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Branched Alkyl Alcohol Propoxylated Sulfate Surfactants for Improved Oil Recovery

This investigation considers branched alkyl alcohol propoxylated sulfate surfactants as candidates for chemical enhanced oil recovery (EOR) applications. Results show that these anionic surfactants may be preferred candidates for EOR as they can be effective at creating low interfacial tension (IFT) at dilute concentrations, without requiring an alkaline agent or cosurfactant. In addition, some of the formulations exhibit a low IFT at high salinity, and hence may be suitable for use in more saline reservoirs. Adsorption tests onto kaolinite clay indicate that the loss of these surfactants can be comparable to or greater than other types of anionic surfactants. Surfactant performance was evaluated in oil recovery core flood tests. Selected formulations recovered 35–50% waterflood residual oil even with dilute 0.2 wt% surfactant concentrations from Berea sandstone cores.

Key words: Alcohol propoxylated sulfate, Alforterra, ultra-low interfacial tension, enhanced oil recovery, surfactant adsorption, surfactant flooding, chemical flooding

Verzweigte Alkylalkoholpropoxysulfate für die tertiäre Erdölförderung. Diese Studie untersucht verzweigte Alkylalkoholpropoxysulfate für Anwendungen in der tertiären chemischen Erdölförderung (EOR). Die Ergebnisse zeigen, dass diese anionischen Tenside besonders für die EOR geeignet sind, da sie die Grenzflächenspannung (IFT) ohne alkalische Zusatzmittel oder Kotenside effektiv senken. Zusätzlich weisen einige Formulierungen eine geringe IFT bei hohen Salzgehalten auf und könnten daher für den Einsatz in Reservoiren mit hohen Salzgehalten brauchbar sein. Die Adsorptionsmessungen an Kaolin machen deutlich, dass der Verlust dieser Tenside vergleichbar oder größer ist als der anderer anionischer Tenside. Die Tensidwirksamkeit wurde in Bohrkernflutungstests ermittelt. Ausgewählte Formulierungen mit einer Tensidkonzentration von nur 0,2 wt% ermöglichten eine Produktion von 35–50% des Restöls aus den Bereasandsteinkernen.

Stichwörter: Verzweigte Alkylalkoholpropoxysulfate, Alforterra, ultra-niedrige Grenzflächenspannung, tertiäre Erdölförderung, Tensidadsorption, Tensidfluten, chemisches Fluten

1 Introduction

Surfactant enhanced oil recovery (EOR) has been applied commercially for many years, especially starting in the 1970's and 1980's [1–14]. Most of these projects were pilot-scale, but several field-scale projects were also completed.

Now, with the recent surge in crude oil prices, this chemical process has received new impetus.

The basic physics behind the surfactant flooding EOR process is that the residual oil dispersed as micron-sized ganglia is trapped by high capillary forces within the porous media. Increasing the fluid flow viscous forces or decreasing the capillary forces holding the oil in place are required before the oil can be pushed through the pore throats and sent to a production well. The rule of thumb for a successful surfactant flood is that the interfacial tension between the crude oil and the aqueous phase needs to be reduced to ultra-low values (i. e. 0.001 mN/m), several orders of magnitude below that of a typical reservoir brine-crude oil system [1]. This is equivalent to increasing the capillary number N_{cap} by a factor of at least three orders of magnitude. The capillary number is a dimensionless group which represents the ratio of viscous forces that would promote mobilizing oil droplets in the porous media to the interfacial forces that trapped the oil in place.

Besides the requirements to achieve a low in-situ IFT, another major factor that determines the technical and economic success of a surfactant flood project is to minimize the depletion of the injected surfactant, with the major sink usually from solid adsorption onto clays in the reservoir.

A wide variety of surfactants has been investigated for their potential efficacy for chemical EOR applications [1, 15–32]. More recently researchers reported data for branched propoxylated tridecyl alcohol sodium sulfates, guerbet alcohol hydrophobes [33] and alkyl polyglucosides [34–36].

However, there are surfactants not previously available or investigated during the earlier development phase of surfactant EOR technology. In part, for this reason, branched alkyl alcohol propoxylated sulfates were selected for this study. Several studies have investigated some characteristics of these branched alcohol propoxylated sulfates, details are summarized below.

Branched alkyl alcohol propoxylated sulfates have emerged as an effective type of surfactant for the removal of non-aqueous phase liquids (NAPLs) from near surface, aquifer contaminated sites [37, 38], a similar application to EOR. This application to remediate shallow subsurface aquifers by injecting a surfactant solution is a relatively recent technology. This investigation considers the same surfactant class as potential EOR agents for oilfield applications.

Alcohol propoxylated sulfate surfactants have been shown to create middle-phase micro-emulsions versus crude oils, and presumably achieve low interfacial tensions [39]. Another study demonstrated that mixtures of ethoxylated and propoxylated sulfates could be formulated to provide optimum performance for different oils and process conditions [40]. Another motivation for this research is the need for high performance surfactants and that surfactants with branched-chain alkyl groups are shown in a recent study to have lower IFT than those with straight-chain alkyl groups [41].

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Optimum salinity, solubilization ratio at optimum conditions (i.e. minimum IFT), and the influence of number of propylene oxide (= propoxy, PO) groups of alcohol propoxylated sulfates on phase behavior has been investigated [42].

Physico-chemical properties of an array of Guerbet alcohol based-ethoxylated sulfate surfactant formulations were analyzed [43–46] including the critical micelle concentration, surface excess concentration, IFT, Krafft point, dynamic surface tension and dynamic contact angle. IFTs, adsorption on calcite, optimum salinity and the wettability alteration capacity on carbonates of Alfoterra surfactants were investigated [47–52].

