Colloid Polym Sci 273:565–571 (1995)
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ORIGINAL CONTRIBUTION

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Interfacial tension of alkylglucosides in different APG/oil/water systems

Received: 2 November 1994
Accepted: 28 November 1994

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Abstract The interfacial performance of pure alkylglucosides (C_8G_1, $C_{10}G_1$ and $C_{12}G_1$) and of technical grade alkylpolyglucoside (APG) surfactants was investigated in three different water/oil systems (decane, isopropylmyristate and 2-octyldodecanol). From the dependence of the interfacial tension on the surfactant concentration below the CMC the cross-sectional area of the molecules at the decane/water interface was estimated. The plateau values of the interfacial tension at the CMC (σ_c) are independent of temperature and almost independent of added electrolyte in the decane/water system. The ability of the surfactants to lower the oil/water interfacial tension is most pronounced for the nonpolar oil. The partition coefficient of the surfactant between oil and water phase (k_c) was estimated from the CMC and the observed break point of the interfacial tension after equilibration of the two phases. In decane/water, k_c is nearly zero for all surfactants studied. For the polar oils, k_c increases with the chain length of the surfactant up to $k_c \approx 10$ for $C_{12}G_1$ in octyldodecanol/water. The values of σ_c in the different oil/water systems appear to be correlated with k_c and exhibit a minimum near $k_c = 1$.

Key words Alkylglucosides – interfacial tension – surfactants – oil/water interface – partition coefficient

Introduction

Currently, technological developments aiming at the production of chemicals derived from agricultural raw materials are attracting renewed attention. Alkylpolyglucosides (APG) are nonionic surfactants synthesized from fatty alcohols and saccharides [1]. They display dermatological safety, very good biodegradability and interesting surface-active properties. Therefore, these surfactants become increasingly important for use in detergents and cosmetic products [2]. The surface activity of pure alkylglucosides at the air/water interface was first studied systematically by Shinoda et al. [3]. Investigations of surfactant mixtures containing alkylpolyglucosides were recently reported by Nickel et al. [4]. For practical applications there is also a need for reliable data concerning the influence of APG surfactants on the oil/water interfacial tension, both for nonpolar and polar oils, and on the phase behavior of the respective oil-water-surfactant systems. Some studies of the phase behavior have been reported recently [5, 6]. However, little attention has been paid to the interfacial performance of APG surfactants so far.

In this paper, we report a study of the interfacial properties of oil-water-surfactant systems containing alkylglucosides. In particular, the influence of temperature, electrolyte concentration and the amphiphilicity of the oil was investigated for different pure and technical grade alkylglucosides. On the basis of these results it will be possible to compare the interfacial properties of APG with those of the widely used polyoxyethylene glycol ethers (C_nE_m).

Experimental

Substances

The alkylmonoglucosides octyl-, decyl- and dodecylglucoside ($C_8G_1, C_{10}G_1, C_{12}G_1$) and technical grade alkylpolyglucosides C_8/C_{10}-APG, C_{12}/C_{14}-APG and C_{14}-APG were prepared by Henkel by means of Fischer glucosidation using pure or technical grade fatty alcohols [7]. All products represent mixtures of α- and β-glucosides. The monoglucosides (C_nG_1) were purified by distillation and fractional crystallization. Samples of pure decyl-β-D-glucoside, dodecyl-β-D-glucoside and decyl-β-D-maltoside were purchased from Sigma (99%).

n-Decane (> 98%) and isopropylmyristate (> 98%) were obtained from Merck–Schuchardt, 2-octyldodecanol (technical grade) was from Henkel. All chemicals were used without further purification. The water used in this study was distilled and passed through a Milli-Q pure-water system.

Methods

Throughout this work the surfactants were dissolved in water and their concentration was determined by weight. Samples containing a 1:1 mass ratio of oil and aqueous phase were prepared in Teflon-sealed glass tubes and allowed to equilibrate at the experimental temperature (60 °C) in a water bath for at least 48 h before the measurements of interfacial tension were made.

Interfacial tensions of the pre-equilibrated phases were measured using a Krüss SITE 04 spinning-drop tensiometer. Tensions above 10 mN m^{-1} were determined by the pendant-drop method. The temperature of the samples in the tensiometers was controlled to within ± 0.1 K.

