

Surfactant Systems for EOR in High-Temperature, High-Salinity Environments

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Summary

A systematic study was made of phase behavior of alkoxyglycidylether sulfonates (AGESs). These surfactants were screened with either NaCl-only brines or NaCl-only brines and *n*-octane at water/oil ratio (WOR) ~1 for temperatures between approximately 85 and 120°C. All test cases were free of alcohols and other cosolvents. Classical Winsor phase behavior was observed in most scans, with optimal salinities ranging from less than 1% NaCl to more than 20% NaCl for AGESs with suitable combinations of hydrophobe and alkoxy chain type [ethylene oxide (EO) or propylene oxide (PO)] and chain length. Oil solubilization was high, indicating that ultralow interfacial tensions existed near optimal conditions. The test results for 120°C at WOR~1 have been summarized in a map, which might provide a useful guide for initial selection of such surfactants for EOR processes. Saline solutions of AGESs separate at elevated temperatures into two liquid phases (the cloud-point phenomenon), which may be problematic when they are injected into high-temperature reservoirs. An example is provided that indicates that this situation can be alleviated by blending suitable AGES and internal olefin sulfonate (IOS) surfactants. Synergy between the two types of surfactant resulted in transparent, single-phase aqueous solutions for some blends, but not for the individual surfactants, over a range of conditions including in synthetic seawater. Such blends are promising because both AGES and IOS surfactants have structural features that can be adjusted during manufacture to give a range of properties to suit reservoir conditions (temperature, salinity, and crude-oil type).

Introduction

Many reservoirs suitable for surfactant EOR have high temperatures and salinities [i.e., temperatures ranging from 70°C to more than 120°C and brines with substantial hardness and having total-dissolved-solids (TDS) contents up to approximately 200,000 mg/L]. These conditions are challenging for process design because injected surfactants must remain chemically stable at reservoir conditions for the duration of the project, which could last for years. Moreover, precipitation or other undesirable phase separation must be avoided. In addition to meeting these conditions, surfactants should be able to develop ultralow interfacial tensions (IFTs) with crude oil at reservoir conditions, have low adsorption on reservoir rock, and form clear, single-phase aqueous solutions at mixing and injection temperatures, typically at surface temperature. In non-water-wet formations, they should also be able to increase wettability of pore surfaces to water.

It is well known that surfactants with alkoxy chains (i.e., EO and/or PO), can improve surfactant tolerance to high salinities and hardness. Indeed, sulfates having EO and/or PO groups have been used in laboratory and pilot tests of surfactant EOR processes at low temperatures, including some cases with carbonate cores or reservoirs (Adams and Schievelbein 1987; Maerker and Gale 1992; Liu et al. 2008; Levitt et al. 2009). However, sulfates have a sulfur-to-oxygen bond, which is subject to hydrolysis at high temperatures (Talley 1988). Efforts are being made to identify particular conditions where hydrolysis can be minimized as well as

to develop additives that can help achieve these conditions (Adkins et al. 2010). Nevertheless, great caution should be exercised in laboratory screening for using sulfates above 50–60°C. Test results should indicate clearly that surfactant stability can be maintained for the entire range of conditions encountered during the designed EOR process. In contrast, sulfonates, including those with alkoxy groups, have the required stability at high temperatures because they have a sulfur-to-carbon bond, which is not subject to hydrolysis.

Results for several IOSs showing phase behavior expected to yield ultralow IFTs at high temperatures were presented previously (Barnes et al. 2008). Some further information on performance of these surfactants is given here. However, these experiments were conducted with brines containing only NaCl (i.e., no hardness). Designing EOR processes for high-temperature reservoirs with brines having substantial hardness and high values of TDS will be more challenging and will likely require blending of alkoxyated sulfonates with other surfactants such as IOSs, which are also stable at high temperatures.

Some previous laboratory studies of surfactant EOR processes have included experiments with alkoxyated—mainly ethoxyated—sulfonates, used either alone or in combination with other surfactants. Skauge and Palmgren (1989) reviewed the EOR literature on such work and presented their own experiments on phase behavior with *n*-heptane at 90°C for a series of ethoxyated sulfonates in which both hydrophobe and EO chain length were varied systematically. Secondary butanol was used as cosolvent at a concentration equal to surfactant concentration. A few surfactants tested had optimal salinities near and even above 20% NaCl. However, all surfactants having optimal salinities above 16% NaCl either had low solubilization parameters, which would not yield ultralow IFTs, or exhibited precipitation in seawater. Austad (1993) reviewed research on static and dynamic adsorption of ethoxyated sulfonates relevant to their possible use in sandstone reservoirs. Abe et al. (1986) tested ethoxyated sulfonates with various alkanes at temperatures up to 80°C in the absence of alcohol. With suitable choice of branched hydrophobe and EO chain length, they found surfactants with satisfactory solubilization at optimal conditions for salinities up to approximately 20% NaCl. They did not indicate whether these surfactants were soluble in brine and, hence, were suitable for injection. In recent years, ethoxyated sulfonates have been studied as possibilities for reducing IFT and altering wettability in fractured, oil-wet carbonate reservoirs (Seethepalli et al. 2004) and as a means of improving salt tolerance in mixtures with other surfactants at low temperatures (Flaaten et al. 2010).

This paper deals with alkoxyated glycidyl sulfonates (AGESs), whose synthesis and structure were described by Barnes et al. (2008). The AGESs used in the research described here were laboratory samples. They are not currently available as commercial products and would, if commercialized, be more expensive than either the corresponding sulfates or IOSs because more steps are involved in the AGES manufacturing process. Some coreflooding experiments using earlier laboratory samples of AGESs were carried out by Wellington and Richardson (1997), but these did not emphasize high temperatures and salinities. Phase behavior of some AGESs is shown next for temperatures up to 120°C in alcohol-free model systems with *n*-octane as the oil and NaCl brine. Both ethoxyated and propoxyated surfactants are tested, alkoxy and hydrocarbon chain lengths are systematically varied, and some of the surfactants have branching of a different type than in previous studies of alkoxyated sulfonates.

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Fig. 1—Encased-glass-pipette method.

Octane was chosen because optimal salinities of various surfactants against this oil are not greatly different from those of the same surfactants against many crude oils (Cayias et al. 1976; Nelson 1983). However, solubilization parameters of surfactants at similar optimal conditions are lower for crude oils than for octane, which has a lower molar volume (Puerto and Reed 1983); hence, IFTs are higher. In the present paper, a plot is given showing optimal salinities and solubilization parameters for several AGESs at 120°C as a function of lengths of the hydrophobe chains and of EO or PO chains. This plot provides a useful starting point for surfactant selection.

