Effects of Hardness and Cosurfactant on Phase Behavior of Alcohol-Free Alkyl Propoxylated Sulfate Systems

Maura C. Puerto, George J. Hirasaki, and **Clarence A. Miller,** Rice University; **Carmen Reznik, Sheila Dubey, Julian R. Barnes,** and **Sjoerd van Kuijk,** Shell Global Solutions

Summary

The effect of hardness was investigated on equilibrium phase behavior in the absence of alcohol for blends of three alcohol propoxy sulfates (APSs) with an internal olefin sulfonate (IOS) with a $C_{15–18}$ chain length. Hard brines investigated were synthetic seawater (SW), 2*SW, and 3*SW, the last two with double and triple the total ionic content of SW with all ions present in the same relative proportions as in SW, respectively. Optimal blends of the APS/IOS systems formed microemulsions with *n*-octane that had high solubilization suitable for enhanced oil recovery at both $\approx$25°C and 50°C. However, oil-free aqueous solutions of the optimal blends in 2*SW and 3*SW, as well as in 8 and 12% NaCl solutions with similar ionic strengths, exhibited cloudiness and/or precipitation and were unsuitable for injection. In SW at 25°C, the aqueous solution of the optimal blend of $C_{16–17}$ 7 propylene oxide sulfate, made from a branched alcohol, and $IOS_{15–18}$, was clear and suitable for injection. A salinity map prepared for blends of these surfactants illustrates how such maps facilitate the selection of injection compositions in which injection and reservoir salinities differ. The same APS was blended with other APSs and alcohol ethoxy sulfates (AESs) in SW at $\approx$25°C, yielding microemulsions with high *n*-octane solubilization and clear aqueous solutions at optimal conditions. Three APS/AES blends were found to form suitable microemulsions in SW with a crude oil at its reservoir temperature near 50°C. Optimal conditions were nearly the same for hard brines and NaCl solutions with similar ionic strengths between SW and 3*SW. Although the aqueous solutions for the optimal blends with crude oil were slightly cloudy, small changes in blend ratio led to formation of lower phase microemulsions with clear aqueous solutions. When injection and reservoir brines differ, it may be preferable to inject at such slightly underoptimum conditions to avoid generating upper phase, Winsor II, conditions produced by inevitable mixing of injected and formation brines.

Introduction

Recovery of crude oil from a reservoir by means of primary and secondary production methods is estimated to yield approximately 30 to 35% of the original oil in place (Lake and Venuto 1990). The residual oil, trapped predominantly by capillary forces, constitutes a significant prize if it can be mobilized. In chemically enhanced oil recovery (cEOR), the mobilization of this residual oil is achieved through surfactants that generate a sufficiently (ultra) low crude-oil/water interfacial tension (IFT) to produce a capillary number large enough to overcome capillary forces and allow the trapped oil to flow. The development of cEOR for fields with amenable temperatures, crude-oil properties, and salinity profiles has been of significant focus since the 1970s. Recently, there has been increasing focus on the challenges inherent in reservoirs in which temperature, brine alkalinity, and/or hardness are high (Ben Shiau et al. 2013). These harsh reservoir conditions are especially challenging because surfactant performance depends on reservoir characteristics, temperature, and water composition, as well as on the type of crude oil. The surfactant system needs to be tailored to these harsh conditions to achieve ultralow IFT.

Because the potential for recovery from surfactant-based methods is high, there has been significant industry interest in cEOR techniques (Anderson et al. 2006; Dwarakanath et al. 2008; Gao and Gao 2010; Hirasaki et al. 2011). Also, the industry has begun to look to new frontiers, such as offshore cEOR opportunities, in which seawater would ideally be used to make up the injection fluids (Raney et al. 2012). In addition, there are many onshore opportunities in which the industry has significant interest in using cEOR techniques that can make use of available water sources, including the produced water from a waterflood, without carrying out treatment such as softening. The advantage is that total project costs can be significantly reduced.

One of the key criteria and challenges for a surfactant-based enhanced-oil-recovery (EOR) fluid is good aqueous solubility of the surfactant/polymer in the reservoir injection brine at the salinity or total-dissolved-solids (TDS) content in which an ultralow IFT is achieved. Surfactant and surfactant/polymer solutions can precipitate or phase separate at high-TDS and/or divalent-ion (mainly Ca^{2+} and Mg^{2+}) concentrations in the aqueous phase. Certain classes of surfactants such as internal olefin sulfonates (IOSs) are particularly sensitive to divalent-ion content (OilChem Technologies 2013; Southwick et al. 2014). Adding cosolvents has been frequently practiced as a method to achieve injectable solutions. However, their use increases costs and complexity of logistics and may hinder achieving sufficiently low IFT.

In addition, the phase behavior of anionic surfactant systems is more sensitive to changes in concentrations of Ca^{2+} and Mg^{2+} ions than to those of monovalent cations such as Na^+, a phenomenon that is pronounced at lower surfactant/TDS concentrations (Glover et al. 1979; Puerto and Reed 1983). Ion exchange that occurs between the clay, brine, and surfactant micelles in the reservoir can be problematic because it can result in a shift in the phase behavior with the system becoming overoptimum (Hirasaki et al. 2011).This shift is undesirable because (a) it tends to give viscous water-in-oil emulsions, which can become trapped in the formation, and (b) the surfactant migrates to the oil phase, which is often less mobile than the brine, thereby slowing surfactant transport through the reservoir. If the oil becomes trapped, the surfactant it contains can take no further part in the chemical flood.

This paper contains test results evaluating surfactant performance without cosolvent in SW and more-concentrated hard brines and in NaCl brines with ionic strengths equivalent to those of the hard brines. This work has several objectives.

- To study the performance of alcohol alkoxy sulfates [i.e., alcohol ethoxy sulfates (AESs) with ethylene oxide (EO) and alcohol propoxy sulfates (APSs) with propylene oxide (PO) chains]. These are known to provide tolerance for brines of high salinity and hardness. Even at relatively high salinities, they resist precipitation in hard brines more successfully than other surfactants including alkyl aryl sufonates, alpha olefin sulfonates (AOSs), and internal olefin

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% Salt	SW_s	SW	
NaCl	2.7	2.9	4.0
$CaCl_2$	0.13	0.13	
$MgCl_2 \cdot 6H_2O$	1.12	1.12	
$NaSO_4$	0.48	–	
TDS (cm^3/L)	38,300	35,500	40,000
Ionic strength (mol/L)	0.765	0.697	0.684

Table 1—Test brines with similar divalent ions in seawater with (SW_s) and without (SW) sulfate.

sulfonates (IOSs), classes of surfactants that have been used or are being proposed for cEOR. In this study, alcohol sulfates with chains of POs followed by EOs were excluded to limit the scope of work.