2 Experimental Methods

2.1 Materials

The specific surfactants selected for this study were 18 different branched alkyl alcohol propoxy sulfates of the Alfoterra mn ($m = 1-6$, $n = 3, 5, 8$) series supplied by Sasol North America Corporation. In the nomenclature Alfoterra mn, the second digit n (e.g. 5 in Alfoterra 15) indicates the average number of propoxy groups in the molecule. The first number (m) is associated with the size of the branched alkyl chain. Alfoterra 1n, 2n, 3n, 4n, 5n and 6n series have an alkyl chain of approximately C_{13} , C_{12} , C_{14} , $C_{12}-C_{13}$, $C_{14}-C_{15}$ and $C_{12}-C_{13}$, respectively.

The structure of Alfoterra 23 (used in one presented coreflood) is shown in Figure 1. The structures of the other Alfoterra surfactants vary according to the nomenclature in terms of PO groups and alkyl chain branching/length.

Aldrich supplied n-octane, n-decane, 2-propanol and sodium chloride (all ACS grade). We define 2-propanol as a co-solvent although it is a weak amphiphile that adsorbs at the interface (thereby changing the spontaneous curvature of the amphiphilic film). In our studies we use the word “co-surfactant” for comparatively complicated secondary surfactants, e.g. sorbitan esters or sorbitan ester ethoxylates [59, 60] in order to semantically distinguish them from simpler molecules (e.g. 2-propanol or 1-butanol [39, 59]), which we define as “cosolvents”. The de-ionized water was prepared in-house by distilling tap water twice. The n-octane and n-

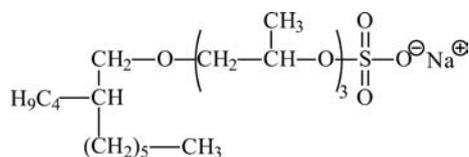


Figure 1 Alfoterra[®] 23; molar mass = 446 g/mol

formulation	surfactant	surfactant concentration	PV surfactant injected	polymer drive solution	PV polymer drive solution	IFT [mN/m]
1	Alfoterra [®] 38	2.00 wt%	0.25	350 ppm Alcoflood 1235 in 1 wt% NaCl brine***	1.0	0.008*
2	Alfoterra [®] 23	0.20 wt%	0.80	350 ppm Alcoflood 1235 in 1 wt% NaCl brine***	1.2	0.009**

* IFT of 2.00 wt% Alfoterra[®] 38 in 3.00 wt% NaCl brine against n-octane

** IFT of 0.20 wt% Alfoterra[®] 23 in 6.00 wt% NaCl brine against n-octane

*** 350 ppm Alcoflood 1235 in 2.00 wt% NaCl brine had a viscosity of $1.5 \text{ mPa} \cdot \text{s}$ at 2.6 s^{-1} , measured with a Brookfield DV-E viscometer and a #18 spindle at atmospheric pressure and a temperature of 25°C . Alcoflood 1235 is a commercial polyacrylamide product commonly used in the petroleum industry, supplied by Ciba Corporation

Table 1 Details of the Alfoterra formulations used in the core flood tests

decane were used as oleic phases because other studies have shown that IFT and phase behavior of crude oils can often be represented well by n-alkanes ranging from n-hexane to n-decane [1]. Two crude oils (crude oil #4 and Gulf of Mexico (GOM) crude) were also used in the IFT measurements. The surfactant floods were performed in a Berea sandstone core which was cut to cylindrical dimensions (25.4 mm diameter, 304.8 mm length) and glued into an aluminum housing with epoxide glue. The core's brine permeability was then determined to be 300 mD, porosity was 20%.

2.2 Interfacial tension and phase behavior

IFT and phase behavior samples were prepared in volumetric tubes adding 5 ml of the aqueous surfactant/co-solvent/salt formulations to 5 ml of hydrocarbon. The samples were mixed well for several hours, and were allowed to equilibrate for at least three weeks at ambient conditions ($T = 25^\circ\text{C}$, atmospheric pressure). The phase characteristics of each system were recorded (i.e. the relative volumes of the aqueous and oleic phases, and, if present, the middle-phase) and the interfacial tensions aqueous phase-oleic phase were determined with a spinning drop tensiometer (Temco Inc.) as described in detail by Cayias [53]. Several experiments were reproduced, showing that the spinning drop method had a maximum standard deviation of approximately 20%, particularly at low IFT.

2.3 Surfactant adsorption onto kaolinite clay

Adsorption of all investigated Alfoterra surfactants onto kaolinite clay was measured. Adsorption is an important physical process leading to surfactant loss during a surfactant EOR flood [1] and should therefore be minimized. Most of the surfactant mass is adsorbed onto clays as they have the largest surface area.

We heated kaolinite clay (more details about this clay can be found in [34]) in an oven at 120°C for two hours and then added the surfactant solutions (1:20 solid to liquid mass ratio). The samples were then shaken for 8 hours at 25°C in an electrical shaker at ambient conditions. The test tubes were next centrifuged to separate the solution and clay. Equilibrium surfactant concentrations and adsorbed surfactant masses were determined.

2.4 Oil displacement core flood experiments

Tertiary oil recovery was determined by first fully saturating the core with brine under vacuum and then injecting n-octane into the core in a primary drainage process with a capillary number [1] $N_{\text{cap}} = 3.36 \cdot 10^{-8}$ until connate water saturation was reached ($S_{\text{wc}} = 40.9\% \pm 2.0\%$). The core was then

subjected to a waterflood in a secondary imbibition process at $N_{\text{cap}} = 7.11 \cdot 10^{-8}$. The residual waterflood oil saturation was $30.2\% \pm 2.0\%$. Then the surfactant formulation, followed by a polymer drive slug, was injected into the core and incremental oil production was measured against time until no further oil production was observed.

Two selected Alfoterra formulations (cp. Table 1) were tested in the corefloods. They were chosen because they showed low IFT and low adsorption behavior onto kaolinite clay.

The surfactant formulations were prepared in 1.00 wt% NaCl brine while the connate brine salinity in the plug was 10.00 wt% NaCl. The surfactant and polymer slugs were injected at a flow rate of 0.06 mL/min. This is approximately a frontal advance rate of 2 ft/day.

