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Separation of Produced Emulsions from Surfactant Enhanced Oil Recovery Processes[†]

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Selected cationic and amphoteric surfactants were effective in separating oil-in-water emulsions representative of produced emulsions expected during a surfactant/polymer (SP) process for enhanced oil recovery. The aqueous phase of the emulsion contained an anionic surfactant blend, alcohol, and partially hydrolyzed polyacrylamide. Brine composition was a suitable mixture of formation brine with brines from the surfactant slug and polymer drive. The crude oil had an American Petroleum Institute (API) gravity of 31°. Bottle tests were conducted at ambient temperature, which is near the reservoir temperature. Conventional non-ionic demulsifier resins and polymeric cationic flocculants were not effective in removing oil from the aqueous phase. The water content of the oil phase was still well above specification upon heating the emulsions to 50−60 °C. However, both oil and water phases of acceptable quality were obtained after 6 h of settling upon the addition of 200 ppm of octyltrimethylammonium bromide (C_8TAB) at ambient temperature. Additionally, a commercial cationic surfactant at the same concentration yielded acceptable results for both phases in 2 h. Optical microscopy showed significant coalescence after only 1 min in the C_8TAB system as the cationic surfactant reduced electrostatic repulsion among drops and shifted system phase behavior toward the balanced state between hydrophilic and lipophilic effects, actions well-known to reduce emulsion stability. Some amphoteric surfactants, such as cocobetaine, were also effective in separating these emulsions. The amount of cationic surfactant required could be reduced by adding it simultaneously with a non-ionic demulsifier resin. A commercial cationic surfactant was also found to significantly improve separation of emulsions produced during an alkaline/surfactant/polymer (ASP) process.

1. Introduction

Chemical enhanced oil recovery (EOR) methods are expected to play a major role in future global crude oil production.[1] However, breaking dilute oil-in-water (O/W) emulsions produced during surfactant/polymer (SP) and alkaline/surfactant/polymer (ASP) processes for EOR is important for process success. These emulsions can be very stable, for example, as discussed by Li et al. for ASP processes.[2] Emulsions for SP processes may have continuous aqueous phases containing an anionic surfactant blend and high-molecular-weight, partially hydrolyzed polyacrylamide. Owing to dilution by mixing with reservoir brine and the polymer drive, surfactant concentrations vary during the process and may range from below 0.1 to perhaps 0.5% by weight, depending upon such factors as injection concentration, reservoir heterogeneity, and process design. Polymer concentrations up to about 0.1% by weight may be expected. Total dissolved solids may be 1−5% by weight with some hardness. A cosolvent, such as an alcohol, may

also be present in the EOR chemical blend. The surfactant is preferentially soluble in the aqueous phase for these conditions and solubilizes some oil. That is, the aqueous phase is an O/W microemulsion. A typical process requirement is to a develop cost-effective separation of such an emulsion, providing an oil phase containing no more than 0.3−0.5% water by volume and an aqueous phase containing no more than 200 ppm oil, preferably 100 ppm.

Much effort has been devoted to breaking crude oil−brine emulsions from normal production operations.[3−5] Emphasis has been on breaking brine-in-crude oil emulsions and, thereby, reducing the brine content of the oil phase to acceptable values. Asphaltene layers at the surfaces of the brine drops are the chief source of emulsion stability in most cases.

Many compounds have been proposed or used as demulsifiers. One type of widely used demulsifier capable of displacing significant portions of the asphaltene layers in such emulsions and promoting coalescence consists of ethoxylated and/or propoxylated alkylphenol formaldehyde resins with molecular

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weights of a few thousand daltons. Experiments have indicated that, for a given emulsion, there is an optimal ratio of hydrophilic and lipophilic properties for these non-ionic demulsifiers, which provides the best separation.[6−9] This behavior is consistent with observations that both oil- and water-continuous emulsions stabilized by surfactants of low molecular weight are least stable near conditions where hydrophilic and lipophilic properties of the surfactant film are balanced and spontaneous curvature is zero.[10−12]

