ORIGINAL ARTICLE



Increased Emulsion Stability for Reverse Y-Shaped Sugar-Based Surfactants

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Abstract A series of reverse Y-shaped surfactants containing aromatic and aliphatic linkers to combine two short hydrocarbon chains and one carbohydrate head group was prepared. Liquid crystalline behavior, air-water interfacial properties, and efficiency as an emulsifier was investigated for each reverse Y-shaped surfactant. All reverse Y-shaped surfactants mediated higher emulsion stabilities for waterin-oil compared to common typical reference surfactants, reflecting an improved ability to cope with a curvature towards water. The introduction of a benzene ring into the linker substantially increased the affinity of the surfactant for hydrophobic media, resulting in improved emulsion stability for both water-in-oil and oil-in-water.

Keywords Reverse Y-shaped surfactant · Sugar-based surfactant · Double alkyl chain · Water-in-oil emulsion · Click chemistry

Supporting information A supplementary data section is provided, which includes full details of the synthetic procedures as well as characteristic data for intermediated products. The material also contains images of NMR spectra, enabling the evaluation of the surfactant purity and pictures of the emulsions before and after separation. Supplementary data can be obtained from the journal webpage.

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Introduction

Glycolipids, whether natural or synthetic, are non-ionic surfactants that are associated with independent environmental performance, biological degradability, and reasonable pricing due to the abundance of renewable resources [1–11]. Their application potential is not much restricted by salinity and pH variations [12]. During recent years, there has been intense interest in the development of new surfactants derived from natural resources. Moreover, the synthesis of surfactants has dramatically increased, reflecting the wide range of applications for these compounds, such as in cleaning and personal care products, cosmetics, emulsion paints, and polishes [6]. Therefore, many studies are now focussed on the industrial processes and formulation of these compounds, in an attempt to optimize the economy of sugar-based surfactants [1, 2, 13, 14].

Almost all synthetic straight-chain alkyl glycosides (AG) and their phase behavior properties have been extensively reported [15]. The same cannot be said for branched-chain alkyl glycosides [16-18]. The latter are considered as low-foaming surfactants compared to straight-chain AG [17, 19]. Over the past few decades, only a few reports had dealt with double-chain alkyl surfactants such as disodium 1,8-bis (alkyloxymethyl)-3,6-dioxaoctane-1,8-disulfates and disodium 5,12-bis (alkyloxymethyl)-4,7,10,13-tetraoxahexadecane-1,16-disulfonates (alkyl = octyl or decyl). Their structure consists of double-chain amphiphilic bearing two ionic head groups, with the molecular structure apparently shaped as a bundle of two typical single-chain surfactants. However, these designs reduce surface tension and enhance interfacial properties [20]. Besides the advantage of the double-chain in a surfactant, the presence of different linkages between

the head group and the hydrocarbon chain affects the surfactant behavior, possibly due to intramolecular H-bonding [21]. This refers not only to the functional group that mediates the connection, but in particular to small molecular spacers and linkers that may be introduced between the two surfactant-antipodes, i.e., head group and tail. The effect of different linkages including triazole and benzene in double-chain glycolipids is not clearly understood.

The current work investigated the benzene and triazole linkages with regard to flexibility on the phase behavior. We successfully synthesized a new series of double-chain glycolipids with different possibilities of linkage. This design of surfactants exhibits greater ability to lower surface tension and increase emulsion stability than could comparable single-chain surfactants, like alkyl polyglucosides (APG) [22] and alkyl triazole glycosides (ATG) [23].

Experimental Section

Chemicals

Chemicals were procured from various suppliers, as indicated in brackets: 3,5-dihydroxybenzoic acid (Merck 97 %), dihexylamine (Merck 99 %), 2-bromoethanol (Merck 95 %), β-D-glucose pentaacetate (Merck 98 %), sodium azide (Merck 99 %), 1-bromohexane (Merck 98 %), propargyl bromide (Sigma-Aldrich solution 80 wt% toluene). 3-chloroperbenzoic acid in (Sigma-Aldrich <77 %), and Allyl alcohol (Merck >99 %). All chemicals were used without further purification. The reaction products were purified by column chromatography using the flash technique on silica gel 35-60 mesh (Merck). TLC was performed on pre-coated plates of silica gel 60 (GF254 by Merck). Visualization was achieved by treatment with 15 % ethanolic sulfuric acid and subsequent heating.

Instrumentation

Structural identities of the reaction products were based on NMR spectra (¹H and ¹³C, recorded on a Bruker AVN-400 MHz spectrometer).

Surface tension measurements were performed at 25 °C under atmospheric pressure using a KSV Sigma 702 tensiometer. This instrument applied the DuNoüy ring method. The critical micelle concentration (CMC) was assessed as the intersection of the linear regressions of the surface tension against the logarithmic surfactant concentration for the concentration-dependent region as well as the concentration. The surface tension at this intersection is called the surface tension at the CMC (γ_{CMC}).

