saturation was measured by recording the total volume of brine collected during oil injection and subtracting the dead volume in the tubing. The volume of oil in the core at residual oil saturation was obtained by measuring the amount of oil produced when water flooding was finished. This value was subtracted from the volume of oil in the core at residual water saturation. The equations are as follows:

\[ V_{o @S_{wr}} = V_{\text{brine produced}} \]  
\[ V_{o @or} = V_{o @S_{wr}} - V_{\text{oil produced}} \]

These values can be used to get the oil saturations. Brine saturations are then:

\[ S_w = 1 - S_o \]
4.5 Summary and Conclusions

This chapter has explained the equipment and procedures used in this thesis for phase behavior, aqueous stability, spinning drop interfacial tensiometer, and core flooding experiments. The equations used to determine experimental results were provided here. Standard protocols are necessary to define techniques, and were discussed in this chapter to improve precision, and to compare the results presented in this thesis with the scientific literature.
Figure 4.1: Core flood experimental setup.
CHAPTER 5: DESIGN OF A SURFACTANT/POLYMER SOLUTION FOR A HIGH HARDNESS CARBONATE RESERVOIR

5.1 Introduction

Traditionally, chemical EOR has been focused on sandstone reservoirs with lower salinity, very low divalent ions, and no gypsum or anhydrite. Typically alkali has been used along with a strong salinity gradient flood. This subset of reservoirs in the United States is limited to relatively few of the potential targets (mainly in the Colorado-Wyoming and Texas Gulf coast areas).

The Eliasville Caddo Unit (ECU) reservoir is located in Stephens County, in Northern Texas. As an enhanced oil recovery target, the ECU reservoir is a stark contrast to published reservoir EOR targets. The ECU is a moldic limestone reservoir with gypsum and anhydrite present. Additionally, the reservoir brine has a high concentration of divalent ions (>5,000 ppm divalent ions). Because of the differences in the ECU reservoir from traditional targets, the experimental methodology in this thesis is unique among published research. The challenge is to design a surfactant-polymer flood that can be used at connate reservoir conditions to efficiently recover the largest amount of oil possible. To this end, the issue of divalent ions was held paramount.

As has been noted above, past research has dealt with divalent ions by substituting them with softened brine, by pre-flushing them away in core floods, using very strong salinity gradients, or (when feasible) by adding chelating agents. Typically an ASP or SP formulation is designed so that it will have its optimum salinity and aqueous stability below the reservoir salinity. This is commonly done using NaCl or sodium carbonate and anticipates the injection slug mixing with the reservoir brine.

However, the research in this thesis is based on the idea that a strong salinity gradient is not feasible, pre-flushing does not work, hard brine must be used whenever possible, and chelating agents are insufficient and inefficient. These stances are taken because of the detachment of the ECU reservoir from traditional EOR targets and due to
the correspondingly higher technical and economic risks. It is believed that by taking such an approach the divalent ion issue can be overcome.

5.2 Eliasville Caddo Unit Description

5.2.2 Crude Oil and Brine

Three brine analysis reports were collected from the ECU field produced water. The details of these analyses can be found in Table 5.1. The two brine analyses performed by Champion Technologies were for two different wells; AA Atkins-Texaco #3 and AA Atkins #37. The last analysis was done by Tiorco and came from the AA Atkins #21 well. The AA Atkins #21 produced water was presumably collected before the separator, for it contained approximately 1 vol% oil when received from the field.

The total dissolved solids content and total amount of divalent ions of each sample agree well. Additionally, the divalent ion concentration of the two Champion Technologies analyses agree. However, the Champion Technologies and Tiorco analyses differ in the divalent ion composition. The Tiorco analysis contains less calcium, less barium and more strontium. Initially, the aqueous stability and phase behavior experiments were done with an average of the Champion Technologies analyses and called New Synthetic Field Brine (see Table 5.2). (The original Synthetic Field Brine sought to include the bicarbonate from the brine analysis. The bicarbonate was found to cause precipitation in the brine and was subsequently replaced with an ionic strength equivalent of chloride ions.) However, once a sample of the field brine was sent to Tiorco and the discrepancy discovered, all subsequent analysis were done with New Strontium Synthetic Field Brine (Table 5.2).

An additional complication of the Eliasville Caddo Unit reservoir is its location and how that impacts the brine chemistry. Because the reservoir is located in Stephens County of Northern Texas, fresh water resources are scarce and a continuing drought has caused the freshwater situation to deteriorate. It is not economic to incur costs by drilling new wells for freshwater or for disposing of waste water from the field. While some water may be available for a salinity gradient injection scheme, such a salinity gradient
will likely be weak and consist of mildly diluted reservoir brine with freshwater lake or river water. For these reasons the aqueous stability and phase behavior experiments were conducted with synthetic field brine diluted with DI water.

Table 5.1: Brine Chemistry Analyses

<table>
<thead>
<tr>
<th>Company</th>
<th>Champion Tech.</th>
<th>Champion Tech.</th>
<th>Tiorco</th>
</tr>
</thead>
<tbody>
<tr>
<td>Well Name</td>
<td>AA Atkins #37</td>
<td>AA Atkins-Texaco #3</td>
<td>AA Atkins #21</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>3368</td>
<td>3368</td>
<td>2810</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>1264</td>
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<td>-</td>
<td>998</td>
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<td>Na$^+$</td>
<td>15802</td>
<td>15080</td>
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<td>-</td>
<td>89.2</td>
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<td>Fe$^+$</td>
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<td>0</td>
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<tr>
<td>Cl$^-$</td>
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<td>33000</td>
<td>33000</td>
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<td>129</td>
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<tr>
<td>CO$_2$</td>
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<td>220</td>
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<tr>
<td>Bromide</td>
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<td>-</td>
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<td>Fluoride</td>
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<td>2.76</td>
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<td>H$_2$S</td>
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<td>TDS</td>
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<td>53834</td>
<td>53600</td>
</tr>
<tr>
<td>Sum</td>
<td>55639</td>
<td>54252</td>
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</tr>
<tr>
<td>pH</td>
<td>6.17</td>
<td>6.37</td>
<td>6.97</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>1.0384</td>
<td>1.0374</td>
<td>-</td>
</tr>
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<td>-</td>
</tr>
<tr>
<td>Pressure</td>
<td>150</td>
<td>150</td>
<td>-</td>
</tr>
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<td>Ionic Strength (calculated)</td>
<td>1.1</td>
<td>1.08</td>
<td>1.13</td>
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<tr>
<td>Conductivity</td>
<td>-</td>
<td>-</td>
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Table 5.2: New Synthetic Field Brine

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<th>AA Atkins #37</th>
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<th>Mean</th>
<th>molecular weights</th>
<th>Ion</th>
<th>Ionic Strength</th>
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<tr>
<td>mg/L</td>
<td>mg/L</td>
<td>mg/L</td>
<td>g/mol</td>
<td>mol/L</td>
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<tr>
<td>Ca(^{2+})</td>
<td>3368</td>
<td>3368</td>
<td><strong>3368</strong></td>
<td>40.078</td>
<td>0.084</td>
<td>2</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>1264</td>
<td>1264</td>
<td><strong>1264</strong></td>
<td>24.305</td>
<td>0.052</td>
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<tr>
<td>Ba(^{2+})</td>
<td>425</td>
<td>690</td>
<td><strong>557.5</strong></td>
<td>137.327</td>
<td>0.004</td>
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<tr>
<td>Sr(^{2+})</td>
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<td></td>
<td></td>
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<td><strong>15441</strong></td>
<td>22.99</td>
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<tr>
<td>Mn(^{2+})</td>
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<td>0</td>
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<td>Cl(^{-})</td>
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<td><strong>33500</strong></td>
<td>35.453</td>
<td>0.945</td>
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<td>HCO(_3^{2-})</td>
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<td>415</td>
<td>406</td>
<td>45.011</td>
<td>0.009</td>
<td>1</td>
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<td>CO(_2)</td>
<td>209</td>
<td>220</td>
<td>214.5</td>
<td>44.01</td>
<td>0.005</td>
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<td>H(_2)S</td>
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<td>198</td>
<td>186</td>
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<td>TDS</td>
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<td>53834</td>
<td><strong>54545</strong></td>
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</tr>
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<td>Sum</td>
<td>55639</td>
<td>54252</td>
<td><strong>54945.5</strong></td>
<td>1.906</td>
<td>1.093</td>
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</table>

sum of bold: 54536.5
5.3 Aqueous Stability and Phase Behavior Measurements

All aqueous stability and phase behavior experiments are presented in the Appendix. Details on the specifics of surfactants, alkalis, co-solvents, brines, experiment range, and experiment precision can be found there. Experimental results are also provided in the Appendix.

5.3.1 First Set of Screening Tests

The original objective of the phase behavior and aqueous stability tests was to get an optimum salinity at the reservoir salinity of approximately 5.36-5.50 wt% TDS, with strong and broad solubility, and aqueous stability to at least 5.50 wt% TDS but preferably 6.00 or 6.50 wt% TDS. Later, it was decided that enough fresh water could be obtained to try a salinity gradient. The target salinity for the fourth screening was 4.5 wt% TDS. The first surfactant solutions used were single surfactant mixtures with no alkali and no polymer. This was done to gauge the relative hydrophilic-lipophilic interaction of the crude oil, brine, and surfactants. Initially it was desired that only one surfactant be used for the EOR flood to mitigate the risks of chromatic separation of surfactants within the reservoir. However, it was quickly found that one surfactant alone would not be able to provide adequate phase behavior and aqueous stability. A list of the surfactants used through all screenings is displayed in Table 5.3. Table 5.4 displays the abbreviations used for describing the surfactant structures. All surfactants were either too hydrophilic or hydrophobic and did not show both good solubilization and aqueous stability at the reservoir salinity. The best surfactant candidates based on phase behavior precipitated at reservoir salinity and temperature.
Table 5.3: List of surfactants used in experiments.

<table>
<thead>
<tr>
<th>Trade Name</th>
<th>Chemical Structure</th>
<th>Chemical Details</th>
<th>Charge</th>
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</thead>
<tbody>
<tr>
<td>S-2</td>
<td>IOS</td>
<td>C15-18 IOS</td>
<td>Anionic</td>
</tr>
<tr>
<td>S-3</td>
<td>IOS</td>
<td>C20-24 IOS</td>
<td>Anionic</td>
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<tr>
<td>S-8A</td>
<td>BAPS</td>
<td>C13-4PO-Sulfate</td>
<td>Anionic</td>
</tr>
<tr>
<td>S-8B</td>
<td>BAPS</td>
<td>C13-7PO-Sulfate</td>
<td>Anionic</td>
</tr>
<tr>
<td>S-8C</td>
<td>BAPS</td>
<td>C13-9PO-Sulfate</td>
<td>Anionic</td>
</tr>
<tr>
<td>S-9A</td>
<td>BAPS</td>
<td>C14-15-4PO-Sulfate</td>
<td>Anionic</td>
</tr>
<tr>
<td>S-9B</td>
<td>BAPS</td>
<td>C14-15-7PO-Sulfate</td>
<td>Anionic</td>
</tr>
<tr>
<td>S-9C</td>
<td>BAPS</td>
<td>C14-15-9PO-Sulfate</td>
<td>Anionic</td>
</tr>
<tr>
<td>S-10B</td>
<td>BAPS</td>
<td>C16-17-7PO-Sulfate</td>
<td>Anionic</td>
</tr>
<tr>
<td>S-13A</td>
<td>APS</td>
<td>C13-4PO-Sulfate</td>
<td>Anionic</td>
</tr>
<tr>
<td>S-13B</td>
<td>APS</td>
<td>C13-7PO-Sulfate</td>
<td>Anionic</td>
</tr>
<tr>
<td>S-13C</td>
<td>APS</td>
<td>C13-9PO-Sulfate</td>
<td>Anionic</td>
</tr>
<tr>
<td>S-13D</td>
<td>APS</td>
<td>C13-13PO-Sulfate</td>
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</tr>
<tr>
<td>S-14</td>
<td>AES</td>
<td>C13-6EO-Sulfate</td>
<td>Anionic</td>
</tr>
<tr>
<td>Neodol-25-12</td>
<td>EA</td>
<td>C12-15-12EO</td>
<td>Non-ionic</td>
</tr>
<tr>
<td>C-9</td>
<td>AES</td>
<td>C6-10 high Ethoxy Sulfate</td>
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<td>TDA-45PO-10EO-Sulfate</td>
<td>APES</td>
<td>C13-45PO-10EO-Sulfate</td>
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<tr>
<td>TDA-45PO-20EO-Sulfate</td>
<td>APES</td>
<td>C13-45PO-20EO-Sulfate</td>
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<td>TDA-45PO-30EO-Sulfate</td>
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<tr>
<td>TDA-45PO-60EO-Sulfate</td>
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<tr>
<td>TDA-45PO-60EO-Carboxylate</td>
<td>APEC</td>
<td>C13-45PO-60EO-Carboxylate</td>
<td>Anionic</td>
</tr>
<tr>
<td>T-Soft SA97</td>
<td>ABS</td>
<td>C12-Sulfonate</td>
<td>Anionic</td>
</tr>
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</table>

Table 5.4: Abbreviations for chemical structures.

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>ABS</td>
<td>Alkyl Benzene Sulfonate</td>
</tr>
<tr>
<td>APEC</td>
<td>Alkyl polyoxy propylene/ethylene (alkoxy) Carboxylate</td>
</tr>
<tr>
<td>AES</td>
<td>Alkyl Ethoxy Sulfate</td>
</tr>
<tr>
<td>APES</td>
<td>Alkyl polyoxy propylene/ethylene (alkoxy) Sulfate</td>
</tr>
<tr>
<td>APS</td>
<td>Alkyl Propoxy Sulfate</td>
</tr>
<tr>
<td>BAPS</td>
<td>Branched Alkyl Propoxy Sulfate</td>
</tr>
<tr>
<td>EA</td>
<td>Ethoxylated Alcohol</td>
</tr>
</tbody>
</table>

The first surfactants used were commercially available through Tiorco/Stepan under the Petrostep brand name. These surfactants included C9, Neodol 25-12, S-2, S-8A, S-8B, S-9A, S-13A, S-13B, S-13C, and S-13D. Initial screening tests were done in
sodium chloride, synthetic formation, and field brines. The first screening results are summarized in the tables in the Appendix. What follows is a summary of the surfactants from the first screening and their behavior.

S-8A and S-8B are both C13 sulfates made from an iso-tridecyl alcohol stock, which, according to the chemical supplier, is a multi-branched alcohol. S-8A has 4 PO groups and S-8B has 7 PO groups. The phase behavior of S-8A can be seen in Figure 5.1 and Figure 5.2 and the phase behavior of S-8B is shown in Figure 5.3. Figure 5.1 was done with S-8A in SFB and can be compared with Figure 5.2, which was done in NaCl brine. The S-8 series surfactants are similar to the S-13 series, but the S-8 series is branched and supposedly slightly more hydrophobic. The S-13 series of surfactants are made from a straight chain tridecyl alcohol stock. Comparing PB 18 and PB 21 (Figure 5.1 and Figure 5.4), it seems that S-8A and S-13A have similar optimum salinities, with S-13A’s being lower. Both also have similar solubilization ratios, but S-13A’s may be higher. Of the single surfactants used, S8-A and S-13A showed the highest optimum solubilization ratio and had optimum salinities closest to 5.4 wt% TDS SFB.

Surfactant S-13B is a straight chain C8-13-7PO-Sulfate molecule. Its optimum salinity is about 2.25 wt% TDS in synthetic formation brine. It causes viscous macroemulsions above its optimum salinity. Figure 5.5 displays PB 6, which contained only S-13B.

Surfactant S-13C is a straight chain C8-13-9PO-sulfate molecule. This molecule is slightly more hydrophobic than S-13A and S-13B, but not as hydrophobic as S-13D. Its optimum salinity is somewhere between 1.50 and 3.00 wt% NaCl and it causes viscous macroemulsions above the optimum salinity. The phase behavior of S-13C can be seen in Figure 5.6.

Surfactant S-13D, along with S-13C and C-9, would become the subject of intense scrutiny in the second screening. S-13D has the same structure as S-13A, S-13B, and S-13C except that it has 13PO groups and is therefore more hydrophobic. In the first screening, S-13D was mostly combined with C-9 and Neodol 25-12, after tests with S-
13A and S-8A were found to be aqueous unstable at reservoir conditions. S-13D also contributes to macroemulsions above the optimum salinity.

Surfactant S-2 is a C15-18 IOS and is much more lipophilic than the other surfactants tested in this screening. 0.50 wt% S-2 was tested by itself in sodium chloride brine and synthetic formation brines in PB 2 and PB 4. Both experiments scanned from 0.00 wt% TDS to at least 8.00 wt% TDS. No middle phase was observed, which indicated that the surfactant was exceedingly hydrophobic.

The surfactant C-9 is a highly ethoxylated sulfate and is very hydrophilic. Neodol 25-12 is also a very hydrophilic surfactant, but it is non-ionic. Initially these hydrophilic surfactants were used to try to make the surfactants solutions more hydrophilic. AS’s 37 through 44 and 46, 50, 51, 56C, and 59A were done to see how C-9 and Neodol 25-12 improve the aqueous stability of hydrophobic surfactants. Later, C-9 and Neodol 25-12 were used primarily in combination with the hydrophobic surfactants to increase the optimum salinity of the solution. C-9 was found to help prevent the formation of viscous macroemulsions.

Most of the initial experiments were salinity scans, but occasionally a surfactant concentration, co-solvent, or co-surfactant scan was done. For example, PB 24 through PB 28 were done to observe how changing WOR and surfactant concentration influenced the solubilization ratio with S-13A surfactant in field brine. PB 29 through PB 33 were similar, but with S-8A surfactant. The results showed that the solubilization ratio was constant above approximately 0.10 wt% surfactant. However, S-13A and S-8A were not aqueously stable at reservoir conditions. AS 34 through AS 46 and beyond attempted to try to keep these surfactants from forming cloudy solutions. Figure 5.7 shows AS 34 with S-8A, S-8B, and S-13A forming cloudy solutions. AS 35 was similar to AS 34, but sodium metaborate was used to try and chelate some of the hard ions and improve aqueous stability. Figure 5.8 Shows that not only did this not work, but sodium metaborate precipitated in the brine without any surfactant added.

Experiments AS 40 through AS 44 were co-surfactant scans in which Neodol 25-12 was added to the S-13A and S-13B mixtures with field brine at different
concentrations. AS 40 showed that over 1.0 wt% Neodol 25-12 was needed to stabilize 0.30 wt% of S-8A in field brine. The stability of S-13A was better. AS 41 showed that less than 0.30 wt% Neodol 25-12 would stabilize 0.30 wt% S-13A. AS 44 sought to identify the cloud point of 0.30 wt% S-13A. It was found that at least 0.08125 wt% N-25-12 was needed to solubilize 0.30 wt% S-13A (see Figure 5.9). Thus, for S-13A, the requisite amount of ratio of surfactant to co-surfactant for stability is about 2.25:1. A ratio higher than this would lead to instability in reservoir brine at reservoir temperature. AS 46 showed that with co-surfactant C-9, this ratio increased to 3:1, indicating that C-9 is more hydrophilic and a better stabilizer than N-25-12. Also, since N-25-12 is a non-ionic surfactant, which is known to have reversed solubility with temperature, N-25-12 could be losing its solubility at reservoir temperature.

The higher the ratio of surfactant to co-surfactant, the better. Since the co-surfactants are known to be very hydrophilic, they will increase the optimum salinity of the solution as well as the aqueous stability. This is an undesirable consequence that typically causes the optimum salinity to go too high, which is countered with more hydrophobic principal surfactants. The higher concentration of hydrophobic surfactants is offset with higher concentrations of co-surfactant to achieve aqueous stability. In some cases this problem can be offset with co-solvent, but as will be seen later, the impact of co-solvent on the aqueous stability of hard brines is very slight.

Experiment AS 50 showed that with S-13B, the amount of C-9 needed increased so that the ratio of S-13B to C-9 for stability was 2:1, indicating that S-13B is more hydrophobic. Test AS 51 did the same with S-8B and the ratio decreased to 1.71:1. It should be noted that experiments AS 50 and AS 51 were done with new synthetic formation brine instead of field brine.

The next step was to see how the stabilized mixtures would perform in phase behavior tests. Experiments PB 48 through PB 63 investigated the impacts that co-solvent had on the pure surfactant mixtures. As can be seen in PB 48 and 48B, a surfactant mixture of 0.75 wt% S-13A and 0.25 wt% C-9 had an optimum salinity in the 9.00 to 10.00 wt% range with new synthetic brine, where just S-13A had an optimum salinity.
around 5.00 wt% in synthetic brine. The change in brines is not enough to explain the difference in optimum salinity, especially since the divalent ion and TDS content remain the same (the new synthetic brine just substituted sodium carbonate for an ionic strength equivalent of sodium chloride, which is relatively small). Thus, it can be seen that S-13A would not be a suitable primary surfactant because the amount of C-9 it requires to make it aqueously stable pushes the optimum salinity too high.

Because the requisite amount of C-9 and Neodol 25-12 co-surfactant with S-8A or S-13A shifted the optimum salinity too high, it was decided to bring the optimum salinity down by using even more hydrophobic surfactants than S-8A and S-13A. This was accomplished by progressively introducing more hydrophobic surfactants such as S-8C, S-13C, and S-13D to the formulation. PB 52 through PB 64 were designed to meet this objective.

Phase behavior experiments PB 52 through PB 55 were done using New Synthetic Formation brine. PB 52 and PB 53 combined 0.50 wt% S-13D with different co-surfactants. PB 52 used 0.15 wt% N-25-12, whereas PB 53 used 0.15 wt% C-9. Both solutions showed that the optimum salinity was below 4.00 wt% TDS. They also contained viscous macroemulsions.

Since PB 52 and PB 53 had optimum salinities that were too low, PB 54 and PB 55 were designed to be more hydrophilic. PB 54 used 0.75 wt% S-13C and PB 55 used 0.75 wt% S-8C. Both solutions also contained 0.25 wt% C-9 in New Synthetic Formation Brine. The optimum salinities of PB 54 and PB 55 were above 10.00 wt% TDS, and were thus too hydrophilic.

PB 56A through PB 64 were done in sodium chloride brine. PB 56A (see Figure 5.10) was a salinity scan of 0.90 wt% S-13A and 0.10 wt% C-9. The optimum salinity of this combination was about 10.00 wt% TDS in the NaCl brine and would be lower in the New Synthetic Formation Brine. However, this surfactant combination would still have its optimum salinity above that of the ECU. AS 56C was an aqueous stability test that showed that 0.90 wt% S-13A and 0.10 wt% C-9 would become cloudy at 4.00 wt% NaCl, which would be even lower with New Synthetic Formation Brine. Aqueous
stability test PB 60 used 0.75 wt% S-13A and 0.25 wt% C-9 in NaCl brine and was cloudy at 8 wt% TDS, or twice the salinity of AS 56C. Small changes in the surfactant to co-surfactant ratio can make a large difference in aqueous stability.

Since more C-9 was needed to make the solution aqueously stable, it was apparent that S-13A and S-13B would be too hydrophilic for optimum salinity purposes. PB 57 through PB 64 were done mostly with S-13D and C-9. PB 57 was a test of just S-13D in NaCl and confirmed that the optimum salinity of S-13D is very low, in the 1.00 wt% TDS range. PB 59 was a phase behavior test that showed a solution of 0.75 wt% S-13D and 0.25 wt% C-9 had an optimum salinity between 3.00 and 4.00 wt% NaCl, as can be seen in Figure 5.11. The subsequent coarse aqueous stability test, AS 59A (see Figure 5.12), showed that while the solution was slightly hazy at 4.00 wt%, progress was being made. Since the optimum salinity and aqueous stability limit were both below their targets, it was believed that S-13D could be blended with C-9 to achieve an optimum salinity and aqueous stability near the reservoir brine salinity because both of these properties would increase with more C-9.

Phase behavior test PB 62 blended 0.50 wt% S-13D, 0.40 wt% C-9, and 0.10 wt% S-2 together, but the optimum salinity was above 7.00 wt% NaCl. In hindsight it is recognized that 0.40 wt% C-9 is too much, even for the more hydrophobic S-2 and S-13D molecules. In the second screening it was observed that concentrations of more than 0.35 wt% C-9 (or about 3:1 surfactant to co-surfactant ratio) would lead to the optimum salinity being pushed above 6.50 wt% TDS. PB 62 marked the point where experiments began to incorporate three surfactants in an attempt to use the phenomena of synergy to achieve stability and good phase behavior.

PB 63 was a phase behavior experiment with 0.75 wt% S-13D and 0.25 wt% IBA. This experiment was similar to PB 57, which did not have the IBA co-solvent. The IBA was meant to lower the amount of viscous macroemulsions, but they were still present in PB 63. The IBA appeared to have no effect.

PB 64 was a three surfactant phase behavior test with 0.50 wt% S-13D, 0.25 wt% S-13C, and 0.25 wt% C-9. This combination had an optimum salinity around 5.00 wt%
NaCl. The solubilization ratio for PB 64 was less than ten and viscous macroemulsions appeared at 5.00 wt% NaCl and above. Aqueous stability of the same surfactant composition was done in NaCl brine in AS 64B and showed stability until 6.00 wt% TDS, at which point the solution became cloudy. Phase behavior and aqueous stability tests with New Synthetic Field Brine were done in PB 64CA and AS 64AA. These experiments showed the optimum salinity to be about 4.00 wt% TDS with a very strong solubilization ratio and significant brine solubilization into the oil phase (see Figure 5.13). They also showed that the aqueous stability limit was below 3.00 wt%. However, given the large increases to aqueous stability and phase behavior that co-surfactant C-9 imparts, it was believed that PB 64 could be further modified to achieve aqueous stability at 5.50 wt% TDS or higher and solublization ratio above 10 at 5.50 wt% TDS New Synthetic Formation Brine.

Polymer was not observed to phase separate at reservoir or room temperature. Multiple experiments showed that 0.10 wt% F3330S polymer did not phase separate at salt concentrations up to 7.50 wt% NaCl brine, in field brine at the same concentration, or in a salinity scan up to 7.0 wt% TDS Strontium Synthetic Formation Brine. The polymer stability was higher than the range of each of these tests. Additionally, dry polymer was mixed in field brine at a concentration of 0.50 wt% and did not phase separate at reservoir temperature. While polymer was not observed to phase separate, it did at times slow the phase separation or precipitation chemistry. Since the viscosity of the polymer depends on the salinity of the brine, the additional time for aqueous stability due to polymer varied between a few minutes and a few hours.

**First Set of Screening Tests: Summary**

The first set screening of tests investigated many surfactants and advanced from simple single surfactant solutions to mixtures of two or three surfactants. Alkalis were also investigated and found to cause precipitation in the synthetic and field brines. Many of the solutions tested exhibited viscous macroemulsions in the type II and type III
regions. Obtaining good aqueous stability and phase behavior proved to be difficult because the requirements of each test were antagonistic; more hydrophobic surfactants were needed for phase behavior, and more hydrophilic surfactants were needed for aqueous stability. The PB 64 series had many of the desired properties and appeared to be the best formulation to modify going forward.

5.3.2 Second Set of Screening Tests

After the initial screening, the most promising approach appeared to be a refinement of the S-13D, S-13C, C-9 surfactants with different co-solvents, specifically the PB 64 solution. Aqueous stability continued to be a problem for this round of screening. The experiments were very heavily influenced by slight changes in individual surfactant concentrations. Too much S-13D would drop the aqueous stability below the 5.5 wt% TDS limit. However, too little S-13D or too much C-9 would in some cases cause the optimum salinity to rise above 7.0 wt%. Viscous macroemulsions also continued to appear above optimum salinity.

Throughout these experiments, however, the solubilization ratio at optimum salinity remained relatively low. Very few of these experiments showed a solubilization ratio of 10 or more at 5.5 wt% ECU brine. Those that did were very sensitive to surfactant concentration variations. The breadth of the type III microemulsion region was also more narrow than desired. Many attempts were made to improve solubilization without altering the optimum salinity and the aqueous stability.

The first experiment in the second screening was PB 65, which is presented in Figure 5.14. This phase behavior experiment was done in NaCl brine with the same concentration of PB 64 surfactants, but with 0.25 wt% S-13C replaced with 0.25 wt% S-13A. The optimum salinity of this formulation was between 6.00 and 7.00 wt%. Because the optimum salinity would drop when hard brine was used, the next experiment (PB 65AA) was the same as PB 65 but with New Synthetic Formation Brine. Figure 5.15 demonstrates that the type III region of PB 65AA was broad and extended from 4.00 to 6.50 wt% TDS. The optimum salinity was calculated to be 5.25 wt%, very close to the
desired optimum salinity. The solubilization ratio of 9.0 cc/cc, however, was not as high as required by the 10.0 cc/cc cutoff. Additionally, evidence of macroemulsions existed at 5.50 wt% and viscous plugs formed at 6.00 wt% and above. Due to co-solvents’ tendency to decrease the solubilization ratio, it was decided that while co-solvent would mitigate the macroemulsion problem, it would also make the solubilization problem worse.

AS 65BA and AS 65C were the two aqueous stability tests done with 0.50 wt% S-13D, 0.25 wt% S-13A, and 0.25 wt% C-9. AS 65BA (see Figure 5.16) was done in New Synthetic Formation Brine and AS 65C (Figure 5.17) was done with NaCl brine. Both tests were done without polymer. AS 65C showed phase separation at 6.00 wt% NaCl and AS 65BA phase separated at 4.50 wt% TDS. The poor aqueous stability was further evidence that PB 65 would not work for the ECU SP flood. The phase behavior and aqueous stability experiments were not comparable on an ionic strength basis. More details on an ionic strength comparison of experiments can be found in the section 5.3.6 Ionic Strength

The next series of experiments was the PB 66 series. These tests were done with 0.40 wt% S-13D, 0.25 wt% S-13C, and 0.35 wt% C-9.

Figure 5.18 shows the first phase behavior test PB 66r, which was done with New Synthetic Formation Brine. This experiment had its optimum salinity at 5.4 wt% TDS and had a solubilization ratio of 10.5 cc/cc. The type III microemulsion region of PB 66r was also very broad; it extended from 4.00 wt% to 6.50 wt% and maintained decent solubility between 5.0 wt% and 6.00 wt%. Subject to qualitative observations, the type III microemulsion was very fluid. The presence of viscous macroemulsions only appeared at 7.00 wt% TDS. The analysis of PB 66r is presented in Figure 5.19.

The aqueous stability tests AS 66A and AS 66C were also promising. AS 66A tested the surfactant solution without polymer in NaCl brine and the result can be seen in Figure 5.20. The vials showed stability to at least 7.00 wt% NaCl. AS 66C used New Synthetic Formation Brine without polymer and showed signs of phase separation at 6.00 wt% TDS. A similar result was also obtained when the experiment was re-done with polymer (AS 66D).
One issue with PB 66r, however, was that the solubilization of oil in water was greater than the solubilization of water in oil. It was observed that the type III microemulsion phase displaced more of the oil than water. As the salinity increases, the solubilization of water in oil increases. This may be because most of the surfactant in the solution is hydrophobic and therefore partitions into and solubilizes oil at lower salinities. The hydrophilic surfactant has its optimum salinity at higher salt concentrations and begins to solubilize brine at higher concentrations. Thus, it is the combination of these three surfactants that may be creating a broad type III region that goes from a more water in oil microemulsion to an oil in water microemulsion, rather than a single, well defined, and sharp type III microemulsion.

Because the phase behavior and aqueous stability for the PB 66 series was so good, it was decided to perform additional experiments with the 0.40 wt% S-13D, 0.25 wt% S-13C, and 0.35 wt% C-9 solution. These experiments make up the bulk of the second surfactant screening. The variations on PB 66 were primarily done by adding co-solvents and slight variations to the concentrations of the individual surfactant members.

AS 66E through AS 66L were a series of aqueous stability tests in which different co-solvents were tried. These co-solvents included: IBA, TGBE, DGBE, SBA, 1-Butanol, glycerine, methanol, and ethanol. The only co-solvents that changed the stability limit were the addition of 0.25 wt% TGBE, which raised the aqueous stability limit from 6.00 to 7.00 wt%, and 0.25 wt% Methanol, which raised the aqueous stability to 6.50 wt%.

PB 66M was the phase behavior test done with methanol and PB 66N was done with SBA. The results are presented in Figure 5.21 and Figure 5.22, respectively. As can be seen in the figures, both co-solvents shifted the optimum salinity higher and decreased the solubilization. However, SBA appears to have less of an effect on the optimum salinity shift.

A similar test to the PB 66 series was the AS 67A and 67B tests in which 0.25 wt% S-13C was replaced with 0.25 wt% S-13A. PB 67A was clear to the end of the test range of 8.00 wt% NaCl. PB 67B was clear to at least 7.00 wt% TDS New Synthetic Formation Brine. However, from previous experience it was determined that this
surfactant formulation would be too hydrophilic for good phase behavior, and therefore further experiments were not performed.

PB 68 through PB 110 were all done with New Synthetic Formation Brine. PB 68 was a phase behavior experiment with 0.50 wt% S-13D, 0.25 wt% S-13C, and 0.25 wt% N-25-12 surfactants. No optimum salinity was observed within the range of the test. All of the pipettes were type II microemulsions, which indicate that the optimum salinity of the formulation was below 4.00 wt% New Synthetic Field Brine, the lowest salinity used in the test. This result arises because the increased concentration of S-13D and the decrease in co-surfactant make the formulation more hydrophobic. Additionally, it has been observed that N-25-12 is not as hydrophilic as C-9, which drops the optimum salinity even further. Using this reasoning, an aqueous stability test was not performed.

PB 69 increased the PB 66 S-13D concentration by 0.05 wt% to 0.45 wt% and decreased the C-9 co-solvent by 0.10 wt% to 0.25 wt%. It also used 0.05 wt% IBA as co-solvent. The optimum salinity was found to be 4.35 wt%, but with only a solubilization ratio of 8.0 cc/cc. A photograph of the PB 69 pipettes is presented as Figure 5.23. An aqueous stability scan was not done because of the poor phase behavior.

PB 70 was similar to PB 69, except that it had 0.05 wt% less C-9 and 0.05 wt% more IBA. All the pipettes were type II microemulsions and contained viscous macroemulsion plugs between the oil and brine phases (see Figure 5.24). This experiment further illustrates the ineffectiveness of IBA to eliminate macroemulsions. It also shows just how sensitive the phase behavior is to C-9. Every 0.05 wt% drop in C-9 decreases the optimum salinity of the formulation by about 2.00 wt% TDS. PB 71 further lowered the amount of C-9 and increased the amount of S-13D. Predictably, the phase behavior was poor.

