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Analysis of the Influence of Alkyl Polyglycoside Surfactant and Cosolvent Structure on Interfacial Tension in Aqueous Formulations versus n-Octane

We studied the influence of molecular structural elements of alkyl polyglycoside (APG) surfactants on the interfacial tension (IFT) in aqueous formulations against n-octane. This included the analysis of alkyl and aryl chain length, type and number of sugar-ring head, anomers, addition of cosolvents and effect of salt addition. We found that longer alkyl or aryl chains lead to lower IFT, consistent with data recorded for commercial (mixed) APGs. APGs with only one sugar-ring head had lower IFT than their analog maltose derivatives (two-ring head). Intriguingly the stereochemistry of the sugar head (i.e. galactose versus glucose) and the type of anomer showed a significant influence on IFT. The n-octyl- α -D-glucopyranoside anomer had a lower IFT than the corresponding β -anomer. 1-octanol and 1-hexanol were efficient cosolvents consistent with the datasets observed for commercial APGs. Salt addition reduced IFT. Functional groups (aldehyde, amide-methoxy) integrated into the molecular architecture of the APG skeleton were efficient in terms of significantly reducing IFT, suggesting a strategy for the molecular design of advanced APG surfactants. We discuss the results in the context of the hydrophilic-lipophilic deviation (HLD) concept, which we modified so that IFT values are discussed instead of phase behavior.

Key words: Alkyl polyglucoside, cosolvent, interfacial tension, nonionic surfactant, structure-property relation

Analyse des Einflusses der Struktur von Alkylpolyglucosiden und von Ko-Lösungsmitteln auf die Grenzflächenspannung von wässrigen Formulierungen gegen n-Oktan. Wir untersuchten den Einfluss molekularer Strukturelemente von Alkylpolyglucosiden (APG) auf die Grenzflächenspannung (IFT) von wässrigen Formulierungen gegenüber n-Oktan. Dies schloss die Analyse der Alkyl- und der Arylkettenlänge, den Typ und die Anzahl der Zucker-Kopfgruppen, Anomere, die Zugabe von Ko-Lösungsmitteln und den Effekt von Salzzugabe ein. Wir fanden in Übereinstimmung mit den Daten für kommerzielle APG (-Mischungen), dass mit längerer Alkyl- oder Arylkettenlänge die IFT abnimmt. APGs mit nur einer Zucker-Kopfgruppe wiesen eine niedrigere IFT auf als die analogen Maltosederivate (mit 2 Zu-

ckerringen als Kopfgruppe). Die Stereochemie der Zucker-Kopfgruppe (z.B. Galaktose im Vergleich zu Glucose) und der Typ des Anomers zeigten einen signifikanten Einfluss auf die IFT. Das n-Octyl- α -D-Glucopyranoseanomer senkte die IFT stärker als das analoge β -Anomer. 1-Oktanol und 1-Hexanol waren wirksame Ko-Lösungsmittel; dies ist konsistent mit Daten für kommerzielle APGs. Die Zugabe von Salzen reduzierte die IFT. Funktionale Gruppen (Aldehyde, Amid-Methoxy) in der APG-Molekülarchitektur konnten die IFT signifikant senken. Dies eröffnet neue Moleküldesignstrategien zur Entwicklung verbesserter APG-Formulierungen. Wir diskutieren unsere Ergebnisse im Zusammenhang mit dem Konzept der hydrophilen-lipophilen Abweichung (HLD), das wir so modifizierten, dass wir IFT-Werte anstatt des Phasenverhaltens analysieren.

Stichwörter: Alkylpolyglucoside, Ko-Lösungsmittel, Grenzflächenspannung, nichtionisches Tensid, Struktur-Eigenschaftsbeziehung

1 Introduction

Alkylpolyglycosides (APG) are an important surfactant class used in a diverse range of industrial applications, including cosmetics, household detergents, agricultural products, pharmaceutical products or enhanced oil recovery [1–6].

APG surfactants were synthesized initially over 100 years ago by E. Fischer [7, 8]; they have a green chemistry character as their toxicity is low and they can be manufactured from renewable resources. APGs can be prepared with sugars (e.g. glucose or maltose) and fatty alcohols; industrially, the synthesis is usually accomplished with starch and fat as raw materials [2].

APGs are nonionic surfactants with large sugar-based polar head groups and a hydrophobic hydrocarbon tail. Pure APGs readily available include molecules with alkyl chain lengths with up to sixteen carbon atoms (hexadecyl-) and sugar heads comprising one (-glucose, -galactose) or two (-maltose) sugar head groups. Commercial APGs are a complex mixture of molecules [4,9] comprising a spectrum of sugar-head groups and hydrophobic alkyl chain lengths. Understanding APG behavior may help in improving the application of bio-surfactants [10].

APG formulations can reach low to ultra-low interfacial tension (IFT) values against hydrocarbon phases [1–4,11–23] and their IFT is largely independent of temperature and salinity [3, 14, 18, 22, 24]. These are very useful properties for a wide range of applications, e.g. improved oil recovery [25, 26]. Molecular modeling (MM) studies indicate that the large head group in combination with the nonionic charac-

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ter of the APG molecule is consistent with the observation of phase behavior and IFT being largely indifferent to changes in temperature [14].

In the context of industrial applications, it is important to find APG formulations which can generate low IFTs with only low surfactant concentrations. In order to study systematically the relation between molecule architecture and IFT (especially low IFT) and to validate the modeling results [14] we conducted a research program which investigated the influence of sugar-head type, number of sugar rings, alkyl chain length, aliphatic versus aromatic hydrocarbon tails, number of aromatic rings and stereochemistry of the molecules on IFT. Moreover, the influence of the structure and mixing ratio of cosolvent molecules on the IFT of APG/cosolvent formulations was investigated and the effect of brine as compared to deionized water was studied. The main reason for including formulations in deionized water was to simplify the physical system. In addition, the MM computations were completed for deionized water, because ionic solutions are far more difficult to include due to the finite size of the unit cells that are possible with current models, leading to unreasonably high salinity values.

The pure APG molecules which we tested are far too expensive to be used in any industrial application (with the exception of medicine, bioengineering and pharmaceutical production). However, the findings and principles presented in this research article are expected to be consistent with those in commercial APG products. This is indeed the case in terms of APG alkyl chain length and cosolvent influence on IFT [2–4, 14].

2 Materials and Experimental Procedure

An array of pure APG molecules was purchased to investigate the basic principles in the structure-IFT relationships.

2.1 Chemicals

Anatrace Inc. (Maumee, OH, USA) supplied n-octyl- α -D-glucopyranoside (α -APG₈, >99% purity), n-octyl- β -D-glucopyranoside (APG₈, >99% purity), n-octyl- β -D-maltopyranoside (APM₈, \geq 99.5% purity), n-decyl- β -D-maltopyranoside (APM₁₀, =99% purity), n-dodecyl- β -D-glucopyranoside (APG₁₂, 99.8% purity), n-dodecyl- β -D-maltopyranoside (APM₁₂, 99.2% purity), n-tridecyl- β -D-maltopyranoside (APM₁₃, \geq 99% purity), n-hexadecyl- β -D-maltopyranoside (APM₁₆, >99.5% purity), anameg-7 (Methyl-6-O-(N-heptyl-carbamoyl)- α -D-glucopyranoside) (>98.0% purity).