Produced O/W emulsions from SP EOR processes differ from conventional crude oil emulsions in that the injected surfactants and, in alkaline/surfactant processes for oils with significant acid content, acids and corresponding soaps can be concentrated at the oil−water interfaces. Because the injected surfactants, soaps, and polymers are anionic, electrostatic and steric effects can result in enhanced emulsion stability. If the approach of the preceding paragraph is followed, the demulsifier should shift spontaneous curvature from its initial value favoring O/W emulsions and microemulsions toward zero. Such a shift can be achieved by adding a more lipophilic surfactant than that used for the EOR process and/or increasing the ionic strength of the produced fluid. It is also desirable to reduce electrostatic repulsion between oil drops. As reported below, the addition of certain cationic or amphoteric surfactants at ambient temperature was effective in separating emulsions typical of one SP process into oil and water phases, which met required crude oil pipeline and produced water-handling/disposal specifications. The added cationic surfactant reduced the surface charge sufficiently to produce drop coalescence. In contrast, the addition of conventional demulsifiers of the type described above produced some separation; however, it was incomplete, and the oil content of the water phase was unacceptable. Heating, another conventional approach to break emulsions, yielded an oil phase containing water above specification for a temperature range of 50−60 °C.[13] Adding alum or conventional cationic polymeric flocculants to the emulsion was also unsuccessful at resolving the emulsion and yielded viscous sediment at the bottom.

In a related but separate application, the addition of a cationic surfactant was also found to be useful in causing separation of oil and brine phases produced from an ASP application, as discussed below.

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(13) Lissant, K. J. Demulsification of petroleum emulsions. *Demulsification Industrial Applications*; Marcel Dekker: New York, 1983; Chapter 5, pp 105−134.

2. Experimental Section

2.1. Materials. A crude oil with an American Petroleum Institute (API) gravity of 31°, acid number of 0.34 mg of KOH/g of oil, and viscosity of 13.1 cP at 25 °C was used in the experiments. The asphaltene content of the crude oil was about 1.53%, and the resin content was about 4.49%. The surfactants, Petrostep S-1, the sodium salt of a propoxylated branched C16−C17 alcohol sulfate, and Petrostep S-2, the sodium salt of an internal olefin sufonate, IOS 15-18, were supplied by Stepan Chemical Company. The anionic polymer Flopaam 3330S, a 30% hydrolyzed 8 MM molecular-weight polyacrylamide polymer was supplied by SNF, Inc. Isobutyl alcohol at 99.4% purity was obtained from J.T. Baker Chemical Company. Sodium chloride of greater than 99.9% purity was obtained from Fisher Scientific. Calcium chloride obtained from Fisher Scientific was of 99% purity.

Pure cationic surfactants of the type alkyltrimethylammonium halide were obtained from Alfa Aesar, a Johnson Mathey Company. Commercial cationic demulsifiers P and V were supplied by Nalco Chemical Company. Commercial amphoteric surfactants were supplied by McIntyre, now Rhodia. The commercial non-ionic surfactant Tergitol 15-S-5 was supplied by Dow Chemical Company, and Neodol 25-3 was supplied by Shell Chemical Company. Commercial demulsifiers A and B were supplied by Nalco Company. Water used for solution preparation was deionized (DI). All materials were used as received.

2.2. Methods. *2.2.1. Method To Make Synthetic-Produced Brine.* Using an Acculab SV-100 weighing scale, all chemicals, except DI water, were weighed. In a 5 gallon pail, DI water was added and placed under a Heidolph RZR 2051 control stirrer. Then the mixer was turned on, and the salts were added sequentially followed by the polymer. The polymer particles were slowly tapped into the stirred solution (ca. 30 min) so as not to form clumps commonly known as fisheyes. No undissolved particles were noted in any of the batches made, and therefore, no filtration was performed. The mixing was continued for 1 h. Next, the preweighed surfactants Petrostep S-1 first and then Petrostep S-2 and alcohol were added, and the solution was stirred for 30 min. The synthetic-produced brine contained 1.0 wt % NaCl, 0.18 wt % CaCl$_2$·2H$_2$O, 0.12 wt % Flopaam 3330S, 0.15 wt % (active) Petrostep S-1, 0.05 wt % (active) Petrostep S-2, and 0.40 wt % isobutyl alcohol.

2.2.2. Emulsion Preparation and Bottle Tests. The emulsions were made in 6 oz. (177 mL) glass prescription bottles, an industry standard.[14] A majority of the bottle tests was performed using 70 mL of synthetic-produced brine and 30 mL of the crude oil.

