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Article

Effect of Synthetic Polypeptide – *Bio*-Surfactant Composition on the Formation and Stability of Foams

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Abstract: In recent decades, numerous studies have focused on finding environmentally friendly substitutes for commonly used petrochemical-based compounds. This paper explores the potential use of poly-L-lysine/rhamnolipids and poly-L-glutamic acid/ethyl lauroyl arginate mixtures, for foam formation and stabilization. Two complementary methods were employed to investigate the synergistic and antagonistic effects of these mixed polyelectrolyte/surfactant systems: (1) the thinning and rupture of thin foam films formed under dynamic conditions were monitored using a dynamic fluid-film interferometer (DFI), and (2) foamability tests were conducted using a standard dynamic foam analyzer (DFA). The results demonstrated that adding polyelectrolyte to an oppositely charged surfactant primarily induces a synergistic effect, enhancing foaming properties and extending foam lifetime. Furthermore, interferometric methods confirmed improved stability and slower drainage of thin foam films in systems containing synthetic polypeptides.

Keywords: polyelectrolyte/surfactants systems; foam stability; thin foam film; bio-surfactants; synthetic polypeptides; rhamnolipids; ethyl lauroyl arginate; poly-L-lysine; poly-L-glutamic acid

1. Introduction

Foams represent one of the largest groups of dispersed systems and are widely utilized in industrial, technological, and everyday applications. Examples of the significant demand for foam products include mineral processing [1,2], the food industry [3], firefighting [4], cleaning agents [5], and cosmetic and pharmaceutical applications [6]. Recently, the search for foams capable to response for external stimuli as temperature, light, or electricity is of the growing interest [7,8]. In this term, mixed polyelectrolyte/surfactants (PE/S) systems for stabilization of foams and emulsions have been investigated and applied in modern technologies [9,10]. So far, PE/S systems have found applications in detergency, drug delivery, rheological modifiers, or cosmetics [11,12]. On the other hand, polymers have also been adapted for use in mineral processing technologies such as froth flotation [13,14] and flocculation [15] and thus might present an interesting alternative to nanoparticles/surfactant compositions [16,17]. Therefore, it is of great importance to explore polyelectrolyte – surfactant interactions and their effects on process efficiency in these applications.

The stability of foams is primarily governed by the stability of the microscopic and mesoscopic thin liquid films between the compartments (air bubbles). The interfacial behavior of long alkyl chain polyelectrolytes is strongly influenced by hydrophobic interactions, while the complex formation with short chain surfactants is dominated by electrostatic interactions. In case of quasi-static single standoff foam films, the general observation is that the stabilization via oppositely charged PE/S mixtures leads to stable common black films (CBFs), while other systems (same charge system, or non-ionic/charged compounds system) usually form thinner and less stable Newton black films (NBFs) [18]. Beyond these general rules, the preparation of PE/S systems with desirable features depends on several physicochemical properties, including the charge and hydrophobicity of the

compounds used, PE chain length and conformation, PE/S ratio, type of surfactant's headgroup, as well as the bulk's pH and ionic strength [19–23].

Unfortunately, despite their effectiveness in formulation processes, most commonly used polyelectrolytes and surfactants are petrochemical-based compounds that decompose slowly in the natural environment, contributing to water pollution, eutrophication of water bodies, and accumulation in living organisms [24,25]. Those effects are especially pronounced in mineral industry processes where large numbers of chemical compounds are used, such as in froth flotation [26,27] bitumen extraction [28], and enhanced oil recovery [29]. To counteract these undesirable effects, it is of great importance to search for biodegradable, environmentally friendly compounds with low toxicity for both humans and the environment, especially in terms of mass production and overuse of surfactant systems [30,31].

The main objective of the presented study is to investigate the potential use of bio-polyelectrolytes and bio-surfactants in stabilization of foam films formed under dynamic conditions. The choice of the PE/S system components was driven by their properties, such as biodegradability, biological activity (antiseptic properties), and biocompatibility. The physicochemical properties of the system and each component individually will play an important role in the formation and stabilization of thin liquid films.

Particular attention was paid to potential use of bio-polyelectrolytes based on synthetic polyaminoacids: the polycation poly-L-lysine (PLL) and the polyanion poly-L-glutamic acid (PGA). Both macroions have attracted special interest due to their unique properties and its environmentally friendly, biocompatible behaviors [32,33].

Regarding bio-surfactants, rhamnolipids (RH) and ethyl lauroyl arginate (LAE) were chosen. Rhamnolipids belong to the group of microbial glycolipids. They are defined as an anionic surfactants [34], but their charge is strongly dependent on solution's pH [35,36]. They are considered 'green surfactants' due to their low toxicity, good biodegradability and microbial origin. These properties make them an interesting replacement for standard surface-active compounds used in the industry [37,38]. Ethyl lauroyl arginate is an amino acid-based cationic surfactant [39] with strong antimicrobial activity [40]. It has been found that, when combined with cellulose nanocrystals, it forms stable and environmentally friendly foams [41,42], which makes it interesting in terms of PE/S systems.

Using a complementary approach — applying experimental techniques to study foam films under dynamic conditions — the synergistic and antagonistic effects of mixed polyelectrolyte/surfactant systems on foam film stability were examined.

