

Alkaline/Surfactant/Polymer Processes: Wide Range of Conditions for Good Recovery

Shunhua Liu, SPE, Occidental Oil and Gas Corporation; and Robert Feng Li, SPE, Clarence A. Miller, SPE, and George J. Hirasaki, SPE, Rice University

Summary

Design of an alkaline/surfactant/polymer (ASP) process requires knowledge of the amount of soap formed under alkaline conditions from naphthenic acids in the crude oil. We show here for several crude oils that, when substantial acid is present, the acid number determined by nonaqueous-phase titration is approximately twice that found by hyamine titration of a highly alkaline aqueous phase used to extract soaps from the crude oil. This acid number by soap extraction should provide a better estimate than nonaqueous-phase titration because the extracted soap interacts with the injected surfactant to form surfactant films and microemulsion droplets during an ASP process.

In a previous paper (Liu et al. 2008), an unusually wide range of salinities of ultralow oil/water interfacial tensions (IFTs) was found for one alcohol-free crude-oil/anionic-surfactant system under alkaline conditions where naphthenic soaps were present. Solubilization results indicate that this favorable behavior exists with the same surfactant blend and another crude oil.

In the same paper, a 1D simulator for the ASP process was presented. Here, this ASP simulator has been used for various acid contents, injected-surfactant concentrations, slug sizes, and salinities to show that high recoveries of waterflood residual oil (> 90%) can be expected for a wide range of near-optimal (Winsor III) and underoptimum (Winsor I) conditions for a constant-salinity process, even with relatively small slug sizes. A key factor leading to this good performance is development of a gradient in soap/surfactant ratio, which ensures that a displacement front with ultralow IFT forms and propagates through the formation. Similar high recoveries can be attained for certain Winsor II conditions but only for much larger slug sizes, owing to the tendency for surfactant to partition into the oil phase and become retarded. Large dispersion, such as might be expected for field conditions, can reduce recovery significantly for small surfactant slugs even for near-optimal and underoptimum conditions. However, this problem can be overcome by injecting the slug or drive at salinities below reservoir salinity, thereby creating a salinity gradient.

Introduction

Alkaline/surfactant processes offer considerable promise for enhanced oil recovery (EOR). The alkali converts naphthenic acids in the crude oil to soaps. The combination of the soaps and a suitably chosen injected surfactant reduces interfacial tensions to ultralow values, where residual oil can be mobilized and oil trapping prevented. As discussed more fully in a previous paper (Liu et al. 2008), the alkali reduces surfactant adsorption. Soaps are usually too lipophilic to produce ultralow tensions at reservoir conditions. Effective hydrophilic surfactants can be injected in an alkaline/surfactant process at salinities below their optimal salinities for oil recovery when used in the absence of alkali (Nelson et al. 1984). Injection at lower salinities further reduces adsorption and facilitates finding surfactant-slug compositions where the addition of polymer to provide adequate mobility control does not

cause undesirable separation into polymer-rich and surfactant-rich phases. The drive is also a polymer solution, so that the process is of the ASP type.

Liu et al. (2008) presented phase behavior, IFTs, adsorption isotherms, and results of ASP experiments in silica and dolomite sandpacks for a system with a particular surfactant blend (NI blend) and a west Texas crude oil (Yates). The alkali was sodium carbonate, and all experiments were conducted at ambient temperature. A mixture of a propoxylated sulfate and an internal olefin sulfonate, the NI blend was used with no added alcohol or other cosolvent. It was a single-phase micellar solution for salinities only slightly below its optimal salinity with the crude when minimal soap was present, making it suitable for injection at lower salinities in an ASP process, as already mentioned.

For this system, it was found that the range of salinities where IFT was ultralow (< 0.01 mN/m) was considerably wider when sodium carbonate was present than when it was not for samples comprising a salinity scan with fixed synthetic-surfactant concentration and water/crude-oil ratio. ASP sandpack experiments showed excellent recovery of waterflood residual oil (> 95%). A 1D simulator gave a similar high recovery prediction in this case but lower recovery if ultralow IFTs were present over a narrower salinity range. In this paper, we present solubilization data from phase-behavior experiments that suggest that a similar wide range of ultralow IFTs exists with the same surfactant blend and another crude oil when sodium carbonate is present. That is, such behavior of an ASP system, which clearly is favorable for oil recovery, seems not to be an anomaly exhibited by only a single system.

An important insight provided by the previous simulations was that a gradient in the ratio of naphthenic soap to surfactant develops during an ASP process carried out at constant salinity. Ahead of the displacement front, this ratio is large and conditions are Winsor II, while behind the front, the ratio is small and conditions are Winsor I. At the front itself, IFT is ultralow. In this paper, we use the simulator to examine recovery and process behavior for a wide range of conditions for the NI-blend/Yates system. For each slug size, recovery for a constant-salinity process can be represented by contours on a single plot of salinity as a function of the soap fraction at residual conditions. Soap fraction is defined as the mole fraction of soap in an element of pore volume (PV) at initial S_{or} , as a fraction of surfactant plus soap if the initial brine in the PV is replaced by the surfactant solution to be injected. The contour plot shows that a surfactant slug of 0.2 PV containing 0.2% surfactant can produce high oil recoveries over a wide range of optimal and underoptimum conditions but not at overoptimum conditions, owing to surfactant retention in trapped oil. If large dispersion comparable to field conditions is present for a 0.2-PV slug, recovery is significantly reduced, even for optimal and underoptimum conditions. This problem can be overcome by changing from a constant-salinity process to one where a salinity gradient is imposed by injecting slug or drive at salinities below reservoir salinity.

Determination of Acid Number and Soap Extraction

Nonaqueous-Phase Titration. Nonaqueous-phase titration to determine total acid number was performed using the procedure of Fan and Buckley (2007) except that the electrode used was a

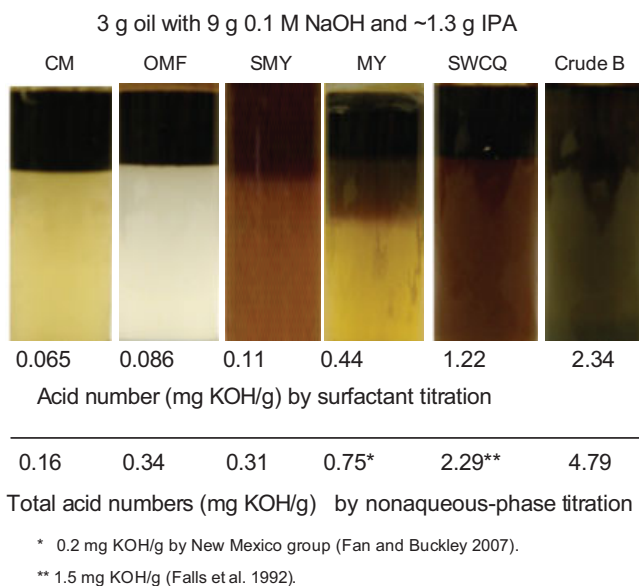


Fig. 1—Soap-extraction behavior and acid numbers by soap extraction and nonaqueous-phase titration.

Metrohm Solvotrode glass electrode (6.0229.100) designed for application in nonaqueous phases. It was preconditioned in organic solvent for 3 minutes between titrations. The organic solvent [50% toluene, 49.5% isopropanol (IPA), 0.5% deionized water] was spiked with stearic acid as in the Fan/Buckley method, and the difference between endpoints with and without added crude oil was used to calculate the acid number. The titrant was 0.0534 M tetrabutyl ammonium hydroxide in ethanol. This procedure has been found to give reliable and reproducible results.

Aqueous-Phase Titration. In an ASP process, soap, which is an anionic surfactant, is generated by saponification of the acidic components in the crude oil with alkali. Because the relative amounts of soap and injected surfactant present in surfactant aggregates and interfacial films dictate phase behavior and IFT, it is important to know the amount of soap formed from a particular crude oil. Nonaqueous-phase titration provides information on the total amount of acid in a crude oil. However, not all soaps formed when the oil contacts an alkaline solution have significant effects on ASP-process behavior. For example, soaps formed from short-chain acids are more hydrophilic and, hence, less surface active than other soaps. As a result, their concentration in interfacial films may be small. Also phenolics and porphyrins in crude oil can consume alkali but do not change interfacial properties as much as surfactant.

Asphaltenes or resins may have carboxylate functional groups but not be extracted into the aqueous phase. Total acid number determined by nonaqueous-phase titration cannot distinguish such species, which do not produce useful surfactant, from acids that generate soaps that do form mixed microemulsions with injected surfactant. Therefore, aqueous-phase titration with hyamine is used to find the amount of soap extracted into an aqueous phase containing 0.1 M NaOH and approximately 13% IPA by weight. The high alkalinity and alcohol both promote extraction.

The following procedure was used for aqueous-phase titration:

1. Mix crude oil, 0.1 M NaOH solution, and IPA with weight ratios of 1:3:0.44. This composition was chosen because it ensures that enough NaOH is present to react with the acid in the oil and still keep pH near 13.

2. Shake the sample well by hand for 1–2 minutes and continue shaking with a rotating shaker for 24 hours.

3. Let the sample settle until the position of the water/oil interface does not change with time. Centrifuge 1.5 hours to ensure phase separation.

4. Sample the aqueous phase and determine the aqueous-phase anionic-surfactant concentration by potentiometric titration with benzethonium chloride (hyamine 1622). For Crude Oil B, the oil and water phases never separated, and the entire emulsion was used for titration.

5. Use mass balance to calculate the acid number.

Fig. 1 shows photographs of six crude oils and the corresponding aqueous solutions after extraction and compares the acid numbers determined by soap extraction and nonaqueous-phase titration at ambient temperature. The former are less than the latter, as expected. Indeed, the acid number determined by soap extraction is approximately half of the total acid number determined by nonaqueous titration (**Fig. 2**). Some deviation from this relationship is seen for oils with low acid numbers. The soap-extraction value should provide a better estimate of the amount of soap that influences phase behavior and IFT.

