Colloid Polym Sci 276:518–523 (1998)
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ORIGINAL CONTRIBUTION

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The thickness and contact angle of sodium dodecyl sulfate foam films depending on the concentration of LiCl

Received: 6 January 1998
Accepted: 11 March 1998

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Abstract In the present study a detailed investigation of the thickness and contact angles of foam films prepared from sodium dodecyl sulfate as a function of LiCl concentration was carried out. Concentration of LiCl was varied in a wide range from 0.05 to 2.0 M. It was found that in the investigated system Newton black foam films are formed at LiCl concentrations higher than 1.4 M. This observation is proved by contact angle measurements and calculated values for the change of interaction free energy between common and Newton black films.

Key words Foam films – film thickness – contact angle

Introduction

Soap films can be easily formed from solutions of ionic surfactant in the presence of electrolytes. After formation the initial thick foam film becomes thinner by drainage of the solution due to the capillary pressure in the meniscus and interactions between two film surfaces. Finally, equilibrium films are obtained with a uniform thickness depending on the concentration of ions in the solution. Two types of black films are exhibited. The thicker common black film (CBF) usually appears at a low electrolyte concentration. Their thickness and stability are controlled by electrical double-layer repulsion, in agreement with DLVO theory [1]. At higher electrolyte concentrations the equilibrium state is a very thin Newton black film (NBF). The thickness of NBF is practically independent of the electrolyte concentration and is given by the direct interaction of the surfactant adsorption layers by short-range forces not included in DLVO theory.

The structure and stability of soap films formed from aqueous surfactant solutions have been extensively studied from both theoretical and practical points of view [2–5]. Measurements of the stability [6], film thickness [7, 8], gas permeability [9, 10], and electroconductivity [11] have been reported. The contact angle between a black film and a bulk surface, as well as the difference in tensions between black and thicker films, have been measured for the foam films stabilized by different surfactants. These studies provide important information on the interaction forces in thin films [12–17].

A frequently used model system is soap films prepared from sodium dodecyl sulfate (NaDoS) in the presence of NaCl or mixtures of NaCl and LiCl [7, 8]. In some studies only LiCl is used as an electrolyte [8, 19]. Large differences between the properties of the films prepared in the presence of these electrolytes have been observed. In the case of NaCl the thickness of the CBF decreases with increasing NaCl concentration. However, at a certain critical salt concentration the thickness decreases stepwise and reaches the constant small value characteristic for NBF. Using LiCl such stepwise decrease at a critical salt concentration has not been observed. Secondly, the thickness measured for films at very high salt concentrations higher than 1.5 M [19] is slightly larger than the thickness of NBF with NaCl.

In this study we carried out a detailed investigation of the thickness and contact angles of films prepared from NaDoS as a function of LiCl concentration. Measurement of the contact angles of the films allows the calculation of the free energy of film formation per unit area. This data supplies us with more information about interactions in the black soap films.

Experimental part

The sodium dodecyl sulfate was of a "surface-chemical purity" grade [20]. It was obtained from Merck and it was purified by means of the purification method described in [21, 22]. The lithium chloride anhydrous p.a. (Fluka) was used without further purification. The solutions were prepared from double-distilled water Milli-Q_{plus} water (specific resistance 18 MΩ cm).

Thickness measurements

The thickness of the foam films was measured with the microinterferometric method as described by Scheludko and Exerowa [23, 24]. In a glass ring (radius $R = 4$ mm) a double-concave meniscus of the investigated solution is first formed. After sucking off part of the solution a horizontal nonequilibrium thick microscopic film is formed. This film thins by the action of the capillary pressure and following by the action of the surface forces in the film. Finally, it reaches an equilibrium thickness. The diameters of the films investigated were in the range of 0.3–0.5 mm.

The glass ring was situated on an inverted direct-light microscope in a small closed cell. The cell was thermostated, and its volume was saturated with the vapor of the film forming solution. A small central part of the film was illuminated with monochromatic light at a wavelength of 546 nm. A part of the light was reflected by the film to a photomultiplier. Special computer soft- and hardware collected and evaluated the data.

From the light intensity reflected from the film, the so-called equivalent water thickness h_w was calculated. For this, a homogeneous refractive index of the film was assumed to be equal to that of the film-forming solution.