A limitation of alkyl alkoxyated sulfonates is that, like alkoxyated nonionic surfactants, their aqueous solutions typically exhibit a cloud point (i.e., separation into two liquid phases as temperature increases). Thus, formulations using alkyl alkoxyated sulfonates alone, while exhibiting favorable phase behavior with oil, may be unsuitable as injectable compositions. IOSs exhibit the opposite behavior, becoming more soluble in aqueous NaCl solutions as temperature increases. Accordingly, their blends with alkoxyated sulfonates offer prospects of having single-phase aqueous solutions over a wider temperature interval, from surface to reservoir temperature, than with alkoxyated sulfonates alone. Moreover, the alkoxyated sulfonates in such blends can provide tolerance to high TDS contents and hardness. We provide an example of such behavior showing that suitable blends of this type are promising for use in EOR processes in high-temperature, high-salinity reservoirs.

Experimental

Surfactant Synthesis and Structures. A description of the synthesis steps for AGES and IOS surfactants and the chemical structures formed was given earlier by Barnes et al. (2008). The AGESs were prepared from three primary alcohol carbon cuts commercially available as NEODOL alcohols. These were a C12,13 alcohol, a C12–15 alcohol, and a *b*-C16,17 alcohol. The C12,13 and C12–15 alcohols are composed of a mixture of 80% linear and 20% branched alcohols, while the *b*-C16,17 alcohol is fully methyl branched. In terms of abbreviations in this paper, *b*-C16,17–3EO GES stands for branched C16,17 alcohol with an average of three ethylene oxide groups and a terminal glycidyl ether sulfonate (GES) group and C12,13–3PO GES for (largely) linear C12,13 alcohol with an average of three propylene oxide groups and a terminal GES group. The IOSs were prepared from internal olefins with carbon cut C20–24 and are abbreviated as IOS 20–24.

Microemulsion Phase Tests. The procedure for sample preparation was previously disclosed and called the glass-pipette method

(Barnes et al. 2008) but is more completely described as the encased-glass-pipette method. The volume of fluids required to accurately determine surfactant properties is approximately 2 cm³ and is contained in heat-sealed pipettes. The small pipettes were made from cutting disposable, 5-cm³ serological pipettes of borosilicate glass with 0.1-cm³ subdivisions having regular tip and standard length. The *n*-octane was 98% reagent grade. Salt solutions were made by adding NaCl to deionized water. All surfactant samples were from the Shell Chemical Company.

Tests were carried out in oil baths. Water, oil, and surfactant were weighed into pipettes using an analytical balance, taking into account their densities. Heat-sealed pipettes, containing water/surfactant (1 cm³) and test oil (1 cm³) were placed inside a 10-cm³ test tube filled with the same fluid as in the bath (see Fig. 1). Samples were mixed in a rotisserie-type mixer immersed in the oil bath. After being mixed, samples were left to equilibrate at test temperature. Typically, they were removed from the oil bath briefly several times during equilibration, shaken by hand a few times, and replaced. This procedure was continued until phase volumes remain unchanged. Photographs were taken at different time intervals.

There are several advantages for inserting the sealed pipette in a test tube filled with the bath fluid:

1. The safety of handling sealed pipettes with hydrocarbons at high temperature is greatly improved compared to equilibrating them in an air bath because the main hazard leading to pipette rupture, sudden large temperature variations within the pipettes, is eliminated.

2. If the sealed pipette leaks, test oil will be diluted by approximately 10 times, which mitigates the hazard of handling low-molecular-weight oils such as *n*-octane at high temperature.

3. The presence of the outer liquid oil jacket will contain any leak or rupture of the glass pipette and prevent contamination of the bath fluid.

4. The outer hot fluid mitigates temperature losses. This makes it practicable to visualize and photograph surfactant phase behavior at high temperatures.

Phase Behavior of AGES Solutions With Octane

Fig. 2 shows optimal salinity (C_ϕ) with octane at 120°C as a function of alkoxy chain length for AGESs having hydrophobes with three different chain lengths. Overall surfactant concentration in each pipette is 2% by weight, and WOR is one. No alcohol or other cosolvent is used. As is evident, a wide range of C_ϕ values can be achieved by varying type and length of the alkoxy chain and surfactant hydrophobe. C_ϕ increases with increasing EO chain length but decreases with increasing PO chain length. Longer-chain hydrophobes lead to lower C_ϕ . Although additional data might reveal that variation of C_ϕ with alkoxy chain length is not linear as indicated, the basic trends are clear.

Maps such as Fig. 2 provide a starting point for selecting surfactants for EOR processes, in this case for an elevated reservoir temperature. Surfactants with hydrophobes and alkoxy chain lengths different from those used to construct the map could be selected to achieve desired values of C_ϕ . Indeed, two or more surfactants may have virtually the same C_ϕ , as shown for *b*-C16,17–3EO GES and C12,13–3PO GES in Fig. 2. Another possibility is to blend surfactants of this type in suitable proportions, for instance one having C_ϕ above and another having C_ϕ below that of the reservoir. The following subsections present results on phase behavior including C_ϕ and solubilization parameters for individual surfactants and provide information on the effect of temperature in the range 85–120°C.

Ethoxylated GES. As depicted in Fig. 2, ethoxylated GESs exhibit phase behavior that suggests that they may be potential candidates for EOR processes in high-temperature, high-salinity reservoirs. The ethoxylated surfactants exhibited optimal salinities with octane up to 21% NaCl at 120°C. EO chain lengths ranged from 3–9 with three hydrophobes being used: C12,13; C12–15; and *b*-C16,17 alcohols.

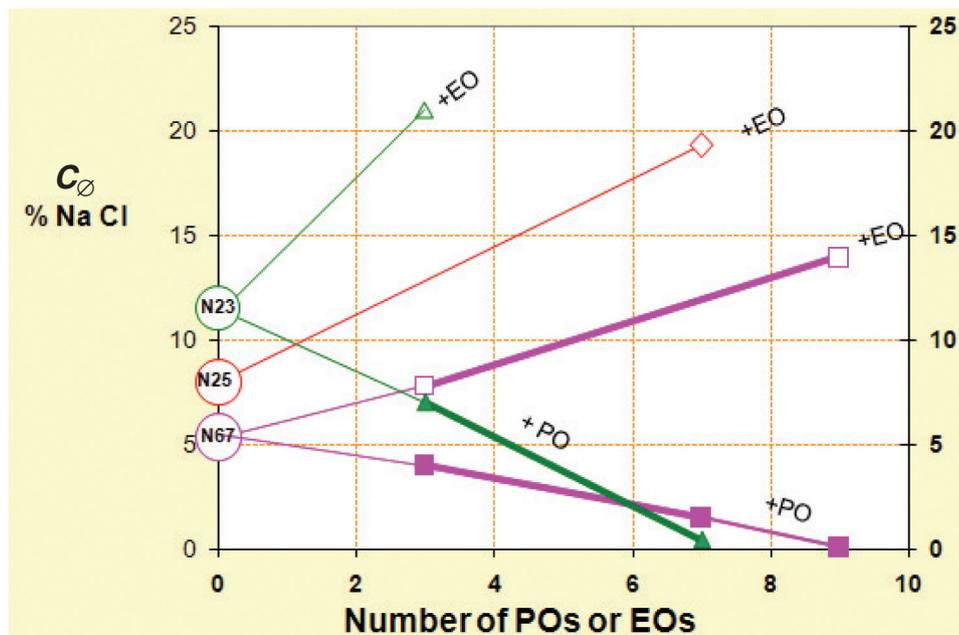


Fig. 2—Optimal-salinity map for glycidylether sulfonates against *n*-octane at 120°C. Circled N23, N25, and N67 are C12,13, C12–15, and *b*-C16,17 alcohols, respectively.

