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Comparative study on interfacial and foaming properties of glycolipids in relation to the gas applied for foam generation†

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Glycolipids are biosurfactants with a wide range of structural diversity. They are biodegradable, based on renewables, ecocompatible and exhibit high surface activity. Still, studies comparing glycolipids and conventional surfactants in terms of interfacial properties and foaming performance are lacking. Here, we compared interfacial and foaming properties of microbial and enzymatically synthesized glycolipids to those of the widely-used, conventional surfactant sodium dodecyl sulfate (SDS). The enzymatically produced sorbose monodecanoate, as well as microbially produced di-rhamno-di-lipids exhibited high foam stabilizing properties, similar to those of SDS. However, sophorolipid and mono-rhamno-di-lipids did not produce metastable foams. An appropriate selection of head and tail groups depending on the application of interest is therefore necessary. Then, glycolipids can serve as an ecofriendly and efficient alternative to petroleum-based surfactants, even at substantially lower concentrations than *e.g.* SDS. Moreover, the influence of three foaming gases on the foaming properties of the glycolipids was evaluated. Slightly higher foam stability and lower coarsening rates were determined for sorbose monodecanoate when using nitrogen as the foaming gas instead of air. Foams generated with carbon dioxide were not metastable, no matter which surfactant was used.

Introduction

Surfactants are amphiphilic molecules with a wide range of applications in industry and in everyday-life, *e.g.* in petrochemistry, in cosmetics, in agriculture, in paints, coatings and detergents, as well as in the food industry.[1–3] Biosurfactants are gaining interest due to growing environmental awareness and the depletion of fossil resources. Glycolipids are a class of biosurfactants containing a sugar moiety and a fatty acid or fatty alcohol moiety. They can be produced based on renewables either by fermentation or by enzymatic synthesis, moreover they are biodegradable and non-toxic.[4–10] However, not only the production and environmental burden must be considered when selecting alternative surfactants, but also their properties compared to conventional ones. In recent studies glycolipids exhibited high potential as emulsion and foam stabilizing agents but comparisons of their properties with conventional surfactants are still lacking.[11,12] Critical micelle concentration

(CMC), dynamic interfacial tension, dilatational interfacial elasticity and dilatational interfacial viscosity are parameters of interest for characterizing interfacial properties as they are correlated with stabilizing effects on disperse systems.[13–18]

Foams are thermodynamically unstable systems with applications in various fields *e.g.* in detergents, cosmetics, foods, pharmaceuticals, agriculture, fire-fighting, oil recovery or wastewater treatment.[19–24] The demands on foamed products are just as diverse as their fields of application, but foam stability is one of the key parameters. While low foaming is desirable in detergents for washing machines, foaming is an important criterion for hand laundry detergents and shampoos due to consumer acceptance. For cosmetics, pharmaceuticals and foods high foam stability with narrow bubble size distribution is desired to achieve a homogeneous product with the expected perception properties and high storage stability.[19,20,22]

Surfactants are applied for stabilizing the dispersion of bubbles in a solution by lowering interfacial tension and by reducing aggregation and coarsening.[13–15,23–25] However, foam stabilization mechanisms are strongly related to the surfactant used.[13,15,24] Reported results of different laboratories may not be comparable as foaming properties are highly dependent on the experimental set-up, as well as the employed measurement protocols, and as disparities are observed between the different methods used.[26,27]

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In this study we compared two microbial glycolipids and an enzymatically synthetized glycolipid with the conventional surfactant sodium dodecylsulfate (SDS) in regard to interfacial and foaming properties. The structural formulae of the investigated molecules are depicted in Fig. 1. SDS was chosen as reference surfactant because it exhibits high foaming power and produces metastable foams.[28] As microbial surfactants, sophorolipid and a commercial rhamnolipid product, Rhapynal V3 800 were selected. Rhapynal V3 800 contains two different rhamnolipids that were further separated by flash chromatography in two fractions (mono-rhamno-di-lipids, R1, and di-rhamno-di-lipids, R3). Sorbose monodecanoate was chosen as a model of enzymatically derived glycolipid because it showed promising results in a previous study dealing with high foaming properties at low surfactant concentrations.[11] Foaming properties were evaluated using three different gases for foam generation, air, nitrogen and carbon dioxide, in order to analyze their influence. Nitrogen was chosen as it exhibits low solubility in water which is beneficial for foam stability and low coarsening rates.[29] Air was selected as second foaming gas due to ubiquitous availability and low price. Carbon dioxide was chosen because of its industrial relevance.

The aim of the study was to evaluate interfacial and foaming properties of glycolipids compared to SDS in order to assess whether they represent suitable, green alternatives to conventional surfactants in terms of foam formation and application.

Experimental

Materials

Lipase B from *Candida antarctica*, immobilized on acrylic resin (iCalB) was acquired from Strem Chemicals (Strem chemicals Europe, Germany). Vinyl decanoic acid was purchased from Tokyo Chemical Industry Co., Ltd. (TCI Europe, Belgium). Celite 545 sodium dodecyl sulfate and solvents (HPLC grade) were acquired from Carl-Roth GmbH & Co. KG (Germany). Sorbose was graciously gifted from Givaudan (France). 6-Decanoyl-D-glucose was purchased from Sohena GmbH (Germany). Rhapynal V3 800 was kindly provided by Biotensidon GmbH (Germany). Acidic, non-acetylated Sophorolipid were acquired from Biosynth s.r.o. (Slovakia).