- To study blends of APS and IOS as well as blends of two alcohol alkoxy sulfates, the latter a previously unreported surfactant combination, to assess how well these combinations perform with hard brines. Performance in aqueous solubility, oil solubilization, and IFT reduction is presented for a number of surfactant systems, both with model oil (*n*-octane) and with crude oil, and at two temperatures.
- To evaluate performance of these surfactant blends in hard brines compared with performance in NaCl solutions of similar ionic strength.

Also explored is the effect of mixing injection brine with reservoir brine during cEOR flooding. These brines often have different salinities. After mixing, the ionic content experienced by the surfactant formulation as well as the surfactant concentration can change significantly, and that can affect process performance, most likely adversely. When a blend of two different surfactants is used in this situation, it is useful for EOR process design to construct a salinity map, in which equilibrium phase behavior with the relevant crude oil at reservoir temperature is plotted against surfactant and brine compositions. This tool aids the selection of a surfactant system with high potential to recover oil when a salinity gradient is present.

Experimental

Sample Preparation. For preparing a set of phase-behavior samples at a water/oil ratio of approximately unity, eleven pipettes of ≈3.0 cm^3 are filled with an aqueous surfactant solution: 2% total or 0.04 g active mass, 1 cm^3 brine(s), and 1 cm^3 oil; volumes are converted to weight by density with surfactant density assumed equal to ≈1 g/cm^3, and each weight is recorded. The 3.0-cm^3 pipettes are made from cutting 5-cm^3 borosilicate, serological pipettes. Pipettes are sealed first at the tip; after being filled, they are sealed at the top with an oxygen-acetylene torch. Samples are well mixed and then equilibrated at the desired test temperatures. Often samples are remixed after a certain period of equilibration to ensure thorough mixing. For the experiments at ≈50°C, each pipette was placed inside a 10-cm^3 test tube filled with transparent silicone oil. This procedure avoids high thermal stresses in the pipettes when the hot samples are exposed to air, and facilitates photographing the samples before cooling alters significantly the equilibrium phase behavior.

Salinity scan tests were performed by either (1) mixing two brines with different concentrations of NaCl and divalent ions or (2) mixing two brines of different NaCl concentrations but with the same divalent-ion concentrations,

Blend scans, for finding an optimal surfactant system for a desired condition, were prepared by either (1) weighing surfactants, measured from a positive displacement pipettor, into pipettes, then adding brine and oil by volume or (2) preparing stock solutions of surfactants, loading weighed aliquots of a stock solution to the pipettes, then adding oil by volume.

Aqueous solutions were prepared at 1% total surfactant concentration. Brines and surfactant solutions were all prepared as wt/vol%. Surfactant-blend ratios were calculated in wt/wt from the active mass in surfactants.

Materials. The compositions of hard brines are disclosed in **Table 1.** Two synthetic seawater compositions were used in the experiments, SW_s with sodium sulfate and SW without it. The latter brine was used to provide greater assurance that no precipitation would occur. As disclosed in the table, 4% NaCl solutions have nearly the same ionic strength as SW. Omitted from the table are 2*SW and 3*SW, having double and triple the salt composition of SW, and the corresponding 8% and 12% NaCl solutions with nearly the same ionic strengths as these multiples of SW. Inorganic salts used in preparing these brines were reagent grade, and the water used was deionized.

The alcohol propoxy sulfate (APS), alcohol ethoxy sulfate (AES), and internal olefin sulfonate (IOS) surfactants used in this work are part of Shell Chemical's ENORDET range of surfactants for enhanced oil recovery (EOR). The hydrophobes of all the alkoxylated sulfates named in **Table 2** were branched to reduce their tendency to form solid phases and lyotropic liquid crystals. For similar reasons, IOS was selected instead of alpha olefin sulfonate.

Oils and alcohols were reagent grade. The crude oil was a relatively light crude oil at ≈50°C.

It is important, as a general rule, to observe and record the appearance of sulfated surfactants regularly. These surfactants when freshly made are alkaline, but, after aging they, by hydrolysis, could become hazy or multiphase with pH lower than neutral, indicating product degradation.

Synthesis/Manufacture of the Surfactants. $C_{15–18}$-based IOSs were manufactured on 1- to 2-ton scale quantities for EOR field trials with the pilot-scale sulfonation facilities at Ballestra, as described in a previous work (Barnes et al. 2008), wherein the properties of these IOSs are described.

The alcohol alkoxy sulfates were prepared either on a laboratory scale yielding a few kilograms of each sample or on a pilot-plant scale yielding approximately 100 kg. Three alcohol feeds were prepared by hydroformulation of the appropriate olefin carbon cut. Two of these were approximately $C_{12–13}$ cuts that had two levels of branching, a higher level ("B") and a lower level ("b").The third alcohol was a largely $C_{16–17}$ cut that had the lower

Hydrophobe	Propoxy Groups –[CH_2- (CH_3)-CH_2–O]-	Ethoxy Groups –(CH_2-CH_2–O]-	Naming Convention
Sulfates			
Branched $C_{16–17}$	7	0	b-C_{67} 7P
Lower branched $C_{12–13}$	7	0	b-C_{23} 7P
Higher branched $C_{12–13}$	7	0	B-C_{23} 7P
Lower branched $C_{12–13}$	0	7	b-C_{23} 7E
Higher branched $C_{12–13}$	0	7	B-C_{23} 7E
Sulfonate			
Internal Olefin 15–18	n.a.	n.a.	IOS

Table 2—Tabulation of surfactants.

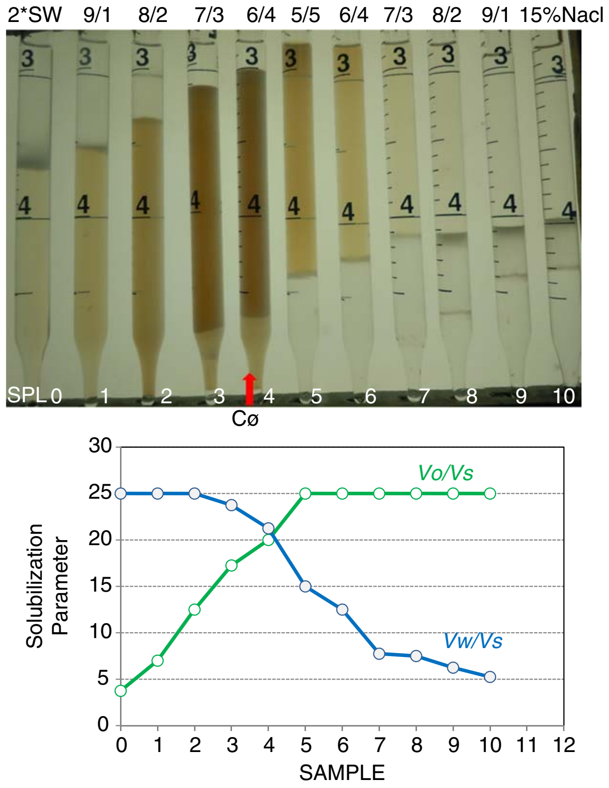

Fig. 1—Picture of salinity-scan test for 2% total b-C_{67}7P/IOS1:1 by weight after 9 weeks of equilibration at ≈25°C and corresponding solubilization parameters plotted below—"Two brines, 2*SW and 15% NaCl, mixed at 10% salinity increments with *n*-octane at WOR ≈1."

