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

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Abstract

The effect of hardness was investigated on equilibrium phase behavior in the absence of alcohol for blends of three **A**lcohol **P**ropoxy **S**ulfates with an **I**nternal **O**lefin **S**ulfonate having C₁₅₋₁₈ chain length. Hard brines investigated were synthetic **S**ea **W**ater, 2*SW, and 3*SW, the last two having double and triple the total ionic content of SW with all ions present in the same relative proportions as in SW. Optimal blends of the APS/IOS systems formed microemulsions with n-octane having high solubilization suitable for EOR at both ~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 wt% and 12 wt% 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 branched alcohol C_{16,17} 7PO sulfate and IOS₁₅₋₁₈ was clear and suitable for injection. A salinity map prepared for blends of these surfactants illustrates how such maps facilitate selection of injection compositions where injection and reservoir salinities differ. The same APS was blended with other APSs and **A**lcohol **E**thoxy **S**ulfates in SW at ~25°C, yielding microemulsions with high n-octane solubilization and clear aqueous solutions at optimal conditions. Two 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 encountering upper phase conditions produced by inevitable mixing of injected and formation brine.

1. Introduction

In **c**hemically **E**nhanced **O**il **R**ecovery (cEOR) mobilization of 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. 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 is dependent 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 in order to achieve ultra low IFT.

Since the potential for recovery from surfactant-based methods is high, there has been significant industry interest in cEOR techniques (Hirasaki *et al* 2011). As well, the industry has begun to look to new frontiers, such as offshore cEOR opportunities, where seawater (SW) would ideally be used to make up the injection fluids. In addition, there are many onshore opportunities where 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 EOR fluid is good aqueous solubility of the surfactant/polymer in the reservoir injection brine at the salinity or Total Dissolved Solids (TDS) content where an ultra-low 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 are particularly sensitive to divalent ion content. 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. Ion exchange which occurs between the clay, brine and surfactant micelles in the reservoir can be problematic since it can result in a shift in the phase behavior with the system becoming over-optimum (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 presents work to evaluate surfactant performance without cosolvent in seawater and more concentrated hard brines and in NaCl brines with ionic strengths equivalent to those of the hard brines. This work has several objectives.

1. 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 sulfonates, alpha olefin sulfonates (AOSs), and internal olefin 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.
2. To study blends of APS and IOS as well as blends of two alcohol alkoxy sulfates, a previously unreported surfactant combination, to assess how well these combinations perform with hard brines. Performance in aqueous solubility, oil solubilization and IFT reduction are presented for a number of surfactant systems, both with model oil (n-octane) and with crude oil, and at two temperatures.
3. To evaluate comparative performance of these surfactant blends in hard brines 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, and upon mixing, the ionic content experienced by the surfactant formulation as well as the surfactant concentration can change significantly, which can impact process performance 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 selection of a surfactant system with high potential to recover oil when a salinity gradient is present.

The APS, AES, and IOS surfactants described here are part of Shell Chemical's ENORDET™ range of surfactants for EOR.

2. Experimental

2.1 Sample preparation

For preparing a set of phase behavior samples at WOR~1, eleven pipettes of ~3.0 cc are filled with surfactant; 2% **total** or 0.04g active mass, 1cc brine(s), and 1cc oil; volumes are converted to weight by density with surfactant density assumed equal to ~1 g/cc, and each weight is recorded. The 3.0-cc pipettes are made from cutting 5-cc 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 certain period of equilibration to ascertain thoroughly mixing.

Salinity scan tests were done by either (1) mixing two brines having different concentration of NaCl and divalent ions or (2) mixing two brines of different NaCl concentration but 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 done at 1% total surfactant concentration.

2.2 Materials

The compositions of hard brines are disclosed in Table 1. Two synthetic **Sea Water** compositions were used in the experiments, one with **no** sodium **sulfate** to assure no precipitation of the hard brines themselves. As the table shows, 4 wt% NaCl solutions have nearly the same ionic strength as SW_{nos}. Omitted are 2*SW and 3*SW having double and triple the same salt composition of SW_{nos} 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 was deionized.

The hydrophobes of all the alkoxyated 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 AOS (alpha olefin sulfonate).

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

It is important to observe and record the appearance of sulfated surfactants regularly. These surfactants when freshly made are "buffered" to pH 8-9, but on aging they, by hydrolysis, could become hazy or multiphase with pH lower than neutral, indicating product degradation.

2.3 Synthesis/Manufacture of the Surfactants

C₁₅₋₁₈ based IOSs were manufactured on 1-2 ton scale quantities for EOR field trials using the pilot scale sulfonation facilities at Ballestra, as described in previous work (Barnes *et al* 2008), wherein the properties of these IOSs are described.

The alcohol alkoxy sulfates were prepared on a laboratory scale yielding a few kg of each sample. The alcohol alkoxyates were prepared via ethoxylation or propoxylation reaction of the alcohol using conventional (KOH) catalyst. Sulfated derivatives were made by reaction of the

alcohol alkoxylate with SO_3 via a laboratory scale falling film sulfonation unit. The chemistry in the propoxylation step has been covered previously (Barnes *et al* 2008).

2.4 Spinning Drop Interfacial Tension

Interfacial tensions (IFTs) were determined using extracted excess brine as the continuous phase and excess oil as a droplet, from equilibrated phase behaviour tubes. A spinning drop tensiometer SVT20N from Dataphysics was used and stable IFTs were determined between 5 – 45 min measurement time and at approximately 5000 rpm. Densities and refractive indices were used as input and determined experimentally for both phases (RI only for the brine) at the relevant temperature ($\sim 50^\circ\text{C}$).

3. Phase Behavior of APS/IOS Systems

3.1 Phase Behavior with Octane

APS/IOS blends have been considered for EOR processes in recent years. In particular, blends of b-C₆₇P and IOS have been used in laboratory studies, e.g., Liu *et al* 2008, Levitt *et al* 2009, and a few pilot tests. Hence initial experiments for this project consisted of salinity scans such as that shown in Figure 1 for a blend of equal parts by weight of the two surfactants. Brines in the scan consisted of mixtures of 2*SW and 15% NaCl. The temperature was $\sim 25^\circ\text{C}$, the oil was n-octane, and water-to-oil ratio (WOR) was approximately one 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_o/V_s) ~ 20 at optimal salinity. This result suggests that low interfacial tension and good oil recovery could be achieved for this system (Huh 1979). This experiment and others with surfactant blends having higher proportions of b-C₆₇P indicated that microemulsions with high solubilization parameters could be obtained for this combination of surfactants for brines between SW and 3*SW.