2. Materials and Methods

2.1. Materials

Poly-L-lysine hydrobromide (PLL) of molecular weight 70–150 kg/mol and poly-L-glutamic acid sodium salt (PGA) of molecular weight 50–100 kg/mol were purchased from Sigma-Aldrich (Merck KGaA, Darmstadt, Germany). Stock suspensions of polyelectrolytes of concentration 1 g/dm³ were prepared in Milli-Q water.

Rhamnolipid biosurfactant (RH) was purchased from AGAE Technologies LLC (Corvallis, OR, USA) as a mixture of different mono- and di- RA homologues. The exact composition of the RH mixture was studied by Legawiec et al. (2023) [36]. A stock solution of 1 g/dm³ were prepared in Milli-Q water.

Ethyl lauroyl arginate (LAE) of molecular weight 421 g/mol was purchased from United States Pharmacopeia Reference Standard (Frederick, MD, USA). A stock solution of 4×10⁻³ mol/dm³ were prepared in pure water, stored in fridge and used within 3 days to avoid influence of the surfactant hydrolysis products [43].

The ionic strength and the pH of solutions were adjusted using respective solutions of analytical grade NaCl (Merck KGaA, Darmstadt, Germany), NaOH, and HCl (Chempur, Piekary Slaskie, Poland).

All necessary solutions were obtained by dilution of the stock solutions. Milli-Q water (Millipore, Burlington, MA, USA) was used throughout preparation of all solutions.

2.2. Methods

The surface tension, σ , measurements were performed using the bubble profile analysis tensiometer PAT-1 (Sinterface Technologies, Berlin, Germany). An air bubble was formed at the tip of U-shaped steel capillary of 1 mm inner and 2 mm outer diameters in a closed cuvette (3.5 cm \times 3.5 cm \times 3.5 cm) filled with studied solution. To attain equilibrium, emerging bubble was retained for 10000–40000 sec.

The diffusion coefficients, D , of polyelectrolytes molecules were determined by the dynamic light scattering (DLS) using Malvern Zetasizer Nano ZS apparatus (Malvern Panalytical, Malvern, United Kingdom). Knowing the diffusion coefficient, one can calculate the hydrodynamic diameter, d_H , of the molecules using the Stokes–Einstein relationship [44]:

$$d_H = \frac{kT}{3\pi\eta D} \quad (1)$$

where k is the Boltzmann constant, T is the absolute temperature, and η is the dynamic viscosity of the solution.

The electrophoretic mobility, μ_e , of polyelectrolytes molecules were measured by the laser Doppler velocimetry technique (LDV) using the same Malvern apparatus. The zeta potential, ζ , of the molecules was calculated using the Henry formula [44]:

$$\zeta = \frac{3\eta\mu_e}{2\epsilon f(\kappa d_H)} \quad (2)$$

where ϵ is the electric permittivity of the electrolyte, $f(\kappa d_H)$ is the Henry correction function.

Foamability and foam stability of pure surfactants and their mixture with polyelectrolytes were measured using a Dynamic Foam Analyzer DFA100 (Kruss GmbH, Hamburg, Germany) [45]. The apparatus consisted of (i) a cylindrical glass column of 40 mm diameter and of 250 mm height and (ii) light scanners for simultaneous automatic measurement of foam and solution heights as a function of time. Before each measurement cylindrical column was carefully cleaned with 5% Mucosol (Schülke & Mayr GmbH, Norderstedt, Germany) solution and thoroughly rinsed with Milli-Q water. Next, the column was placed on the apparatus stand and filled with 50 cm³ of the studied solution. The foam was produced by the air pumped at a flow rate of 0.5 dm³/min for 20 sec thru the air disperser – pure cellulose filter paper with pore sizes 12–15 μ m. Data grabbed by PC was analyzed by Kruss Advance software. All measurements were repeated at least three times.

The data on foaming and foam decay were gathered and used for calculation of the Bikerman unit of foaming [46] and the foam production [47]. The Bikerman unit of foaming, Σ , is defined as [46]:

$$\Sigma = \frac{H_{\max}}{U_{\text{gas}}} \quad (3)$$

where H_{\max} is the maximum height of the foam and U_{gas} is the gas flow rate, while the foam production, f_p , is calculated as [47]:

$$f_p = \frac{\Sigma}{U_D} \quad (4)$$

where U_D is the average rate of foam decay.

The thinning dynamics of the foam thin film formed between colliding bubble and the free surface was monitored using the Dynamic Fluid-Film Interferometer (DFI) showed on Figure 1. The bubble was formed at the capillary orifice of inner diameter 0.051 mm mounted at the bottom of the round glass column. The equivalent diameter of the bubble (d_{eq}) detaching from the capillary was 1.31 \pm 0.02 mm in distilled water. Time delay between two successive bubbles was equal to at least 60 sec

and was adjusted using precise 'bubble-on-demand' generator [48]. The distance (L) covered by the bubble from the moment of its release to the moment of liquid film formation was equal to 1.0 or 10 cm. The interference patterns were acquired using top-view camera UI-3280CP-C-HQ (IDS Imaging Development Systems GmbH, Obersulm, Germany) equipped with a light source LAV-80SW2 (CCS Inc., Kyoto, Japan), Zoom Imaging Lens VZM450 (Edmund Optics, Barrington, NJ, USA), and a tri-band filter Edmund Optics #87245 with pass bands at 457 nm, 530 nm, and 628 nm. The film thickness was obtained by analysis of the reflection interference data, i.e. by mapping the colors in the recorded videos, using the classical light intensity–film thickness relations described in details in ref. [49,50].

