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Foaming behavior of sugar-based surfactants: influence of molecular structure and anticipation from surface properties

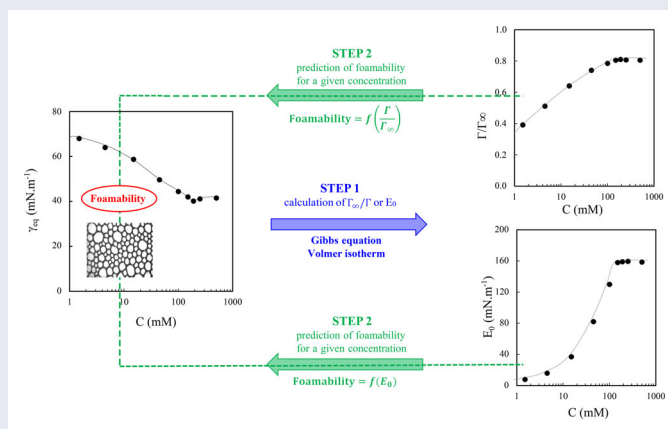
Rémy Bois^a, Isabelle Pezron^a, Patricia Rotureau^b, Elisabeth Van Hecke^a, Guillaume Fayet^{b#}, and Alla Nesterenko^{a#}

^aUniversité de technologie de Compiègne, ESCOM, TIMR (Integrated Transformations of Renewable Matter), Centre de recherche Royallieu, Compiègne Cedex, France; ^bINERIS, Parc Technologique Alata, Verneuil-en-Halatte, France

ABSTRACT

Sugar-based surfactants are a class of environmentally-friendly surface-active molecules well known for their functional performances, good biodegradability and reduced ecological footprint. Many previous studies have explored the surface properties of these surfactants. However, very little research has investigated their foaming properties. The present study examines the foaming behavior of 17 nonionic sugar-based surfactants with gradual structure variation. Foaming properties such as foamability, foam stability and maximum foam density were measured using the gas-sparging method. The influence of surfactant structure and concentration on foaming properties was evaluated. The data on surface adsorption properties, determined in the previous study, and foaming properties were then analyzed using a Principal Component Analysis. It was shown that the foaming behavior of glycolipids can be correlated to concentration and interfacial properties. Predictive models are proposed to anticipate the foaming behavior and provide a useful guide for screening the foamability of bio-based surfactants in various technological applications.

GRAPHICAL ABSTRACT



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KEYWORDS


Natural surfactants; sugar-based surfactants; surface properties; foaming properties; correlation

Introduction


One current trend in various industrial sectors is to reduce the use of petroleum derived and synthetic products, making essential the search for ecofriendly biobased alternatives. The market for surfactants derived from natural resources has steadily increased to counteract serious environmental concerns and satisfy consumer requirements. In addition to surface active properties, renewable surfactants should be less toxic, biocompatible, and biodegradable. Sugar-based surfactants are the most significant biomass-derived

surfactants used at an industrial scale.^[1–3] They have been widely suggested to replace synthetic surfactants in cleaning formulations and have already demonstrated their efficacy and environmentally-friendly nature in applications in cosmetics, household detergents, textile industries, and everyday chemicals.^[4,5]

In a wide range of industrial processes, and for various applications in everyday life, evaluating the foaming properties of surfactants is of great importance. Depending on the target application area, foams may or may not be desirable. Good foam performances are required for a number of

CONTACT Alla Nesterenko ✉ alla.nesterenko@utc.fr  Université de technologie de Compiègne, ESCOM, TIMR (Integrated Transformations of Renewable Matter), Centre de recherche Royallieu, Compiègne Cedex, France.

#These authors made an equal contribution to this work.

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valuable applications in cosmetics, cleaning formulations, food, and oil recovery. On the other hand, foams are unwelcome, and antifoams are used to destroy them in refineries, reactors, and the paper industry. The characterization of foaming behaviors is a challenging issue because the amount and quality of the foam produced is a function of many complex factors.^[6] Aside from the process parameters and concentration, the properties of foams are significantly affected by molecular structure and the nature of surfactants.^[7,8] Several structural parameters, such as length and flexibility of the hydrophobic group, size of the polar group, or rigidity of the linking group can impact surface viscoelasticity, as well as the compactness of the adsorbed surfactant monolayer, and thus, the properties of foam films.^[9] To obtain foam with the desired properties, selecting the appropriate surfactant structure is essential.

Recent research focused on the relationships between the molecular structure of sugar-based surfactants and their surface adsorption and self-assembling properties has complemented the considerable literature available,^[2] more dedicated to petroleum-based surfactants. In particular, the review by Gaudin et al.^[10] combined knowledge on structural features with surface properties and drew conclusions on how glycolipid structure influences surface properties. Predictive models have also been developed to anticipate the properties of surfactants based on their molecular structures,^[11,12] in particular for sugar-based surfactants.^[13–16] Anticipation of dynamic interfacial properties and foaming behaviors nevertheless remains less investigated until now. In a previous study, the relationship between the molecular structure of nonionic glycolipids and their dynamic adsorption properties at the liquid/gas interface was investigated in particular,^[17] and a new way for predicting dynamic properties has been described. This may be useful for reducing both the time and cost of experimental screening.

Despite the fact that active research on sugar-derived surfactants has been on the rise, relatively few studies on their foaming properties have been conducted. The foam-related properties of dodecyl β -maltoside, including the microscopic arrangement of surfactant at the air/water interface, rigidity, thickness, stability and viscoelastic behavior of foam film, have been widely investigated.^[18–23] Few studies have analyzed the foaming behavior of glycolipids with regard to their chemical structure. Mainly, the effect of alkyl chain length on foam formation has been reported for alkoxyethyl β -D-glucopyranosides (manual shaking),^[24] alkylglucuronamides (Ross-Miles method)^[25] and alkylpolyglycosides (manual shaking).^[26] Analyzing data from the literature demonstrates that the maximum amount of foam is obtained for glycolipids with 9–10 carbons in the alkyl chain. In terms of innovation in the field of natural surfactants, detailed and rigorous investigation of the foaming behavior of sugar-based surfactants in relation to their surface properties and molecular structure are still of interest.