3 Results and Discussion

3.1 Interfacial tension measurements

IFTs of the Alfoterra formulations were measured versus n-octane, n-decane and crude oils. Strategically, 2 wt% surfactant solutions with and without cosolvent (2-propanol) were screened initially against n-octane. For the best (= lowest IFT) surfactants this was extended to more dilute surfactant concentrations (0.1 and 0.2 wt%). Then, for selected Alfoterra surfactants, the IFTs were measured against two crude oils at elevated temperature to simulate more representative conditions of an oil reservoir. The influence of salt and addition of a second surfactant on IFT was tested for Alfoterra formulations versus n-decane. By changing salinity and/or cosolvent concentration solubilities in the surfactant formulations were varied (with the objective to achieve low or ultra-low IFT). Would an IFT of zero be achieved, complete miscibility, and by that complete oil recovery, would be established.

3.2 Initial screening versus n-octane

The IFTs of 2 wt% Alfoterra surfactant aqueous solutions were measured as a function of aqueous phase salinity (0–20 wt% NaCl range) versus n-octane as the oleic phase. The IFT was measured with formulations that contained surfactant only and also samples containing 1 wt% 2-propanol as a cosolvent.

Figure 2 shows IFT results for Alfoterra 23. The IFT of this surfactant decreased dramatically with an increase of salinity; at 6 wt% NaCl, its IFT was ultra-low with a value of 0.003 mN/m. The sharp minimum in the IFT indicates the optimal salinity for Alfoterra 23 surfactant is near 6.0 wt% NaCl. It can be seen in this figure that there is little effect from the presence of cosolvent.

For Alfoterra 25 and Alfoterra 28 (not shown), the IFT values indicated an optimal salinity at 3 wt% NaCl. The lowest IFT was approximately 0.01 mN/m. The effect of cosolvent on IFT was very small.

Similar trends were found for Alfoterra 33 surfactant, as shown in Figure 3. The lowest IFT for Alfoterra 33 was 0.005 mN/m at a salinity of 6.0 wt% without addition of cosolvent, and 0.002 mN/m at 3.0 wt% NaCl with addition of 2-propanol.

IFTs measured for Alfoterra 35 (not shown) were comparatively high with around 0.1 mN/m. Addition of 2-propanol had no effect on IFT below a salinity of 1 wt% NaCl, but this effect was significant above that salinity where cosolvent increased IFT.

Figure 4 shows that the IFT of Alfoterra 38 had a fairly broad minimum over a range of salinities. This could be an advantage for EOR, because this behavior makes Alfoterra 38 a candidate for reservoirs with a wide range of salinity. The IFT of this surfactant was as low as 0.008 mN/m and the effect of 2-propanol on IFT was small.

The IFT values observed for the 3n Alfoterra series are consistent with the data reported by Mohanty [48, 51] for Alfoterra 3n-Na₂CO₃ brine formulations. Kelkar [52] however reported IFTs above 0.1 mN/m for Alfoterra 38 formulations (surfactant concentration was 0.05 wt% in 0–0.5 M Na₂CO₃ brine). This discrepancy can be explained with the insufficient equilibration time in Kelkar's experiments (only 3 days), where thermodynamic equilibrium and low IFT were apparently not attained.

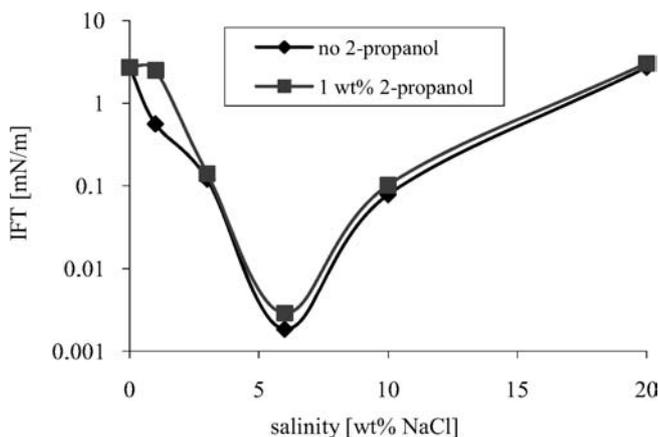


Figure 2 IFT of Alfoterra 23 versus salinity

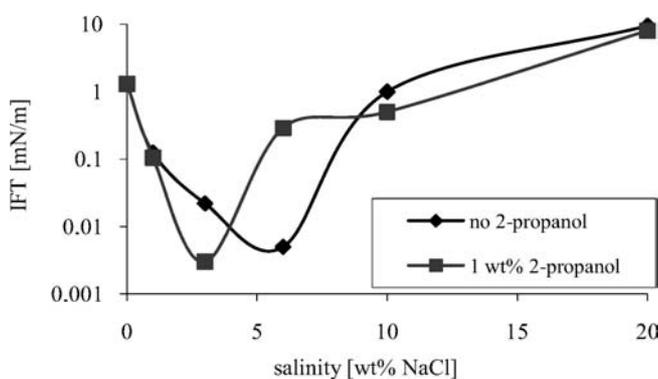


Figure 3 IFT of Alfoterra 33 versus salinity

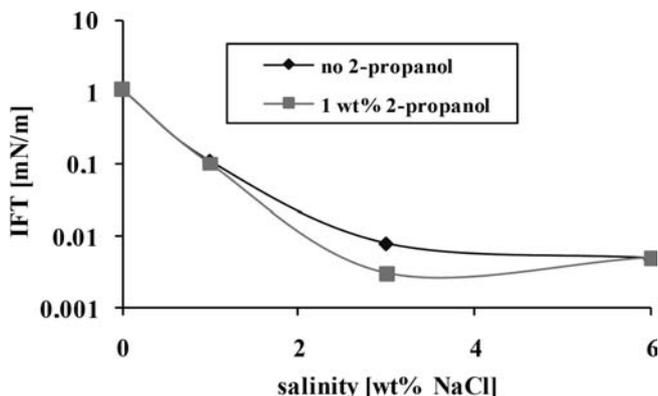


Figure 4 IFT of Alfoterra 38 versus salinity

The IFT curves of Alfoterra 43 (not shown) with or without cosolvent were very similar and a minimum IFT of 0.05 mN/m was reached at a salinity of 6 wt% NaCl (no cosolvent) or 10 wt% NaCl (with cosolvent).

