

Recent Advances in Surfactant EOR

George J. Hirasaki, SPE, Clarence A. Miller, SPE, and Maura Puerto, Rice University

This paper (SPE 115386) was accepted for presentation at the SPE Annual Technical Conference and Exhibition, Denver, 21–24 September 2008, and revised for publication. Original manuscript received for review 19 July 2010. Revised manuscript received for review 22 December 2010. Paper peer approved 18 January 2011.

Summary

In this paper, recent advances in surfactant enhanced oil recovery (EOR) are reviewed. The addition of alkali to surfactant flooding in the 1980s reduced the amount of surfactant required, and the process became known as alkaline/surfactant/polymer flooding (ASP). It was recently found that the adsorption of anionic surfactants on calcite and dolomite can also be significantly reduced with sodium carbonate as the alkali, thus making the process applicable for carbonate formations. The same chemicals are also capable of altering the wettability of carbonate formations from strongly oil-wet to preferentially water-wet. This wettability alteration in combination with ultralow interfacial tension (IFT) makes it possible to displace oil from preferentially oil-wet carbonate matrix to fractures by

oil/water gravity drainage.

The alkaline/surfactant process consist of injecting alkali and synthetic surfactant. The alkali generates soap in situ by reaction between the alkali and naphthenic acids in the crude oil. It was recently recognized that the local ratio of soap/surfactant determines the local optimal salinity for minimum IFT. Recognition of this dependence makes it possible to design a strategy to maximize oil recovery with the least amount of surfactant and to inject polymer with the surfactant without phase separation. An additional benefit of the presence of the soap component is that it generates an oil-rich colloidal dispersion that produces ultralow IFT over a much wider range of salinity than in its absence.

It was once thought that a cosolvent such as alcohol was necessary to make a microemulsion without gel-like phases or a polymer-rich phase separating from the surfactant solution. An example of an alternative to the use of alcohol is to blend two dissimilar surfactants: a branched alkoxyated sulfate and a double-tailed, internal olefin sulfonate. The single-phase region with NaCl or CaCl₂ is greater for the blend than for either surfactant alone. It is also possible to incorporate polymer into such aqueous

surfactant solutions without phase separation under some conditions. The injected surfactant solution has underoptimum phase behavior with the crude oil. It becomes optimum only as it mixes with the in-situ-generated soap, which is generally more hydrophobic than the injected surfactant. However, some crude oils do not have a sufficiently high acid number for this approach to work.

Foam can be used for mobility control by alternating slugs of gas with slugs of surfactant solution. Besides effective oil displacement in a homogeneous sandpack, it demonstrated greatly improved sweep in a layered sandpack.

Introduction

It is generally considered that only approximately one-third of the petroleum present in known reservoirs is economically recoverable with established technology (i.e., primary-recovery methods using gas pressure and other natural forces in the reservoir, and secondary recovery by waterflooding). It has long been an objective of the industry to develop improved processes to increase overall recovery. However, the low oil prices that prevailed from the mid-1980s until recently provided little incentive for research on EOR, especially surfactant processes with substantial initial cost for chemicals. In light of the current higher prices and

accompanying revival of interest, it seems appropriate to review understanding of, and prospects for, surfactant EOR.

Adding surfactant to injected water to reduce oil/water IFT and/or alter wettability and thereby increase recovery is not a new idea [see, for instance, Uren and Fahmy (1927)]. Indeed, a few early field trials where small amounts of surfactant were injected did produce small increases in oil recovery. The increases were probably caused mainly by wettability changes, although the data were inconclusive for assessing mechanisms. The results were not sufficiently promising to stimulate use of surfactants on a larger scale. A related long-held concept for improving recovery is to generate surfactant in situ by injecting an alkaline solution (Atkinson 1927), which is less expensive than synthetic surfactants and converts naphthenic acids in the crude oil to soaps. Early results were not encouraging, and the relative importance of likely process mechanisms was not understood (Johnson 1976). Other references to early work on surfactants are given by Hill et al. (1973).

Two different approaches stimulated significant advances in surfactant EOR processes in the 1960s. The surfactants were made either by direct sulfonation of aromatic groups in refinery streams or crude oils, or by organic synthesis of alkyl/aryl

sulfonates, which allowed for the surfactant to be tailored to the reservoir of interest. The advantages of these surfactants are their low cost, their wide range of properties, and the availability of raw materials in somewhat large quantities.

Miscible flooding was an active area of research, but the solvents being considered, such as enriched gas and LPG, exhibited poor reservoir sweep because the adverse mobility ratio promoted viscous fingering and the low solvent density led to gravity override. Seeking a solvent miscible with oil but having a higher viscosity and density, Gogarty and coworkers at Marathon proposed using a slug of an oil-continuous microemulsion made of hydrocarbon, a petroleum sulfonate surfactant, an alcohol, and water or brine [see review by Gogarty (1977)]. Holm and coworkers at Union Oil advocated a similar process using a “soluble oil,” which was also an oil-continuous microemulsion made mainly of crude oil, some mineral oil, petroleum sulfonate, a cosolvent such as ethylene glycol monobutyl ether, and water, as summarized by Holm (1977). Slugs of these materials miscible displaced oil and with better sweep than previous solvents. However, it was not initially recognized that process success also depended on maintaining ultralow IFT at the rear of the slug, where it was displaced by an aqueous polymer solution and became a Winsor I

microemulsion (Hirasaki 1981).

The other approach involved injection of a surfactant formulation made of a petroleum sulfonate and alcohol in an aqueous electrolyte solution. Key to the success of this approach were systematic studies of oil displacement leading to recognition that a dimensionless capillary number ($N_c = \mu v / \sigma$) controlled the amount of residual oil remaining after flooding an oil-containing core at interstitial velocity v with an aqueous solution having a viscosity μ and IFT σ with the oil (Taber 1969; Stegemeier 1977; Melrose and Brandner 1974; Foster 1973). In situations when gravity is important, the Bond number must be included (Pennell et al. 1996). This work revealed that at typical reservoir velocities, IFT had to be reduced from crude-oil/brine values of 20 to 30 mN/m to values in the range of 0.001 to 0.01 mN/m to achieve low values of residual-oil saturation (<0.05).

Several research groups found that ultralow IFTs in the required range could be achieved using petroleum-sulfonate/alcohol mixtures (Hill et al. 1973; Foster 1973; Cayias et al. 1977). They also found systematic variations of IFT when changing such variables as salinity, oil composition, and temperature. An important contribution was the work of Healy et al. (1976) [see also Reed and Healy (1977)], who demonstrated a relationship between

IFT and microemulsion phase behavior. Core tests using continuous surfactant injection at the optimal salinity also yielded the highest recovery of waterflood residual oil. Their studies used mixtures of an alcohol cosolvent with synthetic alkyl/aryl sulfonates, in particular C₉, C₁₂, and C₁₅ orthoxylene sulfonates, which can be made from oligomers of propylene with more reproducible compositions than those belonging to petroleum sulfonates.

Conventional Phase Behavior for Ultralow IFT.

The understanding of ultralow IFT in oil-recovery processes was advanced when Healy et al. (1976) explained how the Winsor definition of equilibrium microemulsion phase behavior (I, II, and III, or lower-phase, upper-phase, and middle-phase microemulsion, respectively) described the changes of phase behavior, solubilization of oil and water, and IFT as a function of salinity for anionic surfactants. The surfactant is able to solubilize an increasing amount of oil and a decreasing amount of water as salinity is increased. The “optimal salinity” determined from phase behavior is the salinity at which the microemulsion solubilizes equal amounts of oil and water. The optimal salinity at which equilibrium IFTs between the microemulsion phase and excess-oil or excess-water phase become equal (and thus the sum becomes a minimum) is close to

the optimal salinity from phase behavior. There are correlations between the “solubilization parameters” (ratio of oil/surfactant V_o/V_s or water/surfactant V_w/V_s by volume) and the IFTs of the microemulsion with the respective excess phases (Huh 1979). Thus, one can estimate the value of the equilibrium IFT at the optimal salinity from the value of the solubilization parameters at the optimal salinity (where they are equal).

Nelson and Pope (1978) recognized that the appearance of a middle-phase microemulsion (Winsor III) is dependent on the amounts of water, oil, and surfactant present. Thus, they defined the Type III phase environment as the range of salinity at which a middle-phase microemulsion may exist if one was to scan the water/oil/surfactant ternary diagram. This distinction is important at very high or very low surfactant concentrations because the volume of the middle-phase microemulsion is proportional to the surfactant concentration. At high surfactant concentrations, more of the excess phases are solubilized, and thus the excess phases have smaller volume or are not present. If the surfactant concentration is high enough, the “middle-phase” microemulsion phase may appear as a single phase at or near optimal conditions. On the other hand, at low surfactant concentrations but above the critical micelle concentration, the volume of the middle-

phase microemulsion is minute and its presence may not be visually detected or sampled for IFT measurements.

The nanostructure of the microemulsion should be recognized to distinguish it from macroemulsions or liquid-crystal dispersions or phases. Macroemulsions are nonequilibrium dispersions that change with time or may be in a metastable condition. Liquid-crystal phases are condensed, ordered phases that usually are birefringent (rotate polarized light), viscous, and tend to inhibit emulsion coalescence (Healey and Reed 1974). Microemulsions are equilibrium isotropic phases that may have a bicontinuous structure with near-zero mean curvature at or near optimal conditions (Scriven 1976). (Microemulsions are oil-swollen micelles in water at underoptimum conditions and reversed micelles in oil at overoptimum conditions.) It was once thought that it is necessary to have a cosolvent (alcohol) to have a microemulsion with an anionic surfactant. However, it is now recognized that it is possible to have microemulsions without alcohol at room temperature by using branched surfactants (Abe et al. 1986).

Salinity-scan tests are used routinely to screen phase behavior of surfactant formulations before conducting more time-consuming coreflood tests (Levitt et al. 2009; Flaaten et al. 2009; Mohammadi

et al. 2009). The minimum IFT is correlated with the solubilization parameters at the optimal salinity. The presence of viscous, structured, or birefringent phases and/or stable macroemulsions is easily observed. Apparent viscosities of phases present in 5-mL samples in sealed glass pipettes can be measured by the falling-sphere method, even for opaque phases (Lopez-Salinas et al. 2009).

Surfactant Requirements and Structures

In a successful displacement process, the injected surfactant slug must first achieve ultralow IFT to mobilize residual oil and create an oil bank where both oil and water flow as continuous phases (Bourrel and Schechter 1988). Second, it must maintain ultralow IFT at the moving displacement front to prevent mobilized oil from being trapped by capillary forces. Because of the way they are prepared, commercial surfactants are invariably mixtures of multiple species, which raises questions as to whether chromatographic separation (i.e., preferential adsorption on pore surfaces or preferential partitioning into the oil phase of some species) can cause IFT variations with possible adverse effects on oil recovery. When alcohol is used in the formulation, it partitions among the bulk-oil and brine phases and the surfactant films in a manner different from the surfactant. The alcohol must then

be carefully selected and tested to ensure there is no deleterious effect of chromatographic separation (Dwarakanath et al. 2008; Sahni et al. 2010). In the surfactant films, alcohol serves as a cosolvent, making the films less rigid and thereby increasing the rate of equilibration and preventing formation of undesirable viscous phases and emulsions instead of the desired low-viscosity microemulsions. Alcohol can also serve as a cosurfactant, altering, for instance, the optimal salinity required to achieve ultralow IFT. Alcohols with short chains such as propanol increase optimal salinity for sulfonate surfactants, while longer-chain alcohols such as pentanol and hexanol decrease optimal salinity. For petroleum sulfonates and synthetic alkyl/aryl sulfonates with light crude oils, it has been found that 2-butanol acts as a cosolvent but has less effect on optimal salinity than other alcohols.

A disadvantage of using alcohol is that it decreases solubilization of oil and water in microemulsions, and hence increases the minimum value of IFT achievable with a given surfactant (Salter 1977). Also, it destabilizes foam that may be desired for mobility control with the slug and in the drive. For temperatures below approximately 60°C, the need for alcohol's cosolvent effect can be reduced or eliminated by some combination of the following strategies: (1) using surfactants with branched

hydrocarbon chains, (2) adding ethylene oxide (EO) and/or less-hydrophilic propylene oxide (PO) groups to the surfactant, and (3) using mixtures of surfactants with different hydrocarbon-chain lengths or structures. Such measures counter the tendency of long, straight hydrocarbon chains of nearly equal length to form condensed surfactant films and the lamellar liquid-crystalline phase. At high temperatures, increased thermal motion promotes more-flexible surfactant films and disruption of ordered structures, but it does not always eliminate viscous phases and emulsions. Further studies are needed to investigate usefulness of these or other strategies for high temperatures.

The use of branched hydrocarbon chains to minimize or eliminate alcohol requirements was discussed by Wade, Schechter, and coworkers (Abe et al. 1986). An isotridecyl hydrophobe was used in Exxon's pilot test in the Loudon field. The hydrophilic part of the surfactant was a chain consisting of short PO and EO segments and a sulfate group (Maerker and Gale 1992). With this combination of the first two strategies, no alcohol was required. The Neodol 67 hydrophobe developed and manufactured by Shell Chemical has an average of 1.5 methyl groups added randomly along a straight C₁₅–C₁₆ chain that provides another type of branching. A propoxylated sulfate with this

hydrophobe has been blended with an internal olefin sulfonate, which is also branched, and used to displace West Texas crude oils in low-salinity, ambient-temperature laboratory tests, both with (Levitt et al. 2009) and without (Liu et al. 2008) alcohol. In this case, all three strategies were combined.

Long-term surfactant stability at reservoir conditions is another surfactant requirement. Provided that pH is maintained at slightly alkaline levels and calcium concentration is not too high, hydrolysis of sulfate surfactants is limited for temperatures up to 50–60°C (Talley 1988). Surfactants with other head groups, most likely sulfonates or carboxylates, will be needed for reservoirs at higher temperatures. Because the sulfonate group is added at different points along the hydrocarbon chain during synthesis, internal olefin sulfonate (IOS) surfactants consist of species with a twin-tailed structure, a different type of branching. Results of laboratory studies of IOS phase behavior at high temperatures have recently been presented (Barnes et al. 2008, 2010; Zhao et al. 2008, Puerto et al. 2010). Hydrocarbon-chain lengths ranged from C₁₅–C₁₈ to C₂₄–C₂₈. However, the effect of dissolved calcium and magnesium ions, which most likely cause surfactant precipitation, was not investigated in these studies (see Fig. 3 of Liu et al. 2008).

Moreover, the current availability of internal olefins of long chain length, as would be required for low or moderate reservoir salinities, is limited. Alpha olefin sulfonate (AOS) surfactants have the same potential disadvantages and are not as highly branched as IOS surfactants.

Sulfonate groups cannot be added directly to alcohols, including those with EO and/or PO chains. One approach is to prepare sulfonates with glycidyl chloride or epichlorohydrin, where a three-carbon chain is added between the EO or PO chain and the sulfonate group. Wellington and Richardson (1997) described some results with such surfactants. Further information on their synthesis and initial phase-behavior results for propoxy glycidyl sulfonates with the Neodol 67 hydrophobe is given by Barnes et al. (2008). Puerto et al. (2010) presented phase behavior showing that suitable ethoxy or propoxy glycidyl sulfonates could produce microemulsions with high solubilization over a wide range of optimal salinities with *n*-octane as the oil at temperatures up to 120°C. They also noted that because these surfactants typically exhibit phase separation (cloud point) at high temperatures and salinities, it may be necessary to blend them with other surfactants such as IOS, which are also stable at high temperatures.

Until recent years, nearly all work was directed toward EOR in sandstone reservoirs owing to

concerns that in the high-divalent-ion environment of carbonate reservoirs, petroleum or synthetic sulfonates would adsorb excessively and/or form calcium and magnesium salts that would either precipitate or partition into the oil phase. The exception was the work of Adams and Schievelbein (1984), who conducted laboratory experiments and two field tests showing that oil could be displaced in a carbonate reservoir using a mixture of petroleum sulfonates and ethoxylated sulfate surfactants. The ethoxy groups add tolerance to divalent ions. Recent work with carbonate reservoirs used ethoxylated or propoxylated sulfates, as discussed in the later section on wettability.

