Formation and Expansion of Dark Spots in Stratifying Foam Films

P. A. Kralchevsky, A. D. Nikolov, D. T. Wasan,* and I. B. Ivanov

*Laboratory of Thermodynamics and Physico-Chemical Hydrodynamics, Faculty of Chemistry,
University of Sofia, 1126 Sofia, Bulgaria, and Department of Chemical Engineering, Illinois
Institute of Technology, Chicago, Illinois 60616*

The stratification of thin liquid films formed from micellar solutions or latex suspensions can be explained by layer-by-layer destruction of a colloid crystal structure inside the film. The stepwise decrease of the film thickness is due to appearance and growth of dark spots (of less thickness) in the film. This phenomenon is analyzed in the present paper, and an explanation is proposed. The driving force for the stepwise thinning of the film is attributed to the gradient of the chemical potential of micelles at the film periphery. Therefore, the appearance and expansion of spots in the film are controlled by the micellar self-diffusion, rather than by normal instabilities. The spots are considered as condensed states of vacancies in the micellar structure inside the film, and the appearance of dark spots is interpreted as a phase transition. This explanation of the mechanism of stratification phenomenon is supported by the data for formation and expansion of spots.

Introduction

In the beginning of this century, Johnnott[1] and Perrin[2] experimentally observed and described a phenomenon of stepwise thinning of liquid foam films. This phenomenon, called stratification, was later investigated by many authors, both with foam films[3-6] and with emulsion films.[7,8] Several researchers,[5,6] hypothesized that the phenomenon is connected with the formation of liquid crystal structure. Some recent experimental data[9,10] suggest another explanation of the stepwise thinning. Nikolov and Wasan[9] observed stratification with films, formed from a polystyrene latex suspension in water. It is known that the spherical latex particles, bearing a high surface charge, do not form *liquid* crystal structures. However, they form three-dimensional[11,12] and two-dimensional[13,14] *colloid* crystals. In addition, the experiments with micellar solutions of anionic surfactants (at concentrations much lower than needed for formation of liquid crystals) showed that the height of the step during the stratification is approximately equal to the mean distance between the micelles in the solution. Stratification was also observed[10] with micellar solutions of nonionic surfactants. All these data

lead to the conclusion that the stratification is observed with thinning liquid films formed from colloidal solutions containing monodisperse particles of submicron size. Then the stepwise thinning can be explained[9] by a layer by layer destruction of a *colloid* crystal structure formed by these particles in the restricted volume of the film.

To support this idea quantitatively, a model of the micellar structure inside the film was developed,[10,15] and the disjoining pressure of the film was calculated. The contribution of the micellar interactions to the disjoining pressure led to a series of metastable states of the film. The calculated thicknesses of the metastable states turned out to be in good agreement with the experimental data.

Our aim in the present paper is to explain the mechanism of the transition from one metastable state to the next one. The occurrence of this process is the following.

We form a horizontal circular foam film by using a version of the known method of Scheludko.[16] The conditions of the experiment, the materials, and all details of the experimental setup are described in ref 9.

The film is created in a cylindrical capillary by sucking out the solution from a biconcave drop through an orifice in the capillary wall. The resulting horizontal flat film is encircled by a bioconcave liquid meniscus. After the film is formed, it starts to decrease its thickness. When it becomes sufficiently thin, stepwise changes in the film thickness are observed. Each metastable state with uniform thickness exists several seconds or several hundred seconds, depending on its thickness and on the other conditions of the experiment. Then suddenly, one or several dark spots appear amidst the uniform film and start to increase gradually their area—Figure 1. The spots seem darker in reflected light, because they have smaller thickness than the remaining part of the film. After the spots have covered the whole area of the film, it stays for some time in the new metastable state. Then darker spots appear, and after their expansion a subsequent metasta-

---

* Author to whom correspondence should be addressed. Illinois Institute of Technology.

(1) Johnnott, E. S. *Philos. Mag.* **1906**, *70*, 1339.

(2) Perrin, R. E. *Ann. Phys.* **1918**, *10*, 160.

(3) Bruil, H. G.; Lyklema, I. *Nature* **1971**, *233*, 19.

(4) Friberg, S.; Linden, St. E.; Saito, H. *Nature* **1974**, *251*, 494.

(5) Manev, E.; Proust, J. E.; Ter-Minassian-Sarraga, L. *Colloid Polym. Sci.* **1977**, *225*, 1133.

(6) Manev, E.; Sazdanova, S.; Wasan, D. T. *J. Dispersion Sci. Technol.* **1984**, *5*, 111.

(7) Kruglyakov, P. M. *Kolloidn. Zh.* **1974**, *36*, 160.

(8) Kruglyakov, P. M.; Rovin, I. G. *Physical Chemistry of Black Hydrocarbon Films—Biomolecular Lipid Membranes*; Nauka: Moscow, 1978 (in Russian).

(9) Nikolov, A. D.; Wasan, D. T. *J. Colloid Interface Sci.* **1989**, *133*, 1.

(10) Nikolov, A. D.; Wasan, D. T.; Kralchevsky, P. A.; Ivanov, I. B. In *Ordering and Organization in Ionic Solutions*; Ise, N., Sogami, I., Eds.; World Scientific: Teaneck, NJ, 1988; p 362.

(11) Hachisu, S.; Kobayashi, Y.; Kose, A. *J. Colloid Interface Sci.* **1973**, *42*, 342.

(12) Ito, K.; Nakamura, H.; Ise, N. *J. Chem. Phys.* **1986**, *85*, 6136.

(13) Pieranski, P. *Contemp. Phys.* **1983**, *24*, 25.

(14) Van Winkel, D. H.; Murry, C. A. *Phys. Rev. A.* **1986**, *34*, 562.

(15) Nikolov, A. D.; Kralchevsky, P. A.; Ivanov, I. B.; Wasan, D. T. *J. Colloid Interface Sci.* **1989**, *133*, 13.

(16) Scheludko, A. *Adv. Colloid Interface Sci.* **1967**, *1*, 391.

(a)　　　　　　　　(b)
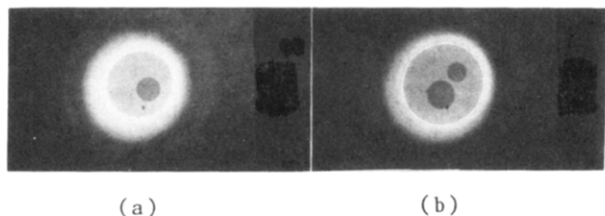
Figure 1. Single dark spot (a) and a couple of spots (b) in a horizontal thin liquid film formed from a 0.1 mol/L solution of NaDS. The circular shape of the spots is due to the action of positive line tension.

ble state is reached. This process is repeated until a final stable state is attained.

There are two traditional mechanisms for explaining instabilities in thin liquid films. The first one is connected with the appearance and spontaneous growth of capillary waves at the film surfaces.[17-22] The applicability of this mechanism to dark spot formation in stratifying films is discussed in the next section. The second mechanism is based on nucleative formation of holes (in our case spots) inside a thin film.[23-28] However, it turns out that neither the first nor the second mechanism can explain the experimental data on spot formation and expansion. That is why we propose below a new diffusive–osmotic mechanism, which explains the stepwise transition by the presence of two types of entities, *vacancies* and *spots*, in the initially uniform film. This mechanism is compared with the available experimental data in the last section of the paper, where the results of this study are discussed.

