

Impact of the Surfactant Structure on the Foaming/Defoaming Performance of Nonionic Block Copolymers in Na Caseinate Solutions*

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Abstract. Systematic experimental study of the physico-chemical factors controlling the foaming and defoaming performance of several Pluronic nonionic block copolymers is performed in solutions of sodium caseinate. Dynamic light scattering measurements and microscopic observations confirm that a significant defoaming is observed above the cloud point of the nonionics, which is almost independent on the polymer structure. However significant differences are observed in the foaming below the cloud point, which do correlate with the polymer structure. Dynamic surface tension measurements allow more detailed analysis of the mechanism of polymer and protein adsorption, and of the role of the individual components for the overall stabilization or destabilization of the foams.

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1 Introduction

Pluronics are linear block copolymers consisting of polyoxyethylene (EO) and polyoxypropylene (PO) blocks [1-3]. These molecules are highly surface active due to the partial hydrophobicity of the PO blocks. Thus varying the molar ratio of the EO and PO groups and their order (PO-EO-PO or EO-PO-EO) one obtains molecules with various tunable properties and applications [1,4]. The Pluronics with ratio PO:EO between 4:1 and 9:1 are widely used as antifoams [3] but almost no data have been published on the mechanism of defoaming. Main

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areas of application of the Pluronic antifoams include dishwashing machines and sugar beet industry [3]. In many of these applications, voluminous dynamic foam is formed, stabilized by proteins and/or sugars [3].

The main aim of our work is to investigate of the physico-chemical factors controlling the foaming and defoaming performance of several Pluronic nonionic amphiphiles in solutions of the milk protein Sodium caseinate.

We have focused our considerations to the dynamic processes only, which occur, *e.g.*, during automatic washing of fabrics and dishes. In these very dynamics foams, gas entraps together with liquid jets circulating in the water bath. New gas bubbles form with high rate (milliliters to liters per minute, depending on the process), which leads to formation of a new surface with a rate of up to several square meters per second [5,6]. Stability of this newly formed foam depends on the stability of the dynamic foam films forming upon bubble collisions.

In absence of surface active substances these films are unstable, however, in presence of surfactants or other foam stabilizing agents, the foam films are stabilized and continuous foam increase is observed. Breaking of otherwise stable films, however, is possible when antifoams substances are present in the foaming media [5-9]. The antifoams could be formally divided into soluble and insoluble ones, the former present under their limiting solubility in the solution while the later forming insoluble globules (droplets and/or solid particles) [5-7,10].

Soluble defoamers are different fatty alcohols and acids, and also some partially soluble organic substances, present in the foaming solution below their limiting solubility [8-10]. The soluble defoamers are believed to contribute for the foam depression mainly by inclusion in the surfactant adsorption layers on the air/water interface, thus hindering the stabilization of the liquid films and foams [8-10].

Insoluble defoamers are called substances present as micron or submicron globules (droplets, solid particles, or their mixtures) in the foaming media. For aqueous foams insoluble defoamers are the hydrocarbon, silicone or fluorocarbon oils, inorganic (silica and alumina oxides, calcium precipitates) or organic (*e.g.* solid fatty alcohols) solid particles, or mixtures of those [5-8]. Various mechanisms have been discussed in the literature for the insoluble antifoams [5-9], *e.g.* bridging-dewetting [7] and bridging-stretching [5,11] mechanisms, realized when an antifoam globule bridges the surfaces of the foam film [5-9,11], or spreading-wave generation observed after an antifoam globule has been compressed in the thinning Plateau channels in the foam [5,12].

When the globules are able to destroy the foam films by either of the bridging mechanisms, the foam disappears very fast (for seconds to several minutes after its formation). If the destruction starts after a globule enters the surface of the Plateau channels, then the foam destruction occurs typically for minutes or even hours. That is why the antifoams were classified also as fast (*i.e.* film breaking), and slow (*i.e.* Plateau channels breaking) [5,6]. Note that in dynamic foams

no “spreading-wave generation” mechanism could be realized since there are no Plateau channels formed.