Alcohol-Free Surfactant Slugs for Injection

The surfactant slug to be injected should be a single-phase micellar solution. Especially when polymer is added to increase slug viscosity, it is essential to prevent separation into polymer-rich and surfactant-rich phases, which yields highly viscous phases unsuitable for either injection or propagation through the formation (Trushenski 1977). At low temperatures, oil-free mixtures of petroleum sulfonate/alcohol or synthetic sulfonate/alcohol mixtures with brine are often translucent micellar solutions at salinities well below optimal, but contain lamellar liquid crystal and exhibit birefringence near

optimal salinity where ultralow IFT is found upon mixing with crude oil (Miller et al. 1986). In the absence of polymer, the lamellar phase is often dispersed in brine as particles having maximum dimensions of at least several micrometers. When polymer is added to such a turbid dispersion of the lamellar phase, it produces a polymer-rich aqueous solution and a more concentrated surfactant dispersion (Qutubuddin et al. 1985). This undesirable behavior can sometimes be avoided by adding sufficient alcohol. However, use of alcohol has disadvantages, as indicated previously.

The lamellar phase was observed in surfactant/brine mixtures in the absence of oil even for Exxon's Loudon formulation mentioned previously (Ghosh 1985), where, as indicated, branching and addition of EO/PO groups allowed low-viscosity microemulsions to be formed and ultralow IFT to be achieved with the crude oil without the need to add alcohol. Exxon avoided phase separation when polymer was added to the injected slug by including a paraffinic white oil of high molecular weight in the formulation. That is, they injected a white oil-in-water microemulsion (Winsor I), which became a bicontinuous microemulsion when mixed with substantial volumes of crude oil in the reservoir (Maerker and Gale 1992).

As temperature increases, the lamellar liquid-

crystal phase may melt. However, the surfactant/brine mixture is still unsuitable for injection if separation into two or more liquid phases occurs near optimal salinity (Benton and Miller 1983). Even if bulk phase separation does not occur, turbid solutions are sometimes observed. These solutions usually have large, anisotropic micelles and separate into surfactant-rich and polymer-rich phases with the addition of polymer. These phases can separate and/or plug the porous media into which they are injected. Adding alcohol can reduce micelle size and prevent phase separation in some cases. As indicated previously, addition of a paraffinic-oil which yields an oil-in-water microemulsion with nearly spherical drops is another approach for preventing phase separation when polymer is present. Within limits, the higher the molecular weight of the oil added to produce an oil-in-water microemulsion, the less oil is needed to formulate single phases with polymer for mobility control.

Another approach to formulate single-phase injection compositions would be to find surfactants or surfactant blends that neither exhibit phase separation nor form turbid solutions or liquid crystalline dispersions at conditions of interest (Flaaten et al. 2009; Sahni et al. 2010). Blends of the branched surfactant Neodol 67 propoxylated sulfate (N67-7POS), having an average of seven PO groups with

the twin-tailed surfactant IOS 15/18, an IOS (Barnes et al. 2010) made from a feedstock containing mainly C_{15} – C_{18} chains, are interesting in this respect. **Fig. 1** shows phase behavior at ambient temperature of 3 wt% aqueous solutions of such surfactant blends containing 1 wt% Na_2CO_3 and varying NaCl concentration but no alcohol or polymer. IOS 15-18 alone precipitates above 4 wt% NaCl in such solutions. In contrast, solutions of the propoxylated sulfate alone do not precipitate but instead become cloudy above the same salinity, as droplets of a second liquid phase form and scatter light. Addition of IOS 15-18 to the propoxylated sulfate makes the mixture more hydrophilic, thereby raising the salinity at which phase separation occurs to a value higher than for either surfactant alone. For instance, the 4:1 blend (hereafter NI blend) (i.e., 80% N67-7POS and 20% IOS 15-18) exhibits phase separation at approximately 6 wt% NaCl (plus 1% Na_2CO_3), although slight cloudiness occurs above approximately 3.5 wt% NaCl. Addition of 0.5 wt% of partially hydrolyzed polyacrylamide to a 0.5 wt% solution of this blend in a solution containing 4 wt% NaCl and 1 wt% Na_2CO_3 produces phase separation, although similar addition of polymer to a solution containing only 2 wt% NaCl does not (Liu et al. 2008). Phase-behavior studies show that the optimal salinity of this blend with a West Texas crude oil is

approximately 5 wt% NaCl (with 1 wt% Na_2CO_3) when the amount of surfactant present is much greater than soap formed from the naphthenic acids in the crude oil. However, in alkaline/surfactant processes, it is best to inject at lower salinities, as discussed later, because the surfactant encounters conditions during the process with greater ratios of soap-to-surfactant and correspondingly lower optimal salinities. Indeed, excellent recovery of the West Texas crude oil was observed in sandpack experiments when a single-phase mixture of the 4:1 blend and polymer was injected at 2 wt% NaCl with 1 wt% Na_2CO_3 (Liu et al. 2008). At 2% NaCl, the surfactant micelles are not highly anisotropic, and polymer and surfactant can coexist in the same phase.

A similar approach was used by Falls et al. (1994) in an alkaline/surfactant field test. They added a small amount of the nonionic surfactant Neodol 25-12 to the main injected surfactant, a blend of IOSs, to make the formulation sufficiently hydrophilic to form a single micellar solution during storage at ambient temperature. Because this surfactant becomes less hydrophilic at higher temperatures, it did not adversely affect process performance at the reservoir temperature of approximately 57°C.

Alkaline/Surfactant Processes: Role of Alkali

Nelson et al. (1984) proposed injection of a solution

containing both surfactant and alkali for EOR. Such processes have attracted and continue to attract considerable interest. They have been labeled by different names, but will be collectively described here as alkaline/surfactant processes (Nelson et al. 1984; Peru and Lorenz 1990; Surkalo 1990; Baviere et al. 1995).

The primary role of the alkali in an alkaline/surfactant process is to reduce adsorption of the surfactant during displacement through the formation and sequestering divalent ions. An additional benefit of alkali is that the soap is formed in situ from the naphthenic acid in the crude oil (Johnson 1976). As indicated previously, the generation of soap allows the surfactant to be injected at lower salinities than if used alone, which further reduces adsorption and facilitates incorporation of polymer in the surfactant slug. Also, alkali can alter formation wettability to reach either more water-wet or more oil-wet states. In fractured oil-wet reservoirs, the combined effect of alkali and surfactant in making the matrix preferentially water-wet is essential for an effective process. These benefits of alkali will occur only where alkali is present. Thus, it is important to determine “alkali consumption,” which controls the rate of propagation of alkali through the formation.

Reduced Surfactant Adsorption. The discussion here will be limited to anionic surfactants (Wessen and Harwell 2000). The primary mechanism for the adsorption of anionic surfactants on sandstone- and carbonate-formation material is the ionic attraction between positively charged mineral sites and the negative surfactant anion (Tabatabal et al. 1993; Zhang and Somasundaran 2006). Thus, the role of the alkali is to be a “potential-determining ion” to reverse the charge on positively charged mineral sites. The potential-determining ions for oxide minerals are the hydronium and hydroxide ions. The pH at which the charge reverses is the “isoelectric point” if measured by electrophoresis (zeta potential) and is the “point-of-zero-charge” if determined by titration. The values are tabulated for most common minerals (Lyklema 1995). Silica is negatively charged at reservoir conditions and exhibits negligible adsorption of anionic surfactants. Clays (at neutral pH) have negative charge at the faces and positive charge at the edges. The clay edges are alumina-like and thus are expected to reverse their charge at a pH of approximately 9. Carbonate formations and sandstone-cementing material can be calcite or dolomite. These latter minerals also have an isoelectric point of approximately pH 9, but carbonate ions, as well as the calcium and magnesium ions, are more significant potential-

determining ions. The zeta potential of calcite is negative even at neutral pH in the presence of 0.1 N carbonate/bicarbonate ions (Hirasaki and Zhang 2004). If a formation contains iron minerals, the oxidation/reduction conditions influence whether the surface iron sites are Fe^{3+} or Fe^{2+} . Adsorption of anionic surfactant for one sandstone was found to be lower by more than a factor of two for reducing rather than for oxidizing conditions (Wang 1993). Surfactant adsorption is only one component of surfactant retention. Phase trapping of surfactant can be more significant and will be discussed later.

Alkaline preflush had been advocated for both sequestering divalent ions and reducing sulfonate adsorption (Holm and Robertson 1981). In subsequent work, alkali has been injected with the surfactant. Adsorption of anionic surfactants on Berea sandstone was reduced several-fold with addition of sodium carbonate for petroleum sulfonate (Bae and Petrick 1977) or with addition of sodium silicate or hydroxide for alcohol ethoxysulfate (Nelson et al. 1984). The reduction of adsorption on Berea sandstone with sodium bicarbonate was 68% in a dynamic experiment (Peru and Lorenz 1990). Static and dynamic adsorption of anionic surfactants on calcite and dolomite was decreased by an order of magnitude with addition of sodium carbonate, but insignificantly with sodium hydroxide (see **Figs. 2**

through 4) (Hirasaki and Zhang 2004; Seethepalli et al. 2004; Zhang et al. 2006; Liu et al. 2008; Tabatabal et al. 1993). (The TC Blend of Figs. 2 through 4 is an earlier blend of isotridecyl 4PO sulfate and C12 3EO sulfate. Research on it was discontinued because its optimal salinity was too high for the application of interest.)

Divalent-Ion Sequestration. The phase behavior of anionic surfactant systems is much more sensitive to a change in divalent ions (e.g., Ca^{2+} and Mg^{2+}) compared to monovalent ions (e.g., Na^+), especially at low surfactant concentrations (Nelson 1981). This is problematic in sandstones because of ion exchange between the clay, brine, and surfactant micelles (Hill et al. 1977; Pope et al. 1978; Hirasaki 1982). This exchange can result in the phase behavior becoming overoptimum, with resulting large surfactant retention (Glover et al. 1979, Gupta 1981). Alkali anions (e.g., carbonate, silicate, and phosphate) that have low solubility product with divalent cations will sequester divalent cations to low concentrations (Holm and Robertson 1981). Hydroxide is not as effective for sequestration of calcium because the solubility product of calcium hydroxide is not very low. Sodium metaborate has recently been introduced as an alkali that may sequester divalent ions (Flaaten et al. 2009; Zhang et al. 2008). A common problem

with alkali injection is that softened water is needed to avoid scaling.

Generation of Soap. The original concept of alkali flooding was the reduction of oil/water IFT by in-situ generation of soap, which is an anionic surfactant, sodium naphthenate (Jennings 1975). Ultralow IFT usually required injection of relatively fresh water with a low concentration of alkali because optimal salinity (total electrolyte concentration) of the in-situ-generated soap is usually low (e.g., <1% electrolyte). If the alkali concentration is too low, alkali consumption reactions may result in a large retardation of the alkali displacement front. The concept of alkaline/surfactant flooding is to inject a surfactant with the alkaline solution such that mixture of the in-situ-generated soap and injected surfactant has an optimal salinity that is tailored to the reservoir fluids (Nelson et al. 1984; Surkalo 1990).

The common method used to determine the amount of naphthenic acid in crude oil is the total acid number (TAN), determined by nonaqueous titration with a base (Fan and Buckley 2007). If sodium naphthenate is to act as a surfactant, it should partition into the aqueous phase at low electrolyte concentrations and be measurable by hyamine titration for anionic surfactants. It was found that the sodium naphthenate determined by extraction into the

aqueous phase and measured by hyamine titration is less than the TAN value (Liu et al. 2010). It is hypothesized that the TAN includes components that are too lipophilic to be extracted to the aqueous phase and/or too hydrophilic to be detected by hyamine titration.

Alkali Consumption. The ASP process should be designed such that displacement fronts of the alkali, surfactant, and polymer travel together. The mechanisms responsible for the retardation of the alkali front include silica dissolution, clay dissolution with zeolite precipitation, anhydrite or gypsum dissolution with calcite (or calcium hydroxide or silicate) precipitation, dolomite dissolution with calcium and magnesium silicate precipitation, hydrogen-ion exchange, divalent-ion exchange with precipitation, and mixing with divalent ions in formation water with precipitation (Ehrlich and Wygal 1977; Holm and Robertson 1981; Southwick 1985; Cheng 1986; Novosad and Novosad 1982; Jensen and Radke 1988; Mohammadi et al. 2009). Naphthenic acids in crude oil also react with alkali and thus contribute to consumption, but the amount is usually small compared to the mentioned inorganic mineral reactions. Silica dissolution can be controlled by using a buffered system such as sodium carbonate or silicate rather than hydroxide (Southwick 1985).

Clay dissolution is strongly dependent on the pH and type of clay, and is kinetically limited (Sydansk 1981). Thus, acidic clay such as kaolinite, as well as high temperature, will increase the importance of this mechanism.

A limitation of the application of sodium carbonate in carbonate formations is that if anhydrite or gypsum is present, it will dissolve and precipitate as calcite (Hirasaki, et al. 2005; Liu, 2007). This is detrimental for dolomite formations because they may have originated from evaporite deposits where gypsum is usually present. An alternative alkali is sodium metaborate (Zhang et al. 2008; Flaaten et al. 2009). However, longer-term experiments and equilibrium calculations indicate that this metaborate will also precipitate.

Alkaline/Surfactant Processes: Wettability Alteration

Wettability is the next most important factor in waterflood recovery after geology (Morrow 1990). The recovery efficiency of a flooding process is a function of the displacement efficiency and sweep efficiency. These efficiencies are a function of the residual-oil saturation (waterflood and chemical flood) and mobility ratio, respectively. The residual-oil saturation to waterflooding is a function of wettability, with the lowest value at intermediate

wettability (Jadhunandan and Morrow 1995). The mobility ratio is a function of the ratio of water relative permeability to oil relative permeability at their respective endpoints or at a specific saturation. The mobility ratio or relative permeability ratio becomes progressively larger as the wettability changes from water-wet to oil-wet (Anderson 1987b). When a formation is strongly oil-wet, it can have both a high waterflood residual-oil saturation and unfavorable mobility ratio. In addition, an oil-wet formation will have capillary resistance to imbibition of water (Anderson 1987a). Formation wettability can be altered by pH (Wagner and Leach 1959; Ehrlich et al. 1974; Takamura and Chow 1985; Buckley et al. 1989, Dubey and Doe 1993), surfactants that adsorb on the minerals (Somasundaran and Zhang 2006) or remove adsorbed naphthenic acids (Standnes and Austad 2000), and acids or bases (Cuiec 1977). These processes are now incorporated into chemical-flood simulators (Anderson et al. 2006; Delshad et al. 2006; Adibhatla and Mohanty 2007, 2008).

Sandstone Formations. Wettability alteration to more water-wet or more oil-wet conditions was proposed as one of the mechanisms of caustic flooding (Wagner and Leach 1959; Ehrlich et al. 1974; Johnson 1976). Our current understanding of

microemulsion phase behavior and wettability is that the system wettability is likely to be preferentially water-wet when the salinity is below the optimal salinity (Winsor I). When the system is overoptimum (Winsor II), macroemulsions tend to be oil-external. An oil-external macroemulsion will trap water and have a low oil and water relative permeability, similar to what one expects with oil-wet porous media. The optimal salinity for a conventional alkali flooding system is dependent on the in-situ-generated sodium naphthenate soap, and is usually below approximately 1% electrolyte strength. Because salinity of reservoir brine typically exceeds this value, a conventional alkali flood often generates overoptimum and oil-wet conditions. We show later in this review that this behavior can be avoided by injecting the alkali and surfactant in the Winsor I region. After mixing with the fluids in the reservoir of interest, it will pass through the Winsor III, low-IFT region. Even a high-salinity sandstone formation that is initially oil-wet may be altered to preferentially water-wet by injecting alkali with a hydrophilic surfactant in the Winsor I region.

Carbonate Formations. Wettability alteration has received more attention recently for carbonate formations compared to sandstones because carbonate formations are much more likely to be

preferentially oil-wet (Treiber et al. 1972). Also, carbonate formations are more likely to be fractured and will depend on spontaneous imbibition or buoyancy for displacement of oil from the matrix to the fracture.

Wettability-alteration tests on plates of calcite, marble, limestone, and dolomite with different surfactants and sodium carbonate have been used to identify many systems that are altered to preferentially water-wet with low anionic-surfactant concentrations (Hirasaki and Zhang 2004; Seethepalli et al. 2004; Zhang et al. 2006; Adibhatla and Mohanty 2008; Gupta et al. 2009). Sodium carbonate has an important role because the carbonate ion is a potential-determining ion for calcite and dolomite (Hirasaki and Zhang 2004).

