



# Foams based on biosurfactants solutions. Part I. Influence of biosurfactant origin on foaming properties

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## Abstract

This paper reviews the literature on various natural and synthetic biosurfactants, which can facilitate the process of foam formation and stabilisation. Biosurfactants are an alternative to classical surfactants. For example, proteins, through their stabilising properties, can be used both in the food industry and in cosmetics, and this confirms their versatile properties and application in many areas of industry. Sugar-based foaming agents, on the other hand, are characterised by their ability to maintain high foam stability, and their natural origin and biodegradability are attractive substitutes for classical compounds of this type. This review aims to compare the effects of various compounds on the properties and stability of foams. Research on such materials will allow the development of innovative foaming technologies that minimise the negative environmental impacts of foaming compounds without losing the properties of the final product.

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Biosurfactants, Foam, Foamability, Foam stabilisation, Proteins, Sugar-based foaming agents, Rhamnolipids, Glycolipids, Synthetic biosurfactants.

## Introduction

Foam is a stable, gas–liquid dispersed structure that forms on the surface of a liquid or inside a solid substrate. The stability of foam is closely related to its colloidal stability, which involves the maintenance of a

dispersed phase within a continuous medium without the phases separating. Ensuring colloidal stability is essential for preventing the collapse of the foam and maintaining its desired properties over time [1,2]. The properties of foam, such as its density, durability and ability to form stable bubbles, make it extremely useful. The key components that enable foam formation are surfactants [1–3]. However, it must be remembered that the method and conditions of foam production are equally important for the obtained foam fraction's physicochemical properties, morphology, and stability [2].

Surfactants are broadly defined as substances that reduce the surface tension of liquids (including the oil-water interface) or liquids with gas, enabling the formation of a stable emulsion or foam (which is why they are referred to as foaming compounds in this context) [1–3]. Properties that enable surfactants to perform this function include lowering the surface tension of liquids, forming monomolecular layers at the interface and stabilising bubbles in liquids [1].

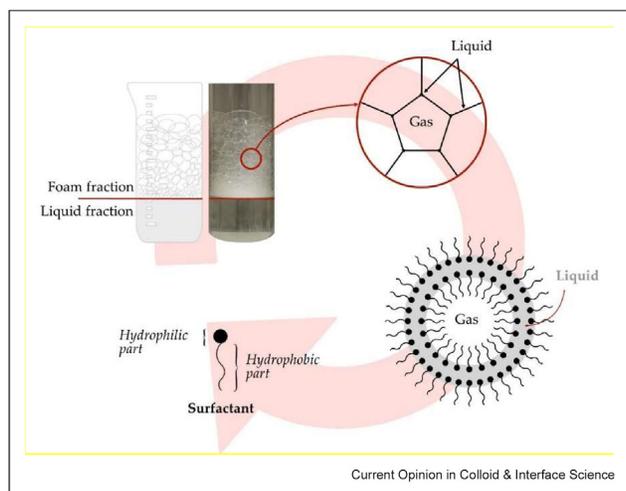
The ability of surfactants to lower the surface tension of liquids is due to their structure and physicochemical properties [3]. These compounds contain two key domains, i.e., a hydrophilic domain, which is prone to interact with water, and a hydrophobic domain, which avoids contact with water. When surfactants are introduced into liquids, their molecules are distributed at the phase interface. The phase interface is where two different states of matter meet. In the case of liquids, the phase interface marks where a liquid meets another state of matter - for example, a gas. The first phase is the liquid since it is the dominant phase within the system. The second phase is the gas phase, which is above the surface of the liquid. Important physical and chemical phenomena occur in the phase interface, such as foam formation due to surfactants. The hydrophilic domain of these compounds remains immersed in the liquid, while the hydrophobic domain faces outward, thus avoiding contact with water. This surfactant positioning contributes to forming a so-called monomolecular layer at the interface. Its compounds (their hydrophilic domains) interact with the water molecules on the surface, thus reducing their surface energy. This, in turn, allows

the formation and stabilisation of bubbles in the liquid, thus creating foam [3].

The scheme of foam formation using a foaming agent (surfactant) has been presented in Figure 1.

The wet foam formation consists of the gas dispersion in the solution, in which the bubbles move under buoyancy and accumulate on the solution interface. The ability to create a stable liquid foam is directly related to the degree of surfactant adsorption coverage of the interface of the bubbles. Foams are thermodynamically unstable systems influenced by many external factors. The main processes affecting foam stability are liquid leakage from the foam film, coalescence of adjacent bubbles and gas diffusion between bubbles in the foam fraction [1,2]. Liquid drainage is the primary physical process in liquid foams under gravitational acceleration. The rate of fluid drainage is also influenced by the viscosity of the liquid and the capillary pressure between adjacent bubbles. The consequence of liquid leakage is the gradual thinning of the foam film. When its thickness exceeds a specific critical limit, the foam falls apart. Coalescence occurring in foam systems combines small gas bubbles into larger ones, reducing the degree of dispersion of the system. This leads to the weakening of the foam structure and its eventual collapse. However, in liquid foams produced from highly viscous liquids (where the processes mentioned above of drainage and coalescence are significantly slowed down), lead the third foam fraction destruction process, gas diffusion between adjacent foam cells (also called “coarsening” or “Oswald ripening”). The processes described above are generally called foam ageing.

Figure 1



Structure–property relation in foams, where the properties of molecular building blocks control macroscopic properties at the interface.

Surfactants, as a group of chemicals that exhibit surface activity, also include biosurfactants, which are an important part of them. There are two main types of biosurfactants: natural and synthetic. Natural biosurfactants are chemical compounds of biological origin that exhibit surface activity [4,5]. Natural biosurfactants can be derived from various sources, such as microorganisms (e.g., bacteria, fungi), plants or animal organisms, and include a diverse group of compounds including, among others, proteins, lipids (including glycolipids or phospholipids), sugar-based chemicals or also lipid–protein complexes. On the other hand, synthetic biosurfactants are compounds obtained by chemical synthesis that demonstrate non-toxicity to humans and the environment and biodegradability [6,7]. It is crucial in their manufacture to meet safety and sustainability requirements while maintaining their surface properties. Examples of such surfactants include a variety of substances, such as alkyl-glucosides [8] or sugar esters [9].