Synthesis of sorbose monodecanoate

Sorbose monodecanoate was synthesized according to Hollenbach *et al.*[11] Briefly, 0.5 M sorbose, 0.5 M vinyldecanoate and 10 mg mL^{-1} iCalB were mixed in a 250 mL round bottom flask in 100 mL acetone at 50 °C and 600 rpm in a Laborota 4000 rotatory evaporator (Heidolph, Germany) at atmospheric pressure for 48 h.

Then, the obtained reaction mixture was filtrated with a Büchner funnel and the filtrate was washed three times with ethyl acetate. The glycolipid containing solvent was mixed with Celite 545 in a ratio of 1 : 3 (w/w) and the solvent was
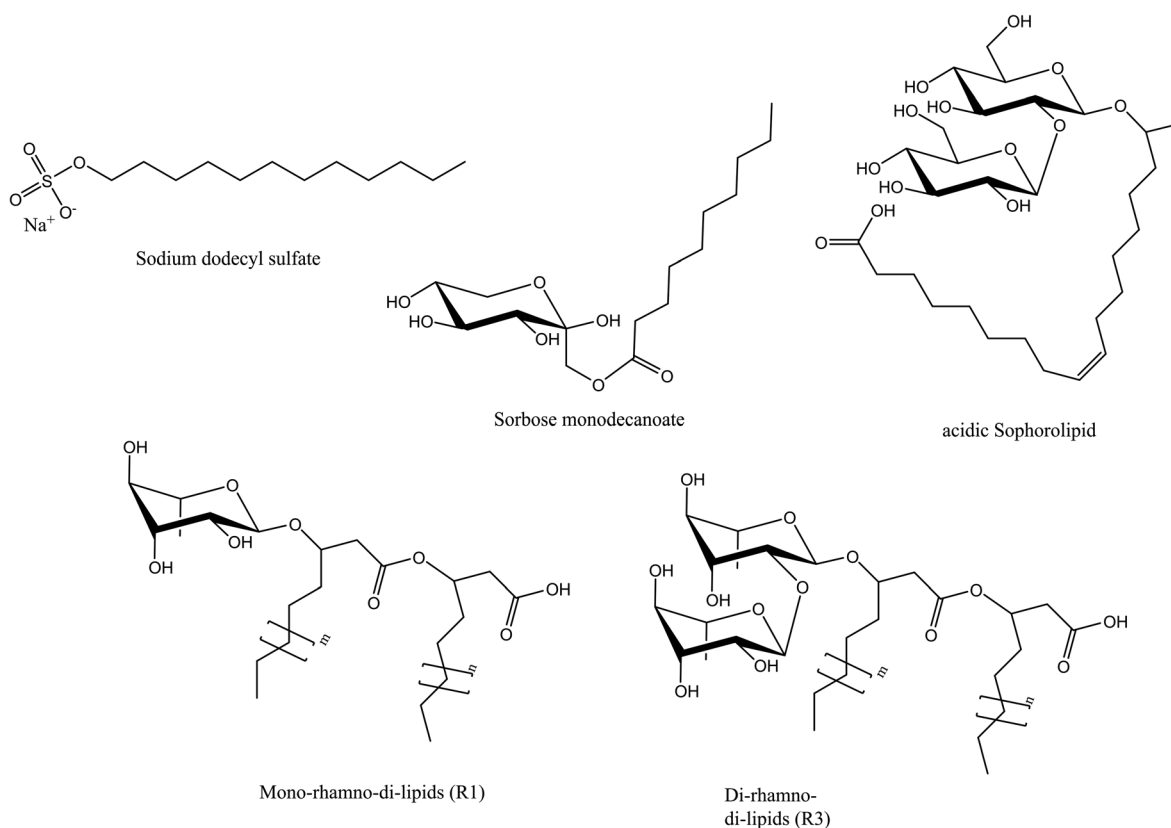

Fig. 1 Structures of the investigated glycolipids. Rhamnolipids were purified from the commercial Rhapynal V3 800, chain length of the β-hydroxyfatty acids is 8 to 14 carbon with $1 \leq m,n \leq 7$. Sorbose monodecanoate was synthesized enzymatically.

subsequently evaporated with a rotatory evaporator at 40 °C and 240 mbar. Solids were purified by flash chromatography using a Reveleris Prep® system from Büchi Labortechnik GmBH (Essen, Germany) and a Flash Pure Silica® column (40 g, 53–80 Å) using solid loading. Mobile phase consisted of chloroform (C) and methanol (M). A gradient was used to separate sorbose monodecanoate and residual substrates: starting from 100% C a linear gradient was applied to 96% C and 4% M within 2 min. This ratio was maintained for 9 min, followed by another linear gradient to 90% C and 10% M within 2 min. After maintaining this ratio for 6 min, a linear gradient to 75% C and 25% M within 2 min was applied and this ratio was hold for 4 min followed by a linear gradient to 100% M in 2 min and the latter was hold for 6 min. Peaks were collected and fractions controlled by TLC. Glycolipid containing fractions were collected and solvents were again evaporated with a S-Concentrator BaVC-300H from Helmut Saur Laborbedarf (Germany). The purity of sorbose monodecanoate was determined by HPLC-ELSD.

