

Drainage of foam films in the presence of nonionic micelles

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Abstract: The stratification (step-wise thinning) of horizontal foam films formed from micellar solutions of nonionic surfactants is studied experimentally. The effects of film area, temperature, oil solubilization, surfactant and electrolyte concentrations are investigated. The data support the colloid crystal model of stratification, according to which the step-wise thinning is due to a layer-by-layer destruction of an ordered structure of spherical nonionic micelles inside the film. The analysis of the data shows that the main factor governing the stratification is the volume fraction of the micelles. This fact leads to an unified interpretation of the observed effects, both with nonionic and with anionic surfactant solutions.

Key words: Foam films; nonionic surfactants; stratifying films; micellar structuring; steric stabilization

Introduction

At present the nonionic surfactants are the subject of intensive research and development with continuously growing fields of application. Their wetting, foaming, dispersing or emulsifying properties are widely utilized in practice. At equal molar concentrations the nonionic surfactants, as a rule, exhibit greater surface activity and lower critical micellar concentrations (CMC) than the ionic surfactants [1, 2].

It was recently observed [3] that foam films formed from micellar solutions of nonionic surfactants exhibit step-wise thinning. This phenomenon, called „stratification“ was observed long ago with anionic surfactants [4, 5]. The step-wise thinning of films from solutions of ionic micelles was explained [3, 6, 7] as a layer-by-layer destruction of a structure of spherical micelles inside the film. The occurrence of the stratification depends strongly on the interaction between the micelles and on their concentration in the solution.

The aim of the present paper is a comprehensive experimental study of the occurrence of stratification with nonionic surfactant solutions. Special attention is paid to the influence of different factors

(surfactant concentration, temperature, film area, solubilization, etc.) on the step-wise thinning. The results are compared with similar data for anionic surfactants. Correlations are found between the micellar aggregation in the surfactant solution and the stratification and stability of the films. The results indicate how one can control (increase or decrease) the stability of microheterogeneous systems containing nonionic surfactant micelles in the disperse medium.

Experimental materials and technique

a) Materials

In our experiments we used a commercial nonionic surfactants Enordet AE 1215-9.4 and AE 1215-30 (products of Shell Co.). Both surfactants are ethoxylated alcohols with straight paraffinic chain containing between 12 and 15 carbon atoms and with a hydrophylic chain containing, on the average, 9.4 and 30 ethylene-oxide groups, respectively. The data of Mitchell et al. [8] for ethoxylated alcohols obtained by small-angle neutron scattering show that these nonionic surfactants in aqueous solutions form liquid crystal phase only at concentrations higher than 30 wt % at room temperature. In our experiments we

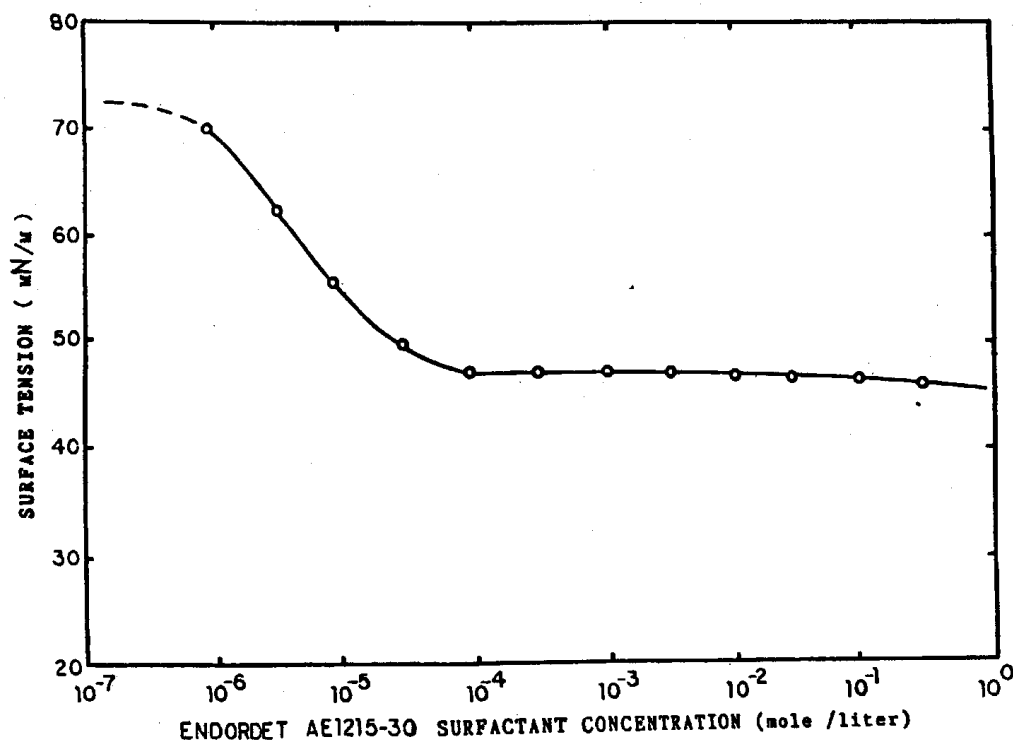


Fig. 1. Plot for the experimental data for the surface tension of an Enordet AE 1215-30 solution vs the surfactant concentration at 25°C

used surfactant solutions of concentrations above CMC, but below 10 wt %. In this concentration-range spherical micelles are formed in the solution (see [1, 2, 8]).

Figure 1 shows surface tension isotherm at 25°C for Enordet AE 1215-30, measured by the Wilhelmy plate technique. There is no minimum on the isotherm, which is an indication of the absence of surface contaminations.

b) Measurements of micellar size and distribution

The available light-scattering data [9] show that at low concentration and room temperature the micellar solutions of nonionic surfactants behave as a solution of hard spheres with a volume fraction that is larger than the surfactant weight fraction. This fact indicates that at low micellar concentrations the surfactant molecules are strongly hydrated. In the case of micellization in solutions of polyoxyethylene surfactants, like those studied by us, the ethylene-oxide groups interact with the water molecules and form a shell enveloping the micellar core, the latter consisting mostly of the hydrocarbon phase [10]. The outer diameter of this shell in fact determines the size of the effective hard sphere characterizing the interaction between micelles.