This review paper comprehensively characterises a variety of biosurfactants that are vital components in the foam formation process. Importantly, in this review, the term “biosurfactants” is used broadly, including classic biosurfactants and hydrocolloids that demonstrate surfactant properties. Hydrocolloids such as agar, alginates, xanthan gum, carrageenan, or pectin constitute biopolymers that can form gels and stabilise emulsions. This is due to their macromolecular structure, making them important materials with surfactant activity. Hence, to comprehensively discuss materials with surface activity, hydrocolloids and classical biosurfactants have been discussed in the article. The paper aims to present the diversity of biosurfactants and their role and application in foam production, which is essential to developing new technologies in this field. The article describes the latest work carried out in this research area, highlighting its ongoing development and its importance to modern science.

### Foaming proteins

The first reports about the surface activity of proteins come from the 1930s. It has already been shown that some proteins adsorb in a specific way, creating a thick surface layer and significantly lowering the surface tension. Due to the protein’s complex structure, it was impossible to determine the conformation of adsorbed molecules of these biosurfactants [10]. Only the introduction of sophisticated research methods, i.e. neutron scattering [11], allowed in selected cases to determine the exact structure of the adsorption layer for some proteins, e.g., for  $\beta$ -lactoglobulin [12]. The surface activity of proteins is strictly related to a balance between their hydrophobicity and charge residues in the polypeptide chain [4,10]. Therefore, the most common way to increase protein hydrophobicity is to reduce surface

charges due to the addition of electrolytes or pH adjustment [13]. It should also be pointed out that these biopolymers can aggregate, promoting the stabilisation of the foam structure. Hence proteins constitute promising agents in fabrication of stable foams [14], even in construction industry [15].

In the case of protein-based foams, much of the work has been devoted to plant-derived proteins [16]. For example, in the article [17], studies on the foam-stabilising properties of various fractions of mung bean protein are presented. The following fractions were examined: dry fractional fine fraction (FF), protein fraction with mildly purified protein content (PM), globulin-rich fraction (GLOB), albumin-rich fraction (ALB) and protein colloids (COL). The foam-forming ability of protein fractions was investigated by evaluating the amount of excess foam after whipping and the size of bubbles after nitrogen spray. The globulin-rich FF, PM and GLOB fractions showed lower excesses than the ALB fractions. Bubbles were larger for FF, PM and GLOB (0.39 mm, 0.34 mm, 0.20 mm) than for ALB (0.06 mm). PM stabilised foam had the smallest air bubbles (0.06 mm) and the highest excess among the GLOB fractions. It was also demonstrated that large starch granules in FF may have affected the anti-foaming process.

Another promising foaming protein is soybean protein. For example, Wang *et al.* [18] investigated the impact of electric field intensity on foaming properties of soybean 7S globulin. The conducted research showed that moderate electric field (MEF) treatment improved the foaming properties of soybean 7S globulin. The electric field positively affected the formation of aggregates, leading to changes in the spatial structure of the protein. The protein  $\beta$ -sheet content was reduced, and the partially buried tryptophan side chain groups originally buried inside the 7S globulin molecule were exposed to polar conditions. Due to the MEF treatment, the protein unfolded and exposed hydrophobic side chains, which previously were inside the globulin. As a result, the hydrophobicity of the protein rose. Soybean 7S globulin aggregates subjected to MEF were characterised by higher solubility, higher turbidity and larger particle size than the protein in its natural state. The results suggest that MEF treatment may be an effective method to improve the foaming properties of 7S globulin.

Xia *et al.* [19] demonstrated that the proteolysis of  $\beta$ -conglycinin 7S of soy protein isolate (SPI) increased surface activity and better foaming properties. Peptides larger than 14 kDa enhanced the stiffness of the air–water interface, while those smaller than 14 kDa hindered the formation of the interface network. Hydrolysates with a lower degree of hydrolysis demonstrated much better foam stability than those with a

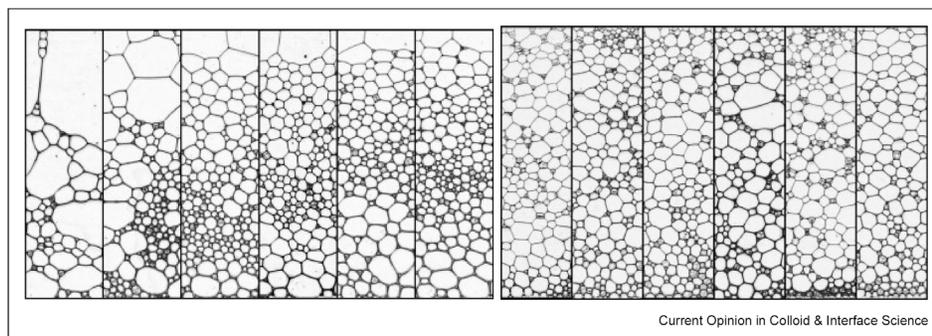
higher degree of hydrolysis. Hence, it may be concluded that selective proteolysis of  $\beta$ -conglycinin may improve the foaming properties of SPI.

So far, performed research has demonstrated that proteins of animal origin, including, among others, bovine albumin [20] and egg white protein [21,22] have the foaming ability.

