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Critical thickness of foam films stabilized by nonionic, ionic surfactants and their mixtures

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Abstract: The critical thickness (h_{cr}) for foam films of *n*-dodecyl β -D maltoside ($C_{12}G_2$) and of its mixed solutions with dodecanol ($C_{12}E_0$), hexaethyleneglycol dodecyl ether ($C_{12}E_6$) and dodecyl trimethylammonium bromide ($C_{12}TAB$) of different molar ratio (50:1; 1:1; 1:50) at low and high ionic strength was measured interferometrically. It was found that the h_{cr} increases with the increase of the film radius independently of solutions composition. At low ionic strength the type of surfactant affects the critical thickness and the equilibrium state of the film. h_{cr} for the films of mixture with $C_{12}E_0$ increases with the increase of the total surfactant concentration, while h_{cr} for the films of mixture with $C_{12}TAB$ decreases. For the values of the critical thicknesses for films from individual surfactant solutions the following sequence $h_{cr}(C_{12}TAB) > h_{cr}(C_{12}E_6) > h_{cr}(C_{12}G_2)$ is found. At high ionic strength the quantity of nonionic additive does not substantially affect the value of h_{cr} , while the quantity of ionic additive influences it by two different ways (i) in 50:1 mixture $C_{12}TAB$ supports $C_{12}G_2$ in the reducing of negative charge; (ii) in 1:1 mixture $C_{12}TAB$ recharges the film surfaces.

Keywords: foam films; *n*-dodecyl β -D maltoside ($C_{12}G_2$); mixed solutions of nonionic and ionic surfactants; molar ratios 50:1; 1:1; 50:1; experimental critical thickness.

Introduction

Surfactants are used in many chemical, biochemical, pharmaceutical industries because of their capability to modify the surfaces (hydrophilisation or hydrophobization), to defend the colloidal particles from aggregation and to organize themselves to micelles in the bulk (nanoparticles) in which some useful substances (proteins, enzymes, metals), or harmful (stable organic pollutions) are solubilized. There is no doubt about the usefulness of the surfactants but their toxicity is also proved. That is why their use in practice must be so realized that their usefulness to dominate many times their harmful action. In practice it is achieved by using mixtures of surfactants with proven positive synergism. In the studies of equilibrium properties [1-2] and the kinetic stability [3-5] of foam films (FF) during the last years are used mixtures of surfactants. A subject of the presented study are foam films obtained from mixtures of the surfactants: *n*-dodecyl β -D maltoside ($C_{12}G_2$ or G_2); hexaethyleneglycol dodecyl ether ($C_{12}E_6$ or E_6); dodecanol ($C_{12}E_0$ or E_0); dodecyl trimethylammonium bromide ($C_{12}TAB$ or TAB) at wide varied

experimental conditions – low and high total surfactant concentration, low and high ionic strength and different molar ratios between the components in the mixed solutions. One of the parameters of importance for the kinetic stability of foam film is its critical thickness (h_{cr}). It is the averaged film thickness in its critical state which could be a thickness of rupture h_{br} or thickness of black spot formation in the film h_{bl} . It can be measured interferometrically [2-5], or calculated on the bases of equations suggested in the literature [6-7]. A new procedure for determination of critical thickness by interferometric method from film evolution video has been suggested in [8-9]. Its advantages are that the film thickness can be determined in specially chosen places - the area of critical state generating and in some of the thinnest places in the film. Realizing of this procedure and its comparison with interferometric method with photomultiplier showed its advantage in getting of correct experimental data of h_{cr} . Experimental data of h_{cr} of films from mixed solutions can be used in two directions: (i) to check if the dependences of the h_{cr} on the surface tension and film radius correspond to those suggested by theory; (ii) to check how the surfactant's type and molar ratio of the components in the mixture at low and high ionic strength influence on the value of h_{cr} . The above mentioned considerations determine the aim of the presented study which is - *to obtain systematic experimental data of critical thickness for films with varied radii obtained from mixed $C_{12}G_2$ solutions with $C_{12}E_0$, $C_{12}E_6$ and $C_{12}TAB$ of different concentration and molar ratios of the components in them at low and high ionic strength.*