To calculate the real physical thickness h of the film we used the formalism given in [25]. There the foam film is considered as being constructed of three layers of different refractive indices: A core of aqueous solution with thickness h_1 and refractive index n_1, which includes the surfactant head groups. This core is sandwiched by the two layers with thickness h_2 and refractive index n_2 consisting of the hydrophobic part of the NaDoS molecules. The real physical film thickness

$$h = h_1 + 2h_2 \tag{1}$$

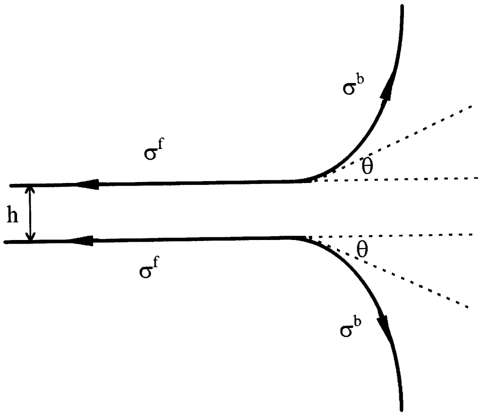
can be calculated using the following relation:

$$h_1 = h_w - 2h_2[(n_2^2 - 1)/(n_1^2 - 1)] . \tag{2}$$

Contact angle measurements

The contact angle θ between film and surround meniscus can provide us with information on the interaction forces in the thin foam films [2, 13, 15, 18]. It is defined [13–15] as the angle between the surfaces of the extrapolated Plateau border and the plane parallel film at their line of contact (Fig. 1). There are different methods for measuring the contact angle [2]. In the present paper the contact angles were measured using the expansion method described by Kolarov et al. [12, 13]. These measurements were performed in the same cell as the thickness measurements. The initially thick nonequilibrium film (Fig. 2a) has a radius r_1 and a contact angle θ_1 equalizes zero. In the process of approaching the equilibrium film, small black spots appear. The spots grow, coalesce, and finally cover the whole film area (Fig. 2b). However, in this moment the film tension and the surface tension of the meniscus surface are not in equilibrium, and the film diameter expands. After reaching a radius r_2, an equilibrium state is reached with a contact angle $\theta_2 > 0$.

Fig. 1 Profile of the film and surrounding meniscus: θ – contact angle; σ^b – surface tension of the bulk solution; σ^f – surface tension of the film surface



