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# Alkyl Polyglycoside-Sorbitan Ester Formulations for Improved Oil Recovery

We measured interfacial tensions (IFT) of aqueous alkyl polyglycoside (APG) systems formulated with sorbitan ester-type cosurfactants against n-octane. The study focused on low to ultra-low IFT systems which are relevant for enhanced oil recovery (EOR). In addition, we measured equilibrium adsorption concentrations of these surfactants and cosurfactants onto kaolinite clay, commonly found in oil reservoirs. We present one surfactant EOR laboratory flood experiment with one selected APG-sorbitan ester formulation with which we recovered 94% of initial oil in place (IOIP).

**Keywords:** Alkyl polyglycoside, sorbitan ester, cosurfactants, Span, Tween, ultra-low interfacial tension, enhanced oil recovery, surfactant flood, chemical flood

**Formulierungen mit Alkylpolyglucosiden und Sorbitanestern für die tertiäre Erdölförderung.** Wir präsentieren hier Messergebnisse für Grenzflächenspannungen zwischen n-Okтан und wässrigen Alkylpolyglucosidsystemen (APG), die mit Sorbitanester/Co-Tensiden formuliert wurden. Diese Studie konzentriert sich auf niedrige bis ultraniedrige Grenzflächenspannungen, die für die tertiäre Ölförderung (EOR) relevant sind. Zusätzlich haben wir die Adsorptionsgleichgewichtskonzentrationen für diese Tenside und Co-Tenside an Kaolinit gemessen. Kaolinit ist eine Tonerde, die in Ölreservoirs häufig auftritt. Wir präsentieren außerdem ein Tensid-EOR Flutungsexperiment mit einer ausgewählten APG-Formulierung. Mit ihr konnten wir 94% des Öls fördern.

**Stichwörter:** Alkylpolyglucoside, Sorbitanester, Co-Tenside, Span, Tween, ultraniedrige Grenzflächenspannung, tertiäre Erdölförderung, Tensidfluten, chemisches Fluten

## 1 Introduction

Global economic growth is associated with an increase in energy consumption. In order to supply this increasing demand, people rely on several energy sources, among which oil is still a major contributor. However, conventional reserves are diminishing; this is particularly the case in the USA and it is therefore essential to develop advanced technologies to produce unconventional oil reserves and ensure energy security. Primary and secondary oil recovery techniques – here defined as conventional – produce only 5–50% of the initial oil in place (IOIP) [1], and there is clearly potential to increase oil production by recovering this residual oil. One promising way to accomplish such additional (tertiary) oil recovery is surfactant flood enhanced oil recovery

(SEOR). This technology has been studied intensively (compare for example [1–5] among others) and several SEOR pilot-scale and industrial-scale projects have been completed [6–11].

In this work we present new surfactant formulations, which are key to successful SEOR, and test their effectiveness in terms of additional oil recovery. These new formulations may be used in SEOR projects. We focus on alkyl polyglycoside-sorbitan ester formulations, where both, alkyl polyglycosides (APG) and sorbitan esters are nontoxic, renewable, green chemicals which are environmentally friendly and already used in such industries as food, beverages, pharmaceuticals, cosmetics or detergents. Large quantities of these materials are produced worldwide, 80000 t/a of APG, 8000000 t/a sorbitol and 20000 t/a sorbitan esters [12, 13], which is clearly an economic advantage in terms of surfactant pricing. Moreover, as established previously, APGs have many useful physical properties in the context of EOR, including their capability of creating low to ultra-low IFTs against hydrocarbons if formulated with cosolvents [14–20] and their quasi-independent IFT of temperature or salinity [12, 16, 21–23]. This is very useful in terms of EOR, because in oil bearing formations, significant temperature and salinity variations can be expected. These variations reduce control and

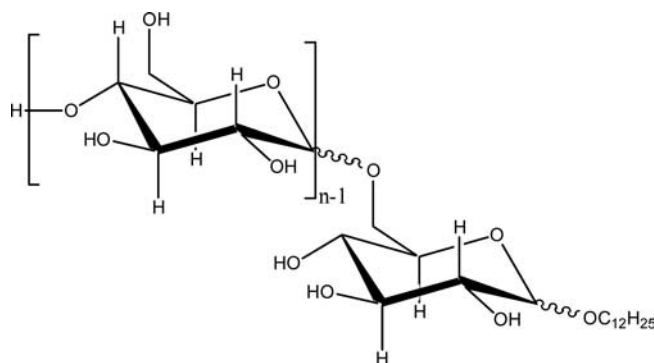


Figure 1 Molecular structure of a typical alkyl polyglycoside [21]