All experiments were carried out at room temperature of 21 ± 3 °C.

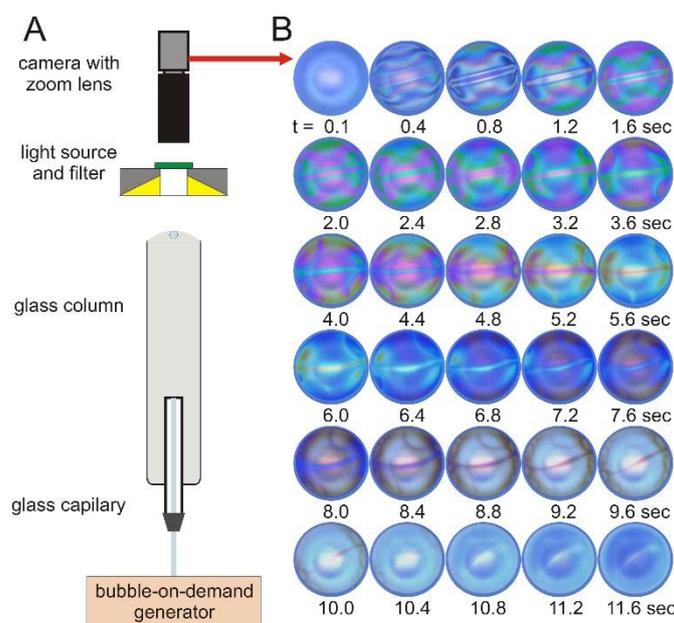


Figure 1. (A) Schematic view of the Dynamic Fluid-Film Interferometer and (B) sequence of experimentally acquired DFI images of a foam film formed at $L = 1.0$ cm for $CLAE = 253$ mg/dm³ and $C_{PGA} = 100$ mg/dm³.

3. Results and Discussion

Figure 2 presents the bulk physicochemical properties of the studied polyelectrolytes. The results in Figure 2A show that at pH 5.8, the electrokinetic potential remains highly positive for PLL and highly negative for PGA, with only slight changes as ionic strength increases. These results indicate that both polyelectrolytes are highly charged, which affects their conformation. Indeed, the hydrodynamic diameter shown in Figure 2B suggests that both macromolecules exhibit a rather elongated conformation [51,52], which may influence the mechanism of foam stabilization.

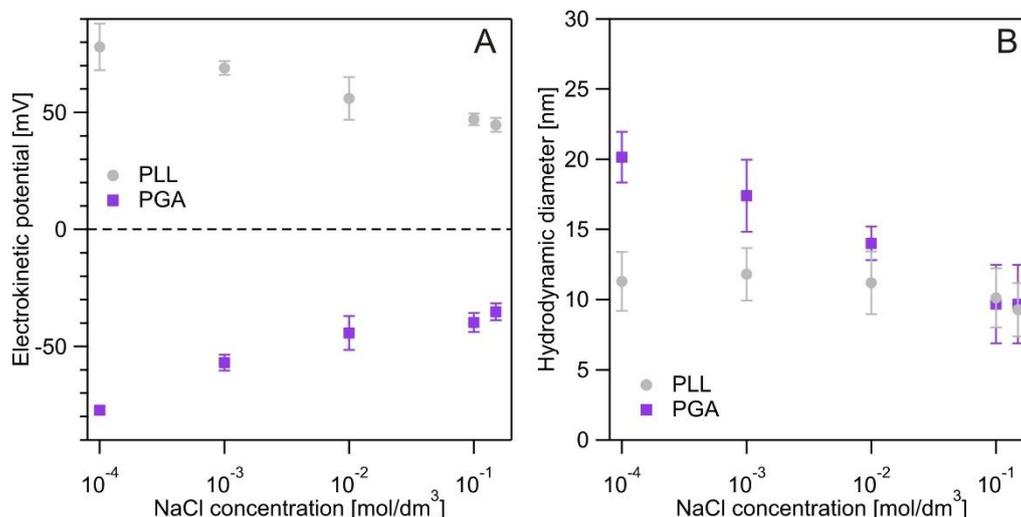


Figure 2. (A) Electrokinetic potential and (B) hydrodynamic diameter of poly-L-lysine and poly-L-glutamic acid in function of NaCl concentration in pH 5.8.

The basic information about the interaction between the surfactant and oppositely charged polyelectrolyte was obtained from surface tension measurements. Figures 3A and 3B show the surface tension as a function of surfactant concentration for PGA/LAE and PLL/RH compositions, respectively. In both cases, the polyelectrolyte concentration was 100 mg/dm³. Additionally, data for surfactants without polyelectrolytes are presented. This polyelectrolyte concentration was chosen after a series of preliminary measurements, which showed it to be optimal. At lower PE concentrations, the effect of the added polyelectrolyte was imperceptible, or a second phase appeared in the bulk, significantly reducing the concentration range in which the study could be conducted. On the other hand, higher PE concentrations led to significantly increased research costs without notable improvements in foam stability. It is worth mentioning that polypeptides alone have no adsorption properties at the water/air interface [53,54].