Surface Waves in a Film Stabilized by Intermicellar Repulsion

In principle, the presence of symmetrical surface waves (Figure 2) can lead to local decreases of the film thickness and hence to formation of dark spots. Let us denote the local deviation from the flat surface by ζ (Figure 2). For surface waves, ζ can be presented in the form[17-22]

$$\zeta = A(x_1, x_2)e^{\omega t} \tag{2.1}$$

where t is time and ω is a complex frequency. As known[16-21] when the derivative of the disjoining pressure $\Pi = d\Pi/dh$ (with h being the film thickness) is positive, ω has real positive value. Such is the case when
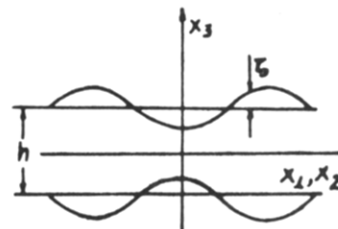
Figure 2. Capillary waves in a thin liquid film of mean thickness h. ζ is the local deviation due to the surface waves.

the van der Waals attractive forces prevail in the film. According to eq 2.1, $\omega > 0$ leads to unbounded increase of the surface corrugations with time and to rupture of the film.[17-21] However, this is not the case of a thin liquid film with micellar structure inside, due to the strong repulsion between the micelles ($\Pi < 0$ around each metastable state ($\Pi = P_c$), see Figure 5 in ref 15). The amplitude of surface waves cannot increase whenever Π is negative. To estimate the amplitude of the film thickness fluctuations in this case, one can use the expression[33]

$$\bar{\zeta} = [\zeta^2]^{1/2} \le \left(\frac{kT}{12\pi\sigma}\right)^{1/2}\frac{h}{R} \tag{2.2}$$

where $\bar{\zeta}$ is the amplitude ζ averaged over a circular parcel of radius, R, σ is surface tension, T is temperature, and k is the Boltzmann constant. For $\sigma = 38.3$ mN/m and $T = 298$ K, one obtains

$$\bar{\zeta} \le 5.33 \times 10^{-9}\frac{h}{R} \text{ cm} \tag{2.3}$$

Using microscope and movie camera, one can record the process of dark spot formation. The radius of the smallest recorded dark spots in our experiments (with micellar solutions of NaDS) is in the range 5–8 μm. The thickness, h, of the studied films is smaller than 0.08 μm. Then one finds from eq 2.3 that the thermal fluctuations of the film thickness cannot exceed 8.5×10^{-11} cm (for $R = 5$ μm). $\bar{\zeta}$ can be of the order of the magnitude Δh of the stepwise transitions of the film thickness (usually $\Delta h \cong 10^{-6}$ cm) only if $R \ll h$. One sees that the capillary wave mechanism can hardly explain the formation of macroscopic dark spots in the stratifying films. Another possible mechanism is considered below.

Nucleation Mechanism (Constant Chemical Potentials)

Derjaguin and Gutop[23] and Derjaguin and Prokhorov[24] proposed a nucleation theory of rupture of very thin (practically bimolecular) films. By analogy with the theory of cavitation in liquids, they suggested that fluctuations can lead to the formation of very small (of molecular size) holes in the film. Their further growth in lateral direction can lead to film rupture. A similar nucleation mechanism was proposed by Kashchiev and Exerowa,[26] who adapted the molecular theory of adsorption by considering the two layers of a bimolecular film as being mutually adsorbed on each other. Recently, Prokhorov and Derjaguin[28] developed a generalized theory of bilayer film rupture combining both concepts: the mechanical[23-25] and the vacancial.[26,27]

In both theories, it is presumed that the phases, surrounding the film, can serve as reservoirs of heat and matter, and therefore the temperature and the chemical potentials are constant during the nucleation process. Under these conditions, the reversible work of forma-

(17) Vrij, A. *Discuss. Faraday Soc.* **1966**, *42*, 23.
(18) Ivanov, I. B.; Radoev, B. P.; Manev, E.; Scheludko, A. *Trans. Faraday Soc.* **1970**, *66*, 1262.
(19) Sche, S.; Fijnaut, H. M. *Surf. Sci.* **1978**, *76*, 186.
(20) Maldarelli, C.; Jain, R. K.; Ivanov, I. B.; Ruckenstein, E. *J. Colloid Interface Sci.* **1980**, *78*, 118.
(21) Maldarelli, C.; Jain, R. K. In *Thin Liquid Films*; Ivanov, I. B., Ed.; Marcell Dekker: New York, 1988; Chapter 8.
(22) Ruckenstein, E.; Sharma, A. *J. Colloid Interface Sci.* **1987**, *119*, 1.
(23) Derjaguin, B. V.; Gutop, V. V. *Kolloidn. Zh.* **1962**, *24*, 431.
(24) Derjaguin, B. V.; Prokhorov, A. V. *J. Colloid Interface Sci.* **1981**, *81*, 108.
(25) Derjaguin, B. V. *Theory of Stability of Colloids and Thin Films*; Nauka: Moscow, 1986 (in Russian); Plenum Press: New York, 1989.
(26) Kashchiev, D.; Exerowa, D. *J. Colloid Interface Sci.* **1980**, *77*, 501.
(27) Exerowa, D.; Balinov, B.; Kashchiev, D. *J. Colloid Interface Sci.* **1983**, *94*, 45.
(28) Prokhorov, A. V.; Derjaguin, B. V. *J. Colloid Interface Sci.* **1988**, *125*, 111.
(29) Rusanov, A. I. *Phase Equilibria and Surface Phenomena*; Khimia: Leningrad, 1967 (in Russian).
(30) Ivanov, I. B.; Toshev, B. V. *Colloid Poly. Sci.* **1975**, *253*, 593.
(31) Clifford, J.; Pethica, B. A. *J. Phys. Chem.* **1966**, *70*, 3345.
(32) Hill, T. L. *An Introduction to Statistical Thermodynamics*; Addison-Wesley: Reading, MA, 1962.

(33) Kralchevsky, P. A.; Nikolov, A. D.; Wasan, D. T.; Ivanov, I. B. *Ann. Univ. Sofia, Fac. Chim.* **1987**, *81*, No. 2 (in press).

tion of a circular hole of radius r is given by the increment of the grand thermodynamic potential:[23-25]

$$\Delta\Omega = -\pi r^2 \gamma + 2\pi r \kappa \qquad (3.1)$$

The first term in the right-hand side corresponds to the work done by the film tension, γ, and the second term is the work for formation of the perimeter of the hole with κ being the line tension of the two-dimensional nucleus. $\Delta\Omega$ has a maximum at hole radius

$$r^* = \kappa/\gamma \qquad (3.2)$$

which must be the radius of the critical hole.

On the basis of eqs 3.1 and 3.2 and the nucleation theory, Derjaguin and Prokhorov[24] derived the following expression for the lifetime τ of a film of radius r_c:

$$\tau = \frac{4\kappa\eta}{r_c^2 \Gamma(kT)^{1/2}\gamma^{3/2}} \exp\left(\frac{\pi\kappa^2}{\gamma kT}\right) \qquad (3.3)$$

Here η (kg/s) is the two-dimensional viscosity of the film and Γ is the number of molecules per unit area of the film.

A straightforward application of the theory of Derjaguin et al.[23-25] can be made for interpretation of the data for dark spot appearance in stratifying films. It is sufficient to consider nuclei of dark spots instead of nuclei of holes and to replace γ by

$$\Delta\gamma_n = \gamma_n - \gamma_{n-1} \qquad (3.4)$$

where γ_{n-1} is the film tension of the spot and γ_n the tension of the surrounding film with n micellar layers inside. Then instead of eqs 3.1–3.3, one can write

$$\Delta\Omega_n = -\pi r^2 \Delta\gamma_n + 2\pi r \kappa \qquad (3.5)$$

$$r_n^* = \frac{\kappa}{\Delta\gamma_n} \qquad (3.6)$$

$$\tau_n = \frac{4\kappa\eta}{r_c^2 \Gamma(kT)^{1/2}(\Delta\gamma_n)^{3/2}} \exp\left(\frac{\pi\kappa^2}{\Delta\gamma_n kT}\right) \qquad (3.7)$$

where Γ is the number of micelles per unit area of the film. τ_n is the time needed for appearance of a spot of thickness h_{n-1} in a uniform film of thickness h_n.

It is known[29,30] that

$$\gamma_n = 2\sigma_n^f + P_c h_n; \quad \sigma_n^f = \sigma \cos\theta_n \qquad (3.8)$$

where σ and P_c are the surface tension and the capillary pressure of the meniscus, h_n and σ_n^f are the thickness and the surface tension of the film at its nth metastable state, and θ_n is the contact angle between the film and the meniscus. Both h_n and θ_n can be measured by interferometry in reflected light using the experimental setup described in ref 9. Then in view of eqs 3.4 and 3.8, $\Delta\gamma_n$ can be calculated from the equation

$$\Delta\gamma_n = 2\sigma(\cos\theta_n - \cos\theta_{n-1}) + P_c(h_n - h_{n-1}) \qquad (3.9)$$

Experimental data for h_n and θ_n are presented in Table I for a 0.1 mol/L solution of NaDS ($\sigma = 36.6$ mN/m, $P_c = 50.5$ Pa). Since the values of $\Delta\gamma_n$, calculated from eq 3.9, decrease with the increase of n (Table I), according to eq 3.7 the metastable states with higher values of n should have greater lifetimes. However, the experimental values of τ_n, also shown in Table I, exhibit the opposite trend.

