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Evolutions and equilibrium parameters of foam films from individual solutions of Bovine serum albumin, *n*-dodecyl - β -D-maltoside and from their mixed solutions

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Abstract: *The evolutions of thinning of films from individual solutions of BSA, C₁₂G₂ and from their mixed solutions with molar ratios 1:1, 1:7.5, 1:50 and 1:100 with pH = 4.9 were recorded by modified (with video camera) interferometric method. Based on them the stages through which the film goes from its formation to the equilibrium state were distinguished. It was shown that: (i) the difference between the kinetic of drainage of films stabilized by high and low molecular surfactants is drastic; (ii) only the change of the pH solution under or above isoelectric point strongly retards the film drainage; (iii) the transition of the kinetic of thinning of films from mixed solutions from a kinetic typical for high molecular substances towards a kinetic for low substances depends on the molar ratio between the components in the solution. From the picture of film corresponding to its equilibrium state the type of film was determined. From the analysis of this picture the equilibrium thickness and contact angle were calculated. It was found that the criterion for Newtonium black films (based on the values of film thickness and contact angle) is not directly applicable for films from protein solutions or mixed solutions with the participation of proteins.*

Keywords: *Bovine Serum Albumin (BSA); *n*-dodecyl - β -D maltoside (C₁₂G₂); mixed BSA/ C₁₂G₂ solutions; film evolution; equilibrium thickness; contact angle.*

Introduction

The pursuit of people to keep the ecological equilibrium, to produce pure and non toxic foods, stable medical compositions and detergents without allergic effects determines the interest to proteins as stabilizers of foam. By this reason foam films (FF) stabilized by different individual proteins (fibrillar or globular) have been subject of many experimental and theoretical studies [1-7dr]. Low molecular surfactants are used in isolating, purifying and storing of the proteins in the detergents and medicine compositions. That’s why in the last years the properties of the thin films of mixed solutions of proteins and low molecular surfactants are intensively investigated [8-12dr]. The information about of the type, structure and equilibrium film parameters as thickness, contact angle at different experimental conditions (protein nature and concentration, electrolyte concentration and pH of the medium) is important for relatively stable foams. Usually, the foams used in the practice are unstable ones. That’s why in these cases the film’s kinetic behavior is more important. The qualitative information about film properties can be drawn from the evolution of the film formation and drainage. The video record of the film evolution not only visualizes its formation and drainage but it gives a crucial qualitative information about its kinetic behavior and equilibrium properties. For example based on it:

- the stages through which the film goes from its formation to the critical state can be distinguished and from the latter one to the equilibrium state, respectively;
- the type of the film in its equilibrium state can be determined;
- the drainage kinetic of the films from solutions of high and low molecular stabilizers can be compared;

- one can check whether the change of the pH solution only under or above isoelectric point could retard the film drainage;
- the molar ratio of the mixed solution at which is established a smooth transition from a kinetic typical for high molecular substances towards a kinetic for low substances can be found;
- one can check if the aging degree of the film surfaces leads to an increase in the time for reaching to a respective moment of the film drainage.

The aim of the present study is: (i) to derive an information about the kinetic behavior of films stabilized by *Bovine serum albumin (BSA)*, *n-dodecyl-β-D maltoside (C₁₂G₂)* and by their mixtures from the videos of their drainage evolution; to check whether the conclusions (from the videos) about the type of the film and its stability correlate with the thermodynamic parameters at its equilibrium state.

Materials and methods

The Bovine Serum Albumin was purchased from Sigma-Aldrich, USA, protein content 96%. (M_w 67 kDa). The nonionic sugar surfactant *n-dodecyl-β-D maltoside*, purity >99.5%) was purchased from Glycon and used as received. BSA is a globular protein which molecular structure [13], volume and interface properties [14,15], as well as its interactions with non ionic low molecular surfactants are well studied [12,16,17]. *n-dodecyl-β-D maltoside* is a well soluble in water, non ionic sugar surfactant with temperature and pH insensitivity. The value of its critical micelles concentration (CMC) is equal to 1.5×10^{-4} mol/l [18].