Phase Behavior and Soap Fraction. The optimal salinity of orthoxylene sulfonate mixtures can be characterized by a mixing rule (Bourrel and Schechter 1988), as shown in Eq. 1. Experimental results show that this relationship fits the experimental data for such surfactants quite well (Puerto and Gale 1977; Bourrel and Schechter 1988). The University of Texas Chemical Composition Simulator also uses this empirical equation as a mixing rule for anionic surfactants.

$$\log(\text{Opt}_{\text{mix}}) = \sum_i X_i \log(\text{Opt}_i), \dots \dots \dots (1)$$

where X_i is the mole fraction of surfactant i in the surfactant mixture, Opt_{mix} is the optimal salinity of surfactant mixture, and Opt_i is the optimal salinity of surfactant i .

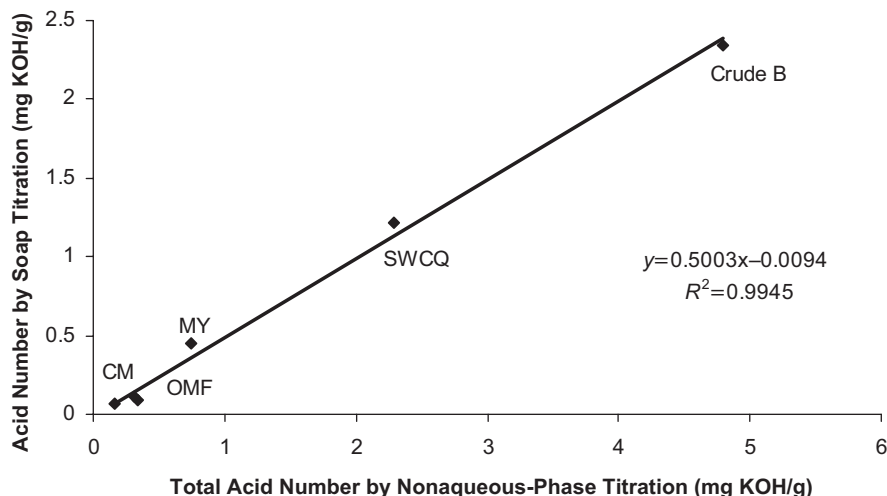


Fig. 2—Acid number by soap extraction as a function of total acid number by nonaqueous-phase titration.

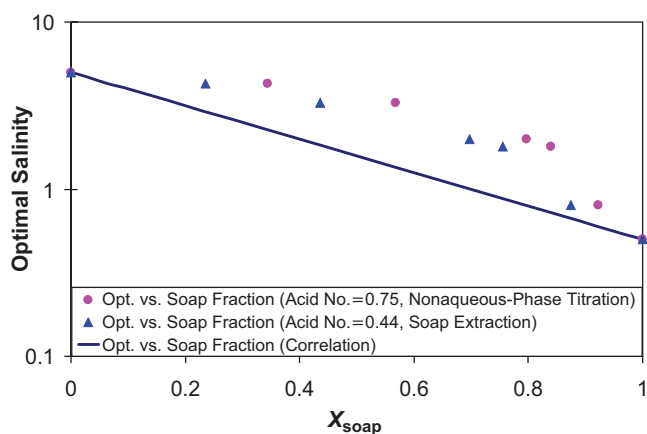


Fig. 3—Relationship of optimal salinity and soap mole fraction by different acid-number methods for NI Blend and Yates oil.

For an alkali/surfactant system, Eq. 1 can be simplified as

$$\log(\text{Opt}) = X_{\text{soap}} \cdot \log(\text{Opt}_{\text{soap}}) + (1 - X_{\text{soap}}) \cdot \log(\text{Opt}_{\text{surfactant}}), \quad (2)$$

where X_{soap} is the mole fraction of soap in a mixture with synthetic surfactant.

Fig. 3 compares the dependence of optimal salinity for the Yates-crude-oil/NI-surfactant-blend system on X_{soap} when the latter is determined by the nonaqueous-phase titration and aqueous extraction methods. The phase behavior of this system was presented previously (Liu et al. 2008). The straight lines represent Eq. 2. Fig. 4 is similar to Fig. 3, except the oil is Crude Oil B, which has an acid number much higher than that of Yates crude oil (MY in Fig. 2). Its phase behavior with NI blend as surfactant and Na_2CO_3 as alkali was recently determined in our laboratory (Liu 2008). Figs. 3 and 4 show that the acid number from soap extraction gives better agreement between the mixing rule and experimental data than the acid number from nonaqueous-phase titration.

Phase Behavior and IFT. During phase-behavior studies of the NI-blend/Yates-crude-oil system (Liu et. al. 2008), it was observed that, below optimal salinity, colloidal material dispersed in the water-continuous microemulsion rose because of gravity over a period of time to the interface with excess oil and formed a thin layer there (Fig. 5). The results indicated that this material, possibly a second microemulsion, had a higher soap/surfactant ratio than the microemulsion in which it was dispersed. As shown in Fig. 5, similar behavior has also been observed for Crude Oil B, which, according to Fig. 2, has a much higher acid number than

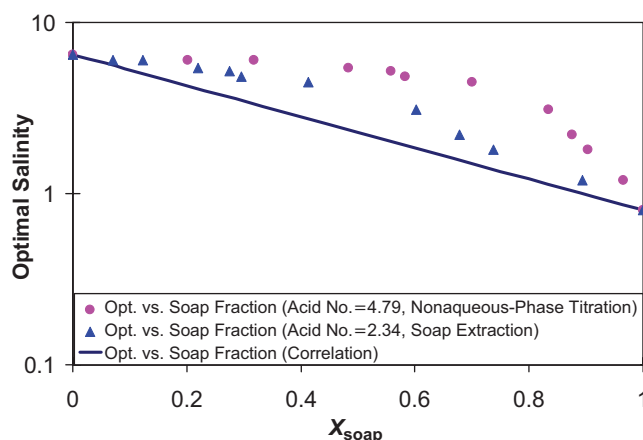


Fig. 4—Relationship of optimal salinity and soap mole fraction by different acid number methods for NI Blend and Crude B.

Yates crude oil (designated MY). It also has much higher viscosity at room temperature (266 vs. 19 cp). Even so, it is a possible candidate for an alkaline/surfactant process. We have conducted a laboratory sandpack experiment with Crude Oil B and such a process, which used foam instead of polymer for mobility control (Li et al. 2008). In the Yates system, it was found that the presence of the colloidal dispersion led to the existence of IFTs below 0.01 mN/m over a wide range of salinities (Fig. 6). The IFT was measured using a protocol that ensured that colloidal dispersion was sampled with the pre-equilibrated microemulsion phase (Liu et al. 2008). Although IFTs in the Crude Oil B system could be not be measured because of the very dark microemulsion phases, IFTs estimated from solubilization parameters using Huh's correlation (Huh 1979) indicated the presence of a wide low-IFT region below optimum salinity in this system as well, as shown in Fig. 6. Estimated IFTs are between microemulsion and oil below optimal salinity (approximately 5.2% NaCl) and between microemulsion and brine above optimal salinity. Values of (V_o/V_s) for samples such as those shown in Fig. 5 were taken as the ratio of all oil not in the excess oil phase to the total synthetic surfactant present. As shown previously, IFTs calculated from measured solubilization parameters in the Yates system showed a wide region of low IFTs, in agreement with the measured-IFT results (Liu et al. 2008).

Simulation of ASP Process

A 1D, two-phase ASP simulator was described previously (Liu et al. 2008). It tracks transport of soap, injected surfactant, alkali, and polymer through the reservoir. Acid in the crude oil is assumed to be completely converted to soap as soon as the alkali front arrives. In this paper, the simulator is modified slightly by using Eq. 2 instead of an earlier method of fitting the experimental data on optimal salinity. IFT is taken as before to be 0.001 mN/m at optimal conditions for all values of X_{soap} , and the experimental IFT data for Yates oil are used to construct the remaining IFT contours, which now fall on straight lines (Fig. 7a). Fig. 6 provides a comparison of experimental IFT data at $X_{\text{soap}} = 0.25$ with the values given by Fig. 7a and used in the simulator. The wider range of low IFT below optimal conditions compared to above optimal conditions is evident from Figs. 6 and 7a. Points on the IFT contours for other values of X_{soap} were located by assuming that a particular IFT (e.g., 0.01 mN/m) was the same percentage below (or above) the optimal value as when $X_{\text{soap}} = 0.25$. The exact equations used to calculate IFT and surfactant and soap partitioning, which are shown in Fig. 7b, are given elsewhere (Liu 2008).

The simulation parameters of an example flood, which we shall call the base case, are given in Table 1. This case is for one of the simulations corresponding to a successful ASP sandpack flood of Yates oil as shown in the earlier paper (Liu et al. 2008). The simulations showed that the width of the low-tension region (IFT < 10^{-2} mN/m) is very important for oil recovery. If the low-tension region is narrow, the oil recovery decreases significantly.

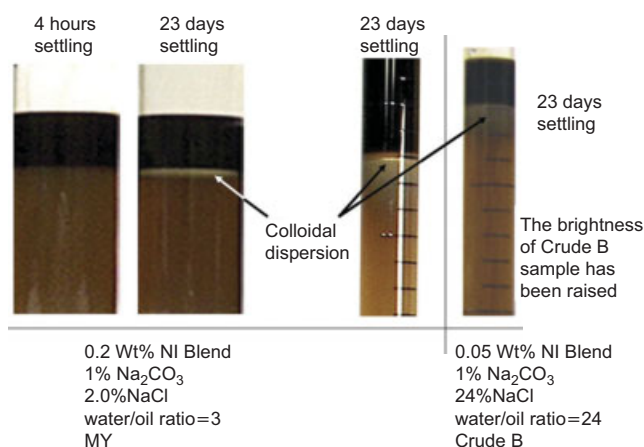


Fig. 5—Colloidal-dispersion region near interface for samples from Yates oil (MY) and Crude B.