The experimental observations show also that the smallest detected dark spots have radii in the range 5–8 μm and grow steadily (without any indication of cirtical behavior) until they cover the whole film area. Then one can assume that the radius of the critical spot, r_n^*, is equal

Table I. Measured Values of the Film Thickness h_n, Contact Angle θ_n, and Lifetime τ_n at a Metastable State[a]

n	h_n, nm	θ_n, deg	$\Delta\gamma_n \times 10^3$, mN/m	τ_n, s (exptl)	r_n^*, μm (from eq 3.6)
0	16.2	1.26			
1	26.1	0.906	9.05	600	42
2	35.9	0.790	2.69	108	142
3	47.0	0.685	2.29	36	166
4	57.9	0.665	0.85	24	447

[a] With n micellar layers inside the film (0.1 mol/L NaDS). r_n^* and $\Delta\gamma_n$ are calculated from eqs 3.6 and 3.9.

to or smaller than 4–8 μm. The estimate

$$\kappa = \sigma\delta_l \qquad (3.10)$$

($\delta_l \cong \Delta h$ is the height of the border around the dark spot) yields $\kappa = 3.8 \times 10^{-5}$ dyn for NaDS of concentration 0.1 mol/L. Using this value of κ and the values of $\Delta\gamma_n$ from Table I, one can calculate r_n^* from eq 3.6. The values of r_n^* thus obtained are much larger than the values measured experimentally (see Table I).

Thus one reaches the conclusion that the nucleation mechanism of Derjaguin et al.,[23-25] in its present form, cannot be applied to the interpretation of the experimental data for the appearance of spots in stratifying films. We believe that this is due to the fact that the chemical potential of the micelles in the restricted area of the film varies during the nucleation process, and thus one of the basic premises of the theory of Derjaguin et al. is violated. That is why we propose below another mechanism of dark spot formation. Since the chemical potential is supposedly not constant, we will use the variation of the free energy, ΔF, instead of the variation, $\Delta\Omega$, of the grand thermodynamic potential.

Diffusive–Osmotic Mechanism

Spots and Vacancies. In ref 15, the disjoining pressure Π_n of a thin film with n micellar layers inside was calculated by means of a model in which the micellar interactions were accounted for. The calculations showed that as large as the capillary pressure P_c might be, it can be counterbalanced by the disjoining pressure, Π_n, which is due predominantly to the intermicellar repulsion. This balance corresponds to a metastable state of the film. More precisely, $\Pi_n = P_c$ is the condition for equilibrium with respect to the forces acting normally to the film surfaces.

The metastable states of the film have a comparatively short lifetime: due to the motion of micelles from the film to the bulk solution, dark spots are formed in the film. The experimental data for expansion of spots, discussed in detail in the next section, show that the chemical potential of the micelles in the film is uniform along the film. Hence, a non-zero gradient of the chemical potential of the micelles must exist in the transition region between the film and the meniscus. This gradient gives rise to a force which is parallel to the film surfaces and which in fact is the driving force of the layer-by-layer thinning of a stratifying film. In other words, the normal stability of the film is accompanied by a lateral instability.

A vacancy appears in place of a micelle, which has left the film. Such a vacancy is shown schematically in Figure 3a. Due to the strong anisometry of the system, the relaxation in direction normal to the film surfaces is much faster than the relaxation in lateral direction. Therefore, it can be expected that due to the intermicellar repulsion the space left by a missing micelle is divided between the other micelles, which are situated along the normal
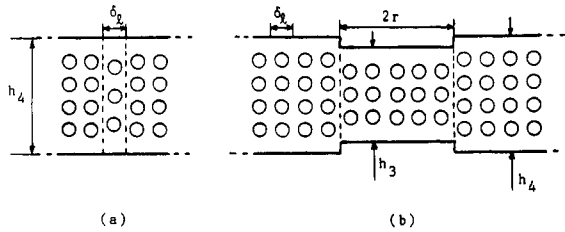
Figure 3. Sketch of a vacancy (a) and of a spot of radius r (b) in a flat thin film. δ_l is the distance between the micelles in lateral direction, and h_3 (h_4) is the equilibrium thickness of film containing three (four) micellar layers.

Figure 4. Model of a film of thickness h, containing two layers of colloid particles (micelles). The cells A and B can be considered as the two components of a two-dimensional solution, representing the film. In particular, each cell B contains a vacancy.

to the film (cf. Figure 3a). Then the thickness of the film in a place with a vacancy will be the same as the thickness of the remaining part of the film. An area δ_l^2 of the film surface corresponds to each vacancy (δ_l is the distance between the micelles in the film in lateral direction; δ_l is supposed to be equal to the mean distance between the micelles in the bulk solution—see ref 15).

Due to the self-diffusion of the micelles, the vacancies can move throughout the film. A vacancy will travel a distance δ_l for time $t = \delta_l^2/(4D)$ with velocity $v = \delta_l/t = 4D/\delta_l$, where D is the coefficient of self-diffusion of the micelles. For a 0.03 mol/L aqueous solution of NaDS, $\delta_l = 1.66 \times 10^{-6}$ cm (ref 15), $D = 1.2 \times 10^{-6}$ cm^2/s (ref 31), and we find $v = 2.9$ cm/s. This high value of v, coupled with the small size of the film (the film radius in our experiments was usually 0.02–0.03 cm), means that it takes only 10^{-2} s for a micelle to go from the meniscus to the film center.

As explained above, we call a vacancy a place in a film containing n micellar layers, where there are $n - 1$ micelles per area δ_l^2 of the film surface, but the film thickness is the same (Figure 3a). In contrast, the film thickness is smaller in the place of a spot—Figure 3b. More precisely, the thickness of the spot is h_{n-1}, whereas the thickness of the remaining part of the film is h_n (h_n and h_{n-1} are the equilibrium thicknesses of a film containing n and $n - 1$ micellar layers, respectively (see ref 15 for details)). According to eq 3.10, the excess energy per unit length of the contact line, encircling a spot, can be interpreted as line tension, κ.

Considering a spot as a result of aggregation of vacancies, one can regard the quantity

$$N = \pi r^2/\delta_l^2 \qquad (4.1)$$

as the aggregation number of a spot of radius r. The formation of a spot by aggregation of vacancies and the equilibrium between a spot and the single vacancies moving throughout the area of the remaining part of the film can be described by means of a two-dimensional lattice model.

Work of Spot Formation. Let us consider a stratifying film of area πr_c^2, where r_c is the radius of the contact line between the film and the liquid meniscus surrounding it. A film of uniform thickness, containing vacancies, can be regarded as a two-dimensional solution, which consists of the components A and B—Figure 4. A cell A, as well as a cell B, has a base with area δ_l^2 and height h_n (n is the number of the micellar layers inside the film). Cell A contains n micelles (one micelle in each layer), whereas there are $n - 1$ micelles in cell B; i.e., cell B contains one vacancy. For the sake of brevity, we will sometimes call the cells of type B "vacancies". (We will not consider cells containing two or more vacancies, because the appearance of such cells has low probability due to the repulsion between the micelles.) The total number
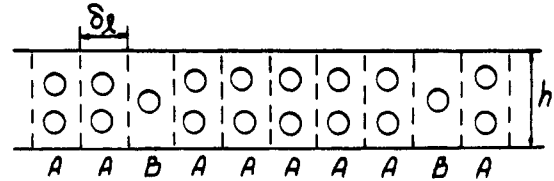
of cells of both types in the film is

$$M = \pi r_c^2/\delta_l^2 \qquad (4.2)$$

The diffusive motion of the vacancies in the film can be identified with the motion of the component B throughout the two-dimensional solution. Since the equilibrium along the normal to the film is established much faster than the lateral equilibrium, we will suppose that the positions of the micelles in the cell type A or B are determined by the electrostatic repulsive forces. Then the lateral equilibrium will be attained by two-dimensional motion of the cells A and B throughout the film area.