PB 72 was a phase behavior test with 0.45 wt% S-13D, 0.25 wt% S-13C, and 0.30 wt% C-9 solution, which is 0.05 wt% more C-9 than PB 69 had. The result was optimum stability at 4.1 wt% TDS New Synthetic Field Brine and solubilization ratio of 13 cc/cc. However, the microemulsion at 4.50 wt% TDS and above was viscous. At 6.00 wt% TDS and onward, viscous macroemulsions were also present. PB 73 tried to lower the amount
of C-9 from PB 72 and use 0.05 wt% IBA, but this made the phase behavior predictably more hydrophobic. PB 74, which can be viewed in Figure 5.25, tried to add co-solvent to PB 72 in an effort to make the middle phase more fluid. While the experiment succeeded in moving the point of high viscosity up 0.50 wt% to 5.00 wt% TDS New Synthetic Formation Brine, viscous macroemulsions were still present from 5.5 wt% onward and the solubilization ratio was lowered to 10.5 wt%. Another interesting observation with PB 74 was that the salinity at which the middle phase became viscous decreased the longer the pipettes were in the oven. After one week, the high viscosity point was at 6.00 wt% TDS. After nearly eight weeks, the point dropped to 5.50 wt% and after 34 weeks the viscous point was 5.00 wt%. This probably occurred as macroemulsions coalesced and condensed. Figure 5.26, Figure 5.27, and Figure 5.28 show the aqueous stability experiments for PB 74. Figure 5.26 and Figure 5.27 show AS 74A with NSFB when settled and agitated, respectively. Figure Figure 5.28 shows AS 74A at room temperature. The aqueous stability test AS 74A was cloudy at 4.50 wt% TDS New Synthetic Formation Brine at reservoir temperature (43.3°C). At room temperature (~22°C) the solution was cloudy at 6.00 wt% TDS. Thus, even a small increase in temperature can have significant impacts to aqueous stability.

PB 75 was another phase behavior experiment, this time with 0.45 wt% S-13D, 0.30 wt% S-13C, 0.25 wt% C-9, and 0.05 wt% IBA solution. This represented a 0.05 wt% increase in S-13C over the previous experiments. The optimum salinity of this test was low, about 4.1 wt% TDS New Synthetic Formation Brine. However, it showed a very strong solubilization ratio of 54 cc/cc. PB 75 also showed strong and persistent macroemulsions above 4.50 wt% TDS.

PB 76 increased the concentration of C-9 by 0.05 wt% from PB 75 and also eliminated the IBA. Strangely, the optimum salinity appeared to have dropped below 4.00 wt% and the solubilization ratio dropped to 10.5 cc/cc. This indicated that the result from PB 75 was imprecise due to macroemulsions that resembled microemulsions, despite seven weeks of equilibration time. Figure 5.29, Figure 5.30, and Figure 5.31 show PB 76 after 6, 33.5, and 42 weeks in the oven, respectively. The decrease in
macroemulsions over time is readily apparent in these photographs. Figure 5.32 is the phase behavior plot used to determine optimum salinity and optimum solubilization. Figure 5.33 shows the phase behavior after the samples were removed from the oven and left at room temperature. The next step was to try to increase the optimum salinity of this formulation by increasing the amount of C-9.

The surfactant composition of PB 77 was 0.45 wt% S-13D, 0.25 wt% S-13C, 0.35 wt% C-9, and 0.05 wt% IBA. As can be seen in Figure 5.34 and Figure 5.35, this combination had an optimum salinity of about 5.5 wt% TDS New Synthetic Formation Brine with a solubilization ratio of approximately 15 cc/cc. Additionally, no viscous macroemulsions were observed and the middle phase flowed freely. The aqueous stability test also showed good results; the solution did not become cloudy until 6.00 wt% TDS content. Despite this good behavior, it was decided to continue screening. AS 77B through AS 77D included 0.25 wt% of methanol, TGBE, and sec-butanol respectively. AS 77B and AS 77D phase separated at 5.5 wt% TDS, but AS 77C with TGBE was clear until 6.0 wt%. Because of its good aqueous stability, a phase behavior experiment with 0.25 wt% TGBE was done. This test, AS 77E, had an optimum salinity above 7.0 wt%, possibly around 7.5 wt% TDS. The TGBE pushed the optimum salinity much higher than what was expected (see Figure 5.36).

Experiments PB 78 through PB 86 all contained 0.45 wt% S-13D with variations to the S-13C, C-9, and IBA concentrations. Most of these experiments had optimum salinities below 5.00 wt% TDS New Synthetic Formation Brine and poor aqueous stability (see Figure 5.37 and Figure 5.38). Figure 5.39 and Figure 5.40 compare the variations in phase behavior of PB 80, 82, 83, and 84 due to relatively small surfactant composition changes.

PB 87r was similar to PB 66 but contained 0.05 wt% more S-13C. This pushed the optimum salinity to 5.9 wt% TDS and the solubilization ratio to 11 cc/cc (see Figure 5.41). PB 89 increased the amount of S-13C by an additional 0.05 wt% and the optimum salinity increased to 6.3 wt% TDS with a solubility of 13 cc/cc (see Figure 5.42). Figure 5.43 shows how PB 90 tried to bring the optimum salinity of PB 87r and PB 89 down by
increasing the concentration of S-13D by 0.05 wt%. While the solubilization ratio increased to 15 cc/cc, the optimum salinity remained high at 6.25 wt% TDS.

Large concentrations of N-25-12 co-surfactant were used in PB 92 through PB 98 to try to improve the solubilization ratio and aqueous stability. These efforts were largely fruitless. Besides PB 93 and PB 97, the pipettes displayed poor solubilization. PB 93 showed decent phase behavior, but the optimum salinity was too high and the solubilization ratio too low, because of the relatively high concentration of surfactant (2.00 wt%). PB 97 showed good solubility, but the middle phase was very narrow and above 6.00 wt% TDS.

Second Set of Screening Tests: Summary

The second screening involved experiments in a narrower surfactant range. S-13D, S-13C, and C-9 were the predominant surfactants used. The second screening experiments sought to make slight variations to the PB 64 series from the first screening. This was done by changing the surfactant concentrations relative to one another and on an overall basis. Iso-Propyl Alcohol (IPA) was used as a co-solvent and was largely ineffective. Viscous macroemulsions were less common in this round of screening and were highly dependent on the amount of C-9 present relative to S-13D and to a lesser extent S-13C.

PB 66 was the solution that met both the phase behavior and aqueous stability requirements. However, the solubilization ratio of PB 66 was not very strong and the solution also demonstrated a significant dependence on surfactant composition. Injection errors or chromatic separation of PB 66 could have led to flood failure. It was decided to continue investigating surfactants to find a less sensitive solution with a stronger solubilization ratio. The main problem was finding surfactants that had synergistic properties such that the solution is both aqueously stable and yet hydrophobic enough to have decent phase behavior around 5.5 wt% TDS.
5.3.3 Third Set of Screening Tests

The third screening was characterized by branching out from the S-13D, S-13C, C-9 combinations. This was done in an effort to identify surfactants that displayed better synergy properties. Synergy has been observed with sulfates and Internal Olefin Sulfonate (IOS) surfactants. These combinations, along with many others, were tried in this screening.

The first 40 experiments of the third screening were mostly aqueous stability tests with S-13D, S-2, C-9, and various co-surfactants. Additionally, most of these experiments were done with hard brines. The exceptions were PB 109 and AS 109A. PB 99 through 110B were done with New Synthetic Formation Brine. AS 111 through 226 were done with Strontium Synthetic Formation Brine. This switch was made after a Tiorco brine analysis indicated the composition of a field brine sample was different from the New Synthetic Formation Brine. The TDS and weight percentage divalent ion content of the brine analyses were approximately the same, but the Tiorco analysis (which was done twice) indicated that the calcium and barium levels were lower and the strontium levels higher.

One concern might be that while the weight percent salt divalent ions are the same, due to the difference in atomic mass, the total number of divalent ions in the two synthetic brines are different. The Champion Technologies water reports appear to have not analyzed strontium; therefore they have recorded strontium atoms as either barium or calcium with approximately equal likelihood. The difference in the number of divalent ions between the two brines is 7.5 Moles/L or 5.6 %. If monovalent ions are added, the total ionic difference between the two brines is 61.84 Moles/L or 3.6 % (see Table 5.5). The Champion brine analysis was used to make the composition of NSFB and Tiorco’s was used to make the SSFB. At the same TDS concentration, the ion difference is a negligible 0.5 wt%. Thus, while there is a slight difference between the brines, it is not likely to have an appreciable impact on the comparability of results with formation brine. The shift in aqueous stability and phase behavior should be approximately 0.25 wt% TDS, well within the margin of error being sought.
Table 5.5: Comparison between total molar ion concentration between the water analyses.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Champion Technologies Analysis</th>
<th>Tiorco Analysis</th>
<th>Mole/L Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Atomic Mass</td>
<td>mg/L</td>
<td>Moles/L</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>40.078</td>
<td>3368</td>
<td>84.04</td>
</tr>
<tr>
<td>Ba$^{2+}$</td>
<td>137.327</td>
<td>557.5</td>
<td>4.06</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>24.305</td>
<td>1264</td>
<td>52.01</td>
</tr>
<tr>
<td>Sr$^{2+}$</td>
<td>87.62</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Na$^+$</td>
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<td>687.04</td>
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<td>Cl$^-$</td>
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<td>34000</td>
<td>959.02</td>
</tr>
<tr>
<td>Total</td>
<td>-</td>
<td>$54991.5$</td>
<td>1786.16</td>
</tr>
</tbody>
</table>

The table above is for the formation brine. While the brine used to perform the experiments has its composition based on the formation brine, the tests are done by wt% TDS. When this is taken into consideration, the Moles/L difference between the two brine total compositions at 5.50 wt% is 9.05, or 0.51%. This difference is effectively negligible given that an increase by 0.50 wt% TDS is equivalent to approximately 90 Moles/L of ions.

PB 99 was an unsuccessful phase behavior trial because it was too hydrophobic. All of the pipettes were type II microemulsions and contained viscous macroemulsions. PB 99 was composed of 0.45 wt% S-13D, 0.25 wt% S-13C, and 0.25 wt% S-2.

The phase behavior tests PB 100 and PB 101 both had optimum salinities above 5.50 wt% TDS; the former at 7 wt% and solubilization ratio of 9 cc/cc and the latter at 8.8 wt% with solubilization ratio of 9.5 cc/cc. PB 100 was composed of 0.45 wt% S-13D, 0.40 wt% S-2, 0.15 wt% C-9 and 0.50 wt% IBA (Figure 5.44). PB 101 replaced S-13D with S-13C. Neither experiment showed signs of macroemulsions and both were fluid throughout the salinity range tested. From the previous experiments working with IBA, this seems to be more of a result of synergy between the surfactants, rather than IBA suppressing macroemulsions. The high optimum salinities of these surfactants was surprising, given that both S-13D and S-2 have optimum salinities by themselves below
2.5 wt% TDS. Previous experience dictated that such a low concentration of C-9 should not have increased the optimum salinity appreciably.

AS 100A showed signs of phase separation at 5.50 wt% TDS and appeared to have been caused primarily by S-2, which is yellow in color. The phase separated fluid was a yellow color, unlike the otherwise clear vial (see Figure 5.45). All of the other surfactants were clear in color. Their phase separations can be observed more easily at 6.50 wt% and 7.00 wt% TDS. Since the aqueous stability was acceptable, but marginal, it was decided to try to bring the optimum salinity of PB 100 down further.

PB 102 and PB 109 through PB 109C are a related series of experiments with 0.60 wt% S-13D, 0.30 wt% S-2, 0.10 wt% C-9, and 0.50 wt% IBA. PB 102 had an optimum salinity of 3.75 wt% and a solubilization ratio of 9.0 cc/cc, but AS 102A phase separated at 4.00 wt% TDS (see Figure 5.46). PB 109 (presented in Figure 5.47) and AS 109A were similar to PB 102 and PB 102A except they contained NaCl brine instead of New Synthetic Formation Brine. These trials had an optimum salinity at 5.9 wt% with 13.5 cc/cc solubilization ratio and stability until 5.50 wt%, at which point phase separation and cloudiness were observed. The phase behavior tests displayed a fluid microemulsion phase until 7.50 wt% NaCl.

Based on the results of PB 109 and AS 109A, it was desired that the same chemical mixture be tested in New Synthetic Formation Brine. AS 109B and PB 109C, as expected, had lower optimum salinity and lower aqueous stability than the NaCl trials. The solution was cloudy at 4.0 wt% TDS and had an optimum salinity of 4.8 wt% (see Figure 5.48 and Figure 5.49). One interesting result was that the solubilization ratio decreased to 8 cc/cc. This could be due to experimental variation, but both samples were prepared at the same time with the same surfactant stock solutions and stored in the same conditions for the same amount of time. It seems likely that the divalent ions in the NSFB contributed to the decreased solubilization, just as they did with the optimum salinity.

The next set of experiments involved 0.55 wt% S-13D, 0.30 wt% S-2, 0.15 wt% C-9, and co-solvent. These mixtures contained an increase in C-9 and a decrease in S-13D from the PB 109 and related series. All trials were in Strontium Synthetic Formation
Brine. The intent was to increase the optimum salinity and surfactant stability. This series of experiments also represents an investigation of different co-solvents. The first experiments, PB 110 and AS 110A, used 0.50 wt% IBA and had aqueous stability that was too low and optimum salinity that was too high. These two experiments serve as a basis for evaluating the subsequent work. The optimum salinity was 6.4 wt% with solubilization of 5.5 cc/cc and phase separation at 5.00 wt% TDS at reservoir temperature. Figure 5.50 and Figure 5.51 show these results.

AS 116 through AS 122 respectively contained 1.0 wt% of methanol, glycerol, 1-Butanol, SBA, TGBE, and DGBE. AS 119 was an attempt to use amyl alcohol as a co-solvent, but failed because amyl alcohol was insoluble in DI water even at concentrations as low as 1.00 wt%. Of all these co-solvents, the only one to show appreciable improvement to aqueous stability was TGBE. However, when phase behavior was done with TGBE in PB 122A, no optimum salinity was observed and all pipettes were type I microemulsions. Thus, it appears that TGBE considerably increased the optimum salinity of the chemical solution.

Since TGBE had been found to be very good at improving aqueous stability, further research was done to bring the optimum salinity to an acceptable level (5.00-6.00 wt% TDS). This is reflected in PB 123 through AS 137. Also, AS 125 and AS 130 through AS 137 represent attempts to improve aqueous stability while minimizing the impact to phase behavior by cutting the surfactant concentration by approximately half.

PB 123 and PB 124 tried to increase the amount of S-13D and C-9 in the formulation, but to no avail; the phase behavior did not change from PB 122A. AS 124A, which was an aqueous stability test, actually showed phase separation at 5.0 wt% TDS, which was much worse than AS 121. This may have been because the concentration of surfactant was becoming too high, or because the concentration of TGBE was lower. The composition of these experiments was 0.60 wt% S-13D, 0.30 wt% S-2, 0.20 wt% C-9, and TGBE. PB 123 had 1.0 wt% TGBE and PB 124 had half of that. Cutting the amount of TGBE to 0.25 wt% in PB 126 did not produce any change from AS 124A. AS 127 and AS 128 stability tests removed C-9 from the solution and all the vials phase separated.
This reiterated the importance of C-9 in maintaining stability of the solution; C-9 affects stability on a first order basis, co-solvents have a second or third order influence. AS 129 decreased the amount of S-2, which is known to be very hydrophobic, but this did not improve stability within the range of the test.

AS 125 was the same as PB 123, except the concentrations of the surfactant and co-solvent were cut in half. The same result as AS 124A and AS 126 was observed: phase separation at 5.00 wt% TDS. Most of the experiments from AS 130 through AS 137 contained 0.30 wt% S-13D, 0.15 wt% S-2, 0.10 wt% C-9, and TGBE. In these experiments S-13D, TGBE, C-9 were varied. An increase in S-13D of 0.05 wt% was observed to drop the aqueous stability by 1.0 wt% TDS. An increase of 0.125 wt% TGBE increased the stability by 0.5 wt%, and an increase of 0.125 wt% C-9 increased the stability by approximately 1.0 wt%.

The next round of tests looked at a new set of surfactants. These chemicals included the alkyl polyoxy propylene/ethylene alkoxy molecules with long chains of PO and EO groups, larger IOS surfactants, C15-17 ABS surfactants, and T-soft. The large alkoxy surfactants were mostly of the form TDA-45PO-xEO, with x being either 30 or 60 for this earlier set of screening. Both sulfate and carboxylate propylene/ethylene alkoxy surfactants were tried. These experiments make up the bulk of AS 139 through AS 160.

AS 139 through AS 143 were a series of aqueous stability tests that all phase separated below 4.50 wt% TDS Strontium Synthetic Formation Brine. AS 139 and AS 141 both used TDA-45PO-30EO-Sulfate and co-surfactants in 0.50 wt% concentrations with 1.0 wt% SBA. AS 160 and AS 160B later revealed that TDA-45PO-30EO-Sulfate is aqueously stable to over 14.0 wt% TDS SSFB. Thus, it is concluded that the co-surfactants are what are making the solution precipitate. These co-surfactants were C15-17 ABS and T-soft. AS 147 and AS 148 were similar experiments with TDA-45PO-60EO-Sulfate and TDA-45PO-60EO-Carboxylate and both were either all cloudy or phase separated below 4.0 wt% TDS. These experiments were done at room temperature, but even when the vials were lowered to room temperature, aqueous stability did not improve within the ranges tested.
AS 140, AS 141, and AS 142 all used S-13D, S-3B (C20-24 IOS), C-9 or S-2, and TGBE. The fact that these tests had such poor phase behavior is probably a result of S-3B being more hydrophobic than S-2.

AS 151 through AS 154 was a series of stability tests with TDA-45PO-60EO-Sulfate and TDA-45PO-60EO-Carboxylate, C-9, and SBA. These experiments showed that the surfactants were all soluble throughout the range of the tests (6.0 to 6.5 wt% TDS SSFB). At this point it was unclear whether the surfactants were soluble because of the co-surfactant or co-solvent. AS 158 through AS 160 were tests done with 0.50 wt% alkyl polyoxy propylene/ethylene alkoxy surfactants, polymer, and SSFB. All the surfactants tested were stable to at least 14.0 wt% TDS. Given the solubility of these surfactants, more hydrophobic alkyl polyoxy propylene/ethylene alkoxy surfactants were tested in AS 163 and 164. These surfactants were made more hydrophobic by attaching less EO groups to the molecule. In SSFB, TDA-45PO-10EO-Sulfate had its stability below the range of the test (4.0 wt% TDS) and TDA-45PO-20EO-Sulfate was stable to about 10.0 wt% TDS. A phase behavior test was run on the 20EO-sulfate because of its stability. The resulting optimum salinity was below the range of the experiment (4.0 wt% TDS) and mostly viscous macroemulsions were observed.

The experiments AS 165 through AS 184 were a return to commercially available surfactants from the Stepan/Tiorco Company. These surfactants included S-3B, S-8B, S-8C, S-9A, S-9B, S-9C, S-10B, S-13B, S-14, and other surfactants that have already been mentioned. The S-9 and S-10 series of sulfate surfactants are made from straight chain alcohols with a single branch. S-14 is made from a straight chain alcohol stock (tridecyl alcohol). The A, B, and C lettering refer to the number of propylene oxide groups attached to the hydrocarbon tail (4, 7, and 9 PO groups, respectively). More details are provided in Table 5.3.

AS 165 through PB 169A and AS 175 through PB 179A were mostly of the composition: 0.40 wt% S13D, 0.25 wt% X, 0.325 wt% C9, and 0.25 wt% SBA, where X represents the varied surfactant. A notable exception was AS 169 which only contained 0.15 wt% S3B because S3B was known to be very hydrophobic. AS 170 to AS 174 were
single surfactant stability tests. AS 180 through PB 184A had varying compositions, but most of the experiments sought to find a suitable replacement with S13D while keeping S13C, C9, and SBA concentrations the same.

Of the phase behavior experiments done in the AS 165 to AS 184 range, only PB 179A showed a type III microemulsion in the tested salinity interval. The optimum salinity of this test was above 7 wt% TDS and the type III emulsion extended beyond 8.5 wt% TDS. PB 179A was composed of 0.40 wt% S13D, 0.25 wt% S10B, 0.325 wt% C9, and 0.25 wt% SBA. It was thought that S10B would be on a comparable level of hydrophobicity as S13D, but this experiment showed that it is actually more hydrophilic than S13C and is probably comparable to S13B.

Most of the AS 165 to AS 184 experiments were too hydrophilic. In addition, many of them exhibited poor aqueous stability. The difference between the S13 and S9 surfactants is the feedstock alcohol for the hydrocarbon tail. The S13 series has a C8-13 tail, whereas the S9 series has a C14-15 tail. S10 has an even longer tail: C16-18. For surfactants like S-9A and S-9B the hydrophilic nature is not too surprising. However, S9C should be more hydrophobic than S13C because both molecules contain the same number of PO groups, the same sulfate head groups, and the same alkyl arrangement, but S9C has a longer hydrocarbon tail. Likewise, S10B should also be more hydrophobic than S13C. The increased length of the S9 and S10 hydrocarbon tails is apparent in the aqueous stability tests where these molecules have lower stability than the S13 molecules. Therefore, S9 and S10 have the opposite behavior of what is desired; they are more hydrophilic and have lower aqueous stability.

S14 was also explored as a possible alternative to C9 in AS 180. Despite having good stability by itself (AS 174), S14 was not nearly as hydrophilic as C9 and did not have good stability when mixed with S-13C and S-13D. In AS 192 the amount of S14 was increased to 0.50 wt% TDS from 0.35 wt% TDS in AS 180, but stability only increased from 4.00 wt% to 4.50 wt% TDS. Increasing S14 seemed to have marginal results and phase behavior was not attempted by replacing C9 with S14.
AS 185 to PB 247 mostly involved large alkoxy surfactants, IOS, C9, and SBA. These mixtures showed much promise with extremely high solubilization ratios, broad type III microemulsions, and good aqueous stability with strontium synthetic formation brine at the formation temperature and salinity. In a few cases, ABS, Tsoft, and Gemini surfactants were used, but those experiments were not very fruitful.

The main alkoxy surfactants used were TDA-45PO-10EO-Sulfate and TDA-45PO-20EO-Sulfate. From AS 163 through PB 164A we know that the 10EO surfactant has an aqueous stability below 4.0 wt% TDS at reservoir temperature and that 20EO has stability to approximately 10 wt% TDS. In addition, the 20EO surfactant has an optimum salinity below 4.0 wt%. These were promising properties and the first set of experiments (AS 185 – PB 191A) sought to use the large alkoxy molecules as co-surfactants with S13D and C9. AS 185 to AS 187 and AS 190 to AS 191 showed that mixtures of 0.40 wt% S13D, 0.25 wt% TDA-45PO-XEO-Sulfate, 0.35 wt% C9, and SBA typically had stability at 5.50 wt% TDS at room temperature, but most had stability exceeding the 6.00 wt% TDS upper limit of the experiments. On the other hand, the phase behavior for the large alkoxy surfactants showed mostly type I microemulsion with some type III microemulsion at the upper end of the experiments (6.00 to 7.00 wt% TDS). This indicated that the large alkoxy surfactants were slightly more hydrophilic than S13C.

The ability of the large alkoxy surfactants to promote good aqueous stability, while also having an optimum salinity only slightly higher than S13C, led to their extensive testing in the latter portion of the third surfactant screening. Because a more hydrophobic surfactant than S13D was needed, and because IOS’s show good synergy with sulfates, it was decided to use the S-2 and S-3 IOS surfactants from Tiorco with the University of Texas manufactured large alkoxy surfactants. In these experiments, the large alkoxy molecules were used as the primary surfactant and IOS and C9 were used as the co-surfactants. SBA was retained as co-solvent because it appeared to have the best ability for improving aqueous stability and mitigating macroemulsions without significantly altering the optimum salinity or solubilization ratio. While co-solvent was
not necessary for aqueous stability, it did help with macroemulsions during phase behavior screening.

AS 192 through AS 198 were a series of aqueous stability experiments with 0.40 wt% TDA-45PO-XEO-Sulfate, S-2, and C9, where X is 10 or 20. No co-solvent was used. AS 199 through AS 206 used S-3B instead of S-2. In both cases, the solutions displayed exceptional aqueous stability. All of the tests were stable through the range tested, which was typically 6.50 wt%. A good example of this is AS 206, which had stability to at least 6.00 wt% TDS and was composed of 0.40 wt% TDA-45PO-10EO-Sulfate, 0.25 wt% S-3B, and 0.15 wt% C-9. With S-13D and S-13C, such a low C-9 content would have led to phase separation. The good stability is surprising given that the large alkoxy surfactant was unstable at 4.00 wt% TDS and that S-3B is more hydrophobic still.

The AS 214 through AS 222 experiments had aqueous stability components as well. This new round of testing had higher salinity concentrations, and went to 8.00 wt% TDS. With similar compositions as AS 199 through AS 206, most of these tests had stability to at least 8.00 wt%.

The AS 214 through PB 247 experiments showed a vast improvement in performance over previous tests. These experiments used TDA-45PO-XEO-Sulfate surfactants, with the exception being experiments PB 232, PB 239, and PB 240, which used Gemini carboxylate surfactants. Most tests used S-3B and C-9 as co-surfactants.

The most successful experiments from this round of screening were the AS 215, AS 219, and PB 236 series. The AS 215 series used a 45PO-10EO large alcoxy surfactant and can be seen in Figure 5.52 through Figure 5.57. The AS 219 and PB 236 series used 20EO and are presented in Figure 5.58, Figure 5.59, and Figure 5.60. These experiments showed strong and broad type III phase behavior in the desired range. They also had superb aqueous stability. Viscous macroemulsions and gels were present, even with the presence of SBA co-solvent. However, these macroemulsions were present at salinities significantly higher (~7.0 wt% TDS) than the reservoir salinity (5.4 wt% TDS). All of
these experiments had aqueous stability to at least 8.0 wt% TDS SSFB and optimum solubilization ratios of 20 cc/cc or greater.

Experiments with S-2 instead of S-3B (AS 217 through AS 218 and AS 221) showed good stability, but had optimum salinities that were higher than 9.0 wt% TDS SSFB. Similar observations were made for the TDA-45PO-30EO sulfate surfactants (AS 216, PB 216A, AS 222, PB 235A). PB 238 used a TDA-45PO-60EO sulfate as a hydrophilic co-solvent, but the result was all type II phase behavior, which indicated that the 60EO molecule was not as hydrophilic as desired.

In an effort to simplify the surfactant slug, it was suggested that the HLB of the AS 215 series be determined, and a single surfactant with a similar HLB be tested. It has been proposed that the HLB of a solution of surfactants is determined according to a linear mixing rule whereby the HLB impact of each individual surfactant is proportional to weight or molar fraction (Kruglyakov, 2000, pp. 230-231) (Anton, Anderez, Bracho, Vejar, & Salager, 2008, p. 84). In other words:

\[
\text{HLB}_{\text{mixture}} = \sum_{i} x_i \text{HLB}_i
\]

Where \(i\) is the surfactant species in the solution and \(x\) is the weight or molar fraction of surfactant \(i\). The weight average HLB for AS 215 (0.40 wt% TDA-45PO-10EO-Sulfate, 0.25 S-3B, 0.25 C-9) was determined to be 28.8. The closest available surfactant that had a similar HLB was TDA-27EO-Carboxylate, which had an HLB of 32.975. PB 228 used this surfactant by itself and the phase behavior did not appear to be impacted at all. The response was similar to a DI water and oil combination (a null result). There are three explanations for the null result: 1) The carboxylate head group did not have as favorable properties as sulfate in the solution, 2) the HLB of the carboxylate surfactant was not close enough to the mixture HLB, or 3) the linear mixture principle was not applicable. The last explanation seems most plausible because the linear mixture principle is based on the surfactants being relatively similar. The mixing rule is not linear if the products are extremely different (Anton, Anderez, Bracho, Vejar, & Salager, 2008, p. 97). The AS 215 mixture contained sulfate and sulfonate surfactants some of which were very large and hydrophobic whereas others were very small and hydrophilic. It is likely that the
combination of these surfactants have selective partitioning into the aqueous and oil phases, which can be viewed as a type of synergy. Single component surfactants will not exhibit selective partitioning, which may limit their behavior.

A Gemini surfactant was also tested. PB 232, PB 239, and PB 240 all used a C-18-DEG-70PO-30EO-2Carboxylate Gemini surfactant (where DEG is a diethylene Glycol bridge molecule between the two hydrocarbon tails). The phase behavior with this molecule was poor and no type III region was observed in any of the three experiments.

The other experiments in the AS 221 through PB 247 were done with TDA-45PO-XEO-Sulfate, S-3B, and C-9, where X is 10 or 20. These experiments had varying surfactant concentrations and brines. Many were done with formation brine, which was diluted by the addition of surfactant. The result was typically type I microemulsions. Even when the mixing procedure was adapted to use stock synthetic brine to compensate for the diluting effect of the surfactant solutions, the phase behavior was still in the type I region. Such variations were made for PB 215F, PB 215G, PB 219D, PB 236A, and PB 246A, with no effect.

**Third Set of Screening Tests: Summary**

The third screening was composed of approximately 200 aqueous stability and phase behavior tests. Field brine, new synthetic field brine, and strontium synthetic field brine by themselves were not found to precipitate at reservoir temperature. Experiments such as PB 124A and PB 125 showed that aqueous stability was not improved by cutting the surfactant concentration in half. This may have been because the level of improvement was smaller than the 0.5 wt% TDS resolution of the experiments.

The most promising experiments from this round of testing were the PB 66, PB 77, PB 215, and PB 219 series. These series all had an optimum salinity near the 5.5 wt% target salinity. The PB 215 and PB 219 series showed the strongest solubilization ratios yet seen, had broad type III regions, and had fluid microemulsions. These series also had aqueous stability beyond 8.0 wt% TDS SSFB. The PB 66 and PB 77 series, while still
performing better than many of the other experiments, had marginal solubilization ratios and moderate to poor aqueous stability. Many additional experiments were done with the PB 66 and PB 77 series (or variations of them), but their shortcomings were not surmounted.

The most promising chemicals were the moderately hydrophobic large alkoxy sulfate surfactants mixed with very hydrophobic IOS and very hydrophilic ethoxylated sulfates. Various co-solvents were used predominantly to improve aqueous stability. Most co-solvents proved to be either ineffective or to increase the optimum salinity too much. Sec-buty alcohol (SBA) proved to be an adequate co-solvent because it slightly improved aqueous stability, it had low impacts to optimum salinity and solubilization ratio, it minimized the presence of viscous macroemulsions, and it decreased the viscosity of the microemulsion phase. Most of the other surfactants and co-solvents that were tested were too hydrophilic. Many exhibited poor solubilization ratios as well. The PB 109 series of experiments mixed IOS with APS surfactants and showed strong solubilization, but poor aqueous stability.

Experiments in the third screening were also done with formation brine. After compensating for the diluting effects on the formation brine due to the stock surfactant solutions, phase behavior continued to display type I microemulsions. This indicated that either the optimum salinity had shifted upwards, or the solution salinity was still too low.

5.3.4 Fourth Set of Screening Tests

The fourth screening was characterized by a change in phase behavior objectives and continued investigation of formation brine experiments. In March of 2013 it was decided that adequate fresh water could be obtained for a salinity gradient. This necessitated that the optimum salinity of the surfactant formulation be approximately 80% of the formation salinity. With the formation salinity accepted as 53,600 ppm TDS, the target optimum salinity would be 4.5 wt% TDS and the drive salinity would be 3.375 wt% TDS.
Tweaking of the PB 215 and PB 219 series continued and ultimately three surfactant mixtures were found to have excellent aqueous stability and phase behavior characteristics. PB 242 was composed of 0.50 wt% TDA-45PO-10EO-Sulfate, 0.25 wt% S-3B, and 0.25 wt% C-9. A photograph of the phase behavior is presented in Figure 5.61. The optimum salinity was found to be 4.8 wt% TDS SSFB with a low solubility ratio of just 6 cc/cc. However, this formulation did show very high water solubility and, when measured with the spinning drop interfacial tensiometer, had comparable IFT values to other well performing surfactant formulations. PB 246 had a similar composition as PB 242, except that it had 0.275 wt% C-9. Its optimum salinity and solubilization ratio were 5.5 wt% TDS and 24 cc/cc. The phase behavior of PB 246 is available for viewing in Figure 5.62. PB 247 was composed of 0.40 wt% TDA-45PO-10EO-Sulfate, 0.25 wt% S-3B, and 0.225 wt% C-9. PB 247 did not have a distinctive optimum salinity in the range tested. However, the point of maximum water solubilization (16.6 cc/cc) occurred at approximately 4.5 wt% TDS SSFB and had an oil solubilization of 55.8 cc/cc, which indicates strong solubilization properties. Figure 5.63 shows the phase behavior of PB 247.

Given the success of these experiments in SSFB, an effort was made to test the surfactant formulations in formation brine (FB #1), which was augmented with concentrated SSFB to offset the decrease in salinity caused by adding the stock surfactant solutions. The aqueous stability results for AS 242D and AS 247B are displayed in Figure 5.64: AS 242D with reservoir brine. and Figure 5.65: AS 247B with reservoir brine.. The corresponding phase behavior experiments, PB 242E and PB 247C, are displayed in Figure 5.66 and Figure 5.67. As can be seen in the pictures, the samples are aqueously stable at reservoir temperature. The phase behavior, on the other hand, was very poor.

In an effort to better understand the discrepancy between the phase behavior of FB #1 with SSFB and just SSFB, a spinning drop interfacial tensiometer was used to determine the IFT versus salinity. The IFT tests were all done by placing aqueous surfactant solution into a capillary tube and then introducing a drop of ECU crude oil. The samples were not pre-equilibrated, but were allowed to equilibrate in the machine for
at least one hour before measurements were taken. In one instance a sample with a WOR of one was equilibrated for two days at reservoir temperature and then tested. The result was the same as the unequilibrated samples.

The IFT experiments were done on the most promising candidates for core flooding: solution series 242, 246, and 247. Figure 5.68 shows AS 242A, which is the same formulation that was used in PB 242, and therefore the IFT measurements can be directly compared to the phase behavior. Doing so shows that the measured IFT data agrees well with the phase behavior data in that both have the optimum salinity at 4.8 wt% TDS SSFB. However, the Chun Huh equation constant at S* is \( C = 0.0906 \text{ dynes cm}^{-2} \), not 0.3 as is often assumed. Also important to note is that the IFT does not reach the “ultra-low” value traditionally targeted for high oil recoveries (see section 1.2 A Brief Overview of Chemical EOR). To see how co-solvent was impacting the IFT, AS 242B removed the SBA from the solution. A graph of PB 242B is presented in Figure 5.69. The impact of SBA on IFT seemed to be negligible. Next, AS 242C and AS 242D both eliminated SBA and used different brines. The former used NaCl brine and the latter FB #1 with SSFB. The graphs of AS 242C and AS 242D are displayed in Figure 5.70 and Figure 5.71. These figures have multiple readings at each salinity to portray the variation in oil bubble diameter (and ultimately IFT) that is observed when taking measurements. As can be seen, the NaCl brine has an optimum salinity that is much higher than the other brines. In addition, the IFT with the NaCl solution is almost an order of magnitude lower than with the other brines (0.007 dynes/cm at the lowest point). Figure 5.71 with PB 242D in FB #1 and SSFB has similar IFT trends as PB 242B and 242C in only SSFB. This is an interesting result given that the phase behavior is very different. The similarities in IFT but differences in phase behavior may serve as evidence that the field brine contains emulsion breakers (or other solvents) which will be discussed further in section 5.3.8 Synthetic Brine Versus Field Brine.

The IFT results with AS 246 with SSFB is presented in Figure 5.72. This IFT data is also directly applicable to phase behavior data (PB 246). Comparing the IFT data to the phase behavior’s S* (5.5 wt% TDS SSFB), we get a value of 0.01 dynes/cm and a \( \sigma^* \) of
24 cc/cc. This gives a Chun Huh constant of C=0.24 dynes/cm, which is much closer to the standard assumed value of 0.3. Unlike the phase behavior data, the IFT results indicate that the interfacial tension continues to decrease with salinity.