Following our earlier work, the major purposes of the present study are: (1) to investigate the effect of sugar-based surfactant structure and concentration on their foaming behavior, and (2) to access deeper quantitative understanding of the relationships between the surface properties of sugar-based surfactants and their foaming behavior.

Combined with dynamic surface properties previously investigated for the same molecules,^[17] foaming properties were measured using the gas-sparging method. By using data mining approaches, correlations between foaming and the surface properties of surfactants were established. The proposed methodology makes it possible to anticipate the foamability of sugar-based surfactants directly from surface tension versus concentration curve. To our knowledge, such in-depth investigation on predicting the foamability of bio-based surfactants has not been carried out before.

Experimental section

Surfactants studied

Seventeen nonionic sugar-based surfactants with gradual variation in their molecular structure were investigated in this study: 11 molecules of commercial origin and 6 molecules synthesized in a laboratory. Alkyl β -glucosides as well as alkyl- α/β -maltosides (purity > 99%, HPLC) were purchased from Anatrace (Maumee, OH, USA). Octyl β -galactoside (purity > 99%, HPLC) was purchased from Carbosynth (Compton, Berkshire, UK). These molecules were used as received without further purification. Two families of synthesized surfactants (purity > 99%, NMR spectroscopy) were produced following the methodologies described in previous studies: alkyl-uronates series^[27] and sugar-based esters (C_8 - β MeGal and C_8 - α MeGlu).^[28] The structures of studied glycolipids are presented in Table 1.

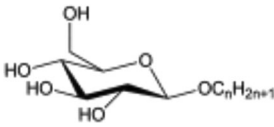
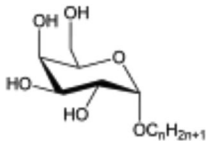
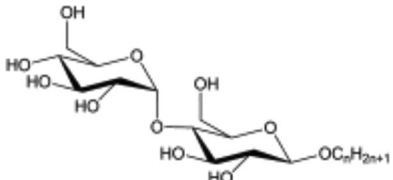
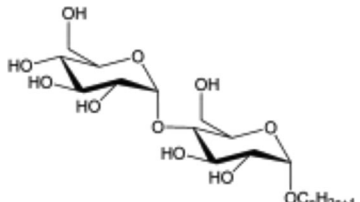
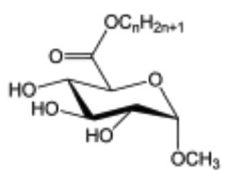
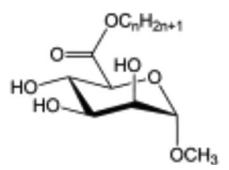
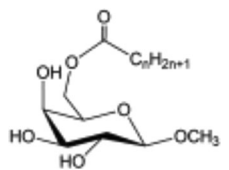
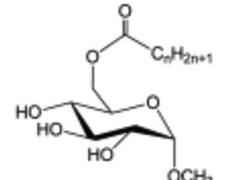
Surfactant solutions were prepared by dissolving a certain amount of each surfactant in water (millipore filtration, resistivity of 18.2 M Ω cm) to obtain a target concentration. In this study, the maximal glycolipid concentration for determining all surface and foaming properties was set at the critical micelle concentration (CMC). Consequently, all solutions analyzed were considered to be in the same thermodynamic state (monomer form). The concentration varied between 0.001 and 1 C/CMC. All the sugar-based surfactants studied were soluble in water at 25 °C.

The procedure for determining the different surface properties, summarized in Table SD1, and notably the CMC, equilibrium surface tension (γ_{eq}), excess surface concentration (Γ_{∞}), surface concentration (Γ), limiting elasticity (E_0) and maximum rate of surface tension reduction (V_{max}), is detailed in the previous study.^[17]

Determining foaming properties

The instrument used to generate and characterize the foams was a commercially available automated Foamscan apparatus (Teclis, France). The foams were generated by blowing gas through a porous frit at the bottom of a glass column (diameter 3.5 cm, height 30 cm) at a controlled flow rate. The conductivity measurement and image analysis made it possible to analyze different foam properties, such as foamability, foam stability, liquid fractions, drainage rate and foam density. For each experiment, 40 mL of surfactant solution at different concentrations was introduced into the

Table 1. Structures and CMC values of studied glycolipids.

Surfactant		<i>n</i> - carbon number in alkyl chain	CMC (mM)
Alkyl- β -glucoside ¹ (C _n - β Glc)		7	72.3
		8	21.2
		9	6.9
		10	1.9
Alkyl- α -galactoside ¹ (C _n - α Gal)		8	51.3
Alkyl- β -maltoside ¹ (C _n - β Malt)		6	150.0
		8	23.0
		10	2.0
		12	0.2
Alkyl- α -maltoside ¹ (C _n - α Malt)		10	1.5
		12	0.2
Alkyl (methyl- α -glucosid) uronate ² (Uro C _n - α MeGlc)		6	55.0
		8	6.0
		10	0.65
Alkyl (methyl- α -mannosid) uronate ² (Uro C _n - α MeMan)		8	5.5
6-O-alcanoyl methyl- β -galactoside (C _n - β MeGal) ³		8	8.5
6-O-alcanoyl methyl- α -glucoside (C _n - α MeGlu) ³		8	9.8

1: commercial surfactants, 2 and 3: surfactants synthesized in laboratory using methodology described in (Lu et al., 2016) and (Khan et al., 2011), respectively.

Table 2. Investigated regression formulas and best equations obtained for each foaming property by systematic investigation.

List of investigated regression formulas	Equations with best correlations	R ²	MAE
$y = ax^2$	Foamability = $0.23\log E_0 - 0.25$	0.88	0.11
$y = ax + b$	Foamability = $1.5\left(\frac{\Gamma}{\Gamma_{\infty}}\right)^2$	0.89	0.09
$y = a\sqrt{x} + b$	MD(%) = $11.3 + 2.4\log C$	0.79	1.0
$y = a\log x + b$	Stability = $3.45 - 1.90\log \gamma_{eq}$	0.54	0.18
$y = \frac{a}{x} + b$			
$y = ax^2 + bx + c$			

column equipped with frit porosity of grade P1 ($\phi=100\text{--}160\mu\text{m}$), at ambient temperature ($24 \pm 2^\circ\text{C}$). Foam was generated by injecting pressurized air (0.5 bar) at a flow rate of $300\text{ mL}\cdot\text{min}^{-1}$ for 40 s. The foamability or foaming capacity determined at the end of bubbling was calculated from the following equation:

$$\text{Foamability} = \frac{V_{\text{foam},0}}{V_{\text{gas}}} \quad (1)$$

where $V_{\text{foam},0}$ is the volume of foam at the end of gas injection and V_{gas} is the volume of sparged gas.