Subsequently, systematic blend scans with n-octane and WOR ~ 1 were conducted at $\sim 25^\circ\text{C}$ 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-C₆₇P but also b-C₂₃P, and B-C₂₃P. In this way the effects of hydrophobe structure could be determined. Samples were made with 10% intervals in blend ratios by weight, e.g., 100/0, 90/10 . . . 0/100).

Table 3 summarizes 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°C and 50°C . Figure 2 shows a blend scan of b-C₆₇P/IOS in 2*SW at 25°C , which has optimal blend ratio and solubilization parameter of 65/35 and 12 respectively.

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 having high oil and brine solubilization parameters (many >15) near optimal conditions, which indicates 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 in 2*SW and 3*SW and soft brines of the same ionic strength showed little 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 hydrocarbon chain length of the APS for fixed length of 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 APS's

less hydrophilic by reducing the water of hydration of their PO chains. The results in Table 3 allow the APSs tested to be arranged from most-to-least hydrophilic as $b\text{-C}_{23}7\text{P} > \text{B-C}_{23}7\text{P} > b\text{-C}_{67}7\text{P}$. Both $b\text{-C}_{23}7\text{P}$ and $\text{B-C}_{23}7\text{P}$ 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 utilizing a blend of two surfactants, salinity of the injected brine differs from that of formation brine. 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 brine are indicated on the two axes. Such a plot is shown for $b\text{-C}_{67}7\text{P}/\text{IOS}$ with octane at 25°C in Figure 3. In this case the injection brine is taken as SW and formation brine 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 because the surfactant is preferentially soluble in oil and hence may be transported through the formation more slowly than if it were in the aqueous phase or even be trapped as residual oil. Moreover, water-in-oil emulsions are favored in the Winsor II region and can become highly viscous as water content increases. For a hypothetical case with injection in SW, the injected blend should be in the Winsor I region and hence not exceed 30 wt% IOS, according to Figure 3. Mixing of the injected surfactant solution with formation brine at constant blend ratio is represented by the horizontal arrow shown in the figure and leads to undesirable overoptimum conditions if the proportion of formation brine in the mixture exceeds 50%.

3.2 Phase Behavior of Aqueous Solutions

Similar blend scans of oil-free aqueous solutions at 1 wt% overall surfactant concentration were made for the same APS/IOS combinations, temperatures, and salinities as in Tables 1 and 2 using 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.

In general, the results are much less favorable than those reported above with n-octane. For all three APS/IOS blends the samples in 2*SW, 3*SW and 4% and 8% NaCl solutions having corresponding ionic strengths were cloudy, separated into two phases on standing, or were plagued with precipitate for all blend ratios at both 25°C 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.

The aqueous phase results in SW for the three APS/IOS blends are summarized in Figures 4 and 5 for 25°C and 50°C respectively. A favorable result is obtained for $b\text{-C}_{67}7\text{P}/\text{IOS}$ at 25°C in SW in that the aqueous solution is clear and injectable for the optimal blend ratio. As indicated previously, the $b\text{-C}_{23}7\text{P}/\text{IOS}$ and $\text{B-C}_{23}7\text{P}/\text{IOS}$ 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, where oil-water interfaces have zero spontaneous curvature, is also favorable to forming the lamellar liquid crystalline phase in aqueous solution. Using 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 $b\text{-C}_{67}7\text{P}/\text{IOS}$ aqueous solutions at low salinities, which may be applicable to other APS/IOS blends where IOS is the more hydrophilic surfactant. In the absence of IOS an aqueous solution of 1% $b\text{-C}_{67}7\text{P}$ 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 (Figure 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 Na₂CO₃ having ionic strengths comparable to sea water (Liu *et al* 2009). 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. It seems that in general blends with high contents of IOS should be avoided owing to precipitation in aqueous solution even though microemulsion phase behavior with oil present may be acceptable.

Because, as indicated above, 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-C₂₃7P/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% of cosolvents secondary butyl alcohol (SBA) and diethylene glycol butyl ether (DEBE)
- 0.25% of commercial nonionic surfactant C₁₂₋₁₃EO₁₂
- 0.25% of benzene sulfonate (a hydrotrope)
- 1% of a white oil (branched paraffinic hydrocarbon) having molecular weight of 540

The cosolvents and hydrotrope hinder formation of solids and liquid crystals. The nonionic surfactant shifts 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 having spherical drops, thereby minimizing the tendency for separation into two phases having different concentrations of surfactants. Because its molecular weight or molar volume is much greater than for octane, it forms a Winsor I (lower phase) microemulsion under the same conditions that near optimal microemulsions are seen with n-octane. This approach was used by Exxon in the 1980's 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-C₂₃7P/IOS. However, because this range includes the optimal blend ratio of (85/15), according to Table 1, this formulation could be used for EOR at 2*SW. In 3*SW none of the additives was successful in producing injectable solutions. Of course, other white oils could be used, a topic of current research in our laboratory.

4. Blends of Alkoxylated Sulfates

As discussed in the preceding section, it is difficult to find APS/IOS blends having clear aqueous solutions near conditions exhibiting optimal microemulsion phase behavior with n-octane and hence presumably for most crude oils. Especially when IOS content of the optimal blend exceeds 20-30 wt%, its sensitivity to brines with moderate salinity and hardness usually results in precipitation. Because the EO and/or PO groups of alkoxylated sulfates provide tolerance to salinity and hardness, a study of blends of alkoxylated sulfates with no IOS was initiated. In order 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 study of blends of b-C₆₇7P with other APSs b-C₂₃7P and B-C₂₃7P and ethoxylated sulfates b-C₂₃7E and B-C₂₃7E. Blend scans were conducted in SW at 25°C with n-octane present at WOR ~ 1 and for the corresponding oil-free aqueous solutions.

Optimal blend ratios B_ϕ and aqueous phase behavior are shown in Figure 6. A photograph of the blend scan with octane for b-C₆₇7P/b-C₂₃7E may be seen in Figure 7.

It is noteworthy in Figure 6 that, in contrast to the blends with IOS, aqueous solutions of the alkoxyated sulfate blends exhibit clear solutions for all blend compositions except for bC₁₆₋₁₇PO₇ sulfate itself, which, is above its cloud point in SW at 25°C. A photograph of the aqueous phase scan for b-C₆₇7P/ b-C₂₃7E is shown in Figure 8.

The ability of blends of alkoxyated sulfates to produce clear aqueous solutions over a wide range of blend ratios is encouraging and merits further study including experiments at higher temperatures up to 60°C and higher salinities.