Nonionic surfactants are a special class of substances which are soluble in water and usually promote the foaming below their cloud point (CP), however, they form surfactant enriched (oily) droplets above their cloud point. These surfactant enriched (coacervate) globules are believed to cause heterogeneous type of foam destruction, similarly to the insoluble antifoams [8,13].

In fact, the nonionic surfactants might not enhance foaming even below their cloud point, if they do not form well packed adsorption monolayer on the water/air interface and do not contribute to the stabilization of the foam films by steric repulsion. In this case, the foaming is very low and the reason is the instability of the foam films *per se*.

Summarizing, the nonionic amphiphilic copolymers could act as both soluble and insoluble antifoams, and as foam stabilizers, depending on the specific substance, concentration, temperature, and other experimental conditions.

The aim of the present work is to clarify the physico-chemical factors controlling the foaming and defoaming performance of several Pluronic nonionic amphiphiles in solutions of the milk protein sodium caseinate.

2 Experimental

2.1 Materials

We have used four different nonionic surfactants of Pluronic[®] type, whose properties are summarized in Table 1. Note that three of the Pluronics (PE XXXX) were with a central polypropylene glycol group, connected to two end polyethylene glycol groups, while the fourth one (RPE 2520) had central polyethylene glycol group and two end propylene oxide groups [2].

Table 1. Description of the used Pluronic copolymers. Approximate molecular weight is taken from the Technical information by the producer [2]. The number of EO (ethylene oxide) and PO (propylene oxide) are average values calculated after the Technical information. CP was determined from DLS measurements with 0.2 % solutions in water (see the experimental results)

Commercial name	Short name used in the text	Molecular weight, g/mol	EO content, m%	CP, deg C
Pluronic [®] PE 6100	PE 6100	approx. 2000	approx. 10	25 ± 2
Pluronic [®] PE 8100	PE 8100	approx. 2600	approx. 10	19 ± 2
Pluronic [®] PE 10100	PE 10100	approx. 3500	approx. 10	17 ± 2
Pluronic [®] RPE 2520	RPE 2520	approx. 3100	approx. 30	25 ± 2

Foam measurements were performed with solutions containing Pluronics with concentrations of 0.0002, 0.002 and 0.02 wt.%. Measurements were carried out in absence and in presence of 0.1 wt.% Na caseinate (Alanate 185, from NZMP, New Zealand).

All solutions were prepared with deionized water from Millipore Elix purification system (Millipore, USA). pH was adjusted to 12 using 1 M stock solution of NaOH (analytical grade sodium hydroxide, Merck). Analytical grade $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ (Merck) was added to some of the solutions to explore the impact of 0.01 wt.% Ca on the solution properties. All concentrations referred below as % corresponded to wt.%.

2.2 Methods

Foam Test: Ross-Miles Test (RMT or Circulation Test)

The foam was formed in a graduated cylinder of total volume ≈ 600 mL. The cross-section area of the cylinder was 10.5 cm^2 and a foam volume of 100 mL had a height of ≈ 10 cm.

The foam was formed by a circulation of 350 mL solution for 1 minute (see Figure 1A). The liquid circulation was realized by a pump, which sucked the solution from the bottom of the cylinder and poured it on top of the solution surface through a nozzle (5 mm diameter), placed at 25 cm above the liquid level.

During the circulation of the liquid, dynamic foam was formed which had almost constant height/volume after, *e.g.*, 30 seconds of circulation, see Figure 1B. The steady-state height of the dynamic foam was measured and called hereafter the Dynamic Foam Height (DFH) – this height was used as a quantitative measure for the foamability of the solutions.

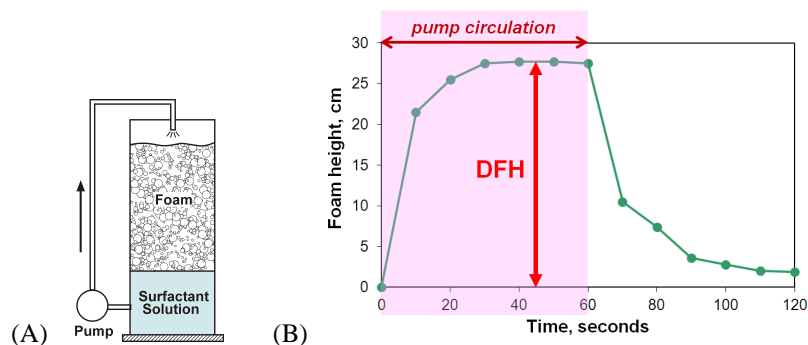


Figure 1. (A) Schematic presentation of the column used for the foaming experiments by the circulation Ross-Miles test (RMT); (B) Change of the foam height during the liquid circulation for 1 min and the determined dynamic foam height (DFH).