The experimental data for expansion of spots (see the next section) show that the velocity of formation of vacancies at the film periphery is much smaller than the velocity of diffusion of the vacancies in the film. That is why one can consider the two-dimensional solution AB as uniform. In accordance with the lattice theory of the solutions, in the Bragg–Williams approximation,[32] the free energy, F, of the solution can be written in the form

$$\frac{F}{kT} = N_A\left[\frac{g_A^{\circ}(h_n)}{kT} + \ln x_A + u_{AA}(h_n) - u(h_n)(1 - x_A)^2\right] +$$
$$N_B\left[\frac{g_B^{\circ}(h_n)}{kT} + \ln x_B + u_{BB}(h_n) - u(h_n)(1 - x_B)^2\right] \quad (4.3)$$

where k is the Boltzmann constant, N_A and N_B are the numbers of the cells A and B ($N_A + N_B = M$)

$$x_A = N_A/M; \quad x_B = N_B/M \qquad (4.4)$$

u_{AA}, u_{BB}, and u are connected with the interaction energies w_{AA}, w_{BB}, and w_{AB} between the respective components as follows:

$$u_{AA} = \frac{cw_{AA}}{2kT}; \quad u_{BB} = \frac{cw_{BB}}{2kT}$$

$$u = \frac{c}{2kT}(w_{AA} + w_{BB} - 2w_{AB}) \qquad (4.5)$$

Here c is the number of the nearest neighbors; in our model, $c = 4$ because the cells A and B are supposed to fill a two-dimensional square lattice. g_A° and g_B° in eq 4.3 are the standard Gibbs free energies of a cell A or B, respectively. In the Bragg–Williams approximation, this free energy is proportional to the logarithm of the internal statistical partition function of the corresponding cell.[32] From eqs 4.3 and 4.4, one obtains

$$f_n = \frac{F}{MkT} = x_A\left[\frac{g_A^{\circ}(h_n)}{kT} + \ln x_A + u_{AA}(h_n)\right] +$$
$$x_B\left[\frac{g_B^{\circ}(h_n)}{kT} + \ln x_B + u_{BB}(h_n) - u(h_n)x_A\right] \quad (4.6)$$

Let us now consider a film in which a spot of radius r has been formed. The aggregation number, N, of the spot is defined by eq 4.1. The free energy, F_1, of such a

film can be written in the form

$$\frac{F_1}{kT} = (M - N)f_n + N\left[\frac{g_A{}^\circ(h_{n-1})}{kT} + u_{AA}(h_{n-1})\right] + \frac{2\pi r\kappa}{kT}$$

(4.7)

Here κ is the line tension of the line, which encircles the spot. We have supposed in eq 4.7 that there are no vacancies in the spot. (It can be shown[33] that the concentration of vacancies in a spot should be extremly low and should not affect the process of spot formation.) From eq 4.1, one finds

$$r = \delta_l(N/\pi)^{1/2}$$

(4.8)

It is convenient to introduce the dimensionless parameters

$$\theta = N_t/M; \quad x = N/M; \quad \beta = \frac{2\delta_l{}^2\kappa}{r_c kT}$$

(4.9)

where N_t is the total number of the micelles which have left the film. The molar fractions of the components A and B in the two-dimensional solution, surrounding the spot, can be expressed as

$$x_B = \frac{\theta - x}{1 - x}; \quad x_A = 1 - x_B = \frac{1 - \theta}{1 - x}$$

(4.10)

Then eq 4.7 can be transformed into

$$\frac{F_1}{MkT} = (1 - \theta)\left[\frac{g_A{}^\circ(h_n)}{kT} + \ln\frac{1 - \theta}{1 - x} + u_{AA}(h_n)\right] +$$

$$(\theta - x)\left[\frac{g_B{}^\circ(h_n)}{kT} + \ln\frac{\theta - x}{1 - x} + u_{BB}(h_n) - u(h_n)\frac{1 - \theta}{1 - x}\right] +$$

$$x\left[\frac{g_A{}^\circ(h_{n-1})}{kT} + u_{AA}(h_{n-1})\right] + \beta x^{1/2} \quad (4.11)$$

The work of formation of a spot with aggregation number $N = xM$ in a film containing initially $N_t = \theta M$ vacancies is

$$\Delta F(\theta, x) = F_1(\theta, x) - F_1(\theta, 0)$$

(4.12)

Then from eqs 4.11 and 4.12 one derives

$$\Delta\bar{F}(\theta, x) = \frac{\Delta F}{MkT} = -(1 - \theta)\ln(1 - x) + (\theta - x)\ln\frac{\theta - x}{1 - x} -$$

$$\theta\ln\theta - xQ + u(h_n)\frac{x}{1 - x}(1 - \theta)^2 \quad (4.13)$$

where the quantity

$$Q = [g_B{}^\circ(h_n) - g_A{}^\circ(h_{n-1})]/(kT) + u_{BB}(h_n) - u_{AA}(h_{n-1})$$

(4.14)

depends neither on θ nor on x.

Equilibrium Spot. A necessary condition for a spot (or a nucleus of a spot) to be in equilibrium with the surrounding part of the system is for ΔF to have an extreme value.[29] Hence, the equilibrium value of x at given θ must satisfy the equation

$$\left(\frac{\partial(\Delta F)}{\partial x}\right)_\theta = 0$$

(4.15)

The substitution of ΔF from eq 4.13 into eq 4.15 yields the equation

$$G(\theta, x) = Q$$

(4.16)

where the function G is defined by the expression

$$G(\theta, x) = \frac{\beta}{2x^{1/2}} - \ln\left(\frac{\theta - x}{1 - x}\right) + u(h_n)\left(\frac{1 - \theta}{1 - x}\right)^2 \quad (4.17)$$

The solution of eq 4.16 for x determines the radius

$$r = r_c x^{1/2}$$

(4.18)

(cf. eqs 4.2, 4.8, and 4.9) of the spot, which is in equilibrium with the single vacancies in the surrounding film of radius r_c. The equilibrium spot is stable, when it corresponds to a minimum value of ΔF; if ΔF has a maximum, the spot is unstable. The equilibrium size of the spot, determined from eq 4.16, will obviously depend on the total concentration of the vacancies in the film, θ.

Equation 4.16 can be interpreted as a two-dimensional analogue of the Gibbs–Thomson equation. Indeed, by using eqs 4.9, 4.10, and 4.17, one can transform eq 4.16 to read

$$x_B = x_B{}^\infty \exp\left(\frac{\kappa}{r}\frac{\delta_l{}^2}{kT}\right)$$

$$x_B{}^\infty = \exp\left[-Q + u\left(\frac{1 - \theta}{1 - x}\right)^2\right] \quad (4.19)$$

where x_B is the equilibrium value of the molar fraction of the vacancies in the film surrounding the spot. The comparison of eq 4.19 with the Gibbs–Thomson equation for the vapor pressure

$$p = R^\infty \exp\left(\frac{2\sigma}{r}\frac{v_l}{kT}\right)$$

of a spherical drop of radius r and surface tension σ shows that $\delta_l{}^2$ is a counterpart of the molar volume, v_l, of the liquid in the drop, and κ/r of the capillary pressure $2\sigma/r$.

Numerical Results and Discussion. A closer inspection of eq 4.16 shows that at sufficiently large values of θ it has two different roots, $x = x_{cr}$ and $x = x_{st}$, which correspond to a maximum and a minimum of ΔF, respectively. The parameters in eqs 4.16 and 4.17 are estimated in the Appendix of this paper by using some data and model results from ref 15. For the last transition (1 $\rightarrow$ 0) of a stratifying film, formed from 0.1 mol/L aqueous solution of NaDS, we thus calculated $u = 0.059$ and $Q = 15.1$. The respective dependences of ΔF and G on x/θ, calculated from eqs 4.13 and 4.17 for three different values of θ, are shown in Figure 5. We have used the experimental values $r_c = 170$ μm, $\sigma = 36.6$ mN/m, and $\delta_l = 10.4$ nm, and we calculated from eqs 3.10 and 4.9 $\kappa = 0.38$ nN and $\beta = 0.118$. These values of the model parameters, corresponding to a real experimental situation, are used below to illustrate quantitatively the theoretical results.