5. Phase Behavior with Crude Oil in SW at ~50°C

As a means of testing whether systems such as those discussed above can be used for a practical application, a formulation was sought which 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 considered that the amount of IOS needed in an optimal blend with b-C₆₇7P would cause precipitation to occur in the aqueous solution. Hence, preliminary experiments were conducted with several blends of alkoxyated sulfates. Although several suitable blends could likely be found with an adequate inventory of alkoxyated sulfates, a blend of b-C₆₇7P/b-C₂₃7E was selected based on knowledge of phase behavior of the individual surfactants. A photograph of a blend scan with crude oil for this system at ~50°C in SW may be seen in Figure 9. It indicates that the optimal blend is near 70 wt% b-C₆₇7P. A salinity map for this system at ~50°C extending from SW to 3*SW is shown in Figure 10. For comparison it includes optimal blends of NaCl solutions having 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.

With n-octane as the oil the optimal blend is between 60% and 70% b-C₆₇7P in SW at ~50°C (photograph not shown). This value is not far from that of crude oil, which indicates that octane could be used in initial screening to find optimal phase behavior with crude oil in this system.

An aqueous solubility blend scan in SW at ~50°C for the same surfactant pair shows clear, single-phase solutions at 60% or less of b-C₆₇7P (Figure 11). The solution at 70% is only slightly cloudy, while those with higher contents of b-C₆₇7P are considerably cloudier. That is, the aqueous solution at the optimal blend for crude oil is questionable for injection. However, it would be preferable to inject at slightly lower contents of b-C₆₇7P for mitigating the possibility of reaching overoptimum conditions with its risk of generating viscous Water/Oil emulsions due to (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.

Using blends of alkoxyated 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 ~50°C. Figure 12 shows 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-C₂₃7P/B-C₂₃7E with crude oil and n-octane respectively are 83/17 and 87/13. The small difference again indicates that n-octane is a good choice of model oil to be used for initial screening purposes in this system.

Figure 13 is a chart showing 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-C₂₃7E, which exhibit clear solutions in SW. As discussed above, it may be preferable in

many cases to inject at such blend ratios instead of at the optimal ratio in SW.

Additional evaluation of the b-C₂₃7P/B-C₂₃7E/crude oil system by IFT measurement was carried out on the equilibrated system (after one week), at ~50°C. In the salinity scan of Figure 14 the blend ratio for all samples is the optimal blend shown in Figure 12 for SW. The first three samples have lower salinities than SW, the last three samples higher salinities. The fourth or central sample, which is in SW, shows Winsor III behavior. IFT measured between excess oil and brine phases for this sample was ~10⁻² mN/m. Based on discussion by Sottmann and Strey (1997), IFT values for microemulsion/oil and microemulsion/brine interfaces are individually less than this value. Thus, substantial residual oil should be displaced for these conditions.

6. Conclusions

In this work, it was found that blends of branched APS's with IOS can form alcohol-free microemulsions with n-octane having high oil and brine solubilization at optimal conditions for salinities up to about three times that of seawater (3*SW) and temperatures up to 50°C. As well, optimal conditions with n-octane for 2*SW and 3*SW were generally similar for hard brines and NaCl solutions having the same ionic strengths.

In general, in the absence of oil, aqueous solutions at optimal conditions for these higher salinity formulations were cloudy and/or exhibited precipitate 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 the observed 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 salinity, which should prove useful in situations where compositions of injection and formation brines differ.

Initial experiments with blends of alkoxyated 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. As well, two APS/AES blends formed suitable microemulsion phases with a crude oil in SW at ~50°C. While it was found that aqueous phases of the optimal blends were 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 due to ion exchange phenomena or mixing of injection and formation brines.

The test results from different APS and AES based systems with model oil 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.

7. References

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Table 1 Test brines with similar divalent ions in SW with and without sulfate

Wt% Salt	SW	SW _{nos}	
NaCl	2.7	2.9	4.0
CaCl ₂	0.13	0.13	
MgCl ₂ ·6H ₂ O	1.12	1.12	
NaSO ₄	0.48	—	
TDS (mg/L)	38,300	35,500	40,000
Ionic strength mol/L	0.765	0.697	0.684

Table 2 Tabulation of Surfactants

Hydrophobe	Propoxy Groups -(CH ₂ - (CH ₃)-CH ₂ -0)-	Ethoxy Groups -(CH ₂ -CH ₂ -0)-	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	na	na	IOS

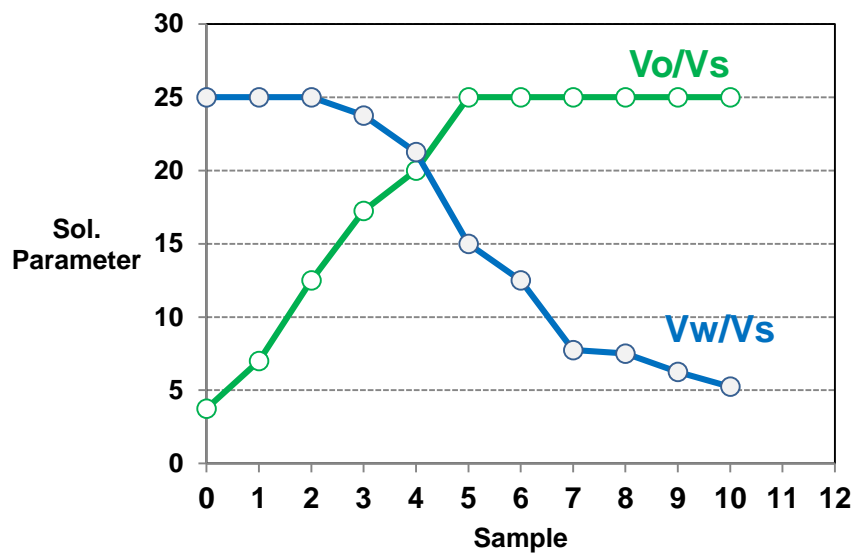
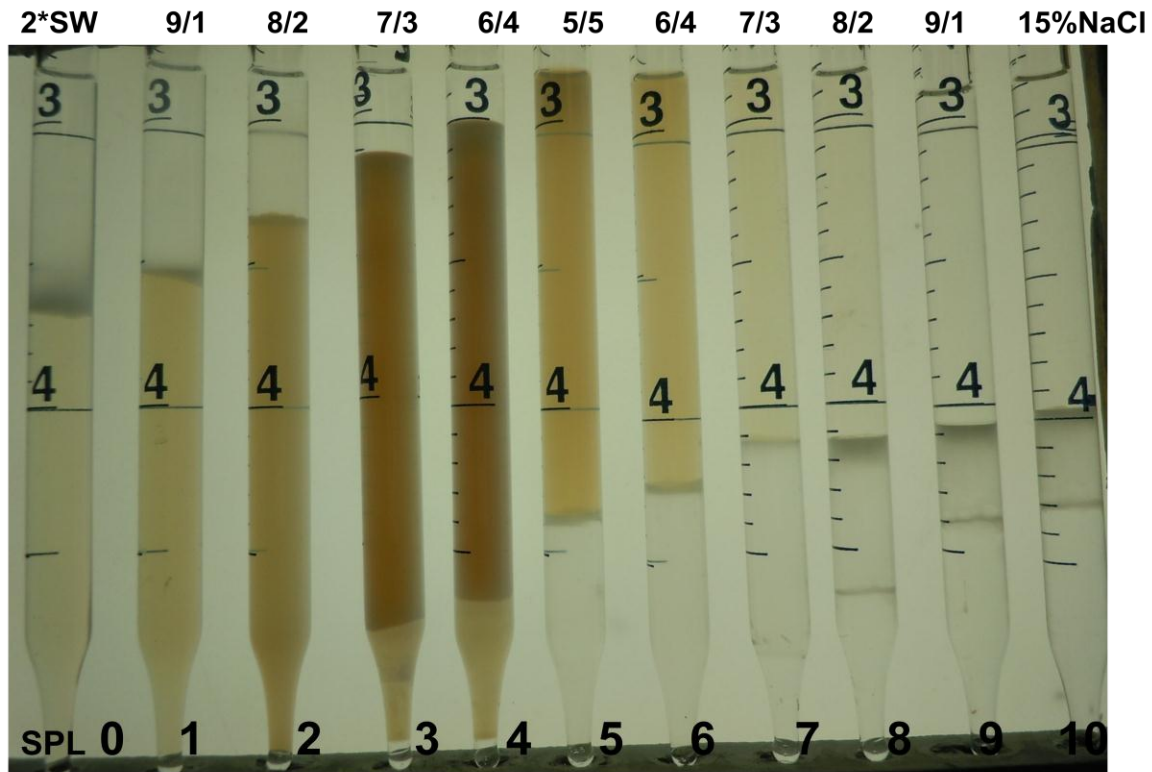