Results and discussion

Alkyl chain length of the surfactant

Figure 1 shows the interfacial tension of aqueous solutions of the surfactants C_8G_1, $C_{10}G_1$ and $C_{12}G_1$ against decane after equilibration at 60 °C. The tension σ is plotted vs. the logarithm of the initial surfactant concentration in the

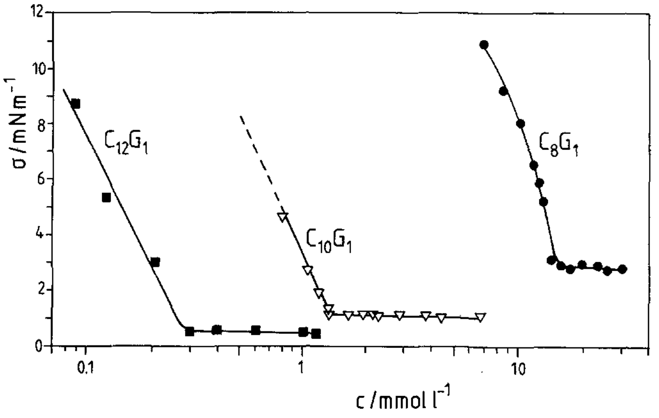


Fig. 1 Influence of alkylglucoside surfactants C_8G_1, $C_{10}G_1$ and $C_{12}G_1$ on the decane/water interfacial tension at 60 °C. Equilibrium values of the tension σ are plotted vs. initial concentration c of the surfactants in the water phase

Table 1 CMC-values determined from surface tension (ST) or interfacial tension (IFT) measurements

Substance	T/°C	cmc/mol l^{-1} (ST)	c_b/mol l^{-1} (IFT)	Reference
β-D-C_8G_1	25	$2.5 \cdot 10^{-2}$	–	[3]
C_8G_1 (75% α/25% β)	25	$1.8 \cdot 10^{-2}$	–	[4]
	40	–	$1.8 \cdot 10^{-2}$	this work
	60	–	$1.8 \cdot 10^{-2}$	this work
α-D-$C_{10}G_1$	60	–	$1.7 \cdot 10^{-3}$	this work
β-D-$C_{10}G_1$	25	$2.2 \cdot 10^{-3}$	–	[3]
	60	–	$2.0 \cdot 10^{-3}$	this work
$C_{10}G_1$ (70% α/30% β)	60	–	$1.4 \cdot 10^{-3}$	this work
β-D-$C_{10}G_2$	60	–	$3.0 \cdot 10^{-3}$	this work
β-D-$C_{12}G_1$	25	$1.9 \cdot 10^{-4}$	–	[3]
	60	–	$2.0 \cdot 10^{-4}$	this work
$C_{12}G_1$ (70% α/30% β)	60	$1.7 \cdot 10^{-4}$	–	[4]
	60	–	$2.0 \cdot 10^{-4}$	this work

Table 2 Interfacial tensions σ_0 and σ_c, and the increments $\Delta\sigma = \sigma_0 - \sigma_c$ at 60 °C (all values in mN m^{-1})

Oil		C_8G_1		$C_{10}G_1$		$C_{12}G_1$	
	σ_0	σ_c	$\Delta\sigma$	σ_c	$\Delta\sigma$	σ_c	$\Delta\sigma$
Decane	48.7 (± 0.9)	2.8 (± 0.2)	45.9	1.0 (± 0.1)	47.7	0.5 (± 0.1)	48.2
IPM	27.9 (± 0.7)	2.1 (± 0.2)	25.8	0.6 (± 0.1)	27.3	0.4 (± 0.1)	27.5
OD	24.2 (± 0.7)	0.9 (± 0.1)	23.3	0.7 (± 0.1)	23.5	1.2 (± 0.2)	23.0

aqueous phase. The break in the curves is attributed to the CMC of the surfactant in the aqueous solution. The respective break point concentrations (c_b) are in good agreement with the respective CMC values as determined from surface tension measurements (see Table 1). This finding indicates that after equilibration the surfactant has remained almost entirely in the aqueous phase and its concentration in the decane phase is virtually zero. As seen in Fig. 1, the CMC decreases with increasing chain length of the surfactant, in agreement with the Traube rule. For a given surfactant, the interfacial tension remains nearly constant above the break point, there is just a slight decrease of the tension with increasing concentration. Such a behaviour has been observed for the surface tensions of many surfactant systems [8]. The interfacial tension at the break point, σ_c, decreases with increasing chain length of the surfactant in the decane/water system (see Table 2). This behavior is discussed later in connection with the other oils.