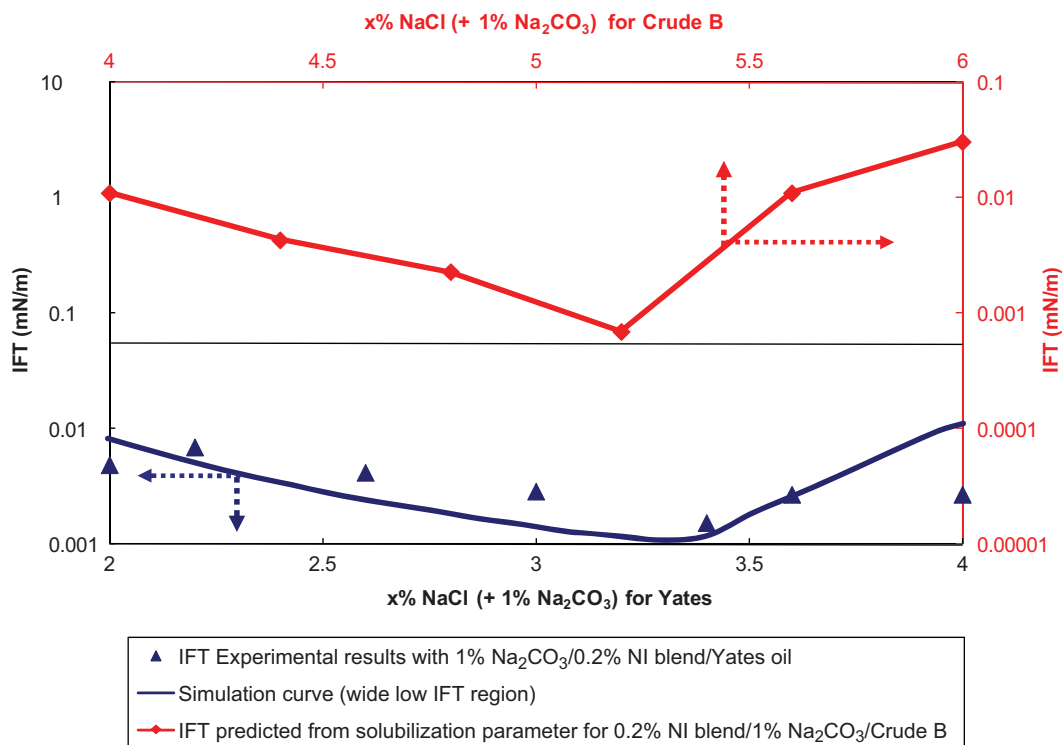


Fig. 6—IFT variation with salinity for 0.2% NI blend and 1% Na_2CO_3 with Crude B (from solubilization data, upper curve) and Yates crude (experimental data and line used in simulations, lower curve). Water/oil ratio = 3.

Good mobility control was also shown by the simulations to be essential for ASP-process success. Oil recovery falls if viscosity of the surfactant slug and polymer drive decreases.

Characteristic Soap Fraction

A characteristic soap fraction is defined to characterize the concentration of soap initially present in the residual oil relative to the concentration of the injected surfactant. The characteristic soap fraction and dimensionless salinity are defined as follows:

$$X_{\text{soap}}^{\text{Sor}} = \frac{C_{\text{soap}} \cdot S_{\text{orw}}}{C_{\text{soap}} \cdot S_{\text{orw}} + C_{\text{surfactant}} \cdot (1 - S_{\text{orw}})}, \quad (3)$$

where C_{soap} is the soap molar concentration in the oil, S_{orw} is initial oil saturation for the EOR process, and $C_{\text{surfactant}}$ is injection surfactant molar concentration.

Characterization of Dispersion; Péclet Number

Convective dispersion in porous media is proportional to the fluid interstitial velocity (Lake 1989):

$$K_{\ell} = \alpha_{\ell} v, \quad (4a)$$

where α_{ℓ} is the longitudinal dispersivity and v is the interstitial velocity. When the mass-balance equations are made dimensionless with respect to the system length, L , the dispersion coefficient appears in the Péclet number.

$$\text{Pe} = \frac{vL}{K_{\ell}} = \frac{L}{\alpha_{\ell}} \quad (4b)$$

A Péclet number of 500 was selected to represent laboratory experiments because this value [in addition to numerical dispersion,

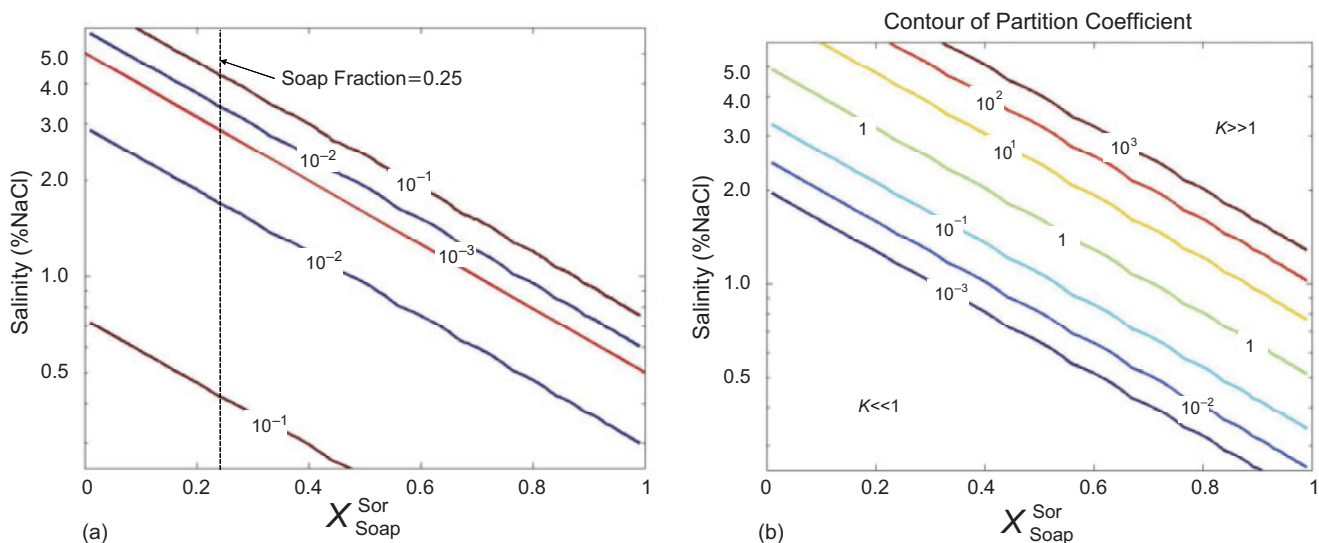


Fig. 7—(a) Contours of IFT, mN/m. (b) Contours of partition coefficient.

TABLE 1—SIMULATION PARAMETERS OF AN EXAMPLE CASE

Initial Oil Saturation	0.3
Formation Brine	2.0% NaCl
Acid Number of Crude Oil	0.2 mg KOH/g
Injection Na ₂ CO ₃ Concentration	1.0%
Injection Salinity	2.0% NaCl
Surfactant Concentration	0.2% (NI blend)
Surfactant Slug Size	0.5 PV
Injection Polymer Concentration (Flopaam 3330S)	5,000 ppm
Injection Solution Viscosity	40 cp
Crude Oil Viscosity	19.7 cp
Polymer Adsorption	20 µg/g
Surfactant Adsorption	0.2 mg/g
Surfactant Retardation Caused by Adsorption β_1^*	0.03
Péclet Number	50, 200, 500
Polymer Retardation Caused by Adsorption β_2^*	0.01
Optimum Salinity of Pure Soap	0.5% NaCl
Optimum Salinity of Pure Surfactant	5.0% NaCl
IFT Assumption	Wide low IFT region
NX (Gridblock Number)	100
dt_D/dx_D	0.05

$$\frac{1}{Pe_{num}} = D_{num} = \frac{f'}{2}(\Delta x_D - f' \Delta t_D) \approx \frac{1}{200}] \text{ matched the dispersion of}$$

a sandpack experiment to measure adsorption (Zhang et al. 2006). The Péclet number of 50 for field application was taken from a representative value of α_i (20 m) measured for a displacement distance of 1000 m (Lake 1989). The base case has 100 gridblocks. Increasing the number of gridblocks to 200 and 1,000 made no significant difference, other than in computing time.

The effect of dispersion on spreading and self-sharpening (shock) waves typical of EOR processes was described by Lake and Helfferich (1978). Delshad et al. (1985) measured the dispersivity of multiphase systems and showed that the dispersivity was different for different phases and depended on saturation. However, here we assume that the dispersivity is same for all phases and is constant. Dispersivity is a constant for a 1D, homogeneous, single-phase system. However, Lake and Hirasaki (1981) showed that 2D heterogeneous systems with transverse dispersion will have effective dispersivity that is a function of the distance traveled. This dependence of dispersivity on the system length is further discussed by Mahadevan et al. (2003).

Jessen et al. (2004) describe the effect of the interplay of numerical dispersion on phase behavior in compositional simulations. They showed that waves of local minimum or maximum concentration calculated in the absence of dispersion cannot be duplicated with finite difference simulations unless the numerical dispersion is made very small. Hirasaki (1981) showed that a surfactant flood in a Winsor II environment can have good oil recovery either with a continuous surfactant slug or with a finite slug in the absence of dispersion. However, in the presence of dispersion, a finite slug in a Winsor II environment will dissipate and fail to propagate. Pope et al. (1979) showed that changing the level of dispersion had little effect with continuous surfactant injection. With finite surfactant slugs, they found that a salinity gradient (with higher than optimal salinity ahead of the surfactant slug and lower than optimal salinity behind the surfactant slug) is effective in the presence of dispersion. Hirasaki et al. (1983) showed that a salinity gradient could remobilize a finite surfactant slug that was injected in a Winsor II environment.