Materials, methods and procedures

The nonionic surfactants: $C_{12}G_2$ purchased from Glycon; $C_{12}E_0$ purchased from Merck; $C_{12}E_6$ purchased from Fluka. The cationic $C_{12}TAB$ was supplied from Prof. C. Stubenrauch. NaCl and NaBr were obtained from Merck and Sigma, respectively.

In order to be able for comparison the results for different mixtures, all concentrations are given in terms of the critical micelle concentration (CMC) which was chosen as a reference concentration. Total concentrations from 0.01 to 1.0 CMC were used for experiments with foam films at ionic strength 0.1, or 0.001M. The equilibrium surface tension of mixed solutions from which the foam films were formed was measured by Wilhelmy plate method. All experiments were done at $25^\circ\text{C} \pm 1^\circ\text{C}$.

In this study the foam films stabilized by individual surfactants or mixtures of them were investigated by microscopic interferometric method with a procedure proposed in [8]. The new element in the procedure is the determination of the reflected light intensity from a video recording of the film evolution.

Results and Discussion

In the present paper the critical thickness: (i) just before (0.2 s) appearance of the first black spot h_{bl} (for films which transform into common black film (CBF)); (ii) just before (0.2 s) appearance of the Newtonian black spot h_{bl} (for films which spontaneously pass from common film (CF) to Newtonian black films (NBF)) was experimentally determined.

Experimental data of the critical thickness for films obtained from solution with 0.001 M ionic strength.

Data about the influence of surfactant's type and concentration (from 0.1 to 1.0 CMC) on the critical thickness at low ionic strength are presented in Fig. 1. The experimental data show that the value of h_{cr} increases with increasing of the film radius, irrespectively of the solution composition – it is in line with theory. The close values of h_{cr} for films from mixed solutions at the respective radii show that the type of nonionic additive ($C_{12}E_6$, $C_{12}E_0$ with short and long chain head) at CMC does not affect the value of h_{cr} . Clearly, two opposed tendencies for the influence of the surfactant concentration on h_{cr} can be seen from the figure: increasing in the h_{cr} value with increasing of the total surfactant concentration of mixture with $C_{12}E_0$ and decreasing in the h_{cr} value with increasing of the total surfactant concentration of mixture with $C_{12}TAB$. It probably could be connected with the role of the ionic surfactant. From one hand it adsorbs and decreases the charge in the same direction as $C_{12}G_2$ does, and from the other hand, it acts as an organic electrolyte. We assume that up to concentration 0.5 CMC its effect as an electrolyte dominates and leads to a decrease in film thickness.

A difference in the film equilibrium state is found too - the films are stable NBF when they are formed from mixed solution with $C_{12}E_0$, (as the films from $C_{12}G_2$ in one of their metastable states), while

they are CF when they are from the mixture with $C_{12}TAB$ (as the films from $C_{12}G_2$ in other of their metastable states). According to [9] for films from pure $C_{12}G_2$ (at 1CMC) solution a metastable state was observed - CF or NBF arise.