("b") level of branching. The alcohol alkoxylates were prepared with an ethoxylation or propoxylation reaction of the alcohol by use of a conventional (KOH) catalyst. Sulfated derivatives were made by the reaction of the alcohol alkoxylate with SO_3 by means of either a laboratory-scale falling-film sulfonation unit or (for the larger sample quantities) a pilot-scale sulfonation unit. The chemistry in the propoxylation step was covered previously (Barnes et al. 2008).

Spinning-Drop Interfacial Tension (IFT). IFTs were determined by use of extracted excess brine as the continuous phase and excess oil as a droplet, from equilibrated phase-behavior tubes. A spinning-drop tensiometer SVT20N from Dataphysics was used, and stable IFTs were determined between a 5- and 45-minute measurement time and at approximately 5,000 rev/min. Densities and refractive indices (RIs) were used as input and were determined experimentally for both phases (RI only for the brine) at ≈50°C.

Phase Behavior of Alcohol Propoxy Sulfate/Internal Olefin Sulfonate (APS/IOS) Systems

Phase Behavior With Octane. APS/IOS blends have been considered for enhanced-oil-recovery (EOR) processes in recent years. In particular, blends of b-C_{67}7P and IOS were used in laboratory studies (e.g., Liu et al. 2008; Levitt et al. 2009). Hence, initial experiments for this project consisted of salinity scans, such as that shown in **Fig. 1** for a blend of equal parts by weight of the two surfactants. Brines in the scan consisted of mixtures of 2*SW_s and 15% NaCl. The temperature was ≈25°C, the oil was *n*-octane, and water/oil ratio (WOR) was approximately unity by volume.

As may be seen from the photographs and the solubilization parameter plot, classical Winsor phase behavior was observed for this alcohol-free system with a high solubilization parameter (V/V_s) ≈20 at optimal salinity. This result suggests that low interfacial tension (IFT) and good oil recovery could be achieved for this system (Huh 1979). This experiment and others with surfactant blends with higher proportions of b-C_{67}7P indicated that microemulsions with high-solubilization parameters could be obtained for this combination of surfactants for brines between SW_s and 3*SW_s.

Subsequently, systematic blend scans with *n*-octane and WOR≈1 were conducted at ≈25°C and 50°C in SW, 2*SW, and 3*SW (all with Na_2SO_4 replaced by NaCl, as in Table 1) for blends of IOS with not only b-C_{67}7P but also b-C_{23}7P and B-C_{23}7P. In this way, one could determine the effects of hydrophobe structure. Samples were made with 10% intervals in blend ratios by weight (e.g., 100:0, 90:10 . . . 0:100).

Table 3 is a summary of optimal blend ratios on a weight basis and optimal solubilization ratios (where $V_o/V_s = V_w/V_s$) for these experiments at 25 and 50°C. **Fig. 2** is to disclose a blend scan in 2*SW at 25°C for b-C_{67}7P/IOS, which has an optimal 65:35 blend ratio and a solubilization parameter of 12.

Inspection of Table 3 confirms the tentative conclusion reached from the initial salinity scans that these alcohol-free APS/IOS blends produce microemulsions with *n*-octane with high oil- and brine-solubilization parameters (many >15) near optimal conditions, indicating that they are highly promising for EOR processes. Moreover, microemulsion phase behavior at salinities up to 3*SW demonstrates tolerance to both salinity and hardness. Comparison of phase-behavior test results in 2*SW and 3*SW with soft brines of the same ionic strength indicates little

	Surfactant Blend Weight Ratio		SW	2*SW	8% NaCl	3*SW	12% NaCl
25°C	b-C_{67} 7P: IOS	*Bø*	85:15	65:35	65:35	55:45	45:55
		V/Vs	>10	17	15	13	14
	b-C_{23} 7P: IOS	*Bø*	All Type I	85:15	85:15	65:35	65:35
		V/Vs		16	16	12	12
	B-C_{23} 7P: IOS	*Bø*	All Type I	75:25	75:25	55:45	50:50
		V/Vs		19	19	19	One phase
50°C	b-C_{67} 7P: IOS	*Bø*	Not done	45:55	45:55	25:75	35:65
		V/Vs		16	15	11	10
	b-C_{23} 7P: IOS	*Bø*	Not done	80:20	75:25	45:55	45:55
		V/Vs		One phase	22	11	11
	B-C_{23} 7P: IOS	*Bø*	Not done	65:35	65:35	35:65	35:65
		V/Vs		17	17	18	18

[a] Test conditions: 2% overall concentration, *n*-octane/test-brine ≈1. *Bø* = optimal blend ratio; *V/Vs* = solubilization parameter at *Bø*; *V* = oil or water volume; *Vs* = surfactant volume.

Table 3—Tabulation of test results at ≈25°C, 50°C.[a]

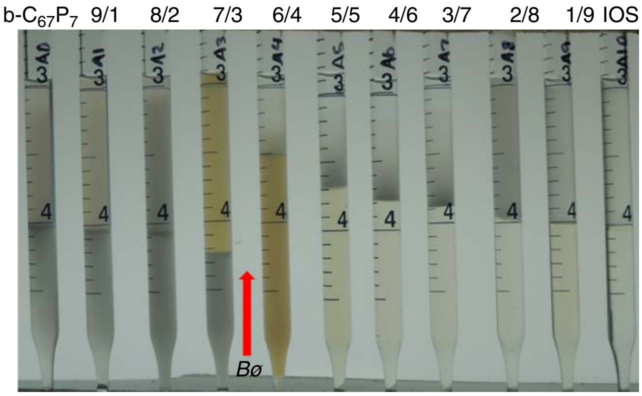

Fig. 2—Picture of blend-scan test for 2% total b-C_{67}7P/IOSin 2*SW and *n*-octane at WOR≈1 and 25°C.

