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Drainage and stability of foam films from aqueous solutions of a single nonionic surfactant $C_{12}E_6$

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The drainage and stability of thin liquids foam films from aqueous solutions of the nonionic surfactant hexaethyleneglycol monododecyl ether ($C_{12}E_6$) is studied as a function of surfactant concentration and film size. The thinning rate is investigated in the range of total surfactant concentrations from 10^{-5} M to 10^{-4} M, at electrolyte concentration of 0.025 M. The value of the drainage coefficient (α) is determined for each film from its "thickness vs. time" dependence. The film thickness was calculated using microinterferometric method.

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1. Introduction

The stability of disperse system is an important and central subject in colloid science. Essential knowledge of the studies on the drainage behaviour of thin liquid films one can obtain from the recent reviews of Manev & Nguyen [1,2], as well as a number of preceding comprehensive publications, like these of Scheludko [3], Ivanov et al [4], Exerowa and Kruglyakov [5] and others.

The necessary condition for obtaining foam films and foam of measurable stability and lifetime, is the presence of a surfactant. Surfactant adsorption at the interface provides the foam films with the ability to resist deformation in the process of thinning (film drainage). The molecular structure and the concentration of the surfactant have strong influence on film stability. The present work on film drainage and stability of foam is dealing with single surfactant aqueous solutions of hexaethyleneglycol monododecyl ether ($C_{12}E_6$), containing 0.025 M NaCl.

The aim of the presented study is to establish the characteristics by investigating thin liquids films stabilized by $C_{12}E_6$ and to compare the results for single surfactants with other results for mixtures containing $C_{12}E_6$. [6, 7] The evolution of the films was studied function of the surfactant concentration (10^{-5} - 10^{-4} M $C_{12}E_6$) and film size (0.05 - 0.25 mm). The thickness of all investigated films was measured interferometrically, using Scheludko cell. [3]

The thin liquid film is regarded as a two dimensional phase with specific properties. [1, 2] Foam is a disperse system in which gas bubbles are separated by thin liquid films (liquid layers). [4,5] The surfaces of foam films are covered by molecules of surface active substances, known as surfactants, and the film core consists of the liquid medium (water in our study). The stability of the film depends on the adsorption of surfactant at the interface. As proved in earlier works [8-10], the simple empirical dependence (Eq. 1), can be effectively employed for the rate of film thinning:

$$h = h_0 \exp(-\alpha t) \qquad (1)$$

which yields:

$$V = dh/dt = \alpha h \qquad (1a)$$

h = film thickness
h_0 = arbitrary initial thickness
α = drainage coefficient
t = time
V = rate of film thinning

The film thickness is a fundamental quantitative characteristic of the deviations in the properties of the thin film from those of the bulk phase. Such deviations are adequately expressed by the so-called disjoining pressure (Π), introduced by Derjaguin [11, 12].

During the film drainage, the capillary pressure causes sucking of the film liquid into the Plateau borders [13]. Upon thinning, below thickness *ca.* 100 nm, when the two film surfaces approach each other, disjoining pressure starts acting as well, which affects the dynamics of the film. The driving force causing the film thinning can be expressed as:

$$\Delta P = P_\sigma - \Pi \qquad (2)$$

If at some thickness the disjoining pressure, is equal to the capillary pressure, P_σ, the driving force ΔP is equal to zero, leading to the formation of an equilibrium film.

Disjoining pressure is the fundamental element in the DLVO theory of stability of colloids. [14,15] The classical DLVO theory incorporates the van der Waals and electrostatic interactions:

$$\Pi = \Pi_{vdW} + \Pi_{el} \qquad (3)$$

2. Methods and materials

2.1 Methods

The solutions were studied with Whilhelmy method for measuring surface tension and the thin liquids films with microscopic interferometric method for measuring the film thickness. [3,5,16] The horizontal foam films were obtained from a biconcave drop of the studied solution in a closed Scheludko cell, with film holder of 2.15 mm inner radius, in the atmosphere of saturated vapours of the studied solution. The experimental setup for studying thin liquid films with microscopic interferometric method are presented in Fig. 1.