When $\theta < 1.77 \times 10^{-4}$, eq 4.16 has no roots, and $\Delta\bar{F}$ is an increasing function of x. For $\theta > 1.77 \times 10^{-4}$, $\Delta\bar{F}$ has a maximum and a minimum (see Figure 5). They are connected with the first and the second term in the right-hand side of eq 4.17. In other words, the maximum is related to the line tension, and the minimum to the equilibrium concentration of the vacancies in the film encircling the spot, i.e., to the "vapor pressure" of the spot.

The maximum at $x = x_{cr}$ corresponds to a spot of critical size. It can grow spontaneously until it reaches size $x = x_{st}$, which corresponds to a spot in stable equilibrium with the remaining part of the film. Once formed, the stable spot can grow futher only due to the condensation of newly created vacancies, which can approach the spot periphery by self-diffusion (increase of θ at $x = x_{st}$).

The presence of a minimum of the excess free energy at $x = x_{st}$ does not guarantee the existence of a stable spot. If $\Delta\bar{F}(x_{st}) > 0$, the formation of the spot will not be thermodynamically favorable. This is the region with
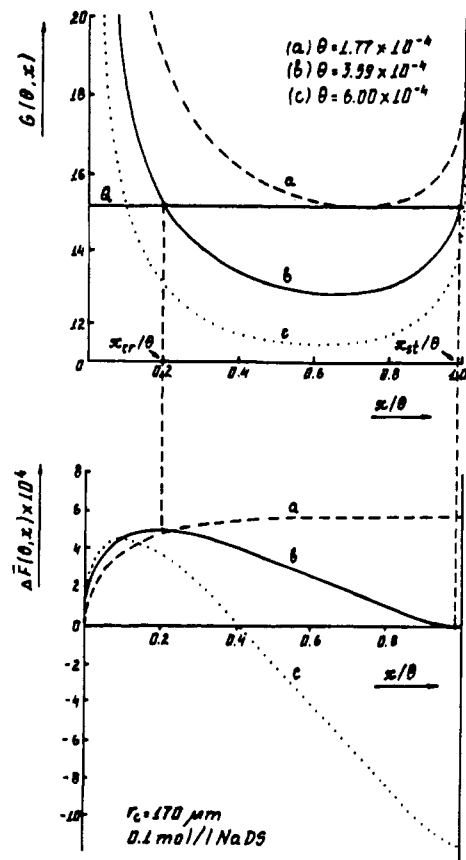
Figure 5. Dependences of $\Delta \bar{F}$ and G on x/θ, calculated from eqs 4.13 and 4.17 for three different values of θ. The intersection points $G = Q$ determine the extrema of $\Delta \bar{F}$ (0.1 mol/L NaDS, transition 1 → 0).

$1.77 \times 10^{-4} < \theta < 3.59 \times 10^{-4}$ in Figure 5. The existence of a stable spot is thermodynamically advantageous for $\Delta \bar{F}(x_{st}) < 0$, i.e., at $\theta > 3.59 \times 10^{-4}$ for the example in Figure 5. The value $\theta = \theta_{cr}$, corresponding to zero excess energy at the minimum, i.e.

$$\Delta \bar{F}(\theta_{cr}, x_{st}) = 0 \qquad (4.20)$$

can be considered as the commencement of stable spot formation. Then $x_{st} = x_{st}(\theta_{cr})$, determined from eq 4.16 at $\theta = \theta_{cr}$, gives the size of the smallest possible stable spot.

$\theta_{cr} = 3.59 \times 10^{-4}$ for the illustrative example in Figure 5. The height of the barrier in this case is $\Delta F(\theta_{cr}, x_{cr}) = 4.1 \times 10^5 kT$. Then the excess energy per one vacancy aggregated in the critical spot is $\Delta F(\theta_{cr}, x_{cr})/(x_{cr}M) = 1.4kT$ (cf. eq 4.9).

For $\theta > \theta_{cr}$ the height of barrier at $x = x_{cr}$ decreases and the depth of the minimum at $x = x_{st}$ increases when increasing θ. In other words, the formation of spots becomes more and more favorable.
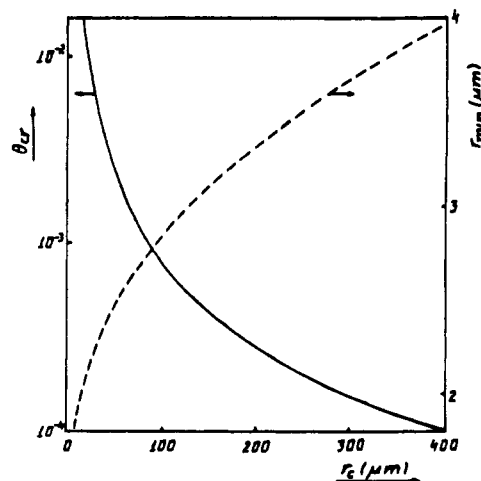
The parameter

$$\beta = a/r_c \qquad \left(a = \frac{2\kappa\delta_l^2}{kT} \right) \qquad (4.21)$$

defined in eq 4.9 decreases with the increase of the film radius r_c. This leads to a dependence of θ_{cr} on r_c, i.e., on the size of the film. The dependence $\theta_{cr}(r_c)$ can be determined by elimination of x_{st} between eq 4.20 and the equation

$$G(\theta_{cr}, x_{st}) = Q \qquad (4.22)$$

and by using eq 4.21 for β.

Figure 6. Dependences of θ_{cr} and r_{min} on the film radius r_c. θ_{cr} is the concentration of the vacancies, which corresponds to the beginning of their aggregation in spots, and r_{min} is the radius of the smallest stable spot.

The result is shown in Figure 6; the same values of the parameters are used as in Figure 5 (in particular $Q = 15.1$, $u = 0.059$, and $a = 20.05$ μm). The dependence of the radius of the smallest stable spot, r_{min}, on the film radius r_c calculated from eqs 4.20, 4.22, and

$$r_{min} = r_c[x_{st}(\theta_{cr})]^{1/2} \qquad (4.23)$$

is also shown in Figure 6. (In fact, eq 4.23 is a special case of eq 4.18.) One sees from Figure 6 that θ_{cr} decreases and r_{min} increases with increasing r_c.

In our experiments, we recorded the process of formation of spots by means of a movie camera at a velocity of 0.125 s/frame. The inspection of the movie film showed that the smallest spots appear suddenly with an initial radius between 4.5 and 8 μm. These values are slightly greater than the respective theoretical value $r_{min} = 3.2$ μm (at $r_c = 170$ μm and 0.1 mol/L NaDS)—see Figure 6. It is possible that the exposure time of 0.125 s/frame has been too large for the fast expansion of the appearing spot to be registered in details.

The experiment also shows the stratification (stepwise thinning) is observed only with foam films, whose radius r_c is greater than a certain threshold value r_c^{th}. This fact can be interpreted in the following way.

In principle, it is possible for the film to reach diffusive equilibrium with the liquid meniscus at some concentration, θ_{eq}, of the vacancies in the film. Let us then consider the following two possibilities:

(i) $\theta_{eq} > \theta_{cr}$. In this case, the thin film will reach equilibrium with the bulk solution in the meniscus at concentration of the vacancies lower than θ_{cr}. Hence, spots of smaller thickness will not appear in the film and stratification will not occur.

(ii) $\theta_{eq} > \theta_{cr}$. The continuous formation of vacancies at the film periphery will cause gradual increase of their concentration, θ, in the film. Hence, at a certain moment θ will become equal to θ_{cr}. The spots with smaller thickness will appear in the initially uniform film. In this way, a stepwise transition will occur before the equilibrium concentration $\theta = \theta_{eq}$ ($\theta_{eq} < \theta_{cr}$) is reached, i.e., before the influx of vacancies has stopped.

These considerations lead to the conclusion that the threshold value, r_c^{th}, of the film radius needed for occur-

rence of stratification can be determined from the equation

$$\theta_{cr}(r_c{}^{th}) = \theta_{eq} \qquad (4.24)$$

In other words, the dependence $\theta_{cr} = \theta_{cr}(r_c)$ at $r_c < r_c{}^{th}$ in Figure 6 must terminate at $r_c = r_c{}^{th}$, because stepwise thinning cannot be observed for smaller r_c. The precise measurement of $r_c{}^{th}$ and θ_{eq} for different solutions at different concentrations needs additional experiments. The fact that under certain conditions formation of spots will not occur and the film will be stable even when it contains several layers of micelles has a simple physical explanation. When the stable spot forms, almost all vacancies present in the film are condensed in the spot $(x_{st}/\theta \cong 1$ in Figure 5). Suppose now that the concentration of vacancies is so small that below a given film radius, r_c, their *total* number in the film becomes smaller than the number of vacancies needed for the formation of the minimum stable spot. Obviously, formation of stable spot will be then impossible, stratification will not occur, and the film will be in a stable equilibrium although it contains one or several layers of micelles.

