

New surfactant mixtures for fine foams with slowed drainage



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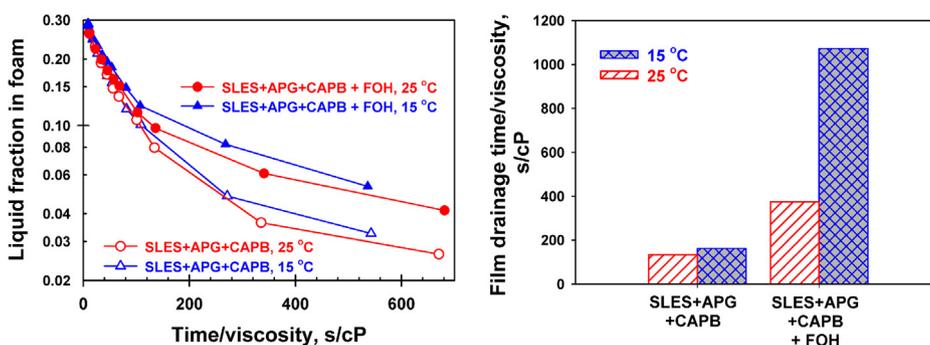
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HIGHLIGHTS

- Stable foams were obtained by a triple surfactant mixture of APG, SLES and CAPB.
- Chelating agent MGDA helped the solubility of additives even in very hard water.
- Foam drainage was slowed by additives for high pH: fatty alcohol and modified starch.
- Temperature decrease further slowed down the drainage of foam and thin films.
- Temperature control on surface rheology was shown.

GRAPHICAL ABSTRACT



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ABSTRACT

We form and investigate foams stabilized by a triple surfactant mixture containing a nonionic alkyl polyglucoside (APG) in addition to the combination of ionic sodium lauryl-dioxyethylene sulphate (SLES) and zwitterionic cocamidopropyl betaine (CAPB) surfactants. APG improves the surfactants compatibility at alkaline pH. The addition of a readily biodegradable chelating agent methylglycinediacetic acid (MGDA) in the mixture contributes further for the excellent performance even in very hard water.

Foam properties are analyzed and compared to those of the single components and to the binary mixture without APG. Foam drainage is successfully controlled by introducing additives suitable for the alkaline conditions: fatty alcohol and/or hydrophobically modified starch.

Systematic model experiments are performed to characterize the surface tension and dilatational rheology, and thin films drainage. Slowed foam and thin films drainage is confirmed to correlate with the increased surface visco-elasticity in the presence of fatty alcohols. Temperature impact on the surface properties is used for fine tuning of the foam drainage.

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1. Introduction

Surfactant foams are used in an increased number of applications including home care (detergents, hand dishwashing

formulations, carpet foam cleaner, clinging spray foam cleaner, etc.), industrial cleaning (car washing, carpets and textile washing, etc.), personal care (shaving foams, liquid soaps, shampoos, toothpaste, etc.), cosmetics (hair mousses, hair dyeing foams, dry makeup foundation foam, etc.), pharmaceuticals (dermal foams, mucoadhesive and anti-inflammatory foams, vaginal foaming tablets, etc.), constructions (e.g. insulating organic or inorganic foams) etc. [1–5]. Control of foam properties and stability, including

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bubble size, liquid content, Ostwald ripening, drainage, are decisive to ensure the sought delivery, cleaning and/or protective effects [1–9].

Mixtures of anionic surfactant sodium lauryldioxyethylene sulphate (SLES) and zwitterionic cocamidopropyl betaine (CAPB) have been proposed as suitable system for foam dynamics studies by Denkov et al. [6,7]. These mixtures form homogeneous solutions with Newtonian behavior and have a significant solubilizing capacity for different fatty acids and alcohols [7]. Fatty acids have been preferably added to different formulations in model studies since they easily form surface condensed phases at air/water interfaces at natural pH and ambient temperature [6–8,10–12]. The concentration and type of fatty acids [7,10,11] and the temperature [7] have been used to ensure high surface modulus and foams with small bubble size and high viscous stress. Besides fatty acids, fatty alcohols [7,13,14], proteins [13–15], polymers [16] or polymer-surfactant combinations [17,18] have been used to tune surface visco-elasticity and foam properties.

We form and study alkaline surfactant mixture containing alkyl polyglucoside (APG) surfactant in addition to the mixture of SLES and CAPB. Besides the readily biodegradability APG surfactants are known and used for their mildness and good stability in wide pH range [19,20]. The presence of APG in the studied mixtures improves significantly the surfactants compatibility and mixed micelles solubilizing capacity at alkaline pH.

To increase the formulation application to very high water hardness we added the readily biodegradable chelating agent methylglycinediacetic acid (MGDA) [21]. Chelating agents are used in many formulations aimed to work at high water hardness [22]. The increased interest toward readily biodegradable substances, as MGDA, should be especially noted [22].

To increase the surface visco-elasticity and to reduce the drainage of the foams we added fatty alcohol and/or a hydrophobically modified starch. These additives were especially selected for the alkaline pH, where the fatty acids would not work [10].

The foams were formed by simple hand shaking method and their volume and stability were registered and compared along with the drainage and bubble size. Surface properties and thin films were characterized in model experiments.

2. Materials and methods

2.1. Materials

The surfactants and additives used by us were products of BASF. Their commercial names, chemical names, together with the short names used in the text, and some additional information for the chemistry are given in Table 1.

Stock solutions with total of 5 wt% surfactant concentration were prepared by using some of the surfactants or their mixtures: anionic SLES, zwitterionic CAPB, and the nonionic APG. The solutions were prepared with deionized water (Elix[®] purification system, Millipore) with preliminary adjusted alkaline pH = 12. Alkalinity was adjusted by using NaOH ($\geq 98\%$, Sigma-Aldrich).