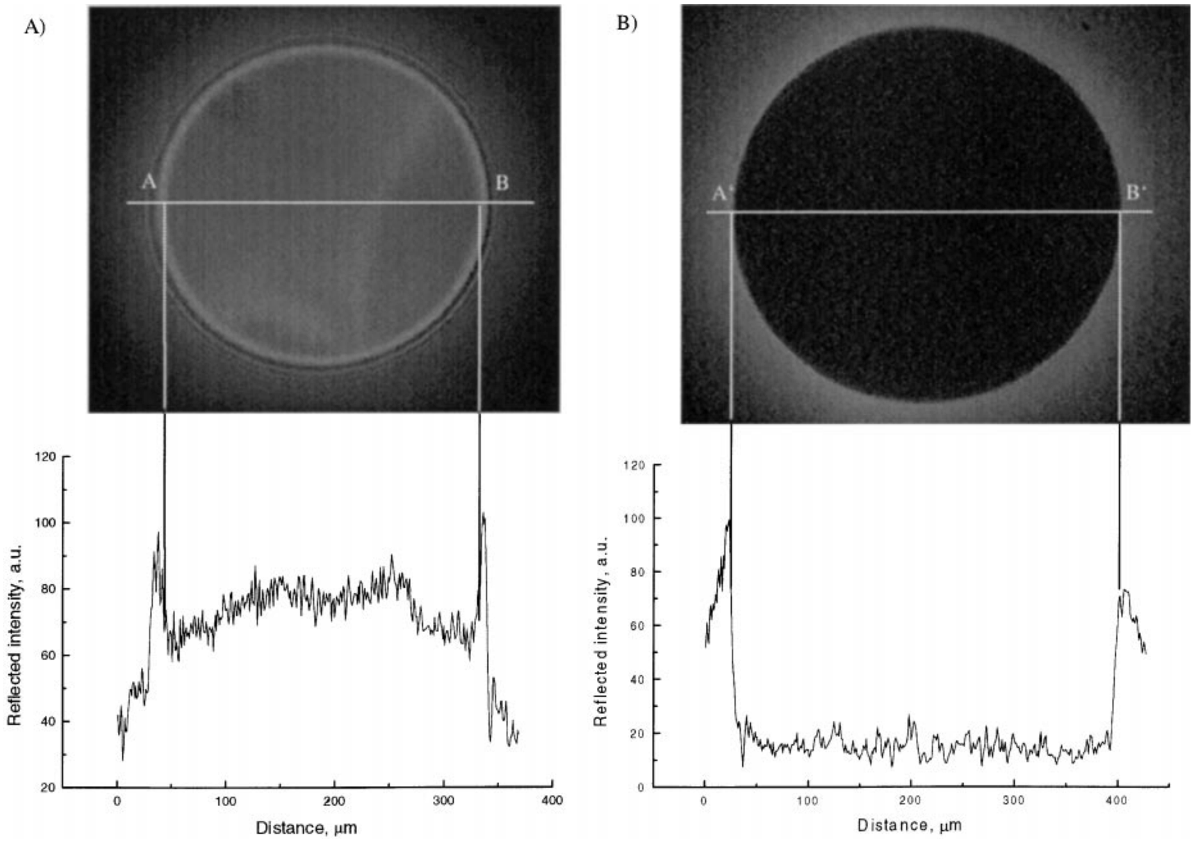


Fig. 2 Typical video images of foam films obtained from solution containing – 1.73 mM NaDoS and 1.7 M LiCl and their densitograms obtained with an image processing programme along the line AB for: (a) a nonequilibrium thick foam film just before first black spots appeared; (b) an equilibrium black foam film

The contact angles were calculated from experimental data using the calculation procedure of the so-called expansion method at constant pressure described in [26]. The capillary pressure in the system film/meniscus is given by the equation:

$$P_\mathrm{c} = \frac{2\sigma^b(R\cos\psi - r\cos\theta)}{(R^2 - r^2)} \tag{3}$$

where σ^b is the surface pressure of the bulk solution, r is the film radius and R is the radius of the capillary in which the film is formed. θ and ψ are the contact angles film/meniscus and meniscus/capillary wall, respectively. The capillary pressure is constant in the first obtained nonequilibrium film and in the finally obtained equilibrium black film. Then one can write

$$\frac{2\sigma^b(R\cos\psi - r_1\cos\theta_1)}{(R^2 - r_1^2)} = \frac{2\sigma^b(R\cos\psi - r_2\cos\theta_2)}{(R^2 - r_2^2)} \,. \tag{4}$$

The following formula can be derived for the calculation of the contact angle in the expansion method from the above equation:

$$\sin\theta_2 = \frac{(\delta_2^2 - \delta_1^2)\cos\psi + \delta_1(1 - \delta_2^2)\sin\theta_1}{\delta_2(1 - \delta_1^2)} \,, \tag{5}$$

here $\delta_1 = r_1/R$ and $\delta_2 = r_2/R$. This formula can be simplified to the following equation if $\psi \approx 0$, $\theta_1 \approx 0$ and $\delta_1^2 \ll 1$:

$$\sin 2\theta = \frac{\delta_2^2 - \delta_1^2}{\delta_2} \,. \tag{6}$$

We need the values of r_1, r_2 and R for the evaluation of the contact angles. The necessary conditions include total wetting ($\psi = 0$) of the tube where the film is formed, small values of the contact angle θ_1, small values of r_1/R, and constant pressure in the film and meniscus during film formation. These conditions are fulfilled in the experimental cell used in our case as it was proved in [26].

The process of film formation was recorded by a video camera. The images were evaluated by a computer equipped with an image processing system. Using this system, the noise in the images was reduced.

The radius of the thick nonequilibrium film was measured just before the moment of appearance of first black spots in the film because film diameter expands slightly in the moment of black spot formation. This leads to an error in the determination of the contact angle. From the densitogram of the image along the film diameter the film radius was obtained as half of the distance between the two points with the smallest darkness. These points correlate with both ends of the diameter of the film (line AB in Fig. 2a). For each experiment, r_1 was determined by averaging the data from three measurements of different film diameters.

The radius r_2 of the thinner film was measured when the expansion stopped and the film approached equilibrium. The same procedure as used for nonequilibrium films was applied to obtain the value. The correlated densitogram is presented in Fig. 2b.

The thickness and contact angle for a certain composition of film forming solution were determined through the mean value of at least 10 measurements of different films. The accuracy is ± 0.2 nm for thickness measurements and $\pm 0.1^\circ$ for contact angles. All measurements were performed at 25 °C. The surfactant concentration of 1.73 mM NaDoS was used in all experiments. It is well above the cmc for all LiCl concentrations. These experimental conditions are comparable with those for earlier experiments carried out with films stabilized with the same surfactant.

The surface tensions of the bulk solutions were measured using Lauda tensiometer equipped with a Du Noüy ring.

Results and discussion

Detailed dependencies of the thickness and the contact angles of foam films prepared from aqueous NadoS solutions on LiCl concentrations were measured. The LiCl concentration was varied in the range of 0.05–2.0 M. Experimentally obtained results are summarized in Table 1.

