Evaluation of extended surfactants with different hydrophilic head groups for enhanced oil recovery

Applications

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Abstract: Extended surfactants (ESs), obtained by inserting an oligomeric oxypropylene segment often together with an oligomeric oxyethylene segment between the hydrophobic tail and an anionic polar headgroup, have attracted considerable interest for enhanced oil recovery (EOR) due to their high salinity tolerance and favorable synergistic interactions with conventional anionic surfactants used for EOR. Sulfated ESs, in particular, have been extensively studied and applied in combination with alkylbenzene sulfonates (ABS) and olefin sulfonates. However, the limited thermal stability of sulfate head groups restricts their application in high-temperature reservoirs. In this study, three ESs with identical hydrophobic tail and the same oxypropylene-oxyethylene chain but different hydrophilic head groups – sulfate, sulfonate, and carboxylate – were synthesized and characterized. The three ESs showed comparable CMC values and excellent salinity tolerance. The sulfonate- and carboxylate-based ESs remained stable for several weeks at 120 °C, whereas the ES with a sulfate end group was rapidly hydrolyzed. All ABS/ES formulations formed Winsor Type III microemulsions with similar solubilization ratios, although the ABS/carboxylate system exhibited lower optimum salinity than the other two systems. Coreflooding using Berea sandstone outcrops achieved a yield of 50–56 % of the original oil in place (OOIP) after waterflooding.

Keywords: extended surfactants; enhanced oil recovery; phase behavior; thermal stability

1 Introduction

Surfactant flooding is an established chemical EOR technique that improves oil recovery primarily through reduction of the oil–water interfacial tension and alteration of reservoir rock wettability toward more water-wet conditions.[1–4] Effective surfactant formulations must be capable of forming Winsor Type III microemulsions with appropriate oil and water solubilization ratios, while maintaining adequate aqueous solubility and thermal stability under reservoir conditions.[2,5–11] These requirements are critical to ensure effective transport of surfactants through the reservoir and sustained interaction with oil, water, and rock to mobilize residual oil after water flooding. In addition to technical performance, economic and environmental considerations also play an important role in the selection of surfactants for field applications.[12,13]

Reservoirs differ significantly in crude oil composition, permeability, brine salinity and hardness, temperature, and lithology. Consequently, surfactant systems must be tailored to specific reservoir conditions.[14–17] Among the various surfactant classes investigated for EOR, anionic surfactants are most widely applied due to their favorable performance, availability, and cost-effectiveness. The fact that they are negatively charged is also advantageous because loss by adsorption at the reservoir rock will be less of a problem than with nonionic or cationic surfactants since most rock surfaces carry a negative net charge. Common examples include alkylbenzene sulfonates, petroleum sulfonates, long-chain internal or alpha-olefin sulfonates, and, extended surfactants,[18–23] which is the topic of this paper.

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Extended surfactants represent an important development in surfactant flooding technology. These surfactants are made by propoxylation and subsequent ethoxylation of fatty alcohols followed by introduction of a negatively charged polar headgroup at the end of the polyoxyethylene segment. They combine the salt tolerance of nonionic surfactants with the adsorption characteristics of surfactants with anionic headgroups. Extended surfactants have demonstrated strong synergistic behavior when formulated with conventional anionic surfactants such as hydrophobic ABS and olefin sulfonates, and their performance has been validated in both laboratory studies and field trials.[6,19,24–26] To date, sulfate-based ESs are the most commonly used, particularly in reservoirs with temperatures below 70 °C. However, they are monoesters of sulfuric acid and as such susceptible to hydrolysis, in particular acid catalyzed hydrolysis, which prevents their use in high-temperature reservoirs.[27–29] To address this limitation, ESs with carboxylate or sulfonate headgroups as an alternative to sulfate have been proposed to improve the thermal stability and extend the applicability of surfactant flooding with ESs to harsher reservoir environments.[27,28,30,31] In this work, three ESs with identical hydrophobic tail and the same oxypropylene-oxyethylene chain but different hydrophilic headgroups were synthesized and systematically evaluated. Their CMC, aqueous stability at various brine salinity/hardness, long-term thermal stability, phase behavior, and displacement properties were evaluated under conditions relevant to surfactant flooding. This study provides a direct evaluation and comparison of sulfate-, sulfonate-, and carboxylate-based extended surfactants and offers practical guidance for selecting ES systems for EOR applications.

2 Experimental and discussions

2.1 Synthesis of extended surfactants

The nonionic surfactant fatty alcohol alkoxylate (FAA), synthesized in the laboratory of Shandong GINZRE New Materials Development Co., Ltd. via sequential propoxylation and ethoxylation of 1-octadecanol, was used as the precursor for the synthesis of the three extended surfactants. The target molecular structure of FAA was designed to be $C_{18}H_{37}$–$(PO)_{20}$–$(EO)_{10}$–H. The three batch synthesis procedures are briefly described below.

Sulfation. A known mass of fatty alcohol alkoxylate (FAA), sulfamic acid, and amide catalyst was charged into a 500 ml three-necked flask. The molar ratio of sulfamic acid to FAA was maintained at 1.2, and the catalyst loading was 5 wt % of the total charge. Nitrogen blanketing was applied throughout the reaction to minimize oxygen exposure and obtain a light-colored product. The reaction was conducted at 95 °C for 3–4 h. Samples were withdrawn at 1-h intervals, and the conversion was determined by two-phase titration in accordance with ISO 2271:1989. The reaction was terminated when the conversion exceeded 95 %.