The working solutions used for foam preparations and model characterizations were obtained by 25 times dilution of the 5 wt% stock solutions to 0.2 wt% surfactant content. Dilution was performed with water containing either 2.5 or 5 mM CaCl₂. CaCl₂·2H₂O ($\geq 98\%$, Chem-Lab) was used for water hardness adjustment.

Additives used to slow down the foam drainage were added to the 5 wt% stock solutions with concentrations of 0.2 wt% for the fatty alcohol, and 0.1 wt% for the polymer HMS. After the 25 times dilution their concentrations in the working 0.2 wt% surfactant formulation was 0.008 and 0.004 wt% respectively. We measured the viscosity of the used 0.2 wt% surfactant formulations by a capillary

viscometer and we found no significant differences to the viscosity of water.

2.2. Foams

Foams were formed following the Bartsch method [23,24] by 10 vigorous shakings by hand of a closed cylinder (130 mL total internal volume, graduated to 100 mL with an increment of 1 mL) containing 40 mL solution and 90 mL air.

The upper and the lower boundaries of the foams in the cylinders were monitored during 10 min (600 s). Thus one records the total volume of foam and liquid beneath, V_{F+L} , which is the upper boundary, and the volume of the drained liquid, V_{DrL} , which is the lower boundary. Afterwards we calculated the global liquid fraction in the foam $\varepsilon = (40 - V_{DrL}) / (V_{F+L} - V_{DrL})$. The first measurement was recorded 10 s after shaking in order to have well-defined upper and lower foam boundaries.

All foam tests were performed at least twice. Reproducibility of the results was typically within 5%.

Most of the measurements were performed at 25 °C in a tempered environment (± 1 °C). Several series at 15 °C were carried out as well.

2.3. Bubble size

Bubble size was determined by using the procedure of Garrett et al. [25,26]. Freshly formed foam in a cylinder was spread in a small petri dish. An optical triangular prism was placed on top of the dish in a direct contact with the foam. The foam was illuminated by diffuse white light through one of the prism side-walls, whereas the foam observation was made by video-camera, through the other side-wall of the prism. In the recorded images one sees as bright polygonal spots the wetting films, formed between the bubbles and the prism wall, whereas the Plateau borders around the films are seen as dark interconnected areas. The diameter of each bubble was calculated by using the relation $d_B = 2(A_{BP}/\pi)^{1/2}$, where A_{BP} is the projected area of a given bubble in contact with

the prism wall [25,26]. The average diameter $d_{32} = \frac{\sum_{i=1}^N d_i^3}{\sum_{i=1}^N d_i^2}$ was calculated afterwards for each image containing typically $N = 20$ –200 bubbles.

The foam images taken during 10 min were processed via a shareware computer program Image J, released by the National Institute of Health (NIH).

Observations were performed at 15 and 25 °C using a specially designed tempering holder (± 0.2 °C).

2.4. Surface tension and surface dilatational rheology of the solutions

We formed and observed buoyant bubbles on the tip of a J-shaped hollow needle dipped in the aqueous solution by means of the instrument DSA100R (Krüss GmbH, Germany). The instrument is equipped with a tempering chamber TC40 allowing precise control (± 0.1 °C) of the temperature during measurement. Most of the measurements were performed at 25 °C. Several series at 20 and 15 °C were carried out as well.

The surface tension σ was determined by axisymmetric drop shape analysis with the software DSA1 (Krüss GmbH, Germany). The surface dilatational storage and loss moduli, E' and E'' , were determined using the oscillating bubble method as described in Ref. [27]. For this goal, the variation of σ was recorded for sinusoidal

Table 1
List of surfactants and additives used in the experiments.

Short name used in the text	Chemical name	Commercial name	Additional information according to the manufacturer
SLES	sodium lauryl ether sulphate	Texapon® N 70	Based on fatty alcohol C12-C14; 2 mol EO; sulphated
CAPB	cocamidopropyl betaine	Dehyton® K	–
APG	alkyl polyglucoside	Glucopon® 225 DK	based on fatty alcohol C8-C10
FOH	fatty alcohol	Lorol® Technisch	C12-18
HMS	hydrophobically modified starch	Polyquart® Ecoclean	–
MGDA	methylglycinediacetic acid sodium salt	Trilon® M Liquid	–

oscillations of the bubble area A with a period of 5 s. The bubble was observed in transmitted light during the whole experiment and its profile was processed to calculate the surface tension, bubble area, volume, and the error of the Laplace fit [28].

2.5. Thin foam films

Experiments with individual foam films were performed with the Scheludko-Exerowa (SE) cell [29–31]. The films were observed in reflected monochromatic light by using the method of Scheludko and Exerowa [30,31]. Jenavert microscope (Carl Zeiss, Jena) equipped with a long working distance objective ($\times 5$) and an interference filter (564 nm) was used.

In the SE cell, the investigated solution is loaded in a cylindrical capillary through an orifice in its wall. Next, liquid is sucked from the formed biconcave drop until a film appears in the central part of the cell. By injecting or sucking of liquid through the side capillary, one can vary the radius of the formed film. We formed and observed films with a diameter of 450–500 μm and we measured the time from the film formation until the whole film reached a homogeneous equilibrium thickness, which we call a drainage time, τ_{Dr} . It is worth noting in advance that all observed films reached an equilibrium thickness of 15 ± 3 nm, i.e. primary films formed at the applied capillary pressure [31,32].

Measurements at 25 and at 15 °C were performed in a tempered environment (± 1 °C).