AS 247A, shown in Figure 5.73, is comparable to the phase behavior experiment PB 247, although PB 247 has 0.5 wt% SBA whereas AS 247A does not. AS 247A shows that the IFT continues to decline as the salinity increases, a result that was seen with AS 246 as well. AS 247B used FB #1 and SSFB and is charted in Figure 5.74. The results are similar to AS 247A, however, the formation brine appears to cause the IFT to increase slightly. The error in making measurements makes it difficult to confirm this trend with certainty.

Further experiments were attempted to characterize the chemical formulations. AS 248 through PB 254A and PB 268 through PB 274 used S-13D, S-2 or S-3B, C-9, and SBA. AS 255 through PB 267A used TDA-45PO-XEO-Sulfate, S-2 or S-3B, C-9, and SBA, where X is 20 or 30. Almost all of these additional experiments were done with Formation Brine #2 (FB #2) augmented by concentrated Strontium Synthetic Formation Brine (SSFB) in order to offset the decrease in salinity brought about by adding the surfactant solutions. The salinity of AS 248 through PB 267A was 4.60-4.70 wt% TDS. At reservoir temperature (43.3°C) all of the formulations either had poor aqueous stability or poor phase behavior. However, at room temperature a few of the pipettes showed very good solubilization. These experiments include PB 74C, 80C, 145B, 248A, and 250A, all of which have S-13D as the principal surfactant. For reservoir conditions, none of these further surfactant solutions were suitable.

5.3.5 Experiments with additional Co-solvents

A number of experiments were done in which the co-solvent was varied. This is most evident in PB 66, PB 77 and PB 116 through PB 144. Primarily these experiments investigated the improvement to aqueous stability, but a few were also done to look at phase behavior.
The principal co-solvents used in experiments up to PB 110 were IBA and N-25-12. When sulfates and IOS surfactants were combined, IBA raised the optimum salinity significantly (see PB 100) and controlled macroemulsions very well. IBA also improved aqueous stability substantially (see AS 100A). However, with only sulfate surfactants, the impact of IBA on the solution behavior was negligible. This may have been due to the fact that lower concentrations of IBA were used with sulfate only solutions. The influence of N-25-12, which is actually a non-ionic surfactant, on solution behavior was found to be negligible (see AS 92 through PB 98).

Glycerol and 1-Butanol had no observed effect on aqueous stability. Methanol, Ethanol, Sec-Butanol, and DGBE had minor improvements to stability. They typically improved stability by 0.0 to 0.5 wt% TDS over solutions with weak or no co-solvent, depending on the concentration of surfactant and co-solvent. TGBE performed the best in terms of increasing aqueous stability. It was observed to raise the cloud point by 0.5 wt% to 1.0 wt% TDS over solutions with weak or no co-solvent.

Glycerol, 1-Butanol, Ethanol, and DGBE were not used in phase behavior experiments. Methanol, SBA, and TGBE all increased the optimum salinity. PB 66M had 0.25 wt% Methanol and showed an increase in optimum salinity from PB 66, which did not have co-solvent, from 5.4 wt% to approximately 7.1 wt% TDS SSFB. The solubilization ratio also decreased from 10.5 to 9 cc/cc. PB 66N had 0.25 wt% SBA and the optimum salinity was 6.75 wt% TDS SSFB with a solubilization ratio of 9. PB 66N also displayed good solubilization at 6.0 and 6.5 wt% TDS. PB 122A through PB 126A all should have been hydrophobic mixtures with optimum salinity in the 4.0 to 5.0 wt% TDS range. However, the inclusion of TGBE pushed the optimum salinity above 6.5 wt% TDS in all cases. PB 77E had 0.25 wt% TGBE and had an optimum salinity of about 7.5 wt% with a solubilization ratio of 6.5 cc/cc. The optimum salinity and solubilization ratio of PB 77, which did not have co-solvent, was 5.5 wt% TDS and 15 cc/cc. From these results it is apparent that Methanol and TGBE increased the optimum salinity too much. Additionally, TGBE was very detrimental to the solubilization ratio (and to IFT). SBA was used ubiquitously throughout the third and fourth screenings because 1) it had
acceptable improvements to aqueous stability, 2) it did not increase optimum salinity to unreasonable levels, 3) it did not impact the solubilization ratio substantially, 4) it mitigated some of the effects of viscous gels and macroemulsions at elevated temperatures and salinities, and 5) it accelerated the equilibration time.

5.3.6 Ionic Strength

A number of samples were tested with hard brine and with NaCl brine. This section analyzes some of those experiments. The ionic strength of the SSFB brine at 5.36 wt% is 1.06 mol/ml, which is equivalent to 62,000 g/L NaCl. Figure 5.75 is a chart comparing the ionic strengths of NaCl and SSFB at different concentrations. Table 5.6 shows the solubilization ratio, optimum salinity, and optimum salinity ionic strength for experiments done with hard and soft brines. Surfactant composition, temperature, and oil were held constant. Table 5.7 shows the cloud point and cloud point ionic strength for experiments done with hard and soft brines. While the phase behavior experiments with only sulfate surfactants do not show similar performance characteristics on an ionic strength basis, the experiments that blend IOS with sulfates do show comparable behavior when normalized with respect to ionic strength. This may not be true for the large hydrophobe surfactants such as TDA-45PO-10EO-sulfate, which is present in PB 219A’.

Temperature may also play a role in determining ionic strength equivalency. As will be discussed in the following section (5.3.7 Temperature Effects), temperature influences both the solubilization and the optimum salinity of surfactant formulations. The consequence of this is that phase behavior based on ionic strength equivalency may shift with temperature changes.

While phase behavior and aqueous stability do not always equate on an ionic strength basis, the results presented here echo those by Gogarty and Tosch in that ionic strength can be a useful means for predicting the phase behavior of micellar solutions (Gogarty & Tosch, 1968).
Table 5.6: Phase behavior experiments with hard and soft brines.

<table>
<thead>
<tr>
<th>Brine</th>
<th>Experiment</th>
<th>Solubilization Ratio (cc/cc)</th>
<th>S* (wt% TDS)</th>
<th>Ionic Strength S* (mol/dm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>PB 64</td>
<td>6.9</td>
<td>4.75</td>
<td>0.813</td>
</tr>
<tr>
<td>Hard</td>
<td>PB 64C</td>
<td>18</td>
<td>2.8</td>
<td>0.557</td>
</tr>
<tr>
<td></td>
<td>PB 65</td>
<td>18</td>
<td>7.9</td>
<td>1.352</td>
</tr>
<tr>
<td>Hard</td>
<td>PB 65AA</td>
<td>9.5</td>
<td>5.33</td>
<td>1.06</td>
</tr>
<tr>
<td>NaCl</td>
<td>PB 109</td>
<td>9.75</td>
<td>6.2</td>
<td>1.061</td>
</tr>
<tr>
<td>Hard</td>
<td>PB 109C</td>
<td>9</td>
<td>4.85</td>
<td>0.965</td>
</tr>
<tr>
<td>Hard</td>
<td>PB 66Q</td>
<td>4.7</td>
<td>8.4</td>
<td>1.671</td>
</tr>
<tr>
<td>NaCl</td>
<td>PB 66V</td>
<td>2.6</td>
<td>9.8</td>
<td>1.677</td>
</tr>
<tr>
<td>Hard</td>
<td>PB 219A’</td>
<td>32</td>
<td>5.6</td>
<td>1.114</td>
</tr>
<tr>
<td>NaCl</td>
<td>PB 219G</td>
<td>6</td>
<td>9.0</td>
<td>1.534</td>
</tr>
</tbody>
</table>

Table 5.7: Aqueous stability experiments with hard and soft brines.

<table>
<thead>
<tr>
<th>Brine</th>
<th>Experiment</th>
<th>Cloud Point (wt% TDS)</th>
<th>Ionic Strength at Cloud Point (mol/dm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>64B</td>
<td>6.0</td>
<td>1.027</td>
</tr>
<tr>
<td>Hard</td>
<td>64AA</td>
<td>4.0</td>
<td>0.796</td>
</tr>
<tr>
<td></td>
<td>PB 65BA</td>
<td>6.0</td>
<td>1.027</td>
</tr>
<tr>
<td>Hard</td>
<td>PB 65C</td>
<td>4.5</td>
<td>0.895</td>
</tr>
<tr>
<td>NaCl</td>
<td>PB 66A</td>
<td>7.0</td>
<td>1.198</td>
</tr>
<tr>
<td>Hard</td>
<td>PB 66B</td>
<td>6.0</td>
<td>1.193</td>
</tr>
<tr>
<td></td>
<td>PB 109A</td>
<td>5.5</td>
<td>0.941</td>
</tr>
<tr>
<td>Hard</td>
<td>PB 109B</td>
<td>4.0</td>
<td>0.796</td>
</tr>
<tr>
<td>NaCl</td>
<td>PB 66S</td>
<td>6.5</td>
<td>1.112</td>
</tr>
<tr>
<td>Hard</td>
<td>PB 66T</td>
<td>5.5</td>
<td>1.094</td>
</tr>
</tbody>
</table>
5.3.7 Temperature Effects

The effects of temperature were also monitored in many of the aqueous stability and phase behavior experiments. The results can be found in the tables at the end of this chapter. Only two temperatures were done with these temperature experiments: reservoir temperature (43.3 °C) and room temperature (~22 °C).

In most cases the aqueous stability had an inverse relationship with temperature (i.e. it decreased with increasing temperature). Some experiments that had failed stability through the range of the test did not see any change with temperature. This is probably because the cloud point was too far below the range of the test for temperature to make a difference. No surfactant/polymer experiments had improved stability with increasing temperature. The alkali scans, however, did have improved stability with increasing temperature, but this is not surprising because most salts have higher solubilities at elevated temperatures.

The experiments that did have a drop in aqueous stability with increasing temperature typically had stability decrease by 0.5 to 1.5 wt% TDS. However, this number is dependent upon many parameters, including: brine type, surfactant type, surfactant concentration, co-solvent type, and co-solvent concentration. The phase behavior was influenced by similar variables.

The general trend for phase behavior experiments was for the solubilization ratio and optimum salinity to decrease with increasing temperature. A good example of this was PB 76, which had $S^*$ increase by about 0.5 wt% TDS and $\sigma^*$ increase by 2 cc/cc. Figure 5.32 and Figure 5.33 demonstrate the shift in phase behavior with temperature for PB 76. Other solutions had much greater changes in phase behavior with temperature. For example, PB 72 had $S^*$ increase by 1.5 wt% and $\sigma^*$ increase by 25 cc/cc. PB 219A had $S^*$ increase by 0.8 wt% and $\sigma^*$ increase by 25 cc/cc.

The effects of temperature were recorded in the tables in the appendix. In all cases, the two temperatures studied were reservoir temperature (43.3°C) and room temperature (~23°C).
5.3.8 Synthetic Brine Versus Field Brine

A very significant problem that arose during phase behavior screening was that the results from the Strontium Synthetic Formation Brine (SSFB) were not transferable to the field brine. This result was troubling because the SSFB composition was based on multiple water analyses that had comparable compositions (see above). Work done with alkali (see section 7.4 Sodium Metaborate and EDTA-4Na) also indirectly showed comparable brine characteristics between SSFB and FB #1. The SSFB was used for ease of screening and was supposed to accurately reflect the field brine. In the phase behavior experiments, careful attention was paid to make sure that the SSFB and field brine salinities were as close as possible. Since adding surfactant to the field brine diluted the salinity, some concentrated SSFB was added to bring the salinity back up to the original formation salinity (5.36 wt% TDS). Very strong type III solubilization ratios in the SSFB were often either type I microemulsions, or poor type III microemulsions in the field brine. This signaled an upward shift in optimum salinity, all things being equal. One possible explanation for the shift in phase behavior was the presence of chemicals in the field brine that were not recorded by the water analyses. In the field, emulsion breakers were added to the produced oil and brine before they entered the separator. The produced brine was then reinjected into the reservoir. While the second field brine sample was taken before the chemicals were added and the separator was reached, it was possible that these emulsion breaking chemicals circulated through the reservoir in a loop. Corrosion inhibitors may similarly have circulated through the reservoir and remained entrained in the brine. It seems abundantly logical that emulsion breaking chemicals would disrupt microemulsion based phase behavior experiments. Another explanation was that the difference in phase behavior might be due to bacterial action because the same oil and brine had been used over the course of 14 months of study. However, fresh brine and oil samples from the field gave the similar results.

Another field brine water analysis was performed. Interestingly, the divalent ion components had nearly the same concentrations as in the Tiorco water analysis. However, the sodium and chloride concentrations were significantly lower than the previous three
water analyses. The TDS content of the brine was measured to be 45,960 ppm, a 14.4% decrease from the Tiorco water analysis (53,600 ppm). Communication with the field revealed that the sample collected had been diluted with freshwater from a nearby source.

The decrease in salinity in the new field brine sample is sufficient to explain the shift from type III to type I microemulsion from SSFB to the new field brine sample. However, the original field brine sample had been tested by Tiorco and gave salinity results similar to SSFB. The difference in behavior for the original field brine sample remains unresolved.

5.3.9 Screening Summary

During this first screening, individual surfactants were initially used to gauge their interaction with the crude oil and brine. Later, combinations of surfactants were tried in order to try to improve the solubilization of the surfactants and enhance their aqueous stability. The first in this series of experiments mainly tried to improve the aqueous stability of the solution by adding more hydrophilic surfactants. Both C-9 and Neodol 25-12 were tried; however, it was found that the requisite amount of co-surfactant with S-8A or S-13A shifted the optimum salinity too high. It was then decided to try to bring the optimum salinity down by using even more hydrophobic surfactants than S-8A and S-13A. This was accomplished by progressively introducing more hydrophobic surfactants such as S-13C and S-13D to the formulation.

The second screening refined the investigation of a chemical solution for the hard brine. The brines used in the second screening were various (NaCl, SFB, NSFB, SSFB, formation brine), which, in the case of NSFB, was a result of precipitation reactions when mixing the stock brine, intellectual curiosity (NaCl), or updated water analysis reports (SSFB). The result of the second screening was PB 66 (0.40 wt% S-13D, 0.25 S-13C, 0.25 C-9), which had an optimum salinity of 5.4 wt% TDS, optimum solubilization ratio of 10.5 cc/cc, broad type III behavior, low presence of macroemulsions, and stability to at least 5.5 wt% TDS.
The third screening saw a return to searching for new surfactant mixtures. Both commercial and UT manufactured surfactants were used, as were various co-solvents. TDA-45PO-(10 or 20)EO-Sulfates with S-3B and C-9 were found to have excellent phase behavior (optimum solubilization of at least 20 cc/cc) and aqueous stability (to at least 8.0 wt% TDS). Spinning drop tensiometer tests also revealed very favorable IFT values (on the order of 0.001 dynes/cm).

In the fourth screening it was decided to use a salinity gradient in the flood design, which necessitated that the new optimum salinity be below the reservoir salinity. The new target optimum salinity was 4.5 wt%.

The main conclusions from the screening tests are:

- PB 242, PB 246, and PB 247 were all identified as suitable candidates for further testing and core flooding.
- PB 242 was used in three core floods that are detailed in the following chapter. The formulation was 0.5 wt% TDA-45PO-10EO-Sulfate, 0.25 wt% S-3B, and 0.25 C-9.
- TDA-45PO-(10 or 20)EO-Sulfates have very good synergy with S-3B and C-9. They are also moderately hydrophobic yet highly soluble.
- Reducing surfactant concentration had no influence on aqueous stability.
- It is difficult to get good aqueous stability with S-13D and S-2 surfactant mixtures because they are very hydrophobic and have poor solubility.
- SBA improves aqueous stability slightly, has low impact on solubilization, does not significantly influence optimum salinity, improves microemulsion viscosity, and decreases the amount of macroemulsions.
- Surfactant solution behavior is not always equivalent on an ionic strength basis when using different brines.
- Increasing experimental temperature decreases optimum salinity, optimum solubilization ratio, and cloud point.
- Sodium metaborate precipitated in SSFB and field brine, but was stable past 2.0 wt% NaCl at reservoir temperature (43.3 °C).
Figure 5.1: PB 18. After 11 weeks in the oven.
Figure 5.2: PB 9 after 15 weeks at 43.3°C. WOR=1. S*=~ 2.25 wt% TDS.
Figure 5.3: PB 5 after 22 weeks at 43.3 °C. WOR=1. S* between 1.80 and 2.20 wt% TDS. Viscous macroemulsions at 3.75 wt% TDS and above.
Figure 5.4: PB 21 after 13 weeks in the oven.

Figure 5.5: PB 6 after 25 weeks at reservoir temperature of 43.3°C. WOR=1. S*=~ 2.25 wt% TDS. Viscous macroemulsions at 4.50 wt% TDS and above.
Figure 5.6: PB 3. WOR=1. S around 1.5 wt% TDS. Viscous macroemulsions at 2.25 wt% TDS and above.

Figure 5.7: AS 34. Different surfactants in ECU Field Brine at reservoir temperature (43.3 °C) after agitation. From left to right: no surfactant, 0.50 wt% S-8B, 0.50 wt% S-8A, and 0.50 wt% S-13A. All of the surfactants cause a phase separation reaction.
Figure 5.8: AS 35. Sodium metaborate trials in ECU Field brine at (43.3 °C) after agitation. All vials have 0.50 wt% sodium metaborate. The vial on the left contains no surfactant, the middle vial contains 0.50 wt% S-8A, and the vial on the right contains 0.50 wt% S-13A. All vials showed precipitation reactions.
Figure 5.9: AS 44 indicating at least 0.8125 wt% N-25-12 is needed to prevent precipitation.
Figure 5.10: PB 56A. After 6 weeks in the oven.
Figure 5.11: PB 59. After 7 weeks in the oven.
Figure 5.12: AS 59A in NaCl brine.
Figure 5.13: PB 64CA. After 7 weeks in the oven.
Figure 5.14: PB 65 after 43 weeks in the oven.
Figure 5.15: PB 65AA after 7.5 weeks in the oven.
Figure 5.16: AS 65BA. Phase separation at 4.5 wt%.

Figure 5.17: AS 65C. Phase separation at 6.0 wt%.
Figure 5.18: PB 66r after 7.5 weeks in the oven.
Figure 5.19: PB 66r analysis.
Figure 5.20: AS 66A with NaCl brine. All vials are stable.
Figure 5.21: PB 66M after 13 weeks at reservoir temperature.
Figure 5.22: PB 66N after 13 weeks at reservoir temperature.
Figure 5.23: PB 69 after 5 weeks in the oven.
Figure 5.24: PB 70 after 5 weeks in the oven. 0.05 wt% less C9 than PB 69, but all type II with macroemulsions.
Figure 5.25: PB 74 after 33.5 weeks in the oven. More C9 and some co-solvent.

Figure 5.26: AS 74A at reservoir temperature.
Figure 5.27: AS 74A after agitation at reservoir temperature.

Figure 5.28: PB 74 after agitation at room Temperature.
Figure 5.29: PB 76 after 6 weeks in the oven.
Figure 5.30: PB 76 after 33.5 weeks in the oven.

Figure 5.31: PB 76 after 42 weeks in the oven.
Figure 5.32: PB 76 analysis after 294 days.
Figure 5.33: PB 76 analysis after 30 days at room temperature.
Figure 5.34: PB 77 after 32 weeks in the oven.
Figure 5.35: Analysis of PB 77.
Figure 5.36: PB 77E after 13 weeks at reservoir temperature.
Figure 5.37: PB 78 with new synthetic formation brine after 32 weeks in the oven.
Figure 5.38: AS 78A. Cloud point at 5.0 wt% TDS.
Figure 5.39: Impacts of slight surfactant composition changes. 40 days in the oven.
Figure 5.40: Impact on phase behavior of increasing S-13C. After 40 days in the oven
Figure 5.41: PB 87r after 39 weeks at reservoir temperature.
Figure 5.42: PB 89 after 5 weeks in the oven.
Figure 5.43: PB 90 after 5 weeks in the oven.
Figure 5.44: PB 100 with new synthetic formation brine after 19 weeks.
Figure 5.45: AS 100A with phase separation of S-2 at 5.50 wt% TDS.

Figure 5.46: AS 102A showing different levels of stability failure from phase separation of S-2 at the low end, to cloudiness and phase separation of other surfactants in the high salinity end.
Figure 5.47: PB 109 in NaCl brine after 12 weeks.
Figure 5.48: AS 109B. All phase separate.
Figure 5.49: PB 109C with New Synthetic Formation Brine after 12 weeks at reservoir temperature.
Figure 5.50: PB 110 in new synthetic formation brine after 21 weeks.
Figure 5.51: AS 110A. Phase separation at 5.0 wt% TDS.
Figure 5.52: PB 215A after 8.5 weeks in the oven.
PB 215A: 0.40 wt% TDA-45PO-10EO-Sulfate, 0.25 S-3B, 0.25 C-9

Figure 5.53: PB 215A analysis.
Figure 5.54: PB 215A and A’ after 8.5 weeks in the oven.
Figure 5.55: PB 215A’ analysis.
Figure 5.56: PB 215B after 8.5 weeks in the oven.
Figure 5.57: PB 215B analysis.
Figure 5.58: PB 219A after 8.5 weeks.
Figure 5.59: PB 219B after 8 weeks.
Figure 5.60: PB 236 after 7 weeks.
Figure 5.61: PB 242 after 6 weeks in the oven.
Figure 5.62: PB 246 after 6 weeks in the oven.
Figure 5.63: PB 247 after 6 weeks in the oven.
Figure 5.64: AS 242D with reservoir brine.
Figure 5.65: AS 247B with reservoir brine.
Figure 5.66: PB 242E with reservoir brine.
Figure 5.67: PB 247C with reservoir brine.
Figure 5.68: AS 242A IFT with SSFB.

Figure 5.69: AS 242B IFT with SSFB.
Figure 5.70: AS 242C IFT with NaCl brine.

Figure 5.71: AS 242D IFT with FB #1 augmented by SSFB.
Figure 5.72: AS 246 IFT with SSFB.

Figure 5.73: AS 247A IFT with SSFB.
Figure 5.74: AS 247B IFT with FB #1 augmented by SSFB.

Figure 5.75: SSFB vs. NaCl ionic strength equivalent.
CHAPTER 6: CORE FLOOD EXPERIMENTS

After completing hundreds of phase behavior and aqueous stability screening experiments, spinning drop interfacial tension experiments were performed on the most promising surfactant mixtures. Ultimately chemical formulation PB 242 with 0.5 wt% TDA-45PO-10EO-Sulfate, 0.25 wt% S-3B, and 0.25 C-9 was chosen for core flooding. Co-solvent and alkali were not used in any of the core floods. PB 242 had aqueous stability far beyond (greater than 8.0 wt% TDS SSFB) the reservoir salinity (5.36 wt% TDS). It was also aqueous stable in reservoir brine. Despite poor phase behavior with reservoir brine at reservoir temperature (43.3°C) - which was characteristic of all phase behavior experiments with reservoir brine at reservoir temperature - PB 242 showed comparable IFT results with both Strontium Synthetic Formation Brine (SSFB) and Formation Brine #1 (FB #1). Furthermore, the phase behavior optimum salinity of PB 242 was in the desired 3.5-4.5 wt% TDS range that was desired for implementing a salinity gradient.

The salinity gradients in each core flood were set up in such a manner that the initial brine in the core prior to chemical flooding would be FB #1 or SSFB (depending on the core flood), both at 5.36 wt% TDS. The surfactant slug would be injected at 4.5 wt% TDS, which is the approximate optimum salinity. Next, the polymer flood would be done at 3.4 wt% TDS. This follows the standard salinity gradient design of connate brine being 1.20 times the optimum salinity (s*), the surfactant brine being equal to s*, and the polymer flood being done at 0.75 times s*.

The polymer used in all cases was Flopaam 3330S. The concentration of polymer used was kept constant through the surfactant and polymer slugs, relying on the change in salinity to control the polymer’s viscosity. The Flopaam 3330S viscosity data collected can be observed in Figure 6.11.

In total, three core floods were performed, all of them at ECU reservoir temperature (43.3°C). The first one was done with Eliasville Caddo Unit Limestone core
plugs. The next two were done with Estillades Limestone. A summary of the cores’ properties and core flooding results can be found in Table 6.2 and Table 6.3

6.1 Eliasville Caddo Unit Core Flood ECU-1

6.1.1 Core Description

A photograph of the core plugs used in the ECU SP flood can be seen in Figure 6.1. The plugs were all between 1.5 and 3.0 inches in length and 1.5 inches in diameter. The series of core plugs had already been analyzed by Core Labs and were used as received. The cores arrived with information about each sample’s porosity and permeability. They were arranged in the coreholder from highest to lowest permeability. Vuggy porosity was abundant in each of the samples. Table 6.1 characterizes the core plugs.

Figure 6.2 shows the experimentally obtained relative permeability of the reservoir core plugs after flooding with FB #1 and ECU crude oil with $n_0 = n_w = 2$. As can be seen, the core is the textbook definition of a water wet rock (Peters, 2012, p. 178). The residual water saturation to oil flooding was not as low as reported by initial water saturations from the field. Additionally, the residual oil saturation after water flooding was not as high as was desired. The target for residual oil saturation was 0.30-0.35. An attempt to increase the initial and residual oil saturations by a second oil flood with pressures up to 500 psi were unsuccessful. The values obtained in the second oil and water floods were essentially the same as the first floods (the second flood values are the ones reported in Table 6.2). This serves as further confirmation of the cores’ wettability.
Figure 6.1: ECU plugs used in the field core surfactant-polymer EOR flood.

Table 6.1: ECU core plug porosity and permeability.

<table>
<thead>
<tr>
<th>Order</th>
<th>Length (inches)</th>
<th>Porosity (%)</th>
<th>Permeability (md, Klinkenberg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.57</td>
<td>27.15</td>
<td>348</td>
</tr>
<tr>
<td>2</td>
<td>2.24</td>
<td>18.29</td>
<td>110</td>
</tr>
<tr>
<td>3</td>
<td>2.734</td>
<td>14.45</td>
<td>83.2</td>
</tr>
<tr>
<td>4</td>
<td>2.547</td>
<td>17.22</td>
<td>35.1</td>
</tr>
<tr>
<td>5</td>
<td>2.189</td>
<td>15.13</td>
<td>20.3</td>
</tr>
</tbody>
</table>
Figure 6.2: Assumed ECU core relative permeability curves with n=2 (for the first oil and water floods).

6.1.2 Brine Flood

The ECU core was saturated and flooded with ECU Formation Brine #1 to determine the initial permeability of the core. The permeability was found to be 19.7 md, which is close to the average permeability of the field (11 md with air) (Weiss & Baldwin, 1985). This is also close to the permeability of the last plug in the core. The harmonic mean permeability of the cores was 47.4 md and was calculated using:

$$k = \left(\frac{1}{L} \sum_{i=1}^{N} \Delta x_i \frac{1}{k_i}\right)^{-1}$$  \hspace{1cm} \text{6.1}
One reason why the permeability was not higher was because the Core Labs reported permeability tested each sample independently. When the cores were run together in series, the vugs may not have meshed well. In other words, the discontinuities at core plug interfaces may have negatively affected the overall permeability. In total, 1.0 PV of brine was pushed through the core in the initial permeability test. The flow rate was 14.62 ml/hr (1.01 ft/d).

6.1.3 Oil Flood

The core was flooded with 2.78 PV of ECU crude oil in the first oil flood and 10.25 PV in the second. The flow rates were 5.1 ml/hr (0.35 ft/d) and 6.8 ml/hr (0.47 ft/d). The ECU dead crude oil had a viscosity of 2.5 cp at 0.1 1/s and it had a density of 41 °API (0.82 g/cc) at 110°F (43.3°C). These results are close to the values of 3 cp and 39°API (0.83 g/cc) reported in the literature for the ECU field at 115°F (Weiss & Baldwin, 1985). The residual water saturation of the first oil flood was 0.483 and 0.729 for the second flood. The residual water saturation was much lower in the second flood because of hysteresis effects. The oil relative permeability at residual water saturation for the first oil flood was 0.53 (10.5 md).

6.1.4 Water Flood

After the crude oil flood, ECU FB #1 was again pumped into the core. 4.47 PV were pumped into the core for the first water flood and 15.6 PV for the second water flood. The residual oil saturation for the first flood was 0.191 and for the second flood it was 0.210. The brine was pumped at a rate of 3.9 ml/hr, which is 0.27 ft/d in the first flood and 14.5 ml/hr (1.00 ft/d) in the second.

One cause of the low residual oil saturation may be due to the rocks’ water wet and vuggy nature. In general, the non-wetting phase in a porous medium will tend to reside in the larger pores. In the ECU cores, this means that a large portion of the crude
oil is in the large vugs. When water flooded, the water sweeps out the large vugs and thus produces a large amount of oil.

6.1.5 Chemical Flood Design

The ECU surfactant-polymer slug design is detailed in this section. The surfactant solution injected was similar to PB 242 and consisted of 0.5 wt% TDA-45PO-10EO-Sulfate, 0.25 wt% S-3B, and 0.25 wt% C-9, which is the same formulation used in all of the core floods. 0.25 wt% of F3330S polymer was also added to the surfactant and polymer slugs. The size of the surfactant slug injected was 0.4 PV. The surfactant solution salinity was 4.5 wt% TDS of FB #1, which was diluted from the stock FB #1 solution (5.36 wt% TDS) using DI water. It was injected at a rate of 3.9 ml/hr or 0.27 ft/d. After the surfactant flood, polymer was pushed through the core. The polymer slug salinity was 3.4 wt% TDS of FB #1. It was also injected at a rate of 3.9 ml/hr (0.27 ft/d).

6.1.6 Mobility Control

Mobility in the core flood was maintained with Flopaam 3330S polymer and a salinity gradient. The polymer was used to increase the viscosity of the injected fluids in the SP slugs. Since the polymer concentration was the same in both slugs, the salinity decrease between the surfactant and polymer slugs was relied upon to provide an adequate increase in viscosity in the polymer slug for proper displacement of the surfactant slug. With a crude oil viscosity of 2.5 cp, and realizing that the microemulsion viscosity could be up to (or greater than) two times the oil viscosity, the desired surfactant viscosity was at least 5.0 cp. Using a rheometer, the surfactant slug viscosity was demined to be 4.6 cp at 10 s⁻¹ and 43.3°C. The polymer slug viscosity was 4.80 cp.

An alternative theory for the desired viscosity of the chemical slug uses the total relative mobility of the oil bank (Yang H. T., 2010, pp. 28-29). This theory uses the Corey equations (the same equations that were used to generate Figure 6.2) to determine
the oil and water relative permeabilities at different water saturations. From there the water and oil mobilities can be added to obtain the total mobility defined as:

$$\lambda_{total} = \left( \frac{K_w}{\mu_w} + \frac{K_o}{\mu_o} \right)$$  \hspace{1cm} 6.2

The inverse of the minimum total mobility value then gives the minimum viscosity of the chemical slugs necessary for stable displacement:

$$\mu_{chemical,min} = \frac{1}{\lambda_{total, min}} = \frac{1}{(\frac{K_w}{\mu_w} + \frac{K_o}{\mu_o})_{min}}$$  \hspace{1cm} 6.3

For the ECU chemical flood, the minimum total mobility was $\lambda_{total, min} = 0.0878$ and the slug viscosity necessary for stable displacement was $\mu_{chemical,min} = 11.39$ cp. This is more than twice as viscous as the viscosities of the fluids actually used in the chemical flood.

Using excessively high polymer concentrations to secure an excessively high mobility ratio was not feasible. The relatively low permeability of the core and limitations of the experimental setup prevented such methodology. Injecting high viscosity fluids into a 20 md rock creates very high pressures, but the pressure transducer used could only go up to 180 psi reliably and 215 psi total. Thus, the SP slug viscosities were selected to keep the maximum pressure at 150 psi.

6.1.7 Chemical Flood Recovery

Figure 6.3 shows the results of the chemical flood. No macroemulsions were produced in the flood. The oil recovery attributed to the EOR process after 2.97 PV of EOR fluids injection was 0.0878 PV, which was 17% of the OOIP and 41.9% of the residual oil to water flooding. OOIP was 0.271 PV and waterflooding recovered 22.6% of OOIP. Typically, the objective is to obtain at least 90% of the OOIP after water and oil flooding and to have a stronger oil bank (higher oil cut concentrated in a couple PV). Only 39.7% of OOIP was recovered after the water flood and three pore volumes of the EOR flood. The result of the ECU flood suggests that the oil recovery would continue for
many more pore volumes (which was indeed the case). It was concluded that the high level of heterogeneity in the core, a product of many different core plugs with different permeabilities, porosities, and vuggy nature, caused the drawn out nature of the oil production. In the future this can be remedied by using more polymer in the SP slugs and obtaining higher operating pressure transducers.

Figure 6.3: Eliasville Caddo Unit SP (PB 242) EOR core flood produced oil results.

### 6.2 Estilades Core Flood ECU-2

#### 6.2.1 Core Description

The second core flood was done with Estilades limestone one inch diameter by six inch long core. The Estilades limestone had a uniform granular structure with a
porosity of 21.8% and brine permeability of 35.7 md. The relative permeability curves can be observed in Figure 6.4. Like the ECU core, this Estillades one was also strongly water wet and had a low residual oil saturation to water flooding.

![Relative Permeability Curves](image)

Figure 6.4: Assumed Estillades #1 Core relative permeability curves with n=2.

6.2.2 Brine Flood

The first Estillades limestone core flood was saturated and flooded with 5.36 wt% TDS Strontium Synthetic Formation Brine (SSFB). The permeability was found to be 35.7 md, which is larger than the ECU permeability. In total 20.5 PV of brine was flushed through the core during the brine flood at a rate of 42 ml/hr or 6.52 ft/d.
6.2.3 Oil Flood

The core was flooded with 7.94 PV of ECU crude oil in the oil flood. The flow rate was 10.5 ml/hr (1.63 ft/d) and the residual water saturation was 0.492. This gave an initial oil saturation of 0.508.

6.2.4 Water Flood

After the crude oil flood, ECU 5.36 wt% TDS SSFB was again pumped into the core. 7.30 PV were pumped into the core for the water flood. The residual oil saturation for the flood was 0.319. The brine was pumped at a rate of 8.5 ml/hr, or 1.32 ft/d. The water flood recovered 37.2% of the OOIP. A graph of the production results can be observed in Figure 6.5.

Figure 6.5: Estillades #1 water flood.
6.2.5 Chemical Flood Design

The first Estillades surfactant-polymer slug design is detailed in this section. The surfactant solution injected was similar to PB 242 and consisted of 0.5 wt% TDA-45PO-10EO-Sulfate, 0.25 wt% S-3B, and 0.25 wt% C-9, which is the same formulation used in all of the core floods. In an effort to improve the mobility from the first core flood, 0.35 wt% of F3330S polymer was added to the surfactant and polymer slugs. This represents a 0.10 wt% increase from the ECU SP flood. The size of the surfactant slug injected was 0.4 PV. The surfactant solution salinity was 4.5 wt% TDS of SSFB. It was injected at a rate of 6.5 ml/hr or 1.0 ft/d. After the surfactant flood, polymer was pushed through the core. The polymer slug salinity was 3.4 wt% TDS of SSFB. It was also injected at a rate of 6.5 ml/hr or 1.0 ft/d.