Spontaneous Imbibition. Spontaneous imbibition is the process by which a wetting fluid is drawn into a porous medium by capillary action (Morrow and Mason 2001). The presence of surfactant in some cases lowers the IFT, and thus the capillary pressure, to negligible values. Spontaneous displacement can still occur in this case by buoyancy or gravity drainage (Schechter et al. 1994).

The research group of Austad has investigated spontaneous imbibition into chalk-formation material with enhancement by cationic and nonionic

surfactants and/or sulfate ions present in seawater (Austad, et al. 1998, Standnes and Austad 2000; Milner and Austad 1996a, 1996b; Høgnesen et al. 2004, 2006). Spontaneous imbibition was most effective with dodecyl trimethylammonium or amine surfactants. The mechanism is thought to be removal of adsorbed naphthenic acids through ion pairing with the cationic surfactant. Capillarity may dominate during earlier time, with gravity dominating later.

Laboratory and field testing of surfactant-enhanced imbibition was investigated for the dolomite formation of the Yates field (Chen et al. 2000; Yang and Wadleigh 2000). Both mass-balance and CT scans showed increased oil recovery with 0.35% nonionic and ethoxylated sulfate surfactants compared to reservoir brine. A single-well injection, soak, and production test showed increased oil recovery with decrease in water/oil ratio (WOR). The CT scans showed that with formation brine, the oil recovery involved countercurrent imbibition, but with surfactant, the displacement was dominated by gravity after early time.

An investigation compared the spontaneous recovery of the Yates system with 0.35% ethoxylated alcohol and dodecyl trimethylammonium bromide [C12TAB, Standnes et al. (2002)]. The superior recovery of C12TAB was interpreted to be caused by advancing contact angle of 32° for C12TAB,

compared with 107° for the ethoxylated alcohol and 133° for brine.

Laboratory measurements of spontaneous oil recovery were made on the Yates system or outcrop limestone with alkaline/surfactant solutions with 0.05% anionic surfactant and sodium carbonate (Hirasaki and Zhang 2004; Seethepalli 2004; Zhang et al. 2006; Adibhatla and Mohanty 2008). There was no recovery (Yates cores) or only little recovery (outcrop cores) with brine as the imbibing fluid. However, the alkaline/surfactant solutions recovered as much as 60% of the oil. For a given system, temperature is an important factor for wettability alteration and rate of imbibition oil recovery (Gupta and Mohanty 2010).

Surfactant-aided wettability alteration and spontaneous oil recovery may not have a significant contribution from capillary pressure if the IFT is reduced to ultralow values. However, in these conditions, gravity becomes an important contribution (Babadagli 2001; Hirasaki and Zhang 2004, Zhang et al. 2006; Adibhatla and Mohanty 2007; Gupta and Mohanty 2010, 2008). **Fig. 5** illustrates the simulated velocity field during spontaneous displacement for a cylindrical core immersed in a 0.05% alkaline/surfactant solution. The aqueous phase enters from the sides, and oil flows out from the top of the core. The significance

of gravity-dominated displacement is that time scales proportionally with the characteristic length of the matrix, whereas it would scale with the square of the length if the process were capillary dominated (Hirasaki and Zhang 2004).

Najafabadi et al. (2008) and Delshad et al. (2009) simulated cases of fractured oil-wet systems where negative capillary pressure inhibited oil displacement from the matrix. Wettability alteration and low IFT reduced the unfavorable capillary pressure so that the pressure gradient from flow in the fractures could displace oil from the matrix by viscous forces.

Emulsification of Heavy Oil. Alkali and surfactant can be used to recover viscous, heavy oil by emulsification and wettability alteration along with displacing the oil as a lower-viscosity, oil-in-water emulsion (Liu et al. 2006; Bryan et al. 2008; Li et al. 2010, Kumar and Mohanty, 2010, Kumar, et al. 2010).

Alkaline/Surfactant Processes: Wide Region of Ultralow IFT

Surfactant processes for enhancing oil recovery are based on achieving ultralow IFT (e.g., $<10^{-2}$ mN/m) to either raise the capillary number in forced displacement or to raise the Bond number for gravity-

driven displacement (Pennell et al. 1996) from a matrix that is surrounded by fractures or vugs bearing surfactant solution. For most anionic surfactants, especially those sensitive to divalent ions, ultralow IFT occurs only over a limited range of conditions [Healy et al. (1976); IFT vs. salinity plot shows a narrow region of ultralow IFT]. It has always been a process-design challenge to maintain or pass through these narrow conditions of Winsor III or middle-phase microemulsion to have ultralow IFT during the oil-recovery displacement process. Recently, it was found that blending alkyloxyated sulfate and IOS surfactants in an alkaline environment produced ultralow IFT for a wide range of conditions even when the system has Winsor I phase behavior. This is an important discovery because surfactant retention is much less for Winsor I compared with Winsor III phase behavior. These results are reviewed here.

Middle Layer of Lower-Phase Microemulsion.

When a salinity scan test is conducted at low surfactant concentrations (e.g., 0.05%), the equilibrium phase behavior appears to go from a lower-phase microemulsion to an upper-phase microemulsion over a narrow salinity range (**Fig. 6**) (Zhang et al. 2006; Liu et al. 2008). Middle-phase microemulsions are rarely seen at low surfactant concentrations; thus, IFT measurements for salinity

scans for low surfactant concentration are usually between the upper and lower phases observed in the sample tubes. The phases may be (1) lower-phase microemulsion and excess oil (Winsor I), (2) excess brine and upper-phase microemulsion (Winsor II), or (3) excess brine and excess oil (Winsor III). The value of the IFTs for these systems, measured between the upper and lower phases, was not reproducible until a protocol was developed to include a small volume of intermediate-density material in conducting spinning-drop measurement. In Winsor III, this material would include the middle-phase microemulsion. In Winsor I (lower-phase microemulsion or underoptimum salinity), this intermediate-density material appeared to be a colloidal dispersion in the lower-phase microemulsion (**Fig. 7**). This colloidal dispersion formed a middle layer between the excess oil and lower-phase microemulsion of alkaline/surfactant systems with crude oil with a TAN of 0.3 mg KOH/g or greater. This middle layer was more opaque than the rest of the lower-phase microemulsion, and can be interpreted to be more oil-rich from its intermediate density. When the oil/water ratio is increased, the volume of this layer also increased. Because this layer is not observed in the absence of alkali, it is hypothesized that the dispersed colloidal material is an oil-and-sodium naphthenate-rich

microemulsion that is in equilibrium with the remainder of the lower-phase microemulsion. As shown later, the soap is more lipophilic than the added surfactant. This layer is not just a macroemulsion dispersion that has not yet coalesced because the presence of this material affects the value of the IFT.

IFT With and Without Alkali. The IFT of the system with and without alkali was measured to test the hypothesis that the soap generated by the alkali is responsible for the ultralow IFT in the presence of the colloidal-dispersion material. **Fig. 8** compares the measured IFT with and without alkali. In the absence of alkali, the lower-phase microemulsion was homogeneous, and the ultralow IFT occurred only near the optimal salinity, as expected for conventional surfactant EOR systems. In the presence of alkali and using the protocol to ensure that a small volume of colloidal dispersion was present, a wider, ultralow IFT region was observed, especially for underoptimum conditions. If the colloidal dispersion is not present as a result of creaming or centrifugation, IFT behavior is similar to that in the absence of alkali [Liu et al. (2008), Fig. 14]. Apparently, this colloidal dispersion contains surface-active species responsible for lowering IFT between the lower-phase microemulsion and the

excess-oil phase in a manner similar to behavior of the middle-phase microemulsion between the excess-brine and excess-oil phases.

Consistent With Solubilization Parameter. The wide range of ultralow IFT was verified by comparison with the Huh correlation (Huh 1979). The solubilization ratios of the alkaline NI blend with Yates crude oil are shown in **Fig. 9**. The IFTs calculated from the Huh correlation and measured by spinning drop are shown in **Fig. 10**. Thus, the measured IFT is consistent with the volume of oil that is solubilized into the microemulsion phase(s)/volume of surfactant. The generality of the wide ultralow IFT was tested with another crude oil with a TAN of 4.79 mg KOH/g. The lower-phase microemulsion of this crude oil was too dark to observe the spinning drop for IFT measurements. The IFT estimated from the Huh correlation shows this crude oil to also have a wider, ultralow IFT region of salinities, especially in the underoptimum region (Liu et al. 2010).

Alkaline/Surfactant Processes: Phase

Behavior of Soap/Surfactant

Alkali saponifies the naphthenic acid in crude oil in situ to generate sodium naphthenate, a soap that helps to generate low IFT during the displacement process.

Thus, an alkaline/surfactant system should be considered as a pseudo-two-surfactant system featuring the injected surfactant and the soap. The two surfactants will likely have different optimal salinities. Thus, a mixing rule is needed to model how the optimal salinity changes with surfactant and soap concentrations.

WOR and Surfactant Concentration. Optimal salinity was observed to be a function of surfactant concentration and WOR for an alkaline/surfactant system (**Fig. 11**). However, all of these curves can be reduced to a single curve if plotted as a function of the soap/surfactant ratio (**Fig. 12**). The latter figure compares the curves of optimal salinity for the TC blend and NI blend surfactant formulations and the same crude oil.

Mixing Rule. The modeling of alkaline/surfactant flooding will benefit from a mixing rule for the optimal salinity. When the TAN was used for the soap content, the experimental data deviated significantly from the mixing rule of Salager et al. (1979). An alternative approach to determine the soap content of crude oil is to extract soap from the crude oil into alkaline, alcoholic water and titrate for anionic-surfactant content by hyamine titration. (An alternative to analytical determination of the

extractable soap content is to estimate a value that will result in the best fit to Eq. 1.)

The Salager et al. (1979) mixing rule was found to be followed reasonably well when the aqueous-titration method was used to quantify the soap content of the crude oil (**Fig. 13**, right panel). The expression for the mixing rule is

$$\log(Opt_{mix}) = X_{soap} \log(Opt_{soap}) + (1 - X_{soap}) \log(Opt_{surfactant})$$

where

$$X_{soap} = \frac{\text{Soap}}{\text{Soap} + \text{Surfactant}}, \quad \text{mole fraction} \quad \dots(1)$$

The optimal-salinity mixing rule is used in UTCHEM for simulation of alkaline/surfactant processes (Mohammadi et al. 2009). In addition, the researchers found that the optimum solubilization ratio follows a linear mixing rule:

$$\sigma_M^* = X_{soap} \sigma_{soap}^* + X_{surfactant} \sigma_{surfactant}^* \quad \dots\dots\dots(2)$$

where σ_M^* , σ_{soap}^* , and $\sigma_{surfactant}^*$ are the optimal solubilization ratio of the mixture, soap, and surfactant, respectively.

IFT Measurements. The dependence of the optimal salinity on the soap/surfactant ratio can be used to explain the difference of minimum-equilibrium IFT that may be observed with different surfactant concentrations and WOR. This also explains why the

minimum IFT of small oil drops on a calcite plate occurred at the optimal salinity of the TC blend surfactant with zero soap fraction (i.e., 10–12% NaCl) [Zhang et al. (2006); Figs. 4 and 13]. The WOR of the small drops was very high. Equilibrium IFT measurements had lower optimal salinity because the soap/surfactant ratios were larger owing to lower WORs.

The dependence of optimal salinity on the soap/surfactant ratio also explains the transient minimum IFT observations in spinning-drop measurement of a fresh oil drop in fresh surfactant solution (Liu 2007). The soap concentration of the oil drop is changing as soap is being extracted from the small oil drop into the much larger volume of surfactant solution. Thus, the soap/surfactant concentration ratio of the oil drop changes from a large value to near zero with time, and the minimum IFT (in time) occurs when the soap/surfactant ratio of the oil drop corresponds to the ratio that is optimal for the salinity of the surfactant solution.

Composition Gradients

Displacement of residual oil by surfactant flooding requires reducing the IFT to ultralow values such that disconnected oil droplets can be mobilized. The ultralow IFT generally exists only in a narrow salinity range near the optimal salinity. During the

1970s and 1980s, two schools of thought developed about how ultralow IFT could be achieved in the displacement process (Gupta and Trushenski 1979). One approach is to either preflush the formation to reduce the formation salinity to a value near optimal, or to design the surfactant formulation such that the optimal salinity is equal to the formation salinity, with the surfactant slug and drive injected at the formation salinity (Maerker and Gale 1992). In the former case, success was limited because the more viscous surfactant slug contacted portions of the reservoir that the preflush bypassed. In the latter case, this problem is avoided because there is no change in salinity because of dispersive mixing or crossflow. The other approach is to have a salinity gradient such that the system has overoptimum salinity ahead of, and underoptimum salinity behind, the active region. In this case, the salinity profile is certain to pass through the optimal salinity somewhere in the displacement-front region (Nelson 1981).

Whether the salinity is constant or a salinity gradient is used, the electrolyte composition is further challenged by divalent ions in the formation brine and ion exchange from the clays to the flowing phases (Hill et al. 1977; Pope et al. 1978; Glover et al. 1979; Gupta 1981). It was discovered that the surfactant micelles or microemulsion droplets have an affinity for divalent ions similar to that of the

clays, and thus act as a flowing ion-exchange medium (Hirasaki 1982; Hirasaki and Lawson 1986). The problem of divalent ions is avoided by use of an alkali such as sodium carbonate or sodium silicate (Holm and Robertson 1981).

Salinity Gradient. It was demonstrated that with a salinity gradient,

1. Ahead of the active region, the system is overoptimum; surfactant is retarded by partitioning into the oil-phase.

2. The system passes through the active region of ultralow IFT (Winsor III) where residual-oil displacement takes place.

3. Behind the active region, the system is underoptimum, with lower-phase microemulsion, and the surfactant propagates with the water velocity (Glover et al. 1979; Pope et al. 1979; Hirasaki et al. 1983). Thus, the salinity gradient tended to focus the surfactant near the advancing displacement front where salinity is optimal and the phase behavior is Winsor III (**Fig. 14**). Also, the salinity gradient helps to maintain polymer flow in the same phase with the surfactant for the Winsor I conditions behind the active region. The polymer is in the excess-brine phase in the Winsor II and III phase environments (Gupta 1981, Tham et al. 1983). The example in **Fig. 15** was injected overoptimum only for illustration of

surfactant transport with respect to salinity environment. Overoptimum salinity environments (Winsor II) can have viscous, high-internal-phase, water-in-oil emulsions [Hirasaki et al. (1983), Fig. 14] that may be bypassed by the subsequent lower-salinity fluids. In practice, the surfactant slug is injected in a near-optimal to under-optimum salinity environment. Therefore, the gradient basically provides assurance that if overoptimum conditions are unexpectedly reached during the process, the lower salinity injected later will allow optimal conditions to be achieved and will release surfactant trapped in the oil.

Soap/Surfactant Gradient. It was mentioned earlier that the optimal salinity changes as the soap/surfactant ratio changes. Thus, an alkaline/surfactant flood will have a gradient of optimal salinity because of a gradient in the soap/surfactant ratio unless the soap content is negligible or the surfactant and soap have identical optimal salinity (although surfactant would likely not be used if the soap had a suitable optimal salinity). A gradient in the soap/surfactant ratio exists because soap is generated in situ by interaction between the alkali and the naphthenic acids in the crude oil, while the synthetic surfactant is introduced with the injected fluid.

The role of the soap/surfactant gradient in the ASP process was evaluated with a 1D finite-difference simulator (Liu et al. 2008, 2010). Example composition and IFT profiles (Fig. 15) show the IFT dropping to ultralow values in a narrow region of the profile as the optimal salinity passes across the system salinity, which was constant in this example. There is only a short distance for the oil saturation to be reduced to a low value before the IFT again increases and traps any oil that has not been displaced. The oil saturation that will be trapped is approximately the saturation where the slope of the ultralow-IFT oil/water fractional-flow curve becomes less than the dimensionless velocity of the displacement front (Pope 1980; Hirasaki 1981; Ramakrishnan and Wasan 1988, 1989). Thus mobility control is important for displacement efficiency in addition to sweep efficiency for ASP flooding. Finite-difference simulation showed that recovery decreased from 95 to 86% as the aqueous viscosity decreased from 40 to 24 cp for oil with viscosity of 19 cp (Liu et al. 2008). This is consistent with a pair of experiments that differed only in polymer concentration.