3. Experimental results

3.1. Foaming and foam stability

We formed foams from solutions containing only one of the three basic surfactants (see Table 1), binary surfactant blends of SLES and CAPB and a triple mixture of SLES, APG and CAPB in a ratio 2:2:1. Binary blends with ratio 4:1 and 3.5:1.5 SLES to CAPB were used. The ratio 3.5:1.5 is chosen to be close to the ratio 2:1 used by Denkov et al. [6–8,10,11]. The binary blend 4:1 SLES:CAPB contains the same fraction of betaine as the triple mixture. Notably all formed foams were voluminous, very stable and no coalescence was noticed for the 10 min of observation. To illustrate the foam stability we plot the total volume of the foam and the liquid beneath, V_{F+L} , in the cylinders for the 10 min of observations in Fig. 1 (left ordinate axis) for three of the tested solutions. The data for the other samples are practically the same but have not been plotted to simplify the graph.

Additives that have been proven to have an impact on the foam drainage were mainly fatty acids [6–12], fatty alcohols [7,13,14] and polymers [16–18]. We added the hydrophobically modified starch HMS (see Table 1) in a concentration of 0.1 wt% to the 5 wt% stock solution of the triple mixture SLES + APG + CAPB (2:2:1). The obtained solution was clear, not viscous and its foaming (after 25 times dilution) was comparable to that in the absence of hydrophobically modified starch.

We added fatty alcohol (FOH) to all surfactant solutions to test whether it could act as a surface active additive capable to help

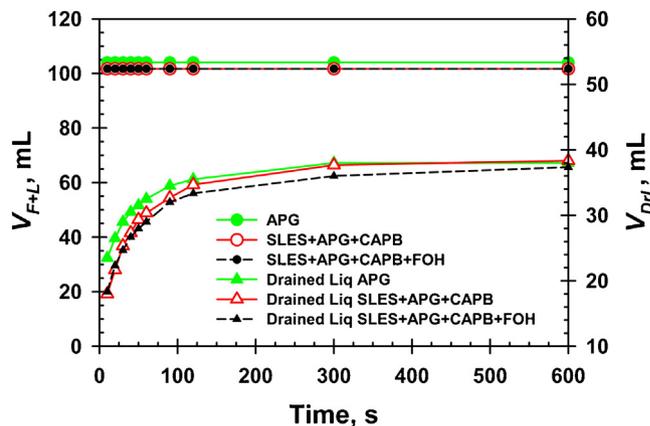


Fig. 1. Typical plots of the total volume of foam + liquid beneath, V_{F+L} (left axis), and the volume of the drained liquid, V_{DrL} (right axis). Data for three surfactant compositions are given as shown in the legend. All observations were performed at 25 °C.

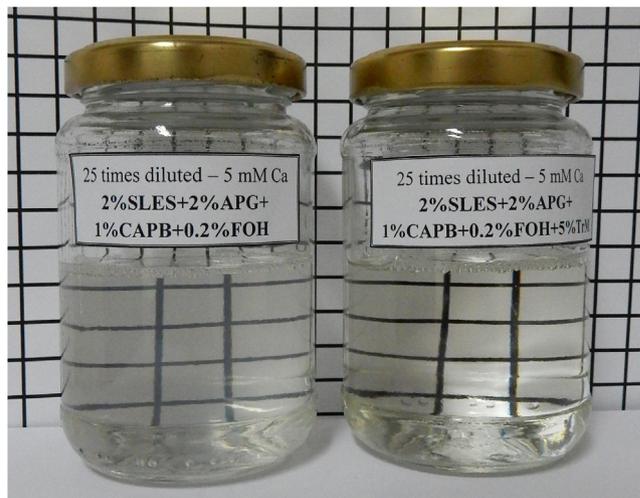


Fig. 2. Photo of glass containers with 25 times diluted working triple mixture of SLES + APG + CAPB (2:2:1) in the absence (left) and in the presence (right) of MGDA. The observations were performed at 20 °C.

the reduction of the foam drainage. We added 0.2 wt% FOH to the 5 wt% stock solutions. Few of the stock solutions have dissolved the added alcohol, i.e. clear solutions formed after intensive stirring and heating to 40 °C, namely the triple mixture. The remaining stock formulations were turbid, some of them viscous, and only after the dilution, clear and not viscous solutions were obtained, with some precipitates in several of them. Remarkably, we have succeeded to dissolve relatively fast the FOH in the mixtures containing the chelating agent MGDA. MGDA was not detected to influence the foaming or foam drainage but contributed for easier mixing and clear solutions formation even at very hard water. Fig. 2 presents a picture from typical diluted surfactant mixtures with and without MGDA before foaming. Although with low surfactant concentra-

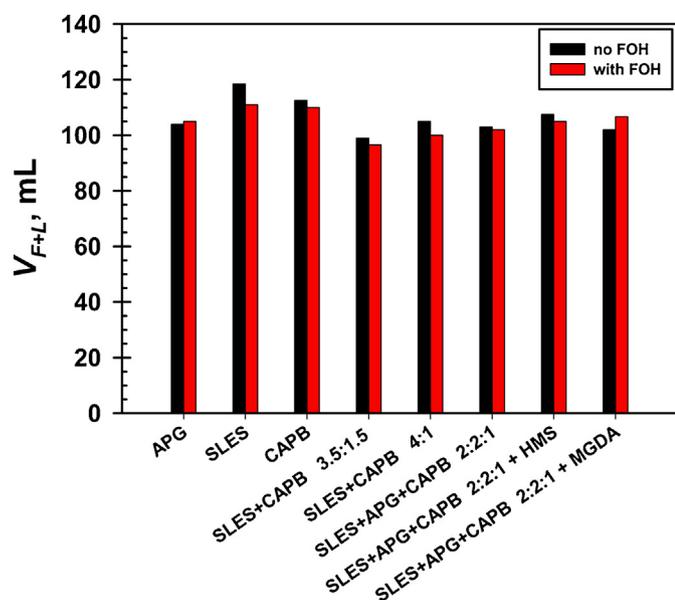


Fig. 3. Total volume of foam+liquid beneath, V_{F+L} , for single, double and triple 0.2 wt% surfactant compositions in the absence and in the presence of fatty alcohol FOH. All observations were performed at 25 °C.

tion (0.2 wt%), the mixture without the complexing agent is visibly turbid due to the formation of Ca^{2+} precipitates.