Carboxylation. Carboxylate extended surfactants are usually synthesized via reaction of the nonionic surfactant with monochloroacetic acid.[32] A known mass of fatty alcohol alkoxylate (FAA) and solid NaOH was charged into a 500 ml three-necked flask. The mixture was heated to 90 °C under continuous stirring and vacuum to remove water generated during the reaction, and these conditions were maintained for 4–5 h. The system was then cooled to 60 °C, and chloroacetic acid (CA) was gradually added through a charging funnel at a CA/FAA molar ratio of 1.2. The carboxylation reaction proceeded for approximately 1 h, after which the product was neutralized with NaOH to a final pH of approximately 9.

Sulfonation. A known mass of fatty alcohol alkoxylate (FAA) and solid NaOH was charged into a 500 ml three-necked flask. Similar to the carboxylation procedure, the mixture was heated to 90 °C under continuous stirring and vacuum for 4–5 h to remove water generated during the reaction. The temperature was then increased to 120 °C, after which 1,3-propanesultone was gradually added through a charging funnel at a fixed molar ratio of 1.2 relative to FAA. The reaction was allowed to proceed for 3 h before cooling to ambient temperature.

2.2 Characterization of the extended surfactants

Table 1 presents detailed information on the FAA and the three extended surfactants (ESs). As shown in Table 1, the nonionic FAA exhibits a purity close to 100 %, as determined by hydroxyl group titration (GB/T 7383-2007), and appears as an opaque, milky white material. All three ESs are paste-like but differ in color and active content. Specifically, the sulfate-based surfactant is pale yellow with an active content of 92 %, and the sulfonate-based surfactant is deep amber in color with an active content of 85 %. The carboxylate-based surfactant has a milky appearance similar to that of the FAA but is more viscous.

The active contents of the sulfate and the sulfonate were determined using the two-phase titration method defined by ISO 2271:1989 (E), which is specifically designed for anionic surfactants. Although carboxylates are also anionic surfactants, they do not fully dissociate in acidic environments. Consequently, the two-phase titration method is not applicable to carboxylates, and no convenient and validated method has yet been established for determining the active content of carboxylate-based extended surfactants. In this study, its active content was therefore calculated assuming 100 % conversion of the FAA. This means that the active content of the carboxylate is likely overestimated.

Table 1: Summary of the FAE and three extended surfactants.

	FAA	Sulfate	Sulfonate	Carboxylate
Molecular structure	R-O-$(PO)_m(EO)_n$-H	R-O-$(PO)_m(EO)_n$-SO_4Na	R-O-$(PO)_m(EO)_n$-SO_3Na	R-O-$(PO)_m(EO)_n$-CH_2_COONa
Active%	~100	92	85	93
Testing standards	GB/T 7383-2007	ISO 2271, 1989 (E)	ISO 2271, 1989 (E)	Theoretical calculation
Appearance				

Notes: (1) GB/T 7383-2020. Non-ionic surface active agents – determination of hydroxyl value. (2) ISO 2271, 1989 (E). Surface active agents – detergents – determination of anionic-active matter by manual or mechanical direct two-phase titration procedure.

To obtain detailed structural information on the extended surfactants – specifically the number of propylene oxide (PO) and ethylene oxide (EO) units incorporated into the molecules – the surfactant samples were analyzed using liquid chromatography–mass spectrometry (LC–MS). Because the same fatty alcohol alkoxylate (FAA) precursor was used to synthesize all three extended surfactants, only the sulfate-based surfactant was analyzed by LC–MS in this study. Figure 1 shows the composition of the sulfate-based extended surfactant. As can be seen, it exhibits a broad homologue distribution with m/z values ranging from 1,100 to 1,800 and a maximum at 1,394. This observation is consistent with previous reports indicating that the use of alkaline catalysts (KOH in this case) during FAA synthesis leads to a broad oligomer distribution.[33–35] The literature suggests that acid-catalyzed ethoxylation can produce a narrower oligomer distribution.[36,37] The oligomer distribution has a significant impact on the physicochemical properties of surfactants, including product viscosity, wetting and permeation behavior, freezing point, and cloud point.[38] Although these properties are important for EOR applications, optimization of the FAA synthesis is beyond the scope of this study but merits further investigation.

2.2.1 Determination of critical micelle concentration (CMC)

The CMC values of the three extended surfactants were determined under ambient conditions (20 °C) using surface tension (γ) measurements. A tensiometer (BZY-203, Shanghai FangRui Instrument Co., Ltd.) was employed to measure the surface tension of aqueous solutions of the surfactants in distilled water over a concentration (C) range from 2.44×10^{-8} to 2×10^{-4} mol L^{-1}. The CMC values were identified from the breakpoint in the γ–log C curves, where a sharp change in slope occurred.

As shown in Figure 2, the three surfactants exhibit very similar surface tension plots, with CMC values in the range 2–3 $\times$ 10^{-6} mol L^{-1}. The carboxylate surfactant displays a slightly lower interfacial tension above the CMC (36 vs. 39 mN/m) compared with its sulfate and sulfonate counterparts. This behavior can be attributed to the lower degree of ionization of the carboxylate in distilled water, which reduces the electrostatic repulsion between the polar headgroups, which is favorable for the self-assembly. Under real EOR conditions, with a high concentration of electrolytes (e.g., NaCl and Na_2CO_3) the electrostatic repulsion will be screened to large extent, which will affect both the CMC and the surface tension at the CMC. It is likely that the electrolyte effect will be more pronounced for the fully ionized sulfate and sulfonate surfactants than for the partly ionized carboxylate.[39] The effect of electrolytes on the CMC and the surface tension at the CMC for the different ESs has not been investigated in this work, however.