Expansion of Spots

After a spot has formed, it starts increasing its area. The expansion of such a spot in a horizontal film can be explained in the following way.

A newly formed stable spot has minimum excess free energy, ΔF, corresponding to $x = x_{st}$ at given θ—see Figure 5. The equilibrium molar fraction, x_B, of the vacancies (the component B) in the film, encircling the stable spot, is very low

$$x_B = \frac{\theta - x_{st}}{1 - x_{st}} \approx \theta\left(1 - \frac{x_{st}}{\theta}\right) \ll \theta$$

see eq 4.10 and Figure 5. Then $x_{st} \approx \theta$, and the new vacancies, formed at the film periphery, will increase θ and simultaneously will increase the size of the stable spot x_{st}. Physically, this means that the new vacancies approach the spot and "condense" on it, thus increasing its area. As illustrated in Figure 5, the minimum excess free energy $\Delta \bar{F}(\theta, x_{st})$ will decrease during this process.

As mentioned above, in the absence of chemical equilibrium the diffusive outflux of micelles from the film to the meniscus will cause an effective influx of vacancies (component B) in the film. Let us denote by J the total value of this influx. It leads to expansion of the spot and therefore

$$\frac{d}{dt}(\pi r^2) = \delta_l{}^2 J \qquad (5.1)$$

Here as usual $\delta_l{}^2$ is the area of a vacancy and πr^2 is the area of the spot. During the expansion of the spot, the physical conditions at the film periphery are not changed, and one can expect that the total influx of vacancies, J, will remain constant. Then eq 5.1 can be easily integrated:

$$r^2 = \delta_l{}^2 Jt/\pi + \text{const} \qquad (5.2)$$

i.e., r^2 should be a linear function of time.

Curve 1 in Figure 7 represents experimental data for expansion of a dark spot in the film with one micellar layer ($n = 1$) inside it at 0.1 mol/L NaDS ($\delta_l = 10.4$ nm) and film radius $r_c = 170$ μm. The process was recorded by movie camera at a velocity of 0.125 s/frame. Curve 2 in Figure 7 corresponds to two spots of approximately equal size in the film with $n = 2$ micellar layers inside and radius $r_c \cong 180$ μm (all other conditions are the same as for curve 1). In both cases, the data can be fitted well

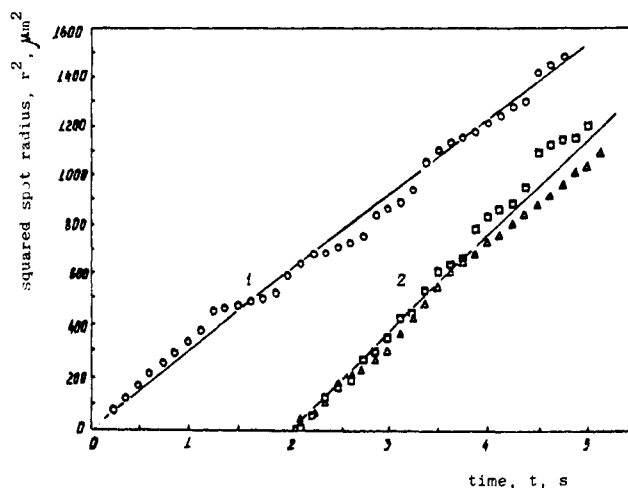**Figure 7.** Data for expansion of spots: (1) a single spot at $n = 1$ and $r_c = 170$ μm; (2) two spots (of approximately equal size) at $n = 2$ and $r_c = 180$ μm (surfactant concentration 0.1 mol/L in both cases).

with a straight line. From the slope of the lines in Figure 7 and from eq 5.2, one determines $J(1) = 3.6 \times 10^6$ s^{-1} for curve 1 and $J(2) = 8.8 \times 10^6$ s^{-1} for curve 2. The difference between the two fluxes can be explained in the following way.

There are $2\pi r_c n/\delta_l$ micellar sites along the periphery of a film with n micellar layers inside. Then

$$J(n) = (2\pi r_{cn}/\delta_l)j; \quad n = 1, 2, 3, \ldots \qquad (5.3)$$

where j is the flux per micellar site. From the above values of $J(1)$ and $J(2)$, we calculated $j \cong 100$ s^{-1}. The decrease of the lifetime of the metastable states when increasing the value of n can be explained with the fact that $J(n)$ in eq 5.3 is proportional to n. The process of stepwise thinning is accelerated by another factor, which is not accounted for in eq 5.3. Usually the spot (or spots) is not centered at the middle of the film. Then the expanding spot will reach the film periphery before the thicker part of the film is entirely replaced by the spot. In this way, two transitions ($n \rightarrow n - 1$ and $n - 1 \rightarrow n - 2$) will take part simultaneously.

The influx $j \cong 100$ s^{-1} can be compared with the flux $j_{sd} = 2D/\delta_l{}^2$ due to the self-diffusion of the micelles. With $\delta_l = 10.4$ nm and diffusion coefficient $D = 6.9 \times 10^{-7}$ cm^2/s for 0.1 mol/L NaDS (ref 31), one finds $j_{sd} = 1.2 \times 10^6$ s^{-1}. Hence, really $j \ll j_{sd}$ and the velocity of the "condensing" and "evaporating" vacancies at the spot border is much greater than the velocity of formation of new vacancies at the film periphery; i.e., there is dynamic equilibrium between the spot and its "vapors". In other words, at every moment the spot can be considered as being an equilibrium one, as supposed in the previous section.

A problem for further investigation is the dependence of the elementary flux, j (see eq 5.3), on n. The difference between the chemical potentials of a micelle in the film and in the bulk solution (the driving force of the film thinning) in principle can depend on the film thickness. To calculate this difference, one needs more information about the state of the micelles in the bulk solution. However, the available data are too scant. Therefore, additional research, both experimental and theoretical, is needed to solve the problem.

Concluding Remarks

Our analysis showed that the formation of spots in a stratifying thin liquid film can be explained neither by

capillary waves in the film nor by the available nucleation theories.[23-26] The derived expression for the amplitude of the fluctuative capillary waves, eq 2.22, implies the conclusion that the smallest detected dark spots are too large to be formed directly by capillary waves. The alternative nucleation mechanism of Derjaguin et al.,[23-25] applied for nuclei of spots in stratifying films (instead of nuclei of holes in equilibrium bimolecular films), leads to contradictions with the experimental data.

The analysis of the experimental observations led us to another mechanism of the stepwise film thinning. This diffusive–osmotic mechanism can be applied both to films containing micelles and to films containing latex or other colloid particles. It provides the following picture of the stratification phenomenon.

During the process of thinning, micellar structure is formed inside the film. The intermicellar repulsion counterbalances all other forces acting normally to the film surfaces. The thinning stops and the film reaches a metastable state with uniform thickness. However, the equilibrium with respect to the normal forces is not accompanied with lateral equilibrium. The radius of the film is much larger than its thickness, and relatively long time is needed for the diffusive equilibrium between the film and the bulk liquid in the meniscus to be reached. Before that, the chemical potentials of the particles (micelles) in the film are higher than their chemical potentials in the bulk solution. The experimental data show that the outflux of micelles from the film is much smaller than their self-diffusive flux. That is why one can suppose that the chemical potential is uniform throughout the film, but it changes sharply across the film periphery. The gradient of the chemical potential at the film periphery is the driving force of the process of stratification. Under the action of this gradient, the micelles leave the film. This leads to appearance of vacancies in the micellar structure inside the film. The concentration of the vacancies, θ, increases with time. At a given concentration, $\theta = \theta_{eq}$, equilibrium between the film and the solution in the meniscus can be reached, which leads to the arrest of the stepwise thinning.