Sigma-Aldrich supplied 2-naphthyl- β -D-galactopyranoside (APGac₁₀*, >99% purity), phenyl- β -D-glucopyranoside (APG₆*, >97% purity), phenyl- β -D-galactopyranoside (APGac₆*, >98% purity), salicylaldehyde- β -D-glucopyranoside (helicin, >99% purity) and fluorescein (>95% purity). The structures are shown in Figure 1a–o.

The critical micelle concentrations (CMC) in deionized water of the surfactants supplied by Anatrace are displayed in Table 1. This information was not available for the products purchased from Sigma-Aldrich.

1-butanol, 1-hexanol, 1-octanol, 1-decanol, 1-dodecanol, 1-eicosanol, 1-naphthol, sodium chloride, SPAN20, n-octane (all ACS grade) were supplied by Aldrich. The deionized water was prepared in-house by distilling tap water twice.

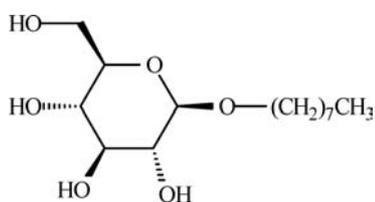


Figure 1a Structure of n-octyl- β -D-glucopyranoside (APG₈)

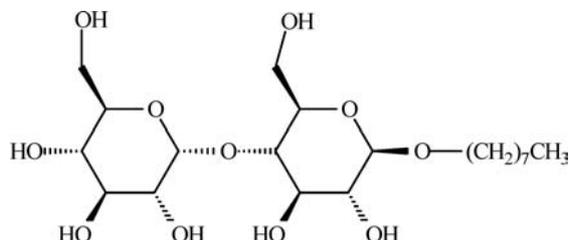


Figure 1b Structure of n-octyl- β -D-maltopyranoside (APM₈)

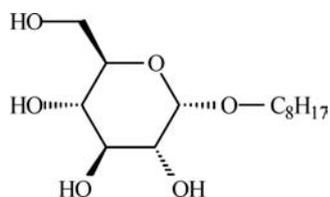


Figure 1c Structure of n-octyl- α -D-glucopyranoside (α -APG₈)

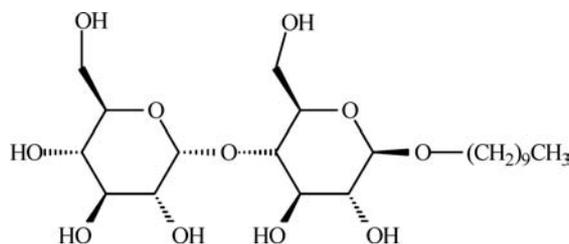


Figure 1d Structure of n-decyl- β -D-maltopyranoside (APM₁₀)

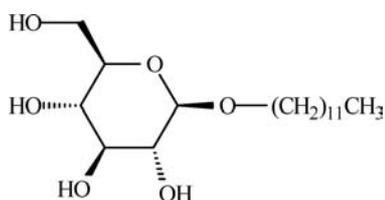


Figure 1e Structure of n-dodecyl- β -D-glucopyranoside (APG₁₂)

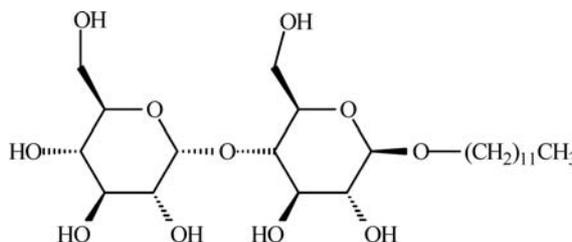


Figure 1f Structure of n-dodecyl- β -D-maltopyranoside (APM₁₂)

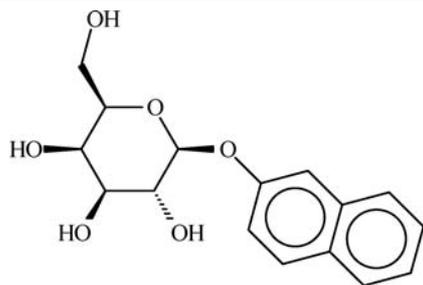


Figure 1g Structure of 2-naphthyl- β -D-galactopyranoside (APGac_{10*})

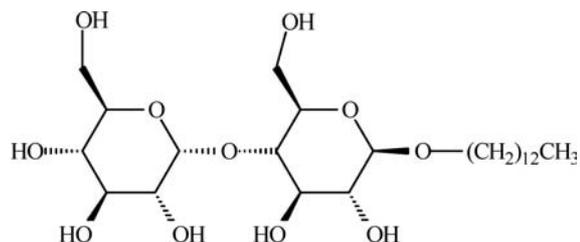


Figure 1h Structure of n-tridecyl- β -D-maltopyranoside (APM₁₃)

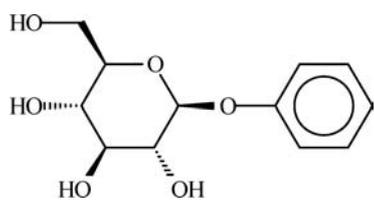


Figure 1i Structure of phenyl- β -D-glucopyranoside (APG_{6*})

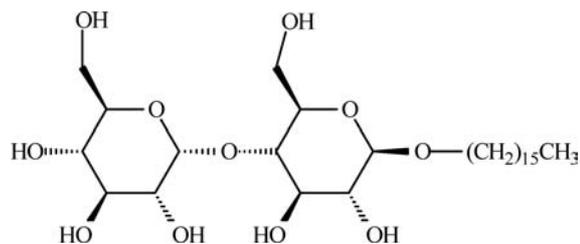


Figure 1j Structure of n-hexadecyl- β -D-maltopyranoside (APM₁₆)

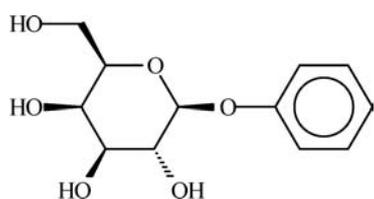


Figure 1k Structure of phenyl- β -D-galactopyranoside (APGac_{6*})

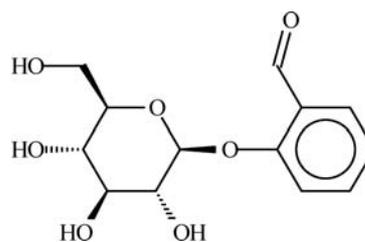


Figure 1l Structure of salicylaldehyde- β -D-glucopyranoside (helicin)