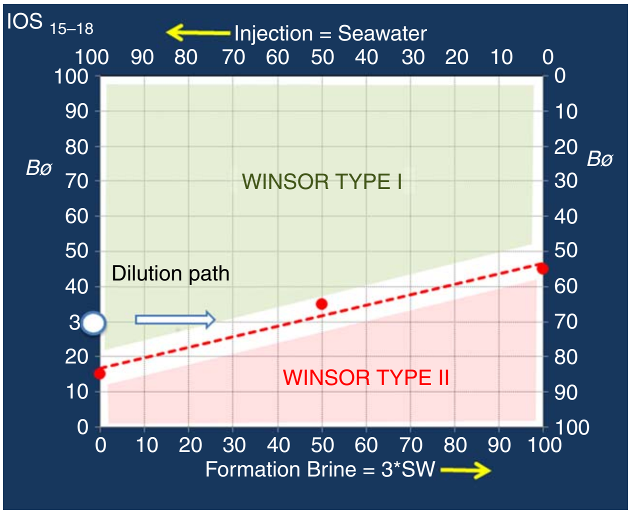

Fig. 3—Salinity map: Hypothetical case for surfactant selection in a variable-salinity cEOR processes. The injection blend for optimal oil recovery should lie in the Winsor Type I region, green-shaded, in between 55:45 and 85:15 of b-C_{67} 7P/IOS blend; lower amounts of b-C_{67} 7P should result in too-high IFT and higher amounts in immediate transition to Winsor Type II in which surfactant will be lost by partitioning into oil, making, for example, heavy emulsion. An example dilution path is indicated by a blue arrow. See Aqueous Solubility subsection for a further constraint.

difference in optimal blend compositions for a given APS/IOS combination. That is, optimal conditions for hard brines of known composition can be estimated from measured optimal conditions for NaCl solutions, at least for these systems at these salinities.

As expected, increasing either salinity or hydrocarbon chain length of the APS for fixed length of propylene oxide (PO) chain (e.g., from $C_{12–13}$ to $C_{16–17}$) decreased the proportion of APS in the optimal blend. Both of these changes make the surfactant blend less hydrophilic at constant blend ratio. Hence, the blend ratio must be changed to incorporate more of the hydrophilic surfactant IOS to regain the hydrophilicity of the initial optimal blend. A similar decrease in APS proportion in the optimal blend was found with increasing temperature because such an increase also makes the APSs less hydrophilic by reducing the water of hydration of their PO chains (Acosta et al. 2012; Puerto et al. 2012). From the test results (see Table 3), the APSs tested can be arranged from most-to-least hydrophilic as c-C_{23}7P>B-C_{23}7P>b-C_{67}7P. Both b-C_{23}7P and B-C_{23}7P were so hydrophilic that all blends with IOS exhibited only lower phase microemulsions (underoptimum conditions) for SW at 25°C.

In many surfactant EOR processes using a blend of two surfactants, the salinity of the injected brine differs from that of formation brine (FB). Because some mixing of injection and formation brines inevitably occurs during the process, it is useful to have a salinity map in which equilibrium phase behavior is shown on a plot in which relative amounts of the surfactants in the blend and relative amounts of injection and formation brines are indicated on the two axes. Such a plot is shown for b-C_{67}7P/IOS with octane at 25°C in **Fig. 3.** In this case, the injection brine is taken as SW and FB as 3*SW. The optimal line separates Winsor I (underoptimum) and Winsor II (overoptimum) regions. It is desirable in EOR processes to avoid the Winsor II region for the reasons stated in the Introduction. This condition requires an injection surfactant blend containing at least 15% IOS, according to Fig. 3. Injection compositions containing more than ≈45% IOS are also undesirable because the horizontal dilution path followed on mixing with FB never reaches the optimal line, and sufficiently low IFT may not be achieved. A further constraint is that the oil-free solution of the injected surfactant blend should be soluble in SW, which is discussed in the next subsection.

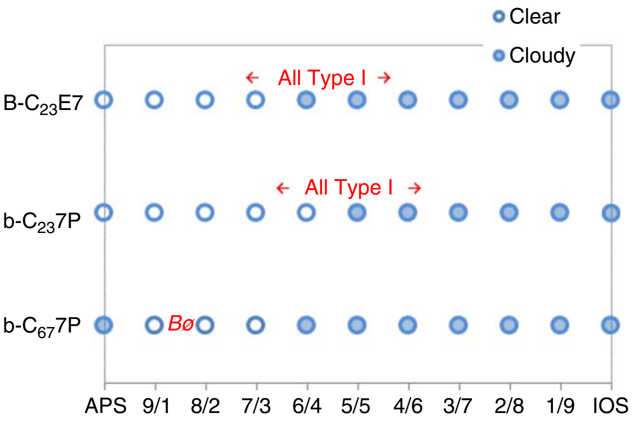

Fig. 4—Aqueous solubility map: APS/IOS blends at 25°C for SW.

Aqueous Solubility. A successful chemically enhanced-oil-recovery (cEOR) formulation requires its aqueous solutions to be stable, single phases when oil is not present (i.e., during injection and subsequent flow in the reservoir until it contacts crude oil). A particular challenge of working with high-total-dissolved-solids systems or systems with divalent ions present such as SW is the limited solubility of some classes of surfactants near the optimal conditions for oil recovery. Often, cosolvents are required in a formulation for achieving the solubility needed for single-phase behavior.

To systematically evaluate surfactant systems for aqueous solubility, similar blend scans of oil-free aqueous solutions at 1% overall surfactant concentration were made for the same APS/IOS combinations, temperatures, and salinities, as in Table 3 by use of SW_{nos}. The purpose of these experiments was to determine whether the solutions were single phase near optimal conditions and hence injectable in a cEOR process. The 1% concentration was chosen because it represents a realistic surfactant concentration for application in typical cEOR processes.

For all three APS/IOS blends, the samples in 2*SW, 3*SW and 4 and 8% NaCl solutions with corresponding ionic strengths were cloudy, separated into two phases on standing, or were plagued with precipitate for all blend ratios at both 25 and 50°C. Thus, it will be necessary to find a suitable additive for formulating single-phase aqueous surfactant solutions if these APS/IOS blends are to be used at these salinities. Similar problems were not encountered in the experiments described previously with *n*-octane because, among other things, inorganic salts of anionic surfactants, especially salts of divalent cations, have substantial solubility in oil.

The aqueous-phase results in SW for the three APS/IOS blends are summarized in **Fig. 4** for 25°C and **Fig. 5** for 50°C. A

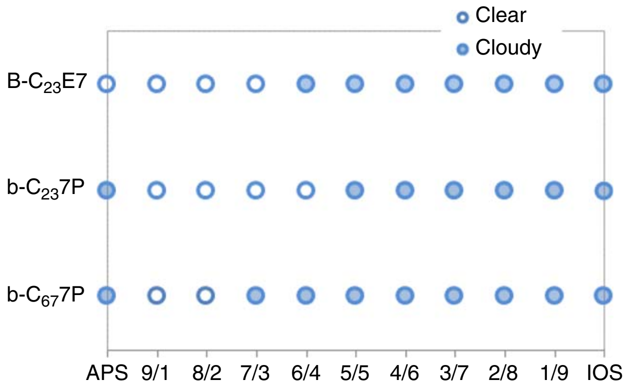

Fig. 5—Aqueous solubility map: APS/IOS blends at 50°C for SW. Optimal blend against *n*-octane undetermined.

favorable result is obtained for b-C$_{67}$7P/IOS at 25°C in SW in that the aqueous solution is clear and injectable for the optimal blend ratio. As indicated previously, the b-C$_{23}$7P/IOS and B-C$_{23}$7P /IOS blends are underoptimum at all ratios for these conditions (i.e., no optimal blend ratio exists).