After injecting 2.44 PV of polymer, no more oil was produced. Given the low yield of produced oil, the surfactant slug was re-injected. This was done to see if more oil could be produced from the core. Typically this is not done because an inverse salinity gradient is created with a mobility ratio slightly below unity. However, by this point, the chemical flood had already failed to meet expectations. 0.83 PV of the surfactant solution was injected at 1.09 ft/d, followed by 4.18 PV of polymer at ~1.00 ft/d.

6.2.6 Mobility Control

Similar to the first flood, mobility in the core flood was maintained with Flopaam 3330S polymer and a salinity gradient. However, with the higher permeability in the Estillades core, a higher viscosity was used. The viscosity of the surfactant slug was 5.32 cp at 10 °C and 43.3°C. The viscosity of the polymer slug was 10.46 cp. The combination of lower heterogeneity in the core and higher mobility ratio gave a sharper defined oil bank which had a higher peak oil cut than in the ECU flood. This was true for both oil banks.
For the EST #1 chemical flood, the minimum total mobility was \( \lambda_{\text{total},\text{min}} = 0.1636 \) and the slug viscosity necessary for stable displacement was \( \mu_{\text{chemical},\text{min}} = 6.11 \text{ cp} \). The surfactant slug viscosity was close to this value, and the polymer slug exceeded it.

6.2.7 Chemical Flood Recovery

Figure 6.6 shows the results of the chemical flood. The oil recovery attributed to the EOR process after 2.84 PV was 0.027 PV, which was 5.4% of the OOIP and 8.6% of the oil left after water flooding. The oil recovery attributed to the EOR process after 7.27 PV was 0.094 PV, which was 18.6% of the OOIP and 29.6% of the oil left after water flooding. The total oil recovery for the water and EOR floods was 57.2% of OOIP. No macroemulsions were produced in the core flood.

The first Estillades limestone core flood did not perform as well as desired. A relatively large surfactant slug was needed to mobilize the remaining oil in the core. Even so, the oil recovery was poor. The sharp oil banks indicate that the mobility of the injected fluids was adequate. Some of the sufficient mobility was due to the increase in slug viscosities, but most of it was probably due to the homogenous nature of the Estillades core. The next core flood sought to repeat the Estillades #1 core flood, but with Field Brine #1 instead of Strontium Synthetic Formation Brine.
Figure 6.6: First Estillades SP EOR core flood produced oil results.

### 6.3 Estillades Core Flood ECU-3

#### 6.3.1 Core Description

The third core flood was also done with Estillades Limestone one inch diameter by 5.75 inch long core. The Estillades Limestone had a uniform granular structure with a porosity of 24.5% and brine permeability of 40.8 md. The relative permeability curves can be observed in Figure 6.7. Like the other cores, this Estillades one was also strongly water wet and had a low residual oil saturation to water flooding.
6.3.2 Brine Flood

The second Estillades Limestone core flood was saturated and flooded with FB #1 (5.36 wt% TDS). The permeability was found to be 40.8, which is larger than the permeability of the other cores. In total 4.84 PV of brine was flushed through the core during the brine flood at a rate of 42.4 ml/hr or 6.59 ft/d.

6.3.3 Oil Flood

The core was flooded with 6.4 PV of ECU crude oil in the oil flood. The flow rate was 164 ml/hr (25.5 ft/d) and the residual water saturation was 0.41.
6.3.4 Water Flood

After the crude oil flood, FB #1 (5.36 wt% TDS) was again pumped into the core (see Figure 6.8). 12.2 PV were pumped into the core for the water flood. The residual oil saturation for the flood was 0.194, which is similar to the values obtained for the ECU and first Estillades cores. The brine was pumped at a rate of 7.0 ml/hr, which is 1.09 ft/d. The oil recovered due to waterflooding was 66.7% of OOIP.

![Figure 6.8: Estillades #2 water flood.](image)

6.3.5 Chemical Flood Design

The second Estillades surfactant-polymer slug design is detailed in this section. The surfactant solution injected was similar to PB 242 and consisted of 0.5 wt% TDA-45PO-10EO-Sulfate, 0.25 wt% S-3B, and 0.25 wt% C-9, which is the same formulation used in all of the core floods. 0.35 wt% of F3330S polymer was added to the surfactant
and polymer slugs. This represents a 0.10 wt% increase from the ECU SP flood. The size of the surfactant slug injected was 0.4 PV. The surfactant solution salinity was 4.5 wt% TDS of SSFB. It was injected at a rate of 7 ml/hr or 1.09 ft/d. After the surfactant flood, polymer was pushed through the core. The polymer slug salinity was 3.4 wt% TDS of SSFB. It was also injected at a rate of 7 ml/hr (1.09 ft/d).

After injecting 4.25 PV of polymer, no more oil was produced. Given the low yield of produced oil, the surfactant slug was re-injected. This was done to see if more oil could be produced from the core. Typically this is not done because an inverse salinity gradient is created with a mobility ratio slightly below unity. However, by this point, the chemical flood had already failed to meet expectations. 0.71 PV of the surfactant solution was injected at 1.09 ft/d, followed by 5.1 PV of polymer at 0.87 ft/d.

6.3.6 Mobility Control

Similar to the other floods, mobility in the core flood was maintained with Flopaam 3330S polymer and a salinity gradient. The viscosity of the surfactant slug was 6.77 cp at 10 1/s. The viscosity of the polymer slug was 10.68 cp. The combination of lower heterogeneity in the core and higher mobility ratio gave a sharper defined oil bank which had a higher peak oil cut than in the ECU flood. This was true for both oil banks.

For the EST #2 chemical flood, the minimum total mobility was $\lambda_{total, min} = 0.0754$ and the slug viscosity necessary for stable displacement was $\mu_{chemical, min} = 13.26$ cp. The surfactant slug viscosity was about half of this value, and the polymer slug was approximately 2.5 cp below it.

6.3.7 Chemical Flood Recovery

Figure 6.9 and Figure 6.10 show the results of the chemical flood. The oil recovery attributed to the EOR process after 4.25 PV was 0.057 PV, which was 9.8% of the OOIP and 29.5% of the oil left after water flooding. Total oil recovery for the entire
flooding process (water flooding and EOR) was 76.7% of OOIP after 4.25 PV of the
EOR flood. The oil recovery after 10.2 PV of the EOR slugs was 0.172 PV, which was
29.3% of the OOIP and 88.6% of the oil left after water flooding. Total oil recovery for
the entire flooding process (water flooding and EOR) was 96.2% of OOIP after 10.2 PV
of the EOR flood.

The sharpness of the oil banks indicate that the viscosity of the EOR slugs was
sufficient. Furthermore, the higher oil recovery from this core flood over the first
Estillades Limestone flood suggests that the EOR chemicals have greater success in the
field brine than in synthetic brine. However, a very large surfactant slug was needed in
order to mobilize this oil. This may be due to high adsorption of the surfactant and high
IFT. The second bank of oil had a considerable amount of microemulsion produced with
the oil. No macroemulsions were produced in the core flood.

Figure 6.9: Second Estillades SP EOR core flood produced oil results.
6.4 Summary and Conclusions

In the core floods performed for potential use in the Eliasville Caddo Unit limestone reservoir, none met the stringent metrics for EOR core flood success. The floods either did not have sufficient mobility to counteract high levels of heterogeneity (ECU-1) or required large surfactant slugs to produce oil (ECU-2 and ECU-3). The Estillades limestone cores were also short in length (~6 inches) and capillary end effects may have had a strong impact on the floods. A contributing factor to the EOR failure may have been the strong water-wet nature of all of the cores. The ECU reservoir is known to be mixed-wet and have a higher residual oil saturation to water flooding than what was achieved in the core floods. A higher oil saturation could make a more successful chemical EOR flood because a stronger oil bank might be formed. Additionally, only one surfactant formulation was used for all of the floods (PB 242). Other (PB 246 and PB
247) surfactant solutions may have greater success. Co-solvent was also not used in any of the core floods because the phase behavior experiments showed low viscosity microemulsion behavior without any macroemulsions present. At this time, it is recommended that further phase behavior and core flood studies be done before progressing to field injection. The additional core floods should: 1) use longer cores (particularly for the Estillades cores), 2) age the cores, 3) use various surfactant mixtures, concentrations, and slug sizes, and 4) investigate chromatic separation behavior.
Table 6.2: Summary of EOR Floods.

<table>
<thead>
<tr>
<th>Property</th>
<th>Flood</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ECU</td>
</tr>
<tr>
<td>Core Diameter (in)</td>
<td>1.5</td>
</tr>
<tr>
<td>Core Length (in)</td>
<td>11.34</td>
</tr>
<tr>
<td>Porosity</td>
<td>17.7</td>
</tr>
<tr>
<td>Pore Volume (ml)</td>
<td>58</td>
</tr>
<tr>
<td>Permeability (md)</td>
<td>19.7</td>
</tr>
<tr>
<td>$S_{wr}$</td>
<td>0.483</td>
</tr>
<tr>
<td>$k^p_{ro}$</td>
<td>0.533</td>
</tr>
<tr>
<td>$S_{orw}$</td>
<td>0.191</td>
</tr>
<tr>
<td>$k^p_{rw}$</td>
<td>0.17</td>
</tr>
<tr>
<td>Water Flood Flowrate (ft/d)</td>
<td>1.00</td>
</tr>
<tr>
<td>Original Surfactant Slug Size (PV)</td>
<td>0.4</td>
</tr>
<tr>
<td>Surfactant Viscosity (cp, at 10 s$^{-1}$, 43.3°C)</td>
<td>4.6</td>
</tr>
<tr>
<td>Polymer Slug Size (PV)</td>
<td>3.00</td>
</tr>
<tr>
<td>Polymer Viscosity (cp, at 10 s$^{-1}$, 43.3°C)</td>
<td>4.8</td>
</tr>
<tr>
<td>Chemical Flood Flowrate (ft/d)</td>
<td>0.27</td>
</tr>
<tr>
<td>Chemical Flood Oil Recovery (PV)</td>
<td>0.088</td>
</tr>
<tr>
<td>Residual Oil Saturation at EOR Flood Termination</td>
<td>0.115</td>
</tr>
<tr>
<td>EOR Efficiency (% of OOIP)</td>
<td>22.22</td>
</tr>
<tr>
<td>EOR Efficiency (% of $S_{orw}$)</td>
<td>41.86</td>
</tr>
<tr>
<td>Total % of OOIP Recovered (Water + EOR Floods)</td>
<td>55.0</td>
</tr>
</tbody>
</table>
Table 6.3: EOR coreflood results after 2 PV of chemical injection.

<table>
<thead>
<tr>
<th>Property</th>
<th>Flood</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ECU</td>
</tr>
<tr>
<td>Chemical Flood Oil Recovery (PV)</td>
<td>0.076</td>
</tr>
<tr>
<td>Residual Oil Saturation after 2 PV of EOR injection</td>
<td>0.134</td>
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<tr>
<td>EOR Efficiency (% of OOIP)</td>
<td>14.72</td>
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<tr>
<td>EOR Efficiency (% of Sorw)</td>
<td>36.28</td>
</tr>
<tr>
<td>Total % of OOIP Recovered (Water + EOR Floods)</td>
<td>50.65</td>
</tr>
</tbody>
</table>

Figure 6.11: Viscosity data of EOR fluids at 43.3°C.
CHAPTER 7: EXPERIMENTS WITH EDTA-4Na AND NaB(OH)4 ALKALIS IN HARD BRINES

7.1 Introduction

As mentioned in chapters 2 and 3, alkaline agents in chemical enhanced oil recovery help to reduce surfactant adsorption, limit surfactant (particularly sulfate) degradation, react with naphthenic acids to generate in situ surfactants, and change the wettability of the formation rock (see section 2.2.4 Properties of Alkalis). Numerous researchers have cited sodium metaborate (NaB(OH)4) and EDTA-4Na as good alkalis for hard formation brines (see section 3.7 Alkali Behavior in Hard Brines). The experiments in this chapter investigate such claims.

A number of aqueous stability experiments were done using sodium metaborate, sodium acetate, and tetrasodium EDTA as alkali. The pH of the samples was also recorded in these experiments. Different salts and salt concentrations were used in the tests. The main salts in the brines were CaCl2, MgCl2, SrCl2, and NaCl. Some BaCl2 was present in the Strontium Synthetic Formation Brine (SSFB). Formation Brines #1 and #2 were also tested. Their compositions can be found elsewhere (Table 5.1, Table 5.2, and Table 5.5). In addition, the concentration of alkali was varied and two temperature intervals were investigated. Thus, the experiments investigated five dimensions of alkali in hard brines: aqueous stability, pH, cationic element, concentration of ions, and temperature.

Aqueous stability is defined elsewhere in this thesis (2.3.2 Aqueous stability) and its meaning is consistent in this chapter; a stable mixture is clear and translucent with no cloudiness or precipitation. pH was measured with a single Hanna Instruments 99104 pH tester with a range of 0.00 to 14.00, resolution of 0.01 pH, accuracy of ± 0.2 pH at 20 degrees Celcius, and operating range of 0 to 50 degrees Celsius. The pH meter was calibrated approximately twice every hour when in use with a two point manual calibration procedure using standard pH solutions. Calibrations were done at room temperature, however, after a fresh calibration, the same standard pH solutions were
tested at elevated temperature and found to be consistent. While the accuracy of the pH meter may be considered low, the instrument recorded consistent readings months apart. It is also believed that constant calibration improved the accuracy of the readings to perhaps ±0.05 pH. The concentration of ions was varied in fixed intervals, typically 0.5, 1.0, 1.5, and 3.0 wt% for pure salts. Salt mixtures such as 9:1 NaCl: CaCl2 or MgCl2 had a broader range, as did experiments with SSFB. Except where specified, no surfactants or co-solvents were used. All samples were mixed with de-ionized (DI) water on a weight basis using a Mettler PL200 scale that had been recently (<2 months) calibrated. The two temperatures investigated were room temperature (~23 degrees Celsius) and Eliasville Caddo Unit (ECU) reservoir temperature (43.3 degrees Celsius).

The data has been tabulated at the end of this chapter. Table 7.1 presents the data collected for sodium acetate solutions and Table 7.2 shows EDTA data. Table 7.3 contains the relevant brine details for the alkali experiments. The information includes brine type, wt% TDS, wt% divalent ions, molar concentrations, and ionic strength. Table 7.4a and 7.4b present the pH data collected for alkali-brine solutions at reservoir temperature (43.3°C). Table 7.5a: EDTA-4Na at 23 degrees Celsius. and 7.5b show the information for room temperature (~23°C) pH measurements. Table 7.6a and Table 7.6b show the pH values for samples after re-heating to reservoir temperature from room temperature. Hysteresis can be noted by discrepancies between Table 7.4a, Table 7.4b, Table 7.6a, and Table 7.6b. Finally, Table 7.7 presents the pH data gathered at four temperatures for establishing trends.

The research done with EDTA-4Na expands upon that done by Winters in his 2012 master’s thesis at the University of Texas at Austin (Winters, 2012). Winters’ research involved experiments investigating the aqueous stability and pH of 1.0 to 1.5 wt% EDTA-4Na at 55°C with different concentrations of calcium and magnesium. He also did equilibrium simulations on how the concentration of EDTA-4Na, temperature, and divalent ion concentration effect the pH. His simulations showed that the pH of EDTA-4Na in DI water does not increase much after approximately 5,000 ppm EDTA-4Na. He also reported an approximately linear dependency of pH with temperature for a
given concentration of EDTA-4Na in DI water. The slope of this relationship was $-1.0 \frac{pH}{100^\circ C}$. Finally, his simulations showed a sharply declining pH with multivalent ion concentration that levels off at about 7.3 pH after 1,000 ppm divalent ions when 1% EDTA-4Na is present in DI water at 25°C. This leveling off seems to correlate with a 10:1 weight percent ratio of EDTA-4Na to multivalent ions, which is close to the 9:1 ratio given earlier (3.10.2 Infeasibility of Sequestering Divalent Ions).

The similarities between Winters’ observations and those made for this thesis are: a change in pH with temperature, similar characteristics in decline of pH with increasing multivalent ion concentration, larger decline in pH with the presence of calcium, and precipitation reactions. The differences are as follows. Winters simulated that the pH would stay above a pH of 7 in DI water. In the experiments done with multivalent ions for this thesis, all the solutions leveled off significantly below 7 pH. Many were in the 3.5-5.5 pH range. Winters thesis seems to indicate a 10:1 EDTA-4Na:divalent ion correlation with pH. This thesis finds that EDTA (without the 4Na) chelates with calcium and strontium ions on an approximately 1:1 molar basis, and slightly higher with magnesium. Given the differences in molecular weights, the weight percent ratio varied between 6.28:1 and 28.5:1 EDTA-4Na:divalent ion, with calcium and magnesium brines being significantly above the 10:1 ratio from Winter’s deionized results. This thesis finds that calcium lowers pH more than magnesium and strontium, whereas Winters’ only looked at calcium and magnesium. This thesis also observes effects caused by monovalent ions, mixing of ion solutions, and formation brines, whereas Winters’ did not. This thesis investigated certain aspects of the sharp decline in pH with increasing divalent ion concentration. Finally, possible hysteresis effects due to cycling temperatures were investigated in this thesis.

7.2 Sodium Acetate

The experimental results for sodium acetate and field brines or their derivatives are given in Table 7.1 (end of chapter) and Figure 7.1 (below). As can be seen, the
sodium acetate pH is lower in the strontium synthetic formation brine (SSFB) and the formation brine (sample #2) than in the NaCl brines. The 6.4 wt% NaCl brine is an ionic strength equivalent to the SSFB, which is an indication that the divalent ions are influencing the pH.

Figure 7.1: Sodium acetate pH in different brines.

Additional evidence of divalent ions influencing the pH was recorded by direct observation of precipitates. All of the hard brine samples precipitated. Samples at and above 5 wt% sodium metaborate were at risk of forming crystalline solids that plugged up much of the vials. NaCl samples also exhibited precipitation, but not to the degree of the hard brines. The NaCl samples also were able to tolerate over 2.0 wt% sodium metaborate.

AS 211 through AS 213 tested the aqueous stability and pH of sodium acetate solutions in SSFB. All vials tested were clear. These experiments were done at 5.50 wt% TDS of SSFB and NaCl and Sodium Acetate concentrations up to 7.0 wt%. Sodium
Acetate solutions all had pH’s between 7 and 8.2 and appeared to be independent of divalent ion and alkali concentration.

7.3 EDTA

AS 230 and 230A tested the aqueous stability of EDTA (not to be confused with EDTA-4Na) at reservoir temperature (43.3°C). PB 230 was done with Formation Brine 2 (see section 5.3.9). AS 230A used SSFB at a concentration of 5.50 wt% TDS. All vials in both experiments showed precipitation, even with EDTA concentrations as low as 0.25 wt% and as high as 10 wt%. These samples also had pH values on the order of 1.8 to 2.0. The low pH values for EDTA solutions were used later to better understand the chemical’s chelating characteristics. Low concentrations of EDTA-4Na had low pH, which may indicate that not all of the divalent ions were being chelated.

7.4 Sodium Metaborate and EDTA-4Na

AS 231 through AS 231E tested the aqueous stability of sodium metaborate at reservoir temperature. AS 231 was done with Formation Brine 2 and AS 231A was done with SSFB at 5.50 wt% TDS. Figure 7.2 is a photograph of AS 231. All vials in both AS 231, AS 231A, and AS 231E precipitated. AS 231B through AS 231C were done with sodium chloride brines and had stability limits between 2.5 and 5.0 wt% NaCl. The concentration of sodium chloride in AS 231C and AS 231D is 6.4 wt%, which is the ionic strength equivalent of 5.5 wt% SSFB. The results of these experiments are summarized in the Appendix.

AS 230 through AS 231E show that EDTA (not EDTA-4Na) and sodium metaborate are not good chemicals for the Eliasville Caddo Unit at reservoir conditions. The chemicals appear to interact with divalent ions to form precipitates (see Figure 7.2).

AS 230AA through AS 230EE used EDTA-4Na with various brines; namely Strontium Synthetic Formation Brine (SSFB), NaCl, and Formation Brine #1 (FB #1).
The pH responses of AS 230AA and AS 230CC (5.5 wt% SSFB and FB #1) are similar enough to indicate that the divalent ion concentration and TDS of both samples are similar, as was expected based on the water analysis reports. However, as detailed in Chapter 5, the phase behavior of the two solutions did not match. Formation brine typically showed type I microemulsion where SSFB showed type III microemulsion. The shift in phase behavior is likely a result of emulsion breakers (added before the process separator) or corrosion inhibitors circulating through the reservoir and mixing with the field brine.

AS 275 through AS 298 investigated \( \text{MgCl}_2, \text{CaCl}_2, \) and \( \text{SrCl}_2 \) brines in different concentrations with EDTA-4Na and sodium metaborate \( (\text{NaB(OH)}_4) \). AS 299 through AS 310 investigated mixtures of NaCl with divalent salts. The ratio of NaCl:divalent salts was kept at 9:1 on a weight basis. The results of these experiments will be discussed further below.

Figure 7.2: AS 231. Sodium metaborate in formation brine #2. All samples precipitate.
7.5 EDTA-4Na

7.5.1 pH Drops Below 7.0

As seen in Figure 7.3, the pH of EDTA-4Na salt solutions is below 7 when the concentration of alkali is low relative to the amount of divalent ions in the solution. Increasing the EDTA-4Na concentration raises the pH, but not uniformly. As can be seen in the figure, incrementally raising the alkali concentration has a higher impact at low divalent ion concentrations and slowly propagates to higher concentrations. The result is a backwards “s” shaped curve that resembles a clinoform. It is unclear whether the clinoformal drop in pH is a feature unique to EDTA-4Na or is present in all chelating alkali agents. Sodium metaborate did not exhibit such behavior over the range tested.

For low concentrations of EDTA-4Na relative to the divalent ion concentration, the equilibrium pH is almost always less than 5.0 pH. The pH is typically less than 4.0 in the presence of calcium, which is much lower than the values obtained with magnesium and strontium based brines. Magnesium brines typically have a lower equilibrium pH than strontium brines, but the pH’s are close in value.

With high concentrations of EDTA-4Na relative to divalent ion concentration, the pH of each type of brine approaches an upper limit of approximately 9.4 pH. This value is less than the 10.0 needed to create insitu soaps and reverse the zeta potential of calcite. However, it may be enough to prevent sulfate surfactant degradation at elevated temperatures.

The reason for the sudden shift in solution pH likely deals with how EDTA acts like an acid by itself and a base with higher concentrations of EDTA-4Na. This is likely determined by EDTA’s ability to chelate divalent ions, the topic of the next section.

7.5.2 EDTA Chelating

Another behavioral characteristic worth noting in Figure 7.3 is the pH inversion. For calcium, the pH is lower than magnesium and strontium at low EDTA-4Na
concentrations, but after the inversion, the calcium brine pH is higher than that of the other brines. This is likely due to the manner in which the divalent ions are chelating with the EDTA molecule. A linear interpolation was done between points on either side of the phase inversion to determine the alkali concentration at neutral pH. This should give an indication of the chelating properties of EDTA for a given divalent ion. EDTA-4Na is an alkali (given a sufficiently low concentration of divalent ions) that displays a low tendency to precipitate, whereas just EDTA is an acid with a very low pH and a high tendency to precipitate. It seems that at high concentrations of divalent ions, EDTA-4Na is unable to properly chelate the divalent ions. This may be because of competition between the cations to be captured by the anionic EDTA molecule. However, once the chelating action is taking hold, the EDTA-4Na molecule begins to act like an alkali and the pH raises sharply. A linear interpolation on the pH inflection gives an indication of the concentration of EDTA needed to chelate a divalent ion molecule.

Figure 7.4 and Figure 7.5 show how the results of the linear interpolation to a pH of 7 on the pH inflection. As can be seen, all the brines require an EDTA: divalent ion ratio of slightly above unity. This ratio is even higher for magnesium and strontium than it is for calcium. With the intercept set to zero, the EDTA: divalent ion ratio is 1.285 for calcium chloride brines and 1.582 for magnesium chloride brines. Figure 7.5 shows how the chelating ratio changes with increasing concentration of divalent ions. The amount of EDTA needed to chelate calcium and strontium increases with increasing divalent ion concentration. Brines with magnesium display the opposite behavior; the chelating ratio decreases with increasing ionic concentration.

The reason for the differences in EDTA’s ability to chelate different divalent ions may be caused by the divalent ions’ size. Magnesium and strontium might be mechanically bigger or smaller than the EDTA chelating site’s maximum efficiency. This conjecture would require more advanced experimental means to fully vet.

The chelating ratio can be converted to a weight percent basis. Similar trends are observed to the molar basis. The amount of EDTA-4Na needed to get to neutral pH increases with calcium and strontium concentrations, but decreases with magnesium.
Figure 7.6 and Figure 7.7 shows that strontium ratios are low (6.28 to 7.03:1 wt% EDTA-4Na:Sr), whereas calcium and magnesium are high (11.2 to 12.4:1 and 24.3 to 28.5:1, respectively). The ratio for Formation Brine #1 was 13.6:1. These results indicate that the blanket 9:1 or 10:1 wt% ratio is inaccurate and should be tailored to the brine based on divalent ion molarity.
Figure 7.3: pH dependence on EDTA-4Na concentration and Mg++, Ca++, and Sr++ salts at 43.3°C.
Figure 7.4: EDTA-4Na needed for pH 7.0 at 43.3°C.
Figure 7.5: EDTA-4Na:divalent ion chelating ratio dependency with divalent ion type and concentration at 43.3°C.
Figure 7.6: Wt% EDTA-4Na to wt% divalent ion for different brines at pH 7.0 and 43.3°C.
Figure 7.7: Wt% EDTA-4Na to divalent ion chelating ratio trends at pH 7.0 and 43.3℃.
7.5.3 Large Temperature Impacts

The influence of temperature on pH has also been found to be substantial at low pH. This influence is likely a manifestation of reaction equilibriums changing with temperature. At high pH (i.e. above the pH inversion), the pH is much less dependent on temperature. Many of the experiments were done only at room temperature (≈ 23°C) and ECU reservoir temperature (43.3°C). However, seven of the alkali-brine combinations were tested at four temperatures: 23°C, 35°C, 43.3°C, and 49.5°C. These values were chosen based on the limitations of the pH probe, which could only tolerate temperatures up to 50°C. Multiple temperature points were necessary to determine the nature relationship of pH with temperature (i.e. linear, exponential, etc.). In order to assure accuracy in the readings, samples were occasionally measured at room temperature, reservoir temperature, room temperature, and then reservoir temperature again, with a pH meter calibration between each temperature measurement. The values obtained were in good agreement with each other.

Figure 7.8, Figure 7.9, Figure 7.10, and Figure 7.11 show a typical variation in pH with temperature with magnesium. The pH decreases with increasing temperature. The amount of the decrease is dependent on divalent ion concentration in the brine. The higher the divalent ion concentration, the more significant the decline in pH with increasing temperature. It was not unusual to observe pH declines of 1.0 or more with 3.0 wt% \( MgCl_2 \) and a temperature increase from 23°C to 43.3°C. \( SrCl_2 \) brines saw a decrease of up to 0.15 pH with the same increase in temperature (shown in Figure 7.12 and Figure 7.13). The pH decrease becomes much less pronounced above pH 6 for both \( MgCl_2 \) and \( SrCl_2 \) brines. Brines that contain mixtures of divalent and monovalent ions also have decreases in pH with increasing temperature (see Figure 7.14 and Figure 7.15, which contain Formation Brine #1 and 5.5 wt% Strontium Synthetic Field Brine, respectively). As can be seen in Figure 7.16 and Figure 7.17, \( CaCl_2 \) does not experience a change in pH with temperature.
Figure 7.18, Figure 7.19, and Figure 7.20 show how the pH is affected by temperature for different brines with 0.25 wt%, 0.50 wt%, and 5.0 wt% EDTA-4Na respectively. The lines of best fit show a high correlation with linear trends. Additionally, the slopes agree well for the different brine types at the same pH values. At low pH, the slope is approximately $-1.1 \frac{\text{pH}}{100^\circ C}$ and at high pH the slope is $-0.34 \frac{\text{pH}}{100^\circ C}$. Similar trends are observed at other concentrations of EDTA-4Na.

Figure 7.8: EDTA-4Na Temperature effect on pH in 0.5 wt% MgCl2 (AS 287).
Figure 7.9: EDTA-4Na Temperature effect on pH in 1.0 wt% MgCl₂ (AS 288).

Figure 7.10: EDTA-4Na Temperature effect on pH in 1.5 wt% MgCl₂ (AS 289).
Figure 7.11: EDTA-4Na Temperature effect on pH in 3.0 wt% MgCl2 (AS 290).

Figure 7.12: EDTA-4Na Temperature effect on pH in 1.0 wt% SrCl2 (AS 296).
Figure 7.13: EDTA-4Na Temperature effect on pH in 3.0 wt% SrCl₂ (AS 298).

Figure 7.14: EDTA-4Na Temperature effect on pH in Formation Brine #1 (AS 230CC).
Figure 7.15: EDTA-4Na Temperature effect on pH in 5.5 wt% SSFB (AS 230AA).

Figure 7.16: EDTA-4Na Temperature effect on pH in 1.0 wt% CaCl2 (AS 284).
Figure 7.17: EDTA-4Na Temperature effect on pH in 3.0 wt% CaCl₂ (AS 286).

Figure 7.18: pH trend with temperature at 0.25 wt% EDTA-4Na.
Figure 7.19: pH trend with temperature at 0.50 wt% EDTA-4Na.

Figure 7.20: pH trend with temperature at 5.0 wt% EDTA-4Na.
7.5.4 pH Hysteresis

Hysteresis was observed in the solution pH with higher concentration magnesium brines when the temperature was cycled between reservoir and room temperatures. Figure 7.21 through Figure 7.23 show that the severity of the hysteresis increased as the magnesium concentration increased. When measuring the pH at reservoir temperature, cooling, and then measuring at room temperature again, the difference in pH readings at elevated temperature was as high as 0.81 pH. The hysteresis always caused the pH to increase upon reheating. Hysteresis was also more prominent at higher EDTA-4Na concentrations, but below the pH inversion (before high pH). Hysteresis was not observed with calcium or strontium brines.

The hysteresis of EDTA-4Na with $Mg^{2+}$ seems to be related to the chelating properties of $Mg^{2+}$, which has a high ratio of EDTA: divalent ion concentration on a molar basis. Experiments with just EDTA (AS 230 and AS 230A) also showed hysteresis. Magnesium ions could be concentrating around EDTA molecules and competing with each other very strongly to be chelated, thereby preventing EDTA from chelating and securing one divalent ion indefinitely. As the temperature is changed, perhaps some EDTA-divalent ion pairs are made easier or harder to break apart. Once broken, the EDTA-divalent ion pairings may be difficult to reform, which is manifested as pH hysteresis. Temperature may also impact the hydration of magnesium ions, which then affect EDTA’s ability to chelate them.

When $MgCl_2$ was mixed with other salts, as in AS 310 (10 wt% 9:1 NaCl: MgCl$_2$) and AS 230AA (5.5 wt% SSFB), the hysteresis effects were eliminated. This behavior is not well understood. One possibility is that other ions interfere with $Mg^{2+}$ ions’ strong interaction with the EDTA molecules. Monovalent ions may help shield the EDTA molecule from $Mg^{2+}$ and allow EDTA to sequester and release ions easier with changes in temperature.
Figure 7.21: EDTA-4Na with 1.0 wt% MgCl2; pH hysteresis due to temp (AS 288).

Figure 7.22: EDTA-4Na with 1.5 wt% MgCl2; pH hysteresis due to temp (AS 289).
Figure 7.23: EDTA-4Na with 3.0 wt% MgCl2; pH hysteresis due to temperature (AS 290).

7.5.5 Monovalent and Divalent Brine Mixtures

When pH is plotted versus the multivalent ion molarity, mixing NaCl with multivalent ions had the interesting effect of lowering pH more than pure multivalent salts. It appears that monovalent ions can influence the pH when present in multivalent mixtures. Monovalent ions are not as impactful as multivalent ions, but they still appear to be affect pH, as Figure 7.24 and Figure 7.25 suggest.
Figure 7.24: EDTA-4Na pH dependence on magnesium brine mixtures at 43.3°C.
Figure 7.25: EDTA-4Na pH dependence on calcium brine mixtures at 43.3°C.

7.6 Sodium Metaborate

The data shows that sodium metaborate (NaB(OH)4) is prone to precipitation. In only a few instances did it not induce a precipitation or scale reaction. Magnesium ions caused very hard scales that were difficult to remove, even by mechanical means. On the other hand, sodium metaborate did have a fairly stable pH over the tested intervals. The pH of sodium metaborate solutions was less effected by temperature and divalent ion type than EDTA-4Na. Only at very high concentrations of alkali (or low concentrations of multi-valent ions) did sodium metaborate manage to break the 10 pH barrier, which is
required to form insitu soap and reverse the zeta potential in order to lower surfactant
adsorption to calcite (limestone). However, the real limitation of sodium metaborate is its
extremely low tolerance to multivalent ions. No solution was able to contain more than
0.50 wt% of sodium metaborate without precipitating. Even AS 299, which contained
only contained 5000 ppm TDS (including 181 ppm $Ca^{2+}$ ions), precipitated at 0.25 wt%
sodium metaborate.

While sodium metaborate does exhibit decent alkali characteristics in that it raises
the pH above 8, even at low concentrations of alkali and high concentrations of divalent
ions, and that it has good tolerance to temperature changes, its inability to properly
dissolve and tendency to form precipitates or scales is a colossal limitation to this
chemical’s use in the field. The recommendation is to not use sodium metaborate in hard
brines. This recommendation runs contrary to many documents of the literature (Flaaten,
2007) (Zhang, Nguyen, Flaaten, & Pope, 2008) (Sahni V. M., 2009). However, of those
that tout sodium metaborate’s abilities, Chandrasakhar and Bataweel observed
precipitates even at relatively low concentrations of divalent ions (Chandrasekar, 2010)
(Bataweel & Nasr-El-Din, 2011).

Figure 7.26 shows how the pH varies based on brine type, $NaB(OH)_4$
concentration, and TDS. Similar to EDTA-4Na, sodium metaborate shows a decline in
pH with increasing divalent ion concentration. The pH increases as the alkali
concentration is increased, but not in as drastic a fashion as EDTA-4Na. The type of
divalent ion affects pH, but not to the same extent as with EDTA-4Na. pH dependence on
temperature was not significant with Sodium metaborate. pH hysteresis with temperature
was likewise insignificant.