We foamed all diluted mixtures and we found that the presence of precipitates did not affect significantly the volume of the formed foam. V_{F+L} for all compositions was practically the same and furthermore it was not affected by the presence of the fatty alcohol as well – see Fig. 3.

Fig. 3 presents the volume of the foam together with the volume of the liquid beneath, V_{F+L} , for all studied compositions in the absence and in the presence of FOH. As seen from the bars all compositions dispersed at least 60 mL of air to give the total volume of 100 mL (containing 40 mL liquid).

The solution containing only SLES formed largest foam volume (~120 mL that almost filled the cylinders) which was to be expected since lauryl ether sulphate surfactants are known and used for their excellent foaming properties [1–4]. The mixtures of SLES and CAPB have significant foaming as well, although the smallest foam volume among all studied compositions. Notably the replacement of part of the lauryl ether sulphate with the alkyl polyglucoside surfactant resulted in an excellent foaming as well. Furthermore, it allowed for the introduction of a hydrophobically modified starch without any precipitate formation.

In summary, all studied surfactant formulations foamed very well and without significant differences under the applied foaming method and procedure. However, the obtained foams differed in drainage and bubble size. These differences are presented and discussed in the next sections.

3.2. Foam drainage

Some differences in the drainage of the foam could be seen even if one compares the volumes of the drained liquid – see the plots corresponding to the right ordinate axis in Fig. 1. Better comparison could be made, however, when the evolution of the global liquid fraction, ε , is inspected. Fig. 4A presents ε for single, double and triple surfactant mixtures, two of which contain fatty alcohol. Note that the solutions of the single surfactants formed foams with a lower liquid fraction although with larger total volume (cf. Fig. 3). The foams stabilized by combinations of two or three surfactants, contained more liquid ten seconds after formation, i.e. ~25% vs

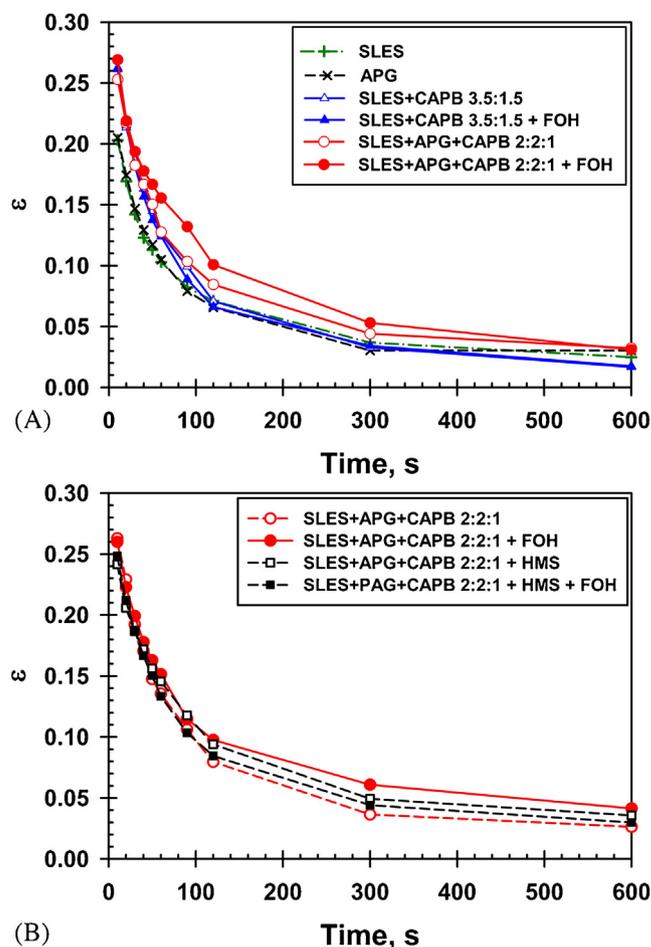


Fig. 4. Evolution of the global liquid fraction $\varepsilon = (40 - V_{DRL}) / (V_{F+L} - V_{DRL})$ in foams obtained with different surfactant compositions: (A) single, double and triple mixtures in the absence and in the presence of FOH; (B) triple mixture in the absence and in the presence of FOH and/or HMS. All observations were performed at 25 °C.

~20% for the single surfactants. The slowest drainage was observed with the triple mixture SLES + APG + CAPB with addition of FOH. However, no impact of FOH was noticed for the double mixture of SLES + CAPB.

Detailed comparison of the impact of the different additives on the drainage of foams stabilized with the triple surfactant mixture is presented in Fig. 4B. Having in mind that the reproducibility of ε is within ± 0.01 , one could conclude that there is drainage retarding impact with all additives. Most significant drainage retardation is seen however when only FOH is added to the triple mixture SLES + APG + CAPB.

The observed impact of FOH could be explained with a predominant adsorption of fatty alcohol molecules on the air/water interface similarly to other observations with fatty alcohol [14] or acids [11]. No effect of the bulk viscosity could be expected, similarly to Ref. [16], since all solutions had viscosity almost the same as that of the water.