Fig. 3 is a photograph of a salinity scan at 120°C for 4 wt% aqueous solutions of *b*-C16,17–9EO GES equilibrated with equal volumes of *n*-octane in the absence of alcohol. The horizontal red bars indicate positions of interfaces difficult to see in the photograph. Transition from Winsor III to Winsor II (middle to upper) phase behavior is observed with increasing salinity. At lower salinities than shown, Winsor I (lower) phase behavior would be seen. Also included is a plot of solubilization parameters (V_o/V_s) and (V_w/V_s) for the scan, where V_o , V_w , and V_s are volumes of oil, brine, and surfactant in the microemulsion phase, as estimated from phase volumes. Optimal salinity, C_ϕ , where the two solubilization parameters have equal values (V/V_s) $_{C_\phi}$, is approximately 14% NaCl (w/v), as also shown for this surfactant in Fig. 2. The high value for (V/V_s) $_{C_\phi}$ of 22 suggests, according to Huh's correlation (Huh 1979), that IFT is ultralow near C_ϕ and should provide high oil recovery in corefloods. Indeed, values of (V/V_s) $_{C_\phi}$ exceeding 10 should lead to sufficiently low tensions for good recovery, a criterion met by all surfactants discussed in this and the next subsection for the conditions cited. As noted previously, values of (V/V_s) $_{C_\phi}$ for crude oils will be less than those for *n*-octane.

The lower line of Fig. 4 shows that C_ϕ with *n*-octane for this surfactant decreases as temperature increases from 85°C to 120°C, the slope being approximately 0.15%NaCl/°C. The decreasing trend is expected for surfactants with EO chains, which become less hydrated with increasing temperature. However, the decrease may not have the same slope or even be nearly linear for other systems or temperature ranges. Values of (V/V_s) $_{C_\phi}$ remain high and exhibit little change over this temperature range.

Fig. 5 is similar to Fig. 3 except that the surfactant is C12,13–3EO GES. Again, the temperature is 120°C and horizontal red bars have been added to indicate interfacial positions. In this case, the scan includes Winsor I and III regions, but not Winsor II, which would occur at even higher salinities. C_ϕ is higher (21% NaCl) than in Fig. 3, owing to the shorter chain length of the hydrophobe, which outweighs the tendency of the shorter EO chain length to decrease optimal salinity. Here, too, a large value of 19 for (V/V_s) $_{C_\phi}$ is found.

Fig. 6 shows dependence of solubilization parameters on salinity at 120°C for the surfactant C12–15–7EO GES equilibrated with octane. The photographs of the sample at 19.8% NaCl for several times after removal from the oil bath illustrate another way of

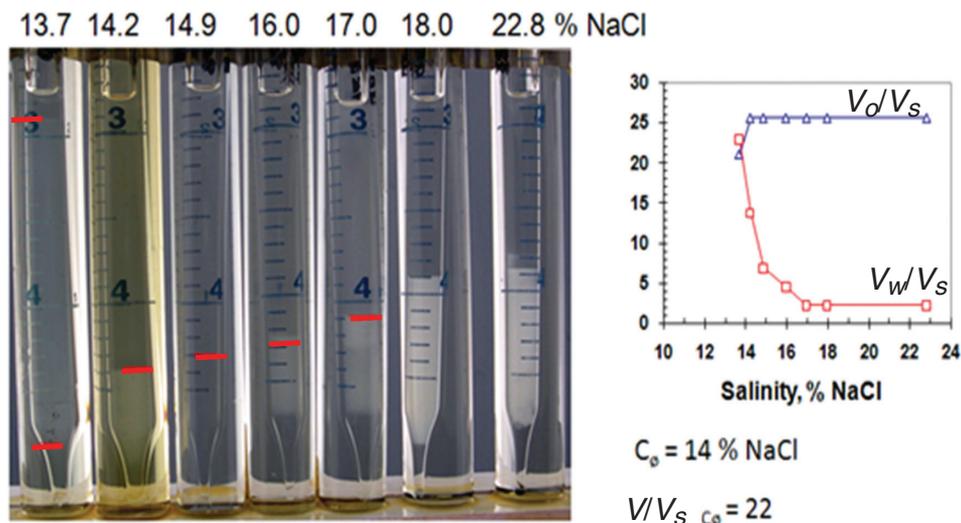


Fig. 3—2% *b*-C16,17–9EO GES salinity scan, WOR~1, *n*-octane at 120°C.

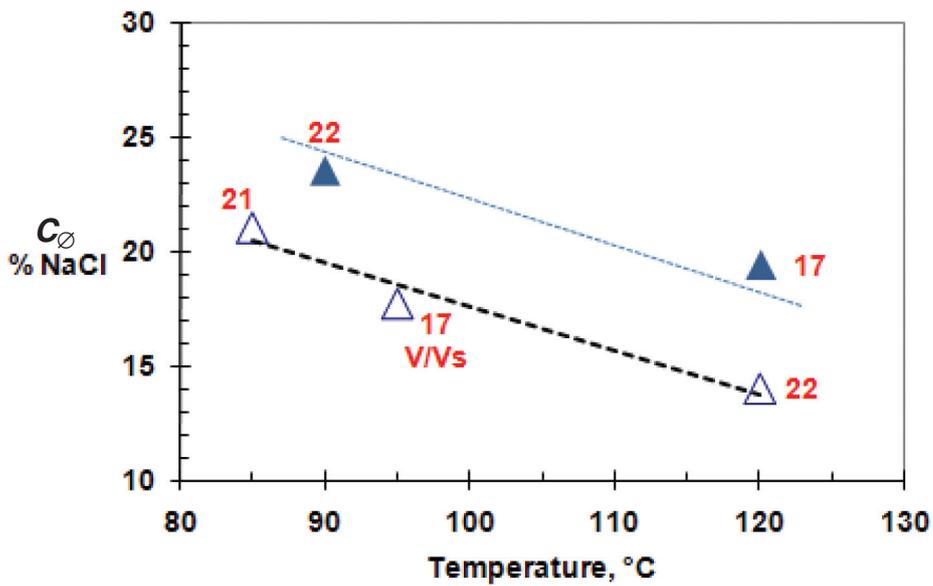


Fig. 4—Effect of temperature on C_ϕ of *b*-C16,17-9EO GES, open triangles, and C12-15-7EO GES, closed triangles, with *n*-octane at 120°C. The optimal salinity C_ϕ decreases approximately 0.15%NaCl/°C. Numbers by data points are values of $(V/V_s)_{C_\phi}$.