The micellar size and the distribution in the nonionic surfactant solutions studied by us have been measured by Malvern 4700 dynamic light-scattering technique. All measurements were done by Malvern Instruments Inc., Southborough, Mass., USA.

c) Measurements of foam film thickness

Horizontal microscopic foam films were formed from the studied solutions of nonionic surfactants in a vertical cylindrical capillary. The latter has a hydrophylic inner wall of radius 1.5 mm. The films were formed by sucking out the liquid from a biconcave drop inside the capillary through an orifice in the capillary wall. The same technique was applied previously [3, 6] for studying foam films formed from micellar solutions of anionic surfactants. The horizontal film was observed from above by means of a microscope with illumination through the objective. We used monochromatic light of wavelength $\lambda = 546$ nm. Stratification is observed, both with anionic and nonionic surfactants.

After the film is formed, it immediately starts to decrease its thickness. When the latter becomes smaller than about 104 nm (this thickness corresponds to the last interference maximum) step-wise changes in the film thickness can be observed. The film remains for a few seconds in a metastable state with almost constant thickness. Then one or several dark spots (thinner than the rest of the film) appear and rapidly increase their area. Soon the spots cover the whole film and the film stays for several seconds in the new metastable state. Then new darker spots appear and spread, and then a subsequent metastable state is reached. Eventually the film reaches a stable state and step-wise transitions no longer occur.

The thickness of the film during the step-wise thinning was recorded using reflected light interferometry tech-

nique. The light reflected from a portion of the film is conducted to a photomultiplier by means of a fine optic fiber. The resulting photocurrent is recorded as a function of time. The experimental setup is described in details in [6]. A typical interferogram is presented in Fig. 2. The minimum and the maximum intensities of the reflected light correspond to the last interference minimum and maximum. The instantaneous film thickness can be calculated from the instantaneous intensity of the reflected light as reported in [6]. The calculated heights of the steps are also shown in the interferogram.

The steps in the interferogram correspond to the metastable states of the film. Their width is the lifetime of the respective metastable state. The irregularity of some of the upper steps (Fig. 2) is due to the consecutive passage of several similar dark spots through the scope field of the optic fiber.

Interferograms obtained at different experimental conditions are shown and discussed below.

Experimental results

Preliminary experiments showed that the stratification of films formed from aqueous solutions of nonionic surfactants depend on several factors: film area, temperature, surfactant concentration, concentration of added electrolyte, oil solubilization, etc. In the following, we will separately consider the role of each factor, holding the other physical conditions constant.

a) Effect of film area

Since the capillary used is cylindrical, the horizontal films have circular shape. The radius r_c of the three-phase contact line encircling the film can be controlled by changing the capillary pressure as explained in [6]. The two interferograms shown in Figs. 2 and 3 represent the step-wise thinning of foam films formed from 0.052 mol/l (8 wt %) solution of Enordet AE 30 at temperature 32°C. The difference between the figures is due to the different film radii: $r_c = 0.4$ mm for Fig. 2, and $r_c = 0.2$ mm for Fig. 3. Six transitions are observed with the larger film, whereas their number is only 4 with the smaller one. (As explained above, the upper transitions sometimes are not very distinct in the interferograms, but they are visually well observed.) In both cases the stratification starts when the film thickness becomes around 70 nm and the mean height of a step is the same and equal to 9.7 nm. However, the thinning of the smaller film stops at thickness 34 nm (vs 14 nm for the larger one) and the last two transitions (observed with the larger film) do not take place. Therefore, the decrease of the film area can stop the stratification. In the case illustrated in Fig. 3 the final stable film contains two layers of micelles, which are in diffusional equilibrium with the bulk micellar solution in the biconcave meniscus surrounding the film.