Figure 1 Salinity Scan by mixing 2*SW with 15%NaCl, ~25°C

2%total b-C₆₇7P/IOS_1/1 by wt. after ~9weeks of equilibration

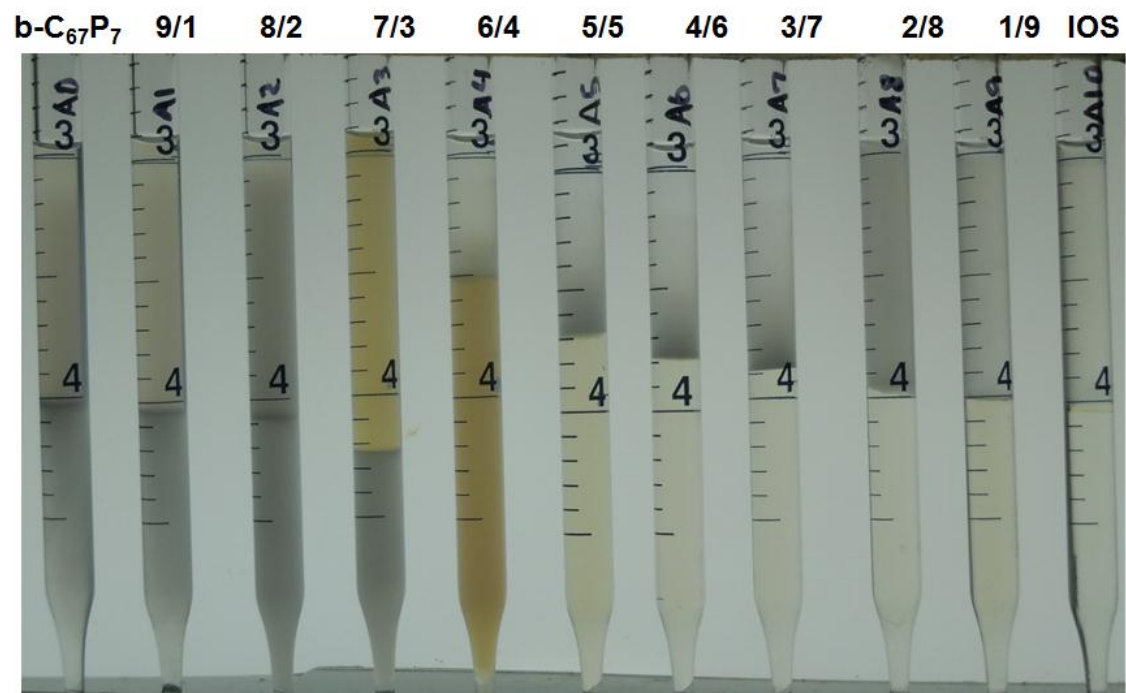


Figure 2 Blend Scan WOR-1: 2% total b-C₆₇ 7P/IOS in 2*SW and n-octane at 25°C

Table 3 Tabulation Test Results ~ 25°C, 50°C

Test conditions: 2% overall concentration, n-octane/test-brine ~1

B \emptyset = optimal blend ratio
V/V_s = solubilization parameter at B \emptyset
V = oil or water volume
V_s = surfactant volume

Surfactant Blend Weight Ratio			SW	2*SW	8% NaCl	3*S W	12% NaCl
25 °C	b-C ₆₇ 7P : IOS	B \emptyset	85:15	65:35	65:35	55:45	45:55
		(V/V _s)	>10 ?	17	15	13	14
	b-C ₂₃ 7P : IOS	B \emptyset	All type I	85:15	85:15	65:35	65:35
		(V/V _s)		16	16	12	12
	B-C ₂₃ 7P : IOS	B \emptyset	All type I	75:25	75:25	55:45	50:50 ?
		(V/V _s)		19	19	19	1 \emptyset
50 °C	b-C ₆₇ 7P : IOS	B \emptyset	Not done	45:55	45:55	45:55	45:45
		(V/V _s)		16	15	11	10
	b-C ₂₃ 7P : IOS	B \emptyset	Not done	80:20	75:25	45:55	45:55
		(V/V _s)		1 \emptyset	22	11	11
	B-C ₂₃ 7P : IOS	B \emptyset	Not done	65:35	65:35	35:65	35:65
		(V/V _s)		17	17	18	18