The IFT of Alfoterra 45 decreased to less than 0.01 mN/m with an increase of salinity to 6 wt% NaCl (cp. Figure 5). With addition of cosolvent, its IFT decreased to as low as 0.002 mN/m. The IFT of Alfoterra 48 (cp. Figure 6) without cosolvent remained almost a constant at about 0.2 mN/m; whereas with addition of 2-propanol, the IFT was lowest at 3.0 wt% NaCl (approximately 0.01 mN/m).

The strong sensitivity of IFT to salinity is expected given that these surfactants are anionic [1]. The results suggest that the optimal salinity (salinity of minimum IFT [1, 42]) can be as high as several percent NaCl concentration. This is consistent with the trends observed in Na_2CO_3 brines [51, 52] and for similar Guerbet alcohol based alkyl propoxylated sulphate surfactant molecules [42]. Hence, these surfactants may be included in an EOR design for relatively saline reservoirs. In addition, the surfactants with more PO groups had a lower optimal salinity which was again consistent with the data reported in the literature [42] and with the notion that more PO groups make the surfactant more hydrophobic.

Another trend is that the addition of 2-propanol as a cosolvent had little effect. Possible exceptions are higher IFT values for Alfoterra 35, lower IFT values for Alfoterra 38 and a shift in optimum salinity for Alfoterra 33. This is contrary to the behavior of nonionic alkyl polyglucosides where cosolvents strongly reduce IFT [34].

In general, added cosolvents pack at the interface so as to decrease the curvature of the interfacial layer and thereby re-

duce the IFT [54–57]. Sabatini [58] suggested the concept of a “hydrophobic linker” as a physical model for the action of these cosurfactants. That is, an additive may work by linking the oil and surfactant molecules better at the interface. However, this phenomenon had only marginal effect on the IFT of the investigated Alfoterra surfactants systems.

3.3 Influence of salt on IFT of Alfoterra formulations and phase behavior examples

In Figure 7, the influence of salt and number of PO groups on IFT is displayed for a 3n Alfoterra surfactant series. The oleic phase was n-decane in these samples and the surfactant concentration was 1 wt% in 2 wt% NaCl brine or deionized water. All measurements were conducted at ambient conditions ($T = 25^\circ\text{C}$, atmospheric pressure). Salt strongly reduced IFT as compared to deionized water, which is consistent with Mohanty’s [48, 51] observations for crude oil systems and with the behavior observed for nonionic alkyl polyglucoside surfactants [34, 59, 61, 62]. The number of PO groups had no effect on IFT for these salinities, the recorded data lie within the range of experimental error.

Salt also had a strong effect on phase behavior, cp. Figures 8 and 9. In samples prepared with deionized water, all oil was solubilized while in brine samples, all water was solubilized. In deionized water, with an increasing number of PO groups, more water was solubilised. Alfoterra 38 which has 8 PO groups solubilized all oil and deionized water and formed a 100% microemulsion. Mohanty [48, 51] recorded for an Alfoterra 38 in deionized water/crude oil formulation