Head-group size and isomerism

The influence of head-group size of the surfactant molecules on the decane/water interfacial tension was investigated by comparing two anomerically pure compounds, decyl-β-D-glucoside (β-D-$C_{10}G_1$) and decyl-β-D-maltoside (β-D-$C_{10}G_2$). As seen in Fig. 2, substitution of the glucoside head group by maltoside has no significant influence on σ_c, but the CMC is shifted to a somewhat higher value (from 2.10^{-3} to 3.10^{-3} M). This finding supports results for the corresponding dodecyl-surfactants by Böcker and Thiem [9] and by Drummond et al. [10], according to which the CMC of the β-D-maltoside is about a factor 2 higher than that of the β-D-glucoside. A similar trend, i.e., a weak increase of the CMC with increasing head-group size, is also well-known for alkyl ethoxylates (C_nE_m) [11]. The α-anomer of decyl-D-glucoside has a somewhat higher cmc than the β-anomer (cf. Table 1), again in agreement with results published by Böcker and Thiem [9].

To obtain a quantitative estimate of the minimum head-group area a_m required by the surfactant molecules at the oil/water interface, the concentration dependence of the interfacial tension $\sigma = \sigma(c)$ at surfactant concentrations up to the CMC was analyzed using the equation

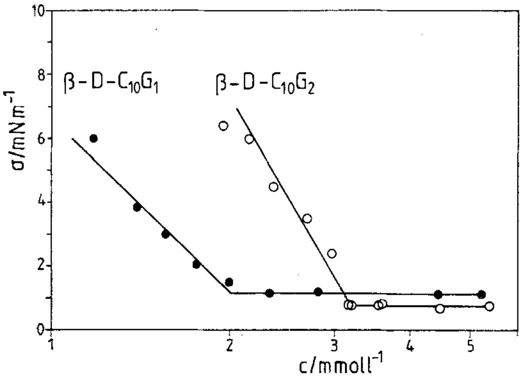


Fig. 2 Influence of decyl-β-D-glucoside (β-D-$C_{10}G_1$) and decyl-β-D-maltoside (β-D-$C_{10}G_2$) on the decane/water interfacial tension at 60 °C. The symbols σ and c have the same meaning as in Fig. 1

$$(1 - x)\exp\left(\frac{\sigma - \sigma_0}{\alpha}\right) + x\exp\left(\frac{\sigma - \sigma_c}{\alpha}\right) = 1 \,, \qquad (1)$$

where $x = c/\text{cmc}$ is the relative concentration of the surfactant in the aqueous phase, σ_0 and σ_c represent the interfacial tensions at $x = 0$ and $x = 1$, respectively. The fit parameter α is related to the minimum area per surfactant molecule, a_m, by $\alpha = kT/a_m$, where k is the Boltzmann constant and T is the temperature. Equation (1) is based on a simple surface layer model for mixtures composed of molecules of equal sizes, neglecting nonideality effects in the bulk solution and in the monolayer [12]. In the literature [13], Eq. (1) was applied to the adsorption of amphiphiles at the air/water interface, but it may also be used for oil/water interfaces if the equilibrium concentration of the amphiphile in the aqueous phase is known, or if it is completely insoluble in the oil phase. This restriction limits the application of Eq. (1) to the data for the decane/water interface in the present study. Best fit values of a_m for these systems are summarized in Table 3. As in other cases, the values of a_m for the alkane/water interface are significantly greater than corresponding values for the air/water interface.

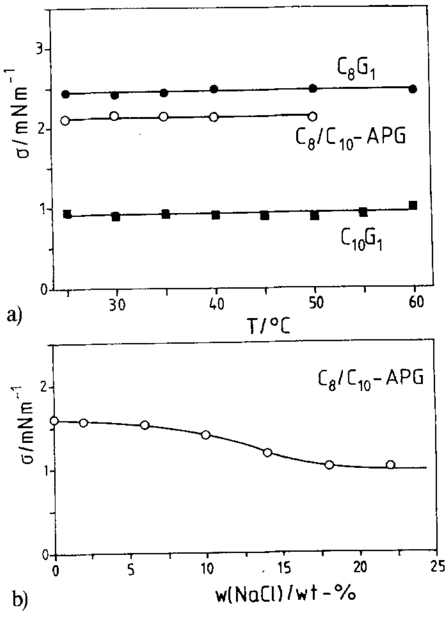
Table 3 Cross-sectional area a_m of surfactant molecules at the air/water and alkane/water interface