The total duration of one experiment was set to 30 min to measure foam stability. This property represents the whole behavior of the foam collapse process as a function of time. The stability was determined from the experimental plot $V_{\text{foam}} = f(\text{time})$:

$$\text{Stability} = \frac{\text{Experimental area}}{\text{Maximal area}} \quad (2)$$

Where the experimental area is under the plot $V_{\text{foam}}=f(\text{time})$ starting at the end of gas-injection and the maximal area corresponds to the ideal behavior in which any foam destabilization is observed throughout the experiment.

The total amount of liquid in the foam is characterized by maximum foam density (MD):

$$\text{MD} (\%) = \frac{V_{\text{solution},0} - V_{\text{solution},F}}{V_{\text{foam},0}} \times 100 \quad (3)$$

$V_{\text{solution},0}$ is the initial volume of liquid, $V_{\text{solution},F}$ is the volume of liquid at the end of gas-injection determined by conductivity measurement within the bottom solution.

The bubble size was monitored at the end of bubbling using a CDD camera, and the mean bubble radius was calculated using Cell Size Analysis (CSA) software.

All foaming experiments were carried out in triplicate and mean values were used for statistical analysis.

Statistical methods

Principal component analyses (PCA) were carried out using the SIMCA P+ software (SIMCA P+, Version 12.0. Umetrics AB, Umeå, Sweden). This method consists in projecting an initial set of independent variables (here, the concentration and surface adsorption properties), which can be more or less intercorrelated, into a reduced set of new orthogonal (i.e., non inter-correlated) variables, called principal components (PC). These projections represent new variables accounting for the maximum variance explained in the data set. The PCA results are presented with score plots

that represent the samples investigated (here, the surfactant solutions) in the new space defined by the first two PCs (which encountered most of the explained variance). The variables are represented on loading plots depending on their contribution to each PC. The samples can then be colored on the scatter plot to evidence possible classifications or trends connecting the variances investigated to a defined criterion or property (here, foaming behaviors).

Linear and non-linear regressions were also developed between the concentration and surface adsorption properties (x) and the foamability properties of the glycolipid solutions (y). Various mathematical formulae, presented in Table 2, were tested. Their goodness-of-fit was evaluated based on the determination coefficient (R^2) and the mean absolute error (MAE).

Foaming behavior of glycolipids

From a physical point of view, aqueous foam is defined by the nonequilibrium dispersion of gas bubbles in a low volume of liquid containing amphiphilic molecules. The stability of the dispersion produced is favored by the adsorption of these molecules at the gas/liquid interfaces and reduction of interfacial tension between them. Due to high interfacial energy, the foam system is thermodynamically unstable. During the destabilization phase, different self-destructive processes take place simultaneously in foam. The main phenomena limiting the foam stability are drainage of the liquid from the action of gravity, and foam aging mechanisms such as coalescence (film rupture) and ripening (inter-bubble gas diffusion due to pressure differences).^[29,30] These processes cause the transformation of foams into their most thermodynamically stable state, i.e., their complete destabilization back to the initial liquid solution.

According to existing literature, various factors may have an impact on foaming properties: experimental process parameters, liquid solution characteristics, and the nature and chemical structure of the foaming agent.^[6,31,32] The present study focuses on the effects of two key parameters which control foaming properties: surfactant chemical structure and solution concentration.

Influence of surfactant structure on foaming properties

First, the effect of surfactant structure on its foaming properties was investigated. For this comparison, an appropriate concentration of surfactant solution had to be chosen: the same molar (mass) concentration or the same C/CMC ratio. In the first case, the dynamic diffusion phenomena during