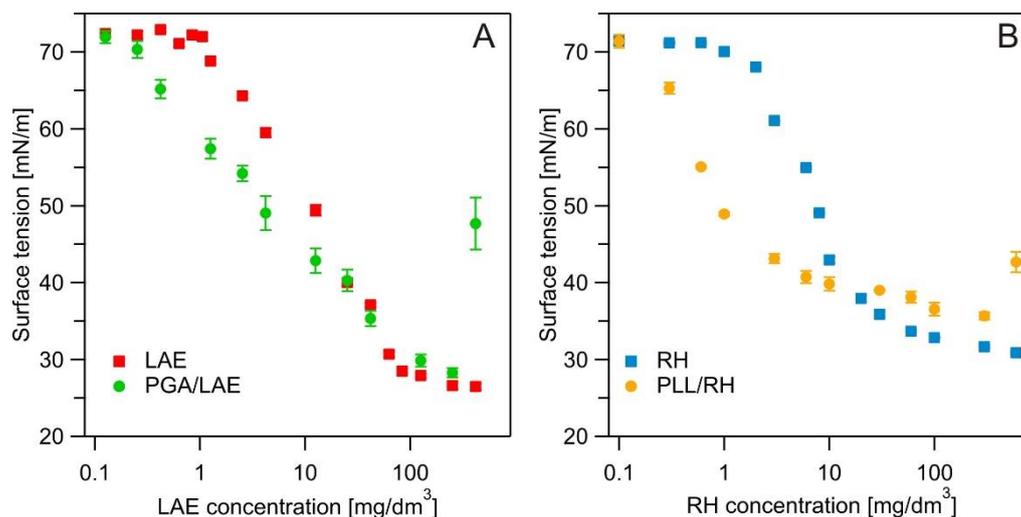


Figure 3. Surface tension of (A) pure LAE and PGA/LAE mixture and (B) RH and PLL/RH mixture in function of surfactant concentration. PGA and PLL concentration was 100 mg/dm³.

The critical micelle concentration (CMC) was found to be ca. 90 mg/dm³ and 30 mg/dm³ for LAE and RH, respectively, what is in good agreement with literature data [36,43]. As seen in both figures, the addition of polyelectrolyte caused a decrease in surface tension compared to the pure surfactant solution. This effect is more pronounced at low to intermediate concentrations, while at higher concentrations, the effect diminishes, leading to a slight increase comparing to the pure surfactant

solution. The observed decrease can be related to two effects: (i) presence of polyelectrolytes can influence adsorption coverage of ionic surfactant over the liquid/gas interface and/or (ii) polymer/surfactant complexes were formed on the liquid/gas interface [55–57]. In both cases, measurements were concluded at the concentration where a second phase appeared, as indicated by a significant increase in the measured surface tension meaning that polyelectrolyte/surfactant complexes desorb, resulting in reduced adsorption of surfactant at the interface [55,58].

While surface tension measurement is an excellent tool for studying the behavior of surface-active substances at the fluid interface and the mechanism of adsorption, the investigation of foams often requires different techniques. For this purpose, dynamic foam analysis is an effective method for evaluating foamability and foam decay. This technique provides quantitative information, such as foam height and the rate of foam decay. Both parameters can be further used to calculate the Bikerman unit of foaminess [46] and the foam production [47], which are interchangeable measures of foamability.

Figures 4 and 5 present foam height as a function of time for PGA/LAE and PLL/RH compositions, respectively, at various surfactant concentrations. In all measurements, the first 20 seconds was the stage during which air was pumped and the foam was formed, reaching its maximum height at the end of this period. Once the air pumping was stopped, foam decay began, and in most cases, the foam disappeared within 100 sec.

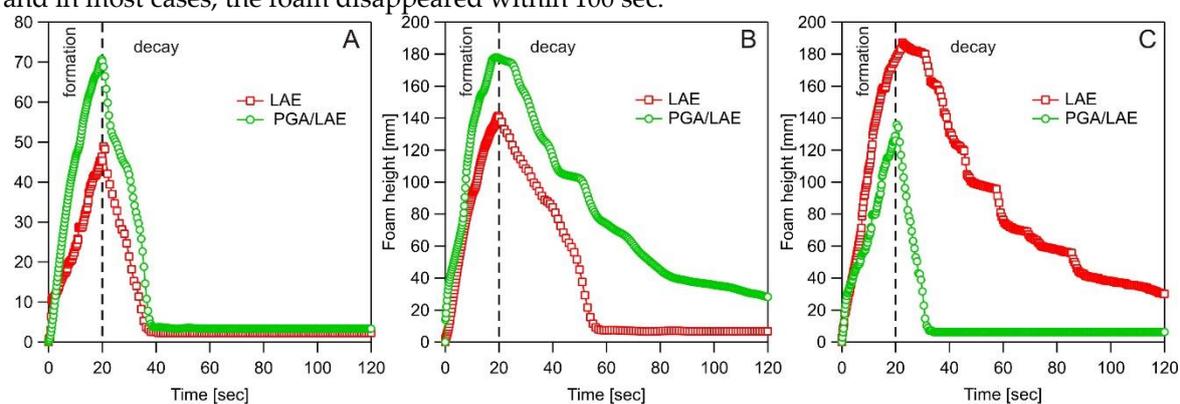


Figure 4. Foamability and foam decay for pure LAE and PGA/LAE mixture for (A) $C_{LAE} = 42.1 \text{ mg/dm}^3$, (B) $C_{LAE} = 253 \text{ mg/dm}^3$, and (C) $C_{LAE} = 421 \text{ mg/dm}^3$. PGA concentration was 100 mg/dm^3 .