Product	Agrimul 2067	Agrimul 2069	Agrimul 2062
alkyl chain (wt%:wt%)	8/10 (45:55)	9/10/11 (20:40:40)	12/14/16 (68:26:6)
average alkyl chain length k (C-atoms)	9.1	10.1	12.5
average n (number of sugar groups)	1.7	1.6	1.6
HLB	13.6	13.1	11.6
activity (wt%)	70	50	50

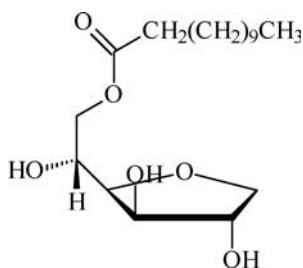
Table 1 Chemical structure information for commercial APG products investigated [24, 25]

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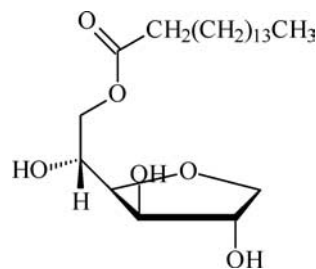
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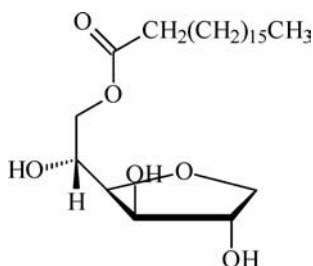
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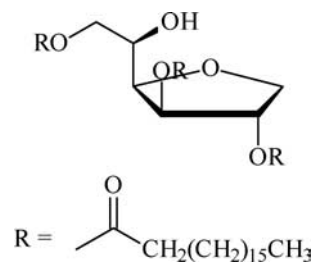
**Figure 2a** Sorbitan monolaurate; Span 20 contains approximately 50 wt% lauric acid (C12:0) ester balanced primarily with myristic (C14:0), palmitic (C16:0) and linolenic (C18:3) acid esters



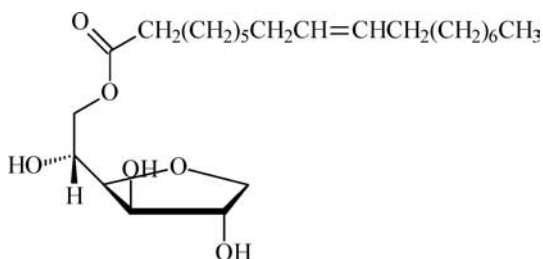
**Figure 2b** Sorbitan monopalmitate; main component of Span 40



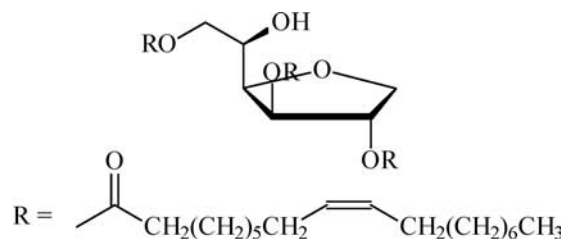
**Figure 2c** Sorbitan monostearate; Span 60 contains approximately 50 wt% stearic acid (C18:0) ester balanced primarily with palmitic (C16:0) acid ester



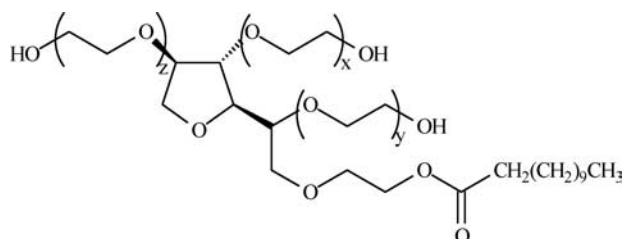
**Figure 2d** Sorbitan tristearate; main component of Span 65



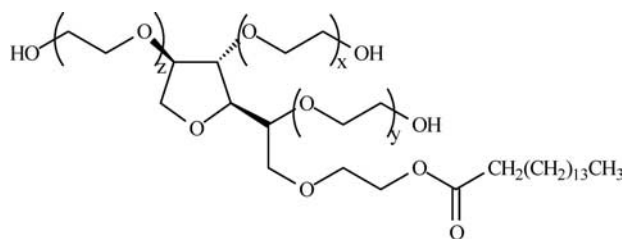
**Figure 2e** Sorbitan monooleate; Span 80 contains approximately 75 wt% oleic acid (C18:1) ester balanced primarily with linoleic (C18:2), linolenic (C18:3) and palmitic (C16:0) acid esters