Flash chromatography of Rhapynal V3 800

Rhapynal V3 800 was dissolved in chloroform : methanol (2 : 1, v/v) and subsequently absorbed on a diatomaceous matrix (Rhapynal : Celite 545, 1 : 3) for further solid loading onto the flash chromatography. The obtained solid was purified using flash chromatography. For the purification of Rhapynal V3 800 a mobile phase of chloroform (C) and methanol (M) was used. The program started with an isocratic phase of 100% C for 3 min. Afterwards a linear gradient to 92% C was applied over 3 min, followed by a linear gradient to 90% C in 4.5 min, then up to 82% C in 3.6 min and further to 74% C in 4.5 min. Finally, a step gradient to 100% M was applied which was held for 3.5 min. Mono-rhamno-di-lipids (R1) eluted between 9-12 min and di-rhamno-di-lipids (R3) between 20–24 min. Peaks were collected and checked for rhamnolipids by TLC-analysis.

Thin layer chromatography (TLC)

For TLC analysis 5 µl of samples were spotted on Alugram® Xtra SIL G plates from Machery-Nagel (Düren, Germany). A mobile phase consisting of chloroform : methanol : acetic acid (65 : 15 : 2, v/v/v) was applied for elution. Compounds were visualized by anisaldehyde dying (anisaldehyde : sulfuric acid : acetic acid 0.5 : 1 : 100, by vol). A Jeneil JBR 425 standard (Saukville, Wisconsin, USA) was applied as a reference substance for the identification of the samples.

HPLC-ELSD

Glycolipids were quantified by reversed-phase chromatography using a Kinetex EVO C18 (2.6 µm, 250 × 4.6 mm) column from Phenomenex (Aschaffenburg, Germany) with an accompanying guard column (4 × 3.0 mm ID) of the same phase and an Agilent (Germany) 1260 series liquid chromatograph equipped with a quaternary pump, an autosampler and a column oven. HPLC analysis was performed according to Hollenbach *et al.* (2020)(11). Briefly, an evaporative light scattering detector from BÜCHI Labortechnik (Essen, Germany) was used for detection.

Mobile phase was a gradient of acetonitrile and water with a total flow rate of 1 mL min^{-1}.

Determination of interfacial tension and critical micelle concentration

Interfacial tension was determined by Du Noüy-ring method using a Lauda Tensiometer TD1 (Germany). The tensiometer was prepared by calibration with a 500 mg calibration weight. A test vessel was filled with at least 2 mL glycolipid solution and placed on the stage of the tensiometer and a Du Noüy ring (19.1 mm diameter) was submerged at least 2–3 mm below the solution surface and equilibration time of 15 min was applied. Then, the measurement was started by lowering the stage manually. The maximum normal force before the lamella formed between ring and solution breaks is the uncorrected interfacial tension σ_{unc}. The absolute interfacial tension σ_{abs} is obtained by multiplying σ_{unc} with a correction factor f. The correction factor f for the used ring was calculated as follows:[30,31]

$$f = 0.8759 + \frac{0.0009188}{\rho}, \tag{1}$$

where ρ is the density of the test liquid.

Dynamic interfacial tension and interfacial rheology measurements

The dynamic interfacial tension and interfacial viscoelasticity of all solutions were determined using a pendant drop tensiometer (PAT1, Sintaface, Berlin, Germany). The interfacial tension was calculated from the drop shape over a period of 10 000 seconds maintaining a constant surface area of 20 mm^2. Drops were produced from a cannula with 1 mm diameter.

The interfacial tension, interfacial viscosity, and interfacial elasticity were determined as described in Loglio *et al.* (2011) from oscillatory dilation experiments with frequencies of 0.05, 0.1, 0.33, 0.5 and 0.67 Hz.[32] The surface area of the drop was then sinusoidally dilated with an amplitude of 2 mm^2 for at least 10 oscillations, followed by an oscillation pause at a constant surface area of 15 min.

Foam generation

For foam generation 16 mL of surfactant solution (concentration = 2 × CMC) were filled into a 50 mL VitaPor suction filter funnel (Por.4, 10–16 µm) from ROBU Glasgeräte GmbH (Hattert, Germany). Foam formation was initiated by a gas flow of 60 mL min^{-1} through the funnel outlet. Either nitrogen, air or carbon dioxide were applied as gases. Gas flow was stopped at a foam height of 5.3 cm and the measurements were started.