All the films investigated under the experimental conditions were stable for at least the time period of the experiment. This is in discrepancy with other results in [8, 19], where unstable films at small LiCl concentrations have been observed. The higher stability in our experiments may result from the very small area of our microscopic films.

Results for the dependence of the film equilibrium thickness on electrolyte concentration are presented in Fig. 3. The equilibrium film thickness was calculated from an experimentally obtained equivalent solution thickness

Table 1 Experimentally obtained values and their standard sample deviation (Δ) for the film thickness and contact angles film/bulk solution for foam films obtained from solutions containing 1.73 M NaDoS and different amount of LiCl. The thickness of thinner films is presented in brackets for these LiCl concentrations where both thick and thin films were observed

LiCl concentration [M]	Film thickness h [nm]	Δh [nm]	Contact angle θ [deg]	$\Delta\theta$ [deg]	Surface tension σ [mN/m]
0.05	9.11	0.55	0.83	0.09	33.65
0.10	7.30	0.25	—	—	33.66
0.20	6.91	0.41	0.80	0.07	33.63
0.30	6.23	0.22	—	—	33.26
0.40	6.06	0.13	0.91	0.12	32.92
0.50	5.67	0.15	0.82	0.15	32.65
0.60	5.31	0.34	0.98	0.08	32.42
0.70	5.19	0.11	0.75	0.10	32.22
0.80	5.17 (4.65)	0.14	0.85	0.08	32.13
0.90	5.15	0.13	1.20	0.10	32.03
1.00	5.02 (4.60)	0.13	1.25	0.05	31.89
1.10	4.84 (4.63)	0.13	1.37	0.05	31.59
1.20	4.75	0.15	1.63	0.05	31.54
1.30	4.74	0.19	1.54	0.07	31.18
1.40	4.57	0.18	1.68	0.08	31.05
1.50	4.60	0.13	2.30	0.21	30.92
1.60	4.56	0.11	2.60	0.10	30.73
1.70	4.61	0.12	—	—	30.62
1.80	4.62	0.13	2.50	0.18	30.57
1.90	4.61	0.18	—	—	30.01
2.00	4.61	0.17	2.51	0.17	29.76

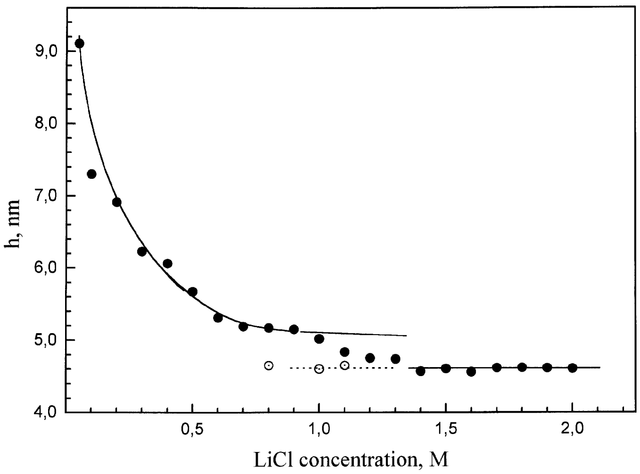


Fig. 3 Dependence of the real physical film thickness on the LiCl concentration for the investigated films

using Eqs. (1) and (2). The parameters h_w and n_1 in Eq. (2) were measured in the present work. The values for h_2 and n_2 are estimated from published data. For n_2 the refractive index of pure dodecane (1.4212) was used. The value of $h_2 = 1.055$ nm is taken from X-ray data recently published in [19] for the system NaDoS + LiCl. It is shown in that the thickness of the surfactant monolayers of the film does not depend on the film type (NBF or CBF).

The film thickness h decreases with increasing electrolyte concentration. This is in qualitative agreement with the changes in electrical double-layer repulsion as predicted by DLVO theory. The value of the double-layer potential is not known for this system. Because of the different properties of the systems containing LiCl or NaCl [8, 27, 28] the known double-layer potential of the latter case cannot be used. Therefore, we are not able to perform calculations of the double-layer interaction.

Film thickness does not depend on the electrolyte concentration at concentrations higher than 1.4 M LiCl (Fig. 3). From this we can follow that film thickness in this range is not controlled by double-layer forces. Therefore, we can consider these films as NBF. This is in accordance with results in [19]. In some experiments films with a thickness typical for NBF appeared at concentrations below 1.4 M LiCl. These results are presented in Fig. 3 as open points. Contrary to films with NaCl in the system with LiCl we can observe only a small step in thickness, if it exists at all.