Krzan *et al.* [20] compared protein foam properties and possible applications with classic synthetic surfactants. They generated foams based on BSA (Bovine Serum Albumin) and SDS (sodium n-dodecyl sulfate) solutions were compared under the same generation conditions. BSA is a serum protein obtained on a large scale from beef blood. It is commonly used in biochemistry and molecular biology as a neutral, non-reactive protein that does not interfere with most reactions and does not have its enzymatic activity. BSA has surface activity, which can be used as a foaming agent or emulsifier, inhibiting foam falling and coalescence. The dependencies of changes in surface tension and foam-forming ability (and foam stability) for the entire (full) concentration profile were presented for the SDS surfactant and the BSA biosurfactant. From concentrations several dozen or even several hundred times lower than the critical micellisation concentration (for SDS) or critical aggregation concentration (for BSA) to concentrations several dozen times higher than the critical ones. BSA and SDS foams were formed in a rotating flat Hele-Shaw cell, and the ageing processes were observed using video-microscopic methods. It has been demonstrated that creating a stable foam based on BSA protein solutions is possible. However, the results proved that the foam generated in systems based on biosurfactants differs entirely from foams based on synthetic surfactants. Foams based on the protein system were much more heterogeneous (with various sizes of foam cells). Foam stability was associated with a foam film that was many times thicker (than in SDS foam – see Figure 2). A comparison of the liquid content in the foam film showed that the drainage rate in BSA foams is many times lower than in SDS (see Figure 3). It can be assumed that the observed differences are related to the much higher surface viscosity of the BSA solutions compared to the SDS solutions tested in the comparison. Therefore, the obtained foam based on the BSA solution was much more stable than the foams produced based on the synthetic surfactant SDS.

When describing protein foams, it is also necessary to refer to their characteristic phenomenon of changing the conformation of their dissolved molecules during adsorption in the interphase layer and contact with atmospheric air. Studies describing the adsorption of BSA protein have shown that its adsorption is slower than predicted by appropriate diffusion-controlled models. The study's authors showed that this behaviour might

Figure 2



Comparison of morphological images of two-dimensional foam fractions in BSA (left) and SDS (right) solutions. In the case of BSA, photo sections for the following concentrations are presented from the left:  $1.5 \times 10^{-7}$  M,  $3 \times 10^{-7}$  M,  $4.5 \times 10^{-7}$  M,  $6 \times 10^{-7}$  M,  $9 \times 10^{-7}$  M and  $1.2 \times 10^{-6}$  M and  $1.5 \times 10^{-6}$  M. In the case of SDS, concentrations of 0.006 M, 0.008 M, 0.01 M, 0.02 M, 0.035 M and 0.05 M are presented from the left [20].

indicate a change in the molecule's orientation at the interface, which causes an increase in the surface density with little effect on the surface tension [23]. Due to the above, the phenomenon of protein adsorption, due to its large molecular size (compared to classic synthetic surfactants), is irreversible. This significantly impacts the properties of the produced foams, which are, on the one hand, super stable but, at the same time, inflexible.

In Table 1, we compiled the foaming potential of selected additional plant-derived proteins (see Table 1).

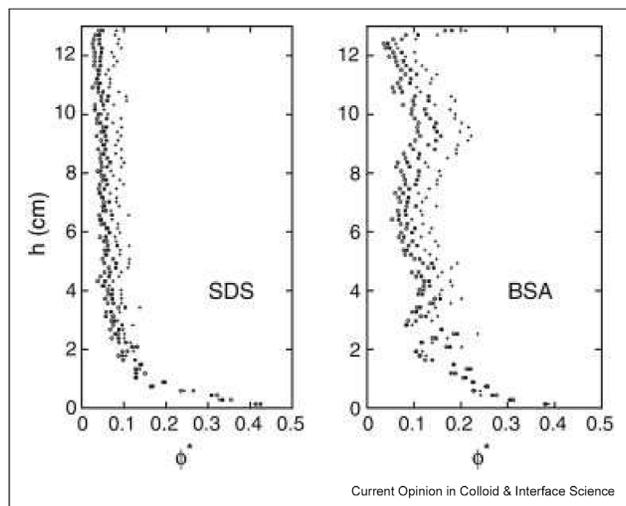
In summary, proteins have great potential for application as biosurfactants and stabilising foam in various

industrial and food sectors. Ongoing research aims to improve their foaming abilities and understand their mechanisms of action at the molecular level. Numerous studies are being conducted to optimise the foaming ability of proteins, including assessing the impact of various salts on this property [31]. Additionally, it was observed that proteins combined with polysaccharides through the Maillard reaction have an increased ability to create foam [32]. Continuing research aims to fully exploit the potential of proteins as biosurfactants, which contributes to progress in various fields and enables innovations in foam stabilisation technology.

### Foams based on sugar-based low and high-molecular-weight foaming agents

The most known sugar-based biosurfactant is saponin. Saponins are chemical compounds of plant origin, classified as glycosides. The saponin structure consists of a non-polar aglycone (glycoside: triterpene or steroid ring) and one to three oligosaccharide chains. The name comes from the Latin word "sapo", which means "soap". This is due to the foaming properties of saponins. Saponins are large molecules and contain a hydrophobic part consisting of a triterpenoid (30 carbon atoms) or a steroid (27 carbon atoms with a 6-ring spirostan or a 5-ring furostan structure) and a hydrophilic part consisting of several saccharide residues attached to a hydrophobic scaffold glycosidic bonds. Terpenoid and steroidal saponins are typically found in dicots and monocots, respectively. Saponins are present in representatives of many plant families, including those constituting the basis of the daily human diet, e.g. in soybeans, peas, chickpeas, peanuts, beans, lentils, oats, garlic, asparagus, tea, spinach, beets and quinoa. Saponins can also be found in many inedible plants used in folk cosmetic and medicinal recipes for centuries. Therefore, saponins are widely used as food preservatives and, emulsifiers or foaming agents in cosmetics.

Figure 3



Distribution of the thickness of the liquid fraction as a function of the vertical position  $h$  above the foam/liquid interface. The fluid fraction  $\phi^*$  is estimated based on image analysis. The free flow of liquid from the foam is considered because the liquid fraction is applied three times after foam generation: 40 s, 150 s and 300 s. Two cases are illustrated: (left) SDS-water mixture at  $2 \times 10^{-2}$  M and (right) BSA-water mixture at  $6 \times 10^{-7}$  M [20].