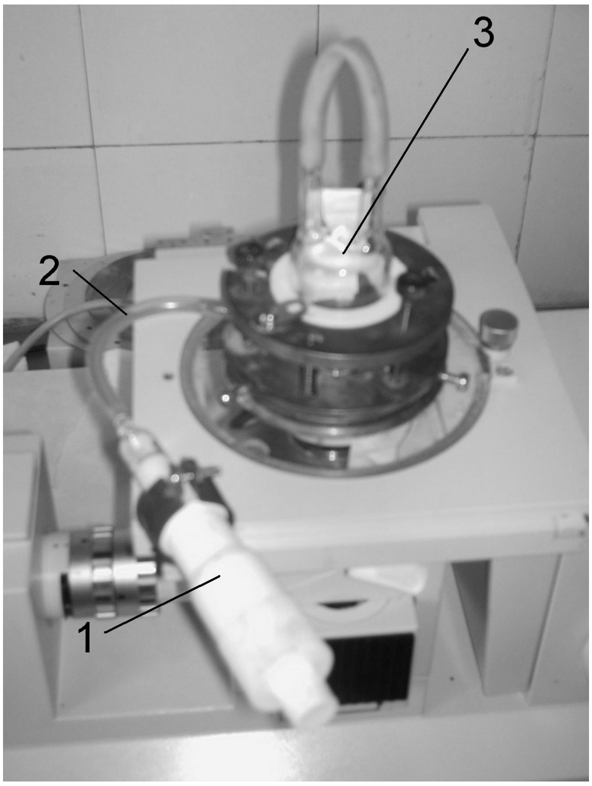

Fig. 1. Experimental setup for studying thin liquid films by the microinterferometric method.

1 = micro-syringe
2 = capillary tube
3 = Scheludko cell

The foam films were observed in reflected monochromatic light (wavelength λ= 551 nm). A CCD-OS45D photo camera was used for recording the film thinning. The cell was enclosed in a thermo stating jacket to maintain a constant temperature throughout the experiment (25°C). The kinetics of film thinning was determined by recording the photocurrent from a small part of the film near its periphery as a function of time. It was registered until reaching equilibrium state, or rupture of the film. Eq. 4 was used to determine the film thickness:

$$h = \frac{\lambda}{2\pi n_\circ}\left(k\pi + \arcsin\sqrt{\frac{I - I_{\min}}{I_{\max} - I_{\min}}}\right) \qquad (4)$$

h = film thickness
λ = the wavelength of monochromatic light source
n_0 = the refractive index of the solution from a film with thickness h
I = intensity of reflected light
I_{max}, I_{min} = maximal and minimal intensity of reflected light
k = the order of the interference (in our case $k = 0$)

From each solution with identified composition were formed at least 15 films of different radii. The kinetics of film thinning was determined by recording the photocurrent from a small part of the film periphery as a function of time (t). It was registered up to the state of equilibrium. From the kinetic curve of each film, the drainage coefficient (α) [17-19] was computed.

2.2 Materials

The non-ionic surfactant hexaethyleneglycol monododecyl ether ($C_{12}E_6$) was purchased from *Fluka* and it was used without further purification. The structure of this surfactant is presented in Fig. 2.

Fig. 2. Structure of hexaethyleneglycol monododecyl ether ($C_{12}E_6$).

Sodium chloride (NaCl) was purchased from *Sigma* and roasted 4h at 600°C to remove organic contaminants.

3. Results and discussion

The drainage of microscopic foam films formed from aqueous solutions of the nonionic surfactant $C_{12}E_6$ is studied as a function of the surfactant concentration and film size (0.05 – 0.25 mm radius). The thinning rates are investigated in the range of total surfactant concentration from 10^{-5} to 10^{-4} M at electrolyte concentration 0.025 M. The thinning behaviour of all films was characterized via their drainage coefficients, α (see Eqs. 1). The experimental values for α were obtained from the *ln h vs t* dependences of the films.

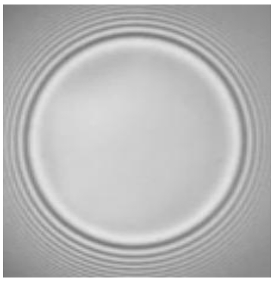

Fig. 3. Microinterferometric image of thin liquid film.

The surface tension of the aqueous solutions containing $C_{12}E_6$ and 0.025 M NaCl was measured for the concentrations used in our study (10^{-5}, 3×10^{-5} and 10^{-4} M), but also for the cmc 7.3×10^{-5} M. [20] The results are presented in Fig. 4:

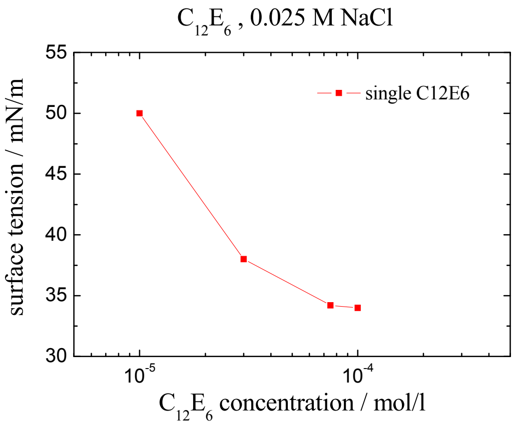

Fig. 4. Surface tension measurements for aqueous solutions $C_{12}E_6$, in the presence of 0.025 M NaCl.