2.3 Effect of brine salinity and hardness on the solubility of the extended surfactants and of their mixtures with alkylbenzene sulfonates

The aqueous solubility of the three extended surfactants varies depending on the nature of their hydrophilic

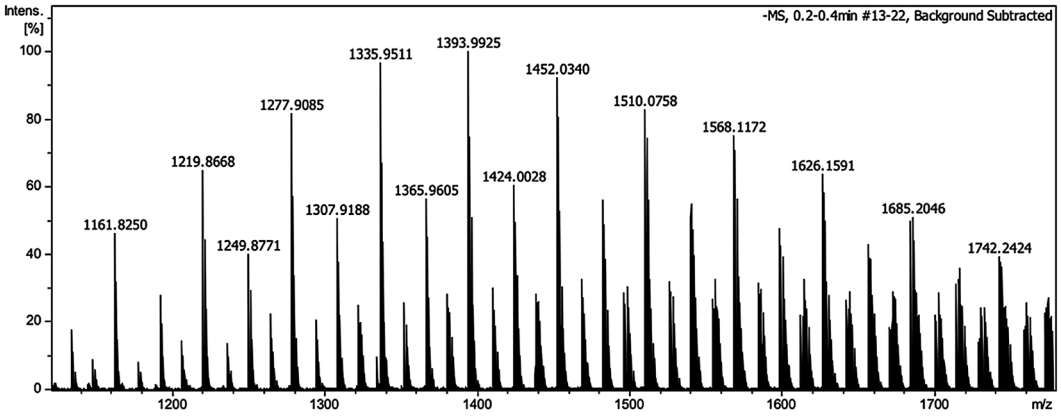

Figure 1: LC-MS analysis of the sulfated extended surfactant.

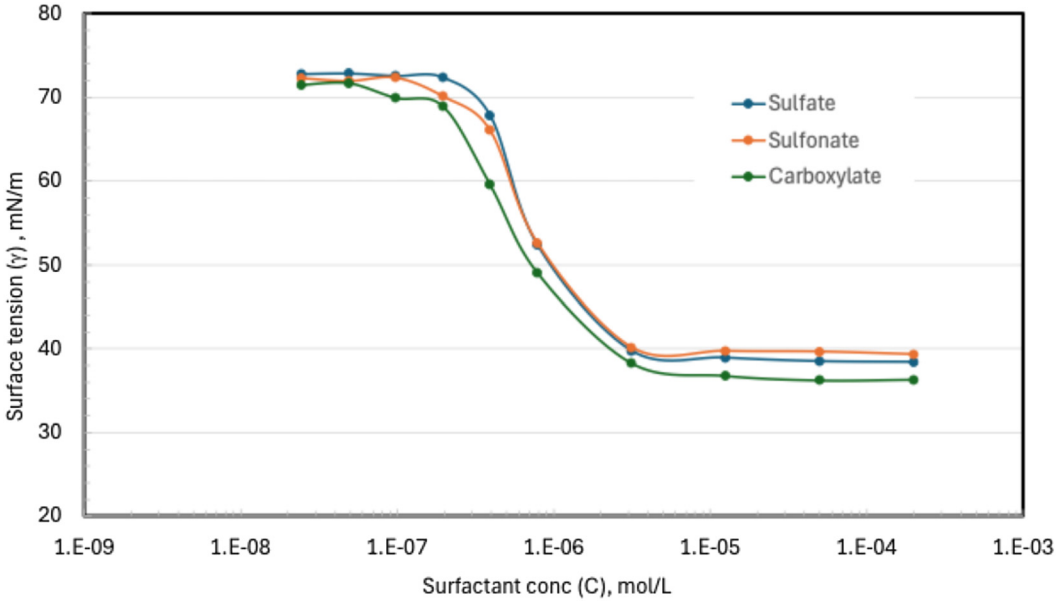

Figure 2: Surface tension versus log surfactant concentration for the extended surfactants.

headgroups. Both the sulfonate and the carboxylate remain soluble at salinities of at least 230,000 ppm NaCl, whereas the sulfate-based surfactant becomes cloudy at a salinity of approximately 210,000 ppm. These results indicate that the extended surfactants exhibit an exceptionally high solubility in aqueous media with high salt content. Such high salt tolerance is an important asset for the application of extended surfactants in high-salinity reservoir environments (Figure 3).

Surfactant mixtures. As mentioned earlier, surfactant mixtures are commonly used to tailor the performance of the formulation to specific reservoir conditions. In this study, the solubility of mixtures of the extended surfactants with an alkylbenzene sulfonate (ABS, molecular weight = 390) was evaluated at a weight mixing ratio of 6:4. As shown in Figure 4, the ABS/sulfate and ABS/carboxylate mixtures remain clear at salinities of up to 75,000 ppm and 60,000 ppm, respectively. The ABS/sulfonate mixture becomes turbid at a slightly lower salinity, approximately 50,000 ppm. Thus, the sulfate ES, which by itself was the most sensitive to electrolytes, turned out to be the least electrolyte sensitive when combined with the ABS.