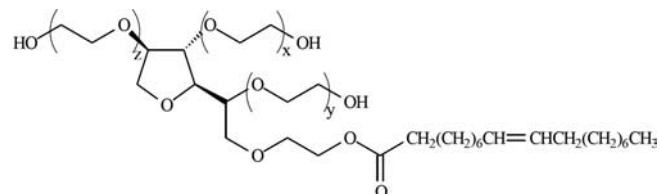
**Figure 2f** Sorbitan trioleate; Span 85 contains approximately 74 wt% oleic acid (C18:1), 7 wt% linoleic acid (C18:2), 2 wt% linolenic acid and 7 wt% palmitoleic acid (C16:1) esters balanced primarily with palmitic (C16:0) acid ester



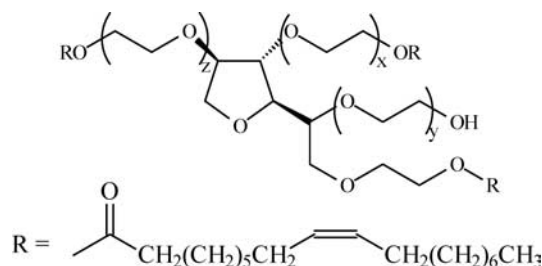
**Figure 2g** Polyoxyethylene sorbitan monolaurate; Tween 20 contains approximately 40 wt% lauric acid (C12:0) ester balanced primarily with myristic (C14:0), palmitic (C16:0) and stearic (C18:0) acid esters



**Figure 2h** Polyoxyethylene sorbitan monopalmitate; Tween 40 contains approximately 90 wt% palmitic acid (C16:0) ester balanced primarily with stearic (C18:0) acid esters



**Figure 2i** Polyoxyethylene sorbitan monooleate; Tween 80 contains approximately 70 wt% oleic acid (C18:1) ester balanced primarily with linoleic (C18:2), palmitic (C16:0) and stearic (C18:0) acid esters



**Figure 2j** Polyoxyethylene sorbitan trioleate; Tween 85 contains approximately 70 wt% oleic acid (C18:1) ester balanced primarily with elaidic, linolenic (C18:3) and palmitic (C16:0) acid esters

**Figure 2** Structures of Span and Tween type sorbitan esters used in this study [17, 29]

predictability of surfactant EOR processes, directly increasing technical and economic uncertainty.

## 2 Experimental Methodology

### 2.1 Materials

We focus on three different commercial alkyl polyglycoside surfactant products, whose basic structure is shown in Figure 1. These products were supplied by the Cognis Corporation (Agrimul 2067, Agrimul 2069, and Agrimul 2062).

The difference among these three products lies in the number of sugar head groups  $n$  and alkyl chain lengths  $k$  (Table 1).

Activity is the mass percentage of surfactant in the mixture, the rest is water. The HLB (hydrophilic-lipophilic balance) for these surfactants were given by the suppliers. We obtained from Aldrich the various sorbitan esters used as cosurfactants. All products were mixtures of sorbitan esters with varying fatty acid ester chains, but they all had a main component. These main components are presented in Figures 2 a–j with a brief listing of the additional fatty acid ester chains in the Span and Tween mixtures. In the Tween products, the number of EO (ethylene oxide) groups add up to 5 or 20 ( $x + y + z = 5$  or 20). Sorbitan esters are industrially produced by a one-step or two-step process [13, 26–28]. Here sorbitol is dehydrated to sorbitan which is then esterified with a fatty acid; commonly used fatty acids include lauric acid (Span 20), palmitic acid (Span 40), stearic acid (Span 60) or oleic acid (Span 80). Depending on the attached fatty acids, hydrophilic-lipophilic balances range between 1 and 8.

These relatively lipophilic molecules can be partly derivatized with ethylene oxides to yield sorbitan ester ethoxylates (Tween) [26], which have a significantly higher HLB (10–17), depending on the fatty acid rest in the ester group and the length and number of attached EO units.

Additional information about these products including CAS number, HLB and number of EO groups in the molecules are displayed in Tables 2 and 3.

As hydrocarbon phase *n*-octane was used (Aldrich, ACS grade). 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]. The brine used was de-ionized water with 2 wt% sodium chloride (Aldrich, ACS grade). The deionized water was distilled twice in-house.