The reproducibility of the results for the DFH from independent measurement runs (separately prepared solutions) was within ± 2 cm foam height.

All measurements presented and discussed below were performed at ambient temperature $25 \pm 1^\circ\text{C}$.

Dynamic surface tension

We measured the dynamic surface tension (DST), $\sigma(t)$, by the Maximum bubble pressure method (MBPM) using Bubble Pressure Tensiometer BP2 (Krüss GmbH, Germany).

Optical microscopy

Some of the studied solutions were inspected by light microscopy in transmitted light in order to observe the particles and aggregates that cause the solutions opalescence and turbidity and may act as antifoam entities. Microscope Ax-ioplan (Zeiss, Germany) with objective $\times 20$ and $\times 50$ was used for all optical observations.

Dynamic light scattering

To characterize the surfactant aggregates and particles in the solutions with size smaller than the resolution of the optical microscopy ($1 \mu\text{m}$) we applied dynamic light scattering (DLS), using the light scattering system Zetasizer Nano ZS (Malvern Instruments, UK).

3 Results and Discussion

3.1 Foams

We first compare the foamability of the solutions contained only Pluronic or only Na caseinate. The results plotted in Figure 2, show that all used Pluronics had lower foamability than the caseinate solution. The concentration dependences of the foamability of the Pluronics were quite different: the most soluble one, with the lower molecular mass (PE 6100) decreased its foamability with the concentration, while the least soluble and having the largest molecular weight (PE 10100) increased it. The foaming of the intermediate polymers PE 8100 and RPE 2520 passed through a maximum in the studied concentration range, see Figure 2.

At low concentrations ($< 0.01\%$), where no phase separation was expected [1], the foaming of PE Pluronics increased with CP (see Table 1). However, RPE

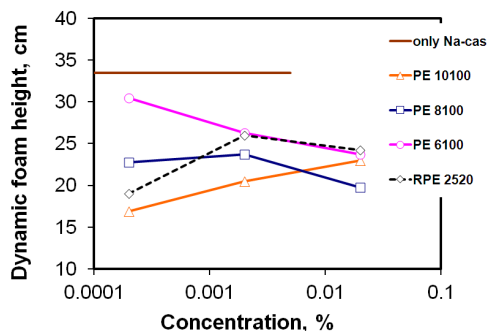


Figure 2. Dynamic foam height for all studied Pluronics and of Na caseinate (Na-cas) solutions, in the working concentration range. All solutions had pH = 12 and did not contain Ca.

2520 did not follow the same dependence on the CP. The later observation shows that, at the same CP, the EO-PO-EO structure ensures better foaming than the PO-EO-PO structure.

The results from the foaming tests with mixed Pluronic-Na caseinate systems are shown in Figure 3. The foamability of the mixed systems is compared to that of the individual components to get better insight on the role of Pluronics. In all systems containing Ca, the mixing of the good foamer Na caseinate with the poor foamer Pluronic resulted in intermediate foaming. The same tendency was observed with Pluronic PE 10100 in absence of Ca. In few systems only, *e.g.* PE 6100 and some concentrations of PE 8100 and RPE 2520, the foaming of the mixed solutions was lower than that of the individual components. One could conclude that all used Pluronics acted as foam suppressors for Na caseinate.