Brine hardness. Divalent ions such as calcium (Ca^{2+}) and magnesium (Mg^{2+}) exhibit strong binding affinity with the hydrophilic head groups of anionic surfactants, which can lead to solution turbidity or even precipitation. Consequently, surfactant formulations must be carefully designed for reservoirs with high formation-water hardness. In some cases, injection brine must be softened prior to alkaline–surfactant–polymer (ASP) flooding to prevent ion precipitation and formation damage.[24] However, the high cost associated with brine softening

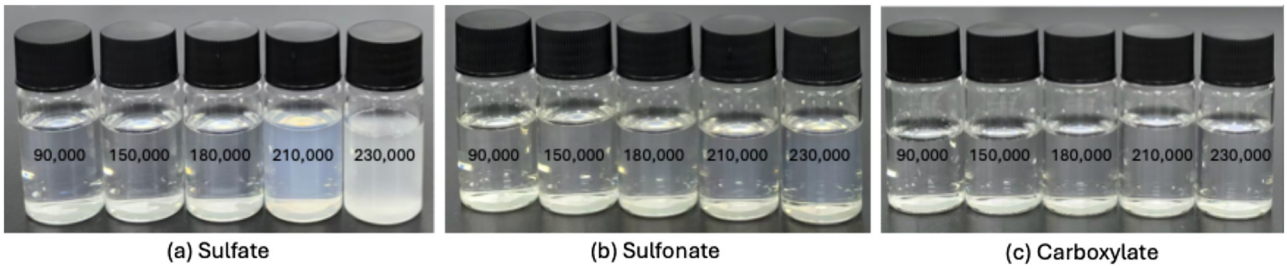

Figure 3: Influence of salinity on surfactant solubility (NaCl was used as the electrolyte and the surfactant concentration was 0.3 %).

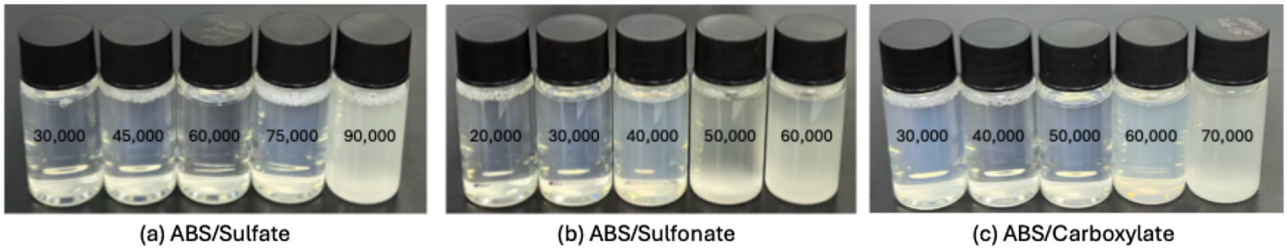

Figure 4: Influence of salinity (NaCl) on solubility of surfactant mixtures (ABS/ES in a 4:6 wt ratio).

can significantly reduce the economic viability of chemical flooding. Therefore, the development and selection of surfactant formulations with high hardness tolerance is a key priority for ASP and surfactant–polymer flooding applications.

In this section, the influence of brine hardness on the solubility of the above surfactant mixtures was investigated. The surfactant mixtures with concentration of 0.3 % were prepared in 30,000 ppm NaCl brine containing various concentrations of divalent ions (Ca^{2+} + Mg^{2+}) at a Ca^{2+}/Mg^{2+} weight mixing ratio of 1:1. As shown in Figure 5, in the presence of divalent ions, the tolerance to brine hardness decreases in the order: sulfate-based > carboxylate-based > sulfonate-based extended surfactants. For example, the ABS/sulfate mixture remains clear at divalent ion concentrations of up to 4,800 ppm, whereas the ABS/sulfonate mixture remains clear only up to approximately 450 ppm. These results indicate that sulfate-based extended surfactants provide the greatest hardness tolerance when blended with alkylbenzene sulfonates.

2.4 Thermal stability of the extended surfactants

The thermal stability of the extended surfactants (ESs) was evaluated at 60 °C and 120 °C. Two parallel sets of surfactant solutions were prepared and placed in ovens maintained at 60 °C and 120 °C, respectively. The concentrations of the sulfate- and sulfonate-based surfactants were fixed at 0.3 %, while the carboxylate-based surfactant was prepared at 0.03 %, which was sufficient for surface tension measurements. Previous studies have shown that pH has a pronounced effect on sulfated extended surfactants, and that an alkaline environment can significantly improve their thermal stability.[28] Accordingly, two sets of sulfate-based surfactant solutions were prepared: one at neutral pH and the other adjusted to a pH of around 9. All samples were monitored for 45 days and analyzed at approximately two-weeks intervals.

As mentioned earlier, the active concentrations of the sulfate- and sulfonate-based surfactants were determined

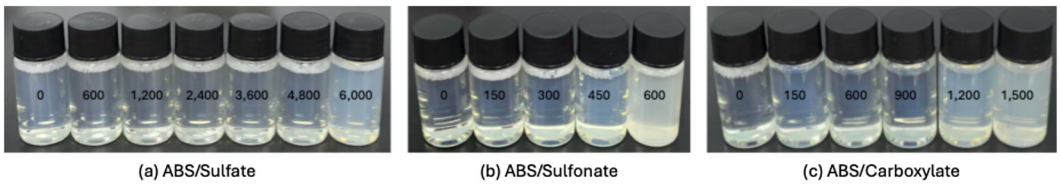

Figure 5: Influence of brine hardness (Ca^{2+} + Mg^{2+} in 1:1 wt ratio) on solubility of surfactant mixtures (total surfactant concentration was 0.3 % with ABS/ES in 4:6 wt ratio) in 30,000 ppm NaCl solutions.

using the two-phase titration method. However, this method is not applicable to carboxylate-based surfactants due to the incomplete dissociation of the carboxylate head group. Instead, surface tension measurements were conducted for the carboxylate-based extended surfactant, and changes in surface tension were used as an indicator of surfactant stability.

As shown in Figure 6, both the sulfonate- and the carboxylate-based surfactants exhibit good stability at 60 °C and 120 °C. For the sulfonate, the active content remained at approximately 90 % of the initial value, while the surface tension of the carboxylate-based surfactants remained relatively stable.