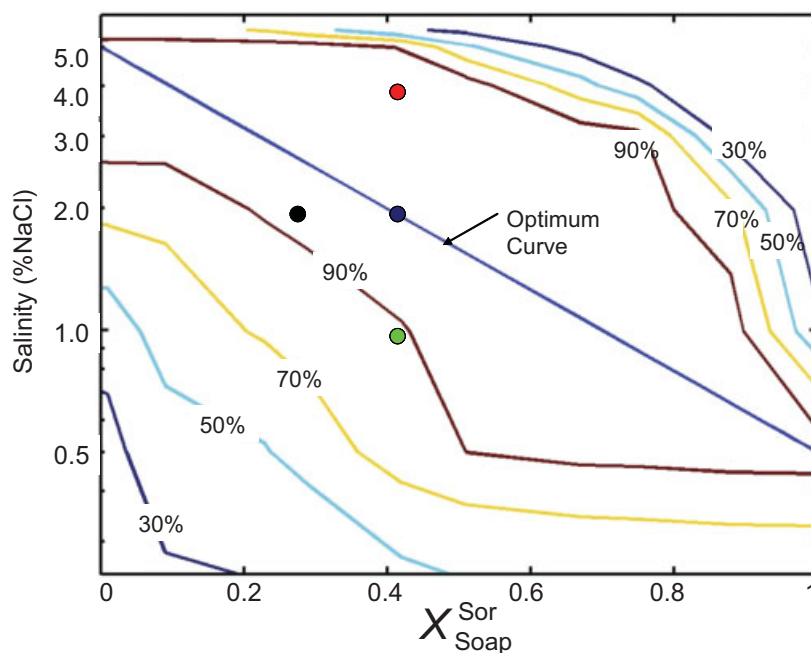
In the following, we investigate the relationships between the level of dispersion, slug size, and constant salinity vs. salinity gradient on the recovery efficiency.

Effects of Injection Strategy and Dispersion on Recovery

Laboratory experiments may identify conditions where ultralow-IFTs occur, but an injection strategy is needed to have the ultralow IFT conditions propagate from the point of injection to the point of production. Propagation of the low IFT is a function of dispersion, slug size, surfactant concentration, and salinity of the formation, surfactant slug, and drive. The salinity may be either constant or varied to generate a salinity gradient. The salinity will be expressed relative to the optimal salinity at the characteristic soap fraction (i.e., optimum, overoptimum, or underoptimum).

Floods with a large surfactant slug (0.5 PV), low dispersion ($Pe = 500$), and constant salinity (NaCl concentration) for the formation, surfactant slug, and drive are first studied for ideal conditions that are representative of laboratory conditions. Obtaining high recovery becomes more challenging with smaller slug size (0.2 PV) and larger dispersion ($Pe = 50$). Application of a salinity gradient compensates for a smaller surfactant slug and large dispersion and will be discussed later.

Large Slug (0.5 PV) and Low Dispersion ($Pe = 500$) With Constant Salinity. A number of cases were simulated with different salinity, surfactant concentration, and soap concentration in the crude oil. The recovery factors (after 2 PV of total fluid injected) of these cases are summarized in Fig. 8. The characteristic soap fraction and injected salinity correlated the numerous cases well enough to plot all results with a contour plot of recovery factor. The line denoted as “optimum curve” corresponds to the curve for the optimal salinity for minimum IFT (see Fig. 7a). The base case of the previous work (Liu et al. 2008) mentioned earlier is denoted by a black point with a characteristic soap fraction of 0.25. The other three points represent overoptimum, optimum, and underoptimum cases with a characteristic soap fraction of 0.42 and are discussed here. The contour intervals show that the recovery factor fall-off is gradual for salinities under the optimum curve. This is because IFT increases gradually below the optimal salinity (see Figs. 6 and 7a). The recovery factor drops rapidly for injected salinity somewhat over the optimum curve. This drop in recovery factor is not because of high IFT because the slug is injected at salinity close to the optimal salinity of the surfactant in the absence of soap. The reason is that the surfactant-and-soap mixture is in the region of



- Acid No.=0.2mg/g, surfactant concentration=0.14%, salinity=4.0% NaCl (overoptimum)
- Acid No.=0.2mg/g, surfactant concentration=0.14%, salinity=2.0% NaCl (near-optimum)
- Acid No.=0.2mg/g, surfactant concentration=0.14%, salinity=1.0% NaCl (underoptimum)
- Acid No.=0.2mg/g, surfactant concentration=0.2%, salinity=2.0 % NaCl (base case)

Fig. 8—Recovery factor with large slug (0.5 PV) and low dispersion ($Pe = 500$).

overoptimum salinity phase behavior where surfactant and soap partition into the oil phase and become retarded (Hirasaki et al. 1981, 1983). In addition, injection of the surfactant slug at a high salinity may result in polymer/surfactant phase separation with loss of mobility control (Liu et al. 2008). However, this effect was not included in the simulations.

Profiles for the near-optimal, 2% NaCl case (blue point in Fig. 8) are shown in **Fig. 9** at 0.5 and 1.0 PV injected. The recovery factor for this case is 98%. The concentration profiles show soap ahead of surfactant. The ratio of soap/surfactant is monotonic, and the IFT reaches 10^{-3} mN/m where the soap/surfactant ratio passes through the optimal ratio of approximately 0.66 for a salinity of 2% NaCl. The IFT at the injection end has a value of 2×10^{-2} mN/m because no soap is injected and 2% NaCl is underoptimum for the injected surfactant in the absence of soap (see Fig. 7a). The oil saturation profile shows that the oil displacement takes place in the narrow region of ultralow IFT ($< 10^{-2}$ mN/m). At 1.0 PV injected, the displacement front is only at $x = 0.85$, even though adsorption accounts for retardation of only 0.04. The additional retardation is caused by surfactant partitioning into the oil phase for soap/surfactant ratios greater than the optimal ratio for minimum IFT and unit partition coefficient. There is little surfactant ahead of the displacement front because, there, the surfactant partitions preferentially into the oil and, thus, is retarded. The shape of the profiles translated from 0.5 to 1.0 PV without spreading. This is the expected behavior of the interaction between a self-sharpening wave and dispersion (Lake and Helfferich 1978). The profile shows considerable surfactant behind the displacement front at 1.0 PV. This suggests that more surfactant was injected than needed.

The underoptimum (1% NaCl) case (green point in Fig. 8) is similar to Fig. 9 except the recovery decreased to 90%, the IFT at injection conditions is 10^{-1} mN/m, and the retardation is less.

The overoptimum (4% NaCl) case (red point in Fig. 8) recovered nearly all of the oil. The injected salinity is near the optimal salinity of the injected surfactant, and the IFT at injection conditions was 2×10^{-3} mN/m. However, retardation is significant as

the displacement front was at $x = 0.68$ at 1.0 PV injected. The higher salinity has optimal soap/surfactant ratio of 0.11, which results in more surfactant in high-partition-coefficient environment, thus more surfactant is retarded. The injected surfactant slug was large enough that the back of the slug did not intersect the displacement front.

Small Slug (0.2 PV) and Low Dispersion ($Pe = 500$) With Constant Salinity. Large surfactant slugs may be used in laboratory experiments to verify that the IFT is low enough for efficient displacement of residual oil. However, such large slugs are seldom used in field application. Evaluation of the propagation of the active, low-IFT region is usually achieved with a slug size scaled to the PV of the region that will be swept. Here, we keep everything the same except we reduce the slug size to 0.2 PV. The recovery factor for different values of characteristic soap fraction and injected salinity is shown in **Fig. 10**. The contours of recovery factor for the small slug are similar to those of the large slug except that the region of high recovery above optimal salinity is much narrower. The surfactant adsorption in the simulation was independent of salinity and small compared to the amount of injected surfactant. There was very little change in recovery between large and small slug for the optimal (blue point) and underoptimum (green point) injected salinity cases. This implies that the large, 0.5-PV slug would have been wasting surfactant for these cases. However, there is a significant reduction in the recovery factor for the overoptimum case (red point).

Profiles of the overoptimum salinity (4% NaCl) case are shown in **Fig. 11** to explain why the recovery dropped from $> 90\%$ to 63% when the slug size decreased from 0.5 to 0.2 PV. At 4% NaCl, the IFT and soap/surfactant profiles show that the minimum IFT occurs at a soap/surfactant ratio of 0.11. This is a factor of 6 less than the case of 2% NaCl. Ahead of the displacement front where the soap/surfactant ratio is greater than 0.11, the partition coefficient is greater than unity. There, the soap and surfactant partition preferentially into the oil and, thus, are retarded. When a large (0.5 PV) surfactant