Figure 7.27 and Figure 7.28 show how magnesium and calcium brine mixtures
behave. When a 10:1 weight ratio of NaCl:divalent salt is present, the curves differ from
pure divalent salt responses. The shapes and trends of the lines are similar, but the 10:1
brines are shifted further to the left on the axes. Since the abscissa is based on divalent
ion concentration, the results indicate that monovalent ions have an impact on pH,
although at a greatly reduced rate.
Figure 7.26: Sodium metaborate pH dependence on divalent ion type and concentration and alkali concentration.
Figure 7.27: Sodium metaborate pH dependence on magnesium brine mixtures.
Figure 7.28: Sodium metaborate pH dependence on calcium brine mixtures.
7.7 Conclusion

- EDTA-4Na is acidic in concentrations less than the chelating equilibrium
  - May lead to:
    - formation dissolution/damage
    - increased release of divalent ions from formation
    - chemical EOR failure due to injection conditions being different from laboratory testing conditions (salinity and hardness might vary considerably in the field from lab results).
- The chelating equilibrium varies based on divalent ions, but is typically between 1.29:1 and 1.58:1 EDTA-4Na:divalent ion on a molar basis.
- The weight percent EDTA-4Na:divalent ion ratio varies based on the divalent ion type and concentration; 10:1 is an inaccurate and arbitrary value.
- EDTA-4Na does not reach pH 10.0
  - Will not cause spontaneous generation of insitu soap
  - But high pH will help limit surfactant degradation and lower adsorption
- EDTA-4Na was completely soluble in all circumstances throughout the range of the experiment (often 10.0 wt% EDTA-4Na)
- The pH of EDTA-4Na varies with concentration, temperature, temperature history (hysteresis), divalent ion type, divalent ion concentration, and mixture with other salts.
- Sodium metaborate has aqueous stability issues and cannot be used in high concentrations (i.e. greater than 0.25 to 0.50 wt%) in many circumstances.
- Sodium metaborate has sustained high pH, but typically precipitates at concentrations much lower than what are needed to obtain pH 10.0.
- Sodium acetate pH did not show any conclusive trends with alkali or divalent ion concentration
- Sodium acetate pH was always below 8.2 in the experiments undertaken.
Table 7.1: Sodium acetate pH experiments at 43.3 degrees Celsius.

<table>
<thead>
<tr>
<th>Expt</th>
<th>Brine</th>
<th>Brine wt%</th>
<th>wt% Brine</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>4.0 5.0 6.0 7.0 8.0 9.0</td>
</tr>
<tr>
<td>AS 207</td>
<td>SSFB</td>
<td>0.10 wt% Sodium acetate</td>
<td>8.17 7.42 7.45 7.42 7.4</td>
</tr>
<tr>
<td>AS 208</td>
<td>SSFB</td>
<td>0.30 wt% Sodium acetate</td>
<td>7.51 7.46 7.41 7.52 7.52</td>
</tr>
<tr>
<td>AS 209</td>
<td>SSFB</td>
<td>0.50 wt% Sodium acetate</td>
<td>7.46 7.08 7.3 7.35 7.55</td>
</tr>
<tr>
<td>AS 210</td>
<td>SSFB</td>
<td>1.0 wt% Sodium acetate</td>
<td>7.44 7.58 7.5 7.3 7.27</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Expt</th>
<th>Brine</th>
<th>Brine wt%</th>
<th>wt% Sodium Acetate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.0 1.0 2.0 3.0 4.0 5.0 6.0 7.0</td>
</tr>
<tr>
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<td>SSFB</td>
<td>5.5</td>
<td>7.46 7.08 7.08 7.1 7.25 7.48 7.49 7.55</td>
</tr>
<tr>
<td>AS 212</td>
<td>SSFB w polymer</td>
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<td>7.15 7.09 7.19 7.28 7.17 7.30</td>
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<tr>
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<td>NaCl</td>
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<td>7.49 7.25 7.19 7.35 7.68 7.42</td>
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Table 7.2: EDTA pH experiments.

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<th>Brine wt%</th>
<th>Temperature (deg. C)</th>
<th>wt% EDTA</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.25 0.5 0.75 1.0 2.5 5.0 7.5 10</td>
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</tr>
<tr>
<td>AS 230</td>
<td>FB #2</td>
<td>-</td>
<td>43.3</td>
<td>1.86 1.86 1.87 1.87 1.84 1.86 1.89 1.91</td>
</tr>
<tr>
<td>AS 230</td>
<td>FB #2</td>
<td>-</td>
<td>23</td>
<td>2.16 2.18 2.21 2.21 2.17 2.19 2.22 2.23</td>
</tr>
<tr>
<td>AS 230</td>
<td>FB #2</td>
<td>-</td>
<td>43.3</td>
<td>1.91 1.91 1.93 1.92 1.90 1.90 1.93 1.95</td>
</tr>
<tr>
<td>AS 230A</td>
<td>SSFB</td>
<td>5.5</td>
<td>43.3</td>
<td>1.93 1.93 1.93 1.93 1.94 1.94 1.94 1.94</td>
</tr>
<tr>
<td>AS 230A</td>
<td>SSFB</td>
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<td>23</td>
<td>2.28 2.29 2.30 2.29 2.30 2.29 2.31 2.29</td>
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<tr>
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<td>SSFB</td>
<td>5.5</td>
<td>43.3</td>
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</tr>
<tr>
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<td>NaCl</td>
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<td>43.3</td>
<td>2.03 2.03 2.03 2.04 2.06 2.06 2.08 2.10</td>
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</table>
Table 7.3: Characterization of brines used in pH experiments.

<table>
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<tr>
<th>Expts</th>
<th>Brine</th>
<th>wt%</th>
<th>divalent ions (ppm)</th>
<th>divalent ions (wt%)</th>
<th>molar (total)</th>
<th>molar (divalent)</th>
<th>Ionic Strength (mol/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AS 275, 277</td>
<td>MgCl₂</td>
<td>0.5</td>
<td>1276.5</td>
<td>0.1276</td>
<td>0.0525</td>
<td>0.0525</td>
<td>0.1576</td>
</tr>
<tr>
<td>AS 276, 278</td>
<td>MgCl₂</td>
<td>1.0</td>
<td>2552.9</td>
<td>0.2553</td>
<td>0.1050</td>
<td>0.1050</td>
<td>0.3151</td>
</tr>
<tr>
<td>AS 279, 281</td>
<td>MgCl₂</td>
<td>1.5</td>
<td>3829.4</td>
<td>0.3829</td>
<td>0.1576</td>
<td>0.1576</td>
<td>0.4727</td>
</tr>
<tr>
<td>AS 280, 282</td>
<td>MgCl₂</td>
<td>3.0</td>
<td>7658.7</td>
<td>0.7659</td>
<td>0.3151</td>
<td>0.3151</td>
<td>0.9453</td>
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<tr>
<td>AS 283, 285</td>
<td>CaCl₂</td>
<td>0.5</td>
<td>1805.7</td>
<td>0.1806</td>
<td>0.0451</td>
<td>0.0451</td>
<td>0.1352</td>
</tr>
<tr>
<td>AS 286, 288</td>
<td>CaCl₂</td>
<td>1.0</td>
<td>3611.3</td>
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<td>0.0901</td>
<td>0.2703</td>
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<tr>
<td>AS 289, 291</td>
<td>CaCl₂</td>
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<td>0.5417</td>
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<td>0.1352</td>
<td>0.4055</td>
</tr>
<tr>
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<td>SrCl₂</td>
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<td>2763.7</td>
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<td>0.0315</td>
<td>0.0315</td>
<td>0.0946</td>
</tr>
<tr>
<td>AS 295, 297</td>
<td>SrCl₂</td>
<td>1.0</td>
<td>5527.4</td>
<td>0.5527</td>
<td>0.0631</td>
<td>0.0631</td>
<td>0.1893</td>
</tr>
<tr>
<td>AS 298, 300</td>
<td>SrCl₂</td>
<td>1.5</td>
<td>8291.1</td>
<td>0.8291</td>
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<td>0.0946</td>
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<td>AS 299, 301</td>
<td>SrCl₂</td>
<td>3.0</td>
<td>16582.1</td>
<td>1.6582</td>
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<td>0.1893</td>
<td>0.5678</td>
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<tr>
<td>AS 302, 304</td>
<td>NaCl:CaCl₂</td>
<td>0.5</td>
<td>180.6</td>
<td>0.0181</td>
<td>0.0045</td>
<td>0.0045</td>
<td>0.0297</td>
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<td>AS 303, 305</td>
<td>NaCl:CaCl₂</td>
<td>5.0</td>
<td>1805.7</td>
<td>0.1806</td>
<td>0.0451</td>
<td>0.0451</td>
<td>0.2965</td>
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<td>AS 304, 306</td>
<td>NaCl:CaCl₂</td>
<td>10</td>
<td>3611.3</td>
<td>0.3611</td>
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<td>0.0901</td>
<td>0.5930</td>
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<td>NaCl:MgCl₂</td>
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<td>255.3</td>
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<td>0.0105</td>
<td>0.0105</td>
<td>0.0638</td>
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<tr>
<td>AS 310, 312</td>
<td>NaCl:MgCl₂</td>
<td>5.0</td>
<td>1276.5</td>
<td>0.1276</td>
<td>0.0525</td>
<td>0.0525</td>
<td>0.3189</td>
</tr>
<tr>
<td>AS 312, 314</td>
<td>NaCl:MgCl₂</td>
<td>10.0</td>
<td>2552.9</td>
<td>0.2553</td>
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<td>0.1050</td>
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<td>230AA</td>
<td>SSFB</td>
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<td>5316.7</td>
<td>0.5317</td>
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<td>1.0367</td>
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<td>0.0000</td>
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<td>1.0951</td>
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<td>-</td>
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<td>SSFB</td>
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<td>230EE</td>
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<td>0.3978</td>
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Table 7.4a: EDTA-4Na at 43.3 degrees Celsius.

<table>
<thead>
<tr>
<th>Expt</th>
<th>Brine</th>
<th>wt%</th>
<th>Alkali (NaB(OH)₄ molar)</th>
<th>0.0181</th>
<th>0.0363</th>
<th>0.0544</th>
<th>0.0725</th>
<th>0.1813</th>
<th>0.3626</th>
<th>0.5440</th>
<th>0.7253</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Alkali (EDTA-4Na molar)</td>
<td>0.0066</td>
<td>0.0132</td>
<td>0.0197</td>
<td>0.0263</td>
<td>0.0658</td>
<td>0.1315</td>
<td>0.1973</td>
<td>0.2630</td>
</tr>
<tr>
<td>AS 275</td>
<td>MgCl₂</td>
<td>0.5</td>
<td>NaB(OH)₄</td>
<td>9.05</td>
<td>9.14</td>
<td>9.08</td>
<td>9.08</td>
<td>9.31</td>
<td>9.60</td>
<td>9.75</td>
<td>9.9</td>
</tr>
<tr>
<td>AS 276</td>
<td>MgCl₂</td>
<td>1.0</td>
<td>NaB(OH)₄</td>
<td>8.94</td>
<td>8.93</td>
<td>8.90</td>
<td>8.92</td>
<td>9.06</td>
<td>9.38</td>
<td>9.57</td>
<td>9.70</td>
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<tr>
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<td>MgCl₂</td>
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<td>NaB(OH)₄</td>
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<td>8.74</td>
<td>8.77</td>
<td>8.73</td>
<td>8.87</td>
<td>9.09</td>
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<td>9.45</td>
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<tr>
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<td>NaB(OH)₄</td>
<td>8.96</td>
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<td>9.05</td>
<td>9.16</td>
<td>9.38</td>
<td>9.71</td>
<td>9.90</td>
<td>10.01</td>
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<td>9.51</td>
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<tr>
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<td>NaB(OH)₄</td>
<td>8.49</td>
<td>8.59</td>
<td>8.58</td>
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<td>8.62</td>
<td>9.33</td>
<td>9.52</td>
<td>9.71</td>
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<td>NaB(OH)₄</td>
<td>8.20</td>
<td>8.26</td>
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<td>CaCl₂</td>
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<td>EDTA-4Na</td>
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<td>4.19</td>
<td>4.19</td>
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<td>8.73</td>
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<td>3.75</td>
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<td>3.69</td>
<td>3.87</td>
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<td>4.69</td>
<td>4.69</td>
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<td>9.21</td>
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<tr>
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<td>MgCl₂</td>
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<td>4.81</td>
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<td>NaB(OH)₄</td>
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<td>8.96</td>
<td>9.04</td>
<td>9.03</td>
<td>9.23</td>
<td>9.56</td>
<td>9.72</td>
<td>9.87</td>
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<td>AS 293</td>
<td>SrCl₂</td>
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<td>NaB(OH)₄</td>
<td>8.74</td>
<td>8.80</td>
<td>8.86</td>
<td>8.88</td>
<td>9.01</td>
<td>9.43</td>
<td>9.68</td>
<td>9.81</td>
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<tr>
<td>AS 294</td>
<td>SrCl₂</td>
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<td>NaB(OH)₄</td>
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<td>8.66</td>
<td>8.65</td>
<td>8.74</td>
<td>8.84</td>
<td>8.97</td>
<td>9.31</td>
<td>9.55</td>
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Table 7.4b: EDTA-4Na at 43.3 degrees Celsius (continued).

<table>
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<th>Expt</th>
<th>Brine</th>
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<th>0.3626</th>
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Table 7.5b: EDTA-4Na at 23 degrees Celsius (continued).

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CHAPTER 8: CONCLUSION

This thesis dealt primarily with the design of a chemical enhanced oil recovery flood for a limestone reservoir containing a hard brine. The development of a surfactant formulation that would perform well at reservoir conditions was an exceptional challenge, but ultimately three formulations were produced using both commercially available surfactants and surfactants created at The University of Texas at Austin. One of these formulations was used in three different core floods. While success was limited in each of the core floods, oil recovery improved with each flood. Further experimentation will be able to refine the chemical injection scheme and improve flood performance.

The foundation of the research done for this thesis was the concerted and concentrated effort to confront the issue of divalent ions present in the field brine. The chemical formulations identified as the best field test candidates were all stable at reservoir conditions (hardness, salinity, and temperature). In fact, many of the formulations developed had aqueous stability and optimum salinity far beyond the reservoir salinity and hardness. A salinity gradient created by diluting hard brine with de-ionized water was ultimately used in the corefloods.

Aqueous stability and phase behavior were a significant challenge early in the project. Using only commercially available surfactants from the Stepan Company, obtaining both good aqueous stability and good phase behavior was found to be difficult; surfactant solutions that had good aqueous stability also had optimum salinities that were higher than the reservoir salinity (i.e. they were too hydrophilic). Surfactant solutions that had good phase behavior had poor aqueous stability because they were too hydrophobic. Many different surfactant solutions were tested before an acceptable final formulation was selected.

The surfactant TDA-45PO-10EO-Sulfate was ultimately identified as having the best properties to serve as the backbone of the chemical formulations. This surfactant, was hydrophobic enough to have a low optimum salinity owing to its high concentration of propylene oxide (PO) groups, but it also had enough ethylene oxide (EO) groups to
make it hydrophilic with good aqueous stability. This led to the surfactant performing well even in elevated salinity, hardness, and temperature conditions. Furthermore, excellent synergistic effects were observed when the TDA-45PO-EO-Sulfate was mixed with internal olefin sulfonate (IOS) surfactants, specifically S-3B. Given S-3B’s low optimum salinity, a small and hydrophilic surfactant (C-9) was used as a counterbalance. The chemical formulations were left to equilibrate for months at a time and no degradation in performance was observed through time. TDA-45PO-EO-Sulfate was developed at The University of Texas at Austin and S-3B and C-9 were Stepan products.

The top three candidates (PB 242, 246, and 247) for core flooding were evaluated with a spinning drop interfacial tensiometer to determine IFT. While the results did not always directly equate to the phase behavior experiments, the match was fairly close. The constant for the Huh equation was observed to be less than 0.3, the typically accepted value. However, this is not overly concerning because the constant is experimentally derived and varies for each set of parameters. The IFT values of from the spinning drop tests did not achieve ultra-low IFT values. Instead the IFT of the formulations was about 0.01 dynes/cm. This may have been a contributing factor to the core flood results. Also important to note was that the phase behavior in field brine was poor, with very small solubilization being observed. However, the IFT data for the field brine #1 and strontium synthetic field brine samples was comparable.

Many of the phase behavior and aqueous stability experiments were evaluated at reservoir temperature (43.3°C) and room temperature (~23°C). The results showed that aqueous stability improved considerably as temperature declined. This has important ramifications in experimental results being transferred to the field. Aqueous stability experiments done at room temperature are likely to have better behavior than field conditions, which can lead to an under-designing of the chemical flood. Phase behavior optimum salinity and solubilization were typically observed to decline as temperature increased. It was not unusual to observe a solubilization ratio decline of 25 cc/cc (a decline of 50%) and optimum salinity decline of 1.0 wt% TDS or more when increasing the temperature by 20°C.
A number of co-solvents were investigated, but most had either detrimental impacts to phase behavior or marginal improvements to aqueous stability. Co-solvents such as IBA had little to no effect on phase behavior or aqueous stability. DGBE and TGBE improved aqueous stability substantially, but also raised the optimum salinity to high levels and effectively destroyed the formation of microemulsions. Most experiments with TGBE ended up having only type I phase behavior. It is advised that this chemical be used sparingly (if at all) in surfactant formulations. SBA was identified as a successful co-solvent, however, it was not needed in the final formulations and was not used in the core flood experiments.

All core flooding was done with formulations of the PB 242 series, which was composed of 0.50 wt% TDA-45PO-10EO-Sulfate, 0.25 wt% S-3B, and 0.25 wt% C-9. The total concentration of surfactant in the chemical floods was 1.0 wt%. The amount of polymer used in the floods varied, but higher viscosities were needed to overcome the extreme heterogeneity of the field cores. All cores were determined to be water wet and had fairly low residual oil saturations to water flooding. The low residual oil saturations may be due to the vuggular nature of the cores. Due to pressure limitations in the experimental set-up and a relatively low permeability core (20 md), compromises were made on the EOR slug viscosities and flow rates for the field limestone core flood. The surfactant and polymer fluid viscosities were 4.6 and 4.8 cp at 10 S\(^{-1}\), whereas the minimum viscosity for stable displacement was calculated to be 11.4 cp. The chemical flow rate was 0.27 ft/d. The low flow rate and viscosities resulted in a drawn out oil bank with relatively low oil cut. Ultimate oil recovery suffered as a consequence.

Core floods were also conducted with Estillades limestone cores at increased flow rates and mobility ratios. On an oil recovery basis, these core floods performed better than the field core flood. The total oil recovery as a percent of OOIP due to water and EOR flooding for the Eliasville and Estillades corefloods was 55.0, 57.2, and 96.2%, respectively. However, with a surfactant slug size of 0.4 pore volumes, recovery was poor. After 2 PV of injected fluids, the three floods recovered 50.7, 43.8, and 69.7% of OOIP. Re-flooding the cores with significantly larger slugs of the same concentration
obtained better results. The final core flood was able to recover 96.2% of the original oil in place with a combination of water and EOR floods.

Since the oil recovery in field cores was not satisfactory, further core flooding needs to be done to better understand and characterize the EOR chemicals’ behavior before field trials can be done. These new core floods should use longer - preferably mixed wet and high permeability - cores. They should involve varying the surfactant slug size and the surfactant concentration. The other surfactant formulations identified as good candidates (PB 246 and PB 247) should also be tried in the core floods. Additionally, surfactant adsorption data should be collected and analyzed.

Chemical EOR in hard brines is less favorable than soft brines because alkalis are precluded from being used in hard brines due to their tendency to react and precipitate with divalent ions. An experimental investigation into alkali with the potential to be used in hard brines was done in this thesis. This investigation mainly focused on sodium metaborate (NaB(OH)$_4$) and EDTA-$4Na$.

Sodium metaborate was found to precipitate in most circumstances and was not recommended for general use in hard brines. The pH of sodium metaborate was always found to be greater than 8.0 and typically less than 10. This pH range is good for slowing the degradation of surfactants at elevated temperatures and limiting surfactant adsorption, but it may be too low for insitu saponification of some naphthenic acids to form natural soaps.

EDTA-$4Na$ was found to have strong sensitivity to divalent ion concentration. High concentrations of divalent ions relative to EDTA-$4Na$ molecules actually resulted in strongly acidic conditions, which are extremely unfavorable for carbonate reservoir EOR floods. Divalent ion type and temperature were also observed to significantly influence the pH of EDTA-$4Na$ solutions. pH hysteresis was observed in the change in temperature of EDTA-$4Na$ with magnesium brines. Finally, the chelating ratio of EDTA-$4Na$ to different divalent ions was determined. The commonly accepted ratio of 9 or 10:1 EDTA-$4Na$:divalent ions was found to be a not generally applicable. Much better tailoring can be done by using a water analysis report or titration with field brine. Given the tendency
for fluids to become diluted in reservoirs and EDTA-4Na’s acidic nature at low concentrations, this chemical is not recommended as a chelating or alkali agent in the field under these conditions.
### APPENDIX

Table A.1: Experiments PB 1 through PB 19.

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<th>Exp. No.</th>
<th>Surfactant Name</th>
<th>Surfactant wt%</th>
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<th>Co-Solvent, Alkali, Polymer wt%</th>
<th>Brine Name</th>
<th>Range (wt%)</th>
<th>Result</th>
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<td>-</td>
<td>-</td>
<td>NaCl</td>
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<td>-</td>
<td>-</td>
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<td>-</td>
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<td>SFB</td>
<td>3-7.0 (0.5 incr.)</td>
<td>S*= 3.75 wt%. WOR=2</td>
</tr>
<tr>
<td>PB 19</td>
<td>S-8A</td>
<td>0.50</td>
<td>-</td>
<td>-</td>
<td>SFB</td>
<td>2.5-7.5 (1.25 incr.)</td>
<td>S*= 5.0 wt%. WOR=4</td>
</tr>
</tbody>
</table>
Table A.2: Experiments PB 20 through PB 28.

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Surfactant</th>
<th>Co-Solvent, Alkali, Polymer</th>
<th>Brine</th>
<th>Range (wt%)</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>PB 20</td>
<td>S-8A</td>
<td>-</td>
<td>SFB</td>
<td>4.5-7.5 (1.25 incr.)</td>
<td>$S^*= 5.5$ wt%</td>
</tr>
<tr>
<td>PB 21</td>
<td>S-13A</td>
<td>-</td>
<td>SFB</td>
<td>4-7.5 (0.5 incr.)</td>
<td>$S^*= 7.0$ wt%</td>
</tr>
<tr>
<td>PB 23</td>
<td>-</td>
<td>Na2CO3</td>
<td>DI</td>
<td>0,2,4-7.5 (0.5 incr.)</td>
<td>No significant crude oil activity observed.</td>
</tr>
<tr>
<td>PB 25</td>
<td>S-13A</td>
<td>-</td>
<td>FB #1</td>
<td>0.1-0.5 (0.1 incr.)</td>
<td>WOR=1.5. Middle Phase increases as surfactant concentration increases for all concentrations. Solubilization ratio constant above about 0.1 wt% surfactant</td>
</tr>
<tr>
<td>PB 26</td>
<td>S-13A</td>
<td>-</td>
<td>FB #1</td>
<td>0.1-0.5 (0.1 incr.)</td>
<td>WOR=1. Middle Phase increases as surfactant concentration increases for all concentrations. Solubilization ratio levels off above about 0.3 wt% surfactant</td>
</tr>
<tr>
<td>PB 27</td>
<td>S-13A</td>
<td>-</td>
<td>FB #1</td>
<td>0.1-0.5 (0.1 incr.)</td>
<td>WOR=0.667. Middle Phase increases as surfactant concentration increases for all concentrations</td>
</tr>
<tr>
<td>PB 28</td>
<td>S-13A</td>
<td>-</td>
<td>FB #1</td>
<td>0.1-0.5 (0.1 incr.)</td>
<td>WOR=0.25. Middle Phase increases as surfactant concentration increases for all concentrations</td>
</tr>
</tbody>
</table>
Table A.3: Experiments PB 29 through AS 37.

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Surfactant</th>
<th>Co-Solvent, Alkali, Polymer</th>
<th>Brine</th>
<th>Range (wt%)</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>PB 29</td>
<td>S-8A</td>
<td>-</td>
<td>FB #1</td>
<td>0.1-0.5 (0.1 incr.)</td>
<td>WOR=4. Middle Phase increases as surfactant concentration increases for all concentrations…effects very apparent</td>
</tr>
<tr>
<td>PB 30</td>
<td>S-8A</td>
<td>-</td>
<td>FB #1</td>
<td>0.1-0.5 (0.1 incr.)</td>
<td>WOR=1.5. Middle Phase increases as surfactant concentration increases for all concentrations</td>
</tr>
<tr>
<td>PB 31</td>
<td>S-8A</td>
<td>-</td>
<td>FB #1</td>
<td>0.1-0.5 (0.1 incr.)</td>
<td>WOR=1. Middle Phase increases as surfactant concentration increases for all concentrations, 0.40 had a leak</td>
</tr>
<tr>
<td>PB 32</td>
<td>S-8A</td>
<td>-</td>
<td>FB #1</td>
<td>0.1-0.5 (0.1 incr.)</td>
<td>WOR=0.667. Middle Phase increases as surfactant concentration increases for all concentrations, 0.10 and 0.20 had been mixed in the pipette improperly and were omitted.</td>
</tr>
<tr>
<td>PB 33</td>
<td>S-8A</td>
<td>-</td>
<td>FB #1</td>
<td>0.1-0.5 (0.1 incr.)</td>
<td>WOR=0.25. No observable middle phase</td>
</tr>
<tr>
<td>AS 34</td>
<td>S-8A, S-8B, S-13A</td>
<td>F3330S</td>
<td>0.10</td>
<td>FB #1</td>
<td>0.5</td>
</tr>
<tr>
<td>AS 35</td>
<td>S-8A, S-13A</td>
<td>F3330S, BNao2</td>
<td>0.50</td>
<td>FB #1</td>
<td>0.5</td>
</tr>
<tr>
<td>AS 36</td>
<td>S-8A, S-13A</td>
<td>F3330S, BNao2</td>
<td>0.10</td>
<td>FB #1</td>
<td>0.3</td>
</tr>
<tr>
<td>AS 37</td>
<td>S-8A, S-13A</td>
<td>Biosoft N25-12 LA</td>
<td>0.5 wt%</td>
<td>FB #1</td>
<td>0.3 and 0.5</td>
</tr>
</tbody>
</table>
Table A.4: Experiments AS 38 through PB 46A.

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Surfactant</th>
<th>Co-Solvent, Alkali, Polymer</th>
<th>Brine</th>
<th>Range (wt%)</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>AS 38</td>
<td>S-8A, S-13A</td>
<td>N-25-12 0.30 S-2 0.30</td>
<td>FB #1</td>
<td>0.3 and 0.5</td>
<td>S-8A samples are cloudy and S-13A samples are clear but have yellow precipitate (S-2?)</td>
</tr>
<tr>
<td>AS 39</td>
<td>S-8A, S-13A</td>
<td>N-25-12 5.0 wt%</td>
<td>FB #1</td>
<td>0.3 and 0.5</td>
<td>All samples are clear (could be evidence of scale on the bottom of the vials)</td>
</tr>
<tr>
<td>AS 40</td>
<td>S-8A 0.30</td>
<td>N-25-12 1.0 to 3.0 wt%</td>
<td>FB #1</td>
<td>1.0 to 3.0 (incr. 0.5)</td>
<td>All Clear except 1 wt% solution.</td>
</tr>
<tr>
<td>AS 41</td>
<td>S-13A 0.30</td>
<td>N-25-12 0.30 to 0.60 wt%</td>
<td>FB #1</td>
<td>0.3 to 0.60 (incr. 0.075)</td>
<td>All clear</td>
</tr>
<tr>
<td>AS 42</td>
<td>S-13A 0.30</td>
<td>N-25-12 0.045 to 0.06 wt%</td>
<td>FB #1</td>
<td>0.045 to 0.06 (incr. 0.0075)</td>
<td>All precipitate</td>
</tr>
<tr>
<td>AS 43</td>
<td>S-13A 0.30</td>
<td>N-25-12 0.30-0.60 (incr. 0.075)</td>
<td>FB #1</td>
<td>0.30-0.60 (incr. 0.075)</td>
<td>Both precipitate</td>
</tr>
<tr>
<td>AS 44</td>
<td>S-13A 0.30</td>
<td>N-25-12 0.06875, 0.08125 to 0.1375 wt% (incr. 0.01875 wt%)</td>
<td>FB #1</td>
<td>0.06875, 0.08125 to 0.1375 (incr. 0.01875)</td>
<td>0.06875 only one to precipitate/cloud...~2.25:1 surf to cosurf</td>
</tr>
<tr>
<td>AS 45</td>
<td>S-13A 0.30, 0.40, 0.50</td>
<td>F3330S 0.10</td>
<td>FB #1</td>
<td>0.30, 0.40, 0.50</td>
<td>All cloudy, some precipitate polymer</td>
</tr>
<tr>
<td>AS 46</td>
<td>S-13A 0.30, 0.40, 0.50</td>
<td>C9 0.10, 0.125, 0.175</td>
<td>FB #1</td>
<td>~3:1 surf to cosurf in increasing concentrations w/ field brine</td>
<td>Cloudy above surf to cosurf of 3:1, precipitate</td>
</tr>
<tr>
<td>PB 46A</td>
<td>S-13A 0.30, 0.40, 0.50</td>
<td>C9 0.10, 0.125, 0.175</td>
<td>FB #1</td>
<td>~3:1 surf to cosurf in increasing concentrations w/ field brine</td>
<td>All type I microemulsions. (same at room temperature)</td>
</tr>
</tbody>
</table>
Table A.5: Experiments AS 47 through PB 51B.

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Surfactant</th>
<th>Co-Solvent, Alkali, Polymer</th>
<th>Brine</th>
<th>Range (wt%)</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>AS 47</td>
<td>S-8A</td>
<td>C9</td>
<td>FB#1</td>
<td>5.36</td>
<td>All cloudy, some precipitate polymer</td>
</tr>
<tr>
<td>PB 48</td>
<td>S-13A</td>
<td>C9</td>
<td>NSFB</td>
<td>1.0-8.0 (incr. 1)</td>
<td>Poor phase behavior throughout. Looks like moving from water in oil to oil in water ME</td>
</tr>
<tr>
<td></td>
<td>C9</td>
<td>-</td>
<td>NSFB</td>
<td>9.0-12.0 (incr. 1)</td>
<td>S*=9.9 wt% TDS, σ*=10 cc/cc. (S*=9.65 wt%, σ*=55 cc/cc at room temp.)</td>
</tr>
<tr>
<td>AS 48C</td>
<td>S-13A</td>
<td>C9</td>
<td>NaCl</td>
<td>2.0-12.0 (incr. 2)</td>
<td>Cloudy at and above 6% TDS. Cloud point somewhere between 4 and 6% NaCl.</td>
</tr>
<tr>
<td>PB 49</td>
<td>S-13A</td>
<td>C9</td>
<td>NSFB</td>
<td>2.0-8.0 (incr. 1)</td>
<td>S* at about 5.6 wt% TDS, but σ* less than 10.</td>
</tr>
<tr>
<td>AS 50</td>
<td>S-13B</td>
<td>C9</td>
<td>NSFB</td>
<td>5.5</td>
<td>Clear for 0.15 and 0.175 wt% C-9, cloudy/precipitation below. Need 50% C9 to make aqueously stable</td>
</tr>
<tr>
<td>PB 50A</td>
<td>S-8B</td>
<td>C9</td>
<td>NSFB</td>
<td>3.50-7.50 (incr. 1.00)</td>
<td>S* = 6.7 wt% TDS, but σ* less than 10.</td>
</tr>
<tr>
<td>PB 50B</td>
<td>S-13B</td>
<td>C9</td>
<td>NSFB</td>
<td>8.50-14.50, (1.50 incr.)</td>
<td>S* =~ 14.5 wt% TDS. Low σ. (All type I at room temperature)</td>
</tr>
<tr>
<td>AS 51</td>
<td>S-8B</td>
<td>C9</td>
<td>NSFB</td>
<td>0.075-0.175 (incr. 0.025)</td>
<td>Clear for 0.175 wt%, cloudy/precipitation below. Need more than 50% C9 to make aqueously stable</td>
</tr>
<tr>
<td>PB 51A</td>
<td>S-13B</td>
<td>-</td>
<td>NSFB</td>
<td>3.50-7.50 (1.00 incr.)</td>
<td>S* =7.0 wt% TDS, σ*=16 cc/cc. (All type I at room temperature)</td>
</tr>
<tr>
<td>PB 51B</td>
<td>S-8B</td>
<td>-</td>
<td>NSFB</td>
<td>8.50-14.50 (1.50 incr.)</td>
<td>S* =~13.0 wt% TDS, σ<em>~20 cc/cc. (S</em>~14.5 wt% at room temp.)</td>
</tr>
<tr>
<td>Exp. No.</td>
<td>Surfactant</td>
<td>Co-Solvent, Alkali, Polymer</td>
<td>Brine</td>
<td>Range (wt%)</td>
<td>Result</td>
</tr>
<tr>
<td>---------</td>
<td>------------</td>
<td>-----------------------------</td>
<td>-------</td>
<td>-------------</td>
<td>--------</td>
</tr>
<tr>
<td>PB 52</td>
<td>S-13D</td>
<td>0.50 Biosoft N-25-12 0.15</td>
<td>NSFB</td>
<td>4.0-10.0 (incr. 1)</td>
<td>S* below range. All type II microemulsions and viscous. (Same at room temperature).</td>
</tr>
<tr>
<td>PB 53</td>
<td>S-13D C-9</td>
<td>0.50 - 0.15 - -</td>
<td>NSFB</td>
<td>4.0-10.0 (incr. 1)</td>
<td>Not much to go on. S* around 5%?</td>
</tr>
<tr>
<td>PB 54</td>
<td>S-13C C-9</td>
<td>0.75 - 0.25 - -</td>
<td>NSFB</td>
<td>2.0-10.0 (incr. 2)</td>
<td>S* greater than 10%</td>
</tr>
<tr>
<td>PB 55</td>
<td>S-8C C-9</td>
<td>0.75 - 0.25 - -</td>
<td>NSFB</td>
<td>2.0-10.0 (incr. 2)</td>
<td>S* above 10%</td>
</tr>
<tr>
<td>PB 56A</td>
<td>S-13A C-9</td>
<td>0.90 - 0.10 - -</td>
<td>NaCl</td>
<td>2.0-12.0 (incr. 2)</td>
<td>S* =~ 10%</td>
</tr>
<tr>
<td>AS 56C</td>
<td>S-13A C-9</td>
<td>0.90 - 0.10 - -</td>
<td>NaCl</td>
<td>2.0-12.0 (incr. 2)</td>
<td>Cloudy at and above 4% TDS. Cloud point somewhere between 2 and 4% NaCl</td>
</tr>
<tr>
<td>PB 57</td>
<td>S-13D</td>
<td>0.75 - - -</td>
<td>NaCl</td>
<td>1.0-5.0 (incr. 1)</td>
<td>S* Less than 1%</td>
</tr>
<tr>
<td>PB 58</td>
<td>S-13D C-9</td>
<td>0.50 - 0.50 - -</td>
<td>NaCl</td>
<td>3.0-7.0 (incr. 1)</td>
<td>All type I microemulsion.</td>
</tr>
<tr>
<td>PB 59</td>
<td>S-13D C-9</td>
<td>0.75 - 0.25 - -</td>
<td>NaCl</td>
<td>1.0-6.0 (incr. 1)</td>
<td>S* =~ 4%</td>
</tr>
<tr>
<td>AS 59A</td>
<td>S-13D C-9</td>
<td>0.75 - 0.25 - -</td>
<td>NaCl</td>
<td>2.0-10.0 (incr. 2)</td>
<td>Cloudy at and above 6% TDS. Cloud point somewhere between 4 and 6% NaCl. Looks like 4% is about the limit for aqueous stability because it has a tinge of cloudiness</td>
</tr>
<tr>
<td>AS 60</td>
<td>S-13A C-9</td>
<td>0.75 - 0.25 - -</td>
<td>NaCl</td>
<td>2.0-12.0 (incr. 2)</td>
<td>Cloudy at and above 8% TDS. Cloud point somewhere between 6 and 8% NaCl</td>
</tr>
<tr>
<td>PB 61</td>
<td>S-13D C-9</td>
<td>0.90 - 0.10 - -</td>
<td>NaCl</td>
<td>1.0-7.0 (incr. 1)</td>
<td>S* around 2%</td>
</tr>
<tr>
<td>AS 61A</td>
<td>S-13D C-9</td>
<td>0.90 - 0.10 - -</td>
<td>NaCl</td>
<td>2.0-10.0 (incr. 1)</td>
<td>Cloudy at and above 4% TDS. Cloud point somewhere between 2 and 4% NaCl</td>
</tr>
</tbody>
</table>
Table A.7: Experiments PB 62 through AS 65BA.