Foam height measurements

Foam height was measured over a period of 60 min. From these measurements, the foam stability was calculated using the parameters r_5 and r_{60}:

$$r_5 = \frac{\text{foam height } (t = 5 \text{ min})}{\text{initial foam height}} \tag{2}$$

$$r_{60} = \frac{\text{foam height } (t = 60 \text{ min})}{\text{initial foam height}} \quad (3)$$

Bubble size distribution measurements

Bubble sizes were analyzed according to Völp *et al.* (2020)[33] using a VHX-950F microscope equipped with a VH-B55 endoscope both supplied by Keyence Deutschland GmbH (Germany). A KL 1500 LCD goose neck lamp from Schott AG (Germany) was used for illumination. The endoscope was equipped with a 90° angle mirror tube and inserted into a customized optical glass cuvette. Pictures were taken every 15 s over a period of 10 min at a height of 22 mm above the filter. The endoscopic pictures were evaluated using a software tool written in Matlab® (MathWorks®, Natick, MA, USA) based on a template matching method as described by Völp *et al.* (2020).[33]

Coarsening rate Ω was determined according to Briceño-Ahumada *et al.* (2017) from the slope of square Sauter diameter *versus* time plots $\left(\Omega = \frac{\mathrm{d}D^2}{\mathrm{d}t} \right)$.[13]

Determination of gas volume fractions

The gas volume fraction φ was determined based on conductivity measurement performed using a SevenCompact conductivity meter equipped with an Inlab® 738 ISM four-electrode conductivity sensor from Mettler-Toledo (Switzerland). The sensor was placed 22 mm above the filter membrane. The conductivity of the surfactant solution (before foaming) and foam conductivity (every 15 s over a period of 10 min) was measured. The relative conductivity κ_{rel} was calculated by:

$$\kappa_{\text{rel}} = \frac{\kappa_{\text{foam}}}{\kappa_{\text{solution}}}, \quad (4)$$

where κ_{foam} is the conductivity of the foam and κ_{solution} is the conductivity of the surfactant solution.

The gas volume fraction φ was calculated as described by Feitosa *et al.* (2005):[34]

$$\varphi = 1 - \frac{3 \times \kappa_{\text{rel}} \times (1 + 11 \times \kappa_{\text{rel}})}{1 + 25 \times \kappa_{\text{rel}} + 10 \times \kappa_{\text{rel}}^2} \quad (5)$$

Table 1 Thin layer chromatography of rhamnolipid samples

Rhamnolipid sample	R_{f}	Rhamnolipid type[a]
Jeneil standard	0.83	Mono-rhamno-di-lipids (R1)
	0.66	Mono-rhamno-mono-lipids (R2)
	0.46	Di-rhamno-di-lipids (R3)
	0.22	Di-rhamno-mono-lipids (R4)
Rhapynal V3 800	0.83	Mono-rhamno-di-lipids (R1)
	0.46	Di-rhamno-di-lipids (R3)
Rhapynal fraction A	0.83	Mono-rhamno-di-lipids (R1)
Rhapynal fraction B	0.46	Di-rhamno-di-lipids (R3)

[a] According to Arino *et al.* (1996), Syldatk *et al.* (1985); Amani *et al.* (2015)[35–37] R_{f} retention factor.

Statistical analysis

Results are given as mean ± standard deviation. Statistical data analysis was performed by ANOVA and Tukey test using the OriginPro 9.6 (version 2019, OriginLab, Nothampton, MA, USA) software. Results were considered significant if *p*-value was <0.05.

Results

In this study two microbial glycolipids, rhamnolipids and sophorolipid, and an enzymatically synthesized glycolipid, sorbose monodecanoate, were compared with the anionic surfactant SDS. In the case of rhamnolipids, the commercially available rhamnolipid mixture Rhapynal V3 800 and two purified fractions of it were tested. TLC analysis of Rhapynal V3 800 revealed that it consists of two rhamnolipids: R1 and R3 (Table 1), therefore it was separated by flash chromatography in the R1 containing fraction A and the R3 containing fraction B. R1 and R3 were obtained in a ratio of 1/5 (w/w) after purification. Interfacial and foaming properties of all surfactants were investigated.

Interfacial properties

Critical micelle concentration, dynamic interfacial tension, dilatational interfacial elasticity and dilatational interfacial viscosity were determined to characterize interfacial properties. Critical micelle concentration was determined in order to identify a suitable concentration for foaming experiments. Dynamic interfacial tension was earlier identified as crucial parameter for foam stabilization by glycolipids and non-ionic surfactants.[11,18]

Results of interfacial tension measurements are summarized in Table 2. CMC of all investigated glycolipids were considerably lower than for SDS. Interfacial tension of the investigated surfactants varied between 26–34 mN m^{-1}. All investigated surfactants lowered the interfacial tension to at least 35 mN m^{-1} within 5 s or less (ESI Fig. S1†).

Interfacial rheology of surfactants was investigated as foam stability and destabilization mechanisms are correlated with interfacial elasticity and interfacial viscosity. Higher interfacial elasticity and interfacial viscosity are reported to result in higher resistance of foams against foam rupture and coarsening and therefore slowdown foam decay.[13–17]

Table 2 Interfacial properties of investigated surfactants

Surfactant	CMC	Interfacial tension[a]
SDS	2.35 g L^{-1}	32.7 ± 0.1 mN m^{-1}
Sorbose monodecanoate	0.325 g L^{-1}	25.7 ± 0.2 mN m^{-1}
Rhapynal (not fractionated)	0.35g L^{-1}	29.0 ± 0.7 mN m^{-1}
R1	0.05g L^{-1}	26.5 ± 0.1 mN m^{-1}
R3	0.125g L^{-1}	34.2 ± 0.7 mN m^{-1}
Sophorolipid	0.23 g L^{-1}	34.0 ± 0.1 mN m^{-1}