It is noteworthy that difficulty in finding clear solutions near optimal conditions in surfactant EOR processes is not unique to the systems studied here, and is indeed widely encountered except when the formulations contain considerable alcohol or other cosolvent. One reason is that achieving the balance of hydrophilic and lipophilic conditions found at optimal conditions, in which oil/water interfaces have zero spontaneous curvature, is also favorable to forming the lamellar liquid crystalline phase in aqueous solution (Miller and Neogi 1980; DeGennes and Taupin 1982; Acosta et al. 2012). We speculate that such ordered phases also promote phase separation/lack of clarity in aqueous solutions. The use of branched hydrophobes and incorporating alkoxy chains makes the interfaces more flexible, but these changes may not be enough to achieve clear, single-phase solutions, especially when polymer is present.

A further remark may be made regarding the b-C$_{67}$7P/IOS aqueous solutions at low salinities, which may be applicable to other APS/IOS blends in which IOS is the more hydrophilic surfactant. In the absence of IOS, an aqueous solution of 1% b-C$_{67}$7P in SW at 25°C is cloudy (i.e., the surfactant is above its cloud point). Addition of only 10% of the more-hydrophilic IOS is sufficient to produce a clear solution, and solutions remain clear even at 30% IOS although exhibiting precipitation whenever IOS content is 40% or more (Fig. 4). Similar improvement in aqueous phase behavior by adding small amounts of IOS was observed previously for the same surfactant pair in aqueous solutions at 25°C containing NaCl and Na_2CO_3 with ionic strengths comparable to SW (Liu et al. 2008). As temperature or salinity increases, more IOS is required to counter the cloud point effect of the APS. Eventually, the amount of IOS required is such that its tendency to precipitate outweighs its ability to lower the cloud point. In general, blends with high contents of IOS should be avoided because of precipitation in aqueous solution even though microemulsion phase behavior with oil present may be acceptable.

Because, as indicated previously, the aqueous solutions for all blends were unsuitable for injection at both temperatures for 2*SW and 3*SW, a few experiments were conducted to assess the potential of additives to obtain single-phase solutions for blends of b-C$_{23}$7P/IOS at these salinities. Accordingly, experiments at 25°C were conducted in which the following individual additives were added to each sample in blend scans in 2*SW and 3*SW:

- 1% secondary butyl alcohol
- 1% diethylene glycol butyl ether
- 0.25% commercial nonionic surfactant $C_{12–13}EO_{12}$
- 0.25% benzene sulfonate (a hydrotrope)
- 1% white oil (branched paraffinic hydrocarbon, MW 540)

The cosolvents and hydrotrope hinder formation of solids and liquid crystals. The nonionic surfactant shifts aqueous phase behavior to more-hydrophilic conditions favoring spherical rather than elongated micelles. The white oil is different in that it is solubilized in the micelles, and can convert a solution of anisotropic micelles into a microemulsion of swollen micelles or spherical drops, thereby minimizing the tendency for separation into two phases with different concentrations of surfactants. Hydrophobic species, which can promote precipitation, may be then incorporated into the micelles. Because the white oil is paraffinic in nature and its molecular weight or molar volume is much greater than that for octane, it forms a Winsor I (lower phase) microemulsion under the same conditions that near-optimal microemulsions form with *n*-octane. This approach was used by Exxon in the 1980s to produce injectable solutions for their Loudon pilot test (Maerker and Gale 1992).

In 2*SW, only the white oil was successful in producing injectable single-phase aqueous solutions and even then only for blend ratios (100:0) – (70:30) of b-C$_{23}$7P/IOS. However, because this range includes the optimal 85:15 blend ratio (see Table 3), this formulation could be used for EOR at 2*SW. In 3*SW, none of the additives was successful in producing injectable solutions. On the other hand, the tests carried out with different cosolvents and hydrotropes were not comprehensive in type and concentration. Thus, further work in this area might produce good aqueous solubility for some systems. In addition, other white oils could be used, a topic of current research in our laboratory.

Constraints imposed by the need for single-phase injection solutions can also be shown on salinity maps, such as that of Fig. 3. As seen in the bottom row of Fig. 4, solubility (a clear solution) is achieved in SW, the injection brine, only for blends between ≈5% and ≈35% IOS. An example dilution path is indicated on Fig. 3. The combination of these constraints imposed by aqueous solubility and those imposed by microemulsion phase behavior discussed in the Phase Behavior With Octane subsection dictates that injection composition in this case must be between 15 and 35% IOS. The final choice for field testing would be made on the basis of coreflooding and simulation-test results.

Blends of Alkoxylated Sulfates

As discussed in the preceding section, it is difficult to find alcohol propoxy sulfate/internal olefin sulfonate (APS/IOS) blends with clear aqueous solutions in hard brines near conditions exhibiting optimal microemulsion phase behavior with *n*-octane and hence presumably with most crude oils. Especially when IOS content of the optimal blend exceeds 20 to 30%, its sensitivity to brines with moderate salinity and hardness usually results in precipitation. Because the ethylene oxide (EO) and/or propylene oxide (PO) groups of alkoxylated sulfates provide tolerance to salinity and hardness, a study of blends of alkoxylated sulfates with no IOS was started. To limit the effort involved in initial work on synthesizing and assessing phase behavior of such blends, only PO and EO sulfates were considered (i.e., sulfates containing both PO and EO chains were excluded).

The main thrust of the investigation was the study of blends of b-C$_{67}$7P with other APSs b-C$_{23}$7P and B-C$_{23}$7P and ethoxylated sulfates b-C$_{23}$7E and B-C$_{23}$7E. Blend scans were conducted in SW at 25°C with *n*-octane present at water/oil ratio of approximately unity and for the corresponding oil-free aqueous solutions.

Optimal blend ratios B_ϕ and aqueous phase behavior are shown in **Fig. 6.** One may see a photograph of the blend scan with octane for b-C$_{67}$7P/b-C$_{23}$7E in **Fig. 7.**

In contrast to the blends with IOS, as seen in Fig. 6, aqueous solutions of the alkoxylated sulfate blends exhibit clear solutions for all blend compositions except for bC$_{16–17}$PO$_7$ sulfate itself, which is above its cloud point in SW at 25°C. A photograph of the aqueous phase scan for b-C$_{67}$7P/b-C$_{23}$7E is shown in **Fig. 8.**

The ability of blends of alkoxylated sulfates to produce clear aqueous solutions over a wide range of blend ratios is encouraging

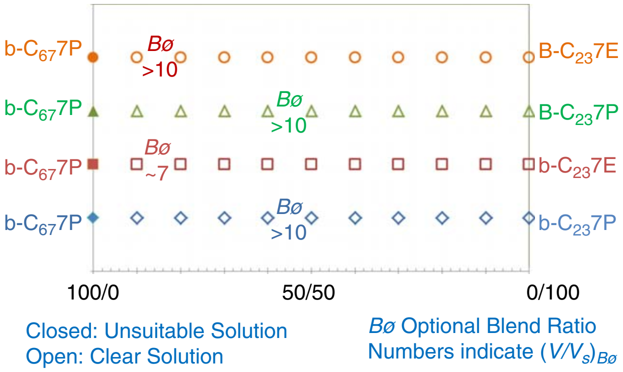

Fig. 6—Aqueous solubility map: 1% total surfactant concentration in SW at ≈25°C.