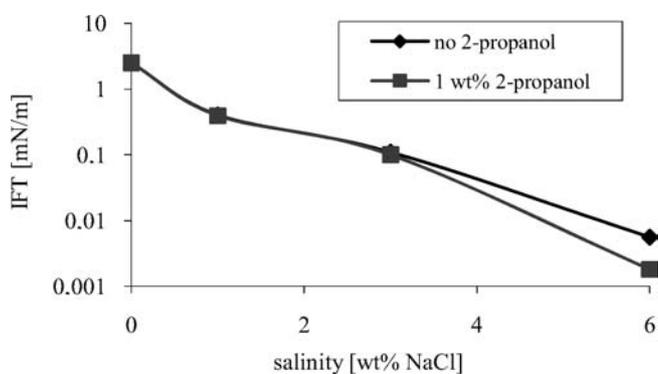


Figure 5 IFT of Alfoterra 45 versus salinity

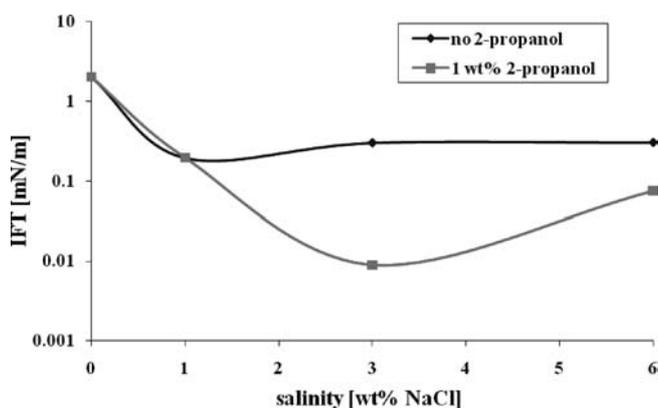


Figure 6 IFT of Alfoterra 48 versus salinity

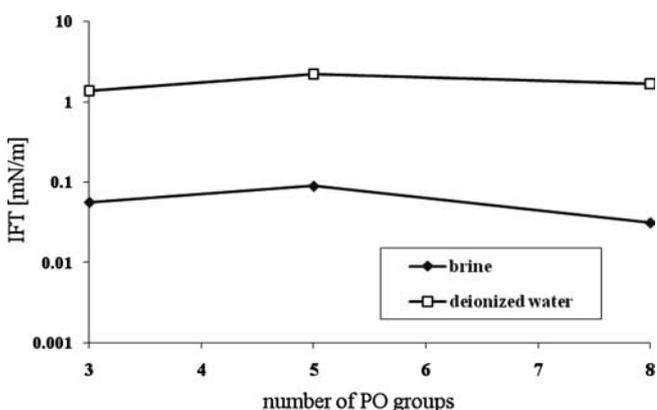


Figure 7 Influence of salt and number of PO groups on IFT of Alfoterra 3n series

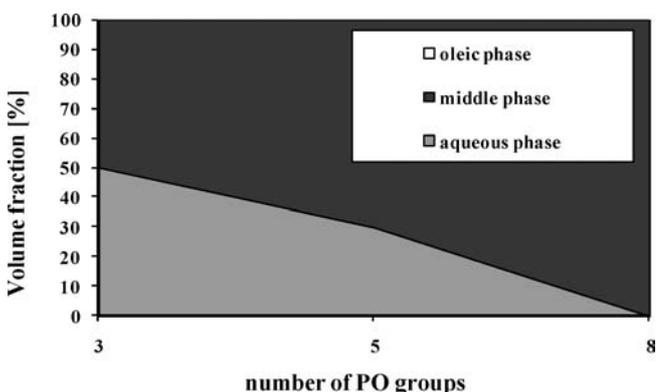


Figure 8 Phase behavior of Alfoterra 3n series in deionized water

that all crude oil and some of the water was solubilized. The difference in results can be explained by the different nature of crude oil as compared to n-decane.

The phase behaviour of Alforterra 38 in brine was consistent with what was observed in 0.1–0.5 M Na_2CO_3 brine at a lower surfactant concentration [51, 52]. As a general trend, low IFT values appear when middle phase microemulsions form [61–63]. The existence of a middle-phase microemulsion is an indicator of hydrophilic-lipophilic balance [63, 65]. Considering the fairly low concentration of Alforterra 38, this is very effective.

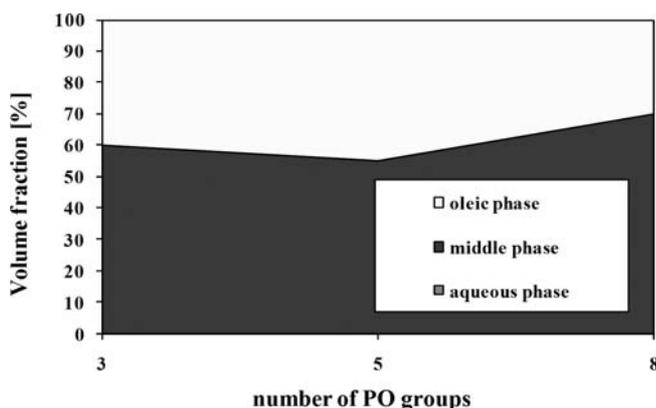


Figure 9 Phase behavior of Alforterra 3n series in brine (2 wt% NaCl)

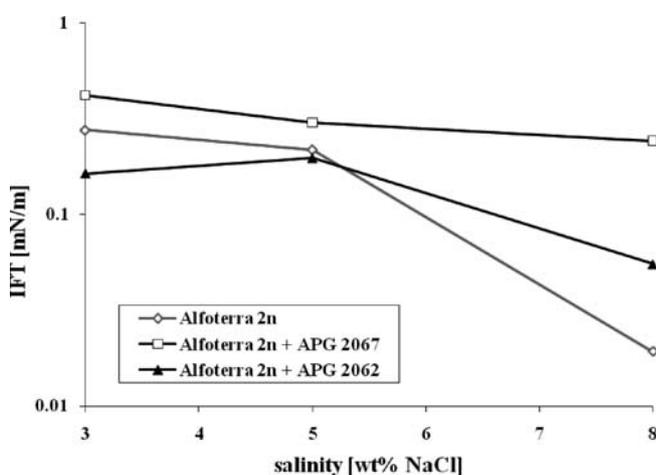


Figure 10 IFT of Alforterra 2n series formulations in brine (2 wt% NaCl)

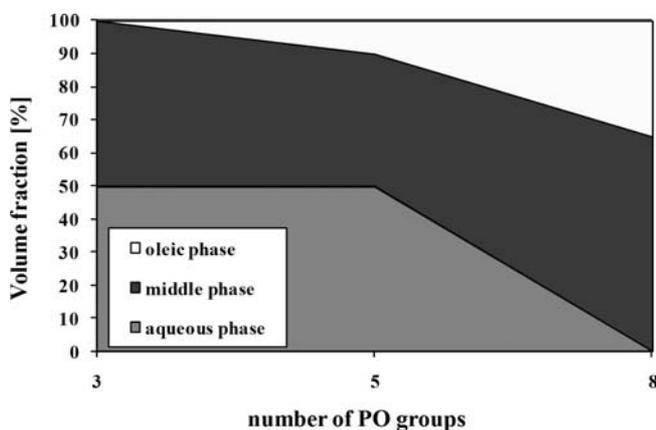


Figure 11 Phase behavior of Alforterra 2n series in brine (2 wt% NaCl)

One test was run at elevated temperature (75°C) to investigate the effect of temperature on IFT. For a 1 wt% Alforterra 35 formulation in deionized water against n-decane, an IFT of 1.45 mN/m was measured as compared to 2.01 mN/m at 25°C . Increasing temperature reduced IFT.

In Figure 10, the IFTs for an array of Alforterra 2n surfactant formulations in 2 wt% NaCl brine are displayed. The Alforterra 2n concentration was 1 wt% in the pure Alforterra mixtures and 0.5 wt% in the formulations where 0.5 wt% APG surfactant was added so that the total surfactant concentration was constant at 1 wt% for all samples. More details about these APG surfactants can be found in [34–36, 61, 62, 67, 68]. The oleic phase was n-decane and all measurements were conducted at ambient conditions ($T = 25^\circ\text{C}$, atmospheric pressure).