Stock solutions of BSA (1×10^{-5} mol/l) and C₁₂G₂ (1×10^{-3} mol/l) were used. The concentration of stock protein solution was determined by measuring the optical density A at $\lambda = 280$ nm using $\epsilon_{1\%}^{1\text{cm}} = 6.7$ equal to 4.489×10^4 l.mol⁻¹.cm⁻¹. The pH value of the solutions (4.9 or 3.8) was adjusted by adding of a small amount of 0.1 mol/l HCl. All experiments were performed at temperature $25^\circ\text{C} \pm 1^\circ\text{C}$.

The BSA concentration was so chosen that the requirement for stable black film formation given in [4] to be kept. pH of the most solutions was equal to the isoelectric point of BSA (pI= 4.9) [19]. Two solutions (1×10^{-4} mol/l C₁₂G₂ and 1×10^{-6} mol/l BSA + 1×10^{-4} mol/l C₁₂G₂) with pH equal to 3.8 (isoelectric point of C₁₂G₂ films) [20] were also used.

The molar ratios 1:1, 1:7.5, 1:50 and 1:100 were chosen based on the surface tension isotherm of mixed BSA (1×10^{-6} mol/l) solutions with C₁₂G₂ given in [21] and they correspond to weak and strong binding of C₁₂G₂ molecules to BSA molecule [22]. In order to differentiate the peculiarities in the evolution, kinetic behavior and equilibrium state of the films from the mixed solutions of BSA and C₁₂G₂, films from the individual substances BSA or C₁₂G₂ have been investigated as well.

From each solution of defined composition at least 20-25 films with fresh surfaces (10 minutes after filling of the glass cell with solution) or with aged surfaces (35 minutes after filling of the glass cell with solution) were formed. A modified interferometric method (with a video registration) [23] was employed to obtain the evolutions of foam films stabilized by pure BSA, C₁₂G₂ or by their mixtures. The calculation of the film equilibrium thickness (h_{eq}) was based on the intensity of the reflected light from the film surfaces [24]. The contact angle was calculated using r_1 and r_2 - the radii of a common film (just before a black spot formation in it) and Newtonium black film respectively and R_c - radius of curvature of the liquid meniscus [23].

The equilibrium surface tension was measured by Sartorius balance using Whilhelmy method with frosted glass plate.

Results and discussion

In Fig. 1 peculiar moments in drainage evolution of films from BSA (1×10^{-6} mol/l) solution with pH= 4,9 are presented. Its thinning is typical for protein black films described in [4] and it goes through all stages of film drainage. The values of the equilibrium thickness, contact angle and the excess of the surface tension in the film are given in Table 1. According to the values of these parameters and the BSA molecular size this film is a black film consisting of double hydrated adsorption layers of BSA. We have tried to shrink the equilibrium film (by filling back the solution in it) in order to disjoin its surfaces. It was found that the film radius does not change, which shows that the solution does not enter the film, but in the transitional zone between the film and meniscus. This is a prove of strong interaction between the film surfaces. The observed picture (185 sec. from Fig.1c) is an indication for a hysteresis of the contact angle - first observed in BSA film by Platikanov [1]. Some moments from the evolution of the films from BSA solutions but with pH = 4 or pH = 8 are presented in Fig. 1ab. The above described drainage kinetic of BSA film at pH = 4.9 was not observed for these films. They reach an equilibrium state (grey films) within 7-15 sec. only without dimple formation

passing only through stages 1 and 3 of the scheme of film thinning [25]. The values of their equilibrium thickness (86 - 98 nm) are a proof for the existence of electrostatic stabilization determined by the charge of BSA molecule at these pH values. The comparison of the thinning of BSA films from solutions with different pH confirms the conclusion given in [4] - black protein films can be really obtained from a solution with $\text{pH} = \text{pI}$ and concentration corresponding to a saturated adsorption layer.

The moments of the evolution of film from C_{12}G_2 solution with concentration equal to 1×10^{-4} mol/l (in vicinity of critical micelle concentration) and $\text{pH} = 4.9$ are presented in Fig.1d. From them it is clear that within 150 sec. the C_{12}G_2 film reaches the equilibrium state without any peculiarity in the kinetic of drainage. The value of its equilibrium thickness is 90 nm and the value of contact angle tends to zero. It shows, that the film is strongly electrostatic stabilized and its surfaces are charged. From the above mentioned it follows that in the C_{12}G_2 adsorption layer (independently that it is with a saturation equal to 0.85 [25]) there is a strong residual charge. The information about C_{12}G_2 films at $\text{pH} = 4.9$: (i) is not in line with the literature data of thickness of the films stabilized by nonionic surfactants (C_{12}E_5 or C_{12}E_6) given in [26, 27]. According to these studies the film thickness in the vicinity of cmc should be decreased substantially, because of the negative surface charge compensation by the adsorbed non-charged C_{12}E_5 or C_{12}E_6 molecules; (ii) is in a contradiction with the fact that non-charged BSA molecules compensate the negative surface charge, when their concentration correspond to the saturation adsorption layer - a proof for this is black film formation.