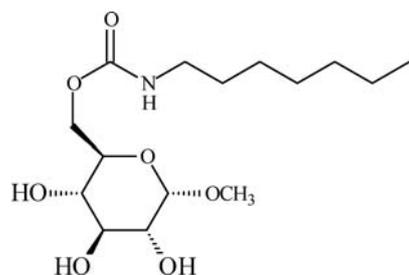


Figure 1m Anameg -7 (methyl-6-O-(N-heptylcarbamoyl)- α -D-glucopyranoside)

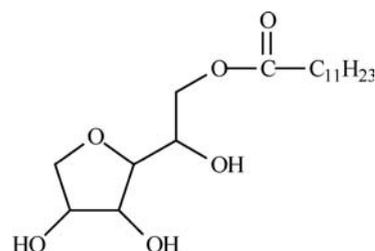


Figure 1n Molecular structure of SPAN20, a sorbitan ester [13]

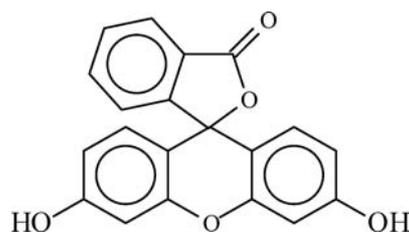


Figure 1o Fluorescein

surfactant	CMC (mM)	CMC (wt%)
anameg-7	19.5	0.65
APG ₈	18–20 23.4 (in 0.1 M NaCl)	0.53
α-APG ₈	0.01	0.0002
APM ₈	19.5*	0.89*
APM ₁₀	1.8 1.8 (in 0.15 M NaCl)	0.087
APG ₁₂	0.19	0.0066
APM ₁₂	0.17 0.12 (in 0.2 M NaCl)	0.0087
APM ₁₃	0.033 0.024 (in 0.15 mM NaCl)	0.0017 0.0013 (in 0.15 mM NaCl)
APM ₁₆	0.0006	0.00003

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

Table 1 CMC of investigated surfactants [27, 28]

2.2 Interfacial Tension and Phase Behavior Measurements

Test tube samples were prepared with 5 ml of aqueous surfactant/co-solvent/salt formulations and 5 ml of hydrocarbon. After mixing well for several hours, they were allowed to stand for at least three weeks to allow the fluids to come to phase equilibrium at ambient conditions (25 °C and ambient 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 [29]. Several experiments were reproduced, showing that the spinning drop method had a maximum (peak) standard deviation of approximately 20%; the average standard deviation was between 5–10%. This comparatively high standard derivation is due to the low IFTs measured.

3 Results and Discussion

It is well established that an array of variables influences the interfacial tension of a water/(salt)/oil/APG/cosolvent system [2, 3, 15, 18–20, 22, 30].

This includes surfactant type and concentration, cosolvent type and concentration, salt type and concentration, oil type, water-oil ratio and pressure.

These relationships directly highlight the complex underlying mechanistic principles which lead to the establishment of the interfacial tension in surfactant systems. This complexity is also reflected by our attempts to model the exact molecular dynamics via quantum mechanical methods [14] with which we were able to predict qualitative IFT trends, but could not calculate exact IFT numbers for these complex surfactant-cosolvent systems. Ultimately the main reason for this was the limitation of computer power or equivalent a limited number of molecules in the model.

Moreover, from an experimental point of view, the IFT is comparatively difficult to measure, so the traditional approach in the literature has been to observe phase behavior of such systems and relate back such phase behavior to IFT. The empirical fundament for this approach is the concept of optimal phase behavior. Optimal phase behavior is defined

as the maximum solubilization of water and oil in the formed microemulsion when an equal amount of oil and water are solubilized [31–33]. The formed microemulsion phase [37–39] is also called middle phase or Winsor III phase and contains oil, water and a relatively large fraction of the surfactant and co-surfactant. Very low IFT values can be reached if optimum phase behavior is selected [6, 19, 20].

In the presented work we will further investigate this relationship between phase behavior and IFT, though the focus was on observing IFT directly.

Now, for a formal discussion of our results, we base our analysis on a formal mathematical description (2), which allows us to analyze the observed characteristics in a phenomenological approach. Again, as outlined above, a rigorous first-principle approach via quantum mechanical calculations is at this point in time not feasible because of limited computing time/power, so that we conclude that a phenomenological approach for the description of IFT in surfactant systems and the parameters influencing it is currently the best way to move forward analysis of this complex variable.

Equation 2 is closely related to the hydrophilic-lipophilic deviation (HLD) concept (1). The HLD concept relates phase behavior to physical parameters including oil type (“alkane number” or “equivalent alkane number”), salinity, temperature, surfactant type (e. g. average number of ethylene oxide groups or alkyl chain length in an ethoxylated alkylphenol [33]) and concentration, alcohol cosolvent type and concentration. The HLD equation has been applied to ethoxylated alkyl alcohols [31, 33, 34], sodium salts of dodecyl sulfate, alkyl sulfosuccinates, alkyl ethylene oxide sulfates, extended alkyl ethylene oxide sulfates and extended alkyl propylene oxide sulfates [35], and to alkylsulfonates and alkylbenzenesulfonates [36]. A recent study also applied the HLD concept to a decylglucoside/sorbitan mono-laurate mixture [6].

$$\text{HLD} = \sum c'_j X_j = \alpha - \text{EON} - k' \text{ACN} + bS + \Phi(A) + c_T(T - T_{\text{ref}}) \quad (1a)$$

$$\text{HLD} = \sum c'_j X_j = P \left(\sum \Delta\mu^* - RTQ \right) \quad (1b)$$

Where X_j are the formulation variables which influence the phase behavior and c'_j are the corresponding coefficients, which are determined experimentally [34]. α is a linear function of the number of carbon atoms in the alkyl group, ACN is the number of carbon atoms in the alkane oil (EACS if the oil is not an alkane), S is the salinity, $\Phi(A)$ is a function of the alcohol type and concentration and T is the temperature. R is the universal gas constant, k' , b , c_T , P and Q are proportionality constants and $\Delta\mu^*$ is the partial free energy of transfer from water to oil.

We propose an analog relationship for IFT, where optimum IFT is equal to minimum IFT (2). This is quasi the HLD equation projected into the “IFT space”. The reason for this parameter transformation is mainly that for many applications the IFT is the relevant parameter, including its absolute value, and not the phase behavior – the phase behavior is an elegant way to efficiently evaluate surfactant systems behavior, but it does not reveal exact IFT numbers because as mentioned before the mechanisms determining IFT are very complex. The in equation 2 formulated partial differential coefficients can be understood as analogs to

the coefficients in the HLD equation (1), e.g. k' in equation 1 is analog to $\frac{\partial \text{IFT}}{\partial \text{O}}$ in equation 2.