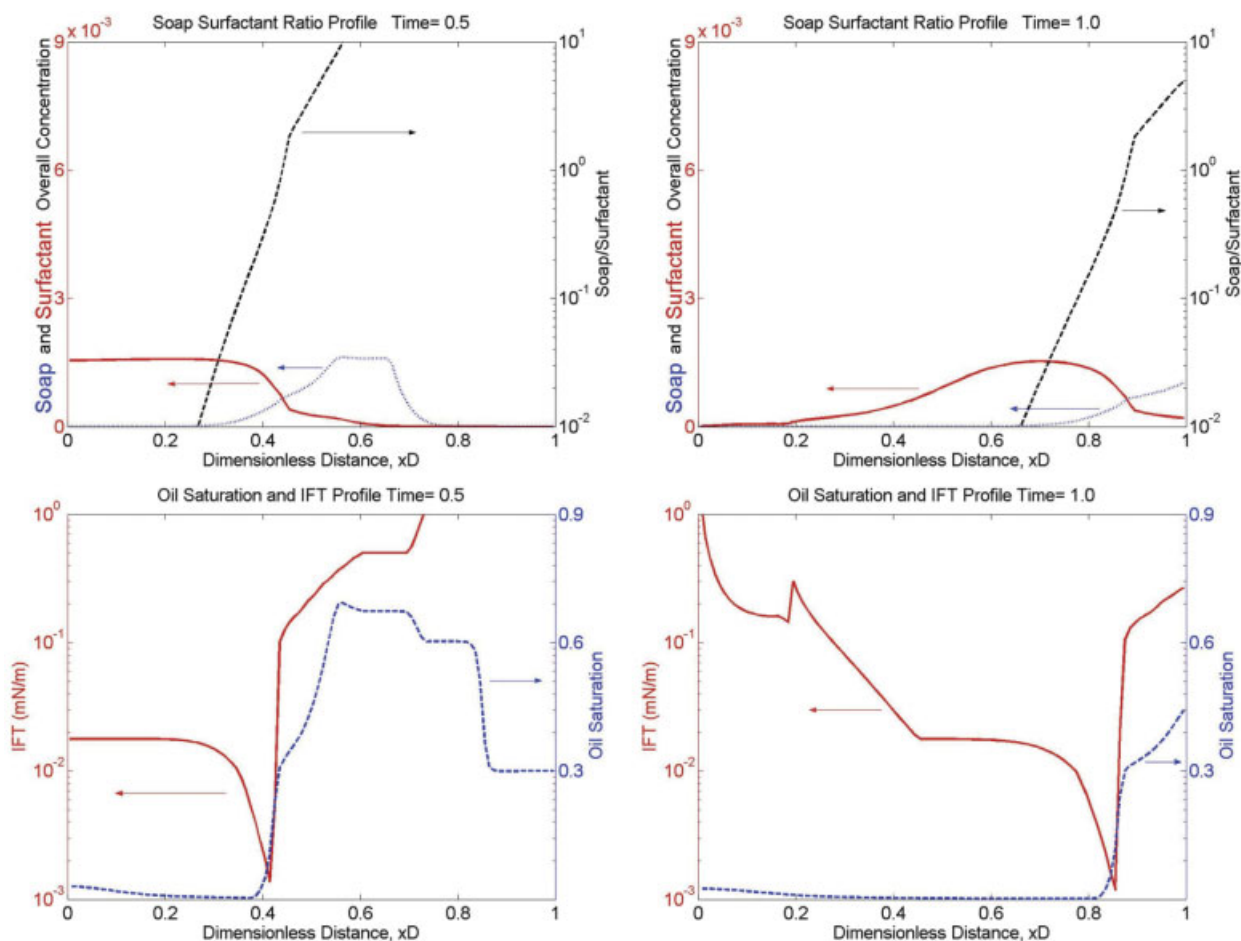
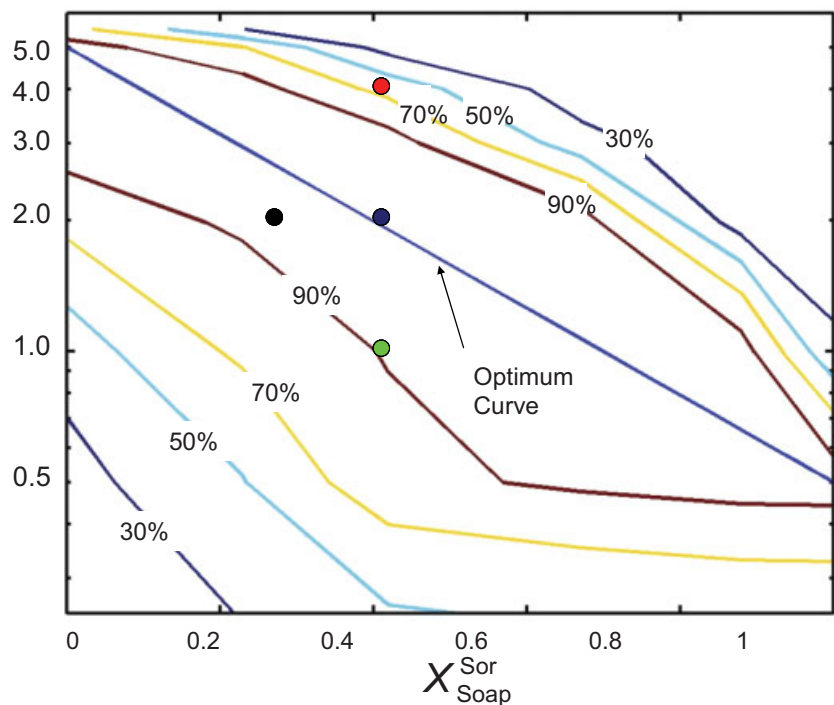


Fig. 9—Profiles for large slug (0.5 PV) and near-optimal salinity (2% NaCl).



- Acid No.=0.2mg/g, surfactant concentration=0.14%, salinity=4.0% NaCl (overoptimum)
- Acid No.=0.2mg/g, surfactant concentration=0.14%, salinity=2.0% NaCl (near-optimum)
- Acid No.=0.2mg/g, surfactant concentration=0.14%, salinity=1.0% NaCl (underoptimum)

Fig. 10—Recovery factor with small slug (0.2 PV) and low dispersion ($Pe = 500$).

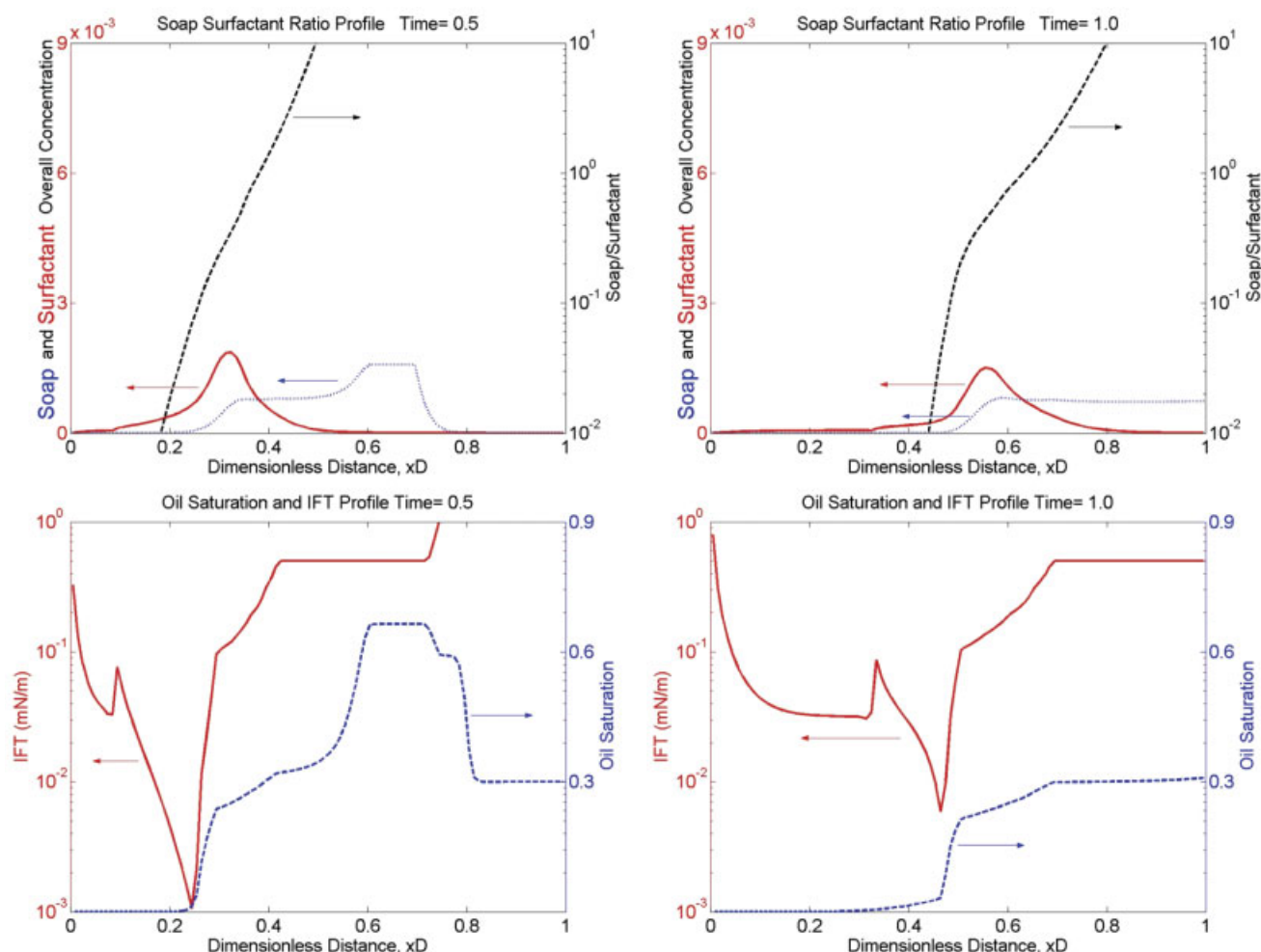


Fig. 11—Profiles for small slug (0.2 PV) with overoptimum salinity (4% NaCl).

slug is injected, the profiles of the surfactant, soap, their ratio, and IFT translate from 0.5 to 1.0 PV. However, with the small (0.2 PV) surfactant slug, the wave of decreasing surfactant concentration at the back of the surfactant slug overtakes the displacement front and lowers the surfactant concentration. Because the displacement front is restricted to a soap/surfactant ratio of 0.11, it is further retarded. This result is analogous to the failure of an overoptimum small slug with conventional surfactant flooding (Hirasaki 1981).

Effect of Dispersion

The dispersion ($Pe = 500$ in addition to numerical dispersion) of the previous results corresponds to laboratory sandpack experiments. A Péclet number of 50 will be used to represent field-scale dispersion. Field-scale dispersion is much larger because it represents mixing at all length scales in proportion to the distance traveled (Mahadevan et al. 2003). The base case against which the effect of dispersion is compared is the 2% NaCl case of Table 1 and the black point in Fig. 8. With a large (0.5 PV) slug size, the recovery factor changes from 96 to 95% as the Péclet number changes from 500 to 50. However, with a small (0.2 PV) slug size, the recovery factor drops from 96 to 57% as the Péclet number changes from 500 to 50.