In Fig. 2 are presented moments from the evolutions of films from mixed solutions of BSA and C_{12}G_2 with molar ratios 1:1, 1:7,5, 1:50 and 1:100 and with $\text{pH} = 4,9$ and 3,8 (only for films from a solution with molar ratio 1:100). The evolution of the films from mixed solutions with molar ratio 1:1 and 1:7,5 is similar to that for films from protein solutions. It is seen that they form themselves passing through all the stages typical for one film evolution and reach to equilibrium stable black films faster than the films from BSA solution. In these films a dimple is formed as well which remains until the transition of the film to a black one. Thinning from the periphery to the centre which is typical for protein films is clearly pronounce. Some black spots arise in the area around the periphery but the dimple remains in the centre of the film. The velocity of spots increasing is high because of that some of the liquid does not succeed to drain from the film and remains as lenses (see Fig.2 ab moments 66, 72 sec.). It is seen that around the big lens is formed an interferometric picture which is a proof that the solution in the lens is in an equilibrium with the meniscus. From the pictures shown in Fig. 2ab it follows that: (i) the kinetic of drainage of films from the mixed solutions 1:1 и 1:7,5 is several times faster than that of BSA films (Fig. 1c); (ii) the films are much more non-homogeneity in thickness and in them are formed some cylindrical channels with different thickness. The latter one means that their surfaces are with higher capability of corrugation in comparison with the surfaces of pure BSA film. It is a result of the interaction between protein and low molecular surfactant in the mixed solutions 1:1 and 1:7,5. According to fluorimetric and tensiometric data in the mixed solution 1:1 one C_{12}G_2 molecule binds to each third BSA molecule, but in the solution 1:7,5 each BSA molecule binds one C_{12}G_2 molecule.

Table 1. Parameters of the solutions and the foam films obtained from them
CF (common film); CBF (common black film); NBF (Newtonium black film)

$C_{BSA} : C_{C_{12}G_2}$	σ mN/m	pH	h_{eq} nm	Film type	θ deg.	$\bar{\Delta} \times 10^2$ mN/m
1:0	54.6	4.0	86.5 ± 1.1	CF	$\rightarrow 0$	
		4.9	11.1 ± 1.2	NBF	1.1 ± 0.4	1.87
		8.0	97.8 ± 0.7	CF	$\rightarrow 0$	
1:1	54.4	4.0	96.8 ± 1.9	CF	$\rightarrow 0$	
		4.9	17.0 ± 2.0	NBF	1.7 ± 0.2	4.77
		8.0	90.8 ± 1.0	CF	$\rightarrow 0$	
1:7.5	52.2	4.9	17.3 ± 0.3	NBF	1.0 ± 0.1	1.48
1:50	45.4	4.9 fresh surfaces	18.3 ± 0.1	CBF		
		4.9 aged surfaces	13.3 ± 1.4	CBF**		
1:100	35.2	3.8	45.2 ± 0.5	CF	$\rightarrow 0$	
		4.9 fresh surfaces	67.9 ± 0.8	CF	$\rightarrow 0$	
		4.9 intermediate surfaces	8.7 ± 1.5	NBF*		
		4.9 intermediate surfaces		CBF*		
		4.9 aged surfaces		CBF**		
		4.9 strong aged surfaces	9.6 ± 0.8	NBF	3.2 ± 0.7	8.7
0:1	35.61	3.8	7.4 ± 1.1	NBF	4.9 ± 0.5	26
		4.9	91.5 ± 0.9	CF	$\rightarrow 0$	
0:1 + 0.1M NaBr		5.8	6.5 ± 0.3	NBF	4.7 ± 0.2	24