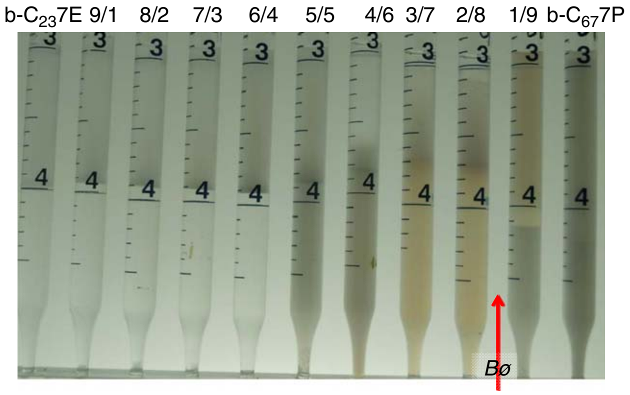

Fig. 7—Picture of blend-scan test for 2% b-C_{67}7P/b-C_{23}7E with *n*-octane and SW at 25°C, water/oil ratio of approximately unity.

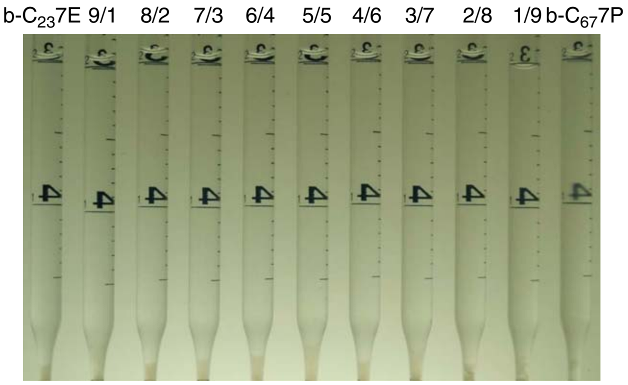

Fig. 8—Picture of blend-scan test of 1% b-C_{67}7P/b-C_{23}7E in SW at 25°C.

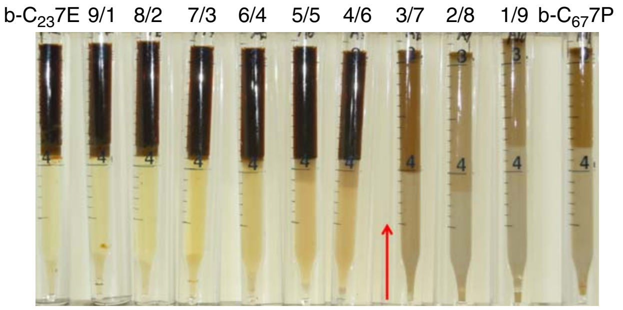

Fig. 9—Blend scan: water/oil ratio of approximately unity: 2% b-C_{67}7P/b-C_{23}7E with crude oil and SW at ≈50°C. Red arrow indicates optimal blend ratio.

and merits further study, including experiments at higher temperatures up to 60°C and higher salinities.

Phase Behavior With Crude Oil in SW at Approximately 50°C

As a means of testing whether systems such as those discussed previously can be used for a practical application, a formulation was sought that would have a clear aqueous phase near optimal conditions at ≈50°C for a crude oil. Although experiments were performed at various salinities, only the work to find a formulation for injection in SW is described here. For these conditions, it was expected that the amount of internal olefin sulfonate (IOS) needed in an optimal blend with b-C_{67}7P would cause precipitation to occur in the aqueous solution. Hence, preliminary experiments were conducted with several blends of alkoxylated sulfates. Although several suitable blends could likely be found with an adequate inventory of alkoxylated sulfates, a blend of b-C_{67}7P/b-C_{23}7E was selected on the basis of knowledge of phase behavior of the individual surfactants. One can see a photograph of a blend scan with crude oil for this system at ≈50°C in SW in **Fig. 9.** It indicates that the optimal blend is near 70% b-C_{67}7P. A salinity map for this system at ≈50°C extending from SW to 3*SW is shown in **Fig. 10.** For comparison, it includes optimal blends of NaCl solutions with the same ionic strength as SW, 2*SW, and 3*SW. Agreement between results for hard and soft brines is reasonable for all three salinities.

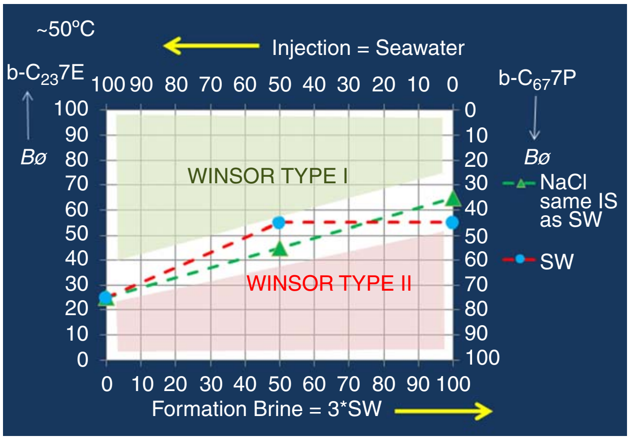

Fig. 10—Salinity map for crude oil: SW and crude oil: NaCl-only brine of same ionic strength as SW at ≈50°C.

With *n*-octane as the oil in SW at ≈50°C, the optimal blend is between 60 and 70% b-C_{67}7P (photograph not shown). This *Bø* value is not far from that of crude oil, which indicates that one could use octane in initial screening to find optimal phase behavior with crude oil in this system.

An aqueous blend scan in SW at ≈50°C for the same surfactant pair produced clear, single-phase solutions at 60% or less of b-C_{67}7P **(Fig. 11).** The solution at 70% is only slightly cloudy, whereas those with higher contents of b-C_{67}7P are considerably cloudier (i.e., the aqueous solution at the optimal blend for crude oil is questionable for injection). However, it would be preferable to inject at a slightly lower contents of b-C_{67}7P for mitigating the possibility of reaching overoptimum conditions with its risk of generating viscous water/oil emulsions caused by (a) possible slight differences between reservoir conditions and those of the laboratory experiments, (b) ion exchange and related phenomena, and (c) inevitable mixing between the surfactant slug in SW and higher-salinity brine in the reservoir (Nelson 1982; Flaaten et al. 2009).