Table 1

## Compilation of the studies on selected plant-derived proteins with foaming potential.

No.	Protein	Purpose of the research	Main findings	Ref.
1.	Pea protein extracts	Analysis of the impact of pea protein extraction processes on its structure and foam-forming properties, in particular the interactions between albumins and globulins and their impact on foam stability.	<ul style="list-style-type: none"> <li>- Heating pea proteins, both by spray drying and high-temperature heating, resulted in an increase in the surface hydrophobicity of the proteins and/or their aggregates.</li> <li>- As a result of heating, globulins (vicilin and legumin) aggregated, resulting mainly in a soluble fraction containing albumin.</li> <li>- Albumins had a dominant effect on the interface and foam stabilising properties after heating, which was confirmed by interface rheology and ellipsometry studies.</li> <li>- Heating had a significant impact on the properties of plant protein, especially on its foam stability.</li> </ul>	[24]
2.	Pea protein; tested fractions: pea protein concentrate (PPC), globulin-rich fraction (GLB-RF) and albumin-rich fraction (ALB-RF).	Analysis of the impact of specific pea protein fractionation steps on these protein fractions' foaming and emulsifying properties.	<ul style="list-style-type: none"> <li>- Pea protein fractionation enables control of individual protein fractions' foaming and emulsifying properties.</li> <li>- Albumins exhibiting smaller size and lower net protein charge exhibited strong interfacial interactions at the air–water interface, forming stiff and cohesive interface layers, resulting in high foam cross-section and stability.</li> <li>- Globulin, which predominated in the pea protein concentrate (PPC) and the globulin-rich fraction (GLB-RF), was characterised by lower foam and emulsion stability compared to albumin.</li> </ul>	[25]
3.	Lentil protein isolate (LPI)	Analysis of the air–water interface behaviour, interface structures and foaming properties of mildly purified lentil protein isolate. These properties were next compared with properties of two proteins of animal origin commonly used in the food industry, i.e. whey protein isolate (WPI) and egg white protein isolate (EPI).	<ul style="list-style-type: none"> <li>- LPI showed rapid adsorption at the air–water interface and exhibited effective foam formation, comparable to WPI and EPI.</li> <li>- LPI formed interface structures consisting of relatively intact globulin particles.</li> <li>- Proteins in LPI showed weaker in-plane interactions at the air–water interface compared to WPI.</li> <li>- Despite lower interface stiffness, LPI resisted large deformations, suggesting its ability to stabilise foam under dynamic processing conditions.</li> <li>- LPI had promising foaming properties comparable to both WPI and EPI, suggesting that it may be a good substitute for animal protein in preparing foaming food products.</li> </ul>	[26]
4.	Pumpkin ( <i>Cucurbita moschata</i> Duch.)-seed protein isolates (PSPI)	Analysis of the effect of high-intensity ultrasound (HIU) on the physicochemical, structural and foaming properties of pumpkin seed protein isolates and determining the optimal ultrasonic conditions to improve these properties.	<ul style="list-style-type: none"> <li>- Treatment of pumpkin seed protein isolates with ultrasound resulted in the transformation of PSPI aggregates into smaller aggregates with a more uniform distribution.</li> <li>- Ultrasound treatment significantly affected the chromaticity and turbidity of pumpkin seed protein isolates.</li> <li>- Ultrasonic modification had a positive effect on improving and increasing the foaming efficiency of PSPI.</li> <li>- The foaming ability and stability of PSPI were significantly improved after ultrasonic treatment.</li> </ul>	[27]
5.	Oat protein concentrate	Analysis of the air–water interface properties and foaming properties of oat protein concentrates produced by enzymatically assisted ultrafiltration, with and without deamidation.	<ul style="list-style-type: none"> <li>- Oat protein concentrate subjected to deamidation and ultrafiltration (DE-UF-OPC) showed higher surface tension compared to oat protein concentrate subjected to only ultrafiltration (UF-OPC).</li> <li>- Both DE-UF-OPC and UF-OPC showed some but limited foaming ability.</li> <li>- Removing non-polar lipids significantly improved the foaming properties and</li> </ul>	[28]

(continued on next page)

Table 1. (continued)

No.	Protein	Purpose of the research	Main findings	Ref.
6.	Protein Z (PZ)	Analysis of the interactions between PZ and humulinone, a common component of aged hops, and the impact of these interactions on the foam properties of PZ.	stability of DE-UF-OPC and UF-OPC, while removing polar lipids only improved the foaming properties of DE-UF-OPC. - Under the influence of humulinone, both the foamability, foam stability and foam texture of PZ improved.	[29]
7.	Wheat aqueous phase (WAP) protein	Analysis of the foam properties and interface properties of wheat protein in the aqueous phase and its soluble (ES) and insoluble (NES) fractions in ethanol.	- The ES fraction exhibited exceptional foaming ability at both pH 5 and 7, while the NES fraction exhibited lower foaming ability but excellent foam stability at pH 5 and 7. - The ES fraction showed a higher initial surface pressure, indicating stronger surface activity and, consequently, excellent foaming ability. In contrast, the NES fraction showed a faster adsorption rate. - The NES fraction showed increased sensitivity to oscillations, suggesting its ability to form a stable adsorption layer at the interface, which contributes to foam stability. In WAP protein, the ES and NES fractions together influence its foam properties, with the ES fraction mainly influencing foaming properties and the NES fraction playing a more important role in foam stability.	[30]

Li et al. recently studied saponin surface activity and foamability for non-purified water extracts and purified tea saponins [33]. They found almost no effect of purification. Both saponin samples exhibited limited micelle size (average 434.1 nm), effective viscosity (0.15 Pa s), surface tension (43.9 mN/m) and the foam abilities were comparable. Only in the foam stability was higher in the case of non-purified saponins. Gonzales and Sorensen obtained similar results for extract from soapwort (*Saponaria officinalis*) [34]. They found very high critical micelle concentration (CMC) of the compounds compared to other natural bio-surfactants, almost no affect of pH and a slightly ionic character of saponin studied. The foams obtained in the saponin solutions were meta-stable, even in the highest studied concentrations.