* unstable, ** unequilibrium

This binding leads to the formation of BSA/C₁₂G₂ associates with decreased hydrophobicity in the area of one of the Trp residual. From the above mentioned it follows that the adsorption layers of films from pure BSA solution are built only from native highly hydrophobic BSA molecules which realize contacts between themselves. Because of that these layers have properties of a solid body. It is the reason for their lower capability of corrugation and retarded film thinning. The adsorption layers of the films from mixed solutions are built of native BSA molecules and BSA/C₁₂G₂ associates (at ratio 1:1) or of BSA/C₁₂G₂ associates (at ratio 1:7.5) in which the interaction should be weaker. It is the reason for a higher capability of the film surfaces for corrugation and the formation of more domains in them, which leads to an acceleration in thinning. The information given for the films from mixed solutions with ratios 1:1 and 1:7.5 is in line with the model for thinning of non-homogeneity in thickness films suggested in [28] for films of nonionic surfactants. According to this model the film is separated into several smaller sections of accelerated thinning rate. The bigger the non-homogeneity in film thickness, the bigger the numbers of the domains and the bigger acceleration in film thinning.

In Fig. 2 $c_{1,2}$ are presented moments from the evolutions of films (with fresh and aged surfaces) from mixed solution of BSA and C₁₂G₂ with molar ratio 1:50 and with pH = 4,9. It is seen that in the evolution of thinning of these films there are some stages which are typical for low molecular substances films (there is no dimple

formation, the black spot does not deform the rings) and stages typical for films from protein solutions (formation of a dark grey ring in the periphery of film and arising of a spot in it). The evolution of film with fresh surfaces much more looks like the evolution of film from low molecular surfactant, while the evolution of film with aged surfaces to the critical state repeats the protein film evolution. Based on the times given in the pictures it follows that the thinning of film with aged surfaces is strongly retarded. Besides, the spot arisen in it expands 8 – folds slower than the spot in the film with fresh surfaces. In both cases the films reach to equilibrium state with thermodynamic parameters corresponding to common black films (CBF) (see Table 1). The kinetic of thinning of films from mixed solution 1:50 with aged surfaces is slower than that for films stabilized by mixtures 1:1 и 1:7,5. It follows that in the films with fresh surfaces $C_{12}G_2$ molecules dominate which increases the mobility of the film surfaces, while in the films with aged surfaces they are replaced by BSA/ $C_{12}G_2$ associates. The described peculiarities in the thinning of films from mixed solution 1:50 are an additional proof to the tensiometric, frumetic and AFM data [29] for the formation of mixed adsorption layers on the film surfaces. The difference in the evolution pictures of the films with fresh and aged surfaces is connected with the fact that firstly is adsorbed the low molecular surfactant and at a later stage - BSA/ $C_{12}G_2$ associates which are with lower surfactant activity because of their decreased hydrophobicity.

In Fig. 2d are presented moments from the evolutions of films from mixed solution of BSA and $C_{12}G_2$ with molar ratio 1:100 and with pH = 4,9. The evolutions noted from film2 to film 13 are for films with different degree of aging of their surfaces, because the video records are taken 5,15,17, 25 and 35 minutes after filling of the solution in the glass cell, respectively. According to Fig. 2d₁ the film with fresh surfaces thins to thick grey film with a thickness around 67 nm and a contact angle tending to zero. Its evolution is similar to that of film from $C_{12}G$ (1×10^{-4} mol/l) solution with pH = 4.9 (see Fig. 1d). It permits us to suppose that on the film surfaces $C_{12}G_2$ molecules adsorb predominantly. The evolutions of the films with intermediate times of aging (films 4 and 9) are similar and they look like the evolution of films stabilized by low molecular surfactants. A dimple does not form in them and they thin through the formation of globes, or channels in them. The evolutions of these films become different after their critical state. In some of them (see film 4) mobile black spots are formed. They expand, fuse and fill the film, which becomes instable and it ruptures. In some others of them (see film 9) a lot of small black spots are formed, which freeze in the film and it can non reach to an equilibrium state. In the films with aged surfaces the black spots appear earlier in time, but their spreading is much slow and they freeze before to spread in the whole film. At film contraction the spot fills up the film, but after its expansion it becomes clear that the spot has kept its radius, which is an evidence that the film surfaces have become solid (see film 10). The evolution of film with strong aged surfaces (see film 13) is similar to that of film from $C_{12}G_2$ solution with electrolyte (see Fig. 1f).