The effects of salinity, surfactant concentration, acid number, slug size, and dispersion on oil recovery are illustrated for a 0.2-PV slug and laboratory-scale dispersion ($Pe = 500$) in **Fig. 16** (Liu et al. 2010). The

system is the one discussed in the IFT and phase-behavior sections, and the black dot in **Fig. 17** represents conditions of the successful sandpack experiment mentioned previously. The effects of surfactant concentration and acid number (soap content of the crude oil) are combined in a single parameter—the soap fraction at the waterflood residual-oil saturation. The range of salinity for greater-than-90% oil recovery is a function of the soap fraction. The salinity for maximum oil recovery decreases from optimal salinity of the surfactant to that of soap as the soap fraction increases (straight line in the figure). The range of salinities for potentially high oil recovery is substantial, especially in the underoptimum region below the optimal line.

If the dispersion is increased to a representative field-scale value [$Pe = 50$, Lake (1989)] with constant salinity and a 0.2-PV slug, the region of greater-than-90% recovery all but disappears. Dilution by mixing at the front and back of the surfactant slug lowers the surfactant concentration more than the soap concentration, and the propagation velocity of the soap/surfactant ratio for optimal salinity is greatly retarded. However, if the system is operated with a salinity gradient, high oil recovery is again possible (Liu et al. 2010). The lower salinity of the drive compensates for the lower surfactant concentration such that the region of optimal salinity again

propagates with a near-unit velocity. In addition, injection of the surfactant slug and polymer drive with a salinity that is less than the optimal salinity of the surfactant alone makes it possible to inject the surfactant slug with polymer without separation of the surfactant and polymer into separate phases (Gupta 1981; Liu et al. 2008). Also, the salinity gradient avoids the large surfactant retention from microemulsion trapping by the polymer drive (Glover et al. 1979; Hirasaki et al. 1983).

Foam Mobility Control

Foam is usually considered as a means of mobility control for gas-injection processes such as steam foam or CO₂ foam. Foam mobility control for surfactant flooding is a natural progression because the system already has surfactant present (Lawson and Reisberg 1980). Moreover, at high temperatures, foam may be favored because polymer degradation is a concern (Srivastava and Nguyen 2010). In fact, foam was used for mobility control for alkaline/surfactant flooding in China (Zhang et al. 2000; Wang et al. 2001). Recently, it has been used to improve sweep in surfactant/polymer flooding (Kang et al. 2010). It has also been used as mobility control for surfactant aquifer remediation (Hirasaki et al. 1997, 2000). Nonionic surfactants have been evaluated for mobility control of CO₂ EOR (Adkins

et al. 2010a, b). They can be injected dissolved in the CO₂ phase and have less adsorption on carbonate formations compared with anionic surfactants. If, in addition, the oil/water IFT can be reduced to ultralow values, a low-tension CO₂ EOR process may be applicable for reservoirs with pressures below the minimum miscibility pressure.

ASP Foam. The reduction of surfactant adsorption with alkali may result in the polymer being the most expensive chemical in the ASP process. Experiments in 1D sandpacks have shown that an ASP process with the polymer drive replaced by a foam drive is equally efficient. Fig. 17 is an experiment in which the ASP slug is alternated with equal-sized slugs of gas. The foam drive consists of slugs of the better-foaming surfactant component (without polymer) alternated with equal-sized slugs of gas (Li et al. 2010). Practically all of the 19-cp oil was recovered after 1.2 TPV injected, but with only 0.6 PV of liquid injected. Experiments with different sands indicated that foam reduced mobility more in higher-permeability media, making it particularly attractive in layered systems.

ASP foam was used to recover a 266-cp, 4.8-mg KOH/g TAN crude oil (**Fig. 18**). What was remarkable is that the apparent viscosity of the displacement process was only 80 cp or less.

Apparently, the viscous oil was being transported as an oil-in-water emulsion with much less resistance than that of the crude oil.

Sweep of Layered Sands. Fig. 19 compares sweep in two cases of a 19:1 permeability contrast layered sandpack initially filled with water dyed green. The sandpack is nearly completely swept with 1.0 TPV of surfactant alternating with gas (SAG) while the low-permeability layer is only one-quarter swept with water only (Li et al. 2010). The sweep efficiency is compared in Fig. 20 as a function of the PV of liquid injected for SAG, water alternating gas, and waterflooding.

Potential for Fractured Formations. The improvement of sweep in layered sands suggests that foam may be helpful in the sweep of a system of fractures. Yan et al. (2006) showed that pregenerated foam does improve the sweep of parallel plates with different apertures to simulate heterogeneous, parallel fractures. Also, the increased pressure gradient caused by foam flow in the fractures increases the driving force for displacement of oil from the matrix (Haugen et al. 2010; Abbasi-Asi et al. 2010). Farajzadeh et al. (2010) describe how the viscous pressure gradient caused by foam flow in fractures can accelerate the production of oil that would

otherwise be produced from the matrix by gravity drainage.

Field Pilots

A pilot of the alkaline/surfactant process is described by Falls et al. (1994). This pilot was tested without polymer, with the intention of a subsequent test with polymer. Nevertheless, the interpretation of induction logs suggested 100% displacement efficiency in the region swept by the injected fluids.

A refinement of the alkaline/surfactant process with recent understanding about the IOS is described by Buijse et al. (2010). The paper also discusses the importance of the crude-oil composition. The process was tested in the field with a single well chemical-tracer test. Stoll et al. (2010) describe pilot tests in Oman.

Gao and Gao (2010) summarized the pilots in Daqing oil field.

Conclusions

The technology of surfactant flooding has advanced to overcome many of the past causes of failures and to reduce the amount of surfactant required. These developments are summarized as follows:

1. Surfactant adsorption can be significantly reduced in sandstone and carbonate formations by injection of an alkali such as sodium

- carbonate. The alkali also sequesters divalent ions. The reduced adsorption permits lower surfactant concentrations.
2. A wide selection of surfactant structures is now available to meet requirements for specific applications.
 - a. Branched alcohol alkoxyate sulfates and sulfonates are tolerant of divalent ions. Ethoxylation increases optimal salinity; propoxylation decreases optimal salinity. In both cases, EO or PO, the optimal salinity decreases with increasing temperature.
 - b. Alkyloxyated glycidyl ether sulfonate is more expensive than sulfate but is stable at elevated temperatures.
 - c. IOSs are low-cost, double-tailed surfactants.
 3. Aqueous solutions of a blend of N67-7PO sulfate and IOS1518 with alkali have a larger single-phase region extending to higher salinities and calcium-ion concentrations than either alone. This blend, without alcohol, can form a single phase for injection with polymer but can form microemulsions with crude oil without forming a gel.
 4. Soap generated in situ by the alkali is a cosurfactant that can change the phase behavior of the injected surfactant solution from lower- to middle- to upper-phase microemulsions. It is lower phase when injected, middle phase at the displacement front, and upper phase ahead of the displacement front.
 5. Injection of the surfactant and polymer at salinity that is underoptimum with respect to the injected surfactant avoids surfactant/polymer phase separation and microemulsion trapping.
 6. The soap generated in situ by the alkali causes a middle layer to form and coexist with the lower-phase microemulsion, which results in ultralow IFT over a wide range of salinity.
 7. Anionic surfactants and sodium carbonate can alter wettability for either sandstone or carbonate formations. Spontaneous oil displacement can occur by gravity drainage.
 8. Foam can be used as the drive of the alkaline/surfactant process in place of the polymer drive.
 9. Foam can efficiently sweep layered and fractured systems.

Acknowledgments

The authors acknowledge the financial support by DOE grant DE-FC26-03NT15406 and the Rice University Consortium on Processes in Porous Media. The information and insight we gained from

our long collaboration with Gary Pope and Kishore Mohanty are also acknowledged.

References

- Abbasi-Asi, Y., Pope, G.A., Delshad, M. 2010. Mechanistic Modeling of Chemical Transport in Naturally Fractured Oil Reservoirs, SPE 129661, paper presented at the SPE IOR Symposium, Tulsa, OK, 24-28 April.
- Abe, M., Schechter, D., Schechter, R.S., Wade, W.H., Weerasooriya, U., and Yiv, S. 1986. Microemulsion Formation with Branched Tail Polyoxyethylene Sulfonate Surfactants, *JCIS*, Vol. 114, No. 2, 342-356.
- Adams, W.T. and Schievelbein, V.H. 1984. Surfactant flooding carbonate reservoirs, SPE/DOE 12686, presented at Symp. on EOR, Tulsa, OK.
- Adibhatia, B. and Mohanty, K.K. 2007. Simulation of Surfactant-Aided Gravity Drainage in Fractured Carbonates, SPE 106161 presented at the SPE Simulation Symp., Houston, TX, 26-28 Feb.
- Adibhatia, B. and Mohanty, K.K. 2008. Oil Recovery from Fractured Carbonates by Surfactant-Aided Gravity Drainage: Laboratory Experiments and Mechanistic Simulations, *SPE&E*, Feb., 119-130.
- Adkins, S. S., Chen, X., Chan, I., Torino, E., Nguyen, Q. P., Sanders, A., and Johnston, K. P., 2010. Morphology and Stability of CO₂-in-Water Foams with Nonionic Hydrocarbon Surfactants,” *Langmuir*, 26(8), 5335-5348.
- Adkins, S. S., Chen, X., Nguyen, Q. P., Sanders, A. W., and Johnston, K. P., 2010. “Effect of branching on the interfacial properties of nonionic hydrocarbon surfactants at the air-water and carbon dioxide-water interfaces,” *J.C.I.S.* 346 455–463
- Anderson, G.A., Delshad, M., King, C.B., Mohammadi, H, Pope, G.A. 2006. Optimization of Chemical Flooding in a Mixed-Wet Dolomite Reservoir, SPE 100062 presented at the SPE/DOE IOR Symp., Tulsa, OK, 22-26 April.
- Anderson, W.G. 1987a. Wettability Literature Survey – Part 4: Effects of Wettability on Capillary Pressure, *JPT*, Oct., 1283-1300.
- Anderson, W.G. 1987b. Wettability Literature Survey – part 5: The Effect of Wettability on Relative Permeability, *JPT*, Nov., 1453-1468.
- Atkinson, H. 1927. U.S. Patent 1,651,311.
- Austad, T., Matre, B., Milter, J., Saevareid, A., and Oyno, L. 1998. Chemical flooding of oil

- reservoirs 8. Spontaneous oil expulsion from oil- and water-wet low permeability chalk material by imbibition of aqueous surfactant solutions, *Colloids and Surfaces A. Physicochemical and Engineering Aspects*, Vol. 137, 117-129.
- Babadagli, T. 2001. Scaling of Cocurrent and Countercurrent Capillary Imbibition for Surfactant and Polymer Injection in Naturally Fractured Reservoirs, *SPEJ*, Dec., 465-478.
- Bae, J.J. and Petrick, C.B. 1977. Adsorption/Retention of Petroleum Sulfonate in Berea Cores, *SPEJ*, Oct., 353-357.
- Barnes, J., Smit, J.P., Smit, J.R., Shpakoff, P.G., Raney, K.H., and Puerto, M.C. 2008. Development of surfactants for chemical flooding at difficult reservoir conditions, SPE 113313, presented at SPE/DOE IOR Symp., Tulsa, OK, 19-23 April.
- Barnes, J.R., Dirkzwager, H., Smit, J.R., Smit, J.P., On, A., Navarrete, R.C., Ellison, B.H., and Buijse, M.A. 2010. Application of Internal Olefin Sulfonates and Other Surfactants to EOR. Part 1: Structure – Performance Relationships for Selection at Different Reservoir Conditions. SPE 129766, paper presented at the SPE IOR Symposium, Tulsa, OK, 24-28 April.
- Baviere, M., Glenat, P., Plazanet, V., and Labrid, J. 1995. Improved EOR by Use of Chemicals in Combination, *SPEE*, Aug., 187-193.
- Benton, W.J. and Miller, C.A. 1983. Lyotropic liquid crystalline phases and dispersions in dilute anionic surfactant-alcohol-brine systems. 1. Patterns of phase behavior, *J. Phys. Chem.*, 87, 4981-4991.
- Bourrel, M. and Schechter, R.S. 1988. *Microemulsions and related systems*, Surface Science Series, Vol. 30, Marcel Dekker, Inc., New York.
- Buckley, J.S., Takamura, K., and Morrow, N.R. 1989. Influence of Electrical Surface Charges on the Wetting Properties of Crude Oil, *SPEE*, Aug., 332-340.
- Buijse, M.A., Prelicz, R.M., Barnes, J. R., and Cosmo, C. 2010. Application of Internal Olefin Sulfonates and Other Surfactants to EOR. Part 2: The Design and Execution of an ASP Field Test. SPE 129769, paper presented at the 2010 SPE IOR Symposium, Tulsa, OK, 24-28 April.
- Bryan, J, Mai, A., and Kantzas, A. 2008. Investigation into the Process Responsible for Heavy Oil Recovery by Alkali-

- Surfactant Flooding, SPE 113993, paper presented at the SPE/DOE Symposium on IOR, Tulsa, OK, 20-23 April.
- Cayias, J.L., Schechter, R.S., and Wade, W.H. 1977. The Utilization of Petroleum Sulfonates for Producing low Interfacial Tensions between Hydrocarbons and Water, *J. Colloid Interface Sci.*, 59.1, 31-38.
- Chen, H.L., Lucas, L.R., Nogaret, L.A.D., Yang, H.D., and Kenyon, D.E. 2000. Laboratory Monitoring of Surfactant Imbibition Using Computerized Tomography, SPE 59006 paper prepared for presentation at the 2000 SPE IPCE, Villahermosa, Mexico, 1-3 February.
- Cheng, K.H. 1986. Chemical Consumption During Alkaline Flooding: A Comparative Evaluation, SPE/DOE 14944 presented at the SPE/DOE Fifth Symposium on EOR, Tulsa, OK, 20-23 April.
- Cuiec, L. 1977. Study of Problems Related to the Restoration of the Natural State of Core Samples. *J. of Canadian Pet. Tech.*, Oct.-Dec., 68-80.
- Delshad, M., Najafabadi, N.F., Anderson, G.A., Pope, G.A., and Sepehmooi, K. 2006. Modeling Wettability Alteration in Naturally Fractured Reservoirs, SPE 100081 presented at the SPE/DOE Symposium on IOR, Tulsa, OK, 22-26 April.
- Delshad, M., Najafabadi, N.F., and Sepehmooi, K. 2009. Scale Up methodology for Wettability Modification in Fractured Carbonates, SPE 118915, paper presented at the SPE Reservoir Simulation Sympisum, Woodlands, TX, 2-4 February.
- Dubey, S.T. and Doe, P.H. 1993. Base Number and Wetting Properties of Crude Oil, *SPE*, August, 195-200.
- Dwarakanath, V., Chaturvedi, T., Jackson, A.C., Malik, T., Siregar, A., and Zhao, P. 2008. Using Co-Solvents to Provide Gradients and Improve Oil Recovery during Chemical Flooding in a Light Oil Reservoir, SPE 113965, paper presented at the SPE/DOE IOR Symp., 19-23 April.
- Ehrlich, R., Hasiba, H.M., and Raimondi, P. 1974. Alkaline Waterflooding for Wettability Alteration-Evaluating a Potential Field Application, *JPT*, Dec. 1335-1342.
- Ehrlich, R. and Wygal, R.J. 1977. Interrelation of Crude Oil and Rock Properties with the Recovery of Oil by Caustic Waterflooding, *SPEJ*, Aug., 263-270.
- Falls, A.H., Thigpen, D.R., Nelson, R.C., Claston, J.W., Lawson, J.B., Good, P.A., Ueber,