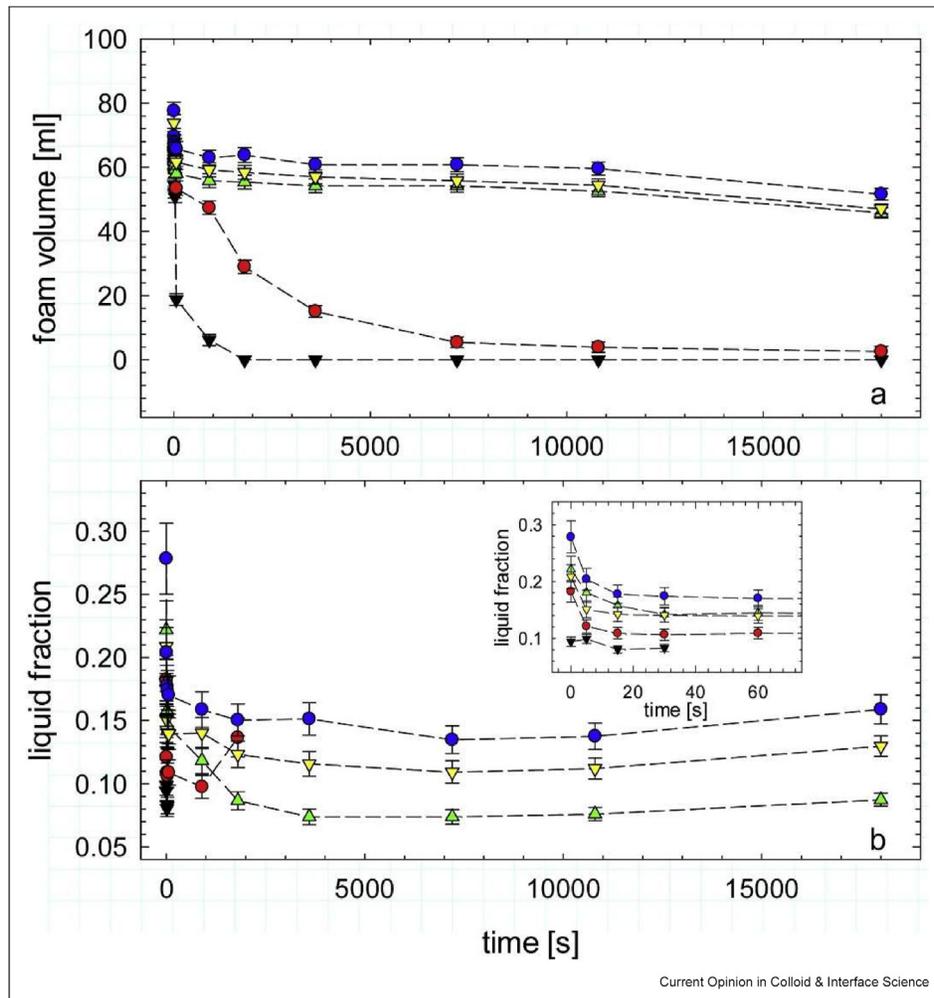
Results presented by Santini et al. [35] confirmed that studied saponin foams are meta-stable. The foam height at a concentration of  $6 \times 10^{-5}$  M (ca. 10 times below CMC) is reduced by half to the initial foam height in up to 30 min. A stable foam that remains at 80% of the initial foam height requires concentration above  $1.8 \times 10^{-4}$  M (see Figure 4 [35]).

Chen et al. used saponin extract from *Camellia oleifera* as a foaming agent [36]. The authors showed that saponin has a lower foamability than solutions of sodium n-dodecyl sulfate or Tween 80. The authors proved that the foaming ability (foam height) of the studied saponin solutions depends (rise) on concentration. It was also shown that the stability of foams developed based on saponin solutions without any additives can only be considered for a very short period of up to 5 min.

These conclusions are consistent with the data presented by Goral and Wojciechowski [37]. However, in this work, the stability of foams based on extracts of various saponins was tested only for up to 30 s after production, concerning the initial foam height.

Sugar-based foams are not only systems based on saponin solution. In the work of Bois et al. [38], foaming, biological and self-organising properties of selected sugar-based biosurfactants — i.e. N-dodecyl-6-O-sulfo-D-gluconamide (GlcCC12S), 6-O-sulfo-N-( $\beta$ -D-glucopyranosyl) dodecanamide (GlcNC12S) and N-dodecyl-6-O-sulfo-D-xylonamide (XylCC12S) — have been compared to the properties of commercial anionic surfactants including sodium lauryl sulfate (SDS) and sodium lauryl sulfate (SLES). The study was designed to evaluate the potential of these new compounds in replacing traditional petroleum-based surfactants. The study showed that the three tested sugar-based biosurfactants demonstrate surface properties and foaming abilities comparable to commercial SDS. Moreover, their cytotoxic and irritant potential is significantly lower compared

Figure 4



Evolution of the foam volume (a) and liquid fraction in foam (b) by the Membrane method for saponin solutions in pure water at various concentrations:  $3 \times 10^{-5}$  M (black triangle),  $6 \times 10^{-5}$  M (red circle),  $1.8 \times 10^{-5}$  M (green triangle),  $3 \times 10^{-4}$  M (yellow triangle) and  $4.8 \times 10^{-4}$  M (blue circle). Data calculated by the foam and drained liquid heights recorded during the destabilisation. The insert in panel b is to expand the scale at the short time [35].

to conventional compounds, suggesting their potential use as replacements for petroleum-based surfactants.

In turn, the study by Kang *et al.* [39] examined the effects of various sugar-based compounds, including surface-active sodium alginate, on solution viscosity, surface tension, foaming ability and foam stability in water-film foams. As a result of the study, it was confirmed that adding sugar-based compounds, such as sodium alginate or xanthan gum, may significantly affect the foam properties of aqueous film-forming foams (AFFFs). The results show that adding these compounds can affect the viscosity, surface tension and foaming ability of AFFFs. Of particular interest is that the combination of xanthan gum and sodium alginate can effectively balance the foaming capacity and foam stability in AFFFs. The mechanism of foam stabilisation by sugar-based compounds in AFFFs is based on the formation

of appropriate intermolecular interactions, which significantly increase the strength of the foam film surface and retard water diffusion in the liquid film, effectively slowing down the drainage process and coalescence of foam bubbles. Research on using sugar-based additives in AFFFs is important for both theoretical exploration and practical application in foam properties.