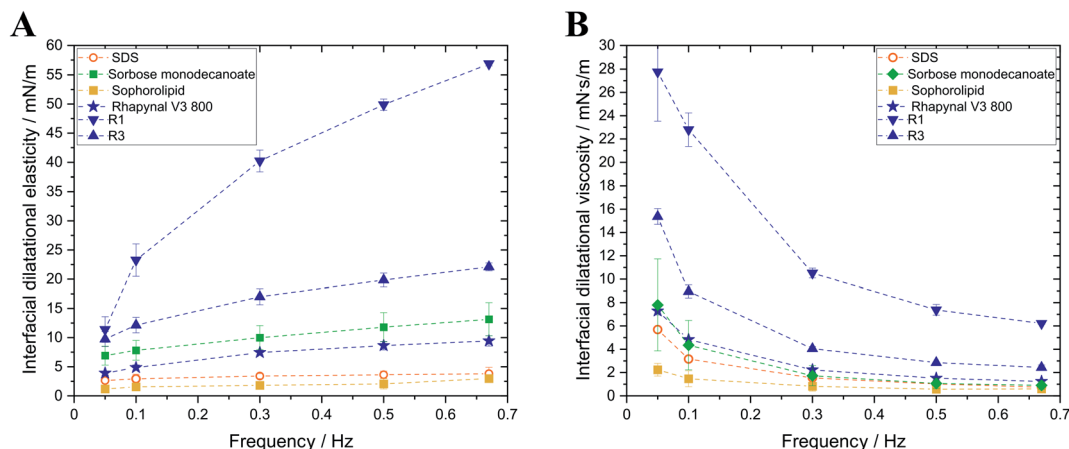[a] Concentration (surfactant) = 2CMC

Fig. 2 Interfacial rheological properties of investigated surfactants. (A) shows interfacial dilatational elasticity, (B) shows interfacial dilatational viscosity. R1 exhibits highest dilatational interfacial elasticity and viscosity while dilatational interfacial viscosity of the other investigated surfactants was similar.

Sophorolipid and SDS exhibited the lowest dilatational interfacial elasticities of the investigated surfactants (Fig. 2). Concerning the rhamnolipids, interfacial elasticity of commercial Rhapynal V3 800 (9.4 ± 0.9 mN m^{-1}; 0.67 Hz) is lower than that of both separated rhamnolipid fractions with R1 (56.9 ± 0.4 mN m^{-1}; 0.67 Hz) exhibiting highest interfacial elasticity. Evaluation of dilatational interfacial viscosities revealed similar findings. R1 showed highest dilatational interfacial viscosity of 6.2 ± 0.1 mN s m^{-1} (0.67 Hz) while the dilatational interfacial viscosities of SDS, sorbose mono-decanoate, sophorolipid and Rhapynal V3 800 exhibited no significant differences for high frequencies (0.6–1.2 mN s m^{-1}; 0.67 Hz).

Foam stability

Foam stability is an important parameter in designing foamed commercial products. The requirements for foam stability can vary considerably depending on the field of application.[19,20]

Foams made of sorbose monodecanoate solution and SDS solution showed highest transient foam heights while foam height of sophorolipid solutions decreased sharply with time (Fig. 3). For R3, more stable foams were observed than for the commercial Rhapynal V3 800. In contrast, foams stabilized by R1 were highly unstable and exhibited also lower foaminess as the initial foam height of 5.3 cm could not be reached despite its high interfacial elasticity.
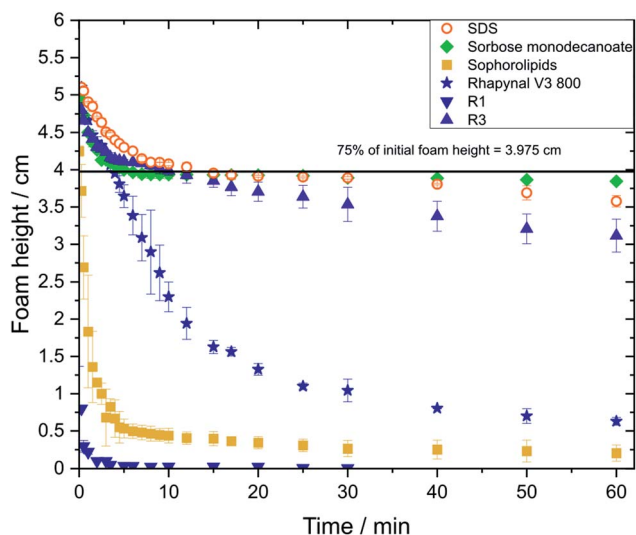

Fig. 3 Transient foam height of investigated surfactant solutions over time (foams prepared with nitrogen). Initial foam height was 5.3 cm. Foams stabilized by SDS, sorbose monodecanoate and R3 showed most stable foams while R1 and sophorolipid were weak in stabilizing foams.