The use of blends of alkoxylated sulfates provides a wide scope of surfactant choices. Another blend was also found to have suitable phase behavior with the crude oil studied in SW at

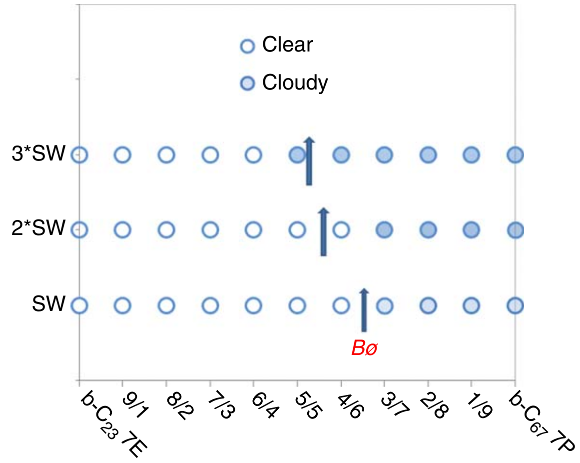

Fig. 11—Aqueous solubility map for 1% b-C_{23}7E and b-C_{67}7P extending from SW to 3*SW at ≈50˚C.

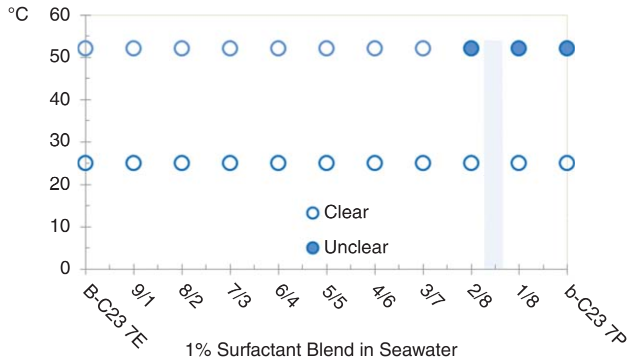

Fig. 13—Aqueous solubility map for 1% blend of b-C_{23}7P/B-C_{23}7E. Shaded blue area to indicate optimal blend ratio, *Bø*, against *n*-octane at ≈50˚C (left boundary) or crude oil (right boundary).

≈50°C. **Fig. 12** is a plot of optimal blend ratio as a function of oil molar volume, a parameter found useful in correlating phase behavior by Puerto and Reed (1983). Optimal blend ratios for b-C_{23}7P/B-C_{23}7E with crude oil and *n*-octane, respectively, are 83:17 and 87:13. The small difference in blend ratios again indicates that *n*-octane is a good choice of model oil, to be used for initial screening purposes in this system. **Fig. 13** shows aqueous phase behavior in SW at 25°C and ≈50°C for this surfactant blend. Here, too, aqueous solutions are cloudy at optimal conditions at ≈50°C for both oils but not greatly different in composition from underoptimum compositions (in SW) containing less b-C_{23}7E, which exhibit clear solutions in SW. As discussed previously, it may be preferable in many cases to inject at such blend ratios instead of at the optimal ratio in SW.

Evaluation of a similar b-C_{23}7P/b-C_{23}7E/crude-oil system at ≈50°C (0.6% total surfactant concentration) by interfacial-tension (IFT) measurement was carried out on the system after 1-week equilibration. In the salinity scan of **Fig. 14**, the blend ratio for all samples is the optimal blend shown in Fig. 12 for the b-C_{23} 7P/B-C_{23} 7E system. The fourth tube from the left at 2.75% total salt in a hard brine showed Winsor III behavior. The IFT measured between excess oil and brine phases from this sample was ≈10^{-2} mN/m. On the basis of discussion by Sottmann and Strey (1997), IFT values for microemulsion/oil and microemulsion/brine interfaces are each less than this value. Thus, substantial residual oil should be displaced for these conditions.

Conclusions

It was found that blends of branched alcohol propoxy sulfates (APSs) with internal olefin sulfonate (IOS) can form alcohol-free

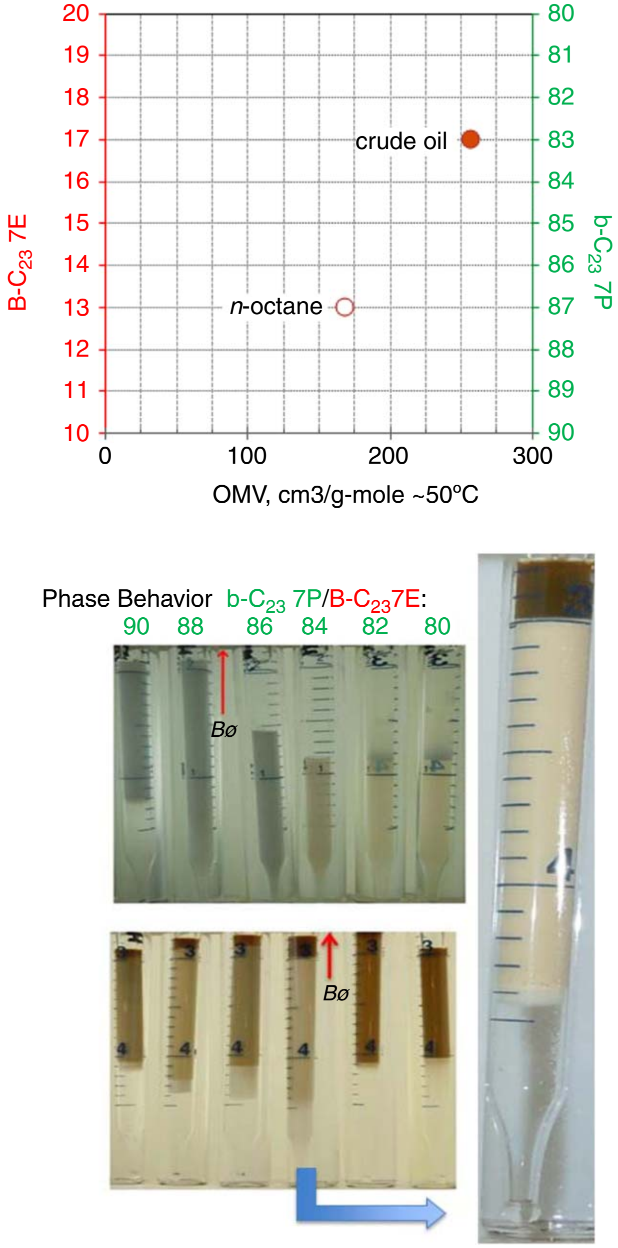

Fig. 12—Phase behavior for b-C_{23}7P/B-C_{23}7E in SW at ~50*C. Optimal blend for crude is slightly more lipophilic than for *n*-octane. The small difference in *Bø* indicates that *n*-octane is a good choice of model oil to be used for initial screening purposes in this system. The picture of near-optimal blend is enlarged to show a near-optimal microemulsion without alcohol; it is of low viscosity.

microemulsions with *n*-octane with high oil and brine solubilization at optimal conditions for salinities up to approximately three times that of seawater (3*SW) and temperatures up to 50°C. Also, optimal conditions with *n*-octane for 2*SW and 3*SW were generally similar for hard brines and NaCl solutions with the same ionic strengths.