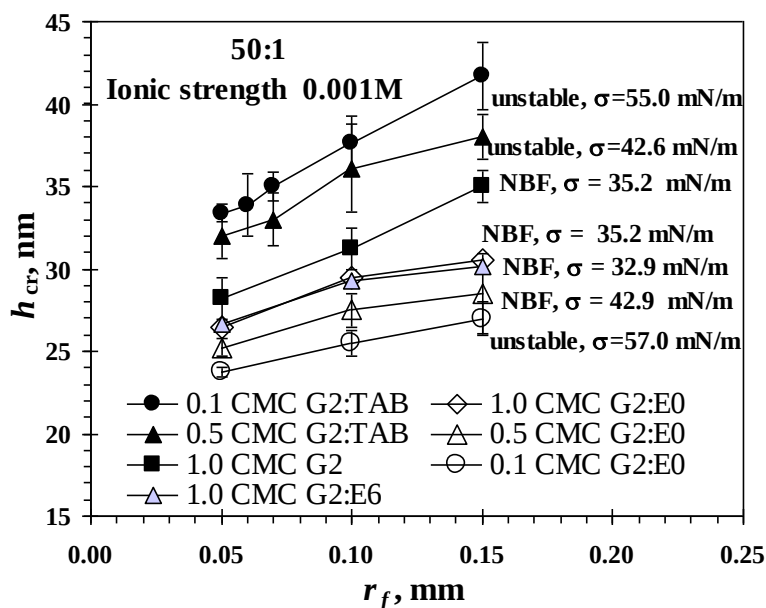


Fig.1. Experimental data of critical thickness for foam films of different radii, obtained from individual solution of $C_{12}G_2$ and from its mixed solutions with $C_{12}E_6$, $C_{12}E_0$ or with $C_{12}TAB$ at molar ratio 50:1.

Experimental data of the critical thickness for films obtained from solution with high ionic strength 0.1 M.

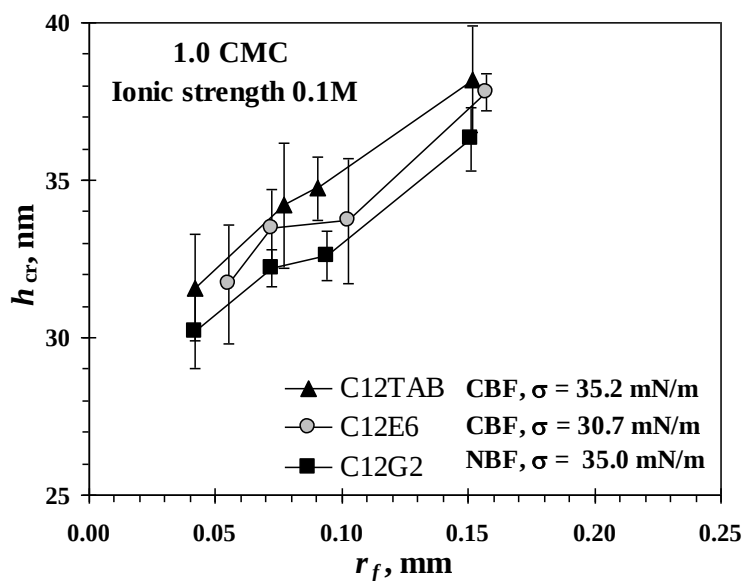


Fig. 2. Critical thickness for foam films of different radii, obtained from individual surfactant solutions

In Fig.2 the experimental data of critical thickness for films from solutions of individual surfactants – the nonionic $C_{12}G_2$, $C_{12}E_6$ and cationic $C_{12}TAB$ are juxtaposed. The total surfactant concentration is 1.0 CMC and the ionic strength is 0.1 M in order the electrostatics in the film to be suppressed. One can see that the critical thickness for films formed from $C_{12}G_2$ solution are lowest, while those obtained from $C_{12}TAB$ solution are highest. Since the investigated systems are placed at the same conditions as it is to be expected, the observed differences in the values of critical thickness are not substantial. Regardless of the close values for the surface tension of $C_{12}G_2$ and $C_{12}TAB$ solutions the critical thickness for films of these solutions are different, which probably is due to their different hydrophilic parts- noncharged, or charged ones. At CMC the interfaces of films from $C_{12}TAB$ solution are positively charged. According to [2] the surface potential for films from $C_{12}TAB$ solution is an order higher than that for films from $C_{12}G_2$