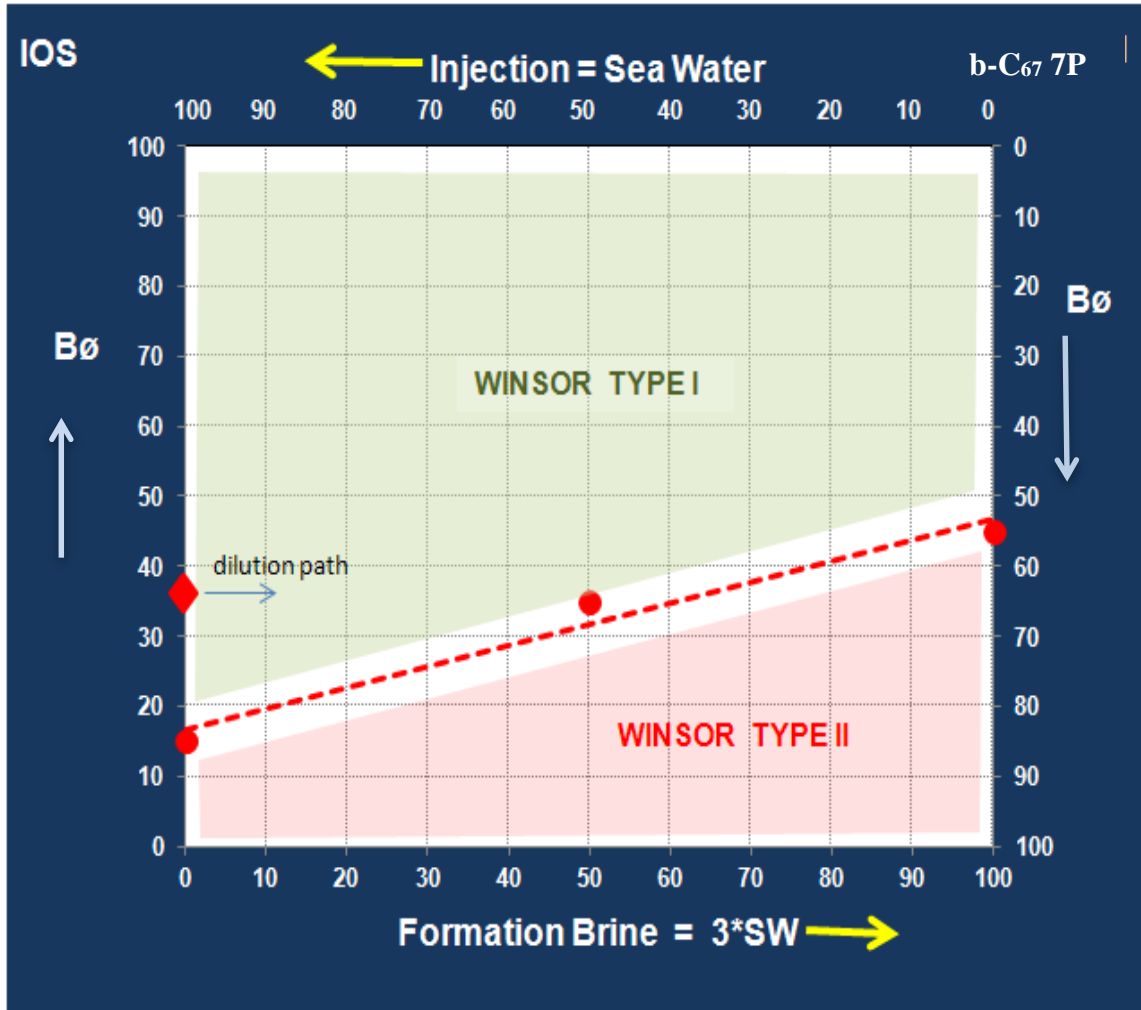


Figure 3 Salinity Map: Hypothetical Case for surfactant selection in a variable salinity cEOR processes. For this case, the injection blend for optimal oil recovery should lie in between 60/40 and 75/25 of b-C₆₇ 7P:IOS blend; lower amount of b-C₆₇ 7P should result into too high IFT and higher amount into transition to Winsor Type II where surfactant will be lost by partitioning into oil, making heavy emulsion, etc.