In order to explain the found non typical evolution of the films from mixed solution 1:100 the following hypothesis has been suggested. According to the composition of solution, surface activity and adsorption kinetics of the used surfactants [29] first should be adsorbed $C_{12}G_2$ molecules. The fact that the films with fresh surfaces are common (see Table 1) indicates that this adsorption does not lead to fully screening of the electrostatic in the film. It is additionally suppressed by the adsorbed later BSA/ $C_{12}G_2$ associates. The formed black spots and metastable state of the film with intermediate aging times prove it. The rearranging of the BSA/ $C_{12}G_2$ associates in the adsorption layer leads to a congestion and to an increase in its modulus of elasticity [30], which is a reason for the black spots freezing and stopping their expansion. When the times of aging are long it is possible some of BSA/ $C_{12}G_2$ associates to be displaced by $C_{12}G_2$ ones. If it is realized the films surfaces become more mobile and will reach to equilibrium Newtonian films (NF), which really takes place in our study. It follows that the suggested hypothesis supposes a formation of a mixed adsorption layer with a dominantly presence of $C_{12}G_2$, as well as and co-adsorbed BSA/ $C_{12}G_2$ associates. It has been checked by a comparison of the evolution of film with strong aged surfaces (film 13) from mixed solution (BSA: $C_{12}G_2$ = 1:100, pH = 4.9) with that of film (Fig.1f) from $C_{12}G_2$ solution (with fully suppressed electrostatic stabilization achieved by an addition of electrolyte 0.1 M NaBr). From Fig. 2d₅ it is seen that the correlation between thinning of these films is a good one (in both cases the films reached to NB). The films from the mixture thin slowly, nevertheless they also reach to the same equilibrium state (NF), but their transition to NF is realized more slowly. It allows the expansion of the Newtonium black spot to be followed up, which is impossible in the case for pure $C_{12}G_2$ films with suppressed electrostatic. The slowly thinning, as well as the kinetic of spot spreading prove the presence of BSA/ $C_{12}G_2$ associates on film interfaces.

According to the evolutions of thinning the films from solutions of BSA and its mixed solutions with $C_{12}G_2$ with molar ratios 1:1, 1:7.5 и 1:100 (with strong aged surfaces) and with pH = 4.9 are NB. This conclusion should be correlated with data for the film thickness and its contact angle from Table 1. According to the accepted criterion for NBF from low molecular surfactants (values of thickness below 10 nm and contact angle above 1 degree) data for these parameters do not correspond to NF. If the dimensions of the BSA

molecule is taken into account and its possibility to adsorb in position side – on or side – in then the films of pure BSA solution and from its mixed solutions with molar ratios 1:1 and 1:7.5 could be accepted as Newtonian black by the following reason: the thickness of films from BSA solution (11 nm) corresponds to two hydrated adsorption layers, in which one BSA molecule with dimension of 4 nm is in side – on position; thickness of the films from the mixed solutions with molar ratios 1:1 (17 nm) and 1:7.5 (17.3 nm) also corresponds to two hydrated adsorption layers, which however are from BSA molecules and BSA/C₁₂G₂ associates for 1:1, or from BSA/C₁₂G₂ associates for mixture 1:7.5.