$$\begin{aligned} \text{HLD}^* = \min(\text{IFT}) &= \left(\frac{\partial \text{IFT}}{\partial T}\right) dT + \left(\frac{\partial \text{IFT}}{\partial p}\right) dp \\ &+ \left(\frac{\partial \text{IFT}}{\partial \text{SAT}}\right) d\text{SAT} + \left(\frac{\partial \text{IFT}}{\partial \text{SAC}}\right) d\text{SAC} + \left(\frac{\partial \text{IFT}}{\partial \text{O}}\right) d\text{O} \\ &+ \left(\frac{\partial \text{IFT}}{\partial \text{WOR}}\right) d\text{WOR} + \left(\frac{\partial \text{IFT}}{\partial \text{COST}}\right) d\text{COST} \\ &+ \left(\frac{\partial \text{IFT}}{\partial \text{COSC}}\right) d\text{COSC} + \left(\frac{\partial \text{IFT}}{\partial \text{ST}}\right) d\text{ST} + \left(\frac{\partial \text{IFT}}{\partial \text{SC}}\right) d\text{SC} \\ &= \sum \left(\frac{\partial \text{IFT}}{\partial X_i}\right) dX_i \end{aligned} \quad (2)$$

where

IFT = interfacial tension
 T = temperature
 p = pressure
 SAT = salt type
 SAC = salt concentration, salinity
 O = oil type
 WOR = water-oil ratio
 COST = cosolvent type
 COSC = cosolvent concentration
 ST = surfactant type
 SC = surfactant concentration
 $\frac{\partial \text{IFT}}{\partial X_i}$ = partial differential coefficient for each physical parameter influencing IFT

The terms $\left(\frac{\partial \text{IFT}}{\partial \text{COST}}\right) d\text{COST}$ and $\left(\frac{\partial \text{IFT}}{\partial \text{ST}}\right) d\text{ST}$ can be further subdivided into terms describing the influence of the individual structural elements, e.g. alkyl chain length in the APG (k) or the sugar head number (SH). This approach will be used in the following discussion. Each molecular structural element of the surfactant will be discussed and an estimate of the related coefficients will be derived. Moreover, the effect of the alkyl chain length of the 1-alcohol cosolvents will be formally described in this way. As the coefficient $\left(\frac{\partial \text{IFT}}{\partial T}\right)$ is zero or close to zero [3, 14, 18, 22, 24], we will not further discuss this coefficient. The coefficient $\left(\frac{\partial \text{IFT}}{\partial p}\right)$ is different from zero, but small [30], and we will not discuss this coefficient further in this text.

3.1 Influence of APG alkyl chain length on IFT

The IFTs of alkyl polyglycosides and alkyl polymaltosides (APM) with different saturated linear aliphatic alkyl chain lengths k are presented in Figure 2, and selected phase behavior plots in Figures 3 and 4. The surfactant concentration of these samples was 0.1 wt% in deionized water, and 1-octanol was added as a cosolvent.

A longer alkyl chain led to lower IFT values, consistent with results found for commercial APGs [3]. This was the case for both, APM and APG. This effect was independent of cosolvent (1-octanol) concentration. 1-octanol was selected as cosolvent, because it was previously identified as the best

performing cosolvent in terms of decreasing IFT versus n-octane [3, 14].

With increasing alkyl chain length the alkyl polymaltoside solubilized more oil forming a middle phase microemulsion. APM₈ solubilized small amounts of oil which were constant versus increasing 1-octanol concentration; APM₁₂ and APM₁₆ solubilized large quantities of oil, from 100% oil solubilization at a low cosolvent concentration to

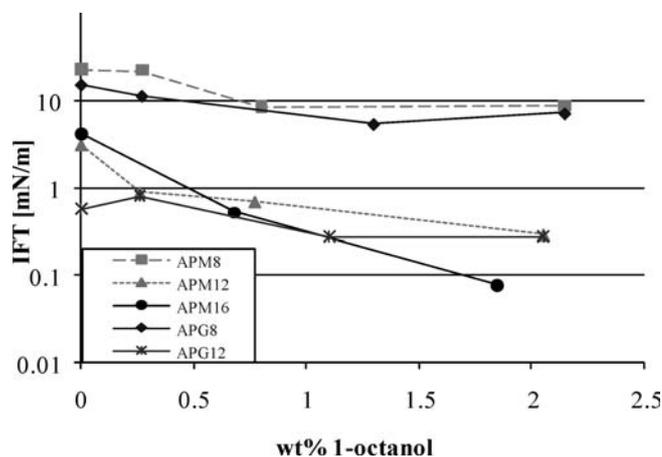


Figure 2 IFT of 0.1 wt% APG and APM/1-octanol formulations in deionized water

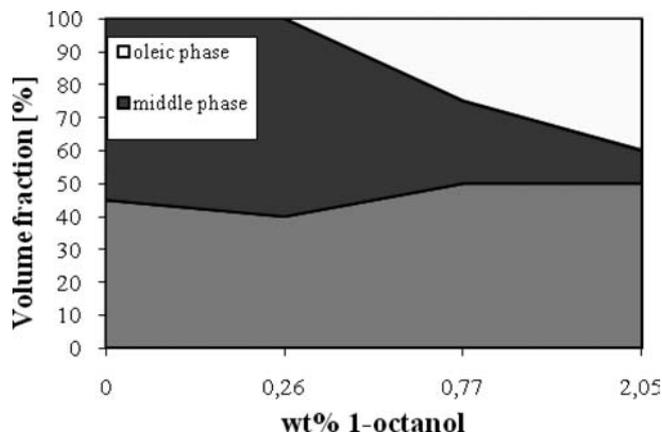


Figure 3 Phase behavior of APM₁₂/1-octanol formulations in deionized water

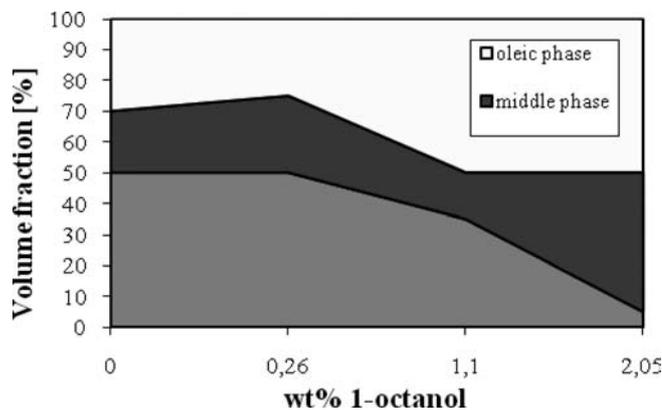


Figure 4 Phase behavior of APG₁₂/1-octanol formulations in deionized water

5–15% at a cosolvent concentration around 2 wt%. APM₁₆ solubilized slightly more oil than APM₁₂. Both, APM₁₆ and APM₁₂ solubilized only a small amount of water at low cosolvent concentration. Larger solubilization of the oil phase with increased *k* can be explained by the higher lipophilicity of the surfactant molecule. Generally it was observed that with a more equal amount of oil to water solubilized, the IFT decreased, which is consistent with the HLD concept [34].

Analog to the alkyl polymaltosides, APG₁₂ solubilized more oil than APG₈. Phase behavior of the APG₈ was constant against 1-octanol concentration, though IFT decreased. The addition of 1-octanol to the APG₁₂ formulation shifted the system to solubilizing more water (cp. Figure 4). At 2 wt% cosolvent concentration circa 90% of the water was solubilized. Lower IFTs were associated with higher 1-octanol concentrations.