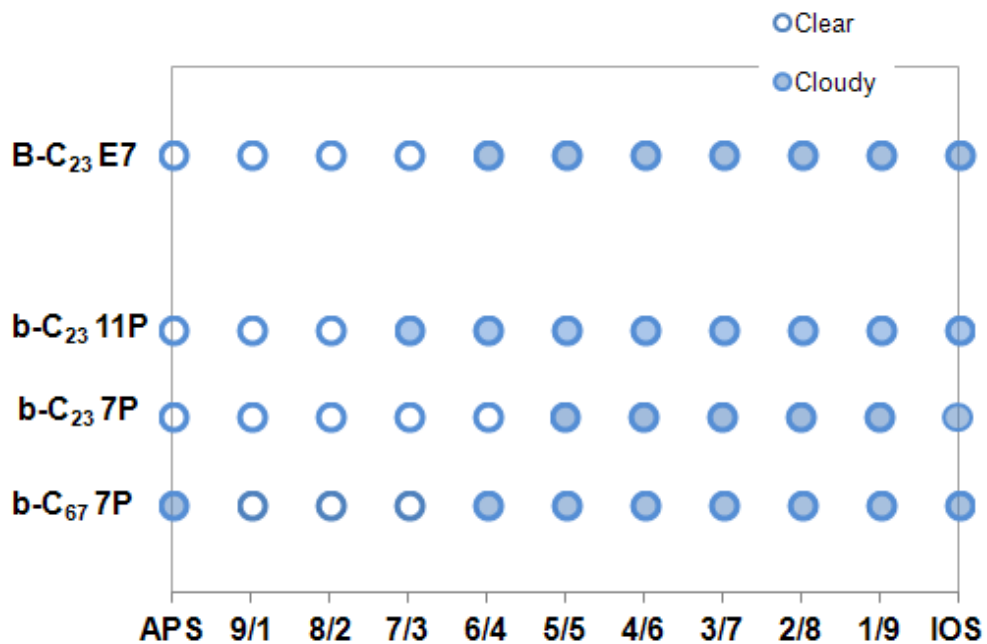


Figure 4 Aqueous Solubility Map: APS/IOS Blends at 25°C for SeaWater

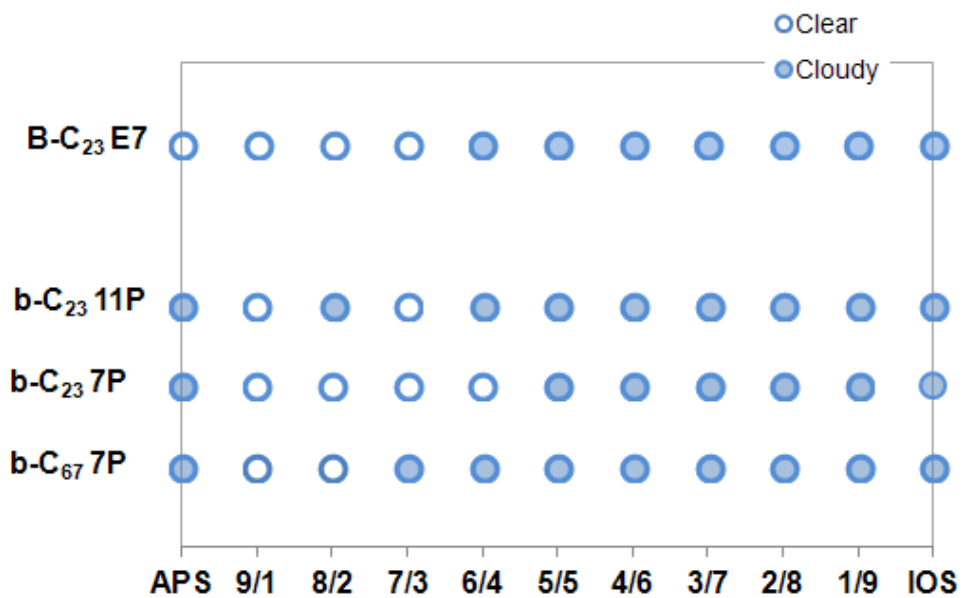


Figure 5 Aqueous Solubility Map: APS/IOS Blends at 50°C for SeaWater

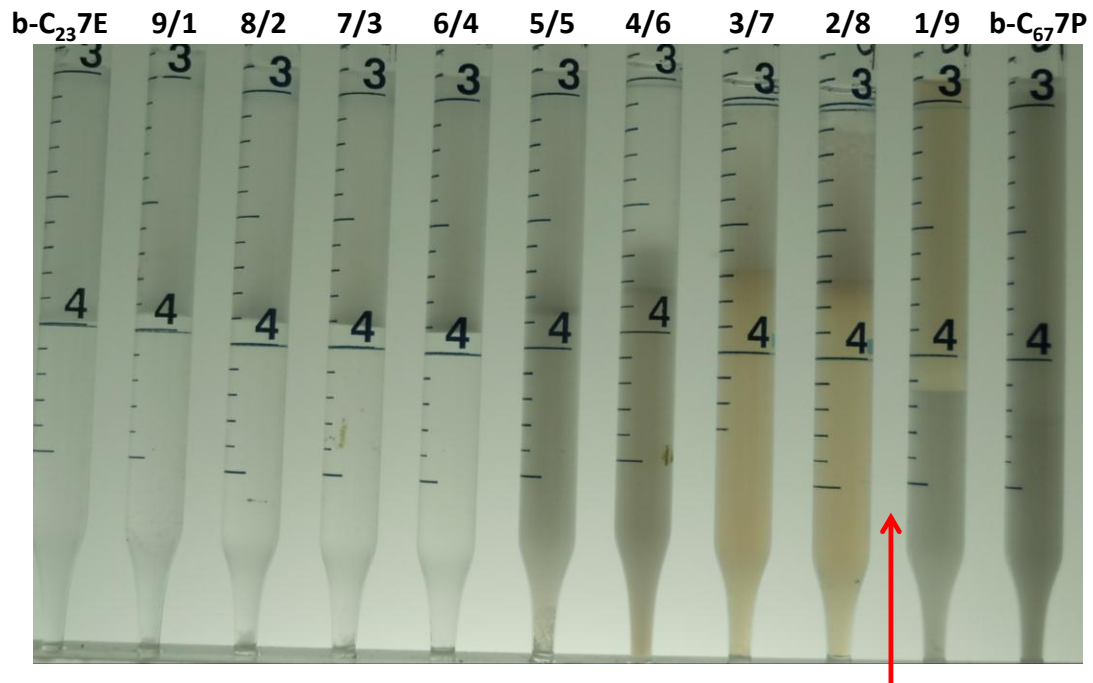


Figure 7 Blend Scan _WOR~1: 2% b-C₂₃7E/b-C₆₇7P with n-C₈ in SW at 25°C

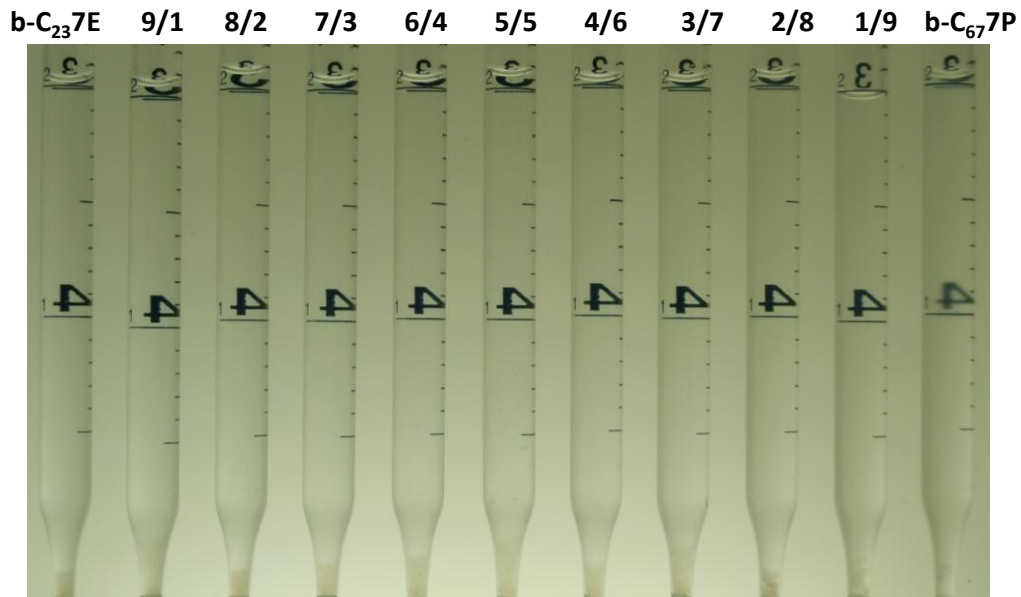


Figure 8 Blend Scan _aqueous: 1% b-C₂₃7E/b-C₆₇7P in SW, 25°C