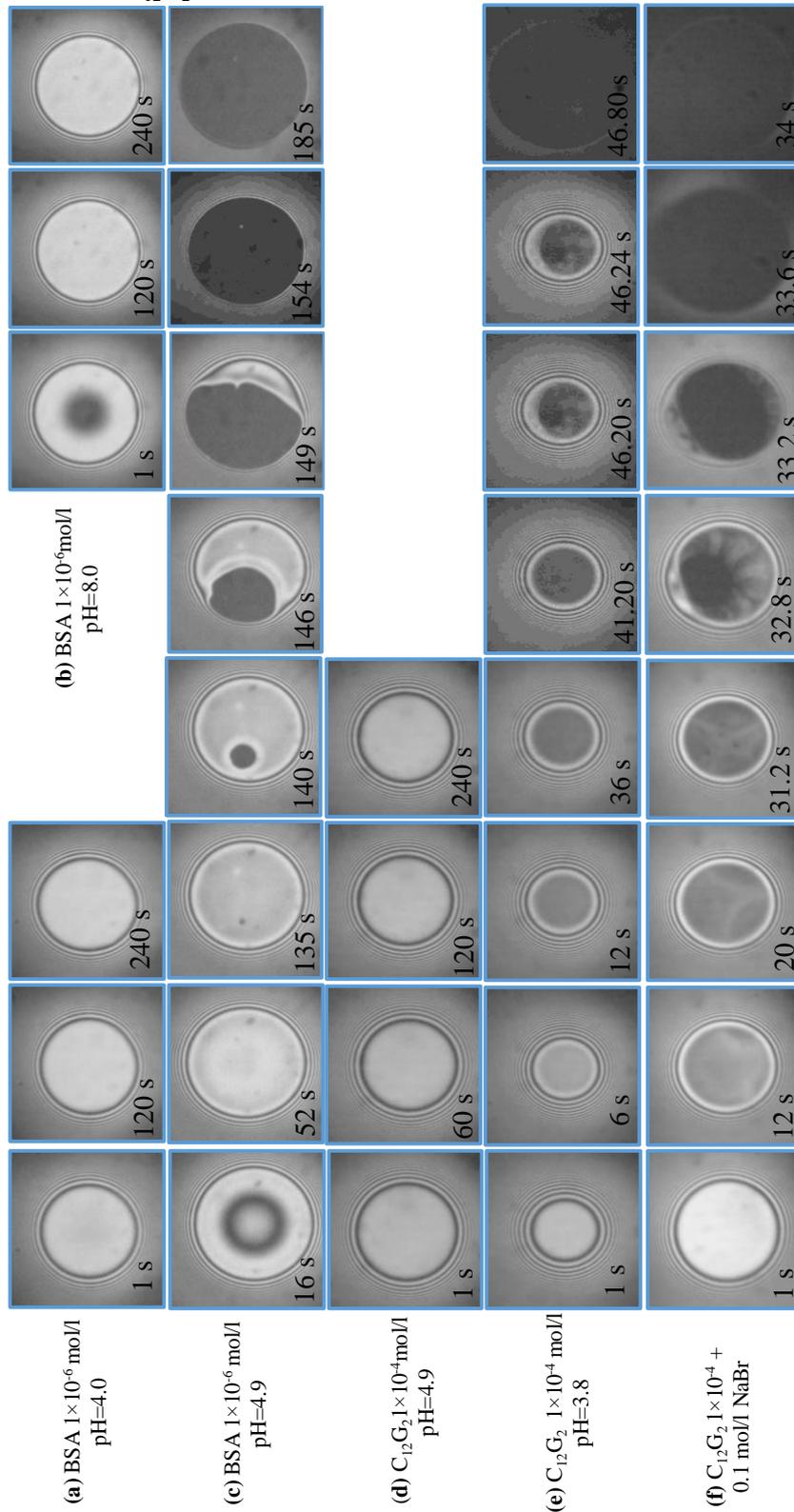
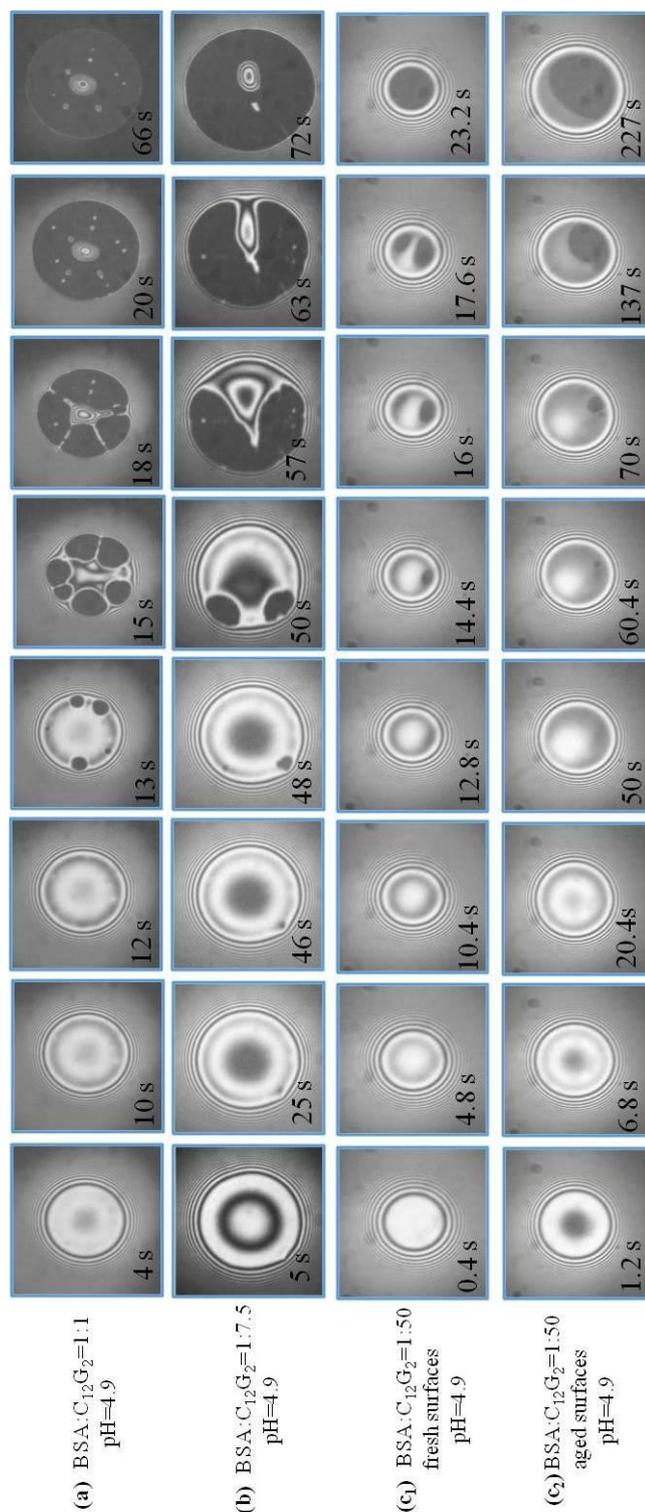