To check further the effect of FOH we performed foam evaluations at 15 °C. No significant differences were recorded in volume and stability of the foams at 15 and 25 °C – see Table 2. However, the foams formed at 15 °C contained 27–28% water 10 s after formation and drained slower than those at 25 °C. Solution viscosity slightly increased with the decrease of the temperature, but this effect could not explain fully the displacement of the drainage curves shown in Fig. 5A. To account quantitatively on the effect of bulk viscosity increase as the temperature decrease in Fig. 5B we plot ε vs the

Table 2
Viscosity of solutions of the triple mixture SLES + APG + CAPB with and without FOH at 15 and 25 °C, and the respective foam volumes.

Solution composition	Viscosity, cP		Total foam + liquid volume, V_{F+L} , ml	
	15 °C	25 °C	15 °C	25 °C
SLES + APG + CAPB 2:2:1	1.106	0.895	99	103
SLES + APG + CAPB 2:2:1 + FOH	1.119	0.881	99	102

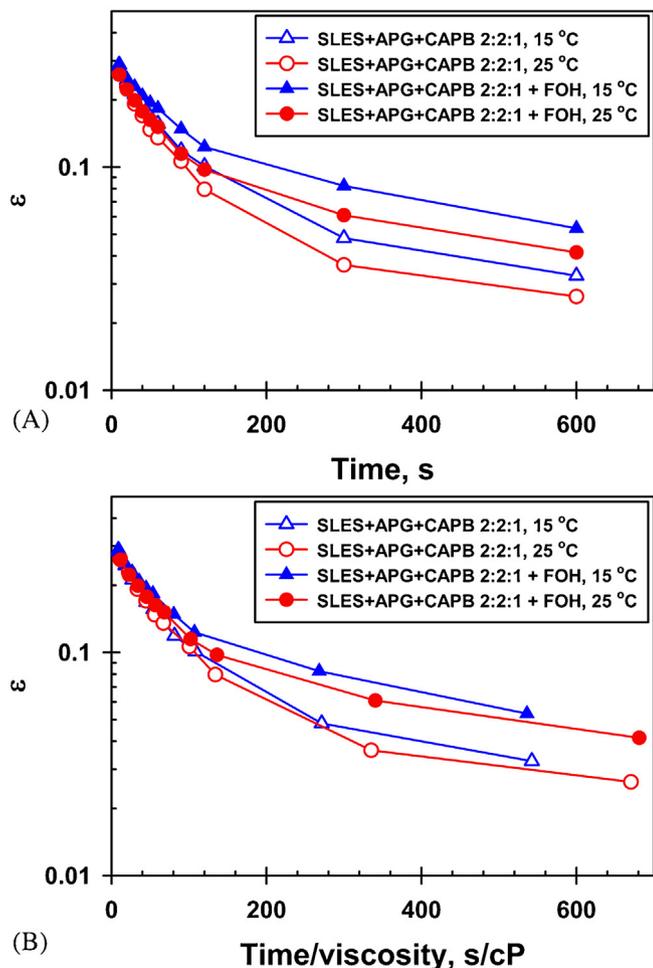


Fig. 5. Evolution of the global liquid fraction $\varepsilon = (40 - V_{Drl}) / (V_{F+L} - V_{Drl})$ in foams obtained with the triple mixtures in the absence and in the presence of FOH at 25 and 15 °C with (A) the time, and (B) time scaled by the viscosity of the respective solutions.

time scaled by the viscosity of the respective solutions. Even after the scaling, the reduced foam drainage at lower temperature is well seen. Thus one could further trace the origin of the reduced drainage either in the bubble size or to changes of surface properties. These are discussed in the following sections.

3.3. Bubble size

We measured the diameter of the bubbles in foams stabilized with the triple surfactant mixture SLES + APG + CAPB 2:2:1 in the absence and in the presence of additives FOH and HMS at 15 and at 25 °C. The aim of these measurements was to check whether the characteristic bubble size was influenced by the temperature or by the presence of additives.

The determined d_{32} values at 15 and 25 °C are shown in Fig. 6 as a function of time for 10 min of observation. The initial bubble diameter was between 0.5 and 0.7 mm for all solutions, which is 2–3 times larger than the diameters reported by Tcholakova et al.

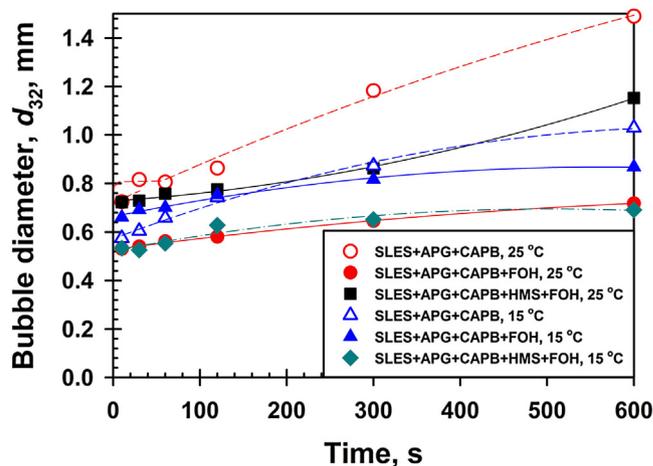


Fig. 6. d_{32} diameter of bubbles in foams stabilized with the triple surfactant mixture SLES + APG + CAPB 2:2:1 in the absence and in the presence of additives FOH and HMS as a function of time at 15 and at 25 °C.

[8] for compositions of SLES and CAPB with high surface modulus and reduced Ostwald ripening. A very important difference to Ref. [8], besides the surfactant concentration and the precise chemistry, is the method of foam formation: Tcholakova et al. have used a method with a syringe where significant shear rates have been applied and thus finer foams have been obtained. We used the foams obtained in the cylinders by the hand Bartsch test directly (see Section 2.2) and we have not tried another method.