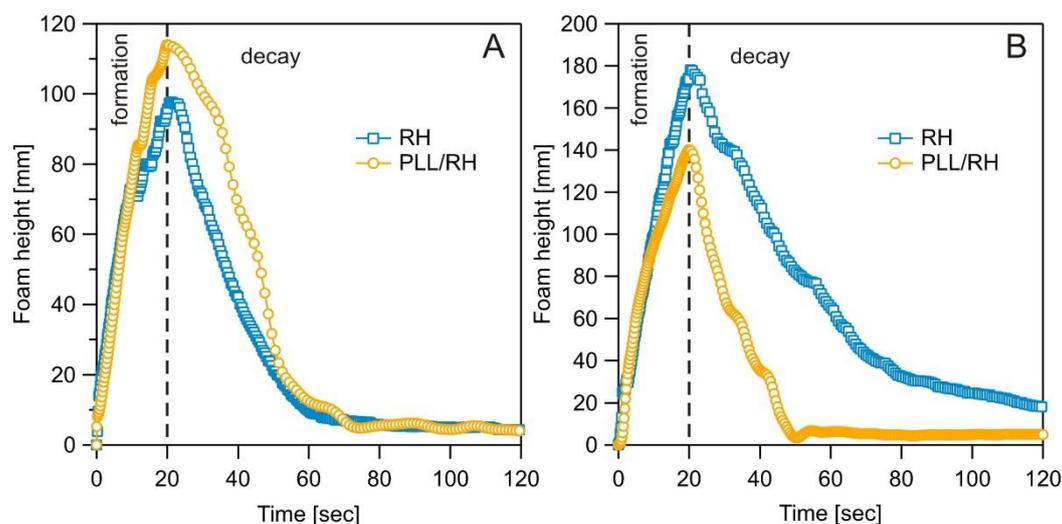


Figure 5. Foamability and foam decay for RH and PLL/RH mixture for (A) $C_{RH} = 100 \text{ mg/dm}^3$ and (B) $C_{RH} = 600 \text{ mg/dm}^3$. PLL concentration was 100 mg/dm^3 .

In the case of the PGA/LAE system, the presence of polyelectrolyte increased the maximum foam height (H_{max}) and slowed down foam decay compared to the pure surfactant. At the highest studied concentration, a substantial decrease in both foam height and stability was observed, which correlates

well with the surface tension data. A similar qualitative effect of increased maximum foam height was observed for the PLL/RH compositions and at the highest concentration, both parameters deteriorated significantly. When it comes to foam stability, it showed no significant improvement – for both, pure surfactant and its mixture with polyelectrolyte, sharp foam decay was observed.

To our surprise, the PGA/LAE composition exhibited better foaming properties than PLL/RH, which is contrary to the data from the surface tension measurements. Therefore, for a thorough quantitative analysis, the Bikerman foaminess and the foam production were determined across the entire range of studied surfactant concentrations. As the gas flow was the same through all measurements, thus calculated values of Bikerman foaminess are directly proportional to the maximum foam heights. In case of the foam production, this parameter is a resultant of two effects: foaminess and foam decay.

The calculated values of both parameters are presented in Figures 6 and 7 for the PGA/LAE and PLL/RH systems, respectively. In both systems, at low surfactant concentrations, there was no difference between the surfactant alone and the polyelectrolyte/surfactant composition, even though surface tension measurements showed a clear effect of macromolecules. The effect of polyelectrolyte addition was observed in the concentration range where the pure surfactant solution also showed increased foaming. The increase in foamability of the studied solutions was noted starting at concentrations close to the CMC of the pure surfactant.

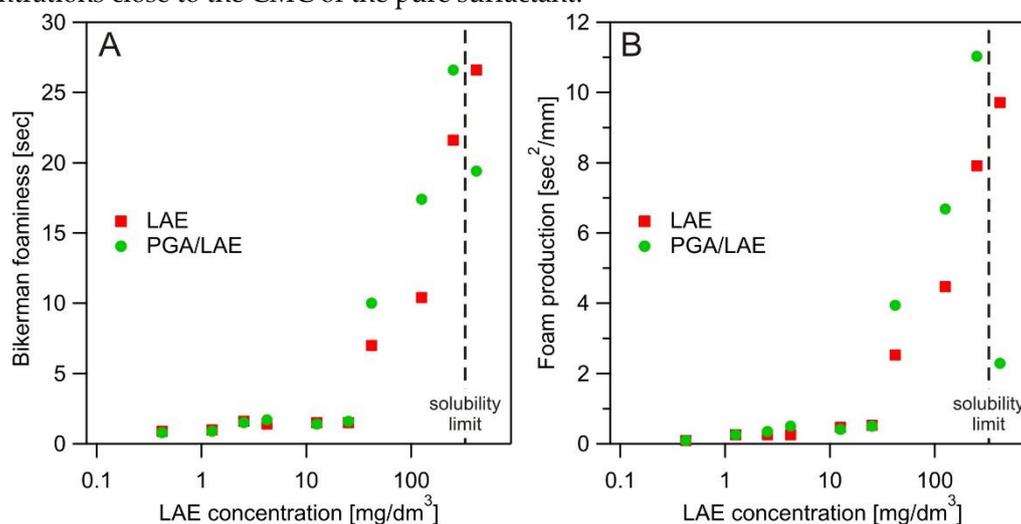


Figure 6. (A) Bikerman foaminess and (B) foam production for pure LAE and PGA/LAE mixture in function of surfactant concentration. PGA concentration was 100 mg/dm^3 .