The prescription bottles were marked at 70 and 100 mL levels, and then the brine was added to the 70 mL mark. The container of relatively high-gravity crude oil was shaken by hand for about 10 min to mix well, and then, using VWR Tripour plastic beakers, crude oil was poured into each of the prescription bottles to the 100 mL mark. Next, the bottles of emulsion were placed on Eberbach shakers on high speed for 10 min. Then, chemicals for demulsification and water clarification were added on the basis of the total weight of emulsion. Again, the bottles of emulsion were placed on Eberbach shakers on high speed (ca. 240 shakes/min) for 10 min. The bottles were removed from the shaker, and emulsion separation was recorded at various time intervals. Further details are illustrated in Figure 1 and in the literature.[15] Water drop readings were recorded in milliliters as a function of time. They were used to gauge emulsion stability, with

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(15) Manning, F. S.; Johnson, R. E. *Oilfield Processing*; PennWell Corporation: Tulsa, OK, 1995; Vol. 2, Crude Oil.
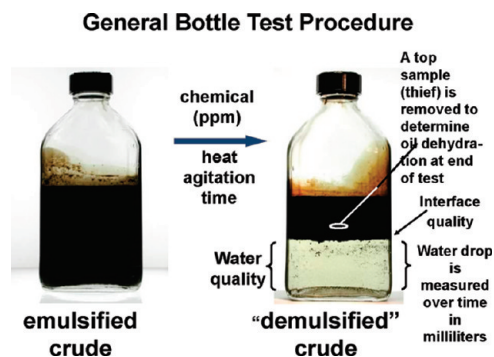
General Bottle Test Procedure

Figure 1. General bottle test procedure.

Figure 2. Water content of oil when emulsion heated to 60 °C versus the addition of cationic demulsifier. Settling time = 3 h.

a faster water drop indicating lower emulsion stability. Water samples were taken from the bottoms of the bottles using a syringe, and the oil concentrations in water were measured by extraction with hexane using the EPA 1664A method.[16]

After the water drop readings, the resolved or partially resolved oil from each bottle was analyzed for water content. Using a syringe with a blunt-tipped needle, a small portion of the oil (about 6 mL) was withdrawn. The tip of the syringe was set to 15−20 mL above the theoretical oil−water interface as determined by the slug grindout value (a procedure that measures the water content of the emulsion).[15] The aliquot of oil was added to a graduated API centrifuge tube containing an equal volume of an aromatic solvent, and the contents were shaken by hand. The centrifuge tubes were then centrifuged at high speed for 3 min. After centrifugation, the percent residual emulsion, typically referred to as basic sediment (BS), and the percent water (W) were noted for each bottle. After recording BS&W values, an alkyl sulfonate surfactant (a chemical known to resolve the remaining emulsion) was added to the centrifuge tube. Such chemicals are generally called "slugging or knockout chemicals" and are typically low-molecular-weight sulfonate-based materials. After slugging, the tube was again shaken and centrifuged as previously described. The BS was therefore completely eliminated and only water remained in the bottom part of the tube. The slug grindout number is reported as a percentage. Smaller values of BS&W and slug indicate drier oil.

Phase behavior studies were performed in capped, 13 mm inner diameter, flat-bottomed test tubes instead of bottles because they afforded a clearer view of the oil−water interface. The solutions were shaken vigorously by hand for 2 min and allowed to equilibrate. Observations were recorded over a time period of several hours up to 24 h.

Surfactants, diluted to either 1 or 5 wt % actives in DI water, were added to the emulsions. The polymeric demulsifiers A and B were diluted to 5 wt % in heavy aromatic naphtha (HAN) before the addition to the emulsion. A control with no added chemicals was included in all experiments.

2.2.3. Microscopy Observations. A drop of emulsion at 70% water cut was immediately transferred to a microscope slide and imaged at 10× magnification on an Olympus BX51 trinocular polarized light microscope. The droplet size at several locations on the slide was monitored as a function of time, and the images were recorded.

3. Results and Discussion

The produced brine contains micelles for the conditions indicated but does not appear to have any liquid crystalline phases, as indicated by the absence of birefringence.
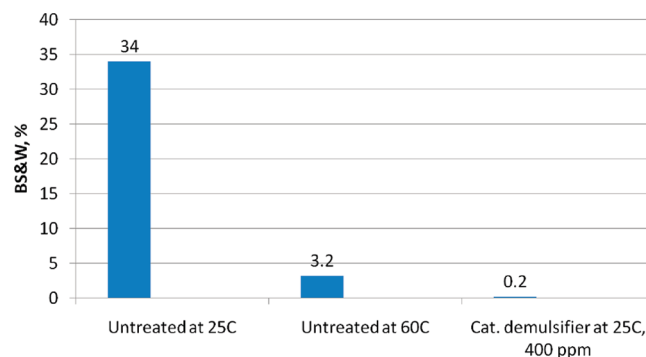
A salinity scan was performed using the 70:30 synthetic-produced brine/crude oil emulsion in test tubes to study phase behavior and determine the region of optimum salinity for the formulation. The results of this study indicated that inversion from O/W emulsion to water-in-oil (W/O) emulsion occurs in the range between 3.9 and 6.0 wt % sodium chloride. Levitt et al. reported that, with 1% total active surfactant, a 3:1 ratio of surfactants, 2% *sec*-butyl alcohol, and this crude oil, i.e., the same proportions of the surfactants and alcohol as in this work but 5 times more concentrated, optimum salinity with NaCl alone as the electrolyte is approximately 4% NaCl with no polymer and a temperature of 38 °C.[17] At room temperature, optimal salinity would be slightly higher. From these results, it is clear that the aqueous phase of the initial emulsion is below optimum salinity and, hence, is an O/W microemulsion.