The IFT decreased with increasing number of PO groups. The maximum for Alforterra 25 formulated with APG2062 lies within experimental error. The phase behavior was similar for all these Alforterra 2n formulations, though in case of including APG2062 a bit more water was solubilized and in case of APG2067 a bit more oil was solubilized if compared to the pure Alforterra 2n base case. Figure 11 displays the phase behaviour of the pure Alforterra formulations.

Comparing the solubilization behavior of the Alforterra 2n series to the Alforterra 3n series, then clearly a difference can be observed. While the Alforterra 3n series solubilized all water, this was not the case for the Alforterra 2n series except for a PO number of 8. For a PO number of 3 and 5, Alforterra 2n solubilized no water but a lot of oil, contrary to Alforterra 3n where all water and some oil was solubilized. Addition of APG2062, which has a longer alkyl chain than APG2067, solubilized more water than either the pure Alforterra 2n or the Alforterra 2n mixed with APG2067.

Addition of APG2067 increased IFT, while addition of APG 2062 decreased IFT except for the Alforterra 28 case, where it also increased IFT. Lower IFT values associated with APG2062 as compared to APG2067 are consistent with previous experiments [34, 59].

In summary, Alforterra 3n surfactants reached low IFT values (0.03–0.08 mN/m), while Alforterra 2n surfactants showed higher IFTs (0.27 mN/m for Alforterra 23 and 0.22 mN/m for Alforterra 25) except for Alforterra 28, which also reached a low IFT value with 0.02 mN/m.

3.4 Interfacial tension measurements – low Alforterra surfactant concentrations

IFTs were also measured at much lower surfactant concentration (0.10 and 0.20 wt%) at the expected optimal salinity. The measurements used n-octane as oleic phase and were performed at ambient conditions. Selected low IFT results are tabulated in Table 2. In most cases low IFTs were reached with low (0.05–0.10 wt%) to zero cosolvent concentration. Low IFTs at these low surfactant concentrations are attractive for further study towards a field application.

Surfactants Alforterra 13, 15 and 18 were included later in the test program because they showed relatively low adsorption on kaolinite clay (cp. Table 4). Samples Alforterra 63, 65 and 68 were also added later because the supplier indicated that these 3 surfactants might be the least expensive to manufacture in large volumes. Because previous results already demonstrated some of the other Alforterra products could achieve quite low IFT at low surfactant concentration, we focused immediately on more severe test conditions. The IFT results indicated that the optimal salinity for some of

these six Alfoterra surfactants may exceed even 10 wt% salinity. None of the measured values were especially low as compared to the best Alfoterra systems reported earlier. The IFT ranged from 0.04 mN/m to 1 mN/m for the Alfoterra 1n series and from 0.02 mN/m to 1 mN/m for the 6n series; IFTs generally decreased with increasing salinity. The results observed for the Alfoterra 6n series are consistent with the data reported for Na₂CO₃ brines [48, 51]

In summary, it is encouraging that for several cases the IFT was quite low at all three surfactant concentrations. The Alfoterra 23 perhaps had the best results, followed by the Alfoterra 45 at 6.0 wt% NaCl and Alfoterra 28 at 3.0 wt% NaCl and without 2-propanol addition. In some cases, the IFT did not increase monotonically with a decrease in the Alfoterra surfactant concentration. This behavior could be associated with experimental errors in the IFT measurement and/or reflect that the optimal salinity can shift with a change in surfactant concentration.

3.5 IFT measurements for crude oil systems

All the previous IFT results were measured against n-octane or n-decane as oleic phase. While n-octane or n-decane can be a reasonable proxy for crude oil for phase behavior/IFT studies [1], measurement with actual crude oil is more relevant. Two different crude oil samples were selected for IFT measurements. The first one was crude oil #4, which had a density of 857 kg/m³ at 45 °C, and the other one was Gulf of Mexico (GOM) oil, whose density was 812 kg/m³ at 45 °C. A density of 695 kg/m³ was measured for n-octane at 45 °C. We selected a test temperature of 45 °C and brine salinity of about 3 wt% NaCl, which is representative of conditions at the oil #4 reservoir. The GOM oil was a light, waxy crude oil. The measured IFT results for different Alfoterra surfactants and the two crude oils and n-octane at 45 °C are listed in Table 3. All measurements were conducted at ambient pressure. These results indicate that the IFT values are lower for the crude oils than for n-octane at identical measurement conditions. We speculate that the IFT values could be

surfactant	surfactant concentration [wt%]	2-propanol concentration [wt%]	NaCl concentration [wt%]	IFT [mN/m]
Alfoterra [®] 23	0.20	0.00	6.00	0.009
Alfoterra [®] 23	0.20	0.10	6.00	0.006
Alfoterra [®] 28	0.20	0.10	3.00	0.019
Alfoterra [®] 33	0.20	0.10	3.00	0.006
Alfoterra [®] 38	0.20	0.00	3.00	0.081
Alfoterra [®] 38	0.20	0.10	3.00	0.121
Alfoterra [®] 38	0.20	0.10	6.00	0.249
Alfoterra [®] 45	0.20	0.00	6.00	0.012
Alfoterra [®] 45	0.20	0.10	6.00	0.011
Alfoterra [®] 48	0.20	0.10	3.00	0.014
Alfoterra [®] 23	0.10	0.00	6.00	0.016
Alfoterra [®] 23	0.10	0.05	6.00	0.011
Alfoterra [®] 33	0.10	0.05	3.00	0.011
Alfoterra [®] 45	0.10	0.00	6.00	0.018

Table 2 IFT results for Alfoterra[®] surfactant formulations

surfactant	brine salinity [wt% NaCl]	IFT for GOM crude oil [mN/m]	IFT for crude oil #4 [mN/m]	IFT for n-octane [mN/m]
Alfoterra [®] 23	Na/Ca brine*	n. d.	0.94	n. d.
Alfoterra [®] 28	Na/Ca brine*	0.49	0.22	n. d.
Alfoterra [®] 38	Na/Ca brine*	0.72	0.23	n. d.
Alfoterra [®] 45	Na/Ca brine*	n. d.	0.65	n. d.
Alfoterra [®] 48	Na/Ca brine*	n. d.	0.31	n. d.
Alfoterra [®] 68	Na/Ca brine*	n. d.	0.69	n. d.
Alfoterra [®] 28	1.00	0.11	n. d.	0.14
Alfoterra [®] 28	3.00	0.003	n. d.	0.007
Alfoterra [®] 28	4.00	0.078	n. d.	0.22