Table 3 Foam stability parameters r_5 and r_{60}, as well as time where drainage-controlled foam decay ends t_{DEV}

Surfactant	Gas	r_5	r_{60}	t_{DEV}
SDS	N$_2$	0.81 ± 0.00	0.68 ± 0.01	20 min
	Air	0.81 ± 0.00	0.65 ± 0.02	20 min
	CO$_2$	0.41 ± 0.02	0.10 ± 0.03	
Sorbose monodecanoate	N$_2$	0.75 ± 0.00	0.73 ± 0.00^a	>60 min
	Air	0.75 ± 0.02	0.69 ± 0.01	40 min
	CO$_2$	0.19 ± 0.01	0.14 ± 0.01	
Rhapynal	N$_2$	0.69 ± 0.03	0.12 ± 0.01	2 min
	Air	0.73 ± 0.01	0.13 ± 0.03	2 min
	CO$_2$	0.18 ± 0.03	0.08 ± 0.00	
R3	N$_2$	0.78 ± 0.00	0.59 ± 0.04	12 min
	Air	0.77 ± 0.00	0.59 ± 0.02	12 min
	CO$_2$	0.24 ± 0.02	0.17 ± 0.03	
R1	N$_2$	0.01 ± 0.00		
	Air	0.002 ± 0.00		
	CO$_2$	—	—	
Sophorolipid	N$_2$	0.10 ± 0.02	0.04 ± 0.02	
	Air	0.11 ± 0.04	0.04 ± 0.01	
	CO$_2$	—	—	

^{a} r_{60} of sorbose monodecanoate shows significant difference between nitrogen and air.

Table 4 Parameters of bubble size distribution in relation to the gas used for foam generation

Surfactant	Gas	Coarsening rate Ω	Q_{3Span} (0.25 min)	Q_{3Span} (10 min)
SDS	N_2	0.007	0.41 ± 0.06^a	0.86 ± 0.07
	Air	0.007	0.38 ± 0.05^a	1.10 ± 0.26
Sorbose	N_2	0.008	0.89 ± 0.08	0.81 ± 0.12
monodecanoate	Air	0.017	1.30 ± 0.17	1.10 ± 0.13
Rhapynal	N_2	0.014	1.12 ± 0.09	1.07 ± 0.13
	Air	0.014	1.35 ± 0.27	1.16 ± 0.22
R3	N_2	0.008	0.91 ± 0.10	1.08 ± 0.09
	Air	0.015	1.01 ± 0.18	1.15 ± 0.20

[a] Q_{3Span} of SDS at 0.25 min is significantly smaller than all the other Q_{3Span} measured.

Comparing the foaming properties depending on the gas used for foam formation, only for sorbose monodecanoate solutions foam stability r_{60} was higher using nitrogen in comparison to using air while for the other investigated glycolipids both gases are merely the same (Table 3). With carbon dioxide, significantly lower foam stabilities were achieved for all 6 tested surfactants in comparison with the other two gases (ESI Fig. S2†). The r_5 value with carbon dioxide was below 0.5 for all surfactants investigated. When using carbon dioxide, no foam could be generated with R1, sophorolipid exhibited lower foaminess and the obtained foams collapsed within less than 5 min.

Regarding the phases of foam decay, the initial drainage-controlled foam decay, as characterized by a ratio of 1 for change in foam height to change in solution height,[23] is substantially longer for sorbose monodecanoate than for the other investigated glycolipids. The drainage-driven foam decay was longer for R3 (12 min) than for of Rhapynal (2 min). No drainage-controlled phase could be observed for foams made of R1 and sophorolipid solutions which collapsed almost completely within 5 min.

Concerning the investigated gases, a longer drainage-driven phase with nitrogen than with air was only observed for sorbose monodecanoate. For carbon dioxide, no drainage-controlled foam decay was observed with any of the surfactants investigated.

Bubble size distribution

Bubble size distribution is known to effect quality of foamed products by influencing perception properties, foam texture and flow, as well as storage stability.[21,22]

Determination of bubble size distribution was only possible for SDS, Rhapynal, R3 and sorbose monodecanoate due to the low foam stability of foams produced with sophorolipid and R1.

Foam stabilized by SDS, sorbose monodecanoate (using nitrogen) and R3 (using nitrogen) showed similar coarsening rates ($\Omega = 0.007$–0.009 μm^2 s^{-1}), while coarsening rates using air for sorbose monodecanoate and R3 were higher and like the coarsening rates of foams from Rhapynal solutions ($\Omega = 0.014$–0.017 μm^2 min^{-1}) (Table 4). Coarsening rates of foams made of SDS and Rhapynal solutions exhibited no differences between the two foaming gases, air and nitrogen (ESI Fig, S3†).

Initial bubble size was significantly higher for foams generated with carbon dioxide compared to those generated with nitrogen or air regardless of the surfactant used (ESI Fig. S4†).

The width of the cumulative volumetric bubble size distribution Q_3 is described by the span $\left(\text{span} = \dfrac{d90 - d10}{d50} \right)$. Initial Q_{3Span} determined at 0.25 min is significantly lower for foams made from SDS solutions than for the other investigated surfactants. There is a significant difference in the Q_{3Span} between 0.25 min and 10 min for SDS. However, no changes in Q_{3Span} over time were observed for the other surfactants. Furthermore, for all the investigated surfactants Q_{3Span} was the same no matter whether the foams were generated with air or nitrogen. With carbon dioxide no metastable foams were obtained and therefore Q_3 could not be determined.