The plot in Fig. 6 does not show any clear impact of the temperature on the bubble size that might be related to the slowed drainage at 15 °C as compared to 25 °C, see Fig. 5. Furthermore, no clear discrimination of the changes in the bubble size could be determined from Fig. 5 in respect to the additives, capable to slow down the Ostwald ripening.

To distinguish reliably the rates of Ostwald ripening in the different systems we calculated and plotted the relative change of the surface area of the bubbles vs the time, see Fig. 7. For comparison data by Tcholakova et al. (from Fig. 2 in Ref. [8]) are also added on the plot at 15 °C (Fig. 7A). Clear discrimination between the systems without and with additives can be made, based on the slopes of the lines in Fig. 7: Although the difference in the initial bubble diameter (~ 0.6 mm in our triple mixture at 15 °C vs 0.4 mm for BS – the SLES + CAPB mixture of Tcholakova et al. in Ref. [8] at 20 °C), the rates of Ostwald ripening in the foams without additives are the same – see Fig. 7A. In the presence of additives (FOH and/or HMS in our mixture, or lauryl alcohol, named LOH, for BS) the rates of Ostwald ripening is also almost the same and it is 2–3 times slower than in the absence of additives, as seen from Fig. 7.

Temperature influences the rate of Ostwald ripening only for the compositions without FOH. In this case the slowed ripening could be related to the decreased rate of gas transfer through the liquid phase due to the increased viscosity as the temperature decreases from 25 to 15 °C.

Tcholakova et al. [8] have shown that the slow rates of Ostwald ripening ensured by surfactant mixtures containing fatty acid or fatty alcohol are related to specific surface properties, and par-

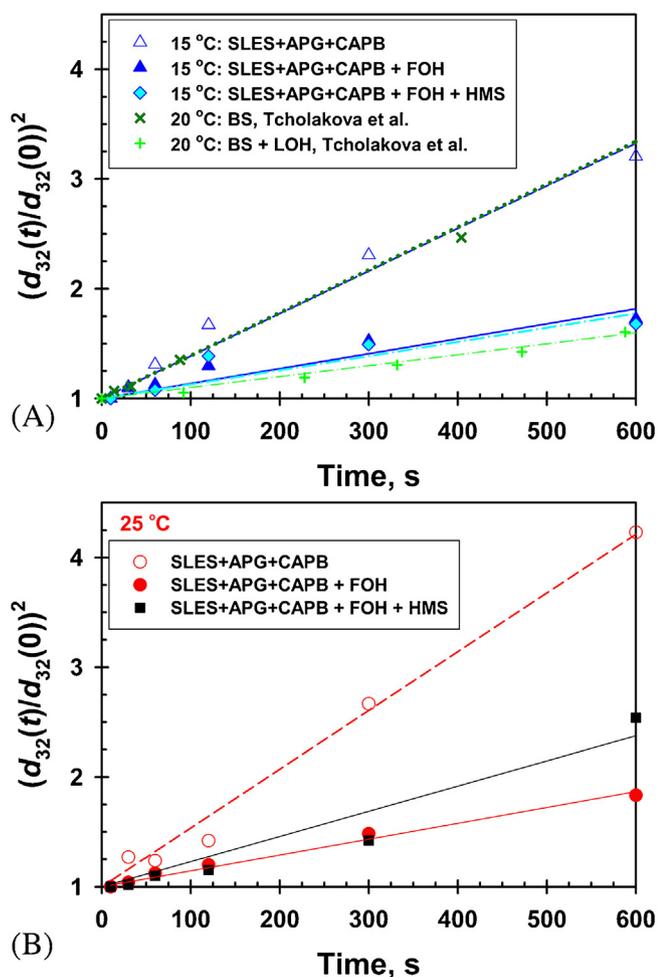


Fig. 7. Relative increase of the bubble surface in foams stabilized with the triple surfactant mixture SLES + APG + CAPB 2:2:1 in the absence and in the presence of additives FOH and HMS as a function of time at (A) 15 °C, and (B) 25 °C. Data from Fig. 2 in Ref. [8] are plotted in (A) for comparison, where BS stands for SLES + CAPB 2:1 mixture and LOH for lauryl alcohol.

ticularly to the high surface modulus. Surface properties of the solutions studied by us are presented in the following section.

3.4. Surface properties

We measured the surface tension of all studied solutions at 25 °C. In addition, for the binary and triple surfactant mixtures we performed measurements in the absence and in the presence of additives at 15 and 20 °C. Notably, in the absence of additives, the surface tension reached a constant value within ~30 s. However, in the presence of FOH a characteristic kink was observed, which could be an indication for a phase transition on the surface [10,14,28,33,34], see Fig. 8. The time for the appearance of the kink was not very reproducible but clear tendency for its shortening with the temperature was observed, as seen from the illustrative plots in Fig. 8. Furthermore, lower values of the surface tension were reached in the presence of FOH as the temperature decreased. Vollhardt et al. [33] have observed qualitatively similar behavior of the surface tension of SDS-dodecanol mixtures. These authors have visualized the surface with a Brewster Angle Microscopy (BAM) and showed directly the formation of condensed phase of dodecanol on the surface of SDS solution.