- R.C., and Shahin, G.T. 1994. Field Test of Cosurfactant-Enhanced Alkaline Flooding, *SPE*, Aug. 217-223.
- Fan, T. and Buckley, J.S. 2007. Acid Number Measurements Revisited, *SPEJ*, Dec., 496-500.
- Farajzadeh, R., Wassing, B., and Boerrigter, P. 2010. Foam Assisted Gas Oil Gravity Drainage in Naturally-Fractured Reservoirs, SPE 134203, paper presented at the SPE ATCE, Florence, Italy, 19-27 September.
- Flaaten, A.K., Nguyen, Q.P., Pope, G.A., and Zhang, J. 2009. A Systematic laboratory Approach to Low-Cost, High-Performance Chemical Flooding, *SPE Res. Eval. Eng.*, 12(5), 713-723. SPE-113469-PA)
- Foster, W.R. 1973. A low-tension waterflooding process, *JPT*, 25, 205.
- Gao, S. and Gao, Q. 2010. Recent Progress and Evaluation of ASP Flooding for EOR in Daqing Oil Field, SPE 127714, paper presented at the SPE EOR Conference at Oil & Gas West Asia, Muscat, Oman, 11-13 April.
- Ghosh, O. 1985. Liquid crystal to microemulsion transitions in anionic surfactant-oil-brine systems, PhD thesis, Rice University.
- Glover, C.J., Puerto, M.C., Maerker, J.M., and Sandvik, E.L. 1979. Surfactant Phase Behavior and Retention in Porous Media, *SPEJ*, June, 183-193.
- Gogarty, W.B. 1977. Oil recovery with surfactants: history and a current appraisal, in *Improved Oil Recovery by Surfactant and Polymer Flooding*, D.O. Shah and R.S. Schechter (eds.), Academic Press, New York, 27-54.
- Gupta, R. and Mohanty, K.K. 2010. Temperature effects on Surfactant-Aided Imbibition Into fractured Carbonates, *SPEJ*, September, 587-597.
- Gupta, R. and Mohanty, K.K. 2008. Wettability Alteration of Fractured Carbonate Reservoirs, SPE 113407 presented at the 2008 SPE/DOE IOR Symp., Tulsa, OK, 19-23 April.
- Gupta, R., Mohan, K., and Mohanty, K.K. 2009. Surfactant Screening for Wettability Alteration in Oil-Wet Fractured Carbonates, SPE 124822, presented at the SPE ATCE, New Orleans, LA, 4-7 October.
- Gupta, S.P. 1981. Dispersive Mixing Effects on the Sloss Field Micellar System, SPE/DOE 9782 presented at the SPE/DOE Second Joint Symp. on EOR, Tulsa, OK, 5-8 April.
- Gupta, S.P. and Trushenski, S.P. 1979. Micellar Flooding – Compositional Effects on Oil

- Displacement, *SPEJ*, April, 116-128; *Trans.*, AIME, 267.
- Haugen, A, Ferno, M.A., Graue, A., and Bertin, H.J. 2010. Experimental Study of Foam Flow in Fractured Oil-wet Limestone for Enhanced Oil Recovery, SPE 129763 paper presented at the SPE IOR Symposium, Tulsa, OK, 24-28 April.
- Healey, R.N. and Reed, R.L. 1974. Physicochemical Aspects of Microemulsion Flooding, *SPEJ*, Oct. 491-501; *Trans. AIME* 265.
- Healy, R.N., Reed, R.L., and Stenmark, D.G. 1976. Multiphase Microemulsion Systems, *SPEJ*, Vol. 16, 147-160; *Trans. AIME* 261.
- Hill, H.J., Helfferich, F.G., Lake, L.W., and Reisberg, J. 1977. Cation Exchange and Chemical Flooding, *JPT*, Oct., 1336-1338.
- Hill, H.J., Reisberg, J., and Stegemeier, G.L. 1973. Aqueous surfactant systems for oil recovery, *J. Pet. Technol.*, 25, 186-194.
- Hirasaki, G.J., 1981. Application of the Theory of Multicomponent, Multiphase Displacement to Three-Component, Two-Phase Surfactant Flooding, *SPEJ*, April, 191-204.
- Hirasaki, G.J. 1982. Ion Exchange with Clays in the Presence of Surfactant, *SPEJ*, April, 181-192.
- Hirasaki, G. J. et al.: 1997. "Field Demonstration of the Surfactant/Foam Process for Aquifer Remediation," SPE 39292, paper prepared for presentation at the 1997 ATCE San Antonio, TX, 5-8 October.
- Hirasaki, G.J., Jackson, R.E., Jin, M., Lawson, J.B., Londergan, J., Meinardus, H., Miller, C.A., Pope, G.A., Szafranski, R., and Tanzil, D. 2000. Field Demonstration of the Surfactant/Foam Process for Remediation of a Heterogeneous Aquifer Contaminated with DNAPL. *NAPL Removal: Surfactants, Foams, and Microemulsions*, S. Fiorenza, C.A. Miller, C.L. Oubre, and C.H. Ward, ed., Lewis Publishers.
- Hirasaki, G.J. and Lawson, J.B. 1986. An Electrostatic Approach to the Association of Sodium and Calcium with Surfactant Micelles, *SPEJ*, March, 119-130.
- Hirasaki, G.J., Miller, C.A., Pope, G.A. 2005. Surfactant Based Enhanced Oil Recovery and Foam Mobility Control; 2nd Annual Report to DOE, DE-FC26-03NT15406, July.
- Hirasaki, G.J., van Domselaar, H.R., and Nelson, R.C., 1983. Evaluation of the Salinity Gradient Concept in Surfactant Flooding, *SPEJ*, June, 486-500.
- Hirasaki, G.J. and Zhang, D.L. 2004. Surface Chemistry of Oil Recovery from Fractured,

- Oil-Wet, Carbonate Formations, *SPEJ*, June, 151-162.
- Høgnesen, E.J., Standnes, D.C. and Austad, T., 2004: Scaling Spontaneous Imbibition of Aqueous Surfactant Solution into Preferential Oil-Wet Carbonates. *Energy & Fuels*, 18, 1665-1675.
- Høgnesen, E.J., Olsen, M, and Austad, T. 2006. Capillary and Gravity Dominated Flow Regimes in Displacement of Oil from an Oil-Wet Chalk Using Cationic Surfactant, *Energy & Fuels*, Vol. 20, 1118-1122.
- Holm, L.W. 1977 Soluble oils for improved oil recovery, in *Improved Oil Recovery by Surfactant and Polymer Flooding*, D.O. Shah and R.S. Schechter (eds.), Academic Press, New York, 453-485.
- Holm, L.W. and Robertson, S.D. 1981. Improved Micellar/Polymer Flooding with High-pH Chemicals, *JPT*, January, 161-171.
- Huh, C. 1979. Interfacial Tensions and Solubilizing Ability of a Microemulsion Phase the Coexists with Oil and Brine, *JCIS*, Vol. 71, No. 2, 408-426.
- Jadhunandan, P.P. and Morrow, N.R. 1995. Effect of Wettability on Waterflood Recovery for Crude-Oil/Brine/Rock Systems, *SPERE*, Feb., 40-46.
- Jennings, H.Y, Jr. 1975. A Study of Caustic Solution-Crude Oil Interfacial Tensions, *SPEJ*, June, 197-202.
- Jensen, J.A. and Radke, C.J. 1988. Chromatographic Transport of Alkaline Buffers Through Reservoir Rock, *SPERE*, Aug., 849-856.
- Johnson, C.E., 1976. Status of Caustic and Emulsion Methods, *JPT*, Jan., 85-92.
- Kang, W., Liu, S., Meng, L., Cao, D. and Fan, H. 2010. A Novel Ultra-low Interfacial Tension Foam Flooding Agent to Enhance Heavy Oil Recovery. SPE 129175, paper presented at the SPE IOR Symposium, Tulsa, OK, 24-28 April.
- Kumar, R. and Mohanty, K.K. 2010. ASP Flooding of Viscous Oil, SPE 135265, paper presented at the APE ATCE, Florence, Italy, 19-22 September.
- Kumar, R., Dao, E., and Mohanty, K.K. 2010. Emulsion Flooding of Heavy Oil, SPE 129914, presented at the SPE IOR Symp. Tulsa, OK, 24-28 April.
- Lake, L.W., 1989. *Enhanced Oil Recovery*, Prentice Hall, Englewood Cliffs, NJ, pg. 166.
- Lawson, J.B. and Reisberg, J. 1980. Alternate Slugs of Gas and Dilute Surfactant for Mobility Control during Chemical Flooding, SPE 8839 presented at the SPE/DOE EOR Symposium, Tulsa, OK, 20-23 April.

- Levitt, D.B., Jackson, A.C., Heinson, C., Britton, L.N., Malik, T., Varadarajan, D., and Pope, G.A. 2009. Identification and evaluation of high-performance EOR surfactants, *SPE Res. Eval. Eng.*, 12(2), 243-253. (SPE-100089-PA)
- Li, R.F., Yan, W. Liu, S., Hirasaki, G.J., and Miller, C.A. 2010. Foam Mobility Control for Surfactant EOR, *SPEJ*, Vol. 15, No. 4, Dec. 928-942.
- Liu, Q., Dong, M., and Ma, S. 2006. Alkaline/Surfactant Potential in Western Canadian Heavy Oil Reservoirs, SPE 99791, paper presented at the SPE/DOE Symposium on IOR, Tulsa, OK, 22-26 April.
- Liu, S. 2007. Alkaline Surfactant Polymer Enhanced Oil Recovery Processes, Ph.D. thesis, Rice University.
- Liu, S., Zhang, D.L., Yan, W., Puerto, M., Hirasaki, G.J., and Miller, C.A. 2008. Favorable attributes of alkaline-surfactant-polymer flooding, *SPEJ*, 13, 5-16. (SPE-99744-PA)
- Liu, S., Li, R.F., Miller, C.A., and Hirasaki, G.J. 2010. Alkaline/Surfactant/Polymer Processes: Wide Range of Conditions for Good Recovery, *SPEJ*, 15, 282-293. (SPE-113936-PA)
- Lopez-Salinas, J.L., Miller, C.A., Koo, K.H.K., Puerto, M., and Hirasaki, G.J. 2009. Viscometer for opaque, sealed microemulsion samples, SPE 121575 presented at Intl. Symp. on Oilfield Chem., The Woodlands, TX.
- Lyklema, J. 1995. *Fundamentals of Interface and Colloid Science, Vol. II Interfaces*, Academic Press Inc., San Diego, A3.1-A3.6.
- Maerker, J.M. and Gale, W.W. 1992. Surfactant flood process design for Loudon, *SPEE*, 7, 36-44.
- Melrose, J.C. and Brandner, C.F. 1974. The role of capillary forces in determining microscopic displacement efficiency for oil recovery by waterflooding, *J. Canad. Petrol. Tech.*, 13, 54-62.
- Miller, C.A., Ghosh, O., and Benton, W.J. 1986. Behavior of Dilute Lamellar Liquid Crystalline Phases, *Colloids and Surfaces*, 19, 197-223.
- Milner, J. and Austad, T. 1996a. Chemical flooding of oil reservoirs 6. Evaluation of the mechanisms for oil expulsion by spontaneous imbibition of brine with and without surfactant in mixed-wet, low permeability chalk material, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, Vol. 117, 109-115.

- Milner, J. and Austad, T. 1996b. Chemical flooding of oil reservoirs 7. Oil expulsion by spontaneous imbibition of brine with and without surfactant in mixed-wet, low permeability chalk material, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, Vol. 117, 109-115.
- Mohammadi, H., Delshad, M., and Pope, G.A. 2009. Mechanistic Modeling of Alkaline/Surfactant/Polymer Floods, *SPE RE&E*, Vol. 12, No. 4, 518-527.
- Morrow, N.R. 1990. Wettability and Its Effect on Oil Recovery, *JPT*, Dec., 1476-1484.
- Morrow, N.R. and Mason, G. 2001. Recovery of oil by spontaneous imbibition, *Current opinion in Colloid & Interface Science*, Vol. 6, 321-337.
- Najafabadi, N.F., Delshad, M., Sepehrnoori, K., Nguyen, Q.P., and Zhang, J. 2008. Chemical Flooding of Fracture Carbonates Using Wettability Modifiers, SPE 113369 presented at the SPE/DOE IOR Symposium, Tulsa, OK, 19-23 April.
- Nelson, R.C., 1981. Further Studies on Phase Relations in Chemical Flooding, in *Surface Phenomena in Enhanced Oil Recovery*, Shah, D.O., ed., Plenum Press, New York, 73-104.
- Nelson, R.C., Lawson, J.B., Thigpen, D.R., and Stegemeier, G.L. 1984. Cosurfactant-Enhanced Alkaline Flooding, SPE/DOE 12672 presented at the SPE/DOE Fourth Symp. on EOR, Tulsa, OK April 15-18.
- Nelson, R.C. and Pope, G.A. 1978. Phase Relationships in Chemical Flooding, *SPEJ*, Vol. 18, 325-338.
- Novosad, Z. and Novosad, J. 1982. The Effect of Hydrogen Ion Exchange on Alkalinity Loss in Alkaline Flooding, SPE 10605 presented at the SPE 6th Int. Symp. on Oilfield and Geothermal Chemistry, Dallas, TX, 25-27 January.
- Pennell, K.D., Pope, G.A., and Abriola, L.M. 1996. Influence of Viscous and Buoyancy Forces on the Mobilization of Residual Tetrachloroethylene during Surfactant Flushing, *Environmental Science & Technology*, Vol. 30, No. 4, 1328-1335.
- Peru, D.A. and Lorenz, P.B. 1990, *SPE RE*, August, 327-332.
- Pope, G.A., Lake, L.W., Helfferich. 1978. Cation Exchange in Chemical Flooding: Part 1 – Basic Theory Without Dispersion, *SPEJ*, Vol. 18, No. 6, 418-434.
- Pope, G.A., 1980. The Application of Fractional Flow Theory to Enhanced Oil Recovery,

- SPEJ*, June, 191-205.
- Pope, G.A., Wang, B. and Tsaur, K. 1979. A Sensitivity Study of Micellar/Polymer Flooding, *SPEJ*, Dec., 357-368.
- Puerto, M., Hirasaki, G.J., and Miller, C.A. 2010. Surfactant systems for EOR in high-temperature, high-salinity environments, SPE-129675 presented at SPE Symposium on Improved Oil Recovery, Tulsa.
- Qutubuddin, S., Miller, C.A., Benton, W.J., and Fort, T., Jr. 1985. Effects of polymers, electrolytes, and pH on microemulsion phase behavior, in *Macro- and Microemulsions*, D.O. Shah (ed.), ACS Symp. Ser. 272, ACS, Washington, D.C., 223-251.
- Ramakrishnan, T.S. and Wasan, D.T. 1988. The Role of Adsorption in High pH Flooding, SPE 17408 presented at the SPE California Regional Meeting, Long Beach, CA, 23-25 March.
- Ramakrishnan, T.S. and Wasan, D.T. 1989. Fractional-Flow Model for High-pH Flooding, *SPERE*, Feb., 59-68.
- Reed, R.L. and Healy, R.N. 1977. Some physico-chemical aspects of microemulsion flooding: a review, in *Improved Oil Recovery by Surfactant and Polymer Flooding*, D.O. Shah and R.S. Schechter (eds.), Academic Press, New York, 383-437.
- Sahni, V., Dean, R.M., Britton, C., Weerasooriya, U., and Pope, G.A. 2010. The Role of Co-Solvents and Co-Surfactants in Making Chemical Floods Robust. 2010. SPE 130007, paper presented at the SPE IOR Symposium, Tulsa, OK, 24-28 April.
- Salter, S.J. 1977. The influence of type and amount of alcohol on surfactant-oil-brine phase behavior and properties, SPE 6843, presented at SPE Annual Meeting, Denver, CO.
- Salager, J.L., Bourrel, M., Schechter, R.S., and Wade, W.H. 1979. Mixing Rules for Optimum Phase-Behavior Formulations of Surfactant/Oil/Water Systems, *SPEJ*, Oct., 271-278.
- Schechter, D.S., Zhou, D., and Orr, F.M., Jr. 1994. Low IFT drainage and imbibition, *J. Pet. Sci. & Eng.*, Vol. 11, 283-300.
- Scriven, L.E. 1976. Equilibrium bicontinuous structure, *Nature*, Vol. 263, No. 5573, 123-125.
- Seethepalli, A., Adibhatla, B., and Mohanty, K.K. 2004. Physicochemical Interactions During Surfactant Flooding of Fractured Carbonate Reservoirs, *SPEJ*, Dec., 411-418.