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Surfactant</th>
<th>Co-Solvent, Alkali, Polymer</th>
<th>Brine</th>
<th>Range (wt%)</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Name</td>
<td>wt%</td>
<td>Name</td>
<td>wt%</td>
<td></td>
</tr>
<tr>
<td>PB 62</td>
<td>S-13D</td>
<td>0.50</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>S-2</td>
<td>0.10</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C-9</td>
<td>0.40</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>PB 63</td>
<td>S-13D</td>
<td>0.75</td>
<td>IBA</td>
<td>0.25</td>
<td>NaCl 2.0-7.0 (incr. 1) A lot of gel. Not clear where S* is, if within range at all</td>
</tr>
<tr>
<td>PB 64</td>
<td>S-13D</td>
<td>0.50</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>S-13C</td>
<td>0.25</td>
<td>-</td>
<td>-</td>
<td>NaCl 2.0-7.0 (incr. 1) S* appears to be around 4.75 wt%, σ* of 6.9 cc/cc</td>
</tr>
<tr>
<td></td>
<td>C-9</td>
<td>0.25</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>AS 64AA</td>
<td>S-13D</td>
<td>0.50</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>S-13C</td>
<td>0.25</td>
<td>-</td>
<td>-</td>
<td>NSFB 3.0-6.0 (incr. 0.5) Precipitation at 4% and above</td>
</tr>
<tr>
<td></td>
<td>C-9</td>
<td>0.25</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AS 64B</td>
<td>S-13D</td>
<td>0.50</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>S-13C</td>
<td>0.25</td>
<td>-</td>
<td>-</td>
<td>NaCl 2.0-10.0 (incr. 1) Cloudy at and above 6% TDS. Cloud point somewhere between 4 and 6% NaCl</td>
</tr>
<tr>
<td></td>
<td>C-9</td>
<td>0.25</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PB 64CA</td>
<td>S-13D</td>
<td>0.50</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>S-13C</td>
<td>0.25</td>
<td>-</td>
<td>-</td>
<td>NSFB 2.0-7.0 (incr. 1) S* at 2.8%, σ* = 18 cc/cc</td>
</tr>
<tr>
<td></td>
<td>C-9</td>
<td>0.25</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>PB 65</td>
<td>S-13D</td>
<td>0.50</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>S-13A</td>
<td>0.25</td>
<td>-</td>
<td>-</td>
<td>NaCl 4.0-9.0 (incr. 1) S* around 7.9%, σ* of 18 cc/cc</td>
</tr>
<tr>
<td></td>
<td>C-9</td>
<td>0.25</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>PB 65AA</td>
<td>S-13D</td>
<td>0.50</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>S-13A</td>
<td>0.25</td>
<td>-</td>
<td>-</td>
<td>NSFB 4.0-7.0 (incr. 0.5) S* at 5.33 wt% TDS, σ* = 9.5 cc/cc</td>
</tr>
<tr>
<td></td>
<td>C-9</td>
<td>0.25</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>AS 65BA</td>
<td>S-13D</td>
<td>0.50</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>S-13A</td>
<td>0.25</td>
<td>-</td>
<td>-</td>
<td>NSFB 4.0-7.0 (incr. 0.5) Phase separation at 4.50% and above</td>
</tr>
<tr>
<td></td>
<td>C-9</td>
<td>0.25</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Exp. No.</td>
<td>Surfactant</td>
<td>Co-Solvent, Alkali, Polymer</td>
<td>Brine</td>
<td>Range (wt%)</td>
<td>Result</td>
</tr>
<tr>
<td>---------</td>
<td>------------</td>
<td>----------------------------</td>
<td>-------</td>
<td>-------------</td>
<td>--------</td>
</tr>
<tr>
<td>AS 65C</td>
<td>S-13D</td>
<td>-</td>
<td>NaCl</td>
<td>4.0-7.0</td>
<td>Phase separation at and above 6% TDS. Cloud point somewhere between 5.5 and 6% TDS.</td>
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<td>S-13A</td>
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<td>(incr. 0.5)</td>
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<td>C-9</td>
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<td>NaCl</td>
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<tr>
<td>PB 66r</td>
<td>S-13D</td>
<td>0.40</td>
<td>NSFB</td>
<td>4.0-7.0</td>
<td>S*=5.4%, σ*= 10.5 cc/cc</td>
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<td></td>
<td>S-13C</td>
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<td></td>
<td>(incr 1)</td>
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<td>C-9</td>
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<td>AS 66A</td>
<td>S-13D</td>
<td>0.40</td>
<td>NaCl</td>
<td>4.0-7.0</td>
<td>Clear</td>
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<tr>
<td></td>
<td>S-13C</td>
<td>0.25</td>
<td></td>
<td>(incr 0.5)</td>
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<tr>
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<td>C-9</td>
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<td>AS 66B</td>
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<td>0.40</td>
<td>NSFB</td>
<td>4.0-7.0</td>
<td>Precipitation at and above 6% TDS.</td>
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<td>S-13C</td>
<td>0.25</td>
<td></td>
<td>(incr 0.5)</td>
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<tr>
<td></td>
<td>C-9</td>
<td>0.35</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>AS 66C</td>
<td>S-13D</td>
<td>0.40</td>
<td>NSFB</td>
<td>4.0-8.0</td>
<td>Cloudy 6% and above</td>
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<tr>
<td></td>
<td>S-13C</td>
<td>0.25</td>
<td></td>
<td>(incr 0.5)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C-9</td>
<td>0.35</td>
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<td>S-13D</td>
<td>0.40</td>
<td>F3330S</td>
<td>4.0-8.0</td>
<td>Phase separation at 6.50 wt%.</td>
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<td>S-13C</td>
<td>0.25</td>
<td></td>
<td>(incr 0.5)</td>
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<tr>
<td></td>
<td>C-9</td>
<td>0.35</td>
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<td>AS 66E</td>
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<td>0.40</td>
<td>TGBE</td>
<td>4.5-7.0</td>
<td>Phase Separation at 7.0 wt% (all stable 7.0 wt%)</td>
</tr>
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<td></td>
<td>S-13C</td>
<td>0.25</td>
<td></td>
<td>(incr 0.5)</td>
<td></td>
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<tr>
<td></td>
<td>C-9</td>
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<td>AS 66F</td>
<td>S-13D</td>
<td>0.40</td>
<td>DGBE</td>
<td>4.5-7.0</td>
<td>Cloudy at 6.0 wt% (phase separation at 6 and 7 wt%, clear at 6.5 wt%)</td>
</tr>
<tr>
<td></td>
<td>S-13C</td>
<td>0.25</td>
<td></td>
<td>(incr 0.5)</td>
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<tr>
<td></td>
<td>C-9</td>
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<tr>
<td>AS 66G</td>
<td>S-13D</td>
<td>0.40</td>
<td>Methanol</td>
<td>4.5-7.0</td>
<td>Phase Separation at 6.5 wt% (phase separation at 7.0 wt%)</td>
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<tr>
<td></td>
<td>S-13C</td>
<td>0.25</td>
<td></td>
<td>(incr 0.5)</td>
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Table A.9: Experiments AS 66H through PB 66Q.

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<th>Surfactant Name</th>
<th>Surfactant wt%</th>
<th>Co-Solvent, Alkali, Polymer Name</th>
<th>Co-Solvent wt%</th>
<th>Brine Range (wt%)</th>
<th>Result</th>
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<td>AS 66H</td>
<td>S-13D</td>
<td>0.40</td>
<td>Ethanol</td>
<td>0.25</td>
<td>SSFB 4.5-7.0</td>
<td>Phase Separation at 6.0 wt% (stability past 7.0 wt% at room temp)</td>
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<tr>
<td></td>
<td>S-13C</td>
<td>0.25</td>
<td>F3330S</td>
<td>0.10</td>
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<td>C-9</td>
<td>0.35</td>
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<tr>
<td>AS 66I</td>
<td>S-13D</td>
<td>0.40</td>
<td>1-Butanol</td>
<td>0.25</td>
<td>SSFB 4.5-7.0</td>
<td>Phase Separation at 6.0 wt% (stability past 7.0 wt% at room temp)</td>
</tr>
<tr>
<td></td>
<td>S-13C</td>
<td>0.25</td>
<td>F3330S</td>
<td>0.10</td>
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<tr>
<td></td>
<td>C-9</td>
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<td>AS 66J</td>
<td>S-13D</td>
<td>0.40</td>
<td>SBA</td>
<td>0.25</td>
<td>SSFB 4.5-7.0</td>
<td>Phase Separation at 6.0 wt% (Phase separation at 7.0 wt% at room temp)</td>
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<td>S-13C</td>
<td>0.25</td>
<td>F3330S</td>
<td>0.10</td>
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<td>C-9</td>
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<td>AS 66K</td>
<td>S-13D</td>
<td>0.40</td>
<td>IBA</td>
<td>0.25</td>
<td>SSFB 4.5-7.0</td>
<td>Phase Separation at 6.0 wt% (Phase separation at 7.0 wt% at room temp)</td>
</tr>
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<td></td>
<td>S-13C</td>
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<td>F3330S</td>
<td>0.10</td>
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<td>C-9</td>
<td>0.35</td>
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<td>AS 66L</td>
<td>S-13D</td>
<td>0.40</td>
<td>Methanol</td>
<td>0.50</td>
<td>SSFB 4.5-7.0</td>
<td>Phase Separation at 6.0 wt%. (Hazy at 7.0 wt% at room temperature)</td>
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<td>S-13C</td>
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<td>F3330S</td>
<td>0.10</td>
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<td>C-9</td>
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<td>PB 66M</td>
<td>S-13D</td>
<td>0.40</td>
<td>Methanol</td>
<td>0.25</td>
<td>SSFB 4.5-7.5</td>
<td>S*= 6.65 wt% TDS, σ* of 9 cc/cc. (All type I at room temp.)</td>
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<td>S-13C</td>
<td>0.25</td>
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<td></td>
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<td>C-9</td>
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<td>PB 66N</td>
<td>S-13D</td>
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<td>SBA</td>
<td>0.25</td>
<td>SSFB 4.5-7.5</td>
<td>S*= 6.75 wt% TDS, σ* of 9 cc/cc. Decent behavior at 6.0 and 6.5 wt% TDS. (S* above 7.5 wt% at room temp.)</td>
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<td>S-13C</td>
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<td>C-9</td>
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<td>AS 66P</td>
<td>S-13D</td>
<td>0.40</td>
<td>Sodium Acetate</td>
<td>0.10</td>
<td>SSFB 4.0-7.0</td>
<td>Phase Separation at 5.50 wt%. (Same at room temperature)</td>
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<td>F3330S</td>
<td>0.10</td>
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<td>C-9</td>
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<td>PB 66Q</td>
<td>S-13D</td>
<td>0.40</td>
<td>Sodium Acetate</td>
<td>0.10</td>
<td>SSFB 4.5-9.0</td>
<td>S* at 8.4 wt%, σ*= 4.7 cc/cc. (S* above 9 wt% at room temp.)</td>
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<td>S-13C</td>
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<td>C-9</td>
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Table A.10: Experiments AS 66S through PB 69.

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<th>Exp. No.</th>
<th>Surfactant</th>
<th>Co-Solvent, Alkali, Polymer</th>
<th>Brine</th>
<th>Range (wt%)</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>AS 66S</td>
<td>S-13D 0.40</td>
<td>Sodium Acetate 0.10</td>
<td>SSFB</td>
<td>5.5-6.0 (incr. 0.1)</td>
<td>All Phase Separate (5.5 wt%). (Same at room temperature)</td>
</tr>
<tr>
<td></td>
<td>S-13C 0.25</td>
<td>F3330S 0.10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C-9 0.35</td>
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<tr>
<td>AS 66T</td>
<td>S-13D 0.40</td>
<td>Sodium Acetate 0.10</td>
<td>NaCl</td>
<td>4.0-7.5 (incr. 0.1)</td>
<td>Phase Separation at 6.0 wt%. (Phase separation at 7.5 wt% at room temperature)</td>
</tr>
<tr>
<td></td>
<td>S-13C 0.25</td>
<td>F3330S 0.10</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>C-9 0.35</td>
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<tr>
<td>AS 66U</td>
<td>S-13D 0.40</td>
<td>Sodium Acetate 0.10</td>
<td>SSFB</td>
<td>5.0-5.4 (incr. 0.1)</td>
<td>All phase separate/cloudy (5.0 wt%). (All clear at room temperature)</td>
</tr>
<tr>
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<td>S-13C 0.25</td>
<td>F3330S 0.10</td>
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<td>C-9 0.35</td>
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<td>PB 66V</td>
<td>S-13D 0.40</td>
<td>Sodium Acetate 0.10</td>
<td>NaCl</td>
<td>5.5-10.5 (incr. 0.5)</td>
<td>S* at 9.8 wt%, σ*= 2.6 cc/cc. (S* above 10.5 wt% at room temp.)</td>
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<td>F3330S 0.10</td>
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<td>C-9 0.35</td>
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<tr>
<td>PB 67</td>
<td>S-13D 0.40</td>
<td>Sodium Acetate 0.10</td>
<td>NaCl</td>
<td>4.0-7.0 (incr. 0.5)</td>
<td>All Type I (Same at room temperature).</td>
</tr>
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<td>S-13A 0.25</td>
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<td>C-9 0.35</td>
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<td>AS 67A</td>
<td>S-13D 0.40</td>
<td>Sodium Acetate 0.10</td>
<td>NaCl</td>
<td>5.0-8.0 (incr. 0.5)</td>
<td>No precipitation</td>
</tr>
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<td>S-13A 0.25</td>
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<td>C-9 0.35</td>
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<tr>
<td>AS 67B</td>
<td>S-13D 0.40</td>
<td>Sodium Acetate 0.10</td>
<td>NSFB</td>
<td>4.0-7.0 (incr. 0.5)</td>
<td>all clear</td>
</tr>
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<td>S-13A 0.25</td>
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<td>C-9 0.35</td>
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<td>PB 68</td>
<td>S-13D 0.50</td>
<td>Sodium Acetate 0.10</td>
<td>NSFB</td>
<td>4.0-7.0 (incr. 0.5)</td>
<td>No real optimum observed.</td>
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<td>N-25-12 0.25</td>
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<td>C-9 0.35</td>
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<td>PB 69</td>
<td>S-13D 0.45</td>
<td>Sodium Acetate 0.10</td>
<td>NSFB</td>
<td>4.0-7.0 (incr. 0.5)</td>
<td>S*= 4.35%, σ*= 8 cc/cc</td>
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<td>S-13C 0.25</td>
<td>IBA 0.05</td>
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<td>C-9 0.25</td>
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262
Table A.11: Experiments PB 70 through PB 75.

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<th>Exp. No.</th>
<th>Surfactant</th>
<th>Co-Solvent, Alkali, Polymer</th>
<th>Brine</th>
<th>Range (wt%)</th>
<th>Result</th>
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</thead>
<tbody>
<tr>
<td>PB 70</td>
<td>S-13D 0.45</td>
<td>IBA 0.10</td>
<td>NSFB</td>
<td>4.0-7.0 (incr. 0.5)</td>
<td>Low optimum solubilization. Macroemulsions</td>
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<td>S-13C 0.25</td>
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<td>PB 71</td>
<td>S-13D 0.50</td>
<td>IBA 0.10</td>
<td>NSFB</td>
<td>4.0-7.0 (incr. 0.5)</td>
<td>Low optimum solubilization. Macroemulsions</td>
</tr>
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<td>S-13C 0.25</td>
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<td>S-13D 0.45</td>
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<td>NSFB</td>
<td>4.0-7.0 (incr. 0.5)</td>
<td>S*= 4.1%, σ*= 13 cc/cc. (S*= 5.65%, σ*= 38 cc/cc at room temp.)</td>
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<td>PB 73</td>
<td>S-13D 0.45</td>
<td>IBA 0.20</td>
<td>NSFB</td>
<td>4.0-7.0 (incr. 0.5)</td>
<td>No optimum salinity in range. Type II microemulsion.</td>
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<td>PB 74</td>
<td>S-13D 0.45</td>
<td>IBA 0.05</td>
<td>NSFB</td>
<td>4.0-7.0 (incr. 0.5)</td>
<td>S*= 3.75%, σ*= 14 cc/cc. (S*= 5.50%, σ*= 27 cc/cc at room temp.)</td>
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<td>AS 74A</td>
<td>S-13D 0.45</td>
<td>IBA 0.05</td>
<td>NSFB</td>
<td>4.0-7.0 (incr. 0.5)</td>
<td>Cloudy at 4.5%. (Cloudy at 6 wt% at room temperature)</td>
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<td>F3330S 0.10</td>
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<td>AS 74B</td>
<td>S-13D 0.45</td>
<td>SBA 0.50</td>
<td>FB #2+</td>
<td>4.65</td>
<td>Phase Separation (Clear, but some precipitation at room temperature)</td>
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<td>SSFB</td>
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<td>C-9 0.30</td>
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<tr>
<td>PB 74C</td>
<td>S-13D 0.45</td>
<td>SBA 0.50</td>
<td>FB #2+</td>
<td>4.65</td>
<td>Type II microemulsion. Viscous macroemulsion present. (Type III at room temp., Oil sol.=32.7 cc/cc water sol.=23.2 cc/cc. Fluid.)</td>
</tr>
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<td>S-13C 0.25</td>
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<td>SSFB</td>
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<td>C-9 0.30</td>
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<tr>
<td>PB 75</td>
<td>S-13D 0.45</td>
<td>IBA 0.05</td>
<td>NSFB</td>
<td>4.0-7.0 (incr. 0.5)</td>
<td>S*= 4.12%, σ*= 54 cc/cc</td>
</tr>
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<td>S-13C 0.30</td>
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<td>C-9 0.25</td>
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Table A.12: Experiments PB 76 through AS 77G.

<table>
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<th>Exp. No.</th>
<th>Surfactant Name</th>
<th>Co-Solvent, Alkali, Polymer Name</th>
<th>Brine Coefficient</th>
<th>Range (wt%)</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>PB 76</td>
<td>S-13D 0.45</td>
<td>-</td>
<td>NSFB</td>
<td>4.0-7.0</td>
<td>$S^<em>= 3.7%$, $\sigma^</em>= 13$ cc/cc ($S^<em>= 4.25%$, $\sigma^</em>= 15$ cc/cc at room temp.)</td>
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<tr>
<td></td>
<td>S-13C 0.30</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
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<td>C-9 0.30</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PB 77</td>
<td>S-13D 0.45</td>
<td>-</td>
<td>NSFB</td>
<td>4.0-7.0</td>
<td>$S^<em>= 5.75$ wt%, $\sigma^</em>= 11$ cc/cc. ($S^* = 7.2$ wt%, $\sigma^* = 16$ cc/cc at room temp.)</td>
</tr>
<tr>
<td></td>
<td>S-13C 0.25</td>
<td>IBA 0.05</td>
<td></td>
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</tr>
<tr>
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<td>C-9 0.35</td>
<td>-</td>
<td></td>
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</tr>
<tr>
<td>AS 77A</td>
<td>S-13D 0.45</td>
<td>IBA 0.05</td>
<td>NSFB</td>
<td>4.0-7.0</td>
<td>Cloudy at 6% (Phase separation at 6 wt% at room temperature)</td>
</tr>
<tr>
<td></td>
<td>S-13C 0.25</td>
<td>F3330S 0.10</td>
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<tr>
<td></td>
<td>C-9 0.35</td>
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<tr>
<td>AS 77B</td>
<td>S-13D 0.45</td>
<td>Methanol 0.50</td>
<td>SSFB</td>
<td>4.5-7.0</td>
<td>Phase Separation at 5.5 wt% (all clear at room temperature)</td>
</tr>
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<td>F3330S 0.10</td>
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<td></td>
<td>C-9 0.35</td>
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<tr>
<td>AS 77C</td>
<td>S-13D 0.45</td>
<td>TGBE 0.25</td>
<td>SSFB</td>
<td>4.5-7.0</td>
<td>Phase Separation at 6.0 wt% (Phase separation at 7.0 wt% at room temp)</td>
</tr>
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<td>S-13C 0.25</td>
<td>F3330S 0.10</td>
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<td>C-9 0.35</td>
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<tr>
<td>AS 77D</td>
<td>S-13D 0.45</td>
<td>SBA 0.25</td>
<td>SSFB</td>
<td>4.5-7.0</td>
<td>Phase Separation at 5.5 wt% (phase separation at 7.0 wt% at room temp)</td>
</tr>
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<td></td>
<td>S-13C 0.25</td>
<td>F3330S 0.10</td>
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<td>C-9 0.35</td>
<td>-</td>
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<tr>
<td>PB 77E</td>
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<td>TGBE 0.25</td>
<td>SSFB</td>
<td>4.5-7.5</td>
<td>$S^* = 7.5$ wt% TDS, $\sigma^* = 6.5$ cc/cc ($S^*$ above 7.5 wt% at room temperature)</td>
</tr>
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<td>S-13C 0.25</td>
<td>F3330S 0.10</td>
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<td></td>
<td>C-9 0.35</td>
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</tr>
<tr>
<td>PB 77F</td>
<td>S-13D 0.45</td>
<td>Sodium Acetate 0.10</td>
<td>SSFB</td>
<td>4.0-7.0</td>
<td>Phase Separation at 5.00 wt% (phase separation at 5.5 wt% at room temperature)</td>
</tr>
<tr>
<td></td>
<td>S-13C 0.25</td>
<td>F3330S 0.10</td>
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<td>AS 77G</td>
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<td>SBA 0.50</td>
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<td>All phase separate (5.0 wt%). (Same at room temperature)</td>
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<td>S-13C 0.25</td>
<td>Sodium Acetate 0.10</td>
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<td>C-9 0.35</td>
<td>F3330S 0.10</td>
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Table A.13: Experiments PB 78 through PB 81.

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<th>Brine</th>
<th>Range (wt%)</th>
<th>Result</th>
</tr>
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<td>Name</td>
<td>wt%</td>
<td>Name</td>
<td>wt%</td>
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<td>0.10</td>
<td>NSFB</td>
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<td>S-13C</td>
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<td>0.10</td>
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<td>F3330S</td>
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<td>0.50</td>
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<td>IBA</td>
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<td>NSFB</td>
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<td>F3330S</td>
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<tr>
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<td>SBA</td>
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<td>FB #2+ SSFB</td>
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Table A.14: Experiments PB 82 through PB 90.

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<th>Exp. No.</th>
<th>Surfactant</th>
<th>Co-Solvent, Alkali, Polymer</th>
<th>Brine</th>
<th>Range (wt%)</th>
<th>Result</th>
</tr>
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<tbody>
<tr>
<td>PB 82</td>
<td>S-13D 0.45</td>
<td>-</td>
<td>NSFB</td>
<td>4.0-7.0 (incr. 0.5)</td>
<td>S* about 4.0 wt%, and σ* = 65 cc/cc</td>
</tr>
<tr>
<td></td>
<td>S-13C 0.35</td>
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<tr>
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<td>C-9 0.25</td>
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<tr>
<td>PB 83</td>
<td>S-13D 0.45</td>
<td>-</td>
<td>NSFB</td>
<td>4.0-7.0 (incr. 0.5)</td>
<td>S* about 6.2 wt%, and σ* = 5.8 cc/cc</td>
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<td>S-13C 0.25</td>
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<td>C-9 0.35</td>
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<td>PB 84</td>
<td>S-13D 0.45</td>
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<td>NSFB</td>
<td>4.0-7.0 (incr. 0.5)</td>
<td>S* about 4.7 wt%, and σ* = 1 cc/cc</td>
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<td>S-13C 0.25</td>
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<td>PB 85</td>
<td>S-13D 0.45</td>
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<td>IBA</td>
<td>4.0-7.0 (incr. 0.5)</td>
<td>S* about 4.5 wt%, and σ* = 55 cc/cc</td>
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<td>S-13C 0.25</td>
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<td>PB 86</td>
<td>S-13D 0.45</td>
<td>-</td>
<td>IBA</td>
<td>4.0-7.0 (incr. 0.5)</td>
<td>S* about 3.8 wt%, and σ* = 30 cc/cc</td>
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<td>S-13C 0.25</td>
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<td>PB 87r</td>
<td>S-13D 0.40</td>
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<td>NSFB</td>
<td>4.0-7.0 (incr. 0.5)</td>
<td>S* about 5.9 wt%, σ* = 11 cc/cc. (All type I at room temperature)</td>
</tr>
<tr>
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<td>S-13C 0.30</td>
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<td>C-9 0.35</td>
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<td>PB 88</td>
<td>S-13D 0.80</td>
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<td>IBA</td>
<td>4.0-7.0 (incr. 0.5)</td>
<td>S* about 4 wt%, and σ* = 58 cc/cc. High σ* may be due to misinterp. of macroemulsions</td>
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<tr>
<td>PB 89</td>
<td>S-13D 0.40</td>
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<td>NSFB</td>
<td>4.0-7.0 (incr. 0.5)</td>
<td>S* about 6.3 wt%, and σ* = 13 cc/cc</td>
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<td>PB 90</td>
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<td>NSFB</td>
<td>4.0-7.0 (incr. 0.5)</td>
<td>S* about 6.25 wt%, and σ* = 15 cc/cc</td>
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<td>C-9 0.35</td>
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<tr>
<td>Exp. No.</td>
<td>Surfactant</td>
<td>Co-Solvent, Alkali, Polymer</td>
<td>Brine</td>
<td>Range (wt%)</td>
<td>Result</td>
</tr>
<tr>
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<tr>
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<td>S-13D 0.45</td>
<td>IBA 1.00</td>
<td>NSFB</td>
<td>4.0-7.0 (incr. 0.5)</td>
<td>Cloudy at 5% and above</td>
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<td>F3330S 0.10</td>
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<tr>
<td>AS 92</td>
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<td>N-25-12 1.00</td>
<td>NSFB</td>
<td>4.0-7.0 (incr. 0.5)</td>
<td>Phase separation around 5.5-6%. Otherwise clear</td>
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<td>F3330S 0.10</td>
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<tr>
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<td>N-25-12 1.00</td>
<td>NSFB</td>
<td>4.0-7.0 (incr. 0.5)</td>
<td>S*= 6.3 wt%, σ*= 8 cc/cc. (All type I at room temperature)</td>
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<td>S-13C 0.25</td>
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<td>NSFB</td>
<td>4.0-7.0 (incr. 0.5)</td>
<td>S*= 4.9 wt%, σ*= 10 cc/cc. (S*= 6.0 wt%, σ*= 16 cc/cc at room temperature)</td>
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<td>C-9 0.35</td>
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<td>SSFB</td>
<td>4.0-6.0 (incr. 0.5)</td>
<td>Phase Separation at 4.0 wt% (All cloudy at room temp)</td>
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<td>N-25-12 1.00</td>
<td>NSFB</td>
<td>4.0-7.0 (incr. 0.5)</td>
<td>S* around 5.5%, σ* less than 10 cc/cc</td>
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<td>S-13C 0.35</td>
<td>C-9 0.25</td>
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<tr>
<td>PB 96</td>
<td>S-13D 0.45</td>
<td>N-25-12 1.00</td>
<td>NSFB</td>
<td>4.0-7.0 (incr. 0.5)</td>
<td>S* above 7%</td>
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<td>S-13B 0.35</td>
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<td>PB 97</td>
<td>S-13C 0.80</td>
<td>N-25-12 1.00</td>
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<td>4.0-7.0 (incr. 0.5)</td>
<td>S* 6.1 wt%, σ* ~ 8 cc/cc</td>
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<td>PB 98</td>
<td>S-13D 0.80</td>
<td>N-25-12 1.00</td>
<td>NSFB</td>
<td>4.0-7.0 (incr. 0.5)</td>
<td>S* 4.2 wt%, σ* ~ 9.5 cc/cc</td>
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Table A.16: Experiments PB 99 through PB 108.

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<th>Brine</th>
<th>Range (wt%)</th>
<th>Result</th>
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<td>PB 99</td>
<td>S-13D 0.45</td>
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<td>NSFB 4.0-7.0 (incr. 0.5)</td>
<td>S* below 4.0 wt%</td>
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<td>S-13C 0.25</td>
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<td></td>
<td>S-2 0.25</td>
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<tr>
<td>PB 100</td>
<td>S-13D 0.45</td>
<td>IBA 0.50</td>
<td>NSFB 4.0-8.5 (incr. 0.5)</td>
<td>S* about 7.0 wt%, σ* = 9.2 cc/cc at room temp.</td>
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<tr>
<td></td>
<td>S-2 0.40</td>
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<td>C-9 0.15</td>
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<td>AS 100A</td>
<td>S-13D 0.45</td>
<td>IBA 0.50</td>
<td>NSFB 4.0-7.0 (incr. 0.5)</td>
<td>Cloudy/Phase separation at 5.5%. Clear at 5%</td>
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<td>PB 101</td>
<td>S-13C 0.45</td>
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<td>NSFB 4.0-7.0 (incr. 0.5)</td>
<td>S* About 8.8 wt%, σ* = 9.5</td>
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<td>S-13D 0.60</td>
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<td>NSFB 4.0-8.0 (incr. 0.5)</td>
<td>S* About 3.75 wt%, σ* = 9.0. (S* = 4.5 wt% at room temp)</td>
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<td>N-25-12 0.50</td>
<td>NSFB 4.0-7.0 (incr. 0.5)</td>
<td>All Type I microemulsion. S* above range of test (7% or higher). Some type III at 7 wt%. (same at room temp.)</td>
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<td>NSFB 4.0-7.0 (incr. 0.5)</td>
<td>S* above 7 wt%. Some type III at 7 wt%. (All type I at room temperature)</td>
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<td>PB 108</td>
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<td>NSFB 4.0-7.5 (incr. 0.5)</td>
<td>All type I microemulsions. (same at room temperature)</td>
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Table A.17: Experiments PB 109C through AS 116.

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<th>Range (wt%)</th>
<th>Result</th>
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<td>(wt%)</td>
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<td>NSFB</td>
<td>4.0-7.5</td>
<td>S*= 4.85 wt%, σ*= 9 cc/cc. (S*= 6.2 wt%, σ*= 9.5 cc/cc at room temp.)</td>
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<td>PB 110</td>
<td>S-13D</td>
<td>IBA</td>
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<td>4.0-7.5</td>
<td>S*= 7.4 wt%, σ*=7.5 cc/cc. (All type I at room temperature)</td>
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<td>Aqueous stability to 4.5%. Phase separation at 5% and higher</td>
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<td>AS 111</td>
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<td>SSFB</td>
<td>4.0-7</td>
<td>Maybe a tiny bit of precipitation in all. Not much though. Not noticeable unless vile is swirled. Same at room temp.</td>
</tr>
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<td>AS 112</td>
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<td>SSFB</td>
<td>4.0-7</td>
<td>Maybe a tiny bit of precipitation in all. Not much though. Not noticeable unless vile is swirled. Same at room temp.</td>
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<td>AS 113</td>
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<td>4.0-7</td>
<td>Phase separation at 4.0%. Looks different at 4% (blob) vs. at 7.0% (blob of tiny beads)</td>
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<td>AS 114</td>
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<td>4.0-7</td>
<td>Phase separation at 4.0%. Looks different at 4% (blob) vs. at 7.0% (blob of tiny beads)</td>
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<td>4.0-7.5</td>
<td>S* =~ 7.5% (or greater). σ* about 8.5. (Same at room temp.)</td>
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<td>AS 115A</td>
<td>S-13C</td>
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<td>SSFB</td>
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<td>All cloudy (4%). (Same at room temperature)</td>
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<td>Methanol</td>
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<td>Cloudy at 5.0 wt%. (Cloudy at 6.5 wt% at room temperature)</td>
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Table A.18: Experiments AS 117 through PB 124.

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<th>Range (wt%)</th>
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<td>AS 117</td>
<td>S-13D</td>
<td>Glycerol</td>
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<td>4.0-7.0</td>
<td>Phase separation at 4.5 wt%. (Phase separation at 5.5 wt% at room temperature)</td>
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<td>AS 118</td>
<td>S-13D</td>
<td>1-Butanol</td>
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<td>4.0-7.0</td>
<td>Phase Separation at 4.5 wt% (phase separation at room temp at 6.0 wt%)</td>
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<td>AS 119</td>
<td>S-13D</td>
<td>Amyl Alc.</td>
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<td>4.0-7.0</td>
<td>ABORTED, Amyl alcohol was insoluble in water even at 1 wt% concentration</td>
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<td>AS 120</td>
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<td>SBA</td>
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<td>4.0-6.5</td>
<td>Phase separation at 4.5 wt% (phase separation at 5.5 wt% at room temperature)</td>
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<td>AS 121</td>
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<td>4.0-7.0</td>
<td>Aqueous stability to 6.5%. Phase separation at 7% and higher. Some precip at 6.5 wt%. (All clear at room temp.)</td>
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<td>AS 122</td>
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<td>4.0-6.5</td>
<td>Aqueous stability below 5% (same at room temp.)</td>
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<td>PB 122A</td>
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<td>TGBE</td>
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<td>4.0-6.5</td>
<td>Type 1 microemulsion. No optimum salinity observed in range. (Same at room temp.)</td>
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<td>F3330S</td>
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<td>0.10</td>
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<td>4.0-7.0</td>
<td>Type 1 microemulsion. No optimum salinity observed in range. (Same at room temp.)</td>
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Table A.19: Experiments AS 124A through AS 131.