Molecules with an even number of carbon atoms in a straight hydrocarbon chain are easily biodegradable, while those with an uneven carbon number, a ring or a branched structure have a lower biodegradability. Sorbitan esters are therefore expected to reduce biodegradability of the APG for-

Trade Name	CAS-number	number of EO groups	HLB
Tween 20	9005-64-5	20	16.7
Tween 40	9005-66-7	5	13.3
Tween 80	9005-65-6	20	15.0
Tween 81		5	10.0
Tween 85	9005-70-3	20	11.0

Table 3 Properties of investigated polyoxyethylene sorbitan esters [17, 29]

mulations if compared to APGs formulated with linear alcohol molecules with an even number of C atoms.

### 2.2 Interfacial Tension Measurements

A key factor in improving oil recovery via SEOR is to lower the interfacial tension (IFT) between the oleic phase and the aqueous phase. This is equivalent to increasing the capillary number; if the capillary number is increased by a factor of 1000 or more, then this directly leads to higher oil recoveries [1].

Experimentally, we formulated 5 mL of aqueous surfactant/cosurfactant/salt phase with 5 mL of *n*-octane. This mixture was shaken several times over several hours and then equilibrated for at least three weeks at ambient conditions (ambient pressure and 25 °C). IFT values were then determined via the spinning drop technique (with a Temco tensiometer instrument) as described in detail by Cayias [33]. The average standard deviation was determined to be 5–10%; this relatively high value in standard deviation is due to the low to ultra-low IFTs measured.

### 2.3 Surfactant/cosurfactant solid adsorption on rock

Another significant parameter relevant for a successful SEOR design is surfactant loss by adsorption onto the porous medium [1].

We analyzed adsorption behavior of the surfactant/cosurfactant molecules onto kaolinite clay. This is a worst case scenario as clay adsorbs much more surfactant than sandstone because of its much larger surface area. Typical values for surfactant adsorption of standard Berea sandstone range from 0.1–1.2 mg/g rock [34–37]. Most of the adsorption that occurs in Berea sandstone is due to the few percent of kaolinite clay that is within this sandstone.

To measure equilibrium adsorption values, surfactant/cosurfactant solutions with known concentrations were prepared and kaolinite was added so that a liquid/solid mass ra-

Trade Name	CAS number	number of EO groups	HLB	solubility parameter $\delta_o$ (cal/cm <sup>3</sup> ) <sup>0.5</sup>	$C_w/C_o$ water-oil partitioning coefficient	critical micelle concentration CMC (10 <sup>-5</sup> mol/L)*
Span 20	1338-39-2	0	8.6	13.52	85	2.4
Span 40	26266-57-9	0	6.7	12.58	0.43	1.8
Span 60	1338-41-6	0	4.7	11.59	$1.7 \times 10^{-3}$	1.8
Span 65	26658-19-5	0	2.1			
Span 80	1338-43-8	0	4.3	11.38	$5.5 \times 10^{-4}$	1.9
Span 85	26658-58-0	0	1.8			

\* versus *n*-octane [32]

Table 2 Properties of investigated sorbitan ester cosurfactants [29–31]

tio of 20 was obtained. All tests were conducted at 25 °C and atmospheric pressure. After 8 hours the solid was removed by centrifugation. The water was then removed by evaporation and surfactant concentrations were determined via mass balance. The difference in surfactant concentration (start versus end) is equal to the amount of adsorbed surfactant. The kaolinite clay (supplied by the University of Missouri) consisted of 44.2 wt% SiO<sub>2</sub>, 39.7 wt% Al<sub>2</sub>O<sub>3</sub>, 1.39 wt% TiO<sub>2</sub>, 0.13 wt% Fe<sub>2</sub>O<sub>3</sub> and traces of Na, Mn, Ca, K, P and F (data supplied by the University of Missouri); the clay had a specific surface area of 10 m<sup>2</sup>/g.

#### 2.4 Surfactant enhanced oil recovery displacement test

A surfactant sandpack flood experiment was conducted with a selected APG/sorbitan ester formulation (0.8 wt% Agrimul 2069 mixed with 1.2 wt% Span 20). An IFT of 0.003 mN/m was measured for this system (against n-octane in 2 wt% NaCl brine at 25 °C and atmospheric pressure). A sandpack was used as porous medium. The quartz sand used comprised 75 wt% 149–250 μm (60–100 US standard mesh) and 25 wt% 149–74 μm (100–200 US standard mesh) grain size. The porosity of the sandpack was 29%, the pore volume amounted to 160 mL and the absolute brine permeability was 1 Darcy.

The sandpack was saturated with brine under vacuum and then brought to connate water condition ( $S_{wc} = 28.5\%$ ) in a primary drainage oil flood at a capillary number of  $3.36 \times 10^{-8}$ . The sandpack was then subjected to a waterflood in a secondary imbibition process at a capillary number of  $7.11 \times 10^{-8}$ . The residual oil saturation was 15.0%. Capillary numbers in this range are representative of flow in oil reservoirs, and they have to be increased by at least an order of three magnitudes to enable additional oil production [1].