In contrast, the sulfate-based ES shows a rapid decline in active content at 120 °C, confirming that sulfate head groups readily undergo hydrolysis at elevated temperatures. At 60 °C, however, the sulfate surfactant is much more stable. The effect of pH on the stability is also clear from the figure. After 45 days, the active content remained at approximately 92 % of the initial value in an alkaline environment, whereas it decreased to about 76 % under neutral conditions. These observations are consistent with earlier studies,[27–29] which demonstrate that substituting sulfate head groups with sulfonate or carboxylate groups markedly enhances the thermal stability of extended surfactants. Although sulfated extended surfactants are generally considered suitable for low-temperature reservoirs (below 60 °C), maintaining a mildly alkaline formation environment would be beneficial for improving their stability further.

2.5 Phase behavior tests

Phase behavior tests were conducted using ABS/ES mixtures with a synthetic oil. The oil phase was prepared by blending 82 % crude oil with 28 % kerosene to simulate live oil with a viscosity of 10 cP at 45 °C. The total surfactant concentration was fixed at 0.3 %, which is representative of concentrations typically used in field applications.[24,40,41] NaCl was used in place of alkali such as Na_2CO_3 or NaOH to reduce the risk of formation damage and to simplify produced-fluid treatment.

For each surfactant formulation, aqueous-phase solubility tests and salinity scans were performed at an oil/water ratio of 1. As shown in Figure 7, all three surfactant formulations exhibited excellent aqueous solubility at a surfactant concentration of 0.3 % over the entire investigated salinity range. For both the sulfate/ABS and the sulfonate/ABS mixtures, a middle-phase microemulsion formed at salinities between 1.4 % and 1.8 %, with an optimum salinity of approximately 1.6 %. In comparison, the carboxylate/ABS mixture formed a middle-phase microemulsion at lower salinities, ranging from 1.0 % to 1.3 %, with a reduced optimum salinity of about 1.2 %.

Detailed analysis of the oil, water, and middle-microemulsion phases yielded oil/water solubilization ratios of approximately 12 at the optimum salinity. According to Huh's equation,[42] the corresponding interfacial tensions were estimated to be on the order of 2×10^{-3} mN/m.

2.6 Oil displacement efficiency

Based on the phase behavior tests shown in Figure 7, three core-flooding experiments were conducted using Berea sandstone outcrop cores with blends of ABS and the extended surfactants. The properties of the Berea cores are summarized in Table 2. The cores had dimensions of 1.5 in. × 12 in. and similar porosities of approximately 21 %. Their permeabilities ranged from 167.4 to 259.1 mD, and the initial oil saturation (Soi) varied between 66.6 % and 72.5 %.

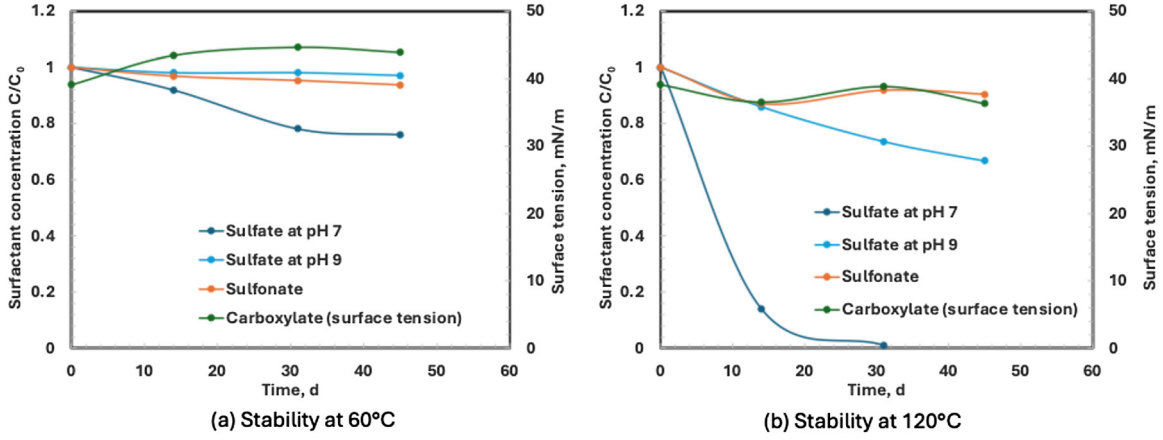

Figure 6: Surfactant thermal stability: (a) at 60 °C; (b) at 120 °C.