solution. Definitely, the added electrolyte will screen the charges in the films of nonionic surfactant, but it is not sure that it would happen to films of ionic surfactant. If on their surfaces there is not a compensated charge the critical state will arise at bigger film thickness. In order to prove the assumed supposition films from $C_{12}TAB$ solution with 1.35×10^{-3} M surfactant concentration and ionic strength 0.4 M were obtained. The films at these conditions were Newtonian ones. It means that indeed, at ionic strength 0.1 M on films surfaces there is some residual charge. The measured critical thickness at higher ionic strength (0.4 M) does not differ substantially from the measured one at lower ionic strength (0.1M). It manifests that actually the effect of ionic strength on the critical thickness is not so crucial as it is for the equilibrium state.

$h_{cr}(r_f)$ dependences for films formed from mixed solution of nonionic surfactants ($C_{12}G_2 + C_{12}E_6$), or of nonionic with cationic surfactants ($C_{12}G_2 + C_{12}TAB$) with molar ratio 1:1 at high ionic strength are presented in Fig. 3.

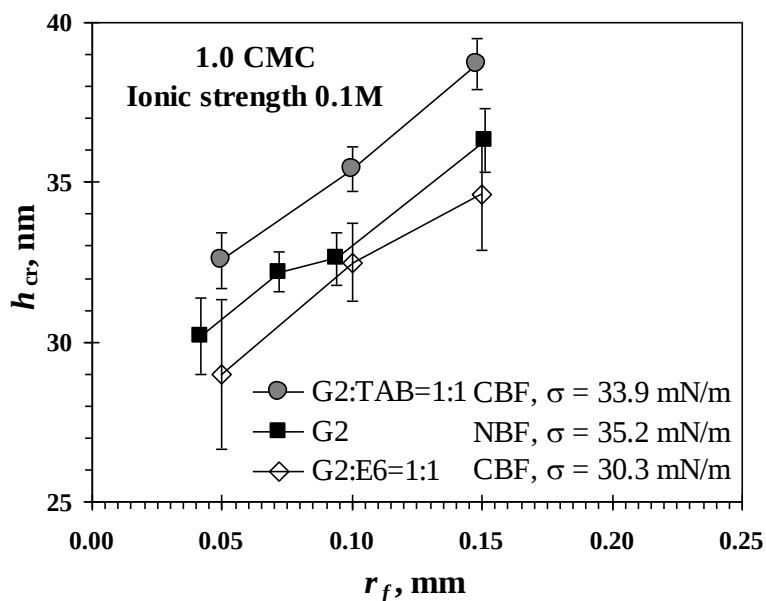


Fig.3. Experimental data of critical thickness for foam films of different radii, obtained from mixed solutions of $C_{12}G_2$ with nonionic $C_{12}E_6$ or with cationic $C_{12}TAB$ of molar ratio 1:1.

The addition of $C_{12}E_6$ does not decrease substantially the value of h_{cr} in comparison with that for the films of individual $C_{12}G_2$ solution. It means that the mixed adsorption layer with dominating participation of $C_{12}E_6$ molecules is formed but without expressed synergism. It is in a good correlation with data in [1], where the mixture of $C_{12}G_2 + C_{12}E_6$ is considered as an ideal mixture. It presumes a weak interaction between $C_{12}E_6$ and $C_{12}G_2$ molecules in the adsorption layer. From the same figure one can see that the h_{cr} for films from mixture of $C_{12}G_2 : C_{12}TAB = 1:1$ is higher again than that for films from $C_{12}G_2$, which proves the specific effect of $C_{12}TAB$ on the critical thickness. According to estimations for the composition of the adsorption layer from mixture of $C_{12}G_2 : C_{12}TAB = 1:1$ the contents of $C_{12}TAB$ in it is 16%. At this condition $C_{12}G_2$ molecules will have a dominating role in the adsorption layer, because of the lower surface activity and higher solubility of $C_{12}TAB$. Although the content of $C_{12}TAB$ in the adsorption layer is relatively low, its presence there makes the layer non-homogeneous and reduces its coherence. The presence of domains of $C_{12}G_2$ and/or $C_{12}TAB$ modifies the adsorption layer corrugation capability and the probability for arising of black spots increases.