- Somasundaran, P. and Zhang, L. 2006. Adsorption of surfactant on minerals for wettability control in improved oil recovery processes, *J. Pet. Sci. & Eng.*, Vol. 52, 198-212.
- Southwick, J.G. 1985. Solubility of Silica in Alkaline Solutions: Implications for Alkaline Flooding, *SPEJ*, Dec., 857-864.
- Srivastava, M. and Nguyen, Q.P. 2010. Application of Gas for Mobility Control in Chemical EOR in Problematic Carbonate Reservoirs, SPE 129840, paper presented at the SPE IOR Symposium, Tulsa, OK, 24-28 April.
- Standnes, D.C. and Austad, T. 2000. Wettability alteration in chalk 2. Mechanism for wettability alteration from oil-wet to water-wet using surfactants, *J. Pet. Sci. Eng.*, Vol. 28, 123-143.
- Standnes, D.C., Nogaret, L.A.D., Chen, H.-C., Austad, T. 2002. An Evaluation of Spontaneous Imbibition of Water into Oil-Wet Carbonate Reservoir Cores Using a Nonionic and a Cationic Surfactant, *Energy & Fuels*, Vol. 16, 1557-1564.
- Stegemeier, G.L. 1977. Mechanisms of entrapment and mobilization of oil in porous media, in *Improved Oil Recovery by Surfactant and Polymer Flooding*, D.O. Shah and R.S. Schechter (eds.), Academic Press, New York, 55-91.
- Stoll, W.M., al Shureqi, H., Finol, J., Al-Harthy, A.A., Oyemade, S., de Kruijf, A., van Wunnik, J., Arkesteijn, F., Bouwmeester, R., Faber, M.J. 2010. Alkaline-Surfactant-Polymer Flood: From the Laboratory to the Field, SPE 129164, paper presented at the SPE EOR Conference at Oil & Gas West Asia, Muscat, Oman, 11-13 April.
- Surkalo, H. 1990. Enhanced Alkaline Flooding, *JPT*, Jan., 6-7.
- Sydansk, R.D. 1981. Elevated Temperature Caustic-Sandstone Interactions – Implications for Improving Oil Recovery, SPE/DOE 9810 presented at the 1981 SPE/DOE Second Joint Symp. on EOR, Tulsa, OK, 5-8 April.
- Tabatabal, A., Gonzalez, M.V., Harwell, J.H., and Scamehorn, J.F. 1993. Reducing Surfactant Adsorption in Carbonate Reservoirs, *SPE RE*, May, 117-122.
- Taber, J.J. 1969. Dynamic and static forces required to remove a discontinuous oil phase from porous media containing both oil and water, *Soc. Pet. Eng. J.*, 9, 3-12.
- Takamura, K. and Chow, R.S. 1985. The Electrical Properties of the Bitumen/Water Interface – Part II. Application of the Ionizable Surface-Group Model, *Colloids and Surfaces*, Vol.

- 15, 35-48.
- Talley, L.D. 1988. Hydrolytic Stability of Alkylethoxy Sulfates, *SPE*, 3, 235-242.
- Tham, M.J., Nelson, R.C., and Hirasaki, G.J. 1983. Study of the Oil Wedge Phenomena through the Use of a Chemical Flood Simulator, *SPEJ*, Oct., 746-757.
- Treiber, L.E., Archer, D.L., and Owens, W.W. 1972. A Laboratory Evaluation of the Wettability of Fifty Oil-Producing Reservoirs, *SPEJ*, Dec., 531-540.
- Trushenski, S.P. 1977. Micellar flooding: sulfonate-polymer interaction, in *Improved Oil Recovery by Surfactant and Polymer Flooding*, D.O. Shah and R.S. Schechter (eds.), Academic Press, New York, 555-575.
- Uren, L.C. and Fahmy, E.H. 1927. Factors influencing the recovery of petroleum from unconsolidated sands by waterflooding, *Petrol. Dev. Technol.*, Petrol. Div. AIME, 318.
- Wagner, O.R. and Leach, R.O. 1959. Improving Oil displacement Efficiency by Wettability Adjustment, *Pet. Trans. AIME*, Vol. 216, 65-72.
- Wang, D., Cheng, J., Yang, Z., Li, Q., Wu, W., Yu, H. 2001. Successful Field Test of the First Ultra-Low Interfacial Tension Foam Flood. SPE 72147 presented at the SPE Asia Pacific Improved Oil Recovery Conference, 6-9 October, Kuala Lumpur, Malaysia.
- Wang, F.H.L. 1993. Effects of Reservoir Anaerobic, Reducing Conditions on Surfactant Retention in Chemical Flooding, *SPE*, May, 108-116.
- Wellington, S.L. and Richardson, E.A. 1997. Low Concentration Enhanced Waterflooding, *SPEJ*, 2, 389.
- Wessen, L.L. and Harwell, J.H. 2000. Surfactant Adsorption in Porous Media, in *Surfactants: Fundamentals and Applications in the Petroleum Industry*, Schramm, L.L., ed., Cambridge University Press, New York.
- Yan, W., Miller, C. A., Hirasaki, G. J., 2006. "Foam sweep in fractures for enhanced oil recovery," *Colloids & Surfaces A: Physico. Eng. Aspects*, 282-283, 348-359.
- Yang, H.D. and Wadleigh, E.E. 2000. Dilute Surfactant IOR – Design Improvement for Massive Fractured Carbonate Applications, SPE 59009, paper prepared for presentation at the 2000 SPE IPCE, Villahermosa, Mexico, 1-3 February.
- Zhang, R. and Somasundaran, P. 2006. Advances in adsorption of surfactants and their mixtures at solid/solution interfaces, *Adv. Colloid Interface Sci.*, Vol. 123-126, 213-229.

Zhang, D.L., Liu, S., Puerto, M., Miller, C.A., and Hirasaki, G.J. 2006. Wettability alteration and spontaneous imbibition in oil-wet carbonate formations, *J. Pet. Sci. Eng.*, 52, 213-226.

Zhang, J., Nguyen, Q.P., Flaaten, A.K., Pope, G.A. 2008. Mechanisms of Enhanced Natural Imbibition with Novel Chemicals, SPE 113453 paper prepared for presentation at the 2008 SPE IOR Symp., Tulsa, OK, 19-23 April.

Zhang, Y., Yue, X., Dong, J., Liu, Y. 2000. New and Effective Foam Flooding To Recover Oil in

Heterogeneous Reservoir. SPE 59367 presented at the SPE/DOE Improved Oil Recovery Symp., 3-5 April, Tulsa, OK.

Zhao, P., Jackson, A.C., Britton, C., Kim, D.H., Britton, L.N., Levitt, D.B., and Pope, G.A. 2008. Development of high-performance surfactants for difficult oils, SPE 113432, presented at SPE/DOE IOR Symp., Tulsa, OK, 19-23 April.

Author Bios

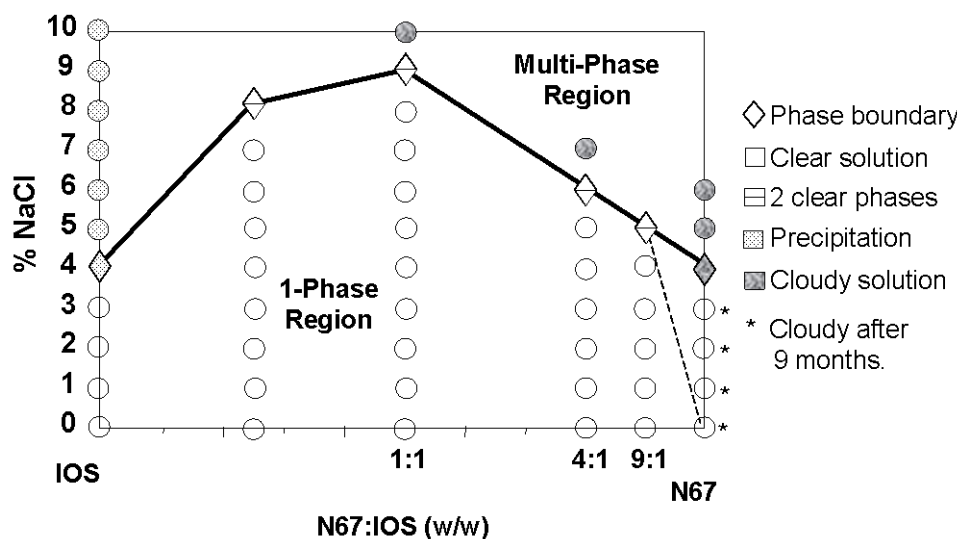


Fig. 1. Effect of added NaCl on phase behavior of 3 wt% solutions of N67/IOS mixtures containing 1 wt% Na_2CO_3 . (Liu, *et al.*, 2008)

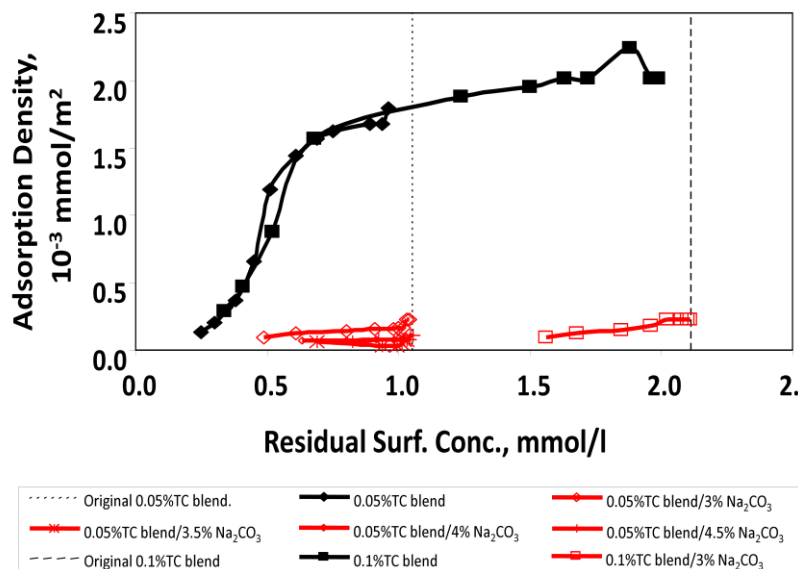


Fig. 2 Static adsorption of TC Blend surfactant on dolomite sand. BET surface area of the calcite: $17.8 \text{ m}^2/\text{g}$ (Zhang, *et al.*, 2006)

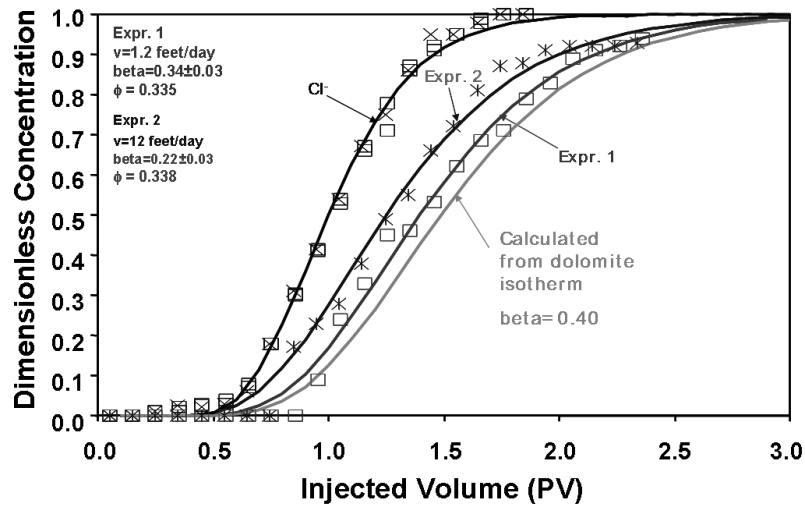


Fig. 3 Dynamic adsorption of 0.2% TC Blend surfactant without Na_2CO_3 on dolomite sand. (Zhang, et al., 2006)

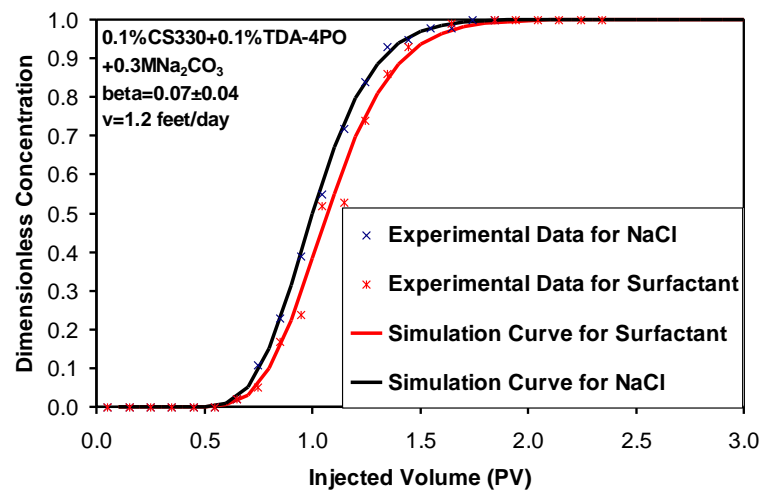


Fig. 4 Dynamic adsorption of 0.2% TC Blend/0.3M Na_2CO_3 on dolomite sand. (Zhang, et al., 2006)

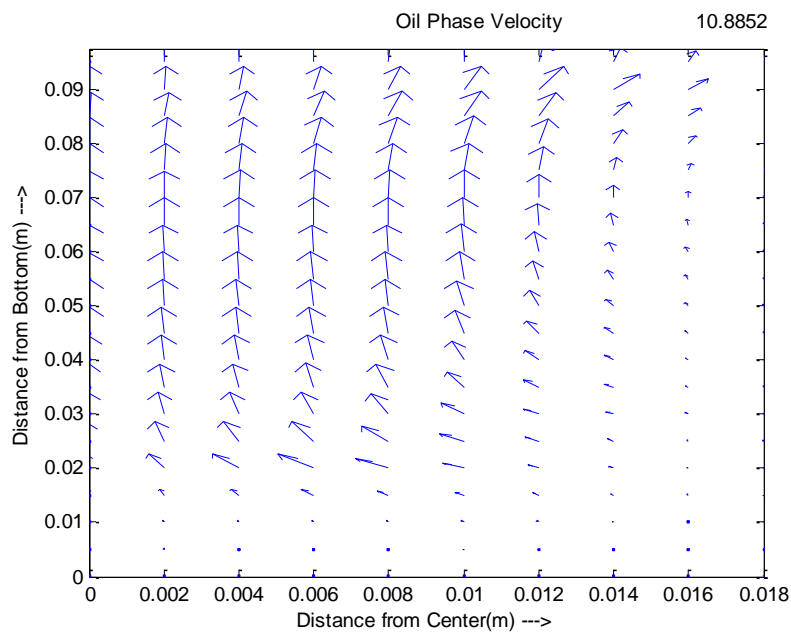
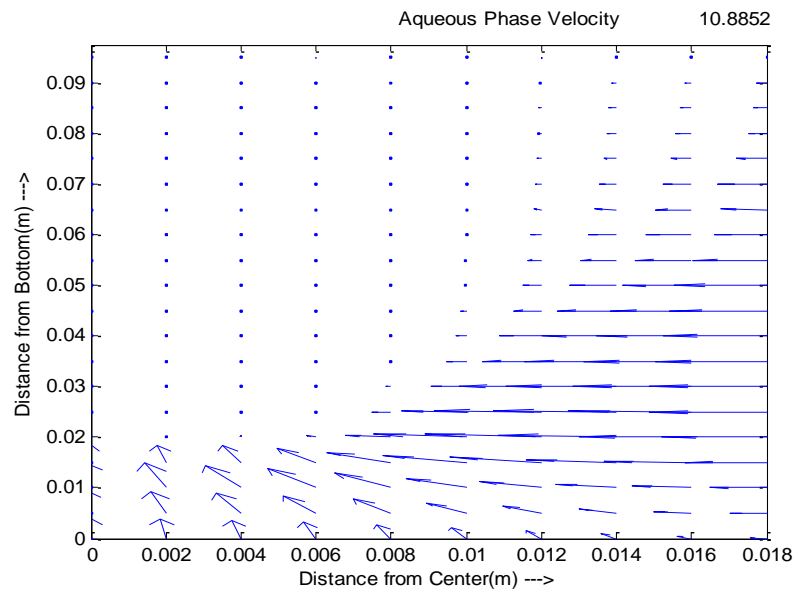


Fig. 5. Velocity field in a cylindrical core immersed in surfactant solution at 10.89 days (a) Aqueous phase (b) Oil phase (from Gupta and Mohanty, 2010)