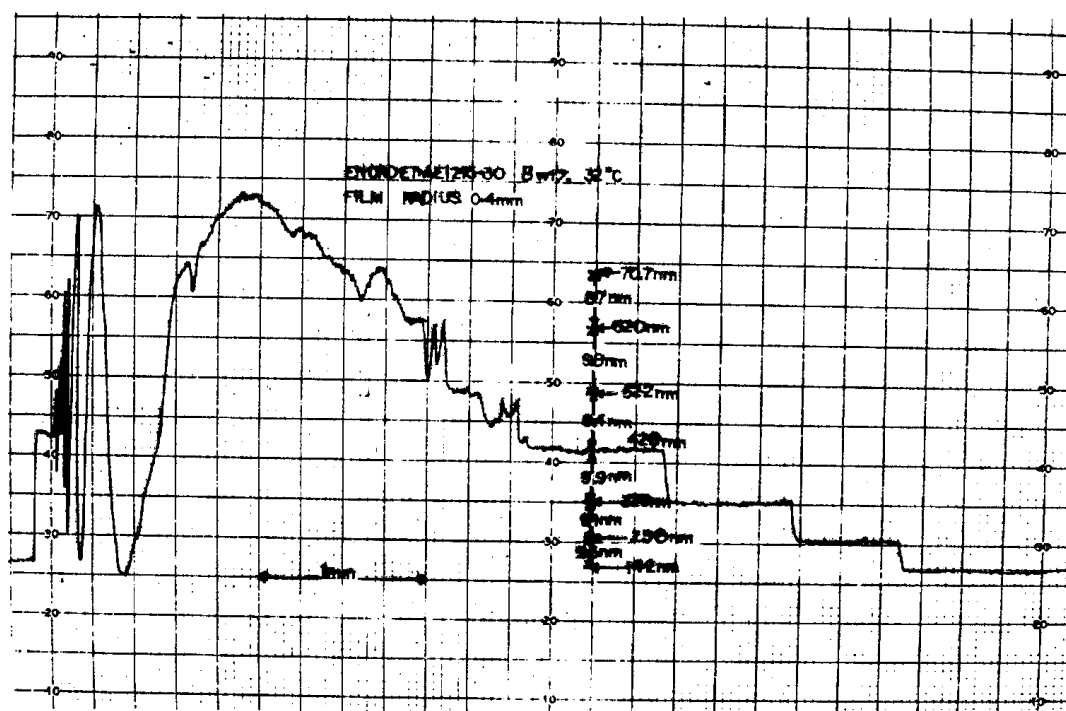


Fig. 2. Photocurrent vs time in the interferogram of thinning of the Enordet AE 1215-30 film at surfactant concentration 5.2×10^{-2} mol/l at 32°C and film radius 0.4 mm

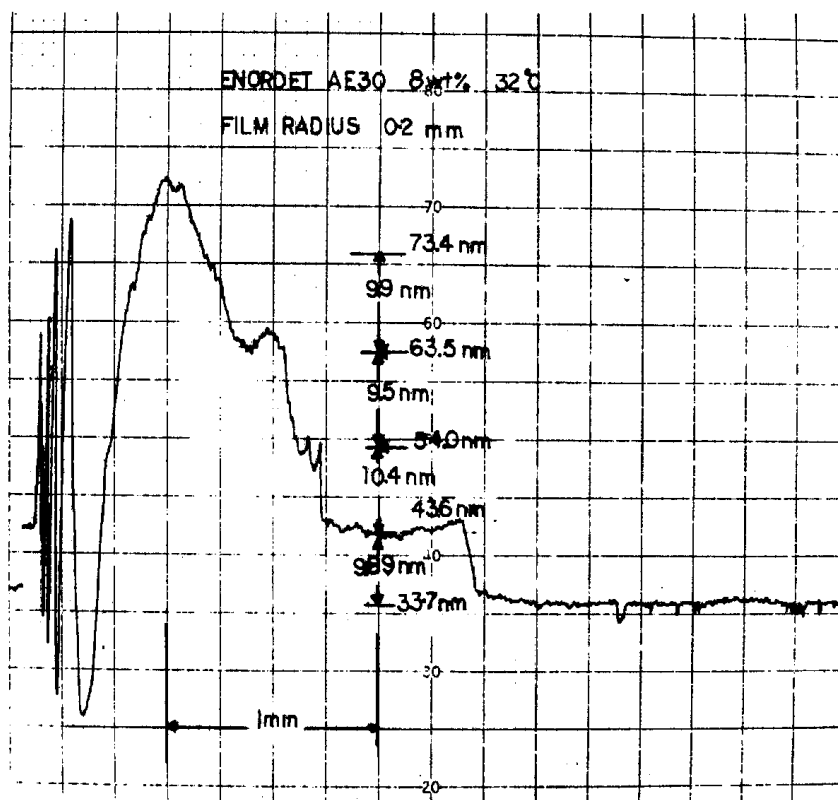


Fig. 3. Photocurrent vs time in the interferogram of thinning of the Enordet AE 1215-30 film at surfactant concentration 5.2×10^{-2} mol/l at 32°C and film radius 0.2 mm

A similar effect was recently observed with stratifying films formed from anionic surfactant solutions. In [11] a diffusive-osmotic mechanism was proposed for interpretation of the data for formation and expansion of spots in the stratifying films. According to this mechanism the appearance of a spot is due to condensation of vacancies in the micellar structure inside the film. The theoretical model predicts that there is a minimum size of the (stable) spots in the film. When the film area is small enough, the total amount of vacancies in the film can be smaller than the one needed for creation of a stable spot. Then spots cannot appear and the stratification stops.

We expect that a similar explanation can be given also for the case of nonionic surfactants, because of the existence of analogous diffusive-osmotic effects. The development of such a model for nonionic surfactants needs, however, additional studies, both theoretical and experimental.

b) Effect of the temperature

A decrease of the temperature, similar to the decrease in the film area, can prevent the occur-

rence of the last few-step-wise transitions. The stratification stops at a larger film thickness. Figure 4 represents an interferogram obtained under the same conditions as those for Fig. 2 ($r_c = 0.4$ mm, 8 wt % solution of Enordet AE 1215-30), except for the temperature, which was 26°C instead of 32°C . One sees that the number of step-wise transitions is reduced to 2 at 26°C , as opposed to 6 at 32°C . The thickness of the final stable film is 14 nm at 32°C , whereas it is considerably greater — 49 nm — at 26°C . Hence, the decrease of the temperature leads to increase of the film stability and thick stable films can be obtained.

The effect of temperature is larger with solutions of nonionic surfactants having lower degree of ethoxylation. Figure 5 represents the interferogram of a thinning film formed from 2 wt % aqueous solution of Enordet AE 1215-9.4 (with an average number of 9.4 ethylene-oxyde groups per molecule) with $r_c = 0.3$ mm at 24°C . One sees that with the surfactant with shorter polyoxyethylene chain step-wise thinning is not observed, the final thickness is larger and the drainage is slower.