Fig. 9 presents the values of the surface tension reached after 300 s as a function of the temperature for four of the studied surfactant compositions. In the absence of FOH the surface tension

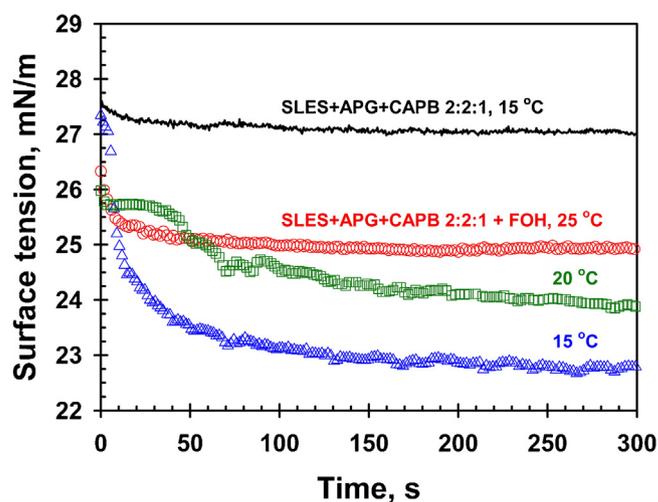


Fig. 8. Surface tension of bubble vs the time after its formation in solution of the triple surfactant mixture SLES + APG + CAPB 2:2:1 in the absence (black line) and in the presence (color symbols) of FOH. Measurements at 15, 20 and 25 °C are shown as indicated in the plot.

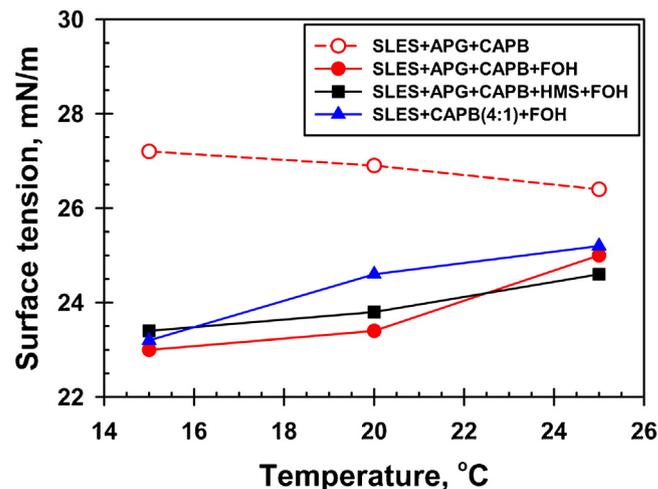


Fig. 9. Surface tension 300 s after bubble formation in solutions of binary and triple (2:2:1) surfactant mixtures in the absence and in the presence of additives FOH and HMS as a function of the temperature.

increased with the decrease of the temperature similarly to pure liquids [35]. All solutions containing FOH, however, decreased their surface tension with decreasing temperature from 25 to 15 °C, similarly to the system in Ref. [33]. Thus we also could hypothesize that FOH dominates the surface and forms a condensed phase. Values of the surface elastic, E' , and loss, E'' , moduli also could be used as an indication for the surface composition [6–8,11]. The measured by us E' and E'' are shown in Fig. 10. In the presence of additives the measured moduli were significantly higher than those of the triple surfactant mixture only. Furthermore, in the presence of additives the moduli E' and E'' start to increase with the decrease of the temperature. Note also that $E'' > E'$, i.e. the surfaces were predominantly viscous. Thus we also could confirm that the reduced drainage of the foams observed in the presence of the additives FOH and HMS (cf. Fig. 4B), and especially at decreased temperature (Fig. 5) was related to the increased surface visco-elasticity.

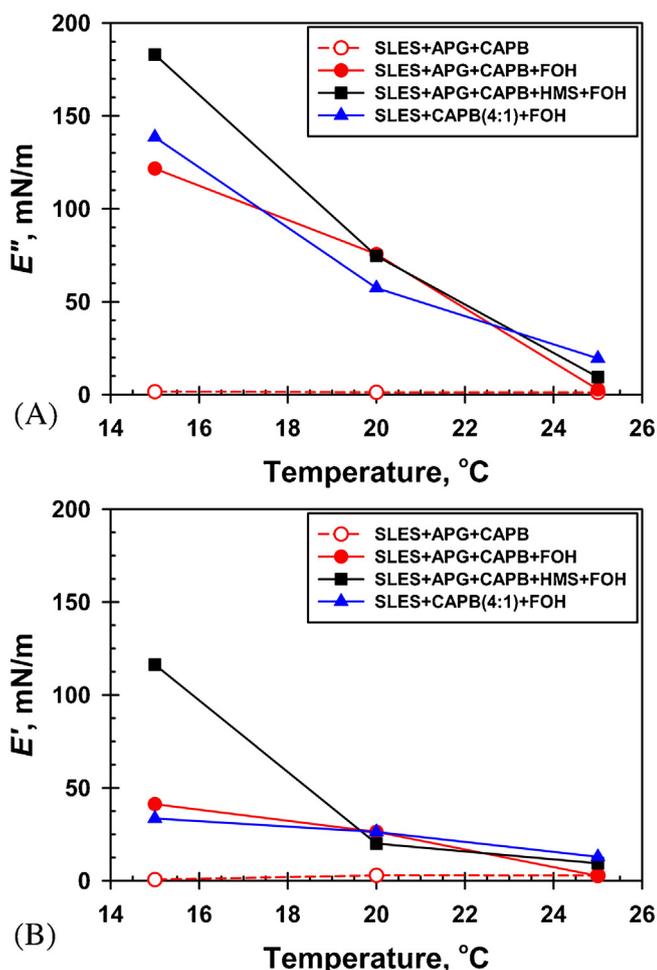


Fig. 10. Typical surface moduli: (A) loss module E'' , and (B) elastic module E' , 300 s after bubble formation in solutions of binary and triple (2:2:1) surfactant mixtures in the absence and in the presence of additives FOH and HMS as a function of the temperature.