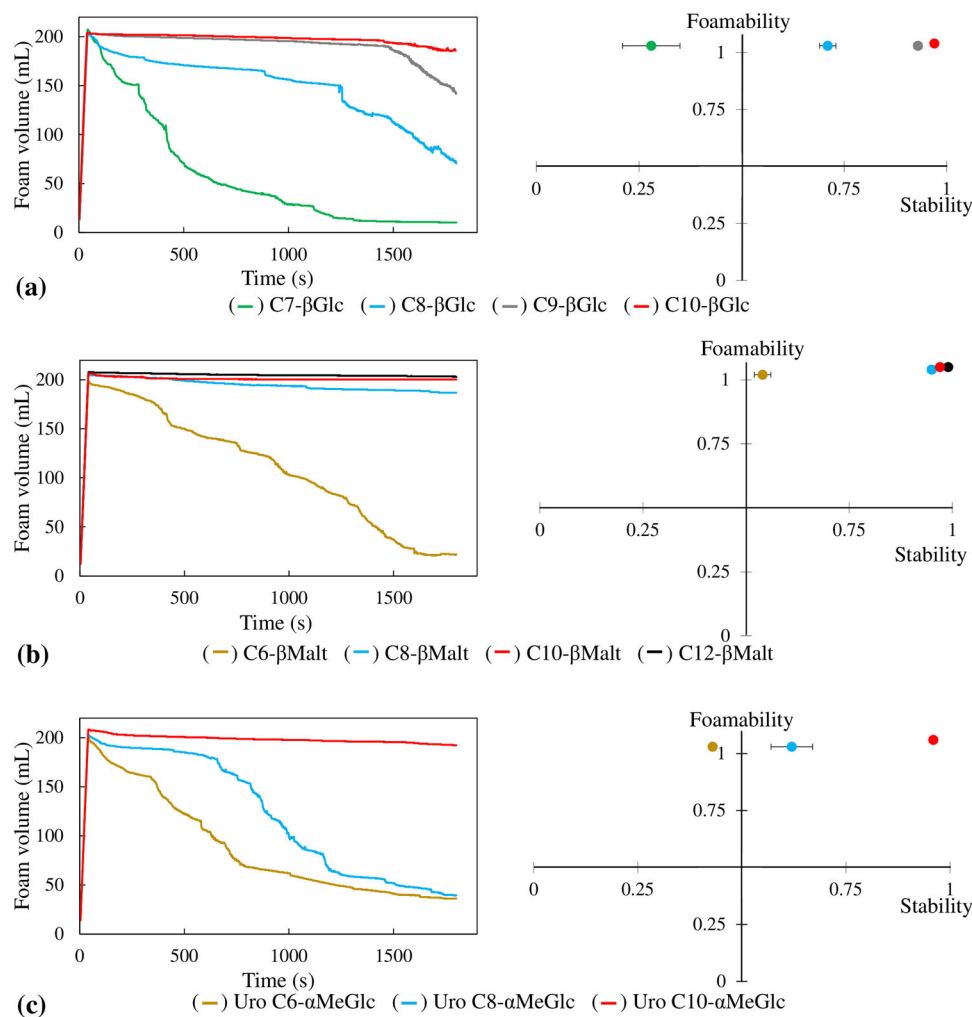


Figure 1. Variation of foam volume as a function of time (left) and mapping of foamability as a function of foam stability (right) for different sugar-based surfactants: (a) alkyl- β -glucosides, (b) alkyl- β -maltoosides and (c) alkyl-(α -methyl)glucoside uronates; C = CMC.

foam formation are similar for surfactants. More importantly, for a sufficiently high concentration, the role of depletion, which is related to the reduction of bulk concentration during foaming, is minimized.^[33] Nevertheless, comparing systems in different thermodynamic states can be tricky when the CMC of surfactants is very different. Below the CMC, surfactants are in monomer form and their adsorption at the gas/liquid interface increases with concentration.^[2] Above the CMC, the form of the surfactants aggregates, and the dynamic stability of the micelles can play an important role. In order to compare the real impact of surfactant structure on foaming behavior, in this study, foams were produced using concentration of solutions close to the CMC. In these conditions, the gas/liquid interface is not saturated with the surfactant molecules. Therefore, moderate foam volume and stability are obtained because of higher drainage, coalescence, and coarsening rates.^[34]

The foamability of glycolipid solutions, characterizing their capacity to produce foam, with variable structures as a function of time, is presented in Figure 1 (left side). These results demonstrate that the whole foam process consists of two stages: the generation of the foam (from 0 s to 40 s) and the destruction of the foam (from 40 s to 1800 s). The first stage corresponds to the gas sparging into the liquid. The

foam volume increases gradually whereas the liquid volume decreases. In the second stage, the foam volume declines because of different destabilization processes resulting in the increase in liquid volume. Classification of surfactants with different structures according to their foaming properties is proposed using the foamability-foam stability cartography (Figure 1, right side). Each cartography consists of four domains and makes it possible to characterize glycolipids into four groups: top right – surfactants with good foamability and good foam stability, top left – surfactants with good foamability and poor stability, bottom right – surfactants with poor foamability and good stability, and bottom left – surfactants with poor foamability and poor stability.

The results highlighted that at $C = CMC$ for the chosen foaming process and experimental conditions, the families of glycolipids investigated had similar foamability values (close to 1), independently of their chemical structure. This means that the totality of the injected gas is retained in the foam at the end of bubbling. However, a clear tendency could be seen in how the size of the hydrophobic part influenced foam stability for each family of surfactants. A rise in foam stability could be observed when the length of the hydrophobic chain increased for all the glycolipids studied. Curves for evolution of foam volume over time indicate that the

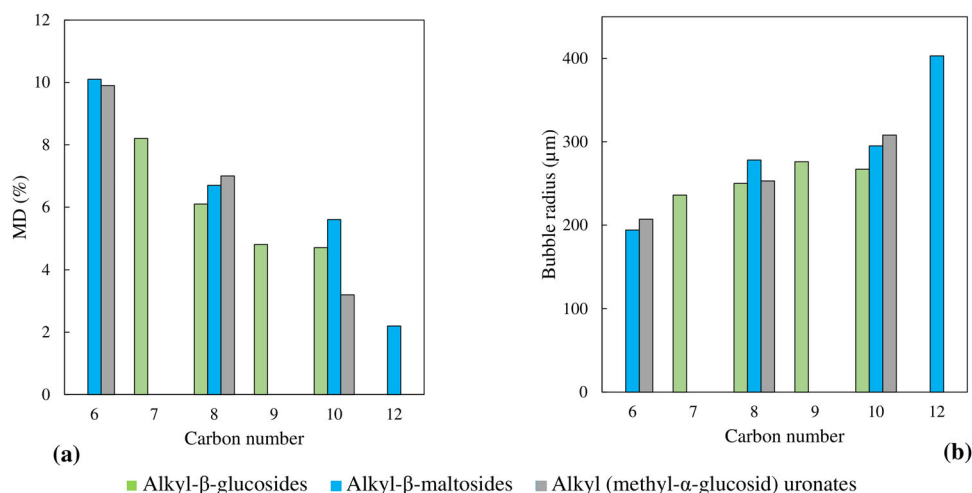


Figure 2. (a) Maximum foam density (MD) and (b) mean air bubble radius in foam for different sugar-based surfactants with various carbon atom number in alkyl chain; C = CMC.