Two examples of drainage coefficient calculation for thin films obtained with aqueous solution containing $C_{12}E_6$, are plotted in Figs. 5 and 6.

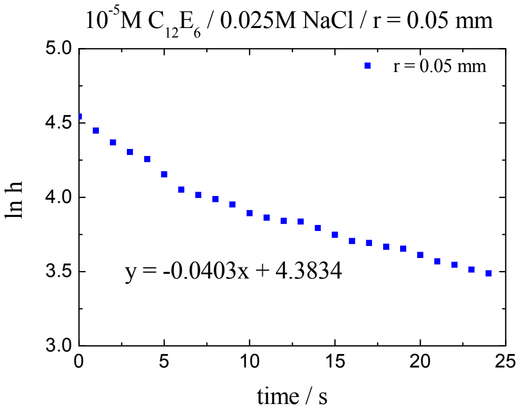

Fig. 5. Calculation of drainage coefficient for a foam films stabilized with 10^{-5} M $C_{12}E_6$, in the presence of 0.025 M NaCl, for film size 0.05 mm ($\alpha = 0.0403\ s^{-1}$).

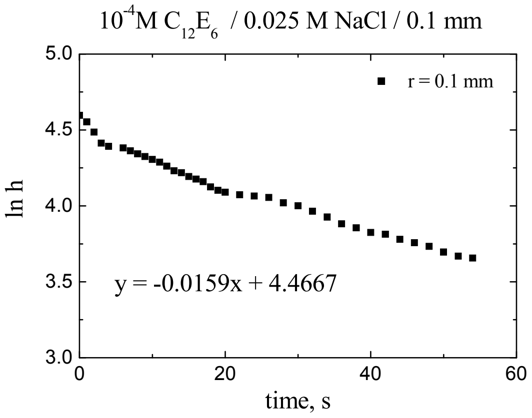

Fig. 6. Calculation of drainage coefficient for a foam films stabilized with 10^{-4} M $C_{12}E_6$, in the presence of 0.025 M NaCl, for film size 0.1 mm ($\alpha = 0.0159\ s^{-1}$).

The experimental data for the drainage coefficients of these films are presented in Figs. 7 and 8.

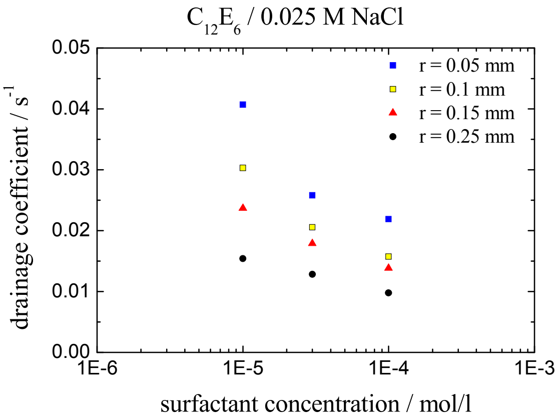

Fig. 7. Drainage coefficient α vs. total surfactant concentration of foam films stabilized with $C_{12}E_6$, in the presence of 0.025 M NaCl, for different film size.

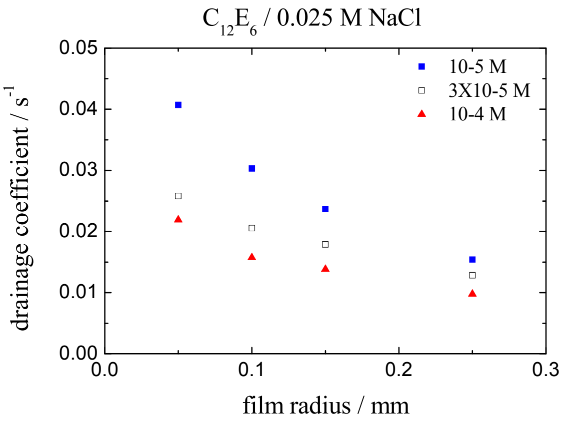

Fig. 8. Drainage coefficient α vs. film radius of foam films stabilized with $C_{12}E_6$, in the presence of 0.025 M NaCl, for different surfactant concentrations (10^{-5} M, $3x10^{-5}$ M and 10^{-4} M).

The experimental dependences for the drainage coefficient α of aqueous foam films stabilized with single $C_{12}E_6$ at different surfactant concentrations and at constant ionic strength of 0.025 M NaCl, are plotted as a function of surfactant concentration in the Fig.7 and as a function of the film radius in Fig.8. It is an expected result that the values of α decrease with increasing surfactant concentration and film size. The present findings complement and confirm previous results on foam films stabilized with surfactants mixtures containing $C_{12}E_6$ [6, 7].