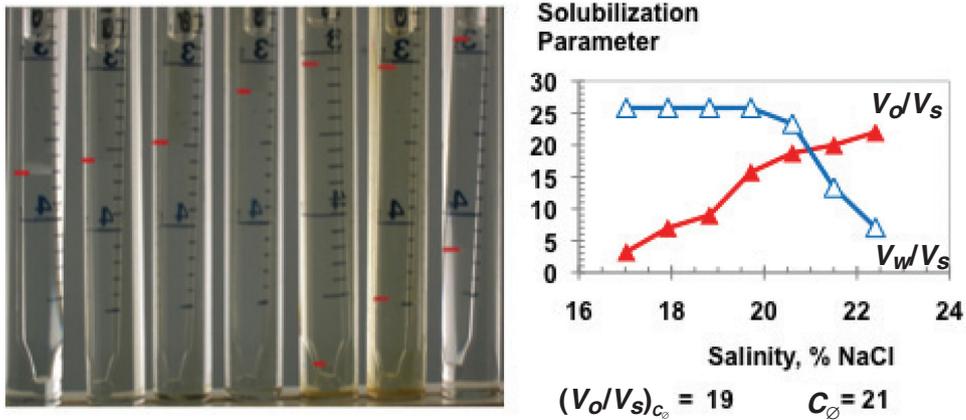


Fig. 5—2% C12,13-3EO GES salinity-scan and solubilization parameters. WOR~1, *n*-octane, NaCl brine.

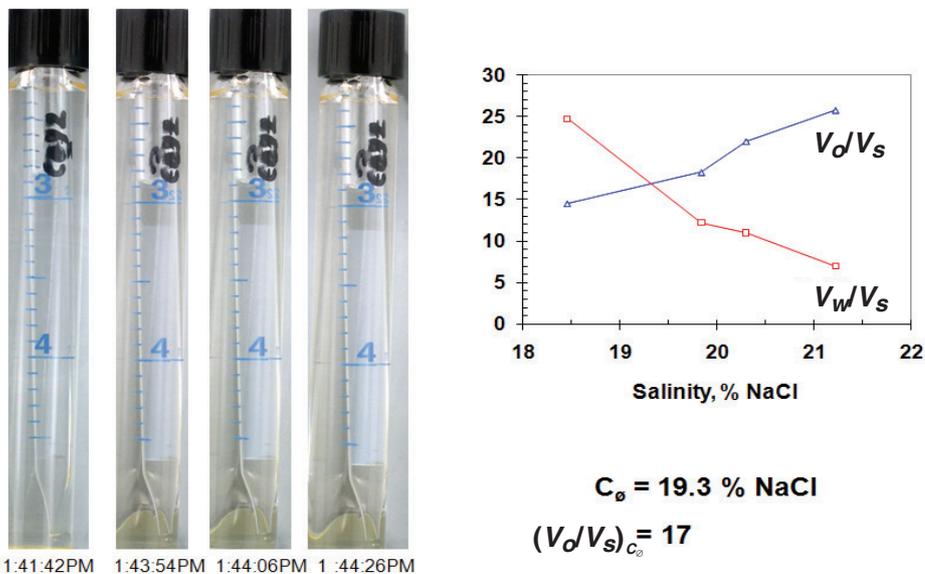


Fig. 6—2% C12-15-7EO GES sample with 19.8% NaCl, WOR~1, *n*-octane, 120°C at four times after removal from oil bath. Plot of solubilization parameters.

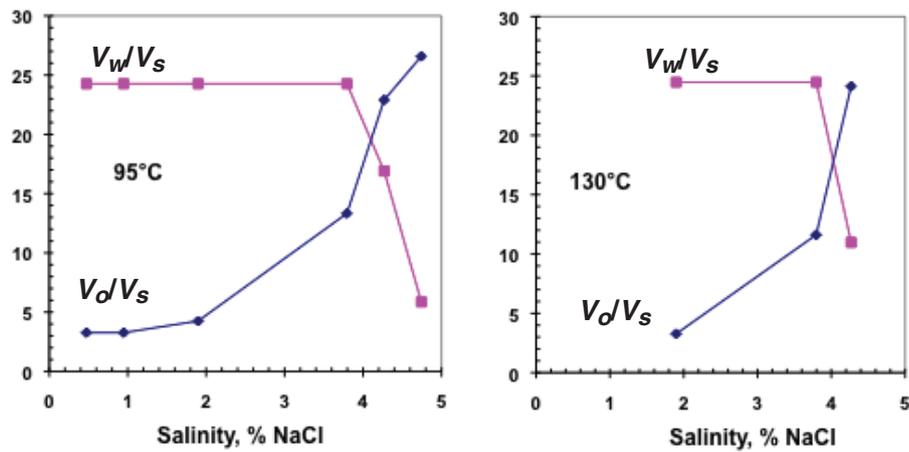


Fig. 7—Solubilization parameters for salinity scans at 95 and 130°C for 2% *b*-C16,17-3PO GES, WOR-1, *n*-octane. Optimal salinity, C_ϕ , appears independent of temperature, but $(V_o/V_s)_{C_\phi}$ decreases as temperature increases.

revealing the positions of interfaces that are difficult to see. On cooling, the microemulsion becomes supersaturated, and the resulting nucleation of small oil droplets causes this phase to become cloudy. C_ϕ is near 19% NaCl, which is intermediate between Figs. 3 and 5 for longer-chain and shorter-chain hydrophobes, respectively. $(V/V_s)_{C_\phi}$ is approximately 17, only slightly lower than for the two surfactants discussed previously. Variation of C_ϕ with temperature for this surfactant is shown by the upper line in Fig. 4. It decreases with increasing temperature, the slope being comparable to that of the lower line for *b*-C16,17-9EO GES discussed previously. Corresponding values of $(V/V_s)_{C_\phi}$ are also shown.