* brine composition was de-ionized water with 2.90 g/L NaCl and 0.10 g/L CaCl₂·2H₂O added

Table 3 IFT for Alfoterra[®] surfactants (0.2 wt%) in brine against crude oil or n-octane at 45 °C

even lower versus these crude oils if the brine salinity would be adjusted to be at their optimal conditions. This is based on previous results of this study where n-octane and Alfoterra surfactants at ambient temperature show an optimal salinity of several percent NaCl.

3.6 Adsorption tests on kaolinite clay

Adsorption was measured as a function of surfactant concentration c_{eq} and showed three trends:

1. Equilibrium surfactant adsorption G increased with increase of bulk surfactant concentration c_{eq} . There were only three exceptions with Alfoterra 15, 25 and 28. For Alfoterra 15 and 25, there were adsorption maxima at a bulk concentration of about 1 wt%. For Alfoterra 28, adsorption decreased with increase of surfactant concentration.
2. The general trend for adsorption sorted by Alfoterra surfactant series from lowest to highest was: Alfoterra 1n's < 2n's < 6 n's < 5 n's < 4 n's < 3 n's (n = 3, 5, 8).
3. Generally adsorption decreased with an increase of the number of PO groups in the surfactant molecule.

The adsorption results for the Alfoterra 2n and 3n series are tabulated in Table 4. Adsorption data for the other Alfoterra surfactants can be found in [59, 60].

Mohanty [49, 51] found that adsorption of Alfoterra 63 on calcite powder increased with an increase in NaCl concentration, temperature and a reduction in pH value.

The mechanisms of surfactant adsorption at the kaolinite/liquid interface have been previously studied [69–73]. It is recognized that two steps, more or less separated, can describe the formation of the adsorption layer. Adsorption onto minerals at low bulk surfactant concentration is gener-

ally due to the interaction between the polar head of the amphiphile molecule and some specific sites of the surface, e.g. H-bonds or electrostatic forces. For higher bulk surfactant concentrations, aggregates are formed at the interface as a result of lateral interactions between hydrophobic chains. This aggregation is due to the same forces as those responsible for bulk micelle formation. In Alfoterra surfactant molecules, more PO groups make the surfactant more hydrophobic, the interaction between hydrophobic chains therefore becomes stronger, which relatively weakens the interaction between the polar head of the surfactant molecules and the specific sites on the kaolinite clay surface. This might explain a decrease of adsorption of Alfoterra surfactants with an increase of the number of PO groups in their molecules.

On the other hand, adsorption of surfactant on mineral surfaces also depends on many other factors. Several physicochemical processes can be expected to occur, such as hydrolysis of surface species, ion-exchange, electrostatic adsorption and dissolution of the clay constitute, and adsorption or precipitation of resultant complexes.

Similar to some other studies of surfactant adsorption from aqueous solutions onto kaolinite clay, an adsorption maximum was found in some cases here. Several researchers proposed a mechanism responsible for the adsorption maximum [74–76]. When aqueous surfactant solution contacts with kaolinite clay, the concentration of Ca^{2+} and Mg^{2+} in the solution increases due to the ion-exchange process. At low surfactant concentration, surfactant molecules exist in the solution as monomers. Meanwhile, the adsorption of surfactant increases with increase in the concentration. At high concentration, when the adsorption density of surfactant on kaolinite surface is high enough to make the concentration product of the adsorbed surfactant anion and Ca^{2+} and Mg^{2+} greater than their solubility products, a precipitate will form on the kaolinite surface. However, with a further increase in surfactant concentration in aqueous solution, surfactant molecules aggregate and micelles are formed in the bulk solution, which enhance the solubility of the precipitate. Consequently, the micelles compete with the surface of kaolinite for the adsorbed molecules and dissolve some of the precipitate on the surface. As a result, the adsorption decreases at high concentrations.

The adsorption levels for the Alfoterra surfactant series onto kaolinite (roughly 5–50 mg/g) are comparable or greater than that reported for some other anionic surfactants tested under similar conditions (moderately concentrated NaCl brine, near ambient temperature). For example, one investigator reports adsorption onto kaolinite of 5–10 mg/g for a series of linear alkyl benzene sulfonates, and another study for petroleum sulfonates shows 5–50 mg/g [23, 76].

3.7 Core flood tertiary oil recovery tests

Based on the IFT and adsorption measurements, we selected Alfoterra 23 and Alfoterra 38 for tertiary oil recovery core flood tests. Note that in these experiments the connate brine salinity was quite high, 10 wt% NaCl, and the chemical slugs were formulated at a much lower 1 wt% NaCl salinity. This was designed to test two aspects, namely firstly that an Alfoterra surfactant formulation could recover significant tertiary oil when the in-situ brine has a fairly high salinity, and secondly that the so-called “salinity gradient” approach is a reasonable strategy. That is, the in-situ brine has salinity above the optimal salinity (about 3 wt% NaCl) of the chemical formulation, and the injected solutions have a salinity below this optimum salinity. The tertiary oil recovery curves

surfactant	c_{eq} [wt%]	G [mg/g]
Alfoterra 23	0.42	14.5
Alfoterra 23	0.89	20.6
Alfoterra 23	1.78	42.5
Alfoterra 25	0.48	3.2
Alfoterra 25	0.96	7.9
Alfoterra 25	1.97	5.4
Alfoterra 28	0.50	0.4
Alfoterra 28	1.01	0.0
Alfoterra 28	2.03	0.0
Alfoterra 33	0.39	20.8
Alfoterra 33	0.80	38.3
Alfoterra 33	1.70	55.7
Alfoterra 35	0.36	26.1
Alfoterra 35	0.76	45.1
Alfoterra 35	1.64	66.1
Alfoterra 38	0.44	11.9
Alfoterra 38	0.89	20.6
Alfoterra 38	1.83	30.1

* Solid to solution mass ratio = 1: 20, equilibrium at atmospheric pressure, 25 °C after 8 hours.