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<th>Range (wt%)</th>
<th>Result</th>
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<td>Name</td>
<td>Name</td>
<td>wt%</td>
<td>wt%</td>
<td></td>
</tr>
<tr>
<td>AS 124A</td>
<td>S-13D</td>
<td>TGBE</td>
<td>0.60</td>
<td>0.50</td>
<td>Phase separation at 5.0 wt% (All clear at room temp)</td>
</tr>
<tr>
<td></td>
<td>S-2</td>
<td>F3330S</td>
<td>0.30</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C-9</td>
<td></td>
<td>0.20</td>
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<tr>
<td>AS 125</td>
<td>S-13D</td>
<td>DGBE</td>
<td>0.30</td>
<td>0.50</td>
<td>Phase separation at 5.0 wt% (phase separation at 6.0 wt% at room temperature)</td>
</tr>
<tr>
<td></td>
<td>S-2</td>
<td>F3330S</td>
<td>0.15</td>
<td>0.10</td>
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<td>C-9</td>
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<td>0.10</td>
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<tr>
<td>AS 126</td>
<td>S-13D</td>
<td>TGBE</td>
<td>0.60</td>
<td>0.25</td>
<td>Phase separation at 5.0 wt% (All clear at room temperature)</td>
</tr>
<tr>
<td></td>
<td>S-2</td>
<td>F3330S</td>
<td>0.30</td>
<td>0.10</td>
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<tr>
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<td>C-9</td>
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<td>0.20</td>
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</tr>
<tr>
<td>PB 126A</td>
<td>S-13D</td>
<td>TGBE</td>
<td>0.60</td>
<td>0.25</td>
<td>No S* within range (close to 8%?). (All type I at room temperature)</td>
</tr>
<tr>
<td></td>
<td>S-2</td>
<td>F3330S</td>
<td>0.30</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C-9</td>
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<td>0.20</td>
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<tr>
<td>AS 127</td>
<td>S-13D</td>
<td>TGBE</td>
<td>0.60</td>
<td>0.25</td>
<td>All precipitate. 4% precipitation. (All phase separate at room temperature)</td>
</tr>
<tr>
<td></td>
<td>S-2</td>
<td>F3330S</td>
<td>0.30</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>AS 128</td>
<td>S-13D</td>
<td>TGBE</td>
<td>0.60</td>
<td>0.5</td>
<td>All phase separate (aqueous stability below 4.5%). (All phase separate at room temperature)</td>
</tr>
<tr>
<td></td>
<td>S-2</td>
<td>F3330S</td>
<td>0.30</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>AS 129</td>
<td>S-13D</td>
<td>TGBE</td>
<td>0.60</td>
<td>0.5</td>
<td>Aqueous stability below 4.5% (phase separation at 5.5 wt% at room temperature)</td>
</tr>
<tr>
<td></td>
<td>S-2</td>
<td>F3330S</td>
<td>0.15</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
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<td>C-9</td>
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<td>0.15</td>
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<tr>
<td>AS 130</td>
<td>S-13D</td>
<td>TGBE</td>
<td>0.30</td>
<td>0.25</td>
<td>Aqueous stability below 5.5%. (All clear at room temperature)</td>
</tr>
<tr>
<td></td>
<td>S-2</td>
<td>F3330S</td>
<td>0.15</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C-9</td>
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<td></td>
</tr>
<tr>
<td>AS 131</td>
<td>S-13D</td>
<td>TGBE</td>
<td>0.40</td>
<td>0.25</td>
<td>Aqueous stability below 4.5%. (Phase separation at 5.0 wt% at room temperature)</td>
</tr>
<tr>
<td></td>
<td>S-2</td>
<td>F3330S</td>
<td>0.15</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
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<td>C-9</td>
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Table A.20: Experiments AS 132 through AS 141.

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<tr>
<th>Exp. No.</th>
<th>Surfactant</th>
<th>Co-Solvent, Alkali, Polymer</th>
<th>Brine</th>
<th>Range (wt%)</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>AS 132</td>
<td>S-13D 0.30</td>
<td>TGBE 0.375</td>
<td>SSFB</td>
<td>4.5-6.5 (incr. 0.5)</td>
<td>Aqueous stability below 5.0%. (All clear at room temperature)</td>
</tr>
<tr>
<td></td>
<td>S-2 0.15</td>
<td>F3330S 0.10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C-9 0.10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AS 133</td>
<td>S-13D 0.30</td>
<td>TGBE 0.25</td>
<td>SSFB</td>
<td>5.0-6.5 (incr. 0.5)</td>
<td>Aqueous stability below 5%. (All clear at room temperature)</td>
</tr>
<tr>
<td></td>
<td>S-2 0.15</td>
<td>F3330S 0.10</td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>C-9 0.125</td>
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<td></td>
</tr>
<tr>
<td>AS 134</td>
<td>S-13D 0.30</td>
<td>TGBE 0.25</td>
<td>SSFB</td>
<td>5.0-6.5 (incr. 0.5)</td>
<td>All phase separate (aqueous stability below 5%). (All clear at room temperature)</td>
</tr>
<tr>
<td></td>
<td>S-2 0.15</td>
<td>F3330S 0.10</td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>C-9 0.10</td>
<td></td>
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<tr>
<td>AS 135</td>
<td>S-13D 0.30</td>
<td>Ethanol 0.50</td>
<td>SSFB</td>
<td>5.0-6.5 (incr. 0.5)</td>
<td>Aqueous stability below 5.0% (below range of test). (Cloudy at 6.0 wt% at room temperature)</td>
</tr>
<tr>
<td></td>
<td>S-2 0.15</td>
<td>F3330S 0.10</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>C-9 0.10</td>
<td></td>
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</tr>
<tr>
<td>AS 136</td>
<td>S-13D 0.30</td>
<td>TGBE 0.375</td>
<td>SSFB</td>
<td>5.0-6.5 (incr. 0.5)</td>
<td>Aqueous stability below 6.0%. (All clear at room temperature)</td>
</tr>
<tr>
<td></td>
<td>S-2 0.15</td>
<td>F3330S 0.10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>C-9 0.125</td>
<td></td>
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</tr>
<tr>
<td>AS 137</td>
<td>S-13D 0.35</td>
<td>TGBE 0.375</td>
<td>SSFB</td>
<td>5.0-6.5 (incr. 0.5)</td>
<td>Phase separation at 5.0 wt% (Phase separation at 6.5 wt% at room temp)</td>
</tr>
<tr>
<td></td>
<td>S-2 0.15</td>
<td>F3330S 0.10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C-9 0.125</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AS 139</td>
<td>TDA-45PO-30EO 0.50</td>
<td>SBA 1.00</td>
<td>SSFB</td>
<td>4.5-7.0 (incr. 0.5)</td>
<td>Phase Separation at 4.5 wt% (all phase separate at room temperature)</td>
</tr>
<tr>
<td></td>
<td>Sulfate  C15-17 ABS 0.50</td>
<td>F3330S 0.10</td>
<td></td>
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</tr>
<tr>
<td>AS 140</td>
<td>S-13D 0.30</td>
<td>TGBE 0.375</td>
<td>SSFB</td>
<td>4.5-6.5 (incr. 0.5)</td>
<td>Phase Separation at 4.5 wt% (all phase separate at room temperature)</td>
</tr>
<tr>
<td></td>
<td>S-3B 0.15</td>
<td>F3330S 0.10</td>
<td></td>
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<tr>
<td></td>
<td>C-9 0.125</td>
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</tr>
<tr>
<td>AS 141</td>
<td>TDA-45PO-30EO 0.50</td>
<td>SBA 1.00</td>
<td>SSFB</td>
<td>4.5-7.0 (incr. 0.5)</td>
<td>Phase Separation below 4.5 wt% (all cloudy at room temperature)</td>
</tr>
<tr>
<td></td>
<td>Sulfate  T-Soft 0.50</td>
<td>F3330S 0.10</td>
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Table A.21: Experiments AS 142 through AS 148.

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<th>Co-Solvent, Alkali, Polymer</th>
<th>Brine</th>
<th>Range (wt%)</th>
<th>Result</th>
</tr>
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<td></td>
<td>Name</td>
<td>wt%</td>
<td>Name</td>
<td>wt%</td>
<td></td>
</tr>
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<td>SSFB</td>
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<tr>
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<td>F3330S</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C-9</td>
<td>0.125</td>
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<td>S-13D</td>
<td>0.30</td>
<td>TGBE</td>
<td>0.50</td>
<td>SSFB</td>
</tr>
<tr>
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<td>S-3B</td>
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<td>F3330S</td>
<td>0.10</td>
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<tr>
<td></td>
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<td>AS 144</td>
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<td>0.30</td>
<td>F3330S</td>
<td>0.10</td>
<td>SSFB</td>
</tr>
<tr>
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<td>S-2</td>
<td>0.15</td>
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<td>AS 145</td>
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<td>SSFB</td>
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<td>S-13C</td>
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<td>AS 145A</td>
<td>S-13D</td>
<td>0.40</td>
<td>SBA</td>
<td>0.50</td>
<td>FB #2+</td>
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<tr>
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<td>S-13C</td>
<td>0.25</td>
<td></td>
<td></td>
<td>SSFB</td>
</tr>
<tr>
<td></td>
<td>C-9</td>
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<tr>
<td>PB 145B</td>
<td>S-13D</td>
<td>0.40</td>
<td>SBA</td>
<td>0.50</td>
<td>FB #2+</td>
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<tr>
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<td>S-13C</td>
<td>0.25</td>
<td></td>
<td></td>
<td>SSFB</td>
</tr>
<tr>
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<td>C-9</td>
<td>0.30</td>
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<td>AS 146</td>
<td>S-13D</td>
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<td>SBA</td>
<td>0.50</td>
<td>SSFB</td>
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<td>C-9</td>
<td>0.30</td>
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<tr>
<td>AS 147</td>
<td>TDA-45PO-60EO Sulfate</td>
<td>0.50</td>
<td>SBA</td>
<td>1.00</td>
<td>SSFB</td>
</tr>
<tr>
<td></td>
<td>T-Soft</td>
<td>0.50</td>
<td>F3330S</td>
<td>0.10</td>
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</tr>
<tr>
<td>AS 148</td>
<td>TDA-45PO-60EO Carboxylate</td>
<td>0.40</td>
<td>SBA</td>
<td>1.00</td>
<td>SSFB</td>
</tr>
<tr>
<td></td>
<td>T-Soft</td>
<td>0.50</td>
<td>F3330S</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>Exp. No.</td>
<td>Surfactant</td>
<td>Co-Solvent, Alkali, Polymer</td>
<td>Brine</td>
<td>Range (wt%)</td>
<td>Result</td>
</tr>
<tr>
<td>---------</td>
<td>------------</td>
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<tr>
<td>AS 149</td>
<td>S-13C</td>
<td>SBA</td>
<td>SSFB</td>
<td>4.5-6.0 (incr. 0.5)</td>
<td>Phase Separation at 4.5 wt% (phase separation at 5.5 wt% at room temperature)</td>
</tr>
<tr>
<td></td>
<td>0.40</td>
<td>0.50</td>
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<tr>
<td></td>
<td>S-13D</td>
<td>F3330S</td>
<td>SSFB</td>
<td>4.0-6.0 (incr. 0.5)</td>
<td>Phase Separation at 5.0 wt% (Hazy at 6.5 wt% at room temperature)</td>
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<td>0.20</td>
<td>0.10</td>
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<td></td>
<td>S-13C</td>
<td>SBA</td>
<td>SSFB</td>
<td>4.0-7.0 (incr. 0.5)</td>
<td>S*= 6.90 wt% TDS, σ*=7.8 cc/cc. (All type I at room temp.)</td>
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<tr>
<td></td>
<td>0.25</td>
<td>0.10</td>
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<td>C-9</td>
<td>N-25-12</td>
<td>SSFB</td>
<td>4.0-6.0 (incr. 0.5)</td>
<td>All clear (6 wt%) (All stable at room temp 6.0 wt%)</td>
</tr>
<tr>
<td></td>
<td>0.325</td>
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</tbody>
</table>

**Table A.22: Experiments AS 149 through AS 157.**

AS 151  | TDA-45PO-60EO Sulfate | SBA | SSFB  | 4.0-6.0 (incr. 0.5) | All clear (6 wt%) (All stable at room temp 6.0 wt%) |
|         | C-9         | 0.50 | 1.00 | | |
|         | 0.50       | F3330S | 0.10 | | |

AS 152  | TDA-45PO-60EO Carboxylate | SBA | SSFB  | 4.0-6.0 (incr. 0.5) | All clear (6 wt%) (All stable at room temp 6.0 wt%) |
|         | C-9         | 0.50 | 1.00 | | |
|         | 0.50       | F3330S | 0.10 | | |

AS 153  | TDA-45PO-60EO Sulfate | SBA | SSFB  | 4.0-6.5 (incr. 0.5) | All clear (6.5 wt%) (All clear at room temp) |
|         | C-9         | 0.50 | 1.00 | | |
|         | 0.25       | F3330S | 0.10 | | |

AS 154  | TDA-45PO-60EO Carboxylate | SBA | SSFB  | 4.0-6.5 (incr. 0.5) | All clear (6.5 wt%) (All clear at room temp) |
|         | C-9         | 0.50 | 1.00 | | |
|         | 0.25       | F3330S | 0.10 | | |

AS 155  | S-13D      | SBA | SSFB  | 4.0-6.5 (incr. 0.5) | Phase separation at 5.0 wt% (Phase separation at 6.5 wt% at room temp) |
|         | 0.40       | 0.50 |       | | |
|         | S-13C      | F3330S | SSFB  | 4.0-6.5 (incr. 0.5) | Phase Separation at 4.0 wt%. Hazy at 6.0 wt% at room temperature |
|         | 0.25       | 0.10 | | | |
|         | C-9        | 0.325 | | | |

AS 156  | S-13D      | SBA | SSFB  | 4.0-6.0 (incr. 0.5) | Phase Separation at 4.5 wt% (all clear at room temp 6.0 wt%) |
|         | 0.40       | 0.50 | | | |
|         | S-13C      | F3330S | SSFB  | 4.0-6.0 (incr. 0.5) | Phase Separation at 4.5 wt% (all clear at room temp 6.0 wt%) |
|         | 0.25       | 0.10 | | | |
|         | C-9        | 0.325 | | | |

AS 157  | S-13D      | SBA | SSFB  | 4.0-6.0 (incr. 0.5) | Phase Separation at 4.5 wt% (all clear at room temp 6.0 wt%) |
|         | 0.43       | 0.50 | | | |
|         | S-13C      | F3330S | SSFB  | 4.0-6.0 (incr. 0.5) | Phase Separation at 4.5 wt% (all clear at room temp 6.0 wt%) |
|         | 0.25       | 0.10 | | | |
|         | C-9        | 0.325 | | | |
Table A.23: Experiments AS 158 through AS 163.

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Surfactant</th>
<th>Co-Solvent, Alkali, Polymer</th>
<th>Brine</th>
<th>Range (wt%)</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>AS 158</td>
<td>TDA-45PO-60EO Sulfate</td>
<td>0.50 F3330S 0.10 SSFB</td>
<td></td>
<td>4.0-6.0 (incr. 0.5)</td>
<td>All clear (6.5 wt%). (Same at room temperature)</td>
</tr>
<tr>
<td>AS 158B</td>
<td>TDA-45PO-60EO Sulfate</td>
<td>0.50 F3330S 0.10 SSFB</td>
<td></td>
<td>8.0-14.0 (incr. 2.0)</td>
<td>All clear (14.0 wt%). (Same at room temperature)</td>
</tr>
<tr>
<td>AS 159</td>
<td>TDA-45PO-60EO Carboxylate</td>
<td>0.50 F3330S 0.10 SSFB</td>
<td></td>
<td>4.0-6.0 (incr. 0.5)</td>
<td>All clear (6.5 wt%). (Same at room temperature)</td>
</tr>
<tr>
<td>AS 159B</td>
<td>TDA-45PO-60EO Carboxylate</td>
<td>0.50 F3330S 0.10 SSFB</td>
<td></td>
<td>8.0-14.0 (incr. 2.0)</td>
<td>All clear (14.0 wt%). (Same at room temperature)</td>
</tr>
<tr>
<td>AS 160</td>
<td>TDA-45PO-30EO Sulfate</td>
<td>0.50 F3330S 0.10 SSFB</td>
<td></td>
<td>4.0-6.5 (incr. 0.5)</td>
<td>Slightly hazy below 6.0 wt%. (Same room temperature)</td>
</tr>
<tr>
<td>AS 160B</td>
<td>TDA-45PO-30EO Sulfate</td>
<td>0.50 F3330S 0.10 SSFB</td>
<td></td>
<td>8.0-14.0 (incr. 2.0)</td>
<td>All clear (14.0 wt%). (Same at room temperature)</td>
</tr>
<tr>
<td>AS 161</td>
<td>S-13D 0.40 SBA 0.25 SSFB</td>
<td>F3330S 0.10</td>
<td></td>
<td>5.0-6.0 (incr. 0.25)</td>
<td>Phase Separation at 5.5 wt%. (All clear at room temperature)</td>
</tr>
<tr>
<td></td>
<td>S-13C 0.25</td>
<td>F3330S 0.10</td>
<td></td>
<td>4.75-6.25 (incr. 0.25)</td>
<td>S* above 6.25 wt%. Mostly type I microemulsions. (Same at room temperature)</td>
</tr>
<tr>
<td></td>
<td>C-9 0.325</td>
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<tr>
<td>PB 161A</td>
<td>S-13D 0.40 SBA 0.25 SSFB</td>
<td>F3330S 0.10</td>
<td></td>
<td>5.0-6.0 (incr. 0.25)</td>
<td>Phase separation at 5.75 wt%. (All clear at room temperature)</td>
</tr>
<tr>
<td></td>
<td>S-13C 0.25</td>
<td>F3330S 0.10</td>
<td></td>
<td>4.75-6.25 (incr. 0.25)</td>
<td>S* above 6.25 wt%. All type I microemulsions. (Same at room temperature)</td>
</tr>
<tr>
<td></td>
<td>C-9 0.325</td>
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<td></td>
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<tr>
<td>AS 162</td>
<td>S-13D 0.40 SBA 0.25 SSFB</td>
<td>F3330S 0.10</td>
<td></td>
<td>5.0-6.0 (incr. 0.25)</td>
<td>Phase separation at 5.75 wt%. (All clear at room temperature)</td>
</tr>
<tr>
<td></td>
<td>S-13C 0.225</td>
<td>F3330S 0.10</td>
<td></td>
<td>4.75-6.25 (incr. 0.25)</td>
<td>S* above 6.25 wt%. All type I microemulsions. (Same at room temperature)</td>
</tr>
<tr>
<td></td>
<td>C-9 0.325</td>
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<tr>
<td>PB 162A</td>
<td>S-13D 0.40 SBA 0.25 SSFB</td>
<td>F3330S 0.10</td>
<td></td>
<td>4.0-14.0 (incr. 2.0)</td>
<td>Phase separation at or below 4 wt% (all precipitate at room temperature)</td>
</tr>
<tr>
<td></td>
<td>S-13C 0.225</td>
<td>F3330S 0.10</td>
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<tr>
<td></td>
<td>C-9 0.325</td>
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<tr>
<td>AS 163</td>
<td>TDA-45PO-10EO Sulfate</td>
<td>0.50 F3330S 0.10 SSFB</td>
<td></td>
<td>4.0-14.0 (incr. 2.0)</td>
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Table A.24: Experiments AS 164 through AS 169.

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<th>Exp. No.</th>
<th>Surfactant</th>
<th>Co-Solvent, Alkali, Polymer</th>
<th>Brine</th>
<th>Range (wt%)</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>AS 164</td>
<td>TDA-45PO-20EO Sulfate</td>
<td>0.50 F3330S 0.10</td>
<td>SSFB</td>
<td>4.0-14.0 (incr. 2.0)</td>
<td>Clear to ~10 wt%, cloudy after (cloudy at room temperature at ~12%)</td>
</tr>
<tr>
<td>PB 164A</td>
<td>TDA-45PO-20EO Sulfate</td>
<td>0.50 - -</td>
<td>SSFB</td>
<td>4.0-16.0 (incr. 2.0)</td>
<td>S* below 4.0 wt%. All type II microemulsions. (Same at room temperature)</td>
</tr>
<tr>
<td>AS 165</td>
<td>S-13D</td>
<td>0.40 SBA 0.25</td>
<td>SSFB</td>
<td>4.0-6.5 (incr. 0.5)</td>
<td>Phase separation at 5.5 wt% (all stable at room temp 6.5 wt%)</td>
</tr>
<tr>
<td></td>
<td>S-13B</td>
<td>0.25 F3330S 0.10</td>
<td>SSFB</td>
<td>4.0-6.5 (incr. 0.5)</td>
<td>S* above 6.5 wt%. All type I microemulsions. (Same at room temperature)</td>
</tr>
<tr>
<td></td>
<td>C-9</td>
<td>0.325</td>
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<tr>
<td>PB 165A</td>
<td>S-13D</td>
<td>0.40 SBA 0.25</td>
<td>SSFB</td>
<td>4.0-6.5 (incr. 0.5)</td>
<td>S* above 6.5 wt%. All type I microemulsions. (Same at room temperature)</td>
</tr>
<tr>
<td></td>
<td>S-13B</td>
<td>0.25 F3330S 0.10</td>
<td>SSFB</td>
<td>4.0-6.5 (incr. 0.5)</td>
<td>Phase separation at 5.5 wt% (Phase separation at 6.5 wt% at room temp)</td>
</tr>
<tr>
<td></td>
<td>C-9</td>
<td>0.325</td>
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<tr>
<td>AS 166</td>
<td>S-13D</td>
<td>0.40 SBA 0.25</td>
<td>SSFB</td>
<td>4.0-6.5 (incr. 0.5)</td>
<td>S* above 6.5 wt%. All type I microemulsions. (Same at room temperature)</td>
</tr>
<tr>
<td></td>
<td>S-8B</td>
<td>0.25 F3330S 0.10</td>
<td>SSFB</td>
<td>4.0-6.5 (incr. 0.5)</td>
<td>Phase separation at 5.0 wt% (Phase separation at 6.5 wt% at room temp)</td>
</tr>
<tr>
<td></td>
<td>C-9</td>
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<tr>
<td>PB 166A</td>
<td>S-13D</td>
<td>0.40 SBA 0.25</td>
<td>SSFB</td>
<td>4.0-6.5 (incr. 0.5)</td>
<td>S* above 6.5 wt%. All type I microemulsions. (Same at room temperature)</td>
</tr>
<tr>
<td></td>
<td>S-8B</td>
<td>0.25 F3330S 0.10</td>
<td>SSFB</td>
<td>4.0-6.5 (incr. 0.5)</td>
<td>Phase separation at 5.0 wt% (Phase separation at 6.5 wt% at room temp)</td>
</tr>
<tr>
<td></td>
<td>C-9</td>
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<tr>
<td>AS 167</td>
<td>S-13D</td>
<td>0.40 SBA 0.25</td>
<td>SSFB</td>
<td>4.0-6.5 (incr. 0.5)</td>
<td>S* above 6.5 wt%. All type I microemulsions. (Same at room temperature)</td>
</tr>
<tr>
<td></td>
<td>S-8C</td>
<td>0.25 F3330S 0.10</td>
<td>SSFB</td>
<td>4.0-6.5 (incr. 0.5)</td>
<td>Phase separation at 5.0 wt% (Phase separation at 6.5 wt% at room temp)</td>
</tr>
<tr>
<td></td>
<td>C-9</td>
<td>0.325</td>
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<tr>
<td>PB 167A</td>
<td>S-13D</td>
<td>0.40 SBA 0.25</td>
<td>SSFB</td>
<td>4.0-6.5 (incr. 0.5)</td>
<td>S* above 6.5 wt%. All type I microemulsions. (Same at room temperature)</td>
</tr>
<tr>
<td></td>
<td>S-8C</td>
<td>0.25 F3330S 0.10</td>
<td>SSFB</td>
<td>4.0-6.5 (incr. 0.5)</td>
<td>Phase separation at 5.0 wt% (All clear at room temp)</td>
</tr>
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<td>C-9</td>
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</tr>
<tr>
<td>AS 169</td>
<td>S-13D</td>
<td>0.40 SBA 0.25</td>
<td>SSFB</td>
<td>4.0-6.5 (incr. 0.5)</td>
<td>Phase separation at 5.0 wt% (All clear at room temp)</td>
</tr>
<tr>
<td></td>
<td>S-3B</td>
<td>0.15 F3330S 0.10</td>
<td>SSFB</td>
<td>4.0-6.5 (incr. 0.5)</td>
<td>Phase separation at 5.0 wt% (All clear at room temp)</td>
</tr>
<tr>
<td></td>
<td>C-9</td>
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Table A.25: Experiments PB 169A through PB 177A.

<table>
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<th>Exp. No.</th>
<th>Surfactant</th>
<th>Co-Solvent, Alkali, Polymer</th>
<th>Brine</th>
<th>Range (wt%)</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>PB 169A</td>
<td>S-13D 0.40</td>
<td></td>
<td>SBA 0.25</td>
<td>SSFB 4.0-6.5 (incr. 0.5)</td>
<td>S* above 6.5 wt%. All type I microemulsions. (Same at room temperature)</td>
</tr>
<tr>
<td></td>
<td>S-3B 0.15</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C-9 0.325</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AS 170</td>
<td>S-9A 0.50</td>
<td>F3330S 0.10</td>
<td>SSFB</td>
<td>2.0-8.0 (incr. 1.0)</td>
<td>Phase separation below 2.0 wt% (all phase separate). (Same at room temperature)</td>
</tr>
<tr>
<td>AS 171</td>
<td>S-9B 0.50</td>
<td>F3330S 0.10</td>
<td>SSFB</td>
<td>2.0-8.0 (incr. 1.0)</td>
<td>Phase separation below 2.0 wt% (all phase separate). (Same at room temperature)</td>
</tr>
<tr>
<td>AS 172</td>
<td>S-9C 0.50</td>
<td>F3330S 0.10</td>
<td>SSFB</td>
<td>2.0-8.0 (incr. 1.0)</td>
<td>Phase separation below 2.0 wt% (all phase separate). (Same at room temperature)</td>
</tr>
<tr>
<td>AS 173</td>
<td>S-10B 0.50</td>
<td>F3330S 0.10</td>
<td>SSFB</td>
<td>2.0-8.0 (incr. 1.0)</td>
<td>Phase separation below 2.0 wt% (all phase separate). (Same at room temperature)</td>
</tr>
<tr>
<td>AS 174</td>
<td>S-14 0.50</td>
<td>F3330S 0.10</td>
<td>SSFB</td>
<td>2.0-8.0 (incr. 1.0)</td>
<td>All clear (8.0 wt%) (all clear at room temp.)</td>
</tr>
<tr>
<td>AS 175</td>
<td>S-13D 0.40</td>
<td></td>
<td>SBA 0.25</td>
<td>SSFB 4.0-6.0 (incr. 0.5)</td>
<td>Phase separation below 4.0 wt%. (Same at room temperature)</td>
</tr>
<tr>
<td></td>
<td>S-3B 0.25</td>
<td></td>
<td>F3330S 0.10</td>
<td></td>
<td></td>
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<td>C-9 0.325</td>
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<tr>
<td>AS 176</td>
<td>S-13D 0.40</td>
<td></td>
<td>SBA 0.25</td>
<td>SSFB 4.0-6.0 (incr. 0.5)</td>
<td>Phase Separation at 5.5 wt% (all clear at room temperature)</td>
</tr>
<tr>
<td></td>
<td>S-9A 0.25</td>
<td></td>
<td>F3330S 0.10</td>
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<tr>
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<td>C-9 0.325</td>
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<tr>
<td>PB 176A</td>
<td>S-13D 0.40</td>
<td></td>
<td>SBA 0.25</td>
<td>SSFB 4.0-6.5 (incr. 0.5)</td>
<td>No S* within range (all type I microemulsion). (Same at room temperature)</td>
</tr>
<tr>
<td></td>
<td>S-9A 0.25</td>
<td></td>
<td></td>
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<tr>
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<td>C-9 0.325</td>
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</tr>
<tr>
<td>AS 177</td>
<td>S-13D 0.40</td>
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<td>SBA 0.25</td>
<td>SSFB 4.0-6.0 (incr. 0.5)</td>
<td>Phase separation at 5.0 wt%. (Hazy at 6.0 wt% at room temp.)</td>
</tr>
<tr>
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<td>S-9B 0.25</td>
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<td>F3330S 0.10</td>
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<tr>
<td>PB 177A</td>
<td>S-13D 0.40</td>
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<td>SBA 0.25</td>
<td>SSFB 4.0-6.5 (incr. 0.5)</td>
<td>No S* within range (all type I microemulsion)</td>
</tr>
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<td>S-9B 0.25</td>
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<td>C-9 0.325</td>
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<tr>
<td>Exp. No.</td>
<td>Surfactant</td>
<td>Co-Solvent, Alkali, Polymer</td>
<td>Brine</td>
<td>Range (wt%)</td>
<td>Result</td>
</tr>
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<td>AS 178</td>
<td>S-13D</td>
<td>SBA</td>
<td>SSFB</td>
<td>4.0-6.0</td>
<td>Phase separation at or below 4.0 wt%. (Hazy at 5.5 wt% at room temperature)</td>
</tr>
<tr>
<td></td>
<td>S-9C</td>
<td>F3330S</td>
<td></td>
<td>(incr. 0.5)</td>
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<td>C-9</td>
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<td>PB 178A</td>
<td>S-13D</td>
<td>SBA</td>
<td>SSFB</td>
<td>4.0-6.5</td>
<td>No S* within range (all type I microemulsion). (Same at room temperature)</td>
</tr>
<tr>
<td></td>
<td>S-9C</td>
<td>F3330S</td>
<td></td>
<td>(incr. 0.5)</td>
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<tr>
<td>AS 179</td>
<td>S-13D</td>
<td>SBA</td>
<td>SSFB</td>
<td>4.0-6.0</td>
<td>Phase separation at 4.5 wt%. (Hazy at 6.0 wt% at room temperature)</td>
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<td>S-10B</td>
<td>F3330S</td>
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<td>(incr. 0.5)</td>
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<td>PB 179A</td>
<td>S-13D</td>
<td>SBA</td>
<td>SSFB</td>
<td>4.0-6.5</td>
<td>S*= 8.1 wt% TDS, σ*= 8.8 cc/cc. (All type I at room temperature)</td>
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<tr>
<td></td>
<td>S-10B</td>
<td>F3330S</td>
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<td>(incr. 0.5)</td>
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<td>AS 180</td>
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<td>SSFB</td>
<td>4.0-6.0</td>
<td>Phase separation at or below 4.0 wt%. (Same at room temp.)</td>
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<tr>
<td></td>
<td>S-13C</td>
<td>F3330S</td>
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<td>(incr. 0.5)</td>
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<td>AS 181</td>
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<td>SSFB</td>
<td>4.0-6.0</td>
<td>Phase Separation at 6 wt% (all stable at room temp.)</td>
</tr>
<tr>
<td></td>
<td>S-13C</td>
<td>F3330S</td>
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<td>(incr. 0.5)</td>
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<td>PB 181A</td>
<td>S-10B</td>
<td>SBA</td>
<td>SSFB</td>
<td>4.0-7.0</td>
<td>No S* within range (all type I microemulsion). (Same at room temperature)</td>
</tr>
<tr>
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<td>S-13C</td>
<td>F3330S</td>
<td></td>
<td>(incr. 0.5)</td>
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<td>C-9</td>
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<tr>
<td>AS 182</td>
<td>S-9B</td>
<td>SBA</td>
<td>SSFB</td>
<td>4.0-6.0</td>
<td>Phase Separation at 6 wt% (all stable at room temp.)</td>
</tr>
<tr>
<td></td>
<td>S-13C</td>
<td>F3330S</td>
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<td>(incr. 0.5)</td>
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<td>C-9</td>
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<td>PB 182A</td>
<td>S-9B</td>
<td>SBA</td>
<td>SSFB</td>
<td>4.0-7.0</td>
<td>No S* within range (type I microemulsion). (Same at room temperature)</td>
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<tr>
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<td>S-13C</td>
<td>F3330S</td>
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<td>(incr. 0.5)</td>
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Table A.27: Experiments AS183 through AS 187.

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<th>Surfactant wt%</th>
<th>Co-Solvent</th>
<th>Alkali Name</th>
<th>Alkali wt%</th>
<th>Polymer Name</th>
<th>Polymer wt%</th>
<th>Brine</th>
<th>Range (wt%)</th>
<th>Result</th>
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<td>0.25</td>
<td>SSFB</td>
<td>4.0-6.0 (incr. 0.5)</td>
<td>Phase Separation at 6 wt% (all stable at room temp.)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>S-13C</td>
<td>0.25</td>
<td></td>
<td>F3330S</td>
<td>0.10</td>
<td>SSFB</td>
<td>4.0-7.0 (incr. 0.5)</td>
<td>No S* within range (type I microemulsion). (Same at room temperature)</td>
<td></td>
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<tr>
<td></td>
<td>C-9</td>
<td>0.35</td>
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<td></td>
<td>S* above 7.0 wt%. (All type I at room temperature).</td>
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<tr>
<td>PB 183A</td>
<td>S-9C</td>
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<td>SBA</td>
<td>0.25</td>
<td>SSFB</td>
<td>4.0-6.0 (incr. 0.5)</td>
<td>Clear at 6 wt% (all stable at room temp.)</td>
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<td></td>
<td>S-13C</td>
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<td>F3330S</td>
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<td>SSFB</td>
<td>4.0-7.0 (incr. 0.5)</td>
<td>No S* within range (type I microemulsion). (Same at room temperature)</td>
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<td>C-9</td>
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<td>Clear at 6 wt% (all stable at room temp.)</td>
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<td>SSFB</td>
<td>4.0-7.0 (incr. 0.5)</td>
<td>No S* within range (type I microemulsion). (Same at room temperature)</td>
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<td>4.0-6.0 (incr. 0.5)</td>
<td>Clear at 6 wt% (all stable at room temp.)</td>
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<td>SSFB</td>
<td>4.0-7.0 (incr. 0.5)</td>
<td>No S* within range (type I microemulsion). (Same at room temperature)</td>
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<td>C-9</td>
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<td>4.0-6.0 (incr. 0.5)</td>
<td>Clear at 6 wt% (all stable at room temp.)</td>
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<td>TDA-45PO-10EO Sulfate</td>
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<td>F3330S</td>
<td>0.10</td>
<td>SSFB</td>
<td>4.0-7.0 (incr. 0.5)</td>
<td>S* above 7.0 wt%. (All type I at room temperature).</td>
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<td>C-9</td>
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<td>SSFB</td>
<td>4.0-6.0 (incr. 0.5)</td>
<td>Clear at 6 wt% (all stable at room temp.)</td>
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<td>F3330S</td>
<td>0.10</td>
<td>SSFB</td>
<td>4.0-7.0 (incr. 0.5)</td>
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<td>SSFB</td>
<td>4.0-6.0 (incr. 0.5)</td>
<td>Clear at 6 wt% (all stable at room temp.)</td>
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<td>F3330S</td>
<td>0.10</td>
<td>SSFB</td>
<td>4.0-7.0 (incr. 0.5)</td>
<td>No S* within range (all type I microemulsion). (Same at room temperature)</td>
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<tr>
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<td>C-9</td>
<td>0.35</td>
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<td>SSFB</td>
<td>4.0-6.0 (incr. 0.5)</td>
<td>Clear at 6 wt% (all stable at room temp.)</td>
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<td></td>
<td>F3330S</td>
<td>0.10</td>
<td>SSFB</td>
<td>4.0-7.0 (incr. 0.5)</td>
<td>No S* within range (all type I microemulsion). (Same at room temperature)</td>
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<tr>
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<td>C-9</td>
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<td>Clear at 6 wt% (all stable at room temp.)</td>
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<td>SSFB</td>
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<td>No S* within range (all type I microemulsion). (Same at room temperature)</td>
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<tr>
<td></td>
<td>C-9</td>
<td>0.35</td>
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Table A.28: Experiments AS 188 through AS 193.