Propoxylated GESs. Plots of solubilization parameters as a function of salinity at 95 and 130°C are shown in Fig. 7 for *b*-C16,17-3PO GES, again with *n*-octane as the oil. C_ϕ (where the two curves intersect) is approximately 4% NaCl in both cases, much lower than for the ethoxylated sulfonates shown in Fig. 2. However, $(V/V_s)_{C_\phi}$ appears to decrease slightly with temperature, from 19 at 95°C to 16 at 130°C, remaining high enough to indicate good oil recovery. The value at 130°C has considerable uncertainty because there are no data points in the narrow three-phase region.

C_ϕ decreases with increasing PO chain length for a fixed hydrophobe (*b*-C16,17) and constant temperature, as shown in Fig. 8. In this case, C_ϕ is nearly independent of temperature for fixed PO chain length.

However, highly viscous phases were observed in the salinity scans for the surfactants with seven and nine POs. For instance, Fig. 9 shows the scan at 110°C for *b*-C16,17-7PO GES. The volume of the aqueous phase at 1% NaCl is greater than its initial value, which suggests a lower phase microemulsion (Winsor I). Similarly, the large volumes of the oleic phase at 4 and 5% NaCl are indicative of upper phase microemulsions (Winsor II). However, the surfactant-contain-

ing phase at 2% NaCl, also shown in the inset, is not a microemulsion. Instead, it is a highly viscous phase or dispersion that does not move when the pipette is gently tilted. These types of viscous phases have been called “very condensed phases” or VCPs (Puerto and Reed 1983). Similar viscous material was seen in the scan for *b*-C16,17-9PO GES. Conventional Winsor behavior was observed with no highly viscous phases for the other propoxylated surfactants used to construct Fig. 2, C12,13-3PO GES and C12,13-7PO GES.

It should be mentioned that VCPs can be eliminated by alcohol addition, raising test temperature, increasing/decreasing oil molar volume of test oil (Puerto and Reed 1983), or combinations of these measures. As an example, the VCPs found in *b*-C16,17-9PO GES when the test oil was *n*-octane were eliminated by changing the oil to *n*-hexadecane and increasing temperature to 130°C. This indicates that the lipophilic *b*-C16,17-9PO tail can be solvated by heavy crude oils. However, addition of too many PO groups to a large lipophile such as *b*-C16,17 will yield a molecule that is extremely lipophilic at elevated temperatures and hence is unsuitable for many reservoirs.

Aqueous Surfactant Solutions of AEGSs and IOSs

In addition to exhibiting suitable phase behavior with oil, the surfactant or surfactant blend for an economic EOR process should have an aqueous solution that is a single phase for injection conditions and that remains so until it enters the reservoir and contacts oil. Otherwise, the surfactant may be distributed in a nonuniform and unpredictable manner in the reservoir. Typically, this requirement means that single-phase conditions are required from a relatively low injection temperature to reservoir temperature, which may be much higher. If mixing with reservoir brine occurs before the injected solution contacts oil, it should remain a single phase for the combinations of salinity and temperature encountered.

Aqueous, oil-free solutions of AEGSs are generally single-phase micellar solutions at low temperatures but separate into surfactant-rich and surfactant-lean liquid phases above a cloud-point temperature, so called because the appearance of droplets of the second phase causes the solution to appear cloudy. Clouding also occurs at constant temperature with increasing salinity. This behavior is similar to that of nonionic surfactants with alkoxy chains.

Aqueous NaCl solutions of IOSs frequently exhibit the opposite trend, being multiphase at low temperatures and single phase at high temperatures for fixed salinity. Solubility decreases with increasing salinity at constant temperature. An example of such behavior is shown in Fig. 10 for 2% solutions of three IOS 20-24 surfactants (Batches A, B, and C of Table 1 in Barnes et al. 2008).

Photographs of salinity scans at 78, 94, and 120°C for Batch C with *n*-octane as the oil and no added alcohol are given in Fig. 11. Classical Winsor phase behavior is seen with high solubilization and no VCPs. Variation of C_ϕ and $(V/V_s)_{C_\phi}$ is shown in Fig. 12 (blue curves). Comparison of Figs. 10c and 12 reveals that single-phase aqueous solutions are found at C_ϕ for all three temperatures for

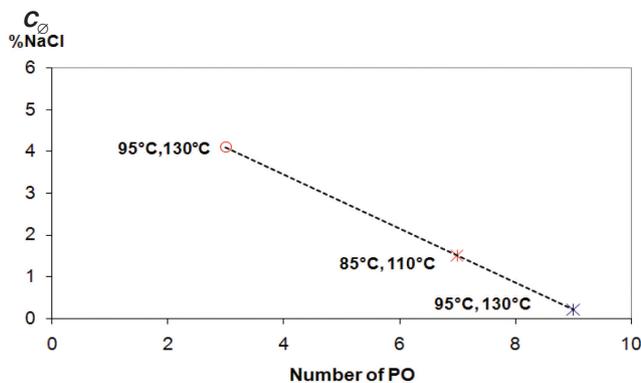


Fig. 8—Optimal salinities for salinity scans of 2% *b*-C16,17-*x*PO GES with octane at selected temperatures. C_ϕ is independent of temperature in this range.