In summary, sugar-based natural chemicals show great potential as foaming agents due to their properties, such as their high viscosity, ability to form network structures, and ability to form complexes with proteins. Various sugar-based foaming agents can reduce the surface tension of liquids, facilitating foam formation and stabilisation. Their natural origin, biodegradability and low risk of sensitisation make them attractive alternatives to synthetic foaming agents. Importantly, research into the use of sugar-based compounds as foaming

agents covers a wide range of applications, from food production to tissue engineering [40–42].

### Foams based on lipids and their derivatives

These compounds with foaming properties include lipids, glycolipids, and rhamnolipids [43]. These compounds show significant potential in creating stable and effective foam [44]. Glycolipids are characterised by their ability to reduce the surface tension of liquids, facilitating bubble formation [45]. Conversely, Rhamnolipids can form foam with high surface area and stability [46]. Some glycolipids, i.e., mannosylerythritol lipids, have surface-active and antibacterial properties [47]. These properties and biodegradability make them useful foaming agents [48]. The various applicability of glycolipid-based biosurfactants has also been emphasised in many recent papers by Faivre and Rosilio [49] and Lourith and Kanlayavattanukul [50].

For example, Hirata et al. [51] studied sophorolipids (SLs), a type of glycolipids produced mainly by the non-pathogenic yeast *Candida bombicola*. SLs have been shown to exhibit extremely low foamability over a wide range of concentrations, comparable to commercial block-copolymer surfactants. In addition, studies have shown that SLs retain their surfactant properties even in water with high mineral content, suggesting their potential for applications in various industrial environments. Interfacial activities of surfactants containing carboxyl groups generally decrease in hard water due to their binding to calcium and magnesium ions. Therefore, authors believe that SLs have the potential to be utilised as low-foaming detergents for washing machines such as laundry machines, automated dishwashers and washer–disinfectors for cleaning medical devices. In an environmental context, it is also important to note that SLs are readily biodegradable, making them attractive from an industrial sustainability perspective. In the same paper, Hirata et al. [51] present foamability and foam stability results of two lipopeptides (surfactin and arthofacin). In the case of these lipid derivatives, the foam properties were comparable with co-studied sodium n-dodecyl sulfate in a whole range of concentrations.

Interesting conclusions were drawn from the study of glycolipids by Sekhar et al. [52]. Their study aimed to investigate the foaming properties of mixtures of two glycolipids with different hydrophobic chain lengths to better understand their interactions at the air–water interface and assess their potential as surfactants. Mixtures of glycolipids have been shown to exhibit synergistic effects, especially at a molar ratio of 0.25, leading to increased surface activity at the interface.

In turn, the studies by Hollenbach et al. [53] investigated the structure-function relationship of seven enzymatically synthesised glycolipids concerning their interfacial and foaming properties. They evaluated four

different head groups, glucose, glucuronic acid, sorbose and sorbitol of glycolipids with unsaturated and branched tail groups. It was proved that unsaturated tail groups in the fatty acid tails increase micellar concentration and decrease elasticity and viscosity at the interfacial surface, leading to lower foam stability. In contrast, branching in the tails reduces flexibility and viscosity but increases foam stability. The observed differences were explained by various adsorption kinetics of compounds, which were associated with different hydration rates of the biosurfactant head group. It was also found that glycolipids with different head groups showed little difference in rheological properties on the interfacial surface and in foam elasticity. However, glycolipids with ketose and uronic acid heads showed higher foam stability than those with aldose or alditol heads.

In turn, investigations performed by Dhar et al. [54] focused on analysing the frothing, interface and flotation properties of three biosurfactants (acidic glucolipid (GL), acidic sophorolipid (ASL) and alcoholic glucoside (GS)) in the context of mineral separation by froth flotation. It was reported that ASL effectively separates copper sulfides, GL is less effective, while GS is a poor collector. The foaming properties of ASL and GL change depending on the pH of the solution, which affects how they are organised at the air–water interface. Moreover, it was concluded that GS is not an effective sulfide collector due to the non-selective transport of ore particles through the foam.

Next, Cohen and Exerowa's study [55] described that the composition of rhamnolipids affects the properties of foam films. The concentration of biosurfactants and the conditions leading to different types of foam films are also significant. Various mixtures of rhamnolipids can yield stable foams with similar stability, which is of practical importance due to the cost of separation. Other studies [56] focused on understanding the effect of the degree of unsaturation of lipids on their foaming properties, mainly by analysing the interaction between unsaturation and foaming ability. It was found that increasing the degree of unsaturation resulted in better foaming and wetting properties. Lipids with once-unsaturated tails proved effective in dissolving and loading hydrophobic substances, while lipids with twice-unsaturated tails showed better foaming properties.

The best summary of the description of the properties of surface-active lipids is the subsequent results obtained by Hollenbach et al. [57], who undoubtedly experimentally proved that selected surface-active lipids have surface activity and foaming ability comparable to classic synthetic surfactants (e.g. sodium n-dodecyl sulfate). Usually, foam based on these biosurfactants is much more stable than synthetic surfactants with similar surface activity. In connection with

the above, it should be stated that similar systems have a chance of finding wide applications.

### Synthetic surfactants showing biodegradability and non-toxicity

Recently, a new group of compounds, which can generally be called synthetic biosurfactants, has appeared on the market. Typically, it can be assumed that these are artificially developed and industrially produced surfactants with zero or very low toxicity/cytotoxicity and high biodegradability. Examples of such compounds include Lauroyl Ethyl Arginate (LAE), amino acid surfactants (AAS) or various sugar-based surfactants, alkyl polyglycosides, AGPs [58,59] or pectin-amides [60].

Synthetic biosurfactants also include cardanol, fatty acids, furfural and isosorbide, and other similar compounds, the syntheses of which have recently been developed from various biowaste materials. Ravazzanno and Ferreira proposed surfactants based on cardanol, a compound abundant in the cashew nutshell liquid [61]. Ghatta *et al.* [62] developed a furan-based surfactant that originated solutions with enhanced foam ability compared to SDS solutions with the same concentration. Zhang *et al.* [63] obtained castor oil-derived zwitterionic surfactants, which form solutions with foamability, wetting and dispersion capabilities adequate for applications in the field of enhanced oil recovery.