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<th>Exp. No.</th>
<th>Surfactant</th>
<th>Co-Solvent, Alkali, Polymer</th>
<th>Brine</th>
<th>Range (wt%)</th>
<th>Result</th>
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<tr>
<td>AS 188</td>
<td>S-13D</td>
<td>SBA</td>
<td>SSFB</td>
<td>4.0-6.0 (incr. 0.5)</td>
<td>Clear at 6 wt% (Phase separation at 6 wt% at room temp)</td>
</tr>
<tr>
<td></td>
<td>T-Soft</td>
<td>F3330S</td>
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<tr>
<td></td>
<td>C-9</td>
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<tr>
<td>AS 188</td>
<td>S-13D</td>
<td>SBA</td>
<td>SSFB</td>
<td>4.0-7.0 (incr. 0.5)</td>
<td>No S* within range (type I microemulsion). (Same at room temperature)</td>
</tr>
<tr>
<td></td>
<td>T-Soft</td>
<td>SBA</td>
<td></td>
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<td>C-9</td>
<td>F3330S</td>
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<tr>
<td>AS 189</td>
<td>S-13D</td>
<td>SBA</td>
<td>SSFB</td>
<td>4.0-6.0 (incr. 0.5)</td>
<td>All cloudy 4 wt%. (All cloudy at room temperature)</td>
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<tr>
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<td>C15-17 ABS</td>
<td>F3330S</td>
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<tr>
<td>AS 190</td>
<td>S-13D</td>
<td>SBA</td>
<td>SSFB</td>
<td>4.0-6.0 (incr. 0.5)</td>
<td>Phase Separation at 5.5 wt%. (All clear at room temperature)</td>
</tr>
<tr>
<td></td>
<td>TDA-45PO-10EO Sulfate</td>
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<td>C-9</td>
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<tr>
<td>AS 190</td>
<td>S-13D</td>
<td>SBA</td>
<td>SSFB</td>
<td>4.5-6.5 (incr. 0.5)</td>
<td>S* difficult to determine. All pipettes look like type I. (S*= 6.4 wt%, σ*= 30 cc/cc at room temp)</td>
</tr>
<tr>
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<td>TDA-45PO-10EO Sulfate</td>
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<td></td>
<td>C-9</td>
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<tr>
<td>AS 191</td>
<td>S-13D</td>
<td>SBA</td>
<td>SSFB</td>
<td>4.0-6.0 (incr. 0.5)</td>
<td>All Clear. (Same at room temperature)</td>
</tr>
<tr>
<td></td>
<td>TDA-45PO-20EO Sulfate</td>
<td>F3330S</td>
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<td>AS 191</td>
<td>S-13D</td>
<td>SBA</td>
<td>SSFB</td>
<td>4.4-6.5 (incr. 0.5)</td>
<td>S* 5.5 wt%, low σ*. (All type I at room temperature)</td>
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<td>TDA-45PO-20EO Sulfate</td>
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<td>C-9</td>
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<td>AS 192</td>
<td>S-13D</td>
<td>F3330S</td>
<td>SSFB</td>
<td>4.0-6.0 (incr. 0.5)</td>
<td>Phase Separation at 4.5 wt%. (All clear at room temperature)</td>
</tr>
<tr>
<td></td>
<td>S-13C</td>
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Table A.29: Experiments AS 194 through AS 202.

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<th>Range (wt%)</th>
<th>Result</th>
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<td>Name</td>
<td>wt%</td>
<td>Name</td>
<td>wt%</td>
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<td>TDA-45PO-20EO Sulfate</td>
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<td>F3330S</td>
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<td>SSFB 4.0-6.5 (incr. 0.5)</td>
</tr>
<tr>
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<td>S-2</td>
<td>0.15</td>
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<td>C-9</td>
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<td>F3330S</td>
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<td>SSFB 4.0-6.5 (incr. 0.5)</td>
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<td>F3330S</td>
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<td>SSFB 4.0-6.5 (incr. 0.5)</td>
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<td>TDA-45PO-10EO Sulfate</td>
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<td>F3330S</td>
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<td>SSFB 4.0-6.5 (incr. 0.5)</td>
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<td>F3330S</td>
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<td>SSFB 4.0-6.5 (incr. 0.5)</td>
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<td>AS 199</td>
<td>TDA-45PO-20EO Sulfate</td>
<td>0.40</td>
<td>F3330S</td>
<td>0.10</td>
<td>SSFB 4.5-6.5 (incr. 0.5)</td>
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<tr>
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<td>S-3B</td>
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<td>S-3B</td>
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<td>S-3B</td>
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Table A.30: Experiments AS 203 through AS 210.

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<th>Co-Solvent, Alkali, Polymer</th>
<th>Brine</th>
<th>Range (wt%)</th>
<th>Result</th>
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<td>TDA-45PO-10EO Sulfate 0.40</td>
<td>F3330S 0.10</td>
<td>SSFB</td>
<td>4.5-6.5 (incr. 0.5)</td>
<td>All clear (6.50 wt%). (All clear at room temperature)</td>
</tr>
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<td>S-3B 0.15</td>
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<tr>
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<td>F3330S 0.10</td>
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<td>4.5-6.5 (incr. 0.5)</td>
<td>All clear (6.50 wt%). (All have precipitate at room temp.)</td>
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<td>S-3B 0.25</td>
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<td>F3330S 0.10</td>
<td>SSFB</td>
<td>4.0-6.0 (incr. 0.5)</td>
<td>All clear (6.50 wt%). (All hazy at room temperature)</td>
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<td>C-9 0.15</td>
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<tr>
<td>PB 205A</td>
<td>TDA-45PO-20EO Sulfate 0.40</td>
<td>F3330S 0.10</td>
<td>SSFB</td>
<td>3.0-10.0 (incr. 1.0)</td>
<td>Mostly type II. Some type III at 3 and 4 wt%. S* below 3 wt%. (S*=3.7 wt%, σ*=14.5 cc/cc at room temp.)</td>
</tr>
<tr>
<td></td>
<td>S-3B 0.25</td>
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<td>C-9 0.15</td>
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<tr>
<td>AS 206</td>
<td>TDA-45PO-10EO Sulfate 0.40</td>
<td>F3330S 0.10</td>
<td>SSFB</td>
<td>4.0-6.0 (incr. 0.5)</td>
<td>Phase separation at 4.5 wt% and above. (All hazy/cloudy at room temperature)</td>
</tr>
<tr>
<td></td>
<td>S-3B 0.25</td>
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<td>C-9 0.15</td>
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<tr>
<td>PB 206A</td>
<td>TDA-45PO-10EO Sulfate 0.40</td>
<td>F3330S 0.10</td>
<td>SSFB</td>
<td>4.0-9.0 (incr. 1.0)</td>
<td>All type II. Macroemulsions present. (Mostly type II at room temperature, but some type III at 3 wt%. Low σ)</td>
</tr>
<tr>
<td></td>
<td>S-3B 0.25</td>
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<tr>
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<td>C-9 0.15</td>
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</tr>
<tr>
<td>AS 207</td>
<td>Sodium Acetate 0.10</td>
<td>F3330S 0.10</td>
<td>SSFB</td>
<td>4.0-9.0 (incr. 1.0)</td>
<td>All clear (9.00 wt%). (Same at room temperature)</td>
</tr>
<tr>
<td>AS 208</td>
<td>Sodium Acetate 0.30</td>
<td>F3330S 0.10</td>
<td>SSFB</td>
<td>4.0-9.0 (incr. 1.0)</td>
<td>All clear (9.00 wt%). (Same at room temperature)</td>
</tr>
<tr>
<td>AS 209</td>
<td>Sodium Acetate 0.50</td>
<td>F3330S 0.10</td>
<td>SSFB</td>
<td>4.0-9.0 (incr. 1.0)</td>
<td>All clear (9.00 wt%). (Same at room temperature)</td>
</tr>
<tr>
<td>AS 210</td>
<td>Sodium Acetate 1.00</td>
<td>F3330S 0.10</td>
<td>SSFB</td>
<td>4.0-9.0 (incr. 1.0)</td>
<td>All clear (9.00 wt%). (Same at room temperature)</td>
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### Table A.31: Experiments AS 211 through PB 215B.

<table>
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<th>Exp. No.</th>
<th>Surfactant Name</th>
<th>Surfactant wt%</th>
<th>Co-Solvent, Alkali, Polymer Name</th>
<th>Co-Solvent, Alkali, Polymer wt%</th>
<th>Brine</th>
<th>Range (wt%)</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>AS 211</td>
<td>-</td>
<td>-</td>
<td>Sodium Acetate</td>
<td>0.0 - 7.0 (incr. 1.0)</td>
<td>SSFB</td>
<td>5.5</td>
<td>All clear (7.00 wt%). (Same at room temperature)</td>
</tr>
<tr>
<td>AS 212</td>
<td>-</td>
<td>-</td>
<td>F3330S</td>
<td>0.10</td>
<td>SSFB</td>
<td>5.5</td>
<td>All clear (9.00 wt%). (Same at room temperature)</td>
</tr>
<tr>
<td>AS 213</td>
<td>-</td>
<td>-</td>
<td>Sodium Acetate</td>
<td>0.0 - 7.0 (incr. 1.0)</td>
<td>NaCl</td>
<td>5.5</td>
<td>All clear (5.00 wt%). (Same at room temperature)</td>
</tr>
<tr>
<td>AS 214</td>
<td>TDA-45PO-20EO Sulfate</td>
<td>0.40</td>
<td>-</td>
<td>-</td>
<td>SSFB</td>
<td>4.0-8.0 (incr. 0.5)</td>
<td>All clear (8.0 wt%). (All hazy at room temp.)</td>
</tr>
<tr>
<td>PB 214A</td>
<td>TDA-45PO-20EO Sulfate</td>
<td>0.40</td>
<td>-</td>
<td>-</td>
<td>SSFB</td>
<td>3.0-8.0 (incr. 1.0)</td>
<td>Optimum salinity above 8.0 wt%. Mostly type I behavior. (Same at room temperature).</td>
</tr>
<tr>
<td>AS 215</td>
<td>TDA-45PO-10EO Sulfate</td>
<td>0.40</td>
<td>F3330S</td>
<td>0.10</td>
<td>SSFB</td>
<td>4.0-6.0 (incr. 0.5)</td>
<td>All clear (8.0 wt%). (All hazy at room temperature)</td>
</tr>
<tr>
<td>PB 215A</td>
<td>TDA-45PO-10EO Sulfate</td>
<td>0.40</td>
<td>-</td>
<td>-</td>
<td>SSFB</td>
<td>3.0-8.0 (incr. 1.0)</td>
<td>S*= 5.6 wt%, σ* ~ = 21 cc/cc. Viscous macroemulsion at 8.0 wt%. Strong and broad phase behavior. (S*= 6.8 wt%, σ* ~ = 60 cc/cc at room temp)</td>
</tr>
<tr>
<td>PB 215A'</td>
<td>TDA-45PO-10EO Sulfate</td>
<td>0.40</td>
<td>-</td>
<td>-</td>
<td>SSFB</td>
<td>4.5, 6.5, and 5.0-6.0 (incr. 0.1)</td>
<td>S*= 5.6 wt%, σ* ~ = 32 cc/cc. Viscous macroemulsion at 8.0 wt%. Strong and broad phase behavior. (S*= 6.25 wt%, σ* ~ = 45 cc/cc at room temperature)</td>
</tr>
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<td>PB 215B</td>
<td>TDA-45PO-10EO Sulfate</td>
<td>0.40</td>
<td>SBA</td>
<td>0.50</td>
<td>SSFB</td>
<td>4.0-9.0 (incr. 1.0)</td>
<td>S*= 5.3 wt%, σ* ~ = 20 cc/cc. Viscous macroemulsion at 7.0 wt%. Strong and broad phase behavior. (S*= 6.5 wt%, σ* ~ = 62 cc/cc at room temperature)</td>
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Table A.32: Experiments PB 215C through PB 217A.

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<th>Exp. No.</th>
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<th>Brine</th>
<th>Range (wt%)</th>
<th>Result</th>
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<td>S-3B</td>
<td>0.25</td>
<td>SBA 0.50</td>
<td>FB #1</td>
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<td>C-9</td>
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<td>PB 215D</td>
<td>TDA-45PO-10EO Sulfate</td>
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<td></td>
<td>S-3B</td>
<td>0.25</td>
<td>SBA 0.50</td>
<td>FB #1</td>
</tr>
<tr>
<td></td>
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<td>PB 215E</td>
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<td></td>
<td>S-3B</td>
<td>0.25</td>
<td>SBA 0.50</td>
<td>FB #2</td>
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<td>PB 215F</td>
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<td>S-3B</td>
<td>0.25</td>
<td>SBA 0.50</td>
<td>FB #2</td>
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<td>PB 215G</td>
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<td>SBA 0.50</td>
<td>NaCl</td>
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<td>AS 216</td>
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<td>S-3B</td>
<td>0.25</td>
<td>F3330S 0.10</td>
<td>SSFB</td>
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<td>PB 216A</td>
<td>TDA-45PO-30EO Sulfate</td>
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<td>S-3B</td>
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<td>-</td>
<td>SSFB</td>
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<td>F3330S 0.10</td>
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<td>PB 217A</td>
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<td>S-2</td>
<td>0.25</td>
<td>-</td>
<td>SSFB</td>
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Table A.33: Experiments AS 218 through AS 222.

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<th>Surfactant</th>
<th>Co-Solvent, Alkali, Polymer</th>
<th>Brine</th>
<th>Range (wt%)</th>
<th>Result</th>
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<tbody>
<tr>
<td>AS 218</td>
<td>TDA-45PO-20EO Sulfate</td>
<td>0.40</td>
<td>F3330S</td>
<td>0.10</td>
<td>SSFB 4.0-6.0 (incr. 0.5) All clear (8 wt%). (Same at room temperature)</td>
</tr>
<tr>
<td></td>
<td>S-2</td>
<td>0.25</td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>C-9</td>
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<tr>
<td>PB 218A</td>
<td>TDA-45PO-20EO Sulfate</td>
<td>0.40</td>
<td>-</td>
<td>-</td>
<td>SSFB 3.0-9.0 (incr. 1.0) All type I microemulsions. (Same at room temperature)</td>
</tr>
<tr>
<td></td>
<td>S-2</td>
<td>0.25</td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>C-9</td>
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<tr>
<td>AS 219</td>
<td>TDA-45PO-20EO Sulfate</td>
<td>0.40</td>
<td>F3330S</td>
<td>0.10</td>
<td>SSFB 4.0-6.0 (incr. 0.5) All clear (8 wt%). (All hazy at room temperature)</td>
</tr>
<tr>
<td></td>
<td>S-3B</td>
<td>0.25</td>
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<td>C-9</td>
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<td>PB 219A</td>
<td>TDA-45PO-20EO Sulfate</td>
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<td>-</td>
<td>-</td>
<td>SSFB 4.0-9.0 (incr. 1.0) S* = 5.6 wt%, σ*= 17 cc/cc. Viscous macroemulsion at 7.0 wt% and up. (S* = 6.4 wt%, σ*= 42 cc/cc at room temperature)</td>
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<td>C-9</td>
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<tr>
<td>PB 219B</td>
<td>TDA-45PO-20EO Sulfate</td>
<td>0.40</td>
<td>SBA</td>
<td>0.50</td>
<td>SSFB 3.0-6.0 (incr. 1.0) S* = 5.55 wt%, σ*= 20 cc/cc. No macroemulsions. (S<em>~6.0 wt%, σ</em>~30 cc/cc at room temp.)</td>
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<td>PB 219C</td>
<td>TDA-45PO-20EO Sulfate</td>
<td>0.40</td>
<td>SBA</td>
<td>0.50</td>
<td>FB#2+SS FB 4.41-5.36 All type I microemulsions. (same at room temperature)</td>
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<td>PB 219D</td>
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<td>0.40</td>
<td>SBA</td>
<td>0.15</td>
<td>FB #2+SSFB 5.36 Type I microemulsion. (Type I at room temperature also)</td>
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<td>C-9</td>
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<tr>
<td>AS 221</td>
<td>TDA-45PO-20EO Sulfate</td>
<td>0.40</td>
<td>F3330S</td>
<td>0.10</td>
<td>SSFB 4.0-8.0 (incr. 1.0) All clear (8 wt%). (Slightly hazy at 8 wt% at room temperature)</td>
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<tr>
<td>AS 222</td>
<td>TDA-45PO-30EO Sulfate</td>
<td>0.40</td>
<td>F3330S</td>
<td>0.10</td>
<td>SSFB 4.0-8.0 (incr. 1.0) All cloudy/phase separate. (Same at room temp.)</td>
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<tr>
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<td>S-3B</td>
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Table A.34: Experiments PB 223 through AS 230BB.

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<th>Exp. No.</th>
<th>Surfactant</th>
<th>Co-Solvent, Alkali, Polymer</th>
<th>Brine</th>
<th>Range (wt%)</th>
<th>Result</th>
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<td>TDA-45PO-10EO Sulfate</td>
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<td>S-3B</td>
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<td>0.20-0.50 (incr. 0.10)</td>
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<td>0.60-0.90, (incr. 0.10)</td>
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<td>C-9</td>
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<td>0.20-0.50 (incr. 0.10)</td>
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<td></td>
<td>S-3B</td>
<td>0.25</td>
<td></td>
<td></td>
<td>3.0-6.0 (incr. 0.5)</td>
</tr>
<tr>
<td></td>
<td>C-9</td>
<td>0.25</td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>S-13D</td>
<td>0.10</td>
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</tr>
<tr>
<td>AS 230</td>
<td>-</td>
<td>-</td>
<td>EDTA</td>
<td>0.25-10.0</td>
<td>FB #2</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
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</tr>
<tr>
<td>AS 230A</td>
<td>-</td>
<td>-</td>
<td>EDTA</td>
<td>0.25-10.0</td>
<td>SSFB</td>
</tr>
<tr>
<td></td>
<td>-</td>
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<td></td>
<td></td>
<td>5.5</td>
</tr>
<tr>
<td>AS 230B</td>
<td>-</td>
<td>-</td>
<td>EDTA</td>
<td>0.25-10.0</td>
<td>NaCl</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
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<td></td>
<td>5.5</td>
</tr>
<tr>
<td>AS 230AA</td>
<td>-</td>
<td>-</td>
<td>4Na-EDTA</td>
<td>0.25-10.0</td>
<td>SSFB</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td>5.5</td>
</tr>
<tr>
<td>AS 230BB</td>
<td>-</td>
<td>-</td>
<td>4Na-EDTA</td>
<td>0.25-10.0</td>
<td>NaCl</td>
</tr>
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<td>6.4</td>
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### Table A.35: Experiments PB 230CC through PB 236A.

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Surfactant</th>
<th>Co-Solvent, Alkali, Polymer</th>
<th>Brine</th>
<th>Range (wt%)</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>AS 230CC</td>
<td>-</td>
<td>4Na-EDTA</td>
<td>FB #1</td>
<td>-</td>
<td>All Clear</td>
</tr>
<tr>
<td>AS 230DD</td>
<td>-</td>
<td>4Na-EDTA</td>
<td>SSFB</td>
<td>4.0</td>
<td>All Clear</td>
</tr>
<tr>
<td>AS 231</td>
<td>-</td>
<td>NaB(OH)4</td>
<td>FB #2</td>
<td>-</td>
<td>All samples precipitate</td>
</tr>
<tr>
<td>AS 231A</td>
<td>-</td>
<td>NaB(OH)4</td>
<td>SSFB</td>
<td>5.5</td>
<td>All samples precipitate</td>
</tr>
<tr>
<td>AS 231B</td>
<td>-</td>
<td>NaB(OH)4</td>
<td>NaCl</td>
<td>5.5</td>
<td>Precipitate at 2.5 wt% alkali</td>
</tr>
<tr>
<td>AS 231C</td>
<td>-</td>
<td>NaB(OH)4</td>
<td>NaCl</td>
<td>6.4</td>
<td>All clear</td>
</tr>
<tr>
<td>AS 231D</td>
<td>-</td>
<td>NaB(OH)4</td>
<td>NaCl</td>
<td>6.4</td>
<td>Clear to 2.5 wt%. Precip. At 5.0%</td>
</tr>
<tr>
<td>AS 231E</td>
<td>-</td>
<td>NaB(OH)4</td>
<td>FB #1</td>
<td>-</td>
<td>All samples precipitate</td>
</tr>
<tr>
<td>PB 232</td>
<td>Gemini C18-DEG-70PO-30EO 2carboxylate</td>
<td>0.40</td>
<td>SSFB</td>
<td>3.0-8.0 (incr. 1.0)</td>
<td>All type I microemulsions. (same at room temperature)</td>
</tr>
<tr>
<td></td>
<td>S-3B</td>
<td>0.25</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C-9</td>
<td>0.25</td>
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<tr>
<td>PB 233</td>
<td>TDA-45PO-10EO Sulfate</td>
<td>0.50</td>
<td>SBA</td>
<td>0.50</td>
<td>SSFB</td>
</tr>
<tr>
<td></td>
<td>S-3B</td>
<td>0.30</td>
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<td>C-9</td>
<td>0.25</td>
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<td>PB 235A</td>
<td>S-13D</td>
<td>0.40</td>
<td>SBA</td>
<td>0.50</td>
<td>SSFB</td>
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<td>S-3B</td>
<td>0.30</td>
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<td></td>
<td>TDA-45PO-30EO Sulfate</td>
<td>0.25</td>
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</tr>
<tr>
<td>PB 236</td>
<td>TDA-45PO-20EO Sulfate</td>
<td>0.40</td>
<td>SBA</td>
<td>0.50</td>
<td>SSFB</td>
</tr>
<tr>
<td></td>
<td>S-3B</td>
<td>0.30</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>C-9</td>
<td>0.20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PB 236A</td>
<td>TDA-45PO-20EO Sulfate</td>
<td>0.40</td>
<td>SBA</td>
<td>0.50</td>
<td>FB #2+SSFB</td>
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Table A.36: Experiments PB 237 through AS 242A.

<table>
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<th>Exp. No.</th>
<th>Surfactant</th>
<th>Co-Solvent, Alkali, Polymer</th>
<th>Brine</th>
<th>Range (wt%)</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>PB 237</td>
<td>TDA-45PO-20EO Sulfate</td>
<td>SBA</td>
<td>SSFB</td>
<td>3.0-6.0 (incr. 1.0)</td>
<td>S* ≈ 3.0 wt%, σ* ≈ 20 cc/cc. (S* around 3.0 wt% at room temperature)</td>
</tr>
<tr>
<td></td>
<td>S-3B</td>
<td>0.25</td>
<td>0.50</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>C-9</td>
<td>0.15</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>PB 238</td>
<td>S-13D</td>
<td>SBA</td>
<td>SSFB</td>
<td>4.0-8.0 (incr. 1.0)</td>
<td>All type II microemulsions. Viscous macroemulsions present. (same at room temperature)</td>
</tr>
<tr>
<td></td>
<td>S-3B</td>
<td>0.25</td>
<td>0.50</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>TDA-45PO-60EO Sulfate</td>
<td>0.25</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PB 239</td>
<td>Gemini C18-DEG-70PO-30EO 2carboxylate</td>
<td>-</td>
<td>SSFB</td>
<td>3.0-8.0 (incr. 1.0)</td>
<td>Strange behavior. Viscous gels, lots of oil droplets trapped in aqueous phase. Possibly type I microemulsions. (Same at room temp.)</td>
</tr>
<tr>
<td></td>
<td>S-3B</td>
<td>0.50</td>
<td></td>
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<tr>
<td>PB 240</td>
<td>Gemini C18-DEG-70PO-30EO 2carboxylate</td>
<td>-</td>
<td>SSFB</td>
<td>3.0-8.0 (incr. 1.0)</td>
<td>All type I microemulsions. (same at room temperature)</td>
</tr>
<tr>
<td></td>
<td>S-3B</td>
<td>0.35</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>C-9</td>
<td>0.15</td>
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<tr>
<td>PB 241</td>
<td>TDA-45PO-10EO Sulfate</td>
<td>SBA</td>
<td>SSFB</td>
<td>4.0-6.0 (incr. 0.5)</td>
<td>Most type II microemulsions. Viscous macroemulsions present. Fluid at 4 wt% with oil sol.=64 cc/cc, water sol.=10. (at room temp, S* ≈ 3.8 wt%. σ* ≈ 58 cc/cc.)</td>
</tr>
<tr>
<td></td>
<td>S-3B</td>
<td>0.25</td>
<td>0.50</td>
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<tr>
<td></td>
<td>C-9</td>
<td>0.20</td>
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<tr>
<td>PB 242</td>
<td>TDA-45PO-10EO Sulfate</td>
<td>SBA</td>
<td>SSFB</td>
<td>4.0-6.0 (incr. 0.5)</td>
<td>S* = 4.8 wt%, σ*= 6 cc/cc. High water solubility below S*. Oil solubility about constant at 6.</td>
</tr>
<tr>
<td></td>
<td>S-3B</td>
<td>0.25</td>
<td>0.50</td>
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</tr>
<tr>
<td>AS 242A</td>
<td>TDA-45PO-10EO Sulfate</td>
<td>SBA</td>
<td>SSFB</td>
<td>2.0-8.0 (incr. 1.0)</td>
<td>All Clear (8.0 wt%)</td>
</tr>
<tr>
<td></td>
<td>S-3B</td>
<td>0.25</td>
<td>0.50</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C-9</td>
<td>0.25</td>
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</tbody>
</table>
Table A.37: Experiments AS 242B through PB 243.

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Surfactant</th>
<th>Co-Solvent, Alkali, Polymer</th>
<th>Brine</th>
<th>Range (wt%)</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>AS 242B</td>
<td>TDA-45PO-10EO Sulfate</td>
<td>-</td>
<td>SSFB</td>
<td>2.0-10.0 (incr. 2.0)</td>
<td>All Clear (10.0 wt%). Cloudy at room temp at 8.0 wt%</td>
</tr>
<tr>
<td></td>
<td>S-3B 0.25</td>
<td>C-9 0.25</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PB 242B'</td>
<td>TDA-45PO-10EO Sulfate</td>
<td>-</td>
<td>SSFB</td>
<td>2.0, 8.0, 10.0</td>
<td>No type III observed. Some macroemulsion at 8 and 10 wt%. (Same at room temperature)</td>
</tr>
<tr>
<td></td>
<td>S-3B 0.25</td>
<td>C-9 0.25</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>AS 242C</td>
<td>TDA-45PO-10EO Sulfate</td>
<td>-</td>
<td>NaCl</td>
<td>2.0-12.0 (incr. 2.0)</td>
<td>All Clear (12.0 wt%). Precipitation at room temp. at 10.0 wt%</td>
</tr>
<tr>
<td></td>
<td>S-3B 0.25</td>
<td>C-9 0.25</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PB 242C'</td>
<td>TDA-45PO-10EO Sulfate</td>
<td>-</td>
<td>SSFB</td>
<td>4.0-12.0 (incr. 2.0)</td>
<td>No type III observed. (some at 10 wt% at room temperature)</td>
</tr>
<tr>
<td></td>
<td>S-3B 0.25</td>
<td>C-9 0.25</td>
<td></td>
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</tr>
<tr>
<td>AS 242D</td>
<td>TDA-45PO-10EO Sulfate</td>
<td>-</td>
<td>FB #1+SSFB</td>
<td>2.0-5.36 (incr. 1.0)</td>
<td>All Clear (5.36 wt%). (All clear at room temperature also)</td>
</tr>
<tr>
<td></td>
<td>S-3B 0.25</td>
<td>C-9 0.25</td>
<td></td>
<td></td>
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<tr>
<td>PB 242E</td>
<td>TDA-45PO-10EO Sulfate</td>
<td>-</td>
<td>FB #1+SSFB</td>
<td>2.0-5.36 (incr. 1.0)</td>
<td>Some type III microemulsion at 5.0 and 5.36 wt%. Low solubilization. (All type I at room temperature)</td>
</tr>
<tr>
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<td>S-3B 0.25</td>
<td>C-9 0.25</td>
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<tr>
<td>PB 242F</td>
<td>TDA-45PO-10EO Sulfate</td>
<td>-</td>
<td>FB #1+SSFB</td>
<td>4.0 wt%</td>
<td>Spinning drop IFT test at 4.0 wt%</td>
</tr>
<tr>
<td></td>
<td>S-3B 0.25</td>
<td>C-9 0.25</td>
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<tr>
<td>PB 243</td>
<td>TDA-45PO-10EO Sulfate</td>
<td>SBA 0.50</td>
<td>SSFB</td>
<td>4.0-6.0 (incr. 0.5)</td>
<td>S* =~4.55 wt%. σ* =~7.6 cc/cc. No macroemulsions. (All type I at room temp.)</td>
</tr>
<tr>
<td></td>
<td>S-3B 0.25</td>
<td>C-9 0.25</td>
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</table>
Table A.38: Experiments PB 244 through AS 247A.

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Surfactant</th>
<th>Co-Solvent, Alkali, Polymer</th>
<th>Brine</th>
<th>Range (wt%)</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>PB 244</td>
<td>TDA-45PO-20EO Sulfate 0.40</td>
<td>SBA 0.50</td>
<td>SSFB</td>
<td>3.0-7.0 (incr 1.0)</td>
<td>All type I microemulsions. (same at room temperature)</td>
</tr>
<tr>
<td></td>
<td>S-2 0.40</td>
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<td></td>
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</tr>
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<td>C-9 0.05</td>
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<tr>
<td>PB 245</td>
<td>C15-17 ABS 0.50</td>
<td>SBA 0.50</td>
<td>SSFB</td>
<td>2.0-6.0 (incr 1.0)</td>
<td>All type II microemulsions. Viscous macroemulsions present. (same at room temperature)</td>
</tr>
<tr>
<td></td>
<td>S-2 0.50</td>
<td></td>
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<tr>
<td>PB 246</td>
<td>TDA-45PO-10EO Sulfate 0.50</td>
<td>SBA 0.50</td>
<td>SSFB</td>
<td>4.0-6.0 (incr 0.5)</td>
<td>S* = 5.5 wt%. σ* = -24 cc/cc. No macroemulsions. (S* = 5.25 wt%. σ* = 18 cc/cc at room temp.)</td>
</tr>
<tr>
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<td>S-3B 0.25</td>
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<tr>
<td></td>
<td>C-9 0.275</td>
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<tr>
<td>PB 246A</td>
<td>TDA-45PO-10EO Sulfate 0.50</td>
<td>SBA 0.50</td>
<td>FB #2+SSFB 5.36</td>
<td></td>
<td>Type III microemulsion. Oil and water solubilizations less than 10 cc/cc. (Type I at room temp.)</td>
</tr>
<tr>
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<td>S-3B 0.25</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>C-9 0.275</td>
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</tr>
<tr>
<td>PB 246B</td>
<td>TDA-45PO-10EO Sulfate 0.50</td>
<td>SBA 0.50</td>
<td>SSFB</td>
<td>3.0-7.0 (incr 1.0)</td>
<td>WOR=3. S*-6.5 wt%. σ* = -9.5 cc/cc. Mostly type I behavior. (Type I at room temperature)</td>
</tr>
<tr>
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<td>S-3B 0.25</td>
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</tr>
<tr>
<td></td>
<td>C-9 0.275</td>
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<tr>
<td>PB 246C</td>
<td>TDA-45PO-10EO Sulfate 0.50</td>
<td>SBA 0.50</td>
<td>SSFB</td>
<td>3.0-7.0 (incr 1.0)</td>
<td>WOR=0.333. All type I microemulsions. (same at room temperature)</td>
</tr>
<tr>
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<td>S-3B 0.25</td>
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<td></td>
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</tr>
<tr>
<td></td>
<td>C-9 0.275</td>
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<tr>
<td>AS 246D</td>
<td>TDA-45PO-10EO Sulfate 0.50</td>
<td>-</td>
<td>SSFB</td>
<td>2.0-8.0 (incr 1.0)</td>
<td>All clear.</td>
</tr>
<tr>
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<td>S-3B 0.25</td>
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</tr>
<tr>
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<td>C-9 0.275</td>
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<tr>
<td>PB 247</td>
<td>TDA-45PO-10EO Sulfate 0.40</td>
<td>SBA 0.50</td>
<td>SSFB</td>
<td>4.0-6.0 (incr 0.5)</td>
<td>S* = 4.00 wt%. σ* = 40 cc/cc. No macroemulsions. (S* = 4.55 wt%. σ* = 58 cc/cc at room temp.)</td>
</tr>
<tr>
<td></td>
<td>S-3B 0.25</td>
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<tr>
<td></td>
<td>C-9 0.225</td>
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<tr>
<td>AS 247A</td>
<td>TDA-45PO-10EO Sulfate 0.40</td>
<td>-</td>
<td>SSFB</td>
<td>2.0-8.0 (incr 1.0)</td>
<td>All clear.</td>
</tr>
<tr>
<td></td>
<td>S-3B 0.25</td>
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</tr>
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<td>C-9 0.225</td>
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<tr>
<td>Exp. No.</td>
<td>Surfactant Name</td>
<td>Co-Solvent, Alkali, Polymer Name</td>
<td>Brine</td>
<td>Range (wt%)</td>
<td>Result</td>
</tr>
<tr>
<td>-----------------</td>
<td>-----------------</td>
<td>-----------------</td>
<td>-------</td>
<td>-------------</td>
<td>--------</td>
</tr>
<tr>
<td>AS 247B</td>
<td>TDA-45PO-10EO Sulfate 0.40</td>
<td>-</td>
<td>FB #1 + SSFB</td>
<td>2.0-5.36 (incr. 1.0)</td>
<td>All clear.</td>
</tr>
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<td></td>
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<td>All type I microemulsions. (same at room temperature)</td>
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<td>Phase Separation (Clear at room temperature)</td>
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<td>S-13C 0.30</td>
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<td>SBA 0.50</td>
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<td>4.64</td>
<td>Type I microemulsion. (Type I at room temperature also)</td>
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<td>Type III microemulsion. Oil sol.=39.5 cc/cc, water sol.=5.1 cc/cc. (Type III at room temp., oil sol.=22.3 water sol.=29.4)</td>
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Table A.40: Experiments AS 251 through PB 254A.

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<th>Result</th>
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<td>Name</td>
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<td>SBA</td>
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Table A.41: Experiments AS 255 through AS 259.

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<th>Alkali</th>
<th>Polymer</th>
<th>Brine</th>
<th>Range (wt%)</th>
<th>Result</th>
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Table A.42: Experiments PB 259A through AS 264.

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<th>Co-Solvent wt%</th>
<th>Alkali Name</th>
<th>Alkali wt%</th>
<th>Polymer Name</th>
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<th>Range (wt%)</th>
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<td>FB #2+ SSFB</td>
<td>4.67</td>
<td>Type I microemulsion. (Type I at room temperature also)</td>
</tr>
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Table A.43: Experiments PB 264A through PB 270.

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<th>Co-Solvent, Alkali, Polymer Name</th>
<th>Co-Solvent wt%</th>
<th>Brine</th>
<th>Range (wt%)</th>
<th>Result</th>
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<td>SBA</td>
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<td>S*= 5.5 wt%. σ*=~10 cc/cc. (All type I at room temperature)</td>
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Table A.44: Experiments PB 271 through AS 286.

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<th>Co-Solvent, Alkali, Polymer wt%</th>
<th>Brine</th>
<th>Brine Range (wt%)</th>
<th>Result</th>
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<td>S* slightly above 5.5 wt%, perhaps 6 to 6.5 wt%. (All type I at room temperature)</td>
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<td>S*= 4.15 wt%. σ*= 5 cc/cc. (S* slightly above 5.5 wt%, perhaps 6.5 wt% at room temp.)</td>
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<td>S* above 5.5 wt%</td>
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BIBLIOGRAPHY


http://austintexas.gov/department/frequently-asked-questions-about-h2o