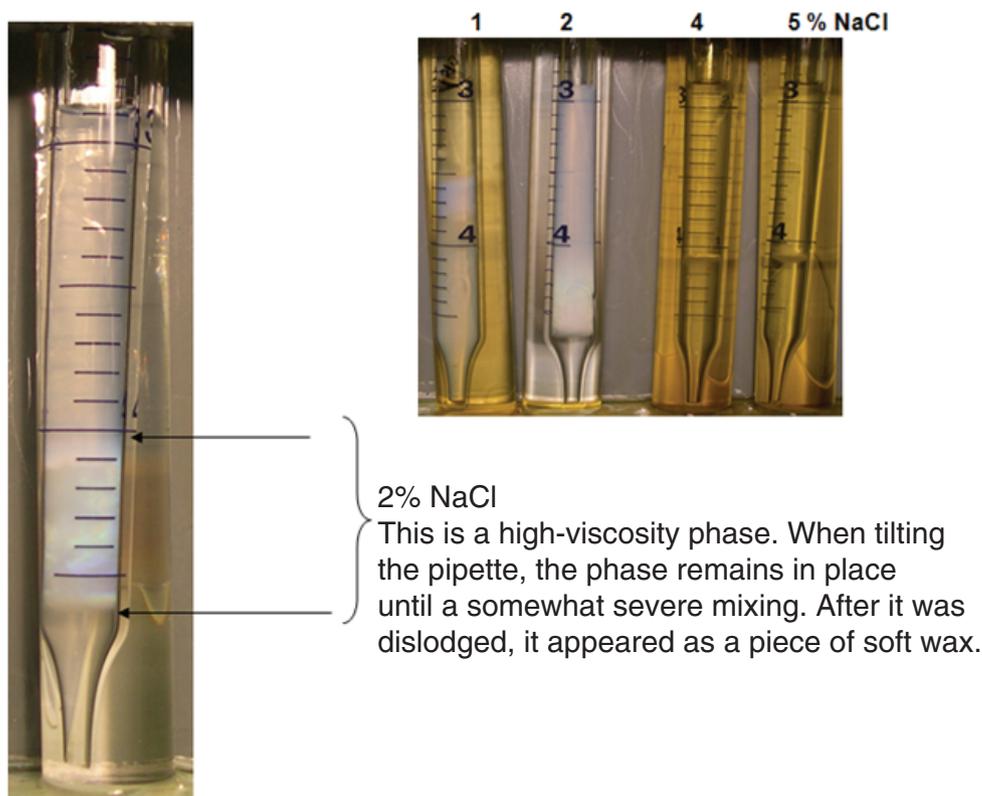


Fig. 9—Salinity scan of 2% *b*-C16,17-7PO GES with octane at 110°C. Enlarged view of sample at 2% NaCl illustrating highly viscous phase.

salinities up to and including C_ϕ with octane. This single-phase behavior, which makes the solutions suitable for injection in EOR processes, also extends to somewhat lower temperatures, though not generally to ambient temperature.

Solubility in aqueous solutions for IOS 20-24 Batches A and B, which have the same average molecular weight as Batch C, is shown in Figs. 10a and 10b. The basic trend of higher solubility in NaCl solutions with increasing temperature is the same, but the lines separating soluble and insoluble regions are shifted to considerably lower salinities, indicating that these surfactants are much less soluble. The corresponding values of C_ϕ shown in Fig. 12 are also well below those for Batch C, as is that for a fourth IOS 20-24 with the same average molecular weight but not discussed by Barnes et al. (2008). Differences also exist in behavior of $(V/V_c)_{C_\phi}$, although all are high enough to indicate ultralow IFTs. For instance, $(V/V_c)_{C_\phi}$ for Batch C increases with increasing temperature, while that for Batch B shows no trend, and those for the other two batches decrease with increasing temperature.

The large variations in C_ϕ among the batches are caused by different proportions of individual surfactant species resulting from differences in internal olefin feedstock and in sulfonation reaction conditions. Barnes et al. (2008) provide this information for Batches A, B, and C (see their Table 1) and discuss the differences in behavior. Among other things, the percentage of disulfonates, which are more hydrophilic than monosulfonates, increases for the batches in the order B, A, C, the same order as for the increase in values of C_ϕ in Fig. 12. However, because it seems unlikely that the high solubilization for Batch C is caused by disulfonates, other factors, such as the ratio of hydroxyalkane sulfonates to alkene sulfonates, must make significant contributions to the observed behavior. Further research is needed to clarify the effects of feedstock and of variations in the sulfonation process on phase behavior of these surfactants.

Test results in Fig. 10 indicate that solutions of Batch A are not suitable for injection at temperatures below approximately 40°C for any salinity. Moreover, single-phase solutions do not exist near the C_ϕ value of 4% NaCl for any temperature below 100°C. In contrast, the solubility limit for solutions of Batch B is near the optimal salinity of 1% NaCl with *n*-octane near 80°C. Above approximately

90°C, the surfactant may be soluble at its optimal salinity with *n*-octane. It is noteworthy that for these surfactants, aqueous solubility and optimal salinity do not exhibit a one-to-one correspondence. Solubility increases in the order A, B, C for the batches, which is different from the order B, A, C for C_ϕ discussed previously.

Phase Behavior for an IOS/AGES Blend

As discussed in the preceding section, phase separation of their aqueous NaCl solutions at high temperatures and salinities (cloud-point effect) greatly limits application of AGESs and their blends in EOR for such conditions even when they exhibit favorable phase behavior with oil. However, the increase in solubility of IOSs with increasing temperature (Fig. 10) suggests that AGES/IOS blends may be able to meet the requirements of clear aqueous solutions for injection and phase behavior with oil yielding sufficiently low IFTs to displace oil.

In this section, we describe behavior of a blend of *b*-C16,17-9EO GES, an AGES, with IOS 20-24 (Batch C). Behavior of both surfactants when used alone was presented previously. For simplicity, the focus here is on behavior of this blend at 90°C with octane as the oil and two different brines, a synthetic seawater whose composition is given in **Table 1** and a synthetic reservoir brine having TDS content of approximately 120,000 mg/L. Both of these brines contain some Ca^{+2} and Mg^{+2} ions, in contrast to results presented up to now for NaCl solutions with no hardness.

Fig. 13 shows a photograph of a blend scan (i.e., where the ratio of the two surfactants in the blend is varied at 90°C) with all samples made by mixing and equilibrating equal volumes of *n*-octane and a 4% w/v surfactant solution in the synthetic reservoir brine (i.e., surfactant concentration is 2% in the overall sample). C_ϕ occurs at a blend composition between 50:50 and 40:60 of AGES/IOS because the former exhibits Winsor I and the latter Winsor II phase behavior. That is, blends with high contents of AGES are underoptimum, and those with high contents of IOS are overoptimum for these conditions. $(V/V_c)_{\text{opt}}$ is approximately 15, although there is considerable uncertainty because the scan does not include any samples in the three-phase region. When the aqueous phase is made with synthetic seawater, all blend compositions exhibit Winsor I behavior at 90°C,