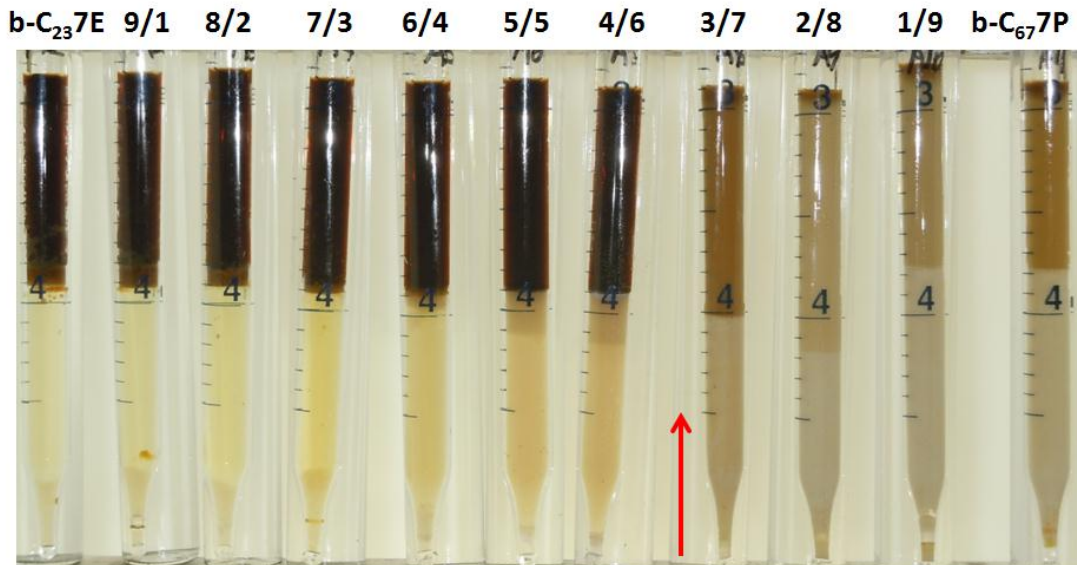


Figure 9 Blend Scan _WOR-1: 2% b-C₂₃7E/b-C₆₇7P with Crude Oil and SW, -50°C

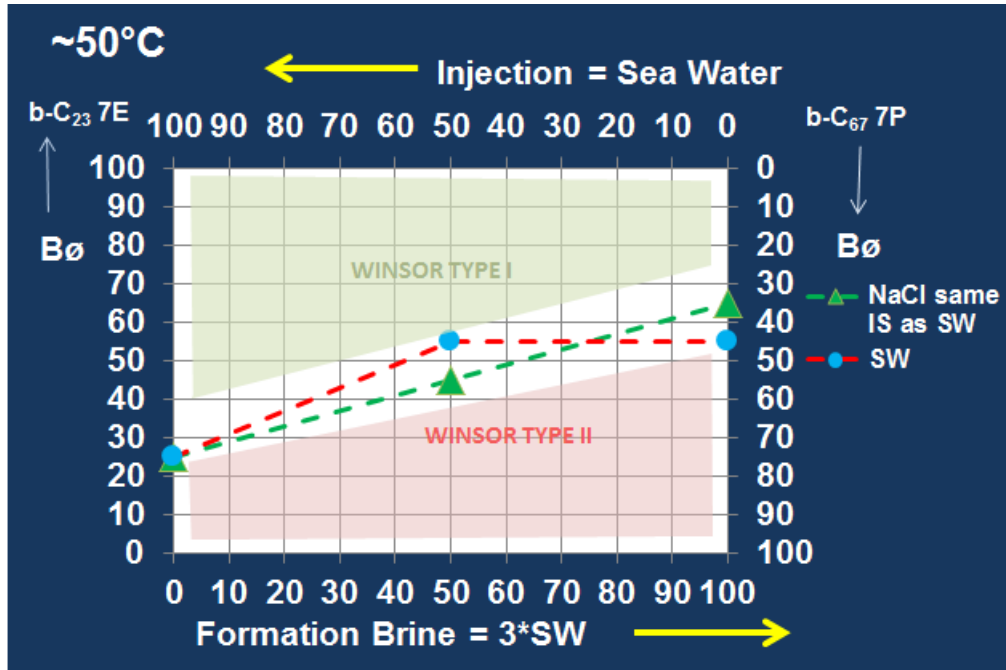


Figure 10 Salinity Map for Crude Oil for SeaWater and NaCl-only brine of same Ionic Strength as SeaWater

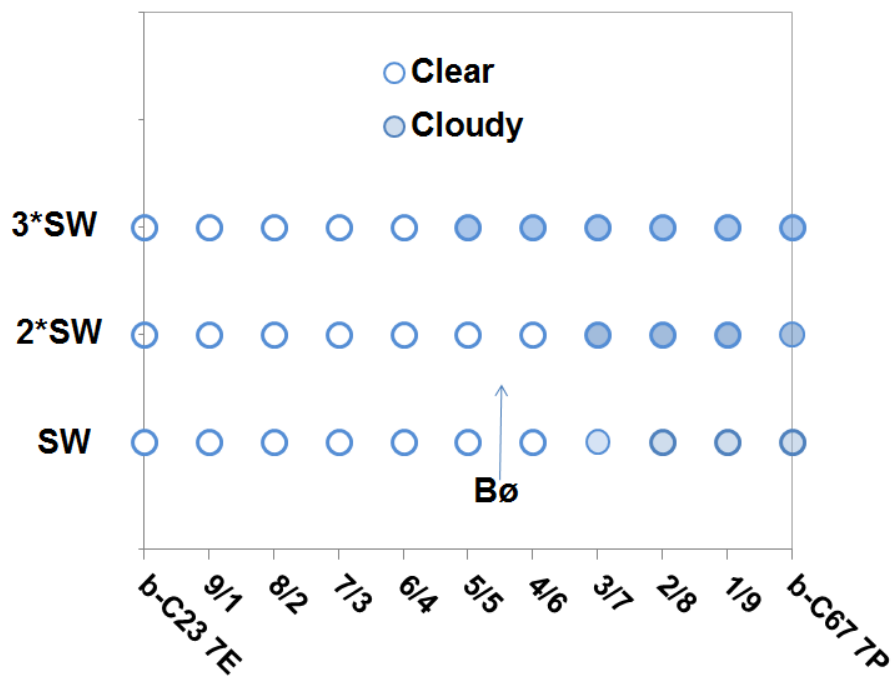


Figure 11 Aqueous Solubility Map for b-C₂₃:7E and b-C₆₇:7P extending from SW to 3*SW at ~-50°C