The profiles for the case the small (0.2 PV) slug with constant, near-optimal salinity (2% NaCl) and large dispersion ($Pe = 50$) are shown in Fig. 12. Even though this case is near-optimal salinity, large dispersion results in the decreasing surfactant concentration at the back of the surfactant slug intersecting the displacement front and lowers the surfactant concentration. The displacement front is constrained to a soap/surfactant ratio of 0.66. Thus, the displacement front is retarded further and IFT increases after surfactant concentration falls below critical micelle concentration.

The propagation of the displacement fronts is illustrated with trajectories in the distance/time diagram, Fig. 13. Trajectories with unit slope for the front and back of the surfactant slug are shown for reference in viewing retardation. Cases with large slug and small dispersion have little retardation because of absence of interaction of the back of the slug with the displacement front. The case with small slug and large dispersion has significant retardation.

Salinity Gradient. All previous simulation cases have been with constant salinity (NaCl concentration). Here, we show that the surfactant retardation with a small slug and large dispersion can be overcome if a salinity gradient is used. Fig. 14 gives the profiles for the case of a small slug (0.2 PV), large dispersion ($Pe = 50$), and a salinity of 2% NaCl for the waterflood, 2% NaCl in the surfactant slug, and 1% NaCl in the drive. The recovery for this case is 99%, in contrast to the recovery of 57% with constant salinity of 2% NaCl. Nevertheless, the displacement-front retardation is still significant. The front is only at $x = 0.66$ at time of 1.0 PV. The distance/time diagram is shown in Fig. 15.

The salinity was reduced further to a constant salinity of 1% as a further effort to reduce retardation of the displacement front (Fig. 16). This was successful in reducing the retardation, as the displacement front was at $x = 0.88$ at time of 1.0 PV. The displacement front is at a soap/surfactant ratio of 2.3 at 1% NaCl. This permits the displacement front to travel at a higher soap concentration than in the higher-salinity cases. However, the recovery of the waterflood residual oil fell to 92%. The profile of oil saturation shows that the trapped oil is only near the inflow end. We are not certain whether this is real or if it is a numerical artifact.

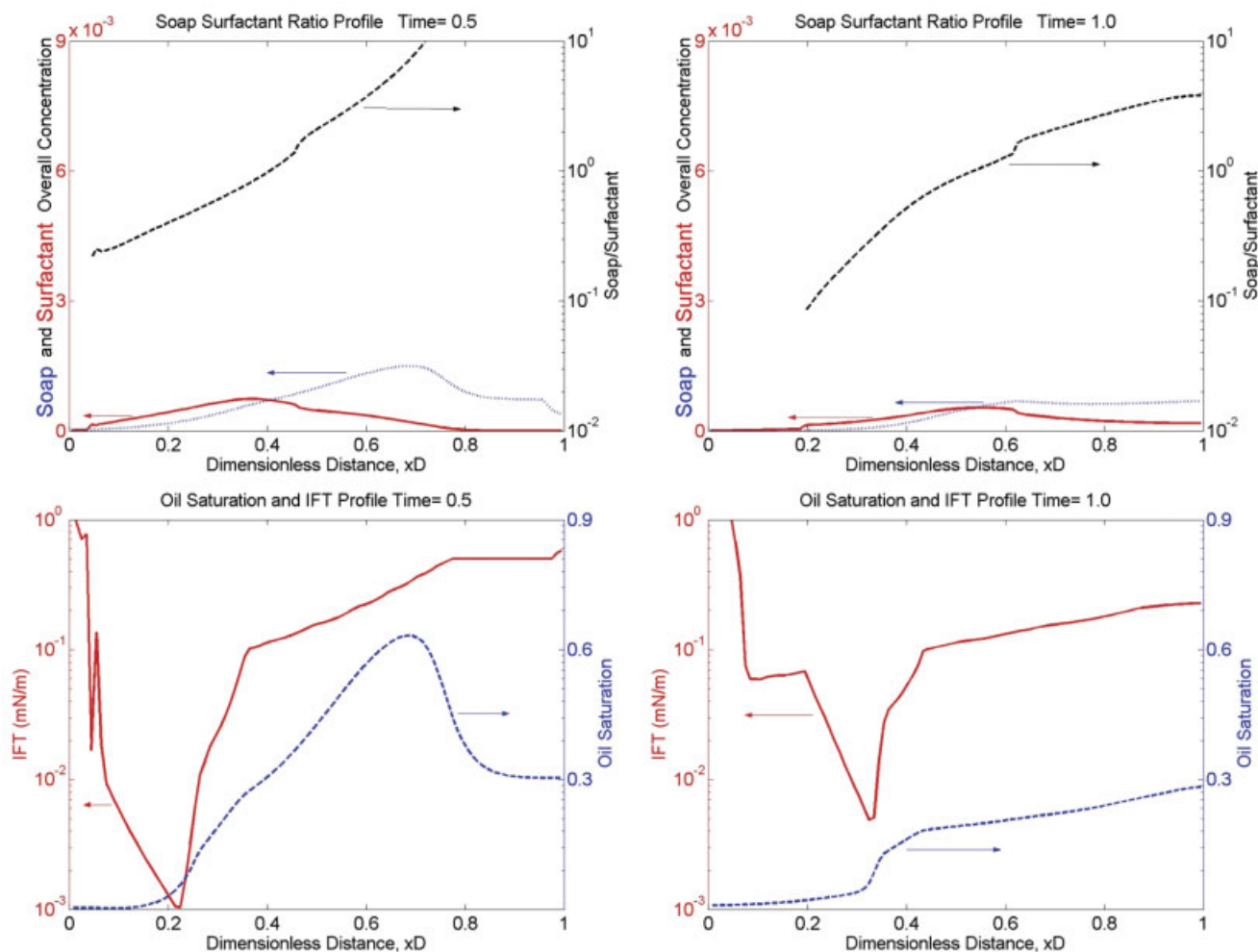


Fig. 12—Profiles for small surfactant slug (0.2 PV) and large dispersion ($Pe = 50$); base case, 2% NaCl.

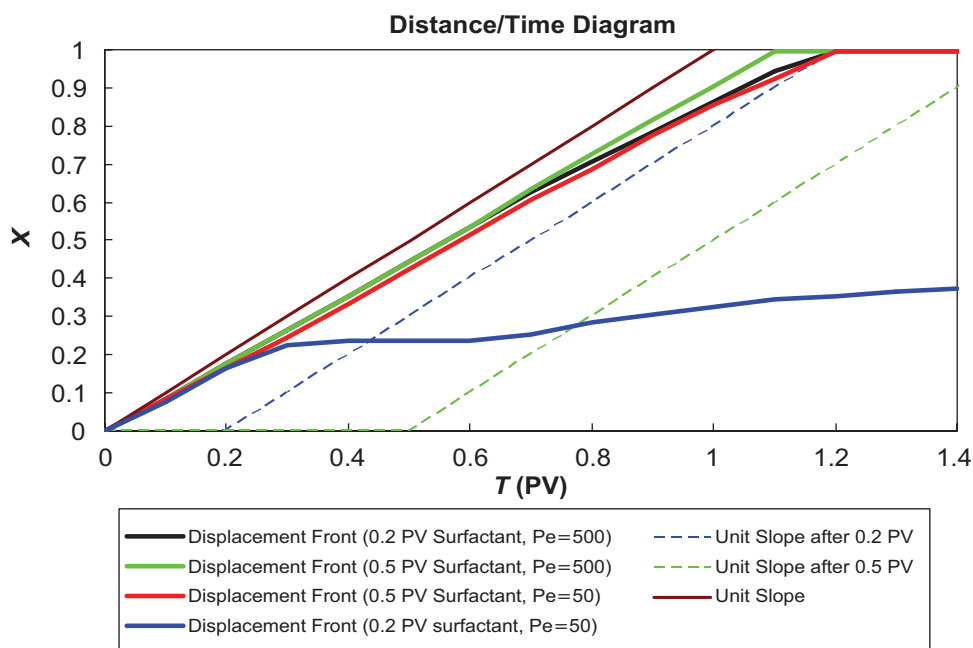


Fig. 13—Distance/time diagram for different surfactant-slug sizes and dispersion with constant salinity.