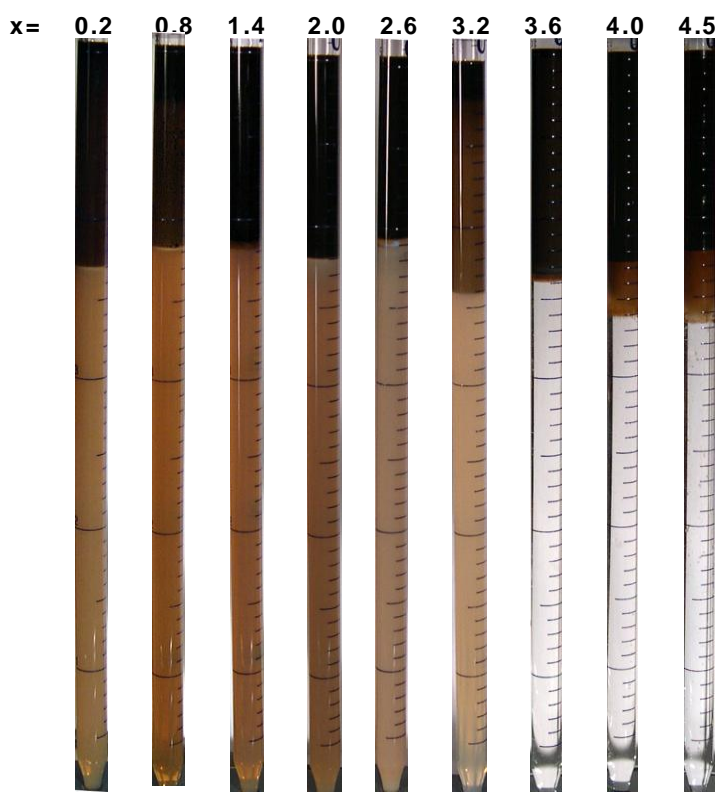


Fig. 6 Salinity scan for 0.2% NI blend, 1% Na_2CO_3 with MY4 crude oil for WOR=3 after settling time of 28 days at 25°C. x = wt.% NaCl. (from Liu, *et al.*, 2008)

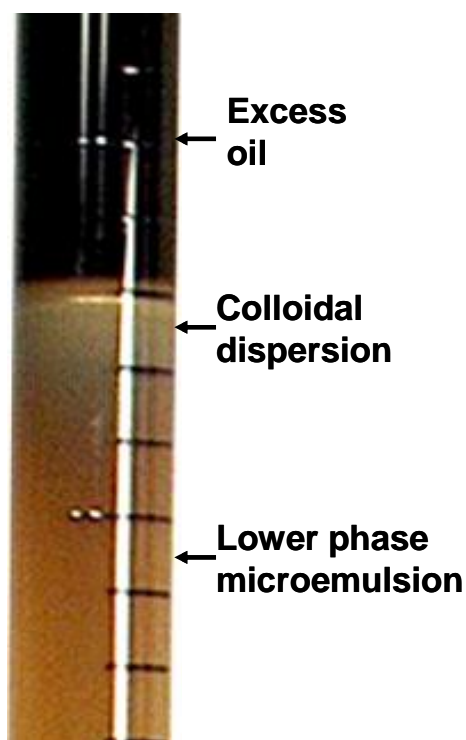


Fig. 7 View of colloidal dispersion region near interface for 2% NaCl sample from salinity scan after 23 days settling. (from Liu, *et al.*, 2008)

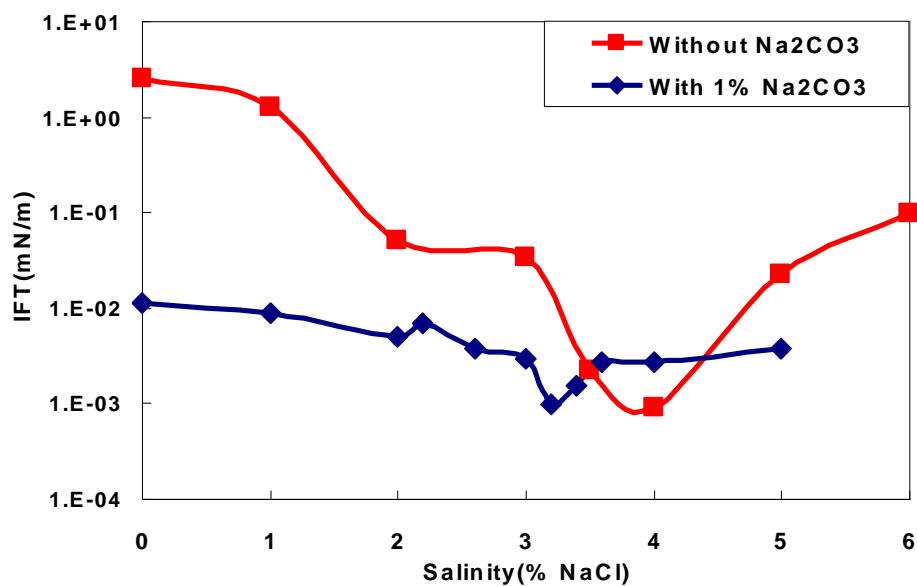


Fig. 8 Measured IFT of system with and without Na₂CO₃ (from Liu, *et al.*, 2008)

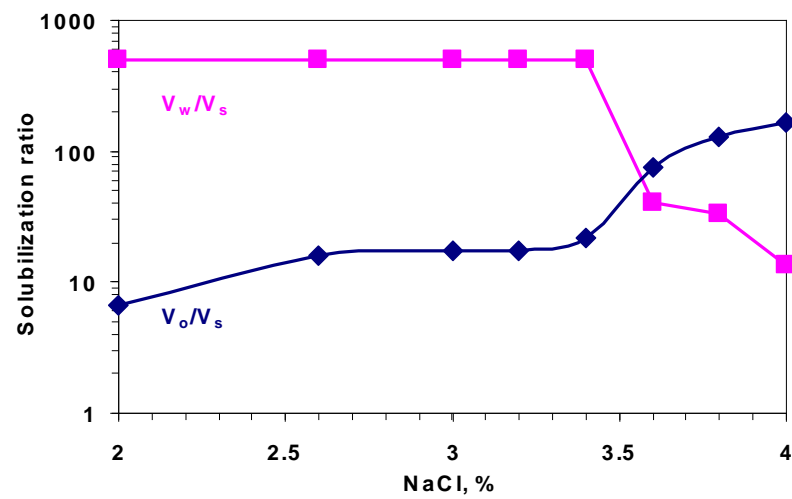


Fig. 9 Measured solubilization ratios of salinity scan (from Liu, *et al.*, 2008).

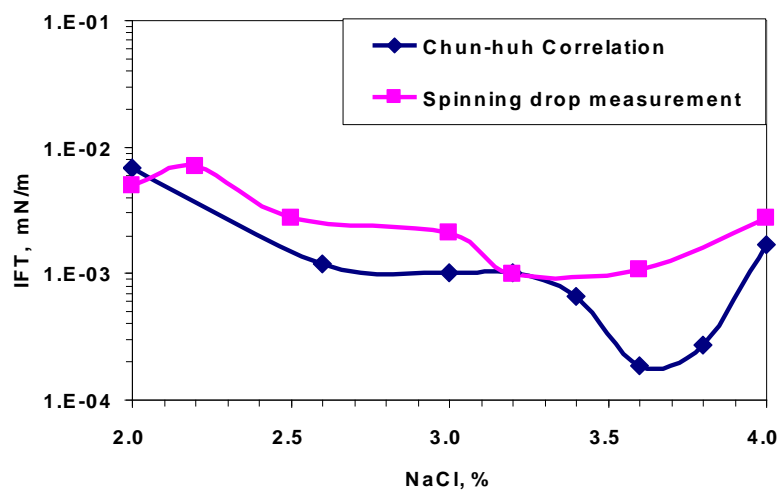


Fig. 10 Comparison of the IFT from the solubilization parameter and spinning drop measurements (from Liu, *et al.*, 2008)

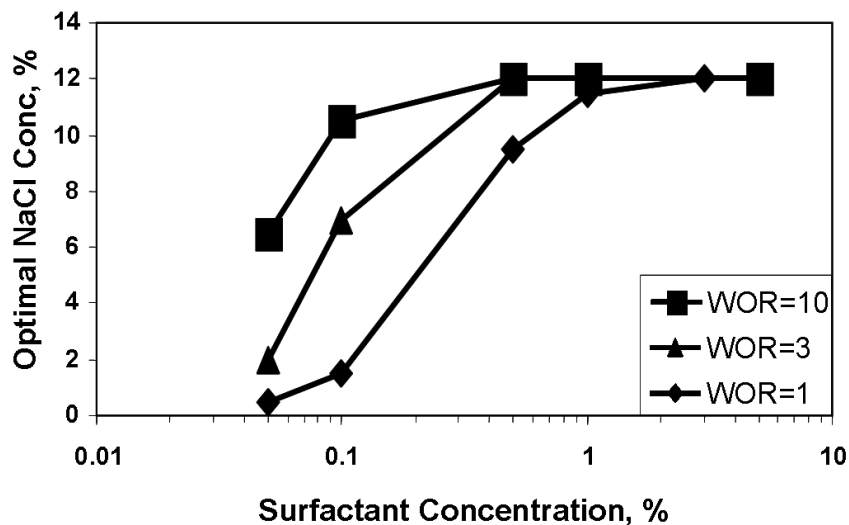


Fig. 11 Optimal sodium chloride concentration of TC blend as a function of WOR and surfactant concentration (settled for more than 6 months). (from Zhang, *et al.*, 2006)

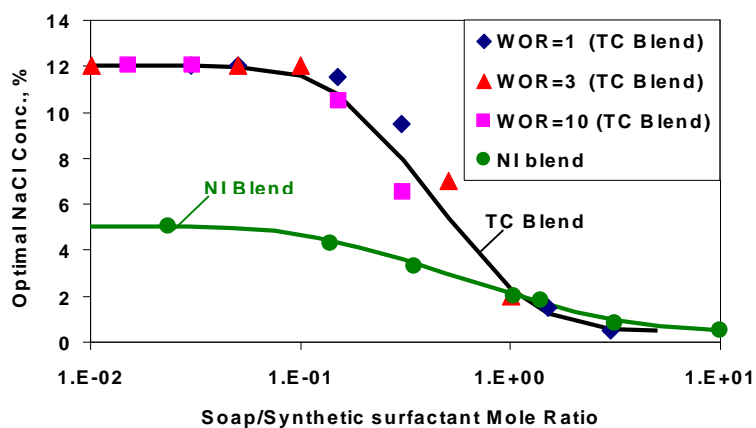


Fig. 12 Optimal salinity as a function of soap-surfactant ratio for NI and TC surfactant blends with MY4 crude oil. (Liu, *et al.*, 2008)

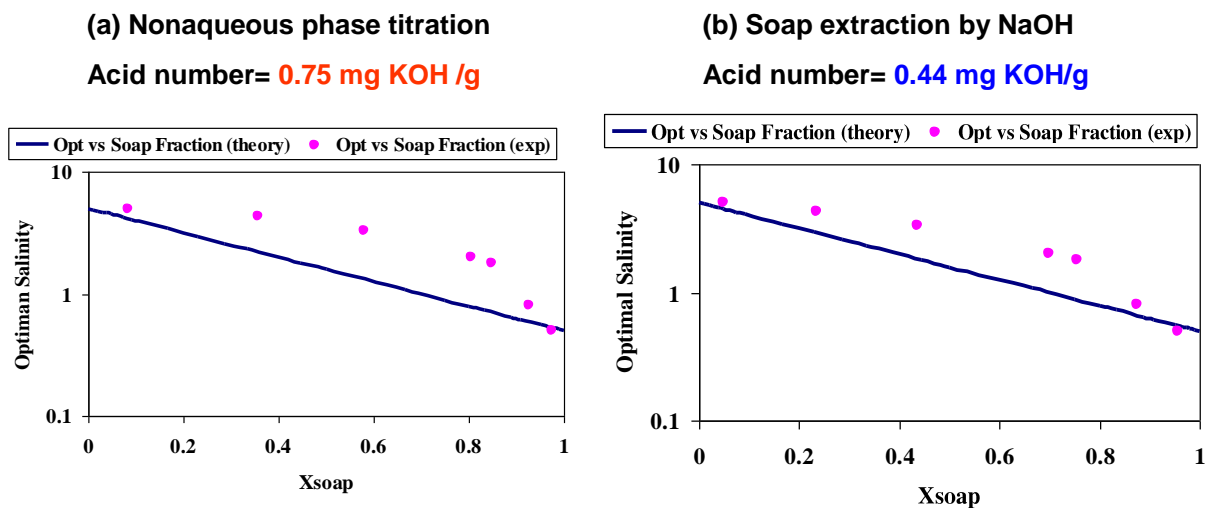


Fig. 13. Relationship of optimal salinity and soap mole fraction by different acid number methods for NI Blend and Yates oil. (from Liu, *et al.*, 2010)

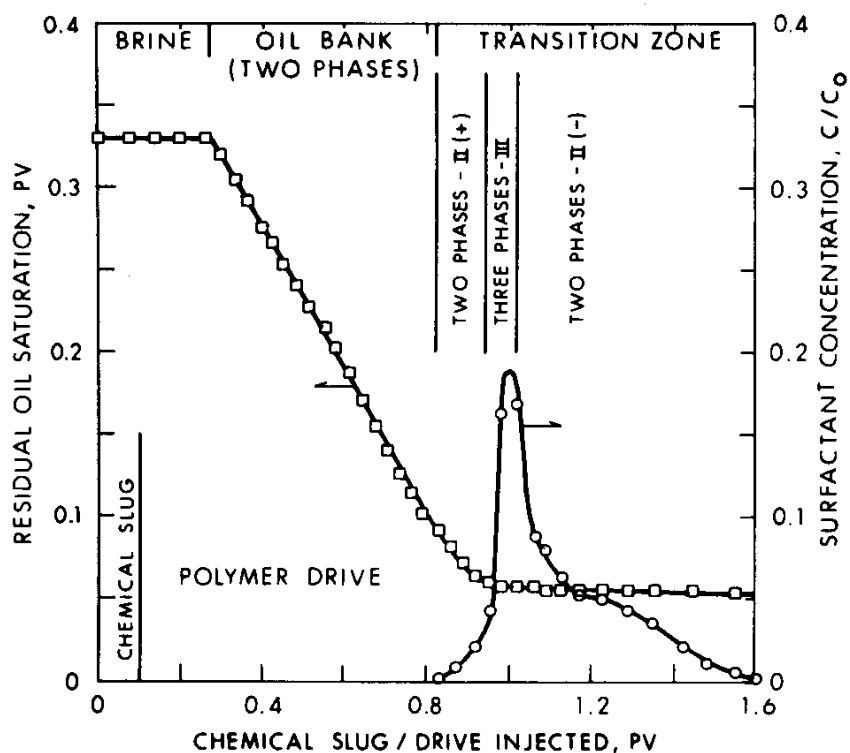


Fig. 14 Oil saturation and surfactant production during experiment with finite, over-optimum surfactant slug and salinity gradient (Hirasaki, *et al*, 1983).