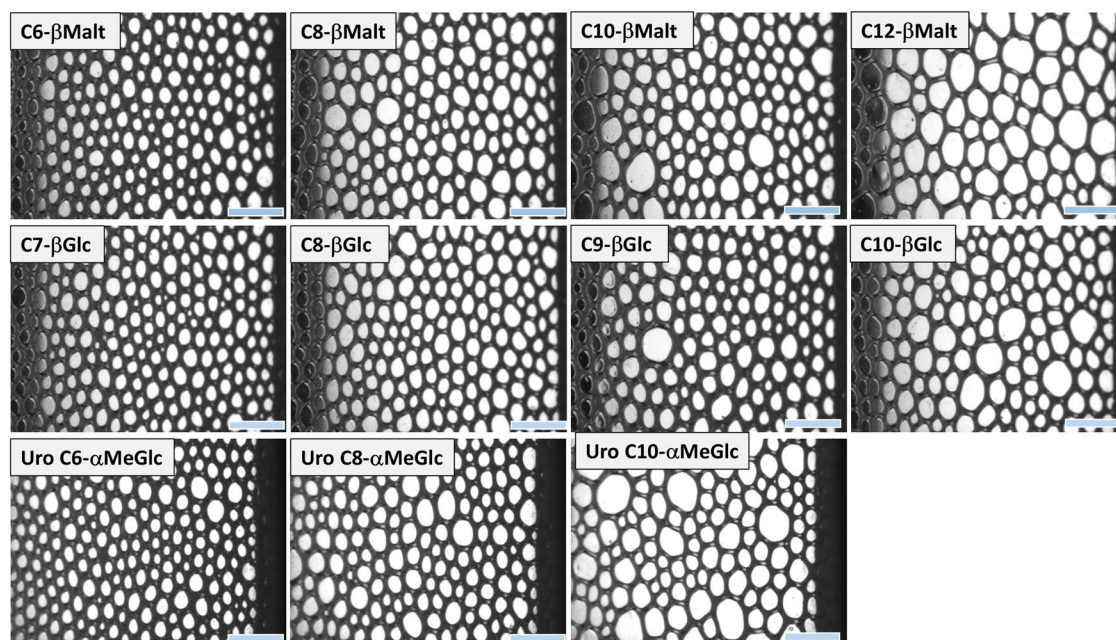


Figure 3. Bubble size analysis (CSA) images for different sugar-based surfactants with various structure at C = CMC. Pictures taken at the end of the bubbling. Scale bar – 1 mm.

destabilization rate for C₁₀₋₁₂ glycolipids is slower than that of C₆₋₈ glycolipids. For example, for the surfactants C7- β Glc, C6- β Malt and Uro C6- α MeGlc with short alkyl chains, stability was comprised between 0.28 and 0.43, whereas for C10- β Glc, C10- β Malt and Uro C10- α MeGlc stability was 0.96–0.99. The stability of foams close to 1 indicates that the volume of foam produced was unchanged during the analysis time (30 min). This observation is supported by optical images of foams at different periods of time (Figure SD1), showing that foams formed with short chain glycolipids are rapidly destroyed by film rupture and coalescence. On the other hand, foams stabilized by long chain glycolipids were mainly destabilized by the ripening mechanism. This probably could be linked to the effectiveness of long-chain surfactants in reducing surface tension and in reinforcing intermolecular van der Waals interactions and cohesive forces at the gas/liquid interface.^[9] Several studies have

suggested that the adsorption behavior of surfactants is enhanced by increasing alkyl chain length for the different families of surfactants.^[4,35] It has been reported that for sugar-derived surfactants, an alkyl chain length of 10 carbons is advantageous for reaching full potential in viscoelasticity and optimizing the stabilization of foam films.^[4,24,26]

Simultaneous occurrence of high foamability and low foam stability can be observed for solutions containing glycolipids with a short chain length (C7- β Glc, C6- β Malt and Uro C6- α MeGlc), despite their high CMC (72.3 mM, 150 mM, and 55 mM, respectively) corresponding to the highest molar concentrations among the solutions analyzed. On the contrary, more stable foams with C10- β Glc, C10- β Malt and Uro C10- α MeGlc were produced with solutions containing significantly lower amounts of surfactant: 1.9 mM, 2 mM and 0.65 mM, respectively. This fact is probably related to the low capacity of