In our previous work, with mixtures containing $C_{12}E_6$ and $C_{12}G_2$ [6, 7], the drainage coefficient decrease also with increasing film size and surfactant concentration. We present here results close to 0.5 CMC for $C_{12}E_6$ as well ($3x10^{-5}$ M) and for mixtures containing $C_{12}G_2$:$C_{12}E_6$ 1:1 ($5x10^{-5}$ M) from the previous work [6, 7]. We can compare all of these (Fig. 9), with respect to different ionic strength.

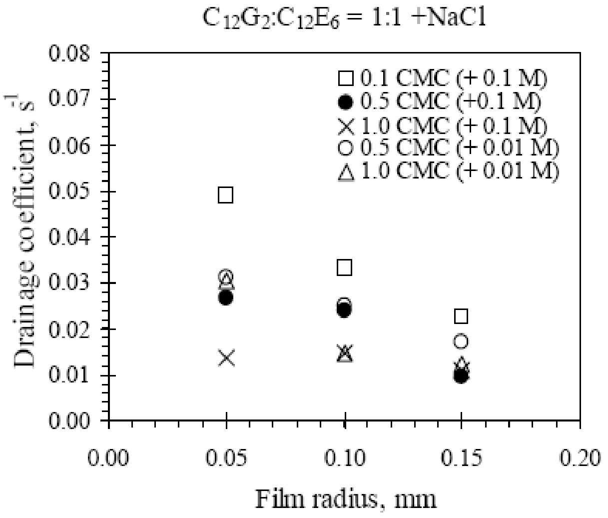

Fig. 9.Drainage coefficient α vs. film radius of foam films stabilized by mixtures of β-$C_{12}G_2$:$C_{12}E_6$ = 1:1, in the presence of NaCl, for different surfactant concentrations (0.1, 0.5, 1.0 and 10.0 CMC). [6]

As it can be seen from Fig. 9, the drainage coefficient values do not differ significantly with ionic strength (the values of the drainage coefficient are close), in the range 0.01 – 0.1 M NaCl [6]. The ionic strength used in this study for single $C_{12}E_6$ solutions is intermediate, as compared to the mixtures (0.025 M NaCl). The drainage coefficient values are lower for the films containing single $C_{12}E_6$ then for films containing $C_{12}G_2$:$C_{12}E_6$ 1:1, at the film size 0.05 and 0.1 mm, but the values are nevertheless very close. [6, 7] We can say that at these film sizes the influence of $C_{12}E_6$ in this mixture on the film behaviour is significant. But, still it is very difficult to compare these results, because we do not know how exactly the behaviour of the films will be changed by ionic strength for other surfactant concentrations. As we expected for the films of the mixture $C_{12}G_2$:$C_{12}E_6$ of ratio 50:1, the influence of $C_{12}E_6$ is weak, because of its low content.

For film size 0.15 mm, the values of the drainage coefficient for films containing $C_{12}E_6$ alone are higher then those for films containing the mixture $C_{12}G_2$:$C_{12}E_6$ 1:1, and lower then the values for the mixture $C_{12}G_2$:$C_{12}E_6$ 50:1 (at different ionic strength). So, for this or larger film size, only further measurements will provide an explanation for that, at the same ionic strength. In the previous experiments we have no measurements at a film size larger then 0.15 mm.

Moreover, in the previous work [6], from the measurements of films containing single $C_{12}E_6$ at CMC ($7.3x10^{-5}$ M), in the presence of 0.001 and 0.01 M NaCl (film size 0.1 mm), it has been observed that the drainage coefficient value is slightly larger at higher electrolyte concentration. In our case, the sodium chloride concentration is even higher then 0.01 M (more then double). Unfortunately, we do not have results in the present work for the CMC. The value of the drainage coefficients at the same film size (0.1 mm) in the present work, below CMC (3×10^{-5} M) is higher then the values for the CMC [6] and above CMC (10^{-4} M $C_{12}E_6$) is lower. In this case, we can observe also that the drainage is faster when the surfactant concentration is lower.

4. Conclusions

The results of the present study of foam films from aqueous solutions of single surfactant confirm the findings of previous classical and more recent investigations on the drainage of foam films [6 - 9, 16 - 19, 21 - 25]. Naturally, for all films, the increase in size (radius) and surfactant concentration causes a decrease of drainage coefficient, that is, the larger the film size, the slower the thinning. The film drainage rates decrease also with the increase in surfactant concentration. The latter effect may be one of the major factors for the variation of the decay rate of foam when varying its surfactant content.

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