In the absence of demulsifiers, both oil and water phases are far above acceptable standards (0.5% water in oil and 200 ppm oil in water), as shown in the first bar in Figure 2 for the oil phase and by the dark color of the aqueous phase in the corresponding sample of Figure 3. Early in the study, it was observed that clarification of the O/W emulsions occurred rapidly when they were heated to 50 and 60 °C, which produced a clear aqueous phase in 1 h. Results of BS&W analysis in this case indicated higher than expected water levels of 3.2 wt % in the separated oil when the emulsion was heated to 60 °C. It is to be noted that heating the emulsion or the produced brine alone to 50 °C for 24 h did not appear to produce any precipitation of solids.

Demulsifier B, an ethoxylated resin, was found to be effective in reducing the water content to 0.4 vol % in the oil phase at 100, 200, and 300 ppm levels after 2.75 h of settling time, while the aqueous phase contained visibly significant quantities of oil even after several hours of settling. Other similar polymeric demulsifiers were also found to be effective in reducing the water content of the oil to acceptable limits but were ineffective at reducing the oil content in the water to acceptable levels.

3.1. Cationic Surfactants with SP Flood. Cationic surfactants of the type alkyltrimethylammonium bromide were used to determine the effect on water and oil separation of produced emulsions resulting from surfactant−polymer floods. A clear separation of the aqueous phase was found upon the addition of around 200 ppm *n*-octyltrimethylammonium bromide (C_8TAB). The addition of 200 ppm C_8TAB to

(16) United States Environmental Protection Agency (U.S. EPA). *EPA Method 1664, Revision A, n-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated n-Hexane Extractable Material (SGTHEM; Nonpolar Material) by Extraction and Gravimetry*; U.S. EPA: Washington, D.C., 1999.
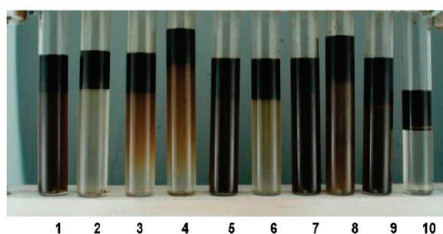
(17) Levitt, D. B.; Jackson, A. C.; Heinson, C.; Britton, L. N.; Malik, T.; Dwarakanath, V.; Pope, G. A. The identification and evaluation of high-performance EOR surfactants. *SPE Reservoir Eval. Eng.* **2009**, *12* (2), 243–253.

Preliminary Experiments, 18 Hours Equilibration

1 – 200ppm EO/PO Demulsifier A   **6 – 200ppm Cationic Demulsifier P**
2 – 200ppm C₈TAB   7 – 200ppm Neodol 25-3
3 – 1000ppm C₈TAB   8 – 2000ppm Neodol 25-3
4 – 2000ppm C₈TAB   9 – No additives
5 – 200ppm Cationic Demulsifier V   **10 – No additives, heated to 50C**
Added chemicals at 1 wt% in water except A diluted in Heavy Aromatic Naphtha

**Low-conc. C₈TAB (best), cationic demulsifier P promising in clearing water
Demulsifiers A (EO/PO) & V, nonionic surfactant (Neodol 25-3) poor
Heating clears the water but this treatment is often unacceptable to oil
producers since heating water is cost prohibitive**

Figure 3. Preliminary screening experiments for emulsions with 30% oil cut at 25 °C.
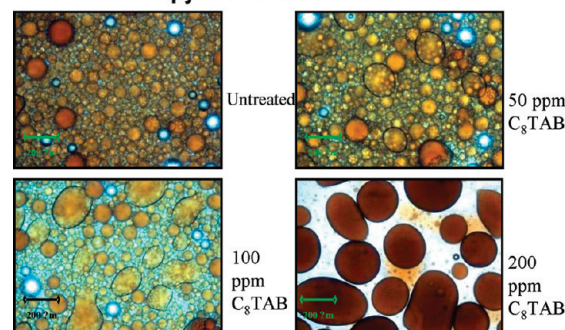
Microscopy of Emulsions after 1 Minute

Figure 4. Microscopy of emulsions with 30% oil cut at 25 °C.