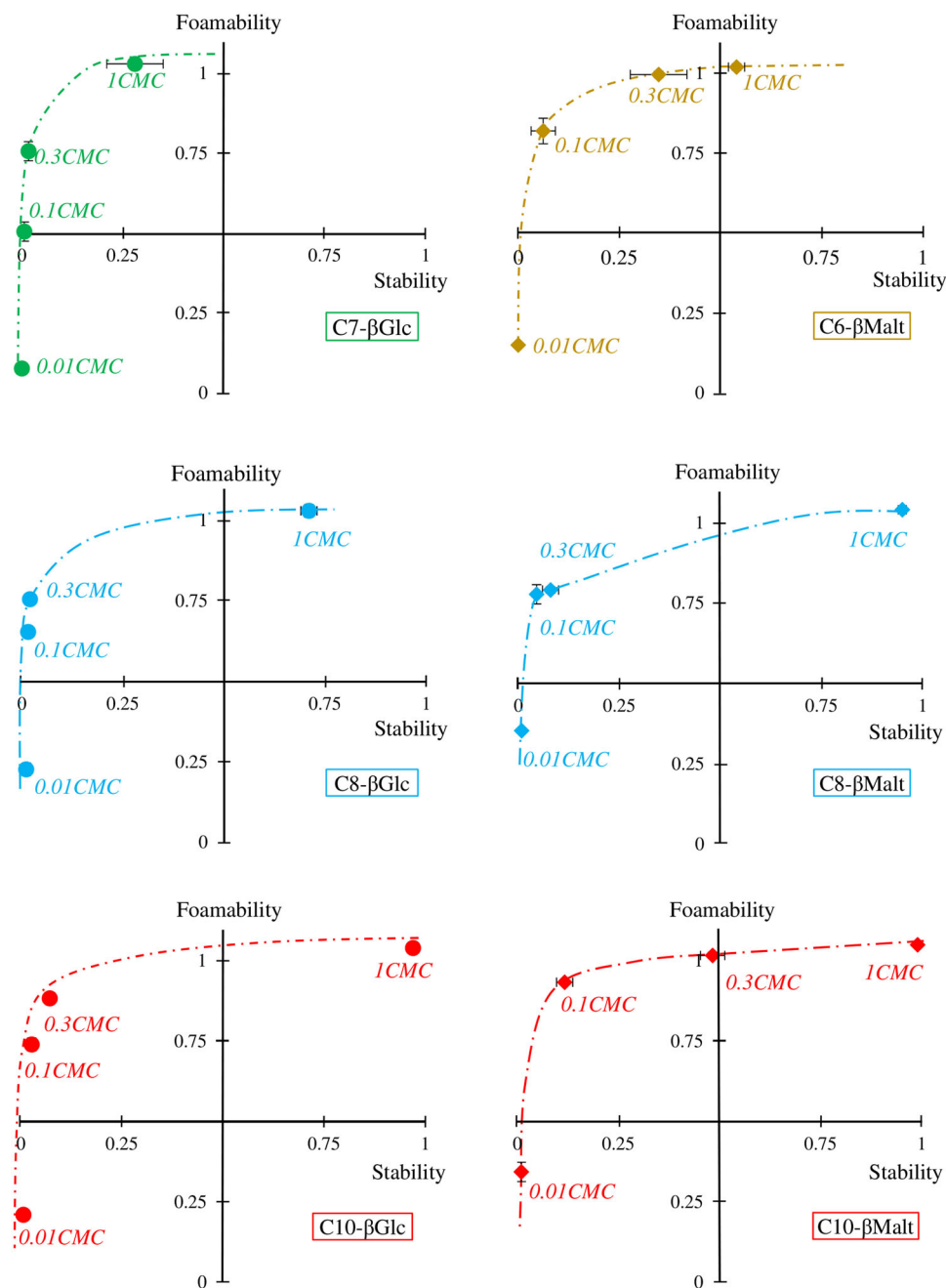


Figure 4. Mapping of foamability as a function of foam stability for different sugar-based surfactants at various concentrations. Dotted lines are used as a guide only.

surfactants to adsorb at the new gas/liquid interface, and form monolayers with sufficient packing density to efficiently stabilize this interface.^[9] The adsorption of surfactants seems to be the key factor for determining their foaming performances.^[19] Despite the significant difference in foam stability between glycolipids with variable chain lengths, no obvious differences were observed between surfactants with the same chain length and variable polar heads.

The effect of surfactant chemical structure on foam morphology can be characterized by measuring foam density and mean bubble size. Figure 2 presents the evolution in the maximal density of foam (MD) and mean air bubble radius in foam at the end of bubbling (Time = 40s). The total surfactant concentration of the solutions was once again

$C = \text{CMC}$. According to these results, no clear dependency was seen between the MD values and the structure of the polar head. For instance, the MD for C_8 glycolipids was 6.1–7%, and 3.2–5.6% for C_{10} glycolipids. However, the increase in hydrophobic chain length led to the formation of more dry foams with lower MD. Consequently, the mean size of the bubbles in the foam increased for long alkyl chain glycolipids (Figure 3) for three families of molecules. For the same foaming process, glycolipids with short alkyl chains formed a higher number of microbubbles per unit of volume, implying the creation of a larger interfacial area. On the other hand, the area of the gas/liquid interface produced, as well as bubble size, were affected by the molar concentration of surfactant. In the case of C_{6-8} glycolipids with a higher CMC, more molecules were available to

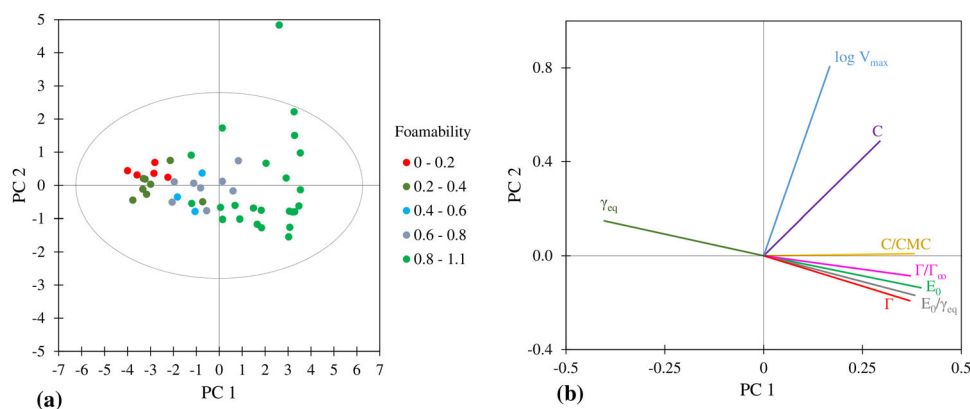


Figure 5. Score scatter (a) and loading (b) plots for the 48 sugar-based surfactant solutions. Solutions are colored according to their Foamability (FC) on the score scatter plot.

stabilize the newly-created gas/liquid interface. However, as highlighted above, the long-term stability of foam was strikingly influenced by alkyl chain length which, in turn, was controlled by molecular packing of the surfactant at the interface.^[36]

Influence of surfactant concentration on foaming properties

Second, how variations in concentration influenced foaming properties was investigated, based on the foamability-foam stability maps in Figure 4. At a very low concentration, $C = 0.01\text{CMC}$, the foamability of the surfactants was poor, and the bubbles coalesced faster than they stabilized due to an insufficient quantity of surfactant molecules. In all cases, the small amount of foam formed in these conditions collapsed very quickly after the end of bubbling and the stability of the foam was close to 0. The increase in total concentration made it possible to enhance foam stability and foamability for all glycolipids. An increase in bulk concentration led to rapid adsorption at the gas/liquid interface, which was formed easily. Consequently, more surface area was obtained, forming greater amount of foam. This result is in accordance with the literature on other types of surfactant in which the same tendencies have been observed.^[2,6,9]

When comparing surfactants with different structures, the evolution in foaming properties with concentration varies. For example, in the case of C7- β -Glc, foamability rises with concentration, whereas foam stability only increases slightly. The concentration of surfactant was lower or close to the CMC, and thus the gas/liquid interface was non-saturated in surfactant. Foam formation and stabilization depend mainly on surfactant diffusion and adsorption properties. As explained in the previous section, for short chain surfactants, reduced stability is related to weak cohesion of the alkyl chains and the stringency of the surfactant interfacial layer.^[9] Conversely, formation of foams with maximum stability close to 1 was observed for C10- β Glc and C10- β Malt. This indicates that the rate of drainage, coalescence, and ripening is slower for surfactants with longer hydrophobic chains.^[9,37]

To sum up, analyzing 17 glycolipids made it possible to highlight that for these particular experimental conditions, foamability is mainly affected by surfactant concentration; while foam stability seems to be predominantly influenced by the alkyl chain length of the surfactant. Higher bulk molar concentration of the surfactant leads to higher foam density and lower bubble size at the end of bubbling. It should also be mentioned that all measurements in this study were performed at 25 °C, but it is well known that temperature has an important influence on both the surface properties^[38] and foaming properties^[39] of surfactants. Further experimental investigations are needed to study the impact of temperature on the behavior of glycolipids.