The lyotropic phase behavior of the glycolipids was investigated based on a contact penetration study observed under an optical polarizing microscope (OPM). The investigation was carried out at room temperature (about 27 °C), applying two different solvents, one of which was polar (water) and the other non-polar (1-undecanol).

Experimental Procedure

General Method for Click Chemistry I

A solution of sugar azide (4.5 mmol) and terminal alkyne compound (4.9 mmol) in 40 mL MeOH was treated with CuCl (40 mg). The solution was stirred at room temperature overnight and subsequently filtered through Celite. After the solvent had evaporated, the residue was purified by filtration through 5 cm silica gel. Elution with 2:1 ethyl acetate:hexane removed any remaining starting materials, after which the product was eluted with 4:1 methanol:CHCl₃.

General Procedure for Deacetylation II

Deprotection was carried out by using a catalytic amount of NaOMe in methanol. The mixture was stirred for 4 h at room temperature. The catalyst was removed by neutralization with Amberlite IR120 (H^+) before the solvent was evaporated to give the final surfactant.

Emulsion Stability

The water-in-oil emulsion preparation applied a composition of 1:19 ratio of water and oil (methyl laurate) containing 0.5 % (wt/vol) surfactant. The formulation was mixed with a homogenizer for approximately 2 min at room temperature at a speed of 14,450 rpm. The emulsion samples were stored at room temperature and monitored for phase separation over a few weeks. A similar procedure was applied for the stability investigation of oil-in-water emulsions with a 19:1 ratio of water and methyl laurate, and containing about 0.5 % surfactant.

Results and Discussion

Surfactant Synthesis

Glucose was selected and fixed as a hydrophilic domain for all reverse Y-shaped surfactants, whereas the hydrophobic domain comprised two C₆-hydrocarbon chains. This distribution of a C_{12} domain was most economical with respect to chemical synthesis. The investigated reverse Y-shaped sugar surfactants (compounds **2**, **4**, **6** and **8**) are

C₆H₁₃. H H

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HO

HC





Fig. 2 Synthesis scheme for the hydrophobic building blocks



displayed in Fig. 1. For purpose of comparison, two structurally closely-related single-chain sugar surfactants (9 and 10) were chosen, resembling previously investigated alkyl polyglucosides (APG) [22] and alkyl triazole glycosides (ATG) [23], respectively.

All surfactants were prepared with a sequential approach, in which the alkyl chains were first attached to a linker. The latter was subsequently coupled to the carbohydrate by glycosylation [2], alkylation of an amine [24] or CuAAC-based click-chemistry [25]. The synthesis of hydrophobic precursors is presented in Fig. 2, while the route to the carbohydrate precursors is shown in Fig. 3. All surfactants were obtained in overall yields ranging from 29 to 56 % based on glucose pentaacetate. Chromatographic purification was required due to the presence of remaining starting material and side products. The ¹H-NMR spectra of the surfactants indicated high purity for all products and confirmed the complete removal of protecting groups in the final surfactants.

ΔcC

όΑο

20 R₂ = CHCH₂ 21 R₂ = CH(O)CH₂ 22 R2 = CHOHCH2N3

Liquid Crystalline Behavior

The lyotropic liquid crystal phases were investigated by optical polarizing microscopy (OPM) at room temperature using a contact penetration technique [26, 27]. There was no liquid crystalline phase observed for surfactants 2, 6 and 8 when in contact with water. On their own the compounds appeared as viscous fluids (syrup) at room temperature. While no texture was observed for compound 2, probably reflecting an isotropic liquid based of rather low viscosity, compound 6 exhibited dark coloring, which made it impossible to observe liquid crystalline textures. In the case of compound 4, low water solubility was observed. This reflected the presence of a benzene ring, which increased the hydrophobicity of the surfactant. However, at the contact zone with water a phase showing birefringence emerged. The texture, depicted in Fig. 4b, suggested a hexagonal phase. The compound alone also exhibited birefringence, as displayed in Fig. 4a. However, in contrast to the water penetrated assembly, the fan shape texture for the anhydrous compound was more in line with a smectic A phase (lamellar). The observation of a smectic phase for the pure compound and an $L\alpha$ phase at low water concentration suggested that the aromatic ring with its two short alkyl chains could balance the surface area of the carbohydrate head group, thus promoting the lamellar phase.

Upon contact with the non-polar solvent 1-undecanol, surfactants **6** and **8** did not show visible solubilization. However, the exposure led to a swelling of the surfactant. No liquid crystalline phase was observed. Compounds **2** and **4**, on the other hand, exhibited significant solubility in 1-undecanol. Like **6** and **8**, **2** did not form a liquid crystalline phase in undecanol. **4** however exhibited a texture that closely resembled that of the pure surfactant, as shown in Fig. 4c, thus confirming the stability of the lamellar phase in the non-polar solvent.

In terms of molecular assembly, a preference for the lamellar phase was expected for reverse Y-shaped surfactants, owing to a balance of the domain surface areas, like that found in natural lipids. However, only surfactant **4** matched this expectation. The reason might be found in the rather short alkyl chains applied in this investigation, requiring substantial participation of the linker to balance the cross section of the sugar head group.