The tertiary SEOR step started by injection of 0.25 pore volumes (PV) of surfactant slug, which was followed by 0.75 PV drive polymer solution (350 ppm Alcoflood 1235 in 2 wt% NaCl brine. 350 ppm Alcoflood 1235 in 2 wt% NaCl brine had a viscosity of 1.5 mPa.s at 2 rpm shear rate measured with a Brookfield DV-E viscometer and a #18 spindle. Alcoflood 1235 (supplied by Ciba) is a commercial polyacrylamide product commonly used in the petroleum industry). Chemical injection rate was constant at 0.06 ml/min, which is approximately a three ft/day frontal advance rate. Incremental oil recoveries were measured against time and plotted against cumulative PV injected.

### 3 Results and Discussion

#### 3.1 Interfacial tension measurements

##### 3.1.1 Influence of cosurfactant type on interfacial tension

The Span type cosurfactants evaluated included saturated linear aliphatic alkyl sorbitan mono esters with alkyl chain lengths ranging from C<sub>13</sub>–C<sub>19</sub>, sorbitan monooleate (one double bond in the alkyl chain), and two tri-esters, sorbitan tristearate and sorbitan trioleate. The HLB values were very low for the tri-esters (1.8 and 2.1) and low for the mono-esters (4.3–8.6).

Investigated Tween type cosurfactants included polyoxyethylene sorbitan mono esters with lauric, palmitic, stearic or oleic alkyl rests and 5 or 20 EO groups. Two polyoxyethylene sorbitan trioleates with either 5 or 20 EO groups were also included. HLB values were medium for

the Tween monoesters (10.0–16.7), but significantly higher than HLBs for the Span cosurfactants. The two Tween tri-esters had an HLB of 10.0 and 11.0.

The aqueous phase contained 2 wt% combined APG/cosurfactant concentration and a salinity of 2 wt% NaCl. The APG surfactants alone (2 wt%) did not form micro-emulsion middle phases, and the IFT reached low, but not ultra-low numbers (Table 4). A micro-emulsion middle phase is an indicator of low or ultra-low IFT [16, 18, 19, 38, 39]. The lowest IFT was observed for Agrimul 2062, the most lipophilic molecule of the set. The phase behavior of the surfactant systems is also listed;  $V_o$  is the relative volume of the oleic phase,  $V_m$  of the middle phase and  $V_{aq}$  of the aqueous phase.

surfactant product	$V_o/\%$	$V_m/\%$	$V_{aq}/\%$	average alkyl chain length k	HLB	IFT/mN m <sup>-1</sup>
Agrimul 2062	0	60	40	12.5	11.6	0.735
Agrimul 2067	60	0	40	9.1	13.6	2.4
Agrimul 2069	50	0	50	10.1	13.1	1.08

Table 4 Properties of brine/n-octane/2 wt% APG surfactant systems

cosurfactant product	average alkyl chain length k	HLB	IFT/mN m <sup>-1</sup>
Span 20	13	8.6	2.4
Span 40	17	6.7	2.3
Span 60	19	4.7	1.85

Table 5 Surfactant properties of 2 wt% Span/brine/n-octane mixtures

APG Agrimul	Span	APG concentration/wt%	Span concentration/wt%	IFT/mN m <sup>-1</sup>
2069	20	0.80	1.20	0.0035
2069	40	0.40	1.60	1.40
2069	60	0.40	1.60	0.33
2069	85	0.40	1.60	1.55
2069	85	1.50	0.50	0.8
2069	85	1.60	0.40	1.2
2062	20	0.80	1.20	0.90
2062	20	1.20	0.80	0.75
2062	40	0.40	1.60	0.85
2062	60	0.40	1.60	1.00
2062	60	0.80	1.20	0.73
2062	80	0.40	1.60	1.20
2062	85	0.40	1.60	0.68
2062	85	0.80	1.20	0.25
2062	85	1.20	0.80	0.40

Table 6 Measured IFT values for APG/Span surfactant mixtures in a 2 wt% NaCl brine versus n-octane

### SPAN cosurfactants

The Span cosurfactants (2 wt% in 2 wt% NaCl brine) also reached low IFTs against n-octane on their own, approximately 2 mN/m, cp. Table 5. IFTs of the pure Tween products were not measured.

Our first formulation test series was based on Agrimul 2062 or Agrimul 2069 as they showed the lowest IFT values on their own (cp. Table 4). They were combined with Span 20, Span 40, Span 60, Span 80 and Span 85 over an APG concentration range of 0.40–1.60 wt%. The total amount of surfactant and cosurfactant was kept constant at 2 wt%.