Gas volume fraction

The gas volume fraction has a strong impact on the flow behaviour and perception properties of foamed products.[21,22] Conductivity measurements were only possible for the metastable foams and revealed no differences in gas volume fraction between foams generated with air and nitrogen. As with carbon dioxide no metastable foams were achieved, gas volume fractions could not be determined. The initial gas volume fraction of SDS (0.73 ± 0.01 with nitrogen; 0.74 ± 0.01 with air) was lower than that of the biosurfactant foams, while the sorbose monodecanoate foam (0.87 ± 0.01 with nitrogen; 0.90 ± 0.00 with air) had the highest initial gas volume fraction (Fig. 4). However, for all biosurfactant foams the gas volume fraction reaches values of 0.92–0.94 within 4 min, while it took about 8 min for the SDS foams to reach that level.

Discussion

Foams are classified into metastable foams and foams of low stability by the parameter r_5,[38] which indicates the foam height after 5 min compared to the initial foam height. Foams made of sophorolipid and Rhapynal fraction R1 exhibit r_5 values of less than 0.5 and are therefore of low stability. SDS, sorbose monodecanoate, Rhapynal and Rhapynal fraction R3 foams are classified as metastable instead. All foams generated with carbon dioxide are classified as nonstable as r_5 <0.5.
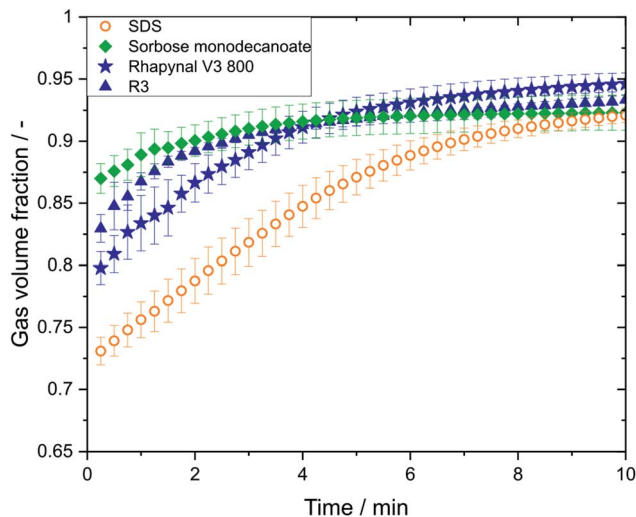
Fig. 4 Gas volume fraction over time of foams generated with nitrogen. SDS foams showed the lowest initial gas volume fraction while sorbose monodecanoate foams exhibited the highest initial gas volume fraction. No stable foams could be produced with sophorolipid and R1. The gas volume fractions of the different foams approached each other with time.

r_5 values of 0.8 were reported in literature for SDS[28,38] which is in good accordance with our measured value of 0.81.

Sophorolipid is classified as weak foaming agent, foams even when made from solutions concentrations up to 100 times their CMC.[4] The determined r_5 of sophorolipid is 0.1 and the r_{60} is 0.04 which confirms their poor foaming properties. Still, R1 exhibited even lower foam stability and foaminess than sophorolipid. In contrast, R3 stabilizes foams more effectively than R1 and exhibits r_5 and r_{60} values close to those found for SDS foams. In literature, foam half-life times, *i.e.* the time when foam height drops to half of its initial value, of 17–35 min are reported for 0.5–1.5% solutions of rhamnolipid mixtures.[39] Half-life time of foams made of R3 solutions were longer than 60 min and for foams of Rhapynal a half-life time of 10 min was determined. The differences in our measured foam half-life times and those reported in literature are due to different compositions of rhamnolipid samples and different concentrations. A higher CMC value was determined for Rhapynal than for the two purified rhamnolipids R1 and R3. This is related to the presence of other components in the commercial formulation. CMC of rhamnolipids is reported to decrease with increasing purity of the samples.[40]

Rhamnolipids cover a wide range of hydrophilic–lipophilic balance (HLB) with R3 being highly hydrophilic and R1 being the least hydrophilic rhamnolipids. HLB is reported to have a significant effect on surfactant properties, *e.g.* CMC values or emulsification, detergent properties and foaming behaviour.[40,41] R1 with its lower HLB exhibits weak foamability and lower foam stability than the more hydrophilic R3 and sorbose monodecanoate. High HLB values were also previously reported to correlate with higher foamability and foam stability.[42,43] However, the weakly foaming sophorolipid has a similar HLB to sorbose monodecanoate. A characteristic of the sophorolipid,

though, is the double bond in the fatty acid chain. Unsaturation was previously shown to reduce the foam stabilizing properties of glycolipids.[11] The double bond causes a change in the molecular geometry of the fatty acid chain and thus van der Waals interactions between the tails are weaker than for the saturated glycolipids Therefore, the alkene in the lipophilic group of the sophorolipid is an explanation for the reduced foamability compared to sorbose monodecanoate solutions despite similar HLB.