The velocity of drainage of the stratifying films depends strongly on the temperature. Let us define



Fig. 4. Photocurrent vs time in the interferogram of thinning of the Enordet AE 1215-30 film at surfactant concentration 5.2×10^{-2} mol/l at 26°C and film radius 0.4 mm

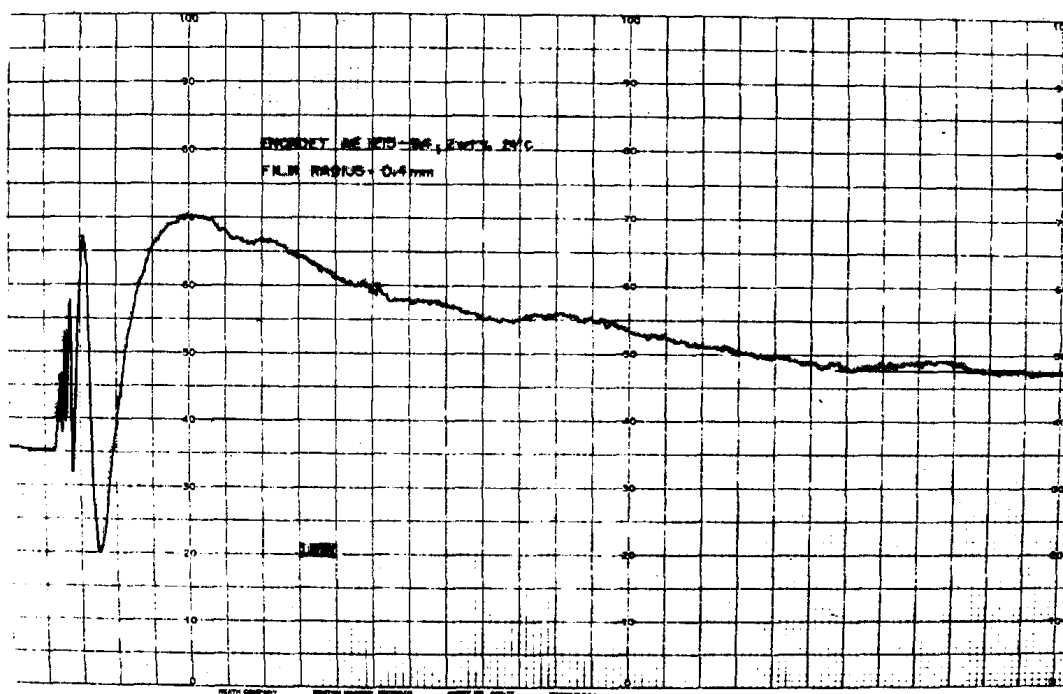


Fig. 5. Photocurrent vs time in the interferogram of thinning of the Enordet AE 1215-9.4 film at surfactant concentration 3.2×10^{-2} mol/l at 24°C and film radius 0.4 mm

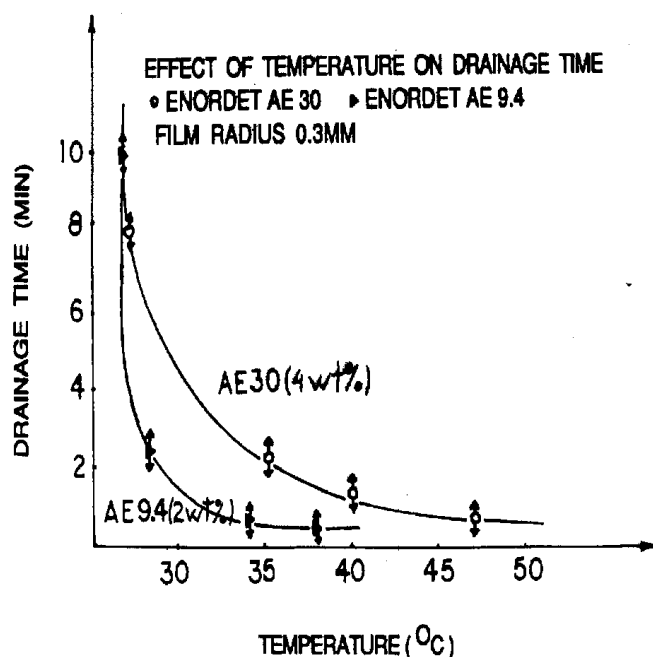


Fig. 6. Effect of temperature on drainage time (○ Enordet AE 1215-30, ◆ Enordet AE 1215-9.4). Film radius 0.3 mm

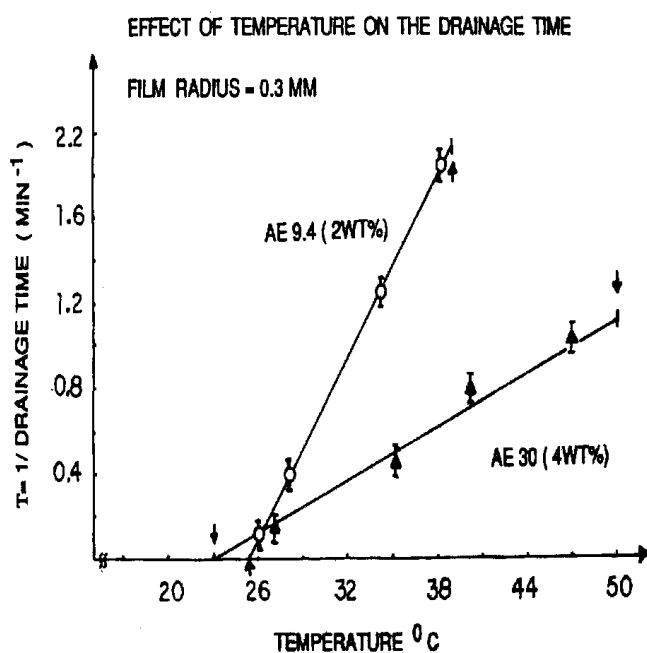


Fig. 7. Effect of temperature on drainage time (○ Enordet AE 1215-30, ◆ Enordet AE 1215-9.4). Film radius 0.3 mm

drainage time of the film by the time elapsed between the appearance of the last interference maximum (it is well seen in the interferograms and corresponds to film thickness about 104 nm) and the moment when the final stable thickness is reached. The data for the dependence of the drainage time so defined on the temperature are shown in Fig. 6 for Enordet AE 1215-30 at concentration 4 wt % (upper curve) and Enordet AE 1215-9.4 at concentration 2 wt % (lower curve). Both curves refer to film radii 0.3 mm. For temperatures below 30°C the drainage time sharply increases and the step-wise transitions are either few or there are none. The final film thickness in this temperature range is about 60 nm or greater and increases with the decrease of temperature.