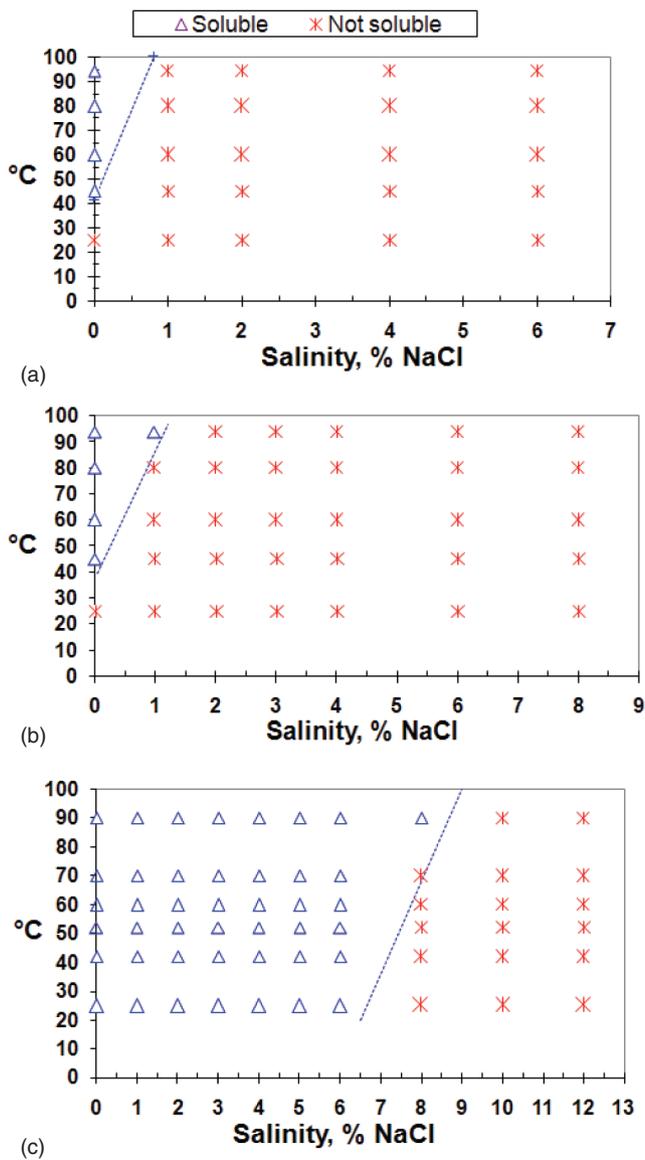


Fig. 10—Solubility maps for IOS 20-24 (Batches A, B, and C).

as might be expected with the much lower TDS content. Phase behavior with *n*-octane for intermediate salinities and temperatures resulting from mixing of a surfactant solution in seawater with the reservoir brine has not been determined.

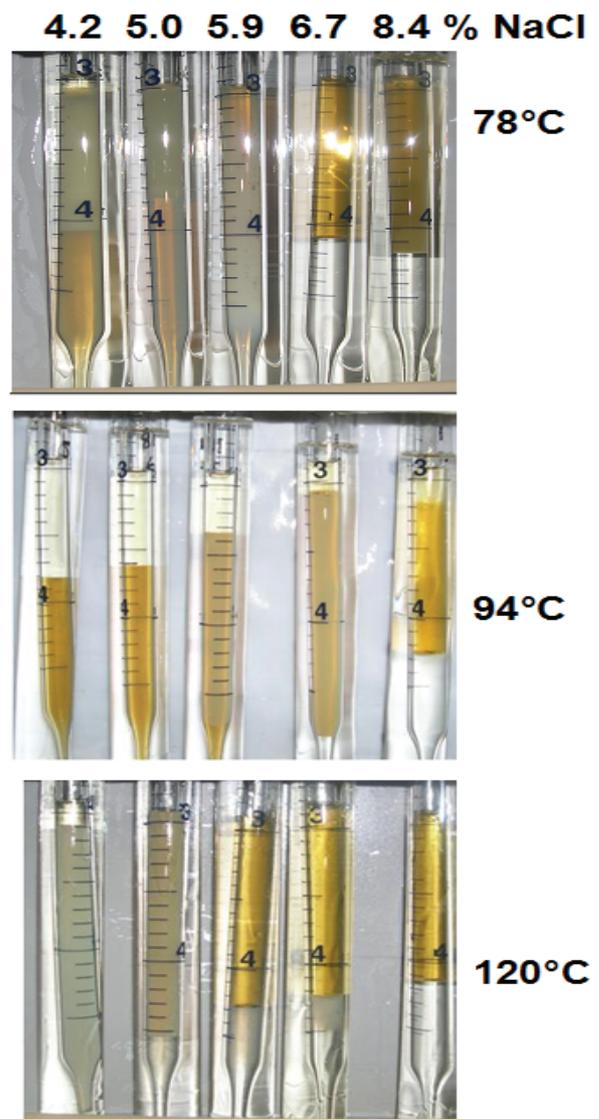
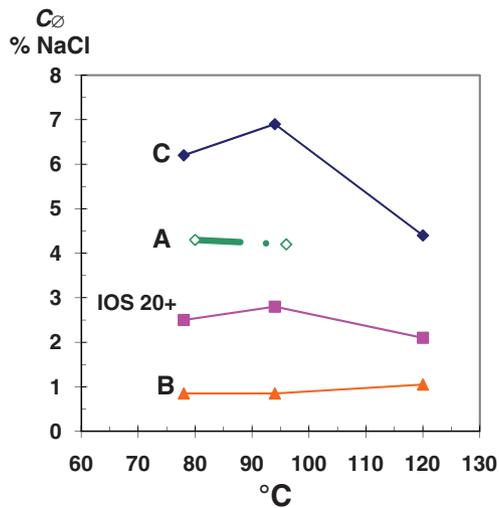


Fig. 11—Salinity scans at temperatures indicated for IOS 20-24 (Batch C) with octane.

Phase behavior of all blend compositions (2% w/v) in synthetic seawater, assumed to be the water available for injection in an EOR process, is shown by the solubility map in Fig. 14. Solutions of all blends are transparent, single-phase solutions at 25°C. However, at

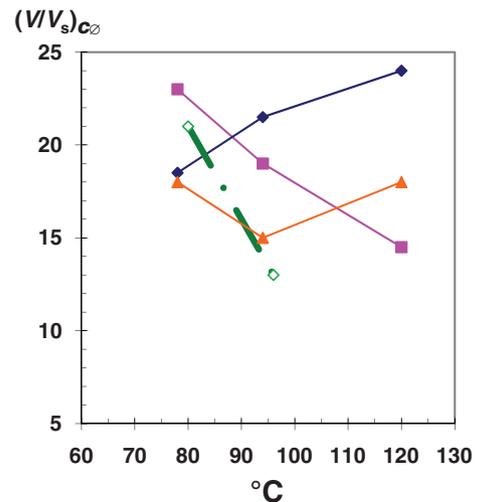


Fig. 12—Optimal salinities and optimal solubilization parameters for four IOS 20–24 surfactants.

Salt	%w/v
NaCl	2.70
CaCl ₂	0.13
MgCl ₂ ·6 H ₂ O	1.12
Na ₂ SO ₄	0.48

70°C, only blends containing at least 50% AGES are transparent. At 90°C, taken to be reservoir temperature in this example, only blends containing 50–80% AGES are transparent (i.e., the cloud point has been reached at 90 and 100% AGES), and two liquid phases coexist. Thus, addition of IOS in this case allows single-phase solutions to exist for some blends at reservoir temperature, even though this temperature is above the cloud point of the AGES. It is noteworthy that solutions of the IOS itself are not transparent single phases at temperatures above 70°C. This behavior, which may seem surprising in that solubility increases with increasing temperature in NaCl solutions (Fig. 10), is presumably caused by the presence of hardness in the seawater. Further study of this behavior is desirable. In any case, the greater solubility exhibited by some blends compared with that of the individual surfactants at 90°C (and higher temperatures) demonstrates a synergism between these two surfactants with respect to mutual solubility.