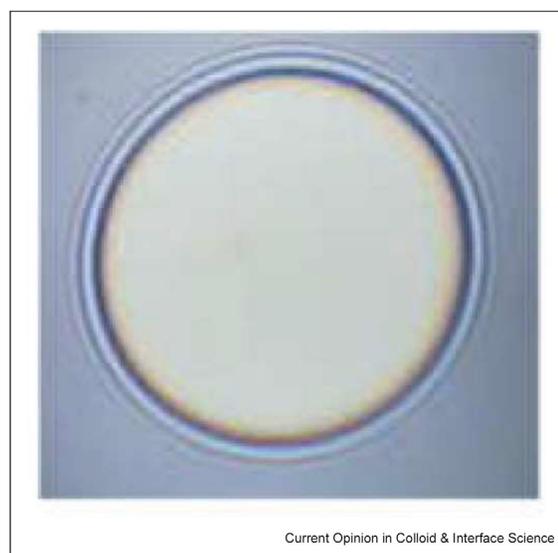
Lauroyl Ethyl Arginate is a positively charged surfactant synthesised from L-arginine and lauric acid with low toxicity and antimicrobial activity. Its molecular weight is  $421 \text{ g mol}^{-1}$ , pKa is approximately 10–11, and the isoelectric point is above  $\text{pH} = 12$ . It is stable at room temperature in a closed container for over two years. In an aqueous solution at  $25^\circ\text{C}$ , its half-life decreases from more than 1 year at  $\text{pH} = 4$ , to 57 days at  $\text{pH} = 7$ , and 34 h at  $\text{pH} = 9$  [64,65], indicating its decomposition by base-catalysed hydrolysis into surfactants: N- $\alpha$ -lauroyl-L-arginine (LAS) or dodecanoic acid (lauric acid). Toxicological studies have demonstrated LAE's low toxicity as it can be hydrolysed by chemical and metabolic pathways into easily metabolised components [66]. Lauroyl Ethyl Arginate has strong antimicrobial activity against various microorganisms, including forms, yeasts, Gram-positive, and Gram-negative bacteria. As a cationic surfactant, it can penetrate the bacterial cytoplasmic membrane, causing its deformation and the loss of cell viability [67]. It is widely used as a food preservative and food packaging ingredient [68].

In our recent papers, we measured the surface tension and foamability properties of LAE solutions and determined its dependence on the surfactant concentration [66] and time of solution deposition. The surface tension isotherm of LAE was compared with ones obtained

for some model cationic and non-ionic surfactants. The onset of the surface activity of LAE was between those measured for classical cationic and non-ionic surfactants with the same hydrocarbon chain length [69]. The tested  $2.4 \times 10^{-4} \text{ M}$  LAE solutions allowed the formation of only a metastable thin foam film [70], which ruptured (coalesced) in time below 100 s (see Figure 5). In this case, obtaining a stable foam is required using the LAE concentration above its critical micelle concentration. Foams formed in the tested LAE solutions, produced using membrane or double syringe methods, disintegrated at a similar time.

In turn, Borkowski *et al.* [71] investigated the foaming properties of biosurfactants with amino-acid heads (AASs), including N-lauroyl-L-leucine ( $\text{C}_{12}$ -LEU), N-lauroyl-L-alanine ( $\text{C}_{12}$ -ALA) and N-lauroyl-L-phenylalanine ( $\text{C}_{12}$ -PHE) in combination with n-octanol ( $\text{C}_8\text{OH}$ ). The results showed that AASs exhibit poor foaming capabilities. It has been proposed that mixtures of AASs with  $\text{C}_8\text{OH}$  be used, which produces a synergistic effect in foaming. The study points to the need for further research into the mechanism of aggregate formation, which can act as reservoirs of surfactant molecules, enhancing the foamability of mixtures. Experimental results suggest that aggregates affect the stability of the air/liquid interface, increasing foam efficiency. It is important to understand further the dynamics of foam formation and the role that aggregates play in the foaming process. The use of AAS mixtures with n-octanol may allow foamability to be controlled more effectively, which could significantly impact the development of foaming technologies.

Figure 5



Snapshots of microscopic foam films from aqueous solutions of lauroyl ethyl arginate  $2.4 \times 10^{-4} \text{ M}$  LAE [70].

Table 2

Characterisation of properties for selected biosurfactants from the described groups of compounds in this chapter [37,70,72–80].

Type of biosurfactants	Examples	Properties					
		Molecular Structure	CMC	Solubility	Minimum Surface Tension	Foam Stability	Chelating Properties
Proteins	<i>BSA</i>	Globular protein with a molecular weight of approximately 66.5 kDa. It consists of 583 amino acid residues.	It is not a typical surfactant, so it does not have a classical CMC. Its surface properties depend on conditions such as pH, temperature, and ionic strength.	It is well soluble in water, especially at neutral pH.	It can reduce the surface tension of water to about 50–40 mN/m under appropriate conditions.	Foam is relatively stable but less durable than foams formed by synthetic surfactants.	It has the ability to bind metal ions due to the presence of carboxyl, amino, and thiol groups in its structure.
	<i>SPI</i>	It is a fraction of soy proteins, mainly globulins, with a molecular weight of about $3 \times 10^{-5}$ – $6 \times 10^{-5}$ kDa.	Similar to BSA, SPI does not have a classical CMC.	It has good solubility in water, depending on pH and temperature.	It can reduce the surface tension to around 55-45 mN/m.	It has the ability to form foam, used in food applications.	It has chelating abilities, though weaker compared to dedicated chelators.
Polysaccharides	<i>Saponins</i>	Glycosides of triterpenes or steroids, consisting of an aglycone (sapogenin) and a sugar part	Depending on the specific saponin and conditions, they have a CMC in the range of 0.3–1.1 g/L.	Well soluble in water.	They can reduce the surface tension of water to about 30–25 mN/m.	The foam formed by saponins is very stable.	Limited chelating properties.
	<i>Sodium Alginate</i>	The sodium salt of alginic acid is a polysaccharide composed of mannuronic acid and guluronic acid residues.	It is not a classical surfactant and does not have a defined CMC.	Well soluble in water, forming a viscous solution.	It has limited ability to reduce surface tension, usually to around 75-60 mN/m.	The foam formed by sodium alginate is not very stable.	It has good chelating properties, especially for calcium ions.
Lipids	<i>SLs</i>	Biosurfactants consist of fatty acids linked to sophorose (a disaccharide).	Typically in the range of 40–70 mg/L.	Soluble in water and also in organic solvents.	They can reduce the surface tension of water to about 40–30 mN/m.	The foam formed by sophorolipids is relatively stable.	Limited chelating properties.
	<i>Rhamnolipids</i>	Biosurfactants composed of rhamnose (a sugar) and fatty acids.	Typically in the range of 1–400 mg/L.	Well soluble in water.	They can reduce the surface tension of water to about 72–30 mN/m.	The foam formed by rhamnolipids is stable.	Limited chelating properties.
Synthetics	<i>LAE</i>	Quaternary ammonium compound consisting of ethyl, lauroyl, and arginine residues.	Typically in the range of 1.0–1.1 mM/L.	Well soluble in water.	It can reduce the surface tension of water to about 70–20 mN/m.	The foam formed by LAE is relatively stable.	It has limited chelating properties but can bind some metal ions.