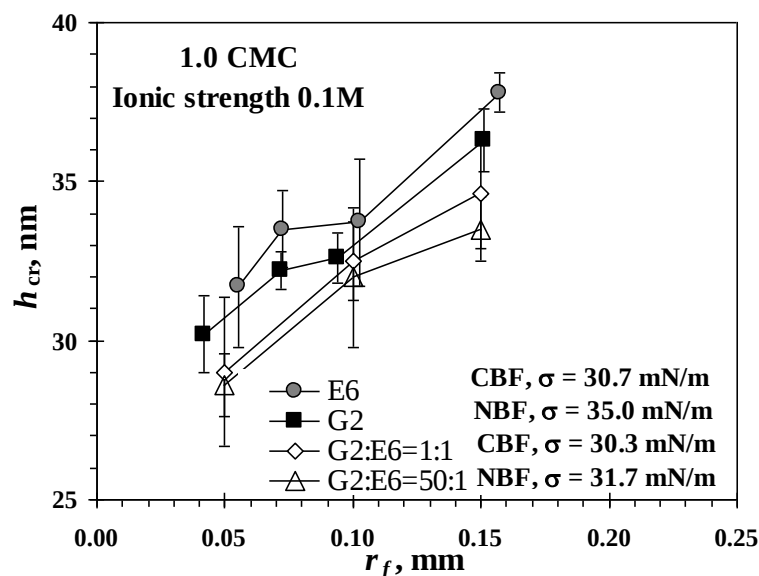


Fig.4. Comparison of the values of critical thickness for foam films of different radii, obtained from solution of $C_{12}G_2$, $C_{12}E_6$ and their mixtures of molar ratio 1:1 и 50:1 at 0.1 CMC

In Fig. 4 four $h_{cr}(r_f)$ dependences are shown - for films stabilized by individual $C_{12}G_2$, or $C_{12}E_6$ and by their mixture, but at high ionic strength. One can see that $h_{cr}(r_f)$ dependence for film from solution of pure $C_{12}E_6$ lies in a highest position. Although the value of surface tension of $C_{12}G_2$ solution is highest, the films produced from it have not the lowest values of the critical thickness. The difference between $h_{cr}(r_f)$ dependences for films from mixtures $C_{12}G_2 : C_{12}E_6 = 1:1$ and 50:1 is not substantial but they are situated below the $h_{cr}(r_f)$ dependence for films from solution of pure $C_{12}G_2$. The lower values of h_{cr} for films from mixed solutions show that the covered mixed adsorption layers are more packed and thus the films drain uniformly to smaller thickness e.g. the probability for arising of the critical state diminishes.