Table 4 Adsorption* of Alfoterra surfactant on kaolinite clay from 2.00 wt% NaCl aqueous solutions

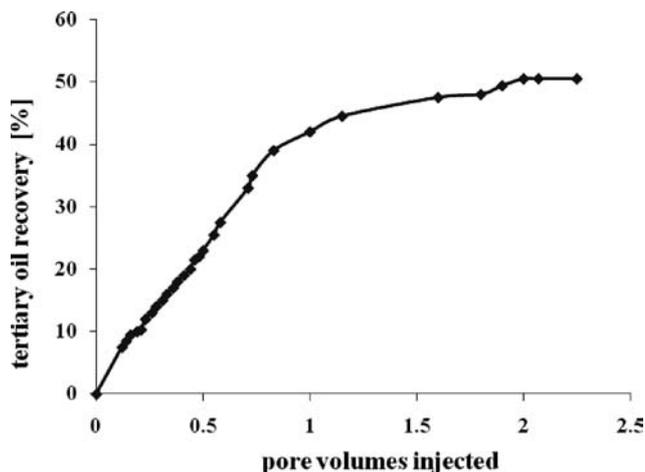


Figure 12 Tertiary oil recovery observed for the Alfoterra 38 formulation

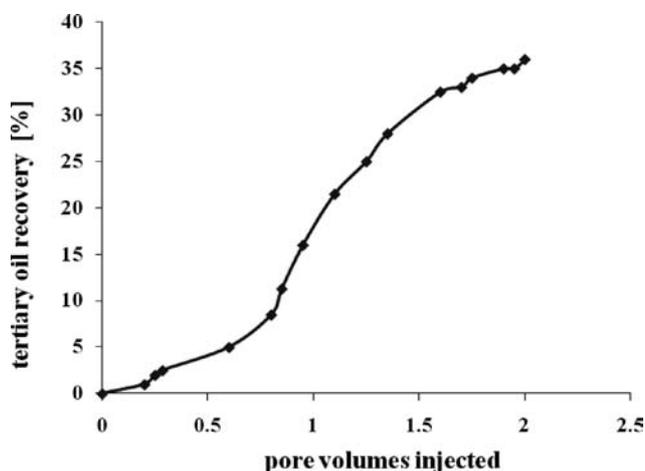


Figure 13 Tertiary oil recovery observed for the Alfoterra 23 formulation

are shown in Figures 12 and 13. After surfactant flooding, the tertiary oil recovery was found to be 50% of the waterflood residual oil in case of Alfoterra 38 and 35% for Alfoterra 23.

While the tertiary oil recovery of Alfoterra 23 was only mediocre, the chemical efficiency of this coreflood experiment was relatively good. The mass of Alfoterra 23 surfactant injected was less than that used in the Alfoterra 38 test, and the percent tertiary recovery was just slightly less with the Alfoterra 23. Both formulations were efficient in terms of waterflood residual oil recovery even with the connate brine salinity being a relatively high 10 wt% NaCl.

Though not directly comparable, Mohanty [49, 51] recorded an oil recovery of 40–60% initial oil in place after 100 days of spontaneous imbibition of a 0.2 wt% Alfoterra

38 formulation (in 0.3 M Na₂CO₃ brine) into an outcrop limestone. This is consistent with our EOR observations (though lower) for Alfoterra 38 even though the displacement mechanism and the porous medium were different. This illustrates the EOR efficiency of branched alkyl alcohol sulfate surfactant formulations.

4 Conclusions

We measured IFT, phase behaviour and solid adsorption of a large array of branched alkyl alcohol sulfate surfactant formulations. Such data for these specific surfactants is scarce in the literature but vital for designing EOR projects and selecting suitable surfactant formulations for this task. We present coreflood forced-displacement oil recovery experiments not previously reported in the literature for this surfactant class.

Key findings from this study include:

- Branched alkyl alcohol propoxylate sulfate surfactants at concentrations as low as 0.1 wt% can create an IFT of 0.01 mN/m or less between brine and n-octane, n-decane or a crude oil.
- The optimal salinity (minimum IFT condition) is several percent NaCl for the products tested, the optimal salinity decreased with an increase of propoxy groups.
- Generally, adsorption of these surfactants on kaolinite clay decreased with an increase of the number of propoxy groups. The amount adsorbed was in a range of 3–25 mg per gram kaolinite at bulk surfactant concentrations 0.4 wt% or lower; and 4–65 mg per gram clay at around 2 wt% concentration.
- Alkyl alcohol propoxy sulfate sodium salts were effective in terms of tertiary oil recovery (from 35–50% additional oil was produced) with surfactant concentrations as low as 0.2 wt%.

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Nomenclature

IFT	interfacial tension [mN/m]
PO	propylene oxide (= propoxy) group
n	number of propylene oxide groups
m	branched alkyl chain of Alfoterra surfactant
HLB	hypophilic-lipophilic balance
EOR	enhanced oil recovery
NaCl	sodium chloride

Na ₂ CO ₃	sodium carbonate
CaCl ₂	calcium chloride
ppm	parts per million
wt%	weight %
S _{or}	residual oil saturation
S _{wc}	connate water saturation
G	equilibrium surfactant adsorption [kg/kg]
c _{eq}	bulk surfactant concentration [wt%]
N _{cap}	capillary number [-]
PV	pore volume [-]
GOM	Gulf of Mexico
Ca ²⁺	divalent calcium cation
Mg ²⁺	divalent magnesium cation

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