At temperatures higher than 30°C pronounced stratification is observed. All possible consecutive step-wise transitions occur and the final film thickness is about 15 nm and probably corresponds to a film that does not contain any micelles.

At temperatures higher than 35°C the step-wise transitions become irregular: two or more transitions can occur at once. At even higher temperatures the step-wise transitions are absent: the final stable state is directly reached. At temperatures close to the surfactant cloud point (but below

it) the films rupture when they reach the critical thickness (stable states do not exist).

It is interesting to note that the dependences in Fig. 6, become linear when the reciprocal drainage time is plotted as a function of temperature — see Fig. 7.

c) Effect of surfactant concentration

Due to the strong effect of the film area and the temperature on the stratification, we studied the role of the surfactant concentration at fixed film radius, $r_c = 0.3$ mm, and at constant temperature 27°C. Data for stratifying films at different surfactant concentrations are presented in Table 1. The film thicknesses corresponding to the different steps were calculated from the experimental interferograms. Both for Enordet AE 1215-9.4 and for Enordet AE 1215-30 the number of the step-wise transitions increases with the increase of the surfactant concentration. For the lowest concentrations studied only one step-wise transition was observed. Five to six transitions occurred at higher concentrations. The surfactant with longer polyoxyethylene chain (Enordet 1215-30) exhibits more step-wise transitions for a given molar concentration.

Table 1. Experimental data for stratifying films from aqueous solutions of Enordet AE

		Enordet AE 1215-9.4			Enordet AE 1215-30		
Surfactant concentration (mol/l)		0.008	0.064	0.130	0.026	0.052	0.100
Final film thickness		17.3	16.8	16.0	16.1	15.0	14.5
Transition number and respective film thickness (nm)	1	32.1	31.0	29.9	27.1	25.5	24.4
	2	—	45.0	42.8	—	36.5	34.4
	3	—	59.4	56.2	—	47.2	43.4
	4	—	74.0	69.2	—	57.7	53.3
	5	—	—	82.9	—	68.7	63.3
	6	—	—	—	—	—	72.5
Mean height of a step (nm)		15.0 ± 0.6	14.2 ± 0.4	13.4 ± 0.4	11.2 ± 0.6	10.8 ± 0.5	9.9 ± 0.4
Micelle diameter (nm)		15.0 ± 1.5	13.7 ± 1.5	—	10.6 ± 2.1	—	—

To check the hypothesis that the thickness of a stratifying film is determined by the number of the micellar layers inside it, we compared the mean height of a step with the diameter of the micelles (the last two rows of Table 1). The mean diameter of the micelles was measured by means of Malvern technique as explained above. One sees that the mean values of the micellar diameter and the height of the step coincide in the framework of the experimental accuracy. This fact implies that the step-wise thinning can really be interpreted as a layer-by-layer destruction of a micellar structure inside the stratifying film. Analogous experiments with thinning films containing anionic surfactant micelles or latex particles reveal [3, 6, 7] that the stratification is typical for films containing almost monodisperse spherical colloidal particles.

We will note also that the micellar diameters as well as the heights of the steps presented in Table 1 exhibit a weak tendency to decrease when increasing the nonionic surfactant concentration.

d) Other factors affecting the stratification

The stratification of foam films, formed from solutions of *anionic* micellar surfactant solutions, is strongly depressed by addition of neutral electrolyte [6, 7]. This effect is due to the shrinking of

the double electric layer around the micelles. Although nonionic micelles have no electric layers, our experiments with *nonionic* surfactants still showed that neutral electrolyte can suppress the stratification.

In our experiments we added NaCl to aqueous solutions of Enordet AE 1215-9.4, -20, and -30 (nonionic surfactants containing 9.4, 20, and 30 ethylene oxide groups, respectively). It turned out that the minimum concentration of NaCl needed for complete suppression of the stratification was dependent on the number of ethylene oxide (EO) groups. That is why we presented the experimental data in Fig. 8 as a diagram showing the number of EO groups vs NaCl concentration. The line divides the regions of stratifying and nonstratifying films. The high values of the NaCl concentration indicate that the effect of neutral electrolyte on stratification is connected with dehydration of the micellar EO groups (salting out).

We also studied the effect of pH. We found out that variation of pH between 2 and 10 does not affect the stratification if the ionic strength is held constant (about 10^{-2} mol/l).

To investigate the role of the solubilization of oil on the step-wise transitions, we used 5.2×10^{-2} mol/l solution of Enordet AE 1215-30 pre-equilibrated for 48 h with n-decane. It is known that under these conditions the decane is solubilized

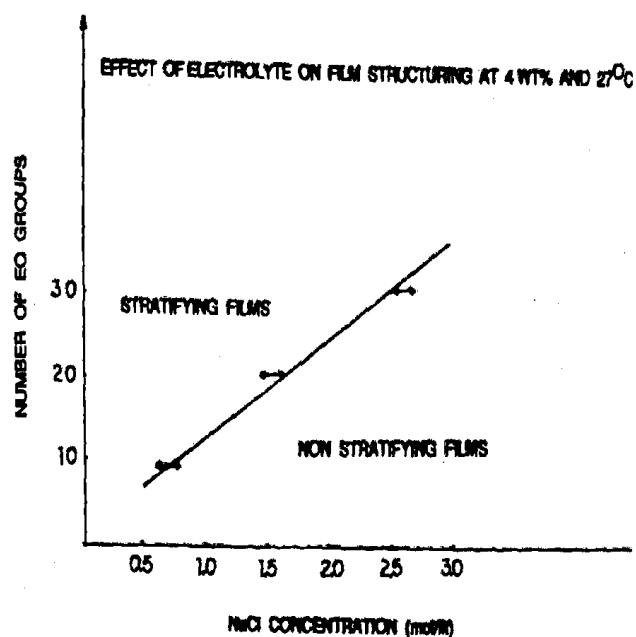


Fig. 8. Effect of electrolyte on film stratification at 27°C and 4 wt % surfactant concentration