Fig. 1. Moments of film evolution for protein foam films (1×10^{-6} mol/l BSA) and for $C_{12}G_2$ foam films (1×10^{-4} mol/l with and without electrolyte), at different pH values.

According to the video pictures for the equilibrium state the films from mixed solution with molar ratio 1:50 are common black films with a good interferometric picture around them. This is in a good correlation with data for film thickness (13 nm) and contact angle (below 1 degree) (see Table 1).



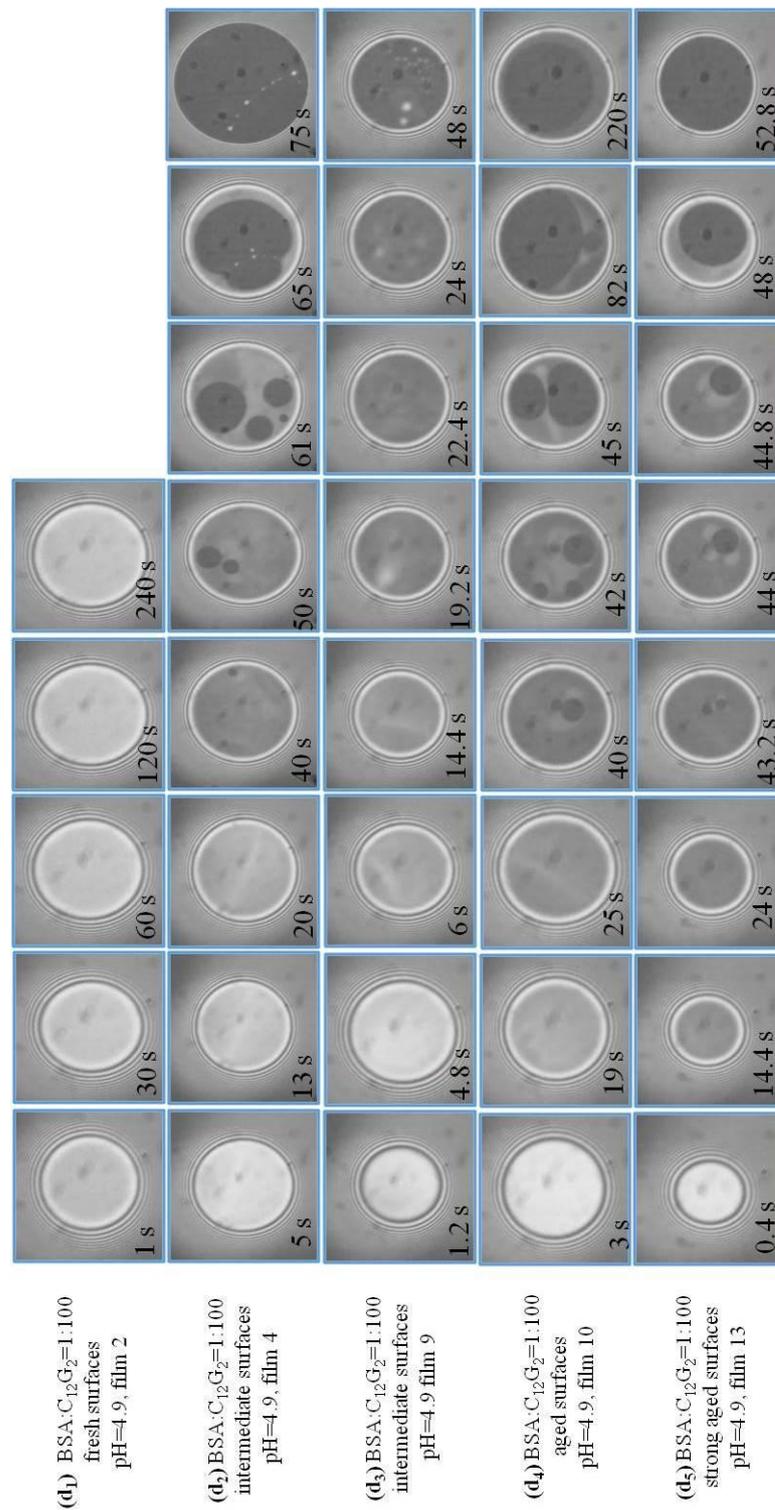


Fig. 2. Moments of film evolution for mixed solution of BSA (1×10^{-6} mol/l) and C₁₂G₂ (1×10^{-6} ; 7.5×10^{-6} ; 5×10^{-5} ; 1×10^{-4} mol/l), at different pH values.

The evolution pictures of films from a solution 1:100 with surfaces with different degree of aging as the data from Table 1 are an indication for a competitive adsorption between $C_{12}G_2$ and the lyophilized BSA/ $C_{12}G_2$ associates. $C_{12}G_2$ molecules dominate in the films with fresh surfaces, but as their concentration is below CMC they do not succeed to neutralize the negative charge, that is why the film thickness is around 70 nm. With time single BSA/ $C_{12}G_2$ associates adsorb, the charge is neutralized and the film stability decreases. Further stabilization of the films and the decreasing of the velocity of spot spreading are a sign of a new BSA/ $C_{12}G_2$ associates adsorption. However in the films with strong aged surfaces they are replaced by $C_{12}G_2$ molecules and the films are with thickness and angle corresponding to Newtonian.

The correlation between the visual pictures and the values of thermodynamic parameters is a good one for the films obtained from BSA solutions with pH different of isoelectric point- equilibrium yellow thick films with thickness around 90 nm and contact angle tending to zero.

Conclusions