Fig. 14 shows that the 50:50 blend in seawater is soluble from 25°C to reservoir temperature of 90°C and is only slightly under-optimum with *n*-octane at 90°C. Thus, it could be a suitable choice for injection in an EOR process. It is not unusual to inject at slightly underoptimum conditions. This procedure ensures that overoptimum conditions are avoided, where surfactant partitions into the oil and may be retarded or even trapped, thus making the surfactant ineffective in maintaining low IFT at the displacement front.

Of course, once the injected solution enters the reservoir it may, after most of the oil in a region surrounding the wellbore has been displaced, mix with reservoir brine before encountering substantial amounts of oil and forming microemulsions. As a result, the injected blend will experience higher salinities as it is heated to reservoir temperature. The solution of the 50:50 blend in synthetic reservoir brine at 90°C is somewhat cloudy but does not (at least in glass pipettes) exhibit separation into two bulk phases. Experiments have not been conducted with mixtures of seawater and synthetic reservoir brine at 90°C to determine the degree of mixing with reservoir brine required to produce cloudiness. However, if cloudiness is a problem, it may be possible to remove it by adding a small amount of a paraffinic oil of high molecular weight to convert the cloudy solution into a transparent oil-in-water microemulsion (Maerker and Gale 1992).

This example indicates that use of suitable blends of AGES and IOS surfactants is a promising approach for designing surfactant EOR processes for high-temperature, high-salinity reservoirs. The reservoir

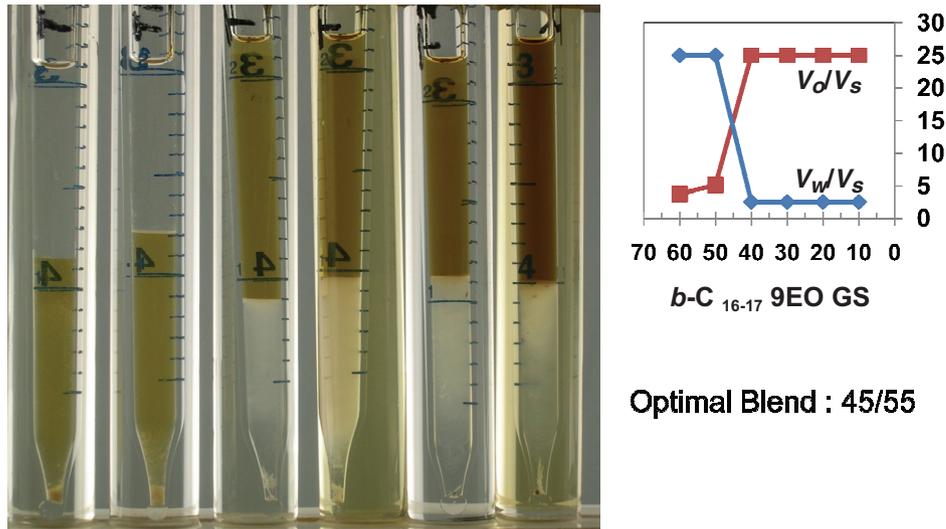


Fig. 13—Blend scan and solubilization parameters with octane and synthetic reservoir brine at 90°C for *b*-C16,17–9EO GES and IOS 20-24 (Batch C). Overall surfactant concentration is 2% in each sample.

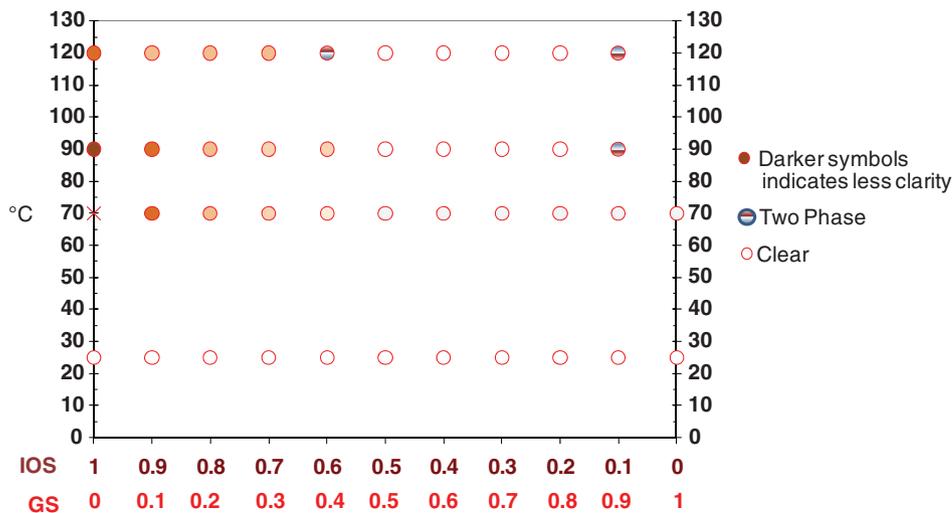


Fig. 14—Solubility map of blends of *b*-C16,17–9EO GES and IOS 20-24 (Batch C) in synthetic seawater.

brine in this case has a TDS content of approximately 120,000 mg/L. Blends for high-temperature reservoirs with more-saline brines could be developed by using surfactants having higher values of C_{ϕ} (e.g., having hydrophobes with shorter carbon chains than those in the example). Nevertheless, extensive laboratory work with reservoir crude oil and brine at reservoir temperature would be required to confirm effectiveness of such blends for EOR application.

Conclusions

Many AGES/*n*-octane/NaCl-brine systems exhibit classical Winsor phase behavior with no added alcohol or other cosolvents for temperatures between approximately 85 and 120°C. Optimal salinities from less than 1% NaCl to more than 20% NaCl have been observed with suitable choice of hydrophobe and alkoxy chain type (EO or PO) and chain length. Oil solubilization is high, indicating ultralow IFTs near optimal conditions. Maps such as those shown here (e.g., Figs. 2, 10, and 14) can provide useful tools for initial surfactant selection. Of course, experiments with crude oil are required before a final formulation can be chosen.

A limitation of AGES surfactants is that their aqueous saline solutions separate into two liquid phases at elevated temperatures. An EOR process would be compromised if such separation were to occur for an injected surfactant solution before it entered the reservoir and advanced far enough to mix with crude oil.

Blends of AGES and IOS surfactants have promise for overcoming this limitation while still providing the ultralow IFTs that are required to displace oil. IOS surfactants, as well as being appropriate for high-temperature reservoir conditions, can be adjusted to work over a wide range of optimal salinities by varying the internal olefin feedstock and the conditions of the sulfonation reaction with internal olefin.

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