In the first couple of minutes of foam decay, foams made of SDS, sorbose monodecanoate, Rhapynal V3 800 and R3 show a similar behaviour. This phase is characterized by rapid foam drainage. No differences between these four surfactants were observed in this regime as herein drainage is not controlled by stabilizing effects of different surfactants due to the high thickness of the foam lamella.[38] Afterwards, stabilizing effects of surfactants start to play a role and the pattern of foam decay differs significantly between the different surfactants. However, the typical pattern of rapid foam drainage could not be observed for foams from sophorolipid and R1 solutions, most likely because these foams are so unstable that rupture of lamellae already starts during foam formation. Foam decay is characterised by three phases: the drainage driven phase 1, phase 2, where drainage and rupture coexist, and phase 3, where foam film rupture is the controlling mechanism.[23] In the case of R1 and sophorolipid, where phase 1 did not exist, phase 3 started already at early foam ages as the drained solution height remained constant.

Interfacial rheological properties, *i.e.* interfacial elasticity and interfacial viscosity, affect rupture of foam lamellae and therefore foam stability.[13,14,16,17] However, no correlation between interfacial rheological properties and foam stability, coarsening rates or the time of drainage-controlled foam decay could be observed in this study. Indeed, sophorolipid showed the lowest values for interfacial elasticity and interfacial viscosity and had low foam stabilizing properties. However, sorbose monodecanoate, showing 5 times higher interfacial elasticity than sophorolipid, exhibited high foam stability and the longest time of drainage-controlled foam decay albeit low interfacial viscosity. Moreover, R1 showed low foam stabilizing effects even though it has the highest interfacial elasticity and the highest interfacial viscosity of the investigated surfactants. In another investigation, it was already reported that foaming properties of enzymatically produced glycolipids cannot be directly correlated to interfacial rheological parameters.[11] In this study, we observed slightly lower interfacial elasticity (13.2 ± 2.9 mN m^{-1} at 0.67 Hz) for sorbose monodecanoate than previously reported in literature (16.4 ± 0.05 mN m^{-1}) which is most likely due to higher purity (98.5% *vs.* 96.4% in the previous study). Also interfacial viscosity was slightly lower for low frequencies but with increasing frequency interfacial viscosity gets similar to the ones previously reported.

Different gases are known to influence foams. Diffusivity and solubility of gases differ and have an impact on coarsening and foam stability.[29,44–47] In this study, we investigated the effect of pure nitrogen, carbon dioxide and the gas mixture air on foam stability, coarsening rates, and bubble size distribution of

different glycolipids and SDS. Foams generated with carbon dioxide showed much lower stability and bigger bubble sizes. This is due to the higher diffusivity and solubility of carbon dioxide in water and in good accordance to literature.[29,46,47] Moreover, carbon dioxide is reported to cause hydrolysis of SDS at the surface.[45,48] Similar effects of carbon dioxide may occur with glycolipids. Therefore, carbon dioxide is no suitable foaming gas for glycolipids and SDS in order to obtain metastable foams.

For sorbose monodecanoate and R3 coarsening rates of foams generated with nitrogen were smaller than the ones generated with air. However, no differences in the coarsening rates for foams made of Rhapynal and SDS were observed. Foam stability and drainage-controlled foam decay also showed different influences of the foaming gases depending on the surfactants applied. For these parameters, a difference between the foaming gases air and nitrogen was only found for sorbose monodecanoate. These results indicate that the surfactant type influences the role of the foaming gas. Surfactants producing an ordered interfacial surfactant layer are reported to show less pronounced differences between foaming gases than surfactants which produce a more disordered arrangement at the interface.[47] Sun *et al.* (2016) reported that the reduced foam stability and faster rupture of foam lamellae due to the oxygen present in air could be reduced by increasing the concentration of SDS.[47] This explains the similar behaviour of SDS foams generated with nitrogen and air as we applied SDS concentrations of twice the CMC in our study.

The results of this investigation indicate that certain glycolipids exhibit similar foamability and foam stabilizing properties as conventional surfactants. Foams made from sorbose monodecanoate solutions showed similar foam stability and coarsening rates as foams made from the conventional surfactant SDS which is known for its good foaming power and for producing metastable foams.[28] R3 solutions also produced metastable foams at similar coarsening rates as observed for SDS and sorbose monodecanoate, whereas the other two microbial glycolipids, R1 and sophorolipid, did not yield stable foams.

Conclusions

The aim of this study was to investigate the interfacial and foaming properties of glycolipids in comparison to the conventional surfactant SDS.

Sorbose monodecanoate, an enzymatically synthesized glycolipid, and the microbially produced R3, produced highly stable foams while sophorolipid and R1 showed poor foam stabilization. Sorbose monodecanoate exhibited similar foaming properties as the widely used conventional SDS indicating that glycolipids are competitive in foam stabilizing to conventional surfactants. Moreover, sorbose monodecanoate was more efficient in foam stabilization than SDS as substantially lower molar concentrations were applied.

Consequently, glycolipids present an ecofriendly and efficient alternative to petroleum-based surfactants for foam stabilization if the head and tail groups are chosen appropriately.

Author contributions

Conceptualization, R. H.; methodology, R. H. and A. V.; formal analysis, R. H.; investigation, R. H., S. O., A. D.; writing—original draft preparation, R. H.; writing—review and editing, R. H., A. D., A. V., J. R., K. O., N. W. and C. S.; supervision, N. W. and C. S.; funding acquisition, N. W. and C. S. All authors have read and agreed to the published version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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