Table 3

Typical drainage time of horizontal foam films with diameter $\sim 500 \mu\text{m}$. The values are averaged from 3 to 5 films.

Compositions before 25 times dilution	Drainage time (min)	
	15 °C	25 °C
2%SLES + 2%APG + 1%CAPB	3 ± 0.3	2 ± 0.3
2%SLES + 2%APG + 1%CAPB + 0.2%FOH	20 ± 5	5.5 ± 0.3
2%SLES + 2%APG + 1%CAPB + 0.2%FOH + 0.1%HMS	15 ± 5	6 ± 0.3

3.5. Thin liquid films

We formed and observed horizontal foam films with diameter $\sim 500 \mu\text{m}$ from the triple surfactant mixture in the absence and in the presence of additives FOH and HMS. We registered the thickness and the drainage time of the films. Notably all films reached almost the same equilibrium thickness of $15 \pm 3 \text{ nm}$ and no significant impact of the additives on the thickness was noticed. However the drainage time was significantly affected by the additives and by the temperature. The determined drainage time at 15–25 °C is shown in Table 3. Data clearly show that the drainage time for all compositions increases with the decrease of the temperature. However, the presence of FOH was the key additive with the strongest impact on the drainage: 2–3 times slowing down at 25 °C and 5–6 times slowing down at 15 °C. Rescaling the film drainage time by the bulk viscosity of the solutions, as done for the foam drainage in

Fig. 5 changes the values in Table 3 by 20% only and cannot wane the surface viscosity effect due to FOH condensed phase on the surface.

Most probably the increase of the drainage time is related to the increased surface viscosity (cf. Fig. 10) as predicted by theories for thin film drainage [32,36,37]. The effect has been observed experimentally in many protein [13,38] and surfactant [7,17,18] systems as well.

4. Discussion

The performed systematic investigation of foams stabilized by single, double or triple surfactant mixtures of the nonionic alkyl polyglucoside (APG), anionic sodium lauryl dioxyethylene sulphate (SLES) and zwitterionic cocamidopropyl betaine (CAPB) showed marginal differences in their foaming (cf. Figs. 1 and 3) when compared at the same total concentration of 0.2 wt% in alkaline water with high water hardness.

Fatty alcohol (FOH) and hydrophobically modified starch (HMS) added to the different mixtures were found to reduce significantly the drainage (Figs. 4 and 5) and the Ostwald ripening (Fig. 7) of the foams. The effect was especially visible with decreasing the temperature to 10–15 °C (see Fig. 5) since at lower temperature the surface visco-elasticity, and especially the viscous modulus E'' , strongly increased. Along with moduli increase, we observed surface tension decrease with the temperature decrease. Such changes in the surface tension and visco-elasticity have been observed and explained with a formation of surface condensed phase [33,34], which would consist of fatty alcohol molecules in our systems.

Increased surface visco-elasticity contributed for a significant increase of the drainage time of model foam films formed from several solutions, see Table 3. In the presence of FOH the drainage time increased 5–6 times at 15 °C. Bulk viscosity also increased with the decrease of the temperature, but only with $\sim 20\%$ (see Table 2). This effect deserves better quantitative description and comparison with available theories of film drainage; it might be a matter of a consecutive study especially on the thin films thinning, similarly to the work by Angarska et al. [39].

The increased visco-elasticity contributed for significant decrease of the rate of Oswald ripening in the foams. Despite the different initial bubble size and polydispersity, we have observed similar rates of bubble growth as those by Tcholakova et al. [8] – see Fig. 7A.

The presence of surface active additives that contributed for high surface visco-elasticity, such as fatty alcohol (FOH) or hydrophobically modified starch (HMS) (Fig. 10) did not affected significantly the foaming (Fig. 2).

The added FOH was fully solubilized in the concentrate of the triple mixtures. The remaining stock formulations were turbid and some of them viscous. After 25 times dilution, in most cases clear, non viscous solutions were obtained. We have succeeded to dissolve fully the FOH in the formulations by the addition of the chelating agent MGDA. MGDA was found to improve formulations homogeneity without influencing their foaming in any direction.

In summary, we have successfully dissolved additives: fatty alcohol and a hydrophobically modified starch, contributing for high surface visco-elasticity in solutions containing triple surfactant mixture of SLES+APG+CAPB at alkaline pH and very high water hardness. The addition of APG helped for better surfactant compatibility. The drainage of the foams produced with these mixtures could be successfully controlled by varying the temperature.

5. Summary and conclusions

We performed systematic investigation of foams stabilized by a triple surfactant mixture containing a nonionic alkyl polyglucoside,

an ionic sodium lauryl dioxyethylene sulphate and zwitterionic cocamidopropyl betaine. The foaming of the triple surfactant mixture is comparable to those of the single components and to the binary mixture without alkyl polyglucoside at alkaline pH.

Fatty alcohol and/or hydrophobically modified starch added to the different mixtures successfully reduced the drainage and the Ostwald ripening of the foams. Systematic model experiments showed that the surface tension and dilatational rheology were also strongly dependent on the presence of the additives.

The effects were strongly temperature dependent: drainage slowed down with decrease of the temperature from 25 to 15 °C. Most significant drainage retardation was observed at 15 °C in the presence of additives, where the surface tension was lowest and the surface visco-elasticity was highest.

Drainage of thin horizontal films was also dependent on the presence of additives and the temperature, and was significantly slower when the surface visco-elasticity increased.

The obtained results demonstrated that additives leading to increased surface visco-elasticity of surfactant solutions, could be used successfully for tuning the foam properties of complex surfactant mixtures, of three and more surfactants even at alkaline pH, thus increasing the application range of the foams and ingredients to harsh conditions and requirements.

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