Substance	Interface	a/A^2	Reference
β-D-C_8G_1	air/water	42	[3]
α-D-$C_{10}G_1$	decane/water	53 (± 3)	this work
β-D-$C_{10}G_1$	air/water	47	[3]
	decane/water	57 (± 2)	this work
β-D-$C_{10}G_2$	decane/water	54 (± 2)	this work
β-D-$C_{12}G_1$	air/water	36	[3]
	decane/water	52 (± 3)	this work

Temperature and electrolyte

Figure 3a shows the σ_c-values of the decane/water interfacial tension as a function of temperature for C_8G_1, $C_{10}G_1$ and technical grade C_8/C_{10}-APG. The values are independent of temperature in the experimental range 25° to 60 °C. Figure 3b shows the decane/water interfacial tension for solutions containing 0.5 wt.-% C_8/C_{10}-APG plotted as a function of the concentration of electrolyte (NaCl) in the aqueous phase; σ_c exhibits only a weak decrease with increasing electrolyte concentration up to 20 wt-% NaCl. These results demonstrate that neither temperature nor added electrolyte has any significant influence on σ_c in these systems. The insensitivity against temperature or electrolytes is in marked contrast to the interfacial performance of other nonionic surfactants [14]. This difference may be explained by the different nature of the hydration of alkylglucosides and oxyethylene surfactants.

Fig. 3 a) Plateau values σ_c for C_8G_1, $C_{10}G_1$ and C_8/C_{10}-APG at the decane/water interface as a function of temperature T; b) influence of added electrolyte (NaCl) on the interfacial tension of a 0.5 wt-% aqueous solution of C_8/C_{10}-APG against decane at 40 °C



In the case of the alkyl polyoxyethylene surfactants (C_nE_m) the hydrocarbon/water interfacial tension exhibits a characteristic temperature dependence with a pronounced minimum of σ near the so-called phase inversion temperature T_m [15, 16]. Well below T_m the surfactant is predominantly hydrophilic due to the hydration of the head-group, and it stabilizes oil-in-water microemulsions; well above T_m it is predominantly hydrophobic with increased oil solubility, and it stabilizes water-in-oil microemulsions. In both these cases the oil-water interfacial tension is relatively high far away from the inversion temperature. As discussed above, the C_nG_1 and APG surfactants of the present study do not partition between water and a non-polar oil like decane in the experimental temperature range, but remain in the aqueous phase due to their high hydrophilicity. This behavior corresponds to that of C_nE_m surfactants well below T_m, where one expects relatively large but temperature-independent oil/water interfacial tensions, as indeed found for the present systems.

For the present alkyl glucosides a phase inversion has not been observed in three-component oil-water-surfactant systems at temperatures up to 100 °C. An alternative possibility to promote a phase inversion with the appearance of a middle-phase microemulsion in hydrocarbon-water-surfactant systems is to add a co-surfactant. In the case of APG surfactants, middle-phase microemulsions can be obtained by the addition of medium-chain alcohols [17] or alkyl glycerol ethers [18] which render the surfactant mixture to be effectively more hydrophobic than APG without co-surfactant. It is found that the width of the three-phase region promoted by the addition of medium-chain alcohols is not significantly affected by temperature or electrolyte addition [17]. Studies of the behavior of quaternary oil-water-APG-alcohol systems are in progress in our laboratories.

Nature of the oil

Three different oils were chosen to study the influence of the nature of the oil: *n*-decane as a non-polar oil, isopropylmyristate (IPM) as an ester oil and the long-chain branched alcohol 2-octyldodecanol (OD). These compounds are representative for important types of oils for various practical applications; they differ in their amphiphilic nature and other respects.