Wen *et al.* [59] comprehensive studies of adsorption and foaming processes on the entire homologous series of selected alkyl polyglycosides showed that the compounds behave almost exactly like synthetic ionic surfactants. The stability of foams increases with the length of the hydrocarbon chain in the range from 8.0 to 10.9; only below this value, it decreases (which may be related to the reduced solubility of the compound). Moreover, the stability of foams varies with increasing ionic strength and the presence of metal ions.

Ravazzano and Ferreira studied cardanol-derived surfactants [61]. They found that the foaming properties of such aqueous systems are strongly temperature-dependent. Foam ability was related to the length of the hydrocarbon chain. Enhanced foam stability was attributed to the higher bulk viscosity due to the presence of elongated micelles in solution and surface viscoelasticity of the resulting, which decreased the liquid drainage, coalescence and coarsening in the obtained foam.

This group of biosurfactants has all the advantages and disadvantages of both synthetic ionic surfactants and natural biosurfactants. Common advantages are low toxicity and high biodegradability of such systems. The disadvantages are the relatively low surface activity and low foaming ability of the solutions described in the literature. The biggest disadvantage is the very low stability of the foams obtained in the tested systems. Better results are only possible in mixtures where electrolyte additions or pH changes modulate the foaming ability and stability, or various additives increase foam stability.

## Summary

This publication presents significant biosurfactants in forming wet foams, including proteins, lipids, and sugar-based surface active chemicals with different properties. Table 2 presents the characteristics of the basic properties for selected compounds described in this mini review.

These compounds and their application in obtaining foams open new industrial perspectives that oppose traditional surfactants. Continued scientific work in this area can contribute to further innovations in many industrial sectors.

Below, we present the most essential conclusions obtained from the literature review:

1. Biosurfactants of natural origin, proteins, polysaccharides and lipids adsorb on the interfacial surface completely differently than classic surfactants. They have much larger molecules and molecular weights, and their structure cannot distinguish the classic hydrophilic “head” and hydrophobic “tail”.

Despite this, they can undoubtedly adsorb to the interfacial surface while lowering the surface tension. The exact mechanisms of adsorption processes for most natural biosurfactants have not been studied. We mostly have to analyse these processes based on semi-theoretical hypotheses.

2. Proteins are the only biosurfactants to create stable foams in relatively low solution concentrations. This is related to the irreversible adsorption mechanism characteristic of most proteins. After reaching the interfacial surface, protein macromolecules with a molar mass of several dozen kD change their structural conformation to adapt to the environmental change. Virtually irreversible dehydration of the molecule occurs. Therefore, adsorption is irreversible. The consequence is the creation of stable, relatively thick foam films and stable foams. Due to the high packing of the adsorption layer with protein molecules, the ageing process occurs mainly through liquid leakage in these foams, and coalescence and gaseous diffusion are not correctly observed. The foam disappears rapidly after some time and practically completely when the dehydration limit of the foam film is exceeded.
3. Polysaccharides and lipid derivatives are currently the most promising biosurfactants in foam-forming research. Foams based on these systems do not have negative features similar to protein foams. It can be speculated that this is related to the much smaller molecular sizes of these biosurfactants than proteins. It has been shown that foams with similar properties (foamability and foam stability) can be produced based on these biosurfactants, as in the case of classic synthetic surfactants. These systems have not yet been as thoroughly researched in adsorption and foaming processes as the proteins used in the food industry.
4. Synthetic biosurfactants, as ionic compounds, are characterised by relatively low surface activity, and the foams produced on their basis are, by definition, meta-stable or unstable. Obtaining a stable foam requires significantly exceeding the Critical Micelle Concentration, exactly as in the case of ordinary synthetic cationic or anionic surfactants. Another solution is introducing foam-stabilising additives, e.g. solid particles, into the system.

## Additional informations

Due to the rules of preparing a review for Current Opinion in Colloids and Interface Sciences, the authors had to finish their summary of the topic here, leaving undescribed biosurfactant mixtures and mutual interaction between biosurfactants with other compounds or particles and the impact of these additives on the foam stability. Therefore, the authors prepared a second review article, titled: “Foams based on biosurfactant mixtures. Part II. “Influence of mixture composition on

foam stability” in *Current Opinion in Colloids and Interface Sciences*.

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## CRedit authorship contribution statement

**Marcel Krzan:** Conceptualisation, Formal analysis, Investigation, Writing – original draft, Writing – review & editing, Supervision, Funding acquisition. **Anna Drabczyk:** Investigation, Formal analysis, Writing – original draft, Writing – review & editing. **Sonia Kudłacik-Kramarczyk:** Investigation, Formal analysis, Writing – original draft, Writing – review & editing. **Mateusz Jamróży:** Writing – original draft, Figures preparation.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. Figures were taken from the first author’s previous papers (M.K.), with the publisher’s permission (please see Acknowledgements).

## Data availability

No data was used for the research described in the article.

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