MM simulations [14] found that the APM₁₆ alkyl chain attained its lowest Gibb's energy if folded into a "S-shaped" conformation, while the APM₈ maintained a "stretched" (linear) alkyl chain conformation in a set of 300 water, *n*-octane, cosolvent and surfactant molecules. We conclude that a bent alkyl chain allows a higher packing density within the *n*-octane phase by optimizing the van der Waals interactions, in the same way polyethylene crystals show a tilt of the packing and backbone angles [40]. This leads to lower IFT.

We then investigated another set of APMs with different alkyl chain lengths *k*, but this time a different cosurfactant (SPAN20, a sorbitan ester, cf. Figure 1n) was added. The formulations contained 6.60×10^{-3} M surfactant (constant molar surfactant concentration) and 6.60×10^{-3} M (= 0.24 wt%) cosurfactant. The results recorded are presented in Table 2; again a longer alkyl chain *k* led to lower IFT.

Depending on the sugar head type and whether a cosurfactant was present, the coefficient $\left(\frac{\partial \text{IFT}}{\partial k}\right)$ varied (cp. Table 3). Based on the experimental data, we conclude that this coefficient is linear and negative, with other words IFT decreases with *k*. Though not identified in our data because

surfactant	surfactant conc. [wt%]	IFT [mN/m]
APM ₈	0.30	4.19
APM ₁₀	0.32	3.88
APM ₁₂	0.34	3.57
APM ₁₃	0.35	3.18
APM ₁₆	0.37	2.72

Table 2 IFT results for APM-SPAN 20 formulations

system	$\left(\frac{\partial \text{IFT}}{\partial k}\right)$
0.1 wt% APM _k surfactant	-2.34
0.1 wt% APG _k surfactant	-3.66
0.0066 M APM _k surfactant + 0.24 wt% SPAN20	-0.18
0.4 wt% APGAc _k + 1.2 wt% 1-octanol	-0.97
0.4 wt% APGAc _k + 1.2 wt% 1-naphthol	-2.48

Table 3 $\left(\frac{\partial \text{IFT}}{\partial k}\right)$ coefficients, for distilled water systems

of limited amount of data, we expect a minimum in IFT versus *k* as the lipophilicity of the surfactant will increase so that at one point it almost exclusively dissolves in the oil phase. An interesting experiment would be to further evaluate APG surfactants with larger *k*. Moreover, the sorbitan cosurfactant decreased the magnitude of the coefficient $\left(\frac{\partial \text{IFT}}{\partial k}\right)$.

Consistent with the observed decreasing IFT with increasing *k* in the investigated APG and APM systems are the associated decreasing CMC values (cp. Table 1).

We observed that APM₁₆ was very efficient in reducing IFT even at very low concentrations and conducted a few more experiments in that area to explore further, cp. Table 4. This is of industrial importance, because costs can be reduced if low IFTs can be achieved by addition of only small amounts of surfactant.

A low APM₁₆ concentration of 0.1 wt% solubilized circa half of the water and led to a low IFT value. The very low APM₁₆ concentration of 0.01 wt% showed only a minute middle phase, but also reduced IFT to a low level.

The analysis was then extended to aromatic hydrocarbon tails in the APG molecules (APGAc_{6*} and APGAc_{10*} which were commercially available). The concentrations of the formulations were 0.4 wt% surfactant and 1.2 wt% cosolvent (1-octanol).

The longer two-ring aromatic chain (in APGAc_{10*}) generated a significantly lower IFT than a single phenyl ring (APGAc_{6*}), (cp. Table 5), which is consistent with the trend observed for saturated linear aliphatic hydrocarbon tails. The APGAc_{6*} solubilized more oil ($V_o = 25\%$; $V_m = 25\%$), while the APGAc_{10*} solubilized a more equal amount of oil/water ($V_o = 45\%$; $V_m = 5\%$). The more optimal phase behavior and associated lower IFT in the APGAc_{10*} system is consistent with the HLD concept. The $\left(\frac{\partial \text{IFT}}{\partial k}\right)$ coefficient is also negative for aromatic tails, but again we expect that this coefficient turns positive when the aromatic tail is sufficiently long turning the surfactant molecule sufficiently lipophilic – analog to the effect we expect for alkyl tails. It

wt% APM ₁₆	wt% 1-octanol	IFT [mN/m]	V _o [%]	V _m [%]	V _{aq} [%]
0.1	1.8	0.022	50	23	27
0.01	1.98	0.038	50	0.5	49.5

Table 4 IFT and phase behavior data of dilute APM₁₆/1-octanol formulations in deionized water

APG surfactant	IFT [mN/m]	V _o [%]	V _m [%]	V _{aq} [%]
APG _{6*}	14.33	45	5	50
APGAc _{6*}	9.105	25	25	50
APG _{6*} (brine)	6.3	50	0	50
APGAc _{6*} (brine)	8.3	50	0	50
APGAc _{10*}	5.2075	45	5	50
APGAc _{10*} (brine)	1.0	45	55	0
helicin	4.12	0	65	35
anameg-7	0.5	50	0	50

Table 5 Effect of stereochemistry, functional groups and salt on IFT for selected APG formulations

should be noted that the HLD theory “converts” non-alkane molecules into alkanes via the EACN (equivalent alkane carbon number) concept. We propose that this EACN concept can also be applied to hydrocarbon tails in the surfactant and/or cosurfactant molecule.

3.2 Influence of APG sugar head type and length on IFT

As shown in Figure 2, two sugar rings (maltose) led to higher IFT than a single sugar ring (glucose). This trend was independent of the presence or concentration of the cosolvent (1-octanol) or the alkyl chain length (C_8 or C_{12}). It appears that the maltose shifts the hydrophilic-lipophilic balance (HLB) to too high levels so that the surfactant molecule is too water-soluble, and which increases IFT.

The coefficient $\left(\frac{\partial IFT}{\partial SH}\right)$ is 7.7. This is however based only on limited experimental data (1 sugar ring – glucose – versus 2 sugar rings – maltose). The conclusion we draw from this limited dataset is that a smaller SH number would be beneficial in terms of further reducing the IFT. This is equivalent to reducing the hydrophilicity of the molecule and could be accomplished by etherizing (or esterizing) the hydroxyl groups of the sugar head with hydrophobic molecules.

3.3 Influence of stereochemistry of the APG molecules on IFT

We studied the influence of sugar stereoisomers (APG heads). We selected APG_{6^*} and APG_{6^*} as test surfactants because they were commercially available. We observed a lower IFT for APG_{6^*} as compared to APG_{6^*} (cf. Table 5). Moreover, the galactose derivative solubilized much more oil. This is an intriguing finding and it means that IFT can be further optimized if the best aldohexose head is identified. It is also interesting to observe that addition of salt changes the IFT of both surfactant systems in a different way (Table 5). This provides evidence that galactose and glucose heads in the APG are hydrated in a different way and that electrolytes apparently change this hydration in a way specific to the exact stereoisomer.