Summary of results at 6 hours with 200 ppm demulsifier and 30% oil cut

Oil content in water (ppm)*
Untreated	224 ppm
C₆TAB	172 ppm
C₈TAB	**112 ppm**
C₁₆TAB	204 ppm
Cocobetaine	179 ppm

*Using EPA 1664 A method

Thief Grind out (BS&W), percent
Untreated	40
C₆TAB	30
C₈TAB	**0.4**
C₁₆TAB	1
Cocobetaine	0.4

Figure 5. Effect of the C$_n$TAB hydrocarbon chain length on demulsification effectiveness with 30% oil cut at 25 °C.

the produced brine did not appear to produce any precipitation, even when heated to 40 °C. Precipitation can occur in mixtures of cationic and anionic surfactants.[18] With 200 ppm of added C₈TAB, the cationic/anionic surfactant mole ratio is about 1:3, significantly lower than the 1:1 molar ratio where precipitation usually occurs.

The non-ionic surfactants tried (Neodol 25-3 and Tergitol 15-S-5) had low solubility in water and presumably did shift phase behavior in the desired direction to some extent. However, at concentrations of a few hundred parts per million, they did not succeed in producing clear brine phases. The cationics, however, showed promise in yielding clear brines. These surfactants are soluble in water but combine with anionic surfactant present in the brine of the initial emulsion to form ion pairs and reduce electrostatic charge at the oil–water interfaces, thereby shifting phase behavior of the oil/brine/surfactant system in the desired direction. C₈TAB seemed particularly effective at concentrations of 200 and 300 ppm. It produced clear brine phases (by visual inspection) after several hours and reduced water content in the oil to 0.8% by volume after 2.75 h. In practice, the bromide compound would probably be replaced by the corresponding chloride, which presumably has a similar effect. However, only the bromide was used in this study. Figure 3 shows the results of these preliminary experiments.

Microscopy studies showed large oil droplets separating from the emulsion shortly after the addition of C₈TAB, with larger droplets found at higher doses (Figure 4). Rapid separation did not occur below 200 ppm, which is consistent with our observation that the aqueous phase had reduced clarity below that dosage level.

The effect of the cationic surfactant chain length was also studied using the cationic surfactants alone at 200 ppm each. The results are shown in Figure 5. They indicate an optimum in reduction of oil content in water and BS&W for C₈TAB.

Figures 6 and 7 show the effects of dosage and settling time on BS&W and oil content of the water phase for another cationic demulsifier. It can be seen that BS&W decreased

with an increase in demulsifier dosage and settling time. At a demulsifier dosage of 200 ppm, BS&W decreased from 13.6 (untreated) to 0.6% after 40 min of settling time and the oil content in water was reduced from 548 to 70 ppm after 4 h. These results demonstrated that oil–water separation was improved with the use of the demulsifier. Water drop efficiency was also measured as a function of time for the same demulsifier (Figure 8). After 5 min, the emulsion seemed to have been completely resolved in comparison to only 7% resolution for the untreated emulsion and 20% for a conventional demulsifier, an ethoxylated amylphenol formaldehyde resin.

3.2. Amphoteric Surfactants with SP Flood. Amphoteric surfactants were screened for effectiveness in demulsification. The results indicate that cocobetaine used alone at dosage levels of 75 and 100 ppm showed significant clearing of the water phase after 21 h of equilibration time (Figure 9). With cocobetaine bottle tests, 218 ppm oil was found in the water and trace amounts of water in the oil.[19] Water drop efficiency was also measured for cocobetaine and was comparable to that for the cationic demulsifier (Figure 8). After 5 min, the emulsion seemed to have been completely resolved with cocobetaine compared to only 7% resolution for the untreated emulsion and 20% for a conventional demulsifier, an ethoxylated amylphenol formaldehyde resin.

In bulk aqueous solution at neutral pH, a small fraction of betaine molecules is protonated to the cationic form. H⁺ ions

(18) Jonsson, B.; Lindman, B.; Holmberg, K.; Kronberg, B. *Surfactants and Polymers in Aqueous Solution*; John Wiley and Sons: New York, 1998; p 128.