All observed IFT values were similar and ranged from 0.25–1.55 mN/m except for the 0.8 wt% Agrimul 2069/1.20 wt% Span 20 formulation which reached an ultra-low IFT with 0.0035 mN/m (cp. Table 6). This seems to be surprising, however this was not an experimental outlier as this number was reproducible. The observed data is also consistent with literature data [18]. We conclude that a special synergy exists for this specific mixing ratio.

None of the phases (whether aqueous, microemulsion or oleic phase) shown in Table 6 formed a viscous or rigid gel. Other combinations of these APG products and Span cosurfactants created stiff gels in the oil phase (not shown here). Those combinations exhibiting such unfavorable phase behavior are not viable as EOR agents and most were not measured for IFT. Other studies have shown that water-APG-fatty alcohol systems can form lyotropic lamellar phases [23, 40] at certain areas in the phase diagram, and we hypothesize that this might be the origin of the viscous gels observed. Contrary to APG/1-alcohol formulations [16], the alkyl chain lengths in the APG had no clear influence on IFT in APG/Span systems. It seems that the sterically more complex Span structure (as compared to 1-alcohols) leads to more complex mixing behavior resulting in more complex interface and possibly micelle structures.

We then proceeded to include Agrimul 2067 formulations, the results are displayed in Figure 3.

Observed IFT values were fairly constant versus APG concentration for the investigated Span 40 and Span 80 blends, but low IFT numbers were reached with Span 20, Span 60 and Span 85 mixtures. These IFT values reached numbers around 0.05 mN/m and always lied in a sharp minimum for very specific surfactant-cosurfactant mixing ratios, e.g. the Agrimul 2067/Span 85 blend had a sharp

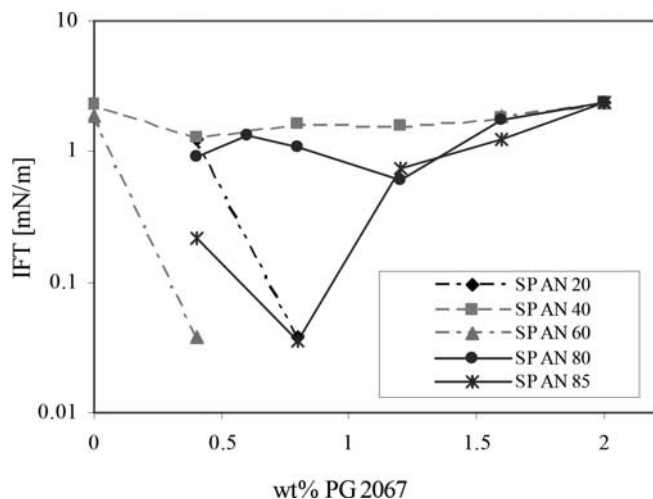


Figure 3 IFT values observed for PG 2067/Span formulations

minimum in IFT at a ratio of 0.75% APG/1.25% Span, but had significantly larger IFT at other mixing ratios.

This peculiar sharp minimum behavior we found is consistent with one available relevant set of data in the literature. Förster et al. [18] measured IFT for APG solutions mixed with Span 20 and equilibrated versus n-dodecane as the oil phase. A low IFT was observed for a narrow range of APG/Span 20 mixing ratios. One explanation for the synergistic action of the added sorbitan ester cosurfactant is that they pack at the interface so as to decrease the curvature of the interfacial layer and thereby reduce IFT [41–44]. Sabatini [45] 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. Our general observation was that virtually all sorbitan ester cosurfactants act to decrease the IFT of the main APG surfactant. This effect was clearly strongest for some very specific mixtures at specific mixing ratios. As a general trend, low IFT values appeared when middle phase micro-emulsions [46] appeared, consistent with observations described by Shinoda and Friberg [47]. The existence of a middle-phase emulsion is an indicator of hydrophilic-lipophilic balance [46].

If IFT is plotted against HLB values for specific surfactant-cosurfactant mixing ratios, then no clear trend can be identified. The same is true if IFT is plotted against the alkyl chain length of the Span molecule. This is not surprising as HLB and alkyl chain length are directly related. However, this finding is inconsistent with the behavior observed for APG/1-alcohol formulations, where a minimum IFT exists if IFT is plotted versus alcohol alkyl chain length [16].

### TWEEN cosurfactants

Measured IFT values for some selected APG-Tween formulations are shown in Table 7.