The concentration dependencies show another interesting effect: in presence of Ca, the increase of Pluronic concentration led to a better foam suppression, while in the absence of Ca the foaming decrease was most pronounced at the lower Pluronic concentrations. The later observation suggested that two different defoaming mechanisms are probably operative in the absence and in the presence of Ca:

1. At the high working pH (≈ 12) Ca forms precipitates which act synergistically with the coacervate droplets [5]. This means that the increased number of droplets with the Pluronic concentration would contribute to better defoaming by a heterogeneous mechanism.
2. Ca^{2+} counterions contribute to formation of denser and more resistant to rupture Na-caseinate adsorption layers, *i.e.* more stable films and foams are formed [15,16]. Thus in the absence of Ca, the molecules Pluronic would easier penetrate and displace the protein from the adsorption layer which would lead to foam destabilization by a molecular (homogeneous mechanism).

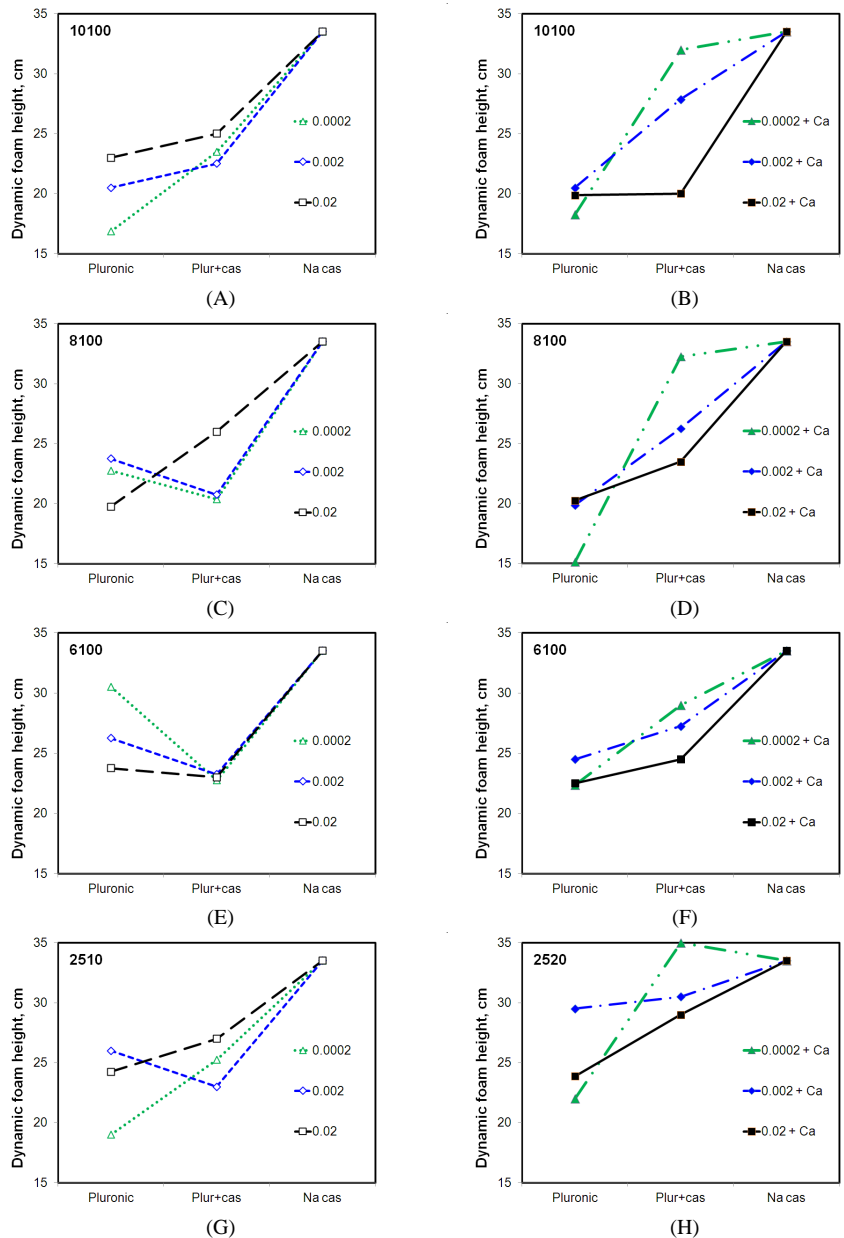


Figure 3. Dynamic foam height, as a function of the solution content: mixed vs single components solutions, at different concentrations of Pluronic, in absence and in presence of 0.01% Ca (see the legend).