(19) Hirasaki, G. J.; Miller, C. A.; Raney, O. G.; Poindexter, M. K.; Nguyen, D. T.; Hera, J. Recovery and separation of crude oil and water from emulsions. *U.S. Patent Application*; Rice University: Houston, TX; Nalco Company: Sugar Land, TX, April 2010.
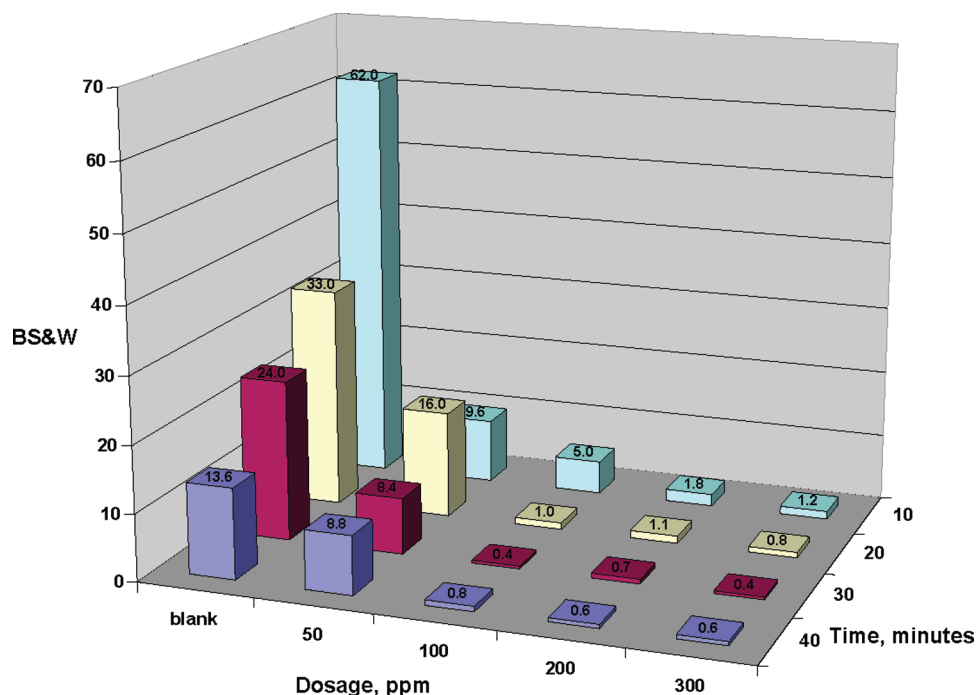
Figure 6. Effects of the cationic demulsifier dosage and settling time on BS&W for emulsions with 30% oil cut at 25 °C.
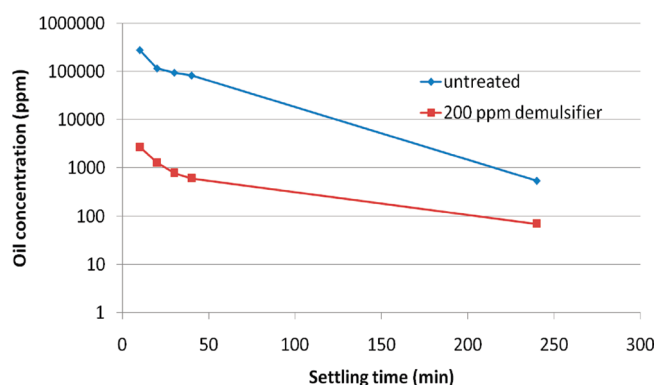

Figure 7. Relationship between the oil concentration and settling time with and without a cationic demulsifier for emulsions with 30% oil cut at 25 °C.
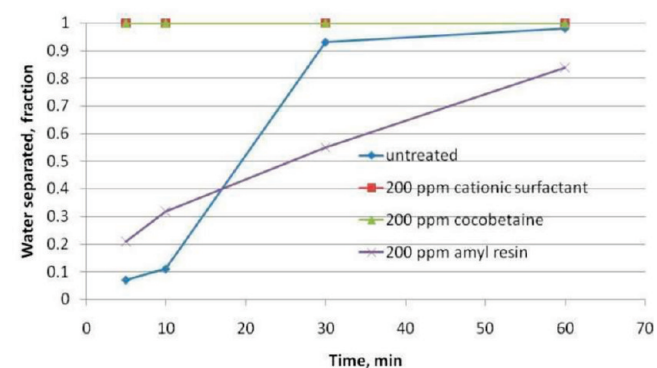

Figure 8. Water separated as a function of time for cationic, amphoteric, and amylphenol formaldehyde resin demulsifiers for emulsions with 30% oil cut at 25 °C.

are attracted to the negatively charged surfaces of the dispersed oil drops, causing surface pH to be lower than bulk pH. As a result, a larger fraction of betaine molecules is in the

Bottle Tests with Amphoteric Surfactants*
21 Hours Equilibration
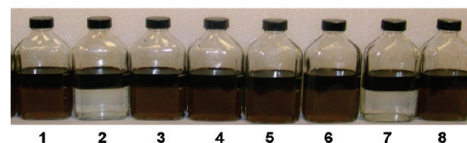
1 – Capryl/capramidopropyl betaine
2 – Cocobetaine
3 – Octyl betaine
4 – Caprylamidopropyl Betaine
5 – Lauramidopropylhydroxysultaine
6 – Sodium Cocoamphopropionate
7 – Cocobetaine
8 – Octyl betaine

Surfactants diluted to 5 wt.% in water.
Added to emulsion at 100 ppm except 75 ppm for samples 7,8.