and swollen micelles are formed [18]. Interferograms of the step-wise thinning before and after solubilization of decane are compared in Fig. 9a, b. Although the number of steps is the same, the lifetimes are shorter for the solutions containing swollen micelles, and the time for draining to the final film thickness was, respectively, 5.3 and 3.7 min. In addition, the steps in Fig. 9b are not as distinct as those in Fig. 9a. These facts suggest that the solubilization leads to less stable micellar structuring.

Discussion

As mentioned above, a colloid crystal model of stratifying films was proposed in [3, 6, 7, 11]. According to this model the step-wise thinning is due to the layer-by-layer destruction of the structure formed by spherical colloidal particles inside the film. An argument in favor of this model is the fact that the height of a step is approximately equal to the colloid particle diameter; (see Table 1 for nonionic micelles and [3, 6, 7] for anionic micelles and polystyrene latex particles). The effective micellar diameter of anionic micelles was defined in [6] as

$$2R_{\kappa} = 2(R_p + 1/\kappa), \quad (1)$$

where R_p is the particle (micellar) radius and $1/\kappa$ is the effective thickness of the double electric layer around the particle.

According to the colloid crystal model any factor suppressing formation of particle ordering inside the film will also restrain the stratification. The parameter determining the disorder-order transition in a system of hard spheres is the volume fraction ϕ of the particles [20]. Then one can expect that any factor decreasing the volume fraction of the colloidal particles will depress the particle ordering inside the film and hence — the stratification. Our aim below is to demonstrate that such a conclusion is supported by the experimental data, both for anionic and nonionic surfactants.

For anionic surfactants the effective volume fraction of the micelle is

$$\phi = C_{\text{mic}} \left(\frac{4}{3} \pi R_{\kappa}^3 \right), \quad (2)$$

where C_{mic} is the number density of the micelles in the solution. For nonionic surfactants the micellar volume fraction is simply

$$\phi = C_{\text{mic}} \left(\frac{4}{3} \pi R_p^3 \right). \quad (2)$$

Let us first briefly consider the case of *anionic* surfactants. In [3, 6, 7] stratification with micellar solutions of sodium dodecylsulfate (NaDS) was studied. Both NaDS and NaCl are strong electrolytes. However, addition of NaDS or NaCl to the surfactant solution leads to quite different effects on stratification. The increase of NaDS concentration increases the number of the step-wise transitions and the time for drainage of the film [6]. This correlates with the fact that the addition of NaDS increases C_{mic} and, thereby, the micellar volume fraction ϕ , calculated by means of Eqs. (1) and (2). Hence, this favors the micellar structuring inside the thinning film.

The addition of NaCl to the surfactant solution leads to the exact opposite effect: the number and the regularity of the step-wise transitions decreases and the drainage of the stratifying film accelerates. The influence of added neutral electrolyte on the micellar volume fraction ϕ can be analyzed with the help of the experimental results of Sigter and Mysels [12]. These data and the calculated values of