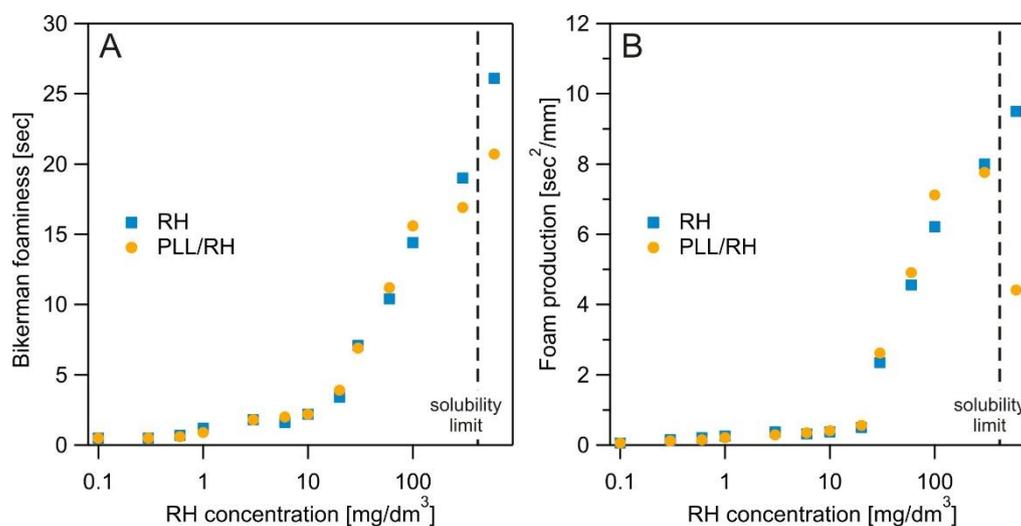


Figure 7. (A) Bikerman foaminess and (B) foam production for RH and PLL/RH mixture in function of surfactant concentration. PLL concentration was 100 mg/dm^3 .

The data in Figures 6A and 6B show that poly-L-glutamic acid had a synergistic effect when mixed with ethyl lauroyl arginate. For the surfactant alone, both parameters describing foam formation and stability increased with surfactant concentration starting at the CMC. The addition of PGA further improved foaming, but at the highest LAE concentration, a second phase precipitated. This phenomenon had a moderate influence on the maximum foam height, but it caused a rapid foam decay and decomposition within 20 seconds, as shown in Figure 4C.

The results for Bikerman foaming and foam production for RH alone and the PLL/RH mixture are presented in Figures 7A and 7B. Similar to ethyl lauroyl arginate, rhamnolipids alone showed an increase in both parameters with increasing surfactant concentration, starting at the CMC. Additionally, both surfactants, LAE and RH, exhibited similar properties regarding maximum foam height and foam decay rate within a comparable concentration range. However, there was a slight shift toward lower concentrations for rhamnolipids, which can be correlated with their CMC values.

As previously mentioned, the addition of PLL to rhamnolipids had an insignificant impact on foam formation and stability. This result might seem surprising in light of the surface tension measurements, but it is important to note that stable foam is typically obtained at surfactant concentrations above the CMC. Therefore, surface tension is not a very accurate indicator of foaming for either the PGA/LAE or PLL/RH systems.

The limited effectiveness of PLL in the PLL/RH composition is likely related to the ionic nature of rhamnolipids. As reported in the literature [35,36], at pH 5.8, rhamnolipids exhibit rather weak ionic/non-ionic properties. Therefore, additional measurements were conducted at pH 10, where the dominant form of rhamnolipids is ionic. It should be noted that the electrokinetic potential of PLL at pH 10 and 1×10^{-4} mol/dm³ NaCl concentration exhibits strongly positive value equal to 62 mV. The foam production increased from 2.6 sec²/mm at pH 5.8 to 4.3 sec²/mm at pH 10, and from 4.9 sec²/mm at pH 5.8 to 6.1 sec²/mm at pH 10 for rhamnolipids concentrations of 30 mg/dm³ and 60 mg/dm³, respectively. These data highlight the importance of pH on the foaming properties of the PLL/RH system.

To gain a more comprehensive understanding of the foaming properties of the studied polyelectrolyte/surfactant compositions, Dynamic Fluid-Film Interferometry (DFI), which allows for the investigation of single foam films, was applied. During a typical DFI experiment, when a rising bubble approached the free surface, a thin liquid film was formed. Due to light reflection at the liquid/air interfaces, colorful patterns were observed, as shown in Figure 1B. These recorded patterns were analyzed to provide information about the lifetime and thinning velocity of the single foam film. Moreover, by adjusting the distance between the point where the bubble was formed and the free surface, various states of the dynamic adsorbed layer (DAL) on the bubble surfaces were obtained [59,60]. Thus, for a 'close' distance, it was expected to have surfactant molecules uniformly distributed over bubble surface. In contrast, at a 'far' distance, surfactant depletion was expected at the front (upstream) part of the bubble, with accumulation in the rear.

Figure 8A,B show the thin liquid (foam) film (TLF) lifetime as a function of surfactant concentration for PGA/LAE and PLL/RH compositions, respectively, at two different distances. In both cases, three characteristic ranges can be distinguished. The first range occurs at low surfactant concentrations, where the thin liquid film was completely unstable, rupturing almost immediately after its formation. In the intermediate surfactant concentration range, i.e., below the surfactant CMC, the TLF lifetime oscillated around 5 sec. In the final range, above the CMC, film stability increased, with TLF lifetimes exceeding 10 sec. However, at the highest surfactant concentration, in the presence of polyelectrolyte, a significant decrease in stability was observed.