We extended this study to include the influence of the anomeric effect on IFT. We measured the IFTs of two anomers, α - APG_8 and β - APG_8 , in deionized water (cf. Table 5). The samples contained 10 mM (0.30 wt%) surfactant. This idea was inspired by the completely different CMC values of these APG compounds (the CMC of β - APG_8 is 20 mM while the CMC of α - APG_8 is 0.01 mM ([2, 27, 28], cp. Table 1). We measured an IFT of 6.56 mN/m for α - APG_8 , and an IFT of 9.44 mN/m for β - APG_8 . Note that the surfactant concentration is above the CMC for the α -anomer and below the CMC for the β -anomer.). This is a significant difference and we conclude that anomers can have a significant effect on IFT. In this anomer-context, we carried out MM calculations [14], which indicated that there is more internal hydrogen-bonding in the α -anomer than in the β -anomer, which renders the β -anomer more water-soluble and leads to a greater CMC. This apparently increases IFT. Separating or directly synthesizing pure anomers is of course an expensive way to reduce IFT, however, for medical or pharmaceutical applications where stereochemistry can be paramount, this may be a feasible route.

In summary, stereochemistry can have a significant influence on the IFT; this observation also highlights that IFT is a highly complex phenomenon, at least in surfactant systems, and that it can be significantly influenced by molecular de-

tails. Because of the limited amount of data and the difficulty associated with mathematically quantifying stereochemical structures we refrain from deriving HLD* coefficients at this point.

3.4 Effect of functional groups in the APG molecule on IFT

To study the effect of functional groups in the surfactant molecule, we bought Helicin and anameg-7, which are commercially available (though quite expensive) and tested them in terms of their IFT reduction potential. Results of IFT and solubilization behavior are shown in Table 5. The concentration of the formulations shown in Table 5 were 0.4 wt% surfactant and 1.2 wt% cosolvent (1-octanol) in deionized water or brine. The brine used was a 2 wt% NaCl solution.

The aldehyde group on the phenyl rest in the helicin lowered the IFT by a factor of 3.5 if compared to the analog APG_{6^*} (without aldehyde group). Helicin solubilized all oil, which was significantly more than what the APG_{6^*} solubilized, which was only marginal (5%).

The IFT observed for anameg-7 was comparatively low with 0.5 mN/m, while neither oil nor water was solubilized. The reason for the reduced IFT in anameg-7 may be the alkylamide function in the hydrophobic side chain of the molecule or the additional methoxy group.

Based on these observations we conclude that functional groups can be efficient in reducing the IFT. This is again an interesting finding as it supports the idea of designing more efficient APG molecules by adding functional groups.

We again refrain from determining the HLD* coefficients because of limited amount of data and the complexity associated with quantifying functional groups in a mathematical way.

3.5 Influence of salt on IFT in the APG formulations

In Figure 5 the influence of salt on the IFT of APM_{16} /1-octanol formulations is presented. The mass of APM_{16} /1-octanol was held constant at 2 wt%, and the mixing ratio was varied.

The IFT decreased with addition of salt, a result consistent with the trends found for other selected APG surfactants (Table 5) and for commercial APG products [14]. Moreover, if salt was added, less oil was solubilized and more water was solubilized, shifting the surfactant towards higher hydrophilicity in the brine systems.

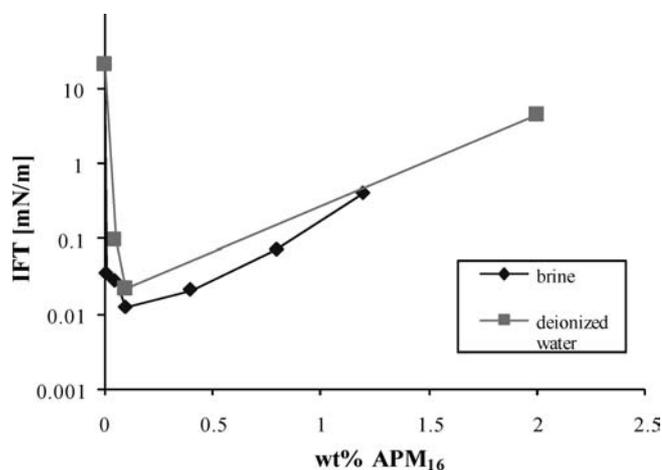


Figure 5 Influence of brine on IFT for APM_{16} /1-octanol formulations

In order to extract the HLD^* coefficient $\left(\frac{\partial IFT}{\partial SAC}\right)$ for the specific system presented in Figure 5, we plotted least square polynomial fits through the datapoints. The difference between these two fits is ∂IFT as a function of APM_{16} concentration for a salt concentration difference $dSAC = 2$ wt% NaCl. The resulting coefficient is presented in equation 3 (see bottom).

Based on this limited dataset, the coefficient $\left(\frac{\partial IFT}{\partial SAC}\right)$ appears to be almost constant versus the surfactant concentration SC at a constant salt concentration difference of 2 wt% NaCl. We therefore simplify equation 3 and derive $\left(\frac{\partial IFT}{\partial SAC}\right) = 0.0375 \text{ mN}/(\text{m} \cdot \text{wt}\% \text{ NaCl})$. Such a simplification is supported by the literature where only a small influence of salt concentration on IFT in APG systems was identified; however, more data varying the salt concentration is required to verify this simplification.

3.6 Effect of Cosolvent structure on IFT

Alcohol cosolvents can significantly reduce IFT [3, 14, 20, 30, 41] by entering the surfactant monolayer and thereby changing its curvature [42, 43] or rigidity [44]. Sabatini et al. [45] suggested the concept of a “hydrophobic linker” as a physical model for the action of these cosurfactants.

We investigated an array of 1-alcohol cosolvent molecules ranging from 1-butanol to 1-eicosanol (C_4 to C_{20}), but also included one aromatic alcohol (1-naphthol) and fluorescein, a molecule with a highly delocalized electron structure (cp. Figure 10). We included cosolvent molecules with delocalized electron clouds as we found that this has an impact on IFT [3, 11, 14, 21]. Apart from describing structure-IFT relationships, the quest was to identify cosolvents which create low to ultra-low IFT. We will also derive the HLD^* coefficients $\left(\frac{\partial IFT}{\partial COST}\right)$ which describe the influence of alcohol cosolvent type on IFT. Specifically, COST is the alkyl chain length in the 1-alcohol cosolvents.

3.7 NaCl-water-1-alcohol- APM_{16} -n-octane systems (quintenary systems)

We focused on APM_{16} as we found that longer alkyl chains lead to lower IFT (cp. Figure 2; also compare [3, 14]). Brine was used as it is more relevant to industrial applications, e.g. enhanced oil recovery [25]).

The experimental results for these IFT measurements (NaCl-water-1-alcohol- APM_{16} -n-octane systems) are shown in Figure 6 (IFT versus wt% APM_{16}).