Our experimental results at low LiCl concentrations are similar to those obtained in [8] where films prepared from lithium dodecyl sulfate in addition of LiCl were investigated. The NBF range was not investigated in detail in this paper. Our results are in favor with results in [19] where the same system as ours was investigated and at high LiCl NBF were observed. This observation was proved in the present work by more experimental points and additionally by the dependence of the interaction free energy of film formation on the electrolyte concentration.

The interaction free energy of the plane parallel equilibrium film with thickness h can be calculated from the data for contact angle and surface tension of the bulk solution (Table 1). Following de Feijter's thermodynamic analysis of the system [15, 18] the interaction free energy per unit film area $\Delta F(h)$ is defined as

$$\Delta F(h) \equiv -\int_{\infty}^{h} \Pi(h)\,\mathrm{d}h \;, \tag{7}$$

where $\Pi(h)$ is the thickness-dependent disjoining pressure. $\Delta F(h)$ is the contribution of interaction forces to the whole energy of the system film/meniscus.

A relation between surface tension on the film surface σ^{f} and $\Delta F(h)$ is [15]

$$2\sigma^{\mathrm{f}} = 2\sigma^{\mathrm{b}} + \Delta F(h) \;. \tag{8}$$

From the force balance at the contact line we have (see Fig. 1)

$$2\sigma^{\mathrm{f}} = 2\sigma^{\mathrm{b}} \cos\theta \;. \tag{9}$$

When Eq. (9) is substituted in Eq. (8) we find the following relation between interaction free energy and contact angle:

$$\Delta F(h) = 2\sigma(\cos\theta - 1) \;. \tag{10}$$

One has to take into account that surface tension is not a surface energy. The value of the free surface energy is numerical equal the surface tension only in the case of pure liquids. This equation is correct in our case under the condition of constant adsorption. It gives the difference ΔF^{f} of the film free energy between the states of the film, which are different only by the state of interaction between the film surfaces and not by composition of the solution, temperature, capillary pressure or other thermodynamic parameters.

The dependence of the free energy of film formation $\Delta F(h)$ on the concentration of LiCl is presented in Fig. 4. The free energy has a small constant value at low electrolyte concentrations. It increases steeply with increasing electrolyte concentration after 0.8 M LiCl and becomes constant in the limits of the experimental error at LiCl concentrations higher than 1.6 M. It is known that transition from CBF to NBF takes place at the salt concentration where the slope of the curve $\Delta F(h)C_{\mathrm{salt}}$ sharply increases. The shape of the curve in Fig. 4 proves our conclusion that NBF can be observed in the investigated system at high LiCl concentrations.

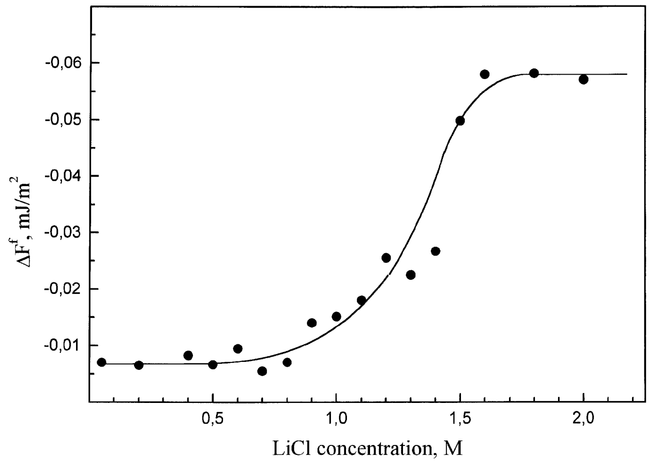


Fig. 4 Dependence of the free energy of film formation (ΔF^f) on the LiCl concentration for the investigated films

Conclusions

Detailed experimental results on both film thickness and contact angles show that Newton black films prepared from NaDoS in the presence of LiCl can be obtained. A smooth transition from CBF to NBF takes place in the concentration range from 0.8 to 1.4 M LiCl. Newton black films are formed at concentrations higher than 1.4 M LiCl. This transition in the NaDoS + LiCl system is not so well defined as in the system NaDoS + NaCl where the transition is well established and the thickness and interaction free energy jump [7, 8].

Acknowledgements The authors acknowledge with thanks the fellowship support for R. Krustev from the "Dr. Anton Kalojanof" foundation. We also acknowledge the fruitful discussion on the paper with Prof. H. Möhwald. Dr. Lunkenheimer kindly supplied us with "surface-chemical pure" NaDos prepared in his laboratory.

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