To check these hypotheses we performed systematic characterization of the bulk and surface solution properties, and the respective results are presented and discussed in the following sections.

3.2 Bulk Properties

We performed Dynamic Light Scattering (DLS) measurements with solutions of the used Pluronics, by varying the temperature from below to above the CP. Note that the concentration of the solutions for DLS was 0.2%, *i.e.* 10 times higher than the highest used in the foam measurements. We tried to work with 0.02 % solutions, however, the signal was rather noisy, due to the low particle/aggregate concentration. Comparison of the samples below and above CP by naked eye showed transparent solutions below CP at all concentrations, transparent solu-

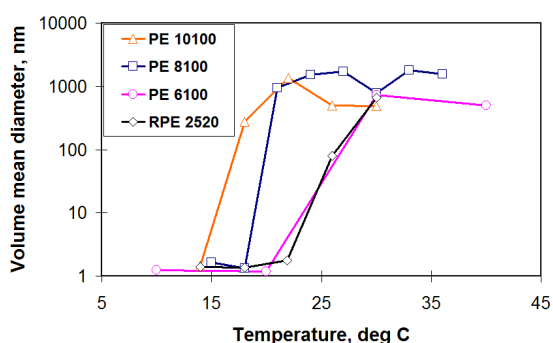


Figure 4. Volume averaged diameter in 0.2% Pluronic solutions, as determined by DLS upon temperature variation.

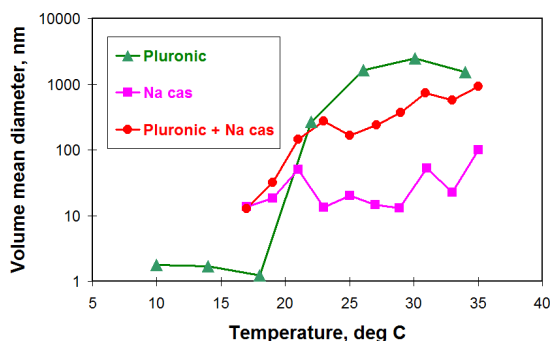


Figure 5. Volume averaged diameter, as a function of the temperature, for solutions of 0.2% Pluronic PE 8100, 0.1% Na caseinate, and their mixture as determined by DLS.

tion with few droplets flowing above CP of 0.02% solutions, and turbid solution with many submicrometer droplets upon clouding of 0.2% solutions.

The obtained results for the volume averaged diameters, measured by DLS with 0.2% Pluronic solutions, are presented in Figure 4. Sharp increase of the size of the aggregates in the solution was observed upon clouding: micrometer droplets formed above the CP, while probably submicellar aggregates formed below CP [1].

Presence of Na caseinate in the solutions was not found to cause any significant change on the clouding. A representative plot of the DLS data in the absence and in the presence of Na caseinate is shown in Figure 5.

We performed optical microscopy observations of the solutions at 25°C (above CP) and we did observe large coacervate phase droplets in all Pluronic solutions with concentration 0.02% or larger, see Figure 6A. We observed also crystals of CaCO₃ in all solutions containing 0.01% Ca (Figure 6B) which sometimes formed mixed aggregates with the coacervate droplets (Figure 6C). All droplets and crystals observed in the solutions of high concentration could act as heterogeneous antifoams, as already shown in the literature for similar systems [5,6].

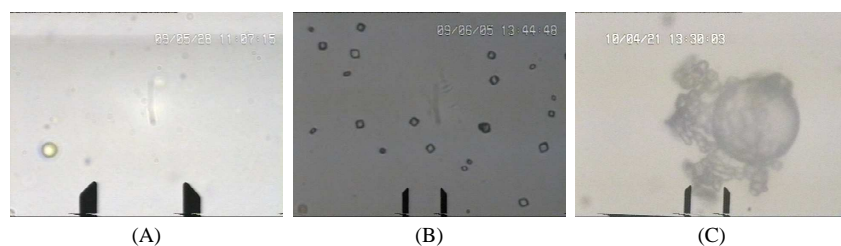


Figure 6. Transmitted light optical microscopy images of (A) droplet of coacervate phase observed in 0.02% solution of PE 8100; (B) crystals of CaCO₃; (C) mixed aggregates of CaCO₃ crystals and coacervate droplets. The distance between the reference bars is 20 μm .