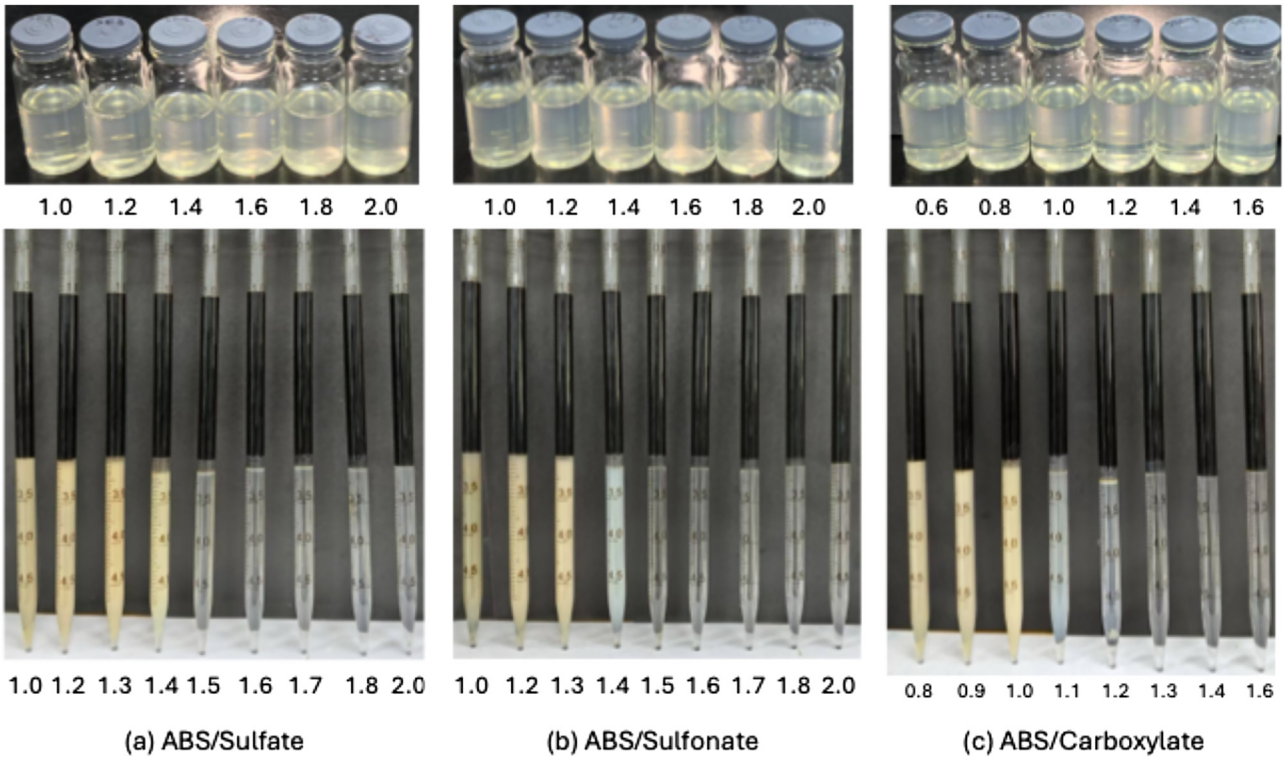

Figure 7: Aqueous solubility and phase behavior of the three ESs in combination with ABS. The ABS/ES ratio was 4:6 and the total surfactant concentration was 0.3 %. (a) ABS/sulfate, (b) ABS/sulfonate, and (c) ABS/carboxylate.

For each core-flooding experiment, after oil saturation, the cores were aged at 45 °C for 12 h and then subjected to water flooding at a flow rate of 0.4 ml/min until no oil was detected in the effluent. Following water flooding, a 0.3 pore volume (PV) salt/surfactant/polymer (SSP) slug was injected, followed by a 0.2 PV polymer drive (PD) and an extended water post-flush until oil production became negligible. Throughout the entire process, the pressure drop across the core was continuously monitored using two pressure transducers positioned 1 in from the inlet and outlet, respectively. The viscosities of the SSP and PD solutions were approximately 40 cP.

For the ABS/sulfate and the ABS/sulfonate systems, the NaCl concentration was 1.6 %, and 2,600 ppm partially hydrolyzed polyacrylamide (HPAM) was added. In contrast, a lower HPAM concentration of 2,400 ppm was applied for the ABS/carboxylate system due to the lower injection brine salinity (1.2 % NaCl). The polymer drive solution had an HPAM concentration of 1,800 ppm. The core-flooding results are summarized in Table 3.

2.7 ABS/sulfate coreflooding performance

As shown in Table 3, water injection of 0.58 PV recovered 37.9 % of the OOIP at a flow rate of 0.4 ml/min. Subsequently, the injection of 0.3 PV SSP + 0.2 PV PD + 0.87 PV water post-flush resulted in an additional oil recovery of 58.2 % OOIP. Consequently, the cumulative oil recovery during the ABS/sulfate core flooding reached 96.2 %, and the residual oil saturation decreased to 2.8 % after the flooding. This indicates that more than 90 % of the residual oil remaining

Table 2: Properties of Berea sandstone outcrops.

No.	Surfactants	Length, in.	Diameter, in.	Mass, g	Porosity, %	Permeability, mD	S_{oi}, %	S_{ow}, %
1	ABS/sulfate	12	1.5	720.0	22	259.1	72.5	27.5
2	ABS/sulfonate			714.5	20	198.5	69.7	30.3
3	ABS/carboxylate			713.9	21	167.4	66.6	33.4

Table 3: Summary of coreflooding.

	ABS/sulfate	ABS/sulfonate	ABS/carboxylate
Water flooding			
PV injected	0.58	0.64	0.81
Oil recovery, %OOIP	37.9	42.6	43.7
SSP flooding			
Surfactant, %	0.3	0.3	0.3
Polymer, ppm	2,600	2,600	2,400
NaCl, %	1.6	1.6	1.2
Viscosity, cp	40.1	41	39
PV injected	0.3	0.3	0.3
Polymer drive			
Polymer, ppm	1,800	1,800	1,800
Viscosity, cp	42	42	41.5
PV injected	0.2	0.2	0.2
Water postflush			
PV injected	0.87	1.37	1.37
Incr oil recovery, % OOIP	58.2	51.0	52.3
Cum oil recovery, % OOIP	96.2	93.6	96
$(S_{or})_{SSP}$, %	2.8	4.5	2.7

after water flooding was recovered by the SSP injection. As shown in Figure 8, the water cut reached 100 % at the end of the water flooding and then began to decrease upon the SSP injection, reaching a minimum value of 43.8 % during the flooding. The pressure-drop profile remained within a reasonable range throughout the process, indicating that no plugging occurred during the chemical injection. This behavior can be attributed to the excellent aqueous solubility of the surfactant formulation (see Figure 7).