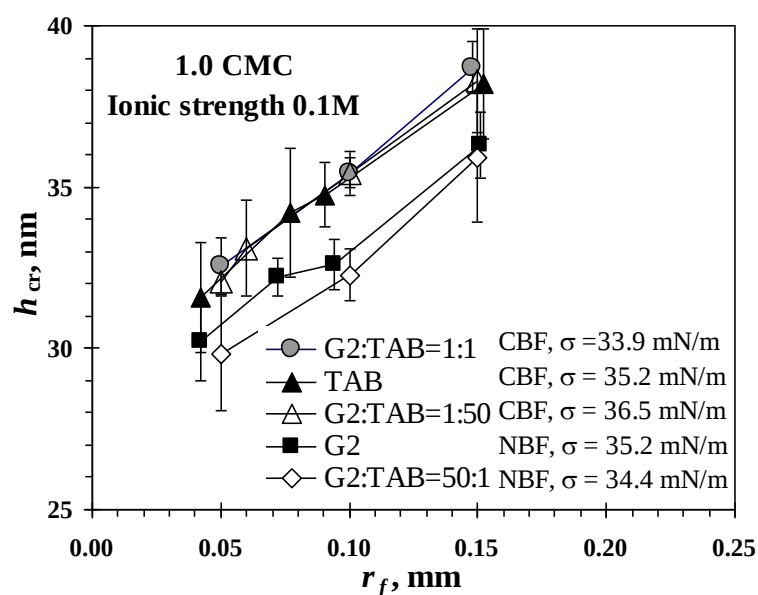


Fig.5. Experimental data of critical thickness for foam films of different radii, obtained from solution of $C_{12}G_2$, $C_{12}TAB$ and their mixtures of molar ratio 50:1; 1:1 and 1:50

The measured critical thicknesses for films from individual solutions of the nonionic $C_{12}G_2$, or cationic $C_{12}TAB$ as well as from their mixed solutions are compared in Fig.5. The total surfactant concentration of the solutions is 1.0 CMC and the ionic strength is equal to 0.1 M. From the figure it is clear that values of h_{cr} for films from solution of single $C_{12}TAB$ and from its mixture with $C_{12}G_2$ (with molar ratios 1:1, 1:50) are the biggest, while those for films from the mixture $C_{12}G_2 : C_{12}TAB = 50:1$ are

the smallest ones. The $h_{cr}(r_f)$ dependence for films from mixture of 1:1 molar ratio is situated close to that for films stabilized by pure $C_{12}TAB$, which is a proof for the determining role of $C_{12}TAB$ for the charge of the mixed adsorption layer. Probably, its adsorption on the interface carries in a charge and film interfaces recharge. A proof for this is the type of the obtained films- they are CBF instead of NBF, as the films from $C_{12}G_2$ solution. The lower position of the $h_{cr}(r_f)$ dependence for films from mixed solution of 50:1 molar ratio shows that the both substances affect the film kinetic behavior. The high contents of $C_{12}G_2$ in the mixture determines its dominating role and in the adsorption layer (0.992 molar parts). In this mixture $C_{12}TAB$ has a role of additive and although its presence in the adsorption layer is only 0.008 molar parts, it leads to a full reduction of the charge. It follows that, in this case, the influence of the adsorption of both components on the charge is in the same direction, which leads to a transition to NBF.

Conclusions

The critical thickness for foam films (with radii from 0.05 to 0.15 mm) of $C_{12}G_2$ and its mixed solutions with $C_{12}E_0$, $C_{12}E_6$ and $C_{12}TAB$ at low and high ionic strength are measured interferometrically.

From the experimental data presented in Figs 1-5 the following conclusions have been drawn:

1. The critical thickness increases with the increase of the film radius independently of solutions composition.
2. For the values of the critical thicknesses for films from individual surfactant solutions the following sequence $h_{cr}(C_{12}TAB) > h_{cr}(C_{12}E_6) > h_{cr}(C_{12}G_2)$ is found.
3. The critical thicknesses for films from mixed solutions of $C_{12}G_2$ with $C_{12}E_6$ of different molar ratios are close, but they are lower than those for films of individual $C_{12}G_2$ solution.
4. At low ionic strength the type of surfactant affects the critical thickness and the equilibrium state of the film. h_{cr} for the films of mixture with $C_{12}E_0$ increases with the increase of the total surfactant concentration, while h_{cr} for the films of mixture with $C_{12}TAB$ decreases. In both cases at 1.0 CMC the films are stable and their thicknesses tend to the metastable forms of $C_{12}G_2$ films.
5. At high ionic strength the quantity of nonionic surfactant does not substantially affect the value of critical thickness, while the quantity of ionic surfactant influences it by two different ways, according to its molar ratio in the mixture: (i) in mixture of molar ratio 50:1 $C_{12}TAB$ acts as an additive and supports $C_{12}G_2$ in the reducing of negative charge; (ii) in mixture of molar ratio 1:1 $C_{12}TAB$ has a dominating role for the charge and it recharges the film surfaces.

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