Toward predictive trends with surface properties

To complement this analysis of foaming properties, trends were also looked for between the foaming behaviors observed and the static and dynamic surface properties measured on the surfactant solutions.

At first, a principal component analysis was carried out to map 48 surfactant solutions characterized from the 17 surfactants studied at different concentrations (detailed in [Supplementary Data](#), Table SD1), according to concentration and interfacial properties: concentration (C), its ratio on the surfactant CMC (C/CMC), maximum rate of surface tension reduction (in line with its logarithm, $\log V_{\max}$), surface excess concentration (Γ), relative surface concentration or ratio of Γ on the limiting adsorption at the saturation of the interface (Γ/Γ_{∞}), equilibrium surface tension (γ_{eq}), the limiting value of elasticity (E_0) and the E_0/γ_{eq} ratio. These properties were chosen notably on the basis of the detailed analyses of dynamic interfacial properties described in a previous work.^[17] The foaming properties of different solutions, such as foamability, maximum foam density and foam stability are summarized in the [Supplementary Data](#) (Table SD2).

As shown in the scattered plot in Figure 5a, the solutions were mainly distributed according to the first principal component (PC1), which encoded most of the variance (74%) associated with these physical and chemical properties among the solutions investigated. The loading plot for this

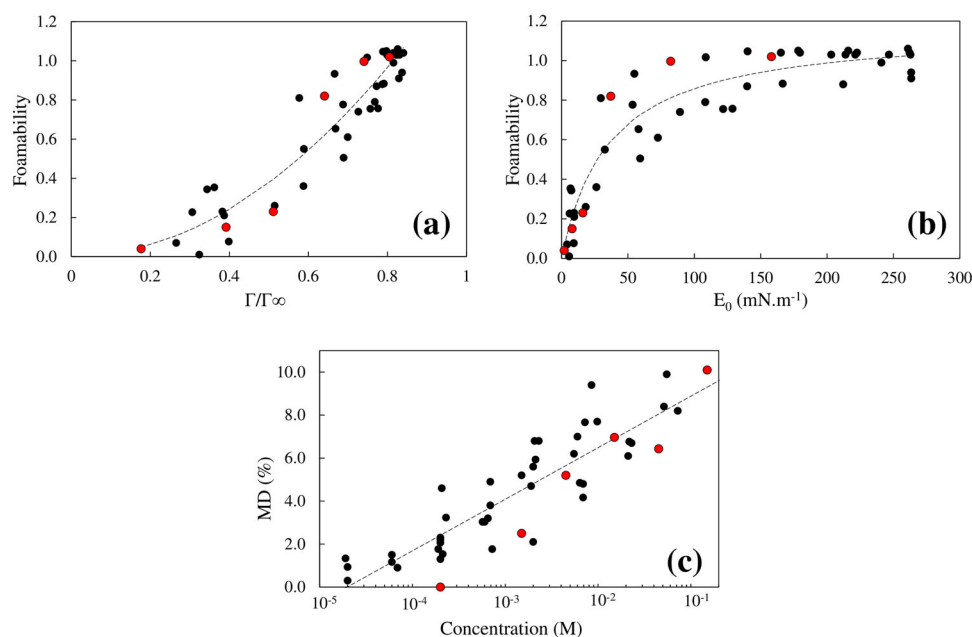


Figure 6. Experimental and model plots of the (a) foamability as a function of normalized surface concentration Γ/Γ_∞ , (b) foamability as a function of limiting elasticity E_0 and (c) maximum foam density as a function of the concentration: experimental data for all surfactants at different concentrations (black symbols), experimental data for C6- β Malt at different concentrations (red symbols), model plot (dotted line) obtained from corresponding equation in Table 2.

PCA (Figure 5b) confirms that all surfactant properties contribute relatively homogeneously to this first component, except $\log V_{\max}$, which is nevertheless the main contributor to the second principal component (PC2), accounting for 14% of the variance. The results confirmed that some properties are correlated: E_0 , E_0/γ_{eq} , Γ , Γ/Γ_∞ , according to the trends identified in a previous study.^[17] Interestingly, the C/CMC ratio introduced additional pieces of information compared to C.

The scatter plot highlights one solution falling outside the cloud of points constituted from the other 48 samples. It concerns the C6- β Malt surfactant at CMC. This singularity was observed in relation to the PC2 axis due to the high CMC value of this molecule (150 mM) compared to the other molecules analyzed ($\text{CMC} \leq 72.3$ mM). Nevertheless, it is not an outlier to the main principal component PC1, which encoded 74% of the variance observed (compared to only 14% for PC2).

When coloring the surfactant solutions according to their foamability, a trend was observed: the foamability values increased with the positive values of PC1. It can be noticed that the properties of E_0 , E_0/γ_{eq} , Γ , Γ/Γ_∞ had a strong impact on the foamability of glycolipid solutions. As shown in the Supplementary Data (Figure SD2), a trend was also observed for maximum foam density (MD) even if it was not only oriented by PC1 but also by PC2. For foam stability, the trend was less obvious, even if the lower stabilities were observed on the negative side of PC1.

This PCA analysis encouraged the search for quantitative relationships between the foaming behaviors and the physical and chemical properties of the surfactant solutions. Linear and non-linear regressions, following the mathematical forms, were then systematically considered to correlate the foamability behaviors (foamability, foam stability and foam density) with each of the concentration and interfacial

properties. The best regressions obtained for each foaming property are listed in Table 2 with their respective R^2 and MAE.

The satisfactory performances with high correlations ($R^2 > 0.88$) found for foamability imply the limiting elasticity, E_0 , and relative surface concentration, Γ/Γ_∞ . These results are in line with the trends observed with the PCA analysis, as it mainly contributed to PC1 of the PCA, which guided the trend observed.