The additive concentration (APM_{16} and cosolvent) amounted to 2 wt% for APM_{16} concentrations above 0.2 wt%. For APM_{16} concentrations below or equal to 0.2 wt%, the APM_{16} concentration was halved to observe IFTs at further reduced surfactant concentrations, e.g. at an alcohol concentration of 1.6 wt%, 0.2 wt% APG_{16} were

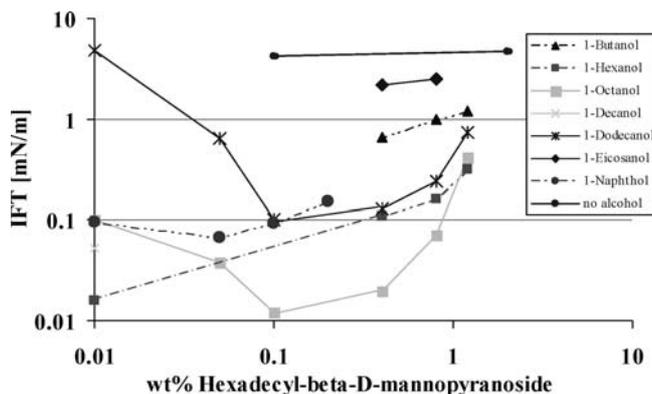


Figure 6 Measured IFT results for APM_{16} -alcohol cosolvent systems

added instead of 0.4 wt%. This was to monitor IFT and phase behavior at very low surfactant concentrations which are relevant for many industrial applications, e.g. necessary to conduct economic surfactant floods [25]. The aqueous phase contained 2 wt% NaCl in all of these samples.

1-octanol and 1-hexanol showed low IFTs. 1-octanol reached a minimum IFT at 0.1 wt% APM_{16} concentration or a molar mixing ratio (alcohol:surfactant) of circa 100, which is low. The 1-hexanol showed a low IFT at even lower concentrations (= 0.01 wt% APM_{16}) or a molar mixing ratio of > 1000, which is very low.

Based on this data and the data presented in Figure 5, we derive the HLD^* coefficients $\left(\frac{\partial IFT}{\partial SC}\right)$ (cp. Table 6). This we did by fitting the data curves with least square fits and then differentiated these fitting functions with respect to SC.

This statistical analysis reveals two aspects, namely a) the HLD^* coefficients $\left(\frac{\partial IFT}{\partial SC}\right)$ increase monotonically with increasing surfactant concentration, starting with a negative value, via a zero-value (which is equivalent to minimum IFT – this zero-value is attained at low APM_{16} concentration, below 0.3 wt% APM_{16} and even lower, depending on the exact system and lowest for the 1-naphthol system.) to positive values which continue to increase; and b) only fairly complicated polynomials fit these curves which means that the underlying physico-chemical mechanism is also complicated and cannot be described by simple exponential, logarithmic, linear or parabolic equations. It should be noted that at much higher SC, we expect $\left(\frac{\partial IFT}{\partial SC}\right)$ to decrease again and attain a zero value because at sufficiently high SC, a one-phase system should be formed.

We also conducted this type of analysis for the HLD^* coefficient $\left(\frac{\partial IFT}{\partial COST}\right)$, specifically the change in IFT with varying alkyl chain length of the linear 1-alcohols (cp. Table 7). For simplicity we executed this analysis at constant

$$\left(\frac{\partial IFT}{\partial SAC}\right) = \frac{\partial(0.349 SC^6 - 1.5955 SC^5 + 2.6495 SC^4 - 2.847 SC^3 + 2.1733 SC^2 - 0.6738 SC + 0.0759)}{2 \text{ wt}\% \text{ NaCl}} \quad (3)$$

with

SC = surfactant concentration, APM_{16} concentration

system	$\left(\frac{\partial IFT}{\partial SC}\right)$
APM ₁₆ /1-octanol in dist. water	$2.0945SC^5 - 7.9775SC^4 + 15.154SC^3 - 15.0612SC^2 + 7.4562SC - .0695$
APM ₁₆ /1-octanol in 2 wt% NaCl brine	$4.556SC^3 - 6.5202SC^2 + 3.1096SC - 0.0406$
APM ₁₆ /1-dodecanol in 2 wt% NaCl brine	$142.398SC^5 - 501.35SC^4 + 657.8SC^3 - 392.85SC^2 + 104.658SC - 9.4675$
APM ₁₆ /1-naphthol in 2 wt% NaCl brine	$(42E + 06)SC^5 - (25E + 06)SC^4 + (8E + 06)SC^3 - 742944SC^2 + 42114SC - 907.77$

Table 6 $\left(\frac{\partial IFT}{\partial SC}\right)$ for selected surfactant systems

surfactant concentration and selected two surfactant concentrations for which we have most experimental data (0.4 wt% APM₁₆ and 0.8 wt% APM₁₆). It is interesting to note that the shape of these fitting curves is almost identical for both concentrations, they are only shifted by a constant ΔIFT , which appears to be constant until a $k = 12$ is reached, above this, ΔIFT widens, but still appears to be constant. Both coefficients have a parabolic-like shape and a minimum at $k = 8$ (1-octanol).

Selected phase behavior for these formulations is displayed in Figures 7–9. Note that the x-axis is not to scale in Figures 8 and 9.

The addition of alcohol cosolvents shifted the phase behavior of these surfactant systems towards more optimal conditions. In fact all investigated brine-APM₁₆-cosolvent-n-octane formulations had a middle phase microemulsion except the 1-hexanol at very low (0.01 wt%) APM₁₆ concentration. The solubilized oil volume in the 1-butanol formulation and the solubilized water volume in the 1-dodecanol and 1-eicosanol formulations were constant versus cosolvent concentration. The other three cosolvents showed peak oil solubilities at 0.8 wt% APM₁₆ (1-hexanol) and 1.2 wt% APM₁₆ (1-octanol) concentration or peak water solubility at 0.2 wt% APM₁₆ (1-naphthol; note that no 1-naphthol formulations with higher APM₁₆ concentrations were measured.) concentration. Oil was solubilized if smaller 1-alcohols were added, while addition of large 1-alcohols solubilized water. The relative volume of the microemulsion was not directly proportional to IFT reduction.

As we found low IFTs for formulations with very low APM₁₆ concentrations, we extended the analysis to more dilute mixing ratios and additional cosolvents. IFT and phase behavior data for these selected APM₁₆ formulations in 2 wt% NaCl brine are listed in Table 8. The APM₁₆ concentration was kept constant at a very low concentration of 0.01 wt%.

The 1-decanol and 1-octanol formulations with 1.8–1.98 wt% alcohol showed low IFTs (0.02–0.05 mN/m), which is very effective considering that the surfactant concentration was only 0.01 wt%. By halving the alcohol concentration the IFT increased by a factor of 2.8 for 1-octanol; a similar IFT was measured for 1-naphthol as a cosolvent. This is again efficient IFT reduction considering the surfactant/cosolvent concentrations. Formation of a microemulsion phase happened for several formulations, but not for others. IFT was not directly proportional to the volume of the microemulsions in the formulations.