In general, in the absence of oil, aqueous solutions at optimal conditions for these higher-salinity formulations, 2*SW and 3*SW, were cloudy and/or exhibited precipitation in both the hard brines and the corresponding NaCl solutions. Apparently, the higher IOS blend content required to achieve optimal phase behavior at higher salinities caused phase separation/precipitation.

One APS/IOS blend tested exhibited a clear aqueous solution with *n*-octane for the optimal blend ratio at 25°C in SW. The optimal conditions at this and higher salinities were used to construct a salinity map showing optimal blend ratio as a function of

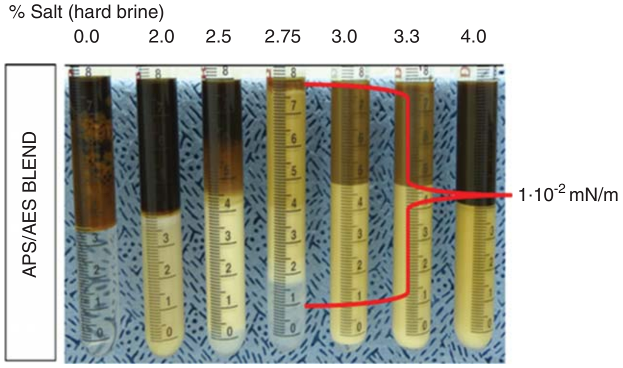

Fig. 14—Phases selected for IFT measurements from phase-behavior salinity scan with crude oil: 1% 83 b-C_{23}7P/17 b-C_{23}7E, SW at $\approx$50°C.

salinity. Such maps should prove useful in situations in which compositions of injection and formation brines differ.

Initial experiments with blends of alkoxylated sulfates with *n*-octane as oil indicated that they have more favorable prospects of having clear aqueous solutions over a range of optimal blend ratios, at least at low temperatures in SW. Also, three APS/alcohol ethoxy sulfate (AES) blends formed suitable microemulsion phases with a crude oil in SW at $\approx$50°C. Although it was found that aqueous phases of the optimal blends were slightly cloudy, relatively small shifts in composition into the lower phase region produced clear solutions suitable for injection. Injection for slightly underoptimum conditions may be desirable to avoid/mitigate phase behavior shifting into overoptimum conditions during the process because of ion-exchange phenomena or mixing of injection and formation brines.

The test results from different APS- and AES-based systems with model oil *n*-octane and hard brines provide proof of concept for applying this approach for real projects. In this case, the approach was confirmed by testing with a representative crude oil.

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Maura C. Puerto is a research scientist at Rice University. She retired from ExxonMobil as a research associate after more than 25 years of service in the Reservoir Division. Puerto is recognized as an expert in the application of surfactants to processes involving flow through porous media and is skilled in the area of designing laboratory coreflood testing and history matching the results by simulation. She holds a chemical engineering degree from Oriente University in Cuba. Before joining Exxon in 1974, Puerto was employed in quality control and product development by Almay Hypoallergenic Cosmetics and was technical director of the cosmetic branch at the Cuban Institute of Soap and Cosmetics. She was the recipient of the 1980 SPE Cedric K. Ferguson Award, and in 1996 she received, on the basis of her work on CO_2 solubility in low-vapor-pressure solvents for aerosols, the Quality Award from Exxon Chemicals for turning environmental regulations into opportunities. Since her retirement from Exxon, Puerto has participated on a part-time basis in research on enhanced oil recovery (EOR) and aquifer remediation at Rice University.

George J. Hirasaki earned 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, EOR, and formation evaluation. At Rice, his research interests are in nuclear-magnetic-resonance (NMR) well logging, reservoir wettability, EOR, gas-hydrate recovery, asphaltene deposition, emulsion coalescence, and surfactant/foam aquifer remediation. Hirasaki received the 1989 SPE Lester C. Uren Award. Hirasaki was named an Improved Oil Recovery Pioneer at the 1998 SPE/DOR IOR Symposium. He was the 1999 recipient of the Society of Core Analysts Technical Achievement Award. He is a member of the National Academy of Engineers and SPE.

Clarence A. Miller is Louis Calder Professor Emeritus of Chemical and Biomolecular Engineering at Rice University and a former chairman of this department. His BS and PhD degrees were from Rice and the University of Minnesota (1969), 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 (Germany), and Delft University of Technology (The Netherlands). Miller's research interests center on emulsions, microemulsions, and foams and their applications in detergency, EOR, and aquifer remediation. He is coauthor of the book *Interfacial Phenomena*, now in its second edition.

Carmen G. Reznik currently supports Shell Chemicals Operations in Houston. She previously worked in Chemical Enhanced Oil Recovery out of Shell Technology Center, Houston. Before joining Shell, Reznik worked in the field of environmental testing. She holds a PhD degree in physical chemistry from Rice University, and her expertise includes interfacial chemistry and transport, photophysics, and surfactant EOR. Reznik has a number of publications, representing each of these fields.

Sheila Dubey has worked in research and technology for Shell Oil Company for 35 years. Dubey's areas of expertise lie in chemical EOR, production chemistry, produced-water treatment, flow assurance, surfactant chemistry, and analytical chemistry. She holds MS and PhD degrees in physical organic chemistry and an MS degree in chemical engineering. Dubey is a member of SPE and American Chemical Society.

Julian R. Barnes is a principal research chemist at Shell's Technology Centre in Amsterdam. His BSc and PhD degrees are in chemistry and NMR spectroscopy from the University of Bristol, UK. In 1980, Barnes joined Shell and, spanning approximately 35 years, has held research-and-development (R&D) positions in the UK, France, Japan, Germany, and, now, The Netherlands. The first part of his career was focused on NMR spectroscopy applications, lubricants and fuels R&D, a technical marketing position, and R&D support for surfactants for household applications. The latter part of Barnes' career has focused on the development and upscaling of new surfactants for EOR. He has published in technical journals over the years and is a coinventor on a number of patents.

Sjoerd R. van Kuijk holds a BSc degree and an MSc degree in chemical engineering from the University of Groningen. As part of his studies, he served an industrial internship on water-system design for conceptual biofuel-production processes, and graduated in 2012 on the creation of aquatic-inspired adhesive products with polyketones. van Kuijke worked at the Shell Technology Centre in Amsterdam for 2 ½ years as a product technologist for surfactants in chemical EOR. Starting in 2015, he will work at the Shell Nederland Chemie Moerdijk plant as an Moerdijk styrene propylene oxide process technologist for water treatment, catalyst production, and energy efficiency.