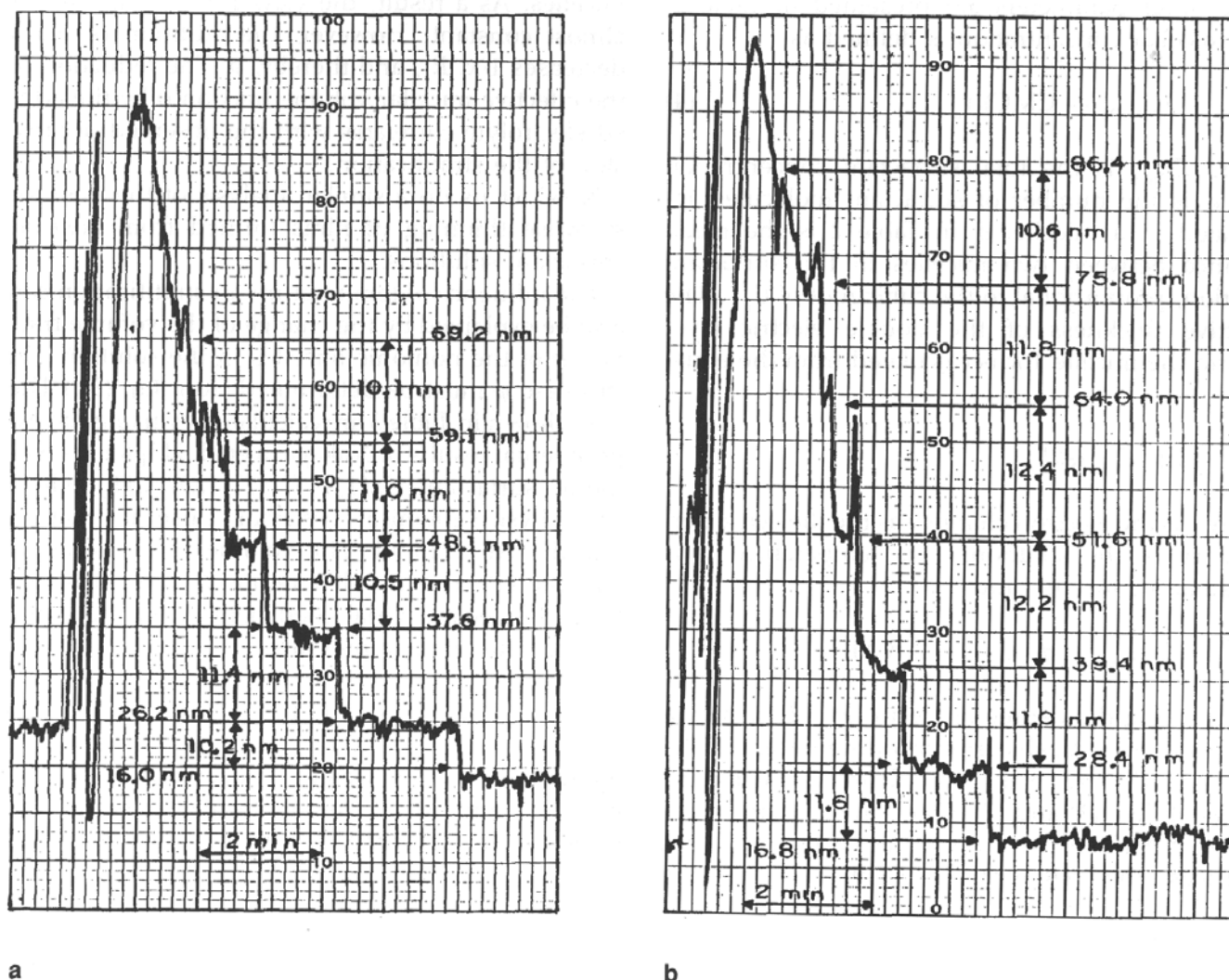


Fig. 9. a) Photocurrent vs time in the interferogram of thinning of the Enordet AE 1215-30 film at surfactant concentration 5.2×10^{-2} mol/l. b) The same as in a) but the solution is preequilibrated with n-decane

Table 2. Effect of concentration of NaCl on the properties of micellar solutions of sodium dodecyl sulfate

C_{NaCl} (mol/l)	CMC (mol/l)	v_a	R_p (nm)	α	$C_{\text{mic}} \times 10^4$ (mol/l)	δ_l (nm)	$1/\kappa$ (nm)	$2R_\kappa$ (nm)	ϕ %
0	8.1×10^{-3}	80	2.15	0.29	2.7	18.3	2.9	10.0	9
0.01	5.3×10^{-3}	89	2.1	0.28	2.8	18.1	1.6	8.8	5
0.03	3.1×10^{-3}	99	2.30	0.29	2.7	18.3	1.6	7.9	3
0.05	2.3×10^{-3}	104	2.34	0.30	2.7	18.3	1.3	7.3	3

some other parameters are presented in Table 2. The micellar concentration is defined as

$$C_{\text{mic}} = (C_{\text{NaDS}} - \text{CMC})/\nu_a, \quad (4)$$

where C_{NaDS} is the total surfactant concentration and ν_a is the number of surfactant molecules aggregated in a micelle. δ_l in Table 2 is the mean distance between two micelles in the surfactant solution, proportional to the cubic root of C_{mic} . The effective thickness of the double electric layer around the micelle $1/\kappa$ is calculated from the equation

$$\kappa^2 = 4\pi e^2 C_{\text{ion}}/(\epsilon kT),$$

where e is the electron charge, ϵ is the dielectric permittivity of the solution, T is temperature, k is Boltzmann constant, and

$$C_{\text{ion}} = 2C_{\text{NaCl}} + a\nu_a C_{\text{mic}} + 2(\text{CMC}),$$

with a being the degree of electrolytic dissociation of the surface ionizable groups of the micelles. The values of R_κ and ϕ in Table 2 are calculated by means of Eqs. (1) and (2). One can see that the increase of NaCl concentration decreases CMC, but increases the aggregation number ν_a of the

micelles. As a result, the values of C_{mic} and δ_l are almost constant. However, the addition of NaCl decreases $1/\kappa$, R_κ , and thereby, ϕ . The reduction of the effective micellar volume fraction ϕ by the added electrolyte correlates with the observed depression of the stratification.

Now, let us do a similar analysis of the data for stepwise thinning of films formed from *nonionic* surfactant solutions.

The influence of temperature on stratification can also be explained by the change of the volume fraction ϕ of the nonionic micelles in the solution. (In this case ϕ must be determined from Eq. (3).) The data shown in Table 3 are calculated by using the experimental results of Nakagawa et al. [13] for the nonionic surfactant $\text{C}_{10}\text{H}_{21}\text{O}(\text{CH}_2\text{CH}_2\text{O})_{12}\text{CH}_3$, which has physico-chemical behavior close to that of Enordet AE 1215-9.4. The volume of a micelle V_p and the effective micellar radius R_p are calculated from the second virial coefficient A_2 in the equation for the osmotic pressure

$$\Pi = C_w RT(1/M_p + A_2 C_w), \quad (5)$$

where C_w is the weight concentration of the micelles, and M_p is the molecular mass of the micelles. In accordance with [2], we assumed that

Table 3. Effect of temperature on the properties of micellar solutions of $\text{C}_{10}\text{H}_{21}\text{O}(\text{CH}_2\text{CH}_2\text{O})_{12}\text{CH}_3$

T °C	CMC $\times 10^3$ (mol/l)	M_p (kg/mol)	ν_a	$C_{\text{mic}} \times 10^4$ (mol/l)	$A_2 \times 10^4$	$V_p \times 10^{26}$ (m ³)	ϕ %
10	2.5	32.9	47	7.4	2.55	11.5	5.2
29	1.6	37.1	53	6.7	2.06	11.8	4.8
51	1.2	45.5	65	5.2	1.36	11.7	3.9

Table 4. Effect of NaCl on the properties of micellar solutions of $\text{C}_{13}\text{H}_{27}\text{O}(\text{CH}_2\text{CH}_2\text{O})_{10}\text{CH}_3$