Fluorescein, a dye, was even efficient in reducing IFT at a concentration of 0.01 wt% mixed with 0.01 wt% APM₁₆. It reached a value of 1.74 mN/m, which is a strong reduction of the water-n-octane IFT (= 50.8 mN/m, [46]), which is amazing for these very low surfactant/cosolvent concentrations. Fluorescein was selected because of its strongly delocalized electron cloud field (cp Figure 10). We observed [3, 11, 14] that strongly delocalized electrons or aromatic sys-

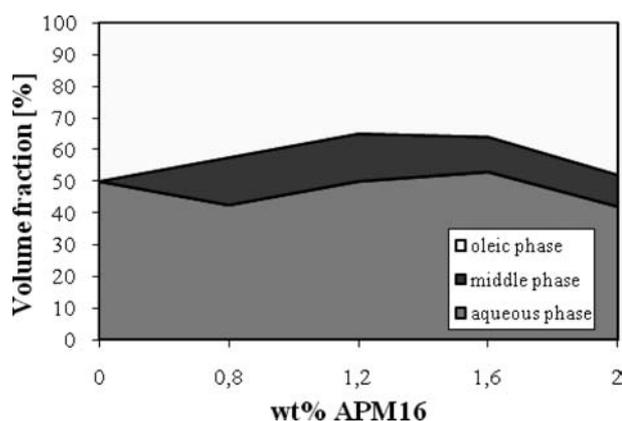


Figure 7 Phase behavior of APM₁₆-1-butanol formulations in brine

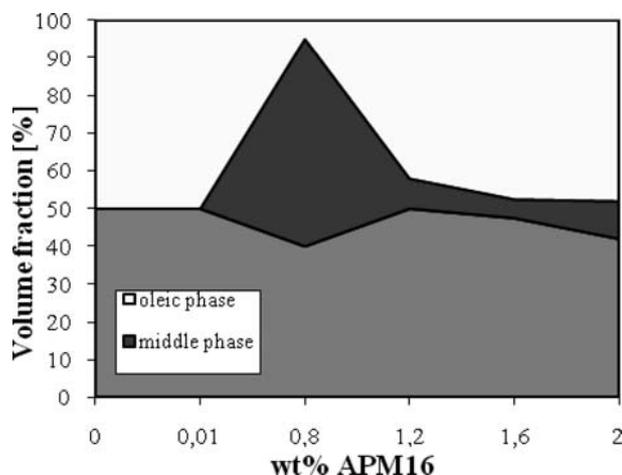


Figure 8 Phase behavior of APM₁₆-1-hexanol formulations in brine

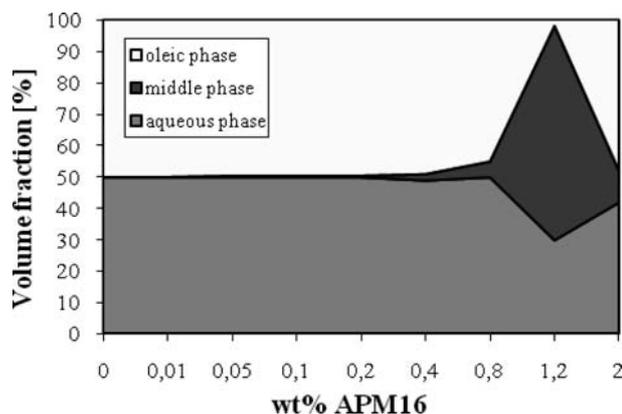


Figure 9 Phase behavior of APM₁₆-1-octanol formulations in brine

system	$\left(\frac{\partial IFT}{\partial COST}\right)$
0.8 wt% APM ₁₆ /2 wt% NaCl brine	$(42E - 06)COST^5 - 0.003COST^4 + 0.0672COST^3 - 0.78COST^2 + 4.36COST - 9.5198$
0.4 wt% APM ₁₆ /2 wt% NaCl brine	$(-20E - 05)COST^4 + 0.0088COST^3 - 0.1533COST^2 - 1.1456COST - 3.1515$

Table 7 $\left(\frac{\partial IFT}{\partial COST}\right)$ for two different surfactant concentrations

cosolvent	cosolvent conc. [wt%]	IFT [mN/m]	V _o [%]	V _m [%]	V _{aq} [%]
1-octanol	1	0.105	50	0	50
1-decanol	1.98	0.053	49.5	0.5	50
1-naphthol	1	0.096	46	10	44
1-octanol	1.98	0.038	50	0.5	49.5
1-octanol	1.8	0.022	50	23	27
fluorescein	0.01	1.74	25	25	50

Table 8 IFT and phase behavior data for APM₁₆-cosolvent formulations with very low 0.01 wt% APM₁₆ concentration

APG ₆ *	phenyl-β-D-galacto-pyranoside
APGac ₁₀ *	naphthyl-β-D-galacto-pyranoside
anameg-7	methyl-6-O-(N-heptylcarbamoyl)-α-D-glucopyranoside
helicin	salicylaldehyde-β-D-glucopyranoside
IFT	Interfacial tension [N/m]
MM	molecular modeling
CMC	critical micelle concentration [mol/m ³]
V _o	volume fraction of oil phase [-]
V _m	volume fraction of middle phase [-]
V _{aq}	volume fraction of aqueous phase [-]
mM	molar concentration [mol/(m ³ × 10 ⁻⁶)]
M	molar concentration [mol/(m ³ × 10 ⁻³)]
wt%	weight %

tems reduce IFT; aromaticity can be introduced into the system in form of the surfactant, cosolvent or oil phase.

4 Conclusions

- An HLD* concept for interfacial tension was developed analog to the HLD concept describing optimal phase behavior.
- Several HLD* partial differential coefficients were derived which describe the influence of system variables on interfacial tension.
- Alkyl polyglucosides can reach very low interfacial tensions (0.01 mN/m) when formulated with 1-alcohol cosurfactants.
- Alkyl polyglycosides with longer alkyl chains reached lower IFT values.
- APGs with one sugar-head ring showed lower IFTs than the analog maltosides.
- The stereochemistry of the sugar-ring in the APG molecule can have a significant influence on IFT.
- An α-anomer (n-octyl-α-D-glucopyranoside) showed a lower IFT than the β-anomer (n-octyl-β-D-glucopyranoside).
- For the n-hexadecyl-β-D-maltopyranoside (APM₁₆), 1-octanol was the best cosurfactant. 1-hexanol, 1-naphthol and 1-dodecanol also significantly lowered IFT values.
- The addition of NaCl salt reduced IFT.

Nomenclature

APG	alkyl polyglucoside
APG ₈	n-octyl-β-D-glucopyranoside
APG ₁₂	n-dodecyl-β-D-glucopyranoside
APM	alkyl polymaltoside
APM ₈	n-octyl-β-D-maltopyranoside
APM ₁₀	n-decyl-β-D-maltopyranoside
APM ₁₂	n-dodecyl-β-D-maltopyranoside
APM ₁₃	n-tridecyl-β-D-maltopyranoside
APM ₁₆	n-hexadecyl-β-D-maltopyranoside
APGac ₆ *	phenyl-β-D-galacto-pyranoside

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