Similar to APG/Span phase behavior, most combinations of APG and Tween surfactants created gels in the oil phase. The phases of the combinations shown in Table 7 were low viscosity fluids, but none of these formulations employing the Tween cosurfactant appeared to be interest-

Agrimul	Tween	APG concentration/wt%	Tween concentration/wt%	IFT/mN m <sup>-1</sup>
2067	21	1.20	0.80	1.07
2067	21	1.60	0.40	1.42
2067	85	0.80	1.20	0.76
2067	85	1.00	1.00	0.38
2067	85	1.20	0.80	0.90
2067	85	1.60	0.40	0.82
2069	21	1.60	0.40	1.25
2069	40	1.60	0.40	1.70
2069	81	1.00	1.00	9.60
2062	21	0.40	1.60	0.05
2062	81	0.40	1.60	1.30
2062	81	0.80	1.20	6.10
2062	85	0.40	1.60	0.76

Table 7 Measured IFT values for APG/Tween surfactant mixtures in 2 wt% NaCl brine versus n-octane

ing as an SEOR candidate because IFT values were not very low, except for the 0.4 wt% Agrimul 2062/1.6 wt% Tween 21 (IFT of 0.05 mN/m). Further work focused on blends of APG and Span 20 as they had the most promising, lowest measured IFT values.

In summary, it appears that highly complex specific molecular interactions are responsible for reducing IFT to low or ultra-low numbers in some very specific sorbitan ester-APG systems. We conducted molecular dynamics calculations [4] for APG-1-alcohol-octane-water formulations, but only IFT trends could be predicted and not exact numbers. As the molecular structure of the sorbitan ester derivatives is more complex we expect that molecular dynamics computations are even more challenging.

### 3.1.2 Interfacial tensions of pure APG molecules formulated with Span 20

This test series included pure APG molecules formulated with Span 20 as cosurfactant. This experimental set was mainly investigated to more rigorously understand the influence of APG and cosurfactant structure on IFT [38], but also to generate experimental data which is directly comparable to molecular dynamics computations which we calculated for deionized water/pure surfactant/pure cosurfactant/n-octane systems [4]. Therefore we prepared these blends in deionized water. We selected Span 20 as it had the lowest IFT value of all APG-Span/Tween formulations tested (cp. Table 6 and 7 and Figure 3).

We chose an array of pure n-alkyl- $\beta$ -D-maltopyranosides APM (which have two sugar rings in the sugar head-group, maltose) with different alkyl chain lengths (e.g. APM<sub>8</sub> is n-octyl- $\beta$ -D-maltopyranoside), critical micelle concentrations (CMC) and HLB. The formulations contained a constant molar surfactant concentration of  $6.60 \times 10^{-3}$  M and  $6.60 \times 10^{-3}$  M cosurfactant (= 0.24 wt% SPAN 20).

surfactant	surfactant conc./wt%	CMC/wt%	IFT/mN m <sup>-1</sup>
APM <sub>8</sub>	0.30	0.89*	4.19
APM <sub>10</sub>	0.32	0.087	3.88
APM <sub>12</sub>	0.34	0.0087	3.57
APM <sub>13</sub>	0.35	0.0017	3.18
APM <sub>16</sub>	0.37	0.00003	2.72

\* in 100 mM NaCl, 20 mM HEPES, pH 7.5; (HEPES = N-(2-hydroxyethyl) piperazine-N'-(2-ethanesulfonic acid))

**Table 8** IFT results and CMC values for APM-Span 20 formulations [48, 49]

surfactant	surfactant concentration/wt%	cosurfactant	cosurfactant concentration/wt%	$\Gamma$ /mg g <sup>-1</sup>	IFT/mN m <sup>-1</sup> *
Agrimul 2067	0.5	—	—	negligible	2.4
Agrimul 2069	0.5	—	—	negligible	1.08
Agrimul 2062	0.5	—	—	61	0.735
Span 20	0.5	—	—	82	2.4
Agrimul 2067	0.4	Span 20	0.6	87	0.04
Agrimul 2069	0.4	Span 20	0.6	121	0.0035
Agrimul 2062	0.4	Span 20	0.6	132	1.5

\* IFT measured against n-octane in a separate experiment, ambient conditions.

**Table 9** Adsorption characteristics of APG products, SPAN 20 and APG/SPAN 20 blends

The results recorded are presented in Table 8 together with literature values for the CMC values. Longer APG alkyl chains led to lower IFT values, consistent with our previous studies for commercial and pure APGs formulated with 1-alcohols [16, 38].