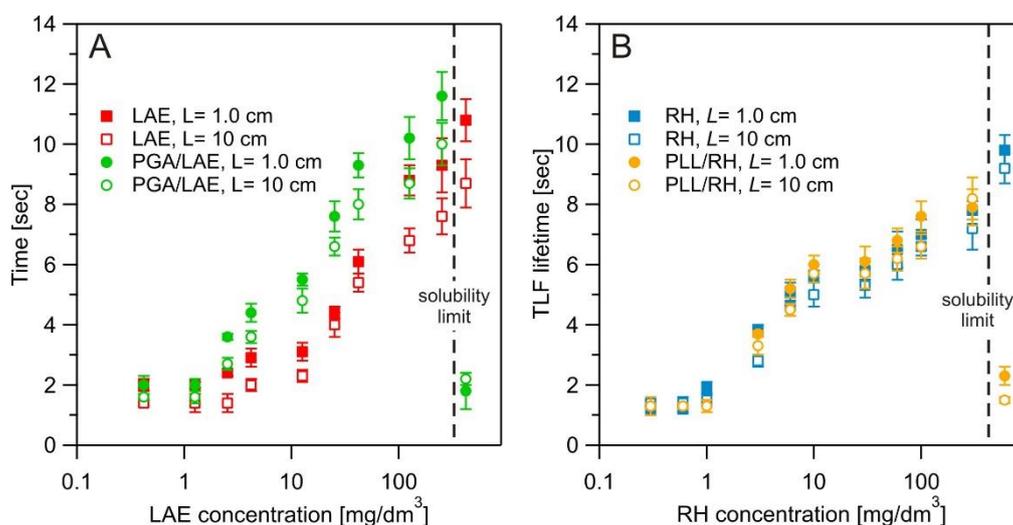


Figure 8. Thin liquid film (TLF) lifetime of (A) pure LAE and PGA/LAE mixture and (B) RH and PLL/RH mixture in function of surfactant concentration. PGA and PLL concentration was 100 mg/dm³.

For both the PGA/LAE and PLL/RH systems, the TLF lifetime data show a qualitative similarity to the results obtained from DFA measurements. A noticeable difference in TLF lifetime was observed between PGA/LAE and LAE alone, while the values for PLL/RH and RH alone overlapped. Thus, it can be concluded that the lifetime of a single thin liquid film correlates much better with the foaminess of the studied compounds than surface tension data.

It is interesting to note that the influence of the dynamically adsorbed layer on TLF lifetime was rather insignificant for all studied solutions, as shown in Figure 8. This lack of a 'distance' effect could be attributed to the rapid formation of the DAL over the bubble surface, resulting in similar coverage states on bubbles colliding with the free surface at both 1 cm and 10 cm. Thus, to investigate the effect of the dynamically adsorbed layer on TLF stability more closely, further measurements at shorter distances or using a 'bubble trap' apparatus are needed [48,61].

In addition to providing information about the lifetime of a thin liquid film, Dynamic Fluid-Film Interferometry also delivers data on film thickness and drainage. Figures 9A and 9B show the thin liquid (foam) film thickness as a function of time for PGA/LAE and PLL/RH compositions, respectively, at various surfactant concentrations.

In the case of pure LAE solution, an increase in surfactant concentration showed two effects: (i) initially, it increased film stability, leading to drainage to a thinner critical thickness before rupturing, and (ii) subsequently, it slowed down film drainage, extending the TLF lifetime. The addition of polyelectrolyte further slowed the drainage of the thin liquid film. The critical rupturing thickness was found to be in the range of 30–50 nm for TLFs with lifetimes exceeding 8 seconds. Once the critical concentration for second-phase precipitation was reached, the thin liquid film ruptured within approximately 2 seconds at a thickness above 1000 nm. However, even during this short period, a significant slowdown in film drainage was observed.

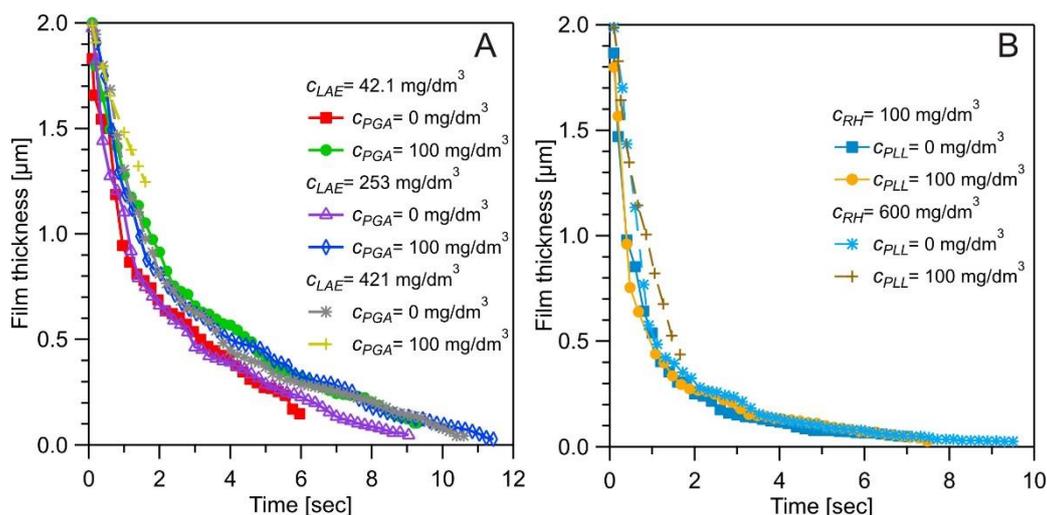


Figure 9. Drainage of the foam film formed at $L = 1.0$ cm of (A) pure LAE and PGA/LAE mixture and (B) RH and PLL/RH mixture in function of surfactant concentration.