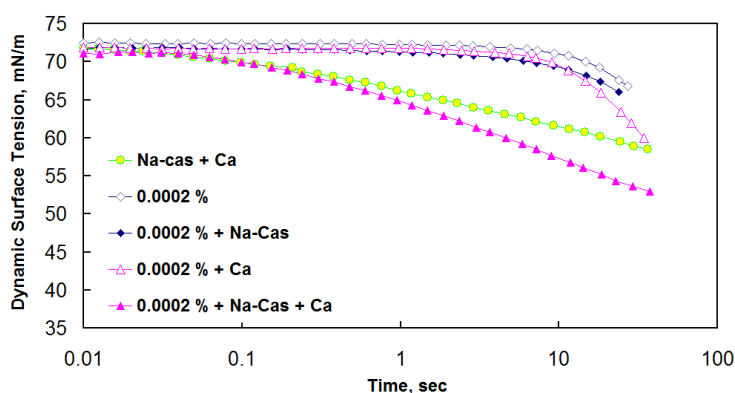
3.3 Dynamic Surface Tension

We measured the dynamic surface tension, $\sigma(t)$, of all solutions used for the foam tests by the Maximum Bubble Pressure Method (MBPM).

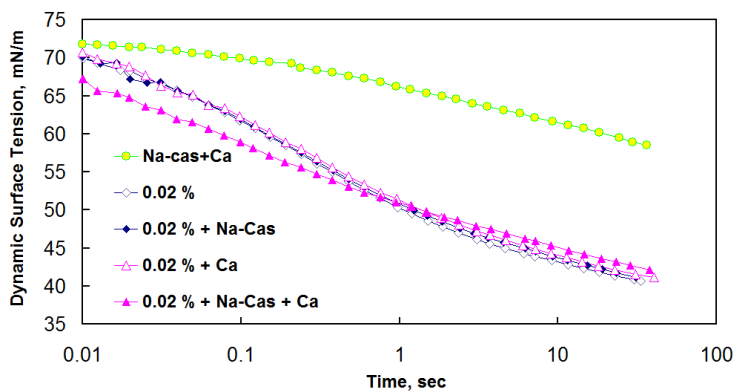
First, it is worth noting that all Pluronics at the same concentration had almost the same DST curves and almost no effect of Ca was noticed, as could be expected for nonionics [1,16]. Note that the used Pluronics differed in their molecular weight and different $\sigma(t)$ curve were to be expected, if the samples were of monomolecular composition. However, we used commercial samples, which were mixtures of molecules with different molecular masses and the referred weights were averaged ones.

The most significant effects found for all used Pluronic were the following:

(i) at low Pluronic concentration (0.0002%) $\sigma(t)$ decreased faster for Na-caseinate solution, *i.e.* the protein was more surface active than the Pluronic. Furthermore, Ca affected the adsorption of Na caseinate, since this protein was charged at pH = 12 [14,15]. As a result, in presence of Ca, the $\sigma(t)$ curves were determined by the Na caseinate, as shown with the illustrative results plotted in Figure 7A. Note also that the mixed solution of RPE 2520 and Na caseinate with Ca decreased its surface tension faster than any of the individual components, which correlated very well with the slight foaming increase observed in this system (see Figure 3H). In absence of Ca, however, the surface tension and the adsorption layers were dominated by the Pluronic, see Figure 7A, which resulted in very low foaming (cf. Figure 3G).



(A)



(B)

Figure 7. Dynamic surface tension, $\sigma(t)$, for solutions of 0.1% Na caseinate and/or 0.0002% (A) and 0.02% (B) Pluronic RPE 2520.

(ii) at high Pluronic concentration (0.02%) the dynamic surface tension curves were determined by Pluronic because it adsorbed faster than the protein, see Figure 7B. In this case, Ca had a negligible effect on the $\sigma(t)$ curves. However, the foaming of the mixture was intermediate, especially in presence of Ca, and one could not exclude the formation of mixed adsorption layers, containing excess of Pluronic which decreased the foaming.