The presence of aromatic groups, reflecting both benzene and triazole, reduced the water-solubility of the surfactants. This was to be expected, because of a substantially increased hydrophobicity of the aglycon comprising not only the alkyl chains, but the linking unit as well. Surprisingly the addition of aromatic rings did not substantially enhance the interactions with an oil phase. This could be due to the selection of the latter, which did not contain aromatic components. The observed low interaction of surfactants involving triazole linkages and oil might discourage the application of click coupling for the preparation of sugar-based surfactants. A more extensive study involving different types of oil as well as a wider range of surfactants would be required to investigate the effect.

Air-Water Interface Behavior

The behaviour of the surfactants at the air-water interphase was investigated by systematic surface tension measurements over a wide range of concentrations, displayed in Fig. 5. With the exception of compound 2, for which a CMC could not be determined despite measurements at high concentration, data regarding the micellar assembly for the surfactants are tabulated in Table 1.

The CMC decreased by one decade upon introduction of a benzene ring, as seen in the lower values for compounds 4 and 8. The drastic reduction in the CMC could be due to the presence of the benzene ring, which had somehow increased the hydrophobicity of the surfactant considerably. On the other hand, the triazole affected the CMC significantly less. This observation was in line with previous observations for ATG [23]. A comparison of compounds 4 and 8 indicated a significant reduction of the minimum surface tension (γ_{min}) upon introduction of the triazole linkage, whereas the CMC itself was not much



Fig. 4 OPM texture for compound 4: a texture of the pure sample. b Water penetration scans showing hexagonal H1 and lamellar phases $L\alpha$ at room temperature. c After 2-h contact with 1-undecanol, indicating penetration of the solvent



Fig. 5 Surface tension measurements; 4 (filled squares), 6 (filled triangles), 8 (cross symbols)

Table 1 Surfactant behavior

Compound	CMC (mM)	$\gamma_{\rm cmc}~({\rm mN/m})$		
4	0.7	34		
6	3.7	37		
8	0.4	28		

affected. An explanation could be found in conformational constraints associated with the linkage of the carbohydrate head group to the hydrophobic domain, because of the directly-linked pyranose ring. Surfactant **8** however, consisted of additional carbon atoms and a triazole ring, resulting in greater flexibility. The lower surface tension of surfactant **8**, compared to **6**, could be attributed to the benzene ring, which increased the efficiency of the rather small hydrophobic domain. Surfactant **4** exhibited an unusual decrease of the surface tension above the CMC. Such behavior has been previously associated with the presence of poly-disperse micelles or the formation of a gel-monolayer at the air–water interface [28].

Emulsion Stability

With the exception of surfactant **2**, all surfactants exhibited reasonable good oil-in-water emulsion stability, requiring 5 days for the separation of a homogenized formulation in the absence of polymeric stabilizers. The data are tabulated in Table 2. The reverse Y-shaped surfactants exhibited a more significant increase of emulsion stability than did the single chain C_{12} -ATG **10** [23], approximately matching the emulsion stability obtained with lauryl glucoside **9**, which, as an APG model, was considered a good emulsifier [22]. These data suggested that the destabilizing effect of a triazole in an O/W emulsion could be compensated by splitting the hydrophobic chain into two units. A similar observation has previously been reported for the introduction of a second head group [29]. The poor emulsion stabilization of compound **2** could be because of repulsive

Table 2 Emulsion	on stability	(O/W	and	W/O)
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Surfactants no.	Time for phase separation		
	O/W (days)	W/O	
2	<1	30 min	
4	5	Gel	
6	5	$\sim 1 h$	
8	5	3 h	
9	6	15 min	
10	<1	10 min	

ionic interactions originating from a partial protonation of the amine in combination with the relatively weak hydrophobic effects of the short alkyl chains. On the other hand, all reverse Y-shaped surfactants exhibited improved emulsion stability for water-in-oil compared to the singlechained reference surfactants. This was expected, considering the molecular shape. The introduction of a second chain reduced the curvature of a surfactant assembly towards the hydrophilic domain, thus simplifying the reverse curving required for an oil-based emulsion. Surfactant 4 exhibited a remarkably good water-in-oil emulsion; no separation was observed within an observation period of 2 months. However, the initially fluid emulsion formed a gel after about 2 months. The latter required heating above 67 °C to liquefy again. The emulsion stability of 4 to that 8, which was remarkable low. It might reflect the effects of interacting head groups at the interphase, as well as enhanced flexibility in surfactant 8 with the introduction of the triazole ring which could prevent these head group interactions. Stability of an emulsion is highly related to the size of the droplet and their viscosity [30, 31]. However, there is no significant difference in the range of droplet size of our emulsions (additional information is in the supplement), so the most possible factor to describe the stability of emulsion of surfactant 4 may be related to the viscosity. This is also consistent with the separation time of the emulsion and gel form of the surfactant 4 as discussed above.

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