C_{NaCl} (mol/l)	ν_a	M_p (kg/mol)	$C_{\text{mic}} \times 10^4$ (mol/l)
0	92	58.7	8.53
0.3	110	70.0	7.11
0.5	141	90.3	5.69

Table 5. Effect of NaCl on the properties of micellar solutions of $\text{C}_{13}\text{H}_{27}\text{O}(\text{CH}_2\text{CH}_2\text{O})_{22}\text{CH}_3$

C_{NaCl} (mol/l)	ν_a	M_p (kg/mol)	$C_{\text{mic}} \times 10^4$ (mol/l)
0	28	32.5	7.7
0.3	29	33.5	7.4
0.5	28	32.5	7.4

$$V_p = M_p^2 A_2 / 4 N_A, \quad (6)$$

where N_A is Avogadro's number. One sees that in spite of the increase of the aggregation number ν_a with the temperature, the volume of a micelle does not change significantly. However, the decrease of the micellar concentration C_{mic} leads to decrease of the volume fraction ϕ of the micelles. This explains why the stratification becomes less pronounced and even disappears entirely when the temperature is raised. On the contrary, when the temperature is sufficiently low, the micellar structure in the film becomes so stable that the film can exist in equilibrium with the bulk surfactant solution. As a result, stable thick films are formed (see Figs. 4 and 5). Such films can contain several micellar layers. It should be noted that the above findings correlate well with the very pronounced effect of temperature on the steric stabilization (see [14, 15]).

An analogous explanation can be given to the effect of neutral electrolyte (e.g., NaCl) on the stratification of thinning films from nonionic surfactant solutions (see Fig. 8). Table 4 contains data for $C_{13}H_{27}O(CH_2CH_2O)_{10}CH_3$, obtained by Becher [16]. One sees that the increase of C_{NaCl} leads to increase of the aggregation number ν_a and to decrease of the micellar concentration C_{mic} . Note that the relative change of C_{mic} without electrolyte and with 0.5 mol/l NaCl in Table 4 are the same as in Table 3 for 10°C and 51°C. Unfortunately, data for the second virial coefficient allowing the use of Eq. (6) for calculation of V_p are not available, so that we could not calculate the micellar volume fraction ϕ . Nevertheless, it is known (see, e.g., [17]) that the salting-out action of the electrolyte, similar to the action of the temperature, leads to a partial

dehydration of the ethylene-oxide chain and reduces the volume of the micelles. Therefore, one can infer that, in this case, the observed depression of stratification can also be explained by reduction of the micellar volume fraction ϕ . In favor of such an assumption are the data presented in Table 5. They show that the dehydration effect due to the added electrolyte is considerably smaller when the ethylene-oxide chain is longer. This result is in agreement with our data in Fig. 8. Accordingly, for 30 ethylene-oxide units a high concentration of 2.5 mol/l NaCl is needed to entirely suppress the stratification.

To interpret our experimental results for the effect of solubilization on the step-wise transitions, we used the data of Nakagawa et al. [18] for aqueous solutions of $C_{10}H_{21}O(CH_2CH_2O)_8CH_3$ preequilibrated with decane. By using Eq. (5), we calculated the volume fraction ϕ of the micelles (see Table 6). Similar to the increase of the temperature, the solubilization leads to an increase of the aggregation number ν_a and to reduction of the second virial coefficient A_2 and of the micellar number density C_{mic} . The volume of a micelle V_p and the respective volume fraction ϕ also decrease, which is consonant with the suppression of the step-wise thinning established in Fig. 9.

Concluding remarks

The present paper is the first experimental study of stratifying films formed from nonionic surfactant solutions. We investigated the effect of film area, temperature, solubilization, surfactant, and salt concentration on the occurrence of the step-wise transitions during the thinning of the film.

Table 6. Effect of solubilization on the properties of micellar solutions of $C_{10}H_{21}O(CH_2CH_2O)_8CH_3$ preequilibrated with n-decane

oil/surfactant (wt %)	ν_a	M_p (kg/mol)	$C_{mic} \times 10^3$ (mol/l)	$A_2 \times 10^3$	$V_p \times 10^{26}$ (m ³)	ϕ %
0	83	43.1	5.73	1.69	13.0	7.4
1.32	87	45.6	5.47	1.13	9.8	5.4
2.33	90	47.8	5.29	0.98	9.3	4.9
3.16	94	50.5	5.06	0.91	9.6	4.8
3.78	96	52.0	4.96	0.68	7.6	3.8
4.93	105	57.5	4.53	0.66	9.1	4.1

The experimental results support the colloid crystal model of the stratification proposed in [3, 6]. According to this model, the step-wise thinning of films from surfactant solutions is due to a layer-by-layer destruction of a structure of spherical micelles formed in the film. We established experimentally that the mean height of a step and the diameter of a nonionic micelle are approximately equal. It also turns out that the main parameter governing the stratification is the volume fraction ϕ of the colloid particles (the micelles) in the solution. All factors causing reduction of ϕ (increase of temperature or electrolyte concentration, or decrease of surfactant concentration) lead to depression or total disappearance of the step-wise transitions and to acceleration of the film drainage. Alternatively, all factors leading to increase of ϕ favor the formation of stable colloid crystal structures inside the film. This concept allows a unified interpretation of the observed effects, both with nonionic and with anionic surfactant solutions.

The practical importance of the studied effects is the following. By investigating the effect of different additives on the stratification one can predict their influence on stability of the respective microheterogeneous systems. When stable dispersions are needed one can utilize the property of nonionic surfactants to form stable, thick films containing several micellar layers at room temperatures (cf. Figs. 5 and 6). For example, this effect can find an application in enhanced tertiary oil recovery [19]. In other cases the opposite effect, that of destruction of the microheterogeneous system and phase separation might be needed. This aim can be achieved by enhancing some factor that reduces the effective micellar volume fraction and depresses the stratification.

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