Figure 4 shows the influence of the surfactants C_8G_1 and $C_{12}G_1$ on the oil/water interfacial tension for the three

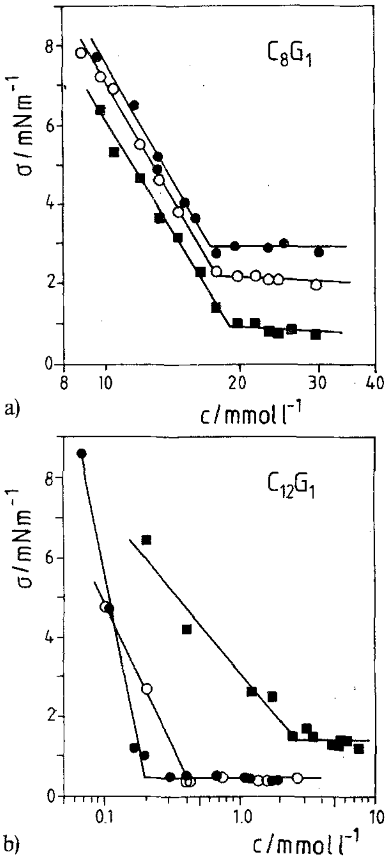


Fig. 4 Effect of alkylglucoside surfactants C_nG_1 on the oil/water interfacial tension for three different oils: ●, *n*-decane; ○, isopropylmyristate (IPM); ■, 2- octydodecanol (OD) at 60 °C. (a) C_8G_1 (upper graph); (b) $C_{12}G_1$ (lower graph) The symbols σ and c have the same meaning as in Fig. 1

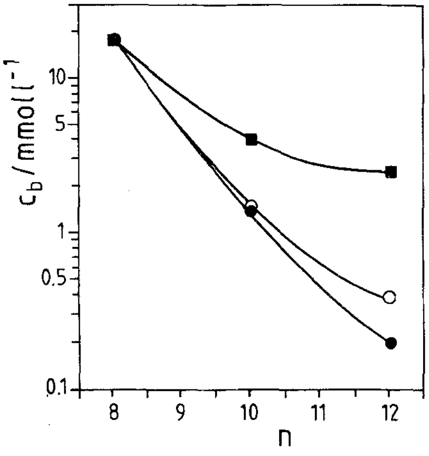


Fig. 5 Break point concentration c_b of C_nG_1 surfactants in three different oil/water systems as a function of *n*, the alkyl chain length of the surfactant (60 °): ●, decane/water; ○, IPM/water; ■, OD/water

Table 4 Approximate values of the partition coefficient k_c for C_nG_1 surfactants in three different oil/water systems

Oil	Decane	IPM	OD
C_8G_1	≈0	≈0	≈0
$C_{10}G_1$	≈0	0, 5	3
$C_{12}G_1$	≈0	1	10

oils. As in Fig. 1, the interfacial tension σ is plotted vs. the initial concentration of surfactant in the aqueous phase. In the case of C_8G_1 (Fig. 4a), the break points of the graphs for the different oils are located at nearly the same concentration c_b for the three oils. Within experimental accuracy this c_b-value agrees with the CMC of the surfactant in water. For $C_{12}G_1$ (Fig. 4b), however, the c_b-value increases in the order decane < IPM < OD. The dependence of c_b on the alkyl chain length of the C_nG_1 surfactants is illustrated in Fig. 5. From the ratio of the concentration c_b and the CMC, one can estimate the partition coefficient k_c of the surfactant between oil-phase and water-phase at the CMC. In the present case, where the surfactant is partitioned between equal masses of oil and water phase, we have

$$k_c = \frac{c^0}{\mathrm{cmc}} = \left(\frac{c_b}{\mathrm{cmc}} - 1\right)\left(\frac{\rho^0}{\rho^W}\right), \qquad (2)$$

where c^0 is the equilibrium concentration in the oil phase at the cmc, while ρ^0 and ρ^W represent the mass densities of oil and water phase, respectively. The resulting values for k_c are summarized in Table 4.

In the systems with the non-polar oil (decane), c_b coincides with the CMC as all three surfactants remain entirely in the aqueous phase, and thus $k_c \approx 0$. In the systems with the polar oils, one finds increasing values of k_c with increasing hydrophobicity of the surfactant. In particular, for $C_{12}G_1$, we obtain $k_c \approx 1$ for IPM/water and $k_c \approx 10$ for OD/water. Hence, $C_{12}G_1$ is partitioned equally between oil and water in the IPM/water system and is predominantly oil-soluble in the OD/water system (cf. Table 4). Generally, an increase of k_c implies a decreasing efficiency of the surfactant in its ability to lower the oil/water interfacial tension. This follows from the fact that part of the surfactant is required to saturate the oil phase at any given equilibrium concentration in the aqueous phase.