Though direct comparison is difficult, it appears that the addition of salt to deionized water reduced IFT (cp. Table 6 and Figure 3 with Table 8). IFT reduction by salt addition has been observed in APG/alcohol systems [16].

### 3.2 Surfactant and cosurfactant adsorption on kaolinite clay

The results we recorded for the equilibrium surfactant adsorption  $\Gamma$  of the APG and Span 20 systems are displayed in Table 9. Data for some APG-Span blends are also included.

While no adsorption was observed for Agrimul 2067 and Agrimul 2069, 61 mg/(g<sub>kaolinite</sub>) of Agrimul 2062 and 82 mg/g of Span 20 were adsorbed which is relatively high if compared to adsorption of linear alkyl benzene sulfonates (5–10 mg/g), petroleum sulfonates (5–50 mg/g) or alkyl alcohol propoxylated sulfates (5–50 mg/g) [50, 51]. Moreover, there was an increased total surfactant adsorption when mixing the Span 20 sorbitan cosurfactant with APG. In this case retention was likely from both surfactants. A positive aspect from the SEOR perspective is the independence of observed adsorption levels of IFT.

### 3.3 Surfactant flood experiment

Figure 4 displays the measured total oil production for the sandpack surfactant flood experiment. A total of 94% of initial oil in place was recovered which is very high. This is equivalent to 60% tertiary oil recovery (TOR). Such a high total oil recovery is mainly due to the high porosity of the sandpack, which results in low waterflood  $S_{or}$  (here 15%) [52, 53]. Moreover, as demonstrated by us previously [5], high permeability leads to high TOR.

## 4 Conclusions

Key findings from this study include

1. Alkyl polyglycoside surfactants may be formulated with Span cosurfactants in brine so that systems with ultra-low interfacial tension approaching 0.001 mN/m versus n-octane are attained.
2. At specific surfactant-cosurfactant mixing ratios, some of the APG/Span formulations showed a sharp minimum in IFT.

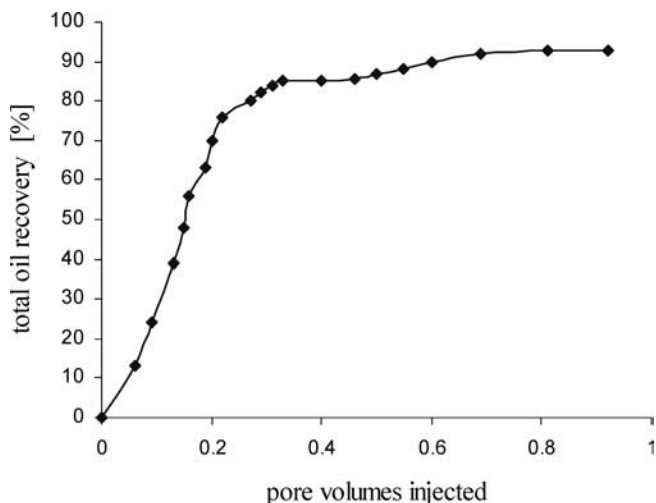


Figure 4 Total oil recovery observed for the Agrimul 2069/Span 20 formulation

- An Agrimul 2069/Span 20 formulation showed excellent enhanced oil recovery in a surfactant sandpack flood experiment, 94 % of initial oil in place were recovered.

#### Nomenclature

APG	Alkyl polyglycoside
APM	Alkyl polymaltoside
IFT	interfacial tension ( $\text{mN m}^{-1}$ )
n	average number of sugar groups in APG
k	carbon number in APG alkyl chain
EO	ethylene oxide group
x + y + z	number of EO groups in Tween molecule
HLB	hypophilic-lipophilic balance
EOR	enhanced oil recovery
SEOR	surfactant enhanced oil recovery
APM <sub>8</sub>	n-octyl- $\beta$ -D-maltopyranoside
APM <sub>10</sub>	n-decyl- $\beta$ -D-maltopyranoside
APM <sub>12</sub>	n-dodecyl- $\beta$ -D-maltopyranoside
APM <sub>13</sub>	n-tridecyl- $\beta$ -D-maltopyranoside
APM <sub>16</sub>	n-hexadecyl- $\beta$ -D-maltopyranoside
NaCl	sodium chloride
IOIP	initial oil in place
wt%	weight %
S <sub>or</sub>	residual oil saturation
S <sub>wc</sub>	connate water saturation
V <sub>o</sub>	relative volume of oleic phase (%)
V <sub>m</sub>	relative volume of middle phase (%)
V <sub>aq</sub>	relative volume of aqueous phase (%)
$\Gamma$	equilibrium surfactant adsorption (kg/kg)
CMC	critical micelle concentration (wt%)

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