The evolutions of thinning of films from individual solutions of BSA, $C_{12}G_2$ and from their mixed solutions of molar ratios 1:1, 1:7.5, 1:50 and 1:100 with pH = 4.9 were recorded by interferometric method. Based on them the stages through which the film goes from its formation to the equilibrium state were distinguished.

1. It was shown that:

- the difference between the kinetic of drainage of films stabilized by high and low molecular surfactants is drastic;
- only the change of the pH solution under or above isoelectric point strongly retards the film drainage;
- the transition of the kinetic of thinning of films from mixed solutions from a kinetic typical for high molecular substances towards a kinetic for low substances depends on the molar ratio between the components in the solution: (i) the evolution of the films from mixed solutions with molar ratio 1:1 and 1:7.5 is similar to that for films from protein solutions; (ii) the evolution of film from mixed solution 1:50 with fresh surfaces much more looks like the evolution of film from low molecular surfactant, while the evolution of film with aged surfaces to the critical state repeats the protein film evolution; (iii) the time for reaching to a respective moment of the film drainage increases as a function of the aging degree of the film surfaces.

2. Based on the analysis of the evolutions of drainage of films from a solution 1:100 with different degree of aging of film surfaces, the comparison between them and the evolution of film from a solution of $C_{12}G_2$ (with suppressed electrostatic) a conclusion for co-adsorption of BSA in the film surfaces was drawn.

3. From the picture of the film corresponding to its equilibrium state the type of the film was determined. From the analysis of this picture by Image program the equilibrium thickness and contact angle were calculated.

4. It was found that the criterion for NBF (based on the values of film thickness and contact angle) is not directly applicable for films from protein solutions or mixed solutions with the participation of proteins.

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