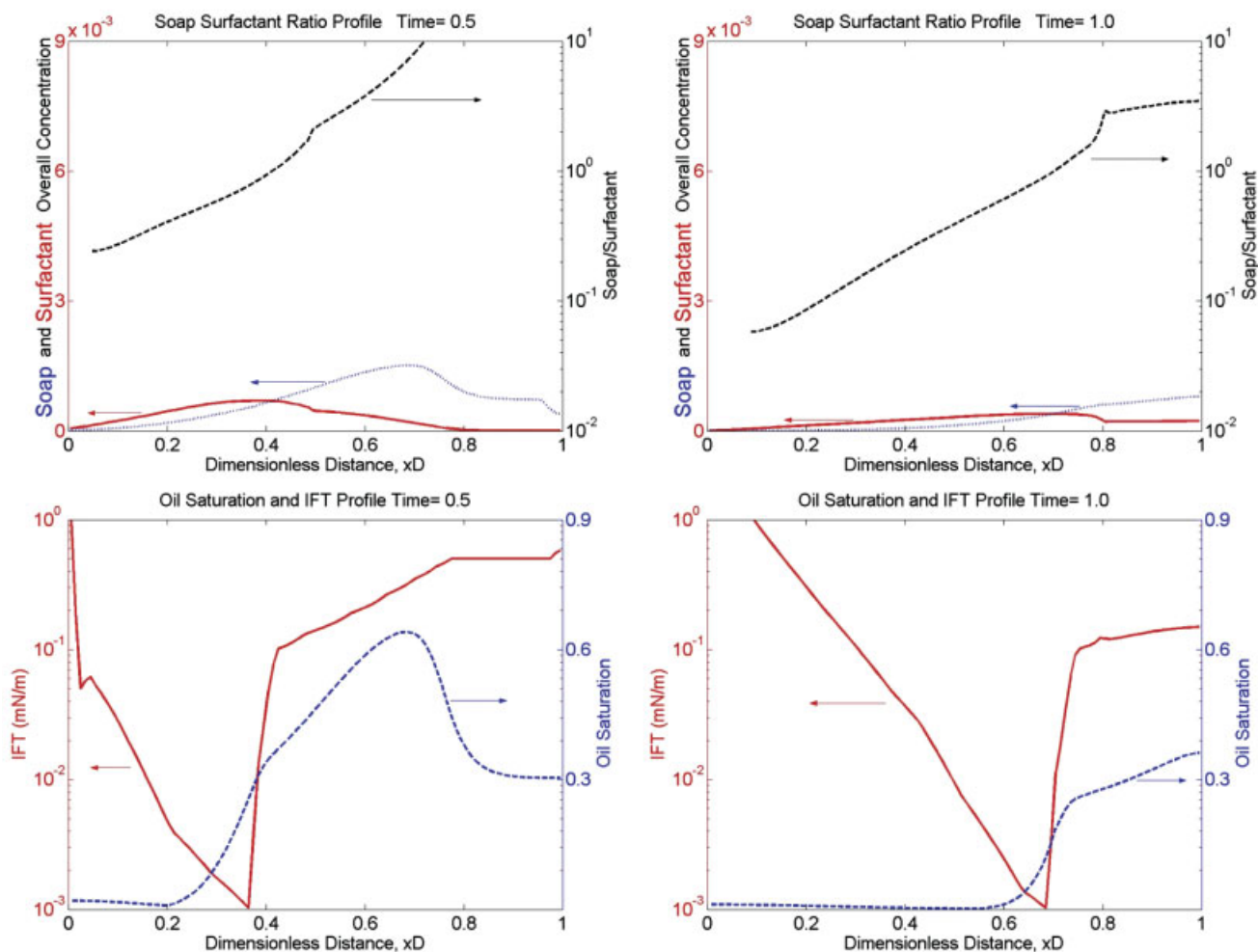


Fig. 14—Profiles of small slug (0.2 PV), large dispersion, and salinity gradient with 2% NaCl initially, 2% NaCl in slug, and 1% NaCl in drive.

Discussion of Results

The effect of dispersion on the ASP process has important consequences that deserve additional discussion. If the injected salinity is somewhere between that of the soap and injected surfactant, then the profile of the soap/surfactant ratio must pass through the

optimal ratio where the IFT is a minimum. If dispersion is small and the injected salinity is below the optimal curve, then the profile of ultralow IFT is narrow and the IFT may increase before all of the mobilized oil is displaced. If dispersion is large and the injected salinity is again below the optimal curve, then the profile of the

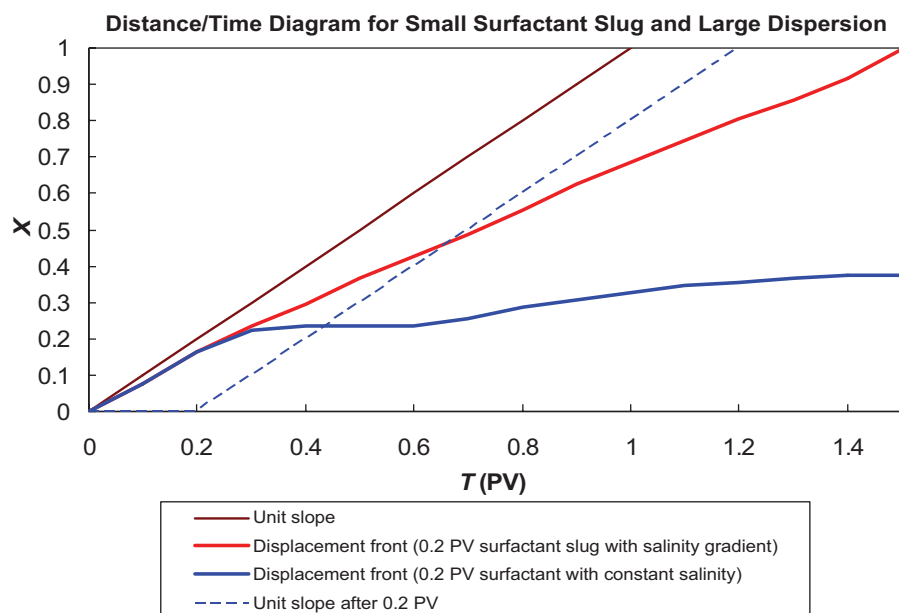


Fig. 15—Distance/time diagrams of salinity gradient and constant salinity with large dispersion ($Pe = 50$).

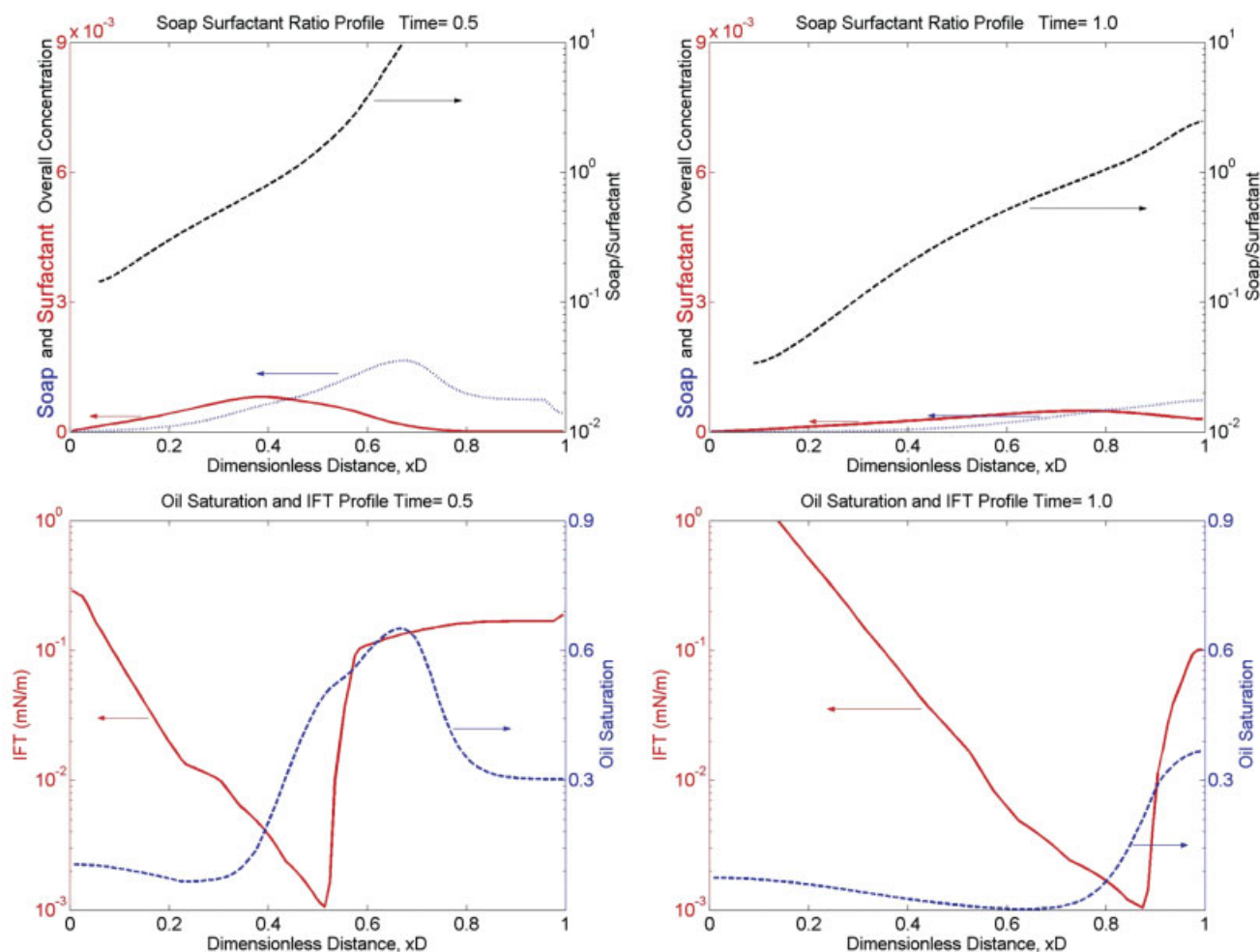


Fig. 16—Profiles of small slug (0.2 PV), large dispersion ($Pe = 50$), and constant (1% NaCl) salinity.

ultralow IFT is wide and the displacement front has more distance to displace the mobilized oil before the IFT increases. In either case, the remaining oil saturation is larger near the inflow end. To test whether this is a numerical artifact, the number of gridblocks was increased from 100 to 1,000. The values of the remaining oil saturation decreased, but the basic profile shape remained.

When the injected salinity is near or above the optimal curve, the effect of dispersion is to retard the displacement front. This occurs because the decreasing surfactant concentration at the back of the surfactant slug interferes with the front of the surfactant slug. This results in the maximum surfactant concentration decreasing. The reduced surfactant concentration increases the soap/surfactant ratio. When the soap/surfactant ratio becomes greater than the optimum ratio at the local salinity, the surfactant and soap partition preferentially into the oil phase and are retarded. Dispersion reduces surfactant concentration faster than soap concentration because the surfactant is a slug with two dispersion mixing zones, while the soap is dispersed on the back side of a bank that grows with displacement.