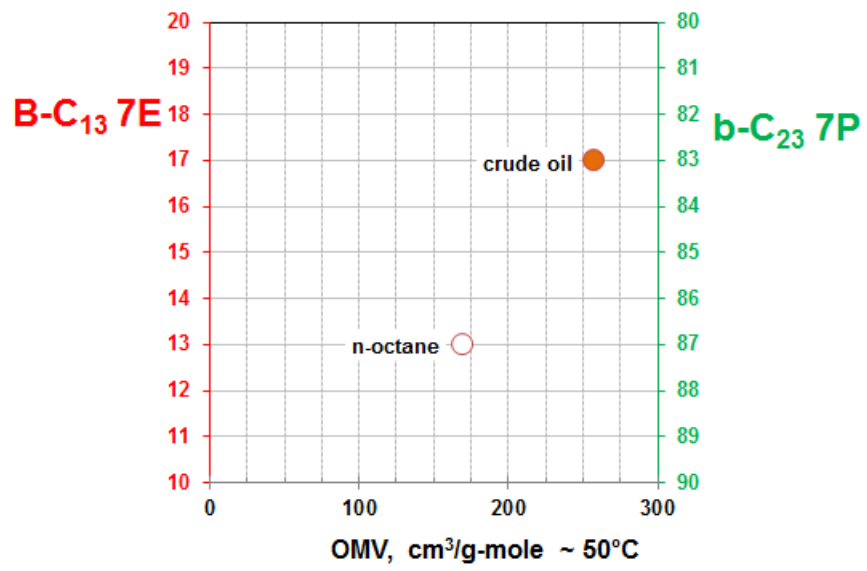


Figure 12 Optimal blend for crude is slightly more lipophilic than for n-Octane.

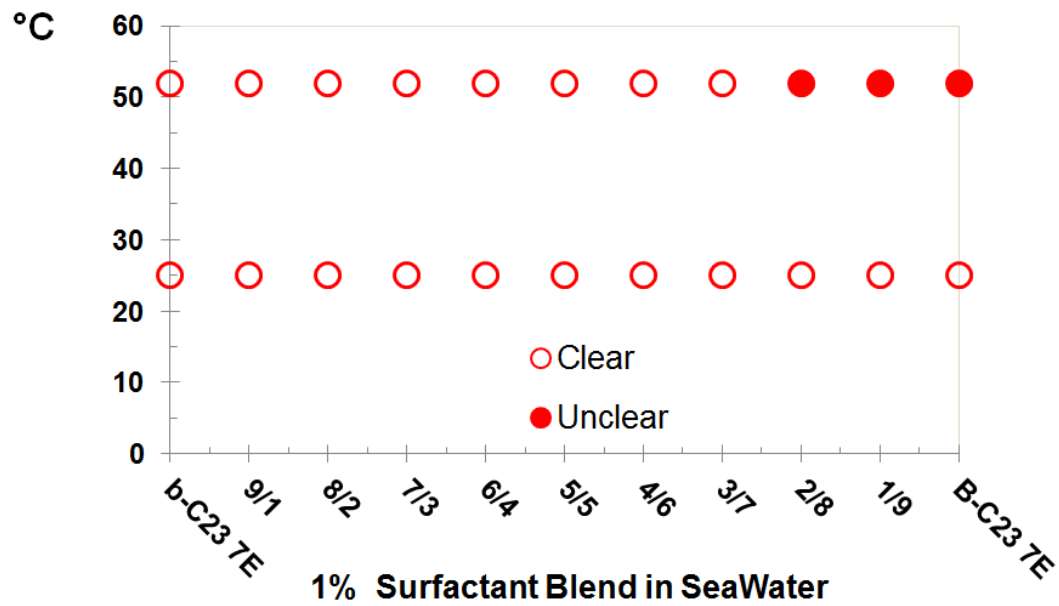


Figure 13 Aqueous Solubility Map for 1% Blend of B-C₂₃7E/b-C₂₃7P. Shaded blue area to indicate optimal blend ratio, Bø, for against n-octane (left boundary) or crude oil (right boundary)

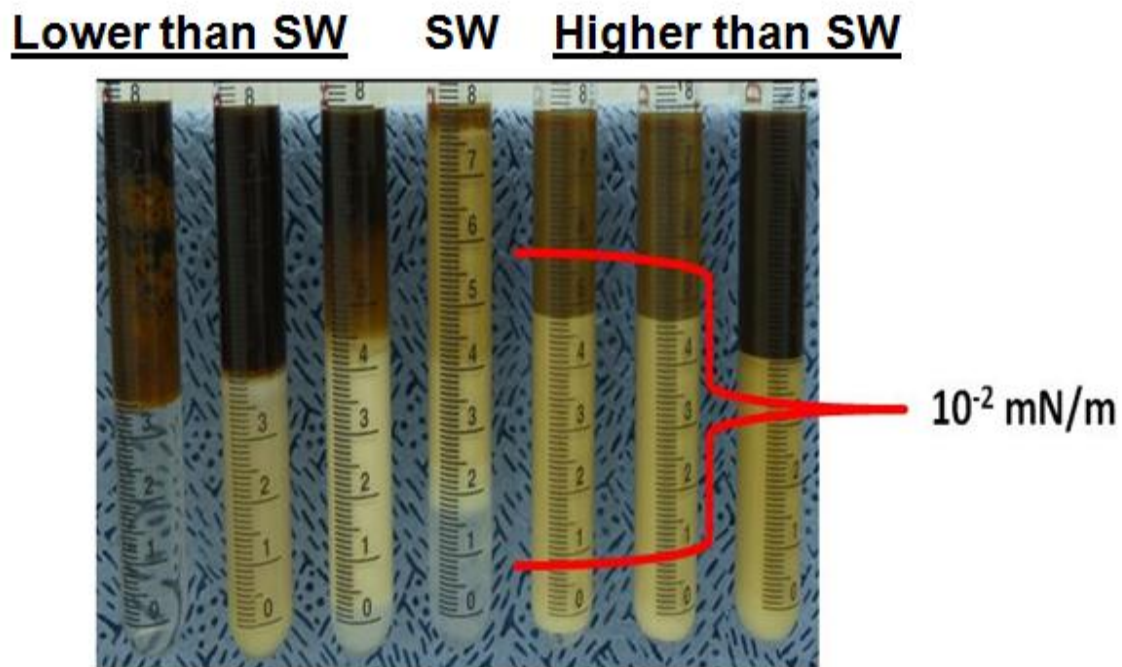


Figure 14 Phases selected for IFT measurements from phase behavior salinity scan with crude oil: 1% b-C₂₃ 7P and at ~50°C.