In the case of the PLL/RH system, the presence of polyelectrolyte did not affect film drainage or the critical thickness at which rupturing occurred. A significant slowdown in TLF drainage was observed only at the highest RH concentration in presence of PLL, but similar to the PGA/LAE composition, the TLF lifetime remained below 2 seconds. This significant slowing of film drainage in the polyelectrolyte/surfactant system could be attributed to the bulk rheological properties, as reported in the literature [23]. However, the appearance of a second phase indicated the desorption of polyelectrolyte/surfactant complexes from the liquid/gas interface, which led to a decrease in film stability.

The presence of large polyelectrolyte/surfactant aggregates in the foam film was evident not only through the slowing of drainage and shortening of the lifetime but also by characteristic changes at the film interface. As seen in Figure 10 (highlighted by yellow circles), there are localized formations that were likely large aggregates, similar to those presented in the literature [56]. Unfortunately, the films formed under these conditions were unstable, making a thorough investigation of this phenomenon impossible. In our opinion, this finding requires further research, which could likely be conducted at higher surfactant concentrations to ensure sufficient stability of the thin liquid film.

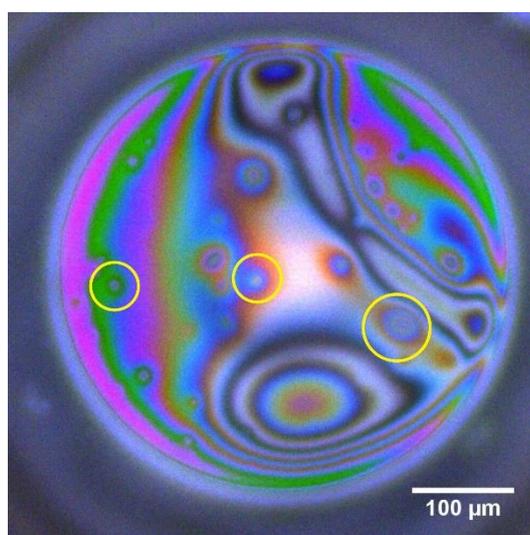


Figure 10. DFI photographic image of a foam film containing interfacial microgels formed at $L = 1.0$ cm for $c_{LAE} = 421$ mg/dm³ and $c_{PGA} = 100$ mg/dm³. Some of the interfacial aggregates are highlighted by yellow circles.

4. Conclusions

As foam systems are crucial for many industrial processes, such as froth flotation, enhanced oil recovery, and flocculation, studying their physicochemical properties, including stability and drainage, is of great interest. To obtain foam with specific and desirable properties, the addition of a surface-active agent is necessary. In this work, foams were produced using *bio*-surfactants, specifically rhamnolipids and ethyl lauroyl arginate, as well as their mixtures with oppositely charged synthetic polypeptides (poly-L-lysine and poly-L-glutamic acid).

Examination of the influence of surfactants alone shows that both compounds exhibit foamability above their CMC. Further increases in concentration led to the production of foams with enhanced stability and reduced foam decay, as confirmed by two independent techniques: dynamic foam analysis and dynamic fluid-film interferometry.

The addition of poly-L-glutamic acid to ethyl lauroyl arginate had a notable impact on foam properties. In terms of foam formation, an increase in maximum foam height and a reduction in the rate of foam decay were observed. These findings were confirmed through the investigation of a single foam film formed under dynamic conditions. The DFI method demonstrated that the presence of PGA prolonged the lifetime of the thin liquid film and resulted in film drainage to thinner critical thicknesses of rupturing.

In the case of the poly-L-lysine/rhamnolipids system, the polyelectrolyte effect was much less significant. This lack of effect was attributed to the primarily non-ionic nature of rhamnolipids molecules at pH 5.8. To examine this hypothesis more thoroughly, preliminary measurements of foam stability for the PLL/RH mixture at pH 10 were conducted. The results showed that the increased charge of the surfactant molecules enhanced the foamability of the studied compositions. Therefore, further investigation into the effect of pH on the foamability of polyelectrolyte/surfactant systems is required.

It should be emphasized that polyelectrolyte/surfactant systems could only be used within a narrow concentration range. Increasing the surfactant concentration while keeping the polyelectrolyte concentration constant caused the formation of a second phase in precipitated form. This phenomenon led to the removal of surfactants and polyelectrolyte/surfactant complexes from the air/water interfaces, resulting in decreased foamability and rapid foam decay.

The presented study showed that polyelectrolyte/surfactant systems could be an interesting and promising alternative to standard foaming formulations, but they require further investigation to optimize their compositions. Thus, further exploration of the influence of pH and ionic strength on foamability is desired, as well as the investigation into the critical concentration of coalescence (CCC) and the formation of the dynamic adsorption layer.

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