2.8 ABS/sulfonate coreflooding performance

When the surfactant system was switched from ABS/sulfate to ABS/sulfonate and ABS/carboxylate, comparable performance was observed. For ABS/sulfonate core flooding, as shown in Table 3 and Figure 9, injection of 0.64 PV water recovered 42.6 % of the OOIP. Subsequent injection of 0.3 PV SSP + 0.2 PV PD followed by a 1.37 PV water post-flush resulted in an additional oil recovery of 51 % OOIP. As a result, the cumulative oil recovery during ABS/sulfonate core flooding reached 93.6 % OOIP, and the residual oil saturation decreased to 4.5 % after the flooding. Figure 9 illustrates the evolution of the water cut throughout the flooding process. The water cut reached 100 % at the end of the water flooding and then decreased upon chemical injection, reaching a minimum value of 48.5 % during the flooding. In addition, the pressure-drop profile indicated that no core plugging occurred during the flooding process.

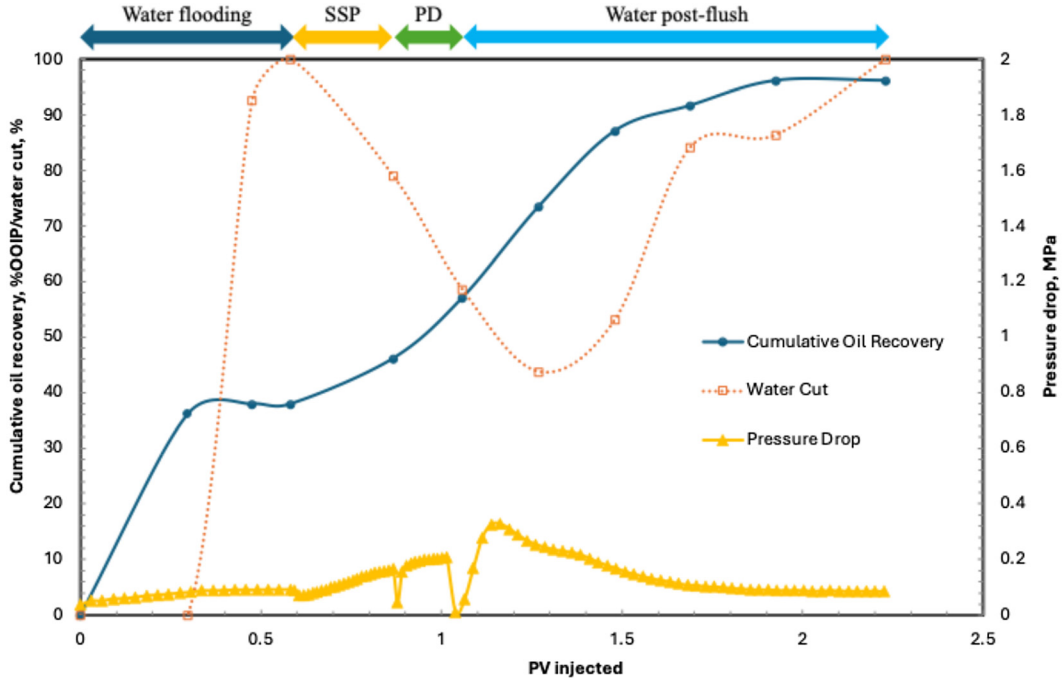

Figure 8: ABS/sulfate coreflooding performance.

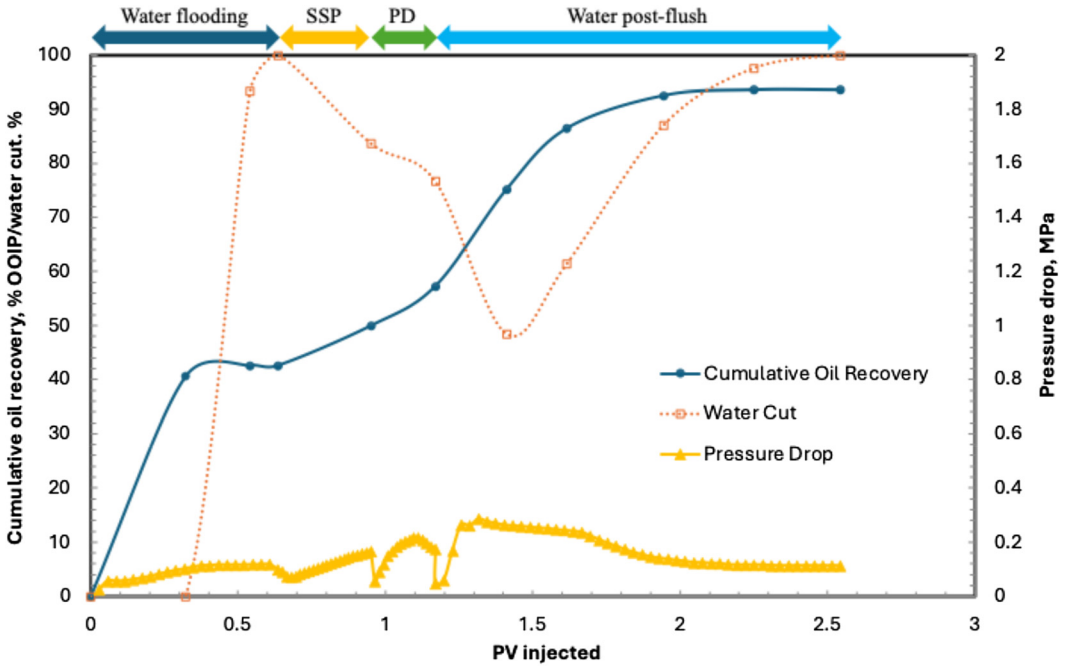

Figure 9: ABS/sulfonate coreflooding performance.