The foamability was then compared with the Γ/Γ_∞ and E_0 parameters. In Figure 6a and 6b, the experimental points for 17 surfactants studied at different concentrations (48 solutions) appeared to follow the nonlinear trends encoded in the equations detailed in Table 2. It can be seen that surfactant solutions with higher Γ/Γ_∞ and E_0 made it possible to form a higher amount of foam. Our previous study reported the existence of a strong correlation between Γ/Γ_∞ and E_0 for nonionic glycolipids ($R^2 = 0.98$)^[17] which may explain the similar dependence of these surface parameters and foamability.

When focusing on each single surfactant, this increase in Γ/Γ_∞ and E_0 was also observed with concentration increases (red symbols for C6- β Malt in Figure 6). The surface excess concentration (Γ) increased for higher concentrations until the limiting adsorption at saturation (Γ_∞), which was constant for a given surfactant.^[2] This reflects the evolution in the Γ/Γ_∞ parameter with concentration. The increase in high frequency limit of elasticity, E_0 , with the rise in concentration demonstrates enhancement of the rigidity of the surface adsorbed film. The same dependence on concentration and E_0 was found by the authors for other surfactants at relatively low concentrations and was non-saturated in surfactant interface, whereas for high bulk concentrations ($C > \text{CMC}$) a plateau value of E_0 could be observed, indicating the maximum possible surface concentration.^[20,21,40]

Furthermore, in the case of E_0 , it can be seen that the model equation produced better performances for low values ($E_0 < 45 \text{ mN.m}^{-1}$) and high values ($E_0 > 200 \text{ mN.m}^{-1}$). Therefore, the predictive model proposed has good accuracy for glycolipids with high and low foamability. In the intermediate zone with surfactant solutions presenting E_0 between 30 and 150 mN.m^{-1} , a significant deviation between model and experimental results can be observed regarding foamability, which oscillated between 0.4 and 1. In this case, the destabilization phenomena, notably coalescence, could occur during bubbling. The simultaneous formation and break-up of bubbles made the foaming process complex and difficult to anticipate.

With regard to maximum foam density, the best correlation was observed in an equation involving $\log C$. This correlation is well illustrated in Figure 6c and fits with the observations made in the PCA analysis. The trend observed for MD on the PCA scatter plot was found to be influenced by both axes (PC1 and PC2). Accordingly, concentration C contributed significantly to the two first components of the PCA. As discussed in the previous section, higher concentrations of surfactant favor the formation and instantaneous stabilization of foam bubbles, limiting coalescence phenomena during bubbling. Bubbles of smaller size and, consequently, more densely packed and humid foams, were formed. The same tendencies were observed for the foams obtained using the gas-sparging method for other surfactants.^[41,42]

In the case of foam stability, no relevant model was found in accordance with the PCA observations, with the best model equation describing foam stability with γ_{eq} presented in Table 2 having a low R^2 coefficient (0.54). This may be due to the fact that this foaming behavior significantly depends on the initial structure of the foam, as highlighted by Boos et al.^[43] At the end of bubbling, foam amount and density vary for different surfactant solutions, and therefore the destabilization mechanisms that occur are very different. To go further with this analysis, foam stability with the same initial structure at the end of formation step should be compared.

In summary, for the foaming process studied and under given experimental conditions, the foamability of glycolipids can be anticipated using established model equations directly from surface tension versus concentration curves, by calculating the Γ/Γ_∞ and E_0 parameters. The bulk solution concentration makes it possible to calculate maximum foam density.

Conclusions

Anticipating the foaming behavior of surfactants is a key issue for various industrial applications. In this work, a systematic investigation of the foaming and surface properties of 17 nonionic biomass-derived sugar surfactants with gradual structure variation was carried out. The study was performed in two steps: measuring the foaming properties and establishing correlations between the foaming and surface properties of surfactants.

The impact of a surfactant's chemical structure and concentration on foaming properties such as foamability, foam stability and maximum foam density was examined. At a fixed concentration, $C = \text{CMC}$, the foamability was only marginally affected by surfactant structure and all molecules demonstrated values close to 1. As expected, a pronounced effect of hydrophobic part size was observed. Namely, the foam stability rose from 0.25 to 1 when the length of the hydrophobic part increased from 6 to 12 carbon atoms. These results indicate that the adsorption behavior of surfactants and their molecular packing at the liquid/gas interface play a key role in stabilizing the interfacial layer. Lower values of foam density were found, and consequently a higher bubble size for glycolipids with a longer chain length. For example, for alkyl- βGlc , the MD declined from 10.1 to 2.2% and bubble radius increased from 194 to $403 \mu\text{m}$, which can be related to different CMC values and thus bulk concentrations of glycolipid. The increase in concentration from 0.001 to 1 C/CMC led to higher foamability, foam stability, foam density and smaller bubble size in all the molecules studied.

Predictive trends were then looked for between foaming behaviors and interfacial properties. Different surface properties were measured experimentally or calculated by applying the Gibbs equation and Völmer isotherm state equation, as described in our previous study for the same surfactant solutions.^[17] Principal component analysis results highlighted that the foamability of glycolipids is strongly impacted by surface adsorption properties such as E_0 , E_0/γ_{eq} , C/CMC , Γ and Γ/Γ_∞ . Investigating the quantitative relationships between foaming behaviors and the physical and chemical properties made it possible to identify model equations with significant correlations ($R^2 = 0.98$), notably between foamability and E_0 , foamability and Γ/Γ_∞ , and foam density and bulk concentration. For this reason, the results obtained in this study provide a new means of anticipating the foamability of glycolipid solutions directly from the surface tension reduction curve versus concentration in a two-step procedure: calculation of E_0 or Γ/Γ_∞ and application of the model equations.

These findings may serve as a solid research basis for in-depth analysis of the complex relationships between the various properties of adsorption layers and the foaming properties of surfactants. The predictive models proposed can be applied to glycolipids with a molecular range similar to that of the molecules studied. In future studies, it would be of interest to expand this investigation to further experiments, enforce evidenced trends, correlate these properties with temperature, and consider other surfactant families and more complex systems, including salts or ionic surfactants, as adsorption mechanisms that can be modified.

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