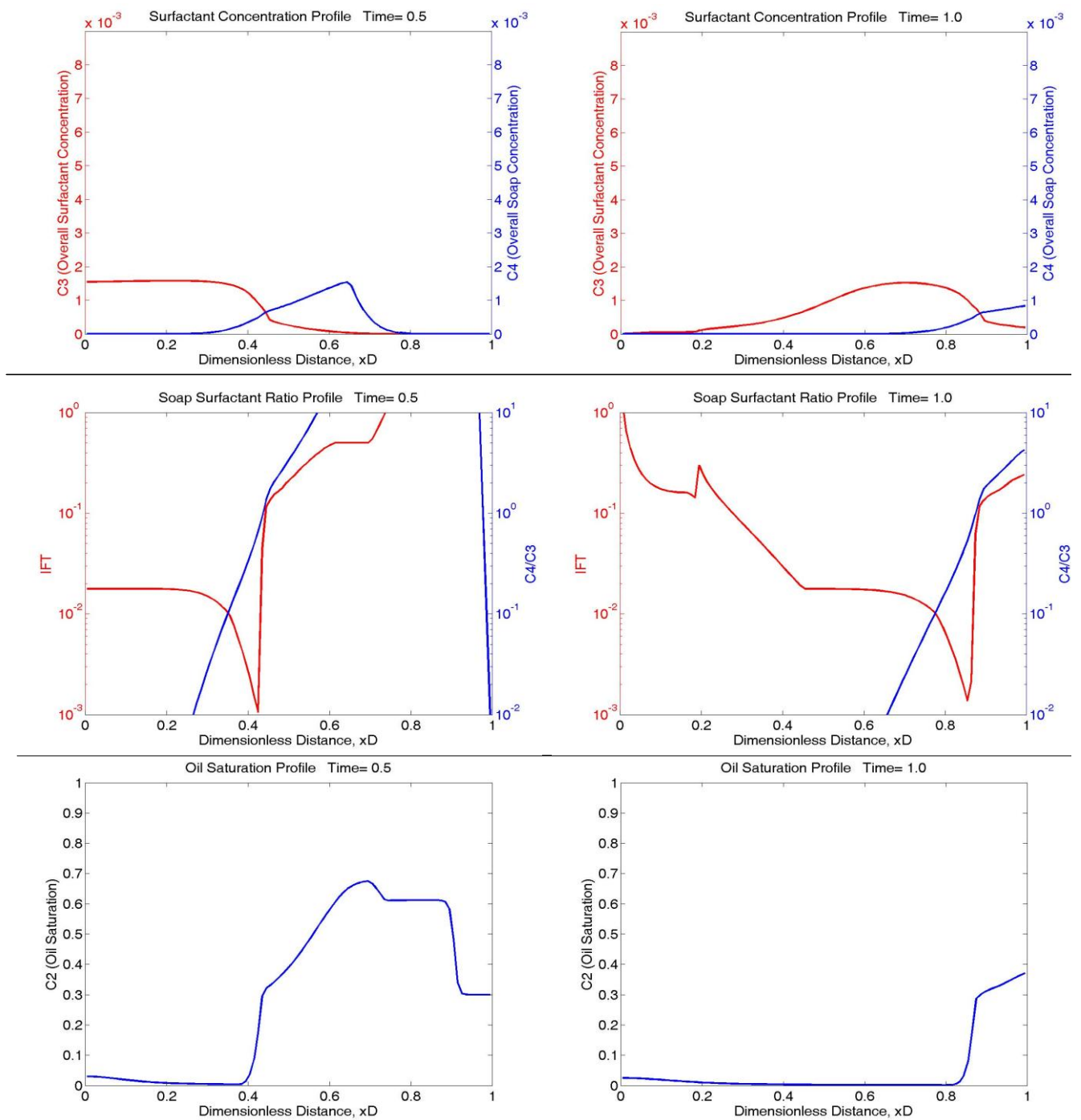


Fig. 15 Profiles for large slug (0.5 PV) with low dispersion near optimal salinity (2 % NaCl). (from Liu, et al., 2010)

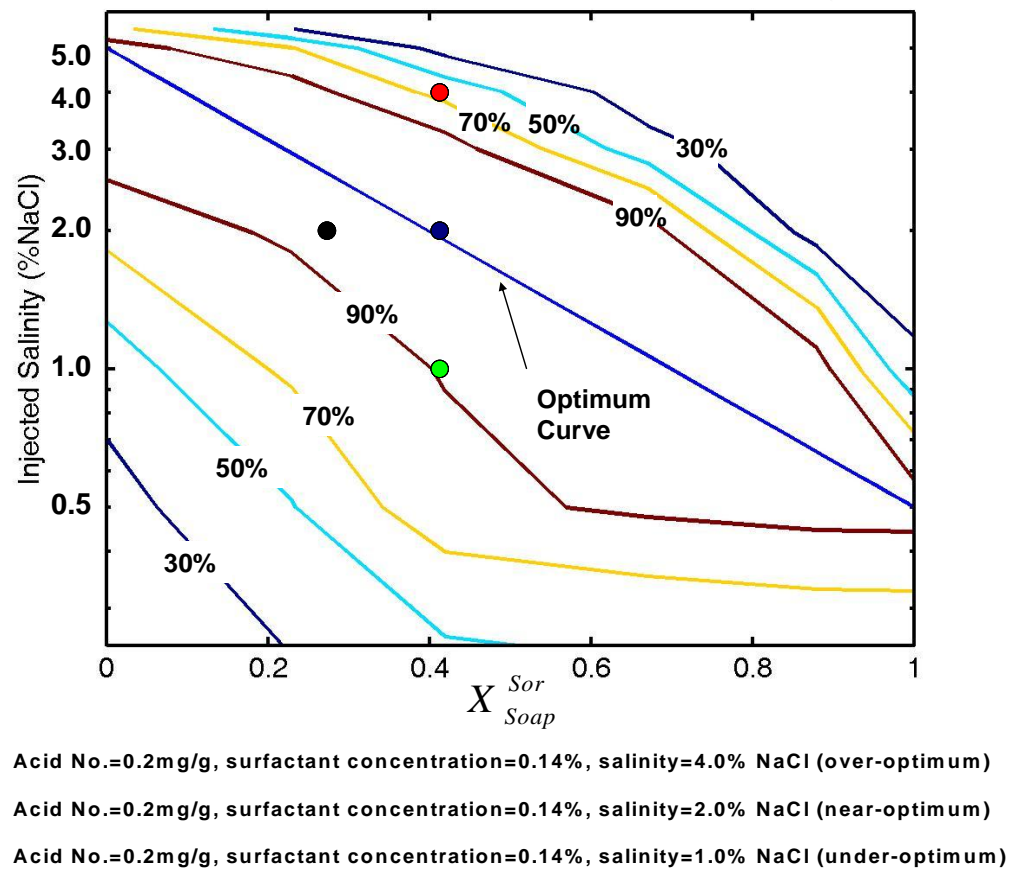


Fig. 16 Recovery factor with small slug (0.2 PV) and low dispersion (Pe=500).
(from Liu, *et al.*, 2010)

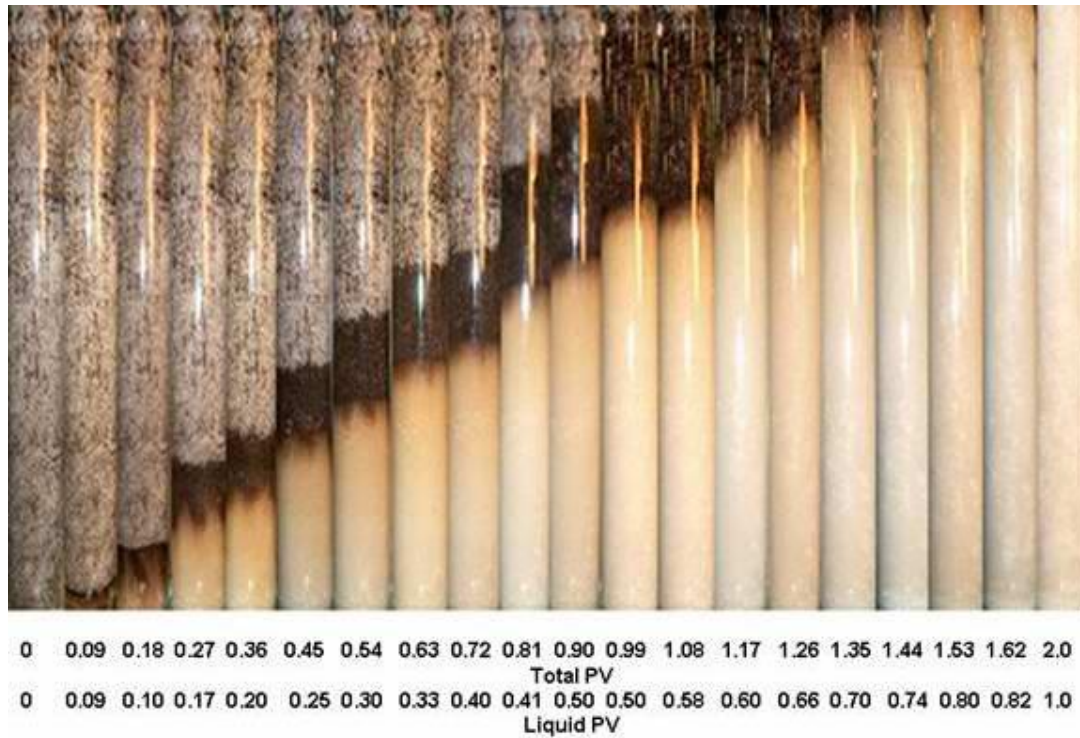


Fig. 17 Displacement profiles for the displacement of MY residual crude oil by ASPF in 40 darcy sandpack. (from Li, *et al.*, 2010)

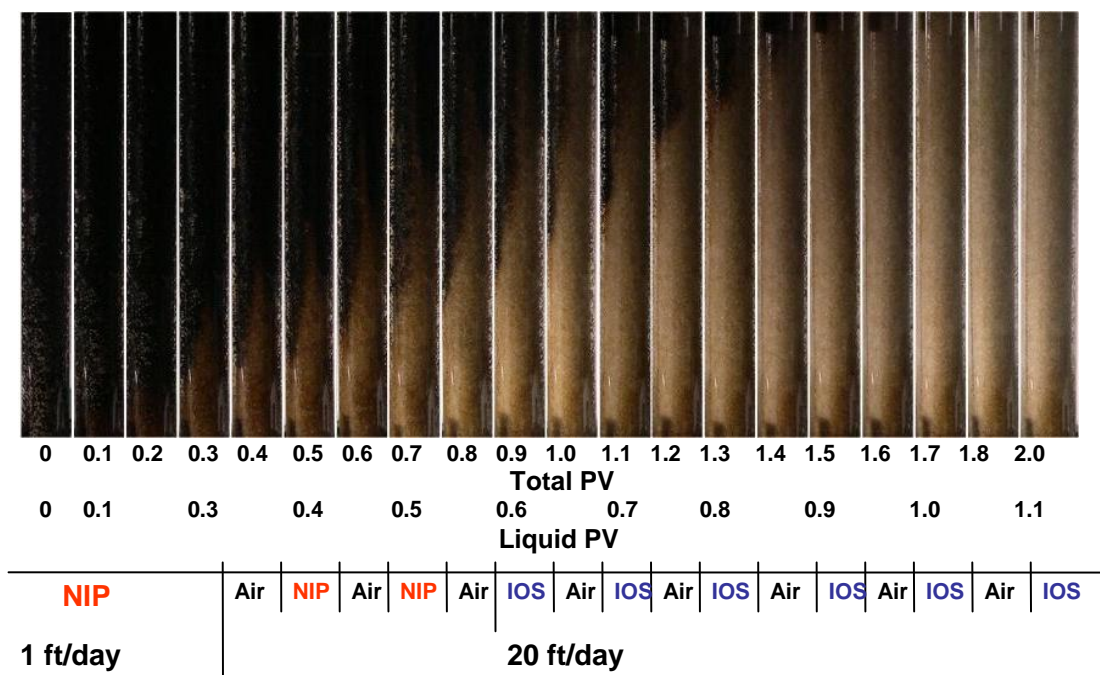


Fig. 18 Profiles of the displacement of 266 cp Crude B with ASP and ASPF. (Li, *et al.*, 2010)

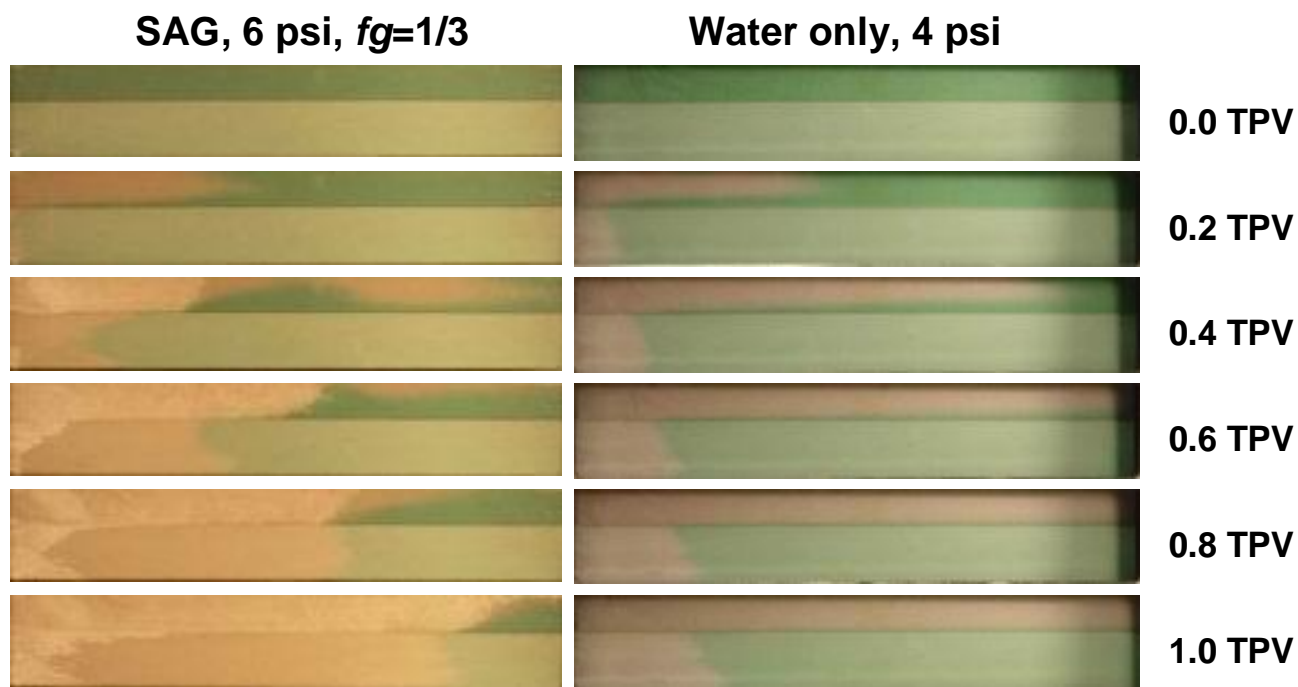


Fig. 19 Comparison of SAG with waterflood in 19:1 permeability ratio sandpack.
(Li, et al., 2010)

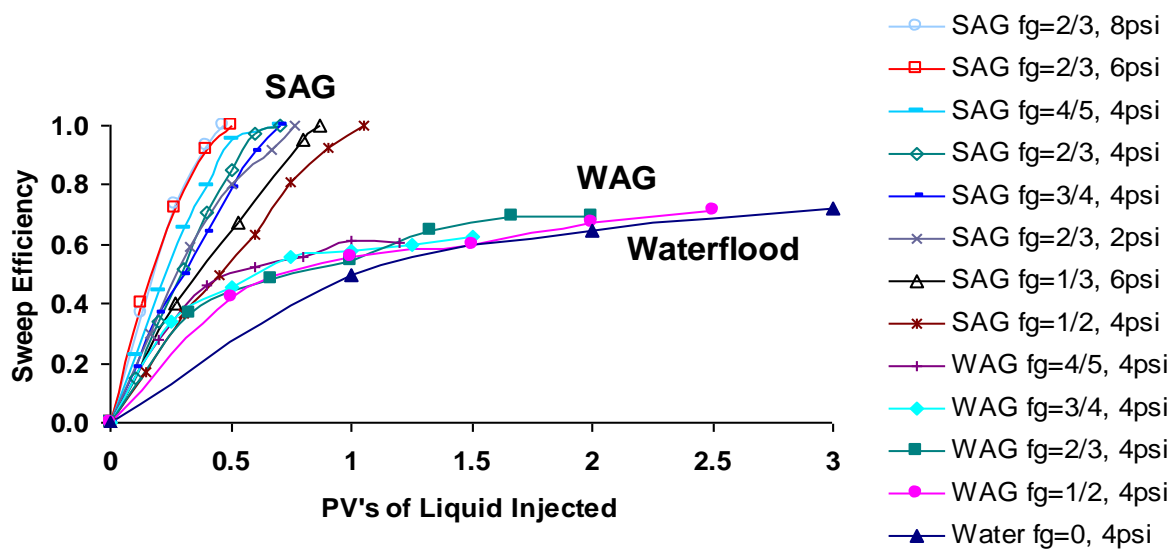


Fig. 20 Sweep in 19:1 permeability contrast sandpack with SAG, WAG, and Waterflood.
(Li, et al., 2010)