To explain the mechanism of stratification, we propose a model which treats the film as a two-dimensional solution composed of two components: A and B (see Figure 4). A cell "A" contains n micelles (one micelle in each layer of the micellar structure inside the film), whereas a cell "B" has the same volume but contains $n - 1$ micelles; i.e., cell "B" contains a vacancy. Both the interaction between the components A and B (in the framework of the lattice theory of Bragg and Williams) and the line energy of the spot perimeter are taken into account in the model.

The model predicts the appearance of spots in an initially uniform film above a given critical concentration, θ_{cr}, of the vacancies. This can happen, however, only if $\theta_{cr} < \theta_{eq}$. In the opposite case ($\theta_{cr} > \theta_{eq}$), spots will not appear in the film, and stratification will not be observed. Besides, the model predicts a pronounced increase of θ_{cr} with the decrease of the film area. In this way, an interpretation is given to the experimental fact that a film with given thickness exhibits stepwise thinning when its area is large but stays in equilibrium when its area is small enough. (In the latter case, $\theta_{cr} > \theta_{eq}$.)

Another result of our model treatment is that an energetic barrier must be overcome for a spot to be formed by aggregation of vacancies in the film. The height of the barrier is determined by an effective osmotic pressure. This effective osmotic pressure exhibits a ten-
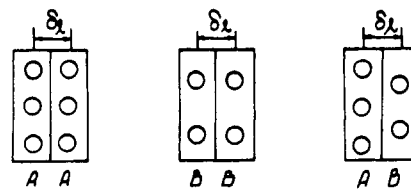

Figure 8. Calculation of the interaction energy between two neighboring cells AA, BB, and AB—see the text.

dency to suck out the excess solvent from the place of a vacancy and to reduce the film thickness—see the Appendix.

Having overcome the barrier, a nucleus of a spot starts to grow spontaneously until it reaches an equilibrium size, i.e., a size corresponding to a stable equilibrium between the spot and the "solution" of single vacancies in its environment. The calculated concentration of the latter tends to be very low at equilibrium; practically all the vacancies are aggregated in the spot. As a result of that, (i) a constant and sufficiently intensive influx of new vacancies is created at the film periphery and (ii) the newly created vacancies "condense" at the spot perimeter, thus increasing its area. In this way, the model predicts that the area of a spot must increase linearly with time, which is in accordance with the experimental data. Besides, the calculated size of the smallest stable spot is in good agreement with the experimental observations.

In conclusion, the model proposed here is able to explain the available experimental data for appearance and expansion of spots in stratifying films. Of course, we are aware of the fact, that the resulting explanation of the stepwise thinning is based on some assumptions, which are liable to additional verifications, correction, or specifying. We believe that a further extension of this theory will provide a quantitative explanation of the micellar outflux from the film and of the total lifetime of the stratifying films.

Appendix

Estimation of the Model Parameters. Calculation of u_{AA}, u_{BB}, and u. It is natural to suppose that the interaction energy w_{AA}, w_{BB}, or w_{AB} of two neighboring cells (AA, BB, or AB; see Figure 4) is determined by the interactions of the micelles contained in these cells. The effective interaction energy of two micelles can be written in the form[34]

$$U^{\text{eff}}(\delta) = U_0 \frac{e^{-\kappa\delta}}{\delta} \qquad (A.1)$$

where δ is the distance between the centers of the micelles, $1/\kappa$ is the Debye thickness of the ionic atmosphere around a micelle, and U_0 is a constant, whose values are given in Table I of ref 15 for different concentrations of NaDS. One can easily realize from Figure 8 that

$$w_{AA}(h_n) = nU^{\text{eff}}(\delta_l) \qquad w_{BB}(h_n) = (n-1)U^{\text{eff}}(\delta_l)$$
$$w_{AB}(h_n) = 2(n-1)U^{\text{eff}}(\delta_l 1.25^{1/2}) \qquad (A.2)$$

where n is the number of micelles contained in cell type A (in accordance with the Bragg–Williams approx-

(34) Beresford-Smith, B.; Chan, D. Y. S.; Mitchell, D. I. *J. Colloid Interface Sci.* **1985**, *105*, 216.

Table II. Values of the Parameters of the Model[a]

n	h_n, nm (exptl)	$u(h_n)$	$(\epsilon_1 + \epsilon_2)\delta_l^2/kT$	Q
1	26.1	0.059	0.157	15.13
2	35.9	0.048	0.145	15.40
3	47.0	0.037	0.110	15.52
4	57.9	0.027	0.088	15.58

[a] Calculated as explained in the text for 0.1 mol/L aqueous solution of NaDS at 25 °C.

imation,[32] we have accounted only for interactions between nearest neighbors). From eqs 4.5 and A.2, one derives

$$u(h_n) = \frac{2}{kT}[(2n - 1)U^{\text{eff}}(\delta_l) - 4(n - 1)U^{\text{eff}}(\delta_l 1.25^{1/2})] \quad (A.3)$$

For a concentration of 0.1 mol/L NaDS, values of $\delta_l = 10.4$ nm and $U_0 = 1.99kT\delta_l$ are determined.[15] The values of $u(h_n)$ for different n are calculated from eq A.3 and listed in Table II. The positive values of $u(h_n)$ mean that the intermicellar interactions lead to an effective repulsion between the vacancies (the component B) in the two-dimensional solution. The reason why they can still aggregate and form spots is connected with some osmotic effects considered below.

Calculation of the Parameter Q. It follows from eqs 4.5 and A.2 that the last two terms in eq 4.14 cancel each other. Then

$$Q = [g_B°(h_n) - g_A°(h_{n-1})]/(kT) \quad (A.4)$$

A cell B of thickness h_n and a cell A of thickness h_{n-1} differ mainly in two respects: (I) in the composition of the solution in these cells and (II) in the interaction energies of the micelles and the parts of the film surfaces, contained in the cells.

Therefore, we can separate the contributions of these effects:

$$QkT = [g_B°(h_n)]^I - [g_A°(h_{n-1})]^I + [g_B°(h_n)]^{II} - [g_A°(h_{n-1})]^{II} \quad (A.5)$$

Effect II can be estimated by using the calculated[15] curves of the excess energy per unit area of the film surfaces, $\omega_n(h)$. Two such curves are shown in Figure 9 (see Note Added in Proof). They correspond to films containing n and $n - 1$ micellar layers, respectively. It is important to note that the quantities w in eq A.2 account for the interaction of the micelles with their lateral neighbors, whereas the quantity ω_n accounts for the interaction energy, due to forces acting normally to the film surfaces.

An excess energy $w_{n-1}(h_{n-1})$ corresponds to a cell A with thickness h_{n-1} containing $n - 1$ micelles. On the other hand the excess energy, which corresponds to a cell B with thickness h_n containing $n - 1$ micelles, is $w_{n-1}(h_n)$. Then using the notation in Figure 9, one can write

$$[g_B°(h_n)]^{II} - [g_A°(h_{n-1})]^{II} = (\epsilon_1 + \epsilon_2)\delta_l^2 \quad (A.6)$$

Data for $(\epsilon_1 + \epsilon_2)\delta_l^2/(kT)$, calculated from the curves in Figure 7 of ref 15, are given in Table II. It turns out that effect II is responsible only for about 1% of the value of Q, which is determined predominantly by effect I. To estimate the latter, we make some additional model considerations.

In accordance with the electroneutrality condition, one can assume that the atmosphere of dissociated counterions around a micelle is brought together with the micelle when it leaves the film. The space of the left micelle is filled with solution from the meniscus, containing bulk concentration of NaDS monomers.
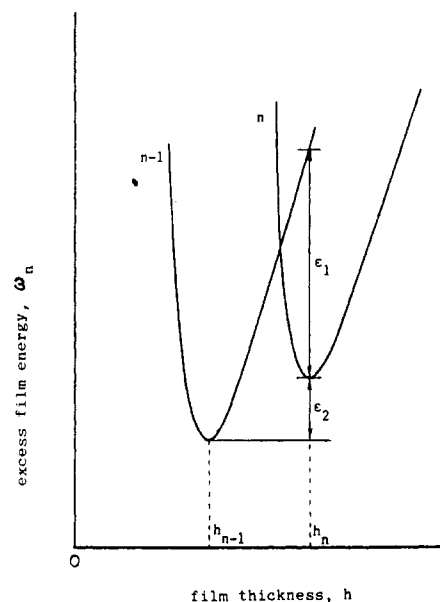
Figure 9. Excess film energy per unit area of the film, ω_n, vs film thickness, h, curves for film with n and $n - 1$ micellar layers inside.