*Patent pending technology

Figure 9. Separation produced by several amphoteric surfactants after 21 h for emulsions with 30% oil cut at 25 °C.

cationic form at the surface of the droplets than in the bulk, with the results that surface charge density is reduced and drop coalesence is more likely. Moreover, incorporation of zwitterionic betaine molecules into the films of anionic surfactant on the drop surfaces also reduces surface charge density. That is, the effect of betaines on drop coalescence is related to that of cationics.

3.3. Cationic/Amphoteric Surfactants and Polymeric Demulsifier with SP Flood. The effect of C_8TAB at levels of 30, 40, and 50 ppm when used in conjunction with 50 ppm of the commercial demulsifier A was investigated. Also, a comparison was made with 200 ppm C_8TAB and cocobetaine and with no added chemicals.

Results of this study (Figure 10) indicate that the clearest aqueous phases were obtained with the combination of 50 ppm demulsifier A and 50 ppm C_8TAB, followed by 50 ppm demulsifier A with 40 and 30 ppm C_8TAB, respectively. These combined systems all have improved clarity of aqueous phases

**Bottle Tests: Cationic and Amphoteric
Surfactants (50 ppm) & Demulsifier A (50 ppm)***
21 hours equilibration

1 – No added chemicals
2 – Demulsifier A + C_8TAB
3 – Demulsifier A + capryl/capraamidopropyl betaine
4 – Demulsifier A + Cocobetaine
5 – Demulsifier A + Octylbetaine

C_8TAB diluted to 2.5wt% in water, Amphoterics diluted to 5wt.% in water, and Demulsifier A diluted to 5 wt.% in Heavy Aromatic Naphtha.

*Patent pending technology

Figure 10. Separation produced by demulsifier A/C_8TAB and demulsifier A/amphoteric surfactant combinations after 21 h for emulsions with 30% oil cut at 25 °C.

1 – No added chemicals
2 – 50ppm Demulsifier A + 50ppm C_8TAB
3 – 50ppm Demulsifier A +100ppm C_8TAB

Figure 11. Effect of the C_8TAB concentration on separation produced by demulsifier A/C_8TAB combination for emulsions with 30% oil cut at 25 °C.

compared to 200 ppm C_8TAB alone, which in turn was better than the system with 200 ppm cocobetaine. The results indicate a minimum threshold at 50 ppm C_8TAB for effective demulsification when used with 50 ppm demulsifier A for this system.

An increasing dosage of C_8TAB to 100 ppm when added with 50 ppm demulsifier A shows that the 50 ppm demulsifier A along with 50 ppm C_8TAB system appears to have the clearer aqueous phase (Figure 11). A further study using C_8TAB at 50, 60, 80, and 100 ppm all dosed with 50 ppm demulsifier A indicated that the clearest aqueous phase was obtained using the composition 50 ppm demulsifier A and 50 ppm C_8TAB (results not shown). Some synergism is suggested in that the total additive concentration of 100 ppm for the best of these demulsifier mixtures is half that required when C_8TAB is used alone.

3.3.1. Effect of Mixtures of Polymeric Demulsifier and Chain Length of Pure Cationic C_nTAB Surfactants. The effect of chain length of the pure cationic surfactant of the alkyltrimethylammonium bromide series was investigated to determine the effectiveness in demulsification. In addition to the study with C_8TAB described in the preceding paragraph, combinations of 50 ppm demulsifier A with 50 and 100 ppm levels of *n*-decyl-, *n*-dodecyl-, *n*-tetradecyl-, and *n*-hexadecyltrimethylammonium

Table 1. ASP Concentrations in Injection Water from ASP Flood for an Oilfield in the U.S.

	produced water
total dissolved solid (ppm)	16000−20000
chloride (ppm)	8500−12000
calcium (ppm)	350
total surfactants (sulfate/sulfonate) (ppm)	3000
polymer (ppm)	1000
Na_2CO_3 (%)	1.75