2.9 ABS/carboxylate coreflooding performance

For the third core-flooding test using ABS/carboxylate, 0.81 PV of water flooding recovered 43.7 % of the OOIP, and the subsequent flooding yielded an incremental oil recovery of 52.3 % OOIP (Table 3). Consequently, the total oil recovery reached 96.0 % OOIP, with a residual oil saturation of 2.7 %. These values are comparable to those obtained for the ABS/sulfate system and superior to those of the ABS/sulfonate system. As shown in Figure 10, the water cut decreased from 100 % at the end of the water flooding to a minimum value of

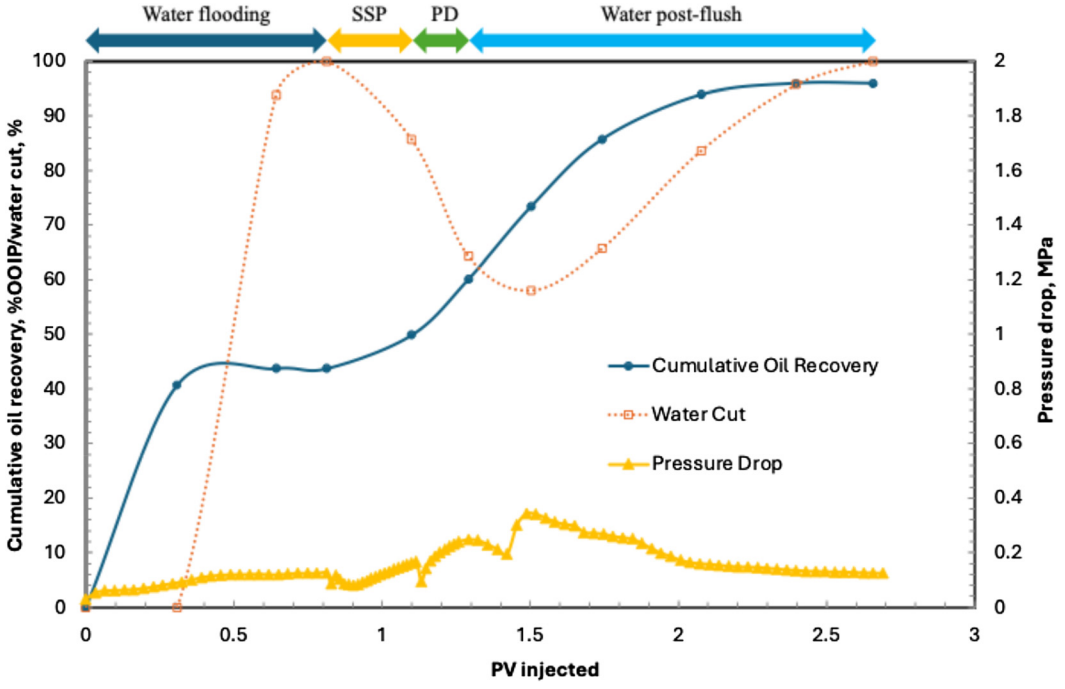

Figure 10: ABS/carboxylate coreflooding performance.

58 % during the chemical flooding. Although this value of minimum water cut is higher than those observed in the other two cases, the low water-cut stage was sustained over a longer period. Similar to the two other core-flooding experiments, the pressure drop for the ABS/carboxylate system remained within a reasonable range, indicating the absence of core plugging.

Taken together, these results demonstrate that, irrespective of the type of hydrophilic head group, the extended surfactants exhibit comparable synergistic potential when combined with a conventional surfactant such as an alkylbenzene sulfonate. All three ESs provide enhanced hard water tolerance and excellent oil recovery performance. Good tolerance to hard water, i.e. essentially to Ca^{2+} and Mg^{2+}, is practically important because the formation water often has a high concentration of these divalent ions. The effect is believed to be due to the extension, the PO/EO chain, giving rise to an increased hydration of the charged end group, which disfavors ion pairing with divalent cations. The extension also leads to a reduction of the Krafft temperature, which also favors solubility in hard water.

3 Conclusions

Extended surfactants (ESs) with different hydrophilic head groups were synthesized via sulfation, sulfonation, and carboxylation using the same fatty alcohol alkoxylate precursor, $C_{18}H_{37}$–O–$(PO)_m(EO)_n$–H. LC–MS characterization and performance evaluation led to the following conclusions:

(1) LC–MS analysis shows that the synthesized ESs exhibit a broad homologue distribution, with m/z values ranging from 1,100 to 1,800. This broad distribution originates from the use of a KOH catalyst during the alkoxylation of fatty alcohol (1-octadecanol).
(2) Sulfate-, sulfonate-, and carboxylate-based ESs display comparable critical micelle concentrations (CMCs) in the range of $(2–3) \times 10^{-6}$ mol/L, as well as similar abilities to reduce surface tension.
(3) The three ESs exhibit similar salinity tolerance. However, when blended with an alkylbenzene sulfonate, their resistance to salinity and hardness follows the order: sulfates > carboxylates > sulfonates.
(4) Thermal stability tests conducted at 60 °C and 120 °C demonstrate that both sulfonate- and carboxylate-based ESs maintain excellent stability at elevated temperatures. In contrast, sulfate-based ESs require a slightly higher pH environment to ensure stability, even at temperatures around 60 °C.
(5) Phase behavior experiments reveal that all three ESs form Winsor Type III microemulsions, with solubilization ratios of approximately 15. Compared with sulfate- and sulfonate-based ESs, carboxylate-based ESs exhibit a slightly lower optimum salinity.
(6) Coreflooding experiments using Berea sandstone outcrops demonstrated that chemical flooding consisting of 0.3 PV SSP injection, followed by 0.2 PV polymer drive and an extended water post-flush, achieved an incremental oil recovery exceeding 50 % of the original oil in place (OOIP).

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