The effects of dispersion are compensated by application of a salinity gradient. There is no benefit of having overoptimum salinity ahead of the displacement front because the soap/surfactant ratio already results in overoptimum conditions there, even in the case of constant salinity. However, underoptimum salinity in the drive behind the surfactant slug is beneficial because it raises the optimal soap/surfactant ratio, transfers the surfactant and soap into the aqueous phase, and increases the velocity of the displacement front. This is the same as in conventional surfactant flooding, where a low-salinity drive can remobilize surfactant trapped in the oil (Hirasaki et al. 1983).

The simulation profiles shown here had characteristic soap fractions of only 0.25 and 0.42. The contour plots of recovery factor

(Figs. 8 and 10) are for a wide range of characteristic soap fraction but were limited to low dispersion ($Pe = 500$). The simulated profiles of the cases used to generate the contour plots are archived in the thesis (Liu 2008).

Conclusions

- For several crude oils with substantial acid content, the acid number determined by measuring soap extracted into the aqueous phase under highly alkaline conditions is approximately half that determined by nonaqueous-phase titration. The value based on soap extraction should be a better estimate of the amount of soap that influences phase behavior and IFT in ASP processes.
- Phase-behavior trends and measured solubilization parameters for an anionic-surfactant/crude-oil system in which the oil has high acid number and high viscosity suggest that ultralow IFTs for alkaline conditions may exist over a wide range of salinities below optimal salinity, similar to what was reported previously for the same surfactant and another crude oil with considerably lower acid number and viscosity.

The following conclusions are the result of a large number of 1D simulations of the ASP process:

- A soap/surfactant-ratio gradient is generated in the ASP process. This gradient not only helps in the profile passing through the optimal condition where the low IFT is achieved but also makes ASP a robust process because surfactant that moves ahead into the soap-dominant region ahead of the major surfactant bank is retarded and surfactant behind the displacement front travels at velocity closer to that of the aqueous phase.
- There is a wide optimum-operation region for constant-salinity ASP processes where recovery is high. It can be determined if the initial natural soap content of the crude oil is known. Then, for a given injected surfactant concentration, good recovery can

be achieved in a certain range of salinity that depends on the relationship between optimal salinity and soap/surfactant ratio.

- High oil recovery is possible with an overoptimum ASP flood, provided that a large surfactant slug is used. However, with a small slug, the process fails.
- With significant (field-scale) dispersion, the recovery for small surfactant slugs may be significantly less than that for large surfactant slugs, even at optimum conditions.
- With a salinity gradient, the ASP process can work well even with a small surfactant slug and large dispersion.

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References

- Bourrel, M. and Schechter, R.S. 1988. *Microemulsions and Related Systems: Formulation, Solvency, and Physical Properties*, Vol. 30. New York: Surfactant Science Series, Marcel Dekker.
- Delshad, M., MacAllister, D.J., Pope, G.A., and Rouse, B.A. 1985. Multiphase Dispersion and Relative Permeability Experiments. *SPE J.* **25** (4): 524–534. SPE-10201-PA. doi: 10.2118/10201-PA.
- Falls, A.H., Thigpen, D.R., Nelson, R.C., Ciaston, J.W., Lawson, J.B., Good, P.A., Ueber, R.C., and Shahin, G.T. 1994. Field Test of Cosurfactant-Enhanced Alkaline Flooding. *SPE Res Eng* **9** (3): 217–223. SPE-24117-PA. doi: 10.2118/24117-PA.
- Fan, T. and Buckley, J.S. 2007. Acid Number Measurements Revisited. *SPE J.* **12** (4): 496–500. SPE-99884-PA. doi: 10.2118/99884-PA.
- Hirasaki, G.J. 1981. Application of the Theory of Multicomponent, Multiphase Displacement to Three-Component, Two-Phase Surfactant Flooding. *SPE J.* **21** (2): 191–204. SPE-8373-PA. doi: 10.2118/8373-PA.
- Hirasaki, G.J., van Domselaar, H.R., and Nelson, R.C. 1983. Evaluation of the Salinity Gradient Concept in Surfactant Flooding. *SPE J.* **23** (3): 486–500. SPE-8825-PA. doi: 10.2118/8825-PA.
- Huh, C. 1979. Interfacial tensions and solubilizing ability of a microemulsion phase that coexists with oil and brine. *Journal of Colloid and Interface Science* **71** (2): 408–426. doi: 10.1016/0021-9797(79)90249-2.
- Jessen, K., Stenby, E.H., Orr, F.M. Jr. 2004. Interplay of Phase Behavior and Numerical Dispersion in Finite-Difference Compositional Simulation. *SPE J.* **9** (2): 193–201. SPE-88362-PA. doi: 10.2118/88362-PA.
- Jha, R.K., John, A., Bryant, S.L., and Lake, L.W. 2009. Flow Reversal and Mixing. *SPE J.* **14** (1): 41–49. SPE-103054-PA. doi: 10.2118/103054-PA.
- John, A.K., Lake, L.W., Bryant, S.L., and Jennings, J.W. 2008. Paper SPE 113429 presented at the SPE/DOE Symposium on Improved Oil Recovery, Tulsa, 19–23 April. doi: 10.2118/113429-MS.
- Lake, L.W. 1989. *Enhanced Oil Recovery*. Englewood Cliffs, New Jersey: Prentice Hall.
- Lake, L.W. and Helfferich, F.G. 1978. Cation Exchange in Chemical Flooding: Part 2—The Effect of Dispersion, Cation Exchange, and Polymer/Surfactant Adsorption on Chemical Flood Environment. *SPE J.* **18** (6): 435–444. SPE-6769-PA. doi: 10.2118/6769-PA.
- Li, R.F., Yan, W., Liu, S., Hirasaki, G.J., and Miller, C.A. 2008. Foam Mobility Control for Surfactant EOR. Paper SPE 113910 presented at the SPE/DOE Symposium on Improved Oil Recovery, Tulsa, 19–23 April. doi: 10.2118/113910-MS.
- Liu, S. 2008. Alkaline Surfactant Polymer Enhanced Oil Recovery Process. PhD thesis, Rice University, Houston, Texas.

- Liu, S., Zhang, D.L., Yan, W., Puerto, M., Hirasaki, G.J., and Miller, C.A. 2008. Favorable Attributes of Alkali-Surfactant-Polymer Flooding. *SPE J.* **13** (1): 5–16. SPE-99744-PA. doi: 10.2118/99744-PA.
- Mahadevan, J., Lake, L.W., and Johns, R.T. 2003. Estimation of True Dispersivity in Field-Scale Permeable Media. *SPE J.* **8** (3): 272–279. SPE-86303-PA. doi: 10.2118/86303-PA.
- Nelson, R.C. and Pope, G.A. 1978. Phase Relationships in Chemical Flooding. *SPE J.* **18** (5): 325–338; *Trans., AIME*, **265**. SPE-6773-PA. doi: 10.2118/6773-PA.
- Nelson, R.C., Lawson, J.B., Thigpen, D.R., and Stegemeier, G.L. 1984. Cosurfactant-Enhanced Alkaline Flooding. Paper SPE 12672 presented at the SPE Enhanced Oil Recovery Symposium, Tulsa, 15–18 April. doi: 10.2118/12672-MS.
- Pope, G.A. and Nelson, R.C. 1978. A Chemical Flooding Compositional Simulator. *SPE J.* **18** (5): 339–354. SPE-6725-PA. doi: 10.2118/6725-PA.
- Pope, G.A., Wang, B., and Tsaur, K. 1979. A Sensitivity Study of Micellar/Polymer Flooding. *SPE J.* **19** (6): 357–368. SPE-7079-PA. doi: 10.2118/7079-PA.
- Puerto, M.C. and Gale, W.W. 1977. Estimation of Optimal Salinity and Solubilization Parameters for Alkylorthoxylene Sulfonate Mixtures. *SPE J.* **17** (3): 193–200. SPE-5814-PA. doi: 10.2118/5814-PA.
- 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. *Journal of Petroleum Science and Engineering* **52** (1–4): 213–226. doi: 10.1016/j.petrol.2006.03.009.

Shunhua Liu holds BS and MS degrees from Tsinghua University, China, both in chemical engineering, and a PhD degree in chemical engineering (2008) from Rice University. He joined Occidental Oil and Gas in 2007 as a reservoir engineer in the Improved Recovery Team in Worldwide Engineering & Technical Services Department in Houston. His areas of expertise are surfactant science, enhanced oil recovery, and numerical simulation.

Robert Feng Li is a PhD candidate in the Chemical and Biomolecular Engineering Department at Rice University. His thesis research involves surfactant EOR and foam mobility control. Li holds a BS degree from the Chemical and Biochemical Engineering Department at Zhejiang University.

Clarence A. Miller is the Louis Calder Professor Emeritus of Chemical and Biomolecular Engineering at Rice University and a former chairman of the department. He holds BS and PhD degrees from Rice University and the University of Minnesota, respectively, both in chemical engineering. Before coming to Rice, Miller taught at Carnegie-Mellon University. He has been a visiting scholar at Cambridge University, the University of Bayreuth, and Delft University of Technology. Miller's research interests center on emulsions, microemulsions, and foams and their applications in detergency, enhanced oil recovery, and aquifer remediation. He is coauthor of the book *Interfacial Phenomena*, now in its second edition.

George J. Hirasaki holds a BS degree in chemical engineering from Lamar University and a PhD degree in chemical engineering from Rice University. He had a 26-year career with Shell Development and Shell Oil Companies before joining the Chemical Engineering faculty at Rice University in 1993. At Shell, Hirasaki's research areas were reservoir simulation, enhanced oil recovery, and formation evaluation. At Rice, his research interests are in nuclear magnetic resonance well logging, reservoir wettability, enhanced oil recovery, gas hydrate recovery, asphaltene deposition, emulsion coalescence, and surfactant/foam aquifer remediation. Hirasaki received the SPE Lester Uren Award in 1989. He was named an Improved Oil Recovery Pioneer at the 1998 SPE/DOR IOR Symposium and was the 1999 recipient of the Society of Core Analysts Technical Achievement Award. Hirasaki is a member of the National Academy of Engineers.