In summary, the dynamic surface tension data show a molecular (homogeneous) mechanism of destabilization of the foams of Na caseinate by the used Pluronics. Ca supported the adsorption of Na caseinate and the foaming and, therefore, the foaming decreased as the Pluronic concentration increased. Note that these considerations did not exclude the prevailing role of the heterogeneous mechanism of defoaming at higher Pluronic concentrations.

4 Summary

Systematic investigation of the foaming of several low foaming Pluronic non-ionics and of their mixtures with Na caseinate was performed at high pH.

The Pluronics of EO-PO-EO type increased their foamability with the CP, while the one of PO-EO-PO type did not follow the same trend. This comparison shows that not only the solubility (expressed as the cloud point of the polymer) is important for the foam stabilization, but the packing in the surfactant adsorption layer is also important.

Analysis of the dynamic surface tension data, along with the foaming performance, show that mixed adsorption layers are formed between Na caseinate and the Pluronics in a wide concentration range. The presence of Ca facilitates the formation of denser adsorption layers of the protein and thus reduces the defoaming activity of Pluronics. At low Pluronic concentration and with Ca, even foam boosting effect was observed with Pluronic RPE 2520.

The adsorption of Pluronic molecules in the mixed adsorption layers increased with the polymer concentration, which led to better defoaming, especially in absence of Ca, *i.e.* defoaming by a homogeneous mechanism occurred.

Heterogeneous defoaming mechanism by coacervate phase droplets additionally contributes to the decrease of Na caseinate foaming, at high Pluronic concentrations (above the cloud point of the polymer).

The obtained results have direct implications for the understanding the foaming and defoaming mechanisms during fermentation and washing processes in various industries.

Acknowledgement

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References

- [1] P. Alexandridis, B. Lindman Eds. (1997) *Amphiphilic Block Copolymers: Self-Assembly and Applications*, Elsevier, Amsterdam.
- [2] BASF Technical information TI/ES 1026 e November 2002 (DFC), TI/ES 1164 e April 2005 (DFC).
- [3] T.G. Blease, J.G. Evans, L. Hughes, P. Loll (1993) In: *Defoaming: theory and industrial applications*, Surfactant Science Series, vol. 45, Marcel Dekker Inc., New York, Chapter 8, p. 299.
- [4] P. Alexandridis (1996) *Curr. Opin. Colloid & Interface Sci.* **1** 490.
- [5] N.D. Denkov (2004) *Langmuir* **20** 9463.
- [6] N.D. Denkov, K.G. Marinova (2006) In: *Colloidal Particles at Liquid Interfaces*, B. P. Binks, and T. Horozov Eds., Cambridge University Press, Cambridge, Chapter 10.
- [7] P.R. Garrett Ed. (1993) *Defoaming: Theory and Industrial Applications*, Marcel Dekker, New York.
- [8] C.A. Miller (2008) *Curr. Opin. Colloid & Interface Sci.* **13** 177.
- [9] D. Exerowa, P.M. Kruglyakov (1998) *Foams and Foam Films: Theory, Experiment, Application*, Elsevier, Amsterdam, Chapter 9.
- [10] T.A. Koretskaya (1974) *Kolloidn. Zh.* **39** 571.
- [11] N.D. Denkov (1999) *Langmuir* **15** 8514.
- [12] E.S. Basheva, D. Ganchev, N.D. Denkov, K. Kasuga, N. Satoh, K. Tsujii (2000) *Langmuir* **16** 1000.
- [13] A. Bonfillon-Colin, D. Langevin (1997) *Langmuir* **13** 599.
- [14] O.D. Velev, B. E. Campbell, R. P. Borwankar (1998), *Langmuir* **14** 4122.
- [15] K.G. Marinova, E.S. Basheva, B. Nenova, M. Temelska, A.Y. Mirarefi, B. Campbell, I.B. Ivanov (2009) *Food Hydrocolloids* **23** 1864.
- [16] P.A. Kralchevsky, K.D. Danov, N.D. Denkov (2002) In: *Handbook of Surface and Colloid Chemistry*, K.S. Birdi Editor, 2nd Edition, CRC Press, New York, Chapter 5.