In view of eq 4.3, $[g_B°(h_n)]^I$ is the (standard) Gibbs free energy of a hypothetical film, containing only component B ($x_B = 1$). Such a film is not observed experimentally, because it cannot exist in equilibrium with the liquid meniscus. The concentration of Na^+ ions in such hypothetical film is obviously different from the respective concentration in a film of the same thickness composed only of pure component A. Indeed, about 18 Na^+ ions are dissociated from a micelle in the concentration interval of consideration.[15] Then a cell B contains less micelles than a cell A (of the same volume), and hence the concentration of the dissociated Na^+ ions will be lower in cell B.

As shown above in a real film, $x_B \ll 1$; i.e., the two-dimensional solution of B in A is very diluted. Then it can be expected that the substance, contained in cell B, is in chemical equilibrium with the surrounding film, composed mainly of cells of type A. In order for this equilibrium to be reached, some amount of dissociated NaDS monomers must be transported from the A cells to cell B. In this way, the initial differences between the chemical potentials in the two types of cells will be transformed in an effective osmotic pressure at the boundary between the cells A and B, cf. Figure 4. The condition for diffusive equilibrium with respect to the ions, which is analogous to the condition for Donnan (membrane) equilibrium, reads[35]

$$x_+^B x_-^B = x_+^A x_-^A \quad (A.7)$$

where x_+ and x_- are the molar fractions of Na^+ and DS^- in the respective cells. Besides, x_+^B and x_-^B can be expressed through the initial concentrations $\bar{x}_+^B$ and $\bar{x}_-^B$:

$$x_+^B = \bar{x}_+^B + \Delta x; \quad x_-^B = \bar{x}_-^B + \Delta x \quad (A.8)$$

where Δx is the change in the concentration of the monomers in the cell B due to the transport of dissociated NaDS molecules across the boundaries of the cell. (The molar fractions x_+^A and x_-^A do not change during this process, because $N_A \gg N_B$.)

In view of the above considerations, the initial compo-

(35) Moelwyn-Hughes, E. A. *Physical Chemistry*; Pergamon Press: London, 1961; Chapter XXI.
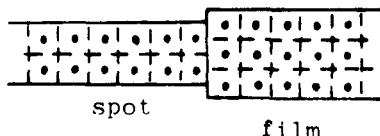
Figure 10. Both the spot and the film can be considered at equilibrium as being built up from identical cubes, each of them containing one micelle.

sition of a cell B is

$$\bar{x}_-^{B} = \bar{x}_-^{A}; \quad \bar{x}_+^{B} = \bar{x}_-^{A} + x_c^{B} \qquad (A.9)$$

where $\bar{x}_-^{A}$ is the bulk molar fraction of DS⁻ in the solution and x_c^{B} is the molar fraction of Na⁺ counterions, dissociated from the micelles in a cell B. Besides

$$x_-^{A} = \bar{x}_-^{A}; \quad x_+^{A} = \bar{x}_-^{A} + x_c^{A} \qquad (A.10)$$

where x_c^{A} is the counterpart of x_c^{B} for a cell A. The substitution of eqs A.8–A.10 in eq A.7 yields

$$\Delta x = [q^2 + \bar{x}_-^{A}(x_c^{A} - x_c^{B})]^{1/2} - q \qquad (A.11)$$

with

$$q = \bar{x}_-^{A} + x_c^{B}/2$$

In accordance with eq 60 in ref 35, the cells can be in equilibrium only if there is a pressure difference

$$P^{A} - P^{B} = \frac{kT}{v_w} \ln \frac{x_w^{B}}{x_w^{A}} \qquad (A.12)$$

between them. Here v_w and x_w are the volume per water molecule and the molar fraction of the water at excluded volume of the micelles. (The motion of the micelles and its contribution to the free energy of the film was already accounted for in section 4 through the entropy of mixing of the components A and B. For the sake of consistency, we will consider the micelles as being fixed at their sites in the cells, the remaining volume being accessible for the thermal motion of the solution molecules.) Since

$$x_w^{A} = 1 - x_+^{A} - x_-^{A}; \quad x_w^{B} = 1 - x_+^{B} - x_-^{B}$$

and having in mind that the molar fractions of the ions are much smaller than 1, we find from eqs A.8–A.12

$$P^{A} - P^{B} = \frac{kT}{v_w}(x_c^{A} - x_c^{B} + 2\Delta x) \qquad (A.13)$$

where we have expanded the logarithm in series. The respective contribution to the film free energy is

$$[g_B^{\circ}(h_n)]^{I} - [g_A^{\circ}(h_n)]^{I} \approx V^{B}(h_n)(P^{A} - P^{B}) \qquad (A.14)$$

where $V^{B}(h_n)$ is the volume of a cell B excluding the volume of the micelles.

Let us consider now the equilibrium of a cell A from the spot (with thickness h_{n-1}) with a cell A from the encircling film (with thickness h_n). As depicted schemati-

cally in Figure 10, the film and the spot can be considered as built up from identical cubes of side δ_l. (The normal deformation, discussed in ref 15, is not significant, and it is neglected here.) Hence, the concentrations of all ions are the same in the two cells A of different thickness, and osmotic effect will not arise. Then we can write $[g_A^{\circ}(h_{n-1})]^{I} - [g_A^{\circ}(h_n)]^{I} = 0$, and in view of eqs A.13 and A.14, we obtain

$$[g_B^{\circ}(h_n)]^{I} - [g_A^{\circ}(h_{n-1})]^{I} = V^{B}(h_n)(kT/v_w)(x_c^{A} - x_c^{B} - 2\Delta x) \qquad (A.15)$$

The substitution from eqs A.6 and A.15 into eq A.5 finally yields

$$Q = \frac{\epsilon_1 + \epsilon_2}{kT}\delta_l^2 + \frac{V^{B}(h_n)}{v_w}(x_c^{A} - x_c^{B} - 2\Delta x) \qquad (A.16)$$

where Δx is given by eq A.11.

Let ν be the number of Na⁺ ions dissociated from a micelle and a_m its radius, then

$$x_c^{A} = (\rho_+ + \rho_-)/\rho_w$$

$$x_c^{B} = x_c^{A} - \nu/(V^{A}\rho_w)$$

$$V^{B}(h_n) = \delta_l^2 h_n - (n-1)\frac{4}{3}\pi a_m^3$$

$$V^{A} = V^{B}(h_n) - \frac{4}{3}\pi a_m^3 \qquad (A.17)$$

where ρ is the bulk concentration (in molecules/cm³) of the respective component and V^{B} (V^{A}) is the free volume of a cell B (A). For a 0.1 mol/L aqueous solution of NaDS, the values of the parameters are respectively ν = 18, δ_l = 10.4 nm, a_{m_4} = 2.4 nm, $v_w \approx 1/\rho_w$ = 3.0 × 10⁻²³ cm³, $\bar{x}_-^{A}$ = 3.43 × 10⁻⁶, and x_c^{A} = 4.79 × 10⁻⁴. See Table I in ref 9 for the values of the ionic bulk concentrations.

The calculated values of Q are given in Table II. One sees that the values of Q (and hence of the extrema of ΔF in Figure 5) are determined mostly by the osmotic therm in eq A.15. It follows from eq A.13 that $P^{A} < P^{B}$; i.e., a sucking pressure $P^{A} - P^{B}$ arises in a cell B. This effect favors the transformation of a vacancy into a spot. However, the excess energy of a single vacancy, $QkT \approx 15kT$, is much smaller than the linear energy of the perimeter of an imaginary single spot: $4\delta_l\chi \approx 3860kT$. That is why a single vacancy (a cell B) does not transform into a spot of area δ_l^2. It is possibile that only much larger spots appear by condensation of vacancies, as described above. The physical reason is that the excess energy of an assembly of vacancies increases proportionally to their number N, whereas the linear energy of the periphery of a spot with the same aggregation number grows proportionally to $N^{1/2}$.

Note Added in Proof: This oscillatory shape of the curves $w_n(h_n)$ was anticipated by J. W. Keuskamp and J. Lyklema (*ACS Symp. Ser.* 1975, *8*, 191).