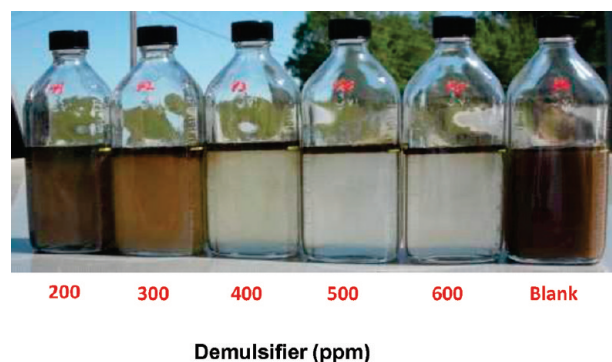200   300   400   500   600   Blank

Demulsifier (ppm)

Figure 12. Effect of the cationic demulsifier concentration on produced emulsion separation after 45 h for ASP flood for an oilfield in the U.S.

bromide were also investigated. Also included were 50 and 100 ppm levels of the amphoteric surfactants cocobetaine and cocaminopropionic acid.

Results of the bottle tests indicate that the best aqueous phase occurred with the 50 ppm demulsifier A + 50 ppm C_8TAB system, followed by 50 ppm demulsifier A + 60 ppm C_8TAB and increasing amounts of C_8TAB up to 100 ppm. This was followed by the systems containing 50 ppm cocobetaine, 50 ppm C_{10}TAB, 100 ppm cocobetaine, 50 ppm cocaminopropionic acid, 50 ppm C_{12}TAB, and 50 ppm C_{14}TAB. A similar concept of using a combination of a water-insoluble, oil-soluble organic demulsifier and a water-soluble surfactant to treat W/O emulsions has been reported. However, the synergism concept does not appear to have been reported in this patent.[20] Rosen has extensively discussed synergism between anionic and cationic surfactants, although not in connection with demulsification of emulsions.[21]

3.4. ASP Flood. Table 1 shows the alkali, polymer, and surfactant concentrations in injection water from a pilot, oilfield ASP flood in the U.S. Surfactants and polymer were mainly responsible for the stability of oil droplets. The polymer increased the interfacial film thickness between water and oil, decreased the ζ potential (more negative), and inhibited aggregation and flocculation of oil droplets by making it more difficult for droplets to approach one another and coalesce. Alkali, such as sodium carbonate, reacted with acidic components of the crude oil and converted them into soaps, which can help stabilize the O/W emulsion. Figure 12 shows the demulsification test photos for ASP-produced fluid with a cationic demulsifier at various dosages at 25 °C and 45 h of settling time. The data demonstrate that the cationic demulsifier was very effective in resolving the emulsion from this ASP

(20) Selvarajan, R.; Sivakumar, A.; Marble, R. A. Aqueous dispersion of an oil soluble demulsifier for breaking crude oil emulsions. U.S. Patent 6,294,093, Sept 25, 2001.
(21) Rosen, M. J. *Surfactants and Interfacial Phenomena*, 2nd ed.; Wiley Interscience: New York, 1989; Chapter 11.

flood at dosages from 400 to 600 ppm at 25 °C. Application of the laboratory findings resulted in the production of on-specification oil for a field experiencing chemical ASP break-through. Before the use of the demulsifier, only a very limited amount of sales oil was produced from the ASP flood because of high BS&W. For example, less than 1.5 barrels of oil was produced/week without treatment, as compared to 588 barrels of oil produced/week when using the cationic demulsifier at 400 ppm.

4. Conclusions

The addition of 200 ppm of suitable cationic surfactants accelerated the separation of O/W emulsions representative of produced emulsions expected during a surfactant/polymer EOR process employing anionic surfactants. Both oil and water phases met specified criteria with either pure C_8TAB or a commercial cationic surfactant. Neither conventional non-ionic demulsifier resins nor heating to 50−60 °C was successful in producing both oil and water phases of acceptable quality. Microscopy confirmed that 200 ppm C_8TAB produced significant coalescence shortly after it was added to the emulsions. Some amphoteric surfactants, such as cocobetaine, produced acceptable results similar to those obtained with cationics.

The amount of cationic surfactant needed to produce a clear water phase was reduced substantially when a non-ionic demulsifier resin was added simultaneously. There seems to be a synergistic effect when the two types of demulsifiers are added simultaneously, a topic that merits further research.

A cationic surfactant was also found to significantly improve separation of emulsions produced during an ASP process.

While these results were obtained in connection with emulsion treatment studies for specific SP and ASP projects, it is anticipated that the basic strategy of using cationic or amphoteric demulsifiers will be applicable to other similar processes employing anionic surfactants.