Figure 6 shows the σ_c-values as a function of chain length *n* of C_nG_1 homologues including the three technical grade APG surfactants. For the decane/water and the IPM/water systems, σ_c decreases with increasing chain length *n*, i.e., with increasing hydrophobicity of the surfactant. Hence, in these two oil/water systems an increase of the surfactant chain length leads to a better balance of the

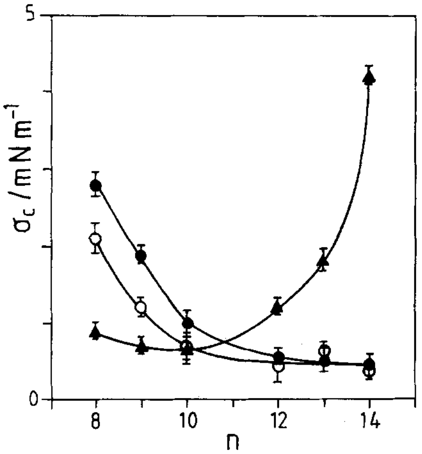


Fig. 6 Plateau values σ_c of the oil/water interfacial tension as a function of n, the alkyl chain length of the C_nG_1 and APG surfactants (60 °C): ●, decane/water; ○, IPM/water; ■, OD/water

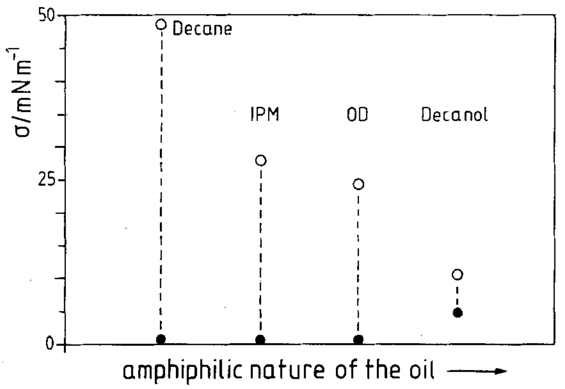


Fig. 7 Oil/water tensions σ_0 (○) and plateau values σ_c (●) for $C_{10}G_1$ in oil/water systems of increasing amphiphilic nature of the oil (60 °C). The increment $\Delta\sigma = \sigma_0 - \sigma_c$ (a measure of the effectiveness of the surfactant) is marked by dashed lines

surfactant with respect to its affinity to water and oil. This trend is analogous to the approach to the inversion temperature T_m from $T < T_m$. For the OD/water systems, on the other hand, σ_c exhibits a minimum for $C_{10}G_1$ and increases sharply for $n \geq 12$. As we have seen, $C_{12}G_1$ is preferentially soluble in the oil-phase in the OD/water system, and the optimum balance of the affinity to oil and water has already been reached for a more hydrophilic surfactant like $C_{10}G_1$. Hence, the observed dependence of the oil/water interfacial tension σ_c correlates with the hydrophilic-hydrophobic balance of the surfactant in the three oil/water systems.

As is to be expected, the effectiveness of the surfactants in lowering the oil/water interfacial tension decreases as the amphiphilic character of the oil becomes more pronounced. This trend is illustrated in Fig. 7, where we have plotted the span from the tension of the pure oil/water interface, σ_0, to the value σ_c at the CMC for a given surfactant ($C_{10}G_1$) in the present oil/water systems, using data from Table 2. The σ_0 value of OD/water is lower than for IPM/water, presumably because the -CH_2OH head-group of OD is more hydrophilic and less bulky than the isopropylate group of IPM. In the OD/water systems, we anticipate an additional effect, namely a direct competition of long-chain alcohols with the surfactant in the interface. This competition becomes even more pronounced if OD is replaced by the linear-chain alcohol decanol as the oil. In this case we expect an oriented monolayer of decanol molecules at the interface [19, 20]. In the presence of such a monolayer of alcohol molecules, surfactant molecules with large head groups like $C_{10}G_1$ will be adsorbed to a lesser extent than at the interface against non-polar or weakly surface-active oils. Accordingly, in the water/decanol system, the σ_c-values for $C_{10}G_1$ is considerably higher than in the case of non-polar or weakly surface-active oils. In conclusion, we may say that the efficiency and effectiveness of the surfactants in lowering the oil/water interfacial tension both decrease markedly with increasing amphiphilicity and surface activity of the oil.

Acknowledgement This collaborative study was performed as a part of the ECLAIR project "Seed oils for new chemical applications (SONCA)". Financial support from the EU (Directorate-General XII) is gratefully acknowledged.

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